



Metals and tributyltin sediment contamination along the Southeastern Tyrrhenian Sea coast



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HIGHLIGHTS

- We explored for the first time four sites in the Southeastern Tyrrhenian Sea coast.
- We reviewed sediment quality from other Southern Tyrrhenian Sea sampling sites.
- Sediments from marinas were more impacted than bays by both metals and TBT.
- Risk characterisation ratios exceeded several times the reference site levels.

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ABSTRACT

Anthropogenic pressures can adversely affect the quality of coastal sediment posing at risk human health and the ecosystem. The Southeastern Tyrrhenian Sea (STS) coast (Italy) is still largely unexplored under this point of view. This study investigated for the first time in the area the seasonal variation and potential impact of selected metals (Cd, Cr, Cu, Ni, and Pb) and tributyltin (TBT) from sediment samples collected along the STS coast (Casalvelino Marina, Casalvelino Bay, Acciaroli Marina and Acciaroli Bay) in the perspective of Water Framework Directive and Marine Strategy Framework Directive. Data were compared to the contamination background levels of Punta Licosa reference site considering elemental enrichment factors (EFs) and single substance- and mixture-based risk characterisation ratios. Further, data were discussed considering the review of Southern Tyrrhenian Sea sediment quality. Results evidenced an increase of contamination levels from March to October showing that marinas are more impacted than bays. Sediment EFs highlighted that contamination levels were always greater than the reference site like risk characterisation ratios, suggesting the presence of potential threats. The sediment quality database generated after literature review revealed a similar situation for the whole Southern Tyrrhenian Sea.

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1. Introduction

Marine pollution in coastal areas is a major concern due to the large number of toxic substances discharged (Arizzi Novelli et al., 2006; Libralato et al., 2010a, 2010b; Prato et al., 2015) and accumulated in sediment that act as sink and source of pollution (Wenning and Ingersoll, 2002; Nikolaou et al., 2009; Rzetala, 2015). Especially in harbours and marinas, where exchange of water with

the open sea is limited, the accumulation of toxic substances can pose major concerns for human and environmental health such as in presence of recreational waters and mariculture activities (Mamindy-Pajany et al., 2010; Schipper et al., 2010). Frequently, contaminants occur as mixtures showing combined effects, which are still largely unknown (Libralato et al., 2009, 2010). Dredging activities in industrial and commercial ports tend to remobilise sediments as well as the associated pollution through the washing out of both short- and long-term contaminant loadings (Arizzi Novelli et al., 2006; Libralato et al., 2008; Krull et al., 2014; Chakraborty et al., 2014). The assessment of sediment quality is compulsory for the right management of the marine environment as required by the Water Framework Directive (2000/60/EC) (WFD)

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and Marine Strategy Framework Directive (2008/56/EC) (MSFD) that considered sediment as one of the key issue for the proper management of surface water bodies.

Metals and organotin compounds (OTCs) are the most widely occurring contaminants in coastal sediments (Mamindy-Pajany et al., 2010). Metals are naturally present in marine sediment, but their concentration drastically increased due to anthropogenic activities. Tributyltin (TBT) was extensively employed as a biocidal agent in marine antifouling paints. Due to its sub-lethal effects and persistence (Kim et al., 2011; Silva et al., 2014), TBT produced shell calcification anomalies in oyster farming and severe sexual disorders mainly in gastropod species (Kotrikla, 2009; Qiu et al., 2011; Choi et al., 2013; Silva et al., 2014). Since September 2008, the use of TBT-based antifouling paints was restricted in many countries (IMO, 2001). Despite such restrictions, TBT still continues to represent a great environmental problem for marine organisms due to its half-life of about 19 years (Adelman et al., 1990) and its illegal use.

Few studies investigated metals and TBT contamination occurrence in sediment along the Southeastern Italian coast (Cicero et al., 2004; Romano et al., 2004; Ferraro et al., 2006; Tranchina et al., 2008; Romano et al., 2009) and, specifically, the Cilento coast (Sprovieri et al., 2006) that is located southward the Gulf of Salerno (40° 20' 55" N – 14° 59' 28" E, and 40° 04' 23" N – 15° 37' 44" E).

Since 1991, a wide part of Cilento was included in the Cilento, Vallo di Diano e Alburni national park becoming a UNESCO World Heritage Site in 1998. In 2009, the area included the Marine Protected Reserve of Punta Licosa renowned for its water quality. Between 2001 and 2003, the Campania Region Environmental Protection Agency (ARPAC) carried out a broad sediment sampling campaign within the SIDIMAR Project along the Campania Region coast, but sediment samples were mainly collected near river mouths and TBT contamination was not taken into consideration.

