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Macro- and microelements in some species of marine life from the Sea of Okhotsk

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Abstract:
Introduction. Residents of northern regions have a diet low in essential macro- and microelements. The Sea of Okhotsk is an enormous source of fish and non-fish products. We aimed to determine mineral contents in marine fish, shellfish, and algae in order to assess if they could satisfy the daily requirement for these elements through fish and non-fish consumption.
Study objects and methods. Our study objects were saffron cod (*Eleginus gracilis* L.), blue-headed halibut (*Reinhardtius hippoglossoides* L.), commander squid (*Berryteuthis magister* L.), northern shrimp (*Pandalus borealis* L.), salted pink salmon caviar (*Oncorhynchus gorbuscham* L.), and kelp (*Laminaria* L.). The contents of 25 macro- and microelements were determined by atomic emission spectrometry and mass spectrometry with inductively coupled argon plasma.
Results and discussion. The absolute contents of macro- and microelements in the marine species were used to assess the proportion of the recommended daily requirement that they account for. Also, we performed a thorough comparative analysis of mineral quantities in the studied species of marine fish, pink salmon caviar, shellfish, and algae from the Sea of Okhotsk. Finally, we examined the elemental status of the coastal residents belonging to the "northern type" and identified their deficiencies of vital chemical elements.
Conclusion. Some chemical elements in the studied marine species from the Sea of Okhotsk (Magadan Region) satisfy over 100% of the daily human requirement for these minerals. Therefore, their products can be recommended as part of a northern diet in order to compensate for the deficiencies of certain minerals.

Keywords: Marine life, the Sea of Okhotsk, macro- and microelements, diet, toxic elements, shellfish

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INTRODUCTION

There is growing concern about chronic diseases such as obesity, diabetes, hypertension, hypercholesterolemia, cancer, and cardiovascular disease resulting from lifestyle changes worldwide [1]. According to a study by S. Shab-Bidar and A. Jayedi, an increase in fish consumption of 100 g/day can reduce overall and cardiovascular mortality, as well as the risk of coronary heart disease, myocardial infarction, stroke, heart failure, depression, and liver cancer. It has no effect on other kinds of cancer. Therefore, fish can be considered a healthy source of animal protein [2].

Oceans cover over 70% of the earth's surface and provide an enormous ecosystem for a wide variety of marine species. These species are a rich source of bioactive compounds that can be used in medicine, pharmacology, and food industry [3].

A number of recent foreign studies have focused on using the by-products of processing fish, marine invertebrates, and plants. These by-products are often discarded as waste, although they contain such valuable components as high-quality proteins, lipids, minerals, vitamins, enzymes, and other bioactive compounds that can be used to fight cancer and some cardiovascular diseases [1, 3, 4].

Nutrition affects our general health and the state of our individual functional systems. Therefore, it should not only be balanced and adequate to gender, age, and the degree of one's physical and mental activity, but also take into account the climatic and geographic conditions, as well as national characteristics and habits. It is especially relevant to the northern regions of Russia.

Fish is an essential component of human diet that provides more than 3 billion people worldwide with about 20% of animal protein [5]. The global fish catch is 182 million tons per annum, of which 2.6–4.5% is produced in Russia [6]. The Far Eastern basin accounts for 64% of the all-Russian catch. Its white fish, salmon, shrimp, squid, and sea kale are the most popular products among consumers. The global production of pink salmon caviar is 173,000 tons, of which 27% (46 700 t) is produced in Russia (30 900 t in the Sea of Okhotsk). Russia boasts its saffron cod (40 500 t/year), commander squid (150 000 t/year), blue-throated halibut (400 kg/year), and kelp (3800–9800 t/year). Shrimp dominates among the crustaceans, but its annual production of 10 000–20 000 tons only satisfies 20% of the Russian demand [6].

Fishing is the leading industry in many coastal regions of Russia, especially in the North and the Far East, where it is the main source of income. Primorsky Krai produces about 50% of all fish in the Far East, followed by Kamchatka and Sakhalin that equally share 2/5 of the total catch. The Magadan Region is also becoming an important player in the Russian fish market. The Far Eastern Basin has 26 million tons of aquatic biological resources, producing 3 million tons of fish per year. An average Russian consumes 16.1 kg fish per year.

Frozen, lightly salted, and smoked fish, as well as cheap canned fish, are among the most popular products in Russia. There is a growth in the consumption of ultra-processed products, which is associated with the standard of living in the country. There is a growing demand for fish delicacies, valuable species of fish, shrimp, crabs, and other invertebrates, as well as caviar, among high-income population [7].

