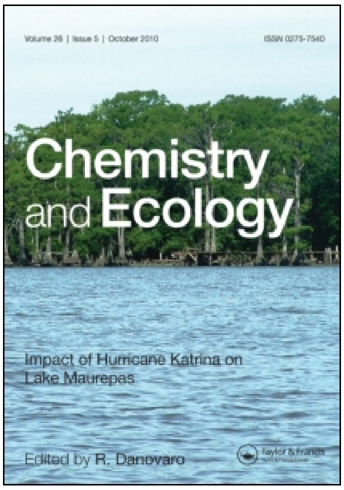

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Determination of heavy metal in seawater and macroalgae of shorelines of Naples and Ischia Island, Italy

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Determination of heavy metal in seawater and macroalgae of shorelines of Naples and Ischia Island, Italy

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In order to develop monitoring of heavy metals (Cd^{2+},Cu^{2+},Pb^{2+}) contamination in marine environment as well as macroalgae we have carried out this work in the Gulf of Naples and in the coastal region of Ischia island. Heavy metals were measured using the ASV (Anodic Stripping Voltammetry) analytical method. This work has given us the chance to underline the link between the state of seawater influences and the state of sessile species on the collected samples. The analyses have highlighted the bioconcentration of metals in sessile organisms.

Keywords: heavy metal; voltammetry; macroalgae; bio-indicator; Naples Gulf; Ischia island

1. Introduction

Contamination of toxic metals in the aquatic environment is a widespread phenomenon, especially in the countries where high-cost remediation technology is not affordable.

While industrialisation, urbanisation and mining activity around the Campania Region coastline can have a negative impact on fisheries, water resources and human health, tourism has a positive economic benefit, however, it may affect pollution through the marine environment. Besides these anthropogenic source contaminations, there are some areas surrounding Campania that seem to have naturally elevated levels of trace metals because of their geological conformation. As marine macroalgae contribute significantly to the primary production of near-shore ecosystems and also accumulate trace metals from solution they have been used extensively for the bio-monitoring of metal contamination of seawater [1].

Seaweeds have been considered for bio-monitoring of trace metals in marine environment by Rainbow and Phillips [2]; some seaweed species satisfy a lot of requirements for effective bio-monitoring, for example, they are sessile, widely distributed, tolerant to physico-chemical variation and exhibit strong net accumulation of trace metals.

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However, use of seaweed as biomonitors makes a lot of problems [3], for example the relationship between growth rate and metal accumulation, species identification and contamination from adherent particles.

The first problem can be reduced by a careful choice of sampling regime which minimises potential differences in growth rate between individuals or population, and by selecting an algal species which is easy to identify [4].

A systematic solution to the latter problem has not been established yet and the most commonly used technique consists of rinsing tissue in pure (i.e. distilled) water or sea water [5–8]. A lot of macroalgae species have a relatively long life span and they can therefore integrate short-term temporal fluctuations in environmental concentrations.

Several studies have been carried out to examine Mediterranean Sea seaweeds in order to assess the degree of metal pollution in the whole Mediterranean region, for instance, in the Northern Adriatic Sea [9] and in Lebanon [10], in the Gulf of Thermaikos [11–15] at Pylos, in the Ionian Sea [16,17], and in the Gulf of Antikyra [18,19].

However, there are not similar studies about the surrounding area of the Campania region. Our study aimed to evaluate the concentration of metals (Cd^{2+},Cu^{2+},Pb^{2+}) in algae that grow along the coastal area of Naples and Ischia island, Italy.

2. Materials and methods

2.1. *Study area and sampling stations*

The Gulf of Naples is located on the south-western coast of Italy (province of Naples, Campania). This Gulf is bounded by the Mediterranean Sea on the west, by Gulf of Pozzuoli (40°47'30,12"N; 14°11'11,18"E) on the north, by Mount Vesuvius (40°49'12,24"N; 14°25'31"E) on the east and by the Peninsula Sorrentina (40°34'8,27"N; 14°19'15"E) on the south, and in the gulf there are three islands: Capri (40°33'0,90"N; 14°13'46,74"E), Ischia (40°43'27, 48"N;13°54'11,87"E) and Procida (40°45'28,24"N; 14°0'55,37"E).

