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Review

Authentication of fishery and aquaculture products by multi-element and stable isotope analysis

Li Li [a,*], Claude E. Boyd [b], Zhenlong Sun [a]

[a] The Key Laboratory of Mariculture, Ministry of Education, Fisheries College, Ocean University of China, Qingdao 266003, People's Republic of China
[b] School of Fisheries, Aquaculture and Aquatic Sciences, Auburn University, AL 36849, USA

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ABSTRACT

The market of fishery and aquaculture products is globalized with increasing numbers of mislabeled products. This highlights the need for approaches to indentify the origin of these products. Among the measures used to identify the origin of other agro-products, multi-element and stable isotope analysis are promising approaches to identify the authenticity and traceability of fishery and aquaculture products. The present paper reviews the use of multi-element and stable isotope analysis to determine the origin of fishery and aquaculture products. Principles and limitations of each method will be illustrated and perspectives for traceability of fishery and aquaculture products will be discussed. The aim of this review is to mediate fundamental knowledge for the interpretation of experimental data on authentication of aquaculture products.

Contents

1. Introduction

Mislabeling of seafood is common in several markets. The USA imported 80% of its seafood and an estimated 30% of the fish and 13% of shellfish sold is mislabeled (Jacquet & Pauly, 2008). In Australia, 23% barramundi and red emperor was incorrectly labeled as other species (Rochfort, Ezernieks, Maher, Ingram, & Olsen, 2013). The development of traceability methods to distinguish aquaculture products is becoming increasingly important to protect consumer's rights and ensure fair competition.

There is a growing interest by consumers in purchasing food items that have been produced in compliance with standards of eco-label certification programs. Several organizations, e.g., the

* Corresponding author.
E-mail address: l_li@ouc.edu.cn (L. Li).

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Aquaculture Stewardship Council, the Global Aquaculture Alliance, Global GAP, and Friends of the Sea certify aquaculture products (Boyd & McNevin, 2015). In order to avoid comingling of certified products with other similar products in the market chain, a chain of custody and traceability system is necessary.

Several methods such as elemental profiling, stable isotope analysis, lipid profiles, DNA barcoding, near infrared spectroscopy etc. are used to determine the geographic origin of food products such as wines, coffee, raw pistachios, tea etc. with promising results (Lavilla, Costas-Rodríguez, & Bendicho, 2013; Liu, You, Chen, Liu, & Chung, 2014; Raco, Dotsika, Poutoukis, Battaglini, & Chantzi, 2015; Sciubba, Capuani, Di Cocco, Avanzato, & Delfini, 2014; Zhao et al., 2014). The assessment of wine traceability and authenticity was carried out much earlier and gained more interest internationally than aquaculture products (Versari, Laurie, Ricci, Laghi, & Parpinello, 2014), while in wine authentication, researchers found the alkaline earth metals, lithium, rubidium and some lanthanides were more relevant to authenticate the geographical origin of wines than other macro and micronutrients (i.e. K, Ca, Fe, Cu, and Zn) (Versari et al., 2014). Life cycle of aquacultural products is usually more complicated than other agro-products such as wine, tea and coffee, and feed – that may include ingredients from more than one geographic area – is also a very disturbing factor in traceability. Hence, using those methods to determine the geographic origin of aquaculture products needs to be comprehensively studied.

Multi-element and stable isotope analysis, which will be the topic of the following review, are two of the most widely used methods in traceability of aquaculture products. The World Wildlife Fund (WWF) conducted the stakeholder dialogs that resulted in the standards for the Aquaculture Stewardship Council. The WWF is considering the possibility of multi-element or stable isotope analysis as a possible means of ascertaining the veracity of the traceability component of aquaculture eco-label certification (McNevin, A.A., Director, Aquaculture, WWF-US, personal communications). The aim of the present review is to mediate fundamental knowledge for the interpretation of experimental data on authentication of aquaculture products. In this study, traceability of aquaculture products represented three issues: species of origin, geographical origin, method of production (wild or farmed, organic or intensive).