According to the federal statistics of 2000 vs. 2019, the annual capita consumption of fish and fish products grew from 14.3 to 21.9 kg and from 12.7 to 22.3 kg in urban and rural areas, respectively. In 2019, the urban citizen consumed 13.9 kg of live and frozen fish and seafood, 4.1 kg of salted, smoked, and dried fish and seafood, 2.1 kg of canned fish, and 1.0 kg of semi-finished and finished fish products. These indicators for a rural consumer were 14.8, 4.6, 1.8, and 0.6 kg, respectively. The data for 2018 were almost identical to those for 2019 [8].

Fish has a more diverse mineral composition than meat, mainly due to microelements [9, 10]. While fish and meat have similar amounts of macronutrients (0.2% phosphorus, 0.3% potassium, 0.1% calcium), the content of some microelements in fish is 10 times higher (20–150 μg/g iodine, 140–700 μg% fluorine, 40–50 μg% bromine). Fish is only low in iron (1 mg%). Other microelements in fish include cobalt (about 20 mg%; 3–4 times more than in meat), zinc (1 mg%), copper (0.1 mg%), nickel (6 mg%), and molybdenum (4 mg%). Its average contents of sodium (100 mg%) and chlorine (165 mg%) are 2–3 times higher than in meat. The total content of minerals in marine fish is about 1.5 times as high as meat. Thus, fish and fish products are an essential source of minerals in human diet. We should also note that fish, especially predatory fish, can accumulate some toxic elements – mercury (up to 0.7 mg/kg), lead (up to 2.0 mg/kg), and cadmium (up to 0.2 mg/kg). However, these concentrations are within permissible levels and, when fish is consumed in generally accepted amounts, they do not pose any health hazard [7].

Non-fish species – crustaceans (crabs, shrimps, lobsters, crayfish), cephalopods (squid, octopus), bivalves (oysters, mussels, scallops), as well as algae (kelp, or sea kale) – contain potassium, sodium, calcium, magnesium, chlorine, sulfur, iron, manganese, phosphorus, aluminum, zinc, and many other macro- and microelements [11]. There is scientific evidence that fish species from tropical areas contain high concentrations of calcium, iron, and zinc, while those from cold seas or pelagic seas and oceans are rich in omega-3 fatty acids [12].

Earlier, we determined the contents of macro- and microelements in muscle tissue and testes of anadromous fish of the salmon (*Salmoidae* L.), chum salmon (*Oncorhynchus keta* L.), coho salmon (*Oncorhynchus kisutch* L.), and pink salmon (*Oncorhynchus gorbuscha* L.) caught in the coastal Sea of Okhotsk, Magadan Region. These species are most frequently eaten by the local population [13]. We found that the interspecific differences in the levels of elements in their biosubstrates were within the permissible standards for food products. However, chum salmon had larger amounts of arsenic, cobalt, copper, sodium, tin, antimony, and zinc than coho salmon. The level of iron in chum salmon and coho salmon was similar to that in freshwater fish. The contents of potassium and phosphorus were quite high, while the contents of lead, mercury, antimony, cadmium, arsenic, and cobalt were significantly below the standards. We also found that the element system of the indigenous small-numbered peoples, who have a traditional way of life in the Magadan Region, was in a better state than the element system of the Caucasian group, despite the imbalance in chemical elements seen in all the groups. This was probably due to the genetic adaptation of the northerners' mineral metabolism to the chronically insufficient intake of macro- and microelements, as well as their diet.

In this work, we determined the contents of chemical elements in the muscle tissue of some species of fish and seafood, as well as in algae, native to the Sea of Okhotsk. These products are the most essential components in the diet of the indigenous northern peoples and general inhabitants of the coastal northern regions. The population of the Magadan Region has a "northern" profile of macro- and microelements with a deficiency of calcium, cobalt, magnesium, zinc, selenium, and iodine [13]. Therefore, we aimed to analyze (qualitatively and quantitatively) the mineral composition of some species of marine life in order to determine whether the consumption of marine fish and seafood can satisfy the recommended daily requirement for minerals.

STUDY OBJECTS AND METHODS

The objects of research were: Far Eastern or Pacific saffron cod (*Eleginus gracilis*, n = 10), black or blue-headed halibut (*Reinhardtius hippoglossoides*, n = 10), commander squid (*Berryteuthis magister*, n = 10), cooked and frozen northern shrimp (*Pandalus borealis*, n = 10), salted pink salmon caviar (*Oncorhynchus gorbuscha*, n = 10), and kelp (*Laminaria*, n = 10) or sea kale. All the objects were caught in the Sea of Okhotsk, the Magadan Region. Each sample of 50 g was packed in a polypropylene container. The contents of macro- and microelements were determined threefold and averaged.

