

Macroalgae and DGT as indicators of available trace metals in marine coastal waters near a lead–zinc smelter

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Abstract The levels of Cd, Cu, Pb, and Zn were determined in the commonest species of green, red, and brown algae collected from five coastal sites in south-western Sardinia (Italy), an area with a long history of mining and smelting. The usefulness of employing *Enteromorpha* sp. and *Padina pavonica* (L.) Thivy to monitor metal pollution was evaluated, while diffusive gradients in thin films (DGT) devices were used to measure dissolved metals in seawater. Levels of Cd and Pb were high enough to be of environmental concern in the whole study area. A significant relationship was found between the content of Pb in *P. pavonica* and DGT-labile Pb in seawater, suggesting that gross elemental concentrations of nonessential metals such as Pb in algal tissues are apparently controlled by the abundance of dissolved metal species in the ambient seawater. The results pointed out the usefulness of using both DGT and algal methods for a better understanding of trace metal availability in coastal waters.

Keywords Biomonitoring · Marine macroalgae · DGT · Trace metals · Smelters · Mediterranean Sea

Introduction

Macroalgae (seaweeds) accumulate trace metals from the dissolved ionic phase in seawater, reflecting the soluble trace metal content of their ambient surroundings with a high degree of time-integration (e.g., Brown and Depledge 1998). Despite the fact that metal uptake can be influenced by various factors—e. g., season, sampling position along the shoreline, coexistence of several metals, salinity, water temperature—algae have been used successfully to monitor metal availability. This has allowed for the assessment of spatial and temporal variation in metal concentration in coastal and estuarine environments and the comparison of trace metal levels between different geographic areas (e.g., Ho 1987; Brown et al. 1999; Haritonidis and Malea 1999; Sawidis et al. 2001; Barreiro et al. 2002; Daka 2005; Zbikowski et al. 2006; Pérez et al. 2007).

Diffusive gradients in thin films (DGT) (Davison and Zhang 1994) have shown much promise as tools for in situ trace metal speciation procedure and as a cost-effective means of measuring labile metals in natural waters. After metal ions freely diffuse through a well-defined

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layer of hydrogel, they are immobilized within a Chelex-100 resin-gel layer. Conventional analysis in the laboratory provides the in situ concentration at the time of deployment. Only labile species such as ionic forms and easily dissociable complexes are taken up by DGTs (Zhang and Davison 1995). Schintu et al. (2008) evaluated the parallel use of transplanted mussels and DGTs for the measurements of Cd, Cu, and Pb in coastal waters. Since the metal uptake in algae has been shown to be proportional to the concentration of free ionic and weakly bound metal species, and not to the total metal concentrations (Sunda and Guillard 1976), the level of elements in algae and DGTs should be comparable.

In this work we present the results of an extensive survey of trace metal concentration in marine algae carried out in south-western Sardinia (Italy), an area with a long history of mining and smelting activities. Both algae and DGTs were utilized in order to evaluate the level and the extent of trace metal pollution.

The aims of this study were:

1. to characterize the most common algal species from trace metals, assessing which alga could be used as a biomonitor of pollution in these coastal waters
2. to evaluate the usefulness of using both DGT and algal methods for a better understanding of trace metal availability in coastal waters

