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Analytical Methods

Stable isotope and trace metal compositions of Australian prawns as a guide to authenticity and wholesomeness

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ABSTRACT

This research has explored the potential of stable isotope and trace metal profiles to distinguish Australian prawns from prawns imported from neighbouring Asian countries. Australian prawns were collected mostly from the Brisbane area. Strong differences in Australian vs. imported prawns were evident from both the isotope and trace element data, with the differences most likely occurring because imported prawns are typically reared in aquaculture facilities and frozen prior to sale in Australia. The aquaculture origins are characterised by comparatively; low δH_{VSMOW}, $\delta^{13}C_{VPDB}$ values, low concentrations of arsenic, zinc and potassium, and high water contents (>80%). Relatively high arsenic and cadmium contents were found within Australian prawns, but the concentrations did not exceed local human health guidelines.

1. Introduction

Access to global markets is increasingly competitive for many food producers from various countries as consumers are well informed and, therefore, more selective on the quality and authenticity of food products. As a result, producers of foods (and many other commodities) are increasingly protective of the cachet which the country, or region of origin may bestow upon their produce. In turn, the consumer will pay a premium price for what is perceived to be a superior product, attributed to a region of renown such as; Russian caviar, French wine and Spanish ham. Consumers will also associate positive characteristics with fresh produce advertised with qualities such as "local" or "free-range" and may purchase these products in preference to those perceived as "imported" or "intensively farmed". The elevated prices of premium products will inevitably lead unscrupulous traders to pass cheaper, inferior goods as authentic products to the detriment of the producer and consumer. The result of these practices is that the brand reputation of the genuine product is degraded as counterfeit or substitute goods are unlikely to be of the substance or quality demanded by the customer.

There has been a significant interest in promoting increased consumption of seafood (including prawns) because of potential health benefits resulting in an increase in seafood production and marketing and in product quality in various markets. There is also a concern from consumers and health regulators that the products available in a marketplace may not come from genuine and good quality producers and may contain chemical residues, including metal contaminants. In such an uncertain marketplace, many techniques have been developed and applied to protect both producers and consumers of premium brands. Manufacturers will, for example, use packaging with features which are difficult to re-produce, incorporating sophisticated designs, metallic strips, holograms etc. Unfortunately, seafood is typically displayed on ice and sold unpackaged such that the only guarantee of a genuine product is the reputation of the seller.

As a means to protect both seller and consumer, food analysts are increasingly looking to stable isotope analysis, often allied with trace metal analysis, as a means to determine geographical origin (Asche, Michaud, & Brenna, 2003; LeBot, Oulhote, Deguen, & Glorennec, 2011). These techniques provide powerful tools to determine the origin of foods and to elucidate other properties such as whether the product is wholesome.

The isotopic composition of prawn chitin has been reported to reflect growth conditions related to nutrients and the surrounding water environment (Nielson & Bowen, 2010). The present study set out to determine which, if any, parameters could best discriminate between Australian prawns and those imported from nearby Asian

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countries by examining the stable isotopic and trace metal compositions of shells (chitin), meat, heads and recoverable water.

As with many studies of food authenticity we encountered difficulty in obtaining truly authentic samples; with the exception of one sample collected directly (and live) from a local prawn farm. In obtaining other samples deemed "*Australian*" our strategy was to seek out reputable vendors with an established supply chain. In general, we were not able to determine the specific origin of samples described as "*Australian*" but in this work we have used the term to identify those samples in which we had reasonable confidence.

Samples which claimed to be the products of Malaysia, China or Vietnam were assumed to be authentic since there was no commercial advantage to be obtained, within Australia, by branding products as such. In this paper we have used the term "*imported*" to identify samples branded as product of these countries although prawns may be imported from as far away as Norway or Colombia. The intention of this study was to identify parameters which may be used to determine the country of origin of prawns. It is envisaged that subsequent studies will test the success of these parameters against regional variations within Australia and against a global survey of prawns and other seafood.

2. Materials and methods

2.1. Samples

Ten samples of prawns were initially purchased, prepared and analysed, to develop a methodology to distinguish *Australian* and *imported* samples. Each sample comprised approximately 1 kg of uncooked prawns which were either whole (heads and shells) or cutlets (tail). These samples were collected to be representative of native Australian and imported species, with both meat and shell present (Table 1, samples 1–10). Australian samples were collected from the Brisbane area. Sample (1) comprised Tiger prawns collected from a Gold Coast prawn farm said to be tenth generation Australian. These prawns had been raised in water taken from the outflow of a local river (the Logan river) and their diet had been supplemented with feed imported from Thailand. Four samples of feed were provided for analysis. Samples 2 and 3 were obtained from a fishmonger (Scarborough, QLD), said to have been freshly caught by local trawlers. Samples 4–6 were purchased from local supermarkets (Sunnybank, QLD) and were sold as frozen and thawed. Four samples of frozen prawn cutlets were purchased from local retailers (Sunnybank, QLD) and were reported to be products of; Malaysia (7, 8), Vietnam (9) and China (10). These ten samples were used to determine which parameters best distinguished *Australian* and *imported* species.

