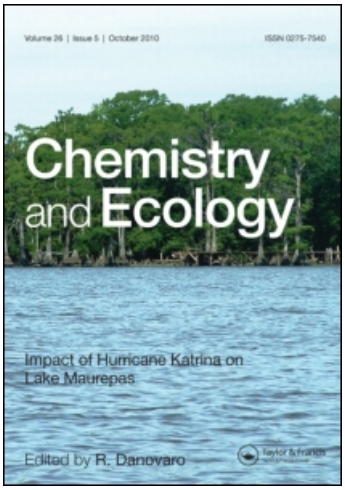

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A Chemical Characterization of A Lagoon Ecosystem: The Sacca Di Goro (Po River Delta, Italy)

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A CHEMICAL CHARACTERIZATION OF A LAGOON ECOSYSTEM: THE SACCA DI GORO (PO RIVER DELTA, ITALY)

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This work reports on the results of a preliminary estimate of the presence and distribution of common and rare elements in a typical estuarine environment of the Po River Delta. Different environmental compartments (sediment, water, macroalgae and benthic animals) were considered, and analysis conducted on samples taken at two different sites characterized by low and high hydrodynamic regime. Resulting evidence of differences between the matrices, especially in relation to their different nature and sampling site are given.

KEY WORDS: Major elements, trace elements, coastal lagoon, eutrophication, River Po delta.

INTRODUCTION

Most of the studies on biogeochemistry of coastal aquatic environments have been addressed to macronutrients, particularly phosphorous and nitrogen, as well as on less abundant elements, viz. sulphur, iron and manganese, which are essential both in plant nutrition and microbial processes. In the last decades, less common and sometimes rare elements have been taken into account, mostly as tracers of heavy anthropogenic impacts. This is the case for rare metals and radionuclides, which can be very useful in identifying pathways and primary sources of environmental pollution.

The study area is a lagoon located along a heavily industrial coastline (Fig. 1), which has always been affected by eutrophication, due to the nutrient load coming from the river. Moreover, this environment acts as a sink against macronutrients and rare elements leading to stressful conditions whose main evidences are eutrophication and episodic dystrophic crises (Viaroli *et al.*, 1992; Viaroli *et al.*, 1993), and accumulation of pollutants like the isotopes of caesium (Bondavalli, 1994).

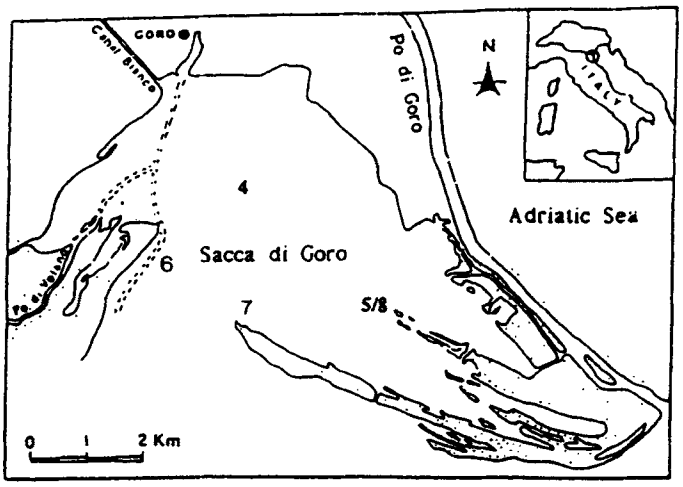

Figure 1 Study area and sampling sites.

MATERIALS AND METHODS

Samples of macroalgae (*Ulva rigida and Gracilaria* sp.) and sediment were collected at two different sites, named stations 4 and 5/8 (Fig. 1), representing two different situations in the environment investigated. Station 5/8 is located in a sheltered area with slow water renewal, while station 4 is directly affected by fresh- and sea water inflows. Samples of benthic animals (*Rapana venosa, Carcinus mediterraneus, Mytilus galloprovincialis*) were collected in an area close to the sea mouth of the sacca.

