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Comparative Analysis of Lipids and Fatty Acids in Beaked Redfish *Sebastes mentella* Travin, 1951 Collected in Wild and in Commercial Products

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Abstract: The lipid and fatty acid profile of muscles in beaked redfish, caught and fixed in the wild versus specimens from food supermarkets ("commercial"), were evaluated, as well as the health implications of this popular food for its consumers based on the calculation of nutritional quality indexes. The contents of the total lipids (TLs), total phospholipids (PLs), monoacylglycerols (MAGs), diacylglycerols (DAGs), triacylglycerols (TAGs), cholesterol (Chol), Chol esters, non-esterified fatty acids (NEFAs), and wax esters were determined by HPTLC; the phosphatidylserine (PS), phosphatidylethanolamine (PE), phosphatidylinositol (PI), phosphatidylcholine (PC), and lysophosphatidylcholine (LysoPC) were determined by HPLC; and fatty acids of total lipids were determined using GC. The TL content was higher in commercial products due to DA and NEFAs, among PL fractions the content of LysoPC was also higher. The results indicated multidirectional processes of slight degradation of lipids in commercial products in comparison to wild. The flesh lipid quality index was lower due to EPA and DHA in commercial specimens while the index of thrombogenicity was significantly higher. The differences in the quantities of lipid classes between muscle biopsy regions in fish apparently corroborate the morphology and physiology of deep-water fish.

Keywords: lipids; fatty acids; beaked redfish; *Sebastes mentella*; "wild" and "commercial" products; mesopelagic zone; North Atlantic

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1. Introduction

The mesopelagic zone, from the standpoint of biodiversity, biomass, and bio-productivity, is considered one of the most promising areas of the oceans [1]. At the same time, "underutilized" mesopelagic species are a potential source of a variety of products for people's daily use and consumption and are thus important for food security programs and actions [2]. Special attention to the study of mesopelagic organisms is due to their increased biological productivity and environmental significance [3–6]. A significant contribution to the development of adaptations of organisms inhabiting mesopelagic ecosystems with relatively stable and at the same time extreme environments is made by metabolic changes of lipids and fatty acids (FA).

Lipids and fatty acids are key multifunctional and physiologically valuable components of an organism, securing its normal functioning [7–17]. An established fact for deep pelagic organisms, for example, is that temperature decline induces changes in the composition and quantities of membrane phospholipids in the brain [7,18,19]. Apart from being energetic components of cells, storage triacylglycerols, cholesterol esters, and wax esters, they participate in the adaptation to depth change (during daily vertical migrations) [20,21]. Decay products of the metabolically interlinked lysophosphatidylcholine and diacylglycerols can be used in the synthesis of bioactive compounds—hormones and neuromediators necessary for muscular activity and coordination [22–24].

As we know, the biggest contribution to the diversity in lipid classes is made by their fatty acid (FA) constituents [25]. Humans have low levels of dietary linoleic acid (LA, 18:2(n-6) and α-linolenic acid (ALA, 18:3(n-3)) conversion to long-chained polyunsaturated fatty acids (PUFA) de novo due to the lack of Δ12- and Δ15-desaturases [26]. They are capable, however, of carbon chain extension by means of the elongase enzyme [27]. Hence, the only way for an animal organism to receive essential polyunsaturated fatty acids (omega-3 and omega-6 PUFAs) is from food. PUFAs are core constituents of polar lipids building biological membranes and are important in cellular signaling, as well as in participating in the regulation of transcription [28]. PUFAs perform a wide range of physiological functions and are pivotal for humans. Eicosapentaenoic acid (EPA) and DHA, which produce immunomodulating and general tonic effects on humans, have been successfully used in the therapy of cardiovascular diseases, autoimmune responses neurodegenerative disorders, critical for learning and memory [26,29,30]. Latest studies showed DHA to be a source for the synthesis of new highly active compounds that promote neural regeneration after traumatic brain injury [31]. Certain PUFAs—EPA, DHA, and arachidonic acids, ARA are the precursors for diverse groups of lipid mediators, such as prostaglandins, thromboxanes, leukotrienes (from ARA); E-series resolvines (from EPA) and protectins, D-series resolvines, maresin (from DHA), which are associated with various physiological effects in the body and regulate various processes, including inflammatory, immune responses, neurotransmitter, and hormonal functions. Recently, it was shown that DHA and EPA are original precursors for novel lipid mediators—elovanoids with important functions for nerve and vision systems [32,33]. A shortage of essential PUFAs, on the other hand, can trigger some somatic diseases: diabetes, tumors, cystic fibrosis, multiple sclerosis, Crohn's disease, Raynaud's disease, myocardial infarction, etc. [34].

There are fragmental data that the mesopelagic fish of the Arctic marine ecosystems contains a complex set of long-chain high-unsaturated FA [35]. This makes these fish a promising resource for bioprospecting and production of especially valuable biologically active products and substances, which increase the adaptive capabilities of humans [36]. Indeed, mesopelagic fish is a potential source of many unique biologically active compounds and substances, such as the indispensable for humans "omega-3" and "omega-6" PUFAs and their optimal ratios, as well as a functional set of long-chain monounsaturated FA. According to the recent data, marine lipids, in particular with a high content of long-chain monounsaturated FA and a certain composition of them, maintain and contribute to the realization of the well-known favorable biological effects of the "omega-3" FA on human health [37–39].

The biomass of mesopelagic fish alone in the Northeast Atlantic and the adjacent exclusive economic zones of the surrounding countries is estimated at 1 to 10 billion tons [5,40–45]. There has been an increased global population demand to consider and explore alternative resources, including high biomass mesopelagic resources, as a potential source of a variety of products for people's daily use and consumption. Indeed, the potential of mesopelagic is multidirectional. For example, it is important to consider the mesopelagic fish as the potential sources of biologically active substances (of a lipid base) for aquaculture, there are few studies on this direction [46], food and cosmetic industry, bioprospecting. One of the primary and most readily available sources of "omega-3" and "omega-6", as well as "omega-9" FAs are marine organisms, namely fish [47].

