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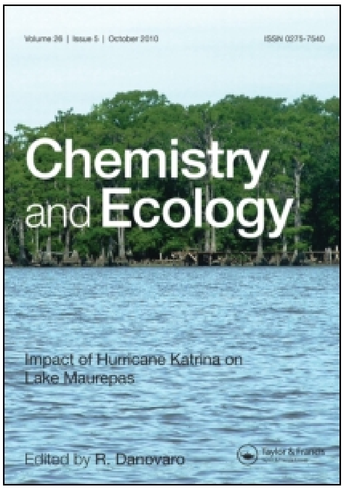

Chemistry and Ecology

Publication details, including instructions for authors and subscription information:
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To cite this Article Fabiano, M. , Baffi, F. , Povero, P. and Frache, R.(1988) 'Particulate Organic Matter and Heavy Metals in Ligurian Open Sea', Chemistry and Ecology, 3: 4, 313 — 323
To link to this Article: DOI: 10.1080/02757548808070850
URL: http://dx.doi.org/10.1080/02757548808070850

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Chemistry and Ecology, 1988, Vol. 3, pp. 313–323
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Particulate Organic Matter and Heavy Metals in Ligurian Open Sea

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(Received March 21, 1988)

Seven stations were sampled along a transect between Imperia and Cape Corso during the C.N.R. "Bannock" survey (8–10 October 1984).

The TSM, PC, PN, and chlorophyll-a concentrations are low and decrease with depth. The AOU values suggest that below 400 m the organic matter is completely inert to further oxidation. Heavy metals concentrations show marked differences in the surface water layer between coastal and offshore stations. The chemical characteristics of total suspended matter are more conservative as an index of waters of coastal origin than the quantity of particulate matter itself or metal concentrations. The Fe:Cd ratio in particles is of interest as an indicator of coastal waters.

INTRODUCTION

The Ligurian Sea is characterized by a very limited fluvial input and consequently the concentration of total suspended matter of terrigenous origin is low. In the offshore waters of the Ligurian Sea the organic fraction constitutes only a small part of the suspended matter, principally of authochthonous origin.

Contribution of the "Gruppo Ricerca Oceanologica-Genova." This work was supported by Research Council of Italy, by International Energy Agency (R.c. No. 3291/EP and No. 3291/R1/ep) and by "Ministero Pubblica Istruzione, Fondi 40%" of Italy.

Previous researches highlighted the distribution of heavy metals in particulate matter of different coastal waters and show the effect of hydrological and biological factors on the levels of trace elements (Baffi *et al.* 1984; Fabiano *et al.* 1985).

The aim of this work is to study and to characterize the particulate matter of areas of open sea and to identify the possible relations between particulate matter and the distribution of particulate heavy metals in water column.

MATERIALS AND METHODS

Sampling

Sampling was carried out from the 8th to the 10th October 1984, on the RV "Bannock" of the National Research Council. Seven stations were sampled along a transect between Impera and Corso Cape (Figure 1). The samples of sea water were collected at the depths of 0, 50, 200, 400, 600, 1200, 1600, 2000 m by using a Niskin bottle of 30 litres. At every depth 2 litres were taken for analysis of

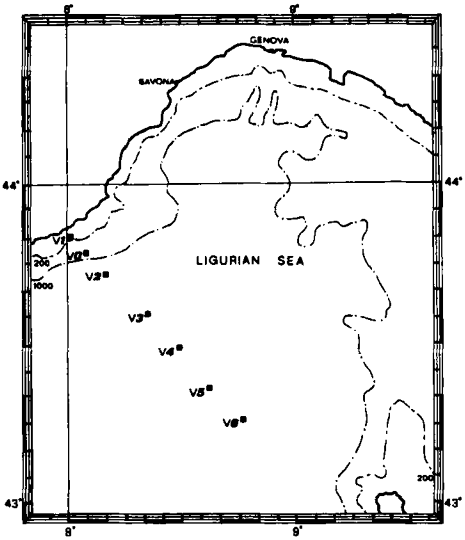

FIGURE 1 Sampling stations.

chlorophyll pigments, 0.3 litres for dissolved oxygen and 1 litre for heavy metals. The water sample for oxygen was fixed and stored immediately. Filtration on Whatman GF/C for particulate carbon and particulate nitrogen on Millipore 0.8 μm for chlorophyll-a, and on Millipore 0.45 μm for heavy metals in the particulate was carried out immediately after sampling and filters were stored frozen.

