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Air-Sea Exchange: Sea Salt and Organic Microcomponents in Antarctic Snow

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AIR-SEA EXCHANGE: SEA SALT AND ORGANIC MICROCOMPONENTS IN ANTARCTIC SNOW

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A characterization of surface active fluorescent organic matter (SAFOM) in Antarctic snow is carried out. Its Fulvic Acids (FA) nature is confirmed. Its enrichment in the smallest aerosol particles is shown.

A tentative explanation of the presence of both natural and man-made organic microcomponents (SAFOMinteracting) is given in terms of marine aerosol transport. Their enrichment ratio appears of the same order as that of SAFOM, and their presence in the atmospheric particulate of marine origin supports the hypothesis on the transport of microcomponents in Antarctica "via marine aerosol".

KEY WORDS: Antarctic snow, air-sea interaction, marine aerosol, humic components, biogeochemical fractionation, pollutants.

INTRODUCTION

The long range transport of pollutants in remote areas via an "atmospheric path" is of increasing interest and so the object of many recent studies. The first results from the SEAREX project' evidenced the importance of the air-sea interaction in long range transport phenomena and showed how, for large areas, in the northern hemisphere the vapour phase appears to be the main state for most organics. These studies covered a vast area, including the Arctic and equatorial regions (Pacific Ocean)'. Evidence of long range transport of organic pollutants in Arctic regions, in the vapour state has also been shown recently²⁻⁴.

On the other hand, marine aerosol is now seen as one of the most important sources of atmospheric particles on a global scale^{1,5} that highly contributes to the nucleating phenomena of clouds and atmospheric precipitations^{δ}. **KY**

Theoretical^{7,8}, laboratory^{9,10} and field studies^{11–13} have shown that the surface active matter and all those components able to interact with surfactants (both of natural and synthetic origin), are involved in the marine microlayer, in aerosol formation and in transport processes. The enrichment of such matter can reach many orders of magnitude with respect to its concentration in marine bulk water 12.13 .

Antarctica, owing to its geographical situation, constitutes a site where the oceanic impact on the continent can be realized. Therefore, studies regarding the formation and transport phenomena of marine aerosol appear particularly attractive.

The evaluation of the organic matter as responsible for the association of other microcomponents in marine aerosol requires, in a first instance, an accurate analysis of its nature. The properties and the ability of the organic matter to distribute in particles of marine aerosol of different sizes must be studied in such conditions that the influence of other factors (i.e. mixing with aerosols of other nature and atmospheric chemistry effects) is reduced. These conditions are reached for rough sea with high coverage of whitecaps. Therefore, Antarctic salt storms¹⁴, together with marine snow precipitations, represent the most favourable conditions. As a consequence, coastal Antarctic snow collected at different heights above sea-level represents interesting sample.

In addition, the study of the transport of pollutants toward Antarctica appears very important to ascertain the increase of certain contaminants in the southern hemisphere. According to us, the organic matter present in marine aerosol could be an important vehicle. This last aspect, that up to now has been largely underestimated, will be particularly addressed in this paper.

In previous studies^{3,15-18}, we have shown that surface active fluorescent organic matter (SAFOM) associated to marine aerosol is present in Antarctic snow. Further confirmation of the large presence of SAFOM in snow (for a major part of fulvic acid nature) could give an explanation for the anomalous excess of minor components in the Antarctic marine aerosol. The organic microcomponents interaction with SAFOM is considered here.

First of all, we characterize the SAFOM present in the snow by analysing a large sample and we discuss it in connection with the characterization of the samples collected in previous campaigns. Second, we try to evaluate the enrichment of natural and anthropogenic organics in the aerosol, using the sea salt as internal reference, in order to compare organics enrichment in the aerosol with the enrichment found for the SAFOM. Our aim is to verify if the hypothesis of transport of these organics by marine aerosol is correct.

