



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

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5
6 **Environmental Context**

7 Due to their long distance from anthropogenic emission sources, Antarctica is an excellent natural
8 laboratory for conducting studies on the behavior of marine aerosols and for monitoring the impact
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21
22 Keywords: aerosol, Antarctica, sugars, ions, carboxylic acids, amino acids, metals, POPs.

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28 characterization of Antarctic aerosol and to investigate its sources. A distinction among anthropic,
29 crustal and biogenic sources was defined using several chemical markers.

30 **Abstract**

31 During the 2010-2011 austral summer, an aerosol sampling campaign was carried out at a coastal
32 Antarctic site (Terra Nova Bay, Victoria Land). In this work, previously published data were
33 merged with novel measurements in order to provide a chemical characterization of Antarctic
34 aerosol and to investigate its sources. Major ions, major and trace elements, carboxylic acids, water
35 soluble organic compounds (anhydrosugars, alcohols sugars, mono and disaccharides, amino acids
36 and phenolic compounds) and persistent organic pollutants (polychlorobiphenyls, polycyclic
37 aromatic hydrocarbons, polychlorinated naphthalenes, polybrominateddiphenyl ethers and
38 organochlorine pesticides) were evaluated using an integrated approach. The persistent organic
39 pollutants were determined using a high volume sampler, able to collect both particulate and
40 gaseous fractions, while remaining compounds were determined by performing an aerosol size
41 fractionation by a PM₁₀ cascade impactor. Ionic species were the most abundant compounds in the
42 Antarctic aerosol due to natural emission. Trace concentrations of persistent organic pollutants
43 highlighted that the occurrence of these species can be due to long-range atmospheric transport or
44 due to the research base.

45 Factor Analysis was applied to the dataset obtained from the samples collected with PM₁₀ sampler
46 in order to make a distinction among anthropic, crustal and biogenic sources using specific
47 chemical markers.

48 Introduction

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

56 Nowadays, the chemical characterization of Antarctic aerosol has been the object of scrappy
57 investigations. Several studies were focused on major ions ^[1-6], or on trace elements ^[7-12], a few
58 organic compounds were also recently investigated ^[13, 14].

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

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

70 We propose a synthesis of all measurements of aerosol samples collected at the Italian research
71 station "Mario Zucchelli" (MZS) (Antarctica) during the austral summer 2010-11. Bazzano et al. ^[15]
72 described the composition of major and trace elements of aerosol samples at MZS during the
73 sampling period. Rella and Malitesta ^[16] performed a qualitative and quantitative analysis of

74 particulate matter surface using X-ray photoelectron spectroscopy (XPS), determining several
75 species as ammonium, nitrate, sulfate, organic sulfur, fluoride and organic fluoride. Barbaro et al.
76 [17, 18] defined the site's composition in amino acids and sugars, while Zangrando et al. [19]
77 investigated several biomass burning markers (levoglucosan and phenolic compounds).
78 Moreover, this study integrates additional groups of compounds in the characterization of the
79 Antarctic atmosphere. These consist of ionic species (Cl^- , Br^- , I^- , NO_2^- , NO_3^- , sulfate, phosphate and
80 methanesulfonic acid (MSA), NH_4^+ , K^+), carboxylic acids (C_2 -oxalic, C_2 -acetic, C_2 -glycolic, C_3 -
81 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 -
82 pimelic, *aC* $_7$ -benzoic, C_8 -suberic) and persistent organic pollutants (POPs) including
83 polychlorobiphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH), polychlorinated
84 naphthalenes (PCN), polybrominated diphenyl ethers (PBDE) and organochlorine pesticides (POC).

85 **Material and Methods**

86 *Sample collection and processing of PM_{10} aerosol*

87 Aerosol samples ($n = 5$) were collected using two analogous high-volume cascade impactors (TE-
88 6070, PM_{10} high volume air sampler) with 10.0 – 7.2 μm , 7.2 – 3.0 μm , 3.0 – 1.5 μm , 1.5- 0.95 μm ,
89 0.95 – 0.49 μm and <0.49 μm particle cut-off diameters, placed at Campo Faraglione (74° 42' S –
90 164° 06' E), about 3 km south of the Italian Research Base MZS (Victoria Land, Antarctica) from
91 November 29th, 2010 to January 23rd, 2011. The average airflow of both air samplers was 1.1 $\text{m}^3 \text{min}^{-1}$
92 and the sampling resolution was about 10 days ($\sim 15,000$ m^3 per sample). One air sampler
93 employed cellulose filters to determine metals in the particulate matter while the second used quartz
94 fiber filters to investigate organic and ionic compounds in Antarctic aerosol. For each sampler, three
95 field blank samples were collected by loading, carrying, and installing the filter on the instrument
96 with the air pump switched off, removing it after ten minutes and following the same procedure
97 used for the sample filters. The device did not employ Teflon O-rings and fluorinated lubricants in
98 order to reduce the risk of contamination.

99 After sampling, the cellulose filters used for the determination of inorganic compounds were placed
100 in acid-cleaned plastic Petri dishes, sealed in double polyethylene bags and stored at -20°C until
101 analysis. Quartz filters used to determine organic compounds were stored at -20°C in double
102 aluminum foil envelopes until analysis.

103 The samples were processed under a laminar flow bench (class 100) to avoid contamination from
104 the laboratory environment. The pre-analytical protocol to determine metals has been described by
105 Bazzano et al.¹⁵. The procedure consisted in a microwave-assisted acid digestion of the cellulose
106 filters followed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and
107 inductively coupled plasma-mass spectrometry (ICP-MS) analysis¹⁵.

108 The XPS measurements were recorded on samples without any pretreatment with an AXIS ULTRA
109 DLD (Kratos Analytical) photoelectron spectrometer using a monochromatic AlK α source (1486.6
110 eV) operating at 225 W^[16].

111 The pre-analytical and sample extraction protocol to determine amino acids, phenolic compounds
112 and sugars has been described elsewhere^[17-19]. Briefly, filters were spiked with a ¹³C labelled
113 internal standard mix (amino acids, phenolic compounds and levoglucosan), ultrasonically extracted
114 with ultrapure water, and filtered through a 0.45 μ m PTFE filter. Amino acids determination was
115 obtained using an high performance liquid chromatography (HPLC) with a chiral column coupled
116 with tandem mass spectrometry^[17]. Phenolic compounds were analyzed using a reverse phase
117 chromatography coupled with tandem mass spectrometry^[19], while sugars were determined using
118 an ion chromatography coupled to mass spectrometry (IC-MS)^[18].