Among fish species inhabiting the mesopelagic zone in the North Atlantic, fish of the genus *Sebastes*, which are represented in the northern seas four species, are well-known commercially valuable redfish. Beaked redfish, *Sebastes mentella*, is the most common species and its largest population is found in the Irminger Sea [48–50]. Our studies [51] and research by our colleagues from other countries [52,53] show PUFA content in the muscles (fillet) of fresh-caught wild beaked redfish is up to 40–45% of total FAs, of which 35–40% is omega-3 FAs (EPA and DHA).

An effective way to preserve the quality of lipids and prevent their oxidation is to deep-freeze tissues. Commercial fisheries in Russia are governed by a requirement of the standard "Frozen fish. Specifications" GOST 32336-2013 [54], stipulating that fish must be frozen at −10–−18 °C. Even then, however, the fish products lose in quality because of lipid hydrolysis and oxidation [55]. Moreover, the storage life and quality of frozen fish can be significantly affected by the temperature and duration of storage before freezing and by transportation conditions [56–59].

In this study, we focused on the lipid and fatty acid profile of muscles in beaked redfish caught and fixed in the wild versus specimens from food supermarkets ("commercial"), both collected in FAO 27 fishery area, and on evaluating the health implications of this popular food for its consumers based on the calculation of nutritional quality indexes. The interest in such a comparison was incited by a recent assessment [51] of lipid profiles in *S. mentella* from the Irminger Sea and the discussion of the role of certain lipids and fatty acids in biochemical adaptations of redfish to the variable biotic and abiotic conditions.

2. Materials and Methods

2.1. Sampling

The material analyzed was obtained in FAO 27, Atlantic, Northeast commercial designation, Fishing Subarea XIV (East Greenland), the "wild" and "commercial" samples were collected from the same stock in the Irminger Sea, the major area for commercial fishery of *Sebastes mentella*, and size category of fish was "2" [60]. Fish were selected of the same size as permitted for fishery catch [61].

Muscle tissue samples from "wild" redfish specimens were collected during field studies in the Irminger Sea (59°60′−64°60′ N, 26°20′−41°50′ W) from aboard R/V "Atlantida". Biological material was sampled from three areas (in the NEAFC regulatory area, in Greenland's fishery zone, and in Iceland's exclusive economic zone) at 250, 325, 375, 400, 650, and 700 m depths. Sampling methods were taken from the Manual for the International Deep Pelagic Ecosystem Survey in the Irminger Sea and Adjacent Waters developed and approved by the Working Group on International Deep Pelagic Ecosystem Surveys (WGIDEEPS) [62]. Sampling was done under the Agreement on Cooperation between the Federal Fisheries Agency and the Russian Academy of Sciences and pursuant to the Joint Research Program of the said parties. The samples were described in more detail in our previous publication [51].

Muscle tissues samples from "commercial" redfish specimens were taken from frozen redfish samples from 6 different suppliers were purchased in chain stores. Interesting that the storage duration of commercial redfish according to labels is 9–10 mouth while in the present study samples stored for 7 months were analyzed. The recommended store temperature is up to −18 °C. Moreover, for the comparison of wild and commercial specimens, samples were drawn from different areas of the fillet parts. Triplicate samples, three vials from each individual specimen, were dissected and prepared for analysis.

Moreover, muscle tissue for lipid analysis was biopsied from three regions in each fish specimen: AD = anterodorsal, MD = mediodorsal, PD = posteriodorsal (Figure 1) to study differences in lipid content and profiles, and nutritional quality among steaks of redfish recently performed in supermarkets besides entire flesh and fillets.

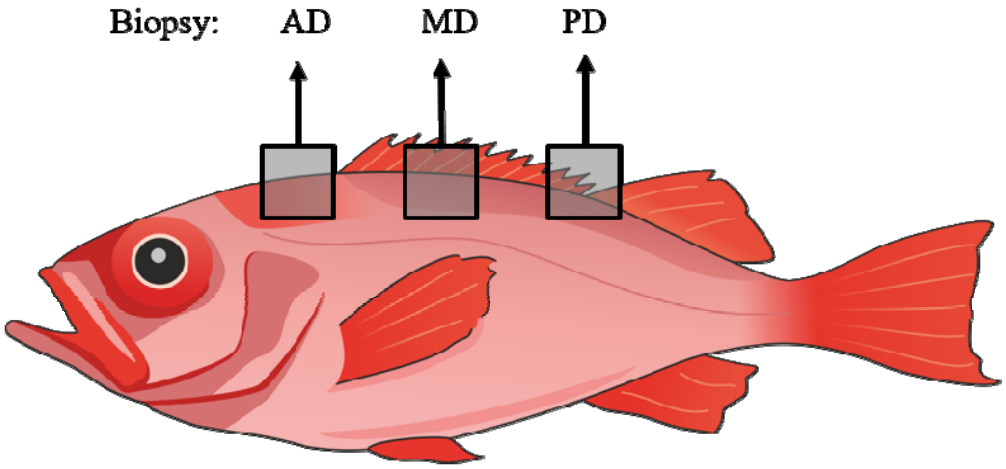

Figure 1. Schematic view of biopsies of muscle tissue from the commercial beaked redfish *Sebastes mentella*.

Notably, there is no sex specificity among the studied samples since the commercial products do not have such identification, and the samples were considered as flesh: fish specimens were beheaded and gutted.

In addition, the samples collected were fixed in 96% absolute ethanol with the addition of 0.05% BHT as an antioxidant to prevent the start of oxidative processes and were frozen on board the vessel to compare the effect of different types of fixations on the lipid content of samples. In the present study, we do not focus on the comparison of protocols of fixation and frozen samples were used.

2.2. Lipid Extraction and Analysis

The total lipids (TL) from muscle tissue were extracted using the Folch methodchloroform-methanol (2:1, *v*/*v*) mixture [63].

