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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

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the Water Framework Directive (2000/60/EC) (WFD) 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 HNO_3 (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 (HNO_3 1%) starting from standard stock solutions (1000 mg/L). Laboratory plasticware and glassware for analytical purposes were cleaned with HNO_3 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 $\mu g\ g^{-1}$ 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).

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

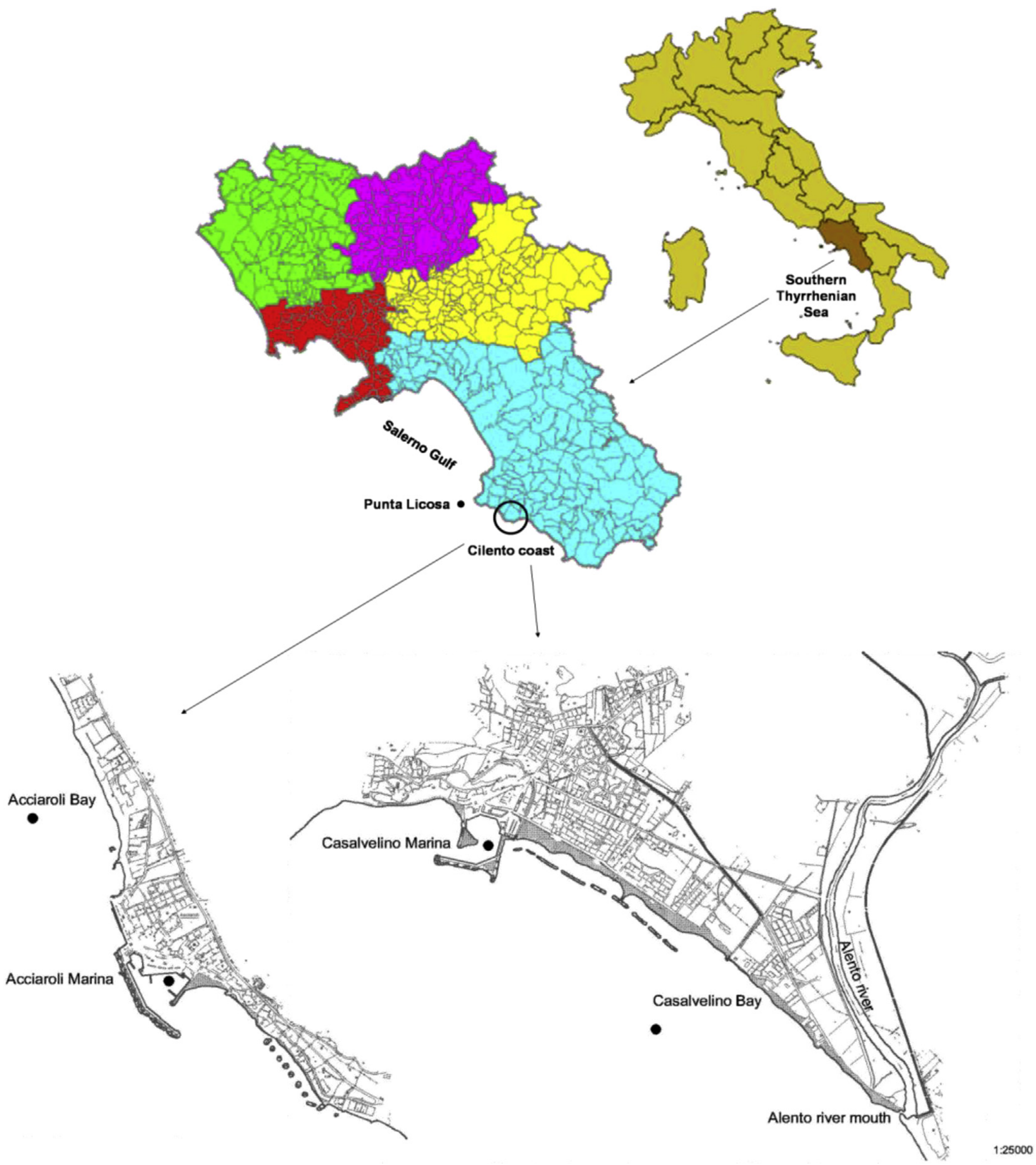

Fig. 1. Sampling (Acciaroli Marina, Acciaroli Bay, Casalvelino Marina and Casalvelino Bay) and reference (Punta Licosa) sites along the Southern Tyrrhenian Sea.