Materials and methods

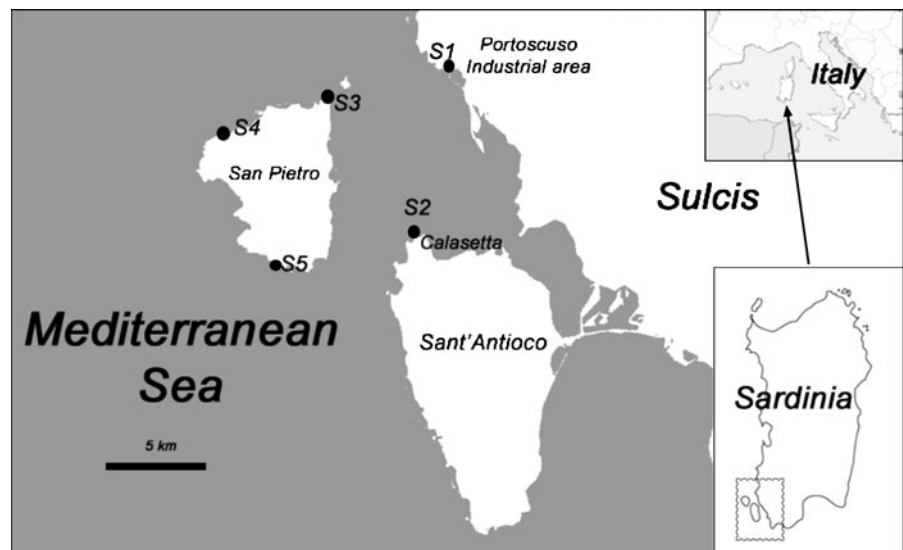
Study area and sampling location

The study area is shown in Fig. 1. A lead–zinc smelter located in Portoscuso (Sulcis district) have been operating since 1972, with a yearly production of 150,000 t of metallic Pb and Zn and 500 t of Cd. Other industrial activities in Portoscuso are based on aluminum production from bauxite-, coal-, and oil-fired power generation. In 1993 the whole territory of Sulcis was identified by the Italian Government as an “environmental high-risk area”. However, no work has been done to evaluate contamination of the coastal waters.

The five sites chosen for collection of algae and deployment of DGTs were (Fig. 1):

- S1 Portoscuso. Algae were sampled from a rocky area south of the industrial harbor of Portovesme ($39^{\circ}11'16''$ N; $8^{\circ}23'50''$ E). In the second sampling campaign (August 2007) *Padina pavonica*

Fig. 1 The study area in south-western Sardinia (Italy) and the location of the sampling sites



was collected from rocky shores north of the harbor (39°12'00" N; 8°23'09" E). The harbor receives major inputs from industrial discharges, runoff from smelter and mining areas, dusts dispersed in the area during shipping operations, and atmospheric fallout. Though mining activity has now been practically abandoned, ores and products to and from the industrial area are still transported. Schintu and Degetto (1999) found extremely high concentrations of Cd and Pb in the sediments of the harbor, mainly to be ascribed to the discharge of the liquid effluent from the smelter.

S2 Calasetta. The sampling station was located in the rocky beach of Calasetta, a tourist and fishing settlement on the island of Sant'Antioco (39°06'36" N; 8°21'55" E).

S3, S4, and S5 San Pietro Island. Sampling points were located in a small island facing the Sulcis coasts. S3 is a rocky area with intertidal pools in the north-eastern coast of the island (39°10'06" N; 8°15'18" E), on the opposite side of Portoscuso; S4 (39°11'11" N; 8°13' E) and S5 (39°06'16" N; 8°15'17" E) are rocky sites on the western coast of San Pietro. S5 is relatively away from mining areas and industrial pollution sources. For these reasons it was assumed to be the least contaminated.

It is difficult to evaluate the exposure of the sampling sites to sea currents, since the circulation in the Western Mediterranean Sea exhibits strong seasonal and inter-annual variability (Millot 1999). The wind-driven circulation originated by the prevailing westerly winds may originate currents which affect the coasts of the study area.

Sampling procedures

Algae were harvested in August 2006. In a second campaign carried out in August 2007 only the brown alga *P. pavonica* was sampled. Algae were collected by hand on the surface of the beach rocks or in the subtidal zone up to at a depth of about 2 m. A pooled sample of each species was collected from each station. All thalli were thoroughly cleaned with seawater, followed by distilled water to remove adhering particulate matter and epiphytes. The samples were stored in plastic bags. Materials were oven-dried at 30°C to a constant weight, and were then ground to powder.

