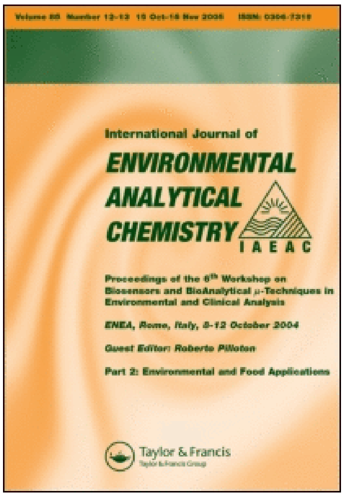

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Spectrofluorimetric Evidence of the Transport of Marine Organic Matter in Antarctic Snow Via Air-Sea Interaction

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SPECTROFLUORIMETRIC EVIDENCE OF THE TRANSPORT OF MARINE ORGANIC MATTER IN ANTARCTIC SNOW VIA AIR-SEA INTERACTION

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This paper considers the importance of marine aerosol in the atmosphere. As a consequence of its peculiar generation mechanism, it is also considered as a possible contributor to the transport of man-made microcomponents via air-sea interaction, especially in remote sites.

In view of future marine aerosol studies, the dominant presence of marine aerosol components in coastal Antarctic snow is discussed. the presence of fluorescent marine organic matter in Antarctic snow is shown. Its "marum" nature is evidenced.

We give a tentative interpretation of the experimental data, and make a hypothesis concerning the variations in marine aerosol composition in correspondence to various altitudes.

KEY WORDS: Aerosol transport, marine aerosol, dynamic surface tension, Antarctic snow fluorescence, marum.

INTRODUCTION

The amount of matter involved in exchange processes due to the dynamic air-sea interaction is very large on a global scale. About 9000–10000 Tg/y[1] of marine aerosol is injected into the earth atmosphere, principally by means of whitecap formation[1,2].

According to the most recent calculations, the annual flux of sea salt is estimated to be about 10000–30000 Tg/y[3].

By comparing this quantity with the total amount of particles produced by synthetic and other natural sources, as estimated by Prospero[4], it is immediately apparent that marine particles play the most important role in the complete aerosol transport phenomena, especially in the presence of particular geophysical conditions.

This appears to be the case of the Antarctica coasts.

Recently, Shaw[5] evidenced the presence of marine aerosol as the principal micro component carrier in Antarctic snow, and showed that during "salt storms" it is particularly abundant; in fact, it was estimated that the contribution of the non-marine aerosol species to the material collected in Antarctic snow is only 5%. The term "Salt Storms" designates perturbed weather conditions with high whitecap coverage on the Antarctic ocean, and with inland winds on the Antarctic coasts.

The presence of marine aerosol components in the snow can be due to:

i) the scavenging effect of snow precipitation.
ii) the nucleation phenomena induced by marine aerosol particles in snow formation;

and

iii) the dry marine aerosol fallout onto deposited snow.

There is now also a general agreement[6] on the presence of organic components in marine aerosol which, as soluble components, can constitute some percentage of the total mass in the fine particles fraction[7].

In some of our previous works[8,9] we used a laboratory procedure which mimics the most important steps of natural aerosol formation during rough sea conditions [10] to study the process of marine aerosol formation.

In these experiments we evidenced the role played by surfactant matter (both natural and man made) in the enrichment process of many microcomponents during the formation of marine aerosol.

Using our laboratory experiments we also evidenced[10] that the fluorescent organic components of marine water were enriched in the aerosolization process; these results were confirmed by our findings on natural marine aerosol samples collected in our meteomarine station[12] on the Tyrrhenian coast.

The fluorescence of the organic matter was similar to that of the humic substances extracted from seawater.

The study of the presence of humic organic matter in Antarctic snow is important for various reasons:

1) its contribution to the knowledge of the organic carbon cycle in the coastal Antarctic environment.
2) to provide a better understanding of the transport mechanism of many microcomponents via air-sea interactions. In fact, both organic and inorganic, natural and man-made microcomponents show strong interacting power with humic components[13].
3) the research concerning the role of humic components in photochemical processes[14].

In previous works[15], we showed for the first time the presence of fluorescent organic matter in the Antarctic snow.

Here, we report further experiments on the presence of humic origin organic matter in Antarctic snow through its characterization by means of physico-chemical processes and parameters. We chose this type of characterization on the basis of the high structural complexity of organic marine matter[14] and its partition between soluble and insoluble fractions.

Fluorescence spectra, turbidity, and surface thermodynamic quantities were considered together with the detection of the most important reference ion species of marine aerosol. The mass balance of particulated matter involved in the enrichment process on the melted snow, considered in our previous papers[9,10], will be the subject of a subsequent work.

