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Levels of Elements in Typical Mussels from the Southern Coast of Africa (Namibia, South Africa, Mozambique): Safety Aspect

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Abstract: The soft tissues of mussels are often used as the main food source, especially in coastal areas. Neutron Activation Analysis was used to measure the content of 24 macro- and microelements in the soft tissues and 18 elements in the shells of selected sets of mussels of the species *Mytilus galloprovincialis*. The mussels were collected in 8 polluted and 4 pristine zones, which included Namibia, the west and east coasts of South Africa, and Mozambique. According to factor analysis Co, Ni, Zn, As, Se, Br, I, Sb could have anthropogenic origin. The concentrations of elements such as Cr, As, Se and partly Zn at polluted stations were above the maximum permissible levels for seafood. The concentrations of Sc, V, Cr, Mn, Co, Ni, Sb, Cs, Th, U in shells and soft tissues of the same mussels were at the close levels. Elements such as Al, Cr, Co, As (partly Zn, Se, and I) are considered to be harmful to human health at the levels of mussels consumption of 200 g/week per person and lower in such zones as Swakopmund, East London, Port Shepstone, Richards Bay, Xai-Xai according to calculated risk quotients and target hazard indices.

Keywords: mussel consumption; bivalves; risk assessment South Africa; Namibia; Mozambique; neutron activation analysis; hazardous trace elements

1. Introduction

Around 40% of the population in South Africa lives within 100 km of the coastline. In the Western Cape Province, the majority of people live within 25 km of the coast, which implies accelerated extensive urbanization and industrialization of the zone [1]. The coastline of South Africa, Namibia, and Mozambique are characterized by different levels and types of anthropogenic pressures. The main sources of trace elements in the coastal water are marine discharges from urban and agricultural runoff, wastewater treatment plants, industries, power stations, shipyards, and recreational activities. Pollution of the coastal and marine environment derives not only from land-based sources but also from atmospheric pollution and maritime sources (e.g., accidental or deliberate discharges, dumping, and antifouling coatings) [1]. Pollution affects marine organisms in the coastal ecosystems, in which the most fundamental role is played by bivalves (mollusks), which filter water, create substrates for benthic communities, and control the environmental conditions for plankton and nekton. Mussels, which are a kind of bivalves spread worldwide, take the pressure of inputs of both anthropogenic and natural origin. They accumulate elements from dissolved and suspended materials to quite high levels in comparison with the other marine organisms. Assessment of the levels and power of anthropogenic and natural inputs of the state of sensitive organisms is the crucial task of coastal pollution control and management.

The importance of mussels in biomonitoring reflects in their ability to the biomagnification process. As filter-feeding organisms, they have accumulated a high amount of available elements from the water and suspended sediments. For example, the concentrations of Cu, Zn, As, Mo, and Cd were significantly higher in mussels than in sediments in the False Bay area [2].

The mussels are widely used as the sentinel organisms for heavy metal, microplastic, different types of organic contamination in coastal pollution monitoring [3]. Bivalves accumulate the heavy metals, trace, and other micro and macroelements to high values due to specific mechanisms of uptake. The gill tissue of mussels is rich in metallothionein that is essential for the uptake of dissolved metals and their further incorporation into lysosomes and their transport in blood plasma and circulating hemocytes [4].

The soft tissues and shells of bivalves are good bioindicators of environmental metal contamination, and therefore provided independent data on metal concentrations. The mussels adequately fulfill the needs of environmental managers as they are sessile, abundant, and readily sampled [5].

In several works, the trace elements in soft tissues of mussels from different regions of South Africa were determined with a focus on a limited set of samples with a variety of obtained levels [1,2,6–8].

The typical species of mussels (*Mytilus galloprovincialis*) was used in Mussel Watch Programmes by the Department of Environmental Affairs to assess the metal concentrations at key sites along the South African coast [2] However, the existence of unstudied zones and the lack of data about levels of the high number of elements and their risks for human health because of the mussel consumption increases the necessity of new studies. The complex work based on the assessment of micro and macroelements in mussels from polluted and protected water areas along a wide region of the African coast could fill the unstudied gaps in locations, the number of elements, and levels of risks caused by the use of these mussels for food.

It is known that the consumption of mussels provides essential vitamins, proteins, and minerals [4]. The mussels in the local coastal sites around the world are constantly used in food. Usually, the state statistical reports include the shellfish in the seafood group, which is characterized by the average consumption per capita. In 2010, in South Africa, 312,000 tons of seafood were eaten annually, which corresponded to 6.25 kg [9]. The average consumption of shellfish in South Africa from 2014 to 2018 was considered at the range of 0.3–0.6 g per day [10]. However, the local inhabitants of the coastal areas can collect and eat the mussels in huge quantities as a main dish constantly or periodically. For different regions of the world, the general consumption of mussels varies greatly. For example, several studies estimated the consumption at levels less than 10 g/day per person (e.g., [11]). On the other hand, the other works considered the possible consumption of mussels at higher than 100 g/day per person levels (f. e. [12]. The majority of studies used the average consumption (CR, consumption rate) at the level of approximately 200 g/week, or 28.6 g/day per person [13–16].

The typical local available species of mussels could be simply collected manually by coastal inhabitants without attention to the ecological state of the site. In this case, the number of such bivalves per person per short period (day or week) could be increased in some cases (from 1–10 g/day to more than 100 g/day per person). It is hard to take into account such an increase in casual consumption. The use of the average consumption with the magnification effect could be taken into account in calculating specific ratios based on guideline limits established by the most reputable organizations, for example, JECFA (Joint FAO/WHO Expert Committee on Food Additives) and USEPA (U.S. Environmental Protection Agency). In this study, such key guideline limits as PTWI (provisional tolerable weekly intake, mg/kg b.w./week) and RfD (oral reference dose, μg/kg bw/day) were used for the assessment of the risks in the mussel consumption in selected coastal zones of Africa from Namibia (West) to Mozambique (East).

The widespread of the studied sites increases the importance of risk assessment of mussel tissues among different climatic zones and coastal conditions. The comparison of the levels of elements in other locations at different climatic zones inside South Africa, the data between other investigations, and recommended levels in a diet were described in detail in our previous work [17].

In this study, the analyzed zones were expanded to new water areas of Namibia, Mozambique (including typical local species such as *Modiolus* sp. and *Mytilus edulis*), and other sites of the Eastern part of South Africa. In addition, the levels of microelements in soft tissues and shells of mussels were compared.

2. Materials and Methods

2.1. Sampling

The mussels were collected at 17 stations along the coasts of Namibia, South Africa, and Mozambique during 2018 (Figure 1). From each site, around 10 individuals of the typical local size groups were chosen (representatives of the size of the mussel population) and one typical substrate based on accessibility for inhabitants. Such size of the sampling set did not harm the small local populations. The majority of mussels were *Mytilus galloprovincialis* with the exceptions-at st. 1 (*Mytilus edulis*) in Namibia and st. 16–17 (*Modiolus* sp.) in Mozambique.

