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Environmental Markers in Remote Areas and Urban Sites. Investigation of the Contribution of Natural and Anthropogenic Sources

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These three years of PhD were a constant source of both professional and personal growth. I would like to thank all the people who have constantly believed in me.

Contents

PREMISE

Stretching from the pre-classical period, before 1900, until now a broad range of scientists stemming from different research fields, such as meteorology, physics, chemistry, engineering etc., have focused their efforts into the developing studies concerning the aerosol. Thanks also to the technological progress, aerosol studies have been initiated and have been continually evolving. Since the end of World War II, aerosol studies has been recognized as an official science [1]. Consequently, nowadays there is a deep interest in the aerosol science mainly focused on the air quality and its relationship with human health. Moreover interest is also on larger scale, focusing on the impact of pollutants on global climate change [2]. These investigations require a wide knowledge of both the natural and anthropogenic emissions sources, of the mechanisms of aerosol transportation and of the chemical and physical characterization and transformation of particles in the atmosphere [3]. Chemical characterization and the study of the size distribution of the particulate matter (PM) are the key instruments needed to investigate both anthropogenic and natural sources of emissions in different areas of the world. There are many potential indicators of different emission sources and different processes that are possible in the atmosphere and they are called *Molecular Markers*. Some of them are defined as *specific*, because their origin is directly connected only to a specific event of emission, while other markers are defined as *non-specific* and their origins can be multiple. Sugars, amino acids, methoxyphenols and polycyclic aromatics hydrocarbons (PAH) are some groups of *specific* molecular markers. Sugars and amino acids are respectively tracers of biogenic activities [4]. Primary saccharides, such as glucose and sucrose, are emitted from bioaerosol, while arabitol and mannitol are tracers for fungal spores and are also concentrated in lichens and bacteria [5], [4]. Among the anhydrosugars the levoglucosan is a *specific* marker of the phenomena of biomass burning, accompanied by low quantities of its isomers: mannosan and galactosan [6]. Methoxyphenols are tracers of biomass burning emitted during the combustion of a particular kind of vegetation [7], but a recent study related the free phenolic compounds to an additional marine source [8]. PAH are mainly emitted from five major sources of emissions: domestic, mobile, industrial, agricultural and natural. PAH are specific tracers of anthropogenic sources of input, due to their low natural emissions [9].

Conversely, elemental carbon (EC), organic carbon (OC) and carboxylic acids (CA) and inorganic and organic ions can be useful to study the main emission sources as *non-specific* molecular markers [10], [11]. This PhD thesis is concerned with the study of environmental molecular markers and their wide applicability as tracers of natural or anthropogenic emission sources. Furthermore, this study focuses on the analysis of aerosol samples coming from three different areas: one remote area, Antarctica, and one urban site, Sernaglia della Battaglia to demonstrate the wide applicability of these environmental molecular markers to extremely different environments, giving valuable information about the air quality in all three.

1 INTRODUCTION

1.1 Particulate Matter

Generally, an aerosol is defined as a suspension of solid or liquid particles in a gas. The particles diameter is between 10^{-4} and 10^{-9} m; the lower limit is for molecules and molecular clusters and the upper limit for rapid sedimentation. Particles diameter vary more than four orders of magnitude, starting from some nanometers (nm) to tens or hundreds of micrometers (μm). Conventionally, particles with a diameter of less than 100 nm are called *ultrafine*, particles smaller than 2.5 μm are defined as *fine* and particles with a diameter greater than 2.5 μm are defined as *coarse.* In environmental research, usually, the term *fine particles* defines all particles with an aerodynamic diameter ≤ 1 μm, called PM1, and ≤ 2.5 μm, called PM 2.5. Sometimes also particles up to 10 μm (PM 10) are included in this definition [12]. Normally, particles are differentiated into *primary particles* and *secondary particles*. *Primary particles* are directly emitted as liquids or solids from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, wind-driven or traffic-related suspension of road, soil, mineral dust, sea salt and biological materials. Whereas, *secondary particles* are formed by gas-to-particle conversion in the atmosphere through reactions like nucleation and condensation with gaseous precursors such as sulphur dioxide, oxides of nitrogen, ammonia and non-methane volatile and semi volatile organic compounds [13] **Figure 1**.

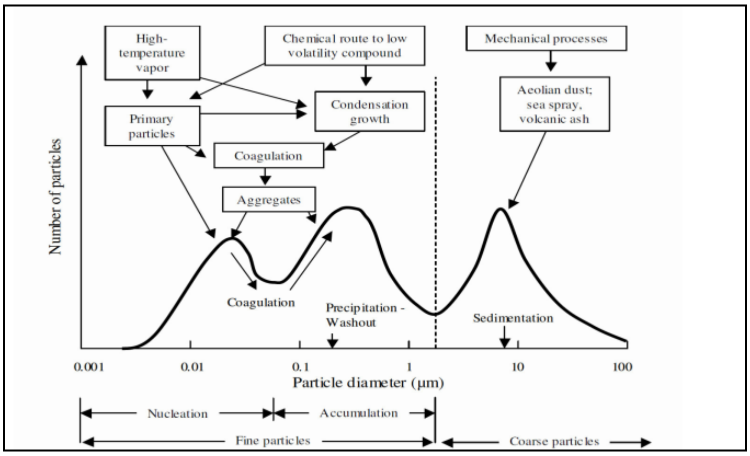

Figure 1. Model of size distribution of the PM with different source of emission and pathways. Adapted from Vallero 2010, [14]

Particles in the atmospheric aerosol can originate from a wide variety of natural and anthropogenic sources. Among the different anthropogenic sources, mainly concentrated in the atmosphere of urban and industrial areas, there are traffic (exhaust emissions, road surface abrasion, brake and tyre wear, particle resuspension from paved roadways), industrial emissions (emissions from power plants, oil refineries, mining) building and housing emissions (excavations, soil movement, demolitions and heating, food cooking). While, the most import natural sources, mainly concentrated in the natural and rural areas, are seas, oceans, deserts, soil, volcanoes, vegetation, wildfires, lightning and biomass burning and emissions coming from farming activities [15].

The wide range of sources generate particles with very different chemical composition, size distribution and concentration of the atmospheric particles in the aerosol are temporally and spatially variable. For example, in the troposphere the total number of particles is in the range of about 102–105 cm^{-3} and the mass concentration typically is in the range of about and 1–100 μgm^{-3} [16]. Usually, the predominant chemical components of air particulate matter are sulphate, nitrate, ammonium, sea salt, mineral dust, organic compounds, and black or elemental carbon, each of which typically contribute about 10–30% to the overall mass load. At various locations, times, meteorological conditions, and particle size fractions, however, the relative abundance of different chemical components can vary by an order of magnitude or even more [17].

The chemical composition of the PM is very complex and varied. It includes inorganic compounds, with a percentage of between 25 and 75%, and organic compounds of around 40%. The predominant species among the inorganic compounds are sulphates, nitrates, ammonium, sea salt and dust components. The composition of the organic matter is much more complex. It includes a wide range of species. PM contains tens of thousands of organic compounds with a different carbon number, functional group and solubility. Among all these compounds only a part has been detected, quantified and studied [18] **Figure 2**.

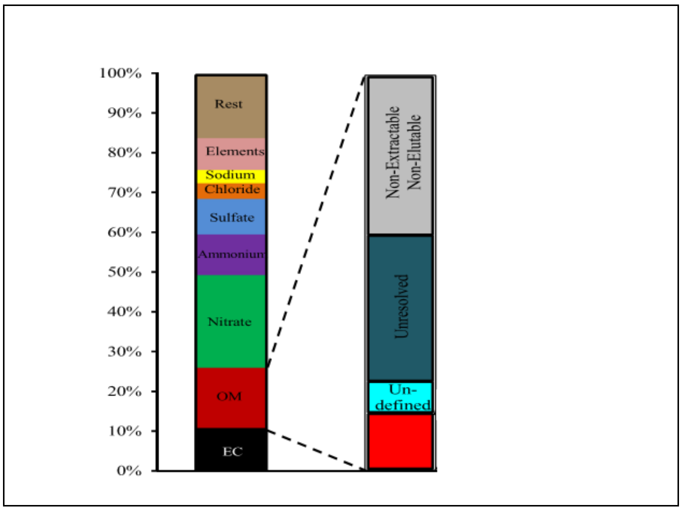

Figure 2. PM chemical composition

1.2 Natural sources

The most relevant natural sources of particulate matter are sea spray, mineral dust, biogenic emissions, volcanic eruptions, and lightning.

The *marine aerosol* is the most important aerosol fraction in the world. Marine aerosol can affect not only the coastal areas, but also the relative high altitudes inland. This is possible due to the phenomena of the long-range transportation of this kind of aerosol [19]. Marine aerosol usually contribute the most to the coarse fraction of the aerosol particles, but nowadays several studies highlight smaller marine particles [20]. Oceans and seas are the main sources of primary marine aerosol and they are responsible of the emission of Na^+ and Cl^-, with a small amount of SO_4^{2-}, K^+, Mg^{2+} and Ca^{2+} [21]. The eruption of rising bubbles on the sea surface, called *bubble bursting*, produces mainly primary marine salt, NaCl. Part of the Cl^- could be changed into gaseous atmospheric reactions with SO_4^{2-} and NO_3^-, this is the phenomena of *chloride depletion*, consequently Na^+ remains the main tracer for particulate matter in marine salt [22].

$$NaCl(s) + HNO_3(g) \longrightarrow HCl(g) + NaNO_3(s)$$

$$2NaCl(s) + H_2SO_4\,(g{+}aq) \longrightarrow 2HCl(g) + Na_2SO_4\,(s)$$

On the surface of the seas and the ocean there could be also phytoplankton which is responsible of the emission of various organic compounds, such as DMS and CH_3SCH_3, considered the most important precursors of atmospheric sulphates in the oceanic regions [3].

Mineral dust, commonly known as *crustal fraction*, is one of the largest contributors to the atmospheric global aerosol and is generated mostly by the action of winds, whose speed regulate the size distribution, on the Earth’s surface. Any type of soil, such as deserts, dry lake beds or semi-arid surfaces, could be a potential source of mineral particles. The emissions of mineral particles are regulated by parameters such as soil surface, moisture, vegetation and climate [23], [24]. The *global dust belt*, formed by deserts like the Sahara in the North of Africa, deserts in the Arabian Peninsula and Oman, Gobi and Taklimakan deserts in China, contribute the most of the total dust emission in the world. Among them the Sahara desert contributes the most in the production of mineral dust [25]. Mineral dust particles are formed by different compounds such as quartz, calcite, clays, dolomite, feldspar, traces of calcium sulphate and iron oxides [26].

Biogenic emissions come mainly from the vegetation and some kind of microorganisms, which produce both primary and secondary aerosol. Primary biogenic aerosol (PBA) comes mostly from plants, animals, bacteria, viruses, carbohydrates, proteins, waxes, ions and has several compounds as tracers: phospholipids, β-1,3-D-glucan, ergosterol, mannitol and arabitol [27], [28], [29], [5]. The biosphere emitted volatile organic compounds (BVOCs) which could be precursors of secondary organic aerosol (SOA), whose markers are mainly isoprene, but also amounts of alcohols, ketones, monoterpenes and sesquiterpenes [30], [31], [32], [33].

Also, *volcanic eruptions* and *lightning* contribute to the particulate matter in the atmosphere. The first one, volcanic eruptions, are important sources of both primary and secondary aerosol. Volcanic eruptions increase the amount of greenhouse gases and sulphur in the atmosphere. Volcanic eruptions emit mainly H_2O, CO_2, SO_2, HCl and other compounds in traces, such as Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Cu, and Zn [34]. These emissions could affect the climate and cause acid rain [35]. Normally the eruptions can reach the troposphere and their lifetime is about one week; in some particular cases, if the eruptions is strong enough, the aerosol emitted could reach the stratosphere and has a lifetime of about one- two years [36].

Lightning emits NO_x: during the lightning events a peak of temperature (around 28.000-31000 K) is reached and air is totally ionised [37]. Then this reaction takes place:

$$N_2 + O_2 \longrightarrow 2NO$$

Subsequently NO could be converted into NO_x [38].

1.3 Anthropogenic sources

The most important anthropogenic sources of particulate matter are traffic, industrial activities, coal burning, biomass burning, cooking emissions, tobacco and fireworks.

In *traffic* emissions, the biggest contribution is from road traffic. This is the main source of both primary and secondary anthropogenic aerosols. Particles vary greatly in size and chemical composition depending on the mechanisms of their formation. Ultrafine particles are directly emitted from petrol and diesel engines. These particles are formed at elevated temperature in the engine, in exhaust pipes or after the emission into the atmosphere. Fine particles, in traffic emissions, are formed by chemical reaction in the atmosphere, while coarse particles are mechanically formed by abrasion of road material road material, tyres and brake linings, soil dust raised by wind and traffic turbulence [39].

There is a large variety of chemical compounds released into the air traffic emissions. From the brake, the tyre and/or waste oil emissions, traces of elements such as strontium, copper, molybdenum, barium, cadmium, chromium, manganese, iron, zinc [40]. From motor emissions, traces of elements like potassium, bromine or chlorine [41].

From catalytic convertor emissions, traces of elements such as platinum, palladium and rhodium [42].

Emissions from other vehicles have been studied, such as railway traffic emissions. These emissions are mainly responsible for iron, aluminium and calcium emissions, due to the re-suspension of mineral dust [43]. Also, air traffic and maritime traffic have been investigated. Aircraft engines are responsible for the emission of metals [44], while ships emitted mostly SO_2, NO_X and carbonaceous particulate matter [45].

Industrial activities emissions depend mainly on the type of production process and the raw material used in production. The activities which generate more particle emissions, during production and transport, are industries producing ceramics, bricks, cement, foundries, mining and quarrying. These activities produce mainly primary aerosol, mostly formed by toxic metals, metalloid and SiO_2 [46]. Fine particles mainly come from activities like fibre production, nitric and sulphuric acid production, oil refineries, coking plants and mineral processing [47].

Another relevant anthropogenic emission source is *coal combustion*. In developing countries, it is used on a large scale and it constitutes a serious problem because it is responsible for emissions of toxic components such as PAHs or trace elements, such as As, Se, Hg, Cr, Cd, Pb, Sb, Zn, mainly in the fine fraction. For this kind of emission coal maturity, coal combustors and burning conditions are relevant [48].

The phenomenon of *biomass burning* is both a natural source and an anthropogenic source of anthropogenic particles. Biomass burning releases into the atmosphere carbonaceous compounds, lower concentrations of inorganic compounds, insoluble dust and ashes, and soluble salts, K^+, NH_4^+, SO_4^{2-}, NO_3^-, mainly concentrated in the fine and ultrafine fractions [49]. The effect of biomass burning is not only at a regional scale, but also at distant sites, due to phenomena like long range transport [50]. Agricultural burning, for example, produces a large amount of CO_2 and NO_x.

Firstly, *food cooking* is an important source of anthropogenic fine particles in urban areas. It is strongly dependent on the cooking method, cooking appliance and food ingredients. Among these factors, cooking temperature is the one that could affect both the chemical composition and the size distribution. In the specific case of meat cooking, 120 compounds have been quantified and they are directly correlated to the meat cooking. Among them, palmitic acid, stearic acid, oleic acid and cholesterol are the most concentrated [51].

Secondly, indoor air quality is also affected by the *tobacco* emissions. Several compounds have been identified as specific markers of tobacco smoke, like iso-alkanes, anteiso-alkanes, nicotine, solanesol, 3-thenylpyridine, nitrosamine [52].

Lastly, emissions from fireworks are an important source of anthropogenic particles. Fireworks are important source of gases, like ozone, sulphur, dioxide and nitrogen oxide, metals, as Sr, K, Ba, Co, Pb, Cu, and organic compounds [53], [54].

1.4 Environmental markers

Different type of natural and anthropogenic sources can be evaluated by using environmental markers, which can estimate if an area of interest is more affected by natural emissions, differentiating which kind of natural sources, or if there is a strong impact of pollution, specifying also which kind of pollutants are involved. Environmental markers are molecules that must not undergo any selective reactions that would preferentially remove the tracers above deposition of the primary particulate matter. Moreover, emissions of these molecular markers must be unique, or at least in limited number, to specific emission sources and conserved in atmospheric transport, neither formed nor destroyed by atmospheric chemical reactions. Environmental markers can not only highlight different emission sources, but they can be also used in tracking the long-range transport of primary emissions. In this case the compound of interest must be in big concentrations so once diluted and mixed with particulate matter coming from other primary sources, the molecular marker is recognizable and quantifiable. The following paragraphs in this thesis describe different environmental markers, which have been applied to study aerosol both in remote areas and urban sites. These environmental markers have been used as indicator of the impact of natural sources and, on the other hand, of the level of pollution and have been used to evaluate the phenomenon of long-range transport.

1.5 Inorganic aerosol compounds

Ionic species are included within the definition: inorganic aerosol, as in some components of the nitrogen cycle such as nitrite (NO_2^-), nitrate (NO_3^-) and ammonium (NH_4^+), components of the sulphur cycle such as sulphate (SO_4^{2-}) and another sulphurous compound such as methanesulfonate (MSA), components of the phosphate cycle such as phosphate (PO_4^{3-}) and other ions chloride (Cl^-), bromide (Br^-), iodide (I^-), sodium (Na^+), magnesium (Mg^{2+}), potassium (K^+).

Some anions such as Cl^-, I^- and some cations, like Na^+, Mg^{2+} and K^+, result mostly from marine sources. Usually sea salt aerosol is found in the coarse mode and its size ranges widely from ~0.05 to 10 μm in diameter. Sea salt aerosol can be originated through many different physical processes over the surface of the ocean. The most common process is the phenomena of *bubble bursting*. It consists in the bursting of bubbles which are entrained by the wind stress during the whitecap formation, reaching the aerosol through sea-air exchange.

Br^- and I^- can have both natural and anthropogenic emissions sources. Br^- in nature is mainly emitted from biogenic sources such as frost flowers, mainly in polar regions, [55] and phytoplankton [56]. Frost flowers are vapor-deposited ice crystal containing high bulk salinity. They have been highly studied in the last decades and have been proposed as a source of sea salt aerosol and a reactive form of bromide to the atmosphere [57].

Some types of phytoplankton such as *Chaetoceros calcitrans, Isochrysis sp., Porphyridium sp., Synechococcus sp., Phaeodactylum tricornutum, Tetraselmis sp., Prorocentrum sp., Emiliania huxleyi and Phaeocystis sp*,, lying on the surface of the water, have been studied and indicated as a possible emission source of CH_3Br in the atmosphere [58].

From anthropogenic emissions, Br^- and I^- can be originated from vehicle exhausts.

1.5.1 Nitrogen ions

Nitrogen is the most abundant element in the atmosphere; approximately 78% of the atmosphere is made up of nitrogen gas (N_2). As part of life processes, nitrogen is transformed from one chemical form to another in the atmosphere, in the land and in living organisms **Figure 3**. N_2, in its gaseous form, cannot be used by most living organisms. N_2 is converted into a usable form through a process called fixation. Fixation can be biological, where bacteria convert N_2 to ammonium ions (NH_4^+), which can be used by plants. Fixation can happen through lightning, which converts atmospheric N_2 into ammonia (NH_3^-) and nitrate (NO_3^-) that enter soil with rainfall. Nowadays, fixation can also be industrial as scientists have learned how to convert nitrogen gas to ammonia (NH_3^-). Then plants take up nitrogen compounds through their roots and animals can obtain these compounds by eating plants. During the waste excretion of animals or when a living organism dies, nitrogen compounds re-enter the soil where they are broken down by microorganisms. This decomposition produces NH_3^-, which can go through the nitrification process where nitrifying bacteria in the soil convert NH_3^- firstly into nitrite (NO_2^-) and secondly into nitrate (NO_3^-). Compounds such as NO_2^-, NO_3^-, NH_4^+ are fundamental part of the biogeochemical nitrogen cycle and through they reaction they can influence atmospheric chemistry. Furthermore, NO_2^-, NO_3^-, NH_4^+ can be adsorbed from soils by plants and then used in the formation of plant and animal proteins.

The process of denitrification completes the nitrogen cycle. Denitrifying bacteria convert NO_3^- back to gaseous N_2. These bacteria instead of oxygen use nitrate to obtain energy, releasing nitrogen gas into the atmosphere.

NO, moreover the highly reactive form NOx, could also be emitted from anthropogenic sources such as combustion processes, the most dominant sources in the troposphere [59]. NH_3 could be directly emitted from agriculture processes such as fertilizer application and production, and also from vehicle exhausts [60].

