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Mercury and methylmercury concentrations in Mediterranean seafood and surface sediments, intake evaluation and risk for consumers

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ABSTRACT

Total mercury and methylmercury concentrations were measured in sediments and marine organisms from the Taranto Gulf to understand their distribution and partitioning. Sediment concentrations ranged from 0.036 to 7.730 mg/kg (mean: 2.777 mg/kg d.w.) and from 1 to 40 μg/kg (mean: 11 μg/kg d.w.) for total mercury (THg) and methylmercury (Me–Hg), respectively. In mollusks THg ranged from n.d. to 1870 μg/kg d.w. while in fish from 324 to 1740 μg/kg d.w. Me–Hg concentrations in fish ranged from 190 to 1040 μg/kg d.w. and from n.d. to 1321 μg/kg d.w. in mollusks. THg exceeded the maximum level fixed by the European Commission (0.5 mg/kg w.w.) only in gastropod *Hexaplex t*. The calculated weekly intake was in many cases over the Provisional Tolerable Weekly Intake established by EFSA for all edible species. These results seem to indicate that dietary consumption of this seafood implicates an appreciable risk for human health.

Introduction

In the marine environment, levels of contaminants have been increasing over the last decades, as a consequence of anthropogenic activities and pollutants are potentially accumulated in organisms and sediments, and subsequently transferred to man through the food chain. Coastal areas, particularly near large urban centres, are of concern, as they receive the largest exposure to chemical contamination, due to source proximity. Contamination of marine organisms with toxic chemicals, such as mercury and its compounds, has been intensively studied in recent years, due to the fact that these contaminants are persistent, toxic, tend to bioaccumulate, and pose human and ecosystem risks.

Mercury may occur naturally in the environment or from anthropogenic sources like mining, fossil fuels combustion, incineration, emission from smelters, fungicides and catalyst activities. Most mercury is volatilized and returned to the atmosphere, but the greater part of this metal introduced into the coastal sea precipitates, because of the very low solubility products of its compounds. It also accumulates in the sediment, which represents the principal sink. Most of inorganic and organic mercury in aquatic environment appears to be bound to particles, colloids and high molecular weight organic matter (Horvat, 1997; Schiff, 2000). In sediments, due to bacterial activity, inorganic mercury may also be converted into methylmercury, the most toxic chemical species which may cause the permanent harm to the central nervous system (Harada et al., 1998), such as behavioural disorders and deficiencies in the immune system and development (Harada et al., 1998; UNEP, 2002). In this form methylmercury dissolves in the water column, becoming readily bioavailable; then it bioaccumulates and biomagnifies up into marine food chains leading to elevated concentrations especially in predatory organisms. Therefore, the consumption of marine products represents a non-negligible exposure pathway to Hg and, thereby, a risk for human health.

The aim of this work was to determine the concentrations of total mercury (THg) and methylmercury (Me–Hg) in the sediments, bivalve molluscs (*Mytilus galloprovincialis, Chlamys varia*), gastropod molluscs (*Hexaplex trunculus*) and fish (*Symphodus melops*) collected at 5 sites from Taranto Gulf, in order to investigate contamination level and public health risks, associated with consuming fish and seafood harvested from these areas. Moreover the goal of this study was also to estimate the weekly intake and compare it with the Provisional Tolerable Weekly Intake (PTWI) recommended by the European Food Safety Authority (EFSA, 2004).

Materials and methods

Study area

Taranto seas, Mar Piccolo and Mar Grande basins (Fig. 1), represent a coastal marine ecosystem example, whose biological balances have been modified step by step, in relation to the anthropic development and, in particular, to the industry settlement (iron and steel factory, petroleum refinery and shipyard). For

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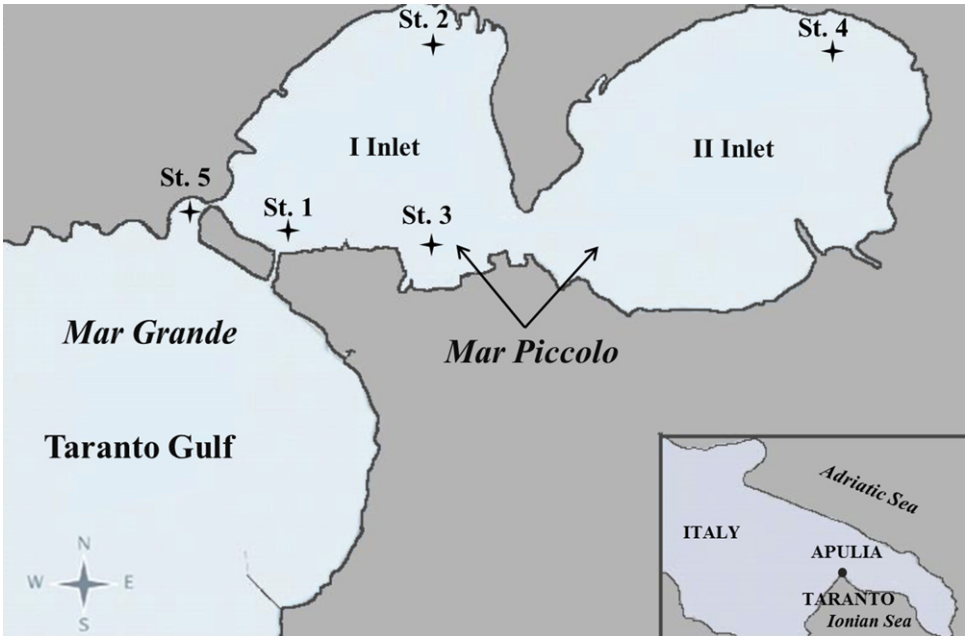