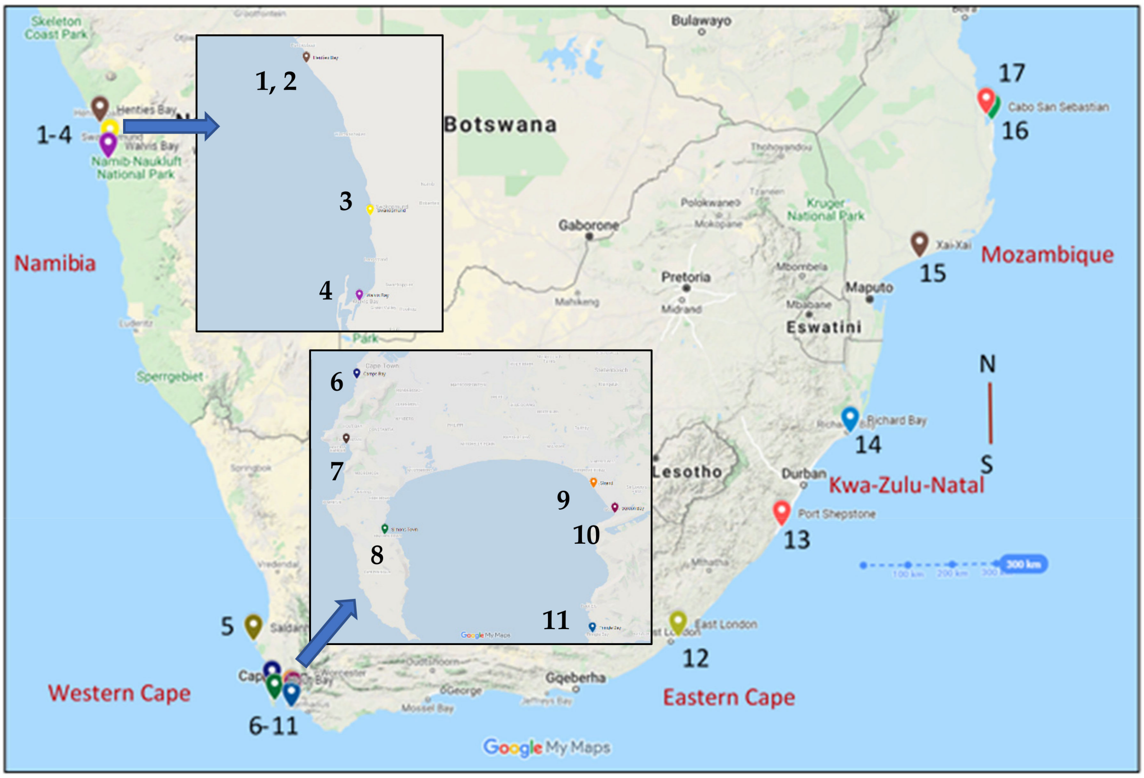

Figure 1. Sampling sites along the south coast of Africa.

The 11 stations were situated at the south-west coast of Africa: 4 in Namibia, 7–in the Western Cape region, and the other 6 were situated at the south-east coast of Africa: (1 in the Eastern Cape; 2 in Kwa-Zulu-Natal (South Africa), and 3 in Mozambique). The several populated cities were chosen as the sites for sampling, where the local inhabitants use the mussels as usual food.

The several stations (13–15) are situated relatively close to rivers, which transport high amounts of terrigenous and anthropogenic materials and increase the total turbidity due to the high content of suspended sediments.

In addition, samples were taken from protected areas: stations 5 (Saldanha outer bay adjacent to Langebaan lagoon), st. 11 (Pringle Bay, in proximity to the Betty's Bay Marine protected area), 16 (near the Cabo San Sebastian protected area), 17.

The Cape Town water area (st. 6–11) was detailed in sampling for determination of the local risky zones for human consumption of mussels in proximity to the Table Mountain National Park.

The climate conditions differ in a wide range: the stations 1–7 corresponded to cool temperate region with influence the Benguela current, 8–12—to warm temperate region with the Agulhas current, and 13–17—to a warm subtropical and tropical region with the particulate influence of the Mozambique current.

The salinity of sampling sites along Namibia (st. 1–4) and Cape Town water area (st. 5–11) usually fall in the range of 34.5–35.2 PSU [18], and the temperature falls in the range of 10–18 °C due to the cold Benguela current with the local reductions connected with cases to upwelling. St. 12–14 is situated at the Subtropical surface water mass, characterized by temperatures 13.1–22.2 °C and salinities 34.8–35.5 PSU. St. 15–17 were included in Tropical surface water mass, which is characterized by 21.5–30.0 °C and 34.4–35.7 PSU [19,20]. Drastic changes were not noted for the temperature and salinity at the studied sites.

In general, st. 1–4 are included in Erongo coastal zone, which presented the marine fisheries and fish processing, aquaculture, salt refining, mining, port, and other transportation activities, and recreational activities and tourism, the latter increasingly nature-based [21]. The port of Walvis Bay (St. 3, 4) is the main port of Namibia specialized in the shipping of different kinds of products, including the transport of ore and ingots from the hinterland mining activities [22].

The maritime transportation and different type of contamination (treated sewage effluent, agricultural, commercial and urban development) in areas of the Western Cape sector of sampling (St. 6–11) are the major contributors to the considerable stress of ecosystems [2]. Among the Cape Town area (including the False Bay) the st. 7 (Hout Bay), st. 8 (Simon's town), st. 10 (Gordon Bay) are considered as the more polluted sites due to fishing or recreational harbors (marinas) that may be affected by metal inputs associated with anthropogenic activities (e.g., discharge of untreated municipal wastewaters and polluting spills from marine traffic) [1].

St. 12–14 (East London, Port Shepstone, and Richards Bay) are considered as the local polluted sites in the eastern zone of South Africa, due to the harbor facilities and industrial development zones.

The Mozambique zone was represented by mussels from st. 15 situated in Xai-Xai (located near the mouth of the Limpopo River), st. 17 (Vilanculos) and 16 situated near Cabo San Sebastian protected area.

The conversion factor (CF) was calculated for typical samples from the Saldanha Bay area (CF [w.w./d.w.] = 0.32, where the w.w.—wet weight and d.w.—dry weight). The samples were frozen and transported for neutron activation analysis to Joint Institute for Nuclear Research, Dubna, Russian Federation.

The lengths of mussels from stations 1, 6, 7, 9, 10, 11, 14, 15 were in the range of 40–50 cm, and at st. 2, 3, 4, 8, 12, 13, 16, 17 were 60–80 cm.

2.2. Neutron Activation Analysis

For neutron activation analysis (NAA) each mussel was dissected with a plastic knife, separated into the shell and soft tissue, rinsed with deionized water to clean them from sediment particles and weighed. Then, after lyophilization, samples were dried to constant weight at 105 °C and homogenized to powder using a planetary mono mill with agate balls at 400 rpm (PULVERISETTE 6, Fritsch Laboratory Instruments GmbH, Germany). The individual material from for each station was analyzed independently. Subsamples of 0.3 g were packed into polythene bags for the determination of short-lived isotopes and aluminum cups for long-lived isotopes of elements.

Neutron activation analysis at the REGATA facility of the reactor IBR-2 (Dubna, Russian Federation) was applied for the determination of 24 macro- and microelements in soft tissues and 18 in shells for each pooled batch of mussels. This method fits well for the determination of specific groups of elements considered as key elements, which allow estimation of the contribution of terrigenous and anthropogenic factors [17]. The basic principles of NAA and characteristics of possible uncertainties are described in [23]. Details of the analysis performed at REGATA facility are presented in [24]. According to the following determination types, the instrumental neutron activation analysis was performed for 3 groups of elements [17]. The subsamples for short-lived isotopes (Mg, Al, S, Cl, Ca, Ti, V, Mn, I) were irradiated at a neutron flux of 1.6×10^{12} n cm^{-2} s^{-1} for 3 min and measured for 15 min. The subsamples for long-lived isotopes were irradiated with epithermal neutrons at a neutron flux of 3.31×10^{11} n cm^{-2} s^{-1} for 3 days after 4 and 20 days of decay samples were measured for 30 min (for such elements as Na, K, As, Br, and U) and 90 min (for Sc, Cr, Fe, Co, Ni, Zn, Se, Rb, Sr, Sb, Cs, and Th), respectively. The spectra of induced gamma activity were measured with HPGe detectors (Canberra) with a resolution of 1.9 keV at 1332 keV of the total absorption peak of ^{60}Co. The detector is calibrated using standard spectrometric and certified reference materials [25].

The Group Standard Sample (GSS) was created by using special software developed in FLNP JINR [25] from standard reference materials (SRMs) irradiated simultaneously with the samples. The GSS is also used to test the quality of the analysis by comparing the obtained and certified concentrations.

The standard reference materials provided by the National Institute of Standards and Technology (NIST), Institute of Nuclear Chemistry and Technology (INCT/ICHTJ), Joint Research Centre (JRC), Institute for Reference Materials and Measurements (IRMM) were used: NIST2709 (trace elements in soil), NIST1566b (oyster tissue), NIST1573a (tomato leaves), NIST1632c (Coal fly ash), NIST1549 (Non-fat milk powder), JRC-IRMM-BCR-667 (Estuarine sediment), NIST1547 (peach leaves), INCT-CTA-FFA1 (Fine fly ash), INCT-OBTL-5 (Tobacco leaves). For the 20 from 24 elements, the concentrations were in the range of 5% deviation between determined and certified values, reflected in the range 95–105% of recovery rates (Table 1). The determined, certified uncertainties and minimal detectable concentrations (MDC. ppm, dry weight basis) were calculated separately for each sample by equations from [24]. The use of standards of different matrices permitted the expansion of the number of determinable elements in the mussel samples [17]. Chemical matrix effects, which could cause errors in the other types of instrumental chemical analysis, are insignificant in NAA. In the case of small samples (size and weight), the use of reference materials with matrices different from the analyzed sample is provided by the insignificant matrix effect in NAA [23].

