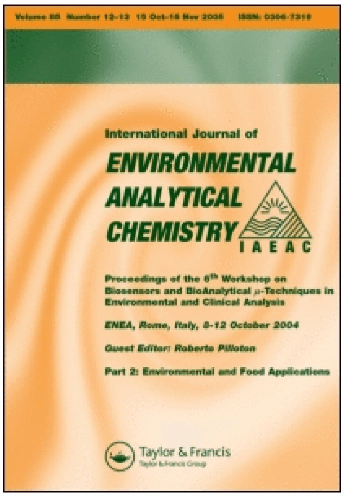

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HUMIC MARINE MATTER AND INSOLUBLE MATERIALS IN ANTARCTIC SNOW

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The aim of the present work is to show that the insoluble components of marine origin are always present, together with the soluble ones, in both the coarse fraction and in the fine fraction of the marine aerosol and that they make up a non negligible part of the insoluble material in Antarctic snow. The results obtained show that a large proportion of the insoluble matter present in high altitude Antarctic snow consists of marine organic matter involved in the aerosolization process and that the thermolabile fraction (400°C), largely consisting of fulvic acids, increases with increasing altitude. The effect of distance from the sea coast is harder to demonstrate for particulate fulvic acids at least over the short distances investigated herein (150 km) and owing to the complex orography of the sample areas.

Keywords: Aerosol; snow; Antarctica; humic substances

INTRODUCTION

The mechanism of both organic and inorganic microcomponents transport in Antarctic snow is of importance as regards to the knowledge and modelling of the global distribution of chemical components, also of a polluting nature, in the atmosphere[1]. Research into these aspects does not however take into account the fine marine aerosol component, including particles of a few hundredths of a micron in size[2–4]. Recent field experiments[5] have revealed the presence of numerous submicronic particles, at least under certain weather conditions, that

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can be attributed to sea spray. Their size distribution reaches a maximum at about 0.1 μm with a quantitatively significant total mass which seems superimposable on the maximum distribution of particles attributed to different origins[6,7]. For atmospheric aerosols this new evidence suggests an interpretative approach[8] to the actual nature and distribution of important additional classes of the fine water soluble fraction.

The first experimental data refering both to marine aerosols (collected in conditions of ascertained prevalence over the other aerosols) and to a coastal Antarctic snowfall, confirm the marine origin (sea spray) of this fine component, prevalently of organic and surfactant nature[5,9,10]. The particles in question are largely composed of marine fulvic acids[7,11]; their particular properties justify the significant excess of concentration in aerosol particulate of ions and molecules, also of a pollutant nature, compared with the respective concentrations in sea water.

The enrichment of the non volatile components as particle size decreases, follows an exponential pattern that, like that of the humic components[9,12], can be interpreted using an adsorption model[8,9,12] (Spray Drop Adsorption Layer Model – SDALM). This model envisages a transition of the marine aerosol particles from a typical saline nature (the same as in sea water) to that of essentially organic particles owing to a convenient size reduction ($\ll 1\,\mu m$). It can explain unsuspected changes in the composition of the marine aerosol.

Moreover, it has been shown how the formation of marine aerosol from the collapse of gas bubbles involves insoluble materials either already present in the sea water or originating from the process of aerosol formation[13]; in certain conditions, this process overlaps that of the demicellization-micellization[13,14] of colloidal dispersions in natural water.

The aim of the present work is to show that the insoluble components of marine origin are always present, together with the soluble ones, in both the coarse fraction and in the fine fraction of the marine aerosol and that they make up a non negligible part of the insoluble material in Antarctic snow. It has also been attempted to relate the presence of this particulate matter with processes of coagulation and flotation due in the first instance to the colloidal properties of the organic material (mainly fulvic acids) present in the marine aerosol, in order to interpret the origin of most of the soluble and insoluble components present both in Antarctic snow and in the fine fraction of atmospheric aerosols.

This topic involves certain global geophysical aspects[15], e.g. pollutant transport over long distances also in remote areas.

Snow and sea water samples were analysed. Sampling, as described previously[12], was performed both on the coast and at various heights above sea level, as well as in internal areas at some distance from the coast. Only surface snow (down to a depth of about 10 cm), sampled immediately after a recent snowfall, was used. These precautions are, nevertheless, subject to certain limitations.

