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Trophic ecology influence on metal bioaccumulation in marine fish: Inference from stable isotope and fatty acid analyses

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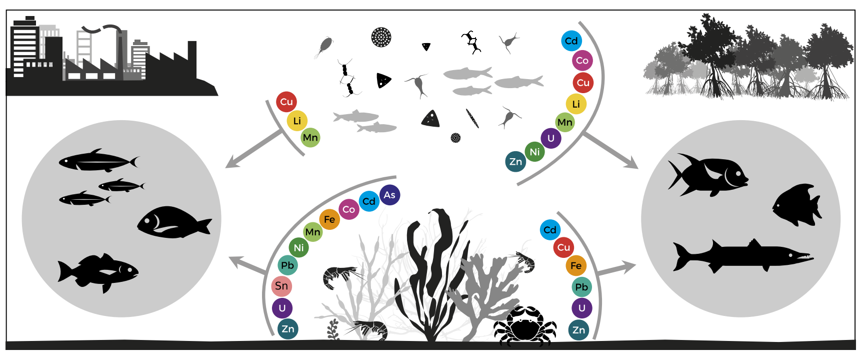
HIGHLIGHTS

- Stable isotope, fatty acid and metal compositions were analysed in marine fish.
- Metal concentrations varied according to trophic group of the fish.
- Benthos was the main pathway for metal transfer in an anthropised region.
- Metal exposition was mainly linked to pelagos in a less anthropised region.
- Combining stable isotope and fatty acid analyses improves determination of source in ecotoxicological studies.

GRAPHICAL ABSTRACT



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ABSTRACT

The link between trophic ecology and metal accumulation in marine fish species was investigated through a multi-tracers approach combining fatty acid (FA) and stable isotope (SI) analyses on fish from two contrasted sites on the coast of Senegal, one subjected to anthropogenic metal effluents and another one less impacted. The concentrations of thirteen trace metal elements (As, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sn, U, and Zn) were measured in fish liver. Individuals from each site were classified into three distinct groups according to their liver FA and muscle SI compositions. Trace element concentrations were tested between groups revealing that bioaccumulation of several metals was clearly dependent on the trophic guild of fish. Furthermore, correlations between individual trophic markers and trace metals gave new insights into the determination of their origin. Fatty acids revealed relationships between the dietary regimes and metal accumulation that were not detected with stable isotopes, possibly due to the trace metal elements analysed in this study. In the region exposed to metallic inputs, the consumption of benthic preys was the main pathway for metal transfer to the fish community while in the unaffected one, pelagic preys represented the main source of metals. Within pelagic sources, metallic transfer to fish depended on phytoplankton taxa on which the food web was based, suggesting that microphytoplankton (*i.e.*, diatoms and dinoflagellates) were a more important source of exposition than nano- and picoplankton. This

Abbreviations: CCLME, Canary Current Large Marine Ecosystem; DHA, docosahexaenoic acid; EPA, eicosapentaenoic acid; FA(s), fatty acid(s); FAME, fatty acid methyl esters; KW, Kruskal-Wallis; MUFA(s), mono-unsaturated fatty acid(s); PCA, principal component analysis; PUFA(s), poly-unsaturated fatty acid(s); SI(s), stable isotope(s); SIMPER, similarity of percentages analyses; SFA(s), saturated fatty acid(s).

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study confirmed the influence of diet in the metal accumulation of marine fish communities, and proved that FAs are very useful and complementary tools to SIs to link metal accumulation in fish with their trophic ecology.

1. Introduction

Increasing concerns regarding metal contamination in marine ecosystems, from both natural and anthropogenic sources, require a better comprehension of the mechanisms that drive their accumulation in organisms. Marine fish are exposed to metals *via* two major pathways, and even if they can assimilate dissolved metals through their gills (Jeffree et al. 2006), the main pathway is thought to be through feeding (Mathews and Fisher 2009). Because marine organisms display a wide range of accumulation patterns, trophic metal inputs therefore depend on the type of prey consumed by marine fish. Furthermore, it has been reported that fish sharing the same habitat do not necessarily share the same levels of metal accumulation (Barhoumi et al., 2009; Siscar et al., 2013), which suggests that considering the feeding habitat (*e.g.*, benthic *vs*. pelagic and coastal *vs*. oceanic) of fish is not a sufficient approach to understand how metals are introduced to fish communities. More accurate methods aiming to characterise the trophic ecology of fish communities are therefore necessary to understand the factors affecting metal bioaccumulation. Studies investigating the link between trophic ecology and metal bioaccumulation report that an organism's metal content is not only dependant on trophic groups, but that this relationship is variable according to the metal considered (Domi et al., 2005; Metian et al., 2013). Moreover, some species can present intraspecific differences in diet, which are reflected in metal accumulation (Das et al., 2000). This highlights the need to apply trophic studies at the individual level to better understand the bioaccumulation drivers.