119 The analytical procedure to determine ionic species consisted in ultrasonic extraction with ultrapure
120 water and a filtration through a 0.45 μ m PTFE filter. Determination and quantification of all anionic
121 compounds and carboxylic acids (see table 1) were performed using an ion chromatograph
122 (ThermoScientific™ Dionex™ ICS-5000, Waltham, US), with an anion exchange column (Dionex
123 Ion Pac AS11 2x250mm) and guard column (Dionex Ion Pac AG11 2x50 mm), coupled with a
124 single mass spectrometer (MSQ Plus™, ThermoScientific™, Bremen, Germany).

125 The sodium hydroxide gradient, generated by an eluent generator (Dionex ICS 5000EG, Thermo
126 Scientific) was: 0-3.5 min gradient from 0.5 mM to 5 mM; 3.5-5 min gradient from 5mM to 10
127 mM; 5-25 min gradient from 10 mM to 38 mM; 25-30 min, column cleaning with 38 mM; 30-
128 35min; equilibration at 0.5 mM. The injection volume was 100 μL and the flow rate was 0.25 mL
129 min^{-1} . Sodium hydroxide was removed by a suppressor (ASRS 500, 2 mm, Thermo Scientific)
130 before entering the MS sources. The MS was operating with an electrospray ionization (ESI)
131 interface in negative mode. Selected ion monitoring (SIM) was used for detection.

132 The ion chromatograph was equipped with a capillary system to simultaneously determine cations.
133 Sodium, ammonium, magnesium and potassium were separated using an Ion Pac CS19-4 μm
134 capillary cation exchange column (0.4 x250 mm) equipped with an Ion Pac CG19-4 μm guard
135 column (0.4x50 mm). The MSA gradient, generated by an eluent generator (Dionex EGC-MSA
136 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
137 equilibration at 1.5 mM. The injection volume was 0.4 μL and the flow rate was 13 $\mu\text{L min}^{-1}$. MSA
138 was removed by a suppressor (CCES 300, Thermo Scientific) before entering the conductivity
139 detector.

140 Each procedure was previously validated to ensure an accurate quantification of each analyte ^{[15, 17,}
141 ^{18, 20]}. All reported values were blank corrected. A summary of each compound reported in this
142 paper and the analytical protocol used for its determination is reported in table 1.

143 *Aerosol mass measurements*

144 During the 2010-2011 austral summer preliminary tests of the direct mass measurements of the
145 different size-segregated aerosol fractions were carried out. The procedure consists in determining
146 the difference between the mass of the exposed filters and their mass before exposure. This
147 procedure was previously setup for the weighing of total PM_{10} ^[21, 22]. A computerized Mettler
148 Toledo (Greifensee, Switzerland) AT261 electronic microbalance (readability 0.01 mg, repeatability
149 $\text{SD} = 0.015 \text{ mg}$) was used.

150 In order to maintain weighing conditions as much stable as possible, a decontaminated polyethylene
151 Atmosbag glove bag (Sigma Aldrich, gas volume 520 L, closure type zipper-lock, not sterilized)
152 was used, and the microbalance was placed inside of it. Temperature and humidity were measured
153 throughout the weighing session using a mini thermos-hygrometer (digital psychrometer Testo,
154 mod. 605-HI). Temperature and relative humidity inside the glove bag were stable throughout all the
155 weighing procedure, varying by $\pm 0.1^{\circ}\text{C}$ and $\pm 0.2\%$, respectively.

156 *Sample collection and processing of aerosol using TE 5000 sampler*

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

167 The samples were processed under a laminar flow bench (class 100) to avoid contamination from
168 the laboratory environment. QFFs were extracted twice with aliquots of 20 mL of hexane/acetone
169 (1:1, v:v) mixture in an ultrasonic bath for 1 h and the recovered organic phases were combined and
170 hold overnight on anhydrous sodium sulfate. 2 mL of isooctane was added to the organic phase and
171 reduced to a volume of about 1 mL in a centrifugal evaporator before the chromatographic analysis.
172 PUFs were extracted twice with aliquots of 150 mL of mixture of hexane/acetone (1:1, v:v) in an
173 ultrasonic bath for 1 h and the recovered organic phase was combined and hold overnight on
174 anhydrous sodium sulfate. The organic phase was then filtered through $0.45 \mu\text{m}$ PTFE filters, then

175 reduced in volume using a centrifugal evaporator and purified by multi-layer solid phase extraction
176 (SPE)cartridges. The analytes were eluted from the SPE column with 10 mL of n-hexane. 2 mL of
177 isooctane was added to the recovered hexane and reduced to a volume of about 1 mL in a
178 centrifugal evaporator before the gaschromatographic analysis.

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

181 Instrumental analysis was performed by a gaschromatograph (5890A, Agilent Technologies, USA)
182 equipped with a MS detector (5973, Agilent Technologies). Chromatographic separation was
183 performed on a HP5-MS capillary column (30m x 0.25mm x 25 μm) using helium as carrier gas at a
184 flow rate of 1 mLmin⁻¹. The oven temperature program was: 60 °C hold for 0.5 min then 15.00 °C
185 min⁻¹ up to 140 °C then 2 °Cmin⁻¹ up to 240 °C then 15 °Cmin⁻¹ up to 300 °C. The injection volume
186 was 50 μL and the PTV temperature program was: 65 °C hold for 0.5 min then 500 °C min⁻¹ up to
187 280 °C. The MS detector operated in SIM mode. The compounds under investigation were: 21
188 congeners of PCBs (-66, -77, -87, -101, -105, -118, -126, -128, -138, -153, -154, -169, -170, -180, -
189 187, -188, -194, -195, -201, -206, -209), 16 congeners of PCN (-2, -6, -13, -28, -52, -66, -73, -75, -
190 27, -36, -46, -48, -50, -53, -69, -72), 46 congeners of PBDE (-1, -2, -3, -7, -10, -15, -17, -28, -30, -
191 47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -139, -140, -153, -154, -156, -169, -153, -
192 171, -180, -183, -184, -191, -196, -197, -201, -203, -204, -205, -206, -207, -208, -209), 6
193 compounds belonging to PAHs (Fluoranthene, Benzo[b]fluoranthene, Benzo[k]fluoranthene,
194 Benzo[a]pirene, Indeno[1,2,3-cd]pirene, Benzo(g,h,i)perylene) and 19 compounds belonging to
195 POC (benfluoralin, trifluoralin, HCH, HCB, HCH-g, metolachlor, tertbutryne, malathion, iProd,
196 heptachloroepoxide A/B, chlordanocis/trans, endosulfan, dieldrin, p-DDE, endrin, endosulfan I/II).