EXPERIMENTAL

Sampling sites of snow and marine water

In the 1991/92 Italian Antarctic Campaign the sampling site for the surface snow was Mt. Melbourne (Lat. **74"** 26 **S,** Long. **164' 45'** E) at 1130 **m** above sea-level. In the same campaign seawater was sampled in a coastal station named "Faraglioni" near the Italian base in Terra Nova Bay.

In the 1990/91 Italian Antarctic Campaign, coastal water samples were taken during a short cruise of the "Cariboo" oceanographic ship in Terra Nova Bay (January, 13 1991). The coordinates of the sampling sites are given elsewhere¹⁶.

Sampling and conservation technique

Snow. The surface snow (30 dm') was sampled by means of a Teflon blade. The present study included the analysis of a very large sample (60 dm') of surface snow

(5-8 cm depth) which should be referred to one of the last (spring/summer-beginning 1991) snow precipitations. The large sampling area could bring to an integration of the possible deposition differences of the surface marine salt that could occur in presence of a typical "salt storm" condition. The large sample permitted also further improvements in the treatment techniques employed for its final characterization.

Seawater. After the sampling, the water was stored in clean polyethylene containers and fast frozen to -70° C. The storage temperature was -30° C. The sampling and conservation techniques of the samples were described in detail in previous papers^{15.16}.

Procedures performed on the samples

On seawater and melted snow samples, we performed the non-foaming gas-bubble enrichment process as previously described¹⁵. This process mimics the first step of the natural aerosolization process taking place in the sea. As a result, we obtain two fractions: the enriched and the depleted fraction. The depleted fraction is given by the water remaining in the gas-bubble enrichment column after the process. This water is consequently "depleted" in its surface active components. The two fractions (enriched and depleted) and the untreated water, are then filtered in a Sartorius apparatus on a 0.45 um Nuclepore membrane.

Measurement techniques

The measurement techniques and apparatus have been described elsewhere $^{25,15-18}$.

Fluorescence spectra. Emission and synchronous spectra were scanned with a Perkin Elmer Fluorescence Spectrophotometer (mod. **LS-SOB).** The intensity values for the emission spectra were normalised using the formula¹⁹:

$$
I_n = I_{\text{max}}/I_{\text{Raman}} \times 100
$$

Where I_n denotes the normalised intensity, I_{max} the maximum intensity, I_{Raman} the Raman scattering peak intensity.

FT-lR. FT-IR spectra were recorded on freeze-dried sample as previously described'*. The IR apparatus was a Bio-Rad FTP 40-PC.

Dynamic surface tension. The surface dilatational and thermodynamic properties were evaluated by surface rheology measurements performed with the Time Resolved Surface Viscoelastometer (TRSV) apparatus as previously described 20,21 .

Weighing procedures. After the filtering operations. performed with a Nuclepore 0.45 μ m filter, the filter membranes were dried and then weighed under vacuum with a Cahn 2000 ultramicrobalance with the procedures described elsewhere¹⁵.

Turbidity. Turbidimeter (mod. 2100). Turbidimetric measurements were performed with a Hach Double Beam

Ion chromatography. The determination of C1 and Na concentration was performed by ion chromatography with the techniques described by Piccardi *et af. ²²*

Other parameters

From the dry mass data, the following parameters were calculated:

- *suspended matter concentration* (PM);

- *mass balance percent excess* (MB%) of the particulated matter, in non-foaming **gas**bubble enrichment process, which can be expressed as follows¹⁶:

 $MB\% = \{ [(PDM_{e} + PDM_{d}) - PDM_{unl}]/PDM_{unl} \} \times 100$

where PDM, denotes the *dry* mass (under vacuum at 20'C) of the particulated matter obtained by filtration of the enriched fraction of the sample, PDM, the *dry* mass of the particulated matter in the depleted fraction of the sample and PDM_{unt} the dry mass of the particulated matter in the untreated sample (all masses are referred to the whole fractions of the sample).