In this area we have investigated only the shoreline of Naples and the coast of Ischia island by sampling 3 stations in Naples and 7 stations in Ischia (Figure 1).

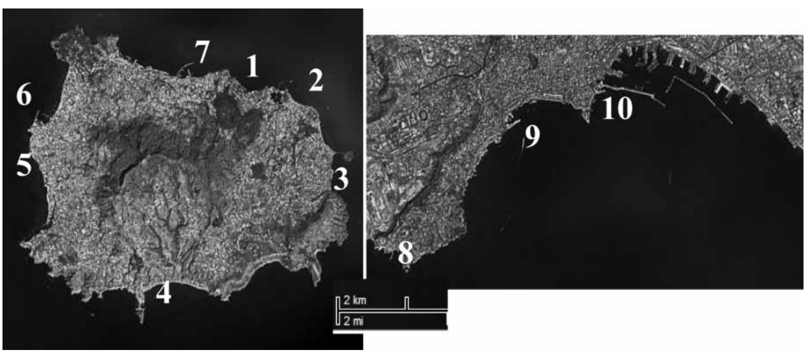

Figure 1. Sampling area: (1) Casamicciola (40°44'51.60"N; 13°54'46.63"E); (2) Ischia Porto (40°44'36.54"N; 13°54'22.07"E); (3) Carta Romana (40°42'24.47"N; 13°54'21.67"E); (4) Sant'Angelo (40°41'51.77"N;13°53'31.79"E); (5) Forio Porto (40°44'18.05"N; 13°51'33.59"E); (6) Forio Cappella (40°44'13.54"N; 13°51'15.8"E); (7) Lacco Ameno (40°45'14.22"N; 13°53'15.19"E); (8) Gaiola (40°47'30,12"N;14°11'11,18"E); (9) Piazza Vittoria (40°49'53.07"N;14°14'29.12"E); (10) Molosiglio (40°50'05.07"N;14°15'09.89"E).

2.2. *Sampling and sample preparation*

The species of algae collected for this study have been chosen because they were easily available in the sampling sites. All species mentioned in Table 1 were not necessarily found in all sites. Table 1 also indicates the number of stations where each species was collected. For example, *Culteria multifida* was found in 3 stations, while *Taonia atomaria* was found in 6 stations. Algae were hand-picked in each sampling station and the age of different algae has been taken into account in order to obtain homogeneous samples, representative of entire algal population living in the studied zone [20].

The harvest was carried out monthly from April to September 2005 in all the ten sampling stations. Algae and seawater were collected at the same time. Samples were brought to the laboratory at 4°C; and algal samples were stored in plastic bags, while seawater was filtered at 0.45 μm and nitric acid was added then it was stored in plastic flasks previously cleaned with nitric acid.

In the laboratory all epiphytes present in the algae were removed by hand and algae were washed with deionised water in order to eliminate salts, sediment and organic debris [21].

Samples were stored at −20°C in flasks. After freeze-drying seaweed samples were crushed and homogenised in a mortar. Tissue samples for trace metal analyses were obtained from seaweed apical and middle parts, where their younger and fast-growing areas are located [22], because only these parts are picked up.

For bio-monitoring the following algal species were chosen as they are easily available in the Gulf of Naples and Ischia shoreline:

- Brown algae: *Culteria multifida* (Smith) Greville, *Halopteris scoparia* L., *Padina pavonia* (L.) Graillon, *Taonia atomaria* (Woodward) Agardh
- Red algae: *Corallina elongata* Ellis et Solander, *Polysiphonia fruticosa* L., *Antithamnion cruciatum* (Agardh) Naegeli
- Green algae: *Enteromorpha sp.* L.