This research study investigated the seasonal variation (March and October) of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and TBT in sediment samples collected from four sampling sites located along the Cilento coast. These pollutants, due to their potential adverse effects on human health and the environment, were further explored reviewing the existing information on sediment contamination falling in the Southeastern Tyrrhenian Sea in the perspective of the WFD and MSFD. The environmental risk of sediments was evaluated considering the potential effects of substances taken singly and as a mixture, providing the state-of-the-art scenario of the contamination in the study area compared to the reference site of Punta Licosa.

2. Materials and methods

2.1. Sampling and sediment collection

Sediment samples were collected in Casalvelino Marina (40° 10' 31" N – 15° 07' 14" E), Casalvelino Bay (40° 10' 10" N – 15° 07' 58" E), Acciaroli Marina (40° 10' 39" N – 15° 01' 39" E) and Acciaroli Bay (40° 11' 07" N – 15° 01' 21" E) (Fig. 1). For marinas, sampling activities took place inside the harbour area, while for bays at 100 m from the coast. Punta Licosa (Fig. 1) was considered as the reference site for sediment according to ARPAC (2003).

Seasonal variability in sediment characteristics (*i.e.* marine traffic and weather conditions) was checked according to two sampling campaigns (March 2010, October 2010). About 1 kg of surface sediment (5 cm top layer) was collected in each sampling site with an Ekman box corer after the on site integration of four sampling replicates. After reducing excess water, sediment samples were stored into polyethylene bags and refrigerated at 4 °C in the dark. Once in the laboratory (in no more than 5 h after collection), coarse materials was removed (*e.g.* shells and organic residues) and

aliquots of homogenised specimen were dried for 2 h at room temperature and, subsequently, in an oven at 105 °C for at least 24 h. Dried sediments were sieved (2 mm mesh) and grounded in a corundum mortar. Pre-treated samples were kept frozen at –20 °C up to the analysis that was carried out in triplicate (ICRAM-APAT, 2007).

2.2. Reagents and materials

Ultrapure HCl (33%) (Carlo Erba, Germany) and HNO₃ (69%) (Fluka Trace Select), and ultra-pure deionised water (Elix 10, Merck Millipore, Billarica, MA, USA) were used for the preparation of standard solutions and samples. All chemicals were of analytical grade. Standard calibration solutions of Cd, Cr, Cu, Ni, and Pb (Sigma–Aldrich, St. Louis, MO, USA) were prepared in acid water (HNO₃ 1%) starting from standard stock solutions (1000 mg/L). Laboratory plasticware and glassware for analytical purposes were cleaned with HNO₃ 2% and rinsed with abundant deionized water before use. The accuracy of the applied analytical methods was checked on Certified Reference Materials BCR 320R and BCR 646 from European Commission – Joint Research Centre (EC-JRC).

2.3. Sample preparation and analysis

Metal concentrations (Cd, Cr, Cu, Ni, and Pb) were determined in triplicate according to ICRAM-APAT (2007) by Atomic Absorption Spectroscopy (AAS). The Limit of Detection (LOD) and Limit of Quantification (LOQ) in µg g⁻¹ were 0.034 and 0.113 for Cd, 0.815 and 2.718 for Cr, 1.000 and 3.400 for Cu, 0.860 and 2.854 for Ni, and 0.140 and 5.000 for Pb. The analysis of TBT as Sn was carried out by 757 VA Computrace polarograph (Metrohm, Origgio, Italy) (LOD(Sn) = 0.5 ng g⁻¹). Details of chemicals characterizations were reported in Supplementary Materials.

2.4. Data analysis

The significance of differences between mean concentration values was assessed by the analysis of variance (ANOVA) considering a significance threshold level always set at 5%. When ANOVA revealed significant differences among treatments, post-hoc tests were carried out with Dunnett's and Tukey's tests. The relationship between variables and the variation present in the dataset matrix were accounted via biplotting both the ordination component scores and the variable loading coefficients through principal component analysis (PCA) (Pearson's correlation matrix). Statistical analyses were performed using Microsoft® Excel 2013/XLSTAT® Pro (Version 7.2, 2003, Addinsoft, Inc., Brooklyn, NY, USA).

2.5. Enrichment factors and risk assessment

In order to assess the rate of contamination and potential sources of anthropogenic inputs to the marine environment, enrichment factors (EFs) were calculated for each metal and TBT using the Equation (1), where [M]_s is the metal concentration of the sample and [M]_{ref} is the concentration of the same metal in the reference area (Punta Licosa) as reported in Table S2. According to this equation, a result ≤0 indicates no metal enrichment in the sample, while values > 0 indicate a metal enrichment in the sample with respect to the control area (Tranchina et al., 2008).

$$EFs = \left(\frac{[M]_s}{[M]_{ref}} - 1 \right) \times 100 \quad (1)$$

In the perspective of an environmental risk assessment, metals and TBT concentrations measured in this study like those reported

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