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Abstract

Distribution of metals (Hg, Pb, Sn, Cu, Cd and Zn) was determined in sediments and in different tissues of *Posidonia oceanica* collected from San Pietro Island, Taranto Gulf (Ionian Sea, Southern Italy). In seagrass, results, compared with metal concentrations in sediments, showed that the highest concentrations of Hg, Pb, Sn and Cu were found in the roots, while in the highest levels of Cd and Zn were found in the green leaves. In contrast, the lowest metal concentrations were found in the basal part of the leaf. Levels of metals in the leaves were similar to those found by other authors in uncontaminated areas of the Mediterranean Sea. Mercury levels in roots were correlated to levels in sediments. This could demonstrate that the plant memorizes sediment contamination. This study reinforces the usefulness and the relevance of *Posidonia oceanica* as an indicator of spatial metal contamination and an interesting tool for environmental quality evaluation.

Keywords: Heavy metals, Mediterranean Sea, *Posidonia oceanica,* Sediments.

Introduction

Coastal ecosystems are exposed to a wide variety of pollutants (Benoit & Comeau, 2005). Of these, metals are among the most widespread and are increasingly reaching marine ecosystems, both from diffuse (including atmospheric) and point sources. Given their potential adverse effects on the environment, wildlife and human health, metals are thus of great concern.

There is currently a great interest in using living organisms as pollution biomonitors in aquatic ecosystems (Goldberg, 1986; Andersen *et al.,* 1996; Pergent-Martini & Pergent, 2000; Morillo *et al.,* 2005; Usero *et al.,* 2005; Demirezen & Aksoy, 2006), given that methods used previously, such as water chemical analysis, do not provide sufficient information on the bioavailability of metals found in the environment (Morillo *et al.,* 2005). In the Mediterranean Sea, the endemic seagrass *P. oceanica* (L.) Delile has been used as a metal bioindicator for two decades (Maserti *et al.,* 1988; Costantini *et al.,* 1991; Malea *et al.,* 1994; Capiomont *et al.,* 2000; Campanella *et al.,* 2001; Lafabrie *et al.,* 2008). The importance of this species lies in its extension, high productivity and stability, and also because its meadows function as spawning areas, hunting territory or permanent habitat for numerous plant and animal species (Ward 1987; Ballesta *et al.,* 2000; Ruiz & Romero 2003; Pergent-Martini *et al.,* 2006).

In addition, the community of organisms living in *P. oceanica* meadows is organized into numerous complex food webs, most of which begin with the consumption of *P. oceanica* leaves and the epiphytes which are associated with them (Ott, 1980). Since marketed species are among the known or potential grazers of *P. oceanica*, the study of metals in this species is not only of ecotoxicological interest, but also of public health concern.

Since the early 60s, the Northwest area of Taranto city (Apulia) has become one of the largest and most complex industrial sites in Europe, including several industrial plants, mainly consisting of an iron and steel factory, oil refinery, military base and many other industrial installations. This has led to growing concerns about the possible health effects caused by environmental exposure of residents until 1990, when the industrial area of Taranto, was declared an "area at high risk of environmental crisis", in accordance with Italian law 349 of 8/7/86.

Sampling sites are located a few kilometres southwest of this industrial area, and are examples of coastal environments with a relatively high influx of industrial effluents. The aim of our study was to evaluate the impact of these industrial discharges on the metal content of *P. oceanica*. Therefore, in this work Hg, Pb, Cd, Sn, Cu and Zn concentrations were determined in *P. oceanica* and in sediments collected at four stations along the San Pietro Island coastline (Taranto Gulf, Ionian Sea, Italy). Moreover, in order to identify bioaccumulation sites, metal distribution in different parts of the plant was determined. In addition, it was investigated whether a relationship exists between metal contamination in sediments and metal levels in plants.

Materials and Methods

Sampling

In the summer of 2009 samples of *P. oceanica* and sediment were collected at four stations in a meadow located along the San Pietro Island coastline (40° 15' N 17° 08' E) (Taranto Gulf, Ionian Sea, Southern Italy) (Fig. 1).

San Pietro Island, together with San Paolo Island, is part of the Cheradi Islands archipelago, located in the inner part of the Taranto Gulf (Ionian Sea), near the Mar Grande basin. The *P. oceanica* meadow covers a triangular shaped area, extending off the island of San Pietro, up to a maximum distance of about 2.5 km in a W and NW direction. However, it extends over 6 km from NW to SE, along the entire Southern coastline of the small archipelago. In recent decades, due to development and, in particular, the large industrial settlement, most of the seagrass meadow has regressed. In the past, the seagrass meadow stretched towards the coast, but now is limited to San Pietro Island. In the meadow, a mean density of 366 shoots /m^2 was determined by Paterno *et al.* (1991). This corresponds to class III-IV, sparse or very sparse meadow according to Giraud's classification (1977) for *P. oceanica* meadows in the Mediterranean.

P. oceanica was collected at 10 ± 1 m depth by scuba divers. At each station, five plants were sampled. After collection, the plants were immediately transported, in polyethylene bags, to the laboratory. At the laboratory, epiphytes and sediment particles were carefully removed from the samples by moderate scraping using a glass slide, according to the method described by Dauby and Poulicek (1995). Plants were divided into the following fractions: roots, rhizomes and leaves. In addition, the leaves were divided into green leaf (upper 5 cm) and basal part (bottom 5cm). Only mature leaves of comparable length were selected for seagrass analysis. For each station, all roots, rhizomes, green leaf and basal part of the leaves were pooled into four samples. Each sample was lyophilized and then manually reduced to a coarse powder.

Superficial sediments (5 cm) were collected in PVC cores by scuba divers. At each station, five samples were collected, then gathered in a single sample. Samples were stored in polyethylene bottles and frozen at -20°C until analysis. At 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. Particle-size analysis by dry sieving was then performed, according to the methods prescribed by the Romano & Gabellini (2001), using a sieve (Retsch AS 200).