2.3. *Sample digestion*

Algae were dried at 80°C until they reached a constant weight. Each sample of seaweeds was ashed in a muffle furnace at 600°C for 24 h. The ashes were dissolved in 3 ml of nitric acid (65%, ultrapure) and the final volume was adjusted to 100 ml by adding distilled water [23].

2.4. *Analytical determination*

In order to determine the concentration of metal ions, we have used a working electrode with Hg: MME (Multi Mode Electrode) with operation system of HMDE (Hanging Mercury Drop Electrode) with Anodic Stripping Voltammetry.

Table 1. Algal species widely detected in the studied areas.

Class	Species	Numer of stations
Brown algae	*C. multifida*	3/10
	H. scoparia	6/10
	P. pavonia	1/10
	T. atomaria	6/10
Red algae	*A. crociatum*	2/10
	C. elongata	8/10
	P. fructicosa	1/10
Green algae	*Enteromorpha* spp.	2/10

Voltammetry involves the application of a potential that varies with time and involves also the measurement of the corresponding current that flows between the working and reference electrodes.

The potential can be considered as the intensive variable (energy in V or J/C) applied to the working electrode, while the current can be seen as the extensive variable (current in A or C/s) corresponding to the rate of an electrode reaction in response to the potential perturbation. Thus, the resulting voltammogram of current versus potential may be either transient or steady-state and a potential ramp serves as the potential perturbation in it.

The 757 Computrace contains a potentiostat whose electronic control includes power supply. Connection to the pc is made by a bus cable and pc interface card, which form part of the standard accessories. The actual electrochemical measuring cell includes three electrodes of 1) Auxiliary electrode: Pt 2) Reference electrode: Ag/AgCl/KCl 3 mol/l 3) Working electrode: Hg.

All samples were analysed three times. Recoveries were reported as 97.5% for cadmium, 95.5% for copper and 94.2% for lead, so if we consider the values obtained, we can easily affirm that the procedures employed are appropriate. All results reported in this work are means of the three measurements. We have not reported all standard deviations because they are always lower than 5% of the measures.

