Environ. Chem. **2016**, *13*, 867–876
doi:10.1071/EN16056_AC

Supplementary material

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

E. Barbaro,[A,B,G] R. Zangrando,[B] T. Kirchgeorg,[A] A. Bazzano,[C] S. Illuminati,[D] A. Annibaldi,[D] S. Rella,[E] C. Truzzi,[D] M. Grotti,[C] A. Ceccarini,[F] C. Malitesta,[E] G. Scarponi,[D] and A. Gambaro[A,B]

[A]Department of Environmental Sciences, Informatics and Statistics, University of Venice, Ca'Foscari,

Via Torino 155, 30172 Venice, Italy.

[B]Institute for the Dynamics of Environmental Processes, Consiglio Nazionale delle Ricerche (CNR),

Via Torino 155, 30172 Venice, Italy.

[C]Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31,

I-16146 Genoa, Italy.

[D]Department of Life and Environmental Sciences, Polytechnic University of Marche, Via Brecce Bianche,

60131 Ancona, Italy.

[E]Department of Biological and Environmental Sciences and Technologies, University of Salento,

Via Monteroni, 73100 Lecce, Italy.

[F]Department of Chemistry and Industrial Chemistry, University of Pisa, Via Moruzzi 13, 56124 Pisa, Italy.

[G]Corresponding author. Email: barbaro@unive.it

Material and Methods

Details of analytical methods to determine anionic and cationic compounds

Determination and quantification of anionic compounds (Cl^-, Br^-, I^-, NO_2^-, NO_3^-, sulfate, phosphate and methanesulfonic acid (MSA)) and 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) were performed using an ion chromatograph (ThermoScientific^{TM} Dionex^{TM} ICS-5000, Waltham, US), with an anion exchange column (Dionex Ion Pac AS11 2x250mm) and guard column(Dionex Ion Pac AG11 2x50 mm), coupled with a single mass spectrometer (MSQ Plus^{TM}, ThermoScientific^{TM}, Bremen, Germany). The sodium hydroxide gradient, generated by an eluent generator (Dionex ICS 5000EG, Thermo Scientific) was: 0-3.5 min gradient from 0.5 mM to 5 mM; 3.5-5 min gradient from 5 mM to 10 mM; 5-25 min gradient from 10 mM to 38 mM; 25-30 min, column cleaning with 38 mM; 30-35min; equilibration at 0.5 mM. The injection volume was 100 µL and the flow rate was 0.25 mL min^{-1}. Sodium hydroxide was removed by a suppressor (ASRS 500, 2 mm, Thermo Scientific) before entering the MS sources. The MS was operating with an electrospray ionization (ESI) interface in negative mode. Selected ion monitoring (SIM) was used for detection.

Determination of cationic compounds were performed using an ion capillary chromatograph coupled with conductibility detector. Sodium, ammonium, magnesium and potassium were separated using an Ion Pac CS19-4µm capillary cation exchange column (0.4 x250 mm) equipped with an Ion Pac CG19-4µm guard column (0.4x50 mm). The MSA gradient, generated by an eluent generator (Dionex EGC-MSA Capillary)was:0-17.3 min; 1.5 mM; 17.3-21.9 min gradient from 1.5 mM to 11 mM; 21.9-30 min equilibration at 1.5 mM. The injection volume was 0.4 µL and the flow rate was 13 µL min^{-1}. MSA was removed by a suppressor (CCES 300, Thermo Scientific) before entering the conductibility detector.

Analytical details to determine Persistent Organic Pollutants in aerosol samples

QFFs were extracted twice with aliquots of 20 mL of hexane/acetone (1:1, v:v) mixture in an ultrasonic bath for 1 h and the recovered organic phases were combined and hold overnight on anhydrous sodium sulfate. 2 mL of isooctane was added to the organic phase and reduced to a volume of about 1 ml in a centrifugal evaporator before the chromatographic analysis. PUFs were extracted twice with aliquots of 150 mL of mixture of hexane/acetone (1:1, v:v) in an ultrasonic bath for 1 h and the recovered organic phase was combined and hold overnight on anhydrous sodium sulfate. The organic phase was then filtered through 0.45 µm PFTE filters, then reduced in volume using a centrifugal evaporator and purified by multi-layer solid phase extraction (SPE)cartridges. The analytes were eluted from the SPE column with 10 mL of n-hexane. 2 mL of isooctane was added to the recovered hexane and reduced to a volume of about 1 mL in a centrifugal evaporator before the gas-chromatographic analysis. QFF and PUF field blanks were spiked with a range of $^{13}C_{12}$-labeled PCB congeners and D_{10}-labeled PAHs to monitor the extraction and clean-up procedures.