Apparatus

A Varian 635 model was used for the spectrophotometric measurement, a CHN Analyzer mod. 1106 C. Erba for the element determinations, and an Inductively Coupled Plasma Atomic Emission Spectrometer model Jobin-Yvon JY38 (with sequential monochromator equipped with a JY2138 Durr plasma torch operating at 2.2 Kw power) for determination of heavy metals.

The transparency of the water column was measured by Secchi disk; temperature, salinity and density with a Neil Brown CTD.

Materials and reagents

Laboratory equipment for heavy metals analysis was made of low density polyethylene and before use it was washed in a standard way (Baffi *et al.*, 1980). Chemicals used were reagent grade and Suprapur (Merk). In the laboratory, analyses were carried out using the following methods:

dissolved oxygen: analysis followed the classic Winkler method;

total suspended matter (TSM): obtained by gravimetric measurement;

C and N (PC and PN): Determination of particulate carbon and nitrogen was made using a CHN Analyzer. Cyclesanone was used as a standard;

chlorophyll-a (CHL): analysis by the spectrophotometric method of Strickland and Parsons (1968); concentrations calculated by the formulae indicated by SCOR-UNESCO;

heavy metals: particulate matter was removed from the filter by ultrasound in 20 ml of water Milli-Q; the suspension was dried at 60°C treated with 2 ml of 8N HNO3, redried and then dissolved in 5 ml of acidified water Milli-Q for ICP determination.

RESULTS AND DISCUSSION

The temperature and salinity values indicated a hydrological situation typical of the Ligurian Sea in October. At the surface (−5 m) temperature was between 15.208°C (V2) and 18.681°C (V1) and salinities between 37.945‰. (V1) and 38.337‰. (V4). A thermocline was evident between 10 and 60 m at the offshore stations (V2–V6) while it was less developed at the more coastal ones (V1 and V0). The temperature salinity diagram (Figure 2) indicates two groups, as Coste and Minas (1977) observed in summer, reflecting a different situation for the superficial waters of the coastal stations (V0, V1 and V2) with respect to the offshore V3, V4, V5 and V6 stations.

Oxygen concentrations at the surface are between 5.42 and 5.60 ml/l. The subsuperficial maximum is present, but not well evidenced (Figure 3) owing to the too scattered depth of sampling. The apparent oxygen utilization was defined by Redfield (1942) as amount of oxygen (AOU) that disappears from the waters owing to the metabolic processes. It was calculated by: $\mathrm{AOU} = \mathrm{O}_2' - \mathrm{O}_2$ where O_2' is the concentration of dissolved oxygen at saturation

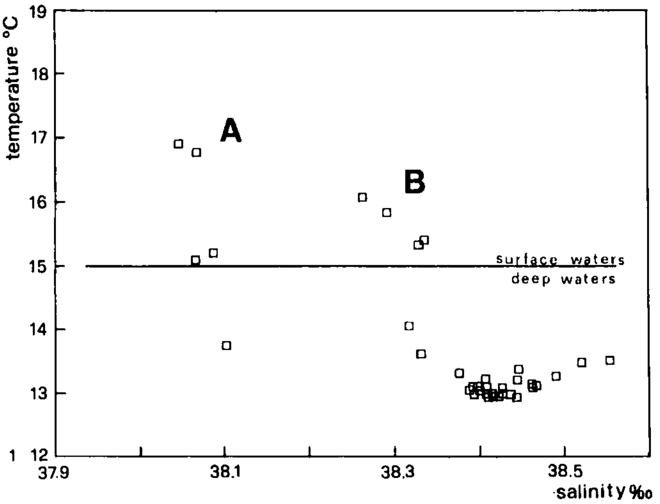

FIGURE 2 Temperature–salinity diagram showing two different surface waters: (A) coastal waters and (B) offshore waters.