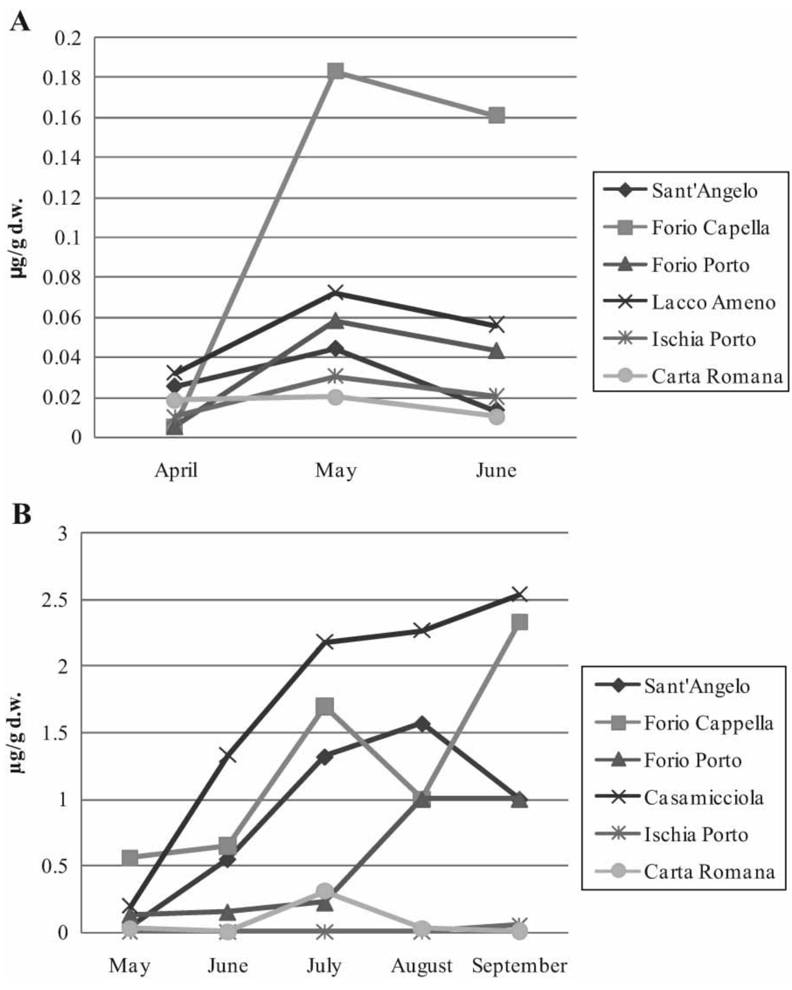

Figure 2. Cadmium trends in (A) *T. atomaria*, and (B) *H. scoparia*.

3. Results and discussion

This study represents work on seaweeds and seawater in polluted and non-polluted areas of the Gulf of Naples. The concentration of different elements in an organism can vary with the seasons and the contents of some elements in an organism may be diluted during the period of its maximum growing.

Cadmium concentration ranged from 0.005–0.183 μg/g dry wt in *T. atomaria* (Figure 2A), from 0.004–2.534 μg/g dry wt in *H. scoparia* (Figure 2B).

In the algal tissues copper oscillated from 0.004 to 0.905 μg/g dry wt in *T. atomaria* (Figure 3A), from 0.160–27.370 μg/g dry wt in *H. scoparia* (Figure 3B).

Lead concentration varied from 0.01–0.98 μg/g dry wt in *T. atomaria* (Figure 4A), from 0.228–8.839 μg/g dry wt in *H. scoparia* (Figure 4B).

H. scoparia metal concentration ranges are apparently wider, probably because it has an accumulation rate higher or it has a longer life cycle so it has more time to absorb metals.

The different contamination between Ischia shoreline and Gulf of Naples is evident in Figure 5A, B & C, where we have reported the metal concentrations in *C. elongata*, which was present in heavily contaminated Naples shoreline, the difference of contamination is clear, in fact the results