Subsequently, the method was applied to seventeen samples of uncooked prawns, of which three claimed to be Australian, two claimed to be imported and the remainder where of unknown origin. For the majority of these samples it was not known if they had been sold fresh, frozen or thawed. Prawns were all larger individuals of >80 mm total length and generally of the family *Penaeidae*.

2.2. Sample preparation

Samples were frozen upon receipt at the laboratory and were defrosted prior to preparation. The meat, shell and head (when present) fractions where separated and coarsely homogenised using a commercial food processor. At this stage of preparation the samples were moist, with a small surface area and were exposed to metal surfaces for approximately 10 s. Previous work within our laboratory has shown that this degree of contact introduces no significant metal contamination. All subsequent stages of handling, in which either contact times or surface areas where large were performed using metal free materials. Samples were then placed in grip-seal polyethylene bags and frozen at −20 °C. The meat, shell and head components from each sample were dried together for approximately 30 h using a Dynavac FD12 freeze-drier (Seven Hills, NSW, Australia). The weigh loss on drying was recorded and the water from each group of samples was recovered from the cold-trap of the freeze-drier and retained for isotopic analysis. To determine the extent of any isotopic fractionation due to the freeze drying processes a sample of MilliQ grade water (approximately 250 g) was frozen, "freeze dried" and re-collected from the cold-trap.

Table 1
Prawn samples obtained for the study.

Sample	Description	State	Country of origin
1	Gold Coast aquaculture tiger prawns	Fresh	Australia[a]
2	Green tiger prawns	Fresh	Australia[b]
3	Green banana prawns	Fresh	Australia[b]
4	Prawn banana raw large fzn	Thawed	Australia[c]
5	Prawn king green xlrge fzn	Thawed	Australia[c]
6	Prawn banana Aust. green lge frzn	Thawed	Australia[c]
7	Raw prawn cutlets peeled-deveined-tail on	Frozen	Malaysia[d]
8	Raw prawn cutlets-tail on	Frozen	Malaysia[d]
9	Frozen raw black tiger prawns	Frozen	Vietnam[d]
10	Vannamei prawns	Frozen	China[d]
11	JW prawn farm		Australia[a]
12	Local fresh green prawns	Thawed	Australia[b]
13	Local king prawns		Australia[b]
14	Frozen raw vannamei	Frozen	Imported[b]
15	Raw prawns peeled	Frozen	Malaysia[c]
16	Raw prawn cutlets		Unknown[b]
17	Prawn meat raw		Unknown[b]
18	Large green king prawns		Unknown[b]
19	Large green prawns		Unknown[b]
20	Raw large king		Unknown[b]
21	Medium king prawn		Unknown[b]
22	Green headless prawns		Unknown[b]
23	Green Pacific king prawn headless		Unknown[b]
24	Medium green king		Unknown[b]
25	Large banana prawns	Thawed	Unknown[c]
26	Prawn meat raw	Frozen	Unknown[c]
27	Prawn green king large	Frozen	Unknown[c]

[a] Prawn farm.
[b] Fishmonger.
[c] Major supermarket.
[d] Local retailer.

The dried samples were de-fatted with hexane (SupraSolv grade, Merck, Darmstadt, Germany), using a Soxtherm automatic extraction system (Perten Instruments, Australia). Chitin was purified from the dried, de-fatted shells according to published methods (Percot, Viton, & Domard, 2002), summarized as follows. Approximately two grams of de-fatted shell were reacted with 80 mL of 0.25 M hydrochloric acid for 24 h and then washed with de-ionised water to neutral pH. The sample was then treated with 80 mL of 1.0 M sodium hydroxide at 80 °C for 18 h and again washed with deionised water to neutral pH. Samples were finally dried in a vacuum oven at 40 °C overnight.

Samples of meat, head, purified chitin or prawn feed were ground to fine powders using a vibratory ball mill equipped with a zirconium oxide mortar and ball (Fritsch, Idar-Oerstein, Germany). Liquid nitrogen was added to chitin samples to make them brittle for grinding. Grinding times were adjusted to achieve a visibly homogeneous product with the consistency of fine flour.

We were aware that the extent of grinding has been reported to affect to amount of exchangeable-hydrogen available within protein samples (Bowen, Chesson, Nielson, Cerling, & Ehleringer, 2005). As a simplified approach we applied a correction for