An integrated study of chemical composition of Antarctic aerosol to investigate natural and anthropogenic sources

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An integrated study of chemical composition of Antarctic aerosol to investigate natural and anthropogenic sources

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Environmental Context

Due to their long distance from anthropogenic emission sources, Antarctica is an excellent natural laboratory for conducting studies on the behavior of marine aerosols and for monitoring the impact of human activities on the globe. The aim of this study is to provide an extensively chemical characterization of Antarctic aerosol and to investigate its sources. A distinction among anthropic, crustal and biogenic sources was defined using several chemical markers.
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Due to their long distance from anthropogenic emission sources, Antarctica is an excellent natural laboratory for conducting studies on the behavior of marine aerosols and for monitoring the impact of human activities on the globe. The aim of this study is to provide an extensively chemical characterization of Antarctic aerosol and to investigate its sources. A distinction among anthropic, crustal and biogenic sources was defined using several chemical markers.

Abstract

During the 2010-2011 austral summer, an aerosol sampling campaign was carried out at a coastal Antarctic site (Terra Nova Bay, Victoria Land). In this work, previously published data were merged with novel measurements in order to provide a chemical characterization of Antarctic aerosol and to investigate its sources. Major ions, major and trace elements, carboxylic acids, water soluble organic compounds (anhydrosugars, alcohols sugars, mono and disaccharides, amino acids and phenolic compounds) and persistent organic pollutants (polychlorobiphenyls, polycyclic aromatic hydrocarbons, polychlorinated naphthalenes, polybrominated diphenyl ethers and organochlorine pesticides) were evaluated using an integrated approach. The persistent organic pollutants were determined using a high volume sampler, able to collect both particulate and gaseous fractions, while remaining compounds were determined by performing an aerosol size fractionation by a PM$_{10}$ cascade impactor. Ionic species were the most abundant compounds in the Antarctic aerosol due to natural emission. Trace concentrations of persistent organic pollutants highlighted that the occurrence of these species can be due to long-range atmospheric transport or due to the research base. Factor Analysis was applied to the dataset obtained from the samples collected with PM$_{10}$ sampler in order to make a distinction among anthropic, crustal and biogenic sources using specific chemical markers.
**Introduction**

The investigation of the chemical composition of Antarctic atmosphere is one of the key points in polar research. Due to its distance from anthropogenic and continental emission sources, Antarctica is an excellent natural laboratory to study the biogeochemical cycles of natural elements and compounds and to investigate chemical transformation of chemical species in the continent’s pristine atmosphere or during long-range atmospheric transport from anthropic areas. Understanding the atmospheric behavior of these compounds will enable the use of these species as markers for specific sources in paleoclimatic studies based on Antarctic ice core data.

Nowadays, the chemical characterization of Antarctic aerosol has been the object of scrappy investigations. Several studies were focused on major ions \cite{1-6}, or on trace elements \cite{7-12}; a few organic compounds were also recently investigated \cite{13,14}.

The goal of this research is to carry out an accurate and wide-ranging chemical characterization of coastal Antarctic aerosol in order to define the aerosol sources for future applications to ice core studies. Here, we report the final results and conclusions of the project “Study of sources and transport processes in the atmospheric aerosol” financially supported by the Italian National Program for Research in Antarctica (PNRA). Five Italian universities contributed to the investigation of aerosol source in Antarctica.

To our knowledge, this is the first study that combines wide range of different chemical measurements to determine organic and inorganic markers of specific sources and analyze the particle size distribution of Antarctic aerosol in order to characterize the Antarctic atmosphere. The occurrence of anthropogenic compounds also allowed us to investigate if the closed research base contributes to Antarctic pollution.

We propose a synthesis of all measurements of aerosol samples collected at the Italian research station “Mario Zucchelli” (MZS) (Antarctica) during the austral summer 2010-11. Bazzano et al. \cite{15} described the composition of major and trace elements of aerosol samples at MZS during the sampling period. Rella and Malitesta \cite{16} performed a qualitative and quantitative analysis of
particulate matter surface using X-ray photoelectron spectroscopy (XPS), determining several species as ammonium, nitrate, sulfate, organic sulfur, fluoride and organic fluoride. Barbaro et al. [17, 18] defined the site’s composition in amino acids and sugars, while Zangrando et al. [19] investigated several biomass burning markers (levoglucosan and phenolic compounds).

