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Mercury and selenium in the grass goby *Zosterisessor ophiocephalus* (Pisces: Gobiidae) from a mercury contaminated Mediterranean lagoon

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ABSTRACT

Mercury (Hg) and its bioaccumulation are important in evaluating the health risk through fish consumption. In the Marano and Grado Lagoon a historical contamination originating from both mining and industrial sources is present.

In this study the Hg levels in the grass goby and the protective effect of selenium (Se) were determined as a function of size, sex, sampling sites and season.

Mercury often exceeded the limit for commercialisation, whereas Se was mostly constant being homeostatically regulated.

The mean Se/Hg molar ratio showed about 40% of data > 1.0 and the HBV_{Se} index was on average equal to 0.0. Thus, grass goby of this area is not a Se source food indicated for pregnant and/or breastfeeding women, but its occasional consumption would appear to have no contraindications if integrated with other Se rich foods: the ingestion of about 10 fish fillets per week can be safely consumed by adults.

1. Introduction

Among pollutants commonly diffused in the environment, mercury (Hg) is of great concern due to its high degree of mobility, exchange through various compartments, and its well-known toxicological effects (Fitzgerald and Clarkson, 1991). This element is present in several chemical forms. In more detail, the elemental form (Hg0) is the most abundant form in the atmosphere, long-lived soil pool of Hg(II) prevails in soils and Hg(0), Hg(II), particulate and colloidal mercury, methylmercury (MeHg) and dimethylmercury (DMeHg) are found in aquatic systems (Selin, 2009). As observed in the most dramatic exposure which occurred at Minamata Bay, Japan (Takeuchi et al., 1962), the organometallic form MeHg causes neurotoxic and genotoxic effects on humans (Clarkson, 1998; Crespo-López et al., 2007, 2011; Li et al., 2010).

The formation of MeHg is a complex process occurring mainly in sediment but also in the water column, and is mediated by specific bacterial communities (Barkay and Wagner-Döbler, 2005) under a well-defined range of chemical and physical conditions (Ullrich et al., 2001). Once formed, MeHg is biomagnified along the whole trophic chain and top-level aquatic predators (e.g., shark, sword fish, tile fish and so on) reaching harmful levels for consumers. As a consequence, a provisional tolerable weekly intake (PTWI) has been set by several international organizations to indicate the human health risk. The last updated release from the European Food Safety Authority (EFSA) established a PTWI for inorganic Hg of 4 μg kg^{-1} body weight (b.w.) per week and of 1.3 μg kg^{-1} (b.w.) per week for MeHg (EFSA, 2012).

Fish and shellfish are among the healthiest foods on the planet because they represent a valuable source of protein, have a low caloric density, a high content of omega-3-long chain polyunsaturated fatty acids (n-3 LC PUFA), minerals and antioxidants such as vitamins D_3 and B_{12}, selenium and so on (Tilami and Sampels, 2017). In particular, selenium (Se) is a trace-element essential for the neuroendocrine tissue and, if present at a low level, provides protection to the nervous system (Behne et al., 2000; Köhrle et al., 2000; Ralston, 2008), whereas at high levels, it is toxic to a range of animals including humans (Gribble et al., 2016 and references therein). Once assumed through food consumption, Se achieves its function in selenium-dependent enzymes that utilise selenocysteine, essential in preventing oxidative damage from reactive oxygen metabolites especially in the brain (Ralston, 2008). Thus, its consumption is strongly recommended by the World Health Organization with a minimal intake level of 40 and 30 μg of Se per day for men and women, respectively (Ralston and Raymond, 2010). Methylmercury is able to cross the blood-brain barrier and to sequester Se at the active site of the selenium-dependent enzymes, thus resulting in an irreversible inhibition particularly when Hg:Se stoichiometry exceeds 1:1 (Squadrone et al., 2015 and references therein). Several authors have hypothesised that the value of the Se:Hg molar ratio could be a

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suitable tool to discriminate between the absence/presence of risk, and that the risks of Hg toxicity to animal life cannot be accurately assessed without considering the moderating effects of Se (Raymond and Ralston, 2004 and references therein; Ralston, 2008).