DGT techniques DGTs consisted of polyacrylamide hydrogel diffusion layers (0.76 mm thick), Chelex-100 impregnated binding phases (0.40 mm thick), and nylon DGT holders (DGT Research Ltd. UK). They were assembled with 0.45-mm pore-size cellulose acetate filters, used as covering membranes. DGTs were deployed in the sampling stations S1, S2, S3, S4, and S5 in the last week of August 2007 and retrieved following a 3-day exposure. Two pairs of DGTs were immersed at approximately 0.5 m below the sea surface in all sampling stations. Water depth ranged from 2 to 3 m. At the retrieval, metals were eluted from the binding gel in 1 ml of 1 M HNO₃. The elution extracts were diluted with Milli-Q water and trace metal analysis (Cd, Cu, and Pb) carried out by GFAAS (Perkin-Elmer Model SIMAA 6000 Zeeman equipped with an AS-72 autosampler). The detection limits were as follows: 0.50 µg l⁻¹ for Cd; 0.50 µg l⁻¹ for Cu; 5 µg l⁻¹ for Pb. The DGT performance was evaluated according to the method used by Zhang and Davison (1995), in two replicates. The mean recovery of metals in acid solution was 80%. The concentrations of metals measured by DGT were calculated using the equations provided by DGT Research Ltd (Lancaster, UK).

Water temperature, pH, and salinity were measured using an YSI DM 6000 Multiprobe. In the study area, the surface water temperature during the experiments ranged between 22.0 and 24°C, salinity was 36.2‰, and pH ranged from 8.10 to 8.15.

Sample analysis and analytical quality control

All chemicals used in sample treatment were of ultrapure grade (HNO_3 , H_2O_2 Merck Suprapur). Ultrapure water (Milli-Q System, Millipore) was used for all solutions. All glassware was cleaned prior to use by soaking in 10% *v/v* HNO_3 for 24 h and then rinsing with Milli-Q water.

About 500 mg (dry weight) of powered algal samples were digested in a microwave oven (Ethos, Milestone) with a mixture of 5 ml of concentrated HNO_3 and 1 ml of 30% H_2O_2 . Cadmium and Pb concentrations were determined by GFAAS (Perkin-Elmer Model SIMAA 6000 Zeeman equipped with an AS-72 autosampler). A mixture of $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Mg}(\text{NO}_3)_2$ was used as a matrix modifier for Cd and Pb, and the method of standard additions was used. Zinc and Cu were determined by flame AAS (Perkin-Elmer 2100). Three replicates subsamples of each sample were processed. The limits of detection for the studied elements were as follows ($\mu\text{g l}^{-1}$): Cd—0.50; Cu—0.50; Pb—5; Zn—2. The accuracy and precision of the analytical measurements were checked based on analysis of NIST (National Institute for Standards and Technology) 1575a “trace elements in pine needles” standard reference material. The obtained results were in good agreement with the certified values (Table 1). Deviations from reference material were generally within the 2–10% range.

All concentrations are presented as milligram per kilogram dry weight (mg kg^{-1} dw) and the quoted values are means. The nonparametric analysis of variance Kruskal–Wallis was used to evaluate statistical significance. A probability of 0.05 or less was considered significant.

Table 1 Analysis of the Standard Reference Material NIST 1575a “trace elements in pine needles”

Element	NIST 1575a (mg kg^{-1})	
	Certified	Found
Cd	0.233 ± 0.004	0.21 ± 0.01
Cu	2.8 ± 0.2	2.6 ± 0.2
Pb	0.167 ± 0.015	0.18 ± 0.02
Zn	38 ± 2	36 ± 2

Certified values and found values (mean \pm SD, $n = 3$)

Results and discussion

Seaweed

The algal species collected from each site and their Cd, Cu, Pb, and Zn content are listed in Table 2. The results pointed out a high variability of metal concentrations among different species from the same sampling site. In fact metal levels are dependent on both biotic parameters and structural differences among the algae species. Furthermore, different species of seaweed have different affinities for different heavy metals, which may reflect competition between metals for binding or uptake sites in seaweed (Phillips 1977; Lobban and Harrison 1994). The algae belonging to the class of *Phaeophyceae* (brown algae, i.e. *P. pavonica*, *Dictyota dichotoma*) accumulated significantly higher concentrations of Cd than green algae (*Chlorophyceae*, i.e. *Enteromorpha* sp., *Ulva rigida*) and red algae (*Rhodophyceae*, i.e. *Corallina mediterranea*, *Amphiroa rigida*) (Kruskal–Wallis test, $p < 0.05$). The capability of some brown algae to accumulate high metal concentrations is due to the high binding capacity of their polysaccharides for divalent metal species and the affinity between metals and polyphenols, even as dead mass when used as biosorbent (e.g. Crist et al. 1992; Volesky and Holan 1995; Amado Filho et al. 1999; Hashim and Chu 2004). Table 2 clearly shows that the concentrations of all metals at S1 (very close to the industrial harbor of Portoscuso) were at least one order of magnitude greater than at other sampling stations. In the rest of the stations significantly higher concentrations of Pb were found in algae at S3.

