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Presence of trace metals in aquaculture marine ecosystems of the northwestern Mediterranean Sea (Italy)

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ABSTRACT

Information regarding chemical pollutant levels in farmed fish and shellfish, along with the risks associated with their consumption is still scarce. This study was designed to assess levels of exposure to 21 trace elements in fish (*Dicentrarchus labrax*), mussels (*Mytilus galloprovincialis*) and oysters (*Crassostrea gigas*) collected from aquaculture marine ecosystems of the northwestern Mediterranean Sea. Metal concentrations showed great variability in the three species; the highest values of the nonessential elements As and Cd were found in oysters while the highest levels of Al, Pb and V were found in mussels. The essential elements Cu, Mn and Zn were highest in oysters, but Fe, Cr, Ni, Se, Co and Mo levels were highest in mussels. Fish had the lowest concentrations for all trace elements, which were at least one order of magnitude lower than in bivalves. The rare earth elements cerium and lanthanum were found at higher levels in mussels than in oysters, but undetectable in fish. The maximum values set by European regulations for Hg, Cd and Pb were never exceeded in the examined samples. However, comparing the estimated human daily intakes (EHDIs) with the suggested tolerable copper and zinc intakes suggested a potential risk for frequent consumers of oysters. Similarly, people who consume high quantities of mussels could be exposed to concentrations of Al that exceed the proposed TWI (tolerable weekly intake).

1. Introduction

Marine ecosystems can receive chemical pollutants, with potential ecological and public health hazards such as metals, through rivers, direct discharges, or atmospheric deposition. Metals can, therefore, be present in marine food items through accumulation and for some elements-such as mercury-by means of biomagnification through the marine food chain.

Some trace elements have nutritional functions and are essential to life (e.g. selenium, copper, cobalt, molybdenum, manganese and zinc), and contribute to maintaining a good health status in humans and animals (Vandermeersch et al., 2015). Other elements, (e.g. lead, cadmium, mercury, arsenic, tin, vanadium and aluminum), have no biological functions and their intake can lead to adverse health effects. The World Health Organization (WHO) recently indicated arsenic, lead, mercury and cadmium on their prioritized list of the top ten chemicals of major public health concern (WHO, 2010). In particular, if toxic metals such as mercury, cadmium and lead accumulate in fish and shellfish, they pose a potential risk to human health. Therefore, European Regulations (1881/2006 and amendments) set maximum limits of these three contaminants in marine products.

Mercury (Hg) is one of the most toxic heavy metals in our environment. Natural, anthropogenic and re-emitted sources are the three major origins of Hg emissions, with the most important anthropogenic sources of Hg pollution in the environment being urban discharges, agricultural materials, mining, combustion and industrial discharges (Zhang and Wong, 2007). The contamination chain of Hg closely follows a cyclic order, namely industry, atmosphere, soil, water, phytoplankton, zooplankton, fish and humans (Kadar et al., 2006). Hg highly bio-accumulates and bio-magnifies throughout the aquatic food chain (Carrasco et al., 2011). The general population is most commonly exposed to mercury primarily by eating fish and shellfish that may contain methyl mercury in their tissues. Methyl-mercury (CH_3Hg) is the most toxic form of mercury, and affects the immune system, alters genetic and enzyme systems, and damages the nervous system.

Fish and shellfish are an important source of cadmium (Cd) intake in the general population. Most of the cadmium content in

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fish or other seafood is highly absorbable in $CdCl_2$ form; Cd is particularly accumulated in the kidneys, while Cd concentrations are low in muscles (ATSDR, 2012). In humans and animals, Cd affects a number of organs, namely kidneys, lungs, bones, placenta, brain and the central nervous system. Cd also causes reproductive toxicity, adverse effects on the hepatic hematological and immune systems, (ATSDR, 2012).

Lead (Pb) is an established contaminant that is mainly exposed to the general population via food and air. Once absorbed, Pb accumulates in high concentrations in bones, teeth, liver, lungs, kidneys, brain and spleen, and it can penetrate the blood-brain barrier and the placenta (Gwaltney-Brant and Rumbeiha, 2002). Much of the Pb in the marine environment is strongly adsorbed onto sediments and suspended particles, reducing its availability to organisms (Falco et al., 2006). In shellfish, Pb concentrations are higher in the calcium-rich shell than in the soft tissue, while in marine fish, Pb levels are higher in the gills and skin than in other tissues (European Food Safety Authority, EFSA, 2012).

In the marine environment, inorganic arsenic (As) predominates in seawater and sediments, while bioaccumulation of the element by organisms generally occurs as organic non-toxic compounds such as arsenobetaine and arsenocholine, which have been suggested to be final products of detoxification processes (Francesconi and Edmonds, 1996). Anthropogenic contamination can modify the environmental bioavailability of arsenic, and influence the relative presence of toxic forms in tissues of exposed organisms such as fish and shellfish (Fattorini et al., 2004).

