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Ecotoxicological and human health risk in a petrochemical district of southern Italy

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ABSTRACT

An ecotoxicological investigation has been carried in the petrochemical district of Priolo (Sicily, Italy), one of the largest in Europe. Results indicated a severe mercury contamination in sediments sampled near a chloro-alkali plant. A clear bioavailability of this element was demonstrated in mussels *Mytilus galloprovincialis* (both native and translocated) and the benthic fish *Mullus barbatus*, which also exhibited marked genotoxic damages. The elevated mercury concentrations in marine organisms are a serious concern for human health; according to the national average fish consumption, the provisional tolerable weekly intake (PTWI) of Hg would be easily exceeded by at least 4 to 12 fold. Such toxicological risk is of particular importance for pregnant women, being possibly involved in the elevated frequency of neonatal malformations.

Since the early 1950s, the industrial area of Priolo (Sicily, Italy) became one of the largest and most complex petrochemical sites in Europe, containing several oil refineries, chemical plants, mineral deposits, a military base and many other industrial installations. Nowadays, it is a high environmental risk area due to the uncontrolled chemical discharges that occurred before the Water Pollution Control Law (Merli law, 1978) and frequent industrial accidents.

The aim of this study was to characterize the main chemical pollutants in the sediments, and to assess their bioavailability and toxicological effects in classical bioindicator species: the mussel (*Mytilus galloprovincialis*) and the red mullet (*Mullus barbatus*) were selected to compare the potential exposure, respectively through the water column or sediments.

Results obtained were discussed in terms of potential risk for human health from seafood consumption of particular relevance for this area where the incidence of neonatal malformations is more than 3-fold higher than the national average (Bianchi et al., 2004).

Sediments and organisms were collected from various sites in the petrochemical area between Augusta and Priolo (Fig. 1A); mussels were also caged for 4 weeks close to an industrial wharf. Chemical analyses included trace metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls and hexachlorobenzene; however only results concerning mercury (Hg) will be presented here since this element appeared as the most relevant pollutant.

Close to a chloro-alkali plant, the Hg concentrations in sediment cores ranged between 25 and 90 $\mu g\, g^{-1}$ dry weight (d.w.) in the superficial layer and between 50 and 350 $\mu g\, g^{-1}$ in the 28–30 cm layer: these results indicate that a massive contamination occurred in the 1970s, and that Hg discharge is still ongoing in this area, which can be certainly defined as the most Hg polluted site in the Mediterranean. The bioavailability of mercury to marine organisms was clearly demonstrated by the analyses on both native and caged mussels. Wild specimens collected in various sites around the plant exhibited concentrations from 2 up to 5 $\mu g\, g^{-1}$, approximately 60-fold higher than those measured in control organisms (Fig. 1B). Bioaccumulation of Hg was also very rapid in caged mussels which, after 4 weeks, exhibited comparable values to those of native organisms. Considering that Hg concentrations rapidly decreased in the water column of polluted sites after the closure of discharges (Francesconi et al., 1997; Sager, 2002), our results further highlight the presence of inputs still releasing this element in the marine environment.

Bioavailability of mercury to marine organisms was even more evident in the benthic fish *M. barbatus* (Fig. 1C). Concentrations in muscle tissues were around 10 $\mu g\, g^{-1}$, while the liver exhibited similar or higher values, up to 30 $\mu g\, g^{-1}$, in organisms sampled in more coastal sites close to the industrial wharf. Levels measured in control specimens were lower than 1 $\mu g\, g^{-1}$ in both the tissues. Despite relatively high mercury concentrations occurring naturally in muscle tissues of Mediterranean fish, due to a geochemical anomaly and biomagnification (Bargagli, 1999), the exceptionally high values measured in this low trophic-level species and the remarkable accumulation in liver indicate that exposure through contaminated sediments has a much greater significance as compared to long term transfer via food-web.