In the perspective of an environmental risk assessment, metals and TBT concentrations measured in this study like those reported by other authors (Table 1 and Table S2) along the Southern Tyrrhenian coasts were compared to three quality standards: Environment Canada-Threshold Effect Level (EC-TEL), Environmental Quality Standards (EQSs) and Ecotoxicological Assessment Criteria (EAC) (Table S3). EC-TEL, EQS and EACs are suggested by the Canadian Marine Sediment Quality Guidelines (1999), Shiga Prefecture (2001), and OSPAR (2004), respectively.

According to Ghekiere et al. (2013), the risk characterization ratio of a single pollutant (RCR) was carried out using Equation (2), where MEC is the Measured Environmental/Exposure Concentration. On the basis of the worst-case scenario approach, the selected MEC value was the highest one measured during the sampling period. If RCR was larger or equal to 1 a potential environmental risk was expected.

$$RCR = \frac{MEC}{EC - TEL} \text{ or } \frac{MEC}{EQS} \text{ or } \frac{MEC}{EAC} \quad (2)$$

For the risk assessment of pollutants as a mixture, the concentration addition approach was taken into consideration. If the value of the risk characterization ratio of the mixture (RCR_m) calculated from Equation (3) was larger or equal to 1 a potential environmental risk was expected.

$$RCR_m = \sum_{i=1}^{n} RCR_i = \sum_{i=1}^{n} \frac{MEC_i}{EC - TEL_i} \text{ or } \sum_{i=1}^{n} \frac{MEC_i}{EQS_i} \text{ or } \sum_{i=1}^{n} \frac{MEC_i}{EAC_i} \quad (3)$$

3. Results and discussion

The concentration of metals (Cd, Cr, Cu, Ni, and Pb) and TBT in bays and marinas were generally higher in October than in March (Fig. 2). The values detected in bays in March were similar to those of the reference site (Punta Licosa), varying significantly only for Cr (Fig. 2B). Within the October sampling, significant differences were observed for Ni (Fig. 2D), Cr (Fig. 2B) and Pb (Fig. 2E). Except for Cd (Fig. 2A), the concentrations of metals from sediment collected in March were similar in both marinas. The highest Cd concentra-

Table 1
TBT sediment concentrations as Sn (ng g^{-1} d.w.) from the Southern Tyrrhenian coast.

Sampling sites		Location	TBT (ng Sn g^{-1} d.w.)	Campaign	Reference
Gulf of Naples	S1	40°48.553′ N 14°12.744′ E	17.81	July 1999	Cicero et al. (2004)
	S2	40°48.630′ N 14°12.841′ E	15.79		
	S3	48°48.782′ N 14°13.574′ E	15.31		
	S4	40°49.000′ N 14°14.300′ E	16.28		
	S5	40°48.884′ N 14°19.370′ E	14.84		
	S6	40°48.490′ N 14°19.090′ E	15.03		
Gulf of Salerno	S7	40°34.311′ N 14°50.301′ E	10.47	July 1999	Cicero et al. (2004)
	S8	40°23.618′ N 14°56.192′ E	10.80		Cicero et al. (2004)
Acciaroli Marina (Cilento)	S9	40°10.651′ N 15°01.640′ E	93 ± 2 344 ± 80	March 2010 October 2010	This study
Acciaroli Bay (Cilento)	S10	40°10.974′ N 15°01.344′ E	1.55 ± 0.06	October 2010	This study
Casalvelino Marina (Cilento)	S11	40°10.535′ N 15°07.251′ E	6 ± 2 7 ± 2	March 2010 October 2010	This study
Casalvelino Bay (Cilento)	S12	40°10.013′ N 15°07.813′ E	0.83 ± 0.01 1.57 ± 0.07	March 2010 October 2010	This study
Gulf of Policastro (Cilento)	S13	40°03.346′ N 15°31.053′ E	8.02	July 1999	Cicero et al. (2004)
	S14	40°02.999′ N 15°31.516′ E	7.41		
Gulf of Santa Eufemia	S15	38°52.715′ N 16°12.841′ E	7.33	July 1999	Cicero et al. (2004)
	S16	38°52.619′ N 16°11.989′ E	7.23		
North-Western Sicilian coasts and Ustica	S17	–	3–27	July–November 1999 May–June 2000	Chiavarini et al. (2003)

tions were detected in Casalvelino Marina, where a significant increase was observed between the two sampling campaigns from 0.32 μg g^{-1} to 0.49 μg g^{-1} from March to October, respectively. Conversely, Cd concentration was significantly lower in Acciaroli Marina (0.32 μg g^{-1}). According to Table S2, the highest Cd concentrations along the Southeastern Tyrrhenian Sea (0.57 μg g^{-1}) were detected in the Gulf of Bagnoli (Naples). Compared to all other monitored elements along Southeastern Tyrrhenian Sea, Cd presented the lowest concentrations ever.