Metal determination in sediments and plants

Mercury concentrations were determined with an Advanced Mercury Analyser (AMA-254, LECO, Stockport, Cheshire, UK), which allows a direct analysis without sample extraction procedure. The instrument consists of a nickel boat in a quartz combustion tube, containing a catalyst (cobalt oxalate and a mixture of manganese oxide, cobalt and calcium acetate) in which the solid sample (about 100mg of dried sample: sediments or plants) is initially dried prior to combustion at 750°C in an oxygen atmosphere. The mercury vapour which is produced is trapped on the surface of a gold amalgamator. After a specified time interval, the amalgamator is heated to 900°C, to release

Fig. 1: Location of the sampling stations.

the mercury which is transported to a heated cuvette (120°C), prior to analysis by AAS using a silicon diode detector at 253.6 nm (Costley *et al.,* 2000; Buccolieri *et al.,* 2006). The detection limit for mercury calculated on the basis of 10 determinations of the blanks as three times the standard deviation was 0.2 ng g^{-1} dry wt.

For the analysis of Cu, Pb, Sn, Cd and Zn about 0.5g of sample (sediments or plants) was digested with 10ml of concentrated HNO_3 in a closed teflon vessel using a MARSX microwave oven (CEM Corporation, Matthews, NC). For each digestion programme, a blank was prepared with the same amount of acid. After mineralization, digests were cooled and the resulting solutions were diluted to a known volume (50 mL) with Milli Q water and stored in polyethylene bottles, until analysis.

Cd, Cu, Pb and Sn were determined by graphite furnace atomic adsorption spectroscopy (GFAAS) using an Analyst 600 spectrophotometer (Perkin Elmer, USA); Zn was determined by flame atomic adsorption spectroscopy (FAAS) using a 1100B spectrophotometer (Perkin Elmer, USA). All chemicals used in sample treatments were ultrapure grade (Merck Suprapur, Daemastadt, Germany). All the glassware was cleaned prior to use, by soaking in 10% v/v HNO_3 for 24 h and rinsed with Milli Q water. Working standard solutions of metals were daily prepared by serial dilution of stock standard solutions of each metal, containing 1000 mg/L of metal (BDH, Poole, UK). The precision and accuracy of the analytical method was checked using standard reference materials CRM 60 (*Lagarosiphon major)* and IAEA 356 (polluted marine sediment). Results were in agreement with certified values and the standard deviations were low, proving good repeatability of the method (Table 1).

Detection limits (LOD) for various metals calculated on the basis of 10 determinations of the blanks as three times the standard deviation were: 0.06 µg g^{-1} dry wt. for Cd, 0.12 µg g^{-1} dry wt. for Cu, 0.09 µg g^{-1} dry wt. for Pb, 0.18 µg g^{-1} dry wt. for Zn and 0.20 µg g^{-1}dry wt. for Sn.

Geoaccumulation index

To assess the degree of sediment contamination, the geoaccumulation index (I_{geo}) was calculated in order to evaluate if metal concentrations represent background levels for the Mediterranean Sea (Loska *et al.,* 1997; Rubio *et al.,* 2000; Ruiz 2001). I_{geo} was originally defined by Müller (1979) in order to determine metal contamination in sediments, by comparing current concentrations with pre-industrial levels. It can be calculated by the following equation:

$$I_{geo} = \log_2 C_n/1.5B_n$$

where C_n is the measured concentration of the examined metal n in the sediment and B_n is the geochemical background concentration of the metal n. Factor 1.5 is used because of possible variations in background values for a given metal in the environment, as well as, very small anthropogenic influences. Müller has distinguished seven classes in the geoaccumulation index (Müller, 1981) (Table 2).

Table 2. Müller's classification for the geoaccumulation index (Müller, 1981).

I_{geo} value	Class	Quality of sediment
0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
> 5	6	Extremely polluted

Several authors (Donazzolo *et al.,* 1981; Karageorgis *et al.,* 1998; Buccolieri *et al.,* 2006) have demonstrated that it is very difficult to establish B_n values, mainly for sediments of the Mediterranean Sea, owing to geochemical variability of various areas and different anthropogenic impact. In this work, Bn values have been estimated by Buccolieri *et al.* (2006), because they have been determined for Taranto Gulf, Ionian Sea. These B_n values are: Hg 0.07 µg g^{-1} d.w., Pb 59 µg g^{-1} d.w., Cu 47 µg g^{-1} d.w. and Zn 97 µg g^{-1} d.w.

Table 1. Metal concentrations (µg g^{-1} dry wt.) in certified reference materials.

Metal	BCR 60 (Lagarosiphon major)		IAEA 356 (Polluted marine sediment)	
	Certified	Found*	Certified	Found*
	(µg g^{-1} dry wt.)		(µg g^{-1} dry wt.)	
Cd	2.20 ± 0.10	2.31 ± 0.29	0.533 ± 0.026	0.556 ± 0.029
Cu	51.2 ± 1.9	50.2 ± 2.1	44.1 ± 1.0	43.6 ± 2.1
Hg	0.34 ± 0.04	0.35 ± 0.06	1.03 ± 0.13	1.01 ± 0.07
Pb	63.8 ± 3.2	66.4 ± 3.6	42.3 ± 1.6	44.0 ± 3.1
Zn	313 ± 8	303 ± 11	142 ± 3	145 ± 5.5

* Number of replicates = 6

Statistical analysis

Two-way analysis of variance (ANOVA) and correlation analysis were used to extract information from the chemical data, in order to find the relationships among metals in plants and sediments. The correlation analysis was performed by Pearson correlation. All statistical analyses were performed using the STATISTICA® software package (StatSoft Inc., Tulsa, OK, USA).