2.3. Statistics

The data was analyzed by Shapiro-Wilk and Levene tests. After that, the nonparametric Kruskal-Wallis test [26] was applied to examine the significance of differences among stations ($p < 0.05$). The multiple comparisons of mean ranks were calculated for all analyzed sets of samples.

The Factor analysis was used for the determination of the main groups of elements. Factor scores were calculated for demonstration of the contribution of factors among stations.

All test was performed by STATISTICA 12 (Stat Soft, Inc., Tulsa, OK, USA)

Table 1. Quality control of neutron activation analysis.

Elements	SRMs	Uncertainties %		Recovery Rate, %	MDC, ppm
		Determined	Certified		
Na	2709a	8.3	2.5	100.5	22
Mg	1566b	10.5	2.1	102	271
Al	1573a	5.6	2	99.7	12
Cl	1632c	8.4	3.6	100.7	141
K	1632c	10	3	103.1	523
Ca	1549	27.8	3.8	97.1	238
Sc	667	5.5	5.1	98.4	0.005
V	1547	11.6	8.1	101.9	0.1
Cr	FFA1	9.4	5.1	102	1.2
Mn	1573a	8	3.3	98.6	0.4
Fe	2709a	5.5	2.1	99.3	22
Co	667	4.2	5.6	101.4	0.02
Ni	FFA1	10	5.9	95.2	0.7
Zn	1632c	9.1	10.7	98.4	0.4
As	1632c	5.7	4.4	97.2	0.07
Se	667	44.2	5	106.9	0.15
Br	OBTL5	4.3	6.2	108.4	0.12
Rb	2709a	16.6	3	93.8	0.06
Sr	667	8.6	30	102.8	1.9
Sb	FFA1	8.9	14.2	98	0.002
I	1547	33.2	30	94.3	0.7
Cs	1632c	5.4	1.7	95.5	0.005
Th	667	4.5	5	103.5	0.007
U	1632c	3.9	2.3	95.5	0.03

MDC–minimal detectable concentrations (ppm, dry weight) for each element.

2.4. Risk Assessment

The risk for human health associated with mussel consumption was assessed by comparing their environmental status, reflected by the concentrations of the metals, and threshold levels, which could cause adverse effects in consumers. Therefore, a risks could be assessed by using the following approaches (based on [14,27,28])

- The concentrations in soft tissues (wet weight basis) could be compared with maximum permissible limits (MPLs), which are established as safety guidelines for several elements (Cr, Ni, Zn, As, Se) in seafood;
- The assessment of differences between estimated weekly intakes (EWI) and PTWI by calculation of risk quotient (RQ) for elements Na, Al, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Sr, Sb, I, U;
- The characterization of the amount of soft tissue (maximal provisional consumption rate MPCR, kg/week) that would need to be consumed per week by the average person to reach the provisional tolerable weekly intake (PTWI) established by the JECFA or related reference limits;
- Target hazardous quotient (THQ) and total hazardous index (HI) which corresponded to the sum of all quotients from elements with recommended RfDs ([29]: Mn, Fe, Co, Ni, Zn, Se, Sr, Sb, I, U) as its combinations for each station for the local coastal population

The key ratios and limits were used in the following specification:

The maximal permissible levels (MPL, μg/g of wet weight) correspond to upper levels of concentrations of trace elements in food, water or soil, which would not cause any adverse effects. The MPLs of elements in seafood were established by organizations such as the European Commission or the United States Food and Drugs Administration (JECFA, [30]) only for Cr, Mn, Zn, As and Se.

PTWI represents the permissible exposure in humans during a week as a result of the natural occurrence of a substance in food and drinking water. PTWI is used for food hazardous substances with cumulative properties. Consumption of seafood containing high levels of the contaminant could lead to the exceedance of its weekly tolerable intake. The assessment takes into account daily variations, the primary concern being prolonged exposure to the contaminant because of its ability to accumulate within the body over a period. For several elements PTWI was calculated on PMTDI–provisional maximum tolerable daily intake, μg/kg bw/day). The PTWI for As was considered as for total arsenic and determined from the equation: 15/0.42 = 35.7 μg/kg bw/week by using the ratio of inorganic/total = 42% from [31]. The PTWI for Cr was calculated based on upper limit of the recommended dietary allowances (0.05–0.2 mg/day) from [32] by using modified equation from [33].

Reference dose (RfD) is a daily oral exposure corresponding to risk from dangerous effects to the whole human population during its lifetime in the studied region, The RfD can be derived from NOAEL (no-observed-adverse-effect level) or LOAEL (lowest-observed-adverse-effect level)

MPCR (kg) is the maximal permissible consumption rate, which can lead to exceeding the PTWI limit. This value was calculated for maximal individual concentrations obtained from each station. The MPCR was calculated only for elements for which PTWI values are available in the literature.

EWI (μg/kg bw/week) is the estimated weekly intake, which was calculated using the equation:

$$\mathrm{EWI} = \frac{\mathrm{C}\cdot\mathrm{CR_W}}{\mathrm{BW}} \tag{1}$$

where C–concentration of element (μg/g); CR_w–weekly consumption rate (200 g/week in our study); BW–body weight (kg). Average BW (body weight, kg)for South Africa, it was calculated from the mean body mass index and height of men and women according to the national survey conducted in 2016 [34]. The mean weight of women aged 25+ was 75.6 kg and for men aged 25+, 71.8 kg. A nominal 70 kg was used as a representative mean value of weight among the whole adult population, including the 18–25 age group.

EDI (estimated daily intake, μg/kg bw/day) was calculated by using a daily consumption rate (200 g/wekk = 28.6 g/day).

Risk quotient (RQ) was assessed as a ratio between estimated weekly intake (EWI) and provisional tolerable weekly intake (PTWI), which was presented by JECFA [35].

Risk quotients were assessed based on the adopted ratio from [13]. RQ > 1 corresponded to a potential human health risk scenario in the case of consumption of mussels with an average and maximum concentrations of each element with existing PTWI.

Target hazardous quotient (THQ), which was developed by USEPA [36], assess the risk for human health from non-carcinogenic elements in the local human population over a lifetime in comparison with the reference oral dose (RfD from EPA's IRIS–Integrated Risk Information System). THQ was calculated using the equation [28]:

$$\mathrm{THQ} = \frac{\mathrm{EF}\cdot\mathrm{ED}\cdot\mathrm{CR}\cdot\mathrm{C}\cdot 10^{-3}}{\mathrm{RfD}\cdot\mathrm{BW}\cdot\mathrm{AT}} \tag{2}$$

where EF is the exposure frequency (365 days); ED is exposure duration (average expectancy is 70 years); CR is consumption rate (28.6 g/day/person), C is the concentration of element (wet weight basis), RfD is reference dose (μg/kg bw/day); BW is body weight (for South Africa the average weight was established as 70 kg); AT is 30 years, an average exposure time for non-carcinogens. THQ > 1 corresponds to the high potential risk for human health in constant dietary conditions over a lifetime.

HI (total hazard index) is calculated as summarize values of THQs of n elements for each station:

$$\mathrm{HI} = \sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{THQ_i} \tag{3}$$

Total hazard index HI > 1 designates the hazard risk on human health for the local population based on multiple elements in mussels.

The assessment was conducted for each individual separately. It is important to note the differences in the accumulation of macro and microelements according to the size of organisms between stations. However, comparing the studied ratios based on the average values of concentrations calculated for each set, and the total consumed amount of soft tissue did not show any effect of size. The risks of mussels consumption for local human populations were not directly connected with the size of the individuals.

Risks were assessed for toxic elements with established guideline levels to identify the potentially hazardous. Depending on the different approaches applied to assess the potential health risk of mussels' consumption for local coastal populations, separated conclusions were suggested.