The *surJace rheological properties* were expressed by:

the limit surface elastic modulus $\varepsilon_0 = d\gamma/d\log\Gamma$,

where γ = surface tension, Γ = surface concentration excess; and the characteristic frequency $\omega_0 = (dc/d\Gamma)^2 D/2$, where $c =$ bulk concentration and $\dot{D} =$ diffusion coefficient.

From the fluorescence and C1 concentration data, the *enrichment ratio* (F,) with respect to the seawater (sw) composition was calculated. As pointed out elsewhere³, the enrichment ratio is expressed as: $F_r = (I_{n\text{ snow}}/Cl_{\text{snow}})/(In_{sw}/Cl_{sw}).$

RESULTS AND DISCUSSION

Characterization of the surface active fluorescent organic matter (SAFOM) present in Antarctic snow

Fluorescence spectra. Marine humic substances show (in the range 320-580 nm) an emission spectra characterised by a large fluorescence band (350–450 nm), when they are excited with near UV light (308 nm)²³. As the emission spectra show frequently very broad bands, in order to get further information, synchronous scan spectra^{24,23} are widely broad bands, in order to get further information, synchronous scan spectra^{24,23} are widely used. In Figure 1 are reported respectively the synchronous scan fluorescence spectra obtained with a $\Delta\lambda$ of 20 nm, for the marine Antarctic water, and for the enriched fraction of the melted snow. These spectra show similar features to those previously reported⁵²⁶.

Figure 1 Synchronous scan spectra of the enriched fraction of the snow sampled at Mt. Melbourne station, and of surface Antarctic seawater sampled in station 46 (campaign 1990-91).

FT-IR spectra. In Figure 2 are reported respectively (a) the infrared spectra of marine fulvic acids (FA) extracted from the above reported sea surface water, and (b) the infrared spectra of the enriched melted snow after lyophilization. Because the lyophilization was done on the gas-bubble enriched fraction^{15.16}, a substantially larger mass of organic matter with respect to the saline component was obtained in the samples. In this case, the interference of SO_4^{2-} is lower than that in the previous spectra¹⁷.

The comparison is done between a class of extracted compounds (FA) and the enriched fraction of all those organic substances, present in the snow, which include fatty acids and lipids in general (collected and selected principally because of their surfactant properties and molecular weight). Notwithstanding these limitations, the similarity appears well pronounced also for IR spectra. This strongly suggests the fulvic acid nature for a large part of the organics in the present sample, selected by the non-foaming gasbubble extraction process²⁷. The extraction and the separation of FA on a large sample (about 1 m³) of Antarctic snow, collected during the 1993–94 campaign²⁶, confirm the above reported findings.

From the inspection of the IR spectra reported in Figure 2, independently from the interference of the SO₄² group, we cannot exclude the presence, in the enriched melted snow, of other surface active components which can have important additional role in the interaction and transport via "marine aerosol" of some particular components.

Figure 2 enriched and lyophilised melted snow (same campaign) (b). IR spectra of marine FA extracted from Antarctic surface seawater (campaign 1990-91) (a);

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Characteristics of SAFOM and physico-chemical properties of natural samples

As reported by Chester²⁸, the microlayer at the air-seawater interface can be considered as a "soup" of many components in the largest part constituted of humic substances, polysaccharides, fatty acids, and their esters.

In the following, we will provide some data to facilitate the comparison of the SAFOM contained in seawater and in snow sampled in different campaigns. In Table 1 are reported the physico-chemical parameters of the large snow sample (1991-92 Antarctic campaign) together with those of the samples which were considered in other previous Antarctic campaigns 5,15,16 .</sup>

In Table 2 are reported the mean values of the same parameters for sea surface water collected in 1990/91 both in a coastal station (6 samples), and during the "Cariboo" cruise in Terra Nova Bay (6 samples).

