Conflicting outcomes of integrated approach for sediment quality assessment in Sardinian coastal area subjected to mining activities

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Introduction: The Sulcis-Iglesiente mining district (SW Sardinia), was exploited for valuable Zn, Pb, Ag and Ba deposits to the end of the last century. Nowadays, large outcrops of sulfide and oxide ores, as well as the products of long-lasting mining activity, are responsible for strong contamination of soil, groundwater, and adjacent coastal marine area[1]. A characterization of superficial and intermediate marine sediments was carried out to evaluate the environmental status through an integrated approach of physical, chemical and ecotoxicological analyses.
The results highlighted high contamination in the most superficial levels for Cd (1.54-75 mg kg^{-1}), Pb (79-857 mg kg^{-1}) and Zn (519-10.610 mg kg^{-1}), with a significant decrease in the deeper levels. Significant concentrations of Hg (0.04-2.72 mg kg^{-1}) are also observed in the deep levels of some cores.
The battery used for bioassays on sediment and aqueous extracts was composed by *Vibrio fischeri* (bacteria), *Dunaliella tertiolecta* (algae) and *Brachionus plicatilis* (rutifera), belonging to different trophic levels. The results with *D. tertiolecta* and *B. plicatilis* did not reveal any toxic effects, while only *V. fischeri* showed medium toxicity in three stations, not among the ones with the highest metal concentrations.

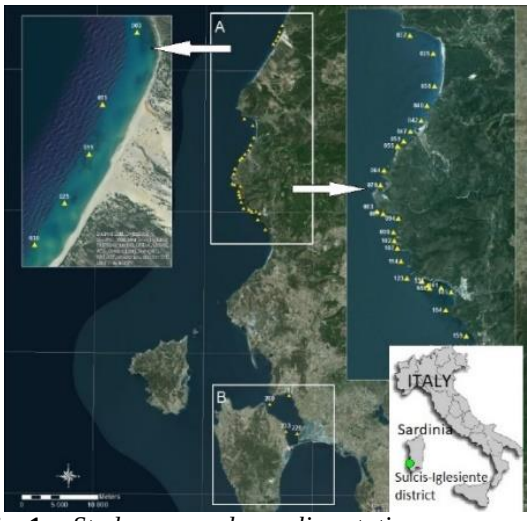

Fig. 1: *Study area and sampling stations*.

To better understand the potential relationships between chemical forms of heavy metals and their bioavailability/mobility in the sediment, extraction analyses was carried out on the same samples where bioassays were performed together with the definition of background levels in the sediments [1].

Methods: Granulometric, chemical and ecotoxicological analyses were carried out on superficial sediments collected by van Veen grab. Al, As, Ba, Cd, Cu, Cr, Hg, Ni, Pb, and Zn were analyzed using ICP-AES; for Hg analysis a Direct Mercury Analyzer (DMA-80, FKV) instrument was used. Metal fractionation from different geochemical phases was evaluated by sequential extraction procedure [2; 3].

Results: Background levels for some elements (As, Cd, Zn, Pb) were significantly higher the natural ones. The sequential extractions highlighted high mobility of these elements (almost 100% of Cd and Zn, and the 80% of Pb). Cd was extracted preferably in the first step that represented the fraction bound to carbonates, while highest percentage of Zn was recorded in the second step, that extracts the metal linked to Mn-Fe hydroxides. Pb was extracted equally in the first and second steps (40% for each one). Hg was mainly divided in the fifth step, that represents the fraction linked to sulfides, and in the insoluble residue.

Discussion: The high recorded concentrations of some heavy metals in the sediments overlap with already higher background values. The maximum concentrations, present in the surface level, indicate that the contribution of these elements is still active and derives from the deposits of mining waste outcrop in the area. The sequential extraction data show an high percentage of mobile fractions of Cd, Pb and Zn in all the samples. On the contrary, the bioassays responses have not revealed any toxicity evidence. This could suggest that bioassay tests are not always able to detect bioavailability and toxicity of the mobile fraction of metals. There could be different reasons for this gap, among which the specific chemical form of metal and the sensibility of organisms used in the battery test.

References: [1] Romano et al. (2017) *Mar Poll Bull* **122**: 331-343; [2] Campanella et al. (1995) *Anal Chim Acta* **309**: 387-393. [3] Maggi et al. (2006);