3. Results and Discussion

3.1. Concentrations of the Elements in Soft Tissues and Maximum Permissible Levels

Mussels from Namibia revealed significantly higher levels of Zn, Se ($p < 0.02$) with the highest values at st. 1 than in the majority of other sets (Table 2). The st. 1 stands out of st. 2–4 due to higher concentrations of Zn, Se. It could be explained by a species-specific accumulation of elements by the individuals of the *Mytilus edulis* at this station.

The levels of elements in the samples from the Saldanha outer bay were close to ranges determined in mussels from Cape Town and False Bay, except for Se, which was on the level of samples from Namibia. The mussels from the Cape Town and False bay water areas revealed insignificant higher values of Ca, Sr, and Zn than several other sets.

The mussels from Eastern South Africa including the polluted harbor area of the Richards Bay (st. 14) revealed significantly higher values ($p < 0.05$) of such elements as Al, Sc, V, Cr, Mn, Fe, Co, Ni, Sb, Cs, Th than the mussels from the majority of the other stations, probably due to the contribution of the river runoff and re-suspended polluted sediments.

Mussels from Mozambique are characterized by significantly higher levels of Na, As, Br, and I. It is interesting to note that mussels at the st. 15 revealed higher levels than the other Mozambique samples (st. 16, 17) and similar levels ($p < 0.01$) as the stations from Eastern South Africa (st. 12–14) for such elements as Al, Cr, Fe, which corresponded to terrigenous suspended material. In addition, this observation could be explained by species-specific accumulation features of *Modiolus* (st. 16, 17).

The concentrations of 4 elements (Cr, Zn, As, Se) were compared with existing maximum permissible levels (according to [37,38]) The maximum permissible levels were converted from recommended wet weight values to dry weight basis using the average conversion factor for analyzed samples to simplify the demonstration of the general picture.

The highest concentrations (interquartile ranges) above MPL (Figure 2):

- Cr content in mussels at st. 3 (Namibia), 12–15 (Eastern SA and Mozambique) reached MPL within the interquartile range. At st. 14 (Richards Bay) and 15 (Xai-Xai), the levels of Cr in all individuals were above MPL and significantly higher ($p < 0.04$) than at the other stations that can be explained by the matter of the terrigenous origin and features of suspended sediments from river runoff, which could be accumulated by mussels
- Zn content reached MPL only at st. 1 (Henties Bay, Namibia) and significantly higher ($p < 0.001$) than at other stations, which is probably associated with high anthropogenic inputs and its higher accumulation by *Mytilus edulis* in comparison with *Mytilus galloprovincialis* (almost the same site, st. 2)
- As content exceeded the MPL at the stations 1–3 (Namibia), 8–11 (Western Cape), 12, 13 (East of SA), and 15–17 (Mozambique) with the significantly higher levels at st. 16 and 17 ($p < 0.01$). The lower levels of As at st. 4–7 could be explained by local shifts of water masses during upwelling
- Se content exceeded the MPL at stations 1–6 (Namibia and Saldanha bay), st. 7 (Hout Bay), st. 13 (Port Shepstone), st. 16 (San Sebastian, Mozambique) with significantly higher levels at st. 1 and 16 ($p < 0.02$). The distribution of Se could be explained by the local growth of the phytoplankton assemblages, which are used by mussels as a food

Table 2. Concentrations of elements (mean±standard deviation, ppm, dry weight basis) in soft tissues of mussels among studied zones.

Zones	**Namibia**	**Saldanha Bay**	**Cape Town**	**False Bay**	**Eastern SA**	**Mozambique**
Stations	**St. 1–4**	**St. 5**	**St. 6–7**	**St. 8–11**	**St. 12–14**	**St. 15–17**
Samples	**n = 36**	**n = 10**	**n = 18**	**n = 40**	**n = 28**	**n = 29**
Elements						
Na	33,110 ± 4970	25,080 ± 4110	37,950 ± 5600	35,280 ± 3850	31,450 ± 5970	39,870 ± 8960
Mg	6020 ± 1010	4350 ± 860	6760 ± 700	6720 ± 750	6020 ± 730	7530 ± 1130
Al	560 ± 270	100 ± 50	440 ± 340	290 ± 110	2880 ± 610	1200 ± 240
Cl	53,920 ± 7850	41,960 ± 6610	57,300 ± 8450	56,000 ± 7800	54,320 ± 10,530	62,210 ± 14,880
K	8510 ± 1520	7720 ± 1530	5570 ± 720	6820 ± 990	4170 ± 630	5030 ± 1580
Ca	4710 ± 1320	3000 ± 560	8570 ± 4490	8370 ± 3860	5700 ± 1120	7140 ± 1810
Sc	0.13 ± 0.08	0.02 ± 0.01	0.09 ± 0.03	0.05 ± 0.02	0.62 ± 0.17	0.34 ± 0.1
V	1.3 ± 0.5	0.8 ± 0.2	0.8 ± 0.3	1 ± 0.3	6.3 ± 1.4	6.6 ± 2.7
Cr	2.9 ± 1.9	2.4 ± 0.7	3.3 ± 1.2	2.4 ± 0.9	12.9 ± 5.3	15.8 ± 9.8
Mn	9 ± 4	3 ± 2	7 ± 3	7 ± 2	34 ± 7	19 ± 8
Fe	550 ± 240	150 ± 70	330 ± 90	250 ± 70	1980 ± 470	1280 ± 380
Co	1.37 ± 0.97	0.64 ± 0.17	0.31 ± 0.06	0.26 ± 0.07	4.68 ± 2.64	1.52 ± 0.32
Ni	9.4 ± 4.9	3.1 ± 0.9	2.5 ± 0.7	1.6 ± 0.6	15.1 ± 7.6	9.4 ± 3.8
Zn	290 ± 170	200 ± 60	240 ± 90	180 ± 60	90 ± 20	100 ± 20
As	6.9 ± 1.3	4.4 ± 1	5.8 ± 0.5	7.2 ± 1.1	9.4 ± 1.7	20.9 ± 7.2
Se	6 ± 1.3	3.9 ± 1	3 ± 0.8	2.2 ± 0.5	3.6 ± 0.6	3.8 ± 0.6
Br	314 ± 48	203 ± 28	336 ± 40	292 ± 24	326 ± 58	559 ± 164
Rb	3.9 ± 0.7	3.7 ± 0.4	3.7 ± 1.3	3.6 ± 0.4	4.4 ± 1	3 ± 0.5
Sr	48 ± 11	30 ± 6	95 ± 32	88 ± 38	60 ± 11	85 ± 12
Sb	0.03 ± 0.01	0.01 ± 0	0.09 ± 0.11	0.03 ± 0.01	0.09 ± 0.03	0.06 ± 0.01
I	16 ± 6	5 ± 2	16 ± 2	12 ± 3	26 ± 4	57 ± 13
Cs	0.07 ± 0.03	0.02 ± 0.01	0.13 ± 0.1	0.06 ± 0.03	0.15 ± 0.04	0.05 ± 0.02
Th	0.21 ± 0.19	0.01 ± 0.01	0.15 ± 0.14	0.07 ± 0.03	0.79 ± 0.25	0.4 ± 0.23
U	0.19 ± 0.08	0.1 ± 0.04	0.31 ± 0.09	0.19 ± 0.06	0.26 ± 0.09	0.35 ± 0.12

It is interesting to note that concentrations of As in soft tissues of mussels from st. 7 (Hout Bay), which were the most polluted, were lower than values reported for mussels collected in the same year [17].

According to this approach (comparison with MPLs), the highest levels were found in mussels at st. 14 and 15 (based on the content of Cr), 16 and 17 (As and Se), and st. 1–4 (Se).

3.2. Groups of Elements

The factor analysis revealed such groups of elements (the proportion of total variance in percent and assumed origin were given in brackets):

- F1 (29%, terrigenous): Al, Sc, V, Cr, Mn, Fe, Rb, Cs, Th.
- F2 (13%, salinity): Na, Mg, Cl
- F3 (9%, shell construction): Ca, Sr
- F4 (13%, mixed): As, Br, I
- F5 (6%, mixed): Zn, Se
- F6 (8%, anthropogenic): Co, Ni, Sb

The assumption of factors origin was determined based on the typical properties of elements reported in the literature [39] and their revealed contribution at studied polluted and protected sites (Figure 3).

