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# Changes in fatty acids, sterols, pigments, lipid classes, and heavy metals of cooked or dried meals, compared to fresh marine by-products

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ABSTRACT

Marine by–products are rich in highly-unsaturated fatty acids (HUFA), but are not usually used as meal because they are composed by a non-homogeneous mix of tissues that are difficult to process and tend to decompose faster than muscle-based meals, like fish meal. They might also contain high levels of some heavy metals that are accumulated in the digestive gland/liver. Here we compared by–product meals as commonly produced by cooking (100 °C/10 min) that has the advantage of preserving meals for a longer shelf-life, against batch drying (60 °C/24 h) which should better preserve the HUFA and other labile lipids, in by–products (scallop viscera, squid viscera, shrimp heads) vs. whole fish (mackerel) as process control. Raw mackerel contained the highest crude protein (668 g/kg dw) while raw squid viscera had more lipids (200 g/kg), HUFA (40 g/kg), pigments (188 mg/kg), and cholesterol levels (26 g/kg), the last similar to levels in shrimp heads. Raw scallop viscera had the lowest content of protein (500 g/kg), lipids (75 g/kg), and cholesterol levels (6 g/kg), but presented the highest levels of different phytosterols, cadmium (303 mg/kg), and lead (16 mg/kg), with high levels of mercury comparable only to mackerel (302–365 μg/kg). Cooking significantly decreased protein to 474 g/kg and HUFA to 15 g/kg in mackerel, phospholipids were significantly reduced in all tested by-products, while triacylglycerides were reduced in almost all, except shrimp heads meal. Lead, cadmium and mercury were significantly reduced in cooked scallop viscera meal. Cooking increased peroxidation in scallop viscera and mackerel meal, but not in squid viscera or shrimp heads meal. Drying reduced cholesterol levels more than cooking, but only in squid viscera and shrimp heads meals. We conclude that cooking should be used in mercury-rich by-products, while drying is better when using scallop viscera or mackerel, particularly for using as alternative to discarding by-products and increasing fishery value.



## 1. Introduction

As fish meal increases in price, it can no longer be used as main high quality protein source feed for aquaculture. Most protein can be substituted by plant protein, and some fish, like salmonids and tilapia, do not need highly unsaturated fatty acids (HUFA) to grow if given plant 18-carbon polyunsaturated fatty acids (PUFA) (Sargent et al., 2002). Nevertheless, other

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animals do require HUFA for adequate growth, and high-HUFA alternatives are being discarded in considerable quantities, either directly in the ocean, or open-air ditched. These alternatives are the by-products of human-focused fisheries, like shrimp, fish, scallop, squid, where only one part of the animal is used, and the rest discarded in the least expensive way. Marine by–products currently represent an environmental problem in most countries (Arvanitoyannis and Kassaveti, 2008), since 30–50% or approximately 45,000 million tons per year globally of raw starting material are not used (Olsen et al., 2014).

By–products are usually not incorporated into the feedstuff market because of: 1) low acceptance by consumers, 2) changing availability and quality through the year, 3) difficulty to process and conserve, and 4) in some places, sanitary regulations restrict their use in food. Another concern is that in contrast to muscle-based meals, by-product meals can concentrate high levels of heavy metals. Marine by–products are highly diverse raw materials, mainly composed of gills, nerve tissue, gonads, and digestive organs, with diverse digestive enzymes that promote rapid decomposition, so ideally, they must be processed quickly, preferably in situ, and in a simple and economic way that preserves quality, particularly the HUFA content. The most common method for producing fish meal from raw material is cooking in boiling water or applying direct or indirect steam, typically for 10–20 min at 90–100 °C, and then drying and milling (Hall, 2011). Cooking inactivates enzymes, disaggregates the protein matrix and releases intracellular and membrane lipids (Chantachum et al., 2000). However, heat applied to an organic matrix can have negative effects on lipids, such as hydrolysis of acylglycerides and phospholipids, producing free fatty acids that are more susceptible to oxidation than their esterified form (Miyashita et al., 1994). This can also happen when producing fish meal, but most fish meals are made using whole fish which have a great proportion of muscle and very low levels of reserve lipids compared to digestive gland or gonads, so the lipid oxidation is less critical. As an alternative to moist cooking, meals can be produced by grinding and then drying. Drying is an easier method to implement directly at the site of recollection/fishing and considerably reduces the cost of producing the meal, which increases the likelihood of using fresh by–products by small locally owned family business.

The aim of the present study was to compare two processing methods: cooking followed by drying or grinding followed by drying, in terms of their effect on the proximate composition, fatty acids, lipid classes, sterols, heavy metals, pigments, and peroxidation products of marine by-products rich in HUFA: pen shell scallop viscera (*Pinna rugosa*), giant squid viscera (*Dosidicus gigas*), heads from brown shrimp (*Farfantepenaeus californiensis*), and whole mackerel (*Scomber japonicus*), in order to assess the nutritional value of the meals obtained.

## 2. Materials and methods

### 2.1. Raw materials

Pen shell scallop (40 kg; mean weigh 450 g) and brown shrimps heads (8 kg; mean weigh 19.5 g) were collected in June 2013 at Bahía Magdalena (24.6° N, 112° W) by local fishermen and transported to a cleaning facility in Puerto San Carlos, B.C.S, Mexico. The scallops were opened with a knife to remove the muscle and separate the viscera from the shell. Cephalothoraxes from shrimp were manually removed. Viscera and heads were placed in clean, food–safe plastic boxes and maintained on ice for transport (<6 h) to laboratory facilities. Frozen whole squid (180 kg; mean weigh 4.6 kg) and mackerel (225 kg; mean weigh 125 g), caught in March 2013, were acquired from a local provider. Squid was gutted at the laboratory. Whole mackerel was used as a control for the processing method, since it is commonly used as fishmeal. All by–products were stored in clean, food–safe plastic boxes at −20 °C until further processing.

### 2.2. Meal production

Experimental meals were prepared in the laboratory following two methods: (1) cooking followed by drying (hereafter called cooked meals) or (2) grinding followed by drying (hereafter called dried meals). Raw materials were defrosted at room temperature for 12 h in an enclosed area to prevent contamination from dust and insects. Cooking meals involved sieving 2 kg batches, in triplicate, of each raw material in a sieve cone (30 cm top diameter, 30 cm depth, 2 mm grid), which was immersed in a large (80 L) stainless steel pot with boiling water for 10 min. The cooked materials were drained and placed in thin layers (less than 0.5 cm) on food–safe plastic trays inside a forced–air oven at 60 °C for 24 h.

The same defrosted by–products were used for dried meals. Each material was ground in a ¾ HP meat grinder with a 1/4 inch mesh. Grinding was repeated four times for each batch. The homogenized products were placed in thin layers on oven–safe silicone pads to prevent adhesion to the food–safe plastic trays when dried in a forced–air oven at 60 °C for 24 h. Samples of the raw homogenized by–products were freeze–dried and used for biochemical analyses as reference of initial state. The cooked–dried or dried products were further ground in a coffee grinder and then sieved to 250 μm. Samples of each cooked or dried by–product were used for biochemical analyses.

### 2.3. Proximate composition

Raw by–products and meal samples were analyzed in triplicate for proximate composition, following standard AOAC (2005) methods: crude protein (2001.11), ether extract (2003.0), crude fiber (978.10), ash (942.05). Gross energy was determined with an adiabatic calorimeter (Parr Instruments, model 1261, Moline, IL).