The Mediterranean is the largest semi-enclosed European sea. It has a narrow shelf and, in the north, is mostly bordered by mountain chains sloping steeply into the sea, resulting in a narrow littoral zone. This semi-closed basin is characterized by several unique features such as low trophic potential, high seawater temperatures, phosphorus limit primary production, low sedimentation rate and high maritime traffic (CIESM, 2007).

Mediterranean aquaculture has experienced a rapid growth in the last three decades. To cope with the continuous increase in production, Mediterranean mariculture has moved from small land-based operations to large enterprises located along the coastline and more recently, to off-shore sites. Several fish marine species are cultured in the Mediterranean, the most commercially-important being the gilthead sea bream (*Sparus aurata*) and European sea bass (*Dicentrarchus labrax*), and regarding shellfish, the European mussel (*Mytilus galloprovincialis*), the European flat oyster (*Ostrea edulis*) and the Pacific oyster *(Crassostrea gigas*) (FAO, 2014).

Adequate information on trace elements present in seafood from aquaculture is often lacking, thus creating potential risks. Where cage farming exists, in addition to the natural presence of metals in the aquatic environment from geochemical and anthropogenic processes, another source of trace metals is from the use of metal (e.g. copper)-based anti-foulants for protecting the nets from fouling (Arechavala-Lopez et al., 2013). Moreover, fish diets are also enriched with various essential metals, such as copper, iron, manganese, cobalt and chromium (CIESM, 2007), which could contribute to the metal burden in fish flesh. As a result, differences between farmed and wild sea bream and sea bass have been found through trace element analysis (Arechavala-Lopez et al., 2013).

Our investigation took place in aquaculture systems of the Ligurian Sea, part of the Mediterranean Sea positioned between the northwestern coast of Italy, the southeastern coast of France, and north of the islands of Corsica and Elba. Previous reports of this area (Giorgi et al., 2009) revealed that wild fish and shellfish are potentially harmful for consumers, as some samples exceeded the maximum residue limits (MRL) set by the regulations for Hg and Pb. To our knowledge, no data are available on the levels of trace elements in fish and shellfish from Northwestern Mediterranean mariculture.

The main objectives of the present study were:

i) to analyze the concentrations of aluminum (Al), antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), cerium (Ce), cobalt (Co), chromium (Cr), iron (Fe), manganese (Mn), mercury (Hg), molybdenum (Mo), lanthanum (La), nickel (Ni), lead (Pb), copper (Cu), selenium (Se), tin (Sn), thallium (Tl), vanadium (V) and zinc (Zn) in European sea bass, European mussels and Pacific oysters from Northwestern Mediterranean aquaculture (Ligurian Sea)
ii) to verify the compliance with the maximum levels established by the European Commission Regulation (1881/2006 and amendments)
iii) to increase the data about the potential risks to human health associated with these contaminants by consuming aquaculture products.

2. Materials and methods

2.1. Study area and collection of samples

The sampling areas were located in a northwestern Mediterranean, Ligurian Sea (Fig. 1).

Samples of mussels (*Mytilus galloprovincialis*) (n. 25) and oysters (*Crassostrea gigas*) (n. 25) were collected in February from aquaculture facilities in the Gulf of La Spezia.

Mussels and oysters are bred, within and outside the east dam, in tanks of varying widths of 500–2000 m^2, consisting of floats attached together by nylon strings, stretched below the level of the wave motion, to which so-called “arbors” or “reste” are knotted, on which the bivalves grow. The morphology and favorable environmental conditions of the area (especially the lack of storms), the depth of the seabed and freshwater undercurrents create optimal conditions for the growth and development of mussels.

European sea bass (*Dicentrarchus labrax*) samples (n. 25) were collected in aquaculture facilities from Porto Venere (in the province of La Spezia). Fish lengths ranged from 30 to 36 cm, and weights ranged from 350 to 450 g. The plant, equipped with floating cages in the sea is an in-shore installation for farming sea bass. Currently, it consists of 76 tanks and occupies an area of 19,000 m^2.

Immediately after collection, fish and bivalve samples were placed into a clean polythene bag, preserved on ice and transported to the laboratory. Each sample of mussels or oysters was prepared by pooling 10 or more individual samples, while at least 10 g of the dorsal muscle from the fish was dissected for subsequent chemical analysis.

2.2. Detection of trace elements

Samples were divided into two sub-samples, one for Hg quantification with a Direct Mercury Analyzer (DMA-80 Analyzer from Milestone, Shelton, CT, USA) and the other for detecting all the other metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS Xseries II, Thermo Scientific, Bremen, Germany). The Direct Mercury Analyzer performs thermal decomposition, catalytic reduction, amalgamation, desorption and atomic absorption spectroscopy without requiring pre-treatment. Between 0.05 g and 0.1 g of samples were directly weighed on graphite shuttles and processed for Hg content.

Determination of Al, As, Be, Cd, Ce, Co, Cr, Cu, Fe, La, Mn, Mo, Pb, Ni, Sb, Se, Sn, Tl, V and Zn, was performed after wet digestion using