197 *Data processing*

198 A statistical approach was used for the dataset obtained from PM₁₀ aerosol with aerodynamic
199 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
200 concentrations values below limit of detection (LOD) were substituted by ½ LOD. Factor analysis
201 (FA) with varimax rotation was performed on the auto-scaled data matrix constituted by 25 rows
202 (samples) and 31 columns (chemical components) using Statistica 8.0 (StatSoft, Inc., 2007). In
203 order to reduce the chemical components, the sum of amino acids (AA), phenolic compounds (PC),
204 carboxylic acids (CA), monosaccharides (MS), alcohol sugars (AS), anhydrosugars (LMG) were
205 considered.

206 **Results and Discussion**

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

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

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

219 Marine input was also identified by Rella and Malitesta^[16], who described the presence of Na⁺ and
220 Cl⁻ and Mg²⁺ in the same samples with XPS. They also demonstrated the occurrence of Ca²⁺, which
221 was not measured by Bazzano et al. ^[15], in the aerosol samples with aerodynamic diameter below 3

222 μm . Two different sulfur species were observed: they proposed a local source for sulfate species,
223 while the origin of organic sulfur species remained unclear. Two species were also found for
224 fluorine: fluoride and organic fluorine, but the origin of the latter could not be identified.

225 Barbaro et al. ^[17, 18] and Zangrando et al. ^[19] characterized the water-soluble organic compounds
226 (WSOC) fraction of Antarctic aerosol. A local marine source was associated with the highest
227 concentration of amino acids in the fine fraction of the aerosol ($<0.49\mu\text{m}$) and the major presence of
228 L-isomers was probably due to planktonic origin^[17]. Primary production of fungi in ice-free areas
229 near MZS was the source of alcohol-sugars^[23] such as mannitol and arabitol in the coarse fraction
230 ($>1\mu\text{m}$), whereas biogenic sources significantly influenced the concentration of glucose in the fine
231 fraction ($<1\mu\text{m}$)^[18]. During biomass burning events, it was also verified that sugars had the same
232 particle-size distribution of levoglucosan when aerosol was affected by biomass burning^[18]. The
233 investigation of biomass burning markers in the Antarctic aerosol was the main aim of a recent
234 paper^[19]. The study of particle size distribution of levoglucosan confirmed the major presence of
235 this long-range atmospheric transport tracer in the fine fraction, but a hygroscopic growth at the
236 coastal site MZS was also observed. The same authors also investigated the occurrence of phenolic
237 compounds because these species are usually used as biomass burning markers, indicating the type
238 of burned plants. Results demonstrated that Antarctic samples had different levoglucosan/phenolic
239 compounds ratios from aerosols directly affected by biomass burning. This difference suggested
240 that other sources influenced the signal. Similar particle size distribution of phenolic compounds
241 with locally produced amino acids may suggest the ocean as a major source: the lignin present in
242 marine environment can undergo photochemical and microbiological degradation, producing
243 phenolic compounds, then emitted in the atmosphere ^[19].

244 *Ionic composition*

245 The determination of major ions was aimed to complete our chemical characterization of these
246 aerosol samples. We determined cations, such as potassium, sodium and magnesium, and anions

247 such as halides (chloride, bromide and iodide), MSA and non-sea-salt sulfate (nss-SO_4^{2-}). The
248 nitrogen cycle was also investigated by determining the concentrations of ammonium, nitrate and
249 nitrite.

250 Figure 1 shows the particle size distribution of ionic species analyzed in the fine (particle diameter,
251 $D_p < 1 \mu\text{m}$) and coarse fraction ($1 \mu\text{m} < D_p \leq 10 \mu\text{m}$). The average concentrations of each fraction were
252 similar to those reported by Fattori et al. [1] for Na^+ , Cl^- , nss-SO_4^{2-} , MSA, NO_3^- and NH_4^+ determined
253 in aerosol samples collected close to the sampling site during the austral summer 2002-2003.

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

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

263 The concentration of NH_4^+ ($33 \pm 9 \text{ ng m}^{-3}$) was very similar to those reported in the literature [13 and
264 references within]. Previous studies [25-27] demonstrated that the emissions of NH_3 from seabirds and
265 penguins could be an important source of NH_4^+ in Antarctica. In fact, our sampling location was
266 placed near the skua nest and a lot of these birds were present near the sampling location. These
267 birds may be potential sources of ammonium. Moreover, the existence of marine sources for aerosol
268 ammonium was also demonstrated in previous studies [28, 29]. The presence of ammonium was also
269 highlighted by the XPS analysis [16].

270 Br⁻ and I⁻ had lower concentrations than other ionic species, representing only 0.05% of the total
271 ionic composition. They were mainly distributed in the fine fraction (142 pg m⁻³ for bromide and 22
272 pg m⁻³ for iodide) (figure 1), probably because these halogens can have similar sources as organic
273 species, e.g. MSA^[30].

274 The sea-salt input in the ionic composition is evident when considering the highest concentration of
275 the major ions in the coarse mode. However, chloride depletion occurred in the aerosol samples and
276 had a mean value of 70%. This value suggests that acidic species, mainly nitrate, sulfate and other
277 organic acids, reacted with NaCl in sea-salt particles and replaced Cl⁻ in the form of gaseous HCl,
278 as also previously demonstrated in literature^[31]. This phenomenon was also confirmed by the Cl⁻
279 /Na⁺ ratio in the coarse fraction (0.4 w/w), lower than that measured in sea water (1.8 w/w)^[31]. This
280 finding is in agreement with XPS results^[16].

281 The contribution of nitrate to the chloride depletion was evaluated by calculating the ratio of
282 measured Na⁺ concentration to the total measured concentrations of NO₃⁻ and Cl⁻. A mean value of
283 4 (±2) was obtained, which is higher than the value (0.85) for unreacted original sea water. Possible
284 explanations of this value are that 1) the chloride depletion can be attributed to sulfate or organic
285 ion formation in sea-salt particles or 2) other sources of Na⁺ are present.

286 Enrichment factors of potassium, calculated as the ratio between K⁺/Na⁺ in the aerosol samples and
287 K⁺/Na⁺ in seawater (0.037w/w), was higher (5-20 w/w) in submicron particle sizes, suggesting that
288 long-range atmospheric transport from biomass burning sources was the main source^[32, 33].