Results and Discussion

Metal concentrations in Posidonia oceanica

Metal concentrations in the different tissues of *P. oceanica* are shown in Table 3. The results show that metal distribution in plants varies according to the considered anatomic compartment. Indeed, the highest concentrations of Hg, Pb, Sn and Cu were found in the roots, while the highest levels of Cd and Zn were found in green leaves. In contrast, the lowest metal concentrations were found in the basal part of the leaves. Similar metal distributions in *P. oceanica* and other seagrass species have been reported by other authors (Nienhuis 1986; Catsiki & Panayotidis 1993).

The relationship between metal concentrations was investigated by Pearson's correlation (Table 4). A highly significant positive correlation ($p<0.05$) was found between Zn and Sn in the roots; a significant negative correlation ($p<0.05$) was found between Cu and Sn in the green leaves and between Pb and Cd in the basal part of the leaves.

In this study *P. oceanica* leaves showed metal contamination levels in the range of the lowest available values for Mediterranean areas (Table 5). Specifically, Cd, Cu and Pb levels determined in the leaves of *P. oceanica* are lower than those reported by other authors, while for Hg the results are comparable to those found in the literature. Mean Zn levels for *P. oceanica* leaves were similar to those of Schlacher-Hoenlinger and Schlacher (1998), but higher than those of Malea *et al.* (1994), Campanella *et al.* (2001) and Conti *et al.* (2010). As regards Sn, it is difficult to compare the results obtained in this study, due to the lack of literature data.

Table 3. Metal concentrations (µg g^{-1} dry wt.) in *Posidonia oceanica* and in sediments (mean* ± S.D.).

Tissue	Sampling station	Cd	Cu	Hg	Pb	Sn	Zn
Green leaf	1	0.47 ± 0.03	3.63 ± 0.52	0.06 ± 0.01	1.71 ± 0.38	0.21 ± 0.03	187 ± 20
	2	0.43 ± 0.06	2.86 ± 0.42	0.08 ± 0.02	1.51 ± 0.20	0.21 ± 0.03	160 ± 15
	3	0.49 ± 0.08	2.21 ± 0.51	0.04 ± 0.01	1.26 ± 0.15	0.23 ± 0.02	129 ± 9
	4	0.57 ± 0.07	6.95 ± 0.62	0.05 ± 0.01	1.31 ± 0.15	0.15 ± 0.04	193 ± 20
Basal part	1	0.09 ± 0.01	1.13 ± 0.23	0.03 ± 0.01	0.43 ± 0.02	0.13 ± 0.04	55 ± 6
	2	0.09 ± 0.01	0.97 ± 0.18	0.04 ± 0.01	0.38 ± 0.06	0.37 ± 0.03	32 ± 3
	3	0.10 ± 0.01	1.43 ± 0.64	0.04 ± 0.02	0.23 ± 0.03	0.15 ± 0.01	25 ± 2
	4	0.10 ± 0.01	1.08 ± 0.46	0.05 ± 0.01	0.23 ± 0.03	0.14 ± 0.03	15 ± 1
Rhizome	1	0.10 ± 0.02	3.27 ± 0.61	0.03 ± 0.02	0.69 ± 0.03	0.15 ± 0.04	68 ± 5
	2	0.16 ± 0.05	2.66 ± 0.30	0.04 ± 0.01	0.35 ± 0.08	0.38 ± 0.03	73 ± 4
	3	0.12 ± 0.04	3.15 ± 0.46	0.03 ± 0.01	0.29 ± 0.04	0.14 ± 0.03	34 ± 3
	4	0.18 ± 0.04	3.49 ± 0.67	0.06 ± 0.02	0.83 ± 0.04	0.15 ± 0.03	36 ± 3
Roots	1	0.25 ± 0.01	7.09 ± 0.65	0.21 ± 0.03	5.38 ± 0.49	0.28 ± 0.04	75 ± 5
	2	0.22 ± 0.03	6.83 ± 0.89	0.05 ± 0.01	3.74 ±0.34	0.73 ± 0.04	132 ± 10
	3	0.32 ± 0.02	5.26 ± 0.76	0.34 ± 0.02	3.30 ± 0.56	0.18 ± 0.03	46 ± 3
	4	0.39 ± 0.03	5.87 ± 0.84	0.15 ± 0.02	5.91 ± 0.35	0.23 ± 0.03	46 ± 4
Sediments	1	0.13 ± 0.04	22.34 ± 1.10	0.54 ± 0.03	29.12 ± 0.50	4.12 ± 0.52	54 ± 6
	2	0.12 ± 0.05	9.58 ± 1.02	0.17 ± 0.02	16.11 ± 0.30	0.44 ± 0.08	38 ± 2
	3	0.16 ± 0.08	8.11 ± 0.85	1.79 ± 0.01	29.19 ± 0.60	0.72 ± 0.09	62 ± 4
	4	0.17 ± 0.08	8.05 ± 0.97	0.10 ± 0.02	14.28 ± 0.45	0.36 ± 0.05	35 ± 3

* mean of three analytical determinations

Table 4. Pearson correlations between metals in the green leaf, basal part, roots and sediments.

	Cu	Hg	Pb	Sn	Cd	Zn
Green leaf						
Cu	1.000					
Hg	-0.206	1.000				
Pb	-0.172	0.490	1.000			
Sn	**-0.985**	0.149	0.285	1.000		
Cd	0.845	-0.682	-0.498	-0.824	1.000	
Zn	0.789	0.135	0.469	-0.708	0.440	1.000
Basal part						
Cu	1.000					
Hg	-0.790	1.000				
Pb	-0.519	-0.112	1.000			
Sn	-0.391	0.318	0.262	1.000		
Cd	0.597	0.000	**-0.982**	-0.433	1.000	
Zn	-0.110	-0.518	0.888	-0.082	-0.797	1.000
Roots						
Cu	1.000					
Hg	-0.710	1.000				
Pb	0.298	-0.413	1.000			
Sn	0.581	-0.717	-0.331	1.000		
Cd	-0.747	0.333	0.407	-0.729	1.000	
Zn	0.702	-0.683	-0.319	**0.978**	-0.850	1.000
Sediments						
Cu	1.000					
Hg	-0.132	1.000				
Pb	0.538	0.764	1.000			
Sn	**0.989**	-0.005	0.639	1.000		
Cd	-0.464	0.433	0.064	-0.349	1.000	
Zn	0.326	0.893	**0.972**	0.440	0.178	1.000

*Correlation significant at $p < 0.05$

Table 5. Means and ranges of concentrations (μg g^{-1} dry wt.) in *Posidonia oceanica* leaves reported in various studies.

