Research Paper

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

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Environmental context. Owing to its remoteness, Antarctica is an excellent natural laboratory for conducting studies on the behavior of marine aerosols and for monitoring the impact of global human activities. The aim of this study is to provide an extensive chemical characterization of Antarctic aerosol and to investigate its sources. A distinction among anthropogenic, crustal, and biogenic sources was defined using several chemical markers.

Abstract. During the 2010–11 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 about water-soluble organic compounds and major and trace elements were merged with novel measurements of major ions, carboxylic acids and persistent organic pollutants (polychlorobiphenyls, polycyclic aromatic hydrocarbons, polychlorinated naphthalenes, polybrominated diphenylethers and organochlorine pesticides) in order to provide a chemical characterisation of Antarctic aerosol and to investigate its sources. The persistent organic pollutants were determined using a high-volume sampler, able to collect both particulate and gaseous fractions, whereas remaining compounds were determined by performing an aerosol size fractionation with a PM_{10} cascade impactor. Ionic species represented 58 % (350 ng m^{-3}) of the sum of concentrations of all detected compounds (596 ng m^{-3}) in our Antarctic PM_{10} aerosol samples 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 the PM_{10} sampler in order to make a distinction between anthropogenic, crustal and biogenic sources using specific chemical markers.

Introduction

The investigation of the chemical composition of the Antarctic atmosphere is one of the key points in polar research. Owing 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 behaviour of these compounds will enable the use of these species as markers for specific sources in paleoclimatic studies based on Antarctic ice core data.

To date, the chemical characterisation of Antarctic aerosol has been the object of disconnected investigations. Several studies have focussed on major ions[1–6] or on trace elements;[7–12] a few organic compounds were also recently investigated.[13,14]

The goal of the present research is to carry out an accurate and wide-ranging chemical characterisation of a coastal Antarctic aerosol in order to define the aerosol sources for future applications to ice core studies.[15–19] Here, we report the final results and conclusions of the 'Study of sources and transport processes in the atmospheric aerosol' project financially supported by the Italian National Program for Research in Antarctica (PNRA). Five Italian universities contributed to the investigation of aerosol sources in Antarctica.

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

We propose a synthesis of all measurements of aerosol samples collected at the Mario Zucchelli (MZS) Italian research station (Antarctica) during the austral summer of 2010–11. Bazzano et al.[20] described the composition of major and trace elements of aerosol samples at MZS during the sampling period. Rella and Malitesta[21] performed a qualitative and quantitative analysis of particulate matter surface using X-ray photoelectron spectroscopy (XPS), determining the presence of several species such as ammonium, nitrate, sulfate, organic sulfur, fluoride and organic fluoride. Barbaro et al.[22,23] determined the site's content of amino acids and sugars, whereas Zangrando et al.[24] investigated several biomass-burning markers (levoglucosan and phenolic compounds).

Moreover, the present study integrates additional groups of compounds in the characterisation of the Antarctic atmosphere. These consist of ionic species (Cl^-, Br^-, I^-, NO_2^-, NO_3^-, SO_4^{2-}, $H_2PO_4^{2-}$ 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; h is hydroxylated, us is unsaturated, a is aromatic) and persistent organic pollutants (POPs) including polychlorobiphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH), polychlorinated naphthalenes (PCN), polybrominated diphenyl ethers (PBDE) and organochlorine pesticides (OCP).

Material and methods

Sample collection and processing of PM₁₀ aerosol

Aerosol samples ($n = 5$) were collected using two analogous high-volume cascade impactors (TE-6070, Tisch Environmental Inc., Cleves, OH, USA; PM₁₀ high-volume air sampler) with 10.0–7.2-, 7.2–3.0-, 3.0–1.5-, 1.5–0.95-, 0.95–0.49- and <0.49-μm particle cut-off diameters, placed at Campo Faraglione (74°42′S, 164°06′E), ~3 km south of the Italian MZS research base (Victoria Land, Antarctica) from 29 November 2010 to 23 January 2011. The average airflow of both air samplers was 1.1 m^3 min^{-1} and the sampling resolution was ~10 days (~15000 m^3 per sample). One air sampler employed cellulose filters for the determination of metals in the particulate matter whereas the second used quartz fibre filters for the investigation of 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 10 min 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 two aluminium foil envelopes 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 (Al, Fe, Mg, Na, Co, Cu, Li, Mn, Mo, Pb, Rb, Y, Cr and V) has been described by Bazzano et al.[20] The procedure consisted of a microwave-assisted acid digestion of the cellulose filters using a two-step procedure: addition of (1) nitric acid, hydrofluoric acid and ultrapure water, and (2) saturated boric acid solution. The analysis was performed using inductively coupled plasma–atomic emission spectrometry (ICP-AES) and inductively coupled plasma–mass spectrometry (ICP-MS).[20]

The XPS measurements to determine Na^+ (e.g. NaCl, Na_2CO_3), N–C, N^+ (NH_4^+), NO_3^-, Cl^-, SO_4^{2-}, silicates, F^-, Ca^{2+} (e.g. $CaCO_3$), Al_2O_3, aluminium silicate, Fe^{III}, Mg^{II}, PO_4^{3-} and Zn^{II} were recorded on samples without any pretreatment with an Axis Ultra DLD (Kratos Analytical) photoelectron spectrometer using a monochromatic Al Kα source (1486.6 eV) operating at 225 W.[21]

The pre-analytical and sample extraction protocol to determine amino acids, phenolic compounds and sugars has been described elsewhere.[22–24] Briefly, filters were spiked with a ^{13}C-labelled internal standard mix (amino acids, phenolic compounds and levoglucosan), ultrasonically extracted with ultrapure water, and filtered through a 0.45-μm polytetrafluoroethylene (PTFE) filter. Amino acid determination was obtained using high-performance liquid chromatography with a chiral column coupled with tandem mass spectrometry (HPLC-MS/MS).[22] Phenolic compounds were analysed using reverse-phase chromatography coupled with tandem mass spectrometry,[24] whereas sugars were determined using ion chromatography coupled with mass spectrometry (IC-MS).[23]

The analytical procedure to determine ionic species consisted in ultrasonic extraction with ultrapure water and 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 (Thermo Scientific Dionex™ ICS-5000, Waltham, MA, USA), with an anion-exchange column (Dionex Ion Pac AS11 2 × 250 mm) and guard column (Dionex Ion Pac AG11 2 × 50 mm), coupled with a single mass spectrometer (MSQ Plus™, ThermoScientific, Bremen, Germany). The ion chromatograph was equipped with a capillary system to simultaneously determine cations using a conductivity detector. Sodium, ammonium, magnesium and potassium were separated using an Ion Pac CS19–4μm capillary cation-exchange column (0.4 × 250 mm) equipped with an Ion Pac CG19–4μm guard column (0.4 × 50 mm). All details about ionic determinations are reported in the Supplementary material (available online).