The ideal conditions for verifying the effect of altitude in the case of the marine aerosol in Antarctic snow are those represented by "salt storms"; owing to the very strong winds, the size distribution of the particles occurs with a gradual variation depending on the altitude[16,17]. Snowfalls associated with such weather conditions do not substantially modify this distribution provided that the snow flakes are formed at altitudes considerably higher than that of sampling; the concentration of marine aerosol particles, which act as seed for the snow flakes, does not appreciably affect the high concentrations of interstitial aerosol in the flakes, which is transported directly into the air mass, together with the snow itself (winds blowing faster than 10–15 m/sec). These are the conditions that account for the experimental results reported previously[9–11].

In the opposite limiting case (snowfalls in the absence of strong winds) the transported aerosol consists of that present inside the snow flakes; the interstitial aerosol is practically eliminated by falling snow in the first few minutes of precipitation. Under these conditions and for snowfalls operating from cloud bodies situated well above the sampling altitude, the altitude effect is practically destroyed. An intermediate case is that of snowfalls produced by very thick cloud systems that include also some of the altitudes of the sampling stations. In this case the data is much more complex and difficult to interpret.

The snow samples from the more internal zones were collected as a function of the distance from the coast at altitudes greater than 1000 m. The altitude and the distance from the coast seemed to be the most favourable conditions for a comparison with the results expected on the basis of the application of the adsorption model (SDALM) for the fine component of the marine aerosol, even if the resuspension of the surface layer, for instance under the effect of katabatic winds, introduces undesirable variations in the surface snow cover.

EXPERIMENTAL

Materials and methods

The geographic coordinates of the snow sampling stations are shown in Table I.

TABLE I Samples from Antarctic campaigns 1995–96 and 1996–97: geographical characteristics of the sampling sites

a

Station/ Campaign	*Altitude m a.s.l.*	*Distance from sea km*	*LAT S*	*LONG E*
Mt. Melbourne (4b) 1995–96	710	10	74°28,307′	164°46,349′
Mt. Melbourne (4c) 1995–96	1130	10	74°25,928′	164°44,969′
Mt. Melbourne (4d) 1995–96	1490	10	74°23,837′	164°41,854′

b

Station/ Campaign	*Altitude m a.s.l.*	*Distance from sea km*	*LAT S*	*LONG E*
Mt. Melbourne (4a) 1996–97	360	10	74°31,8′	164°45,9′
Mt. Melbourne (4b) 1996–97	710	10	74°28,3′	164°46,4′
Mt. Melbourne (4c) 1996–97	1188	10	74°25,9′	164°45,0′

c

Station/ Campaign	*Altitude m a.s.l.*	*Distance from sea km*	*LAT S*	*LONG E*
Tourmaline (5) 1995–96	1800	60	74°13,8′	163°36,1′
Baia Terra Nova (base) (23) 1995–96	0	0	74°41,4′	164°07,2′
Pilot (44)	2267	60	73°16,1′	165°20,2′
Niggli (50)	2520	100	74°42,2′	166°56,4′
Evans (51)	2400	150	72°41,1′	164°30,3′

The samples studied (variable in volume from 30 to 150 1) refer to the 1995–96 and 1996–97 campaigns and were taken in groups depending on the function of the two different types of examination to be carried out.

The samples referred to in Table Ia were subjected to progressive separations and particulate treatment in order to evaluate the organic and inorganic matter content in the soluble and insoluble state as a function of different origins. For this purpose the liquid obtained from melting the snow under controlled conditions in the laboratory was allowed to settle until constant turbidity was reached. An appropriate volume of supernatant was then filtered on an Ag membrane, having a nominal pore size of 0.45 μm. The material remaining on the filter was dried under reduced pressure weighed and then heated in air at 400°C. Thermogravimetric tests run on samples of humic compounds isolated from the snow[7] showed that the latter components are destroyed at this temperature, even though they represent one of the most refractory organic materials of sea origin. The residual particulate was subjected to X-ray photon electron spectroscopy (Electron Spectroscopy for Chemical Analysis-ESCA) technique, while the rapidly settling material was subjected to X-ray diffractometer analysis.

The liquid filtered through the Ag membrane was subjected to aerosolization and the increase in mass of the new aerosol particulate was evaluated by means of filtration through a 0.45 μm Nuclepore membrane.

The techniques for weighing on a Nuclepore membrane in order to evaluate the mass of particulate created in the aerosol, that of the aerosolization process and the measures of the control parameters, fluorescence and turbidity, have already been described[18].