Fig. 1. Location of the sampling stations.

these intense anthropogenic impacts Taranto city has been identified as "High Risk of Environmental Crisis Area" (Law n. 349/86). Later on, the Law n. 426/98 classified it as "Site of National Interest", including the site in the "National Project of Environmental Restoration".

The Mar Piccolo basin is located in the Northern area of the Taranto town, Italy. It is an inner, semi-enclosed basin (surface area of 20.72 km^2), with lagoon features, divided into two inlets, called first and second inlet, which have a maximum depth of 13 and 8 m, respectively. It is connected with the Mar Grande through two channels, the "Navigabile" the "Porta Napoli" channels. Tidal range does not exceed 30–40 cm. The scarce hydrodynamism and the low water exchange with the nearby Mar Grande determine (mainly in summer), a high water stratification. Mar Piccolo basin is the most important area for mussel culture in Italy; it is influenced by urbanization, by harbour activities, by aquaculture and commercial fishing. The main problems of environmental impact are: nine pipes discharge sewages, the ship-yard of the Italian Navy with its dry-docks (located in the first inlet), the largest mussel farm distributed in both the inlets, the fishing-boat fleet localized in the first inlet and small rivers and freshwater springs which drain the surrounding agricultural soils in the basin.

Mar Grande basin is a wide roadstead, which lies to the North-Eastern area of the Taranto Gulf. Twenty-eight urban and five industrial discharges drain directly into the basin. Taranto seas are a noteworthy economic resource, being the site of intensive mussel farming. Mussel farming in Taranto has a long history that dates back to the sixteenth century, so that the typical chestnut stakes, which stick out of the sea, have always been part of the city view. This industry has grown from the idea of an enterprising local to become a big export earner. Actually, the annual output amounts to 30,000 tonnes of mussels. Only a part of the locally harvested seafood is used for home consumption, while most of it is exported to European Economic Community countries, in particular to Spain.

Sampling

Surface marine sediments and marine organisms were collected from four stations of the Mar Piccolo and from one station of the Mar Grande (Fig. 1). Sampling stations were selected by considering distribution of contamination sources, in order to obtain a good evaluation of the monitored area. In particular, station one was near the Navigable Channel, station two was located in proximity to the former shipyard "Tosi", station three was near the Navy Arsenal. Station four was located at the North side of the second inlet of the Mar Piccolo while station five was in proximity of the touristic and commercial port, located in Mar Grande basin.

Surface sediment samples (0–3 cm) were collected with a Van Veen grab in three replicates per station. After sampling, redox potential was determined by a platinum redox electrode Crison (Crison Instruments, Spain). Sediments were stored into a plastic vessel and frozen at −20 °C until analysis. In the laboratory, sediment samples were defrosted at room temperature, dried at 30 °C up to a constant weight, ground and homogenized to a fine powder in a mortar.

Fish species, corkwing wrasse (*Symphodus melops*) was caught with gill nets. Bivalve molluscs (*Mytilus galloprovincialis, Chlamys varia*) and gastropod mollusc (*Hexaplex trunculus*) were collected by scuba divers. Sampling, handling and storage of the specimen were carried out according to the FAO (1976) recommendations. Samples were stored below −20 °C until analysis.

Composite samples of fish species, lower than 100 g, were prepared blending together muscle tissue of three specimens of almost similar size (about 15 cm). For analysis of molluscs, individuals of commercial size were partially thawed, the shell removed and a composite sample of at least 20 individuals was made (mean wet weight 4 g/individual). Dry weight calculation on organism tissues was carried out by oven drying at 105 °C until constant weight.

Total mercury determination

THg concentrations were determined (both for sediments and organisms) with an Advanced Mercury Analyser (AMA-254, LECO) that uses catalytic combustion of the sample, pre-concentration by gold amalgamation, thermal desorption and UV determination at 254 nm. About 100 mg of dry sediments and wet organism's tissue were precisely weighed in a nickel boat, placed in the instrument and automatically introduced into the AMA. The entire analytical procedure was validated by analysing CRM DOLT-2 (dogfish tissue) and IAEA 356 (marine sediment) samples at the beginning