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# Trace elements in seafood from the Mediterranean sea: An exposure risk assessment

Chiara Copat[a,*], Alfina Grasso[a], Maria Fiore[a], Antonio Cristaldi[a], Pietro Zuccarello[a], Salvatore Santo Signorelli[b], Gea Oliveri Conti[a], Margherita Ferrante[a]

[a] *Department of Medical, Surgery Sciences and Advanced Technologies, G. F. Ingrassia, University of Catania, Via Santa Sofia 87, 95123, Catania, Italy*
[b] *Departments of Clinical and Experimental Medicine, University of Catania, Via S. Sofia, 87, 95123 Catania, Italy*

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## ABSTRACT

Fish and shellfish belonging to five different species among pelagic, benthonic and molluscs, were collected from the Gulf of Catania in 2017 to evaluate arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni), selenium (Se) vanadium (V) and zinc (Zn). Risk of developing chronic systemic effects derived from seafood consumption was evaluated with the Target Hazard Quotient (THQ) and compared with the results obtained from the same area and the species, collected in 2012. Hg, Cd and Pb concentrations were found below the limits set by European Community for human consumption in all the analysed species. The total risk is reduced from 1.1 to 0.49, and this result is strongly associated with the lower bioaccumulations levels found for Hg, Mn, Se and V. Others metals such as As, Pb, Ni and Zn bioaccumulation levels remain approximately the same, conversely, it is revealed a slight increase of Cd and Cr. Overall, the present study show a positive picture of the studied area, the Gulf of Catania, highlighting not only a decreased metal availability of the study area, but, above all, a decreased risk to develop chronic systemic effects derived from consumption of local seafood.

## 1. Introduction

Environmental monitoring is a major concern because of the implications that pollutants can exert on the environment, organisms and ecosystems, and therefore on the quality of life of people and on public health. Remarkably, the aquatic environment suffers of pollution more than all others ecosystems, because it is susceptible to various sources of contaminants. It represents the ultimate target for most xenobiotics, because they are directly discharged at sea or in watercourses, or come from hydrological or atmospheric processes (Ferrante et al., 2017c, 2015; García-Hernández et al., 2015; Longo et al., 2013; Mazzei et al., 2014). Today, there are various effective technologies for the restoration of polluted environments and, despite a certain amount of data has been collected during the last twenty years, the implementation of bioremediation projects with proven effectiveness still encounters difficulties (Cristaldi et al., 2017; Ferrante et al., 2018b).

Pollution of the marine environment contributes to pose significant risks for human health and well-being, because of the ingestion of contaminated seafood (Adel et al., 2016, 2018; Conte et al., 2015; Copat et al., 2013, 2014; Dadar et al., 2016; Domingo, 2016; Pappalardo et al., 2017; Storelli et al., 2003, 2010; Vilavert et al., 2017). A wide range of contaminants can be found bioaccumulated in edible tissues of marine organisms, such as metals, organochlorines and polycyclic aromatic hydrocarbons (PAHs) (Conte et al., 2016; Conti et al., 2012; Domingo et al., 2008; Martorell et al., 2010; Quadroni and Bettinetti, 2017; Shen et al., 2017). Nevertheless, the toxicity of each contaminant depends onthe exposure concentrations. Furthermore, even essential metals for human metabolism become toxic when they exceed a certain cytoplasmic concentration (Copat et al., 2013).

Overall, seafood consumption delivers many nutritional benefits, due to its content of high quality proteins (fish provides 17% of total animal protein and 6% of total protein consumed by humans), vitamins and other essential nutrients (Adeyeye, 2002; Ersoy and Celik, 2010; Turyk et al., 2012). Nevertheless, the balance between benefits and risks due to ingestion of seafood has been poorly characterized (Domingo et al., 2007). Therefore, there has been a growing concern about the study on the risk for human to develop chronic systemic effects due to contaminants exposure by seafood consumption, especially in developed countries.