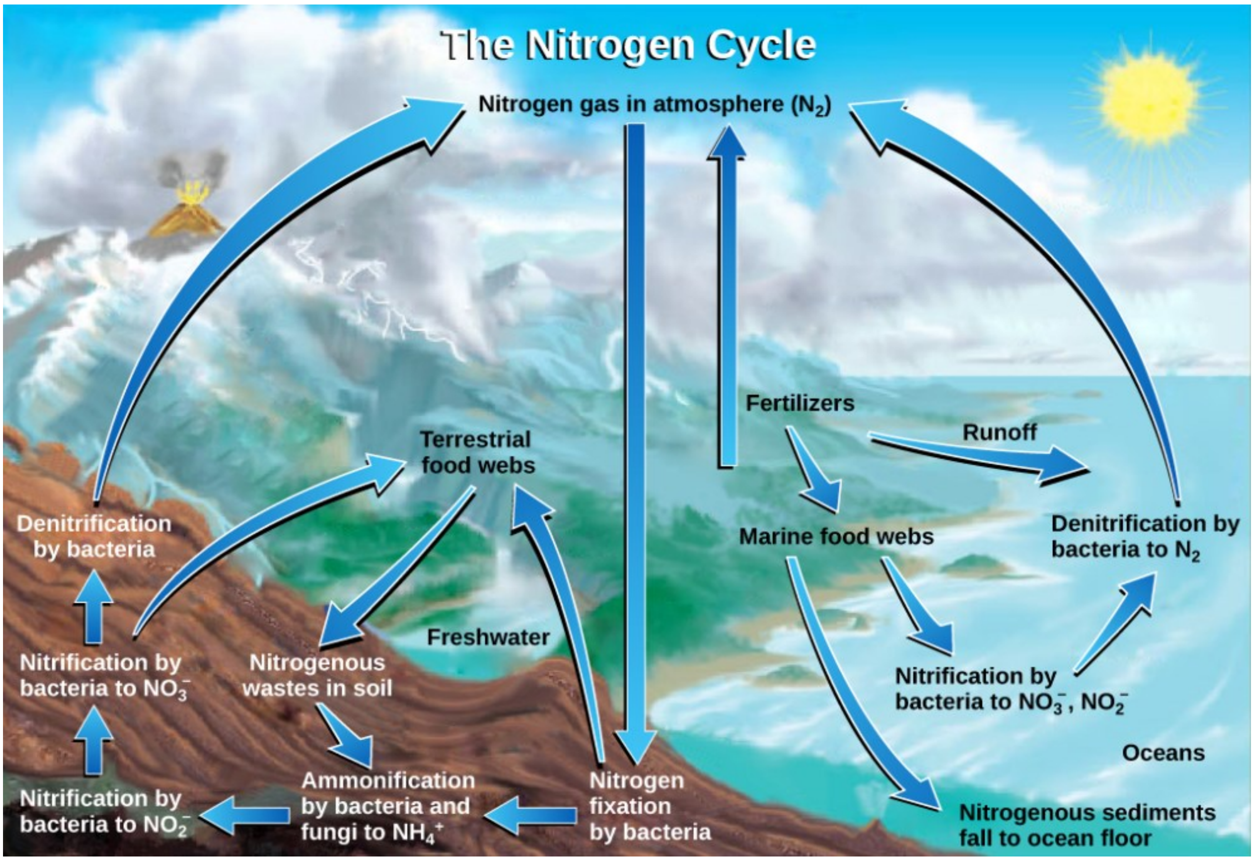

Figure 3. The nitrogen cycle. Adapted from John M. Evans and Howard Perlman, USGS

1.5.2 Sulphate ions

Sulphate (SO_4^{2-}) is one of the chemical participants in the biogeochemical sulphur cycle. The sulphur cycle contains and atmospheric and terrestrial processes. The cycle begins with the weathering of rocks, releasing stored sulphur. In fact, most of the Earth's sulphur is stored underground in rocks and minerals. When the sulphur comes into contact with air it is converted into SO_4^{2-}. Then it can be adsorbed by plants and microorganisms and is converted into organic forms. Then animals consume these organic forms through food they eat, moving the sulphur through the food chain. As organisms die and decompose, some of the sulphur is released again as a SO_4^{2-}. Some of this SO_4^{2-} enters tissues of microorganisms. Sulphur can settle back into the Earth or come down in rainfall. A continuous drainage of sulphur into lakes, streams and oceans leads to a loss of sulphur from terrestrial ecosystem. Sulphur can also enter oceans through fallout from the Earth's atmosphere. Once in the ocean, sulphur cycles can involve marine communities, moving through the food chain. A portion of this sulphur is emitted back into the atmosphere through the phenomena of sea spray. The remaining sulphur is lost to the ocean depths, combining with other compounds.

There are a wide variety of natural sources that can emit sulphur directly into the atmosphere, including volcanic eruptions, the breakdown of organic matter in swamps and tidal flats, and the evaporation of water. Then, SO_4^{2-} derives mainly from the oxidation of the directly emitted precursor sulphur dioxide, SO_2, that can be oxidized both in the gas phase and in the aqueous phase. Conversely, the oxidation of dimethyl sulphur (DMS), directly emitted from oceanic phytoplankton, can be another route which leads to the formation of SO_2 [61]. SO_2 can be directly emitted from anthropogenic sources too, such as fossil fuel combustion or industrial processes.

MSA is a further compound containing a sulphur atom. It can be produced by oxidation of dimethyl sulphoxide (DMSO) and methanesulfonic acid, in the presence of hydroxide ions (OH^-) and DMS. MSA represents an unequivocal indicator of marine biogenic activity [62].

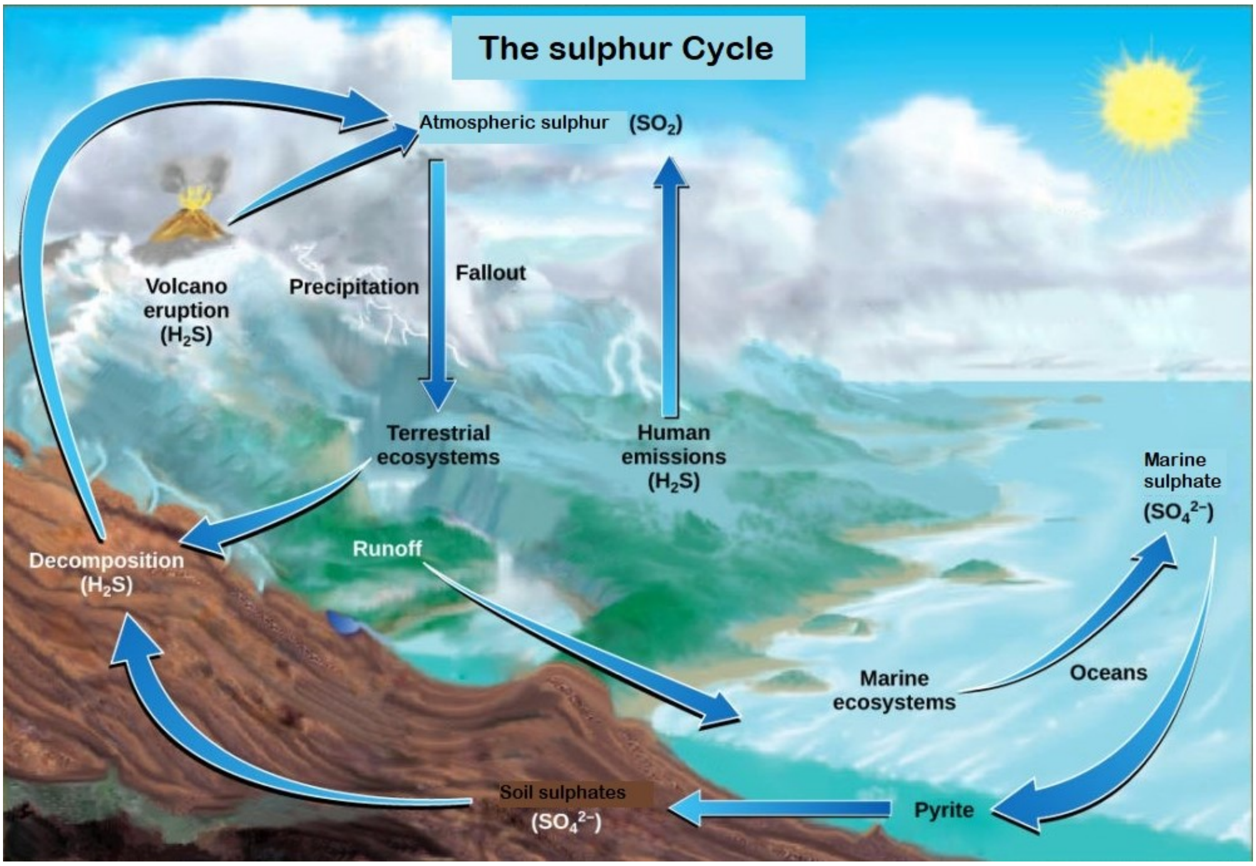

Figure 4. Sulphur cycle. Adapted from by John M. Evans and Howard Perlman, USGS

1.5.3 Phosphate ions

Phosphate (PO_4^{3-}) is one of the chemical compounds which takes part in the biogeochemical phosphorus cycle **Figure 5**. Phosphorus moves in a cycle through rocks, water, soil and sediments and organisms. Weathering and mostly rainfall cause PO_4^{3-} and other minerals to be released from rocks. Then, PO_4^{3-} is distributed in soils and water. PO_4^{3-} is taken by plants from the soil and they may, in turn, be consumed by animals. Once PO_4^{3-} enters plants or animals, it is incorporated into organic molecules such as DNA. After the plant or animal life cycle, when the plant or animal dies, PO_4^{3-} decays and returned to the soil. Within the soil, PO_4^{3-}can be available to plants through bacteria that break down organic matter to inorganic forms of phosphorus, through a process called mineralisation. Phosphorus in soil can end up in waterways and oceans and it can be incorporated into sediments over time. Since most phosphorus compounds are locked up in sediments and rocks, they are not available for plants, so many farmers replaced them using phosphate fertilizers. When fields are overfertilized there is an excess of phosphate that can cause excessive growth of plants in waterways, lakes and estuaries leading to eutrophication.

Furthermore, emission sources of PO_4^{3-} can be both natural and anthropogenic. The PO_4^{3-} can be emitted by natural sources such as the sand, especially in areas near oceans or large reserves of water. However, a large part of PO_4^{3-} can also derive from the anthropogenic sources such as the combustion of fossil fuels and biofuels [63].

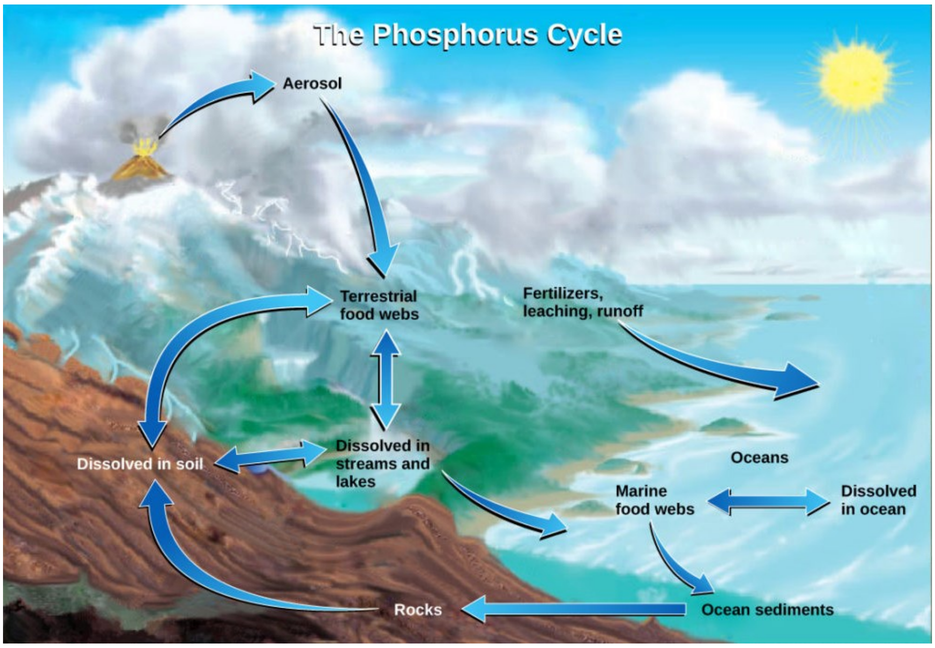

Figure 5. The phosphorus cycle. Adapted from John M. Evans and Howard Perlman, USGS

1.6 Organic aerosol compounds

1.6.1 Carbonaceous Aerosol Compounds

Carbonaceous Aerosol Compounds usually combine a significant fraction of particles in the aerosol. Carbonaceous aerosol compounds are commonly differentiated into two main fractions: black carbon (BC), also known as elemental carbon (EC) and organic carbon (OC). EC is black with a graphitic-like structure also containing high molecular weight, dark-coloured and non-volatile organic materials such as tar, biogenic and coke. EC is classified as a primary pollutant, directly emitted during the incomplete combustion of fossil and biomass fuels. During a combustion process, EC is released directly into the atmosphere and it consists of agglomerations of small spherical graphitic particles in size from 20 to 30 nm. After the nuclei formation they rapidly develop into larger compounds through reaction that occur on the particle surface. These particles form chain-like aggregates of several microns in size, similar to impure graphite [64]. Furthermore, EC is oxidized in combustion analysis above a certain temperature threshold, and only in the presence of an oxygen-containing atmosphere and it is known technically as the residue of ambient samples after the extraction of OC fraction.

OC is a complex mixture of hundreds of hydro-carbons and oxygenates compounds which represent 48–60% of the total amount of organic matter. OC is formed both by anthropogenic and natural sources and can have both primary and secondary origin [65]. Anthropogenic and natural emissions lead to particulate OC, starting with the release of some precursors (volatile organic carbon-VOC) and their subsequent distribution to particulate organic compounds. Particulate OC can be also formed in the atmosphere, as secondary organic aerosol, SOA, through the condensation of low-volatility oxidation products [66].

The EC and OC relative concentration in the PM can indicate the different particle emission source. In addition, the proportion between these two carbonaceous species is indicative of emission sources and is often used as an indicator **Table 1**.

Table 1. EC, OC and OC/EC ratio as indicator of different emission sources

Emission source		EC		OC		OC/EC ratio
Ambient PM$_{2.5}$		2.1		10.8		5.1
Light-duty gasoline vehicles^a		22.6		50.1		2.2
Light-duty gasoline vehicles^b		13.5		30.1		2.2
Heavy-duty diesel vehicles^a		40.5		32.6		0.8
Tunnel^c		25.5		19.3		0.8
Paved road dust^b		1.1		14.7		13.4
Residential wood combustion^b		12.4		51.4		4.1
Meat charbroiling^a		0		33.8		N.A.
Natural gas home aplliances^a		6.7		84.9		12.7
Forest fire^a		3.2		46.9		14.7
Legend:						
1. N.A. = Not Applicable						
^{a} = mass % of fine particle mass						
^{b} = mass % of fine particle mass						
^{c} = mg per vehicle- kilometer						

What is more, EC and OC are studied as important components of atmospheric aerosol because of their light absorbing characteristics and their possible health effects. The effect of the light absorption is a warming on global scale [67] and these light absorbing particles can affect indirectly the tropics, enhancing cloud evaporation [68].

Furthermore, the ratio between organic matter (OM) and OC has been used to do an estimation of the degree of chemical processing in the atmosphere. The OM/OC ratio is strongly dependent on the method of quantification, but several studies proposed 1.6 for OM/OC in urban sites and 2.1 for OM/OC in the rural sites.

1.6.2 Sugars

The organic fraction of the atmospheric aerosol is commonly divided between the water-soluble compounds (WSOC) and non-water-soluble compounds. WSOC are profoundly studied because of their possible relationship with hydroscopity of atmospheric aerosol, having and important role in climate change [69].

Sugars compounds, which include monosaccharides and disaccharides, anhydrosugars and alcohol-sugars, are one of the most relevant WSOC classes in the aerosol **Figure 6**. In the atmospheric aerosol the dominant sugar compounds are primary saccharides, mainly α and β- glucose, sucrose and trehalose, with traces of fructose and xylose. These compounds are emitted by a wide range of different sources, including microorganisms, plants and animals [70]. In the vascular plants, glucose is the most common monosaccharides and it is the source of carbon for bacteria and fungi [71]. In trees CO_2 is present in the leaves reaching the roots in the form of sucrose (glucose + fructose) [72]. Mycose is widely diffused in a large variety of fungi, bacteria and yeast, a few plant and invertebrates as a reserve of carbohydrate and a stress protectant [73].

Among the anhydrosugars, the levoglucosan and in a minor part its isomers galactosan and mannosan, are specific tracers of the biomass burning of cellulose and hemicellulose in the atmosphere. These compounds are very stable for a long time in the atmosphere so they can also be used to investigate the pathway of the aerosol [74].

The sugar-alcohols are usually present in lower concentrations than the other sugar compounds. Among them, arabitol and mannitol are used as tracers airborne fungal spores [5]. Sugars have been used as environment tracers in remote areas like Antarctica [75], in urban areas [76], forests and mountains [77] to investigate organic carbon sources and the aerosol pathway.

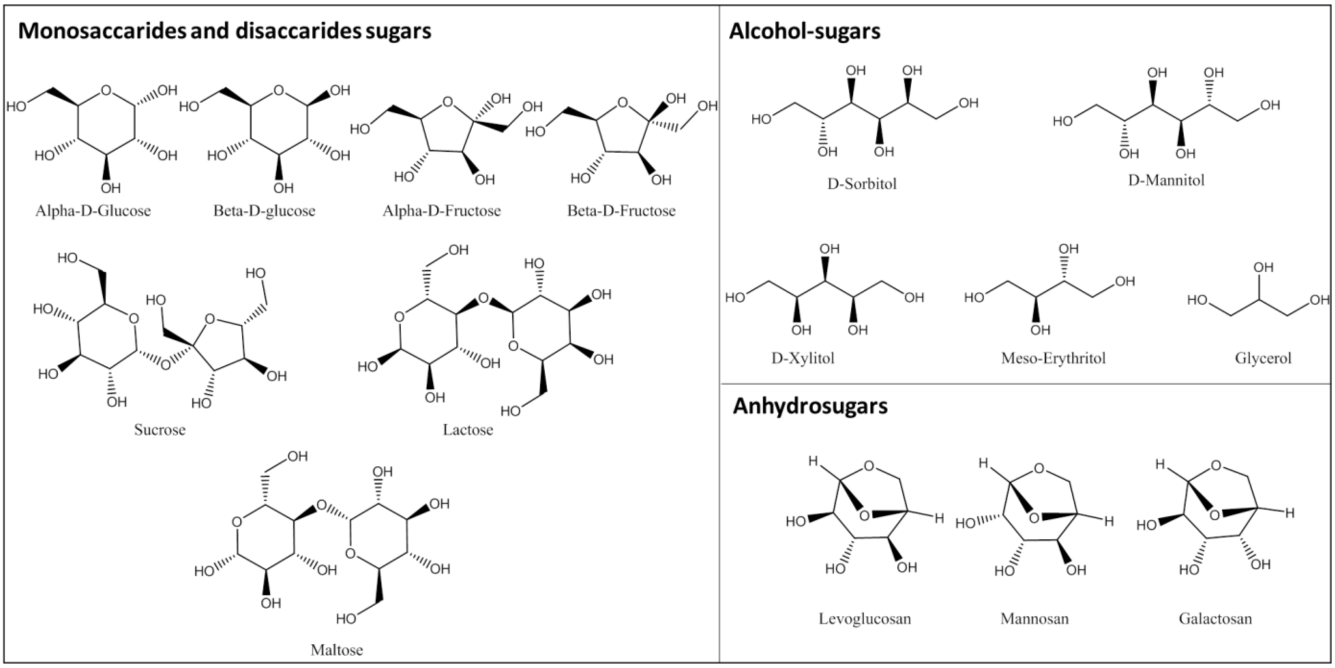

Figure 6. Structure of some main sugars

1.6.3 Amino acids

Amino acids are organic molecules formed by a central carbon atom, called α carbon, to which a hydrogen atom, is bound an amino group (except for one amino acids, called proline, which has an imino group), a carboxylic group and a lateral chain R. The lateral chain R is different for each amino acid and performs different functions. In nature, amino acids are mainly found as constituents of proteins, joined by a peptide bond. The peptide bond is formed thorough the reaction between the carboxylic group of one amino acid and the amino group of the subsequent amino acid, with the release of a water molecule [78]. Depending on the nature of the R side chain it is possible to divide the amino acids into three groups: apolar, neutral polar, acids and basic. Amino acids exist both in the D- and L- spatial configuration. D- and L- amino acids are enantiomers, specular and non-overlapping molecules. They have the same chemical-physical properties, except for the ability to rotate the plane of polarized light; in this case D- and L- amino acids have the same absolute value, but opposite signs for each of the two enantiomers. The L-amino acids are the basic units, with functional and metabolic versatility, for the construction of proteins, through peptide bonds [79]. Whereas, D-amino acids, derive from the peptidoglycan, the main structural component of the bacterial cell wall. The relationship between the two enantiomers can be an important marker for the characterization of organic nitrogen from biogenic sources. Amino acids are recognized as all-over and fundamental components of the atmospheric PM. Normally, glycine is the most concentrated amino acid, followed by alanine, proline, cystine, and threonine [80]. The sources from which amino acids could be emitted are several and this make more complex the identification of their origin. The primary sources of both free and combined amino acids are terrestrial dust, phytoplankton production, bacteria and biological degradation [81]. Some amino acids, like glycine, phenylalanine, threonine, serine, proline and aminobutyric have been detected also in volcanic emissions [82]. Alanine, aspartic acid, glutamine and glycine have also been detected in tobacco smoke [83]. Moreover, alanine can be related with emissions from incinerator, sewage treatment plant and waste collection centres [84] and taurine can originate from livestock manure [85], **Figure 7.**