EXPERIMENTAL

The height distribution of marine aerosol mainly depends on wind speed, particle dimensions, and on path length[16].

Taking into account the marine aerosol generation mechanism[17,18], we can deduce that the particles having the lowest mass are those expected to show the highest enrichment in organic surfactant matter, especially in the case of soluble components.

In very rough sea conditions, which occur during a "salt storm", large quantities of both small and giant particles are generated, which, after appreciable aerial paths[16], are selectively distributed in height from the sea surface. In particular, the giant particles are preferentially distributed at lower altitudes over the sea surface, and for this reason their average lifetimes, and consequently their aerial paths, are shorter. This is the case of the Antarctic coast due to the ice pack present in winter and spring, which are the periods of the highest frequency for "salt storms".

Therefore the highest relative concentration of soluble organic matter in respect to the sea salt is most probable at the highest altitudes.

For these reasons, two sampling sites at different heights were selected at Terra Nova Bay.

Sampling sites

The sampling sites were the following: Mt. Melbourne station (Lat. 74° 26′S–Long. 164° 45′E) at 1130 m above the sea level; Carezza Lake station (Lat. 74° 43′S–Long. 164° 01′E) at 200 m above the sea level.

Sampling and conservation techniques

Surface snow (5–7 cm depth) was sampled by means of a Teflon blade with great care to avoid any contamination from the operator. A volume of about 30 dm^3 was collected for each sample.

The firn sample was collected by means of a drill, which sampled many ice cores, each about 10 cm in diameter and 5–7 cm in depth (about 35 samples collected in a restricted area). The sampled snow was stored in polyethylene containers, previously washed with hydrochloric acid and subsequently treated with water vapor. Then, the snow was stored at −30°C until its arrival in our Florence laboratory. The firn was stored in polyethylene cylinders; the storing procedures were the same as those for the snow.

Samples treatment techniques

a) **melting procedure**: the snow was transferred from the polyethylene container to a large Pyrex vessel, previously washed with hydrochloric acid, ultra pure water and water vapor. The transfer was effected under a laminar flux of filtered air. Then, the snow was melted by immersing the bottle in a thermostatic bath at 21° ± 0.5C

Each short firn core was purified on the surface by partial melting induced by infrared irradiation with contemporaneous rapid rotation of the firn cylinder. Then each piece of firn was melted in a large vessel under laminar flux of purified air with the same procedure of the snow. The final melted firn sample resulted about 12 dm^3.

b) **enrichment process of organic material**: the organic material present in marine aerosol is usually a fraction[19,20,21] of the total marine aerosol mass. In Antarctic snow the marine salt concentration doesn't exceed a few milligrams for cubic decimetre[22]in the studied stations at Terra Nova Bay. Therefore if organic matter is present, its concentration is very low in particular for the soluble surfactant fraction[19,9]. This findings suggest that a previous enrichment is necessary in order to detect organic matter. The non foaming gas bubble enrichment process [23] was used in consequence of these advantages:

1) it mimicks the first step of the natural selective enrichment taking place during the marine aerosol formation under rough sea conditions, according to the Resch model for a breaking wave[2].
2) this process shows the highest efficiency for the lowest surfactant concentrations[24].
3) this process, as a consequence of the above peculiarities, is particularly useful for increasing the concentration of those components present in the melted snow which were previously selected by the natural marine aerosolization process.

Filtered highly pure nitrogen was used as a gas bubble dispersion medium in the enrichment column[23].

Physico-chemical parameters

Dynamic surface tension If organic matter is present in marine aerosol, surfactants must also be present[18,6]. MacIntyre[18]suggests that the surface dilatational properties appear the most correct quantities for the physico chemical characterization of surfactant matter in sea water. The surface dilatational properties and thermodynamic quantities were evaluated by dynamic surface tension measurements (DST)[25,26,27] performed with the Time Resolved Surface Viscoelastometer (TRSV) apparatus as previously described[27,28].

Fluorescence spectra The "marum" i.e. the marine humic substances present in all marine waters which constitute a large class of wet surfactants[18], shows (in the range 320–597 nm) emission spectra characterized by a large fluorescence band (350–450 nm), when excited with near UV light (308 nm)[29] having a maximum in intensity approximately at 440 ± 20 nm (depending on natural characteristics and molecular weight). The spectrofluorimetric measurements were carried out with Perkin Elmer Fluorescence Spectrophotometers mod. MPF 44A and LS-50. The latter being computer controlled. The spectra obtained with the first apparatus were corrected by means of a "Differential Corrected Spectra Unit" using the procedure described in the reference manual. The intensity values were normalized using the formula[30].