Surface active nature of organic matter in natural samples. MacIntyre²⁹ and Bock and Frew 30 suggest that the surface dilatational properties appear the most significant parameter for the physico-chemical characterization of surface active matter in seawater. As noted previously¹⁵, surface dilatational properties could be able to characterise wet and dry surfactants. Taking into account the complex composition of SAFOM, Table 1 evidences, in particular for sample **4** (1991-92), the presence of surfactants as it results from ε_0 and ω_0 values. Moreover, for sample 4 the fitting of the experimental values of

Parameter	Camp. 1988-89 snow $1130 m$ above sea-level	Camp. 1990-91 snow $1130 m$ above sea-level	Camp. 1990-91 snow $200 \, \text{m}$ above sea-level	Camp. 1991-92 snow $1130 m$ above sea-level
	Φ	(2)	ω	⊛
Turbidity-NTU \pm 1%	0.05	0.05	1.90	0.24
P.M. conc. mg.dm ⁻³ \pm 1%	0.073	0.14	1.85	0.37
$MB\% \pm 10\%$	$+91$	$+62$	-42	-23
$I_{\parallel} \pm 2\%$ (filtered)	traces	6.1	3.7	11.1
ε_0 mNm ⁻¹ ± 8%	0.2	21.0	21.5	20.7
ω_{0} Hz \pm 3%	n.d.	49×10^{-4}	51×10^{-4}	35.5×10^{-3}
Cl conc. mg.dm ⁻³ \pm 1%	1.06	2.5	14.2	9.5

Table 1 Physico-chemical properties of Antarctic melted snow (1988-1989. 1990-1991 and 1991-1992 campaigns)

Sample Φ , Φ and Φ = snow, Station Mt. Melbourne (Lat. 74° 26' S, Long 164° 45' E) at 1130 m above sea**level, Sample** *0* = **snow, Station Carezza Lake (Lat. 74' 43' S, Long 164' 01' E) about 200 m above sea-level.**

Table 2 Mean values of physico-chemical properties referred to six samples of Antarctic surface seawater (**1990-91 campaign).**

Parameter	Mean	St. dev.	Ν
Turbidity-NTU \pm 1%	0.38	0.40	12
P.M. conc. mg.dm ⁻³ \pm 1%	1.05	0.67	17
$I_n \pm 2\%$	29.75	11.34	17
ϵ_0 mNm ⁻¹ ± 8%	72.67	21.83	12
ω , Hz $\pm 3\%$	4.81×10^{-2}	4.75×10^{-2}	12

dilatational surface modulus to the diffusional model indicates the wet character of soluble surfactants, in agreement with the prevalent humic nature of the SAFOM. This aspect is reinforced by the large ω_0 value $(\omega_0 = 0$ is the characteristic frequency for an insoluble film).

Particulated matter (PM) and mass balance (MB%). Owing to the involvement of colloidal organic matter in the marine aerosol formation^{15,16}, the MB% information constitutes an interesting characterization parameter, utilised here for the first time for Antarctic snow. Referring to sample **4** (Table 1) it can be seen that the values of particulate matter, turbidity and In_0 are the highest with respect to samples 1 and 2. The interpretation of these data must be given in terms of seasonality, intensity and duration of meteorological events. In this respect, the snow sample **4** is probably referred to a "salt storm" event of stronger intensity than those occurring in samples 1 and 2. A more intense "salt storm" with higher winds could have transported particles of larger size at 1130 m above sea-level. Therefore, the negative mass balance excess (MB%) obtained in the non-foaming gas-bubble enrichment process should indicate that the sample was subjected to a lower oxidating UV action¹⁶ as a consequence of the larger particle dimensions. This hypothesis is in agreement with the previous interpretation' given for sample 3 on the fluorescence enrichment and its negative MB%¹⁸. We may also observe that this finding is in line with particulated matter selection predicted according to the proposed models of MacIntyre and Blanchard^{7,8} for the particles of greater dimensions.