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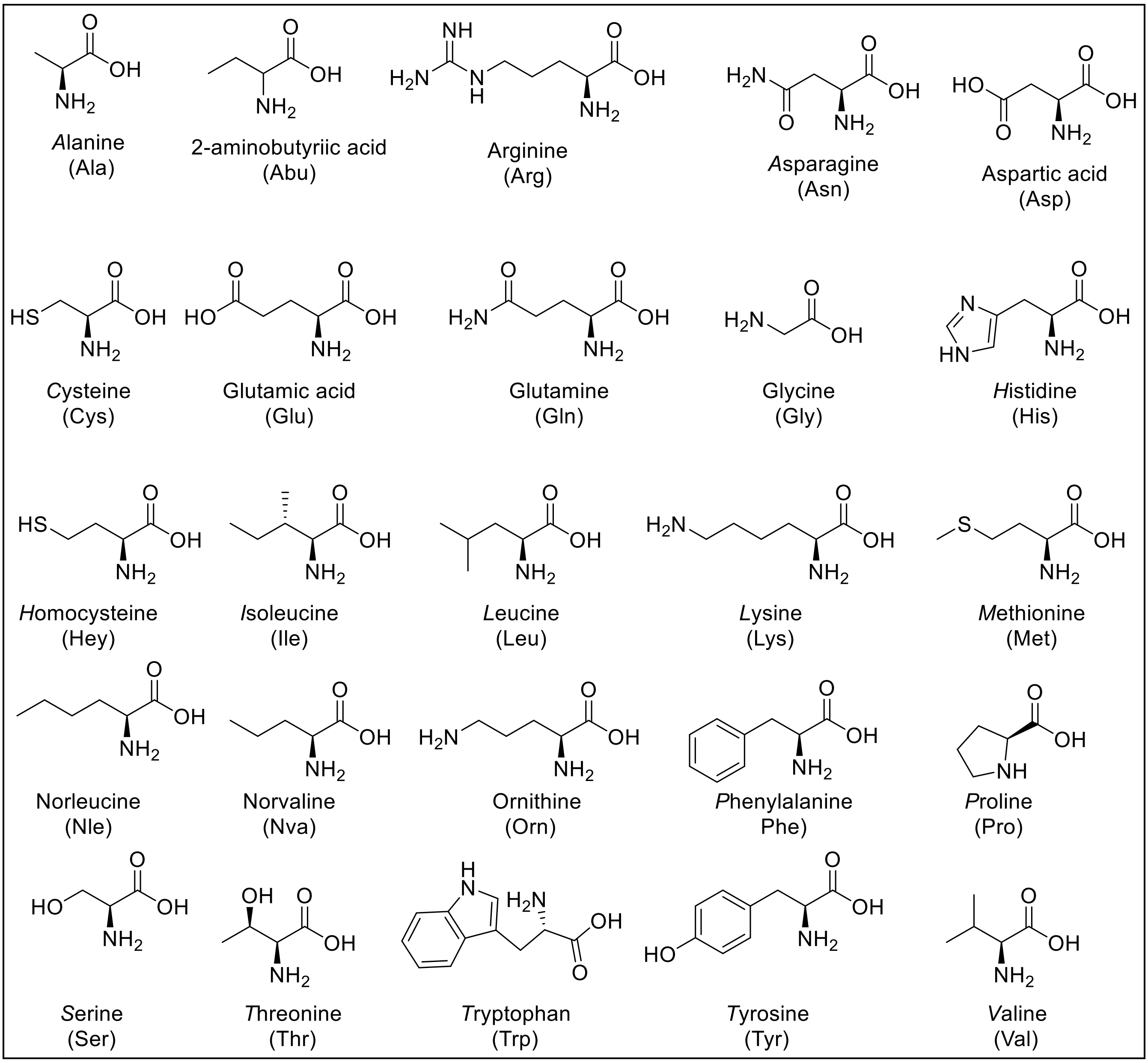


Figure 7. Structure of some main amino acids

1.6.4 Phenolic compounds

Phenolic compounds (PCs) are compounds containing hydroxylated aromatic rings. The hydroxyl group is attached directly to the phenyl, the substituted phenyl or other aryl group **Figure** 8. PCs normally are used as tracers for the lignin combustion or degradation. Lignin is an essential biopolymer of woody tissue, derived from three principal aromatic alcohols: sinapyl, coniferyl and p-coumaryl alcohols. From the combustion or the degradation of these three alcohols derived coumaryl, vanillyl and syringyl moieties, and their relative abundances are proportional to the major plant classes [7]. From sinapyl alcohols, derive homovanillyl alcohol, vanillic acid, vanillin and syringic acid. Coniferyl alcohols produce as dominant phenolic compounds vanillin, homovanillic acid, vanillic acid and homovanillyl alcohol. The most relevant phenolic products produced by the combustion of p-coumaryl alcohols are acetosyringone, syringic acid, vanillin and vanillic acid. Moreover p-coumaryl alcohols are dominant lignin units in grasses [86]. Hardwood lignin, characterized by *angiosperms*, is enriched in sinapyl alcohol and its combustion produces mainly syringyl and vanillyl moieties. Instead, in softwood, characterized by *gymnosperms*, coniferyl alcohol is the most abundant compound and so it developed principally vanillyl moieties [87]. Literature reports studies on MPs in aerosols, in marine and river matrices and sediments. The negative correlation between PCs and levoglucosan, specific marker of the biomass burning, suggest that PCs can originate from an additional marine source[8].

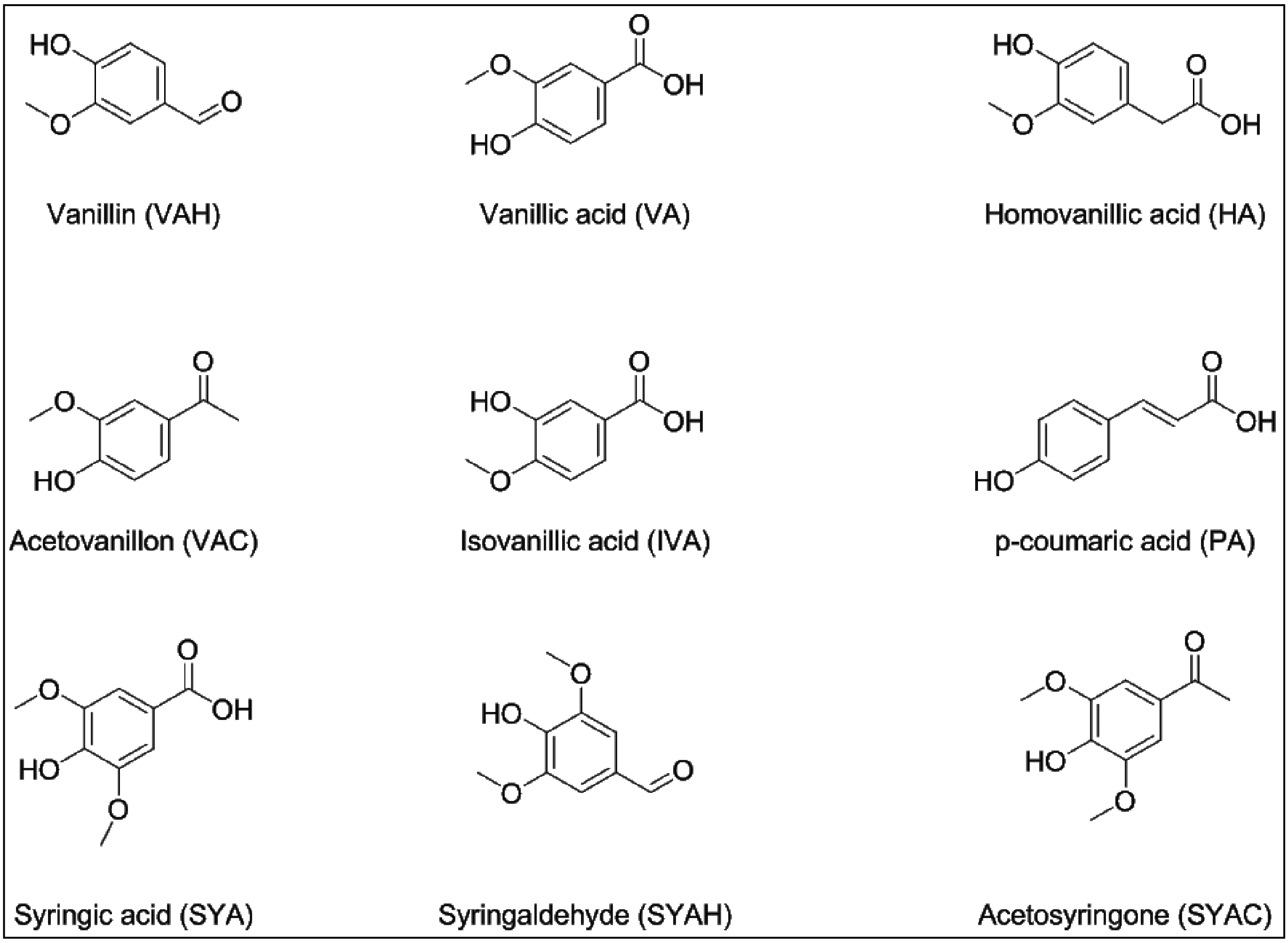


Figure 8. Chemical structure of some phenolic compounds

1.6.5 Carboxylic Acids

Carboxylic acids (CA) are a class of compounds in which a carbon atom is bonded to an oxygen atom through a double bond and to a hydroxyl group through a single bond. A fourth bond links the carbon atom to a hydrocarbon group **Figure 9**. Carboxylic acids are ubiquitous important components of the troposphere, so present in the aerosol. Carboxylic acids are present in a large range of environments, for example continental, marine, urban, and remote atmospheres. They are low molecular weights and polar compounds, so they are water-soluble and mainly concentrated in precipitation such as fog and cloud water [88]. Furthermore, carboxylic acids are involved in important atmospheric transformations Carboxylic acids may have different emissions sources, comprising primary biogenic, anthropogenic emissions and chemical transformation of precursors already present in the aerosol. Normally the shortest carboxylic chains (from C_2 to C_{10}) are the most concentrated in the urban atmospheric aerosol, produced mainly by photochemical reactions of anthropogenic organic compounds already emitted in urban and polluted areas. Furthermore, the long range transport of pollutants in remote areas could allow for the atmospheric reactions which end the formation of carboxylic acids also in this remote environment [89].

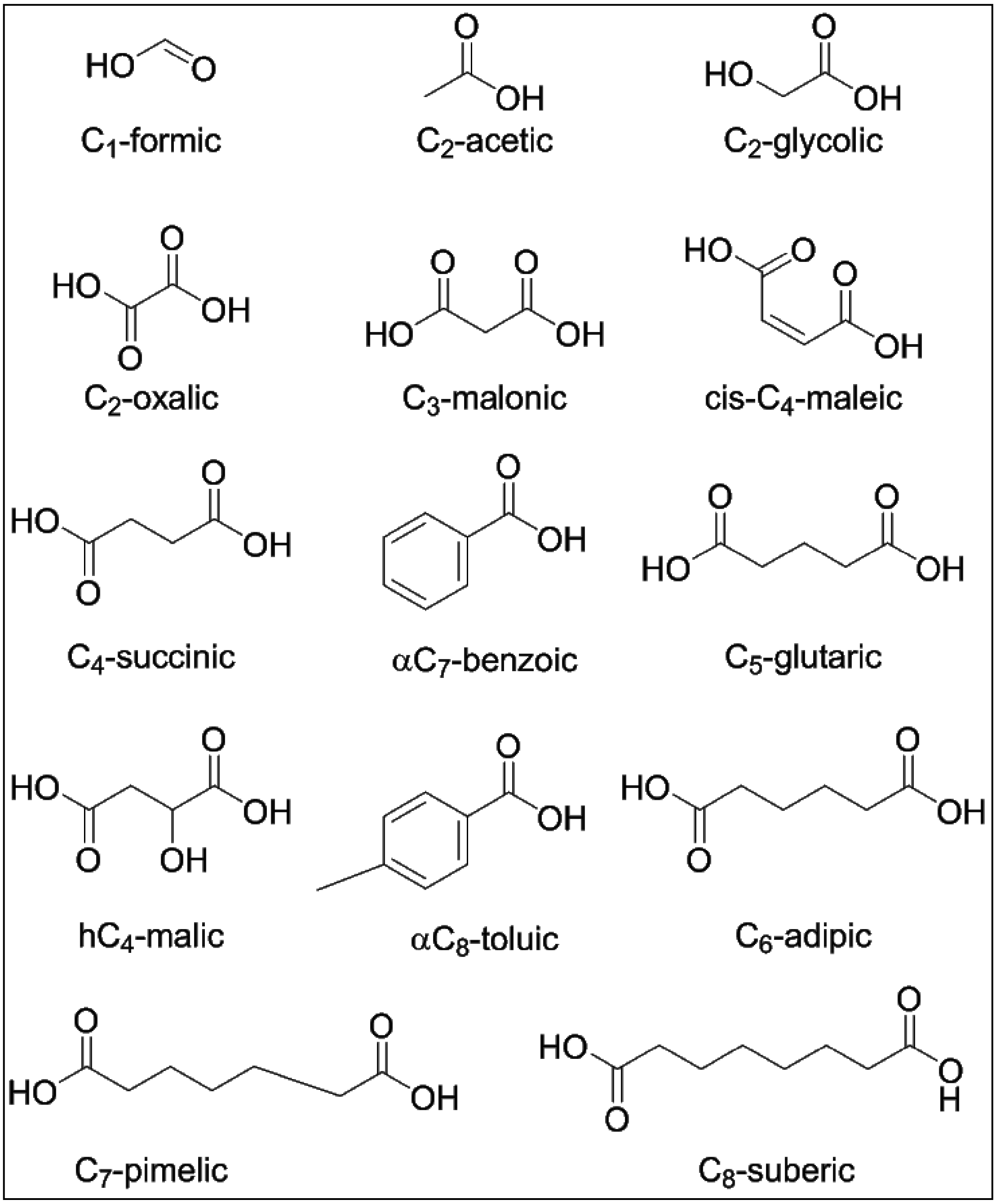


Figure 9. Chemical structure of some carboxylic acids

1.6.6 Polycyclic Aromatic Hydrocarbons and Oxidized Polycyclic Aromatic Hydrocarbon

Polycyclic Aromatic Hydrocarbons (PAHs) are two height ring organic compounds and they are usually formed during incomplete combustion processes, **Figure 10**. PAHs are among the most carcinogenic of the known compounds [9]. They have toxic, mutagenic and carcinogenic effects, through a rapid distribution in a wide range of human tissues, tending to accumulate in body fat [90]. PAHs compounds can be found both in the particulate and in the gaseous phases of the aerosol. PAHs more often occur in complex mixtures rather than single compounds and they have a very high stability in the atmosphere. The major PAHs sources are motor vehicles, home heating, fossil fuel incomplete combustion both for energetic purpose and industrial processes, biomass burning and incinerators [91]. PAHs can originate also from natural emissions such as terrestrial emissions, like volcanic activities, open burning, natural losses of petroleum and coal deposits. PAHs emissions from natural sources are very low, while the emissions from anthropogenic sources predominate and for this reason PAHs are used as tracers of anthropogenic emissions, **Table 2**. PAHs are normally more concentrated in urban environments than in rural and natural environments [7].

Table 2. **PAHs natural and anthropogenic sources**

	PAH sources	
Natural sources		**Anthropogenic sources**
Fires	Incomplete Combustion	Road Dust
Volcanic Eruptions	🔥	Vehicles
		Incineration
		Wood Burning
		Cigarette Smoke
		Cooking Plants
		Industries Processes
		Miscellaneous burning
Natural Petroleum		Petroleum Spills
Vegetative Decay		Pesticide Formulations
Rare Minerals		Sewage Sludge
Plant Synthesis		PAH- contaminated Media

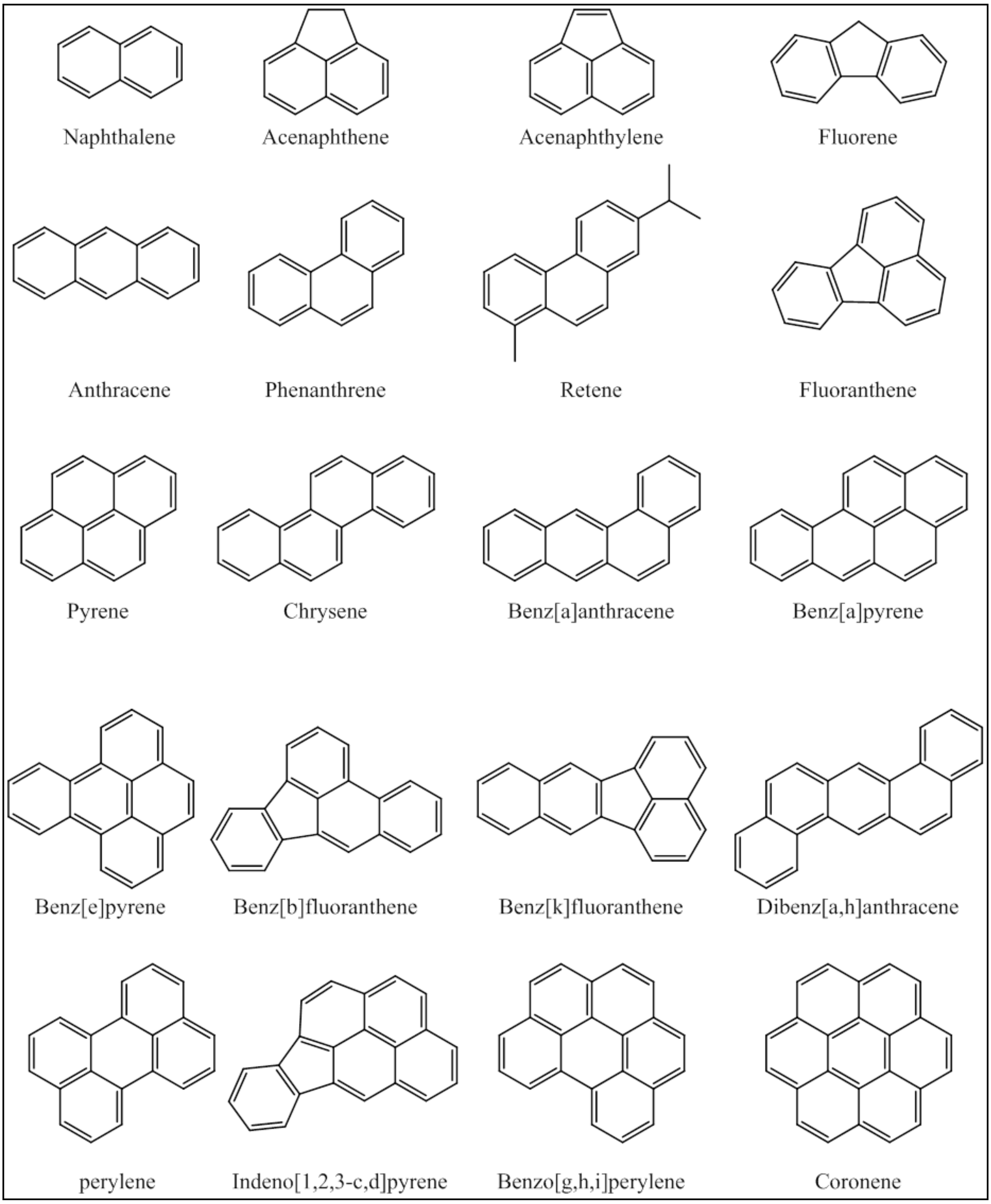
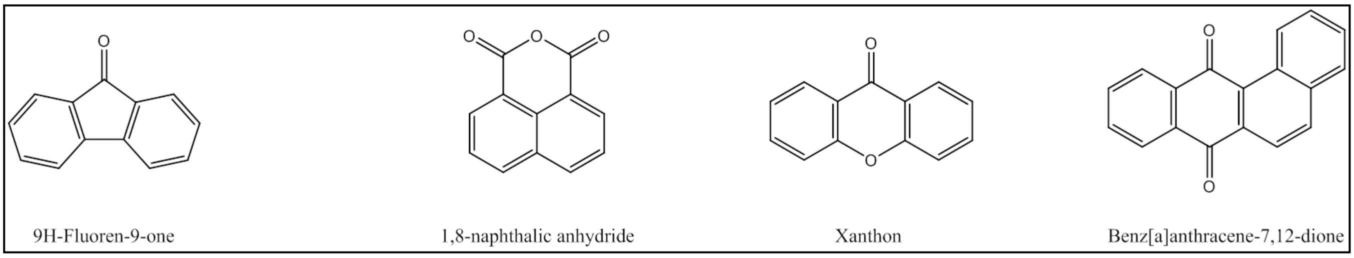


Figure 10. Chemical structure of some PAHs. Adapted from [92]

Oxidized Polycyclic Aromatic Hydrocarbons (O-PAH) are mainly known as the oxygenated derivatives of PAH. O-PAHs are a class of emerging contaminants present in the environment PM and some of them have a certain toxicity. O-PAHs are molecules consisting of one or more oxygen atoms attached to an aromatic ring structure that may also contain other chemical groups [93] **Figure 11**. O-PAHs can derive from incomplete gasoline, diesel, coal or wood combustion. Among these various emission sources, the combustion of a solid fuel such as coal is the one which emits the largest amount of carbonaceous aerosol containing PAH and O-PAH. Furthermore, both PAH and O-PAH are well related to the biomass burning. O-PAH can also derive from the photo oxidation of the PAH precursors deriving from combustion processes [94].