The important factors (according to a higher proportion of total variance) were terrigenous and anthropogenic. Factor 2 (Na, Mg, etc.) includes major salinity ions, connected with marine waters [40]. Analysis of the factor scores showed the high contribution of Factor 1 (Al, Sc, etc.) at st. 12–14. Factor 4 associated with the elements (As, Br, I) of mixed origin is presented with the highest contribution at st. 13–15.

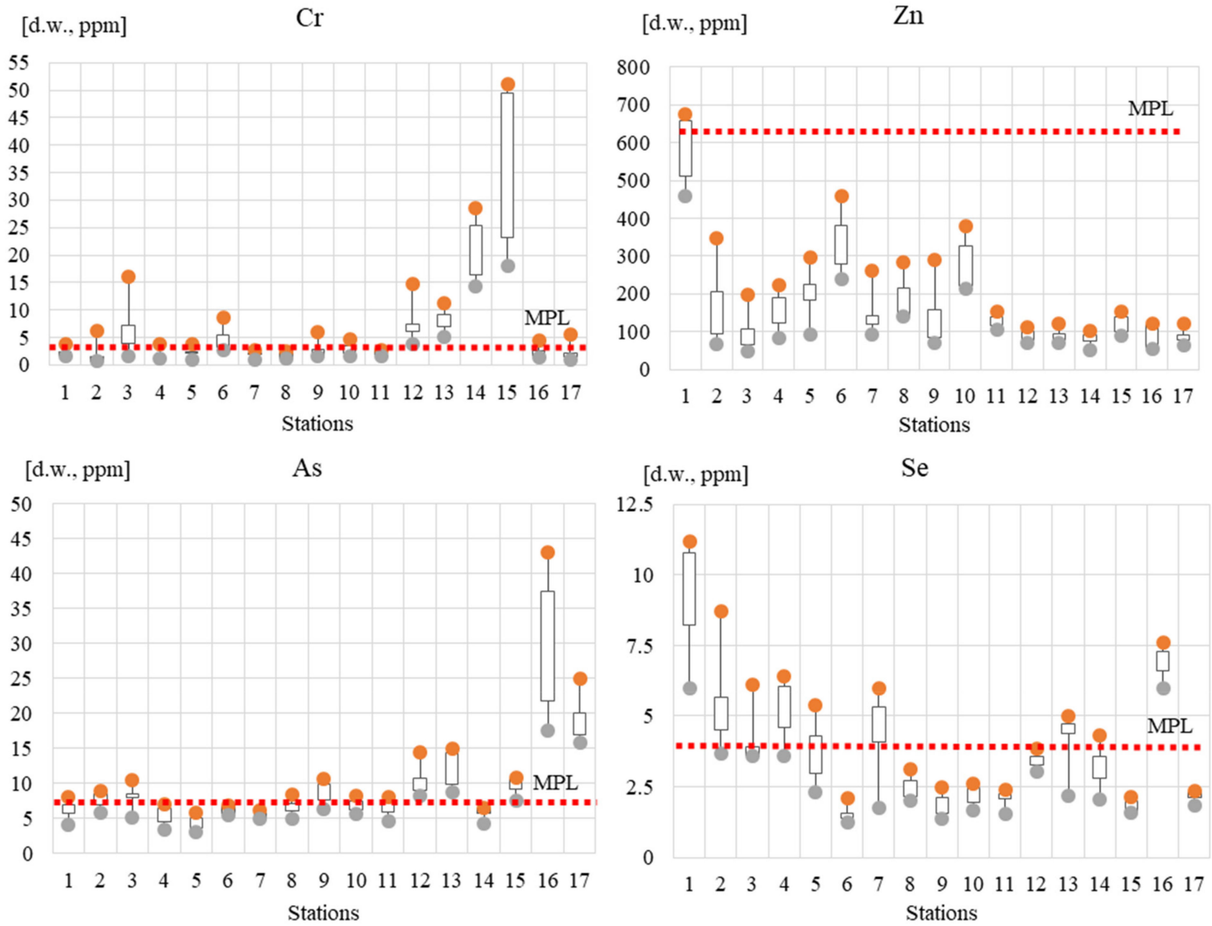

Figure 2. Levels of concentrations in dry weight of soft tissues and maximum permissible levels. The point markers–min and max, boxes–interquartile range. Red dotted line corresponds to MPLs.

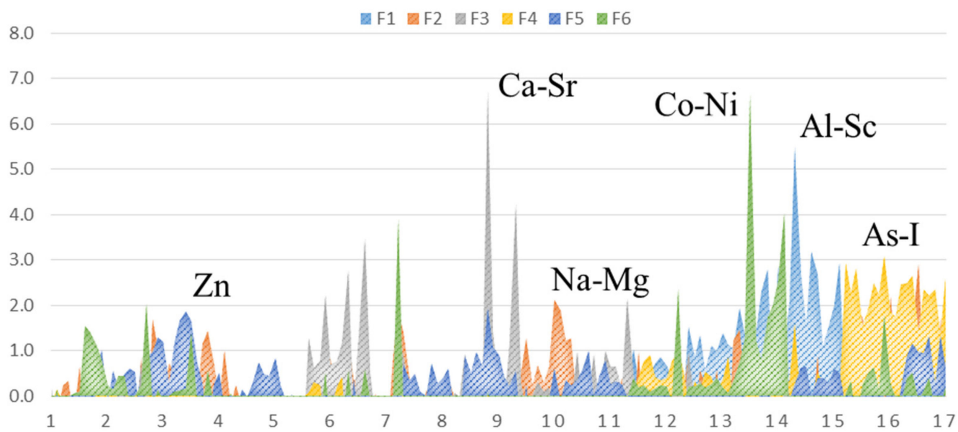

Figure 3. The elements with the highest factor scores in the factor analysis among studied stations.

The influences of the high productivity waters of the Agulhas Retroflection [41] and the high concentrations of chlorophyll-*a* along the west coast tend to increase such elements as Zn, Se (F5), Ca, Sr (F3), and Na, Mg, S, Cl (F2) at the western stations 1–3 and several stations (6, 8, 9). It was probably due to several reasons including the growth of phytoplankton, connected with the upwelling of mineral-rich water from the cold depths of the South Atlantic Ocean, forming the parts of the Benguela Current. Factor 6 (Co, Ni, Sb) was probably also connected with the local pollution features.

According to factor analysis, the main sources of elemental inputs in mussel tissues could conditionally be divided into:

- Terrigenous elements (Al, Sc, V, Cr, Mn, Fe, Rb, Cs, Th)—connected with suspended sediments and river runoff
- Anthropogenic elements (Co, Ni, Zn, As, Se, Br, I, Sb)
- Marine (Na, Mg, Cl)
- Others (K, Ca, Sr, U)

It is important to note the mixed contributions for several elements. The distribution of Zn, Br, and I could be connected with natural influences of mussel diet objects such as phytoplankton, parts of macroalgae, detritus, which are occasionally accumulated by mussels at local sites. In addition, the natural levels of Zn could be considered as constant in the range of salinity 5–30 PSU according to data of [42]. The relatively higher concentrations of such elements as As, Se in mussels from the East part of South Africa and Mozambique could be explained due to the higher salinity. It agreed with the positive relationships between major cations and trace oxyanions (As, Se) found by Liu and Wang [42]. They concluded that the accumulation of arsenobetaine by *Mytilus edulis* depended on seawater salinity (higher concentrations corresponded to the higher salinities). The concentrations of As in soft tissues could be highly dependent on salinity-dependent osmoregulation other than ambient As concentrations. The main source of Se is the ingested food of mussels, but the possible bioaccumulation of Se in bivalves could be related to osmotic regulation (as well as As) due to the predominant presence of Se in organic form [43]. Iodine in several studies was proposed as a hydrochemical indicator of petroleum [44]. Özdemir [44] found a strong relation between organic C and I concentrations in marine sediments, which could be accumulated by mussels in coastal zones. On the other hand, due to the fact, that the tropical water areas of South Africa and Mozambique are characterized by relatively higher temperatures, river sediment, and nutrient-rich runoffs, the microalgae assemblages developed in the coastal zones could increase the content of I in mussels as well.