Each procedure was previously validated to ensure an accurate quantification of each analyte.[20,22,23,25] All reported values were blank-corrected. A summary of each compound reported in the present paper and the analytical protocol used for its determination is reported in Table 1.

Table 1. **Summary of analytes detected in the aerosol collected at the Mario Zucchelli research station (MZS) during the austral summer of 2010–11**
For each class of compounds, sampling system and analytical technique used are reported

Compounds	Sampling system	Analytical technique	Reference
Major elements: Al, Fe, Mg, Na	HV cascade impactor equipped with cellulose filter	ICP-AES	[20]
Trace elements: Li, V, Cr, Mn, Co, Cu, Rb, Y, Mo, Pb	HV cascade impactor equipped with cellulose filter	ICP-MS	[20]
Qualitative analysis: Na^+ (e.g. NaCl, Na_2CO_3), NH_4^+, NO_3^-, Cl^-, SO_4^{2-}, silicates, F^-, Ca^{2+} (e.g. $CaCO_3$), Al_2O_3, Al silicate, Fe^{III}, Mg^{II}, PO_4^{3-}, Zn^{II}	HV cascade impactor equipped with cellulose filter	XPS	[21]
Amino acids (*AAs*): Gly, L-Ala, L-Asp, L-Arg, L-Glu, L-Phe, L-Pro, L-Tyr, L-Thr	HV cascade impactor equipped with quartz filter	HPLC-MS/MS with chiral column	[22]
Phenolic compounds (*PCs*): vanillin, vanillic acid, homovanillic acid, syringic acid, syringaldehyde, *p*-coumaric acid, coniferylaldehyde, ferulic acid	HV cascade impactor equipped with quartz filter	HPLC-MS/MS	[24,25]
Monosaccharides (*MAs*): glucose, fructose, arabinose, galactose, mannose, xylose	HV cascade impactor equipped with quartz filter	HPAEC-MS	[23]
Disaccharide: sucrose	HV cascade impactor equipped with quartz filter	HPAEC-MS	[23]
Alcohol sugars (*ASs*): arabitol, mannitol, erythritol, ribitol, sorbitol and galactitol, xylitol	HV cascade impactor equipped with quartz filter	HPAEC-MS	[23]
Anhydrosugars (*LMG*): levoglucosan, mannosan, galactosan	HV cascade impactor equipped with quartz filter	HPAEC-MS	[23]
Cations: Na^+, NH_4^+, K^+, Mg^{2+}	HV cascade impactor equipped with quartz filter	Capillary cationic chromatography with conductivity detector	Present paper
Anions: Cl^-, Br^-, I^-, NO_2^-, NO_3^-, sulfate, phosphate and methanesulfonic acid (MSA)	HV cascade impactor equipped with quartz filter	HPAEC-MS	Present paper
Carboxylic acids (*CAs*): C_2-oxalic, C_2-acetic, C_2-glycolic, C_3-malonic, C_4-succinic, hC_4-malic, *cis-us*C_4-maleic, *trans-us*C_4-fumaric, C_5-glutaric, C_6-adipic, C_7-pimelic, aC_7-benzoic, C_8-suberic	HV cascade impactor equipped with quartz filter	HPAEC-MS	Present paper
POPs: PCB, PAH, PCN, PBDE, POC	TSP air sampler equipped with polyurethane foam and quartz filter	GC-MS	Present paper

Aerosol mass measurements

During the 2010–11 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 PM_{10}.[26,27] A computerised Mettler Toledo (Greifensee, Switzerland) AT261 electronic microbalance (readability 0.01 mg, repeatability s.d.0.015 mg) was used.

In order to maintain weighing conditions as stable as possible, a decontaminated polyethylene Atmosbag glove bag (Sigma–Aldrich, gas volume 520 L, closure type zipper-lock, unsterilised) was used, and the microbalance was placed inside it. Temperature and humidity were measured throughout the weighing session using a mini thermo-hygrometer (digital psychrometer Testo, model 605-HI). Temperature and relative humidity inside the glove bag were stable throughout the weighing procedure, varying by $\pm 0.1\,°C$ and $\pm 0.2\,\%$ 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 fibre filters (QFF) for contaminants associated with total suspended particles (TSP) and polyurethane foam adsorbent (PUF) for gaseous-phase contaminants. The sampling site and period were 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 ($\sim$2900 m^3 per sample). At the end of each sampling, PUF and QFF were removed from the holder, wrapped in double aluminium foil envelopes, sealed in double polyethylene bags and stored 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 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. The compounds under investigation were: 21 congeners of PCBs (-66,-77,-87,-101,-105,-118,-126,-128,-138,-153, -154,-169,-170,-180,-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), 42 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,-153,-171,-180,-183,-184,-191, -196,-197,-201,-203,-204,-205,-206,-207,-208,-209), 6 compounds belonging to the PAH group (fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c*,*d*]pyrene, benzo(*g*,*h*,*i*)perylene) and 19 compounds belonging to the POC group (benfluoralin, trifluoralin, hexachlorobenzene (HCB), gamma-hexachlorocyclohexane (γ-HCH), metolachlor, terbutryn, malathion, heptachloroepoxides A and B, *cis* and *trans*-chlordane, endosulfan, dieldrin, *p*,*p*-DDE, endrin, endosulfans I and II). All details about the sample

processing and analysis are reported in the Supplementary material.

Data processing

A statistical approach was used for the dataset obtained from the 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 μm. For statistical analysis, the concentration values below the limit of detection (LOD) were substituted by 1/2 LOD. Factor analysis (FA) with varimax rotation was performed on the autoscaled data matrix constituting 25 rows (samples) and 31 columns (chemical components) using *Statistica 8.0* (StatSoft, Inc., 2007).

Chemical components were: (1) major and trace elements detected by ICP-AES and ICP-MS;[20] (2) ionic species determined by high-performance anionic exchange chromatography coupled with mass spectrometry (HPAEC-MS) and IC by conductivity detection (Table S1); (3) amino acids and phenolic compounds detected by HPLC-MS/MS;[22,24] and (4) sugars determined by HPAEC-MS.[23] The concentration values of Na and Mg determined by ICP-AES[25] were used because soluble and insoluble fractions of these species were considered. In order to decrease the number of chemical components, the sum of amino acids (AA), phenolic compounds (PC), carboxylic acids (CA), monosaccharides (MS), alcohol sugars (AS) and anhydrosugars, as the sum of levoglucosan, mannosan and galactosan (LMG) were considered (Table S2).