Moreover, this study integrates additional groups of compounds in the characterization of the Antarctic atmosphere. These consist of ionic species (Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), NO\(_2\)^{+}, NO\(_3\)^{-}, sulfate, phosphate and methanesulfonic acid (MSA), NH\(_4\)^{+}, K\(^{+}\)), carboxylic acids (C\(_2\)-oxalic, C\(_2\)-acetic, C\(_2\)-glycolic, C\(_3\)-malonic, C\(_4\)-succinic, hC\(_4\)-malic, cis-usC\(_4\)-maleic, trans-usC\(_4\)-fumaric, C\(_5\)-glutaric, C\(_6\)-adipic, C\(_7\)-pimelic, aC\(_7\)-benzoic, C\(_8\)-suberic) and persistent organic pollutants (POPs) including polychlorobiphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH), polychlorinated naphthalenes (PCN), polybrominated diphenyl ethers (PBDE) and organochlorine pesticides (POC).

**Material and Methods**

*Sample collection and processing of PM\(_{10}\) aerosol*

Aerosol samples (n = 5) were collected using two analogous high-volume cascade impactors (TE-6070, PM\(_{10}\) high volume air sampler) with 10.0 – 7.2 \(\mu\)m, 7.2 – 3.0 \(\mu\)m, 3.0 – 1.5 \(\mu\)m, 1.5- 0.95 \(\mu\)m, 0.95 – 0.49 \(\mu\)m and <0.49 \(\mu\)m particle cut-off diameters, placed at Campo Faraglione (74° 42′ S – 164° 06′ E), about 3 km south of the Italian Research Base MZS (Victoria Land, Antarctica) from November 29\(^{th}\), 2010 to January 23\(^{rd}\), 2011. The average airflow of both air samplers was 1.1 m\(^3\) min\(^{-1}\) and the sampling resolution was about 10 days (~15,000 m\(^3\) per sample). One air sampler employed cellulose filters to determine metals in the particulate matter while the second used quartz fiber filters to investigate organic and ionic compounds in Antarctic aerosol. For each sampler, three field blank samples were collected by loading, carrying, and installing the filter on the instrument with the air pump switched off, removing it after ten minutes and following the same procedure used for the sample filters. The device did not employ Teflon O-rings and fluorinated lubricants in order to reduce the risk of contamination.
After sampling, the cellulose filters used for the determination of inorganic compounds were placed in acid-cleaned plastic Petri dishes, sealed in double polyethylene bags and stored at -20°C until analysis. Quartz filters used to determine organic compounds were stored at -20°C in double aluminum foil envelops until analysis.

The samples were processed under a laminar flow bench (class 100) to avoid contamination from the laboratory environment. The pre-analytical protocol to determine metals has been described by Bazzano et al. The procedure consisted in a microwave-assisted acid digestion of the cellulose filters followed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) analysis.

The XPS measurements were recorded on samples without any pretreatment with an AXIS ULTRA DLD (Kratos Analytical) photoelectron spectrometer using a monochromatic AlKα source (1486.6 eV) operating at 225 W.

The pre-analytical and sample extraction protocol to determine amino acids, phenolic compounds and sugars has been described elsewhere. Briefly, filters were spiked with a 13C labelled internal standard mix (amino acids, phenolic compounds and levoglucosan), ultrasonically extracted with ultrapure water, and filtered through a 0.45 µm PTFE filter. Amino acids determination was obtained using an high performance liquid chromatography (HPLC) with a chiral column coupled with tandem mass spectrometry. Phenolic compounds were analyzed using a reverse phase chromatography coupled with tandem mass spectrometry, while sugars were determined using an ion chromatography coupled to mass spectrometry (IC-MS).

The analytical procedure to determine ionic species consisted in ultrasonic extraction with ultrapure water and a filtration through a 0.45 µm PTFE filter. Determination and quantification of all anionic compounds and carboxylic acids (see table 1) were performed using an ion chromatograph (ThermoScientific Dionex ICS-5000, Waltham, US), with an anion exchange column (Dionex Ion Pac AS11 2x250mm) and guard column (Dionex Ion Pac AG11 2x50 mm), coupled with a single mass spectrometer (MSQ Plus, ThermoScientific, Bremen, Germany).
The sodium hydroxide gradient, generated by an eluent generator (Dionex ICS 5000EG, Thermo Scientific) was: 0-3.5 min gradient from 0.5 mM to 5 mM; 3.5-5 min gradient from 5 mM to 10 mM; 5-25 min gradient from 10 mM to 38 mM; 25-30 min, column cleaning with 38 mM; 30-35 min; equilibration at 0.5 mM. The injection volume was 100 µL and the flow rate was 0.25 mL min⁻¹. Sodium hydroxide was removed by a suppressor (ASRS 500, 2 mm, Thermo Scientific) before entering the MS sources. The MS was operating with an electrospray ionization (ESI) interface in negative mode. Selected ion monitoring (SIM) was used for detection.