Parameters related with transport phenomena: the fluorescent surfactants enrichment

The enrichment ratio F_r of SAFOM for sample 4 (Table 1) was found to be 1.3×10^{-3} . The In_{sw} of reference was taken the mean value of the seawater samples in all our campaigns (1987–88, 1988–89, 1990–91) which resulted $In_{sw} = 10.9$.

A number of studies have been reported in the literature which show experimentally that the ratio OM/Na increase with the dimensional lowering of the marine aerosol particles. We would like to stress the fact that the SAFOM amount increases with the decrease of the particle diameter, as suggested by the literature for the OM/Na, of which SAFOM makes a major part.

Hoffman and Duce³¹ showed that about 80% of the particulated organic carbon (POC) was present in particles smaller than $2 \mu m$. Barker and Zetlin³² found the highest OM concentration in the smallest sampled particles. We also recently have found similar behaviour for the surfactant fluorescent matter (SAFOM) in samples collected at our meteomarine station in Leghorn (Tyrrhenian sea coast). We report here the samples collected in Leghorn for two reasons. First, the amount of material we have collected for any sampling operation in Antarctica, was not enough to make a comparison between different samples collected in particular weather conditions for different known particles dimensions. Second, we can consider the dependence of the SAFOM amount on the particles diameter during the enrichment and the aerosolization processes, as well as during the long range transport phenomena.

In Figure 3a are reported typical results for a marine aerosol integrated sample, sampled in rough sea conditions, with inland winds $(185^{\circ}-270^{\circ})$ direction and speed $>$ 6 *ds).* An Andersen high volume sampler MP lo00 equipped with a Sierra 235 five stage impactor used in the standard flux, piloted with an intelligent meteorological trigger³³ permitted to reach a final volume of 12700 dm^3 comprehensive of many stormy events. Above each histogram column the Na concentrations, are reported, for the corresponding particle dimension. In Figure 3b are reported the corresponding **F,** vs.

Figure 3a Histogram of the fluorescence intensity of SAFOM **per** unit volume **vs.** particle diameter for the Leghorn aerosol sample. Above each column are reported the Na concentrations of the aerosol.

Figure 3b Enrichment ratio F, of SAFOM vs. particle dimensions for the same sample.

particle diameter values, referred to the mean fluorescence intensity of the seawater samples collected in the same period.

These results, in first instance, evidence for the SAFOM a well defined increase, with the dimensional decrease of the aerosol particles. Therefore, they reinforce the interpretation on our previous findings on Antarctic snow SAFOM F_r^5 in terms of the dimensional selection of the particles due to the altitude effect. They also appear in agreement with our hypothesis that, for our last Antarctic snow sample, a strongest salt storm, should be responsible of particles injection with higher size particles. No direct comparison with Fr of Leghorn SAFOM with that present in Antarctic snow is possible, because the complex mixtures of components that form the adsorption microlayer of the two places are expected different. A further interpretation of the increasing SAFOM Fr with the dimensional lowering of particles will be reported in a work in preparation.

It is necessary here to recall the characteristics of humic substances and the characteristics of the sea microlayer" which are strictly correlated to some aspects of the aerosolization process 7.8 .

As reported by Hunter and Liss³⁴ the dissolved organic carbon (DOC) in seawater is a fraction up to 20% of the total organic carbon (TOC) and consists for the most part, of surface active species much as planctonic lipids and proteinaceous materials. Stuemer and Harvey³⁵ isolated the humic substances from marine water and concluded that they constitute the most important contributor of film forming substances at the air-sea interface. Therefore, the air-sea interface -i.e. the marine microlayer- and the new interface originated by the breaking waves events, undergo an enrichment of the above mentioned "soup" of SAFOM²⁸, together with interacting microcomponents as natural and synthetic organic compounds, transition metals, and microorganisms', both in the dissolved and in the aggregate state³⁶. The whole phenomena are well represented by the proposed scheme of Lion and Leckie 36 .