9H-Fluoren-9-one 1,8-naphthalic anhydride Xanthon Benz[a]anthracene-7,12-dione

Figure 11. Chemical structure of some O-PAH

1.6.7 N- Alkanes

In general, n- Alkanes are compounds containing only carbon or carbon to hydrogen bonds. An example of a general chemical formula for alkanes are C_nH_{2n+2}. N- alkanes can have various chemical structures with different nomenclature and numbering. N-alkanes can be *simple alkanes*, with a linear structure with different lengths. The first ten n-alkanes are called: methane, ethane, propane, butane, pentane, hexane, heptane, octane, nonane and decane **Figure 12**. N-alkanes can be branched alkanes with alkyl substituents on the main chain. N-alkanes can be also cyclo alkanes, with a closed circular structure. Furthermore, all alkanes containing four or more carbon atoms show structural isomerism. Isomers are molecules with the same molecular formula, but a different arrangement of atoms in the space. Iso- and anteiso-alkanes are more concentrated in cigarette smoke particles. The concentration pattern is typical of the tobacco leaf, enriched to a factor of 40 of iso and anteiso- alkanes [95].

n- Alkanes have different emission sources, both anthropogenic and natural, and their homologous distribution can be explained through various sources. Among the anthropogenic sources are fossil fuel combustion or agricultural debris are the most relevant. Instead the natural sources includes suspension of pollens, microorganisms and insects and also from vascular plants [96].

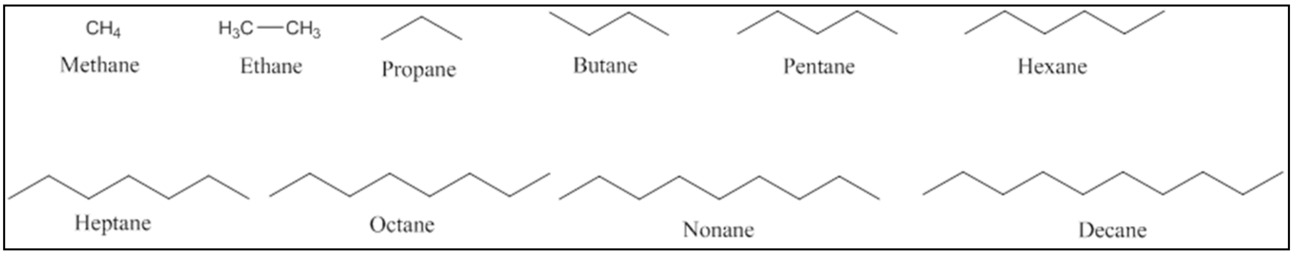


Figure 12. The first ten n-alkanes chemical structures

1.6.8 Resin Acids

Resin acids are a class of compounds found in the tree resins **Figure 13**. They are a mixture of a wide range of carboxylic acids, including levopimaric, pimaric, isopimaric and sandaracopimaric acids, unaltered degradation products, and neoabietic, palustric, dehydroabietic and 7-oxodehydroabietic acids, thermal degradation compounds [97].
All the resin acids present the same basic skeleton structure. They are composed by three fused rings, with the empirical formula $C_{19}H_{29}COOH$. Resin acids, biosynthesized mainly by gymnosperms, are tracers also of biomass burning. DHA, one of the resin acids, has been proposed as a specific tracer of wood combustion, able to distinguish between the combustion of coniferous wood and hardwood. However DHA is a compound also present in anthropogenic emissions being a constituent part of vehicle tyres [98].

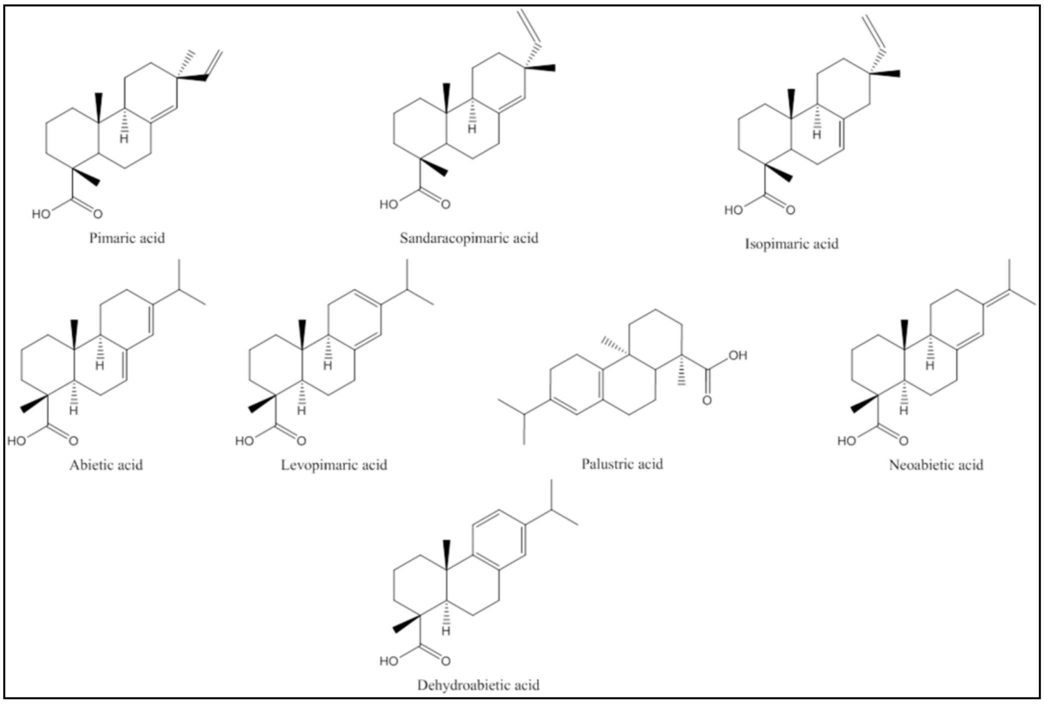


Figure 13. The eight most relevant resin acids and their chemical structures [99]

2 STUDY AREAS

Study areas examined in this thesis are both remote environments, like Antarctica, and urban areas, such as Sernaglia della Battaglia, Treviso. The purpose behind this choice was double. On one hand to demonstrate the wide applicability of several environmental markers even in so different environments. A very clean and preserved environment like Antarctica, that could be compared to an open-air laboratory, and on the other side one urban area, Sernaglia della Battaglia. The second aim was to evaluate the different proportions between natural and anthropogenic sources, through the study of aerosol composition of two different areas, drawing a detailed profile of the study areas and the main emission sources. On one hand Antartica, characterized mostly by natural emissions and on the other hand little urban area, which can have a mix in the aerosol, both natural, but also, in addition, pollutants coming from anthropogenic sources.

Here the detailed geographical, climatic and environmental description of the study areas examined in this thesis through different cases of study, which give a detailed description of the aerosol characteristic of those areas.

2.1 Remote areas

2.1.1 Antarctica

Antarctica is the southernmost continent in the world with an area of more than 14 million km². This continent is situated almost centrally in relation to the south pole and it is completely confined beyond the 60th parallel of the southern latitude. It is a unique continent with no countries, although seven nations, New Zealand, Australia, France, Norway, the United Kingdom, Chile, and Argentina, claim different parts of it. Antarctica has a semicircular shape with an appendix, the Antarctic Peninsula, facing the South America and the Transantarctic Mountains divided the continent into East Antarctica and West Antarctica. Antarctica includes several islands and archipelagos. One group of islands are located near to the Antarctica coast, mainly to the Antarctic Peninsula, and a second group of islands are more distant from the coast, but always inside the Antarctic convergence. The south part of the Pacific, Atlantic, and Indian Oceans surround the Antarctica continent, **Figure 14** [100].

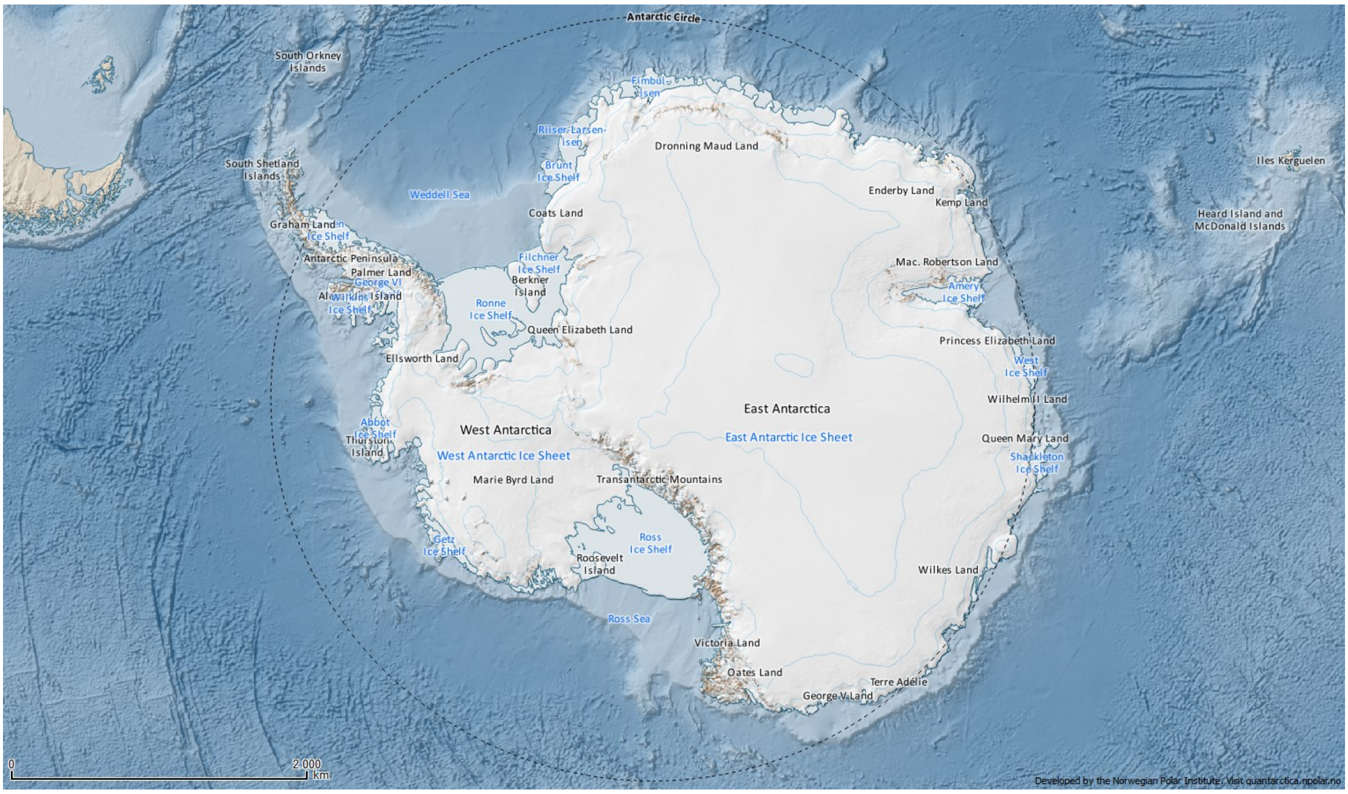


Figure 14. Antarctica (Quantarctica3, packages: SCAR. Antarctic Digital Database. British Antarctic Survey, Cambridge, 2017, http://quantarctica.npolar.no/)

Antarctica is the coldest continent on the Earth; it is a frozen desert with little precipitation. The continent is snow- and ice-covered, with freezing temperatures all year round. Seasons in Antarctica are mainly two: *polar summer*, starting from the end of May and lasting until September, characterized by periods of continual daylight followed by *polar winter*, starting from the end of November to March, characterized by periods of continual darkness. The polar summer presents a daytime with temperatures between -20 °C and -5 °C. The polar winter is characterized by extreme cold temperatures, violent storms and ice-bound seas [101]. Today the dichotomy offered by the Antarctica continent is on the upside a terrestrial ice desert with shadowy forms of plant life and animals, on the downside the adjacent seas are characterized by a thriving underwater life. Antarctic vegetation is limited to a few hundred species, mostly endemic, of mosses, algae, lichens and fungi. Antarctic mushrooms and lichens host a relatively rich fauna of protozoa and small invertebrates. The large fauna on the Antarctic continent is represented by sea birds and sea mammals. The most widespread birds on the continent are penguins, which form large colonies, and the most popolous mammals, mostly on the Antarctic coast, are seals. The Antarctic underwater world is very rich and varied, full of sponges, mollusc, coelenterates, echinoderms. Equally abundant is the fauna composed of large mammals such as cetaceans [102]. Thanks to its isolated position, Antarctica is a natural laboratory for studying atmospheric aerosol [8]. Since the end of the fifties, this isolated territory has become a unique and privileged place for scientific observation and experimentation, from which to obtain valuable information on the origin and the profound history of Earth, and in which to look for answers to some questions about the climatic and environmental future. The Antarctic research programs operate in Antarctica through a series of structures called *bases* or *stations*, specially built to support scientific activity. Bases can be seasonal or annual, temporary or permanent and accommodate several scientific or logistic staff. One of the two Italian research bases in Antarctica is *Mario Zucchelli (MZS)* station. It is located at Terra Nova Bay on the Ross Sea (74 ° 41' 42 " S - 164 ° 07' 23" E, 25 m a.s.l.). The station, active since 1986, is built on a rocky surface, around 25 m altitude, 100 m away from the coastal strip. The base allows for operations on the Victoria Land, but also in the Antarctic plateau. MZS is a permanent structure operating during the austral spring/ summer and it is the reference point for all the Italian research activities. During periods of activity, the base can host up to 90 people per day. The entire infrastructure occupies an area of over 7000 m^2 and is used for scientific studies and research concerning a wide range of scientific topics. The second French-Italian research base in Antarctica is *Concordia* (Dome C). The research base is located on the Antarctic plateau (75° 06’ 02’’ S – 123° 23’ 25’’ E, 3233 m a.s.l.) one of the coldest and most inhospitable places on Earth. Temperatures rarely rise above -25 °C in summer and can reach -80 °C in winter. The humidity is low, and the air is extremely dry with very little rainfall during the year. The construction of the station is the result of a joint agreement, in 1993, between ENEA (Agency for New Technologies, Energy and the Environment), and the French Polar Institute Paul Émile Victor (IPEV). In the beginning of 2005, Dome C became a permanent scientific station. The Concordia Station has a maximum nominal capacity of 65 people; it is able to accommodate 32 people in the summer and a maximum of 16 in the winter and occupies an area of about 1500m^2 [100].

2.2 Urban sites

2.2.1 Sernaglia della Battaglia (TV)

Sernaglia della Battaglia (45° 52' 46" 20 N - 12° 8' 20" 76 E, 117 a.s.l.) is a town located in the province of Treviso, between the left side of the Piave and the Belluno Prealps, in the middle of a large cultivated plain, District of Piave. The area around Sernaglia della Battaglia is almost flat with some altitudes ranging from 89 to 129 m a.s.l. The main watercourse in Sernaglia della Battaglia is the Piave which marks the southern border of the town. The riverbed flows a few metres lower than the surrounding land, forming a sort of wooded escarpment of considerable naturalistic interest. Another important river is the Soligo, which limits the town to the east. In the north-eastern area there are some wetlands, typical of the upper part of Treviso **Figure 15**.

Figure 15. Sernaglia della Battaglia (Open StreetMap)

The climate in Sernaglia della Battaglia is warm and temperate with significant rainfall; in the driest month there is a lot of rainfall and the average annual rainfall is 1026 mm[1].

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[1] https://it.climate-data.org/location/113453/

DISCUSSION

In the following part of the thesis, completely dedicated to the discussion of results, three studies were discussed. These cases of studies have focused on the application of different environmental markers for the careful analysis and characterization of aerosol from two very different areas. The main feature of this PhD thesis was the choice of a wide range of environmental markers able to characterize aerosols coming from such different areas. This wide range of different environmental markers studied permitted the description of both natural and anthropogenic sources in environmental contests that are deeply different, such as one remote site and one urban site. The first two chapters of the discussion part of this thesis concerned the investigation of organic and inorganic compounds in aerosol samples from one remote site, Antarctica. This area thanks to its geographical position, is a perfect open-air laboratory, optimal for studying those exclusively natural sources of emission. In the third chapter of the discussion, the investigation area changed. This chapter is entirely focused on application of environmental markers in a rural site, Sernaglia della battaglia, Treviso. The strong link between these three chapters is the demonstration of the versatile applicability of a wide range of environmental markers in aerosol samples of different atmospheric regions. Each case study has been treated as a stand-alone study, with its own environmental discussion, in the more complex perspective of a summary discussion that unites all studies as a validation of the possible use of environmental markers as a research tool in multiple areas of investigation.

3 STUDY OF THE PARTICLE SIZE DISTRIBUTION OF INORGANIC AND ORGANIC IONS IN ANTARCTIC AEROSOL

This chapter is entirely based on the "Particle size distribution of inorganic and organic ions in coastal and inland Antarctic aerosol" paper, published as co-author with Elena Barbaro, Torben Kirchgeorg, Roberta Zangrando, Giuseppa Toscano, Carlo Barbante and Andrea Gambaro. I took an active part in this work, analysing all samples, evaluating data, quantifying ionic species and making my contribution to the draft of the paper. The aims of this study were the quantification and the particle size distribution of ionic species in Antarctic aerosol samples to evaluate possible sources of emission, chemical evolution and transport. Antarctic aerosol samples came from two different sampling sites: one coastal site, near Victoria Land, close to the Italian Scientific Research base Mario Zucchelli and an inland site, on the Antarctic plateau, close to the Italian-French Scientific Research base Concordia. Anionic compounds were analyzed using ion-chromatography coupled to mass-spectrometry (IC-MS). Cationic compounds were analyzed through capillary ion-chromatography coupled to a conductibility detector.

The chemical characterization of the Antarctic coastal aerosol samples highlighted they were mainly characterized by sea salt species such as Na+, Mg^{2+}, SO_4^{2-}. The study of the particle-size distribution highlighted that these species were mainly distributed in the coarse fraction, confirming the presence of primary aerosol near the ocean source.

Antarctic inland aerosol samples were characterized by species as nss-SO_4^{2-}, NO_3^- and methanesulfonic acid (MSA). These species were mainly distributed in the fine fraction, highlighting a behaviour of a typical secondary aerosol, where several chemical and physical processes occurred[2].

