Food Chemistry 125 (2011) 402–409

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Distribution of trace metals in a ling (*Genypterus blacodes*) fish fillet

Shailini Ashoka [a], Barrie M. Peake [a,*], Graeme Bremner [b], Kimberly J. Hageman [a]

[a] Chemistry Department, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand
[b] Ministry of Fisheries, P.B. 1926, Dunedin 9054, New Zealand

ARTICLE INFO

Article history:
Received 21 July 2009
Received in revised form 28 July 2010
Accepted 2 September 2010

Keywords:
Trace metal distribution
Fish muscle
Red muscle
White muscle
Belly flap
Genypterus blacodes

ABSTRACT

The distribution of trace metals in a ling (*Genypterus blacodes*) fish fillet was determined from ICP-MS measurements of digests prepared using nitric acid and hydrogen peroxide, followed by microwave digestion. Most trace elements were inhomogeneously distributed in the muscle tissue of the ling with a non-linear increase in concentration towards the tail end of the fillet. This distribution pattern may be connected to the size variation of the individual muscle cells or the change in the ratio of connective tissue to muscle tissue, suggesting that the observed inhomogeneity of muscle elemental distribution may be inherent to all fish species. The concentration of an element in a sample of fish muscle tissue thus depends on the physical location within the fish from which the sample was dissected. Significant differences in trace element concentrations were also detected between the red and white muscle fibres of ling, as well as between the belly flap and the rest of the musculature.

1. Introduction

Trace metals have been quantified in muscle tissue from a variety of fish species (e.g. Andreji, Stranai, Massanyi, & Valent, 2006; Cogun, Yuzereroglu, Kargin, & Firat, 2005; Cronin et al., 1998; Emara, El-Deek, & Ahmed, 1993; Prudente, Kim, Tanabe, & Tatsukawa, 1997; Rodriguez-Sierra & Jimenez, 2002; Soegianto & Hamami, 2007; Youssef & Tayel, 2004). These studies have been undertaken for various reasons, many of them concerning food safety and public health interests. Muscle tissue is generally used because it is the major edible portion of the fish; however, there is no consistent protocol for sampling muscle tissue. Sampling protocols include digesting the entire fillet (Bohn & Fallis, 1978), homogenising the entire muscle fillet and taking a subsample for analysis (Plaskett & Potter, 1979; Sepe et al., 2003; Sharif, Mustafa, Mirza, & Safiullah, 1991), dissecting and analyzing only a specific portion of the fillet (Kojadinovic, Potier, Le Corre, Cosson, & Bustamante, 2007; Turkmen, Turkmen, Tepe, Ates, & Gokkus, 2008; Windom, Stickney, Smith, White, & Taylor, 1973), and preparing composite samples from different individual fish (Al-Saleh & Shinwari, 2002; Chale, 2002). In many studies, the sampling protocol is not clearly specified and it is impossible to determine what section of muscle tissue was analysed. Knowing that many different sampling protocols are in use, inter-study comparisons cannot be reliably undertaken without understanding if and how trace metal concentrations vary in different parts of the fish fillet.

Information on the variability of trace metal concentrations in fish muscle is limited to that gained from a small number of studies. Heit (1979) analyzed five samples from the dorsal muscle of a striped bass (*Marone saxatalis*) and reported differences in the concentrations of a number of trace metals in different sections of the muscle. Thurston and MacMaster (1960) measured concentrations of Na and K in different parts of halibut (*Hippoglossus stenolepis*) muscle and also found some noticeable variations in concentrations, particularly for Na. On a related note, concentrations of proteins vary with muscle section and between red and white muscle in mackerel (*Rastrelliger kanagurta*) (Mohan, Ramachandran, Sankar, & Anandan, 2008) and lipids vary among the anterior, posterior, and belly flap regions of Atlantic salmon (Nanton et al., 2007). These studies suggest that further investigation of trace metal concentrations in fish muscle is needed.

The aim of this work was to determine whether trace metal concentrations are homogeneously distributed in the muscle of ling fish (*Genypterus blacodes*). A suite of 40 trace metals was quantified in samples dissected from different positions along ling fillets. Potential differences in trace metal concentrations, between red and white muscle and between the belly flap and adjacent regions, were also investigated. Ling is a large benthic fish found off the shores of New Zealand, southern Australia and southern South America and was selected for this study due to its importance as a commercial fish species in the southern hemisphere.

* Corresponding author. Tel.: +64 3 479 7927; fax: +64 3 479 7906.
E-mail address: bpeake@chemistry.otago.ac.nz (B.M. Peake).

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doi:10.1016/j.foodchem.2010.09.017

2. Materials and methods

2.1. Sample preparation

Samples were obtained from three individual ling fish. The first weighed 5.4 kg and was 96 cm standard length. Sections of ~1 cm^3 of white muscle were dissected along 12 transects within the fillet (Fig. 1) and weighed into polypropylene sample tubes. The approximate distance between sampling sites on this fillet was 5 cm. Five samples of the red muscle, which lies in a narrow band along the caudal section of the lateral line, were also dissected. The second ling fish weighed 1.4 kg and was 86 cm standard length while the third was 1.4 kg and 80 cm standard length. From the second and third fillets, white muscle samples were collected at positions T3e2, T3h2, T7e2 and T10e1 (Fig. 1).