The samples listed in Tables Ib and Ic were intended to be used to find and separate dissolved and particulate humic materials. After melting, the sample was treated as described by Thurman[19] in order to recover the humic compounds from the water, after filtering through a 0.45 μm Millipore polycarbonate membrane. Extraction of the humic substances from the filters was achieved by shaking up with NaOH 0.1 M (200 ml) for 24 h; after removing the filters the solution was acidified and passed through XAD 8 resin (36 ml). The humic substances retained in the column were recovered by counter-current elution using a solution of NaOH 0.1 M (50 ml) subsequently acidified to obtain the separation of the humic acids from the fulvic acids. Whenever present, the humic acids were separated from the solution by centrifuging and dialysed using tubular membranes against distilled and deionized water, while the fulvic acids remaining in solution were purified by ultrafiltration[20].

The humic substances thus obtained were weighed and characterized using spectroscopic and thermogravimetric techniques. In some cases elemental analysis was performed.

Sea water sampling was performed both in Antarctica, Terranova Bay, off Campo Icaro, and in the Tyrrhenian coastal zone near our sea weather station off Livorno[21], in the latter case under rough sea conditions. The peculiar weather conditions involving breaking waves and coastward winds were selected in order to increase the amount of particulate of different origins in the water prior to the process of aerosolization. The abundant presence of these materials would allow their effect on the process itself to be evaluated and would provide further information concerning the validity of the procedures used for the Antarctic samples.

The sample was divided into two sub-samples. The first of these was filtered through a Pyrex G2 porous glass membrane and then on a 0.45 μm Nuclepore polycarbonate membrane. The second was subjected to a single filtration on a G2 porous glass membrane and then allowed to stand for 24 hours. Filtration on G2 porous glass was performed in order to eliminate materials > 100 μm in size that, owing to their nature (algae, coastal wood flotsam) could not be separated out by sedimentation.

The two sub-samples thus treated were subjected under the same conditions to the aerosolization process in a 14 1 column (working height 1.40 m diameter 10 cm)[22], and then the corresponding volumes of collected aerosolized material were filtered on a 0.45 μm nominal size Ag membrane. The particulate separated by the Ag membrane was dried and then weighed under reduced pressure, heated at 400°C for 7 hours in air and then replaced under reduced pressure for further weighing.

The sampling methods at 50 cm from the sea surface and the sample conservation, the artificial aerosolization techniques[13] and those of non foaming gas bubble extraction[23] were as described previously[13,18].

Apparatus

pH values were measured with an ECD (Electro-Chemical Devices) pH meter with an internal temperature correction device.

For weighing on Ag membrane a suitably modified Cahn RH electrobalance[22] was used.

Turbidimetric measurements were effected with a Hach double beam Turbidimeter model 2100.

Spectrofluorimetric measurements were performed with a Perkin Elmer Fluorescence Spectrophotometer model MP44A. The reported values are the maximum fluorescence intensities in an emission spectra that ranged from 320 to 570 nm, the exitation wavelenght was 308 nm. The spectra were corrected by means of the accessory "Differential Corrected Spectra Unit" using the procedures described in the Reference Manual. All the values were normalized.

X-ray photon electron spectroscopy was carried out on particulate material (Ag mambrane). The measurements were performed on an hemispherical electrode energy analyzer equipped with a multichannel detector. Non monochromatized AlKα radiation was used as excitation source. The penetration factor was about 20–30 Å using a Philips PW 1800/10 apparatus equipped with computer and dedicated software.

The aerosolization operation was carried out with a Gershey impactor modified by us which consisted of a column about 1500 cm high with an internal diameter of 4 cm. The column head was espanded to an external diameter of 8 cm, and the underhead wall constituted the impaction surface. The sparger was a glass frit surface (20 cm^2) arranged in an enlarged terminal section at the bottom of the column. The glass frit whose pores had a nominal diameter of 20–40 mm was selected since it produced a very narrow range of bubble dimensions (500–

700 mm diameter) using a pure nitrogen flux of 7±0.05 l h^{-1} at 21°C in artificial sea water.

Since the beginning of each aerosolization operation the water level in the column was rigorously kept at a costant mean distance from the impactor surface (2 cm). In these conditions the collection of jet drops which formed during the second step of the gas bubble rupture mechanism from a 3.5% NaCl water solution (highly purified from surfactants), was assured to be 90% and to be constant in time even if level variations of about 2 mm take place. It is to be observed that the contribution to the aerosol volume of film drops (formed during the first step of bubble collapse) is very small, owing to the above mentioned bubble diameters. With the above nitrogen delivery, the rising gas bubble flow nearly laminarly, so the axial diffusion is much reduced even for a 4 cm column diameter.

