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Macro and trace elements in *Paracentrotus lividus* gonads from South West Atlantic areas

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ABSTRACT

Sea urchin represents one of the most valuable seafood product being harvested and explored for their edible part, the gonads or roe. This species is generally considered a sentinel organism for ecotoxicological studies being widely used in monitoring programs to assess coastal aquatic environments quality, because is directly exposed to anthropogenic contaminants in their habitat. In this context, the aim of this study is to evaluate the concentrations of macro (Cl, K, P, Ca, S) and trace (Zn, Br, Fe, Sr, I, Se, Rb, Cu, Cr, Ni, As, iAs, Cd, Pb, Hg) elements in *Paracentrotus lividus* gonads from three South West Atlantic production areas subjected to distinct environmental and anthropogenic pressures. In all studied areas, the elements profile in sea urchin gonads was Cl > K > P > Ca > S > Zn > Br > Fe > Sr > I > Rb > Cu > Se > Cr > Ni, suggesting an element guide profile with special interest for sea urchin farming development. Concerning toxic elements, the profile was the following: As > Cd > Pb > Hg > iAs. The results evidenced higher levels of Pb and Hg in open areas. Distinct area characteristics and anthropogenic pressures of production areas evidence the importance of biomonitoring contaminants, particularly toxic elements. In general, the levels of these elements were below maximum levels in foodstuffs (MLs) which pose a minimal health risk to consumers.

1. Introduction

Seafood has a great importance in a well-balanced diet, providing several nutritional benefits and being a healthy source of proteins, lipids, n-3 polyunsaturated fatty acids and other important nutrients (EFSA, 2012a). Oligoelements are among the most relevant nutrients provided by seafood like iodine, selenium, zinc, calcium, phosphorus, iron and copper (EFSA, 2014) since they participate in many physiological processes. The essentiality of elements has been intensively discussed, being recommended that daily necessities should be fully covered but avoiding excessive intake since it can lead to toxic effects (e.g. Berdanier, 1998; IoM, 2001). Fish and shellfish products are increasingly promoted as functional foods and nutraceuticals. Yet, sea urchins are one of the least known seafood products, despite their globally increased consumption. Sea urchin roe, gonads represent the edible part of this organism and is one of the most valuable seafood product, being a delicacy like Caviar. It is a good source of proteins, lipids, carbohydrates, fatty acids, vitamins and minerals (Dincer and Cakli, 2007; Zoysa, 2014). The high demand for this delicacy product has led to a great pressure over sea urchin stocks all over the world. Therefore, special attention must be paid to regulate this species harvest activities (Dincer and Cakli, 2007) since their populations are decreasing (Bertocci et al., 2014). Moreover, it is important to understand its nutritional composition to improve the farming of this species.

The purple sea urchin *Paracentrotus lividus* (Lamarck 1816) is distributed in Mediterranean areas and in the north-eastern Atlantic coasts, in rocky intertidal and shallow subtidal environments

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(Boudouresque and Verlaque, 2013). One of the main harvested areas in Europe is the north-western coastal areas of Portugal, where *P. lividus* populations have been commercially harvested to supply nearby region markets, such as Spain (Bertocci et al., 2014). These highly explored areas are inserted within two hydrographical basins where industry sector is well developed and so subjected to possible urban and industrial contamination (Cairrão et al., 2004; Vasconcelos, 2015). In addition, Carreço site is located nearby where the Prestige oil spill occurred in 2002 (Cairrão et al., 2004) and Praia do Norte has an harbour nearby where ship traffic is quite intense, therefore, exposure to oil spills can occur Leather tanning, metal plating and textile industries are the main sources of toxic metal contamination in the Ave river (Gonçalves et al., 1992), once considered the most polluted river in Europe (Soares et al., 1999), that drain less than 10 km north from Vila Chã, one of the harvesting sites in study. Several urban wastewater treatment plants are also present in these areas which can contribute for water degradation (APA, 2015). All these anthropogenic pressures can contribute for distinct elements bioaccumulation patterns in *P. lividus*, including persistent and emerging pollutants (Rocha et al., 2018).

Toxic element contamination is still a potential problem, since elements are frequently found in aquatic environments as an outcome of anthropogenic inputs, mainly from industrial activities (Radenac et al., 2001; Bielmyer et al., 2012), leading to a change in marine communities' structure and in specimen composition (e.g. Rouane-Hacene et al., 2017). Due to its wide distribution, sedentary habits, easy collection, grazer-feeding habits and tolerance to pollutants, the sea urchin *P. lividus* may become contaminated, thus being widely used in monitoring programs to assess coastal aquatic environments quality (Warnau et al., 1998; Salvo et al., 2014). In addition, its gonads are consumed mainly raw or lightly cooked. In this way, consumers are easily exposed to environmental contaminants accumulated in sea urchins. Although marine organisms and humans need trace amounts of elements, such as copper (Cu), zinc (Zn), nickel (Ni) and iron (Fe), they can also play a deleterious effect. Chronic Cu toxicity in humans, for instance, has its most pronounced effects on liver function whilst acute effects of Cu toxicity are primarily observed in the gastrointestinal tract, as a local intestinal irritation effect (EFSA, 2006). Toxic elements, like mercury (Hg), lead (Pb), cadmium (Cd) and arsenic (As), may accumulate in marine organisms and humans potentially causing toxicity (Bielmyer et al., 2012). In areas subjected to industrial, agricultural and mining activities, the levels of toxic elements can increase significantly (Olmedo et al., 2013). The consumption of sea urchin gonads is still hampered by some health risks, since several field studies demonstrate that sea urchins effectively bioconcentrate toxic elements (Augier et al., 1989; Ablanedo et al., 1990; Warnau et al., 1995; Bielmyer et al., 2012; Rouane-Hacene et al., 2017). The accumulation of toxic elements is different within sea urchin body tissues, showing higher concentration levels in the digestive wall (Warnau et al., 1998). In addition, seasonality changes in edible tissues also influence pollutants accumulation, and consequently element bioavailability (Rouane-Hacene et al., 2017). Worldwide, food safety authorities established tolerable upper intake levels (UL) for some elements Cu (1–4 mg day^{-1}), Zn (7–22 mg day^{-1}), Ni (1.0 mg day^{-1}) and Fe (45 mg day^{-1}) in food products (EFSA, 2006; USDA, 2015). Other indicators are tolerable weekly intake (TWI) levels for Cd (2.5 μg kg^{-1} bw; EFSA, 2009b; EFSA, 2011), benchmark dose levels for inorganic arsenic (iAs; 0.3–8 μg kg^{-1} bw day^{-1}, EFSA, 2009a; 3 μg kg^{-1} bw day^{-1}, FAO/WHO, 2011) for seafood products. Maximum limits of toxic elements in sea urchins, however, have not yet been established in the EU. So, the assessment of essential and toxic elements in sea urchins is necessary to evaluate possible environmental contaminations and prevent risks associated with their consumption.