Significant differences in Cr (Fig. 2B) concentrations were evidenced between March and October samplings in both marinas. The highest Cr concentration (50.20 μg g^{-1}) was measured in Acciaroli Marina in October. This value was comparable to Cr concentration (52.49 μg g^{-1}) (Table S2) detected in Palermo city port. Other Cr hot spots along the Campania coast were observed at the Sarno River mouth (84.40 μg g^{-1}) (Table S2) and Naples city port (72.50 μg g^{-1}) (Table S2). The concentration of Cu (Fig. 2C) in Acciaroli Marina in October (492.6 μg g^{-1}) was significantly higher than in Casalvelino Marina (218 μg g^{-1}) and the maximum concentration detected along the Southeastern Tyrrhenian Sea (Palermo city port, 223.06 μg g^{-1}) (Table S2). A significant increase of Cu concentration was recorded between March and October samplings in Acciaroli Marina. Seasonal fluctuations in Ni concentrations were observed (Fig. 2D), but with no significant differences between the two marinas. In October, the concentration of Ni in Casalvelino Marina (46 μg g^{-1}) was higher than those detected along the Southern Italian coast ranging between 2.80 μg g^{-1} (Punta Licosa) and 16.60 μg g^{-1} (Sarno River) (Table S2). The concentration of Pb (Fig. 2E) did not vary significantly between both marinas and the reference site, except for Casalvelino Marina during October (129 μg g^{-1}). The concentration of Cd and Pb in both marinas was significantly higher than those reported for sediment collected in Northern Adriatic Sea marinas (0.068 μg Cd g^{-1}, 14 μg Pb g^{-1}) (Scancar et al., 2007). Their increase in October suggested a potential significant anthropogenic input from summertime leisure activities. Lead in Acciaroli Bay (699 μg g^{-1}) was higher than the concentrations detected in both marinas (129 μg g^{-1} in Casalvelino Marina and 11.9 μg g^{-1} in Acciaroli Marina) and in all sediments collected along Southern Tyrrhenian coast as reported in Table S2. The concentration of Pb observed in Acciaroli Marina was lower than that measured in areas from the Southern Italian coast considered as reference sites such as the Gulf of Termini Imerese (Palermo) (Table S2). According to Table S2, Pb resulted the main contaminant present in Piazza Vittoria (Naples) sampling station. Frequently, Pb is present in antifouling paints, fuels and batteries thus being release also by pleasure boats (Almeida et al., 2007).

In *Acciaroli Marina*, a significant difference in TBT concentration was evidenced between March (93 μg g^{-1}) and October (344 μg g^{-1}) (Fig. 2F) compared to all other investigated sites. The contamination could be due to recent resuspension phenomena of contaminated sediment (boat mechanical resuspension, dredging operations, and sludge dumping), port construction activities and/or illegal use of TBT-based antifouling paints. Lower concentrations of TBT were found in Casalvelino Marina with no seasonal variability. Acciaroli Marina compared to Casalvelino Marina presents docking activities and boatyard. The TBT concentration of Acciaroli Marina sediment was higher than other sites investigated along the Southern Tyrrhenian Sea (Table 1), but none of the sampling stations was located inside a port. Other marinas around the world presented similar contamination levels: 46.2–3935 ng Sn g^{-1} in United Kingdom (Dowson et al., 1992), 25 ng Sn g^{-1} in Portugal