Results and discussion

Several organic and inorganic compounds were analysed in aerosol samples collected at the Antarctic MZS coastal base during the austral summer of 2010–11 (29 November 2010–18 January 2011), as reported in Table 1. Some results have been reported in previous publications but in the present work, these are combined with new measurements and discussed together to identify the sources of Antarctic coastal aerosol using 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 sources of the costal Antarctic atmospheric aerosol. Crustal input was the main source for Al, Co, Fe, Li, Mn, Rb, Y and V whereas Li, Mg, Na and Rb had a marine origin. These elements were mainly distributed in the coarse fraction of the aerosol (7.2–3.0 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 Malitesta,[21] 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.[20] in the aerosol samples with aerodynamic diameter below 3 μm. Two different sulfur species were observed: they proposed a local source for sulfate species, whereas 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. A tentative explanation of the experimental finding could relate to the reported occurrence of organic F species in Antarctica.[28]

Barbaro et al.[22,23] and Zangrando et al.[24] characterised the water-soluble organic compound (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 (<0.49 μm) and the predominant presence of L-isomers was probably due to planktonic origin.[22] Primary production of fungi in ice-free areas near MZS was the source of ASs[29] such as mannitol and arabitol in the coarse fraction (>1 μm), whereas biogenic sources significantly influenced the concentration of glucose in the fine fraction (<1 μm).[23] During biomass-burning events, it was also verified that sugars had the same particle-size distribution as levoglucosan when aerosol was affected by biomass-burning.[23] The investigation of biomass-burning markers in the Antarctic aerosol was the main aim of a recent paper.[24] The study of the 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 MZS coastal site 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 compound ratios from aerosols directly affected by biomass-burning. This difference suggested that other sources influenced the signal. Particle size distribution of phenolic compounds similar to locally produced amino acids may suggest the ocean as a major source: the lignin present in the marine environment can undergo photochemical and microbiological degradation, producing phenolic compounds then emitted into the atmosphere.[24]

Ionic composition

The determination of major ions aimed to complete our chemical characterisation 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 (Table S1).

Fig. 1 shows the particle size distribution of ionic species analysed in the fine (particle diameter, D_p < 1 μm) and coarse fraction ($1 < D_p \leq 10$ μm). The concentration of ionic species in the fine fraction was obtained by summing up the values obtained from filters with 0.95–0.49- and <0.49-μm particle cut-off diameters, whereas the remaining values were summed up to obtain the concentration in the coarse fraction. 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 of 2002–03.

The water-soluble fraction of Na and Mg was 57 ± 25 and 43 ± 33 % respectively of the total concentration determined by Bazzano et al.[20] 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 ($D_p > 1$ μm), 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, owing to their common source by oxidation of dimethylsulfide (DMS) emitted in the atmosphere by the planktonic blooms.[30]

The concentration of NH_4^+ (33 ± 9 ng m^{-3}) was very similar to those reported in the literature by Xu et al.[13] and the references therein. Previous studies[31–33] demonstrated that the emissions of NH_3 from seabirds and penguins could be an
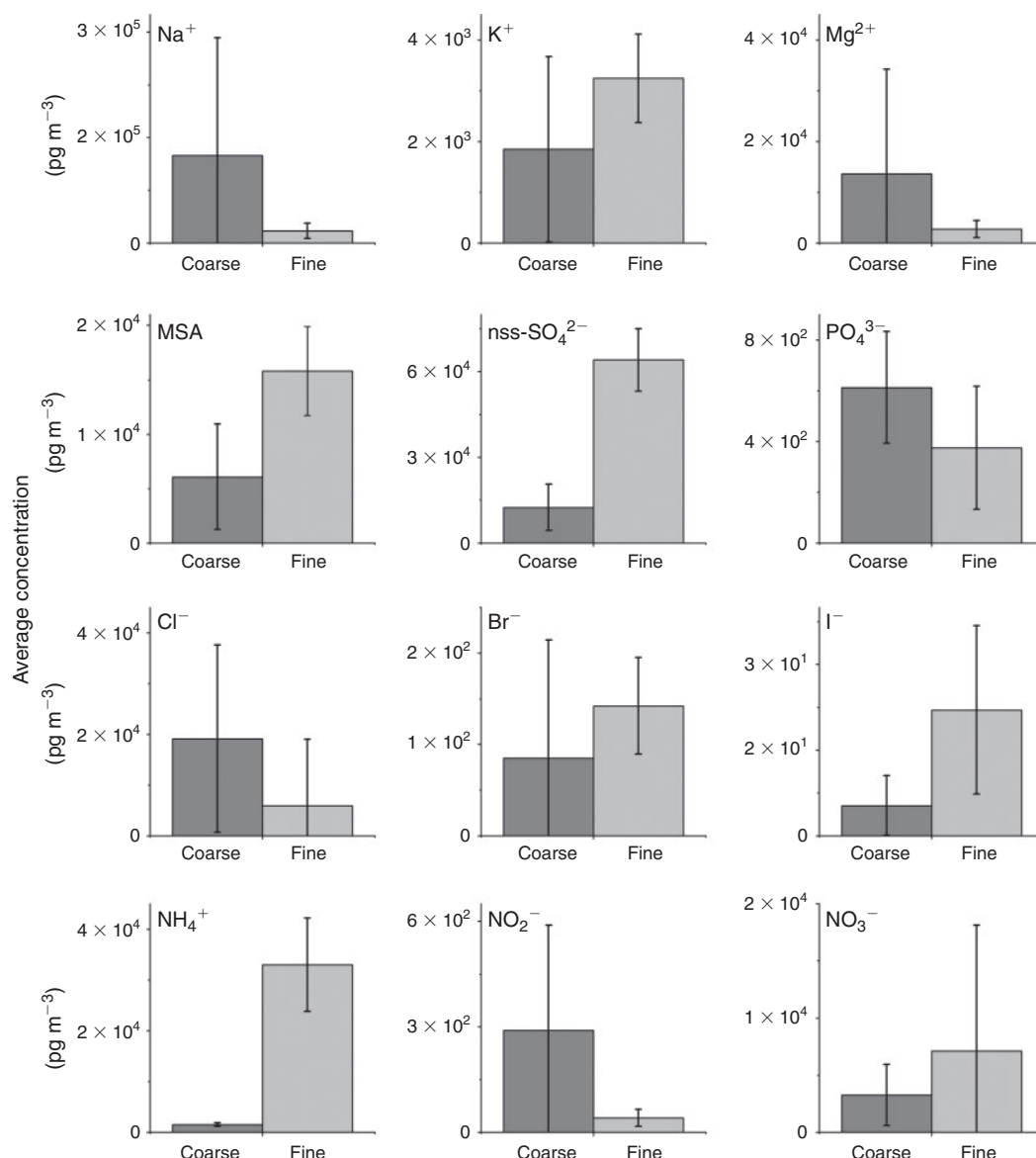
Fig. 1. Average concentration with error bars of ionic species in the coarse (>1, <10 μm) and fine (<1 μm) fractions and standard deviations of aerosol samples collected at the Mario Zucchelli research station (MZS) during the austral summer 2010–11. MSA, methanesulfonic acid; nss, non-sea-salt.

important source of NH_4^+ in Antarctica. In fact, our sampling location was placed near a skua nesting site and many 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.[34,35] The presence of ammonium was also highlighted by the XPS analysis.[21]

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) (Fig. 1), probably because these halogens can have similar sources to organic species, e.g. MSA.[36]

The sea-salt input in the ionic composition is evident when considering the highest concentration of the major ions in the coarse fraction. 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 the literature.[37] 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).[37] This finding is in agreement with XPS results.[21]

The contribution of nitrate to the chloride depletion was evaluated by calculating the ratio of measured Na$^+$ concentration to the total measured concentrations of NO_3^- and Cl$^-$. A mean value of 4 ($\pm$2) was obtained, which is higher than the value (0.85) for unreacted original sea water. Possible explanations of this value are that (1) chloride depletion can be attributed to sulfate or organic ion formation in sea-salt particles, or (2) other sources of Na$^+$ are present.