Locations	Cd	Cu	Hg	Pb	Sn	Zn	References
			(μg g^{-1} dry wt.)				
Tyrrhenian coast (Italy)	2.81 (2.02-3.87)						Taramelli *et al.,* 1991
Antikyra Gulf (Greece)	20.08 (2.7-44.0)	18 (2.8-148)		39.5 (10.5-123)		43.4 (27.1-97.7)	Malea *et al.,* 1994
Calvi (Corsica, France)	2.3	10.2		5.96		154	Warnau *et al.,* 1995
Marseille (France)	2.4	12.1		7.76		179	
Ischia (Italy)	2.1	16.2		8.35		144	
Island of Ischia (Italy)	1	14.1		3.4		168	Schlacher-Hoenlinger and Schlacher 1998
Rosignano (Italy)			0.51 (0.39-0.63)				Capiomont *et al.,* 2000
Tonnara (Corsica)			0.06 (0.05-0.07)				
Favignana Island (Italy)	2.22 (1.13-2.78)	11.6 (5.7-20.2)		0.91 (0.70-1.18)		112 (105-118)	Campanella *et al.,* 2001
Corsican coast (France)	2.35		0.05	1.71			Lafabrie et al., 2008
San Pietro Island (Italy)	0.49	3.91	0.06	1.45	0.20	167	This study

Metal concentrations in sediments

Metal concentrations in sediments, expressed in µg g^{-1} dry weight, are shown in Table 3. Cu, Hg, Pb, Sn, Cd and Zn levels in sediments were in the range of 8.05-22.34, 0.10-1.79, 14.28-29.19, 0.36-4.12, 0.12-0.17 and 35-62 µg g^{-1} dry wt. respectively. Highest Hg, Pb and Zn concentrations were observed at station 3, whereas highest Cu and Sn concentrations were detected at station 1. Cd concentrations were similar at all stations. For grain size distribution, according to the AASHO (American Association of State Highway and Transportation Awards) classification system, all sediments consisted predominantly of pelitic sands. The average grain size composition was: 5.0% gravel, 49.0% sand, 46.0% silt and clay. There are no significant differences among stations as regards grain size.

The two-way ANOVA did not show significant differences in metal distribution between the stations ($p<0.05$). Significant positive correlations in the sediments were observed between Cu-Sn and Zn-Pb concentrations ($p<0.05$) (Table 4). These correlations between metal concentrations suggest either a common or a similar geochemical behaviour or origin. Factors including source rock or soil types, weathering processes, surface adsorption phenomena, and characteristics of depositional environment affect metal distribution in sediments. Therefore, metal/metal relationships may vary significantly (NAVFAC, 2003).

A comparison with results from sediments of other marine coastal areas is shown in Table 6. In general, data show concentration levels more or less similar to those found in other areas. In particular, Hg levels were higher than those reported for the Aegean Sea and Ligurian Sea, except for the Adriatic Sea, Gulf of Trieste and the Venice Lagoon. Cd levels were always higher than those reported for the Aegean Sea and for the Adriatic Sea and Slovenia Coast, except the Ligurian Sea and Venice Lagoon. Concerning Cu, Zn and Pb, levels were lower than those reported by other authors, except for the Slovenia Coast.

Results of the I_{geo} are shown in Figure 2; for Pb, Cu, Zn, Sn and Cd, all the stations are classified in class 0 (the unpolluted class). The I_{geo} class for Hg, ranges between 1

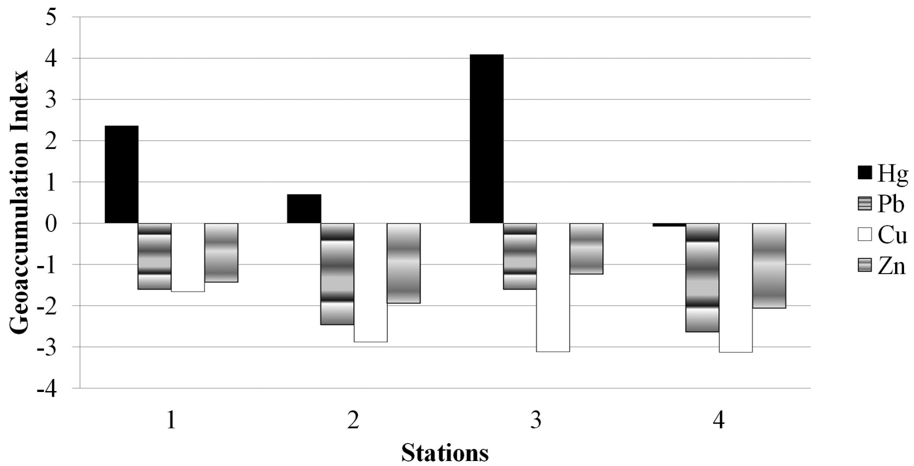

Fig. 2: Geoaccumulation Index (Igeo) in surface sediments from San Pietro Island (Taranto Gulf, Ionian Sea, Italy).

Table 6. Comparisons of metal concentrations (µg g^{-1} dry wt.) in sediments from different marine coastal areas.