Amicon stirred ultrafiltration cell, model 8400, capacity 400 mL, equipped at the bottom with 500 dalton membrane disc (diameter 76 mm). The cell is connected to a reservoir (5 L) containing washing solution (deionized water pH 4.9) which is nitrogen pressurized (4 atm). Varying the operational conditions, the cell can be used under nitrogen pressure (3.5 atm) without interfacing with the reservoir. In this way it can work in preconcentration conditions.

Thermogravimetric analyses were performed with a Perkin Elmer termogravimetric balance model TGA 7, working in nitrogen atmosphere between 50 and 1300°C, heating rate 10°C/min, 1.5 mg of sample.

Na, K, Ca and Mg determinations were performed with an ion chromatographic apparatus Dionex 4500i. Na used as a total marine aerosol reference.

RESULTS AND DISCUSSION

Fraction not destroyed at 400 °C and material separating out by settling

The particulate collected on the Ag membrane after heat treatment was subjected to magnetochemical testing which revealed highly paramagnetic characteristics, probably due to the presence of transition metal oxides.

For the purpose of more detailed investigation the surface of the test material was subjected to X-ray photoelectronic spectroscopy directly on the Ag sheet. The elemental concentrations of Si, O, K, Fe, Cl and Mg, referring to Al=1±10%, were found to be the same within the allowed experimental error for the two samples taken at heights of 1490 and 1130 m a.s.l. (Table II). The elementary species were similar to those of typical crust components, but since tests carried out using the Bubble Interfacial Microlayer Sampler – BIMS[24] had shown that

Al and Fe were involved in marine aerosol, it may be postulated that the transport of these elements on to the Antarctic continent was partly direct and partly associated with transport via marine aerosol.

TABLE II Elemental composition of the colloidal particulate separated after settling from the melted surface snow water after treatment at 400°C

Elemental composition referring to Al = 1 ± 10%						
Mt. Melbourne 1130 m a.s.l.	*Si*	*O*	*K*	*Fe*	*Cl*	*Mg*
	3.20	12.5	0.24	0.17	0.71	0.40
Elemental composition referring to Al = 1 ± 10%						
Mt. Melbourne 1490 m a.s.l.	*Si*	*O*	*K*	*Fe*	*Cl*	*Mg*
	3.50	12.9	0.21	0.16	1.00	0.45

In order to characterize the material separated by sedimentation, it was repeatedly washed with ultrapure water, then dried and subjected to both optical and magnetic microscope examination. Optical microscopy revealed the presence of crystalline particles (< 0.1 mm) mixed with apparently amorphous material. Magnetic examination revealed the presence of ferromagnetic particles that were easily separable from the remaining materials. X-ray diffractometry analysis of the sedimented material revealed that it consisted of a mixture of pyroxene plagioclase (diopside), forsterite olivine and probably also magnetite. In practice, it consisted of basaltic rocks, the traces of which are probably due to direct fall from the top of Mt. Melbourne.

Thermolabile particulate destroyed at 400°C

Table III shows the results of the two experiments carried out on sea water sampled in rough sea conditions off Livorno, the particulate of which is certainly associated with the formation of marine aerosol under rigorously controlled conditions.

A large difference in particulate mass is observed between the two procedures, while the weight loss due to heat treatment is comparable. The abundant presence in sub-sample II of inorganic colloidal and particulate matter (clays and other material of crustal origin) does not seem to have any appreciable effect on the transfer of colloidal organic material to the aerosol. The large difference in volume in the aerosolized liquid is indicative of the substantial effect of reduc-