Samples were taken from April 1992 to June 1992. Sampling techniques are described in detail by Bondavalli (1994).

C, N and P Determination

Total carbon, nitrogen and phosphorus concentrations were determined only in macroalgal thalli. Total carbon and nitrogen content were analyzed with a CHN elemental analyzer LECO 600, which acts via a combustion followed by an oxidation (CO_2) and a reduction (N_2) (Fumagalli and Viaroli, 1987).

The procedure for total phosphorus determination required ashing of 1 g at 550 C, in a muffle furnace. The ash produced underwent specific treatment, according to the modified Aspila method proposed by Isaac (1990), to obtain a solution where phosphorus content was measured by molecular absorption spectrometry (Valderrama, 1981).

Micro and Macroelements Determination with ICP-OES, GF-AAS and ICP-MS

Six elements Cs, Fe, Zn, Co, Mn and Sr were determined on sediment, macroalgae and benthic animals by inductively coupled Plasma Optical Emission Spectrometry

(Fe, Zn and Mn), by Graphite Furnace Atomic Absorption Spectrometry (Co) and by inductively coupled Plasma Mass Spectrometry (Cs). At the same time standard reference materials were analyzed (Achilli *et al.*, 1991).

One gram of macroalgae, 2.5 g of molluscs and crustaceans and 0.5 g of sediment, were accurately weighed, transferred to glass vessels and ashed in a oxygen plasma processor. The ashing was completed after 2–3 days during which the samples were homogenized at least once a day. At the end of this procedure the organic matter was completely destroyed and afterwards the ashes were treated with 15 ml of an acid mixture ($H_2O/HNO_3/HCl = 2.5/2.5/1$) and transferred into a Teflon bomb. Then the samples received 5 ml of H_2O_2. When any residual reaction ended, the bombs were introduced into a microwave oven. After the dissolution, sediment samples were filtered to eliminate the solid residue. The solutions obtained were then analyzed.

Determination of Trace Elements with INAA

Instrumental Neutron Activation Analysis was utilized to determine the amount of Ca, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Rb, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Lu, Hf, Ta, Th and U in macroalgae, benthic animals and sediment.

The irradiation was carried out in the TRIGA Mark II reactor of the University of Pavia; induced radioactivity was measured by gamma-ray spectrometry using a high purity germanium detector.

The analytical procedure follows three main steps:

1. samples (300 mg; sediments, *Ulva*, *Gracilaria*, *Mytilus*, *Rapana*, *Carcinus*) and reference materials (Coal Fly Ash NIST 1633a, Bovine Liver NIST 1577, River Sediment NIST 1645) were irradiated at a thermal neutron flux (1×10^{12}n $cm^{-2}s^{-1}$), for 20 hours;
2. the decay was obtained over 3 days;
3. measurement of the induced γ activity of ^{47}Sc, ^{76}As, ^{140}La, ^{153}Sm, ^{177}Lu, ^{239}Np was first shown, then repeated countings after 7, 14, 21, 30 and 60 days were carried out for ^{46}Sc, ^{51}Cr, ^{59}Fe, ^{60}Co, ^{58}Ni, ^{65}Zn, ^{75}Se, ^{86}Rb, ^{95}Zr, ^{124}Sb, ^{134}Cs, ^{131}Ba, ^{141}Ce, ^{147}Nd, ^{152}Eu, ^{153}Gd, ^{161}Tb, ^{166m}Ho, ^{170}Tm, ^{169}Yb, ^{181}Hf, ^{182}Ta and ^{233}Pa.

To calibrate the method, standard reference materials, such as coal fly ash, bovine liver and river sediment (NIST 1992), underwent the same treatment. By comparing the elemental concentration determined in reference samples with literature data, clues about the accuracy of this analytical procedure can be obtained. As shown in Table I the two data sets are generally in agreement, except for calcium, zinc, antimony and uranium contents in river sediment and chromium, zinc and rubidium in bovine liver.