Locations	Cu	Hg	Pb µg g^{-1} dry wt.	Cd	Zn	References
Gulf of Trieste, Adriatic Sea (Italy)		0.10-23.30				Covelli *et al.,* 2001
Ligurian Sea (Italy)	2.3-74	0.03-0.47	1.2-150	0.03-1.13	13-610	Bertolotto *et al.,* 2004
Slovenia Coast, Northern Adriatic Sea	15.6-87.00		8.0-18.3	0.07-0.13	35-140	Scancar *et al.,* 2007
Venice Lagoon, Adriatic Sea (Italy)		1.2-2.3	38-114	0.2-5.0	101-1115	Bellucci *et al.,* 2002
Gulf of Izmir, Aegean Sea	2.6-50.0	0.05-0.39	14.0-76.0	0.01-0.14	20-249	Bergin *et al.,* 2006
San Pietro Island (Italy)	8.05-22.34	0.10-1.79	14.28-29.19	0.12-0.17	35-62	This study

Table 7. Pearson correlations between metal concentrations in plant and sediment.

	green leaf	basal part	rhizome	roots	sediments
Hg					
green leaf	1.000				
basal part	0.497	1.000			
rhizome	0.084	0.884	1.000		
roots	-0.802	-0.811	-0.610	1.000	
sediments	-0.616	-0.831	-0.753	**0.964**	1.000
Cd					
green leaf	1.000				
basal part	0.607	1.000			
rhizome	0.474	0.826	1.000		
roots	0.953	0.763	0.499	1.000	
sediments	0.833	0.697	0.278	**0.947**	1.000
Pb					
green leaf	1.000				
basal part	0.968	1.000			
rhizome	0.222	0.007	1.000		
roots	0.288	0.078	**0.997**	1.000	
sediments	0.239	0.188	-0.292	-0.290	1.000
Zn					
green leaf	1.000				
basal part	0.185	1.000			
rhizome	0.244	0.731	1.000		
roots	-0.009	0.330	0.867	1.000	
sediments	-0.600	0.415	-0.173	-0.373	1.000
Cd					
green leaf	1.000				
basal part	-0.395	1.000			
rhizome	0.686	0.300	1.000		
roots	-0.058	-0.735	-0.340	1.000	
sediments	-0.131	-0.130	0.154	0.717	1.000
Sn					
green leaf	1.000				
basal part	0.378	1.000			
rhizome	0.278	0.899	1.000		
roots	0.204	0.909	0.901	1.000	
sediments	0.316	-0.463	-0.144	-0.226	1.000

*Correlation significant at $p < 0.05$

(from unpolluted to moderately polluted) and 4 (strongly polluted), indicating an Hg enrichment. Therefore, in this case the examined sediments can only be considered contaminated by Hg. This result may be related to the ILVA iron and steel factory and the ENI refinery in Taranto. In fact, industrial emissions of Hg in the Taranto area are about 1400 kg/year in air and 665 kg/year in sea water (Eper Register, 2012). In fact, several studies have qualified the Taranto Gulf as an Hg contaminated site (Cardellicchio *et al.,* 2009; Annicchiarico *et al.,* 2011).

Metal correlations

It is known that sediments can act as a source of contaminants for organisms (Villares *et al.,* 2001). In fact, marine macrophytes absorb metals in two ways: by direct absorption from water through the leaf surface, or from the sediment and interstitial water through the roots (Brinkhuis *et al*., 1980).

The foliar tissue analysis of these organisms allows us to determine the mean pollution levels over a limited time interval, whereas an analysis of the roots provides an indication of environmental contamination over a much longer period (Ledent *et al.,* 1993). This phenomenon may be due to the long lifespan of the roots and the slow regeneration levels of these structures compared with foliar structures (Ott 1980; Caye 1989; Pergent 1990).

In this work significant positive correlations ($p<0.05$) were found between Hg concentrations in roots of *P. oceanica* and in sediments (Table 7). Several authors (Ferrara & Serriti 1989; Maserti *et al.,* 1991; Sanchiz *et al*., 2001) indicated that the Hg uptake occurs primarily through the root system and only minimally through the leaves. Therefore the Hg levels found in *P. oceanica* provide an indication of sediment contamination, rather than water. Therefore, *P. oceanica* seagrass meadows could be involved in the Hg cycle at two different levels: in the mobilization of metals found in the sediment, and in the storage of Hg (sink) in the "matte", in the form of dead sheaths and rhizomes. Mattes of P. oceanica seagrass are the result of rhizome growth. These mattes can, in places, reach a thickness of several meters, which corresponds to growth over several centuries: this structure thus could represent an important store of mercury (Molinier and Picard 1952; Boudouresque *et al.,* 1980).

Moreover, significant positive correlations ($p< 0.05$) were found in Cd concentrations between the green leaves and roots of *P. oceanica* (Table 7). It has been reported by other authors (Brinkhuis *et al.,* 1980; Ward 1989) that the Cd uptake occurs mainly from the leaves, through passive adsorption, which depends on the leaf surface and Cd moves to rhizomes and roots at a later stage only. Therefore, the fact that no correlations were found between Cd concentrations in *P. oceanica* roots and in sediment could indicate that Cd in *P. oceanica tissues* reflects the Cd in the water column.

Significant positive correlations ($p<0.05$) were observed in Pb concentrations between green leaves and the basal part of *P. oceanica* and in Pb concentrations between roots and rhizomes of *P. oceanica* (Table 7). The fact that no correlation was found between Pb concentrations in roots of *P. oceanica* and in sediment could indicate that Pb in *P. oceanica tissues* reflects the Pb in the water column. The uptake of Pb, like Cd, seems to occur mainly through the water column with a passive process dependent on the leaf surface exposed (Ward 1989). In fact, it has been demonstrated that aquatic plants can remove Pb from the surrounding water (Axtell *et al.,* 2003).

Finally, no correlations were observed in Cu and Zn concentrations among various parts of the plant and the various parts of the plant and sediments, indicating that absorption can take place, both through the roots and the leaves (Lyngby & Brix 1982). However, Cu as well as Zn are essential for the growth and metabolic processes of plants and their accumulation is affected by processes of metabolic regulation.