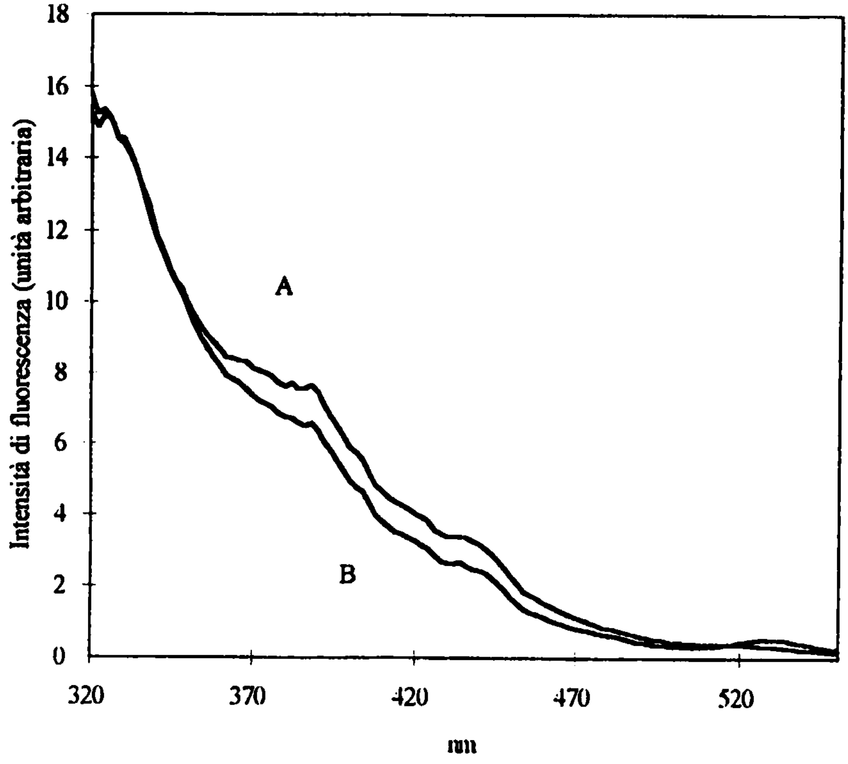

FIGURE 1 Synchronous scanning spectra of a sea water sample (taken on 21/11/96) subjected to aerosolization and filtration on an Ag membrane. Signal A corresponds to the aerosol obtained from a part of the sea water sample pretreated by filtration on a G2 porous glass membrane and subsequently filtered on a 0.45 μm Nuclepore membrane. Signal B corresponds to the aerosol obtained from a part of the sea water sample pretreated only by filtration on a G2 porous glass membrane. Both the aerosols obtained in the laboratory were subsequently filtered on an Ag membrane

tion of the concentration of the dissolved surfactant material (proportional to In) owing to the particulate present in sample II. There is a consequent variation in the process efficiency, in particular with regard to the number and size of the aerosol microdrops originating from the collapse of the gas bubbles, in agreement with the affinity displayed by the surfactant humic matter to the solid particles originating from the crust[25]. The gas bubbles were produced by a nitrogen flow of 6 dm^3/h through a G3 porous glass membrane selected so that it gave rise to bubbles varying in diameter between 0.3 and 0.5μm and therefore capable of producing essentially jet drops[26].

The synchronous scanning spectra for the two aerosol samples after filtering on Ag (Figure 1) confirm the presence of fluorescent surfactant material similar to that of sea water and show that prefiltration using various different techniques makes no appreciable difference to the nature of the fluorescent material. The fluorescence spectra and the normalized fluorescence intensity values shown in Table III for the aerosol give a good indication of the nature of the organic material involved[7,11,12]. It is worth emphasizing that, for sample I, the particulate found in the aerosol after aerosolization of the filtrate was certainly produced during the aerosolization process.

The results of this first experiment thus indicate the presence of particulate matter of an organic, mostly humic, nature associated with the formation of the marine aerosol.

Table IV shows the data refering to a similar experiment carried out on three samples of Antarctic snow taken after a summer snow fall accompanied by sea winds (1995–96 campaign on Mt. Melbourne at altitudes of 1490 m (A), 1130 m (B), 710 m (C) a.s.l., respectively). The particulate separating out from the melted snow, after constant turbidity reaching, was found to be present in greater quantities at the lower level. The greatest weight loss due to thermal treatment was found in the sample collected at the highest altitude. This result seems to be supported by the adsorption model (SDALM) which predicts an increase in organic material content with decreasing particle size as a function of altitude, as reported in the literature for some time[16,17].

The results of the aerosolization process carried out on the filtrate using an Ag membrane for the three snow samples investigated are shown in Table V. The process was performed using a reduced size aerosolization column[13] in view of the small volumes available. The turbidity, measured immediately after Ag filtration, was found to be 0.02 NTU. It subsequently increased spontaneously until it reached constant values of practically the same order as those shown in Table V. This explains why filtering performed several hours later leads to the separation of further particulate, showing that an equilibrium is set up between dispersed and aggregated colloidal matter. The In values for the liquid prior to and after the aerosolization process, which are similar for the three samples, do not appear to contradict this hypothesis. The colour and the weak fluorescence displayed by the particulate retained on the Nuclepore polycarbonate membrane point to the predominant presence of humic substances.