2.2.1. Determination of Certain Lipid Classes by HPTLC

Qualitative and quantitative determination of individual lipid classes—total phospholipids (PL), monoacylglycerols (MAG), diacylglycerols (DAG), triacylglycerols (TAG), cholesterol esters (Chol esters), cholesterol (Chol), non-esterified fatty acids (NEFA), and wax esters was carried out using high-performance thin-layer chromatography (HPTLC). Fractionation of total lipids was carried out on ultrapure glass-based plates—HPTLC Silicagel 60 F_{254} Premium Purity (Merck, Germany). The application of microvolumes of the sample was performed using a semi-automatic Linomat 5 applicator (CAMAG, Switzerland), and the separation of individual lipid classes was carried out using an ADC2 chromatographic chamber (CAMAG, Switzerland) in the solvent system hexane-diethyl ether-acetic acid (32:8:0.8, *v*/*v*) with used supersaturated zinc nitrate ($ZnNO_3$ * $6H_2O$) solution for maintaining humidity (47–49% humidity) [64]. The formation of visible individual lipid spots was stained in a solution of copper sulfate ($CuSO_4$) with orthophosphoric acid (H_3PO_4), followed by heating the plate to 160 °C for 15 min. Qualitative and quantitative determination of lipid components was carried out in the chamber of a TLC Scanner 4 densitometer (CAMAG, Switzerland) [65]. The identification of individual lipid classes was carried out according to the standards of the respective studied components ("Sigma-Aldrich", St. Louis, MO, USA), taking into account the correspondence of the Rf-values.

2.2.2. Determination of Certain Phospholipid Classes by HPLC

Qualitative and quantitative determination of individual phospholipid fractions—phosphatidylcholine (PC), phosphatidylethanolamine (PEA), phosphatidylserine (PS),

phosphatidylinositol (PI), and lysophosphatidylcholine (LysoPC) was performed by high-performance liquid chromatography (HPLC) and described previously in Reference [66].

2.2.3. Fatty Acids Analysis by GC

Qualitative and quantitative fatty acids (FAs) profile of the TL was analyzed by gas-liquid chromatography (GC) with flame-ionized detector (FID) and mass-detector (MS). FAMEs were separated on a GC with mono-quadrupole mass-selective detector "Maestro-αMS" (Saitegra, Russia) for identification of FAs constituents. The separation of FAs was carried out for 120 min in isothermal configuration (200 °C) on a Zebron ZB-FFAP capillary column (Phenomenex, Torrance, CA, USA) using helium as a mobile phase. The SIM/SCAN mode: SIM mode for searching for FAs according to the analytical standards—Supelco 37, Bacterial Acid Methyl Ester (BAME) Mix and PUFA №1 Marine source (all Sigma Aldrich, USA); SCAN mode was used for searching and identification unique FAs with scan parameters 50 to 400 m/z. The data were analyzed using "Maestro Analytic v. 1.025" software with NIST library. Next, after qualitative identification of FA with GC-MS, the quantitative determination was carried out using GC-FID. FAMEs were separated on a "Chromatek-Crystall-5000.2" gas chromatograph with a flame-ionization detector (FID) and an automatic liquid dispenser (Chromatek, Yoshkar-Ola, Russia). The separation of FAs was carried out for 120 min in isothermal configuration (200 °C) on a Zebron ZB-FFA capillary column (Phenomenex, USA) using nitrogen as a mobile phase. Chromatek-Analytik-5000.2 software "Chromatek Analytic V. 3.0.298.1" (Chromatek, Yoshkar-Ola, Russia), the analytic procedure is described in Reference [17]. All GC parameters were identical between GC-MS and GC-FID except mobile phase (helium and nitrogen, respectively).

2.3. The Lipid Quality, Health and Nutritional Indexes from the Fatty Acids Composition

Based on the obtained FA profiles including certain FA the next health and nutritional indexes were calculated:

Index of atherogenicity (IA):

$$IA = [12:0 + (4 \times 14:0) + 16:0]/(\text{n-3 PUFA} + \text{n-6 PUFA} + \text{MUFA})$$

PUFA—polyunsaturated fatty acids
MUFA—monounsaturated fatty acids
12:0—lauric acid, 14:0—myristic acid, 16:0—palmitic acid

Index of thrombogenicity (IT):

$$IT = [14:0 + 16:0 + 18:0]/[(0.5 \times \text{MUFA}) + (0.5 \times \text{n-6 PUFA}) + (3 \times \text{n-3 PUFA}) + (\text{n-3 PUFA}/\text{n-6 PUFA})]$$

PUFA—polyunsaturated fatty acids
MUFA—monounsaturated fatty acids
14:0—myristic acid, 16:0—palmitic acid, 18:0—stearic acid

Flesh-lipid quality (FLQ):

$$FLQ = 100 \times [EPA + DHA]/[\sum FA]$$

EPA—eicosapentaenoic acid (20:5(n-3))
DHA—docosahexaenoic acid (22:6(n-3))
FA—fatty acids

Hypo- to hyper-cholesterolemic ratio (h/H):

$$h/H = (18:1 + \text{PUFA})/(12:0 + 14:0 + 16:0)$$

PUFA—polyunsaturated fatty acids
12:0—lauric acid, 14:0—myristic acid, 16:0—palmitic acid

Health-promoting index (HPI):

$$HPI = UFA/[12:0 + (14:0 \times 4) + 16:0]$$

UFA—unsaturated fatty acids (MUFA + PUFA)
12:0—lauric acid, 14:0—myristic acid, 16:0—palmitic acid

2.4. Statistical Analysis

To perform the statistical analysis, the free R-programming language (v. 3.6.1.) with basic packages and additional "readxl" (v. 1.3.1), "tidyverse" (v. 1.3.0), "corrgram" (v. 1.13), "factoextra" (v.1.0.6), "randomForest" (v. 4.6–14), "quantreg" (v. 5.52), "cowplot" (v. 1.1.1), "gmodels" (v. 2.18.1) packages was used. Statistical significance differences between depths were tested by a non-parametric test, the Kruscal-Wallis test, and between individual depths—the Wilcoxon-Mann-Whitney test [66]. Statistical significance was set at $p \leq 0.05$. Machine learning was carried out using the "random forest" classification; the mean decrease Gini coefficient was used to determine the "significant" classifiers [67]. Multivariate analysis was performed using principal components analysis for FAs, the content of which was more than 1% of the total FA [52].

The biochemical analysis was performed at the scientific center collective usage platform of the Karelian Research Centre of the Russian Academy of Sciences.