Instrumental analysis was performed by a gas-chromatograph (5890A, Agilent Technologies, USA) equipped with a MS detector (5973, Agilent Technologies). Chromatographic separation was performed on a HP5-MS capillary column (30m x 0.25mm x 25µm) using helium as carrier gas at a flow rate of 1 mLmin^{-1}. The oven temperature program was: 60 °C hold for 0.5 min then 15.00 °C min^{-1} up to 140 °C then 2 °Cmin^{-1} up to 240 °C then 15 °Cmin^{-1} up to 300 °C. The injection volume was 50 µL and the PTV temperature program was: 65 °C hold for 0.5 min then 500 °C min^{-1} up to 280 °C. The MS detector operated in SIM mode.

Table S1. Concentrations (pg m^{-3}) of ionic species associated to size-segregated aerosols collected at Campo Faraglione (Mario Zucchelli Station, Antarctica) during the austral summer 2010-2011

<MDL, below method detection limit; n.d., not detected

			Na^+	$NH4^+$	K^+	Mg^{2+}	Cl^-	Br^-	I^-	NO_2^-	NO_3^-	MSA	SO_4^{2-}	PO_4^{3-}
Sample 1	29 November - 09 December	10-7.2 µm	5179	333	132	881	6459	<MDL	<MDL	115	<MDL	138	4627	175
		7.2-3.0 µm	16483	384	330	2424	16391	<MDL	<MDL	41	<MDL	587	5235	152
		3.0-1.5 µm	10984	333	414	1620	19116	8	<MDL	<MDL	736	676	4051	137
		1.5-0.95 µm	16099	307	233	1966	8673	9	10	<MDL	728	1709	10463	386
		0.95-0.49 µm	10420	2448	482	1041	1332	17	6	51	865	2224	11548	645
		<0.49 µm	24214	17382	4030	4128	27913	159	34	<MDL	25873	9830	71750	<MDL
Sample 2	09-19 December	10-7.2 µm	5437	127	177	266	3905	13	<MDL	<MDL	<MDL	130	1427	<MDL
		7.2-3.0 µm	26242	319	646	3367	9473	7	<MDL	335	<MDL	757	3410	<MDL
		3.0-1.5 µm	16953	237	173	964	4543	8	<MDL	359	<MDL	533	10437	117
		1.5-0.95 µm	17278	410	144	1159	1761	14	11	<MDL	754	1007	14329	269
		0.95-0.49 µm	9590	4635	294	871	<MDL	24	7	<MDL	734	3272	14007	<MDL
		<0.49 µm	6445	30874	2102	932	<MDL	191	24	<MDL	1174	8401	41178	<MDL
Sample 3	19-29 December	10-7.2 µm	5154	108	131	105	1232	<MDL	<MDL	<MDL	<MDL	278	<MDL	<MDL
		7.2-3.0 µm	14394	416	209	1036	2921	<MDL	<MDL	49	183	1089	2693	417
		3.0-1.5 µm	9236	342	76	261	1139	8	<MDL	<MDL	1532	993	2430	148
		1.5-0.95 µm	12564	1023	214	989	<MDL	13	<MDL	<MDL	3384	4518	12595	115
		0.95-0.49 µm	4670	9024	209	513	<MDL	7	<MDL	<MDL	505	5455	15169	368
		<0.49 µm	3476	35863	2352	870	<MDL	76	26	60	1185	15284	42308	<MDL
Sample 4	29 December - 08 January	10-7.2 µm	7943	185	644	561	2783	11	<MDL	<MDL	287	502	<MDL	83
		7.2-3.0 µm	21658	60	310	1256	2676	9	<MDL	<MDL	207	1104	7489	<MDL
		3.0-1.5 µm	10776	570	180	530	2245	10	<MDL	517	3507	1613	5157	135
		1.5-0.95 µm	769	342	122	83	<MDL	<MDL	<MDL	<MDL	2974	584	1281	156
		0.95-0.49 µm	7704	7106	268	705	<MDL	14	<MDL	<MDL	1179	4226	17208	346
		<0.49 µm	n.d.	28317	2792	696	<MDL	101	5	39	2026	11149	43673	<MDL
sample 5	08-23 January	10-7.2 µm	40032	<MDL	581	3806	4342	77	<MDL	<MDL	<MDL	336	12673	237
		7.2-3.0 µm	293538	1500	3119	39805	<MDL	186	<MDL	<MDL	319	318	12610	<MDL
		3.0-1.5 µm	44203	363	744	3649	4443	31	<MDL	<MDL	750	3981	10428	151
		1.5-0.95 µm	46292	<MDL	643	3159	3482	21	6	32	931	9543	17396	383
		0.95-0.49 µm	873	5672	436	1570	393	20	<MDL	<MDL	<MDL	5134	20176	516
		<0.49 µm	17607	23658	3251	2244	<MDL	101	9	53	2067	14070	53887	<MDL