Particulate trends per unit volume in the aerosol fraction seem to confirm the presence of a specific quantity of particulate matter in each microdrop, which is essentially due to the aerosolization process. This quantity varies as a function of the stability of the micellization-demicellization equilibrium characterizing the colloidal dispersion in question (in particular the oxidation-induced effect[27]).

TABLE III Data of the coastal seawater samples taken in rough sea conditions at our Tyrrhenian station near Livorno (Italy)

Sub-sample Treatment	*Aerosolized volume cm^3*	*Total volume of aerosol microdrops collected cm^3*	*Tot. particulate in aerosol mg ± 0.01*	*Weight loss after heat treatment at 400 mg ±0.01*	*In^a filtered aerosol °C ± 0.03*	*Weight loss in POC % compared with total*
Sub-sample I prefiltration on G2 porous filter and on 0,45μm Nucleopore filter	12200 ± 10	25 ± 1	19.15	3.15	239.7	8.45
Sub-sample II prefiltration only on G2 porous filter	12200 ± 10	13 ± 1	301.71	3.64	180	1.20

a. Fluorescence, as a first approximation proportional to the dissolved humic matter, is expressed as normalized fluorescence intensity ($In=I_{Raman}/I_{max} \times 100$)

TABLE IV Antarctic Campaign 1995–96: Thermodestruction treatment of surface snow samples (Mt. Melbourne) taken at three different altitudes

Sampling altitude	*Vol. Filtered using 0.45 μm Ag membrane cm^3*	*NTU ± 5%*	*In^a ± 3%*	*Tot Particulate after settling mg ± 3%*	*Tot Particulate after settling mg/l*	*Weight loss after treatment at 400°C mg ± 3%*	*Weight loss %*	*Na μg/dm^3 ± 3%*
1490 (A)	2500	0.07	21.0	0.541	0.216	0.178	32	55.7
1130 (B)	2200	0.10	20.3	0.443	0.201	0.100	22 6	80.4
710 (C)	2500	0.09	21.2	0.930	0.370	0.252	27	141

a. Fluorescence, as a first approximation proportional to the dissolved humic matter, is expressed as normalized fluorescence intensity ($In=I_{Raman}/I_{max} \times 100$)

TABLE V Antarctic Campaign 1995–96: aerosolization process after settling and filtration on 0.45 μm Ag membrane

Sample	*Treatment*	*Turbidity NTU*	*pH*	*Particulate material mg/l*
1490 (A)	As is	0.07	6.27	0.22
	Eluted	0.04	6.62	0.04
	Aerosol	–	–	1.00
1130 (B)	As is	0.10	6.64	0.20
	Eluted	0.08	6.56	0.06
	Aerosol	–	–	2.00
710 (C)	As is	0.09	5.53	0.37
	Eluted	0.06	6.10	0.18
	Aerosol	–	–	2.00

Prevalent nature of particulate thermolabile at 400°C and mean particle size

Table VI (geographic coordinates of the sampling stations in Tables Ib and Ic) shows the concentrations of dissolved fulvic acids (FA) expressed in mg/dm^3, the concentrations of insoluble fulvic acids, the percentage of particulate FA and, lastly, for several samples, the concentrations in μg/dm^3 of Na, K, Mg, and Ca. The most interesting aspect of the reported data is that for the first time a direct measure is available of the concentration of soluble and insoluble FA referring to the same volume of snow.

In the case of Mt. Melbourne the soluble FA content is apparently of the same order for all three samples; the total FA concentrations in the particulate state increase perceptibly with altitude, while those of Na, K, Mg and Ca decrease.

As the Na concentration is known, it can be used to obtain the total effective volume of sea spray expressed as sea water and thus obtain an, albeit only indicative, evaluation of the mean concentration of the soluble and insoluble portions of the fulvic acids in sea spray. By way of example, for the 1188 m sample, bearing in mind that the Na concentration is 0.105 mg/dm^3 and that the total volume of sea spray contained in 1dm^3 of melted snow is 0.0095 cm^3, the concentration of soluble FA in sea spray is found to be about 6.31 mg/cm^3.