3. Results

A comparison of the total lipid (TL) content in muscles of the flesh of beaked redfish from the wild and the commercial samples is shown in Figure 2. The TL content was significantly higher in commercial products—17.64% dry weight in comparison to the wild—7.71% dry weight.

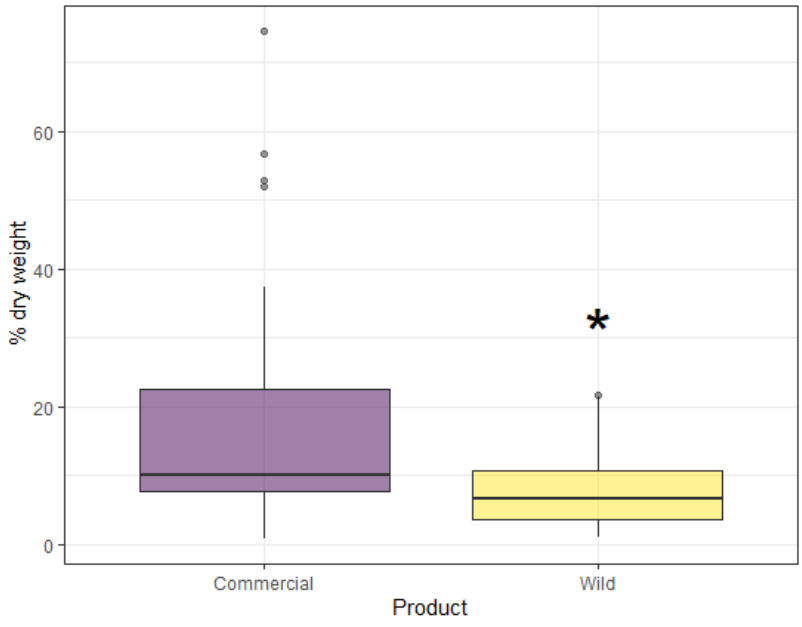

Figure 2. Total lipid (TL) content (% dry weight) in muscle tissue from the wild and commercial samples of beaked redfish *Sebastes mentella*. Note: *—significantly ($p \leq 0.05$) different between wild and commercial product.

The lipid analysis of different biopsy regions (AD, MD, PD) in commercial specimens revealed differences among sites in TL content, with higher levels in the MD region—31.5% vs. 9.62%—in AD and 9.34% dry weight in PD (Figure 3).

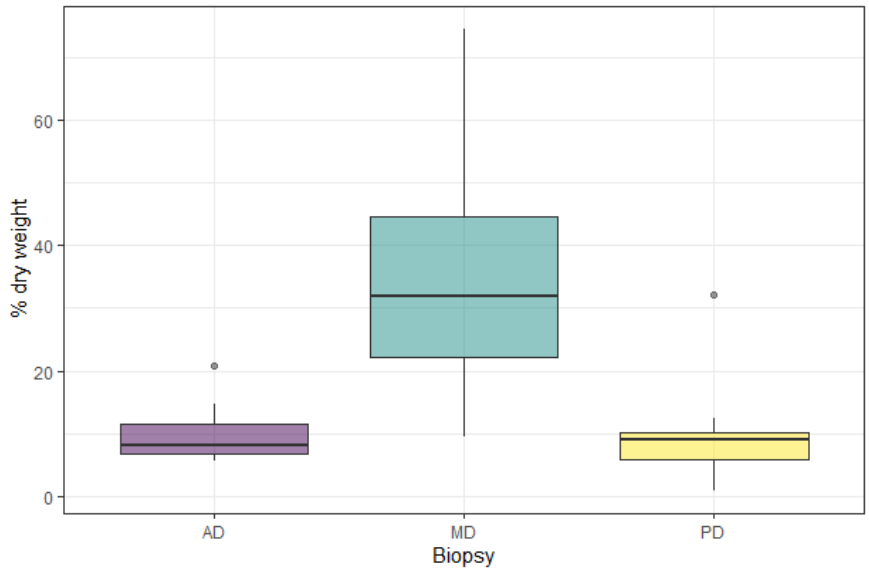

Figure 3. Total lipid (TL) content in anterodorsal (AD), mediodorsal (MD), posteriodorsal (PD) sites of muscle tissue in commercial beaked redfish *Sebastes mentella*.

Figure 4 maps the profiles of individual lipid classes in the two redfish groups. The content of TAG, DAG, Chol, and NEFAs was significantly higher in the commercial product (9.3, 0.6, 1.2, and 2.4% dry weight, respectively) compared to wild specimens (1.4, 0.1, 0.9, and 0.3% dry weight, respectively) (Figure 4). Wild beaked redfish specimens demonstrated a significant prevalence of waxes (0.6 vs. 0.4% dry weight) and an insignificant prevalence of Chol esters (3.0 vs. 2.13% dry weight). The content of PLs and MAG was similar, no significant differences were found, in the two groups: in commercial samples—1.48% and 0.22% dry weight and in wild—1.23% and 0.19% dry weight.