Since different species accumulate metals at differing levels, pollution level at various locations should be compared by using the same species at each site. *Enteromorpha* sp. and *P. pavonica* (L.) Thivy were the algal species occurring at all the sampling stations. Both of them exhibit characteristics considered essential for biomonitors. The use of the green alga *Enteromorpha* sp as monitor of trace metal availability is well documented. *Enteromorpha* sp. is tolerant to metals, sedentary, easily collectable, and widespread along the coast all over the world (Bryan et al. 1985; Ho 1987; Leal et al. 1997; Brown et al. 1999; Zbikowski

Table 2 Mean concentration ($n = 3$) of trace metals (mg kg⁻¹ dw) in pooled samples of the most common seaweed species collected in SW Sardinia (Italy)

	Site	Species	Class	Cd	Cu	Pb	Zn
<p>Variability within different replicates (standard deviation) ranged between 5% and 12%</p> <p><i>C Chlorophyceae,</i> <i>P Phaeophyceae,</i> <i>R Rhodophyceae</i></p>	S1—Portoscuso	<i>Enteromorpha</i> sp.	C	19.2	41.3	386	722
		<i>Padina pavonica</i>	P	27.9	36.4	270	780
		<i>Corallina mediterranea</i>	R	11.5	15.8	352	240
		<i>Dictyota dichotoma</i>	P	31.0	56.2	878	435
		<i>Halopteris scoparia</i>	P	20.0	24.6	436	658
		<i>Jania rubens</i>	R	16.9	45.2	617	130
		<i>Udotea petiolata</i>	C	2.93	9.4	172	660
	S2—Calasetta	<i>Enteromorpha</i> sp.	C	0.41	1.9	17.8	28.6
		<i>Padina pavonica</i>	P	2.93	1.6	71.7	91.3
		<i>Caulerpa prolifera</i>	C	0.50	5.4	80.3	143
		<i>Codium</i> sp.	C	1.04	2.8	42.1	79.2
		<i>Dictyota dichotoma</i>	P	1.83	9.7	19.3	123
		<i>Ulva rigida</i>	C	0.36	4.2	8.4	50.7
		<i>Enteromorpha</i> sp.	C	4.62	3.8	115	88.2
	S3—San Pietro-NE	<i>Padina pavonica</i>	P	5.34	5.7	97.2	78.1
		<i>Amphiroa rigida</i>	R	0.91	2.9	9.4	89.3
		<i>Cladophora prolifera</i>	C	0.43	3.8	72.2	140
		<i>Codium</i> sp.	C	2.05	1.9	11.6	70.1
		<i>Corallina mediterranea</i>	R	2.46	3.5	53.7	154
		<i>Dasycladus claviformis</i>	P	8.01	3.8	70.7	70.2
		<i>Dictyota dichotoma</i>	P	7.36	2.6	46.9	290
		<i>Dilophus fasciola</i>	P	0.67	4.6	61.5	110
		<i>Hypnea</i> sp.	R	0.67	5.7	34.7	97.1
		<i>Ulva rigida</i>	C	0.12	1.9	22.4	28.2
		<i>Enteromorpha</i> sp.	C	1.23	6.5	19.7	96.2
	S4—San Pietro-NW	<i>Padina pavonica</i>	P	1.65	4.6	18.1	102
		<i>Amphiroa rigida</i>	R	0.93	1.3	9.7	42.3
		<i>Cladophora prolifera</i>	C	0.34	1.9	40.8	80.1
		<i>Cystoseira crinita</i>	P	1.07	3.5	7.9	59.1
		<i>Dictyota dichotoma</i>	P	2.45	4.7	39.3	108
		<i>Jania rubens</i>	R	2.26	3.7	50.2	65.4
		<i>Ulva rigida</i>	C	0.43	2.4	5.5	45.4
	S5—San Pietro-SW	<i>Enteromorpha</i> sp.	C	0.63	1.9	4.2	46.7
		<i>Padina pavonica</i>	P	0.54	2.3	8.8	62.6
		<i>Amphiroa rigida</i>	R	0.81	2.1	3.5	52.5
		<i>Ceramium ciliatum</i>	R	1.12	2.1	19.7	40.8
		<i>Corallina mediterranea</i>	R	0.72	1.3	1.7	34.2
		<i>Cystoseira crinita</i>	P	1.72	1.8	10.3	52.4
		<i>Halimeda tuna</i>	C	1.46	3.4	20.8	56.1
		<i>Halopteris scoparia</i>	P	1.26	1.9	18.2	30.3