The data shown in Table VI can also be used to make an approximate calculation of the enrichment ratios, which are defined as $Er=(X/Na)_{aer}/\ (X/Na)_{SW}$ where x = concentration of the element with respect to that of Na both for the aerosol and sea water[12], and to obtain some indication of the mean diameter of the aerosol particles involved in any way in the snow fall investigated. This implies a knowledge of the thickness Δr of the adsorption film on the aerosol microdrops at the time of aerosol formation. On the basis of literature data[9,12] it was assumed to be 0.01 μm.

For the sample at the highest altitude we obtained:

$$\mathrm{ErF} = (\mathrm{mgFA/Na})_{\mathrm{snow}}/(\mathrm{mgFA/Na})_{\mathrm{SW}} = (0.06/0.105)/(0.1/11015)$$
$$0.57/9\ 10^{-6} = 5.7/9\ 10^{-5} = 6.3\ 10^{4} \cong 63000$$

a value that is consistent with that obtained from the data referring to the normalized fluorescence intensity Er In = 92735 (Table IV, $\mathrm{In}^{\mathrm{SW}} = 27.4$), assuming an error of ±15% and taking into consideration that the FA concentrations listed in table VI should be considered as an underestimation of the true values as the fulvic acid extraction yield using the described methods is of the order of 85–90%.

Comparing the values of Er In^{A}=175000, Er In^{B}=92725 and Er In^{C}=62647 with those of ErIn observed directly in the field for aerosols of certain marine origin for defined particle size classes[9] it is found that they are presumably in the <0.49μm class. If Er regularly follows increases in altitude, the trend would seem to be in agreement with the reduction in particle size due to the altitude. Obviously the fluorescence enrichment ratios refer only to soluble FA.

Effect of distance from the coast on FA concentrations

For the samples referring to the other 4 stations above 1800 m. (Table VI) and for a maximum distance of 150 km from the sea, their behaviour, in our opinion, is compatible with the characteristics typical of marine aerosols at high altitudes. At altitudes above 2000 m the aerosol is composed of very small particles ($\ll$ 0.49μm) and is probably present in the form of Cloud Condensation Nuclei (CCN) in view of the FAs' strong tendency to behave as wet-surfactants. On the basis of the SDALM[9,12] it is also to be expected that these particles, as well as having a highly reduced mass ($\sim 10^{-17}$ gr ^{2}), are mainly composed of organic material as well as ammonium salts and methanesulphonic acid (MSA) for snow in the summer period. Therefore the variations in soluble FA content could be accounted for as being due mainly to orographic variations in the deposit surfaces, to the probable resuspension of the surface snow under katabatic wind action and to low-altitude cloud formation with consequent falls of snow having different characteristics owing to the lack of homogeneity of the cloud bodies.

Also the micellization process is reduced (for example, see the sample referring to the Niggli station, which has a high soluble FA content compared with those in a particulate state). In our opinion, these indicative preliminary data suggest that in order to determine the effect of distance from the sea on Antarctic snow composition it would be necessary to take larger distances from the coast into consideration and possibly on the surface of the Antarctic ice-cap, at some distance from the transAntarctic mountain chain, so as to avoid any macroscopic orographic discontinuities on the deposit surface.

As regards the fresh snow sample gathered at the base, at sea level and in the absence of any strong winds, the most immediately observable fact is the high concentration of both soluble and insoluble FA, which is in apparent contradiction with expectations due to the altitude effect based on the adsorption model[12] and demonstrated by the preceding data.

It must nevertheless be borne in mind that this snowfall occurred in the absence of "salt storms", and that the marine aerosol is incorporated in the snow essentially as CCN, in view of the small size of the particles linked to the height of the clouds from which the snow originated. The scavenging effect on pre-existing and interstitial aerosol is probably very low as, at the time of the snowfall, whitecaps were not abundant on the sea surface and the aerosol already present in the air was practically eliminated during the first few minutes of the snowfall. This type of behaviour is supported by the findings of Mangoni et al.[28] in a sequential study on rain in a temperate zone (Florence-Italy). The abundant quantities of FA may thus be attributed to that portion of the fine component of the marine aerosol present at the altitude at which the cloud system from which the snowfall originated was formed.

The meteorological event in question thus represents one of the two limiting cases treated previously.