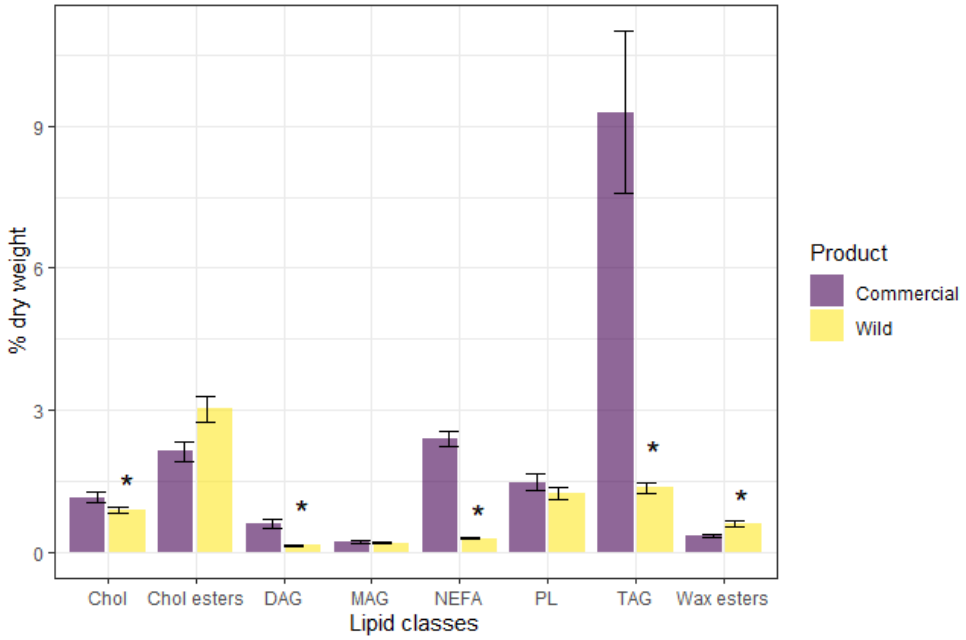

Figure 4. The content of individual lipid classes in muscle tissue from the wild and commercial beaked redfish *Sebastes mentella* samples. Note: *—significantly ($p \leq 0.05$) different between wild and commercial product.

The analysis of lipid classes for different muscle regions in commercial redfish specimens revealed differences between the regions, mainly regarding TAG, Chol esters, and

NEFAs (Figure 5). The MD biopsy region contained the highest amount of TAG compared to AD and PD. Application of the "random forest" machine learning algorithm confirmed that the MD region had a greater variation of the content of lipid classes as opposed to AD and PD—the test set predicted 100% of values for MD, while the prediction accuracy for AD and PD varied within 60–90%. The weightiest classifiers among lipid classes (according to the mean decrease in Gini—MDG) are TAG (MDG = 4.10), as well as DAG (MDG = 3.24) and Chol (MDG = 3.15).

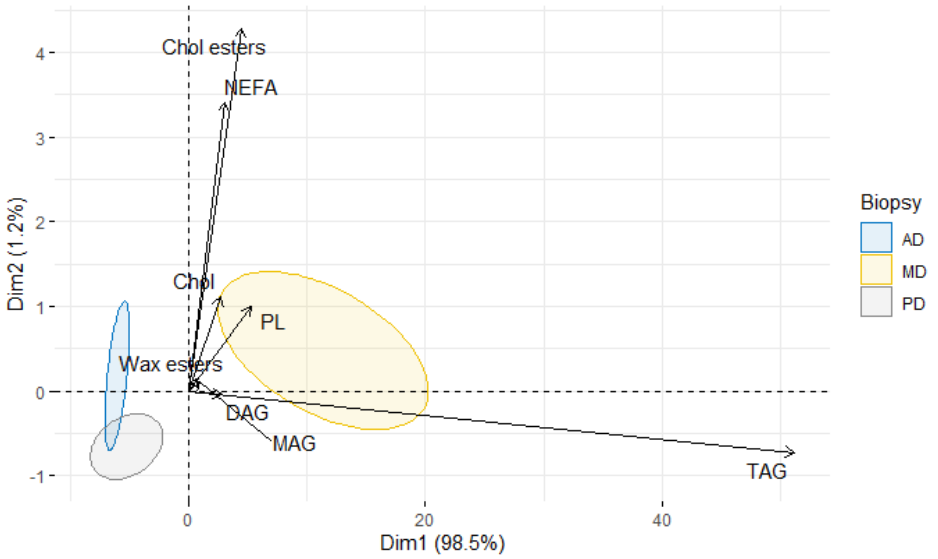

Figure 5. Principal component analysis for different biopsy regions (AD, MD, and PD) in commercial samples of beaked redfish.

A comparison between wild and commercial redfish regarding individual phospholipid classes is shown in Figure 6A. The two samples differ significantly in LysoPC, PEA, and PS contents, whereas PC, a phospholipid metabolically linked with LysoPC and PEA, exhibited no differences. Phosphatidylcholine content was 0.91 and 0.89% dry weight in commercial and wild redfish, respectively. Noteworthy is the significant prevalence of LysoPC in commercial and wild beaked redfish—0.2 and 0.06% dry weight, respectively.

An analysis of phospholipid fractions revealed differences among biopsy regions in the quantities of certain phospholipid classes in "commercial" redfish (Figure 6B). The highest PC content (1.7% dry weight) was found in the MD region, while its levels in the AD and PD regions were 0.6 and 0.5% dry weight, respectively. The content of the metabolically linked PC and PEA was also higher in MD (0.33 and 0.5% dry weight) compared AD (0.1 and 0.2% dry weight) and PD (0.1 and 0.2% dry weight). No significant differences were detected for PS, PI, and SM. The "random forest" machine learning algorithm corroborates the high weight of PC, LysoPC, and PEA as classifiers (MDG = 5.61, 3.74, and 3.71, respectively).

The heat map in Figure 7 illustrates the results of the qualitative and quantitative fatty acid profiling of wild and commercial beaked redfish. The dominant FA in both samples was DHA (22:6(n-3)), but its quantities differed significantly—29.1 and 13.3% of total FAs in wild and in commercial redfish, respectively. It is worth noting that in commercial redfish, quantities similar to that of DHA were found for the following FAs—16:0 (11.5% of total FAs), 18:1(n-9) (11.2% of total FAs), 20:1(n-9) (10.9% of total FAs), and 22:1(n-11) (12.1% of total FAs). In wild redfish, DHA was joined in the first cluster by the saturated 16:0 (palmitic) FA, which contributed 17.0% to total FAs. The next FA cluster comprises 20:5(n-3) and 18:1(n-9)—7.89 and 10% of total FAs; a subcluster "connate", separate from these acids, was represented by "dietary" FAs 20:1(n-9) and 22:1(n-11)—0.2 and 0.6% of total FAs, respectively.