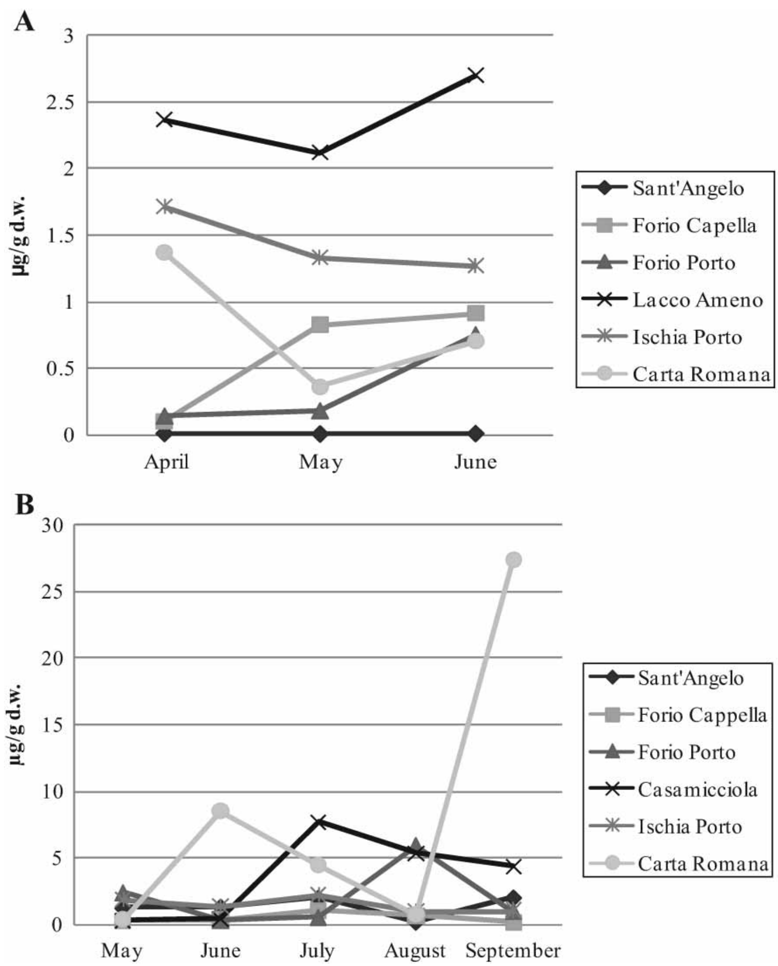

Figure 3. Copper trends in (A) *T. atomatia* and (B) *H. scoparia*.

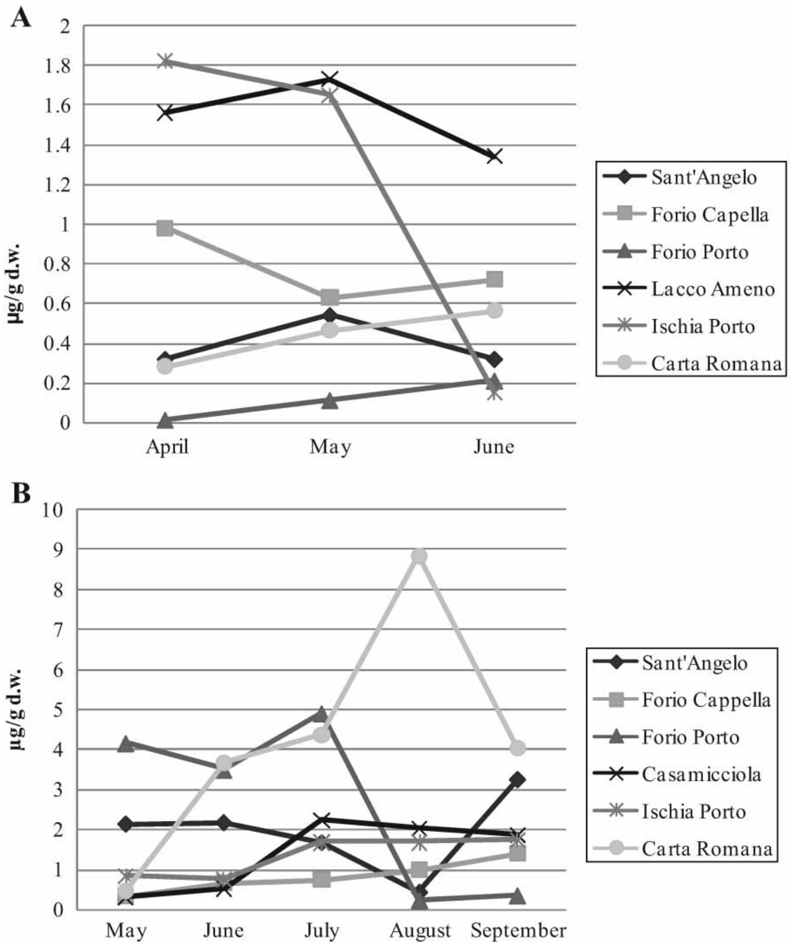

Figure 4. Lead trends in (A) *T. atomatia* and (B) *H. scoparia*.

of analysis of the variances ($\alpha = 0.05$) support this ideas as the hypothesis of equality of the variances can be rejected. This comparison has been done used only *C. elongata* because it is he only specie which grows in both in Naples Gulf and Ischia island.

This is clear evidence that seaweeds can be used as bio-monitors, in fact we have greater concentrations of metals in Naples (more polluted area) than in Ischia (mainly a tourist area). Moreover, the comparison between seawater and algal tissues metal concentration has shown and underlined accumulation capacity of seaweeds (Figures 6, 7 & 8). The statistical evaluation (Levene Test, F-Test and Bertlett Test) showed that algal species had a higher metal concentration.