3.3. Risk Quotients and Maximum Provisional Consumption Rates among 14 Elements

The differences between estimated weekly intakes and provisional tolerable weekly intakes are reflected in ratios of risks quotients.

The highest RQ values (Figure 4) were characteristic for mussels from st. 13–15 (according to intakes of Al), st. 14, 15 (based on intakes of Cr), st. 14 (Ni), and st. 16 (As). The differences between intakes of analyzed elements are explained by two components of the accumulated suspended matter: terrigenous (Al, Cr) and anthropogenic (Al, Cr, Ni, As).

The maximum provisional consumption rate (MPCR) corresponded to risk quotients but showed the amounts of soft tissues, which should be consumed to reach the limit established by JECFA (PTWI) in mg per person per week (Table 3). Usually, the typical average consumption rate for a person consists of 200 g/week as an average size of a meal in coastal cities [14]. The lower values of MPCR reflect the high risks for human health on such constant levels of mussel consumption.

Al as an element corresponding to the terrigenous suspended matter had the minimal MPCR at st. 3, 12–15. Similarly, the other terrigenous elements such as Cr and Fe had high MPCR at st. 14 and 15. According to factor analysis, such elements as As and I are considered anthropogenic, which are probably derived from fertilizers' production and application, emissions of coal-burning power stations [45], and petroleum [44]. MPCRs of As and I were lower at st. 16 and 17. Ni had low MPCR at st. 3 and 14, which was probably connected with the shipping of the metallurgic products.

Therefore, the riskiest sites were considered st. 3, 12–17 according to the minimal levels of MPCR (<0.2 kg/week) for such elements as Al, Cr, Fe, Ni, As, I.

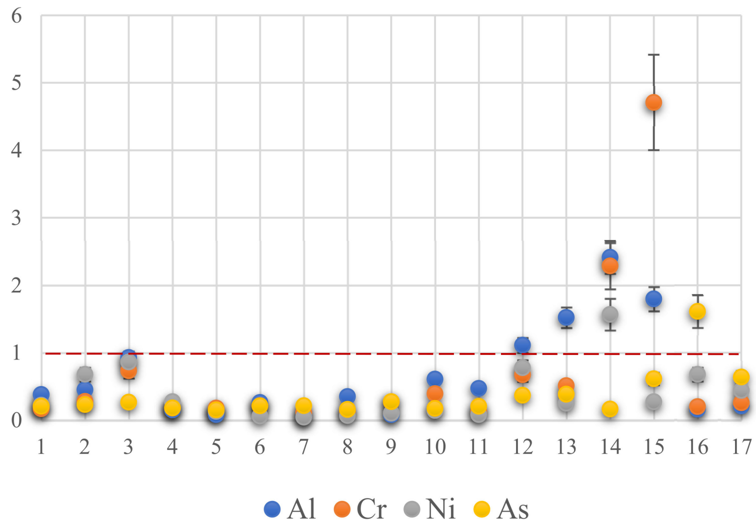

Figure 4. Risk quotients (RQ) of Al, Cr, Ni, and As in mussels from studied sites.

Table 3. The maximum provisional consumption rates (MPCR) for selected elements.

Regions	Species	St.	Sampling Sites	Na	Al	Cr	Mn	Fe	Co	Ni	Zn	As	Se	Sr	Sb	I	U
Namibia	*ME*	1	Henties Bay	138	0.5	1.2	32	1.7	61	0.9	2	1	0.7	13	14	1.3	10
	MG	2	Henties Bay	173	0.4	0.7	21	2.1	37	0.3	4	0.9	0.9	20	22	0.7	26
	MG	3	Swakopmund	120	**0.2**	0.3	7	0.8	25	**0.2**	8	0.8	1.3	12	13	0.6	7
	MG	4	Walvis Bay	111	1.3	1.1	22	1.2	163	0.7	7	1.1	1.2	12	9	1	35
Western Cape	*MG*	5	Saldanha outer bay	165	2.4	1.1	37	4.2	166	1.5	5	1.3	1.4	22	38	3.3	21
	MG	6	Camps Bay	112	0.3	0.5	18	2	333	1.4	3	1.1	3.7	6	5	0.9	9
	MG	7	Hout Bay	117	0.6	1.6	17	3.3	425	2.9	6	1.3	1.3	5	1	2.7	9
	MG	8	Simonstown	128	4.1	1.8	32	3.6	613	4.5	5	0.9	2.5	11	12	1.8	16
	MG	9	Strand	137	2.4	0.7	32	3.4	326	2	5	0.7	3.1	2	14	2.2	12
	MG	10	Gordon Bay	122	0.8	0.9	9	3.2	479	3.3	4	0.9	2.9	10	13	0.9	20
	MG	11	Pringle Bay	134	0.4	1.6	36	2.9	393	2.4	10	1	3.2	6	7	1.8	14
Kwa-Zulu-Natal	*MG*	12	East London	115	**0.1**	0.3	6	0.6	19	0.3	14	0.5	2	14	7	0.7	8
	MG	13	Port Shepston	130	**0.1**	0.4	5	0.5	59	0.8	13	0.5	1.5	8	5	0.6	11
	MG	14	Richards bay	146	**0.1**	**0.2**	4	0.4	7	**0.1**	15	1.2	1.8	16	3	1.3	14
Mozambique	*MG*	15	Xai Xai	125	**0.1**	**0.1**	2	**0.2**	39	0.7	10	0.7	3.6	14	13	1.2	9
	Ms	16	Cabo San Sebastian	85	1.2	1	50	3.3	88	0.3	13	**0.2**	1	6	7	0.3	9
	Ms	17	Vilanculos	88	1	0.8	22	3.1	140	0.5	13	0.3	3.2	7	7	**0.2**	6
	PTWI [mg/kg bw/week]			24500	2	0.02	0.98	5.6	0.7	35	7	0.036	0.035	4.2	0.003	0.12	0.02

Species: *MG—Mytilus galloprovincialis*, *ME—Mytilus edulis*, *Ms—Modiolus* sp. PTWIs for Fe, Co, Se, Sr, Sb, I and U were calculated from PMTDI [35] and corresponding RfD. MPCR ≤ 0.2 are marked in red.

3.4. Target Hazard Quotients and Total Hazard Indices

THQ is a ratio that illustrates the long-term non-carcinogenic exposure probabilities and reflects the risk associated with the consumption of the contaminated mussels [46]. The values below 1 (THQ < 1) are associated with lower levels of exposure, which is not likely to cause any harmful effects for human health during a lifetime in the population.

According to Table 4, the low levels of THQs were obtained for all sites except at the st. 14 and 15 with the THQ > 1 for Co. It agreed with the presence of Ni (which connected with Co) in calculated levels of high risks based on the RQ and MPCR. THQ values for all tested elements (except Co) in all individuals based on medians from mussel samples indicate that no target health risk is present according to established RfD. However, the total hazard indices demonstrated the high (HI > 1) levels at st. 1, 12–17 that correspond to possible risk during high consumption of mussels. The major contributors to HI were such elements as Co (1–6, 12–17), Zn (st. 1), Se (st. 1, 2, 16) and I (st. 3, 12, 13, 16, 17), which are included in the anthropogenic group according to factor analysis (described in Section 3.2).

Table 4. Target hazard quotients and hazard indices from Namibia to Mozambique based on medians.