A number of laboratory experiments have shown that there are significant correlations between metal levels in the tissues and toxicological consequences for the physiological, biochemical and tissue levels (Cristiani *et al*., 1980; Augier *et al.,* 1984). These elements can cause various effects, which can even lead to growth interruption. Other effects include a gradual inhibition of juvenile leaf formation, foliar deformations, tissue and cell necrosis and a loss of pigmentation (Cristiani *et al.,* 1980; Lyngby & Brix 1983; Lyngby & Brix 1984; Augier 1986; Ward 1989; Malea 1994; Malea and Haritonidis 1996).

Conclusions

Research has allowed us to determine the levels of trace metals in different parts of *P. oceanica* and the ability of seagrass to accumulate metals. This shows that the study of the distribution of metals in *P. oceanica* is very important for the monitoring of coastal marine areas. *P. oceanica* is located at the basis of the food web in the Mediterranean and is probably the main source of metals for many animals grazing on its leaves. Therefore, the investigation of trace metal concentrations in the tissues of this species may provide useful information on the transfer of potentially toxic elements from abiotic compartments (water, sediments) to higher consumers. However, even if the use of this species as a biomonitor for trace metals looks attractive for many reasons, further studies are needed in order to evaluate the robustness of the methodology for routine use in marine biomonitoring.

References

Andersen, V., Maage, A., Johannessen, P.J., 1996. Heavy metals in blue mussels (*Mytilus edulis*) in the Bergen Harbor area, western Norway. *Bulletin of Environmental Contamination & Toxicology*, 57 (4), 589-596.

Annicchiarico, C., Buonocore, M., Cardellicchio, N., Di Leo, A., Giandomenico, S. *et al.,* 2011. PCBs, PAHs and metal contamination and quality index in marine sediments of the Taranto Gulf. *Chemistry Ecology*, 27 (Suppl. 1), 21-32.

Augier, H., 1986. L'herbier à *Posidonia oceanica*, son importance pour le littoral méditerranéen, sa valeur comme indicateur biologique de l'état de santé de la mer, son utilisation dans la surveillance du milieu, les bilans écologiques et les études d'impact. *Vie Marine,* 7, 85-113.

Augier, H., Gilles, G., Ramonda, G., 1984. L'herbier *de Posidonia oceanica* et la pollution par le mercure sur le littoral des Bouches-du-Rhône et du Var (France). p. 399-406. In: *First International Workshop on Posidonia Oceanica Beds. 12-15 October 1983, Porquerolles, France*. Boudouresque, C.F., Jeudy de Grissac, A., Olivier, J. (Eds). GIS Posidonie, Marseille.

Axtell, N.R., Sternberg, S.P.K., Claussen, K., 2003. Lead and nickel removal using *Microspora* and *Lemna minor*. *Bioresource Technology,* 89 (1), 41-48.

Ballesta, L., Pergent, G., Pasqualini V., Pergent-Martini, C., 2000. Distribution and dynamics of *Posidonia oceanica* beds along the Albères coastline. *Comptes Rendus de l'Académie des Sciences - Series III: Sciences de la Vie,* 323 (4), 407-414.

Bellucci, L.G., Frignani, M., Paolucci, D., Ravanelli, M., 2002. Distribution of heavy metals in sediments of the Venice Lagoon: The role of the industrial area. *Science of the Total Environment,* 295 (1-3), 35-49.

Benoit, G., Comeau, A. (Eds), 2005. *A sustainable future for the Mediterranean: the Blue Plan's Environment and Development Outlook*. Earthscan, London, UK, 464 pp.

Bergin, F., Kucuksezgin, F., Uluturhan, E., Barut, I.F., Meric, E. *et al.,* 2006. The response of benthic foraminifera and ostracoda to heavy metal pollution in Gulf of Izmir (Eastern Aegean Sea). *Estuarine, Coastal & Shelf Science,* 66 (3-4), 368-386.

Bertolotto, R.M., Tortarolo, B., Frignani, M., Bellucci, L., Albanese, S. *et al.,* 2005. Heavy metals in surficial coastal sediments of the Ligurian Sea. *Marine Pollution Bulletin,* 50 (3), 348-356.

Boudouresque, C.F., Giraud, G., Thommeret, J., Thommeret, Y., 1980. First attempt at dating by ^{14}C the undersea beds of dead *Posidonia oceanica* in the bay of Port-Man (Port-Cros, Var, France). *Travaux scientifiques du parc national de Port-Cros,* 6, 239-242.

Boudouresque, C.F., Gravez, V., Meinesz, A., Molenaar, H., Pergent G. *et al.,* 1994. L'herbier à *Posidonia oceanica* en Méditerranée: protection légale et gestion. p. 209-220. In: *Pour qui la Méditerranée au 21ème siècle? Villes des rivages et environnement littoral en Méditerranée, Montpellier, 28-29 avril 1994. Actes du colloque scientifique Okeanos*. Maison de l'Environnement de Montpellier, Montpellier, France.

Brinkhuis, B.H., Penello, W.F., Churchill, A.C., 1980. Cadmium and manganese flux in the Eelgrass *Zostera marina* II. Metal uptake by leaf and root-rhizome tissues. *Marine Biology,* 58 (3), 187-196.

Buccolieri, A., Buccolieri, G., Cardellicchio, N., Dell'Atti, A., Di Leo, A. *et al.,* 2006. Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). *Marine Chemistry,* 99 (1-4), 227-235.

Campanella, L., Conti, M.E., Cubadda, F., Sucapane, C., 2001. Trace metals in seagrass, algae and molluscs from an uncontaminated area in the Mediterranean. *Environmental Pollution,* 111 (1), 117-126.

Capiomont. A., Piazzi, L., Pergent, G., 2000. Seasonal variations of total mercury in foliar tissues of *Posidonia oceanica*. *Journal of the Marine Biological Association of the UK,* 80, 1119-1123.