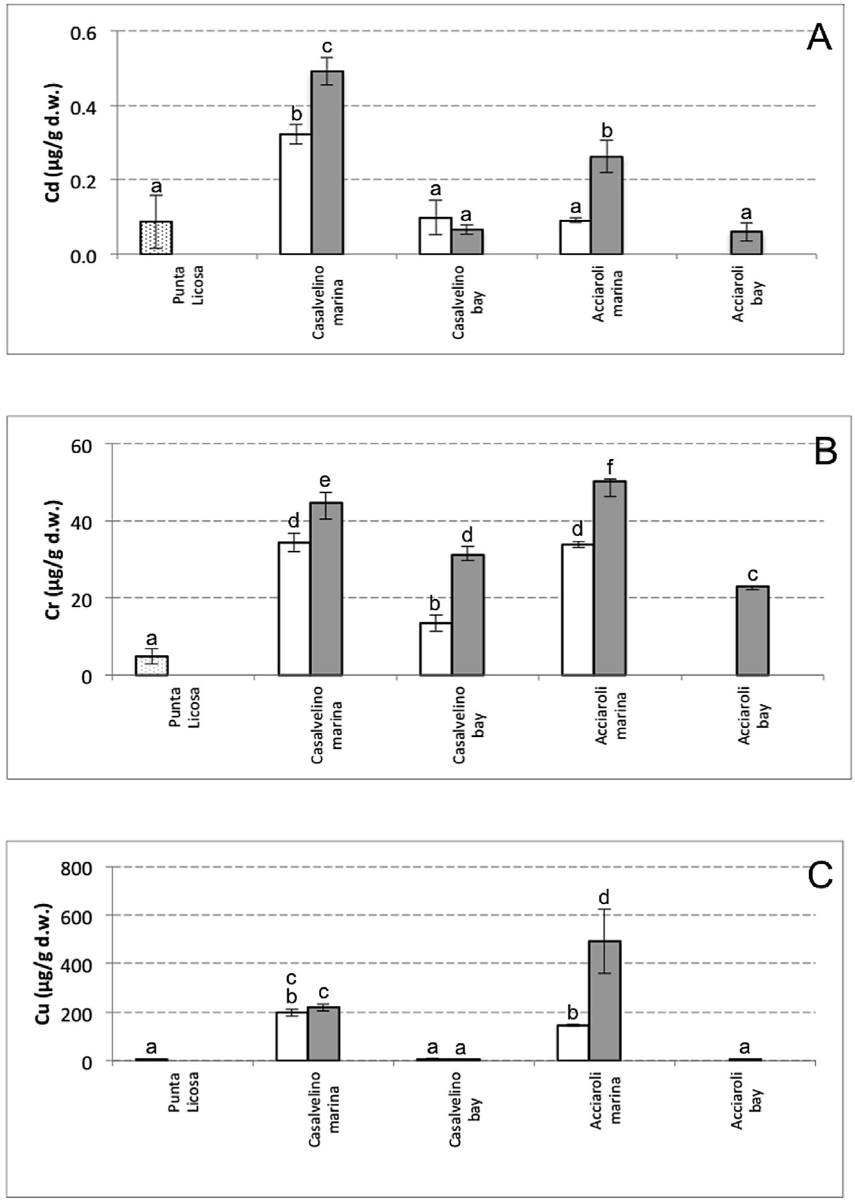

Fig. 2. A, B, C, D, E and F Metals (Cd – A; Cr – B; Cu – C; Ni – D; Pb – E) and TBT (as Sn – F) trend in sediment samples according to seasonality (white = March 2010; grey = October 2010) and in Punta Licosa (dotted bar) as reference site; data with different letters (a, b, c, d, e and f) are significantly different (Dunnett's and Tukey's, $p < 0.05$); d.w. = dry weight).

(Sousa et al., 2007), 920–975 ng Sn g^{-1} in Spain (Diez et al., 2002), and 100–780 ng Sn g^{-1} in Slovenia (Scancar et al., 2007). The berthing capacity and ship traffic in the two marinas could explain the highest Cu, Pb, and TBT levels measured in Acciaroli Marina (460 berths) compared to Casalvelino Marina (120 berths). A similar high concentrations for Cu (698 $\mu g\ g^{-1}$) and Pb (220 $\mu g\ g^{-1}$) were detected in marine sediments of Palermo Gulf, collected inside the Cala Area that is an enclosed zone in which the circulation of water is restricted and domestic sewage coming from the city of Palermo is free to flow (Tranchina et al., 2008).

About the environmental risk assessment, several guidelines were developed dealing with contaminated sediment in response to regulatory requirements (Bay and Weisberg, 2012). For each substance, the MEC was compared to three quality standards for metals (Table 2) and TBT (Table 3). Furthermore, As, Cd, Cu, Cr, Hg, Pb, Ni, and Zn (Table 2), and TBT (Table 3) risk characterisation were investigated for other sampling sites located along the Southeastern Tyrrhenian Sea coast (ARPAC, 2003, 2007; Chiavarini et al., 2003; Cicero et al., 2004; Ferraro et al., 2006; Tranchina et al., 2008; Romano et al., 2009). Threshold values for EQS and EAC (Table S3) were exceeded for several metals and TBT. In most cases, RCR values of single pollutants were larger than 1 suggesting the occurrence of potential environmental risks. Sediment from port areas was the most impacted like in Naples and Palermo (Table 2). The highest RCR values for Cd (MEC/EC-TEL = 1.32, MEC/EAC = 9 and MEC/EQS = 90) and for Hg (MEC/EC-TEL = 10.1, MEC/EAC = 26.4 and MEC/EQS = 2640) were observed in Naples city port and in Palermo city port, respectively; for Zn (MEC/EC-TEL = 4.85, MEC/EAC = 12.04) in Gulf of Bagnoli. Other sediment hot spots were detected at the river mouth of heavily contaminated rivers like the Sarno River (Lofrano et al., 2015). The highest RCR values for Cr (MEC/EC-TEL of 1.61, MEC/EAC of 8.44 and MEC/EQS of 1688) were observed in Sarno River. Due to the volcanic origin of the Campania Region coast, the presence of high