Health benefits and risks vary depending on the fish species, size, harvesting and cultivation practices, as well as the consumed amount and the way it is served. In this study, we present data on metals and metalloids bioaccumulated in highly consumed seafood species, caught in the Gulf of Catania, covering all trophic niches of the marine

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[*] Corresponding author.
*E-mail address:* ccopat@unict.it (C. Copat).

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environment. In particular, we analysed arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), vanadium (V) and zinc (Zn) in edible tissues of *Engraulis encrasicolus*, *Mullus barbatus*, *Scomber scombrus*, *Solea solea* and *Donax trunculus.* The risk for the local population to develop chronic systemic effects due to the consumption of these target species was evaluated through the Target Hazard Quotient (THQ) and compared with the level of risk found for the same species sampled in 2012 in the Gulf of Catania as well (Copat et al., 2014, 2013).

## 2. Material and methods

### 2.1. Seafood collection and sampling area

Fish and shellfish were purchased during March–April 2017 from local fishermen of the Gulf of Catania. The Gulf is an inlet of the Ionian Sea, on the eastern coast of the Italian island of Sicily, which covers about 250 $km^2$. The northern coast is characterized by volcanic rocks of Mt. Etna, where springs the city of Catania, in which the urban waste and the presence of a big commercial harbor bring adverse effects on the marine environment. In the southern coast, there is a sandy coastline of 18 km in length, where San Leonardo and Simeto rivers empty into the Gulf of Catania, carrying nutrients and contaminants from internal agricultural and industrial areas. We selected four different fish species and 250 g of edible part of *Donax trunculus* (Sand Dwelling Mussel). The chosen fish species were *Solea solea* (Flatfish, n = 30), *Mullus barbatus* (Red mullet, n = 30), *Engraulis encrasicolus* (European anchovy, n = 30) and *Scomber scombrus* (Atlantic mackerel, n = 30). Fish and shellfish were transported to the laboratory and stored at −80 °C until analysis.

### 2.2. Heavy metals analysis

From each specimens, aliquots of 0.5 g of muscle tissue were removed, and metals of interest were extracted and quantified. Regarding the species *D. trunculus*, for each specimen the edible parts were separated, collecting up to 250 g, which was homogenized and treated as a single sample. From this, 30 aliquots of 0.5 g were analysed. The samples were mineralized in an Ethos Touch Control (TC) microwave system (Milestone S. r.l., Italy) equipped with pressurized vessels (N. 12), using a heated mixture of strong acids. A digestion solution was prepared with 6 ml of 65% nitric acid ($HNO_3$) (Carlo Erba) and 2 ml of 30% peroxide hydrogen ($H_2O_2$-Carlo Erba) over a 50 min operation cycle at 200 °C. After mineralization, the vessels were opened if a temperature $< 25$ °C was reached, then the content was decanted in falcon tubes and ultra-pure water (Merck) was added to the samples up to 30 ml; for quantification of metals an ICP-MS Elan-DRC-e (Perkin–Elmer, USA) was used. Analytical blanks were processed in the same way as the samples, and concentrations were determined using standard solutions prepared in the same acid matrix. Standards for the instrument calibration were prepared with a multi-elements certified reference solution ICP Standard (Merck). The method detection limits (MDL) estimated with 3r of the procedure blanks were (mg/kg w. w.): As 0.013, Cd 0.002, Cr 0.003, Pb 0.001, Hg 0.025, Mn 0.005, Ni 0.007, V 0.025, Se 0.03 and Zn 0.109. For each batch of mineralization, a laboratory-fortified matrix (LFM) was processed for the quality control and we obtained recovery rates between 91.5 and 110%.

### 2.3. Statistical analysis

The statistical software package IBM SPSS 20.0 was used for statistical analysis. One-way ANOVA and a post hoc Tukey test were performed to evaluate differences in metal concentrations among species.

