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Trace elements in a Mediterranean scorpaenid fish: Bioaccumulation processes and spatial variations

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ABSTRACT

The black scorpionfish *Scorpaena porcus,* a carnivorous sedentary species*,* was studied as an indicator of local trace element (TE) contamination of coastal fish species in the northwestern Mediterranean Sea. Fish were collected in seagrass meadows in winter 2012 at four sampling sites: three were located near Marseille, a highly urbanized and industrial area that is subjected to various types of contaminant inputs, and one was located near Hyères, a less urbanized area. Size, sex, age and diet of fish were determined before stable isotope and TE analyses. C and N isotopic compositions and concentrations of nine TEs (As, Ba, Cd, Cu, Cr, T-Hg, Ni, Pb, and Zn) were determined in dorsal white muscle. Most TEs did not bioaccumulate in *S. porcus*, as no increase in TE concentrations with increasing size, age or trophic level of fish was evident. Total mercury (T-Hg) was the only element to bioaccumulate and biomagnify, displaying strong positive correlations of its concentration with age ($r = 0.88$, $p < 0.01$), length ($r = 0.84$, $p < 0.01$) and $\delta^{15}N$ value ($r = 0.68$, $p < 0.01$). Compared with the reference site, higher concentrations of As, Ba, Cd, T-Hg, Pb, and Zn were recorded in fish collected at one or all of the Marseille site. In contrast, no difference was observed for Cr, Cu, and Ni concentrations with site. Spatial differences in TE concentrations in *S. porcus* were related to differences in isotopic composition and to the primary environmental characteristics and human activities prevailing at each site. Concentrations of Cd, T-Hg and Pb in fish muscle (priority substances for monitoring) were all below the maximum permitted European values.

1. Introduction

Coastal marine environments represent high value eco-socio-systems, but they are also discharge and accumulation areas of anthropogenic compounds, such as trace elements (TEs) (Matthai et al., 2002; Cobelo-García et al., 2004). Such chemical contamination leads to the alteration of marine ecosystems, with an impact at individual, species, population and community levels (Fleeger et al., 2003; Halpern et al., 2008; Tartu et al., 2013). The Mediterranean Sea being a semi-enclosed sea, it is predicted to be a particularly sensitive system to any change in its hydrographic conditions due to either climatic or anthropogenic forcings (Bethoux et al., 1999; The MERMEX Group, 2011). The biogeochemical cycling of TEs at the scale of the Mediterranean Sea is largely governed by atmospheric inputs and air-water exchanges (Migon et al., 2002; Heimbürger et al., 2010; The MERMEX Group, 2011). However, in coastal zones and on continental shelves, rivers, such as the Rhône River in the Gulf of Lions, constitute the main input of terrigenous dissolved organic carbon (DOC) (Sempéré et al., 2000) and particulate metals (Elbaz-Poulichet, 2005; Cathalot et al., 2013; Cossa et al., this issue). In addition, TE input sources include submarine volcanoes, cold seepages and sub-marine freshwater inflows, as well as inputs from large coastal cities, industries, effluents, runoff and marine traffic (Oursel et al., 2013).

Certain TEs have the capability to bioaccumulate within aquatic organisms from the environment because of their persistent nature, chemical speciation and bioavailability (MacDonald et al., 2002; Castro-González and Méndez-Armenta, 2008; The MERMEX Group, 2011, Vieira et al., 2011). Certain TEs have unknown functions in biological systems and are considered to be potentially toxic to organisms at low concentrations, such as barium (Ba), cadmium (Cd), total mercury (T-Hg) and lead (Pb) (Schroeder and Darrow, 1972; Velusamy et al., 2014). Other TEs are essential, such as arsenic (As), copper (Cu), chromium (Cr), nickel (Ni), and zinc (Zn), as they play a specific role in metabolism (Authman et al., 2012; Bosch et al., 2016) and are required

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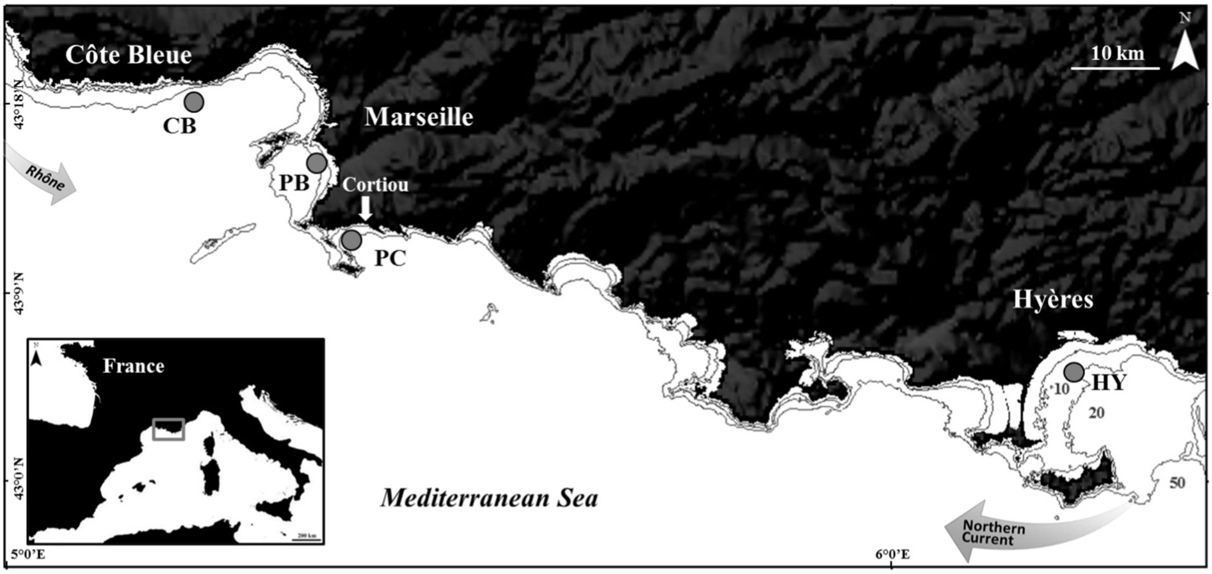