The ion chromatograph was equipped with a capillary system to simultaneously determine cations. Sodium, ammonium, magnesium and potassium were separated using an Ion Pac CS19-4µm capillary cation exchange column (0.4 x 250 mm) equipped with an Ion Pac CG19-4µm guard column (0.4 x 50 mm). The MSA gradient, generated by an eluent generator (Dionex EGC-MSA Capillary) was: 0-17.3 min; 1.5 mM; 17.3-21.9 min gradient from 1.5 mM to 11 mM; 21.9-30 min equilibration at 1.5 mM. The injection volume was 0.4 µL and the flow rate was 13 µL min⁻¹. MSA was removed by a suppressor (CCES 300, Thermo Scientific) before entering the conductivity detector.

Each procedure was previously validated to ensure an accurate quantification of each analyte [15, 17, 18, 20]. All reported values were blank corrected. A summary of each compound reported in this paper and the analytical protocol used for its determination is reported in Table 1.

**Aerosol mass measurements**

During the 2010-2011 austral summer preliminary tests of the direct mass measurements of the different size-segregated aerosol fractions were carried out. The procedure consists in determining the difference between the mass of the exposed filters and their mass before exposure. This procedure was previously setup for the weighing of total PM₁₀ [21, 22]. A computerized Mettler Toledo (Greifensee, Switzerland) AT261 electronic microbalance (readability 0.01 mg, repeatability SD = 0.015 mg) was used.
In order to maintain weighing conditions as much stable as possible, a decontaminated polyethylene Atmosbag glove bag (Sigma Aldrich, gas volume 520 L, closure type zipper-lock, not sterilized) was used, and the microbalance was placed inside of it. Temperature and humidity were measured throughout the weighing session using a mini thermos-hygrometer (digital psychrometer Testo, mod. 605-HI). Temperature and relative humidity inside the glove bag were stable throughout all the weighing procedure, varying by ±0.1°C and ±0.2%, respectively.

Sample collection and processing of aerosol using TE 5000 sampler

Aerosol samples (n = 10) were collected by a TE 5000 High Volume Air Sampler (Tisch Environmental Inc.) using quartz fiber filters (QFF) for contaminants associated with total suspended particles (TSP) and polyurethane foam adsorbent (PUF) for gaseous-phase contaminants. The sampling site and period are the same as those previously indicated for the PM$_{10}$ high volume air sampler. The average airflow was 0.4 m$^3$/min$^1$ and the sampling time was 5 days (~2900 m$^3$ per sample). At the end of each sampling PUF and QFF were removed from the holder, wrapped in double aluminum foil envelops, sealed in double polyethylene bags and stores at -20°C until analysis. During the sampling period, four blank samples were collected by installing PUF and QFF on the instrument with the air pump off and by recovering them according to the procedure used for the exposed ones.

The samples were processed under a laminar flow bench (class 100) to avoid contamination from the laboratory environment. QFFs were extracted twice with aliquots of 20 mL of hexane/acetone (1:1, v:v) mixture in an ultrasonic bath for 1 h and the recovered organic phases were combined and hold overnight on anhydrous sodium sulfate. 2 mL of isooctane was added to the organic phase and reduced to a volume of about 1 ml in a centrifugal evaporator before the chromatographic analysis. PUFs were extracted twice with aliquots of 150 mL of mixture of hexane/acetone (1:1, v:v) in an ultrasonic bath for 1 h and the recovered organic phase was combined and hold overnight on anhydrous sodium sulfate. The organic phase was then filtered through 0.45 µm PFTE filters, then
reduced in volume using a centrifugal evaporator and purified by multi-layer solid phase extraction (SPE) cartridges. The analytes were eluted from the SPE column with 10 mL of n-hexane. 2 mL of isooctane was added to the recovered hexane and reduced to a volume of about 1 mL in a centrifugal evaporator before the gas chromatographic analysis.