Transport of organic microcomponents into the snow

In a previous work¹⁰, it was evidenced the transport of many natural and synthetic organic components, with aerosolization experiments in laboratory, both on artificial and natural seawater samples. The presence in dissolved state of SAFOM was always detected together with other organics transferred from seawater to air. The presence of particulated matter depressed the transfer efficiency. Moreover, for some organics the partition between bulk water, aerosol spray, and surrounding atmosphere, subsequent to the non-foaming gas-bubble process, was evaluated in relation with their vapour pressure.

Desideri *et a1.37-39* reported the concentration of many classes of natural and anthropogenic organic compounds in surface Antarctic water, ice pack and coastal snow.

The question arises if the organic products are present in Antarctic snow as a result of direct transport together with marine aerosol or of their vapour scavenging from the atmosphere by the snow precipitations.

Transport of organics in Antarctic snow. To check this point we evaluated the enrichment ratio F, for four typical products. The selection of the organic compounds was done considering both natural and anthropogenic materials and their behaviour with respect to their surface physico-chemical properties and to their interactions with fulvic acids. Three stations were considered in two different campaigns, respectively: campaign 1987-88 for the Campbell Glacier (920 m above sea-level) and Mt. Crummer (900 m above sea-level) stations'*; and campaign **1990-91** for Mt. Melbourne (1 130 m above sea-level) station. The concentrations of the considered organic compounds in surface seawater were referred to the same campaign for the first two stations³⁸. For the Mt. Melbourne station the enrichments on the snow samples were calculated, in a first approximation, referring to the concentration of the same compounds in seawater sampled in the 1988-89 campaign by the same authors³⁹. The average values of Cl seawater concentration are taken from the literature⁴⁰.

In Tables 3a and 3b are reported the concentrations both in the melted snow and in the surface seawater for the above mentioned stations. In Table 3c are reported the enrichment ratios **F,** as previously defined. Notwithstanding, the above mentioned limitations, the mean values for the snow sampled in the two campaigns appear consistent with those expected for organics interacting with marine aerosol, and with the SAFOM **F,** found in Antarctic snow.

(a)				
	Mt. Crummer 900 m above sea-level	Campbell Glacier 920 m above sea-level	Seawater mean values 1987–88	
(1) C-31	b.d.l.	56	3.30	
(2) Squalene				
(3) Di-iso-butyl-phthalate	102	126	203	
(4) Bis-2-ethyl-hexyl-phthalate	b.d.l.	88	129	
Chlorine (Piccardi et al.) ²²	7.36×10^{5}	1.73×10^{6}	1.98×10^{10}	

Table 3 Concentrations and enrichment ratios (F,) of selected organics in Antarctic snow and seawater (in ng/dm³) (from the data of Desideri *et al.*^{37,38})

 $\overline{1}$

b.d.1.-Below detection limits

The presence of anthropogenic components in Antarctic aerosol of marine origin. The recent finding on the Antarctic atmospheric particulates collected by Ciccioli et al.⁴¹ show that samples collected prevalently from marine air masses are particularly enriched in organics, including phthalates, that, for their physico-chemical properties, are well involved in the process of marine aerosol formation¹⁰. The authors evidence that many of synthetic organics found in their atmospheric particulate samples are the same as those found in marine Antarctic water, ice pack, and $slow^{37-39}$. Taking into account the predicted interactions of these compound with humic substances, and their F, values found in the snow, these results further support the hypothesis that during the "salt storms", many organic compounds present in surface seawater are associated to marine aerosol, both as a result of their surface properties and of their interaction with SAFOM. Therefore, a large part of those synthetic organic compounds found by Desideri *et al.*³⁹ in Antarctic snow should be prevalently associated with the marine aerosol transport, as also our recent laboratory experiments showed".