Our study methods included the inductively coupled plasma atomic emission spectrometry (ICP-AES) and the inductively coupled plasma mass spectrometry (ICP-MS) applied with Optima 2000 DV and Agilent 8900 ICP-MS instruments (Perkin Elmer, USA). The study was carried out in line with Guidelines No. 4.1.985-00 "Determination of toxic elements in food products and raw materials. The autoclave sample preparation technique" and in cooperation with the Micronutrients Company (Moscow).

The study objects were analyzed for the following macro- and microelements: aluminum (Al), arsenic (As), boron (B), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), iodine (I), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), selenium (Se), silicon (Si), tin (Sn), antimony (Sr), vanadium (V), and zinc (Zn).

For statistical analysis, we calculated the average measurement error (M ± m) and tested the normality of frequency distribution. When testing null hypotheses, the critical level of statistical significance was $P < 0.05$. Raw product portions of 100 g were used to determine the degree to which the fish and seafood species satisfied the daily adult requirement for macro- and microelements. For this, we referred to the "Standard physiological requirements for energy and nutrients for various population groups in the Russian Federation" (Methodological Guidelines 2.3.1.2432-08).

The macro- and microelement status of the working-age population in Magadan was examined in compliance with the Declaration of Helsinki and the principles of biomedical ethics. Each participant (study subject) voluntarily provided a written informed consent in line with Federal Law No. 323 "On Health Protection in the Russian Federation" of November 21, 2011 and Federal Law No. 152 "On personal data" of July 27, 2006.

We examined a total of 111 men (70 men aged 22–35 and 41 men aged 36–60) and 270 women (120 women aged 21–35 and 150 women aged 36–55). Hair samples from the back of the head were used as biomaterial for elemental analysis. They were exposed to inductively coupled argon plasma mass spectrometry on an Agilent 8900 ICP-MS instrument in the same laboratory to determine the contents of 25 macro- and microelements: Al (aluminum), As (arsenic), B (boron), Be (beryllium), Ca (calcium), Cd (cadmium), Co (cobalt), Cr (chromium), Cu (copper), Fe (iron), Hg (mercury), I (iodine), K (potassium), Li (lithium), Mg (magnesium), Mn (manganese), Na (sodium), Ni (nickel), P (phosphorus), Pb (lead), Se (selenium), Si (silicon), Sn (tin), V (vanadium), and Zn (zinc).

The data were statistically processed with IBM SPSS Statistics 21.

RESULTS AND DISCUSSION

Table 1 shows the average concentrations of essential (vital) macro- and microelements determined in the aquatic organisms and algae sampled from the Sea of Okhotsk.

We found that macronutrients differed significantly across almost all the studied species. Yet, kelp had a significantly higher ($P < 0.05$) content of calcium, potassium, and magnesium, accounting for 18, 50, and 37% of the daily requirement, respectively. Our calculations were based on 100 g portions of fresh (raw) products, since mineral loss during cooking was outside our study objectives. According to literature, however, the loss of minerals in cooked products is less than 10% [9]. Salted pink salmon caviar showed the highest ($P = 0.01$) concentrations of sodium and phosphorus of 10 040 and 4763 μg/g, respectively, amounting to 77 and 60% of the daily intake.

Our macroelement values slightly differed from the Handbook on the Chemical Composition and Caloric Content of Russian Foodstuffs published by the Institute of Nutrition, the Russian Academy of Medical Sciences (hereinafter "Handbook") [9]. Below are the values from the Handbook (with our values in brackets) for 100 g portions of the following species:

– saffron cod: sodium – 70 mg% (114.4 mg%), potassium – 335 mg% (302.7 mg%), calcium – 40 mg% (22.4 mg%), magnesium – 40 mg% (21.5 mg%), phosphorus – 240 mg% (200.6 mg%);
– halibut: sodium – 55 mg% (140.5 mg%), potassium – 450 mg% (188.6 mg%), calcium – 30 mg% (11.4 mg%), magnesium – 60 mg% (18.5 mg%), phosphorus – 220 mg% (131.1 mg%);
– pink salmon caviar: sodium – 2245 mg% (1004 mg%), potassium – 85 mg% (130.8 mg%), calcium – 75 mg% (60.9 mg%), magnesium – 141 mg% (69.6% mg%), phosphorus – 426 mg% (476.3 mg%);
– boiled and frozen shrimp: sodium – 540 mg% (494.3 mg%), potassium – 220 mg% (143.4 mg%), calcium – 70 mg% (89.6 mg%), magnesium – 50 mg% (63.4 mg%), phosphorus – 225 mg% (128.2 mg%); and
– squid: sodium – 110 mg% (468.4 mg%), potassium – 280 mg% (160.5 mg%), calcium – 40 mg% (23.2 mg%), magnesium – 90 mg% (97.9 mg%), phosphorus – 250 mg% (201.4 mg%).