289 *Carboxylic acids*

290 A homologous series of low-molecular-weight-carboxylic acids (C₂-C₈) were detected in Antarctic
291 aerosol samples (figure 2), with concentrations ranging from 5 to 20 ng m⁻³ (average 9 ng m⁻³).
292 Oxalic acid (C₂) was the most abundant carboxylic acid with concentrations between 0.8 and 15 ng
293 m⁻³ (average 5 ng m⁻³). The values were very similar to those reported in the literature about other

294 sites in the Antarctic site^[34] and in the Southern Ocean^[35]. Oxalic acid accounted for 57% to the
295 quantified acid mass (figure 2), because it is the end-product of various oxidation/decomposition
296 pathways in the atmosphere^[36]. The concentrations of each acid decreased with the increase of the
297 carbon chain length (figure 2).

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

304 In order to investigate the sources of carboxylic acids in Antarctic aerosols, the C_3/C_4 ratio was used
305 as an indicator of enhanced photochemical production of diacids, because succinic acid (C_4) can be
306 degraded to malonic acid (C_3) for decarboxylation reactions activated by OH radicals^[38]. Fu et al.
307^[38] studied the C_3/C_4 ratio in several environments (urban and marine sites) to investigate the real
308 sources of these compounds. Our 1.5 ratio is very similar to what they found from marine areas^[44],
309 suggesting that 1) malonic acid can have a marine source or 2) it is photochemically produced
310 during long-range transport from continents.

311 *Trans* configuration (*trans-us* C_4 -fumaric acid) was more abundant than *cis* isomer (*cis-us* C_4 -maleic
312 acid) (figure 2) with low *cis/trans* ratios ranged between 0.09 and 1.5 (average 0.5). Fu et al.^[44]
313 reported that lower *cis/trans* ratios (0.1-1.5) were generally observed for the marine aerosol than
314 those reported in urban regions (0.9-2.3). *cis*-maleic acid is usually produced through the
315 photochemical oxidation of benzene or toluene in urban regions near the emission sources^[39].
316 Instead, low values of *cis/trans* ratio indicate further isomerization of *cis*-maleic acid to *trans*-
317 fumaric acid during long-range transport^[36, 38]. Moreover, the presence of *trans*-fumaric acid can

318 suggest non-anthropogenic precursors^[40] such as phenolic compounds originated from macroalgae
319 in the sea surface slicks^[41].

320 The photochemical oxidation during long-range atmospheric transport was also confirmed by the
321 sea-salt enrichment factors calculated for C₂-C₇^[42]. Values much greater than 1 were obtained
322 (average value between 7×10³ for maleic acid and 1×10⁵ for adipic acid), demonstrating that these
323 compounds clearly do not originate from sea-salt but are produced in the atmosphere as secondary
324 organic aerosol^[33].

325 *Chemical composition of fine and coarse fraction Antarctic PM₁₀ aerosol*

326 All data of PM₁₀ aerosol samples collected at MZS during the austral summer 2010-11 (reported in
327 this paper) were combined to perform a complete chemical characterization of Antarctic aerosol.
328 Figure 3 describes the chemical composition of coarse (1 μm<D_p≤10 μm) and fine (<1 μm) aerosol.
329 In the coarse fraction, sodium was the most abundant species indicating the contribution from sea
330 spray. Instead, the fine fraction was mainly characterized by sulfur species (sulfate and organic
331 MSA), demonstrating the influence of marine primary production^[1]. Considering that the amino
332 acid concentration is usually lower than that of ionic compounds or major elements, an important
333 percentage of L-Arg (1%) was present in this fraction, due to the correlation of this amino acid with
334 the primary production by marine algal bloom^[17].

335 *Aerosol mass: preliminary results*

336 Due to several technical problems that occurred in the field, the results obtained were not always
337 reliable. Nevertheless, these preliminary tests did allow us to obtain first estimates of the mass
338 concentrations of size-segregated aerosol fractions by direct gravimetry. In particular, for the
339 samples collected in the period from December 29th, 2010 to January 8th, 2011, we obtained the
340 following atmospheric concentrations of size-resolved aerosol: 0.23±0.01 μg m⁻³ for particle
341 diameter (D_p)<0.49 μm; 0.026±0.009 μg m⁻³ for D_p 0.49–0.95μm; 0.17±0.01 μg m⁻³ for D_p0.95–1.5

342 μm ; $0.020 \pm 0.002 \mu\text{g m}^{-3}$ for D_p 1.5–3.0 μm ; $0.25 \pm 0.01 \mu\text{g m}^{-3}$ for D_p 3.0–7.2 μm ; $0.026 \pm 0.003 \mu\text{g m}^{-3}$
343 for D_p 7.2–10 μm . The sum of the aerosol size fraction concentrations gave a total of $0.71 \pm 0.02 \mu\text{g}$
344 m^{-3} and this value is in good agreement with the data reported in the literature for this same
345 sampling area, considering both direct^[8,22] and indirect PM_{10} mass measurements^[1,21].

346 *Persistent Organic Pollutants*

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

350 For each class of pollutants, the total concentration in atmosphere of particulate-associated
351 contamination (QFF samples) and the gaseous-phase contamination (PUF samples) were
352 determined. In general, particulate-associated contamination is lower than gaseous-phase
353 contamination and the differences in total concentration between the samples collected do not show
354 any evident temporal trend over the sampling period. Among the five classes considered, PAH and
355 OCP showed the highest mean total concentration in the atmosphere. Regarding these two classes
356 of pollutants, the highest average concentrations were measured for γ -HCH (0.88 pg m^{-3}), HCB
357 (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})
358 ³), benzo[a]pyrene (0.13 pg m^{-3}), benzo[b]fluranthene (0.18 pg m^{-3}) and indeno[1,2,3-c,d]pirene
359 (0.19 pg m^{-3}). Among OCPs, γ -HCH and HCB represent the organochlorine pesticides that most
360 frequently occur in the ocean and Antarctic atmosphere^[43,44].

361 For PCBs, PBDEs and PCNs, highest average concentrations were found for PCB-101 (0.15 pg m^{-3})
362 ³), PCB-118 (0.06 pg m^{-3}), PCB-38 (0.07 pg m^{-3}), PCB-153 (0.05 pg m^{-3}), PBDE-47 (0.08 pg m^{-3}),
363 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})
364 ³), PCN-46 (0.06 pg m^{-3}) and PCN-52 (0.04 pg m^{-3}). The mean concentrations measured for these
365 pollutants are in agreement with a previous study in which samples from the austral summer 2003-

366 2004 and 2009-2010 were analyzed^[14, 45]. Total concentrations of PCB, PBDE and PCN are similar
367 to other measurements described in the literature. For example, Li et al. ^[46] found a total
368 concentration of indicator PCBs (PCB-28, 52, 101, 118, 138, 152, 180) and a total PBDE
369 concentration at King George Island (Keller Peninsula) respectively of 4.34 pg m^{-3} and 1.52 pg m^{-3}
370 ^[46]; Ockenden et al. ^[47] found at Halley Research Station, a total concentration of 2.45 pg m^{-3} (PCB-
371 28, 52, 101, 153, 132, 138, 180).