QFF and PUF field blanks were spiked with a range of $^{13}$C$_{12}$-labeled PCB congeners and D$_{10}$-labeled PAHs to monitor the extraction and clean-up procedures.

Instrumental analysis was performed by a gas chromatograph (5890A, Agilent Technologies, USA) equipped with a MS detector (5973, Agilent Technologies). Chromatographic separation was performed on a HP5-MS capillary column (30m x 0.25mm x 25µm) using helium as carrier gas at a flow rate of 1 mL/min$^{-1}$. The oven temperature program was: 60 °C hold for 0.5 min then 15.00 °C min$^{-1}$ up to 140 °C then 2 °C min$^{-1}$ up to 240 °C then 15 °C min$^{-1}$ up to 300 °C. The injection volume was 50 µL and the PTV temperature program was: 65 °C hold for 0.5 min then 500 °C min$^{-1}$ up to 280 °C. The MS detector operated in SIM mode. The compounds under investigation were: 21 congeners of PCBs (-66, -77, -87, -101, -105, -118, -126, -128, -138, -153, -154, -169, -170, -18, -187, -188, -194, -195, -201, -206, -209), 16 congeners of PCN (-2, -6, -13, -28, -52, -66, -73, -75, -27, -36, -46, -48, -50, -53, -69, -72), 46 congeners of PBDE (-1, -2, -3, -7, -10, -15, -17, -28, -30, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -139, -140, -153, -154, -156, -169, -173, -171, -180, -183, -184, -191, -196, -197, -201, -203, -204, -205, -206, -207, -208, -209), 6 compounds belonging to PAHs (Fluoranthene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Benzo(g,h,i)perylen) and 19 compounds belonging to POC (benfluoralin, trifluoralin, HCH, HCB, HCH-g, metolachlor, terbutryn, malathion, iProd, heptachloroepoxide A/B, chlordanocis/trans, endosulfan, dieldrin, p-DDE, endrin, endosulfan I/II).

Data processing
A statistical approach was used for the dataset obtained from PM$_{10}$ aerosol with aerodynamic diameters of 10–7.2, 7.2–3.0, 3.0–1.5, 1.5–0.95 and 0.95–0.49 mm. For statistical analysis, the concentrations values below limit of detection (LOD) were substituted by ½ LOD. Factor analysis (FA) with varimax rotation was performed on the auto-scaled data matrix constituted by 25 rows (samples) and 31 columns (chemical components) using Statistica 8.0 (StatSoft, Inc., 2007). In order to reduce the chemical components, the sum of amino acids (AA), phenolic compounds (PC), carboxylic acids (CA), monosaccharides (MS), alcohol sugars (AS), anhydrosugars (LMG) were considered.

**Results and Discussion**

Several organic and inorganic compounds were analyzed in aerosol samples collected at the Antarctic coastal base MZS during the austral summer 2010-2011 (2010, 29th November–2011, 18th January), as reported in table 1. Some results were reported in previous publications but in this work these are combined with new measurements and discussed together to identify the sources of Antarctic coastal aerosol using Factor Analysis (FA).

*Previous results on the aerosol samples collected at MZS (2010-11)*

Bazzano et al.\(^{15}\) determined major and trace elements in the samples in order to identify the source of the costal Antarctic atmospheric aerosol. The crustal input was the main source for Al, Co, Fe, Li, Mn, Rb, Y and V while Li, Mg, Na and Rb had a marine origin. These elements were mainly distributed in the coarse fraction of the aerosol (7.2-30 µm). An anthropogenic source was also identified for Cr, Cu, Mo and Pb, which showed highest concentrations in particles with lower aerodynamic diameters (1.5-0.95 µm).

Marine input was also identified by Rella and Maliesta\(^{16}\), who described the presence of Na\(^+\) and Cl\(^-\) and Mg\(^{2+}\) in the same samples with XPS. They also demonstrated the occurrence of Ca\(^{2+}\), which was not measured by Bazzano et al.\(^{15}\), in the aerosol samples with aerodynamic diameter below 3
µm. Two different sulfur species were observed: they proposed a local source for sulfate species, while the origin of organic sulfur species remained unclear. Two species were also found for fluorine: fluoride and organic fluorine, but the origin of the latter could not be identified.