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[2] This chapter is entirely based on the postprint version of Elena Barbaro, Sara Padoan, Torben Kirchgeorg, Roberta Zangrando, Giuseppa Toscano, Carlo Barbante, Andrea Gambaro. *Particle size distribution of inorganic and organic ions in coastal and inland Antarctic aerosol*. Environmental Science and Pollution Research, 2017, 24: 2724, DOI: https://doi.org/10.1007/s11356-016-8042-x.

3.1 Samples collection and processing

In this case of study, fourteen aerosol samples have been analysed. These aerosol samples were collected during three different Antarctic sampling campaigns, which took place consecutively from 2010 to 2013. Furthermore, samples came from two different sampling sites in Antarctica: one coastal site, Campo Faraglione (74° 42′ S –164° 06′ E) near to the MZS research base, and one inland sampling site, on the Antarctic plateau (75° 06′ S –123° 20′ E), near to the DC research station. From 29 November 2010 to 23 January 2011, during the XXVI Antarctic sampling campaign, five samples were collected at Campo Faraglione, about 3 km south of MZS research base. These samples were re-named *MZS26*. From 19 December 2011 to 28 January 2012, during the XXVII Antarctic sampling campaign, four samples were collected over the Antarctic plateau, near to the DC research base. These samples were re-named *DC27*. From 7 December 2012 to 26 January 2013, during the XXVIII Antarctic sampling campaign, four samples were collected over the Antarctic plateau, near to the DC research base. These samples were re-named *DC28*. **Table 3** presents a more detailed list of samples and the respective sampling dates and places.

Table 3. List of aerosol samples collected during XXVI sampling campaign nearby Mario Zucchelli station and during XVII and XVIII sampling campaign nearby Dome C station, Antarctica

	Sample	Date of sampling
Mario Zucchelli Station	**XXVI sampling campaign**	
	MZS 26 sample 1	29.11- 9.12
	MZS 26 sample 2	9.12- 19.12
	MZS 26 sample 3	19.12- 29.12
	MZS 26 sample 4	29.12- 8.01
	MZS 26 sample 5	8.01-18.01
Concordia Station	**XXVII sampling campaign**	
	DC 27 sample 1	19.12- 29.12
	DC 27 sample 2	29.12- 7.01
	DC 27 sample 3	7.01- 20.01
	DC 27 sample 4	20.01- 28.01
Concordia Station	**XXVIII sampling campaign**	
	DC 28 sample 1	7.12- 17.12
	DC 28 sample 2	17.12- 27.12
	DC 28 sample 3	27.12- 6.01
	DC 28 sample 4	6.01. 16.01
	DC 28 sample 5	16.01- 26.01

For the sampling a multi-stage Andersen impactor, *TE-6000 series, Tisch Environmental Inc.*, was used. Aerosol was collected on six pre-combusted quartz fiber filters. The first five stages were slotted quartz fiber filters, while the last one was a backup filter. The filters were with the respective width of diameter: on slotted filters 10.0–7.2 µm, 7.2–3.0

µm, 3.0–1.5 µm, 1.5–0.95 µm, and 0.95–0.49 µm and <0.49 µm on backup filter **Table 4**. The sampling period was of 10 days per sample and the total air volume sampled was of 15.000 m^3 for each sample. Blank samples were taken, using the Andersen impactor with the pumps switched off. After the sampling, samples and blank samples were stored a -20 °C until analysis.

Table 4. Dimensional fractions collected by the 6 stages of quartz fiber filters

Filter	Stage	Dimensional fraction
Slotted	1	10.0- 7.2 µm
Slotted	2	7.2- 3.0 µm
Slotted	3	3.0- 1.5 µm
Slotted	4	1.5- 0.95 µm
Slotted	5	0.95- 0.49 µm
Backup	6	< 0.49 µm

The samples preparation was performed under a class 100 laminar flow bench, using materials previously cleaned with ultra-pure water by sonication for a period of 30 minutes at room temperature. Each filter was broken into little pieces, using steel tweezers, and it was placed in a polyethylene tube. 7 mL of ultra-pure water were added to the polyethylene tubes containing the slotted filters, while 15 mL of ultra-pure water were added to the ones containing the backup filters. In order to remove all the contaminations, the extracts were filtrated using a 0.45 µm PTFE syringe filter, *ThermoFisher*.

3.2 Instrumental analysis

Anionic analyses were carried out using Ionic Chromatography coupled with Mass Spectrometry (IC-MS). The Ionic Chromatograph was a *ThermoScientific™ Dionex™ ICS-5000, Waltham, US*, equipped with an anionic exchange column, *Dionex Ion Pac AS 11 2×250 mm*, with a guard column, *Dionex Ion Pac AG11 2×50 mm*. As mobile phase NaOH was used and it was directly produced by an eluent generator, inside the instrument, with a specific gradient with a 0.25 mL min flow rate. The gradient was 0 min, 0.5 mM; 0– 3.5 min gradient from 0.5 to 5 mM; 3.5– 5 min gradient from 5 to 10 mM; 5– 25 min gradient from 10 to 38 mM; 25– 30 min, column cleaning with 38 mM; 30– 35 min; equilibration at 0.5 mM. The injection volume was 100 µL. A suppressor, *ASRS 500, 2 mm, Thermo Scientific* was between IC and MS to suppress NAOH before entering MS.

IC was coupled to a single quadrupole mass spectrometer with a MSQ Plus™, Thermo Scientific™, with an electrospray source, *ESI*. ESI operated in negative mode at 500 °C and a needle voltage of 2.5 k. For the detection, Selected Ion Monitoring, *SIM*, was used.

Each mass to charge ratio of $[M\text{-}H]^-$ of each compound had a specific cone voltage and a specific acquisition time, that are provided in **Table 5**.

Table 5. Mass to charge ratios (m/z), cone voltage (V) and time range (min) for each [M-H] of each compounds

Compounds		**$[M\text{-}H]^-$**		**Cone (V)**		**Time range (min)**
Inorganic ions						
Cl^-		35		90		5.00-8.00
NO_2^-		46		100		5.00-7.50
NO_3^-		62		70		7.00-10.00
Br^-		79		40		7.00-9.50
PO_4^{3-}, SO_4^{2-}		97		60		10.00-20.00
I^-		127		40		15.00-20.00
Organic acids						
C_2-acetic		59		40		3.00-6.00
C_2-glycolic		75		40		3.50-5.50
C_2-oxalic		89		100		11.00-14.00
MSA		95		40		3.50-6.00
C_3-malonic		103		70		9.00-12.00
cis-usC4-maleic, trans-usC4-fumaric		115		40		10.00-15.00
C_4-succinic		117		30		8.00-12.00
αC_7-benzoic		121		40		8.00-11.50
C_5-glutaric		131		100		8.00-12.00
hC_4-malic		133		40		8.00-11.00
C_6-adipic		145		50		8.00-11.00
C_7-pimelic		159		40		8.00-12.00
C_8-suberic		173		40		9.00-14.00

The chromatographic separation, with these characteristics, has produced well separated peaks for each analyte, as shown in **Figure 16**, for the anions and for the carboxylic acids in **Figure 17**.

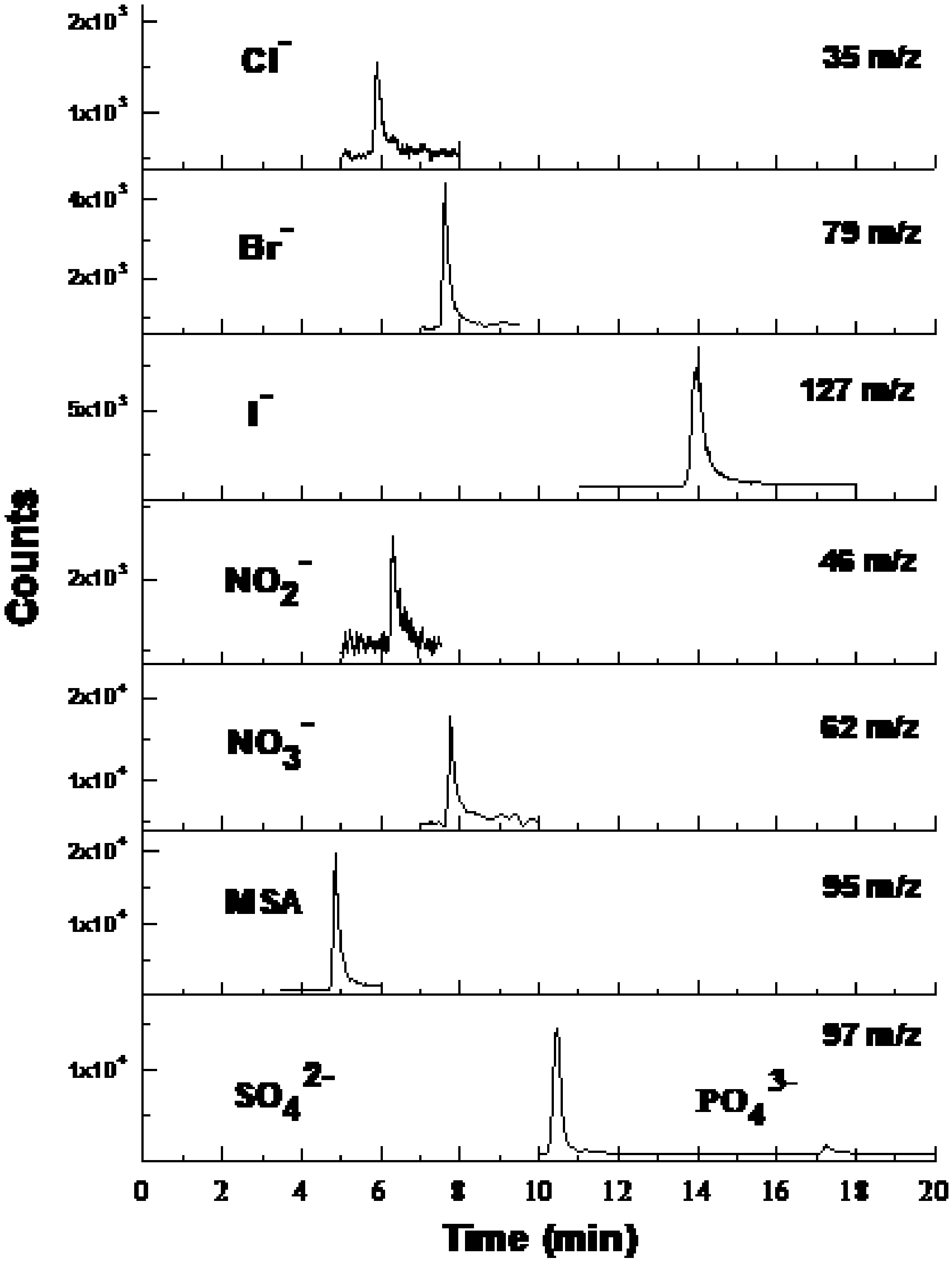

Figure 16. Chromatogram of the anionic species

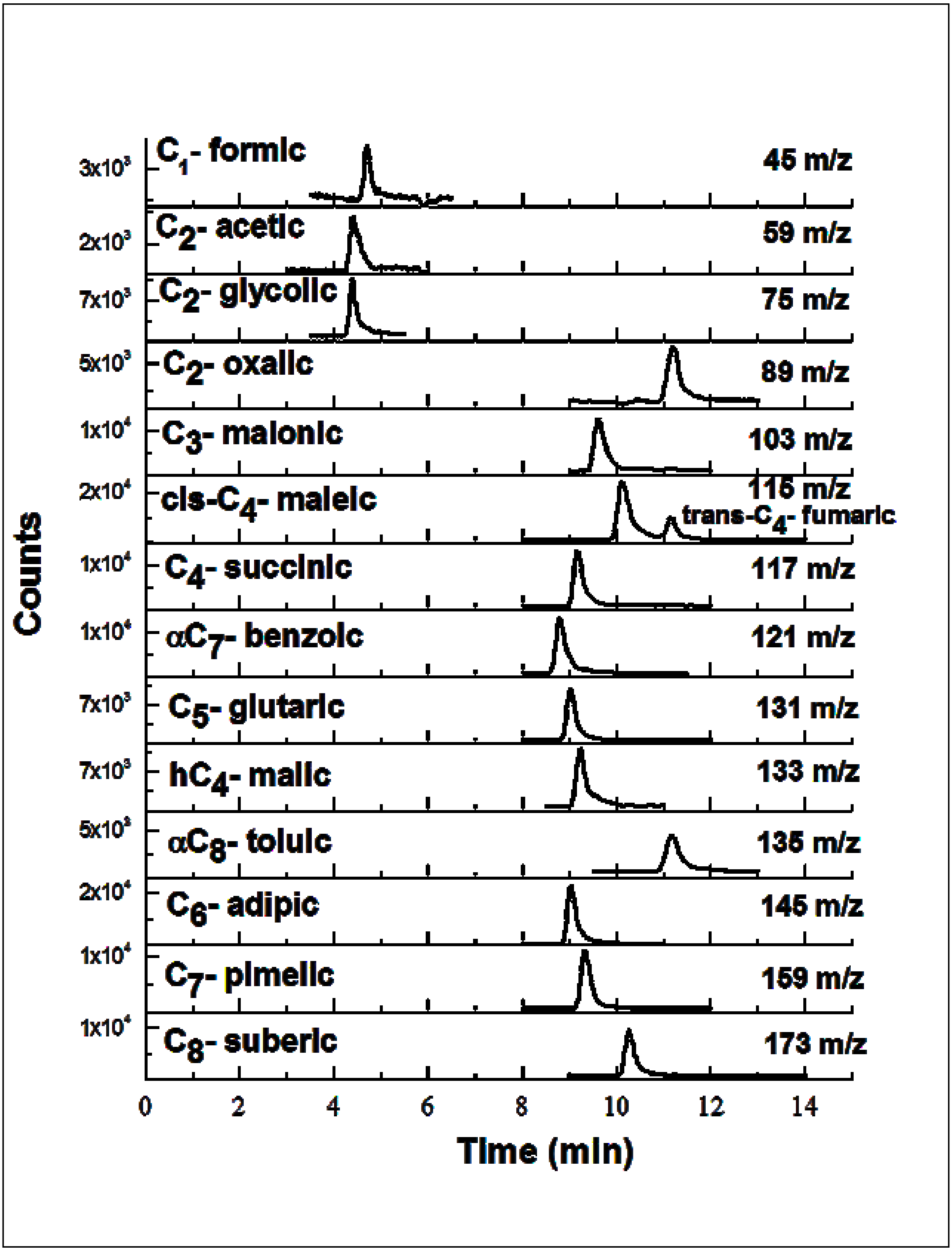

Figure 17. Chromatogram of the carboxylic acids

Cationic analysis were performed using a capillary ion chromatograph coupled with a conductibility detector. The capillary ion chromatograph was a *Thermo Scientific Dionex ICS-5000*, equipped with a capillary cationic exchange column, *Dionex IonPac CS19- 4 µm, 0.4×250 mm*, with a pre-column, *Dionex IonPac CG19-4 µm, 0.4 × 50 mm*. As mobile phase methasulfonic acid, MSA, was used. Mobile phase was directly produced by an eluent generator, *Dionex ICS 5000EG, Thermo Scientific* inside the instrument with a specific gradient with a flow rate of 13 µL min. The MSA gradient was 0–17.3 min; 1.5 mM; 17.3–21.9 min gradient from 1.5 to 11 mM; 21.9–30 min equilibration at 1.5 mM. The injection volume was 0.4 µL. Between the capillary ion chromatograph and the conductibility detector there was a suppressor, *CCES 300, Thermo Scientific*, to remove the MSA entering the conductibility detector. For the acquisition and the data evaluation *Chromeleon 6.8 Chromatography* data system was used.

3.3 Quality control

The anionic analytical method was validated measuring procedural blanks, recoveries, errors and repeatability. Three cleaned quartz fiber slotted filters and three cleaned quartz fiber backup filters were used to evaluated trueness and repeatability. A known quantity of a multi-ion standard solution was spiked on each filter. On each slotted filter were added 7 µg of the anionic standard solution. 15 µg of the anionic standard solution was added to each backup filter. The analytical method was validated for almost all of the anions. Repeatability was below the 10% and percentage errors ranged between – 9 and +10% **Table 6**.

Table 6. Parameters of the validation for anionic species and organic acids

Instrumental method					Slotted filters			Backup filters	
Compounds	**Linear range (ng mL-1)**	**Slope**	**R^2**		**Error (%)**	**RSD (%)**		**Error (%)**	**RSD (%)**
Cl-	11 - 1,000	7	0.985		2	7		-7	1
Br-	3 - 9,999	10	0.980		6	9		-7	1
I-	5 - 750	272	0.982		9	1		-1	3
NO2-	11 - 5,00	12	0.974		-1	1		-4	2
NO3-	8 - 10,000	23	0.995		4	10		-5	9
MSA	0,4 - 14,810	32.3	0.999		7	4		7	5
SO42-	2 - 9,999	46	0.995		4	8		-5	35
H2PO4-	9 - 7,500	13	0.995		-4	1		0	6
C2-oxalic	1 - 10,000	30	0.998		-7	3		-7	3
C2-glycolic	1 - 9,999	22	0.99		10	2		2	5
C2-acetic	13 - 10,000	5	0.999		-2	5		0	8
C3-malonic	1 - 5,000	26	0.997		-1	5		-1	12
C4-succinic	1 - 3030	23	0.989		5	5		-3	1
hC4-malic	1 - 10,013	40	0.993		0.5	0.4		-8	5
cis-usC4-maleic	1 - 9,879	39	0.998		2	2		10	7
trans-usC4-fumaric	4 - 2,025	11	0.998		-1	4		-7	2
C5-glutaric	1 - 1,990	41	0.990		-4	5		-5	4
C6-adipic	1 - 1,860	27	0.991		-9	4		-7	11
C7-pimelic	1 - 5,974	16	0.980		3	3		3	8
αC7-benzoic	2 - 3,400	16	0.995		-4	1		-5	4
C8-suberic	3 - 14,499	11	0.990		6	4		7	1

For the cationic analytical method 14 µg of the cationic standard solution was spiked on the cleaned quartz fiber slotted filters. 30 µg of the cationic standard solution was spiked on each cleaned quartz fiber backup filter. The analytical method was validated for almost all of the cation with repeatability always below 10% and percentage errors below -10 and +10% **Table 7.**

Table 7. Parameters of the validation for cationic species

	Instrumental method				Slotted filters			Backup filters	
	Linear range (µg mL-1)	Slope	R^2		Error (%)	RSD (%)		Error (%)	RSD (%)
Li+	0.1 - 20	0.6	0.990		1	7		-6	10
Na+	0.4 - 20	0.2	0.993		-10	3		-3	10
NH4+	0.2 - 20	0.2	0.991		-3	7		10	9
K+	4 - 20	0.1	0.997		-8	8		-10	8
Mg+	1 - 20	0.5	0.994		10	8		-1	9

For all anionic and cationic species, the signal-to-noise of three and ten times respectively instrumental detection limits (LOD) and instrumental quantification limit (LOQ) were determined. Furthermore, the method detection limit (MDL) and the method quantification limit (MQL) were determined. MDL was determined as three times of standard deviation and MQL was determined as ten times of the standard deviation of the average value of field blanks **Table 8**.

Table 8. LOD and LOQ, MDL and MQL for each ionic specie, in both slotted and backup filters

				Slotted filters				**Backup filters**		
Ionic Compounds	**LOD**	**LOQ**		**Blank**	**MDL**	**MQL**		**Blank**	**MDL**	**MQL**
	ng mL^{-1}	**ng mL^{-1}**		**ng abs**	**pg m^{-3}**	**pg m^{-3}**		**ng abs**	**pg m^{-3}**	**pg m^{-3}**
Cl^-	11	37			29	292			32	318
Br^-	3	10			3	26			1	8
I^-	5	16			0.1	1			0.1	1
NO_2^-	11	37			1	15			2	15
NO_3^-	8	25			13	129			7	67
MSA	0.4	1			5	48			13	127
SO_4^{2-}	2	6			110	1103			206	2058
PO_4^{3-}	9	30			0.5	5			5	45
C_2-oxalic acid	1	4			1	12			11	110
C_2-glycolic acid	1	5			3	26			2	19
C_2-acetic acid	13	44			7	75			39	385
C_3-malonic acid	1	3			1	6			2	16
M	1	3			1	5			1	6
F	4	13			1	8			3	31
C_4-succinic acid	1	3			1	12			3	30
αC_7-benzoic acid	2	7			0.3	3			2	15
C_5-glutaric acid	1	5			0.4	4			2	19
hC_4-malic acid	1	3			1	13			1	11
C_6-adipic acid	1	4			1	12			2	22
C_7-pimelic acid	1	2			1	11			2	20
C_8-suberic acid	3	9			1	7			2	18
Li^+	28	93			1	3			1	2
Na^+	16	52			42	139			119	398
NH_4^+	3	333			4	13			2	8
K^+	2	8333			31	103			134	448
Mg^+	348	1162			38	125			22	74

3.4 Result

In **Figure 18** are shown the mean concentrations of anionic and cationic species in aerosol samples collected during the 26th campaign at MZS, the 27th campaign at DC and the 28th campaign at DC.