372 *Study of aerosol sources*

373 Factor analysis (FA) was performed to identify the sources using specific chemical tracers (figure
374 4). The first three factors explained 64% of the total variance of the data. Loadings of variables
375 seem to be separated into three groups as shown in figure 4. The first group comprised elements
376 having a local source, either marine (e.g. Li, Mg and Na) or crustal (e.g. Al, Fe, Mn, Y), which were
377 correlated with FA1. Anthropogenic species, as Cr, Pb and levoglucosan (LMG) formed a second group,
378 showing a positive correlation with FA2 and negative correlation with FA1. Finally, biogenic
379 compounds like MSA, NH_4^+ and nss-SO_4^{2-} were well separated from the other parameters by FA2
380 and FA3 factors.

381 Figure 4 also shows the scores plot of the samples, identified with a progressive number for the
382 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 ;
383 d: 1.5-0.95 μm ; e: 0.95-0.49 μm). Most of the samples were distributed close to their origin with
384 two exceptions. The samples 1a (29 November-9 December 2010 with particle size between 10 μm
385 and 7.2 μm) have a high score value in the FA 2 that had high correlation with the loadings of the
386 anthropogenic species (e.g., Cr, LMG, Pb). This result was in accordance with the previous
387 evaluations^{18, 19} about the same sampling period. Barbaro et al. ^[18] observed that the particle size
388 distribution of sugars (MA, AS and sucrose) was similar to the levoglucosan trend in the same
389 sample, identifying an anthropic emission during the sampling period.

390 High score value for sample 5b (from 8 to 23 January 2011 with particle size of 7.2-30 μm) can be
391 attributed to high concentrations of sea-salt components (e.g., Na) that increased in the last period
392 of aerosol collection, due to the reduction of the snow coverage and the melting of the sea-ice.

393 **Conclusions**

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

399 Factor analysis permitted to globally consider specific chemical markers. Three groups were
400 identified: 1) local emission, identified by sea salt ion (Na, Li, and Mg) and crustal trace elements
401 (Al, Fe, Co, Mn); 2) anthropic species such as Cr, Pb and levoglucosan, correlated with sugars
402 (MA, AS and sucrose) due to a particular emission occurred during the first sampling period; 3)
403 biogenic compounds, such as MSA, nss-SO_4^{2-} and NH_4^+ .

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411

412

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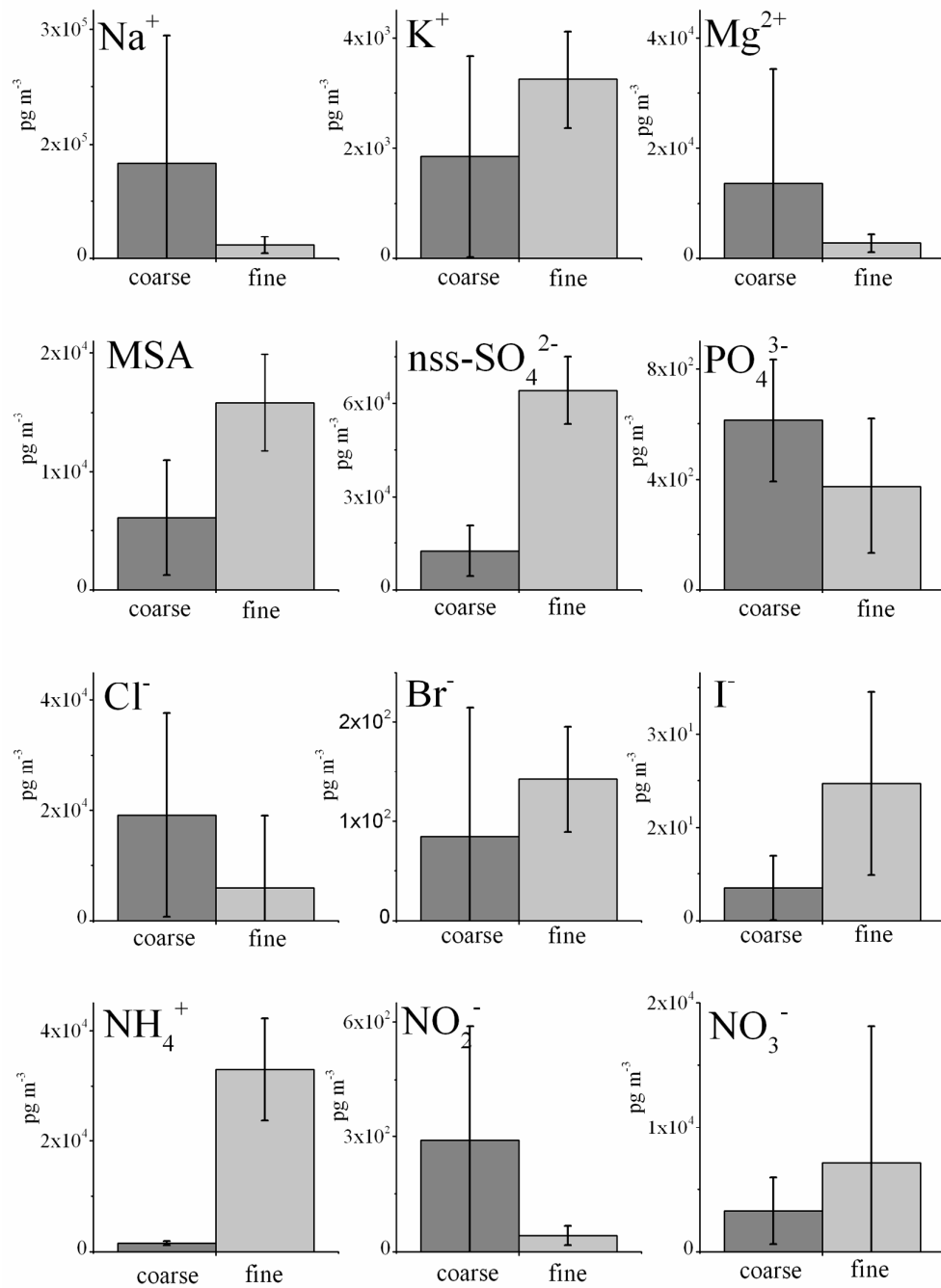
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- 550