Enrichment factors of potassium, calculated as the K$^+$/Na$^+$ ratio in the aerosol samples and K$^+$/Na$^+$ in seawater (0.037 w/w), was higher (5–20 w/w) in submicrometer particle sizes, suggesting that long-range atmospheric transport from biomass-burning sources was the main source.[38,39]
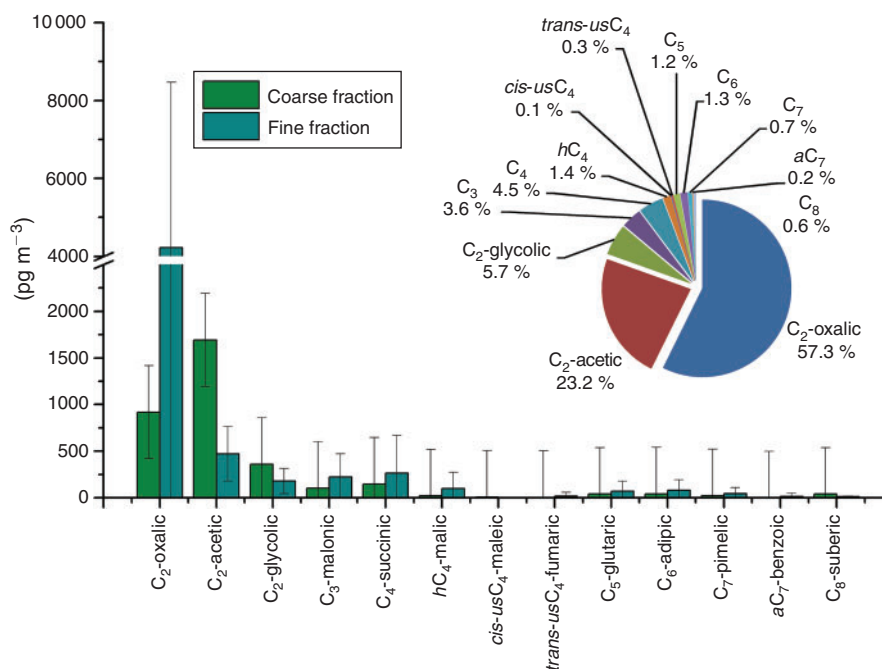
Fig. 2. Particle size distribution with error bars of carboxylic acids and percentage values relative to PM$_{10}$ aerosol samples collected at the Mario Zucchelli research station (MZS) from 29 November 2010 to 18 January 2011.

Ionic balance was evaluated considering the ion concentration in terms of equivalents (eq). The most important alkaline species are Na$^+$ (6 neq m^{-3}; 47%), NH$_4$$^+$ (2 neq m^{-3}; 15%) and Mg^{2+} (1 neq m^{-3}; 10%), whereas nss-SO$_4$$^{2-}$ represents only 15% (2 neq m^{-3}) (Fig. S1). Na$^+$ correlates very well with Mg^{2+}, K$^+$ and Br$^-$ ($r > 0.9$; $P < 0.05$), whereas nss-SO$_4$$^{2-}$ correlates with K$^+$ and Mg^{2+} ($r = 0.94$ and 0.89 respectively; $P < 0.05$), indicating that these species are neutralised by nss-sulfate (Table S3). Examining the anion/cation charge balance, the ratio of the sum of anions to the sum of cations found in each PM$_{10}$ sample was calculated. A mean value of 0.48 was calculated, which is significantly lower than unity and indicates a net deficit of anions when compared with cations.

Carboxylic acids

A homologous series of low-molecular-weight carboxylic acids (C$_2$–C$_8$) were detected in Antarctic aerosol samples (Fig. 2), with concentrations ranging from 5 to 20 ng m^{-3} (average 9 ng m^{-3}). Oxalic acid (C$_2$) 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 for other sites in the Antarctic site[40] and in the Southern Ocean.[41] Oxalic acid accounted for 57% to the quantified acid mass (Fig. 2), because it is the end product of various oxidation–decomposition pathways in the atmosphere.[42] The concentrations of each acid decreased with increase of the carbon chain length (Fig. 2).

All acids, except acetic acid and glycolic acid (called also hydroxyacetic acid), were mainly distributed in the fine fraction (<1 μm) (Fig. 2), owing to their nature as secondary products in the atmosphere. Acetic acid and its hydroxyl derivative have different behaviour than other acids, probably due to their high vapour pressure. Matsumoto et al.[43] 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 oxidation 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$_3$) through decarboxylation reactions activated by OH radicals.[44] Fu et al.[44] 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.

The isomer with a *trans*-configuration (*trans-us*C$_4$-fumaric acid) was more abundant than the *cis* isomer (*cis-us*C$_4$-maleic acid) (Fig. 2), with low *cis/trans* ratios ranging 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 marine aerosols 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 their emission sources.[45] In contrast, low values of the *cis/trans* ratio indicate further isomerisation of *cis*-maleic acid to *trans*-fumaric acid during long-range transport.[42,44] Moreover, the presence of *trans*-fumaric acid can suggest non-anthropogenic precursors[46] such as phenolic compounds originating from macroalgae in sea-surface slicks.[47]

Photochemical oxidation during long-range atmospheric transport was also confirmed by the sea-salt enrichment factors calculated for C$_2$–C$_7$.[48] Values much greater than 1 were obtained (average value between 7×10^3 for maleic acid and 1×10^5 for adipic acid), demonstrating that these compounds clearly do not originate from sea-salt but are produced in the atmosphere as secondary organic aerosol.[39]
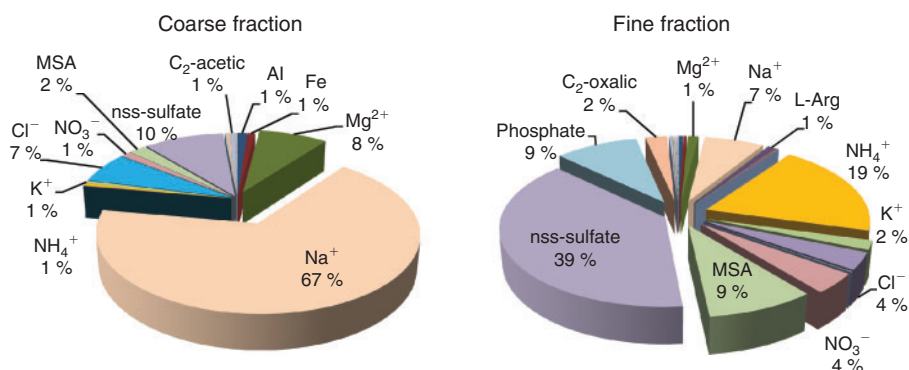
Fig. 3. Chemical composition of PM_{10} aerosol collected at the Mario Zucchelli coastal base during the austral summer 2010–11. All compounds with percentages >1% are reported. The percentage value is related to the sum of all analysed compounds. MSA, methanesulfonic acid; nss, non-sea-salt.