et al. 2006). However, according to Rainbow (1995), there is a lack of robustness in the use of *Enteromorpha* sp. for biomonitoring, because this genus raises the problem of reliable species identification, due to the considerable uncertainty surrounding the taxonomy of *Enteromorpha*. As far as the brown alga *P. pavonica* is concerned, it is easy to identify and to sample, is available all year round and it is widely distributed over Mediterranean coastal areas.

The accumulation ratios of trace metals differ in both *Enteromorpha* sp. and *P. pavonica* from those already identified by other authors in the same algal species collected from areas not affected by human activities. Metals concentrated in both *Enteromorpha* sp. and *P. pavonica* (Table 2) decreased in the order Zn>Pb>Cu>Cd in S1, S4, and S5. In *P. pavonica* collected from S2 the sequence was Zn>Pb>Cd>Cu, while in S3 in both algal species metals decreased in the order

Pb>Zn>Cd≥Cu. In August 2007, the abundance of metals in the *P. pavonica* was in the order Zn>Pb>Cu>Cd in all the five sites, confirming the bioaccumulation trend already shown in the previous campaign.

In *Enteromorpha* sp. collected from different coastal areas of the Mediterranean, Storelli et al. (2001) observed the sequence Zn>Cu>Pb>Cd. The same sequence was observed by Zbikowski et al. (2006) in *Enteromorpha* sp. from the southern Baltic and by Leal et al. (1997) in *Enteromorpha* sp. from Oporto Coast (Portugal). Furthermore, metals decreased in the same order in *P. pavonica* collected from relatively clean areas of the Mediterranean (Campanella et al. 2001; Conti and Cecchetti 2003). However, Sawidis et al. (2001) in the Aegean Sea found in both *Enteromorpha* and *P. pavonica* Zn>Cu>Cd>Pb.

A common industrial origin is a likely reason for the positive correlation coefficients between these elements (Spearman's rank correlation, $n = 40$, $p < 0.05$). Moreover, when considering the metalliferous background of the study area (Boni et al. 1999), the influence of the geochemistry on the metal concentration in the algae cannot be excluded. More information is then necessary to clarify accumulation patterns and to distinguish between anthropogenic contamination and background or natural levels. This will enable an accurate evaluation of the degree of contamination in the area. An estimate of the expected range of Cd, Cu, Pb, and Zn values in *Enteromorpha* sp and *P. pavonica* can be obtained from the literature (Table 3). As far as regards Cd, Pb, and to a lesser

extent Zn, values found in this work are considerably higher than those found in areas relatively free of contamination in the Mediterranean Sea.

DGT

Trace metals in algae vary with respect to their presence in the soluble or particulate fractions of water in a polluted area (Phillips 1994). According to Sanchez-Rodriguez et al. (2001), the combined effect of geochemical and physiological factors will determine how much of an element will be accumulated by algae relative to seawater concentration. Muse et al. (2006) by kinetic speciation showed that the variable that correctly explains heavy metals accumulation in the alga *Ulva lactuca* is the labile metal fraction in seawater.

