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Spatial and seasonal variations of trace elements concentrations in liver and muscle of round Sardinelle (*Sardinella aurita*) and Senegalese sole (*Solea senegalensis*) along the Senegalese coast



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HIGHLIGHTS

- Sardinella and sole sampled along the Senegalese coast were analyzed for trace elements.
- Differences in element concentrations were found between the two species.
- Spatial and seasonal variation in element concentrations were recorded.
- Cd and Pb concentration were below the limit values for edible fish.

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ABSTRACT

Concentrations of 11 elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se,V and Zn) were quantified in liver and muscle from two commercially important fish species from the Senegalese coast. The fish, a small pelagic species (the round sardinella) and a benthic species (the Senegalese sole) were collected from five sites during the dry and wet seasons in 2013. For both species, elements were more concentrated in liver than in muscle. There was no clear seasonal pattern in concentration of elements, however inter-site differences were observed. We found significant differences in element concentrations between the two studied species, likely associated with their behavior, feeding and habitat use. The concentrations of Cd, Fe, and Pb were significantly higher in sardinella whereas concentration of As, Cu, Cr, Mn and Se were highest in sole. The concentration of cadmium was particularly high in the liver of sardinella (from 0.9 to 56 mg kg $^{-1}$, with a mean \pm sd of 17.2 \pm 11.5 mg kg $^{-1}$) and may be related to anthropogenic pressure such as the phosphate industry but also to the upwelling current which brings dissolved elements to the surface that are taken up by plankton. The results showed that concentrations of Cd and Pb were below the limit values established by the European Community and pose no threat to public health.

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1. Introduction

In many countries, substantial development of urban and industrial activities in coastal areas and on lakesides and/or inadequate waste water treatment, results in significant inputs of chemical contaminants to aquatic environments. Knowledge of the

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pollution sources and impacts on ecosystems is important, not only for a better understanding of the ecosystems responses to pollutants, but also for developing sustainable management and conservation of the existing fisheries and aquatic resources. Marine organisms, among them fish, accumulate contaminants from the environment and have been extensively used in marine pollution monitoring programs (e.g. Uthe et al., 1991). Two main objectives are generally pursued in these programs: (i) to determine contaminant concentrations in fish muscle tissue in order to assess the health risk for humans; and, (ii) to use fish as environmental

indicators of aquatic ecosystems' quality (Adams et al., 2002).

Among the large variety of pollutants found in marine environment, metals have been most studied in recent decades. They tend to accumulate in aquatic organism such as fish. Current European Union regulations (EC, 2006, 2014, 2015) have established several maximum levels for Cd, Pb and Hg in fish and other seafood products. Although arsenic may influence human health, this element is not so far governed so far under these regulations. Indeed, several investigations have shown that especially in seafood most of the arsenic is present in organic forms that are less toxic (EFSA, 2009). From a toxicological point of view the amount of inorganic arsenic is considered the most important.

The Senegalese coast, with the Canary Current upwelling ecosystem (CanC), constitutes one of the four main eastern boundary upwelling ecosystems (EBUEs) of the world, which gives rise to highly productive ecosystems and fisheries (Pauly and Christensen, 1995). The fisheries sector, with catches of 400,000 tons per year, provides 75% of protein needs in coastal areas, and employment to 51,931 people (FAO, 2006). About 50% (3.45 million people) of the total population in Senegal live in coastal areas. Dakar, the capital city is home to over 25% of the Senegalese population and more than 80% of its industries (Dumont and Kanté, 2009). At present, few studies on marine pollution or risk assessment for human consumption have been undertaken along the Senegal coast.

The main objective of this work was to evaluate the contamination status of elements in Senegalese coastal fish. The levels of 11 elements (arsenic, As; cadmium, Cd; chromium, Cr; copper, Cu; iron, Fe; manganese, Mn; nickel, Ni; lead, Pb; selenium, Se; vanadium, V and zinc, Zn) were studied in two fish species, *Sardinella aurita* and *Solea senegalensis*, and samples were taken in both dry and wet seasons. These two species are widely distributed along the coast, are among the most important harvested species in Senegal and constitute the main protein resources for local population. Elements were determined in both muscle tissue and livers with the latter chosen as a target organ for comparing element accumulation between sites and seasons. This study also aimed to determine whether Pb and Cd concentrations in these widely consumed fish species exceed the EC's maximum level for human consumption.