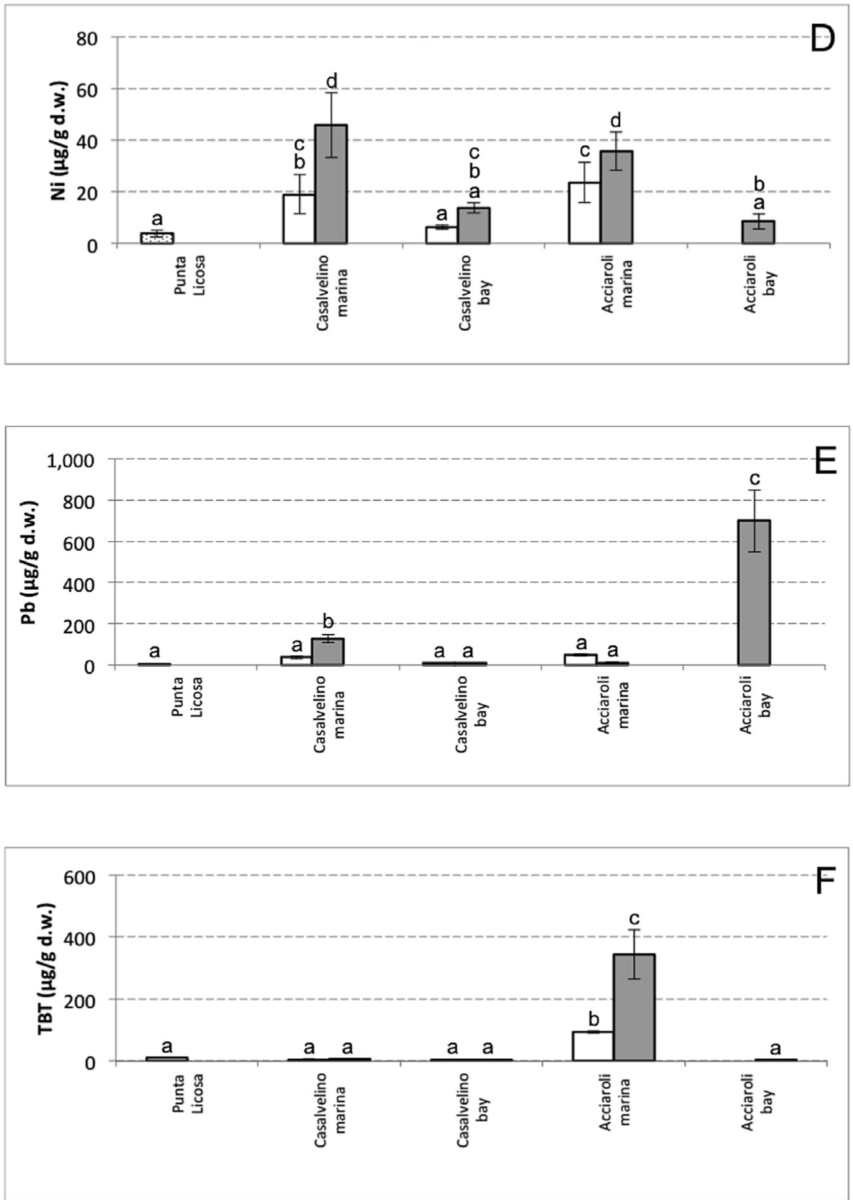

Fig. 2. Continued

RCR values for As was expected (MEC/EC-TEL of 3.16, of MEC/EAC 22.90 and MEC/EQS of 2290) like in Punta Tresino that is frequently assumed as a reference site. The highest RCR values for Cu (MEC/EC-TEL = 26, MEC/EAC = 99), Pb (MEC/EC-TEL = 23, MEC/EAC = 140 and MEC/EQS = 69,934), Ni (MEC/EC-TEL = 2.88, MEC/EAC = 9.16) were observed in Acciaroli Marina, Acciaroli Bay and Casalvelino Marina, respectively.

The risk associated to TBT was high for Acciaroli Marina with values up to 23-fold greater than the Gulf of Naples (Table 3). Data from Casalvelino Marina were similar to other Cilento coastal sampling sites like in the Gulf of Policastro and Santa Eufemia (Cicero et al., 2004). For TBT, the lowest RCR values were found in Casalvelino Bay and Acciaroli Bay. Unfortunately, no reference site (Punta Licosa) data on TBT are currently available thus the potential background level remains still unknown.