Barbaro et al. [17, 18] and Zangrando et al. [19] characterized the water-soluble organic compounds (WSOC) fraction of Antarctic aerosol. A local marine source was associated with the highest concentration of amino acids in the fine fraction of the aerosol (<0.49µm) and the major presence of L-isomers was probably due to planktonic origin [17]. Primary production of fungi in ice-free areas near MZS was the source of alcohol-sugars [23] such as mannitol and arabitol in the coarse fraction (>1µm), whereas biogenic sources significantly influenced the concentration of glucose in the fine fraction (<1µm) [18]. During biomass burning events, it was also verified that sugars had the same particle-size distribution of levoglucosan when aerosol was affected by biomass burning [18]. The investigation of biomass burning markers in the Antarctic aerosol was the main aim of a recent paper [19]. The study of particle size distribution of levoglucosan confirmed the major presence of this long-range atmospheric transport tracer in the fine fraction, but a hygroscopic growth at the coastal site MZS was also observed. The same authors also investigated the occurrence of phenolic compounds because these species are usually used as biomass burning markers, indicating the type of burned plants. Results demonstrated that Antarctic samples had different levoglucosan/phenolic compounds ratios from aerosols directly affected by biomass burning. This difference suggested that other sources influenced the signal. Similar particle size distribution of phenolic compounds with locally produced amino acids may suggest the ocean as a major source: the lignin present in marine environment can undergo photochemical and microbiological degradation, producing phenolic compounds, then emitted in the atmosphere [19].

Ionic composition

The determination of major ions was aimed to complete our chemical characterization of these aerosol samples. We determined cations, such as potassium, sodium and magnesium, and anions
such as halides (chloride, bromide and iodide), MSA and non-sea-salt sulfate (nss-SO$_4^{2-}$). The nitrogen cycle was also investigated by determining the concentrations of ammonium, nitrate and nitrite.

Figure 1 shows the particle size distribution of ionic species analyzed in the fine (particle diameter, $D_p<1\,\mu$m) and coarse fraction ($1\,\mu$m<$D_p\leq10\,\mu$m). The average concentrations of each fraction were similar to those reported by Fattori et al. [1] for Na$^+$, Cl$^-$, nss-SO$_4^{2-}$, MSA, NO$_3^-$ and NH$_4^+$ determined in aerosol samples collected close to the sampling site during the austral summer 2002-2003.

The water-soluble fraction of Na and Mg was 57±25% and the 43±33% respectively of the total concentration determined by Bazzano et al. [15] using microwave-assisted acid digestion and ICP-AES analysis. In both determinations, these elements had the same particle size distribution, showing the highest concentration in the coarse fraction ($D_p>1\,\mu$m), probably due to proximity to the marine primary source.

Non-sea-salt sulfate represented 97% and 74% of the total sulfate in the fine and coarse fractions respectively, and was mainly distributed in the fine fraction, similarly to MSA, due to their common source by oxidation of dimethylsulfide (DMS) emitted in the atmosphere by the planktonic blooms [24].

The concentration of NH$_4^+$ ($33\pm9\,\text{ng m}^{-3}$) was very similar to those reported in the literature [13 and references within]. Previous studies [25-27] demonstrated that the emissions of NH$_3$ from seabirds and penguins could be an important source of NH$_4^+$ in Antarctica. In fact, our sampling location was placed near the skua nest and a lot of these birds were present near the sampling location. These birds may be potential sources of ammonium. Moreover, the existence of marine sources for aerosol ammonium was also demonstrated in previous studies [28, 29]. The presence of ammonium was also highlighted by the XPS analysis [16].
Br⁻ and I⁻ had lower concentrations than other ionic species, representing only 0.05% of the total ionic composition. They were mainly distributed in the fine fraction (142 pg m⁻³ for bromide and 22 pg m⁻³ for iodide) (figure 1), probably because these halogens can have similar sources as organic species, e.g. MSA³⁰.

The sea-salt input in the ionic composition is evident when considering the highest concentration of the major ions in the coarse mode. However, chloride depletion occurred in the aerosol samples and had a mean value of 70%. This value suggests that acidic species, mainly nitrate, sulfate and other organic acids, reacted with NaCl in sea-salt particles and replaced Cl⁻ in the form of gaseous HCl, as also previously demonstrated in literature³¹. This phenomenon was also confirmed by the Cl⁻/Na⁺ ratio in the coarse fraction (0.4 w/w), lower than that measured in sea water (1.8 w/w)³¹. This finding is in agreement with XPS results¹⁶.