2. Material and methods

2.1. Study area and fish sampling

The study area is located along the Senegalese coast in the extreme west of the African continent (Fig. 1). Five sampling sites were selected to represent the Senegalese coast and that differed in terms of anthropogenic pressure (Fig. 1). Site 1 (Saint Louis) is located away from important human anthropogenic pressure but near the Senegal River. Three sites located near Dakar are characterized by strong urban activity and high domestic waste and/or industrial discharge: Soumbedioune (Site 2); Hann (Site 3) and Rufisque (Site 4). Site 2 is dominated by discharges of domestic and hospital waste water and road run-off, being located only a few hundred meters from downtown Dakar and receiving all waste water from surrounding neighborhoods. Site 3 is in the Hann Bay and characterized by permanent discharges of a mixture of urban and food industry waste water, directly discharged to the sea without any treatment. Apart from the presence of sewage and garbage, site 4 was also selected due to the presence of an oil refinery and a cement factory. Site 5 (Joal), is located in the south and distant from significant anthropogenic influences.

Two commercial fish species widely distributed along the Senegalese coast and consumed by the local population were selected:

a small pelagic species, the round sardinella, *S. aurita*; and a benthic species, the Senegalese sole, *S. senegalensis*. *S. aurita* feed mainly on phytoplankton and migrate between Senegal and Morocco to reproduce. *S. senegalensis* is a coastal fish species particularly sensitive to the effects of pollution since they feed on benthic organisms and live in close association with the bottom sediments where many contaminants accumulate (Amara et al., 2009).

At each site and for each season (dry season of January 2013 or wet season of August 2013), ten fish samples of sardinella and ten fish samples of solea were taken. Samples of fish were caught by fishermen's nets in the coastal areas. Each fish was measured for total length (TL, to the nearest 1 mm) and weighed (W, to the nearest 0.1 g). Fish within a limited size range were chosen for chemical analyses in order to reduce the effect of any differences in fish size between sites. For Sardinella, fish of total length 30.6 ± 1.2 cm and weight 272 ± 35 g were analyzed. For Sole, fish with total length 28.8 \pm 3.5 cm and weight 220 \pm 75 g were analyzed. These fish sizes were the most frequently observed in our sampling at the different sites. Fish were dissected using stainless steel scalpels and Teflon forceps using a laminar flow bench (Class 100, US Federal Standard 209a). A part of the muscle (dorsal left fillet without skin) and the whole liver were removed and transferred to polypropylene vials and stored immediately at -20 °C. The muscle tissue was analyzed only in season 2 (wet season) and for sole only in fish from four of the stations (no sole were caught at Saint Louis during the wet season).

2.2. Element analysis in muscles and livers

For each fish muscle tissue and livers were individually lyophilized for 48 h at $-100\,^{\circ}$ C until constant weight, then ground to a powder manually with an agate mortar and pestle. An aliquot of 100 mg from each material was digested in a concentrated solution of nitric acid (65%, Suprapur, Merck) at room temperature for 24 h and then at 100 °C for 4 h. Concentrations of As, Cu, Fe, Mn, Zn were determined by an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Thermo Scientific iCAP 6500) and Cd, Cr, Ni, Pb, Se and V by an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Varian 820-MS). Element concentrations are reported below in mg kg $^{-1}$ dry weight (dw), unless stated otherwise. Limits of quantification (LOQ) were 0.2 mg kg $^{-1}$ for As and Cu, 0.4 mg kg $^{-1}$ for Fe and Zn and 0.02 mg kg $^{-1}$ for Mn (ICP-AES); the LOQ was 0.01 mg kg $^{-1}$ for Cd, Cr, Ni, Pb and V and 0.13 mg kg $^{-1}$ for Se (ICP-MS).

The accuracy and precision of the analyses were assessed using procedural blanks, replicated analyses (done every 25 analysis) and analyses of standard reference material DOLT-4 (dogfish liver, National Research Council, Canada) and DORM-3 (fish protein, National Research Council, Canada). Procedural blanks were less than 2% of the signal and the coefficient of deviation of 3 replicate measurements was consistently below 10% (data not shown). For most elements, except for Ni, the recovery percentages for the DOLT-4 and DORM-3 references materials resulted in ranges from 65% to 110% (Supporting information S1).

2.3. Statistical analysis

Statistics were performed with "XLSTAT-Pro" 2014 (Addinsoft). Inter-species and spatial differences in element concentrations between fish from the five sites were analyzed with a one-way ANOVA, followed by post-hoc Tukey tests. If data did not comply with the parametric assumption of normality and homogeneity of variance, the non-parametric Kruskall Wallis test and MannWhitney U test for post hoc pair-wise comparisons was used. Principal component analyses (PCA) was used to explore

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