To date, no EU guidelines are available to address both human health and environmental assessment of chemical mixtures. Experimental mixture studies in ecotoxicology and human toxicology demonstrated that the concept of dose/concentration addition and independent action provide good approximations of observed combination effects (Kortenkamp, 2007). From data in Tables 2 and 3, the risk assessment of mixtures was investigated according to the concentration addition approach. Frequently, the RCRs exceeded the threshold value for the single substance along the Cilento coast. As consequence, the risk assessment of mixtures leads to even higher potential risks. Although in Punta Licosa most RCRs showed values lower than 1, the relative RCR_m value was >1. This was mainly due to arsenic (not investigated in our study) that is of geogenic origin leading to overestimate the RCR_m in the reference area. For this reason, regional guidelines taking into consideration the specific biogeochemical characteristics of the area should be developed to carry out site-specific risk analysis avoiding misjudgements (Ghekiere et al., 2013).

The PCA analysis (Fig. 3) clustered together Acciaroli Bay and Casalvelino Bay with Punta Licosa reference site due to their low contamination level. Both marinas showed to be impacted,

Table 2
Metal risk characterisation ratios (RCR_s) expressed as MEC/EC-TEL (A), MEC/EAC (B) and MEC/EQS (C); MEC = measured exposure concentration, EC-TEL = Environment Canada-Threshold Effect Level, EAC = Ecotoxicological Assessment Criteria, EQS = Environmental Quality Guidelines and.

Sampling sites		RCR_s	As	Cd	Cu	Cr	Hg	Pb	Ni	Zn	RCR_m	References
Volturno River (Campania)		A	0.69	0.29	0.71	0.51	1.84	0.43	1.02	0.27	6	ARPAC (2003, 2007)
		B	5	2	2.68	2.69	4.8	2.6	3.26	0.66	24	
		C	500	20	–	538	480	1300	–	–	2838	
Gulf of Bagnoli (Campania)		A	0.28	0.84	1.44	0.53	5.38	7.3	0.43	4.85	21	Romano et al. (2009)
		B	2	5.70	5.44	2.80	14	44.22	1.38	12.04	88	
		C	200	57	–	560	1400	22,100	–	–	24,317	
Gulf of Naples (Campania)	Naples city port	A	2.17	1.32	7	1.38	–	4.1	–	2.44	19	Ferraro et al. (2006)
		B	15.70	9	26.2	7.25	–	24.6	–	6.06	92	
		C	1570	90	–	1450	–	12,300	–	–	15,410	
	Piazza Vittoria	A	1.89	0.26	0.7	0.24	3.31	2.9	0.95	0.62	11	ARPAC (2003, 2007)
		B	13.70	1.80	2.8	1.26	8.6	17.38	3.04	1.53	50	
		C	1370	18	–	252	860	8690	–	–	11,190	
	Portici	A	1.80	0.22	1.5	0.34	1.92	0.66	1.01	0.45	8	
		B	13	1.5	5.64	1.78	5	4.02	3.24	1.11	35	
		C	1300	15	–	356	500	2010	–	–	4181	
	Sarno River	A	1.12	0.53	2.7	1.61	2.15	1.92	1.04	0.45	12	
		B	8.10	3.60	10.1	8.44	5.6	11.64	3.32	1.11	52	
		C	810	36	–	1688	560	5820	–	–	8914	
Gulf of Salerno (Campania)	Picentino river	A	0.80	0.22	0.24	0.26	2.15	0.22	0.71	0.55	5	ARPAC (2003, 2007)
		B	5.80	1.5	0.92	1.41	5.6	1.38	2.26	1.37	20	
		C	580	15	–	282	560	690	–	–	2127	
	Punta Tresino	A	3.16	0.06	0.06	0.10	0.61	0.15	0.37	0.35	5	
		B	22.90	0.4	0.26	0.57	1.6	0.94	1.18	8.88	37	
		C	2290	4	–	114	160	470	–	–	3038	
Cilento coasr	Punta Licosa	A	3.04	0.07	0.09	0.09	0.77	0.13	0.33	0.12	5	
		B	22	0.5	0.36	0.52	2	0.8	1.08	0.29	28	
		C	2200	5	–	104	200	400	–	–	2909	
	Acciaroli Bay	A	–	0.09	0.23	0.44	–	23	0.5	–	24	This study (October 2010)
		B	–	0.6	0.86	2.3	–	140	1.7	–	145	
		C	–	6	–	462	–	69,934	–	–	70,402	
	Acciaroli Marina	A	–	0.39	26	0.96	–	1.58	2.25	–	32	
		B	–	2.63	99	5.02	–	9.57	7.14	–	123	
		C	–	26	–	1004	–	4783	–	–	5813	
	Casalvelino Bay	A	–	0.15	0.33	0.60	–	0.31	0.86	–	2.23	
		B	–	0.99	1.23	3.11	–	1.88	2.72	–	9.92	
		C	–	10	–	622	–	939	–	–	1571	
	Casalvelino Marina	A	–	0.72	11	0.86	–	4.25	2.88	–	20	
		B	–	4.9	44	4.48	–	25.7	9.16	–	88	
		C	–	49	–	895	–	12,849	–	–	13,794	
Gulf of Palermo (Sicily)	North West	A	–	–	1.13	0.41	1.42	0.76	–	0.52	4	Tranchina et al. (2008)
		B	–	–	4.23	2.15	3.7	4.64	–	1.29	16	
		C	–	–	–	431	370	2323	–	–	3124	
	Palermo city port	A	–	–	11.9	1.0	10.1	2.46	–	2.57	28	
		B	–	–	44.6	5.2	26.4	14.88	–	6.37	97	
		C	–	–	–	1049	2640	7444	–	–	9133	
	Oreto River	A	–	–	3.9	1.51	7.15	1.94	–	1.63	16	
		B	–	–	14.7	7.93	18.6	11.74	–	4.05	57	
		C	–	–	–	1587	1860	5873	–	–	9320	
	Central Area	A	–	–	2.6	0.9	3.85	1.32	–	0.78	9	
		B	–	–	9.6	4.8	10	8.03	–	1.93	34	
		C	–	–	–	964	1000	4016	–	–	5980	
	North Eastern	A	–	–	1.4	0.99	1.38	0.99	–	0.84	6	
		B	–	–	5.3	5.21	3.6	5.99	–	2.09	22	
		C	–	–	–	1043	360	2999	–	–	4402	
Gulf of Termini Imerese (Sicily)		A	–	–	1.3	0.74	0.61	0.74	–	0.87	4	Tranchina et al. (2008)
		B	–	–	4.9	3.88	1.6	4.48	–	2.16	17	
		C	–	–	–	776	160	2220	–	–	3156	