DGTs are known to measure only soluble fraction of metals (Zhang and Davison 1995) so they have the advantage of offering a direct measure of metal fraction available to algae. The DGT technique is based on the selective diffusion and dissociation of metal species within a gel (Zhang and Davison 1999) and measures a labile metal fraction. The term “DGT-labile” applies to any metal that is diffusible through the polyacrylamide hydrogel and is complexed by the Chelex resin. The labile fraction of dissolved metal sampled by DGT includes free ions, all inorganic complexes, and part of the organic complexes (Zhang and Davison 2000). Lability increases when the dissociation rate constant or the residence time of the metal complex within the hydrogel increase

Table 3 Concentration range (mg kg⁻¹ dw) of Cd, Cu, Pb, and Zn in *Enteromorpha* sp. and *P. pavonica* in Mediterranean areas

Species	Sites	Cd	Cu	Pb	Zn	References
<i>Enteromorpha</i> sp.	Aegean Sea (<i>E. linza</i>)	0.47–0.77	3.4 to 9.8	0.02–12.4	31.5–94.3	Sawidis et al. (2001)
	Southern Adriatic Sea, Italy (<i>E. prolifera</i>)	0.30–1.27	6.1–15.1	ND–1.81	32.6–94.6	Storelli et al. (2001)
	SW Sardinia, Italy	0.39–4.55	1.9–6.5	4.2–115	46–88	This work
<i>P. pavonica</i>	Favignana Island, Sicily, Italy	1.00–2.06	10.4–13.3	5.2–11.4	44–84	Campanella et al. (2001)
	Gulf of Gaeta, Central Italy	0.50 ± 0.07	12.3 ± 1.8	3.98 ± 0.67	51 ± 11	Conti and Cecchetti (2003)
	Aegean Sea	1.2–1.6	3.0–6.1	0.02–2.1	19.3–26.3	Sawidis et al. (2001)
	Syrian coast	0.50–0.78	3.88–5.15	0.77–1.20	32.6–37.1	Al-Masri et al. (2003)
	SW Sardinia, Italy	0.53–5.25	1.6–5.7	8.8–97.2	62–102	This work

The sampling site S1 was excluded from this comparison

Table 4 Means and standard deviation for Cd, Cu, and Pb in pooled samples of *P. pavonica* ($n = 3$; mg kg^{-1} dw) and in seawater ($\mu\text{g l}^{-1}$; $n = 4$)

Site		Cd	Cu	Pb
S1—Portosuso	<i>P. pavonica</i>	6.31 ± 0.65	18.9 ± 1.2	273 ± 15.4
	DGT	0.60 ± 0.05	2.23 ± 0.30	3.13 ± 0.35
S2—Calasetta	<i>P. pavonica</i>	1.45 ± 0.08	3.8 ± 0.4	62.9 ± 8.4
	DGT	0.15 ± 0.06	1.92 ± 0.15	1.26 ± 0.1
S3—San Pietro-NE	<i>P. pavonica</i>	1.52 ± 0.09	3.7 ± 0.4	60.9 ± 7.5
	DGT	0.09 ± 0.03	1.45 ± 0.18	1.51 ± 0.12
S4—San Pietro-NW	<i>P. pavonica</i>	1.24 ± 0.0	1.9 ± 0.2	14.1 ± 1.6
	DGT	0.12 ± 0.07	1.70 ± 0.19	0.92 ± 0.06
S5—San Pietro-SW	<i>P. pavonica</i>	1.15 ± 0.08	1.7 ± 0.3	10.2 ± 1.7
	DGT	0.15 ± 0.01	1.92 ± 0.14	0.82 ± 0.08

(Tusseau-Vuillemin et al. 2003). Upon field testing at both freshwater and seawater sites, Li et al. (2005) found that the DGT-labile metal concentrations measured by different binding phases can be significantly different, suggesting that the DGT-labile metal fractions were dependent on binding strength of the binding phase. However, the use of DGTs to determine metal concentrations is complicated by chemical speciation. For elements such as Cu, speciation is dominated by organic complexes spanning a range of stabilities and size (Twiss and Moffet 2002). Scoullou et al. (2006) in a study carried out on the Aegean Sea found that the percentage of DGT-labile Cu as for total dissolved Cu ranged from 13% to 36%, whereas the corresponding percentage for DGT-labile Cd ranged from 29% to 68%. Cadmium chloro-species and Pb carbonate and chloride species are the major components in seawater in the absence of dissolved organic matter (Fergusson 1990).