Chemical composition of fine- and coarse-fraction Antarctic PM_{10} aerosol

All data of PM_{10} aerosol samples collected at MZS during the austral summer of 2010–11 (reported in the current paper) were combined to perform a complete chemical characterisation of Antarctic aerosol. Fig. 3 describes the chemical composition of coarse ($1 < D_p \leq 10$ μm) and fine (<1 μm) aerosol, showing only species with a percentage >1%. In the coarse fraction, sodium was the most abundant species, indicating the contribution from sea spray. In contrast, the fine fraction was mainly characterised by sulfur species (sulfate and organic MSA), demonstrating the influence of marine primary production.[1] Considering that the amino acid concentration is usually lower than that of ionic compounds or major elements, an important percentage of L-arginine (1%) was present in this fraction, due to the correlation of this amino acid with primary production by marine algal blooms.[22]

Aerosol mass: preliminary results

Owing 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 29 December 2010 to 8 January 2011, we obtained the following atmospheric concentrations of size-resolved aerosol: 0.23 ± 0.01 μg m^{-3} for particle diameter $D_p < 0.49$ μm; 0.026 ± 0.009 μg m^{-3} for D_p 0.49–0.95 μm; 0.17 ± 0.01 μg m^{-3} for D_p 0.95–1.5 μm; 0.020 ± 0.002 μg m^{-3} for D_p 1.5–3.0 μm; 0.25 ± 0.01 μg m^{-3} for D_p 3.0–7.2 μm; 0.026 ± 0.003 μg m^{-3} for D_p 7.2–10 μm. The sum of the aerosol size fraction concentrations was 0.71 ± 0.02 μg m^{-3} and this value is in good agreement with data reported in the literature for this same sampling area, considering both direct[8,27] and indirect PM_{10} mass measurements.[1,26]

Even if these data are only first estimates, it can be noted that ~60% of the PM_{10} mass was found in the fine fraction (particle size ≤1 μm). This finding is in agreement with Teinila et al.[49] and Kerminen et al.[50] who found a similar contribution (more than 70%) of the fine fraction to the total average mass during the summer at the Finnish Aboa Station (western Queen Maud Land).

A more accurate study on the direct measurement of the aerosol mass concentration will allow us to achieve a better evaluation of the aerosol mass distribution over the different size-segregated fractions and the assessment of the seasonal evolution of these PM_{10} fractions.

Persistent organic pollutants

In order to complete the chemical characterisation of Antarctic aerosol, a specific aerosol sampler was used to collect all the suspended particles and the volatile fractions of aerosol to determine POPs.

For each class of pollutants, the total concentration in the atmosphere of particulate-associated contamination (QFF samples) and the gaseous-phase contamination (PUF samples) were determined (Table S4). 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, PAHs and OCPs 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}), benzo[*a*]pyrene (0.13 pg m^{-3}), benzo[*b*]fluoranthene (0.18 pg m^{-3}) and indeno [1,2,3-*c,d*]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.[51,52]

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 pgm^{-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 2003–04 and 2009–10 were analysed.[14,53] Total concentrations of PCB, PBDE and PCN are similar to other measurements described in the literature. For example, Li et al.[54] 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 and 1.52 pg m^{-3};[54] Ockenden et al.[55] found a total concentration of 2.45 pg m^{-3} (PCB-28, -52, -101, -153, -132, -138, -180) at Halley Research Station.

Study of aerosol sources

Factor analysis was performed to identify the sources using specific chemical tracers. Table 2 shows the factor loading of

Table 2. Factor analysis results with factor loadings and scores (bold values above ±0.5)

Scores label 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. AA, amino acid; PC, phenolic compound; MS, monosaccharide; AS, alcohol sugar; LMG, levoglucosan, mannosan, galactosan; MSA, methanesulfonic acid; nss, non-sea-salt

Variables	F1	F2	F3	F4	Cases	F1	F2	F3	F4
Al	0.44	0.04	0.12	**0.80**	1a	−0.26	**3.83**	0.14	**−0.76**
Fe	**0.56**	−0.07	0.16	**0.58**	1b	−0.46	**1.71**	**0.57**	**0.71**
Mg	**0.98**	−0.05	0.02	0.12	1c	−0.44	**0.95**	**0.74**	**1.06**
Na	**0.99**	−0.03	0.03	0.10	1d	−0.26	**0.56**	0.11	**1.20**
Co	**0.50**	−0.08	−0.12	**0.81**	1e	−0.27	**0.75**	**−0.94**	**1.22**
Cu	0.23	**0.81**	−0.01	0.32	2a	−0.47	**−0.68**	**1.03**	**0.58**
Li	**0.95**	0.00	0.05	0.29	2b	−0.13	**−0.73**	**0.70**	**1.89**
Mn	0.46	0.26	−0.01	**0.71**	2c	−0.25	**−0.82**	0.03	**0.96**
Mo	0.08	0.47	−0.01	**0.65**	2d	−0.14	−0.46	0.16	**−2.11**
Pb	−0.08	0.26	0.13	**0.83**	2e	−0.24	−0.38	**−0.77**	0.48
Rb	**0.80**	0.02	0.01	**0.56**	3a	−0.48	−0.35	**1.17**	−0.12
Y	0.24	0.17	−0.01	**0.91**	3b	−0.31	0.02	0.39	**−2.38**
Cr	−0.27	**0.76**	0.13	0.47	3c	−0.39	−0.46	**0.90**	**−1.72**
V	**0.66**	−0.21	−0.11	**0.57**	3d	−0.47	−0.47	−0.05	−0.11
AA	0.37	0.43	0.17	−0.12	3e	−0.42	−0.28	**−2.38**	**−0.62**
PC	−0.27	0.41	−0.21	0.06	4a	−0.42	−0.49	**1.07**	−0.17
MS	−0.14	**0.96**	0.10	0.11	4b	−0.11	**−0.92**	**0.75**	0.26
Sucrose	−0.03	**0.95**	0.04	0.07	4c	−0.17	**−0.53**	0.34	−0.27
AS	0.17	**0.91**	0.19	−0.08	4d	−0.34	−0.39	**0.89**	0.02
LMG	−0.16	**0.83**	−0.20	0.01	4e	**−0.57**	−0.08	**−1.82**	0.01
NH$_4^+$	−0.10	−0.08	**−0.85**	−0.02	5a	**1.36**	0.12	0.14	−0.39
K$^+$	**0.94**	0.00	−0.02	0.15	5b	**4.34**	0.15	0.12	0.09
Cl$^-$	−0.15	0.46	0.34	0.42	5c	**0.67**	−0.41	0.05	0.15
Br$^-$	**0.98**	−0.02	−0.05	0.01	5d	**0.50**	−0.25	**−1.17**	0.01
I$^-$	−0.06	0.01	−0.16	−0.04	5e	−0.26	−0.40	**−2.17**	0.01
NO$_2^-$	−0.09	−0.10	0.12	0.23					
NO$_3^-$	−0.15	−0.20	0.03	−0.11					
MSA$^-$	−0.06	−0.20	**−0.75**	−0.01					
nss-SO$_4^{2-}$	0.25	−0.11	**−0.86**	0.02					
H$_2$PO$_4^{2-}$	−0.17	0.18	**−0.66**	−0.15					
CA	−0.22	0.43	−0.03	−0.08					
Percentage total variance	32	22	10	9					

each variable with the explained variance for each factor. Score values 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) are also reported.