RESULTS AND DISCUSSION

The Po River Delta lagoons are affected by accelerated eutrophication processes due to an excessive nutrient load coming from the river catchment area. During the last

Table I Accuracy evaluation. Element content is given as μg g^{-1} (dry weight) unless otherwise specified.

	River sediment		*Bovine liver*	
	Laboratory	*Literature**	*Laboratory*	*Literature**
Ca%	1.94±0.04	2.9	0.011±0.001	0.0116
Sc	2.02±0.03	2.00	0.015±0.001	–
Cr	2.71±0.05	2.96	0.80±0.05	0.66
Fe%	10.39±0.09	11.30	0.031±0.002	0.026
Co	8.3±0.4	8.0	0.48±0.04	0.17–0.41
Ni	44.5±0.3	45.8	0.36±0.01	0.4
Zn	1507±54	1720	105±5	132
As	65.9±0.9	66.0	0.051±001	0.053
Se	n.d.	–	1.23±0.07	1.08
Rb	43.0±5	–	12.6±0.2	19.5
Zr	n.d.	–	4.0±0.4	4.0
Sb	17.5±0.2	51.0	0.116±0.007	–
Cs	2.4±0.1	–	0.007	0.007
Ba	326±13	–	78.6±0.3	5.1–123
La	8.9±0.4	8.1	0.021	0.017
Ce	23.0±2	–	0.047±0.003	0.046
Nd	12.67±0.07	12.70	0.018±0.001	0.016
Sm	1.46±0.07	–	0.002	0.002
Eu	0.35±0.04	0.37	n.d.	–
Gd	n.d.	–	0.002	0.002
Tb	0.204±0.004	0.210	n.d.	–
Ho	n.d.	–	0.001	0.001
Tm	2.2±0.6	–	n.d.	–
Yb	n.d.	–	0.001	0.001
Lu	0.11±0.01	–	n.d.	–
Hf	1.4±0.2	–	n.d.	–
Ta	0.22±0.01	–	n.d.	–
Th	1.24±0.06	–	1.03±0.04	–
U	2.0±0.2	1.4	0.001	–

(*) Gladney, 1981
n.d. = not determined

few years, in this area there has been an increasing development of large macroalgal beds, in particular *Ulva rigida* and *Gracilaria* sp. Growth and decomposition of these huge biomasses seem to be the most important factors in determining the trophic status of the Sacca di Goro (Viaroli *et al.*, 1992; Viaroli *et al.*, 1993). Many researches have been carried out to investigate different metabolic processes and attention was focused upon nitrogen and phosphorus circulation, in particular nitrogen seems to play a key role in the seasonal evolution of processes that lead to dystrophic crises.

In Figure 2, carbon, nitrogen and phosphorus contents in *Ulva* and *Gracilaria* collected at stations 5/8 and 4 in May 1992 are presented. Nitrogen content in *Ulva* thalli seems to be in relation to both growth rates and dissolved inorganic nitrogen (DIN) concentration in the water column (Naldi, 1993). Dissolved organic nitrogen, DIN, concentration reaches a maximum in winter and decreases rapidly during *Ulva* growth season: the macroalga seems able to accumulate nitrogen. No significant