The contribution of nitrate to the chloride depletion was evaluated by calculating the ratio of measured Na⁺ concentration to the total measured concentrations of NO₃⁻ and Cl⁻. A mean value of 4 (±2) was obtained, which is higher than the value (0.85) for unreacted original sea water. Possible explanations of this value are that 1) the chloride depletion can be attributed to sulfate or organic ion formation in sea-salt particles or 2) other sources of Na⁺ are present.

Enrichment factors of potassium, calculated as the ratio between K⁺/Na⁺ in the aerosol samples and K⁺/Na⁺ in seawater (0.037 w/w), was higher (5-20 w/w) in submicron particle sizes, suggesting that long-range atmospheric transport from biomass burning sources was the main source²⁹,³³.

Carboxylic acids

A homologous series of low-molecular-weight-carboxylic acids (C₂-C₈) were detected in Antarctic aerosol samples (figure 2), with concentrations ranging from 5 to 20 ng m⁻³ (average 9 ng m⁻³). Oxalic acid (C₂) was the most abundant carboxylic acid with concentrations between 0.8 and 15 ng m⁻³ (average 5 ng m⁻³). The values were very similar to those reported in the literature about other
sites in the Antarctic site\(^{34}\) and in the Southern Ocean\(^{35}\). Oxalic acid accounted for 57% to the quantified acid mass (figure 2), because it is the end-product of various oxidation/decomposition pathways in the atmosphere \(^{36}\). The concentrations of each acid decreased with the increase of the carbon chain length (figure 2).

All acids, except acetic acid, were mainly distributed in the fine fraction (<1 µm) (figure 2), due to their nature of secondary products in the atmosphere. Acetic acid has a different behavior than other acids due to its high vapor pressure. Matsumoto et al. \(^{37}\) demonstrated that acetic acid is mainly distributed in the gas phase but a portion is taken into basic coarse particles, such as sea salt. This compound is mainly produced by photochemical production of alkenes released by phytoplankton\(^{13}\).

In order to investigate the sources of carboxylic acids in Antarctic aerosols, the C\(_3\)/C\(_4\) ratio was used as an indicator of enhanced photochemical production of diacids, because succinic acid (C\(_4\)) can be degraded to malonic acid (C\(_3\)) for decarboxylation reactions activated by OH radicals \(^{38}\). Fu et al. \(^{38}\) studied the C\(_3\)/C\(_4\) ratio in several environments (urban and marine sites) to investigate the real sources of these compounds. Our 1.5 ratio is very similar to what they found from marine areas\(^{44}\), suggesting that 1) malonic acid can have a marine source or 2) it is photochemically produced during long-range transport from continents.

Trans configuration (trans-\(\text{usC}_4\)-fumaric acid) was more abundant than cis isomer (cis-\(\text{usC}_4\)-maleic acid) (figure 2) with low cis/trans ratios ranged between 0.09 and 1.5 (average 0.5). Fu et al. \(^{44}\) reported that lower cis/trans ratios (0.1-1.5) were generally observed for the marine aerosol than those reported in urban regions (0.9-2.3). cis-maleic acid is usually produced through the photochemical oxidation of benzene or toluene in urban regions near the emission sources \(^{39}\). Instead, low values of cis/trans ratio indicate further isomerization of cis-maleic acid to trans-fumaric acid during long-range transport\(^{36, 38}\). Moreover, the presence of trans-fumaric acid can
suggest non-anthropogenic precursors\textsuperscript{[40]} such as phenolic compounds originated from macroalgae in the sea surface slicks\textsuperscript{[41]}.

The photochemical oxidation during long-range atmospheric transport was also confirmed by the sea-salt enrichment factors calculated for C\textsubscript{2}-C\textsubscript{7}\textsuperscript{[42]}. Values much greater than 1 were obtained (average value between $7 \times 10^3$ for maleic acid and $1 \times 10^5$ for adipic acid), demonstrating that these compounds clearly do not originate from sea-salt but are produced in the atmosphere as secondary organic aerosol\textsuperscript{[33]}.

\textit{Chemical composition of fine and coarse fraction Antarctic PM\textsubscript{10} aerosol}

All data of PM\textsubscript{10} aerosol samples collected at MZS during the austral summer 2010-11 (reported in this paper) were combined to perform a complete chemical characterization of Antarctic aerosol. Figure 3 describes the chemical composition of coarse ($1 \, \mu m < D_p \leq 10 \, \mu m$) and fine ($<1 \, \mu m$) aerosol.