The Marano and Grado Lagoon (northern Adriatic Sea, Italy) is one of the best conserved wetlands in the whole Mediterranean area. It has been protected by the Ramsar Convention since 1971, and following the implementation of the Habitats Directive (92/43/EC) is also designated as a Site of Community Importance (SCI e IT3320037). Various activities represent a significant economic resource for local inhabitants. Among these fishing, clam harvesting (mainly *Ruditapes philippinarum*) and fish-farming (*Dicentrarchus labrax*, *Sparus aurata*, *Mugil cephalus*) are common (Sladonja et al., 2011).

On the other hand, this system suffers from a high degree of Hg contamination. It is well known that the long period during which Hg ore was mined and processed at the Idrija mine (NW Slovenia, ~500 years), which stopped in 1994, caused serious pollution in the surrounding environment with about 45,500 tons of Hg spread throughout the environment (Dizdarević, 2000). The bulk of roasting residues from the mid-19th century to 1977 was discharged directly into the Idrijca River resulting in serious local contamination of the sediments (up to 1000 mg kg^{-1}). This material was carried into the Gulf of Trieste through the Soča - Isonzo River discharge (Horvat et al., 1999; Covelli et al., 2001) and actively transported into the adjacent Marano and Grado Lagoon as well, especially when extreme flood events are coupled to the influence of an E–NE wind locally referred to as the "Bora" (Covelli et al., 2007). Further and more recent input of Hg in the lagoon is due to the activity of a chlor-alkali plant (CAP), currently decommissioned, located inland at the drainage basin level (Piani et al., 2005; Covelli et al., 2009). The final result is a clear decreasing gradient of Hg levels in the sediment moving from east (> 11 mg kg^{-1}) to west (0.7 mg kg^{-1}) with the fingerprint input from the CAP in the central sector (~5 mg kg^{-1}; Acquavita et al., 2012).

The contaminated sediments are a potential threat to the aquatic trophic chain. Brambati (2001) found that Hg contents in aquatic organisms collected in different areas of the lagoon reflect the bottom sediment concentrations and that the trophic chain level is essential in determining the degree of bioaccumulation. Generally, filter feeders such as the blue mussel (*Mytilus galloprovincialis*) and the common cockle (*Cerastoderma edule*) show lower concentrations than detritus feeders such as prawns (*Palaemon* spp.), whereas high levels are usually detected in common carnivores with values up to approximately 5 mg kg^{-1}.

The grass goby *Zosterisessor ophiocephalus* Pallas, 1814 (Pisces: Gobiidae), is a brackish goby widely distributed in the estuarine and lagoon environment of the Mediterranean basin (Jardas, 1996; Franco et al., 2012) and is particularly abundant in the northern Adriatic Sea, Black Sea and Sea of Azov (Louiz et al., 2013). In the northern Adriatic lagoon (Venice, Marano and Grado Lagoon), where its exploitation has occurred since the twelfth century, it is one of the most important target species of artisanal fisheries (Franco et al., 2012). The life span and reproduction of *Z. ophiocephalus* are associated with seagrass meadows: spawning takes place a few centimetres beneath the seagrass in reproductive nests excavated by males from March to the end of May (Akyol, 2003; Franco et al., 2012; Louiz et al., 2013). It is an iteroparous species living up to 5 years and is reported to reach sexual maturity at 2 or 3 years (Franco et al., 2012 and references therein). Mercury levels in eviscerated grass gobies of the Marano and Grado Lagoon mostly exceed 0.5 mg kg^{-1} (Brambati, 1996), which is the maximum level set for commercialisation according to the Commission Regulation (EC) No 1881/2006. Recently, a health food control carried out at the Marano Lagunare fish market revealed that Hg concentrations in the edible parts ranged around the threshold. It was estimated that on average, about 26 ton a^{-1} of goby is usually caught (period 1998–2007) in the lagoon and this rate shows a constant increase due to the quality of the product and the eco-sustainability of fishing practices which are traditional and have a low environmental impact. Thus, the problem of Hg bioaccumulation in this species is of vital importance to the economy of the area.