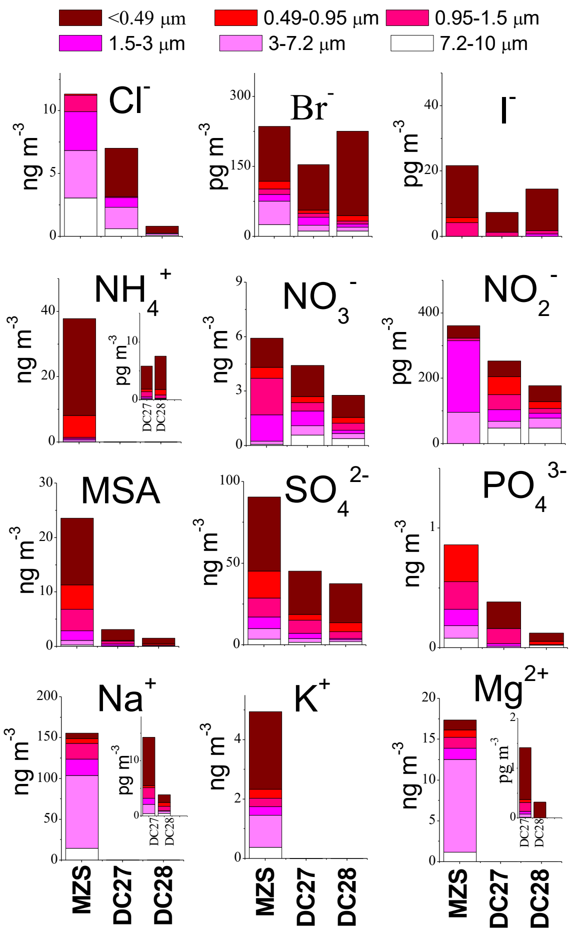

Figure 18. Average concentrations of major ionic species and relative particle size-distribution of aerosol samples collected at Mario Zucchelli Station (MZS) during the 26th sampling and at Concordia Station, Dome C during the 27th sampling campaign (DC27) and the 28th sampling campaign (DC28)

The aerosol collected during the 26th sampling campaign at MZS is highly concentrated in Na^+ (113 ng m^{-3} as mean concentration, 45% of the total sum of all detected ionic species), SO_4^{2-} (90 ng m^{-3}, 26%), NH_4^+ (38 ng m^{-3}, 11%), MSA (24 ng m^{-3}, 7%), Mg^{2+} (17 ng m^{-3}, 5%). Data coming from the first MZS sample, taken from 29 November to 9 December, have been excluded from the calculation of mean values because of their very high concentrations, different from the rest of the samples coming from the same campaign. Cl^-, NO_3^- all the CA have been detected 3 to 10 times higher compared to the other four samples. This is due to a contamination probably coming from local biomass burning combustion [8], [75]. The aerosol collected during the 27th and 28th sampling campaigns at DC shows high concentrations of SO_4^{2-}, NO_3^-, Cl^-, MSA, and CA. In the aerosol samples collected over the Antarctica plateau, SO_4^{2-} was the main ionic compound during both the sampling campaigns. During the 27th campaign, SO_4^{2-} was 45 ng m^{-3}, 72% and during the 28th sampling campaign SO_4^{2-} was 37 ng m^{-3}, 83%. During the 27th campaign at DC Cl^-, with a concentration of 7 ng m^{-3}, 11%, was higher compared to the 28th campaign where its concentration was 0.8 ng m^{-3}, representing the 2% of the total sum of all detected ionic species **Figure 19**.

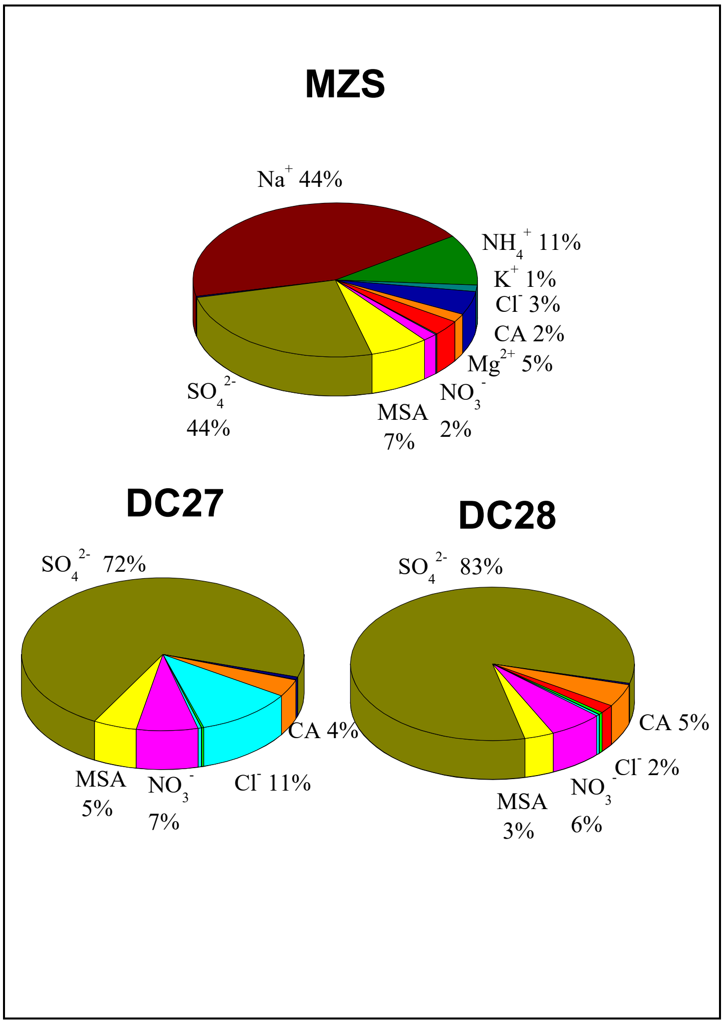

Figure 19. Percentage of ionic species in the different sampling sites. MZS during the 26th sampling campaign. DC during the 27th and 28th sampling campaigns

A first overview of all samples showed that the ionic composition of aerosol samples collected at MZS, the coastal site, was characterized by high concentration of cationic species such as Na^+ and Mg_2^+. On the other hand the ionic composition of aerosol samples collected at DC was characterized by a high concentration of anionic species, such as SO_4^{2-}, NO_3^-, Cl^-, MSA, and CA. Concentrations of the most present ionic species both in MZS and DC samples were similar to those reported in previous publications [103]. The aerosol composition in carboxylic acids is quite similar between the two sampling sites, MZS and DC. The most abundant carboxylic acid was C_2-oxalic acid, with a mean

PM10 concentration of 2.7 ng m^{-3} at MZS. At DC during the 27th sampling campaign C_2-oxalic had a concentration of 1.5 ng m^{-3} and during the 28th campaign its concentration was 1.2 ng m^{-3}. The second most abundant carboxylic acid was C_2-acetic, which had a higher concentration at MZS (2.6 ng m^{-3}) respect to concentrations at DC (0.7 ng m^{-3} and 0.6 ng m-3, respectively). Other carboxylic acids are present in negligible concentrations. Values of CA founded in our samples were comparable to those reported in literature from another Antarctic site [104] and from Southern Ocean [105].

3.5 Discussion

Aerosol samples collected at MZS were dominated by sea spray input, with high concentrations of Na^+, Mg_2^+ and SO_4^{2-}. Cations Na^+ and Mg_2^+ were mainly distributed in the coarse fraction. Higher concentrations are in the first four stages (0.95-1.5 μm, 1.5-3 μm, 3-7.2 μm and 7.2-10 μm) **Figure 19**. In samples collected at DC, over the Antarctic plateau, these chemical species were 10^4 times lower than in MZS. Furthermore, the particle size distribution of these chemical compounds had an evident change in the particle size distribution: Na^+ and Mg^{2+} were mainly distributed in the <0.49 μm fraction. Removal processes affect less fine particles of sea salt aerosol, so this aerosol can eventually move over Antarctica, where some air mass mixes down toward the surface [106]. In MZS samples, the mean concentration of sea-salt particle mass was 505 ng m^{-3}. It is assumed that the original sea salt mass is equal to 3.248 times the sodium mass [107]. This value of sea-salt particle mass was similar to those reported in other investigation at coastal Antarctic stations, such as Halley Bay (160 ng m^{-3}) and at Neumayer (580 ng m^{-3}) [108]. This value of sea-salt particle mass was lower than values reported at Aboa (2100 ng m^{-3}) and at Dumont d'Urville (DDU) (2100 ng m^{-3}) [109].

In the aerosol samples collected at DC, the contribution of sea-salt particle mass drastically decreased. At DC during the 27th sampling campaign, sea-salt particle mass had a mean value of 46 pg m^{-3} and during the 28th sampling campaign a mean value of 12 pg m^{-3}. The different chemical composition and particle size distribution between samples collected at the coastal (MZS) and internal (DC27 and DC28) sampling sites suggest that fresh oceanic emission, through the production of significant amount of sea salt particles was the main source of aerosol at the coastal base. During the long range atmospheric transport over the Antarctic plateau, a depletion of sea salt particles occurred. The total SO_4^{2-}, the total Na^+ concentrations and the Na^+/SO_4^{2-} ratio in bulk seawater show that non-sea salt sulphate (nss-SO_4^{2-}) is >90% of the total sulphate in the fine fraction of the samples taken at MZS. In fact, nss-SO_4^{2-} is mainly concentrated in stages with diameter <0.49 and diameter 0.49-0.95 µm. According to the other markers of sea salt input, such as Na^+ and Mg^{2+}, sea salt sulphate (ss-SO_4^{2-}) was the only form of sulphate found on the stages 3-7.2 µm and 7.2-10 µm **Figure 20**.

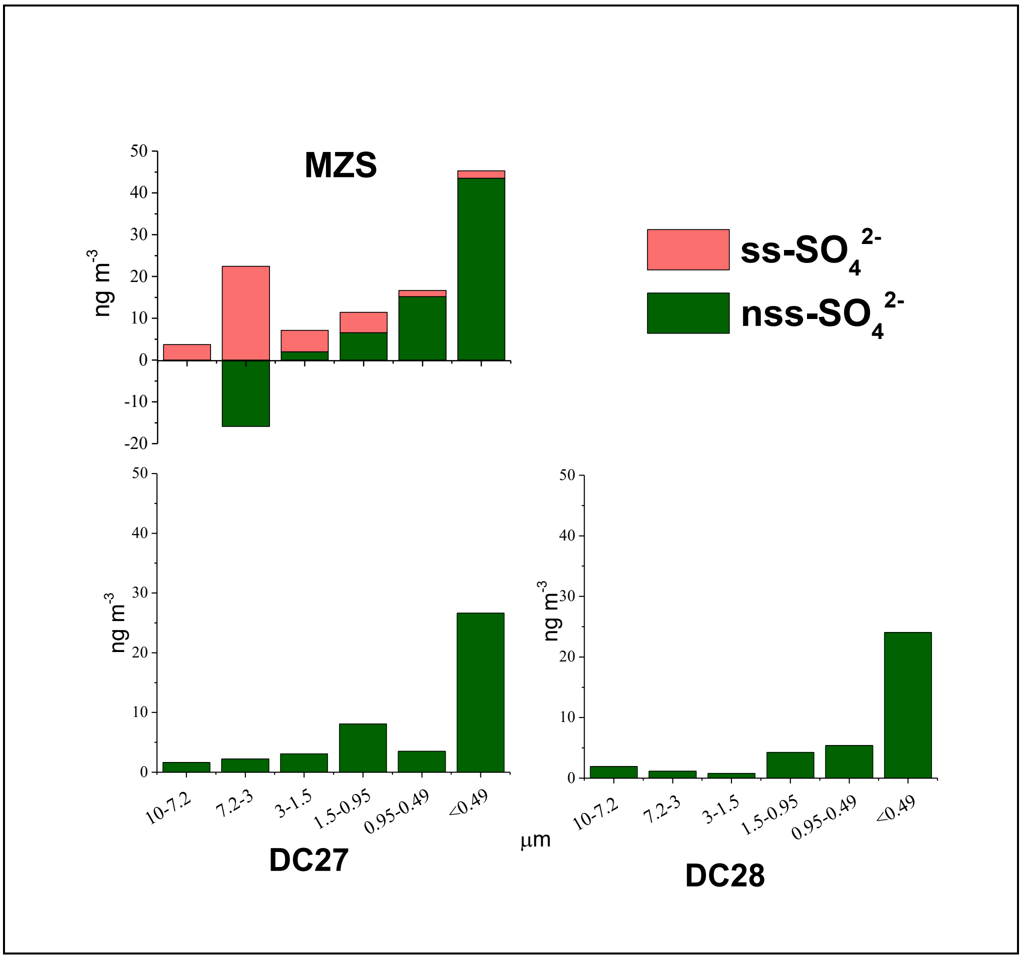

Figure 20. Particle size distribution of mean concentrations of sea salt sulfate (ss-SO_4^{2-}) and non-sea salt sulfate (nss-SO_4^{2-})

On the 3-7.2 µm fraction of MZS samples, it was observed a negative value of nss-SO_4^{2-} along with high salt concentrations, suggesting air masses originates from frost flowers [110]. Over the Antarctic plateau, the ss-SO_4^{2-} was negligible. The nss-SO_4^{2-} was the only species of sulphate present in aerosol samples from DC. The nss-SO_4^{2-} was mostly distributed in the 0.49 µm fraction **Figure 20.** Biogenic sulphur produced by marine phytoplankton in the oceans is the main sources of nss-SO_4^{2-}. Through the evaluation of SO_4^{2-}/Na^+ ratio, the contribution of sea salt in the total sulphate concentration was evaluated **Figure 21**.

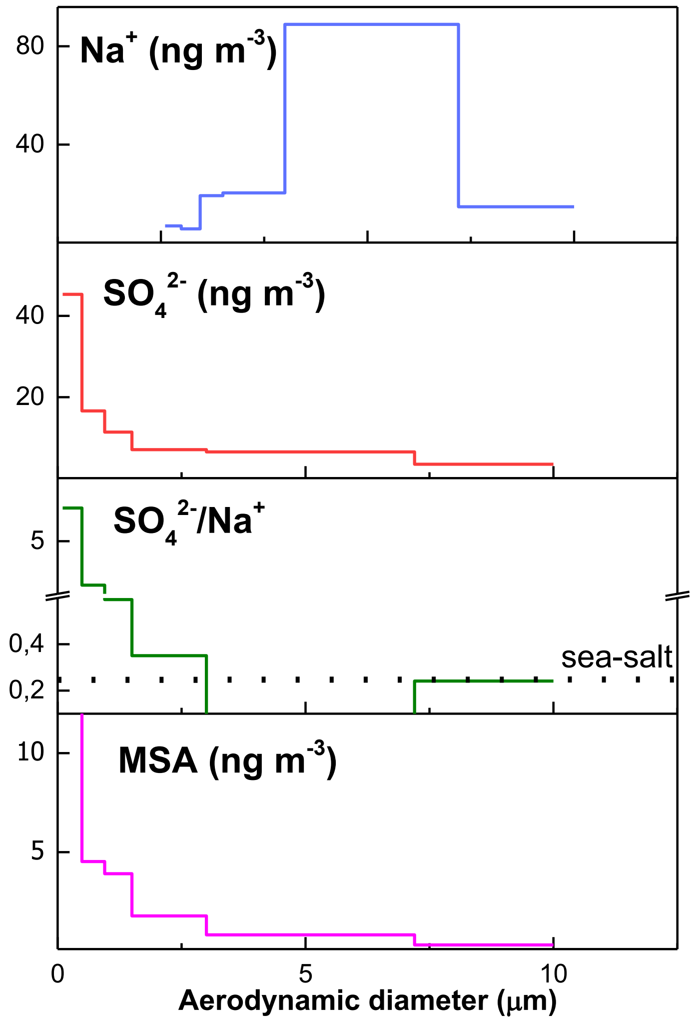

Figure 21. Particle size distribution of mean concentrations of Na^+, SO_4^{2-}, SO_4^{2-}/Na^+ ratio, MSA in the samples collected at Mario Zucchelli Station (MZS) during the 26th sampling campaign

In MZS aereosol samples, collected during the sampling campaign which took place in 2010-2011 austral summer, were calculated ratios higher than seawater value of 0.25, in the <3 fractions. In 3-7.2 μm and 7.2-10 μm fractions were calculated minor or equal ratios respect to seawater value. This SO_4^{2-}/Na^+ ratio particle size distribution was previously obtained at the coastal station of DDU, in Antarctica [111]. In the samples taken at DC, during the sampling campaigns in the austral summer 2011-2012 and 2012-2013, the SO_4^{2-}/Na^+ ratios were always higher than seawater values. This confirmed that the contribution of sea-salt in sulphate concentration was negligible over the Antarctic plateau. In one study Jourdain et al. found an high value of the SO_4^{2-}/Na^+ ratio in samples collected at DC in the month of March, suggesting the heterogeneous conversion of SO_2 on sea-salt aerosol [112]. After the dimethyl sulfide (DMS) emission in the atmosphere, it was oxidized mainly to MSA or SO_2, which is further oxidized to SO_4^{2-}. The contribution of non-biogenic sulphate, for example long-range transport of species containing sulphur, during the polar summer, was less than 10% of the total nss-SO_4^{2-} amount [113]. In samples from MZS and DC were found high concentrations of MSA and nss- SO_4^{2-} on the <0.49 µm fraction. MSA and nss-SO_4^{2-} concentrations decreased over the Antarctic plateau along with a higher distance from the ocean source. MSA and nss-sulphate showed a strong correlation (r^2=0.78), underlining the same biogenic source [103]. The investigation of the MSA/ nss-SO_4^{2-} in aerosol samples was done in several studies [114], [115], [111], [112], [108], [116] giving useful information about Sulphur sources. It can deconvolute marine biogenic emissions from other sulphur sources and it can trace back the latitude of marine source regions influencing nss-SO_4^{2-} and MSA at a precise site; for example, a high ratio suggests high-latitude marine sources. In the MZS samples was found a mean value of MSA/ nss-SO_4^{2-} ratio equal to 0.3±0.1. This value is similar to other values reported in literature about samples collected at coastal sites in Antarctica [115], [111], [108], [113]. In samples collected over the Antarctic plateau, this value of MSA/ nss-SO_4^{2-} ratio strongly decreased. In samples collected at DC during the 27th sampling campaign this value was equal to 0.08±0.02. During the 28th sampling campaign at DC this mean value was equal to 0.04±0.01. This decrease is due to the distance of marine sources. Furthermore, it is also due to the longer atmospheric lifetime of nss-SO_4^{2-} respect to the one of MSA [113]. In samples collected both at MZS and DC, ammonium (NH_4^+) was mainly distributed in the fine fraction, precisely in <0.49 µm fraction. NH_4^+ showed lower concentrations at DC compared to MZS **Figure 18**. This distribution propose ocean [117], [118], [119] emissions of seabirds, penguins colonies or soils exposed to these colonies as the main sources of NH_4^+ [120], [121], [122]. In DC samples, a significantly lower NH_4^+ concentration was observed due to the distance from these potential sources. In MZS aerosol samples nitrate (NO_3^-) was mostly concentrated in the >1 µm fraction (63%). Despite NO_3^- had a similar particle size distribution with sea salt, it had not a marine source. Probably the origin of NO_3^- was the transportation of gaseous compounds. NO_3^- can also be originated from particulate nitrate transferred back to the gas phase before arriving at the lower Antarctic troposphere [108]. The most probable pathway for the NO_3^- formation was the interaction of reactive nitrogen compounds or nitric acid (HNO_3) with sea- salt particles in the Antarctic atmosphere [123]. Thought the atmospheric oxidation of gaseous nitrogen oxides to nitric acid, NO_3^- is produced. Nitrogen oxide come from the reaction of nitrification in soils, phenomena of biomass burning, fossil fuel and oxidation of atmospheric nitrogen by lightning strikes [124], [125]. Nitric acid has a high saturation vapor pressure and for this reason it tend to condense onto existing particles such as sea salt or mineral particles. The formation of NO_3^- is completely different from the formation of MSA or nss-SO_4^{2-}, that originate new particles from the nucleation [110]. Nitric acid and sulphuric acid may react with some species that are condensed on the same particles. An important example of these reactions is the chloride depletion.

$$HNO_3 + NaCl \longrightarrow NaNO_3 + HCl$$

$$H_2SO_4 + NaCl \longrightarrow NaNO_3 + HCl$$

Chloride depletion is important to estimate the amount of NO_3^- and SO_4^{2-} formed on sea-salt particles. To calculate the percentage of chloride depletion in sea-salt depletion the formula is:

$$(\%Cl_{dep}) = ([Cl_{ss}][Cl_{meas}])/[Cl_{ss}]100\%$$

where $[Cl_{ss}]=1.174\ [Na^+_{meas}]$.