In the coarse fraction, sodium was the most abundant species indicating the contribution from sea spray. Instead, the fine fraction was mainly characterized by sulfur species (sulfate and organic MSA), demonstrating the influence of marine primary production\textsuperscript{[1]}. Considering that the amino acid concentration is usually lower than that of ionic compounds or major elements, an important percentage of L-Arg (1\%) was present in this fraction, due to the correlation of this amino acid with the primary production by marine algal bloom\textsuperscript{[17]}.

\textit{Aerosol mass: preliminary results}

Due to several technical problems that occurred in the field, the results obtained were not always reliable. Nevertheless, these preliminary tests did allow us to obtain first estimates of the mass concentrations of size-segregated aerosol fractions by direct gravimetry. In particular, for the samples collected in the period from December $29^{th}$, 2010 to January $8^{th}$, 2011, we obtained the following atmospheric concentrations of size-resolved aerosol: $0.23 \pm 0.01 \, \mu g \, m^{-3}$ for particle diameter ($D_p)<0.49 \, \mu m$; $0.026 \pm 0.009 \, \mu g \, m^{-3}$ for $D_p \, 0.49-0.95 \mu m$; $0.17 \pm 0.01 \, \mu g \, m^{-3}$ for $D_p \, 0.95-1.5 \mu m$. 

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µm; 0.020±0.002 µg m⁻³ for Dₚ 1.5–3.0 µm; 0.25±0.01 µg m⁻³ for Dₚ 3.0–7.2 µm; 0.026±0.003 µg m⁻³ for Dₚ 7.2–10 µm. The sum of the aerosol size fraction concentrations gave a total of 0.71±0.02 µg m⁻³ and this value is in good agreement with the data reported in the literature for this same sampling area, considering both direct [⁸, ²²] and indirect PM₁₀ mass measurements [¹, ²¹].

**Persistent Organic Pollutants**

In order to complete the chemical characterization of Antarctic aerosol, a specific aerosol sampler was used to collect the total suspended particles and the volatile fractions of aerosol to determine persistent organic pollutants (POPs).

For each class of pollutants, the total concentration in atmosphere of particulate-associated contamination (QFF samples) and the gaseous-phase contamination (PUF samples) were determined. In general, particulate-associated contamination is lower than gaseous-phase contamination and the differences in total concentration between the samples collected do not show any evident temporal trend over the sampling period. Among the five classes considered, PAH and OCP showed the highest mean total concentration in the atmosphere. Regarding these two classes of pollutants, the highest average concentrations were measured for γ-HCH (0.88 pg m⁻³), HCB (0.093 pg m⁻³), cis–chlordane (0.056 pg m⁻³) and p,p-DDE (0.23 pg m⁻³), fluoranthene (0.11 pg m⁻³⁻³), benzo[a]pyrene (0.13 pg m⁻³), benzo[b]fluoranthene (0.18 pg m⁻³), and indeno[1,2,3-cd]pyrene (0.19 pg m⁻³). Among OCPs, γ-HCH and HCB represent the organochlorine pesticides that most frequently occur in the ocean and Antarctic atmosphere [⁴³, ⁴⁴].

For PCBs, PBDEs and PCNs, highest average concentrations were found for PCB-101 (0.15 pg m⁻³), PCB-118 (0.06 pg m⁻³), PCB1-38 (0.07 pg m⁻³), PCB-153 (0.05 pg m⁻³), PBDE-47 (0.08 pg m⁻³), PBDE-100 (0.05 pg m⁻³), PBDE-154 (0.09 pg m⁻³), PBDE-183 (0.10 pg m⁻³), PCN-53 (0.073 pg m⁻³), PCN-46 (0.06 pg m⁻³) and PCN-52 (0.04 pg m⁻³). The mean concentrations measured for these pollutants are in agreement with a previous study in which samples from the austral summer 2003-
2004 and 2009-2010 were analyzed\cite{14,45}. Total concentrations of PCB, PBDE and PCN are similar to other measurements described in the literature. For example, Li et al. \cite{46} found a total concentration of indicator PCBs (PCB-28, 52, 101, 118, 138, 152, 180) and a total PBDE concentration at King George Island (Keller Peninsula) respectively of 4.34 pg m$^{-3}$ and 1.52 pg m$^{-3}$; Ockenden et al. \cite{47} found at Halley Research Station, a total concentration of 2.45 pg m$^{-3}$ (PCB-28, 52, 101, 153, 132, 138, 180).