Table S2. Concentrations (pg m^{-3}) of amino acids (AA)[1], phenolic compounds (PC)[2], carboxylic acids (CA), monosaccharides (MS)[3], sucrose[3], alcohol sugars (AS)[3], anhydrosugars (LMG)[3] associated to size-segregated aerosols collected at Campo Faraglione (Mario Zucchelli Station, Antarctica) during the austral summer 2010-2011

<MDL: below method detection limit

			AA	PC	CA	MS	Sucrose	AS	LMG
Sample 1	29 November - 09 December	10-7.2 µm	36	4	1477	196	18	66	24
		7.2-3.0 µm	36	3	1161	114	8	34	8
		3.0-1.5 µm	40	3	680	71	7	20	6
		1.5-0.95 µm	22	3	1550	54	5	18	8
		0.95-0.49 µm	25	5	1186	46	3	15	12
		<0.49 µm	5218	73	13726	876	33	290	134
Sample 2	09-19 December	10-7.2 µm	22	1	334	0.5	<MDL	<MDL	<MDL
		7.2-3.0 µm	24	2	535	0.5	<MDL	0.9	<MDL
		3.0-1.5 µm	30	2	545	<MDL	<MDL	0.3	<MDL
		1.5-0.95 µm	35	3	896	<MDL	<MDL	0.3	7
		0.95-0.49 µm	20	4	619	<MDL	<MDL	0.5	11
		<0.49 µm	556	36	3019	93	1	8	12
Sample 3	19-29 December	10-7.2 µm	11	1	780	<MDL	<MDL	24	<MDL
		7.2-3.0 µm	38	2	804	<MDL	<MDL	25	<MDL
		3.0-1.5 µm	16	3	915	<MDL	<MDL	1	2
		1.5-0.95 µm	17	4	606	<MDL	<MDL	0.4	5
		0.95-0.49 µm	17	1	1065	<MDL	<MDL	<MDL	5
		<0.49 µm	410	15	4218	82	1	0.4	9
Sample 4	29 December - 08 January	10-7.2 µm	15	1	786	<MDL	<MDL	1	<MDL
		7.2-3.0 µm	17	1	659	<MDL	<MDL	0.4	<MDL
		3.0-1.5 µm	31	3	994	2	<MDL	1	1
		1.5-0.95 µm	42	3	454	<MDL	<MDL	1	4
		0.95-0.49 µm	24	3	346	<MDL	2	2	4
		<0.49 µm	322	22	2551	85	1	1	9
Sample 5	08-23 January	10-7.2 µm	32	1	864	2	4	13	1
		7.2-3.0 µm	44	1	4	<MDL	1	26	1
		3.0-1.5 µm	9	2	1470	<MDL	<MDL	7	3
		1.5-0.95 µm	25	2	1476	<MDL	4	2	2
		0.95-0.49 µm	17	2	287	<MDL	<MDL	1	2
		<0.49 µm	397	17	1517	80	<MDL	4	8

Table S3. Correlations matrix of ionic balance with concentration expressed in terms of equivalents

Marked correlations are significant at $p<0.05$

	Na^+	**NH_4^+**	**K^+**	**Mg^{2+}**	**Cl^-**	**Br^-**	**I^-**	**NO_2^-**	**NO_3^-**	**MSA^-**	**nss-SO_4^{2-}**	**$H_2PO_3^-$**
Na^+	1.00											
NH_4^+	-0.26	1.00										
K^+	**0.93**	-0.56	1.00									
Mg^{2+}	**0.99**	-0.33	**0.95**	1.00								
Cl^-	-0.15	-0.84	0.15	-0.07	1.00							
Br^-	**0.93**	-0.38	0.85	**0.93**	-0.05	1.00						
I^-	-0.31	-0.41	-0.23	-0.27	0.75	-0.11	1.00					
NO_2^-	-0.47	0.09	-0.51	-0.50	-0.15	-0.19	0.05	1.00				
NO_3^-	-0.30	-0.72	0.06	-0.22	**0.91**	-0.31	0.49	-0.24	1.00			
MSA^-	0.72	0.32	0.56	0.69	-0.52	0.44	-0.58	-0.72	-0.44	1.00		
nss-SO_4^{2-}	0.86	-0.68	**0.94**	**0.89**	0.38	0.85	0.11	-0.53	0.19	0.40	1.00	
$H_2PO_3^-$	0.39	-0.53	0.60	0.45	0.56	0.18	0.14	-0.87	0.63	0.39	0.65	1.00