In Figures 9, 10 and 11 the metal concentrations in the less common algal species are shown.

Whole sampling data obtained from the measurements of other species showed that metal concentrations were different between the Naples Gulf and Ischia island shoreline.

This work includes a comparison among our data and the bibliographic ones; although present data and bibliographical ones are in different temporal scales and environmental conditions during the period of studies are not known (Table 2).

As copper concentration in *Enteromorpha* spp. in Naples is greater than concentration defined for contaminated sites [10,24,26], we can conclude that Naples marine ecosystem is strongly contaminated.

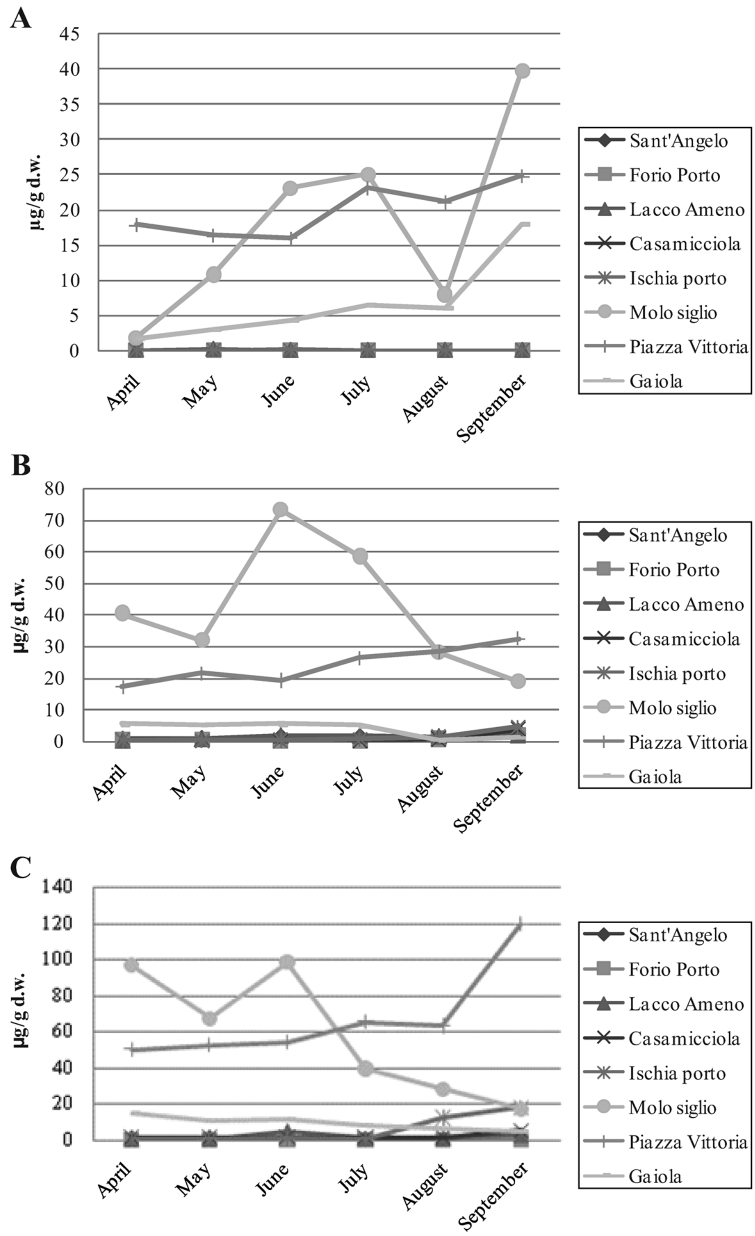

Figure 5. Comparison of heavy metals trend in *C. elongata*: (A) cadmium, (B) copper and (C) lead.

As regards to *P. Pavonia*, found only in the Ischia shoreline, it seemed to be more sensitive to pollution. Regarding the concentration of the three metals measured, contamination is lesser in the sampling points from the Ischia shoreline than in Greece [27].