The differences might be associated with the particular species [14] (in some cases, the Handbook only gives the generic name without specifying the

Table 1 Essential macro- and microelements (M ± m) in the muscle tissue of some species of marine life (the Sea of Okhotsk, Magadan)

ME, mcg/g	Pacific saffron cod *Eleginus gracilis*	Black-headed halibut *Reinhardtius hippoglossoides*	Commander squid *Berryteuthis magister*	Northern shrimp *Pandalus borealis*	Pink salmon caviar *Oncorhynchus gorbuscha*	Kelp *Laminaria*	Daily requirement	% of daily adult requirement (in 100 g)					
					Macroelements								
Ca	224 ± 22 1–2, 1–4, 1–5, 1–6	114 ± 11 2–3,2–4, 2–5, 2–6	232 ± 23 3–4, 3–5, 3–6	896 ± 90 4–5, 4–6	609 ± 61 5–6	2210 ± 221	1250 mg	1.8	0.9	1.9	7.2	4.9	17.7
K	3027 ± 303 1–2, 1–3, 1–4, 1–5, 1–6	1886 ± 189 2–4, 2–5, 2–6	1605 ± 161 3–6	1434 ± 143 4–6	1308 ± 131 5–6	12508 ± 1251	2500 mg	12.1	7.5	6.4	5.7	5.2	50.0
Mg	215 ± 22 1–3, 1–4, 1–5, 1–6	185 ± 18 2–3, 2–4, 2–5, 2–6	979 ± 98 3–4, 3–5, 3–6	634 ± 63 4–6	696 ± 70 5–6	1482 ± 148	400 mg	5.4	4.6	24.5	15.9	17.4	37.1
Na	1144 ± 114 1–3, 1–4, 1–5, 1–6	1405 ± 140 2–3, 2–4, 2–5, 2–6	4684 ± 468 3–5, 3–6	4943 ± 494 4–5, 4–6	10040 ± 1004 5–6	7982 ± 798	1300 mg	8.8	10.8	36	38	77.2	61.4
P	2006 ± 201 1–2, 1–4, 1–5, 1–6	1311 ± 131 2–3, 2–5, 2–6	2014 ± 201 3–4, 3–5, 3–6	1282 ± 128 4–5, 4–6	4763 ± 476 5–6	547 ± 55	800 mg	25.1	16.4	25.2	16.0	59.5	6.8
					Microelements								
Cu	0.392 ± 0.047 1–2, 1–3, 1–4, 1–5, 1–6	0.181 ± 0.022 2–3, 2–4, 2–5	2.52 ± 0.25 3–4, 3–6	8.26 ± 0.83 4–5, 4–6	2.99 ± 0.30 5–6	0.190 ± 0.023	1.0 mg	3.9	2.0	25.2	83.0	29.9	1.9
Fe	3.42 ± 0.34 1–2, 1–3, 1–4, 1–5, 1–6	0.981 ± 0.118 2–3, 2–4, 2–5, 2–6	6.01 ± 0.60 3–4, 3–5, 3–6	1.72 ± 0.17 4–5, 4–6	21.46 ± 2.15 5–6	80.72 ± 8.07	Male – 10 mg	3.4	1.0	6.0	1.7	21.5	80.72
							Female –15 mg	2.3	0.7	4.0	1.1	14.3	53.8
I	6.0 ± 0.6 1–2, 1–3, 1–4, 1–5, 1–6	0.841 ± 0.101 2–3, 2–5, 2–6	0.385 ± 0.046 3–4, 3–5, 3–6	0.773 ± 0.093 4–5, 4–6	7.81 ± 0.78 5–6	2319 ± 278	150 mcg	> 100%	56.1	25.7	51.5	> 100%	> 100%
Mn	0.122 ± 0.015 1–2, 1–3, 1–4,1–5, 1–6	0.042 ± 0.006 2–3, 2–4, 2–5, 2–6	0.553 ± 0.066 3–4, 3–5, 3–6	0.186 ± 0.022 4–5, 4–6	1.07 ± 0.11 5–6	0.960 ± 0.115	2.0 mg	0.6	0.2	2.8	0.9	5.4	4.8
Se	0.509 ± 0.061 1–2, 1–3, 1–4, 1–5, 1–6	0.338 ± 0.041 2–5, 2–6	0.327 ± 0.039 3–5, 3–6	0.265 ± 0.032 4–5, 4–6	2.12 ± 0.21	0.020 ± 0.004	70 mcg	72.9	48.3	46.7	37.9	> 100%	2.9
Zn	10.64 ± 1.06 1–2, 1–5, 1–6	3.58 ± 0.36 2–3, 2–4, 2–5, 2–6	10.65 ± 1.06 3–5, 3–6	12.27 ± 1.23 4–5, 4–6	23.40 ± 2.34 5–6	2.78 ± 0.28	12 mg	8.9	3.0	8.9	10.2	19.5	2.3

