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Different tools to trace geographic origin and seasonality of croaker (*Micropogonias furnieri*)

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ABSTRACT

The aim of this study was to use proximate chemical composition, macro and trace elements, fatty acid profile and stable isotopes as traceability tools to assess geographic origin and seasonality of croaker (*Micropogonias furnieri*). Croaker from Parnaíba contained higher ash in July and lower fat content than croaker from Santos. In contrast, croaker from Santos had statistically higher proportion of 16:1n-9+16:1n-7, 20:1n-11, 20:1n-9, MUFA and n-3/n-6 ratio than croaker from Parnaíba. Concerning seasonality, croaker caught in July had significantly higher amounts of 14:0, 15:0, 16:1n-9+16:1n-7 and saturated fatty acids than fish caught in December. Concerning elements, significant differences were also detected between seasons for Cl, Ca, Fe, Sr and S, whereas differences between geographic origins were only observed with K. $\delta^{13}C$ and $\delta^{15}N$ were statistically different between geographic origins, whereas differences between seasons were only detected in $\delta^{15}N$ ratio of croaker from Santos. Fatty acids, minerals and stable isotope are effective methods to trace geographic origin and seasonality of croaker. Nonetheless, further investigation is still required with larger samples of croaker to enable the implementation of fatty acids, elements or stable isotope as authenticity tools by food control agencies.

1. Introduction

Consumers are increasingly aware about the beneficial effects of fish intake to human health, which enabled the continuous increase in fish consumption worldwide (Mazzeo et al., 2008). As a result, the trade of a wide variety of fish products has increased, and consumers are increasingly concerned about the quality, origin and authenticity of the products, as well as on how they are handled, processed and stored (Herrero, 2008).

Fish adulteration can induce several consequences to consumers, such as the purchase of mislabeling or potentially harmful products and reduce the effectiveness of marine conservation (Civera, 2003). Thus, the authenticity evaluation and origin of species are important requirements to ensure quality, provide adequate security controls and develop effective regulations. Food authentication is part of traceability that includes food components identification to verify the compliance with labeling to prevent fraud. Labeling must provide information about species, origin, age and production systems (Schwagele, 2005).

The conventional fish identification is made by examination of their anatomical and morphological characteristics. However, identification becomes complicated in processed food, such as frozen fillets and precooked shellfish, where these morphological characteristics are removed (Moran & Garcia-Vazquez, 2006). Therefore, there is an urgent need to develop methods to rapidly and accurately identify processed food that can help the authorities and fish industries to comply with the requirements for labeling and traceability, and to ensure product quality and consumer protection (Carrera, Cañas, & Gallardo, 2013).

The use of analytical techniques to determine the geographic origin of food products is the best way to prevent tampering. Gas

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chromatography (Busetto et al., 2008; Thomas et al., 2008), spectroscopy (Cordella, Faucon, Cabrol-Bass, & Sbirrazzuoli, 2003) and IRMS (Thomas, Jasmin, & Lees, 2005) have been proposed for food authenticity in order to identify the presence of main components in the sample or any compounds that may be characteristic of a particular food item.

Isotope ratio mass spectrometry (IRMS) is a powerful tool for the detection of adulterated and counterfeit food products (Calderone et al., 2009) and is recognized as an official method to ensure the authenticity of food products (Martin & Martin, 1995). IRMS has been applied for assessing geographic origin of lamb (Piasentier, Valusso, Camin, & Versini, 2003) beef (Heaton, Kelly, Hoogewerff, & Woolfe, 2008) poultry meat and dried beef (Franke et al., 2007), but limited studies exist of its applicability in seafood.

It is well known that the levels of macro and trace elements in food products clearly reflect the environmental conditions at which they were produced. For this reason, the elemental content has been suggested as a good indicator of the geographic origin of food samples. Thus, techniques such as atomic absorption spectrometry (FAAS) have been successfully employed in food authentication (Gonzalvez, Armenta, & de la Guardia, 2009). Energy dispersive X-ray fluorescence (EDXRF) is another technique that can also be used in elemental determination. This technique is highly sensitive, fast, cheap and accurate to measure multi-elements.

Fatty acids profile is another useful tool to differentiating fish stocks (Joensen, Steingrund, Fjallstein, & Grahl-Nielsen, 2000), production systems (Alasalvar, Taylora, Zubcov, Shahidi, & Alexis, 2002), seasonality (Rasoarahona, Barnathan, Bianchini, & Gaydou, 2005) and geographic origin (Çelik, Diler, & Kuçukgulmez, 2005).

The city of Santos is located in the South East of Brazil in a highly industrialized area, subjected to strong anthropogenic pressure. In contrast, Parnaíba is a small town located in the North East of Brazil, where economy is based on the production of babassu oil, carnauba wax and cotton. Both cities have distinct environmental conditions, water quality and contamination levels. The croaker *Micropogonias furnieri* is considered as one of the most traditional and gastronomically important fish species captured by fisheries in Brazil, Argentina and Uruguay, being a very important resource in Santos and Parnaíba regions (Elsdon & Gillanders, 2002). This species is omnivorous, showing preference for small crustaceans such as shrimp and crabs. Regarding the life cycle, young individuals migrate to estuaries, while adults migrate to coastal areas to breed. The population of croaker varies throughout the year as a result of migration and food availability (Costa & Araujo, 2003).