The first four factors explained 73 % of the total variance of the data. The first factor (F1) comprised elements having a local source, either marine (e.g. Li, Mg and Na) or crustal (e.g. Al, Fe). The high score value in the F1 for sample 5b (from 8 to 23 January 2011 with a particle size of 7.2–3.0 µm) can be attributed to high concentrations of sea-salt components (e.g. Na) that increased in the last period of aerosol collection, owing to reduction of snow coverage and melting of the sea ice. Anthropogenic species, such as Cr, Cu and sugars (MS, AS, sucrose and LMG) have high loading values in the F2. Sample 1 (29 November–9 December 2010) has high score values in the F2, which had high correlation with the loadings of the anthropogenic species (e.g. Cr, LMG, Pb). This result was in accordance with the previous evaluations[23,24] of the same sampling period. Barbaro et al.[23] observed that the particle size distribution of sugars (MA, AS and sucrose) was similar to the levoglucosan trend in the same sample, identifying an anthropogenic emission during the sampling period. Biogenic compounds like MSA, NH$_4^+$ and nss-SO$_4^{2-}$ have a negative

correlation with F3 and high negative score values are obtained for the samples with a particle size of 0.95–0.49 µm, according to the particle distributions of these species in the aerosol.[56] The fourth factor (F4) demonstrates high positive values for major and trace elements with crustal or anthropogenic sources.

Conclusions

An extensive investigation of the chemical composition of Antarctic aerosol was carried out at MZS (Victoria Land, Antarctica) during the 2010–11 austral summer. Several chemical measurements (major ions, major and trace elements, carboxylic acids, WSOCs and POPs) were combined in order to identify 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 the global consideration of specific chemical markers. Three main sources were identified: (1) local emission, identified by sea-salt ions (Na, Li, and Mg) and crustal trace elements (Al, Fe, Co, Mn); (2) anthropogenic species such as Cr, Pb and levoglucosan, correlated with sugars (MA, AS and sucrose) owing to a particular emission that occurred during the first sampling period; (3) biogenic compounds, such as MSA, nss-SO$_4^{2-}$ and NH$_4^+$.

Supplementary material

Details of analytical methods to determine the presence and amount of anionic and cationic compounds and persistent organic pollutants in aerosol samples and tables with all data discussed in the present paper are available from the journal online (see http://www.publish.csiro.au/?act=view_file& file_id=EN16056_AC.pdf).

Acknowledgements

References

[1] I. Fattori, S. Becagli, S. Bellandi, E. Castellano, M. Innocenti, A. Mannini, M. Severi, V. Vitale, R. Udisti, Chemical composition and physical features of summer aerosol at Terra Nova Bay and Dome C, Antarctica. *J. Environ. Monit.* **2005**, *7*, 1265. doi:10.1039/ B507327H

[2] R. Udisti, U. Dayan, S. Becagli, M. Busetto, D. Frosini, M. Legrand, F. Lucarelli, S. Preunkert, M. Severi, R. Traversi, V. Vitale, Sea-spray aerosol in central Antarctica. Present atmospheric behaviour and implications for paleoclimatic reconstructions. *Atmos. Environ.* **2012**, *52*, 109. doi:10.1016/J.ATMOSENV.2011.10.018

[3] K. Budhavant, P. D. Safai, P. S. P. Rao, Sources and elemental composition of summer aerosols in the Larsemann Hills (Antarctica). *Environ. Sci. Pollut. Res. Int.* **2015**, *22*, 2041. doi:10.1007/S11356-014-3452-0

[4] I. Oyabu, Y. Iizuka, R. Uemura, T. Miyake, M. Hirabayashi, H. Motoyama, T. Sakurai, T. Suzuki, T. Hondoh, Chemical compositions of sulfate and chloride salts over the last termination reconstructed from the Dome Fuji ice core, inland Antarctica. *J. Geophys. Res., D, Atmospheres* **2014**, *119*, 14 045. doi:10.1002/2014JD022030

[5] K. Teinilä, A. Frey, R. Hillamo, H. C. Tuelp, R. Weller, A study of the sea-salt chemistry using size-segregated aerosol measurements at coastal Antarctic station Neumayer. *Atmos. Environ.* **2014**, *96*, 11. doi:10.1016/J.ATMOSENV.2014.07.025

[6] R. Hillamo, I. Allegrini, R. Sparapani, V. M. Kerminen, Mass size distributions and precursor gas concentrations of major inorganic ions in Antarctic aerosol. *Int. J. Environ. Anal. Chem.* **1998**, *71*, 353. doi:10.1080/03067319808032638

[7] S. Illuminati, A. Annibaldi, C. Truzzi, G. Libani, C. Mantini, G. Scarponi, Determination of water-soluble, acid-extractable and inert fractions of Cd, Pb and Cu in Antarctic aerosol by square-wave anodic stripping voltammetry after sequential extraction and microwave digestion. *J. Electroanal. Chem.* **2015**, *755*, 182. doi:10.1016/ J.JELECHEM.2015.07.023

[8] A. Annibaldi, C. Truzzi, S. Illuminati, E. Bassotti, G. Scarponi, Determination of water-soluble and insoluble (dilute-HCl-extractable) fractions of Cd, Pb and Cu in Antarctic aerosol by squarewave anodic stripping voltammetry: distribution and summer seasonal evolution at Terra Nova Bay (Victoria Land). *Anal. Bioanal. Chem.* **2007**, *387*, 977. doi:10.1007/S00216-006-0994-0

[9] G. Toscano, A. Gambaro, I. Moret, G. Capodaglio, C. Turetta, P. Cescon, Trace metals in aerosol at Terra Nova Bay, Antarctica. *J. Environ. Monit.* **2005**, *7*, 1275. doi:10.1039/B507337P

[10] C. Barbante, C. Turetta, G. Capodaglio, G. Scarponi, Recent decrease in the lead concentration of Antarctic snow. *Int. J. Environ. Anal. Chem.* **1997**, *68*, 457. doi:10.1080/03067319708030847

[11] G. Scarponi, C. Barbante, C. Turetta, A. Gambaro, P. Cescon, Chemical contamination of Antarctic snow: the case of lead. *Microchem. J.* **1997**, *55*, 24. doi:10.1006/MCHJ.1996.1354

[12] C. Barbante, C. Turetta, A. Gambaro, G. Capodaglio, G. Scarponi, Sources and origins of aerosols reaching Antarctica as revealed by lead concentration profiles in shallow snow. *Ann. Glaciol.* **1998**, *27*, 674.