Note: ME – macro- and microelements; daily requirements were taken from the "Standard physiological requirements for energy and nutrients for various population groups in the Russian Federation" (Methodological Guidelines 2.3.1.2432-08); $^{1-2}$ – reliably significant differences in the amounts of macro- and microelements ($P < 0.05$) among the samples

Table 2 Conditionally essential microelements (M ± m) in the biosubstrates of some species of marine life (the Sea of Okhotsk, Magadan)

ME, mcg/g	Pacific saffron cod *Eleginus gracilis*	Blue-headed halibut *Reinhardtius hippoglossoides*	Commander squid *Berryteuthis magister*	Northern shrimp *Pandalus borealis*	Pink salmon caviar *Oncorhynchus gorbuscha*	Kelp *Laminaria*	Daily requirement
B	0.119 ± 0.014 1–2, 1–3, 1–4, 1–5, 1–6	0.314 ± 0.038 2–3, 2–4, 2–5, 2–6	1.83 ± 0.18 3–5,3–6	1.82 ± 0.18 4–5, 4–6	<0.021 5–6	21.15 ± 2.12	2.0 mg
Co	0.0062 ± 0.00124 1–2, 1–4, 1–5, 1–6	0.0019 ± 0.00039 2–3, 2–4, 2–5, 2–6	0.0063 ± 0.00126 3–4, 3–5, 3–6	0.011 ± 0.002 4–6	0.015 ± 0.002	0.020 ± 0.003	10 mcg
Cr	0.103 ± 0.012 1–2	0.156 ± 0.019 2–4, 2–6	0.128 ± 0.015 3–4	0.08 ± 0.012 4–5	0.117 ± 0.014	0.10 ± 0.012	50 mcg
V	0.0073 ± 0.00146 1–2, 1–3, 1–6	0.0015 ± 0.00031 2–3, 2–4, 2–5, 2–6	0.0033 ± 0.00066 3–4, 3–5, 3–6	0.010 ± 0.002 4–5, 4–6	0.0058 ± 0.00117	0.38 ± 0.046	15 mcg
Si	20.25 ± 2.03 1–2, 1–3, 1–4, 1–6	12.55 ± 1.25 2–3, 2–4, 2–5	27.42 ± 2.74 3–5, 3–6	33.33 ± 3.33 4–5, 4–6	20.83 ± 2.08 5–6	12.66 ± 1.27	5.0 mg
Li	0.012 ± 0.002 1–2, 1–3, 1–4, 1–5, 1–6	0.023 ± 0.004 2–3, 2–4,2–5,2–6	0.080 ± 0.012 3–5, 3–6	0.079 ± 0.012 4–5, 4–6	0.0051 ± 0.00102 5–6	0.130 ± 0.015	100 mcg
Ni	0.054 ± 0.008 1–6	0.048 ± 0.007 2–4, 2–5, 2–6	0.044 ± 0.007 3–4, 3–5, 3–6	0.074 ± 0.011	0.062 ± 0.009	0.080 ± 0.012	n.a.

Note: ME – macro- and microelements; $^{1-2}$ – reliably significant differences in the amounts of macro- and microelements ($P < 0.05$) among the samples; n.a. – not available

species). Additional factors include their habitat, production season, and the methods used to determine macro- and microelements.

The significantly highest content of copper was recorded in the boiled and frozen shrimp sample (83% of the daily requirement). The maximum contents of iron and iodine were found in the kelp sample (54–81% and over 100%, respectively). The highest concentrations of manganese, selenium, and zinc were determined in pink salmon caviar (5%, over 100%, and 19.5%, respectively).

Of all aquatic products, pink salmon caviar was analyzed in a ready-to-eat salted form, since raw caviar is not stored or frozen. Its sodium content was extremely high (10 040 µg/g vs. the recommended intake of 1300 mg/day), as can be seen in Table 1. However, even if a daily diet includes other sodium-containing foods, one caviar sandwich a day will not pose any health risk. On the contrary, it will benefit health since caviar is rich in phosphorus, iron, iodine, zinc, and valuable bioactive substances, such as omega-3-polyunsaturated fatty acids and vitamins.

The contents of conditionally essential elements are presented in Table 2.

The highest boron content was recorded in the kelp sample (21.15 µg/g or 106% of the daily requirement in 100 g). This trace element plays a significant role in the formation of bone tissue by regulating the activity of parathyroid hormone and, therefore, the metabolism of calcium, magnesium, and phosphorus [15, 16]. This makes kelp an essential component in the northerners' diet. Also, kelp had higher concentrations of cobalt (2 µg or 20% of the daily requirement), vanadium (38 µg or 95%), and lithium (13 µg or 13%) than any other of the studied samples. The maximum amount of chromium was determined in the muscle tissue of blue halibut (15.5 µg or 31% of the daily requirement). Northern shrimp was rich in silicon (3333 mcg or 67% of the daily requirement).