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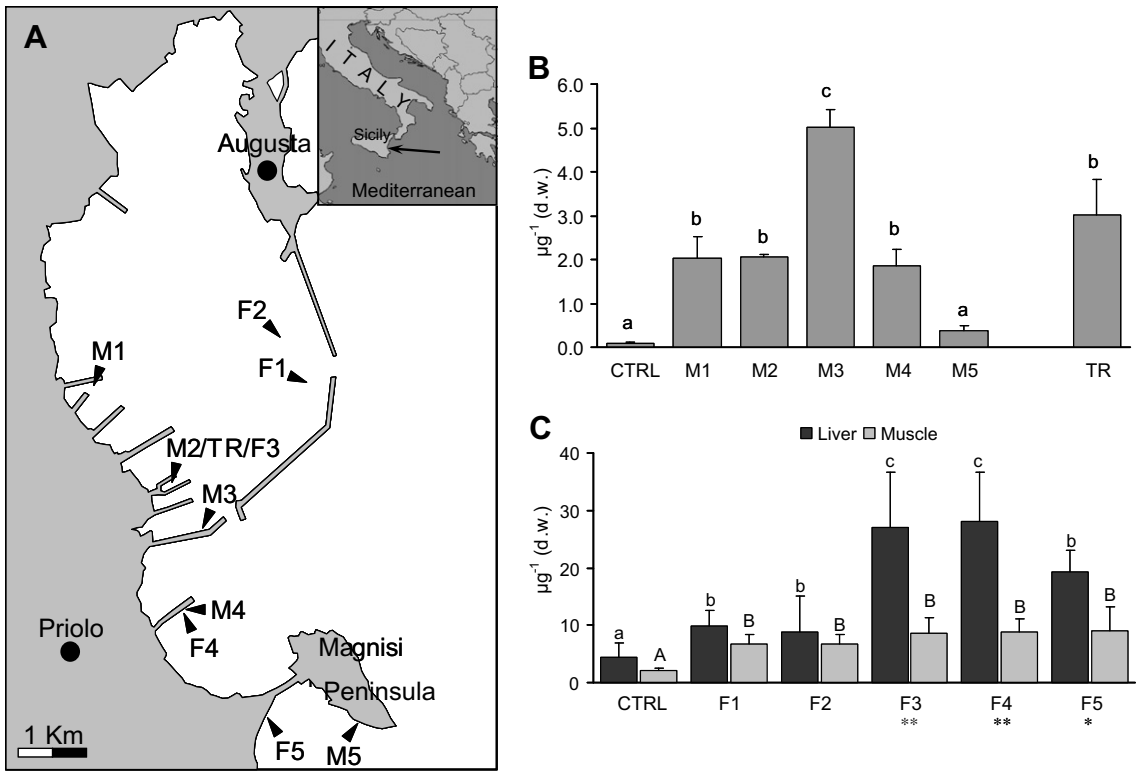

Fig. 1. (A) Sampling locations in the industrial area of Priolo for native mussels (M), transplanted mussels (TR) and fish (F). (B) and (C) Mercury concentrations (μg g^{-1} d.w.) in whole tissues of *M. galloprovincialis* and in liver or muscle of *M. barbatus*. Values are reported as means ± standard deviations ($n = 10$). For mussels different letters indicate significant differences between sites (one way analysis of variance, ANOVA, and post-hoc comparison); for red mullets small letters and capital letters indicate differences between sites for liver and muscle, while asterisks indicate differences between tissues (two ways ANOVA, and post-hoc comparison, $^{*}p < 0.05$; $^{**}p < 0.0001$).

Besides chemical accumulation, there was also evidence of toxicological effects of mercury in both mussels and red mullets. The incidence of micronuclei (MN), respectively in the haemocytes and gills, revealed a frequency up to 11‰ in molluscs and 9‰ in fish (Fig. 2). Similar values have never been previously reported, especially for mussels (Bolognesi et al., 2006), and clearly demonstrate a marked biological reactivity of environmental mercury.