These results could be considered of particular relevance because they are referred to the Antarctic summer period in which the maximum concentration at the vapour state of organic compounds is to be expected.

CONCLUDING REMARKS

The presence in Antarctic snow of fluorescent surface active matter of marine origin is confirmed. The fulvic acids (FA) nature of this matter reinforces its role in the transport phenomena via "marine aerosol" in Antarctica.

The presence of some organic pollutants in Antarctic snow could therefore be explained in terms of transport via this "marine aerosol". The support to this last conclusion is given by the enrichment ratio values here reported, in agreement with those found by measurements of surface active fluorescent organic matter (SAFOM) of fulvic acid nature in Antarctic snow at similar altitude on the sea-level and laboratory experiments following the marine aerosol formation models of MacIntyre and Blanchard.

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References

- I. **R. A. Duce, in:** *Chemical Oceanography* **(J. P. Riley and R. Chester, eds.. Academic Press, London N.Y., Vol. 10, 1989) pp. 1-14.**
- **2. M. Oehme and S.** Man@, *Fresenius Z. Anal. Chem.,* **319, 141-146 (1984).**
- **3. J. M. Pacyna and M. Oehme,** *Afmos. Environ.,* **22.243-257 (1988).**
- **4. M. Oehme,** *Ambio,* **20.293-297 (1991).**
- *5.* **R. Chi, N. Degli Innocenti,** *G.* **Loglio,** *G.* **Orlandi, A. M. Stortini and U. Tesei,** *Intern. J. Environ. Anal. Chem.,* **55,285-296 (1994).**
- **6. D. C. Blanchard and A. H. Woodcock,** *Tellus,* **9, 145-158 (1957).**
- **7. F. MacIntyre,** *J. Geophys. Res..* **77,521 1-5228 (1972).**
- 8. D. Blanchard, Adv. Chem. *Ser.,* **145,360 (1975).**
- **9.** E. **J.** Hoffman and R. Duce, *J.* Geophys. Rex, **81,3667-3669 (1976).**
- 10. R. Cini, P. G. Desideri and L. Lepri, Anal. Chim. Acta, **291, 329-340 (1994).**
- **^I1.** E. J. Hoffman and R. Duce, *J.* Geophys. Res.. **79.4474-4477 (1974).**
- **12. F.** C. Cattel and W. D. Scott, *Science.* **20,429430 (1978).**
- **13.** R. Chi, C. Oppo. **S.** Bellandi, G. Loglio, N. Degli Innocenti, A. M. Stortini, E. Schiavuta, **U.** Tesei. G. Orlandi and F. Pantani, In: Arti del I' *Simposio* Nazionale sulle "Strategie e Tecniche di Monitoraggio sull'Atmosfera", Roma *20-22 settembre 1993* (P. Ciccioli ed., SCI, Rome, **1993)** pp. **168-175.**
- **14.** G. **E.** Shaw, Rev. Geophys., **26,86-112 (1988).**
- **15.** G. Loglio, N. Degli Innocenti. **U.** Tesei, A. M. Stortini and R. Cini, Ann. Chim. (Rome), **79, 571-587** (**1989).**
- **16.** G. Loglio, N. Degli Innocenti, A. M. Stortini, G. Orlandi. **U.** Tesei, P. Mittner and R. Cini, Ann. *Chim.* (Rome), **81,453467 (1991).**
- **17.** R. Cini, N. Degli Innocenti, G. Loglio. **P.** Mittner, A. M. Stortini and **U.** Tesei, In: *IV* Workshop of Italian Research *on* Antarctic Atmosphere (M. Colacino, G. Giovanelli and L. Stefanutti eds., SIF, Bologna, **1992)** Conference Proceedings Vol. **35** pp. **191-203.**