Table 3 Toxic microelements (M ± m) in the biosubstrates of some species of marine life (the Sea of Okhotsk, Magadan)

ME, mcg/g	Pacific saffron cod *Eleginus gracilis*	Blue-headed halibut *Reinhardtius hippoglossoides*	Commander squid *Berryteuthis magister*	Northern shrimp *Pandalus borealis*	Pink salmon caviar *Oncorhynchus gorbuscha*	Kelp *Laminaria*	TPL mg/kg, max.*		
							1,2	3–5	6
Al	1.20 ± 0.12	0.864 ± 0.104	1.0 ± 0.1	0.867 ± 0.104	0.42 ± 0.05	1.82 ± 1.18	–		
As	27.19 ± 2.72	2.07 ± 0.21	0.849 ± 0.102	4.71 ± 0.47	0.294 ± 0.035	6.89 ± 0.69	5.0	5.0	5.0
Cd	0.0024 ± 0.00048	0.0008 ± 0.00023	0.069 ± 0.010	0.075 ± 0.011	0.0016 ± 0.00033	0.130 ± 0.016	0.2	2.0	1.0
Hg	0.034 ± 0.005	0.039 ± 0.006	0.027 ± 0.004	0.028 ± 0.004	<0.0036	0.05 ± 0.008	0.5	0.2	0.1
Pb	0.0043 ± 0.00087	0.0045 ± 0.0009	0.0042 ± 0.00084	0.0031 ± 0.00061	0.0025 ± 0.00051	0.04 ± 0.006	1.0	10.0	0.5
Sn	0.038 ± 0.006	0.004 ± 0.0008	0.0049 ± 0.00097	0.0052 ± 0.00104	0.0092 ± 0.00185	0.008 ± 0.0017	–		
Sr	0.817 ± 0.098	0.636 ± 0.076	4.37 ± 0.44	20.68 ± 2.07	5.42 ± 0.54	193 ± 19	–		

Note: ME – macro- and microelements; TPL – temporarily permissible level

* "Unified sanitary, epidemiological and hygienic requirements for products (goods) subject to sanitary and epidemiological surveillance (control)" (effective from June 1, 2019)

Table 4 Macro- and microelements in the hair samples of working-age residents of Magadan (25–75 percentile)