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

where I_n denotes the normalized intensity, $I_{max.}$ the maximum intensity, I_{Raman} the Raman scattering peak intensity.

All the sample examined, except the fulvic acid solutions, were previously filtered through a Nuclepore membrane (pore diameter 0.45 μm).

Turbidity Although there isn't a direct relation[31] between turbidity and the concentration of suspended matter, this parameter can be used as an additional source of information about the variation of partition on particulated matter involved in the non foaming gas-bubble enrichment process.

Turbidimetric measurements were effected with a Hach Double Beam Turbidimeter mod. 2100.

The turbidity, expressed in Nephelometric Turbidity Units (NTU) was also measured for determining the filtered volumes in order to have approximately the same "impactation charge" for each filtering operation of particulated matter on Nuclepore membrane. This last caution was also taken to achieve the best conditions for PIXE elemental analysis of the collected particulated matter[32].

Ionic chromatography Determination of Cl – Na + concentrations was performed by ionic chromatography with the techniques described by Piccardi[22].

RESULT AND DISCUSSIONS

Evidence of surfactant and fluorescent matter

In Table 1, the data of two snow samples and those of a firn sample collected at Mt. Melbourne and Carezza Lake Station during the campaign 1989/1990 are reported: (Sample 1) fresh surface snow sample, Mt. Melbourne Station, (Sample 2) firn sample, Mt. Melbourne Station; and (Sample 3) snow sample, Carezza Lake Station.

The parameters reported in Table 1 are:

The turbidity in NTU, the normalized fluorescence In; the limiting surface elastic modulus ε_0 given by: $\varepsilon_0 = - d\gamma/d \ln\Gamma$, where γ = surface tension, Γ = excess surface

Table 1 Melted Antarctic Snow (1990–1991 campaign) and Firn (1988–1989 campaign). Sample 1 = Snow—station Mt. Melbourne (Lat. 74° 26′S, Long. 164° 45′E) at 1130 m above the sea level. Sample 2 = Snow—station Carezza Lake (Lat. 74° 43′S, Long. 164° 01′E) at about 200 m above the sea level. Sample 3 = Firn—station Mt. Melbourne (Lat. 74° 26′S, Long. 164° 45′E) at about 1130 m above the sea level.

Treatment	*Turbidity NTU*	I_n ±2%	ε_0 $mN.m^{-1}$ ±8%	ω_0 $Hz.10^{-4}$ ±3%	χ^2	*Cl− mg.dm*$^{-3}$
Sample 1						
Untreated	0.05	6.1	19.9	2.57	2.57	2.5
Depleted	0.11	4.2				-
Enriched	0.32	17.2	17.4	2.94	0.28	-
Sample 2						
Untreated	1.90	3.7	17.3	2.13	2.57	14.02
Depleted	1.39	17.5				-
Enriched	2.80	38.0	30.8	2.34	2.57	-
Sample 3						
Untreated	0.28	5.9	27.0	0.72	0.28	2.01
Depleted	0.11	8.1				-
Enriched	1.01	34.0	23.9	22.7	2.57	-

concentration; the characteristic frequency given by $\omega_0 = (dc/d\Gamma)^2 \times D/2$, where c = bulk concentration and D = diffusion coefficient); the Cl – ion concentration in the melted samples.

This last parameter was taken as an index of the marine aerosol concentration assuming that the amount of Cl – found is the same of that contained in marine aerosol immediately after its formation.

This assumption appears to be valid because the enrichment factor of Cl– in respect to Na+ evaluated by other researchers [22] in snow samples taken at the same stations, is very close to 1. The choice of Cl – concentration as a reference allows us to use the reference values used in other laboratory and field experiments.

The agreement of Cl – /Na + with that of marine water indicates that the marine aerosol trapped in our snow samples is not appreciably subject to the action of sulphuric acid, which is formed in the high Antarctic atmosphere, principally as a consequence of Antarctic coastal DMS (dimethylsulfonic acid) production[33].

Therefore, the photochemical effect should also be limited, at least on the organic components of the aerosol.

From the above reported data, the most evident results are:

I—The abundant presence of surfactants in all the studied samples. This evidence is given by:

a) the ε_0 values;
b) the increase of fluorescence in the enriched fraction;
c) the increase of turbidity in the enriched fraction in all three fractions of each sample;
d) the flotation of particulated matter.