[13] G. Xu, Y. Gao, Q. Lin, W. Li, L. Chen, Characteristics of water-soluble inorganic and organic ions in aerosols over the Southern Ocean and coastal East Antarctica during austral summer. *J. Geophys. Res., D, Atmospheres* **2013**, *118*, 13 303. doi:10.1002/2013JD019496

[14] R. Piazza, A. Gambaro, E. Argiriadis, M. Vecchiato, S. Zambon, P. Cescon, C. Barbante, Development of a method for simultaneous analysis of PCDDs, PCDFs, PCBs, PBDEs, PCNs and PAHs in Antarctic air. *Anal. Bioanal. Chem.* **2013**, *405*, 917. doi:10.1007/ S00216-012-6464-Y

[15] E. Wolff, J. S. Hall, R. Mulvaney, E. C. Pasteur, D. Wagenbach, M. Legrand, Relationship between chemistry of air, fresh snow and firn cores for aerosol species in coastal Antarctica. *J. Geophys. Res.* **1998**, *103*, 11 057. doi:10.1029/97JD02613

[16] N. Kehrwald, R. Zangrando, P. Gabrielli, J. Jaffrezo, C. Boutron, C. Barbante, A. Gambaro, Levoglucosan as a specific marker of fire events in Greenland snow. *Tellus B Chem. Phys. Meterol.* **2012**, *64*, 18 196. doi:10.3402/TELLUSB.V64I0.18196

[17] R. Fuoco, S. Giannarelli, M. Onor, S. Ghimenti, C. Abete, M. Termine, S. Francesconi, A snow/firn four-century record of polycyclic aromatic hydrocarbons (PAHs) and polychlorobiphenyls (PCBs) at Talos Dome (Antarctica). *Microchem. J.* **2012**, *105*, 133. doi:10.1016/J.MICROC.2012.05.018

[18] A. Spolaor, P. Vallelonga, J. Gabrieli, T. Martma, M. P. Björkman, E. Isaksson, G. Cozzi, C. Turetta, H. A. Kjær, M. A. J. Curran, A. D. Moy, A. Schönhardt, A.-M. Blechschmidt, J. P. Burrows, J. M. C. Plane, C. Barbante, Seasonality of halogen deposition in polar snow and ice. *Atmos. Chem. Phys.* **2014**, *14*, 9613. doi:10.5194/ACP-14-9613-2014

[19] M. Vecchiato, E. Argiriadis, S. Zambon, C. Barbante, G. Toscano, A. Gambaro, R. Piazza, Persistent organic pollutants (POPs) in Antarctica: occurrence in continental and coastal surface snow. *Microchem. J.* **2015**, *119*, 75. doi:10.1016/J.MICROC.2014.10.010

[20] A. Bazzano, F. Soggia, M. Grotti, Source identification of atmospheric particle-bound metals at Terra Nova Bay, Antarctica. *Environ. Chem.* **2015**, *12*, 245. doi:10.1071/EN14185

[21] S. Rella, C. Malitesta, X-ray photoelectron spectroscopy characterization of aerosol particles in Antarctica. *Antarct. Sci.* **2015**, *27*, 493. doi:10.1017/S0954102015000176

[22] E. Barbaro, R. Zangrando, M. Vecchiato, R. Piazza, W. R. L. Cairns, G. Capodaglio, C. Barbante, A. Gambaro, Free amino acids in Antarctic aerosol: potential markers for the evolution and fate of marine aerosol. *Atmos. Chem. Phys.* **2015**, *15*, 5457. doi:10.5194/ ACP-15-5457-2015

[23] E. Barbaro, T. Kirchgeorg, R. Zangrando, M. Vecchiato, R. Piazza, C. Barbante, A. Gambaro, Sugars in Antarctic aerosol. *Atmos. Environ.* **2015**, *118*, 135. doi:10.1016/J.ATMOSENV.2015.07.047

[24] R. Zangrando, E. Barbaro, M. Vecchiato, N. M. Kehrwald, C. Barbante, A. Gambaro, Levoglucosan and phenols in marine, coastal and inland Antarctic aerosols. *Sci. Total Environ.* **2016**, *544*, 606. doi:10.1016/J.SCITOTENV.2015.11.166

[25] R. Zangrando, E. Barbaro, P. Zennaro, S. Rossi, N. M. Kehrwald, J. Gabrieli, C. Barbante, A. Gambaro, Molecular markers of biomass burning in Arctic aerosols. *Environ. Sci. Technol.* **2013**, *47*, 8565.

[26] A. Annibaldi, C. Truzzi, S. Illuminati, G. Scarponi, Direct gravimetric determination of aerosol mass concentration in central Antarctica. *Anal. Chem.* **2011**, *83*, 8046. doi:10.1021/AC202408Z

[27] C. Truzzi, L. Lambertucci, S. Illuminati, A. Annibaldi, G. Scarponi, Direct gravimetric measurements of the mass of the Antarctic aerosol collected by high-volume sampler: PM$_{10}$ summer seasonal variation at Terra Nova Bay. *Ann. Chim.* **2005**, *95*, 867. doi:10.1002/ADIC. 200590099

[28] A. Dreyer, I. Weinberg, C. Temme, R. Ebinghaus, Polyfluorinated-compounds in the atmosphere of the Atlantic and Southern Oceans: evidence for a global distribution. *Environ. Sci. Technol.* **2009**, *43*, 6507. doi:10.1021/ES9010465

[29] H. Bauer, M. Claeys, R. Vermeylen, E. Schueller, G. Weinke, A. Berger, H. Puxbaum, Arabitol and mannitol as tracers for the quantification of airborne fungal spores. *Atmos. Environ.* **2008**, *42*, 588. doi:10.1016/J.ATMOSENV.2007.10.013

[30] G. S. Tyndall, A. R. Ravishankara, Atmospheric oxidation of reduced sulfur species. *Int. J. Chem. Kinet.* **1991**, *23*, 483. doi:10.1002/KIN.550230604

[31] M. Legrand, F. Ducroz, D. Wagenbach, R. Mulvaney, J. Hall, Ammonium in coastal Antarctic aerosol and snow: role of polar ocean and penguin emissions. *J. Geophys. Res., D, Atmospheres* **1998**, *103*, 11 043. doi:10.1029/97JD01976

[32] T. D. Blackall, L. J. Wilson, M. R. Theobald, C. Milford, E. Nemitz, J. Bull, P. J. Bacon, K. C. Hamer, S. Wanless, M. A. Sutton, Ammonia emissions from seabird colonies. *Geophys. Res. Lett.* **2007**, *34*, L1080.