In this work, two surveys were conducted (in spring and autumn) at four selected sites of the Marano and Grado Lagoon. The objectives were to determine:

(1) Levels of Hg and Se and their variation according to site location, fish size (total length and weight) and sex;
(2) Se:Hg molar ratio;
(3) Selenium-Health Benefit Value (HBV_{Se}; Kaneko and Ralston, 2007) to provide an assessment of the relationship between fish exposure to Hg and dietary intake of Se;
(4) To suggest good practices for local consumers.

2. Material and methods

2.1. Study area and sampling strategy

The Marano and Grado Lagoon (northern Adriatic Sea, Italy) belongs to an extended transitional system network which includes the Pialassa Baiona, the Venice and Caorle lagoons and less important areas (Fig. 1). The lagoon covers a surface of about 160 km^2 with an average width of 5 km and a length of 32 km. The hydrodynamic circulation is very complex. Recently, Ferrarin et al. (2010) proposed a hydraulic regime-based zonation scheme consisting of six areas taking into account the average values of temperature and salinity, but also their seasonal variability. Tides are semi-diurnal, with a mean range of 0.65 m and spring and neap ranges of 1.05 m and 0.22 m, respectively (Dorigo, 1965).

The lagoon is formally subdivided into two basins (Marano and Grado), which display distinctly different characteristics (i.e., morphology, hydrodynamics, salinity etc.; Acquavita et al., 2015; De Vittor et al., 2012). This study was focused in the Marano area, part of which is above average sea-level and several channels linking the plain spring rivers flowing into its internal edge towards the sea. The main freshwater inputs are the Stella (36.1 $m^3 s^{-1}$) and Cormor (10.7 $m^3 s^{-1}$) rivers and the presence of a drainage pump system localised in the low Friulian plain also contributes to the total water discharge. Salinity is very low (0.5–7) close to the river mouths and increases moving towards the tidal inlets where it reaches values up to 30. This water discharge is responsible for the input of nutrients, mainly as nitrogen ($N\text{-}NO_3^-$), which derives from the massive fertiliser usage for agriculture purposes occurring inland (Acquavita et al., 2015; Saccon et al., 2013): considering the molar Redfield ratio (in some cases up to 2000) the system is phosphorus (P) limited (Redfield, 1963). These inputs, however, are subjected to a dilution effect through the exchange with the open sea water.

The main source of sediments is through exchange at tidal inlets from the sea, mainly as material moving from the Tagliamento and Isonzo River deltas (silty and clayey particles), while the erosion of the barrier islands provides further sandy material. The Marano basin presents coarse sediments (up to 53% sand) close to the tidal inlets and the main channels, while in the rest of the area sand accounts for about 10% (Acquavita et al., 2012).

Specimens of grass goby were collected at four sites (A, B, C and D) with the assistance of local fishermen belonging to the "Cooperativa Pescatori San Vito di Marano Lagunare". Both the sediment and water column have previously been investigated to assess the degree of Hg contamination (Acquavita et al., 2012; WFD, 2000). Briefly, site D was the most contaminated in terms of total Hg in sediment with 6.61 mg kg^{-1}, whereas A, B and C showed a lesser degree of contamination (2.72–2.78 mg kg^{-1}). Methylmercury contents were not correlated with total Hg and ranged from 1.75 to 3.63 μg kg^{-1}. Finally, dissolved Hg (THg_D) ranged from 4.9 ± 2.3 and 6.2 ± 3.4 ng l^{-1}.

A particular fyke net called a *"cogollo"* was employed in fish