Fig. 1. Location of the sampling sites along the northwestern Mediterranean Sea (gray points) (CB: Côte Bleue; PB: Prado Bay; PC: Plateau des Chèvres; and HY: Hyères). Cortiou: location of Marseille sewage output. Bathymetric data from SHOM, 2010.

by living organisms in small concentrations to achieve a normal ontogenetic development (Merciai et al., 2014). However, essential TEs may also have toxic effects at elevated exposure levels (Wood, 2012; Vrhovnik et al., 2013). The sorption of TEs is affected by chemical (e.g., chemical speciation; Vrhovnik et al., 2013), environmental (e.g., pH, temperature and turbidity; Castro-González and Méndez-Armenta, 2008) and biological factors. Contaminants can bioaccumulate during the life of organisms (increases with size or age) and biomagnify with increasing trophic level, but different patterns are observed depending on the contaminant and the organism (Harmelin-Vivien et al., 2012). While the contamination of fish by TEs can come directly from the water through respiration or directly through the skin and membranes, the main way of TE inputs into fish is food through the consumption of contaminated prey (Hall et al., 1997). Bioaccumulation in fish is a complex process that depends on various biological parameters (species, size, age, sex, diet, trophic level and metabolism) (Castro-González and Méndez-Armenta, 2008; Harmelin-Vivien et al., 2012; Wood, 2012), and differs among tissues due to differences in TE absorption, detoxification and storage mechanisms (Has-Schön et al., 2006; Storelli, 2008; Metian et al, 2013). Contaminants, such as TEs, emerged as useful ecotracers of trophic patterns and environmental parameters when used in combination with other chemical tracers, such as C and N isotopic compositions (Dierking et al., 2009; Chouvelon et al., 2014; Cresson et al., 2014b, 2015b), as they provide complementary time- and space-integrated information on bioaccumulation events and trophic positions of fish in the food web.

Environmental monitoring programs for coastal ecosystems are developing in the Mediterranean Sea for providing scientific knowledge in the assessment of the health and sustainability of ecosystems (Tomasello et al., 2012; Copat et al., 2013; Miniero et al., 2014; Personnic et al., 2014; Naccari et al., 2015; Bonito et al., 2016). Studies carried out on TE bioconcentration and/or biomagnification in Mediterranean species investigated magnoliophytes (Pergent-Martini, 1998; Pergent and Pergent-Martini, 1999; Lafabrie et al., 2007, 2009), invertebrates (Perez et al., 2005; Lafabrie et al., 2007; Angeletti et al., 2014), and fish (Canli and Atli, 2003; Copat et al., 2012, 2013). However, most studies on fish concern continental shelf species and are focused on Hg contamination (Harmelin-Vivien et al., 2009, 2012; Cossa et al., 2012; Cresson et al., 2014a, 2015a, 2015b). Thus, there is a lack of knowledge on TE concentrations in fish species living in coastal waters of the northwestern Mediterranean Sea (Uluozlu et al., 2007).

In France, the annual per capita fish consumption ranges from 30 to 60 kg (FAO, 2012; Vieira et al., 2015) and seafood has always been an important part of the diet of Mediterranean populations (Faget, 2009). Given the potential deleterious effects to human health related to the consumption of contaminated fish (Domingo et al., 2007; Martorell et al., 2011; Vieira et al., 2011), it is crucial to better understand the processes of TE accumulation in Mediterranean coastal fishes and to evaluate the subsequent risk due to fish consumption. The black scorpionfish, *Scorpaena porcus* Linnaeus, 1758, while not the most consumed species, is largely used in traditional recipes (fish soup, fried scorpionfish fillets and the famous "bouillabaisse") and is a common component of local fisheries all year round (Leleu et al., 2014). This species is common in all of the Mediterranean Sea between 5 and 30 m depth, but may be occasionally recorded deeper. This a sedentary macrocarnivore living on rocky substrates and seagrass beds (Harmelin-Vivien et al., 1989). It plays an important role in the trophic functioning of these ecosystems, being one of the most common predators and accounting for 18–35% of the total fish biomass (Bell and Harmelin-Vivien 1982; Ourgaud et al., 2015). For these characteristics, *S. porcus* could be used as an indicator of TE contamination in Mediterranean coastal fish species.

Thus, the aim of the present study was to provide some baseline information on the concentration levels of different TEs (As, Ba, Cd, Cr, Cu, Ni, T-Hg, Pb, and Zn) susceptible to revealing anthropic influences in coastal marine fishes or being a threat to health security. For this purpose, *S. porcus* was collected from different locations subjected to different degrees of anthropic inputs. We used a multi-tracer approach (TEs, C and N stable isotopes, stomach contents and otolith analyses) and analyzed muscles that are the main portion of the fish eaten by consumers. The main questions addressed are (1) Did TE concentrations differ among sampling sites and were they related to differences in the biological parameters of fish or characteristics of the environment? (2) Were these differences similar for all TEs analyzed? (3) Could bioaccumulation and/or biomagnification processes be evident for some TEs? (4) Are TE concentrations recorded below European regulations for fish flesh commercialization?

2. Materials and methods

2.1. Study area and sample preparation

This study was carried out in *Posidonia oceanica* seagrass meadows in three sampling sites of the Bay of Marseille, in the vicinity of one of