Over recent years, stable isotope analysis has become a very popular approach to investigate the structure of marine food webs (Valiela, 2015). Among the different strengths of this method for fish communities is the possibility to characterise trophic levels using nitrogen isotopes ($\delta^{15}N$) or to discriminate benthic *vs*. pelagic or continental *vs*. oceanic inputs to the food webs using carbon isotopes ($\delta^{13}C$).

Because stable isotope analysis only provides a two-dimensional discrimination and sometimes fails to discriminate among isotopically similar sources, coupling this approach with fatty acid (hereafter FA) composition analysis has recently been suggested as a solution for a thorough understanding of marine fish trophic ecology (Stowasser et al., 2009; Couturier et al., 2013; Farias et al., 2014). Because different primary producers synthesise different fatty acids and consumers cannot efficiently synthesise them, the composition of FAs reflects the basis of food webs. FA composition analysis has therefore allowed identification of the respective roles of diatoms, dinoflagellates, bacteria or plant detritus in marine food webs (Dalsgaard et al., 2003; Kelly and Scheibling, 2012). Although a number of studies linking stable isotope composition with metal-exposed species have been published (Das et al., 2000; Domi et al., 2005; Chouvelon et al., 2012; Pethybridge et al., 2012), to our knowledge, no study has ever tried to link the metal content in fish tissues with FA trophic markers, except for mercury (McMeans et al., 2015). Furthermore, in contrast to stomach content analysis, these tracers can provide time-integrated information on the dietary habits of the fish for the last few months (Buchheister and Latour, 2010; Beckmann et al., 2014). This time scale is thus more relevant to study the chronic trophic metal exposition because trace elements can take several weeks to accumulate (Berntssen et al., 2001; Kim et al., 2006).

To investigate the link between trophic ecology and metal accumulation, a case study of the Canary Current Large Marine Ecosystem (CCLME) in Western Africa was chosen. This ecosystem is one of the world's major cold-water upwelling currents and includes several countries from Morocco to Guinea including Senegal. It ranks third in the world in terms of primary productivity (Chavez and Messié, 2009) and supports one of the largest fisheries among African large marine ecosystems. These fisheries provide food to local populations but also to foreign countries through the attribution of fishing licences and exportation. This marine ecosystem is prone to metal contamination due to urban effluents and industrial activities (Auger et al., 2015; Diop et al., 2015), including phosphate extraction, which is of special importance for this region (Jasinski, 2015).

Although metals of anthropogenic origin are known to accumulate in marine sediments, they can become available to marine organisms through resuspension processes, in particular due to upwelling activity. Several studies have reported the presence of metals, such as cadmium, in invertebrates from Morocco (Banaoui et al., 2004), Mauritania (Everaarts et al., 1993; Sidoumou et al., 1999) and Senegal (Bodin et al., 2013). Concerning fish communities, although some data are available for the northern part of the CCLME (Roméo et al., 1999; Sidoumou et al., 2005; Chahid et al., 2014), only recent studies have investigated the metal content in fish from the coast of Senegal (Diop et al., 2016a, 2016b). Improved knowledge in this area is of special importance because coastal sediments and waters from this area are known to be impacted by toxic metals such as cadmium, chromium, nickel and lead (Diop et al., 2012, 2014, 2015; Bodin et al., 2013).

In the present study, a multi-tracers approach combining fatty acid and stable isotope analyses was used to investigate the trophic ecology of different fish species from the coast of Senegal. In addition, a metal content analysis was performed on the liver, which is known to be an organ highly involved in metal bioaccumulation by marine fish (Berntssen et al., 2001; Kim et al., 2006; Siscar et al., 2014).

The main objective of this work was to study the repartition of metals between different fish groups characterised by different trophic marker compositions. In addition, correlations between these tracers and trace metal elements were investigated to better understand the pathways leading to the contamination of fish communities.

2. Material and methods

2.1. Study area and sampling

Two sites that were presumed to be impacted differently by metallic contamination were selected (Fig. 1).

The first one was located in the offshore area of Dakar Bay, where urban and industrial wastewaters are directly discharged into the bay (Diop et al., 2012, 2014, 2015).

The second one was located off the Casamance River Estuary, at the extreme southern area of Senegal. Although there are no existing data on metal concentration in marine organisms for this region, this place was considered to be less impacted because of the absence of large cities and/or significant industrial activity.

The samples were collected during the AWA project (Ecosystem Approach to the management of fisheries and the marine environment in West African waters) scientific cruise in March 2014 aboard the RV Thalassa. The fish were caught with a bottom trawl net, packed in plastic bags and frozen on board at −20 °C. Once at the laboratory, the fish were weighed (wet weight) and measured (total length) (Table 1). They were then dissected with ceramic tools to avoid metal contamination, and the liver and a piece of dorsal muscle (a standardised cut on the dorsal muscle just behind the head) were collected. The liver was split into two samples, one for trace metal analysis and one for the fatty acid composition analysis. Stable isotope analyses were conducted on dorsal muscle samples only. Five replicates were analysed for each species and for each type of analysis.