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

Compounds	Samplingsystem	analytical technique	Reference
Major elements: Al, Fe, Mg, Na	HV cascade impactor equipped with cellulose filter	ICP-AES	[15]
Trace elements: Li, V, Cr, Mn, Co, Cu, Rb, Y, Mo, Pb	HV cascade impactor equipped with cellulose filter	ICP-MS	[15]
Qualitative analysis: Na ⁺ (e.g. NaCl, Na ₂ CO ₃), N-C, N+ (NH ₄ ⁺), NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , silicates, F ⁻ , Ca ²⁺ (e.g. CaCO ₃), Al ₂ O ₃ , Alsilicate, Fe(III), Mg(II), PO ₄ ³⁻ , Zn(II)	HV cascade impactor equipped with cellulose filter	XPS	[16]
Amino acids (AA): 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	[17]
Phenolic compounds (PC): vanillin, vanillic acid, homovanillic acid, syringic acid, syringaldehyde, p-coumaric acid, coniferylaldehyde, ferulic acid.	HV cascade impactor equipped with quartz filter	HPLC-MS/MS	[19, 20]
Monosaccharides (MA): Glucose, Fructose, Arabinose, Galactose, Mannose, Xylose	HV cascade impactor equipped with quartz filter	HPAEC-MS	[18]
Disaccharide: Sucrose	HV cascade impactor equipped with quartz filter	HPAEC-MS	[18]
Alcohol-sugars (AS): Arabitol, Mannitol, Erythritol, Ribitol, Sorbitol/galactitol, Xylitol	HV cascade impactor equipped with quartz filter	HPAEC-MS	[18]
Anhydrosugars (LMG): Levoglucosan, Mannosan, Galactosan	HV cascade impactor equipped with quartz filter	HPAEC-MS	[18]
Cations: NH ₄ ⁺ , K ⁺ , Mg ²⁺	HV cascade impactor equipped with quartz filter	Capillary cationic chromatography with conductivity detector	this paper
Anions: Cl ⁻ , Br ⁻ , I ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , sulfate, phosphate and methanesulfonic acid (MSA)	HV cascade impactor equipped with quartz filter	HPAEC-MS	this paper
Carboxylic acid (CA): C ₂ -oxalic, C ₂ -acetic, C ₂ -glycolic, C ₃ -malonic, C ₄ -succinic, <i>h</i> C ₄ -malic, <i>cis-us</i> C ₄ -maleic, <i>trans-us</i> C ₄ -fumaric, C ₅ -glutaric, C ₆ -adipic, C ₇ -pimelic, <i>a</i> C ₇ -benzoic, C ₈ -suberic	HV cascade impactor equipped with quartz filter	HPAEC-MS	this paper
POPs: PCB, PAH, PCN, PBDE, POC	TSP air sampler equipped with polyurethane foam and quartz filter	GC-MS	this paper

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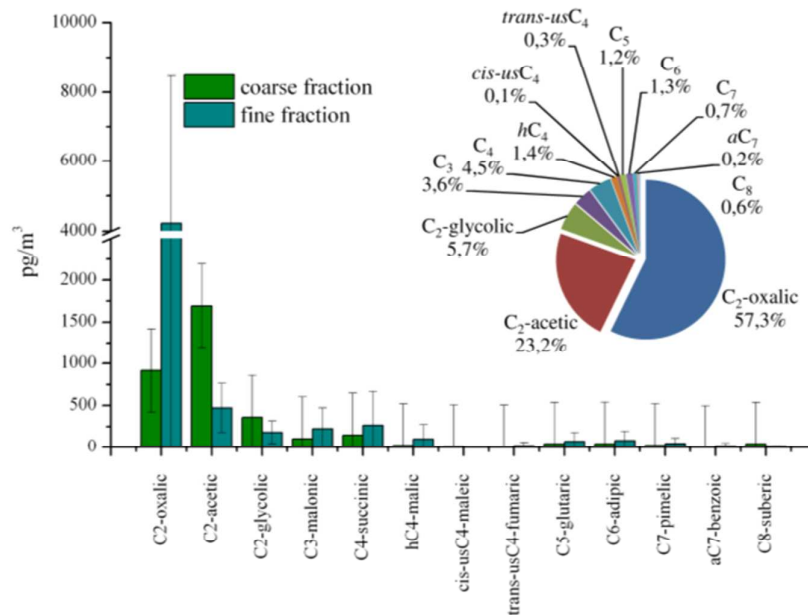


554

555 **Figure 1.** Average concentration of ionic species in the coarse (>1 μm, <10 μm) and fine (<1 μm) fractions and its
 556 standard deviations of aerosol samples collected at MZS during the austral summer 2010-2011.