### 2.4. Target Hazard Quotient

Environmental Protection Agency (US-EPA) provides the “Regional Screening Levels (RSLs) for Chemical Contaminants” online calculator (US EPA, 2017a, 2017b, 2017c, 2017d). For each metal, we calculated the Target Hazard Quotient (THQ) for adults by consuming seafood.

$$\mathrm{THQ} = (\mathrm{EF} \times \mathrm{ED} \times \mathrm{IR} \times \mathrm{C})/(\mathrm{RfD} \times \mathrm{BW} \times \mathrm{AT}).$$

According to EPA guideline, it is assumed a body weight (BW) of 70 Kg, an exposure duration (ED) of 26 yr, and an ingestion rate (IR) mean of the Italian population specific for molluscs (12.34 g/day), demersal (19.25 g/day) and pelagic (12.16 g/day) fish species, provided by FAOSTAT on the “Food Supply - Livestock and Fish Primary Equivalent” database. Furthermore, it is assumed an exposure frequencies (EF) (day/yr) of 365 days/year and a lifetime (LT) of 70 yr. C is the metal concentration in fish mg/Kg, wet weight (w.w.), RfD is the oral reference dose (μg/g/day) specific for each contaminant and AT represents the averaging time (it is equal to EF × LT). Correction factor are automatically included in the calculator, and reference dose (RfD) specific for each metal as well. RfD for lead (Pb) is actually under discussion, so for its risk calculation, we selected from the panel selenium (Se), which has the RfD next to the last provisional tolerable daily intake (PTDI) suggested for Pb by the WHO-Joint FAO expert committee on food additive ($5 \times 10^{-3}$ versus $4 \times 10^{-3}$). Then we inserted on the calculator, concentrations found for Pb and not for Se. Furthermore, As-THQ was calculated assuming the inorganic species as the 3% of the total concentrations. The total risk (HI) derived from consumption of molluscs, demersal and pelagic fish was considered, then we have reworked values found in the same species caught in 2012 from the same area of study and during the same season (with the exception of *S. solea*, whose concentrations were compared with *A. lanterna*, a species with the same ecological niche), applying the methodology above mentioned to compare the total risk for the local population 5 years later. The obtained results of Target Hazard Quotient (THQ) (unitless) for each metal, if above 1 indicates that a risk to develop non-carcinogenic effect during the lifetime can occurs.

## 3. Results and discussion

In Table 1 are summarized mean concentrations and standard deviations of all analysed metals. In order to protect public health, D. Lgs. 1881/2006 established maximum levels for certain contaminants in foodstuff. Among analysedmetals and species, cadmium (Cd) has a limit of 0.050 mg/kg w. w. for muscle meat of fish excluding *E. encrasicolus* and Mackerel species like *S. scombrus,* which have a limit of 0.10 mg/kg w. w. and bivalve molluscs have a limit of 1.0 mg/kg w. w.; lead (Pb) has a limit of 0.3 mg/kg w. w. for muscle meat of fish, whereas bivalve molluscs have a limit of 1.5 mg/kg w. w.; mercury (Hg) has a limit of 0.50 mg/kg w. w. in muscle meat of fish excluding *Mullus* species which have a limit of 1.0 mg/kg w. w. Concentrations found in the three categories of seafood analysed are always below regulatory limits. Nevertheless, the World Health Organization (WHO) and the Environmental Protection Agency (EPA) suggest tolerable intake, reference dose and health risk factors applicable to a large number of pollutants. They allow the evaluation of the lifetime risk to develop chronic systemic or carcinogenic effects on human, derived from the concentrations of contaminants in food, associated with consumption pattern of a specific population or age class. In view of these considerations, we calculated the average THQs for each species and each metal studied, considering the Italian daily ingestion rate, calculated by FAOSTAT for each category of seafood. Then, a total risk derived from each seafood category was considered to understand how much a seafood-based diet could contribute to the overall diet risk for the adult population.

Total arsenic (As) concentration was found significantly higher in muscle tissue of demersal fish, *M. barbatus* and *S. solea* compared to the