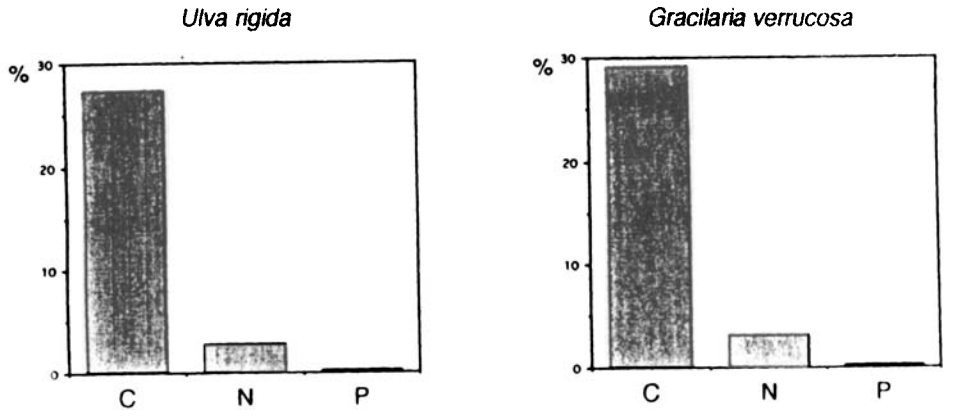

Figure 2 Carbon, nitrogen and phosphorus content in *Ulva rigida and Gracilaria* sp.

seasonal trends were observed for phosphorus in *Ulva* and phosphorus and nitrogen in *Gracilaria* (Naldi, 1993).

Together with macronutrients (C, H, O, P, K, N, S, Ca and Mg) which occur at relatively high amounts in seaweeds, there are micronutrients (Fe, Cu, Zn, Mn, Si, Co, Mo, V, B, Cl, I, Br and Na) which are important as catalysts in metabolic reactions, in osmoregulation and other functions.

The concentration of Cs, Co, Fe, Zn, Mn and Sr are reported in Table II.

The amount of iron in the macroalgae, 4412 $\mu g\, g^{-1}$ (dry weight) in *Gracilaria* and 7917 $\mu g\, g^{-1}$ (dry weight) in *Ulva*, is high if compared with values reported in the literature: on average 300 $\mu g\, g^{-1}$ with a range from 90 to 1500 $\mu g\, g^{-1}$ (DeBoer, 1981).

The same conclusion applies to manganese content which is higher in macroalgal samples. This element is an essential nutrient for plant and almost certainly essential to seaweeds because of its importance in photosynthesis. Manganese is more abundant in *Gracilaria* than in *Ulva*, this could be related to the different structure of the

Table II Element content in different samples, determined by ICP-OES, GF-AAS and ICP-MS (as shown as μg/g).

Sample	*Station*	*Day*	*Cs*	*Co*	*Fe*	*Zn*	*Mn*	*Sr*
Gracilaria	4	7/7/92	0.33	6.52	4412	73	3824	81
Ulva	5/8	7/7/92	0.69	4.73	7917	74	1371	124
Mytilus	6->7	6/5/92	0.06	1.44	806	116	56	62
Rapana	6->7	7/7/92	0.02	0.52	449	74	49	49
Carcinus	6->7	7/7/92	0.07	1.76	668	53	162	1329
Sediment	4	29/7/92	1.49	13.41	17489	71	463	187
Sediment	5/8	29/7/92	2.69	15.38	23970	130	560	187
NIST1566a	–	–	–	0.57	467	784	12	9.6
Cer.Val.	–	–	0.02	0.57	539	830	12.3	11.1

two species. *Gracilaria* presents some structural cells which are not observed in *Ulva*, a species that is formed almost completely by photosynthetic tissue.

The highest concentration of iron caesium and cobalt were found in surficial sediment samples, while macroalgae and the animals analyzed show values rather lower. High amount of strontium was detected for the crustacean *Carcinus*, which probably accumulates this element within the exoskeleton.

Results obtained by INAA on samples of surficial sediment, macroalgae (*Ulva* and *Gracilaria*) and benthic animals (*Rapana, Carcinus and Mytilus*) are shown in Table III.

These results suggest a decrease of trace elements from abiotic matrices to the biotic ones. Many of the studied elements, all classifiable as lithopiles (Sc, Cr, Co, Zr, Cs, Ba, rare earths, Hf, Th and U) seem to be significatively correlated with each other ($R > 0.9$). This provides information about the origin of these elements: they probably come from the sediment compartment and/or from the suspended particu-

Table III Iron(%), calcium(%) and trace elements content ($\mu g\ g^{-1}$) in different matrices from the Sacca di Goro, determined by INAA.