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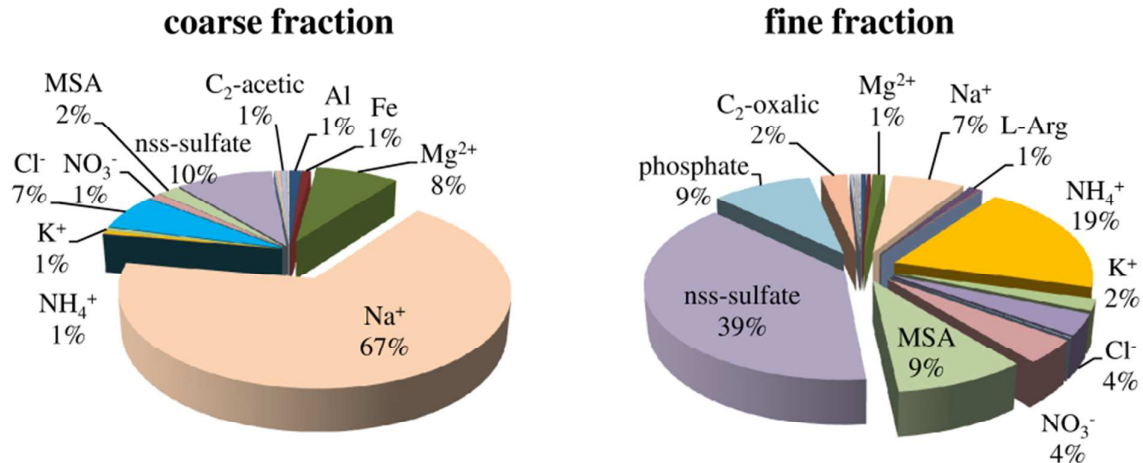
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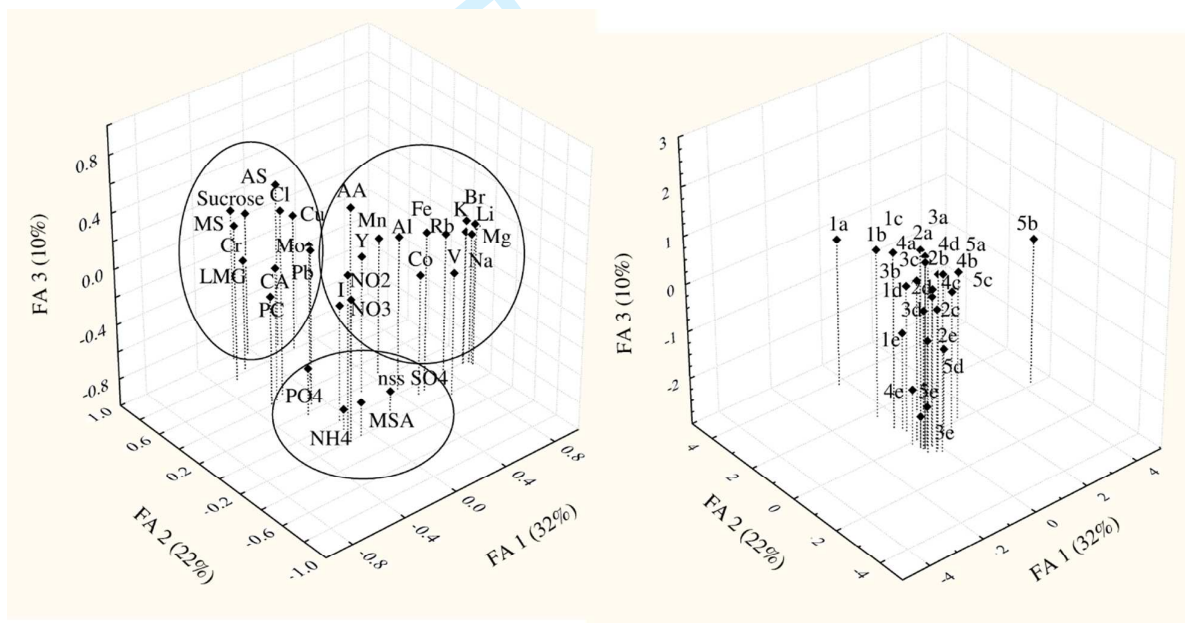
560 **Figure 2.** Particle size distribution of carboxylic acids and percentage values relative to PM₁₀ aerosol samples collected
 561 at MZS from 2010, 29th November to 2011, 18th January.

562



563

564 **Figure 3.** Chemical composition of PM₁₀ aerosol collected at the coastal base "Mario Zucchelli" during the austral
 565 summer 2010-11. All compounds with percentage >1% are reported. The percentage value is related to the sum of all
 566 analyzed compounds.



567

568 **Figure 4.** Factor analysis results: projections of the variables and the cases on the factor-plane 1x2x3. Scores label
 569 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-
 570 3 μm; c: 3-1.5 μm; d: 1.5-0.95 μm; e: 0.95-0.49 μm).

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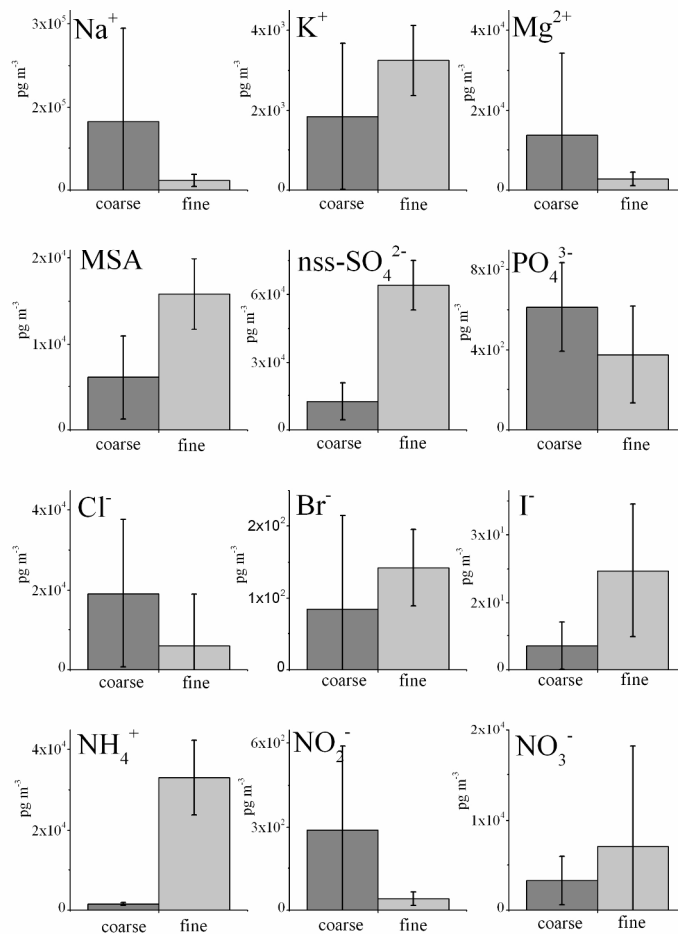


Figure 1. Average concentration of ionic species in the coarse (>1µm, <10 µm) and fine (<1µm) fractions and its standard deviations of aerosol samples collected at MZS during the austral summer 2010-2011. 201x287mm (300 x 300 DPI)

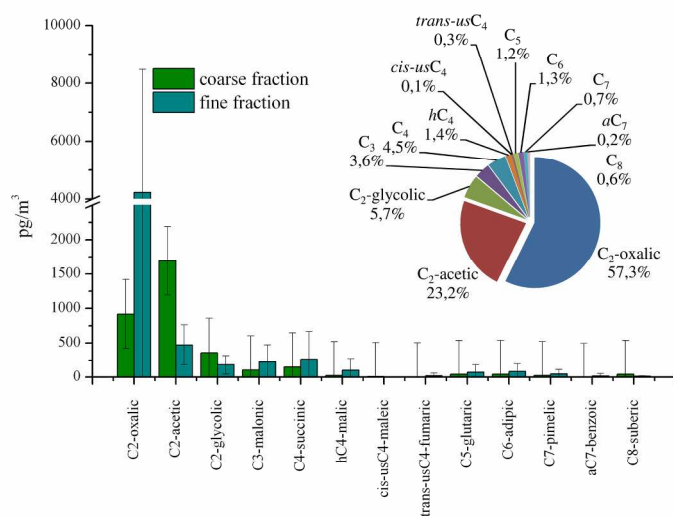


Figure 2. Particle size distribution of carboxylic acids and percentage values relative to PM₁₀ aerosol samples collected at MZS from 2010, 29th November to 2011, 18th January. 209x148mm (300 x 300 DPI)