Table 4 shows the levels of dissolved Cd, Cu, and Pb as measured by DGTs in the sampling stations and the corresponding concentrations in *P. pavonica*. The overall range of concentrations of DGT-labile metals in seawater was 0.15 to $0.60 \mu\text{g l}^{-1}$ for Cd, 1.45 to $2.23 \mu\text{g l}^{-1}$ for Cu, and 0.80 to $3.13 \mu\text{g l}^{-1}$ for Pb. The abundance of metals in *P. pavonica* was in the order $\text{Pb} > \text{Cu} > \text{Cd}$ in all the five sites. Average DGT-labile metal concentrations decreased in the same order in S1, S2, and S3, while in stations S4 and S5 the sequence was $\text{Cu} > \text{Pb} > \text{Cd}$.

In order to evaluate whether the concentrations measured in *P. pavonica* were a function of the DGT-labile metal levels in seawater, regression analysis was performed for each metal (Fig. 2).

A statistically significant correlation was found for Pb and Cd ($p < 0.05$); however, for Cd the experimental points do not cover the concentration range in a roughly uniform fashion. The results suggest that gross elemental concentrations of nonessential metals such as Pb in algal tissues

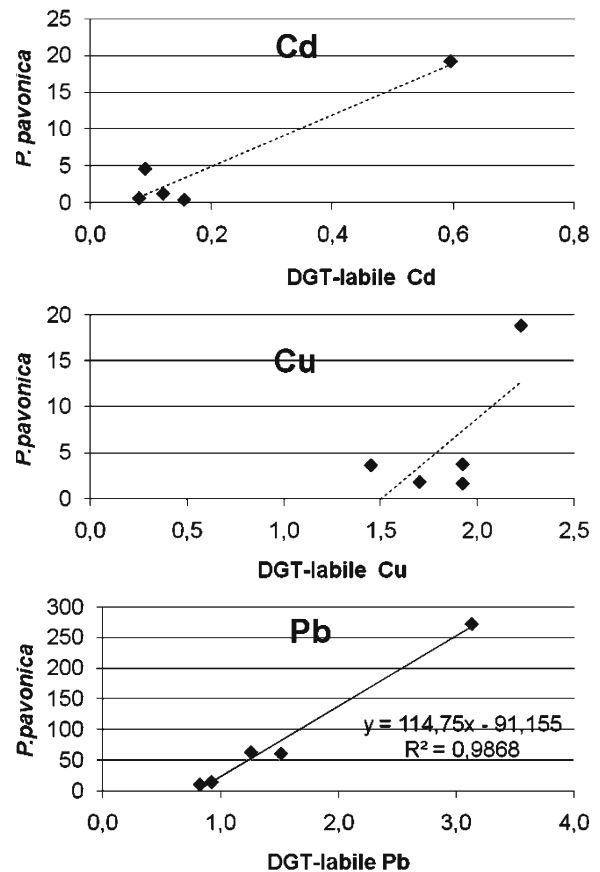


Fig. 2 Relationship between Cd, Cu, and Pb in *P. pavonica* (mg kg^{-1}) and DGT-labile metal in seawater ($\mu\text{g l}^{-1}$)

of *P. pavonica* are apparently controlled by the abundance of dissolved metal species in the ambient seawater. No significant relationship between metal in algae and in seawater was found for Cu. Moreover, Cu is an essential element for algae, and regulatory mechanism cannot be excluded.

Conclusions

The results highlighted the difficulties associated with the utilization of algae as a biomonitor, since different species accumulate metals at differing levels. Among the most frequently occurring species in the study area, the brown algae *P. pavonica* has shown a clear selectivity for Cd and Pb, encouraging its use as biomonitor. Furthermore *P. pavonica* is easy to identify and to sample, and is present in almost all coastal areas of the Mediterranean Sea.

For nonessential metals such as Cd and Pb both algae and DGTs gave a similar picture of the extent and the spatial variability of the contamination. A linear relationship was found between Pb measured in seawater with the DGT technique and Pb accumulated in *P. pavonica*. The results pointed levels of Cd and Pb high enough to be of environmental concern in the whole study area. Although further work is required, the results suggest the usefulness of using both biomonitoring with algae and DGT techniques for a better understanding of trace metal availability in coastal waters.

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