Cardellicchio, N., Buccolieri, A., Di Leo, A., Librando, V., Minniti, Z. *et al.,* 2009. Methodological approach for metal pollution evaluation in sediments collected from the Taranto Gulf. *Toxicological & Environment Chemistry*, 91 (7), 1273-1290.

Catsiki, V.A., Panayotidis, P., 1993. Copper, chromium and nickel in tissues of the Mediterranean seagrasses *Posidonia oceanica* and *Cymodocea nodosa* (Potamogetonaceae) from Greek coastal areas. *Chemosphere,* 26 (5), 963-978.

Caye, G., 1989. *Sur la morphogenèse, le cycle végétatif et le reproduction de deux phanérogames marines de Méditerranée: Posidonia oceanica (Linnaeus) Delile et Cymodocea nodosa (Ucria) Ascherson*. PhD Thesis. Université de Nice, 229 pp.

Costantini, S., Giordano, R., Ciaralli, L., Beccaloni, E., 1991. Mercury, cadmium and lead evaluation in *Posidonia oceanica* and *Codium tomentosum*. *Marine Pollution Bulletin*, 22 (7), 362-363.

Costley, C.T., Mossop, K.F., Dean, J.R., Garden, L.M., Marshall, J. *et al.,* 2000. Determination of mercury in environmental and biological samples using pyrolysis atomic absorption spectrometry with gold amalgamation. *Analytica Chimica Acta,* 405 (1-2), 179-183.

Covelli, S., Faganeli, J., Horvat, M., Bramati, A., 2001. Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic Sea). *Applied Geochemistry*, 16 (5), 541-558.

Cristiani, G., Gassend, R., Augier, H., 1980. Etude de la contamination expérimentale de la phanérogame marine *Posidonia oceanica* (L.) Delile par les composés mercuriques. Partie 1. Modalités de la contamination par le chlorure mercurique. *Environmental Pollution,* 23 (2), 153-162.

Dauby, P., Poulicek, M., 1995. Methods for removing epiphytes from seagrasses: SEM observations on treated leaves. *Aquatic Botany,* 52 (3), 217-228.

Demirezen, D., Aksoy, A., 2006. Common hydrophytes as bioindicators of iron and manganese pollutions. *Ecological Indicators,* 6 (2), 388-393.

Donazzolo, R., Merlin, O.H., Menegazzo Vitturi, L., Orio, A.A., Pavoni, B. *et al.,* 1981. Heavy metal contamination in surface sediments from the Gulf of Venice, Italy. *Marine Pollution Bulletin,* 12 (12), 417-425.

EPER Register, 2006. *The European Pollutant Release and Transfer Register (E-PRTR).* Member States reporting under Article 7 of Regulation (EC) No 166/2006, Nov. 2012.

Ferrara, R., Seritti, A., 1989. Mercury and trace metals in waters of the western Mediterranean. p. 199-207. In: *EROS 2000 (European River Ocean System). First Workshop on the North-West Mediterranean Sea, Paris, 7-9 March 1989.* Water Pollution Research report, No. 13. Commission of the European Communities, Brussel.

Giraud, G., 1977. *Contribution à la description et à la phenologie quantitative des herbiers de Posidonia oceanica (L.) Delile*. PhD Thesis. Université d'Aix-Marseille II, 150 pp.

Goldberg, E.D., 1986. The Mussel watch concept. *Environmental Monitoring & Assessment,* 7 (1), 91-103.

Karageorgis, A., Anagnostou, C., Sioulas, A., Chronis, G., Papathanassiou, E., 1998. Sediment geochemistry and mineralogy in Milos Bay, SW Kyklades, Aegean Sea, Greece. *Journal of Marine Systems,* 16 (3-4), 269-281.

Lafabrie, C., Pergent-Martini, C., Pergent, G., 2008. Metal contamination of *Posidonia oceanica* meadows along the Corsican coastline (Mediterranean). *Environmental Pollution*, 151 (1), 262-268.

Ledent, G., Warnau, M., Temara, A., Jangoux, M., Dubois, P., 1993. Contamination par les métaux lourds et dynamiques de l'accumulation du cadmium chez la phanérogame marine *Posidonia oceanica*. p. 249-252. In: *Qualité du milieu marin: indicateurs biologiques et physico chimiques. 3ème Rencontres scientifiques de la Côte Bleue, Carry-le-Rouet, 20-22 novembre 1992*. Boudouresque, C.F., Avon, M., Pergent-Martini, C. (Eds). GIS Posidonie, Marseille.

Loska, K., Cebula, J., Pelczar, J., Wiechula, D., Kwapuliński, J., 1997. Use of enrichment and contamination factors together with geoaccumulation indexes to evaluate the content of Cd, Cu and Ni in the Rybnik water reservoir in Poland. *Water, Air & Soil Pollution,* 93 (1-4), 347-365.

Lyngby, J.E., Brix, H., 1982. Seasonal and environmental variations in cadmium, copper, lead and zinc concentrations in eelgrass (*Zostera marina* L.) in the Limfjord, Denmark. *Aquatic Botany*, 14, 59-74.

Lyngby, J.E., Brix, H., 1983. Seasonal changes in the concentrations of Ca, Fe, K, Mg, Mn and Na in eelgrass (*Zostera marina* L.) in the Limfjord, Denmark. *Aquatic Botany,* 17 (2), 107-117.

Lyngby, J.E., Brix, H., 1984. The uptake of heavy metals in eelgrass *Zostera marina* and their effect on growth. *Ecological Bulletins,* 36, 81-89.

Malea, P., Haritonidis, S., 1996. Toxicity and uptake of aluminium by the seagrass *Halophila stipulacea* (Forsk) Aschers and in response to aluminium exposure. *Fresenius Environmental Bulletin,* 5, 345-350.

Malea, P., Haritonidis, S., Kevrekidis, T., 1994. Seasonal and local variations of metal concentrations in the seagrass *Posidonia oceanica* (L.) Delile in the Antikyra Gulf, Greece. *Science of the Total Environment,* 153 (2), 225-235.