Stations	Mn	Fe	Co	Ni	Zn	Se	Sr	Sb	I	U	HI
1	0	0.08	0.35	0.01	0.21	0.22	0.01	0.01	0.09	0.01	**1**
2	0.01	0.06	0.36	0.04	0.05	0.12	0.01	0	0.08	0	0.72
3	0.02	0.15	0.48	0.03	0.03	0.08	0.01	0.01	0.15	0.01	0.95
4	0	0.05	0.25	0.02	0.06	0.12	0.01	0.01	0.07	0	0.58
5	0	0.02	0.23	0.01	0.08	0.09	0.01	0	0.03	0	0.48
6	0.01	0.07	0.15	0.01	0.11	0.03	0.02	0.02	0.17	0.01	0.6
7	0	0.04	0.09	0	0.05	0.1	0.01	0.01	0.03	0.01	0.35
8	0	0.02	0.08	0	0.06	0.05	0.01	0.01	0.06	0.01	0.31
9	0	0.03	0.09	0	0.05	0.04	0.02	0	0.05	0.01	0.3
10	0.01	0.05	0.1	0	0.1	0.05	0.01	0.01	0.11	0.01	0.46
11	0	0.05	0.1	0	0.05	0.05	0.02	0.02	0.08	0.01	0.37
12	0.02	0.24	0.92	0.02	0.03	0.08	0.01	0.02	0.19	0.01	**1.55**
13	0.03	0.34	0.8	0.02	0.03	0.1	0.01	0.02	0.22	0.01	**1.59**
14	0.04	0.36	**2.64**	0.05	0.03	0.06	0.01	0.03	0.11	0	**3.33**
15	0.03	0.48	**1**	0.02	0.05	0.04	0.01	0.01	0.1	0.01	**1.76**
16	0	0.05	0.36	0.02	0.04	0.16	0.02	0.02	0.45	0.01	**1.12**
17	0	0.05	0.26	0.02	0.03	0.05	0.02	0.02	0.55	0.02	**1.03**
RfD	140	700	0.3	40	300	5	600	0.4	17	3	

0 corresponded to values less than 0.01. Cr and As were excluded from the analysis due to the unavailability of the data about the percentage of their toxic forms in the mussels. For THQs of Fe, Co, I and U, the RfDs was calculated from maximums PMTDIs.

3.5. Groups of Elements in Shells of Mussels

The obtained concentrations of elements in shells revealed such main features:

- Sc, Cr, Mn, Sb, Cs, Th reached close levels in comparison with soft tissues
- Ca and Sr were accumulated to 10 times higher levels than in soft tissues
- Cl and Zn were accumulated to 10–100 times lower concentrations than in soft tissues
- In polluted zones, V, Co, Ni, Br, U were accumulated at close levels in shells and in soft tissues

The content of elements of terrigenous origin (f. e. Al, Sc, etc.) were higher at st. 1–4, 10, 13, 14 that partly agreed with the data on soft tissues. Iodine revealed higher levels at st. 1–4, 10, 11. Concentrations of other elements, including As, Se in shells are on the level at the detection limits and insignificantly differed between the stations.

Mg/Ca and Zn/Ca ratios in shells characterize the regional patterns in the accumulation of elements by mussels (Figure 5). The samples from the Western Cape water area revealed higher levels of Mg/Ca in comparison with the samples from Namibia (except st. 1), the East coast, and Mozambique. It was probably connected with the state of organisms based on a constant temperature in these localities (mechanism was described in [47]. Fe/Ca, Co/Ca, Ni/Ca were higher in shells from the Namibian st. 1, 2, indicating the possible long-term pollution or specific content of coastal suspended materials. Mn/Ca ratio revealed the higher levels in shells from st. 7, 10, 12–15 and probably connected with the local pollution features of the river runoffs.

Therefore, there were no found similar patterns between the levels of elements in the soft tissues and the shells. This could be explained by the long-term pollution features at the studied stations, which are reflected in the accumulation of trace elements in the shells, while the levels of elements in the soft tissue correspond to the latest period of exposure. In addition, the self-cleaning process regulates the levels of pollutants at the same time.

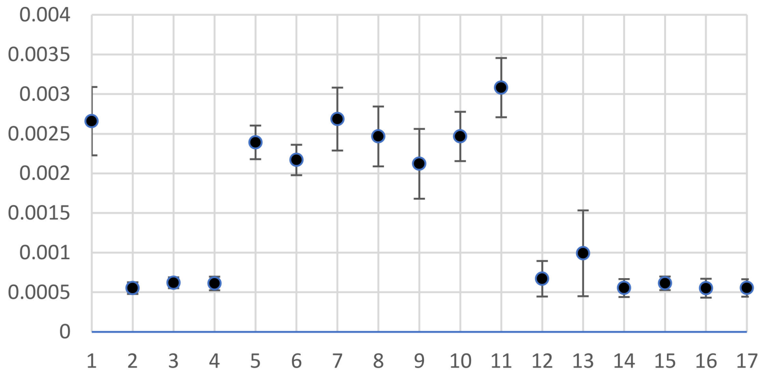

Figure 5. The ratio Mg/Ca in shells of mussels along the African coast.

3.6. *Elements with High Risks in Human Consumption*

After applying four approaches, such elements as Al, Cr, Fe, Co, Ni, Zn, As, Se, I were considered as having the potential risk for human health at the consumption of mussels in the studied areas (Table 5). Exceedance of the guideline limits (MPL and MPCR) by these elements could cause harm to human health in the consumption of mussels from the studied areas.

Table 5. Elements with high risks according to 4 approaches.

	Namibia			Western Cape								East of SA			Mozambique		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
MPL	Zn, As, Se	As, Se	As, Cr, Se	Se	Se	Cr	Se	As	As, Cr	As, Cr	As	As, Cr	As, Cr, Se	Cr	As, Cr	As, Se	As
MPCR (<200 g/week)			Al, Ni									Al	Al	Al, Cr, Ni	Al, Cr, Fe	As	I
RQ>1												Al	Al	Al, Cr, Ni	Al, Cr, Fe	As	I
THQ>1														Co			

■—Al; ■—Cr; ■—Fe; ■—Co; ■—Ni; ■—Zn; ■—As; ■—Se; ■—I.

According to the factor analysis, such elements as Al, Cr, and Fe correspond to terrigenous component with the additional insignificant anthropogenic sources (due to close distribution to such conservative elements as Sc, Th). However, it is important to note that the mussels from st. 3 (Swakopmund), 12–15 (Eastern part of South Africa and Vilanculos in Mozambique) could accumulate Al, Cr, and Fe from pollution sources mentioned earlier due to higher resulting levels in soft tissues. Such elements as Co, Ni, Zn, As, Se, and I were suggested to have an anthropogenic origin. In comparison with the previous data [17], in the present study, the levels of Fe and Ni are considered hazardous.

The nutritional contribution of Co is fundamentally associated with the vitamin B_{12} content in the food. The nutritional requirements for Co are not high (of the order of 0.1 µg/kg/day); therefore, it is usually considered as a toxic metal, which can cause cardiomyopathy or polycythemia when the exposure to it is excessive [4]. According to [4], the average consumption of mollusks represents a contribution of around 40% of the daily requirements of Co for the human body. In our study, the MPCR for Co is much higher than for other elements (Table 3). It corresponds to the safe level of consumption. However, the levels of THQ for Co (2.6, corresponding to the recommended oral RfD) revealed a high risk associated with this element at st. 14 (Richards Bay). It could be explained by the polluted features of the harbor [48].

Nickel plays a physiological role in folate metabolism and is essential for normal growth and reproduction in animals and humans [14]. However, Ni could cause allergic reactions and long-term exposure could result in reproductive diseases [31]. Nickel revealed the high-risk quotient (RQ = 1.6) and MPCR (0.1 kg/week) at st. 14 (Richards Bay). The obtained Co and Ni levels in mussels from this site reflect the polluted features of the harbor (see Section 3.7).

Zinc is an essential trace element; it is known the high number of the requirements for zinc changes throughout life and the health effects associated with zinc deficiency. Zn is a key component of cells and plays a role in the mechanism of action of several crucial enzymes. The natural levels of this element are the highest in oysters. Zinc is utilized as a protective coating of other metals, dye casting, construction industry, fungicide, and other products. Natural emissions results from erosion and forest fires. Rodríguez-Hernández et al. [4] assumed that moderate consumption of mussels contributes to 20% of the nutritional requirements of Zn in adults and up to 35% in children. In comparison with the previous data [17], the Zn content exceeded the MPL only at st. 1 (see Section 3.1).

The high levels of arsenic could be associated with pesticides, manure, mining, and smelting activities. Groundwater contains higher levels of arsenic due to thermal activity or the dissolution of arsenic minerals [49] and could be the source of dissolved As in coastal waters due to submarine discharges. The excess of As could cause dermatitis, lowered neuron transmission, and liver carcinoma may develop [27]. Potentially toxic levels of As could increase to 42% of the total amount [31]. An average consumer of mussels would be exposed to approximately 23–25% of the TDI (tolerable daily intake) of this element according to [4], which, although being relatively high value, is far from representing a real problem for public health. However, it should be noted that mussel consumers in the high percentile would be exposed to up to 75% of the toxicity reference value of this element and could even surpass it if they only consume fresh or frozen mussels. The oral RfD for inorganic As was established by USEPA at the level of 0.0003 mg/kg-day in 2021 [29].