	Sediment	*Sediment*	*Ulva*	*Gracilaria*	*Mytilus*	*Rapana*	*Carcinus*
	*St.*4	*St.*5/8					
Ca%	2.6±0.3	1.9±0.5	1.09±0.03	0.6±0.1	0.75±0.03	0.33±0.02	4.44±0.06
Sc	12.5±0.2	8.8±0.3	3.34±0.06	2.30±0.06	0.34±0.01	0.13±0.03	0.36±0.01
Cr	192±3	142±1	66±1	42±2	7.1±0.2	5.08±0.06	8.00.6
Fe%	0.36±0.08	2.55±0.09	1.01±0.02	0.74±0.02	0.12±0.09	0.074±0.007	0.171±0.003
Co	17.1±0.2	14.0±0.2	11±5	8.6±0.1	1.5±0.2	1.02±0.05	1.64±0.07
Ni	58±4	64±1	34.1±0.3	31±1	n.d.	n.d.	n.d.
Zn	173±8	110±1	76±0.3	80±2	105.7±0.3	76.1±0.5	70±1
As	8.0±0.1	5.16±0.05	7.8±0.2	21±1	12±1	15.4±0.8	9.4±0.2
Se	3.1±0.5	2.2±0.5	1.2±0.1	84±2	1.6±0.1	1.0±0.1	2±1
Rb	105±3	75±2	34.4±0.8	71±2	4.7±0.1	3.33±0.09	8.36±0.06
Zr	149.52±0.03	97±5	n.d.	n.d.	n.d.	n.d.	n.d.
Sb	2.03±0.06	1.02±0.09	0.55±0.01	1.36±0.01	0.097±0.002	0.280±0.003	0.110±0.002
Cs	6.7±0.3	3.7±0.2	1.9±0.1	1.43±0.02	0.232±0.009	0.101±0.009	0.24±0.01
Ba	309±3	261±12	92.6±0.6	61±2	n.d.	37.4±0.6	25.0±0.1
La	31±2	24.9±0.5	9.5±0.3	3.4±0.6	1.29±0.02	1.47±0.04	2.03±0.04
Ce	66±1	48±3	14.7±0.2	7.8±0.6	1.21±0.02	0.722±0.004	2.6±0.1
Nd	33±4	24.2±0.8	8.3±0.1	7.39±0.05	1.165±0.004	1.8±0.3	3.4±0.3
Sm	5.7±0.1	3.9±0.2	1.41±0.07	0.89±0.03	0.160±0.003	0.072±0.001	0.207±0.006
Eu	1.23±0.03	0.99±0.07	0.347±0.005	0.182±0.005	0.040±0.001	0.020±0.004	0.075±0.003
Gd	7.11±0.09	3.5±0.6	1.81±0.06	1.03±0.04	0.19±0.01	0.088±0.006	0.276±0.006
Tb	1.35±0.01	0.86±0.04	0.29±0.04	0.146±0.003	0.030±0.006	0.015±0.004	0.042±0.002
Ho	1.9±0.03	1.25±0.09	0.46±0.01	0.23±0.02	0.048±0.007	0.020±0.001	0.062±0.003
Tm	0.53±0.04	0.40±0.02	0.13±0.04	0.09±0.02	0.020±0.004	0.005±0.001	0.021±0.003
Yb	2.5±0.1	1.98±0.03	0.76±0.03	0.57±0.07	0.10±0.06	0.032±0.001	0.13±0.05
Lu	0.378±0.006	0.26±0.01	0.095±0.007	0.069±0.002	0.015±0.002	0.005±0.001	0.02±0.009
Hf	4.3±0.1	3.18±0.09	1.3±0.2	0.46±0.01	0.561±0.006	0.052±0.03	0.24±0.01
Ta	0.84±0.02	0.578±0.006	0.301±0.009	1.4±0.8±	n.d.	n.d.	n.d.
Th	10.1±0.1	6.9±0.2	2.50±0.08	1.64±0.05	0.27±0.01	0.131±0.005	0.41±0.02
U	3.4±0.4	1.86±0.03	0.712±0.003	n.d.	0.43±0.02	n.d.	n.d.