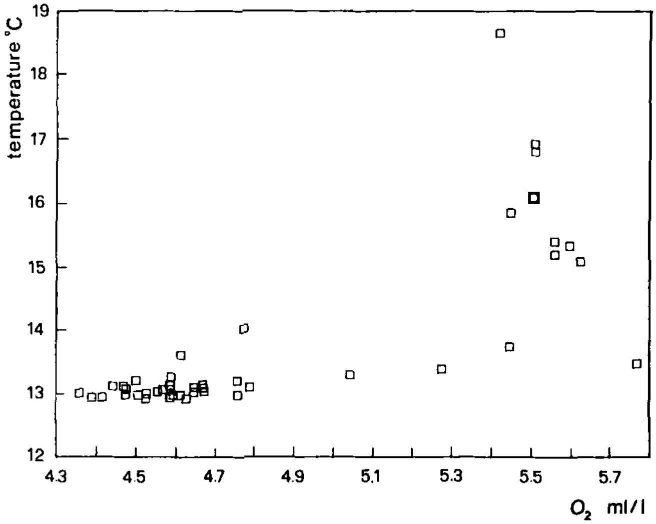

FIGURE 3 Temperature–oxygen diagram showing subsurface maximum of oxygen concentrations between 14°C and 15°C.

obtained by Carpenter's oxygen solubility data and O_2 is the measured dissolved oxygen concentration. The highest values (1.30 ml/l) were found at 200–400 m depth; they suggest that the organic matter is subjected to oxidation particularly in the superficial layer and that, below 400 m, inorganic matter is almost completely inert to the further oxidation; below 400 m, AOU values decrease slightly (Figure 4).

Particulate suspended matter (TSM) is 0.539 mg/l on average. According to the depth, TSM shows a poorly defined behaviour; maxima were found at 600 m and 1200 m (except for the coastal stations V0 and V1). Particulate carbon (PC) mean value is 40.40 μg/l and highest values are found at the surface and progressively lower concentrations with depth. The decrease of particulate nitrogen (PN) concentrations is even more evident with depth (mean value $x = 3.12$ μg/l); the weight ratio C/N varies from 11.7 at 0–50 m to 28.9 at 200–600 m and 35.2 at 1200–2000 m (Table I).

The vegetal component of particulate organic matter, expressed as chlorophyll-a and not corrected for phaeopigments is 0.38 μg/l in the superficial layer, 0.14 μg/l in the intermediate layer and

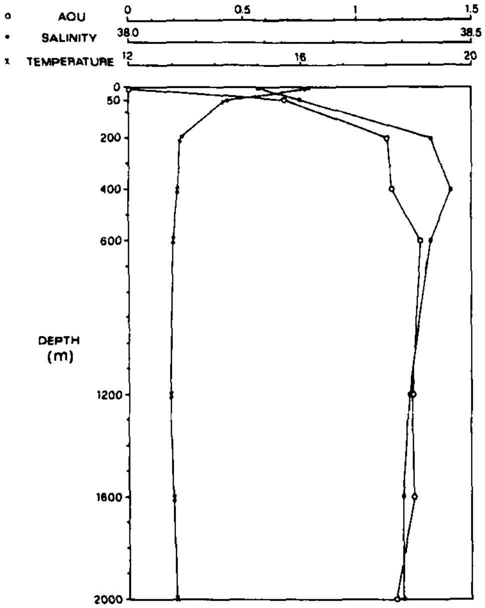

FIGURE 4 Vertical distribution of AOU, temperature and salinity mean values.

0.16 μg/l at depth. To identify the degraded fraction of chlorophyll pigments, we considered the chlorophyll-c/chlorophyll-a ratios (c/a) as representative of degradation of vegetal matter. Obviously this ratio increases with depth (constant = 516.1; regression coefficient = 0.62; degrees of freedom = 44).