$[Cl_{meas}]$ and $[Na^+_{meas}]$ are the equivalent concentrations of the measured Cl^- and Na^+ [126]. At MZS, the coastal sampling site, the percentage of chloride depletion ranged from 87 to 98% during all the sampling period. The highest values of chloride depletion were observed in the fine fraction (< 0.49 µm). In the same fraction the highest concentration of sulphate was observed. In the DC samples, chloride was mainly distributed in the fine fraction. The correlation between Cl^- and Na^+ disappeared due to the extra sea-spray contribution to the Cl^- concentration. In the aerosol over the Antarctic plateau, the main chloride emission source was the fine particles transported in the air masses originating from the ocean. This fine particles contain NaCl and HCl adsorbed on the particle surface [127]. Furthermore, Cl^- could be also re-emitted as HCl into the atmosphere from the snow layer, where NaCl and HCl were previously deposited [128]. Chloride, during the 27th sampling campaign at DC was detected also on the coarse fraction, while during the 28th sampling campaign at DC, chloride was detected only in the fine fraction (< 0.49 µm) **Figure 18**. Using the backward trajectories **Figure 22**, it is possible to establish that during the 27th sampling campaign at DC, air masses arrived in the sampling site in about 36 hours. During the 28th sampling campaign, austral summer 2012-2013, air masses reached DC in 4 to 7 days [79].

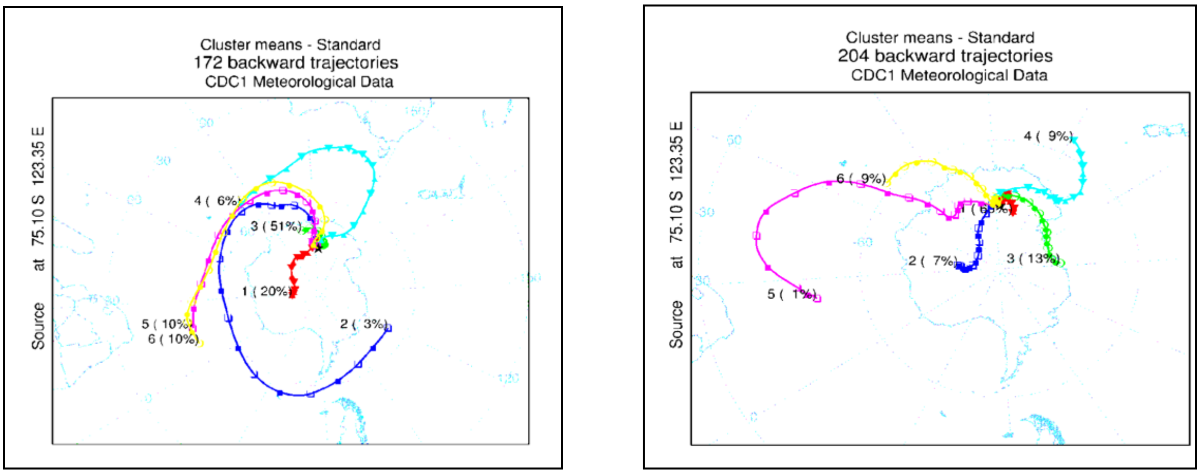

Figure 22. Mean of back trajectories of air masses arriving at the Dome C site during the southern summers 2011-12 (left) and 2012-13 (right)

A key factor in the life duration of the coarse particles composition in the aerosol over the Antarctic plateau, seems to be the time of the long-range transport processes. Br^- and I^- have an important role in environment and climate. But Br^- and I^- data concentrations in Antarctic aerosol are not often available, because of their low concentrations [129], [130]. I^- is concentrated mainly in the underside of sea ice and it is well correlated with phytoplankton's emissions [131]. In MZS samples Br^- and I^- represented the 0.07% of the total ionic content. In DC samples, from the 27th sampling campaign they represented the 0.2% of the total ionic content and in DC samples from the 28th sampling campaign they represented the 0.5% of the total ionic content. In both sampling sites Br^- was 10 times more concentrated than I^- **Figure 18**. In both MSZ and DC sampling sites, Br^- and I^- were mainly found in the fine fraction, precisely in the 0.49 µm fraction. Concentrations values of Br^- were similar to concentration values in bulk aerosol samples collected at DC and DDU reported by Legrand et al. [132]. Biogenic emission, such as phytoplankton or frost flowers are the main sources of Br^- [55]. In MZS samples, there was a high correlation between Br^- and Na^+, R^2= 0.923, with a mean slope of 0.004. This correlation suggested that at MZS, during the 26th sampling campaign, austral summer 2010-2011, sea-salt emission was the main source of the Br^- found in aerosol samples. In MSZ samples, during summer, it was observed a depletion of Br^- relative to Na^+. Br^- to Na^+ mass-based ratio was lower (mean $2x10^{-3}$) compared to the seawater value ($6.25x10^{-3}$). This process is commonly observed at remote marine sites of the Southern Hemisphere [133]. In MZS samples depletion factor (DF) was calculated to evaluate he fraction of bromine lost from aerosol to the gas phase [132].

$$DF= 1- ([Br^-]/[Na^+])_{aerosol}/([Br^-]/[Na^+])_{reference}$$

$([Br^-]/[Na^+])_{reference}$= ratio value considering sea-salt coming from open ocean, for example $6.25x10^{-3}$.

In MZS samples it was found a mean DF value of 0.6. This value was higher compared to values calculated by Legrand et al. in bulk aerosol at DDU, during November, 0.49, December, 0.31 and January, 0.21 [132]. Focusing on the depletion of Br^-, the Br^- to Na^+ mass-based ratio was lower than seawater value in coarse particle (>0.95 μm) while exceeded the seawater value in fine particles (<0.49 μm) **Figure 23**.

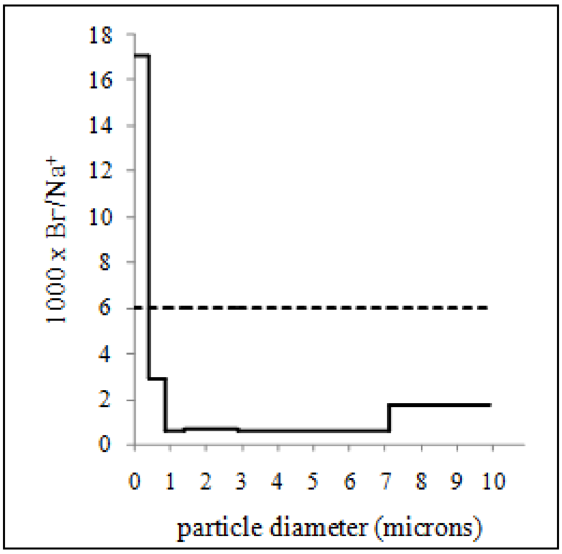

Figure 23. Size-segregated Br^- to Na^+ mass-based ratio in aerosol collected at MZS in austral summer 2010-2011. The dashed line refers to the bromide to sodium mass-based ratio in seawater

This is the confirmation of the trend reported by Legrand et al. [132]. In DC samples from the 27th sampling campaign correlation between Br^- and Na^+ had an R^2=0.96, while in DC samples from the 28th sampling campaign the correlation was very low with an R^2= 0.005. The time of transportation of aerosol over the Antarctica plateau was probably the critical factor for aerosol concentrations obtained at DC. During the 27th sampling campaign, when the air masses arrived over the Antarctic plateau in about 3 hours, the Br^- and Na^+ correlation was quite high. On the other hand, in the samples coming from the 28th sampling campaign, when the air masses took 4 to 7 days to reach the site, the Br^- and

Na^+ correlation was very low. The quantification of carboxylic acids (CA) highlighted that C2-oxalic acid was the most abundant CA in both MZS and DC sampling sites **Figure 24**.

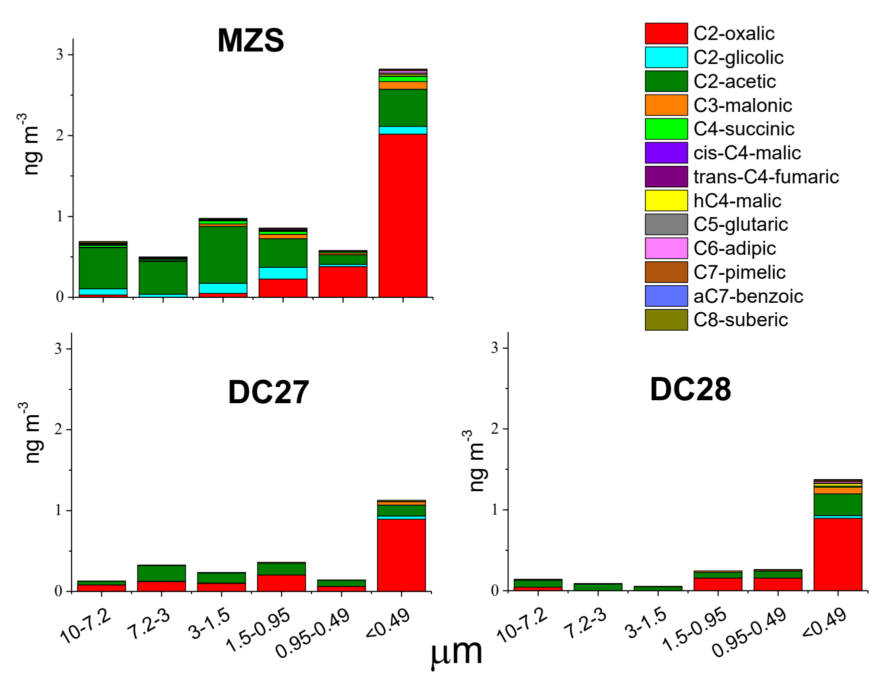

Figure 24. Particle size distribution of the mean concentration of carboxylic acids in the MZS, DC 27 and DC28 aerosol samples

C2-oxalic acid is the end-product of various oxidation/decomposition reactions in the atmosphere [134]. These compounds were mainly produced by photochemical production of alkenes emitted by phytoplankton [135]. In the fine fraction, precisely in the < 0.49 fraction, were found all acids, except for C_2- acetic acid because of their nature of secondary aerosol products in the atmosphere. In contrast, one study at DDU by Jourdain and Legrand reported that C_2-oxalic acid was mainly found in 10 µm fraction of aerosol, highlighting the presence of an evident contribution by ornithogenic, guano-enriched soils [111]. As mentioned before, C_2-acetic acid showed a completely different behavior compared to other acids, because it is mainly concentrated in the coarse fraction. C_2-acetic acid has a high vapor pressure that permit its emission as secondary product in the gas-phase. Then, C_2-acetic acid, is absorbed onto coarse particles, such as sea-salt particles [136]. In DC samples the concentrations of C_2-acetic acid in the coarse fraction is lower. This behavior is probably related with the reduction of sea-salt particles, where the organic acid species can absorb, in the aerosol over the Antarctic plateau. Legrand et al. reported similar trend of C_2-acetic acid in the gas phase at DDU where the C_2-acetic acid showed concentration 105 time higher that our concentrations in the particulate fraction at MZS during the same sampling campaign. Concentrations reported by Legrand et al. are surely heavily influenced by the guano decomposition in the large penguin colonies at DDU [137]. The C_3-malonic/C_4-succinic ratio has been used as indicator of enhanced photochemical production of diacids, to investigate the potential sources of CA IN Antarctic aerosol [138]. Through decarboxylation reactions activated by OH radicals, C_4-succinic acid can be degraded to C_3-malonic acid [139]. In MZS samples the mean C_3-malonic/C_4-succinic ratio was 1.5, very similar to ratios commonly calculated for marine areas [139]. In DC samples from the 27th sampling campaign mean C_3-malonic/C_4-succinic ratio was 5. In DC samples from the 28th sampling campaign mean C_3-malonic/C_4-succinic ratio was 6. These values suggested that C_3-malonic acid was photochemically produced during long-range atmospheric transport over the Antarctic plateau [139]. The ionic balance was evaluated to compare the acidity of aerosol between coastal and inland site. The ionic balance was calculated in terms of equivalent of fine (<0.95 μm) and coarse (>0.95 μm) fraction of aerosol samples collected at MZS and DC, **Figure 25.**

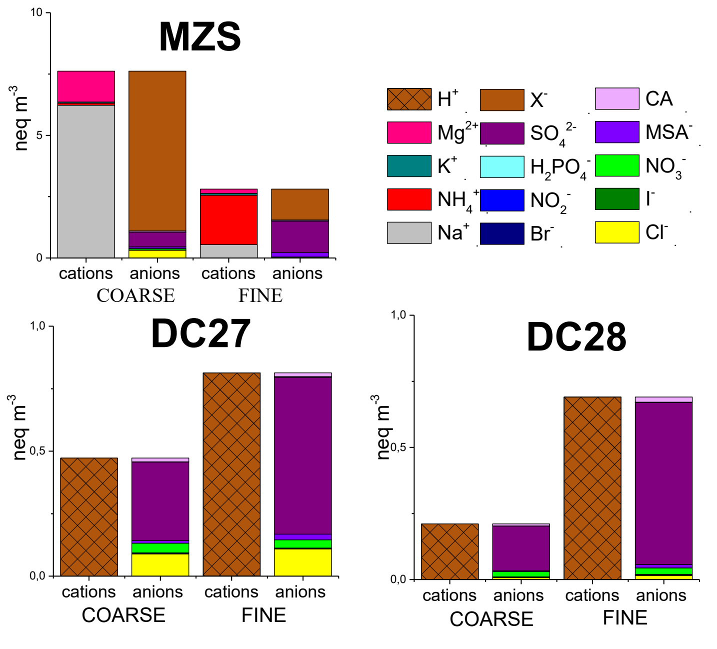

Figure 25. Ion balances (peq m-3) of coarse (>0.95 μm) and fine (<0.95 μm) fraction of MZS, DC27 and DC 28 aerosol samples

In the MZS samples, in both fractions was observed an important anion deficit. To neutralize the MZS aerosol on the coarse fraction, were necessary other anionic species, but we cannot identify them. A possible explanation about the occurrence of these unknown anionic species (X^-) present in the MZS aerosol could be carbonate originating from the ice-free areas near the sampling site. Particle size distribution, with the most of X^- concentrated in the coarse fraction, supported the hypothesis of a local source of this unknown anionic species (X^-). The deficit of anionic species in the fine fractions could be due to the presence of other organic compounds emitted by the ocean nearby. In the DC samples were observed an inverse trend, whit a deficit of cationic species **Figure 25**. This deficit was due to a significant concentration of hydrogen cations in the aqueous solution associated with the aerosols [127].

3.6 Conclusions of this case of study

In this case of study chemical composition and particle size distribution of Antarctic aerosol was investigated. Antarctica is an isolated system that allows scientist to investigate natural sources of aerosol and processes of chemical and physical transformation during long-range transport. For this reason, aerosol samples were collected in two different sites: a coastal site on Victoria Land near the Italian Mario Zucchelli Station, during the 26th sampling campaign, and over the Antarctic plateau at Concordia Station, during two consecutive campaigns, the 27th sampling campaign and the 28th sampling campaign. Sea salt input, Na^+, Mg^{2+} and SO_4^{2-} characterized the aerosol collected in the coastal site. It was differentiated between ss-SO_4^{2-} and nss-SO_4^{2-}. Furthermore, in MZS samples the species more concentrated were found in the coarse fraction, because they are primary species. Ionic species less concentrated were secondary marine biogenic compounds and they are mainly found in the fine fraction, < 0.49 μm fraction. DC samples confirmed that aerosol over the Antarctic plateau was characterized by high concentration of anion species such as, nss-SO_4^{2-}, MSA acid and NO_3^-. The determined ionic species were mainly distributed in the fine fraction due to the atmospheric processes of long range transport. Furthermore, these compounds were produced by chemical reaction in the atmosphere. The DC aerosol showed a high acidity.

4 STUDY OF AEROSOL AND SNOW TRANSFER PROCESSES OF WATER-SOLUBLE ORGANIC COMPOUNDS AND IONIC SPECIES IN ANTARCTICA

This chapter is entirely based on the “Aerosol and snow transfer processes: An investigation on the behavior of water-soluble organic compounds and ionic species” paper published as co-author with Elena Barbaro, Roberta Zangrando, Ornela Karroca, Giuseppa Toscano, Warren R.L. Cairns, Carlo Barbante, Andrea Gambaro. The study conducted in work is a part of the research project "Air-snow exchange and relations for trace elements and organic compounds of climatic interest " (2013 / AZ3.04). This project has been financed by the National Antarctic Research Project (PNRA) for the 2014/2015 campaign (XXX expedition). The main aim of this study was the investigation of the air-snow transfer processes for some water-soluble compounds. These processes were investigated through the quantification of a wide range of chemical compounds, such as ions, carboxylic acids, amino acids, sugars and phenolic compounds. Furthermore, potential specific emission sources of these compounds were investigated. Water-soluble compounds have been determined in samples collected in Antarctica, near the Italian scientific research base Mario Zucchelli, during the 2014-2015 austral summer.

It was measured that water-soluble compounds accounted for 66% of the PM_{10} *of the total mass concentration. The most concentrated ions were* Na^+, Mg^{2+}, Cl^- *and* SO_4^{2-} *and they represented the 99% of the total water-soluble compound, indicating sea spray input was the main source of aerosol.* Na^+, Mg^{2+}, Cl^- *and* SO_4^{2-} *were mainly found in the coarse fraction of the aerosol resulting in enhanced deposition, as reflected by the snow composition. Carboxylic acids, amino acids, sugars and phenolic compounds permitted the identification of biogenic sources. Moreover, in this study there is the first study of the characterization of amino acid and sugars on the snow surface. After snowfall event, high concentrations of amino acids were found on the snow surface and this is probably due to the degradation of biological material scavenged during the snow event. After the snowfall event, alcohol sugars were found with higher concentrations suggesting a deposition of primary biological particles, for example airborne fungal spores*[3].

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[3] This chapter is entirely based on the postprint version of Elena Barbaro, Roberta Zangrando, Sara Padoan, Ornela Karroca, Giuseppa Toscano, Warren R.L. Cairns, Carlo Barbante, Andrea Gambaro. *Aerosol and snow transfer processes: An investigation on the behavior of water-soluble organic compounds and ionic species*. Chemosphere, 2017, 132-138, DOI: https://doi.org/10.1016/j.chemosphere.2017.05.098.

4.1 Samples collection and processing

In this case of study 7 aerosol samples and 8 snow samples were analyzed. Both aerosol and snow samples were collected during the XXX sampling campaign which took place during the austral summer 2014-2015.

Aerosol samples (n=7) were collected using a multi-stage Andersen impactor (TE-6070, Tisch Environmental Inc., Cleves, OH, USA). Sampler was located at the sampling site of Campo Faraglione (74° 41’ S, 164° 06’ E). This sampling site is located 3 km south of the Italian Scientific Research base Mario Zucchelli, in the Bay of Terranova, Southern Antarctica. Samples were collected from the 6th of November 2014 to the 13th of January 2015.

Samples were collected with a time of exposure equal to 10 days, the necessary time to quantify also species with low concentrations [75], [79], [140], [141], **Table 9**. Three field blank samples were collected by loading, carrying and installing the filter on the sampler with the air pump switched off. After 10 minutes each blank filter was removed.

Table 9. List of aerosol samples collected during XXX sampling campaign, nearby Mario Zucchelli station

Mario Zucchelli station (Campo Faraglione)	**Aerosol Samples**	**Date of sampling**
	Sample 1	06.11- 17.11.2014
	Sample 2	17.11 - 27.11.2014
	Sample 3	27.11 - 07.12.2014
	Sample 4	07.12 - 17.12.2014
	Sample 5	17.12 - 27.12.2014
	Sample 6	27.12.2014 - 05.01.2015
	Sample 7	05.01 - 13.01.2015
	Field Blank 1	17.11.2014
	Field Blank 2	17.12.2014
	Field Blank 3	05.01.2015
	Field Blank 4	13.01.2015

Aerosol samples were collected on pre-combusted quartz fiber filters. Filters pre-combustion was done putting filters for 4 hours at 400 °C in a muffle furnace. Each aerosol sample was composed by six stages for accumulation of different particle diameters. The first five stages were slotted filters, which accumulated particles with the following size fractions: 10.0-7.2 μm, 7.2-3.0 μm, 3.0-1.5 μm, 1.5-0.95 μm, 0.95-0.49 μm. The last stage was a backup filter which accumulated a particle diameter <0.49 μm **Table 10**.