ME, mcg/g	Male study subjects		Female study subjects		Significance level (*P*)			
	Aged 22–35 (n = 70)	Aged 36–60 (n = 41)	Aged 21–35 (n = 120)	Aged 36–55 (n = 150)	1–2	3–4	1–3	2–4
Al	10.00 (6.59–14.62)	11.69 (5.82–20.73)	7.62 (4.39–13.73)	7.85 (4.69–14.15)	0.50	0.52	**0.02**	**0.04**
As	0.081 (0.046–0.117)	0.079 (0.046–0.185)	0.042 (0.042–0.062)	0.042 (0.027–0.072)	0.73	0.73	**0.00**	**0.00**
Ca	265.42 (187.85–333.54)	310.60 (221.17–405.60)	449.47 (258.10–750.45)	473.00 (282.48–937.98)	0.07	0.17	**0.00**	**0.00**
Cd	0.027 (0.013–0.052)	0.040 (0.013–0.122)	0.008 (0.004–0.016)	0.012 (0.006–0.034)	**0.03**	**0.00**	**0.00**	**0.00**
Co	0.010 (0.006–0.018)	0.014 (0.008–0.074)	0.012 (0.007–0.022)	0.014 (0.008–0.033)	**0.01**	0.11	0.10	0.41
Cr	0.73 (0.47–1.01)	0.56 (0.24–1.03)	0.35 (0.23–0.54)	0.36 (0.18–0.58)	0.10	0.88	**0.00**	**0.00**
Cu	10.98 (9.87–12.28)	9.89 (8.57–12.54)	10.02 (8.41–11.61)	10.23 (8.99–11.56)	0.31	0.35	0.10	0.66
Fe	18.22 (9.87–12.28)	22.42 (14.52–38.68)	20.35 (14.38–31.04)	18.39 (13.08–26.17)	0.19	0.07	0.37	0.06
K	110.40 (44.76–170.75)	171.00 (73.92–515.07)	38.59 (17.27–77.09)	74.64 (32.62–200.12)	**0.01**	**0.00**	**0.00**	**0.00**
Li	0.015 (0.012–0.027)	0.016 (0.010–0.036)	0.012 (0.012–0.017)	0.012 (0.011–0.022)	0.90	0.16	**0.00**	0.38
Mg	26.85 (19.76–35.93)	27.01 (19.18–40.17)	33.75 (21.61–67.33)	49.41 (26.75–104.32)	0.69	**0.01**	**0.00**	**0.00**
Mn	0.43 (0.28–0.69)	0.71 (0.42–0.95)	0.87 (0.43–1.67)	1.18 (0.48–2.31)	**0.01**	**0.01**	**0.00**	**0.01**
Na	198.51 (62.81–413.94)	392.00 (189.99–866.15)	82.05 (40.52–180.23)	170.20 (79.57–575.95)	**0.00**	**0.00**	**0.00**	**0.00**
Ni	0.22 (0.15–0.35)	0.29 (0.17–0.48)	0.18 (0.11–0.31)	0.17 (0.11–0.30)	0.24	0.94	0.07	**0.02**
P	159.72 (143.80–173.99)	163.00 (149.50–186.12)	151.38 (137.55–165.90)	156.56 (140.38–180.53)	0.19	0.07	0.08	0.170
Pb	0.48 (0.31–0.85)	1.12 (0.48–4.68)	0.16 (0.08–0.33)	0.25 (0.11–0.53)	**0.00**	**0.00**	**0.00**	**0.00**
Se	0.38 (0.30–0.51)	0.51 (0.38–0.80)	0.34 (0.26–0.49)	0.46 (0.27–0.74)	**0.00**	**0.00**	0.22	0.30
Si	32.98 (20.59–48.22)	21.33 (13.83–31.30)	28.81 (17.46–49.81)	23.92 (15.28–40.71)	**0.00**	**0.05**	0.58	0.30
Sn	0.09 (0.06–0.18)	0.12 (0.07–0.20)	0.08 (0.04–0.20)	0.08 (0.04–0.17)	0.21	0.59	0.47	**0.04**
V	0.12 (0.04–0.19)	0.04 (0.01–0.09)	0.04 (0.02–0.08)	0.05 (0.02–0.09)	**0.01**	0.73	**0.00**	0.74
Zn	190.80 (166.86–217.14)	177.00 (131.79–208.30)	176.75 (154.51–211.83)	174.42 (147.13–200.36)	**0.02**	0.17	0.08	0.68
I	0.67 (0.32–1.11)	0.74 (0.38–3.46)	0.49 (0.30–1.00)	0.55 (0.30–1.47)	0.34	0.89	0.37	0.14
Hg	0.53 (0.20–0.89)	0.60 (0.37–0.99)	0.48 (0.30–0.67)	0.51 (0.35–0.68)	0.27	0.28	0.07	0.14
B	0.81 (0.58–1.64)	0.89 (0.56–3.72)	0.56 (0.33–1.29)	0.76 (0.29–1.81)	0.29	0.33	0.20	0.12
Be	0.003 (0.003–0.004)	0.003 (0.001–0.009)	0.003 (0.001–0.003)	0.003 (0.001–0.006)	0.27	0.14	0.27	0.70

Note: ME – macro- and microelements; significant differences are highlighted in bold ($P < 0.05$).

We analyzed the concentrations of toxic microelements in the studied biosubstrates against the "Unified sanitary, epidemiological and hygienic requirements for products (goods) subject to sanitary and epidemiological surveillance (control)" (effective from June 1, 2019) and the hygienic safety requirements for food products established in the Technical Regulations of the Customs Union "On food safety" (TR CU 021/2011). Excessive levels were only found for arsenic: 5.4 times as high in the Pacific saffron cod and 1.4 times as high in the kelp sample (Table 3).

Some studies report fluctuations in the content of total arsenic in various species of fish and shellfish from 5 to 200 μg/g (or mg/kg) [17, 18]. The Russian regulations specify certain contents of total arsenic in food products and materials without differentiating between its inorganic (toxic) and organic (low-toxic) forms, which explains excess concentrations determined in marine hydrobionts. Yet, we know that arsenic is mainly present in the tissues of marine life in its organic, low-toxic forms, such as arsenobetaine, arsenocholine, and arsenosugar [19]. This problem could be solved by introducing an additional maximum permissible concentration for inorganic arsenic in marine hydrobionts into the regulatory documents, such as the Technical Regulations of the Customs Union "On food safety" (TR CU 021/2011) [19].

Besides, our long-term studies of the elemental status did not find any excessive contents of heavy and toxic metals (including arsenic) in the population of the Magadan Region [13, 20].

Thus, since the regulatory documents establish maximum permissible concentrations of total, rather than organic, arsenic in marine life, we can conclude that the population of the Magadan Region is not exposed to a toxic load of arsenic.