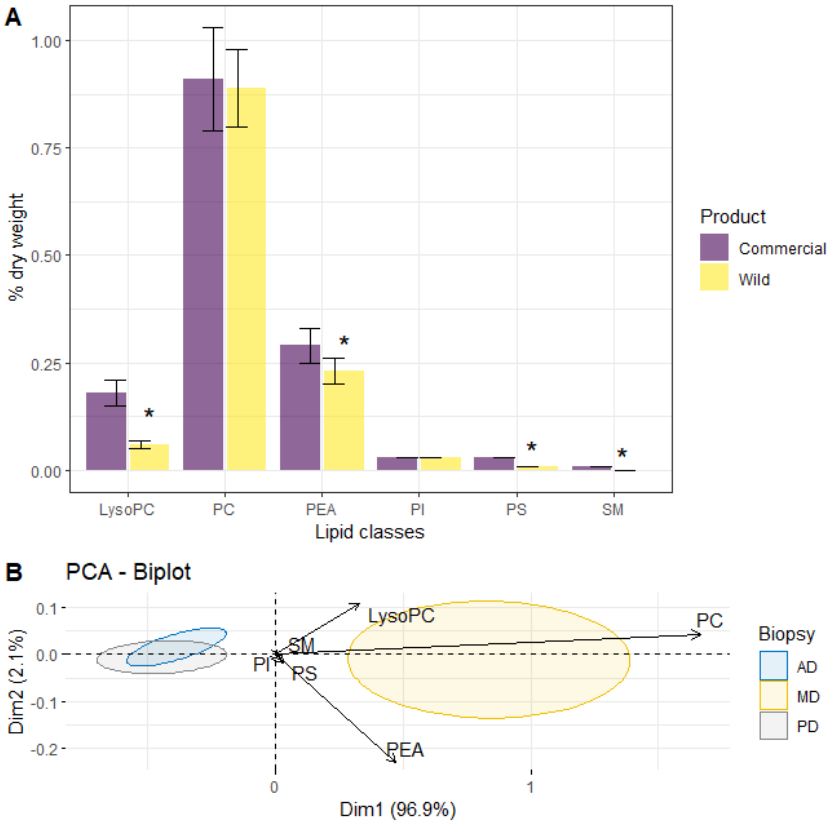

Figure 6. The content of individual phospholipid classes in muscle tissue from the wild and commercial North Atlantic beaked redfish *Sebastes mentella*. Note: (**A**)—comparative characteristics of the content of individual phospholipid classes in wild and commercial fish; (**B**)—principal component analysis for different biopsy regions in "commercial" fish (AD, MD, and PD); *—significantly ($p \leq 0.05$) different between wild and commercial product.

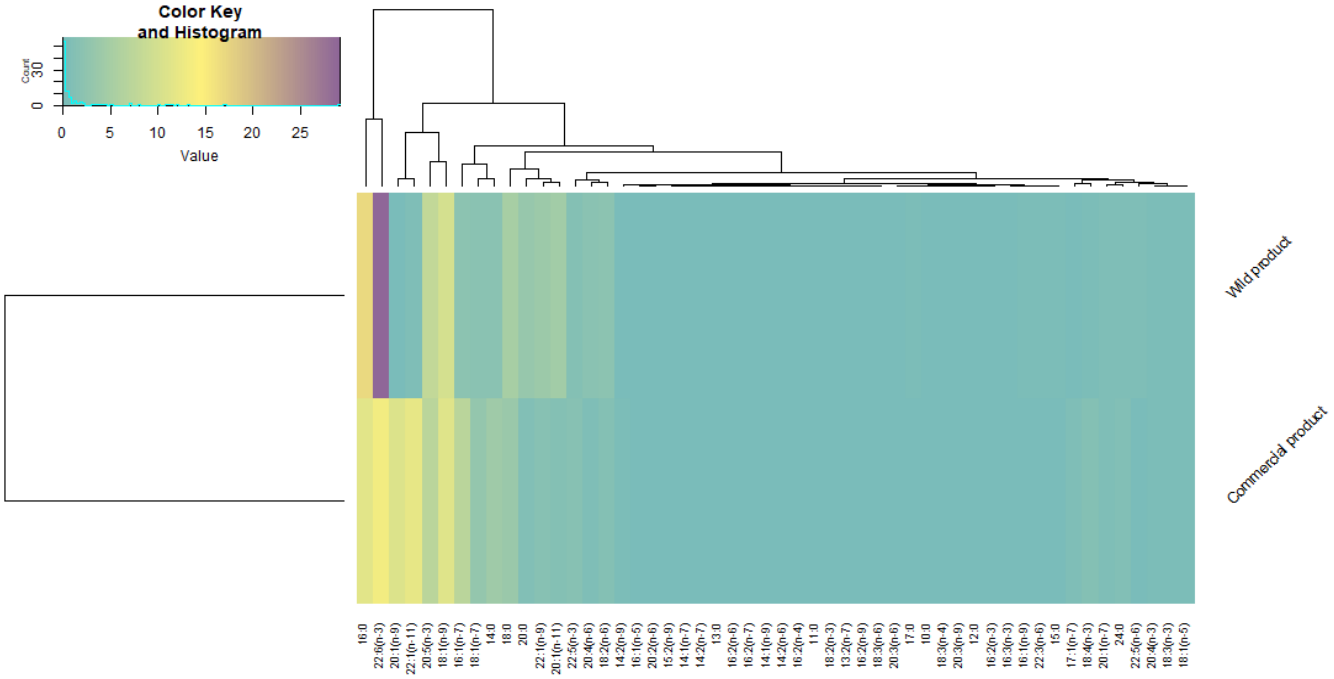

Figure 7. Heatmap of the qualitative and quantitative content of fatty acids (FA) in the muscle tissue from the wild and commercial beaked redfish *Sebastes mentella*.

The differences among main FA classes in a wild and commercial product of beaked redfish are presented in Figure 8. The content PUFA due to (n-3) and (n-6) PUFA was significantly higher in wild specimens than in commercial one's while the content of MUFA was significantly higher in a commercial product. The content of SFA was slightly but significantly higher in muscles of wild samples in comparison to commercial.