II—The presence in the melted snow of fluorescent matter having fluorescence behaviour similar to that of marine humic substances involved in the non foaming gas

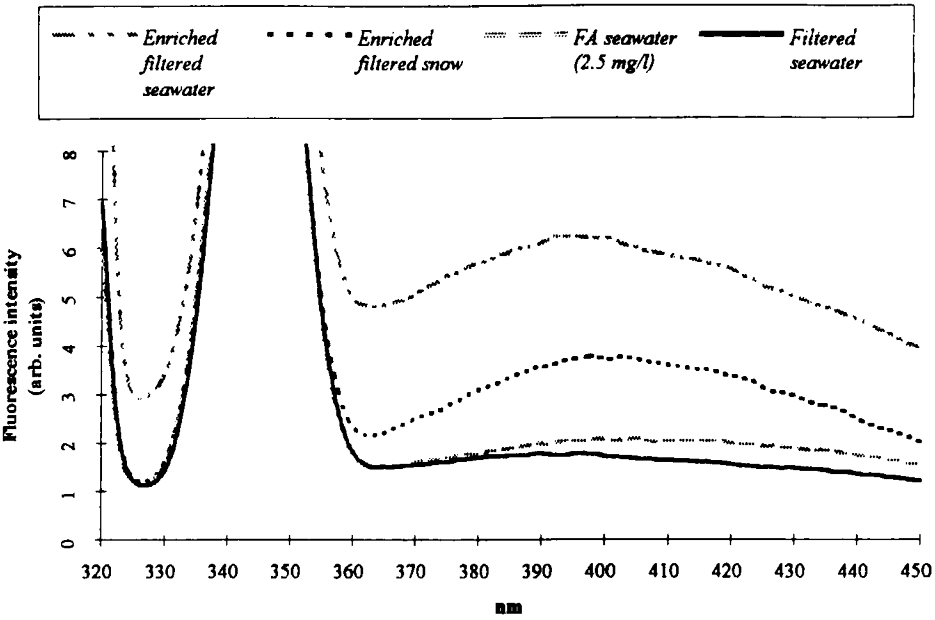

Figure 1 Comparison of snow, seawater and fulvic acids emission spectra.

bubble enrichment and aerosol production processes of Antarctic seawater[9,10,11].

Regarding point I, the quality of the fitting between the experimental values of dilatational quantities and those predicted by the diffusional model, also evaluated from the chi square[25] executed on 15 values, indicate the wet character[18]of the soluble surfactants present both in melted snow and firn.

Estimations of the fluorescent component enrichment

With respect to the fluorescence of the studied sample (point II), Figure 1 reports: I) the typical fluorescence emission spectrum obtained from the marine humic substances (fulvic components) extracted from Antarctic Ross Sea water (coordinates 74° 38′9 Lat S and 167° 14′69 Long E), structurally characterized by Campanella [34], dissolved in artificial seawater according to the Fleming composition; II) the enriched fraction of Antarctic seawater: III) the fluorescence emission spectrum of the enriched fraction of a snow sample. The similarity is evident. All of the solutions, except for those of purified fulvics, were previously filtered on 0.45 µm Nuclepore membrane. It was not possible to carry out the enrichment process on the fulvic acid (FA) solution as well, due to the low amounts extracted.

In Figure 2 we report the calibration curve of normalized intensity (I_n) vs. the concentration of the fulvic components extracted from the Antarctic marine water. It can be seen that there is a linear relationship between I_n and concentration (r = 0.98,