Table S4. Total concentration of Persistent Organic Pollutants (POPs) associated to the particulate fraction (QFF samples) and to the gaseous fraction (PUF samples) of atmospheric aerosol collected at Campo Faraglione (Mario Zucchelli Station, Antarctica) during the austral summer 2010-2011

n.d., not detected

QFF samples	**CF1**	**CF2**	**CF3**	**CF4**	**CF5**	**CF6**	**CF7**	**CF8**	**CF9**	**CF10**	**CF11**
Start sampling	24 November	29 November	4 December	9 December	14 December	19 December	24 December	29 December	3 January	8 January	13 January
End sampling	29 November	4 December	9 December	14 December	19 December	24 December	29 December	3 January	8 January	13 January	18 January
PCN	n.d.	0.19	n.d.	0.06	0.02	n.d.	0.09	0.06	0.03	n.d.	0.08
PBDEs/BFRs	0.14	0.16	1.2	n.d.	0.02	0.08	0.13	0.13	0.26	0.07	0.38
OCP	0.40	0.41	0.28	0.20	0.01	0.22	0.01	0.33	0.33	0.22	0.25
PCB	0.01	0.02	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.01
PAH	0.85	0.23	n.d.	0.30	0.47	0.46	0.25	n.d.	0.52	0.01	0.02

PUF samples	**CP1**	**CP2**	**CP3**	**CP4**	**CP5**	**CP6**	**CP7**	**CP8**	**CP9**	**CP10**	**CP11**
Start sampling	24 November	29 November	4 December	9 December	14 December	19 December	24 December	29 December	3 January	8 January	13 January
End sampling	29 November	4 December	9 December	14 December	19 December	24 December	29 December	3 January	8 January	13 January	18 January
PCN	0.10	0.11	0.04	1.6	0.03	0.01	0.13	0.15	0.05	1.08	1.19
PBDEs/BFRs	0.06	0.58	0.60	0.19	0.09	0.20	n.d.	0.11	0.03	n.d.	n.d.
OCP	1.07	1.54	0.26	0.75	0.10	0.20	1.22	0.94	0.26	4.38	0.68
PCB	0.49	0.34	0.24	0.52	0.14	0.08	0.45	0.48	0.36	0.68	0.42
PAH	1.7	0.79	0.34	3.4	0.33	0.14	1.8	1.7	0.28	0.90	1.2

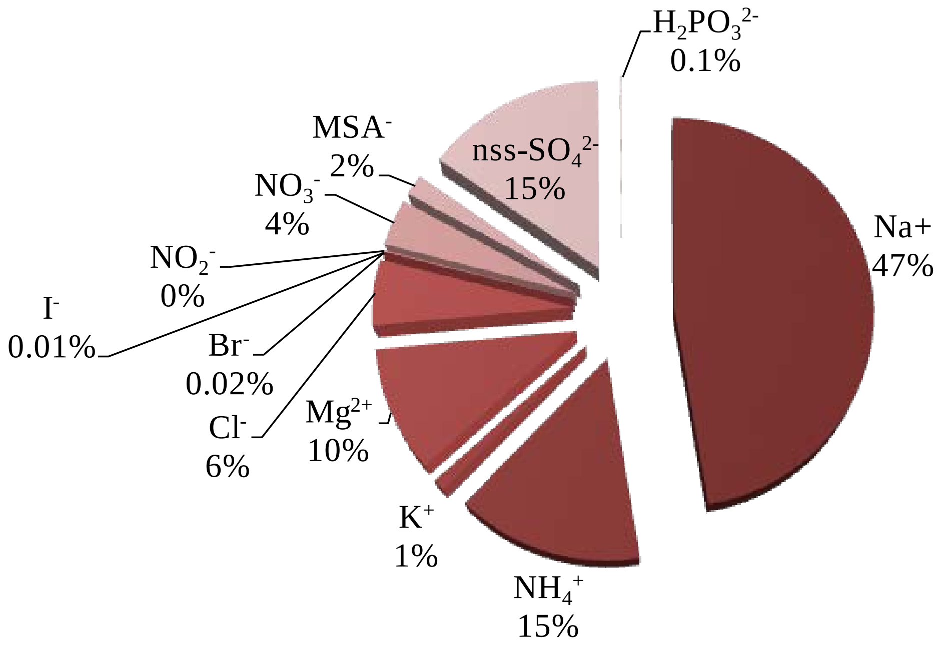

Figure S1. Pie diagram of ionic concentrations (in peq m^{-3}) in the aerosol samples collected at MZS during the austral summer 2011-2012.

References

[1] 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.

[2] 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.

[3] E. Barbaro, T. Kirchgeorg. R. Zangrando. M. Vecchiato. R. Piazza. C. Barbante and A. Gambaro. Sugars in Antarctic aerosol. *Atmos. Environ.* **2015**, *118*, 135.