In this context, this study aimed to assess the traceability of croaker (*M. furnieri*) from two distinct regions, Santos and Parnaíba and harvested in two seasons (July and December). Different traceability tools were employed to assess geographic origin and seasonality of croaker, such as proximate chemical composition, macro and trace elements, fatty acid profile and stable isotopes of carbon and nitrogen.

2. Materials and methods

2.1. Samples

Croakers were caught in two distinct regions of the Brazilian coast, namely in Santos (23° 57′17″S and 46° 19′56″W) and Parnaíba (02° 54′17″S and 41° 46′36″W) in July (winter) and December (summer) of 2011. The regions have two well defined seasons: summer and winter. The specimens' morphological parameters were registered (Table 1), then all fish were eviscerated and transported on ice to the laboratory where they were separated the edible part (muscle), homogenized and frozen. A portion of each frozen sample was freeze-dried for 48 h at −40 °C (Christ, Alpha 2-4 LD Plus, Munchen, Germany) and stored at −80 °C under controlled moisture conditions until further analyses.

Table 1
Weight and length (mean ± standard deviation) of croakers caught in Santos and Parnaíba in different seasons.

Locality/ Seasonality	Weight			Length		
	Mean	Max.	Min.	Mean	Max.	Min.
CSJ ($n = 10$)	1188.5 ± 186.8	1580	965	39.9 ± 2.0	42.5	37.0
CSD ($n = 10$)	712.5 ± 90.2	870.9	591.7	39.5 ± 1.5	42.5	36.5
CPJ[a] ($n = 10$)	244.1 ± 142.2	497.5	96.2	27.1 ± 4.9	34.0	21.2
CPD ($n = 10$)	985.6 ± 104.1	1150	840	45.8 ± 2.1	48.0	42.0

CSJ: Croacker Santos July; CSD: Croacker Santos December; CPJ: Croacker Parnaíba july; CPD: Croacker Parnaíba December.
[a] Weight of eviscerated fish.

2.2. Proximate chemical composition

Moisture, ash, protein and lipid contents were determined according to the Association of Official Analytical Chemists methods (AOAC, 2005). All analyzes were performed in duplicate per specimen. Samples were defrozen for subsequent analyses. Analyses of moisture and ash were carried out by oven drying at 105 °C (method 950.46) and muffle furnace at 550 °C (method 938.08). The total level of nitrogen were determined by the Kjeldahl procedure (method 981.10), and protein levels were estimated using 6.25 conversion factor; and total lipid content was determined with the Soxhlet extraction method using ethyl ether (40–60 °C; 7 h; heater plate SBS Instruments PC6L, Portugal).

2.3. Fatty acid profile

Fatty acid profile was determined in triplicate for each specimen, according to the experimental procedure of Cohen, Vonshak, and Richmond (1988). Each freeze-dried sample (300 mg dry weight) was blended in 5 mL of acetyl chloride/methanol (1:19 v/v; Merck), shaken, and heated (80 °C; 1 h). After cooling, 1 mL of Milli-Q distilled water and 2 mL of n-heptane pro analysis (Merck) were added, and samples were shaken and centrifuged (2000 g; 5 min, Sigma 2k15, Germany) until separation in two phases: an upper organic phase (composed by methyl esters) with n-heptane and a lower organic phase with methyl chloride, methanol and water. The moisture content of the upper phase was removed with anhydrous sodium sulfate (Panreac). An aliquot (2 μL) of the upper phase was then injected (split injector) on a gas chromatograph (Varian Star 3800 Cp, Walnut Creek, CA, USA) equipped with an auto sampler and fitted with a flame ionization detector at 250 °C. The separation was carried out with helium as carrier gas at a flow rate of 1 mL min^{-1}, in a capillary column DB-WAX (30 m length 0.32 mm internal diameter; 0.25 μm film thickness; Hewlett–Packard) programmed at 180 °C for 5 min, raised to 220 at 4 °C min^{-1}, and maintained at 220 °C for 25 min, with the injector at 250 °C. Fatty acids were identified by comparing retention times with those of Sigma standards. Quantitative data were calculated using the peak area ratio (percent of total fatty acids) and the Varian software.

2.4. Trace elements and contaminants

Energy dispersive X-ray fluorescence (EDXRF) was used to quantify the elements S, Cl, K, Ca, Fe, Zn, As, Se, Br and Sr. The spectrometer is a self-constructed system, using a Philips X-ray generator (PW 1140/00/60 3 kV). The EDXRF technique consists of an X-ray tube equipped with a molybdenum secondary exciter. The characteristic radiations emitted by the elements in the sample