[33] J. Schmale, J. Schneider, E. Nemitz, Y. S. Tang, U. Dragosits, T. D. Blackall, P. N. Trathan, G. J. Phillips, M. Sutton, C. F. Braban, Sub-Antarctic marine aerosol: dominant contributions from biogenic sources. *Atmos. Chem. Phys.* **2013**, *13*, 8669. doi:10.5194/ACP-13-8669-2013

[34] T. D. Jickells, S. D. Kelly, A. R. Baker, K. Biswas, P. F. Dennis, L. J. Spokes, M. Witt, S. G. Yeatman, Isotopic evidence for a marine ammonia source. *Geophys. Res. Lett.* **2003**, *30*, 137.

[35] M. T. Johnson, T. G. Bell, Coupling between dimethylsulfide emissions and the ocean–atmosphere exchange of ammonia. *Environ. Chem.* **2008**, *5*, 259. doi:10.1071/EN08030

[36] D. M. Murphy, D. S. Thomson, Halogen ions and NO^+ in the mass spectra of aerosols in the upper troposphere and lower stratosphere. *Geophys. Res. Lett.* **2000**, *27*, 3217. doi:10.1029/1999GL011267

[37] H. Zhuang, C. K. Chan, M. Fang, A. S. Wexler, Formation of nitrate and non-sea-salt sulfate on coarse particles. *Atmos. Environ.* **1999**, *33*, 4223. doi:10.1016/S1352-2310(99)00186-7

[38] A. Virkkula, K. Teinila, R. Hillamo, V. M. Kerminen, S. Saarikoski, M. Aurela, J. Viidanoja, J. Paatero, I. K. Koponen, M. Kulmala, Chemical composition of boundary layer aerosol over the Atlantic Ocean and at an Antarctic site. *Atmos. Chem. Phys.* **2006**, *6*, 3407. doi:10.5194/ACP-6-3407-2006

[39] K. Kawamura, M. Narukawa, S.-M. Li, L. A. Barrie, Size distributions of dicarboxylic acids and inorganic ions in atmospheric aerosols collected during polar sunrise in the Canadian high Arctic. *J. Geophys. Res., D, Atmospheres* **2007**, *112*, D1030.

[40] K. Kawamura, R. Semere, Y. Imai, Y. Fujii, M. Hayashi, Water-soluble dicarboxylic acids and related compounds in Antarctic aerosols. *J. Geophys. Res., D, Atmospheres* **1996**, *101*, 18 721. doi:10.1029/96JD01541

[41] H. B. Wang, K. Kawamura, K. Yamazaki, Water-soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the Southern Ocean and western Pacific Ocean. *J. Atmos. Chem.* **2006**, *53*, 43. doi:10.1007/S10874-006-1479-4

[42] K. Kawamura, F. Sakaguchi, Molecular distributions of water-soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics. *J. Geophys. Res., D, Atmospheres* **1999**, *104*, 3501. doi:10.1029/1998JD100041

[43] K. Matsumoto, I. Nagao, H. Tanaka, H. Miyaji, T. Iida, Y. Ikebe, Seasonal characteristics of organic and inorganic species and their size distributions in atmospheric aerosols over the north-west Pacific Ocean. *Atmos. Environ.* **1998**, *32*, 1931. doi:10.1016/S1352-2310(97)00499-8

[44] P. Fu, K. Kawamura, K. Usukura, K. Miura, Dicarboxylic acids, ketocarboxylic acids and glyoxal in the marine aerosols collected during a round-the-world cruise. *Mar. Chem.* **2013**, *148*, 22. doi:10.1016/J.MARCHEM.2012.11.002

[45] R. Sempere, K. Kawamura, Trans-hemispheric contribution of C2–C10 alpha, omega-dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions. *Global Biogeochem. Cycles* **2003**, *17*, 1069.

[46] K. Kawamura, H. Kasukabe, L. A. Barrie, Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: one year of observations. *Atmos. Environ.* **1996**, *30*, 1709. doi:10.1016/1352-2310(95)00395-9

[47] D. J. Carlson, Surface microlayer phenolic enrichments indicate sea-surface slicks. *Nature* **1982**, *296*, 426. doi:10.1038/296426A0

[48] M. Tedetti, K. Kawamura, B. Charriere, N. Chevalier, R. Sempere, Determination of low-molecular-weight dicarboxylic and ketocarboxylic acids in seawater samples. *Anal. Chem.* **2006**, *78*, 6012. doi:10.1021/AC052226W

[49] K. Teinilä, V. M. Kerminen, R. Hillamo, A study of size-segregated aerosol chemistry in the Antarctic atmosphere. *J. Geophys. Res.* **2000**, *105*, 3893. doi:10.1029/1999JD901033

[50] V. M. Kerminen, K. Teinila, R. Hillamo, Chemistry of sea-salt particles in the summer Antarctic atmosphere. *Atmos. Environ.* **2000**, *34*, 2817. doi:10.1016/S1352-2310(00)00089-3

[51] R. M. Dickhut, A. Cincinelli, M. Cochran, H. W. Ducklow, Atmospheric concentrations and air–water flux of organochlorine pesticides along the western Antarctic Peninsula. *Environ. Sci. Technol.* **2005**, *39*, 465. doi:10.1021/ES048648P

[52] F. M. Jaward, J. L. Barber, K. Booij, J. Dachs, R. Lohmann, K. C. Jones, Evidence for dynamic air–water coupling and cycling of persistent organic pollutants over the open Atlantic Ocean. *Environ. Sci. Technol.* **2004**, *38*, 2617. doi:10.1021/ES049881Q

[53] A. Gambaro, L. Manodori, R. Zangrando, A. Cincinelli, G. Capodaglio, P. Cescon, Atmospheric PCB concentrations at Terra Nova Bay, Antarctica. *Environ. Sci. Technol.* **2005**, *39*, 9406. doi:10.1021/ES0510921

[54] Y. Li, D. Geng, F. Liu, T. Wang, P. Wang, Q. Zhang, G. Jiang, Study of PCBs and PBDEs in King George Island, Antarctica, using PUF passive air sampling. *Atmos. Environ.* **2012**, *51*, 140. doi:10.1016/J.ATMOSENV.2012.01.034

[55] W. A. Ockenden, R. Lohmann, J. R. Shears, K. C. Jones, The significance of PCBs in the atmosphere of the southern hemisphere. *Environ. Sci. Pollut. Res. Int.* **2001**, *8*, 189. doi:10.1007/BF02987384

[56] C. D. O'Dowd, M. C. Facchini, F. Cavalli, D. Ceburnis, M. Mircea, S. Decesari, S. Fuzzi, Y. J. Yoon, J. P. Putaud, Biogenically driven organic contribution to marine aerosol. *Nature* **2004**, *431*, 676. doi:10.1038/NATURE02959