In the samples collected from the Ischia shoreline, *Polysiphonia* spp. appears to be less contaminated by copper and by lead than it appears to be in Venice lagoon [23] and in Greece [27], however it is more contaminated by cadmium.

Corallina spp. results show more contamination in the Naples coastal zone sampled than those collected from Ischia shoreline. From bibliographical sources we know that Ischia results are less contaminated than Greece [27].

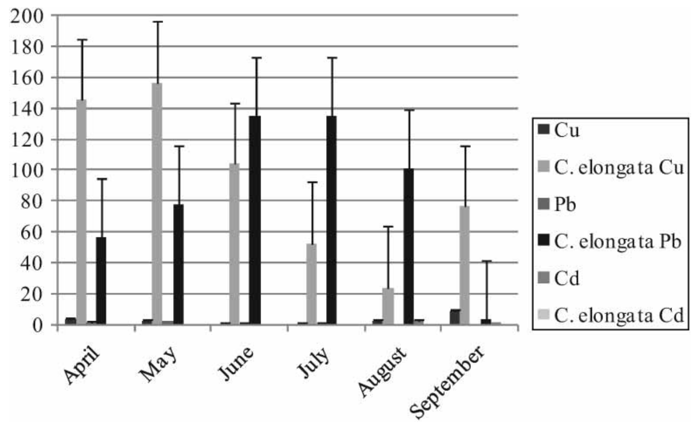

Figure 6. Comparison of metal concentrations between seawater and *C. elongata* at Sant'Angelo, Ischia.

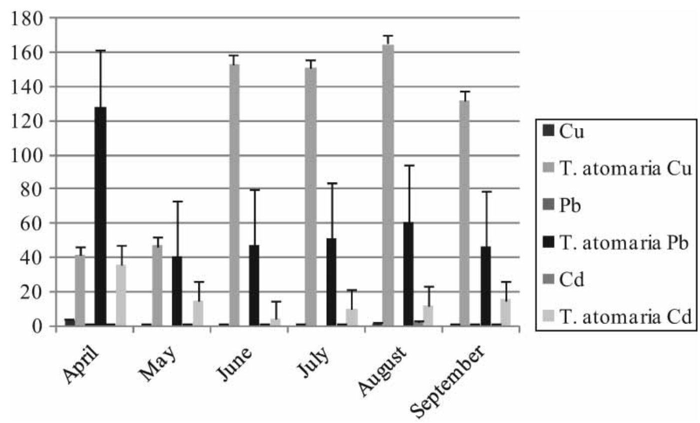

Figure 7. Comparison of metal concentrations between seawater and *T. atomaria* at Forio Porto, Ischia.

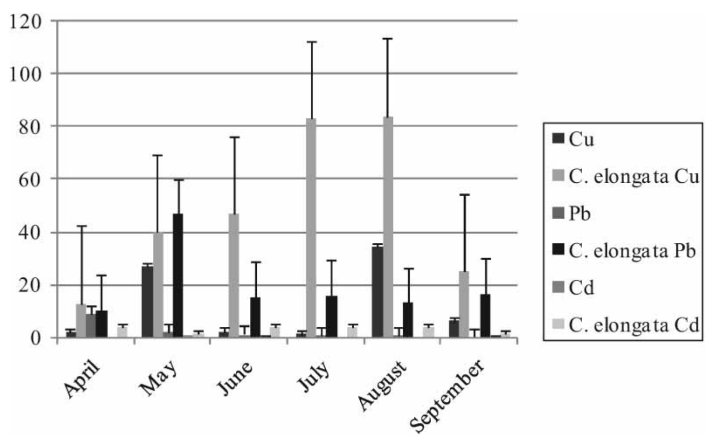

Figure 8. Comparison of metal concentrations between seawater and *C. elongata* at Laccoameno, Ischia.