To minimise risks from metal contamination, all glassware and utensils were rinsed, soaked in an acid bath (5 M nitric acid) for at least 24 h, rinsed with Milli-Q water and dried in a laminar flow cabinet. Concentrated nitric acid was quartz-distilled. Hydrogen peroxide (30% v/v) was Univar grade. Dissections were conducted in a Class 350 clean room using a titanium knife, ceramic tweezers and scissors with ceramic blades. All samples were dried to constant weight in an oven at 105 °C. Concentrations are reported on a dry weight basis. Four samples of ~250 mg of a certified reference material, IAEA-407 Fish Tissue (International Atomic Energy Agency, Vienna) were analyzed concurrently to ensure accuracy and to validate the processes involved. Six laboratory blank samples were also analyzed.

Digestions were conducted by adding 3 ml of nitric acid, 2 ml of hydrogen peroxide and 3 ml Milli-Q water to weighed (±0.001 g) dry muscle samples in a polypropylene sample tube with a screw cap. The sample holder, which was encased in an airtight outer plastic container to prevent acid fumes from escaping and causing corrosion, was placed in a domestic microwave oven (Toshiba model ER-694ETN, 650W) and subjected to the following heating programme: 30% microwave power for 10 min, 0% for 10 min, 30% for 10 min, 0% for 10 min and 30% for 10 min. Each extract was diluted to 100 ml with 0.3 M nitric acid. The advantages of this tissue digestion method compared to others have been described previously (Ashoka, 2009).

2.2. Analytical instrumentation

Quantification of trace metals in digestion extracts was performed with an Agilent 7500ce ICP-MS equipped with an octopole collision cell. Isotopes analysed were ^{7}Li, ^{11}B, ^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K, ^{43}Ca, ^{51}V, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{78}Se, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{107}Ag, ^{111}Cd, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{208}Pb, ^{232}Th and ^{238}U. Due to the large mass range of the elements of interest, five internal standards, ^{45}Sc, ^{103}Rh, ^{115}In, ^{159}Tb and ^{209}Bi, were used to correct for any changes in instrumental conditions during measurement runs and compensate for matrix effects.

Standard solutions for calibration were prepared by diluting commercially-available single element stock solutions (High Purity Standards, 1000 μg/ml) and multi-element stock solutions (Spex Certiprep Claritas PPT multielement solutions, 10 mg/l) with Milli-Q water containing 0.3 M nitric acid. The multi-element standard solutions were matrix-matched to the same average concentrations of Na, K and Ca as the samples.

2.3. Statistical analysis

2.3.1. Preliminary data handling

Final sample concentrations were calculated by subtracting the average blank concentrations from measured concentrations and dividing by the dry sample mass. Outliers in the blank samples, which were detected using the interquartile range test, were removed prior to blank subtraction.

2.3.2. Detection limits

The detection limit for each element was calculated as three times the standard deviation of the apparent concentration in the blanks (Analytical Methods Committee, 1987).

2.3.3. Testing for significant differences

t-Tests were performed using the SPSS statistical software package (Version 17.0) to identify significant differences ($p < 0.05$) between trace metal concentrations in (a) the belly flap versus adjacent muscle tissue and (b) the red versus white muscle of the first fillet.

Univariate analyses of variance were used to test for differences among the four locations sampled in all three fillets. For each element, the mean concentration for the fillet was subtracted from each measured concentration prior to analysis.

2.4. Quality control

The certified reference material (CRM) IAEA-407 Fish Tissue (from the International Atomic Energy Agency) was used for quality control purposes. Experimental values for an element were accepted if the results obtained for the reference material fell

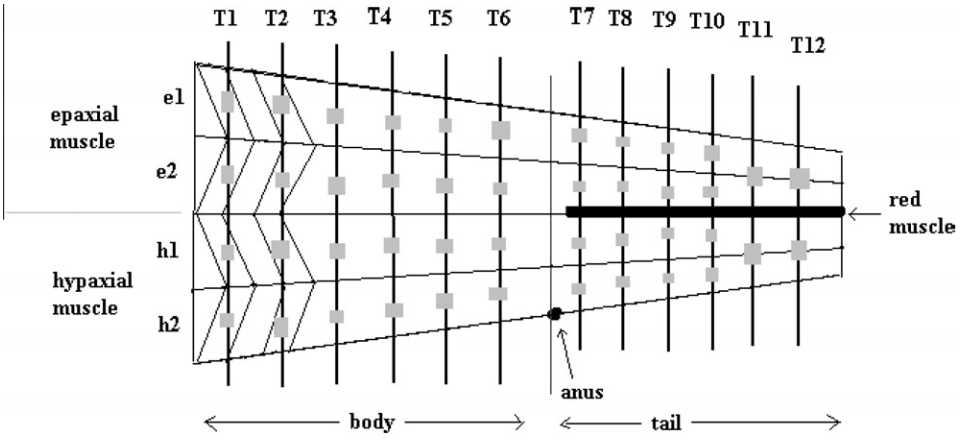

Fig. 1. Diagram of fillet dissection. Shaded boxes indicate positions of dissected samples.