n.d. = not determined

late matter, and their distribution seems not modified when assimilated by one of the different biological components of the studied environment.

The distribution of two major elements (Ca and Fe) may be affected by bioaccumulation processes (viz. calcium in *Carcinus*). On the other hand, the distribution of the other elements (Zn, As, Se, Sb, and Ta) seems to depend mainly on anthrophic contributions.

The analysis of the distribution of rare-earth elements content, normalized with respect to the same content of the chondritic meteorites, was carried out to provide evidence of differences between matrices. Figure 3 and 4 show similar trends for sediment, *Ulva, Gracilaria and Mytilus* from one side and for *Rapana* and *Carcinus*, on the other.

In the first group of samples (Fig. 3), biological matrices (*Ulva, Gracilaria and Mytilus*) reveal no differences compared with that of sediment. On the contrary, *Rapana and Carcinus* (Fig. 4) in addition to an unusual trend, show a depletion of the heaviest rare-earth elements (Eu-Lu) relative to the light ones (La-Sm).

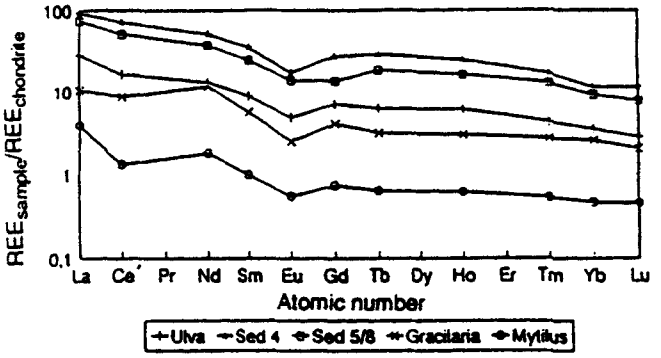

Figure 3 Rare-earth elements (REE) distribution: *Ulva, Gracilaria, Mytilus* and sediments.

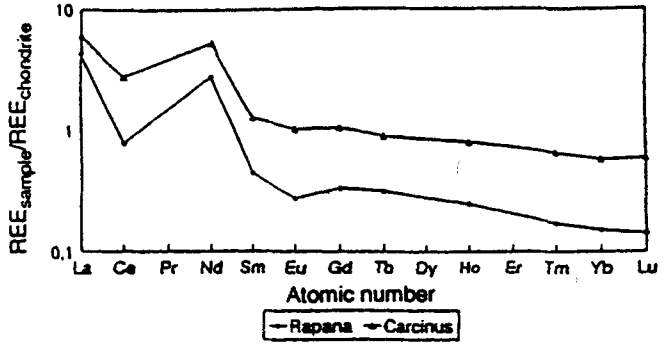

Figure 4 Rare-earth elements (REE) distribution: *Rapana and Carcinus.*

CONCLUDING REMARKS

Chemical characterization of the Sacca di Goro represents an essential preliminary step for investigating the functional ecology of this highly productive environment. In this account, prospective attention has been focused on phosphorus and nitrogen as main determinants of eutrophication and dystrophic events. On the other hand, since the Sacca di Goro receives waters from the Po River, a heavily polluted body of water, it is of extreme importance to investigate accumulation properties of environmental matrices with respect to Fe, Mn, Ca, Zn, Cs and other trace elements. Results presented in this descriptive study will be used in more ecologically oriented investigations that are being carried out on this area.

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