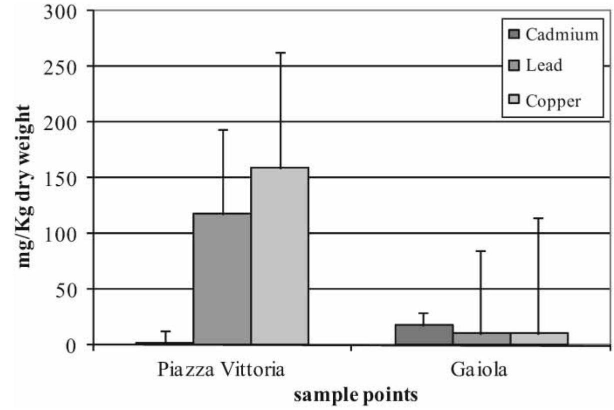

Figure 9. Heavy metal concentrations in *Enteromorpha* spp.

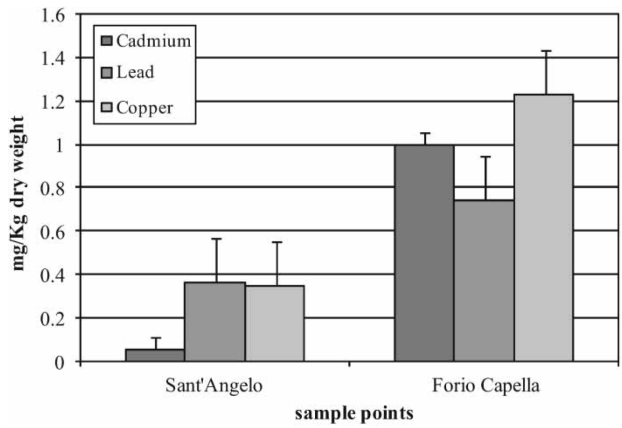

Figure 10. Heavy metal concentrations in *A. crociatum*.

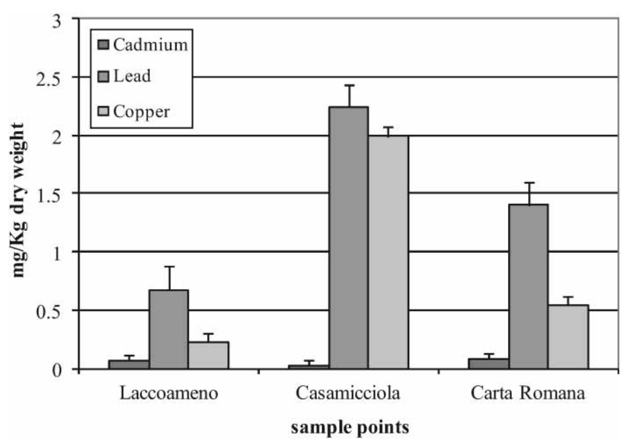

Figure 11. Heavy metal concentrations in *C. multifida*.

Table 2. Comparision with bibliographic references.

	Cd	Cu	Pb	Bibliographic references
		Enteromorpha spp.		
Uncontaminated sites	/	6–12	/	[24]
Contaminated sites	/	20–70	/	[24] [25] [26]
Naples	1,8–17,64	10–158	117,5–98	Present work
		P. Pavonia		
Chalkidiki	1.6	3,700	2,100	[27]
Thira	0,020	3,000	1,200	
Ischia	0,012	0,328	0,219	Present work
		Polysiphonia spp.		
Thermaikos	0,240	13,300	17,700	[27]
Venice Lagoon	0,100	9,000	2,700	[23]
Ischia	1,456	0,004	0,203	Present work
		Corallina spp.		
Crete	2,9	0,85	0,02	[27]
Naples	14,82	23,08	44,76	Present work
Ischia	0,02	0,98	2,05	Present work

So algae can be considered a good bio-monitor, as they absorb metals from seawater. The shorelines of Ischia Island results from these data less contaminated than Gulf of Naples, which issues from comparison with bibliographical data a site strongly contaminated. Moreover it is clear from this sample collection that the contamination of seawater affects the algal community, in fact where the contamination is lesser there are more algal species.

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