2. Multi-element analysis

2.1. Principle of methods

Element profiling is a method widely used in determination the geographic origin of food products (Anderson & Smith, 2005). The feasibility of the method is based on the principle that trace element profile of the food products is related to the true element profile of the environments in which they were produced and is relatively stable from the time of harvest to the time of analysis (Camargo, Resnizky, Marchevsky, & Luco, 2010). The method relies on digestion of samples into ions followed by spectroscopic determination of concentrations. Analytical technology including atomic absorption spectroscopy(AAS), graphite-furnace AAS, X-ray fluorescence spectroscopy etc. with inductively coupled plasma-optical emission spectroscopy (ICP-OES) and ICP-mass spectrometry (ICP-MS) the most frequently used techniques for multi-element analysis (Laursen, Schjoerring, Kelly, & Husted, 2014). The main trace elements analyzed include but are not limited to Cu, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Ba, Sr, Li, Se, Co, Ti, V. Huge database must be produced by chemical analysis and multivariate analysis such as principle component analysis (PCA) and linear discriminant analysis (LDA) etc. used for data exploration.

2.2. Selected studies

Element profiling was used to study the provenance of shrimp, clam, sea cucumber, fish in aquaculture (Iguchi, Isshiki, Takashima, Yamashita, & Yamashita, 2014; Li, Boyd, & Dong, 2015; Li, Boyd, & Odom, 2014; Liu et al., 2012). In a study carried out with short-neck clams of which 156 were from Japan, 56 from China and 60 from the Republic of Korea. The analysis of 10 elements (Li, V, Mn, Co, As, Rb, Mo, Ba, Pb, and U) was made by ICP-MS and these data combined with LDA was able to distinguish the geographic origins of short-neck clams with 80–100% accuracy (Iguchi, Takashima, Namikoshi, Yamashita, & Yamashita, 2013). Similarly, among 15 elements (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Hg and Pb) analyzed by ICP-MS on 39 specimens of sea cucumber from three regions, LDA gave an overall correct classification rate of 100%. The farmed aquaculture products may be mislabeled as the wild caught. Elemental profiling was used to differentiate salmon to geographic origin and method of production. Salmon of three species (king salmon, *Oncorhynchus tshawytscha*; coho salmon, *Oncorhynchus kisutch*; Atlantic salmon, *Salmo salar*) was analyzed for 19 elements from two food production practices, wild and farm raised. Five classification modeling: linear discriminate function, quadratic discriminant function, neural network, probabilistic neural network, and neural network bagging investigated in the study performed well with slightly different accuracy depending on the particular choice of model approaches (Anderson, Hobbie, & Smith, 2010). This method was also successfully used to trace Ictalurid catfish and other aquaculture species to the method of production i.e., wild or farm raised (Li et al., 2015).

Two studies using multi-element analysis to investigate the geographic origin of shrimp were reviewed. The U.S. Customs and Border Protection Laboratory built up an authentic reference database for the eight main shrimp importation countries to the United States: Thailand, Indonesia, Vietnam, Mexico, Ecuador, Malaysia, China, and India with data from more than 100 sampling sites spread over the eight countries. Species of shrimp included Pacific white shrimp, black tiger shrimp, and possibly other species. Shrimp with known country of origin was collected from at least 10 regions of each country to validate that the reference database was capable of discriminating among the eight countries of origin with accuracy of over 90% in most cases (Smith & Watts, 2009). In the other investigation, *Litopenaeus vannamei* cultured in three regions of the United States were collected and analyzed for Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, S, Se, Ti, Zn and Zr. The nonparametric method of discriminant analysis: k-nearest neighbor analysis built a classification model to separate shrimp products to geographic origin and the rate of reliability of the model evaluated by a cross-validation procedure was 100% (Li et al., 2014).

2.3. Elements analyzed

Promising results were obtained for use multi-elements to evaluate aquaculture product authenticity. Table 1 summarized studies committed to the authenticity of seafood based on multi-elements analysis. The elements analyzed varied. The essential elements for living things are classified into four categories: bulk structural elements, macroelements, trace elements and ultratrace elements (Boyd, 2000). Bulk structural elements are elements needed in large amounts such as C, H, O, P, S, and N. Macronutrients which are needed in moderate amounts include: Ca, Cl, K, Na, and Mg. The trace elements include: Cu, Fe, and Zn, and the ultra trace elements include: As, B, F, I, Se, Cd, Cr, Co, Pb, Mn, Mo, Ni, Sn, and V. Seven micronutrients have been identified as essential for plants: B, Cl, Cu, Fe, Mn, Mo, and Zn. Twelve trace elements: As, Cl, Cr, Cu, F, I, Fe, Mn, Mo, Ni, Se, and V are essential for animals