There are some reports on the occurrence of macro and trace elements in commercial sea urchins from production regions like Morocco, France, Spain, Chile, Sardinia, Sicily (Salvo et al., 2015), Algeria coast (Bendimerad, 2014; Rouane-Hacene et al., 2017). However and to the best of our knowledge, there is no information about the assessment of macro and trace elements in sea urchin gonads from production areas in the South West Atlantic coast. So, in this context, the present study intends to assess the macro and trace elements content in *P. lividus* gonads in the harvesting season in different areas subjected to distinct environmental and anthropogenic pressures.

2. Materials and methods

2.1. Study areas and sample preparation

This study was carried out in three sea urchin harvesting areas along the NW Atlantic coast of Portugal: Carreço (C), Praia Norte (PN) and Vila Chã (VC), (Fig. 1A). The areas were chosen due to their relevance in the exploitation of sea urchins and due to the diversity of

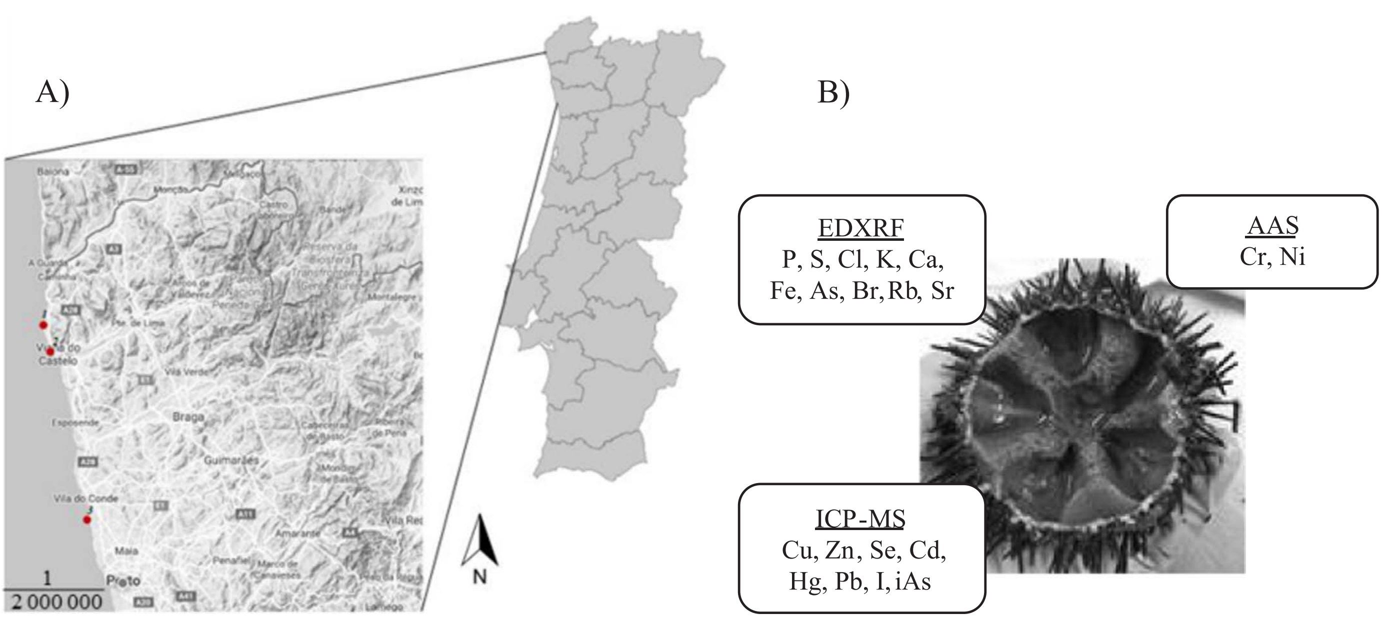

Fig. 1. A) Map showing red dots as sampling areas at South West Atlantic Coast: 1) Carreço (C); 2) Praia Norte (PN); 3) Vila Chã (VC) (adapted from Rocha et al., 2018); B) Example of cracked sea urchin with gonads and indication of which elements were determined by Energy dispersive X-Ray fluorescence (EDXRF), Atomic Absorption Spectrometry (AAS) and Inductively coupled plasma mass spectrometry (ICP-MS) for all samples.