- **18.** R. Cini, N. Degli Innocenti, G. Loglio. A. M. Stortini and **U.** Tesei, In: *V* Workshop *of* Italian Research *on* Antarctic Atmosphere (M. Colacino, G. Giovanelli and L. Stefanutti eds., SIF, Bologna, **1994)** Conference Proceedings Vol. **36** pp. **193-206.**
- **19.** G. Nyquist. "Investigation of some optical properties of seawater with special reference to lignin sulphonates and humic substances". PhD. Thesis, Marine and Analytical Chemistry Dept., Göteborg University **(1979).**
- **20.** G. Loglio, **U.** Tesei and R. Cini, Rev. Sci. Instr., **59,2045-2050 (1988).**
- **21.** G. Loglio, **U.** Tesei and R. Cini, Boll. Oceanolog. Teor. Appl., **4,91-96 (1986).**
- **22.** G. Piccardi, R. Udisti and E. Barbolani, Ann. Chim. (Rome), **79,701-702 (1989).**
- **23.** T. M. Miano, G. Sposito and J. P. Martin. Soil Sci. Soc. Am. *J.,* **52, 1016-1019 (1988).**
- **24.** Tuan Vo-Dinh,Anal. Chem.. **50,396401 (1978).**
- **25. J.** B. **F.** Lloyd, Nature (London), **231.64 (1971).**
- **26.** R. Chi. **B.** M. Petronio. N. Degli Innocenti, A. M. Stortini. C. Braguglia and N. Calace. Ann. Chim. (Roma). **84,424429 (1994).**
- **27.** G. Loglio, **U.** Tesei, **P.** Cellini Legittimo, E. Racanelli and R. Cini, Ann. Chim. (Rome), **71. 251-262 (1981).**
- **28.** R. Chester, Marine Geochemistry (Unvin Hyman Ltd. Boston Sydney Wellington, **1990).** p. **125-129.**
- **29.** F. Maclntyre, J. Recherche Atmospherique, **8.5 15** (I **974).**
- **30.** E. **J.** Bock and N. M. Frew, *J.* Geophys. Res.. **98(C8), 14.599-14.617 (1993).**
- **3 I. E. J.** Hoffman and R. Duce, *J.* Geophys. Res. *Lett..* **4.449452 (1977).**
- **32.** D. R. Barker and H. Zetlin, *J.* Geophys. Res., **77,5076-5086 (1972).**
- **33.** E. Schiavuta. **P.** Mittner and R. Chi, Workshop *I1* Monitoraggio Automatico dell'Inquinamento Marino" CNR-SCI-Taranto *9-10* Aprile *1992.* (N. Cardellicchio and F. Dell'Erba eds., SCI-CNR, **1992).** pp. **3 13-330.**
- **34. K.** A. Hunter and P. *S.* Liss, In: Marine Organic Chemistry (E. **K.** Duursma, L. R. Dawson eds.), Elsevier **Publ.,** Amsterdam, pp. **259-298 (1981).**
- **35.** D. Stuermer and G. Harvey, Deep-sea Res., **24.303-309 (1977).**
- **36.** L. W Lion and J. 0. kckie, Environ, *Ceol.,* **3.293-314,** (1981).
- **37. P.** G. Desideri, L. Lepri, L. Checchini and D. Santianni. *Intern. J.* Environ. An. Chem., **55,3346 (1994).**
- **38.** P. G. Desideri. L. kpri and L. Checchini, Ann. Chim. (Rome), **79.589-605 (1989).**
- **39. P.** G. Desideri, L. Lepri and L. Checchini,Ann. Chim. (Rome), **81,295416 (1991).**
- 40. Chemical Oceanography **(J. P.** Riley and G. Skirrow. eds.. Academic Press. London N. **Y.,** Vol. **1, 1975)** p. *558.*
- **41.** P. Ciccioli, **A.** Cecinato, E. Brancaleoni, M. Montagnoli and I. Allegrini, Intern. *J.* Environ. Anal. Chem.. **55.47-59 (1994).**