In addition, a positive correlation was found between AOU and

TABLE I
Vertical distribution of TSM (mg/l), PC and PN (μg/l) mean concentrations

Depth (m)	TSM	PC	PN
0	0.59	75.26	7.53
50	0.67	49.80	4.16
200	0.20	31.23	2.00
400	0.19	29.13	2.08
600	0.82	27.82	1.45
1200	1.11	40.56	2.70
1600	0.38	30.12	0.70
2000	0.43	32.16	1.60

c/a chlorophyll ratio with $r = 0.57$ ($df = 44$) and a constant $c = 0.069$; we think that with elevated AOU there is the greatest degradation potential for vegetal matter and little active chlorophyll-a, in contrast to AOU near zero, when chlorophyll-a can be considered active. Taking this into consideration we estimate the percentage of undegraded chlorophyll-a in each sample. In the superficial layer, it averages 0.31 μg/l corresponding to 76.2% of the total chlorophyll-a, in the intermediate layer 0.04 μg/l corresponding to 20.8% and in the deep layer 0.03 μg/l corresponding to 18.6%.

For the study of organic matter, the superficial layer (0–50 m) represents the most interesting environment. Analysis of the data reported in Figure 5 shows that the central stations V2, V3 and V4 have a lower TSM content but proportionally a higher organic component. This component, if we observe the absolute values of chlorophyll-a and those of active chlorophyll-a, results in a rather remarkable proportion of organic inactive vegetal-matter (ratio PC/TSM * 1000). The particulate matter of the upper 50 m depth at the stations at the two ends of the transect Imperia-Corso Cape is therefore relatively richer and characterized by a high inorganic component and a little vegetal but active component; while at the central stations of the transect, TSM concentrations are lower and

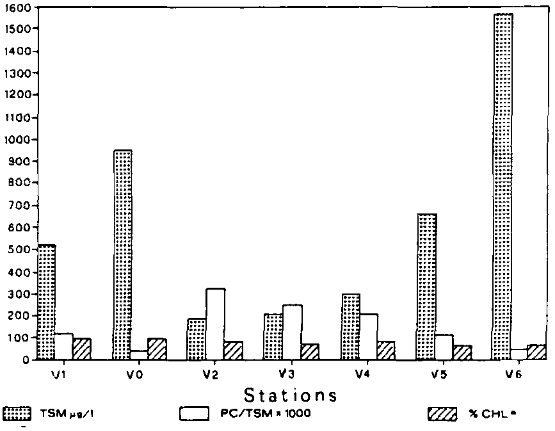

FIGURE 5 Mean values in 0–50 m water layer of active chlorophyll (% CHL *), total suspended matter (TSM) and particulate carbon (PC/TSM * 1000).

the organic matter is both vegetal and heterotrophic in origin. In deep waters, the values of suspended organic matter decrease strongly and even the chemical composition is modified by degradation processes and reach their greatest intensity at 200 m. In deep waters, therefore, we have little organic particulate matter, scarcely significant from a trophic standpoint.

A further aspect of the research is related to differences in heavy metal content of particulate matter between coastal and open waters. If we consider the metals contained in the suspended particles in the superficial layer (Table II; $\mu g/g$) we observe that concentrations in the upper 50 m at stations V0, V2 and V3 are more like those observed in Genoa Gulf (Fabiano *et al.*, in press) while the values of the superficial waters of the V4, V5 and V6 stations are lower; the concentrations at depth >50 m are even

TABLE II
Mean concentrations of heavy metals per litre ($\mu g/l$) and per TSM gram ($\mu g/g$) in the layers 0–50 m and 0-deep level

	Concentrations in ($\mu g/g$)					Concentrations in water ($\mu g/l$)				
Stations	Cd	Fe	Cu	Ni	Cr	Cd	Fe	Cu	Ni	Cr
V0										
0–50	0.495	175	35.3	36.7	17.0	0.283	19.6	3.95	4.11	1.90
200–600	0.347	140	26.4	33.0	18.6	0.041	15.5	7.38	4.23	2.87
V2										
0–50	0.617	180	74.9	56.1	43.0	0.062	17.5	8.15	5.26	4.29
200–2000	0.307	107	21.3	22.0	13.9	0.035	10.0	2.38	2.98	1.73
V3										
0–50	0.442	159	52.9	51.9	24.7	0.041	15.7	4.25	4.92	2.13
200–2000	0.504	139	26.3	32.5	17.5	0.132	74.1	10.4	6.89	5.00
V4										
0–50	0.371	84.7	34.0	17.9	8.62	0.070	14.9	7.19	2.89	1.82
200–2000	0.335	60.3	8.32	19.4	4.30	0.031	5.73	0.721	1.31	0.283
V5										
0–50	0.263	55.3	10.9	10.1	1.42	0.083	18.0	3.57	3.17	0.525
200–2000	0.314	55.0	23.4	14.3	8.10	0.125	27.9	8.97	6.10	2.71
V6										
0–50	0.335	144	13.8	33.1	3.85	0.261	113	10.8	25.9	2.97
200–2000	0.240	63.3	7.03	15.9	1.72	0.093	20.2	2.45	5.36	0.432
Genda gulf										
0–50	0.801	331	49.0	36.7	32.3	0.262	106	16.6	11.6	10.8
200-bott.	0.325	774	242	60.9	102	0.091	238	72	18.3	31.1