CONCLUSIONS

The results illustrated in the present paper show how a large proportion of the insoluble matter present in high altitude Antarctic snow consists of marine organic matter, involved in the aerosolization process. The thermolabile fraction increases with increasing altitude and consists largely of FA. This represents also an indirect confirmation of SDALM applicability to the interpretation of the presence of certain microcomponents in Antarctic[29,30] snow. It is also obvious that the larger particles of marine aerosol (microcomponents present in Antarctic snow at lower altitudes) are also those with a higher content of mainly inorganic insoluble and colloidal particulate components, in agreement with the predictions of Blanchard[26,31] flotation model.

Laboratory experiments carried out on sea water and melted snow have shown that the aerosol formation process is always accompanied by a process of micellization by the surfactant material at least of a humic nature (FA) and that the main FA aggregation takes place already at the time of formation of the marine aerosol (bubble collapse, in agreement with Wallace et al.[32]).

TABLE VI Antarctic Campaign 1996–97: fulvic acid concentration (Mt. Melbourne) both in solution and present in particulate and percentage of fulvic acids in the particulate

Station/ Campaign	*dissolved FA mg/l*	*particulate FA mg/l*	*% di FA in particulate*	*Na µg/l*	*K µg/l*	*Mg µg/l*	*Ca µg/l*
Mt. Melbourne 4a 1996–1997	0.06	n.d.	< 1	1033	40.6	124	51
Mt. Melbourne 4b 1996–1997	0.02	0.09	7.6	468	18	58	25.5
Mt. Melbourne 4c 1996–1997	0.06	0.18	15.6	105	16	104	15.3
Tourmaline (5) 1995–1996	0.05	0.10	9.0				
Pilot (44) 1996–1997	0.14	0.06	9.5				
Niggli (50) 1996–1997	0.19	0.01	2.8				
Evans (51) 1996–1997	0.07	0.01	4.0				
Baia Terra Nova (base) (23) 1995–1996	0.22	0.49	20.0	3070	138	352	182

Direct determination of FA concentrations in Antarctic snow reveals an increase in total FA as a function of altitude and agreement between the respective enrichment ratios obtained using different procedures. While on the one hand again confirming the validity of SDALM, this agreement makes it possible also to obtain useful information concerning the mean size of marine aerosol particles at the time of their formation which are present in the snow samples examined for Δr (thickness of adsorption film = 0.01μm[33]).

The reduction in the sea salt components and the simultaneous increase in soluble and insoluble organic matter, mainly characterized as FA, may be considered a function of the altitude of the Antarctic coastal snow.

From this preliminary investigation it appears that at least a substantial part of the inorganic particulate in high altitude samples is associated with the process of marine aerosol formation. Fragments of crustal material of local origin are instead comparatively abundant in the low altitude snow.

Snow collected at sea level in the absence of strong winds seems to be essentially characterized by marine aerosol particles of a size compatible with the altitude of the cloud system from when the snow originated. In this case, therefore, the effect of varying the altitude is to be expected to be practically insignificant. Conversely, also on the basis of the results obtained by Woodcock and Blanchard[17], the effect of altitude is expected to be strongest for snowfalls occurring together with salt storms.

The effect of distance from the sea coast is harder to demonstrate for particulate FA, at least over the short distances investigated herein (150 km) and owing to the complex orography of the sample areas.

From a general point of view the presence of microcomponents in Antarctic snow is characterized by two transport processes: that associated with marine aerosol formation and that of direct transport (particularly in the gaseous state).

The transport process due to the marine aerosol presents two aspects:

A) one related to the transport of components associated with soluble marine surfactant (<0.45μm) which is essentially dependent on the laws governing physical adsorption

B) the other related to the flotation of organic and inorganic particulate material (>0.45μm) already present in sea water.

The former is always accompanied by mainly organic particulate which is formed at the time of the aerosolization process and is present at all altitudes. Under certain geophysical conditions (e.g. volcanic activity) fine aerosols of different origins may be added to it.

The latter increases with decreasing altitude. In addition to this type of particulate matter there is crustal material of local origin.

In this framework, the role of the fine component of the marine aerosol takes on considerable importance also in remote areas such as Antarctica also as a result of its unexpected abundance, at least in certain weather conditions[5] and it would appear to be, at least in principle, the main factor accounting for the presence of microcomponents also of an anthropogenic nature in Antarctic snow. The proposed transport model-based interpretation referring to the interphase chemistry-physics may suggest satisfactory new elements in the interpretation illustrated[29,30].

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