but with different contamination profiles. Casalvelino Marina was mainly impacted by Cd, whereas Acciaroli Marina by TBT. All other metals (Cr, Cu, Ni and Pb) evidenced a contamination profile changing according to seasonality.

The EFs calculated for Cd, Cr, Cu, Ni, Pb, and TBT were reported in Fig. 4. With the exception of Pb, the highest EFs were observed after summer in marinas: from 144% for Pb up to of 23898% for Cu in Acciaroli Marina, and from 463% for Cd up to 10522% for Cu in Casalvelino Marina. Both marinas showed extremely high EFs especially for Cu (7074% in Acciaroli Marina and 9550% in Casalvelino Marina in March and 23898% in Acciaroli Marina and 10522% in Casalvelino Marina in October). High EFs were observed for Ni (253%) and Cr (541%) in Casalvelino Bay that is influenced by the discharge of the drainage channels collecting water from farmland (Nziguheba and Smolders, 2008) and the overflow of Casalvelino wastewater treatment plant located next to the Alento River mouth (Fig. 1). In Fig. 4, the TBT EFs are available only for Acciaroli Marina according to Fig. 2F. The level of TBT significantly increased from March to October showing EF values of 749% and 3026%, in that order, compared to the background level of Punta Licosa.

Table 3
TBT risk characterisation ratio (RCR) expressed as Measured Exposure Concentration/Ecotoxicological Assessment Criteria (MEC/EAC); sampling sites references are reported in Table 1 (S1–S17).

Sampling sites		RCRs	Sampling campaign	References
Gulf of Naples	S1	3562	July 1999	Cicero et al. (2004)
	S2	3158		
	S3	3062		
	S4	3256		
	S5	2968		
	S6	3006		
Gulf of Salerno	S7	2094	July 1999	Cicero et al. (2004)
	S8	2160		
Acciaroli Marina	S9	18,683	March 2010	This study
		68,782	October 2010	
Acciaroli Bay	S10	310	October 2010	This study
Casalvelino Marina	S11	1233	March 2010	This study
		1404	October 2010	
Casalvelino Bay	S12	167	March 2010	This study
		314	October 2010	
Gulf of Policastro	S13	1604	July 1999	Cicero et al. (2004)
	S14	1482		
Gulf of Santa Eufemia	S15	1466	July 1999	Cicero et al. (2004)
	S16	1446		
North-Western Sicilian coasts and Ustica	S17	600–5400	July–November 1999 May–June 2000	Chiavarini et al. (2003)