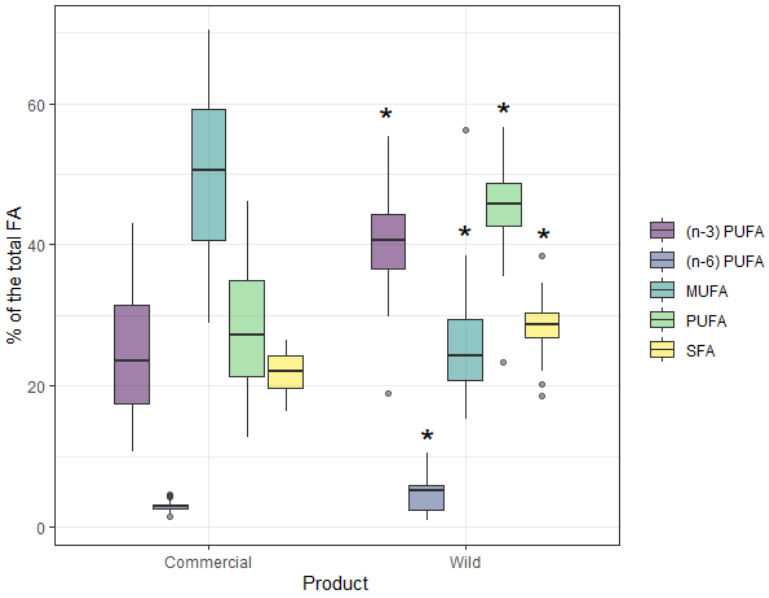

Figure 8. The content of main fatty acids classes in muscle tissue from the wild and commercial beaked redfish *Sebastes mentella*. Note: *—significantly ($p \leq 0.05$) different between wild and commercial product.

The ratios among FAs in these clusters (Figure 7) were significantly different between wild and commercial samples. The data are presented in the Table 1. Notable, no significant differences were found for 20:5(n-3)/18:3(n-3) ratios, the elongation ratio which is characterized possible synthesis of the pivotal product—20:5(n-3) from the precursor—18:3(n-3).

Table 1. Certain significant nutritional indexes and metabolic ratios in muscle of wild and commercial of the studied specimens of beaked redfish *Sebastes mentella*.

Index	Commercial	Wild
(n-3)/(n-6)	8.35 ± 0.32	13.72 ± 1.42
16:0/18:1(n-9)	1.18 ± 0.08	1.79 ± 0.06 *
18:1(n-9)/18:0	3.36 ± 0.24	1.98 ± 0.06 *
18:3(n-3)/18:2(n-6)	0.32 ± 0.01	0.56 ± 0.38 *
20:4(n-6)/18:2(n-6)	0.52 ± 0.04	1.14 ± 0.22 *
20:5(n-3)/18:3(n-3)	18.71 ± 1.46	20.82 ± 0.68
22:6(n-3)/20:5(n-3)	2.14 ± 0.38	3.85 ± 0.15 *
MUFA/SFA	2.36 ± 0.12	0.93 ± 0.04 *
MUFA/PUFA	2.14 ± 0.19	0.59 ± 0.03 *
IA	0.37 ± 0.01	0.35 ± 0
IT	0.2 ± 0.01	0.16 ± 0 *
h/H	2.71 ± 0.08	3.06 ± 0.04 *
HPI	2.78 ± 0.07	2.91 ± 0.04
FLQ	20.41 ± 1.26	37 ± 0.68 *

Note: *—the difference is significant ($p \leq 0.05$).

Moreover, significant differences were detected for main nutritional indexes between the studied groups of fish: FLQ, h/H and IT—20.41, 2.71, 0.20% for commercial *S. mentella* and 37.00, 3.06, 0.16% for wild due to the differences in the contents of certain FA among (n-3) and (n-6)PUFA.

4. Discussion

The depth range inhabited by the beaked redfish in boreal waters extends down to more than 1000 m. All *Sebastes* have certain distinctive characteristics: a complex population structure and a specific life cycle with seasonal, ontogenetic, and vertical (trophic) migrations, longevity, low mortality, late maturing, and slow growth [68,69]. The species' biology, ecology, population structure, and distribution are addressed in several papers, but some aspects remain debatable. Although some studies are available on changes in the lipid metabolism in *Sebastes mentella*, they do not, however, supply full knowledge of the lipid and fatty acid spectrum in redfish at different depths.

In this study, we demonstrate the lipid and fatty acid profiles of muscles in wild beaked redfish in comparison to specimens from food supermarkets and calculate the nutritional quality indexes. There were certain alterations in lipid and FA composition in frozen muscle samples of beaked redfish of a commercial product with 2 months left storage period in comparison to wild samples. Some loss of quality does, however, happen in fish stored frozen over a prolonged time, thus limiting recommended storage life [55]. Furthermore, the quality of fish products and the storage life of frozen fish can also be influenced by several factors: chemical composition of the raw material and handling of it [70], temperature and duration of storage before freezing [56,57], and the conditions in which the frozen product was stored and transported [58]. Quality deterioration due to hydrolysis and oxidation of lipids due to a high degree of unsaturated FA constituents and to protein denaturation affects the product's flavor, nutritive value, texture, yield after defrosting and cooking, as well as the ability of fish muscles to retain natural water [71].

Wild beaked redfish in our study had a lower TL content in muscles (7.71% dry weight) compared to commercial specimens (17.64% dry weight), which probably occurred during storage within the permitted period of product selling, the temperature of storage, and temperature sustainability. As was pointed out, the storage life for beaked redfish according to trade labels was 9–10 months while the commercial samples analyzed were left at 2 months before the expiration date. Personal observations noted that the temperature conditions on storage shells in chain markets varied that could cause freeze-thaw abuse. It is known, in fact, that during prolonged storage, lipolytic enzymes destroy lipids even at −20 °C. Besides, they can be strongly activated during thawing [72]. The result thus indicates that lipid components undergo slow oxidative degradation during prolonged transportation and storage [55,59,73]. In support of this, we show DAG and NEFA content in commercial specimens to be elevated versus the wild sample. The principal reason for the elevated NEFA content is the higher enzymatic activity of lipases, which can continue to cleave labile and active lipid components even after fish death [74]. Beaked trout muscles are known to be rich in PUFA, which makes them more sensitive to lipid hydrolysis [75]. Oxidation of lipids, in particular the high content of NEFA produced through hydrolysis, is the main reason for fish quality deterioration [73]. Another fact pointing to oxidation of lipids, namely phospholipids, is the confidently elevated content of LysoPC, product of the hydrolysis of a principal structural lipid—PC. The decreased content of TAG, increased content of NEFA and lysophospholipids was found for muscles of Atlantic salmon fillets frozen storage at −12 °C for 3 months [75].