Rational nutrition involves a variety of foods in the diet, including those produced in other biogeochemical regions that may have a negative impact on the local population. Thus, the consumption of local food with a significant proportion of essential macro- and microelements is an effective way to prevent regional deficiency or excess of certain chemicals.

According to our data, over 50% of the working-age residents of Magadan have a deficiency of calcium and magnesium (most essential macroelements), as well as cobalt and iodine (microelements). This deficiency, which is typical of the "northern" elemental profile, can decrease the northerners' adaptive reserves. Moreover, a chronic deficiency of basic vital elements in extreme northern conditions can cause dysfunctions in many physiological systems and a wide range of pathologies.

The statistical data for the mineral metabolism in the study subjects are presented in Table 4.

The studied cohorts showed obvious differences related to both age and gender. In a linear approximation, reliably significant (at $P < 0.05$)

differences can be schematically represented as follows (common groups of elements are highlighted in bold).

Gender-related differences:

men (**Si,** V, Zn) ♂ 22–35 > < ♂ 36–60 (**Cd**, Co, **K, Mn, Na, Pb, Se**);

women (**Si**) ♀ 21–35 > < ♀ 36–55 (**Cd**, **K,** Mg, **Mn, Na, Pb, Se**).

Age-related differences:

younger age (**Al, As, Cd, Cr, K**, Li, **Na, Pb,** V) ♂ 22–35 > < ♀ 21–35 (**Ca, Mg, Mn**);

older age (**Al, As, Cd, Cr, K, Na,** Ni, **Pb,** Sn) ♂ 36–60 > < ♀ 36–55 (**Ca, Mg, Mn**).

Noteworthily, age-related differences in mineral metabolism were common for men and women. Younger subjects of both sexes had a significantly higher median of Si concentration. The hair samples of older subjects contained significantly higher contents of toxic cadmium and lead, while no excess of these elements was detected in any of the studied cohorts. In addition, older subjects had higher concentrations of essential potassium, manganese, sodium, and selenium. Thus, we can consider these elements age-related. At the same time, they tended to be in excess at different degrees and frequency of detection, which can be considered as mineral pre-deficiency caused by its increased excretion from the body.

Hormone-determined gender differences in metabolism can be seen in the elemental status of men and women. The female subjects of both age groups had significantly higher concentrations of essential calcium, magnesium, and manganese, while their male counterparts had higher contents of aluminum, arsenic, cadmium, chromium, potassium, sodium, and lead. Our data were in line with some literature sources and our earlier studies [13 , 20–22].

Thus, every individual has unique mineral metabolism that differs between men and women and changes with age. We find it extremely important to regularly monitor the elemental status of the working-age population in the North as a socially significant group. This measure will ease the growing pressure on functional reserves, maintain the immune system, and prevent various pathologies related to mineral imbalance and severe deficiencies. People should support their health, individually or under medical supervision, by rationalizing their nutrition and consuming preventative supplements of macro- and microelements, taking into account the specific features of the "northern" mineral metabolism.

The most common "northern" diseases of a biogeochemical nature include iron deficiency states (deficiency of iron, cobalt, magnesium, and calcium), immunodeficiency conditions (deficiency of selenium, zinc, iodine, and calcium), arthrosis (deficiency or excess of calcium and silicon), urolithiasis (excess calcium or silicon), hypertension (deficiency of magnesium or calcium), dental diseases (imbalance of calcium, fluoride, and magnesium), and thyroid pathologies, most commonly endemic goiter (iodine deficiency and imbalance of selenium, copper, manganese, cobalt, calcium, magnesium, and other elements).

CONCLUSION

We determined the absolute contents of macro- and microelements in some species of marine life and assessed the degree to which they could satisfy the recommended daily requirement for these minerals if included in the daily diet. We compared mineral quantities in the studied species of marine fish, pink salmon caviar, shellfish, and algae from the Sea of Okhotsk. In addition, we examined the elemental status of the coastal residents and specified deficiencies of essential chemical elements common for this "northern" profile.

We found that the studied species of marine life native to the Sea of Okhotsk in the Magadan Region are a valuable source of macro- and microelements that, in some cases, satisfy over 100% of the daily requirement for adult humans. However, the amounts of calcium and manganese in the studied fish and non-fish products (100 g) were lower than required. Therefore, we recommend replenishing their deficiencies with other foods that are rich in these minerals (dairy products and meat), as well as bioactive supplements or pharmaceuticals under medical supervision.

Since the indigenous small-numbered northerners, who lead a traditional way of life, have minimum elemental imbalance and no clinical signs of endemic goiter, we recommend that "outsiders" coming to live in the area optimize their daily nutrition with local foods, mainly marine fish and non-fish products.

CONTRIBUTION

The authors were equally involved in writing the manuscript and are equally responsible for plagiarism.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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