From obtained results, the risk for human health from seafood consumption appears to be a real issue. International Agencies indicate provisional tolerable weekly intake (PTWI) of Hg, ranging from 0.7 μg/kg body weight (b.w.) (USEPA, 2001) to 1.6 μg/kg b.w. (FAO/WHO, 2003). These limits represent safe values which can be accumulated by the human population over lifetime. However, different considerations are recommended for pregnant women, nursing mothers and young children; due to the toxic effects of Hg on the developing nervous system, these categories should avoid the consumption of fish species which normally have a higher mercury content (NRC, 2000; USEPA/ FDA 2004). In this study, the median Hg values for fish muscle (converted to wet weight) were 1.43 μg g^{-1} w.w. when considering all the sites, or 2.06 μg g^{-1} w.w. for only the most impacted. Consequently, a 60 kg women would assume a weekly Hg PTI (0.7–1.6 μg/kg b.w.) from 30 to 67 g or 20 to 46 g of fish caught in different sites of the industrial area of Priolo. Since the national average of fish consumption for the Italian population is estimated to be 33.9 g *per capita* per day (approximately 240 g per week, Turrini and Sermoneta, 2004), a 60 kg women consuming organisms from Priolo would exceed the Hg PTWI by at least 4 to12-fold. In addition, criteria developed to protect human health from mercury in fish products, indicate that calculations for pregnant women should consider a fish consumption 3-fold higher than the national average (USEPA, 2001). The application of this cautionary procedure would further increase the exceeding of recommended safe limits for the area of Priolo, confirming consumption of seafood as a

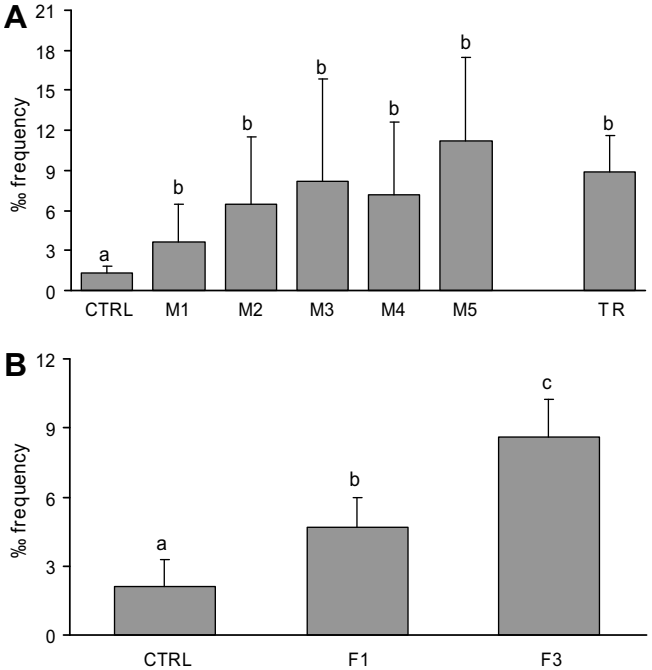

Fig. 2. Frequency (‰) of micronuclei (MN) in haemocytes of *M. galloprovincialis* (A) and gills of *M. barbatus* (B). Values are reported as means ± standard deviations ($n = 10$); different letters indicate significant differences between organism from various sampling sites (one way ANOVA and post-hoc comparison).

serious concern for pregnant women. The hypothesis of human health risk is supported by the frequency of neonatal malformations, which in 2001 was 5.5% for the area of Priolo-Augusta, versus a national average of 1.5% and a risk value indicated by WHO at 2% (Bianchi et al., 2004).

The overall results demonstrated a severe mercury contamination in the area investigated, resulting in a marked bioavailability for marine species and the real possibility for pregnant women to exceed the maximum safe limits for Hg uptake from seafood.

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