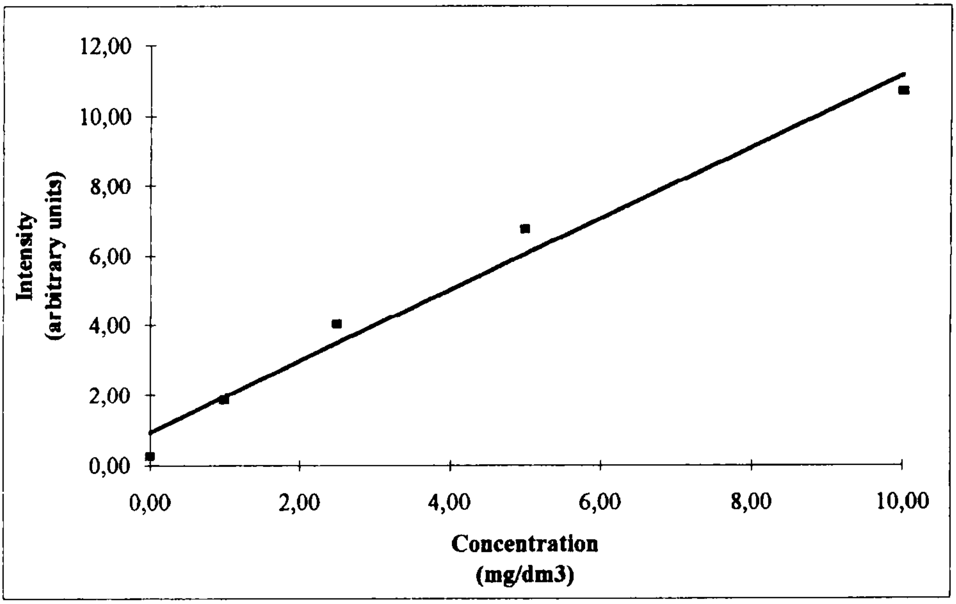

Figure 2 Plot of maximum fluorescence emission intensity vs. concentration of fulvic acids. ■ Experimental data point - — Linear regression curve (r = 0.98).

n = 5) in the considered range. This allows us to make an estimation of the amount of humic component in the marine aerosol trapped in the snow.

As previously stated Cl – can be taken here as a quantitative index of marine aerosol concentration in the snow. The normalized fluorescence intensities, In_{snow} and In_{firn} in untreated samples are, as a mean value, 6.0.

The mean value I_n for untreated filtered fraction[12] calculated from all of the values of seawater samples collected in three Antarctic campaigns (twenty-five samples) is $I_n = 10.4$ i.e. not significantly different from the main value of untreated snow and firn in Mt. Melbourne samples. Therefore, a linear correlation of I_n with the relative concentration can be accepted. The comparison of the two ratios $In_{snow}/Cl_{melted\ snow}$ and $In_{seawater}/Cl_{seawater}$ gives a estimation of the enrichment of fluorescent material in the melted snow with respect to seawater. Therefore, considering the mean values of the snow and firn samples taken on Mt. Melbourne, the ratio

$$(In_{snow}/Cl_{melted\ snow})/(In_{seawater}/Cl_{seawater}) = 2.6/5.4 \times 10^{-4} = 5000$$

can be considered as an estimation of the enrichment of the fluorescent material in the marine aerosol trapped in the snow.

This value appears to be in agreement with the enrichment factors[6] for organic compounds and some transition elements able to interact with the marine organic matter in marine aerosol.

The present data also confirm our suspect that the enrichment of surfactant fluorescent matter in our previous findings was underestimated[15] for Mt. Melbourne sample.

Considering the In_{snow} values for the Carezza Lake sample it is immediately clear that the enrichment estimated with the same procedure is

$$(In_{snow}/Cl_{melted\ snow})/(In_{snow}/Cl_{melted\ snow}) = 2.6 \times 10^{-1}/5.4 \times 10^{-4} = 500$$

Therefore an order of magnitude lower than the samples taken at 1130 m above the sea surface.

Although this estimation is referred only to one sample, the difference is well above the experimental error on the whole adapted procedure and strongly suggests an altitude effect. This is also suggested by the larger absolute concentration of Cl – and the lower I_n/Cl – ratio for the Carezza Lake sample with respect to the other Mt. Melbourne samples. At the same time, it is also important to note that both the Mt. Melbourne snow and the firn samples show very similar In/Cl – ratios, i.e. similar partition of organic matter.

In other words, at high altitude the enrichment is higher, as predicted by the models of aerosol production described by MacIntyre[17] and Blanchard[6]. The largest particles which are preferentially transported at lower altitude correspond to the lowest enrichments of soluble organic matter. We denote here as "soluble" that part of organic matter which is collected in the head of the jet during the gas bubble rupture, therefore in the first jet drop[6] at the surface of the sea.

CONCLUSION

1) The three examined snow and firn samples show the presence of organic matter with fluorescence and surface properties similar to those of the marine humic substances, and confirm our previous results[10,15].

2) The presence of fluorescent organic matter in Antarctic snow appears consistent with the findings of Saxena[35] on the presence of proteinaceous materials in Antarctic marine clouds and the data of Kamamosi[36]on metal organic compounds in Antarctic snow.

3) The ratio between fluorescent matter and marine salt component evidences a possible altitude effect which opens the possibility of studying the variation of marine aerosol composition by means of analysing the Antarctic coastal snow. Despite the small number of samples examined, their volume is so large (30 dm^3) that they enclose a very high number of aerosol particles, thus minimizing any spurious effect.

4) In our opinion, further studies on this topic would be useful in understanding the role of the marine organic matter in the transport via air-sea interaction, of those microcomponents which interact with organic matter and which are also present on the Antarctic sea surface.

5) The present results, in our opinion, strongly suggest that in future campaigns the investigation should be extended, not only with regard to the examination of a larger number of sampling sites, but also other Antarctic coastal sites.

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