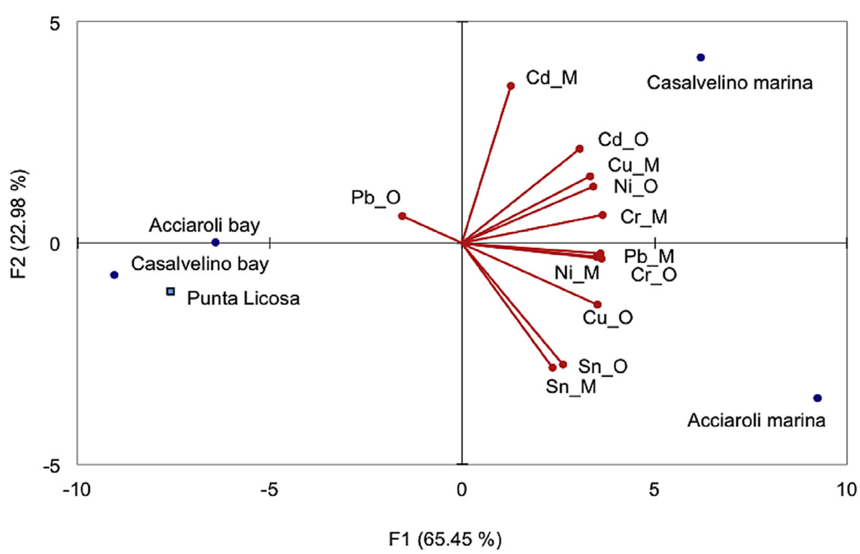

Fig. 3. Principal component analysis biplot of metal concentrations with loadings and scores in the coordinates of the first two principal components (F1 and F2) considering the sampling sites (_M = March 2010 sampling campaign; _O = October 2010 sampling campaign).

4. Conclusion

This was the first survey of Cd, Cr, Cu, Ni, Pb and TBT carried out on four sediment-sampling stations (Casalvelino Marina, Casalvelino Bay, Acciaroli Marina and Acciaroli Bay) from the Cilento coast. Data were compared to the contamination background levels of Punta Licosa reference site and further investigated calculating the relative enrichment factors on a seasonal basis as well as the risk characterisation ratios. Sediment samples evidenced a level of contamination generally increasing from March to October probably due the intensification of human activities along the coast during summertime. The quality of sediment from bays was similar to the reference site, while marinas showed significantly high levels of contamination. The values of risk characterisation ratios, considering both the single substance- and mixture-based approaches, highlighted the occurrence of potential threats. Nevertheless potential misinterpretation may result from the erroneous consideration of geogenic levels of elements, especially in active volcanic areas like Naples area, thus requiring the definition of specific regional guidelines for data interpretation

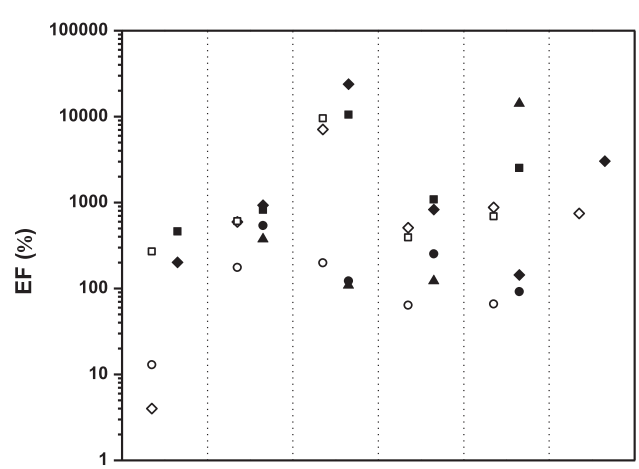

Fig. 4. Metal enrichment factors (EF) of sediment samples from Acciaroli Marina (□ March 2010; ■ October 2010), Casalvelino Marina (◇ March 2010; ♦ October 2010), Casalvelino Bay (○ March 2010; ● October 2010) and Acciaroli Bay (▲ October 2010).

on the basis of contextualised background levels. The database resulting from the review of sediment quality from other Southern Tyrrhenian Sea sampling stations reported an analogous state-of-the-art, showing hot spots in coincidence of river mouths or port activities.

Further studies will be necessary to ascertain the background element concentrations along the Cilento coast, besides the currently available reference site of Punta Licosa, and to carry out ecotoxicological sediment characterisation to integrate the contamination-based assessment with a toxicity-based perspective.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2015.09.002.

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