lower. As for metals in solution (Table II), concentrations (ng/1) are decidedly lower than those observed by the same authors in coastal waters (Fabiano *et al.*, 1985) and in Genoa Gulf (Fabiano *et al.*, in press). The analysis of the ratio between metals in particulate matter is further evidence of differences between the suspended particulate matter of different areas. This analysis points out some qualitative differences between the particulate matter in coastal waters (Genoa Gulf) and that in offshore waters (present study) (Table III). We observe that the greatest differences between two water masses increase in the order:

$$\mathrm{Fe} > \mathrm{Cr} > \mathrm{Ni} > \mathrm{Cu} > \mathrm{Cd}.$$

Therefore iron is the element most influenced by anthropogenic coastal activity and the Fe:Cd ratio can be considered as an indicator of coastal impact on particulate matter in the Ligurian Sea waters.

The differences noted in metals dissolved in 1 liter of sea water compared to that in 1 gram of dry suspended matter do not appear to reflect the quantity of TSM since TSM concentrations at V0, V2, V3 and V4, V5, V6 stations are not significant and remarkably lower than those of coastal waters.

Other possible relations among the studied parameters were therefore considered. We calculated the correlation coefficients between the metal concentrations and the chemical, physical and biological characteristics of the water and the particulate matter that we examined. The relation between Fe, Cr and Ni concentrations

TABLE III
Mean concentration for different groups of stations and for all stations

	Surface layer (0–50 m)		Deep layer (200–2000 m)
Stations	V1, V0, V2	V3, V4, V5, V6	all
AOU ml/l	0.07	0.58	1.21
TSM mg/l	0.55	0.69	0.51
CHL\CHL*	1.07	1.34	3.75
CHL* μg/l	0.29	0.32	0.04
Cd μg/g	0.563	0.352	0.34
Fe μg/g	177	110	87.8
Cu μg/g	55.1	27.9	17.6
Ni μg/g	46.4	28.2	21.2
Cr μg/g	30.0	9.62	9.82

TABLE IV
Mean weight ratios in TSM sampled in Genoa Gulf and Ligurian Sea.

Ratios	Genoa Gulf	Ligurian Sea	Ratio Genoa/Ligurian Sea
Fe:Cr	25.8	8.5	3.0
Fe:Ni	14.9	4.0	3.7
Fe:Cu	15.3	4.4	3.5
Fe:Cd	2578	277	9.3
Ni:Cr	2.6	2.1	1.2
Ni:Cu	1.4	1.1	1.3
Ni:Cd	210.2	69.6	3.0
Cr:Cu	1.2	0.5	2.3
Cr:Cd	203.4	32.5	6.3
Cu:Cd	261.8	63.6	4.1

and oxygen and AOU distribution is most interesting. In the superficial water of coastal origin (V0, C1 and V2), the higher content of some metals per gram of TSM has to be related to the higher content of organic active matter (Table IV). At depth and in the superficial waters at the offshore stations the active organic fraction decreases and, consequently, metal concentration per gram TSM, also.

CONCLUSIONS

Concluding, we believe that the chemical characteristics of total suspended matter are more conservative as an index of waters of coastal origin than the quantity of particulate matter or the metal concentrations. Further, the Fe:Cd ratio can be useful as an indicator of water mass of coastal origin. The vertical distribution of AOU indicates the degradation of organic matter in the water column and the relation between some heavy metals in particles and the percentage of active chlorophyll-a suggests that the phytoplankton population and the degradative action of heterotrophic organisms can play an important role in the distribution of heavy metals in the water column.

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