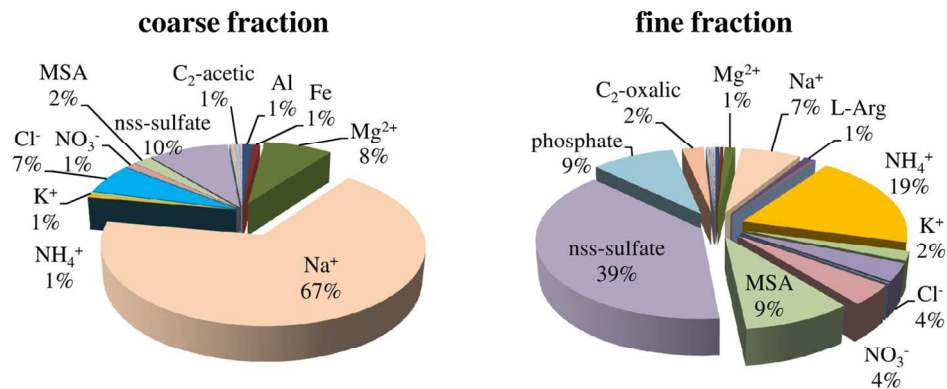


Figure 3. Chemical composition of PM₁₀ aerosol collected at the coastal base "Mario Zucchelli" during the austral summer 2010-11. All compounds with percentage >1% are reported. The percentage value is related to the sum of all analyzed compounds.
120x61mm (300 x 300 DPI)

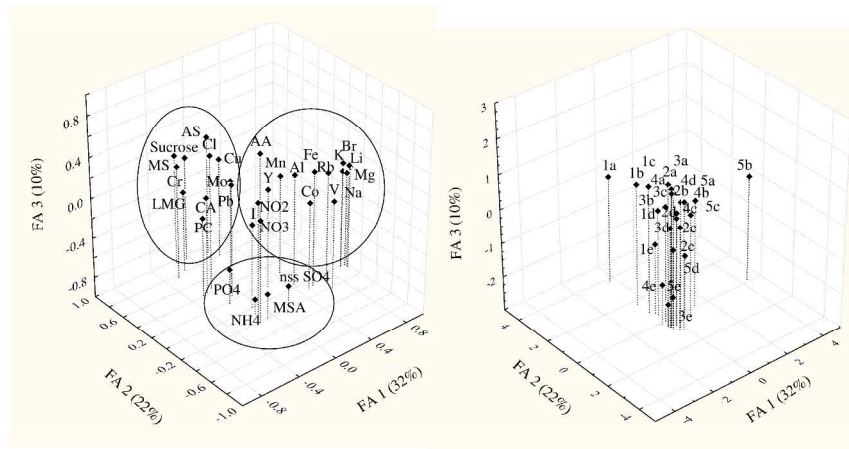


Figure 4. Factor analysis results: projections of the variables and the cases on the factor-plane 1x2x3. Scores label includes a progressive number for the sampling period and a progressive letter for the cut-off size (a: 10-7.2 μm ; b: 7.2-3 μm ; c: 3-1.5 μm ; d: 1.5-0.95 μm ; e: 0.95-0.49 μm).
928x655mm (96 x 96 DPI)

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

Compounds	Samplingsystem	analytical technique	Reference
Major elements: Al, Fe, Mg, Na	HV cascade impactor equipped with cellulose filter	ICP-AES	[15]
Trace elements: Li, V, Cr, Mn, Co, Cu, Rb, Y, Mo, Pb	HV cascade impactor equipped with cellulose filter	ICP-MS	[15]
Qualitative analysis: Na ⁺ (e.g. NaCl, Na ₂ CO ₃), N-C, N ⁺ (NH ₄ ⁺), NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , silicates, F ⁻ , Ca ²⁺ (e.g. CaCO ₃), Al ₂ O ₃ , Alsilicate, Fe(III), Mg(II), PO ₄ ³⁻ , Zn(II)	HV cascade impactor equipped with cellulose filter	XPS	[16]
Amino acids (AA): Gly, L-Ala, L-Asp, L-Arg, L-Glu, L-Phe, LPro, L-Tyr, L-Thr	HV cascade impactor equipped with quartz filter	HPLC-MS/MS with chiral column	[17]
Phenolic compounds (PC): vanillin, vanillic acid, homovanillic acid, syringic acid, syringaldehyde, p-coumaric acid, coniferylaldehyde, ferulic acid.	HV cascade impactor equipped with quartz filter	HPLC-MS/MS	[19, 20]
Monosaccharides (MA): Glucose, Fructose, Arabinose, Galactose, Mannose, Xylose	HV cascade impactor equipped with quartz filter	HPAEC-MS	[18]
Disaccharide: Sucrose	HV cascade impactor equipped with quartz filter	HPAEC-MS	[18]
Alcohol-sugars (AS): Arabitol, Mannitol, Erythritol, Ribitol, Sorbitol/galactitol, Xylitol	HV cascade impactor equipped with quartz filter	HPAEC-MS	[18]
Anhydrosugars (LMG): Levoglucosan, Mannosan, Galactosan	HV cascade impactor equipped with quartz filter	HPAEC-MS	[18]
Cations: NH ₄ ⁺ , K ⁺ , Mg ²⁺	HV cascade impactor equipped with quartz filter	Capillary cationic chromatography with conductivity detector	this paper
Anions: Cl ⁻ , Br ⁻ , I ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , sulfate, phosphate and methanesulfonic acid (MSA)	HV cascade impactor equipped with quartz filter	HPAEC-MS	this paper
Carboxylic acid (CA): C ₂ -oxalic, C ₂ -acetic, C ₂ -glycolic, C ₃ -malonic, C ₄ -succinic, <i>h</i> C ₄ -malic, <i>cis-us</i> C ₄ -maleic, <i>trans-us</i> C ₄ -fumaric, C ₅ -glutaric, C ₆ -adipic, C ₇ -pimelic, <i>a</i> C ₇ -benzoic, C ₈ -suberic	HV cascade impactor equipped with quartz filter	HPAEC-MS	this paper
POPs: PCB, PAH, PCN, PBDE, POC	TSP air sampler equipped with polyurethane foam and quartz filter	GC-MS	this paper

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For Review Only

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