Maserti, B.E., Ferrara, R., Morelli, M., 1991. *Posidonia oceanica*: uptake and mobilization of mercury in the Mediterranean basin. In: *Proceedings of the FAO/UNEP/IAEA consultation meeting on the accumulation and transformation of chemical contaminants by biotic and abiotic processes in the marine environment. La Spezia, Italy, 24-28 September 1990.* MAP Technical Report Series, No. 59. UNEP, Athens.

Maserti, B.E., Ferrara, R., Paterno, P., 1988. *Posidonia* as an indicator of mercury contamination. *Marine Pollution Bulletin,* 19 (8), 381-382.

Molinier, R., Picard, J., 1952. Recherches sur les herbiers de Phanérogames marines du littoral méditerranéen français. *Annales de l'Institut Oceanographique,* 27 (3), 157-234.

Morillo, J., Usero, J., Gracia, I., 2005. Biomonitoring of trace metals in a mine-polluted estuarine system (Spain). *Chemosphere,* 58 (10), 1421-1430.

Müller, G., 1979. Schwermetalle in den Sedimenten des Rheins -Veränderungen seit 1971. *Umschau*, 79, 778-783.

Müller, G., 1981. Die Schwermetallbelastung der Sedimente des Neckars und seiner Nebenflüsse Eine Bestandsaufnahme. *Chemiker-Zeitung,* 105, 157-164.

NAVFAC, 2003. *Guidance for environmental background analyses. Volume II: Sediment*. Naval Facilities Engineering Command, Washington, DC.

Nienhuis, P.H., 1986. Background concentrations of heavy metals in nine tropical seagrass species in Indonesia. *Marine Pollution Bulletin*, 17 (11), 508-511.

Ott, J.A., 1980. Growth and production in *Posidonia oceanica* (L.) Delile. *Marine Ecology*, 1 (1), 47-64.

Paterno, P., Cardellicchio, N., Leone, G., Marra, C., Piraino, S., 1991. Mercury and tin distribution in *Posidonia oceanica* (L.) Delile into the Taranto Gulf (Italy). *Oebalia*, 17 (1), 265-277.

Pergent, G., 1990. Lepidochronological analysis in the seagrass *Posidonia oceanica* (L.) Delile: a standardized approach. *Aquatic Botany,* 37 (1), 39-54.

Pergent-Martini, C., Pasqualini, V., Ferrat, L., Pergent, G., 2006. Ecological data in Integrated Coastal Zone Management: case study of *Posidonia oceanica* meadows along the Corsican coastline (Mediterranean Sea). *Environmental Management,* 38 (6), 889-895.

Pergent-Martini, C., Pergent, G., 2000. Marine phanerogams as a tool in the evaluation of marine trace-metal contamination: an example from the Mediterranean. *International Journal of Environment & Pollution,* 13, 126-147.

Romano, E., Gabellini M., 2001. Analisi delle caratteristiche granulometriche - Sedimenti, scheda 3. In: *Metodologie analitiche di riferimento del programma di monitoraggio per il controllo dell'ambiente marino costiero (triennio 2001 - 2003)*. Cicero, A.M., Di Girolamo, I. (Eds). Ministero dell'Ambiente e della Tutela del Territorio, ICRAM, Rome.

Rubio, B., Nombela, M.A., Vilas, F., 2000. Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. *Marine Pollution Bulletin*, 40 (11), 968-980.

Ruiz, F., 2001. Trace metals in estuarine sediments from the South Western Spanish coast. *Marine Pollution Bulletin*, 42 (6), 481-489.

Ruiz, J.M., Romero, J., 2003. E□ects of disturbances caused by coastal constructions on spatial structure, growth dynamics and photosynthesis of the seagrass *Posidonia oceanica. Marine Pollution Bulletin*, 46 (12), 1523-1533.

Sanchiz, C., García-Carrascosa, A.M., Pastor, A., 2001. Relationships between sediment physico-chemical characteristics and heavy metal bioaccumulation in Mediterranean soft-bottom macrophytes. *Aquatic Botany*, 69 (1), 63-73.

Ščančar, J., Zuliani, T., Turk, T., Milačič, R., 2007. Organotin compounds and selected metals in the marine environment of Northern Adriatic Sea. *Environmental Monitoring & Assessment,* 127 (1-3), 271-282.

Schlacher-Hoenlinger, M.A., Schlacher, T.A., 1998. Accumulation, contamination and seasonal variability or trace metals in the coastal zone - patterns in a seagrass meadow from the Mediterranean. *Marine Biology,* 131 (3), 401-410.

Taramelli, E., Costantini, S., Giordano, R., Olivieri, N., Perdicaro, R., 1991. Cadmium in water, sediments and benthic organisms from a stretch of coast facing the thermoelectric power plant at Torvaldaliga (Civitavecchia, Rome). p. 15-31. In: *Final reports on research projects dealing with bioaccumulation and toxicity of chemical pollutants*. MAP Technical Reports Series, No. 52. UNEP, Athens.

Usero, J., Morillo, J., Gracia, I., 2005. Heavy metal concentrations in molluscs from the Atlantic coast of southern Spain. *Chemosphere,* 59 (8), 1175-1181.

Villares, R., Puente, X., Carballeira, A., 2001. *Ulva* and *Enteromorpha* as indicators of heavy metal pollution. *Hydrobiologia*, 462 (1-3), 221-232.

Ward, T.J., 1987. Temporal variation of metals in the seagrass *Posidonia australis* and its potential as a sentinel accumulator near a lead smelter. *Marine Biology,* 95 (2), 315-321.

Ward, T.J., 1989. The accumulation and effects of metals in seagrass habitats. p. 797-820. In: *Biology of seagrasses: a treatise on the biology of seagrasses with special reference to the Australian region. Aquatic Plant Studies, Vol. 2.* Larkum, A.W.D., McComb, A.J., Shepherd, S.A. (Eds). Elsevier, Amsterdam.