The differences in the quantities of lipid classes between biopsy regions in commercial fish apparently corroborate the conclusions from the morphological studies [76] of redfish skeletal muscles that the diameter and density of fibers varies in different parts of redfish body and that these differences are sex-specific. The muscular tissue variations among body parts and the related metabolic (including lipogenic) differences generally facilitate the growth of this slow-growing species at high depths in boreal waters. In addition to this, latest studies [76] show that the diameter of white muscle fibers in a majority of beaked redfish size groups decreases in the caudal direction.

A major source of "superfoods" is marine organisms, and northern mesopelagic fish are considered as a promising alternative, a multifaceted resource that is not only rich in PUFAs but also features their unique arrays and ratios of components. As a result of

low ambient temperatures, the content of the more valuable n-3 PUFAs in deep pelagic organisms living in northern latitudes is higher than that of n-6 PUFAs. Besides, some favorable biological effects of PUFAs on humans are realized through interaction with monounsaturated fatty acids (MUFAs). Long-chain n-3 PUFAs are known for their anti-atherosclerotic effect. They reduce inflammatory and allergic reactions and are effectively used in clinical practice to treat cardiovascular diseases and neurodegenerative disorders. The lipid and phospholipid classes rich in PUFAs possess membrane-repairing and hepatoprotective properties.

Speaking of the FA profile, both samples of beaked redfish featured a high PUFA content. Interestingly, the dominance of PUFAs in skeletal muscles was noted also for *Sebastes marinus* in both seasons. The quantity sequence was continued by MUFAs and then by saturated fatty acids (SFAs) (unpublished). Thus, this distribution of the main FA families may prove to be shared by all *Sebastes* fishes living in boreal waters.

Among PUFAs, the greatest amounts of 20:5(n-3), EPA, and 22:6(n-3), DHA, as well as of 16:0 FA, which is a "pivotal" NEFA in lipid metabolism, were found in "wild" redfish. As we have demonstrated previously [51], the dominance of essential and physiologically significant EPA and DHA is associated with living at low temperatures and is one of the main pathways for the lipid-involving compensatory reaction in response to changes in the environment. A known fact [7,77,78] is that the content of the essential DHA in fish lipids is influenced by environmental factors such as temperature and depth (pelagic mode of life) and by the natural motility of the fish.

Taking into account that among (n-3) PUFAs, there are EPA and DHA are especially significant for human health due to immunomodulatory, general strengthening properties, and importance in the therapy of cardiovascular diseases the obtained results and the object of study have to be discussed from these positions in special. Indeed, in the present study, it is confirmed by calculating the basic nutritional indicators for fillets of wild and commercial *S. mentella*. According to the data obtained, only the FLQ, h/H, and IT nutritional and health indices differed. The FLQ index indicates the quality of the food source of lipids [79,80]. In the present study, the prevalence of the FLQ index in wild individuals was found to be 2 times. It may make sense to use this indicator to determine the "freshness" of the product since the FLQ calculation considers the content of EPA and DHA, which quickly undergo oxidation. For wild specimens, a significantly high h/H index was found, which indicates a better quality of the food in terms of lowering cholesterol levels in the consumer, compared to the commercial product [81–83]. Saturated FAs as 12:0, 14:0, and 16:0 have the effect of increasing cholesterol levels and, as a result, are considered atherogenic, while MUFA and PUFA of the n-6 and n-3 families have protective properties, reducing the concentration of total cholesterol in plasma and low-density lipoprotein cholesterol [84–86]. It should be noted that both wild and commercial samples showed a high h/H index, in comparison to, for example, dairy products of animals [87].

The values of such important indices as IA and IT prevailed in the commercial samples, but only for IT significant differences were established. It is known that the lower the IA and IT, the more beneficial the product is for health, which is associated with the positive effect of MUFA and PUFA on the cardiovascular system [81]. IT is further defined as the relationship between thrombosis and antithrombotic fatty acids (MUFA, (n-3) and (n-6)PUFA) [88].

For wild individuals, a significant prevalence of FA metabolism ratios was revealed (16:0/18:1(n-9); 18:1(n-9)/18:0; 18:3(n-3)/18:2(n-6); 20:4(n-6)/18:2(n-6); 22:6(n-3)/20:5(n-3)), which might indicate the degradation processes of long-chain FA in commercial samples due to long-term storage. At the same time, no significant differences were found for the 20: 5(n-3)/18:3(n-3) index.

5. Conclusions

In this study, we demonstrate the lipid and fatty acid profiles of muscles in wild beaked redfish in comparison to specimens from food supermarkets and calculate the

health and nutritional quality indexes. Wild specimens are characterized by lower TL content while in the wild sample the TL content was higher, and the qualitative profile was distinguished by slightly higher contents of DAG and NEFA indicate the degradation of lipids. Another fact pointing to oxidation of lipids, namely phospholipids, is the confidently elevated content of LysoPC, a product of the hydrolysis of a principal structural lipid—PC. Even though both samples of beaked redfish featured a high PUFA content the FLQ index was lower due to EPA and DHA in commercial specimens vs. wild fish. Moreover, the IT health index was slightly significantly higher in commercial samples in comparison to wild ones. Thus, we showed the changes in lipids and FAs as well as the difference in the nutritional and health indexes in wild and commercial fillets of redfish. Indeed, freezing is a way to maintain the quality and extend the storage life of redfish, but the duration of transportation, the temperature of storage, and temperature fluctuations must be controlled properly. However, the slight loss and degradation of lipids and the quality of FAs were detected. Quality deterioration due to hydrolysis and oxidation of lipid components affects the product's flavor, nutritive value, and texture, the criteria we had tested analytically and personally.

In addition, we found that the differences in the quantities of lipid classes between biopsy regions in fish apparently corroborate the morphology and physiology of fish inhabited deep-water and perform migrations in the life cycle. Thus, it is expected that trade steaks of redfish are distinguished by the content of lipids based on these steaks could be categorized and offered as a personalized food product.

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