In our study, the levels of As were risky at the majority of stations. The MPL was exceeded for As at st. 1–3, 8–13, 15–17. MPCR was 0.2 kg/week per person at st. 16. The THQ for As was higher than 1.0 at st 2, 3, 8–17, but As was excluded from the resulting Table 4 due to using RfD value for inorganic As.

Selenium is a trace element required for different biological processes and is considered a key nutraceutical component. It is essential due to its association with proteins, known as selenoproteins. However, it could be also a hazardous element due to toxicity at a narrow difference between essentiality and harm. The coastal population is exposed to major sources of aquatic Se through oil combustion, coal-fired power stations, sewage effluent [50]. Chronic toxicity of selenium in humans results in a condition termed selenosis [51]. The contribution of Se from mussels is so striking that children who are large consumers would intake up to 500% of their daily nutritional requirements [4]. This contribution would be even higher (more than double) if only fresh mussels are consumed. In our study, the levels of Se in mussels exceeded MPL at the western stations (1–5; 7) and several eastern stations (13, 16). This approach reflects the specific biochemical processes in local zones. Ibrahim [52] found the absence of a strong and negative correlation of Se with salinity and concluded that the levels of Se in the marine environment are mainly controlled by the utilization of microalgae, redox potential, and diffusion from sediments. According to oral RfD, the lowest MPCRs were found at st. 1 and 2 (0.7 and 0.9 kg/week) that were higher than the assumed average consumption (0.2 kg/week). In addition, the low levels of THQ indicated the absence of risk in consumption according to two other approaches (RQ and MPCR).

Iodine is considered as the key component in the thyroid hormones thyroxine and triiodothyronine. Deficiency can lead to many diseases, ranging from enlargement of the thyroid to severe cretinism with mental retardation. High consumption of iodine by humans can lead to goiter, hypothyroidism, or hyperthyroidism [53]. An upper threshold for iodine concentration in drinking water lies in the range of iodine concentration from 250 to 300 µg/L. The excess of this level leads to an increase of goiter among the children [54]. Marine organisms accumulate iodine on external neritic seafloor together with inorganic matters and in bathyal reduction environment, and in clayed sediments, which are primary sources of iodine in oil and gas reservoir waters [44]. The concentration of I at st. 17 was higher than at st. 2, 4, 5, 7–9, 11 ($p < 0.001$). It is interesting to note that in comparison with the previous data, the highest levels of I were early found at western stations, but in this study, the high levels of RQ and MPCR (0.2 kg/week) for I indicate the possible risk at the eastern st. 17. The increasing contribution of such elements as I in subtropical regions could be connected with the latitudinal variation of temperature and concentrations of nutrients and ions in the marine waters [55,56]. The main component of a mussel's diet is the phytoplankton, which grows in local coastal zones during the quick rise of concentrations of nutrients in the warm conditions and contributes to the high content of the other elements (Na, Mg, Cl, Br, As, etc.) into mussel tissues.

3.7. The Stations with High Risks in Consumption of Mussels

The stations with the high risks are situated in Namibia (3), in the East of South Africa (12–14) and Mozambique (15) (see Table 5). Stations 12–14 are located near the mouths of the rivers and big harbors with the presence of industrial objects and high marine transport facilities. This was expressed in high risks (with the contribution of such elements as Al, Cr, Co, Ni, As) in mussel consumption. Several samples from Namibia (st. 3–Swakopmund) demonstrated the high risks based on the accumulation of Al and Ni according to low MPCR (<0.2 kg/week). In addition, elements such as Zn and Se could cause risk for human health at the higher level of consumption (200 g/week) at Namibia (Zn, Henties Bay), Saldanha Bay (Se), Hout Bay (Se), Port Shepstone (Se), and Mozambique (Se, Vilanculos, and Capo San Sebastian). The two last stations were situated in a pristine water area and revealed risks for such elements as As and I in the consumption of mussels. These two stations could be considered safe according to the particular contribution of toxic As and I in mussel tissue and features of the studied species.

It should be noted that the mussels from the last station in Mozambique (Vilanculos, st. 17) were considered as risk contributors of I, according to the calculated ratios of MPCR (0.2 kg/week) and RQ. It could be connected with specific accumulation features of the *Modiolus* sp., which is the most represented species in the coastal zone. In the same way, the high concentrations of Zn (higher MPL) at st. 1 (The Henties Bay) could be explained by specific accumulation by the most represented species of *Mytilus edulis* in comparison with the *Mytilus galloprovincialis*.

The st. 3 revealed high risks in mussel consumption with Al, Cr, Ni, As, Se as major contributors according to MPLs and low MPCRs. This station is situated at Swakopmund river, which discharges the sediment-rich waters. It is interesting to note that according to the study of Omoregie [57] the indigenous mussels *Choromytilus meridionalis* from Walvis Bay accumulated higher levels of Cu in comparison with similar levels in mussels from Henties Bay and Swakopmund. However, in our study the alien mussels *Mytilus galloprovincialis* accumulated higher levels of the majority of elements (except Zn and Se) at Swakopmund.

The most polluted station 14 revealed the highest risk according to all approaches. St. 14 (Richards bay)–is the deep harbor in South Africa with the export of coal, aluminum, titanium, heavy minerals. The Richards Bay Coal Terminal (RBCT) is the largest coal export facility in Africa. Furthermore, it also contains two aluminum smelters, fertilizer plants, and mining activities. The obtained high levels of risks according to RQ and MPCR for Co and Ni are probably connected with the industries and transport of mining products in the harbor. Al and Cr also revealed high risks at this station, they are associated with the suspended material of the Mhlatuze River.

The st. 15 (Xai-Xai) was considered as dangerous for human health in mussel consumption due to high risks according to all approaches. The main contributors were Al, Cr, Fe, and As. It was connected with the influence of discharges of the Limpopo river and waters from the big harbor of Maputo.

Therefore, after four approaches the riskiest mussels were found at cities Swakompund, East London, Port Shepstone, Richards Bay, Xai-Xai, Vilanculos. Such sites as st. 4–11 (Walvis Bay, Saldanha out of bay, Camps Bay, Hout Bay, Simonstown, Strand, Gordon Bay, Pringle Bay) situated in Namibia, Saldanha and Cape Town region were considered as safe in terms of mussel consumption according to assessed risks (MPCR, RQ, and THQ) based on 25 analyzed elements in soft tissues. Among them, the MPLs exceeded values for such elements as Se (st. 4, 5, 7), Cr (6, 9, 10), and As (st. 7–11) that indicated the high accumulation of such elements in mussels due to different reasons.

It is worth noting that the mussels are not the only source that transports elements into the human organism. Other relevant foods and other sources, such as soil ingestion, dust inhalation, and dermal contact, should be considered as well [4]. Since the risk at human health has to be assessed as the sum of all the exposure pathways, it could be higher than the calculated levels in this study.

4. Conclusions

According to calculated ratios (among all studied elements) Al, Cr, Fe, Ni, As and I could be considered the most dangerous elements (at the levels of consumption less than 100 g/week per person) in such cities as Swakopmund, East London, Port Shepstone, Richards Bay, Xai-Xai, Vilanculos and San Sebastian. The higher level of consumption (200 g/week) of Zn and Se could cause risk for human health in Namibia, Saldanha Bay (Se), Hout Bay (Se), Port Shepstone (Se), and Mozambique (Se, Vilanculos, and Capo San Sebastian). Among the analyzed elements with high risk: the Al, Cr, and Fe were suggested to be of terrigenous origin, while Ni, As, and I of anthropogenic origin. The maximal values of calculated risks correspond to polluted harbours and are influenced by the river runoff. In addition, the higher levels of risks of mussels consumption the tropics (East of South Africa and Mozambique) could be a consequence of the features of shallow water masses in this zone.

The levels of concentrations and analyzed ratios could be used in the calculations of the safe size of seafood dishes in the studied coastal areas. The obtained results and levels of risks could be implemented in the guideline documents for selected studied zones with attention to local conditions and possibilities of coastal treatment.

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