**Study of aerosol sources**

Factor analysis (FA) was performed to identify the sources using specific chemical tracers (figure 4). The first three factors explained 64\% of the total variance of the data. Loadings of variables seem to be separated into three groups as shown in figure 4. The first group comprised elements having a local source, either marine (e.g. Li, Mg and Na) or crustal (e.g Al, Fe, Mn, Y), which were correlated with FA1. Anthropic species, as Cr, Pb and levoglucosan (LMG) formed a second group, showing a positive correlation with FA2 and negative correlation with FA1. Finally, biogenic compounds like MSA, NH$_4^+$ and nss-SO$_4^{2-}$ were well separated from the other parameters by FA2 and FA3 factors.

Figure 4 also shows the scores plot of the samples, identified with a progressive number for the sampling period and a progressive letter for the cut-off size (a: 10-7.2 µm; b: 7.2-3 µm; c: 3-1.5 µm; d: 1.5-0.95 µm; e: 0.95-0.49 µm). Most of the samples were distributed close to their origin with two exceptions. The samples 1a (29 November-9 December 2010 with particle size between 10 µm and 7.2 µm) have a high score value in the FA 2 that had high correlation with the loadings of the anthropic species (e.g., Cr, LMG, Pb). This result was in accordance with the previous evaluations\cite{18,19} about the same sampling period. Barbaro et al. \cite{18} observed that the particle size distribution of sugars (MA, AS and sucrose) was similar to the levoglucosan trend in the same sample, identifying an anthropic emission during the sampling period.
High score value for sample 5b (from 8 to 23 January 2011 with particle size of 7.2-30 µm) can be attributed to high concentrations of sea-salt components (e.g., Na) that increased in the last period of aerosol collection, due to the reduction of the snow coverage and the melting of the sea-ice.

Conclusions

An extensive investigation of the chemical composition of Antarctic aerosol was carried out at MZS (Victoria Land, Antarctica) during the 2010-2011 austral summer. Several chemical measurements (major ions, major and trace elements, carboxylic acids, WSOC and POPs) were combined in order to individuate the possible aerosol sources and evaluate each contribution. The POP determination in the aerosol samples indicated a significant anthropogenic contribution in this remote area.

Factor analysis permitted to globally consider specific chemical markers. Three groups were identified: 1) local emission, identified by sea salt ion (Na, Li, and Mg) and crustal trace elements (Al, Fe, Co, Mn); 2) anthropic species such as Cr, Pb and levoglucosan, correlated with sugars (MA, AS and sucrose) due to a particular emission occurred during the first sampling period; 3) biogenic compounds, such as MSA, nss-SO\(_4^{2-}\) and NH\(_4^+\).

Acknowledgments

This work was financially supported by the Italian National Programme of Antarctic Research (PNRA) through the project “Studio delle sorgenti e dei processi di trasferimento dell’aerosol atmosferico antartico” (2009/A2.11) and the project PON 254/Ric Cod.PONa3_00334. The research was also supported by the National Research Council of Italy (CNR). The authors thank ELGA LabWater for providing the PURE-LAB Option-R and Ultra Analytic, which produced the ultra-pure water used in these experiments.
References


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Table 1. Summary of analytes detected in the aerosol collected at MZS during the austral summer 2010-11. For each class of compounds, sampling system and analytical technique used were reported.

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<td>ICP-AES</td>
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<td><strong>Trace elements:</strong> Li, V, Cr, Mn, Co, Cu, Rb, Y, Mo, Pb</td>
<td>HV cascade impactor equipped with cellulose filter</td>
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<td>XPS</td>
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<td><strong>Amino acids (AA):</strong> Gly, L-Ala, L-Asp, L-Arg, L-Glu, L-Phe, L-Pro, L-Tyr, L-Thr</td>
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**Figure 3.** Chemical composition of PM$_{10}$ aerosol collected at the coastal base "Mario Zucchelli" during the austral summer 2010-11. All compounds with percentage >1% are reported. The percentage value is related to the sum of all analyzed compounds.

**Figure 4.** Factor analysis results: projections of the variables and the cases on the factor-plane 1x2x3. Scores labels includes a progressive number for the sampling period and a progressive letter for the cut-off size (a: 10-7.2 µm; b: 7.2-3 µm; c: 3-1.5 µm; d: 1.5-0.95 µm; e: 0.95-0.49 µm).
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