Table 10. Dimensional fractions collected on the six stages of quartz fiber filters

Filter	Stage	Dimensional fraction
Slotted	1	10.0- 7.2 µm
Slotted	2	7.2- 3.0 µm
Slotted	3	3.0- 1.5 µm
Slotted	4	1.5- 0.95 µm
Slotted	5	0.95- 0.49 µm
Backup	6	< 0.49 µm

The average sampling airflow was of 1.1 m^3 min^{-1}. After the sampling, samples were wrapped in a double layer of aluminium foil and stored at -20 °C until analysis. The pre-analytical procedure for the quantification of ionic species was performed in ISO 4 clean room under a laminar flow hood in order to minimize contamination from the laboratory and operators. Furthermore, all the material used for the samples preparation was previously decontaminated in an ultrasonic bath with ultrapure water in order to avoid contamination from materials. First of all, double aluminium layers, in which filters were had been stored, were opened. For the anionic and cationic analysis, a quarter of each filter was cut with scissor, was chopped into little pieces and was put into a polypropylene tube. An additional volume of 7 mL of ultrapure water was added on the polypropylene tube containing slotted filters and an additional volume of 15 mL of ultrapure water was added on the polypropylene tube containing the backup filters. A 30 minutes extraction by ultrasonic bath was performed. Extracts were filtrated using polytetrafluoroethylene (PTFE) filters, with a porosity of 0.45 µm. These filters were previously activated with ultrapure methanol and subsequently washed the residual of methanol with milliQ water. A small amount of the filtrates was put into vials and was analyzed by ionic chromatography coupled to mass spectrometry (IC-MS) to quantify anionic compounds. Simultaneously ionic chromatography coupled with a conductivity detector was used to quantify cationic compounds. Half of each filter was used to determine amino acids, sugars and phenolic compounds. An additional volume of ^{13}C-labelled internal standard mix, composed by amino acids, phenolic compounds and levoglucosan, was spiked on each filter subsamples. On the slotted filters 100 µL and on the backup filters 300 µL of the mix solution with an average concentration of about 5 µg mL^{-1} were added. For the extraction ultrapure water was used as solvent. For the first extraction 9 mL and 25 mL of ultrapure water were added on the slotted filter and the backup filter respectively. For the second extraction 1 mL and 5 mL of ultrapure water were added on the slotted filter and the backup filter respectively. Each sample was placed in the ultrasonically bath twice for 15 minutes in ultrapure water. Before analysis, each extract was filtered using a 0.45 µm PTFE [75], [79], [8].

Surface snow samples (n=8) were collected at 10-days intervals, concurrently to each start of aerosol sampling (6 November, 17 November, 27 November, 7 December and 27 December 2014) and according to good weather conditions. Three consecutive snow samples were collected (10,12 and 13 January 2015) during a snowfall event that took place from the 8th to the 11th of January 2015. Three field blanks were obtained by filling the 2-L bottles for the sampling with ultrapure water taken in Antarctica. One blank was obtained by filling a 2-L bottle for the sampling with (BTQ) milliQ water coming from Italian milliQ water dispenser. **Table 11** presents a more detailed list of samples and the respective sampling dates. Samples were taken nearby the Italian Scientific Research base Mario Zucchelli, at Campo Faraglione (74° 41' S, 164°, 06' E), about 30 m from the aerosol sampling site.

Table 11. List of surface snow samples collected during XXX sampling campaign, nearby Mario Zucchelli station

Mario Zucchelli station (Campo Faraglione)	**Surface Snow Samples**	**Date of sampling**	
	Sample 1	06/11/2014	
	Sample 2	17/11/2014	
	Sample 3	27/11/2014	
	Sample 4	07/12/2014	
	Sample 5	27/12/2014	
	Sample 6	10/01/2015	**Three consecutive snow samples**
	Sample 7	12/01/2015	
	Sample 8	13/01/2015	
	Field Blank 1	06/01/2014	
	Field Blank 2	07/11/2014	
	Field Blank 3	13/01/2015	
	Blank 1	14/01/2015	

Around 1 cm in depth surface snow samples were collected into 2-L polyethylene bottles. In order to avoid contaminations, all the material was previously cleaned with ultrapure water and methanol. Samples were preserved at -20 °C to minimize contamination and microbial degradation. Subsequently, samples were melted in an ISO 4 clean room and aliquots were put into pre-cleaned vials to determine ionic species and organic compounds. For analysis of amino acids and phenolic compounds an additional volume of C^{13}-labelled internal standard mix was spiked on the melted aliquots: 990 µL of dissolved snow were taken from each sample and 10 µL of the standard mixture containing phenolic compounds and labeled amino acids at an average concentration of 5 µg mL^{-1} were added.

4.2 Instrumental analysis

To quantify anions, cations [141], sugars [75], phenolic compounds [142], and L- and D-amino acids [79], both in aerosol samples and surface snow samples, analytical methods previously developed and validate have been used.

4.2.1 Instrumental analysis for ionic compounds and carboxylic acids

The detection of all anions was performed using an ion chromatograph (Thermo Scientific Dionex™ ICS- 5000, Waltham, MA, USA) coupled to a single quadrupole mass spectrometer (MSQ Plus™, ThermoScientific, Bremen, Germany). Ionic chromatograph was equipped with an anion exchange column (Dionex Ion Pac AS11 2x250mm), preceded by a guard column Dionex Ion Pac AG11 2x50mm. As mobile phase, NaOH was used with a precise gradient. NaOH was removed before entering the MS source using a suppressor (ASRS 500, 2 mm, Thermo Scientific). The detection of all cations was simultaneously performed using the capillary system in the same ion chromatograph coupled to a conductivity detector. Cationic species were chromatographically separated using a capillary cation-exchange column Ion Pac CS19-4 mm (0.4 x 250 mm) equipped with a guard column Ion Pac CG19- 4mm (0.4 x 50 mm). MSA with a precise gradient was used as mobile phase. For the peak acquisition of anions and cations was used the Chromeleon 6.8 Chromatography data system software. More detailed information about the analytical method for anionic and cationic species can be found in the previous chapter of this thesis or in Barbaro et al. [141], where the same analytical method was applied.

4.2.2 Instrumental analysis for sugars

Sugars were determined and quantified using an ion chromatograph (Thermo Scientific™ Dionex™ ICS-5000, Waltham, US) coupled to a single quadrupole mass spectrometer (MSQ Plus™, Thermo Scientific™, Bremen, Germany). A CarboPac PA10™ column (Thermo Scientific, 2mm x 250 mm) equipped with a CarboPac PA10™ guard column (2 x 50 mm) and an AminoTrap column (2 x 50 mm) was used for the separation of six monosaccharides (arabinose, fructose, galactose, glucose, mannose, ribose, xylose), three disaccharides (sucrose, lactose, lactulose) and two alcohol-sugars (erythritol, maltitol). The mobile phase was NaOH with a precise gradient. It was directly generated by an eluent generator (Dionex ICS 5000EG, Thermo Scientific) and the gradient was 0-3 min, 1 mM; 3-20 min gradient from 10 mM to 20 mM; 20-45 min isocratic elution with 20mM; 45-55 min, column cleaning with 100 mM; 55-60 min, equilibration at 1 mM. A CarboPac MA1™ analytical column (Thermo Scientific, 2 mm x 250 mm) equipped with an AminoTrap column (2 x 50 mm) was used for the separation of the alcohol-sugars (mannitol, aribitol, sorbitol, xylitol, galactitol) and anhydrosugars (levoglucosan, mannosan and galactosan). The mobile phase was NaOH with a precise gradient. It was directly generated by an eluent generator (Dionex ICS 5000EG, Thermo Scientific) and the gradient was: 0-23 min, 20 mM; 23-43 min, column cleaning 100 mM; 43-53 min, equilibration, 20 mM. For both the methods the injection volume was 50 µL and the flow rate was 0.25 mL min^{-1}. NaOH was removed before entering the MS source using a suppressor (ASRS 500, 2 mm, Thermo Scientific). For the quantification of all compounds it was used the response factor method and the$^{13}C_6$- levoglucosan as the internal standard. All concentration values obtained were corrected with the blank values. For the peak acquisition and elaboration was used the Chromeleon 6.8 Chromatography data system software. Further information about the analytical method and quality control for sugars are reported in Barbaro et al. [75].

4.2.3 Instrumental analysis for amino acids

Determination and quantification of free L- and D- amino acids has been performed by HPLC-MS/MS. The HPLC system used for this study was an Agilent 1100 Series HPLC System (Waldbronn, Germany) with a binary pump, vacuum degasser and an autosampler. This HPLC system was coupled with an API 4000 Triple Quadrupole Mass Spectrometer (Applied Biosystem/MSD SCIEX, Concord, Ontario, Canada). MS source was a TurboV electrospray source that operated in positive mode, using the multiple reaction monitoring (MRM). The chromatographic separation was performed with a 2.1 x 250 mm Chirobiotic Tag column (Advanced separation Technologies Inc., USA). The mobile phase was a stoichiometric mixture of two mobile eluents. The eluent A was ultrapure water with a 0.1 % v/v of formic acid. The eluent B was ultrapure methanol with 0.1 % v/v of formic acid. The binary gradient elution was: 0–15 min, an isocratic step with 30% of eluent B; 15–20 min, a gradient from 30 to 100% B; 20–25 min an isocratic washing step with 100% of eluent B; 27–30 min, re-equilibration to 30% eluent B, with a flow rate of 0.2 mL min^{-1}. The injection volume was 10 µL. The quantification was performed using internal standard method. Some amino acids where quantify using its isotope forms, but not for all amino acids a labeled standard was available, so another labeled standard was used for the quantification. In both cases, the results were corrected for daily instrumental sensitivity variations by evaluating the instrumental response factors.

4.2.4 Instrumental analysis for phenolic compounds

Phenolic compounds were well separated using HPLC/(−)ESI-MS/MS. It was used an Agilent 1100 Series HPLC system (Agilent, Waldbronn, Germany) accompanied by a binary pump, a vacuum degasser, an autosampler, and a thermostatic column compartment. For the chromatographic analysis a Zorbax Extend C18 (150 mm × 4.6 mm, 3.5 µm, Agilent) column was used. The injected volume for each sample was 100 µL. The eluition flow was of 500 µL min^{-1}. The mobile phase was constituted by a stoichiometric mixture of two different eluents (eluent A and eluent B). Eluent A was ultrapure water with an 0.01% of formic acid, while eluent B was a solution of methanol/acetonitrile 80/20. The elution program with the combination of the two different eluents was as follows: 0−2 min 85% eluent A, 2−3 min gradient to 70% of eluent A, 3−8 min isocratic elution at 70% of eluent A, 8−16 min gradient to 30% of eluent A, 16−17 min gradient to 0% of eluent A, 17−27 min washing from 27 to 29 gradients to 85% of eluent A and equilibration. The total duration of a complete chromatograph run was 34 minutes. Phenolic compounds were quantified using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX, Toronto, Ontario, Canada) with a Turbo V source. Further details about the analytical method for phenolic compounds were reported in Zangrando et al. 2013 [142].

4.3 Results in aerosol samples

4.3.1 Ionic compounds and carboxylic acids

As a general introduction to the results, it can be said that the general ionic composition was very similar to the one found in the samples collected in the same sampling site during the 2010/2011 austral summer [141]. All water-soluble compounds (anions, cations, sugars, carboxylic acid, amino acids and phenolic compounds), analyzed in this case of study, have a total mean concentration in PM10 aerosol samples (calculated with the sum of different size-segregated fractions), equal to 0.6 ± 0.1 µg m^{-3} **Figure 26**.

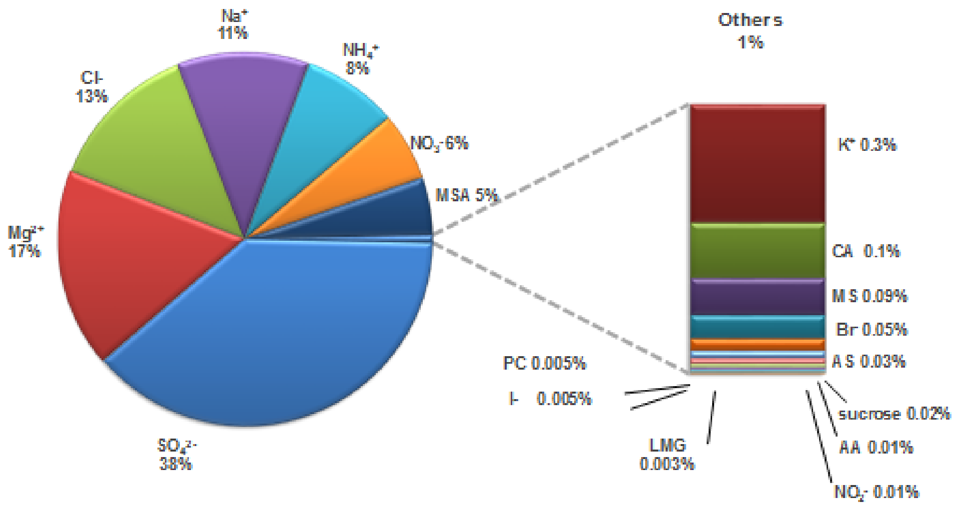


Figure 26. Percentage concentration of water-soluble compounds in the PM10 aerosol samples collected at "Mario Zucchelli Station" (Antarctica) during the austral summer 2014-2015

This total concentration of compounds analyzed in this case of study, represented 66 ± 20% of the PM10 total mass concentrations. This evaluation was done taking into account determinations in other samples which were done by Illuminati et al., 2016 in parallel [143]. Inorganic ions were the preponderant species in the mean composition of PM10 aerosol samples. SO_4^{2-}, whit the mean concentration of 214 ± 53 ng m^{-3} and representing the 38% of the analyzed compounds total concentration, was the most abundant anions in all the samples. The following ionic species were the most concentrated and they are listed in decreasing order: Mg^{2+} (0.10 ± 0.05 µg m^{-3}, 17%), Cl^- (0.07 ± 0.03 µg m^{-3}, 13%), Na^+ (0.07 ± 0.03 µg m^{-3}, 11%), NH_4^+ (0.05 ± 0.02 µg m^{-3}, 8%), NO_3^- (0.03 ± 0.02 µg m^{-3}, 6%) and MSA (0.03 ± 0.01 µg m^{-3}, 5%). The quantification of all the other ionic species highlighted that they represented 1% of the total amount. The chemical composition and the particle size distribution of the aerosol are useful tools to have a further comprehension of the emission sources. In this case of study, it was highlighted that all aerosol samples, collected in the coastal site nearby the MZS station, were characterized by high concentration of ionic species (Na^+, Mg^{2+} and SO_4^{2-}) typically emitted from the sea salt input [144]. Furthermore, these chemical species and also Cl^-, have been founded mainly in the coarse fraction, with a diameter higher than 1 mm, **Figure 27**.

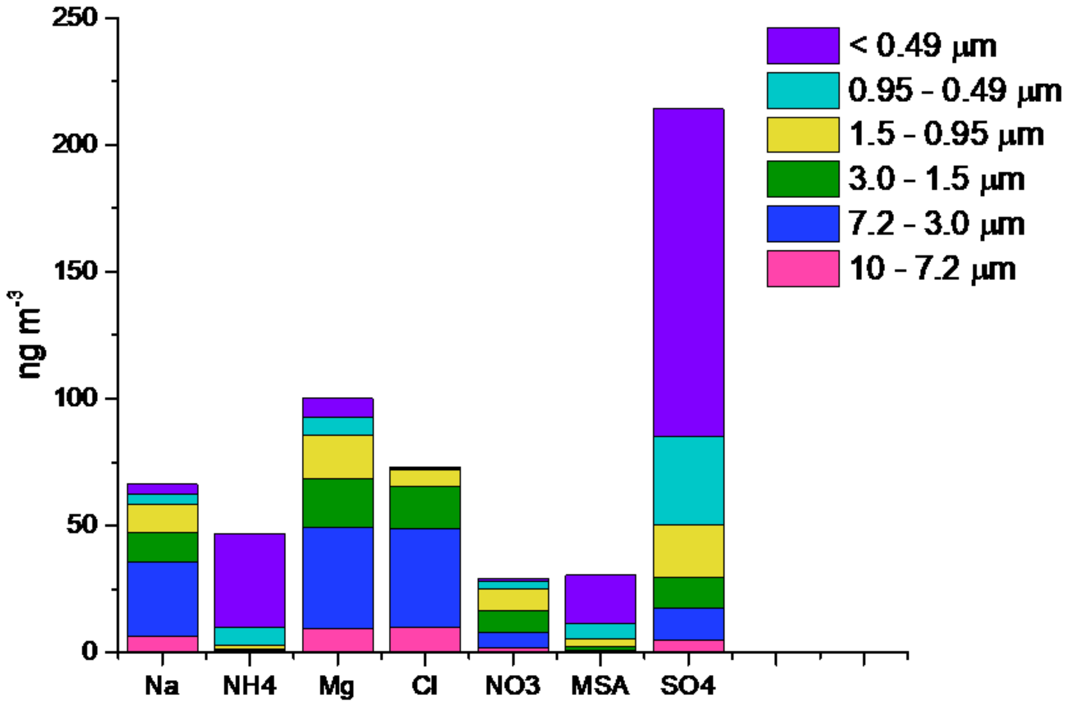


Figure 27. Particle size distribution of the most abundant ionic species in aerosol samples collected at Mario Zucchelli station, Antarctica, from 6 November 2014 to 13 January 2015

The distinction between ss- SO_4^{2-} and nss- SO_4^{2-} permit to study two different emission sources of the SO_4^{2-}. In these samples, sea salt SO_4^{2-} was mainly found on particles with a diameter > 1 mm **Figure 28**.

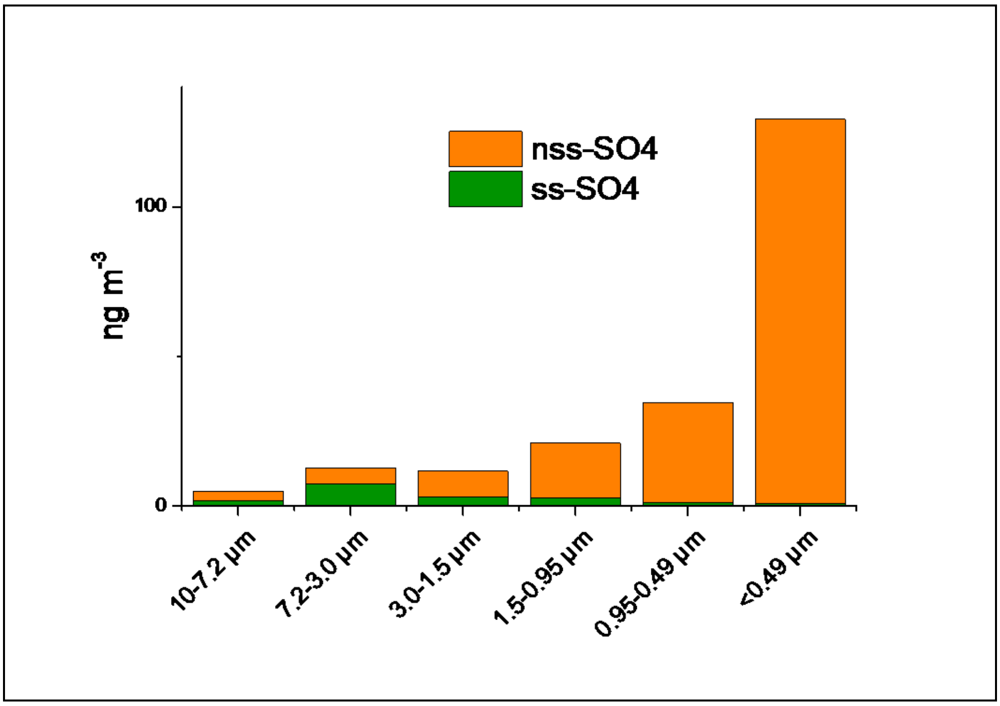


Figure 28. Particle size distribution of sea salt sulfate (ss-SO42-) and non-sea salt sulfate (nss-SO42-) in aerosol samples collected at Mario Zucchelli station, Antarctica, from the 6th November 2014 to the 13th January 2015

Sea salt SO_4^{2-} was compared to Na^+ and Mg^{2+}, which are others sea salt input markers. In samples coming from the 2014/2015 sampling campaign, it was used the SO_4^{2-} to Na^+ ratio to evaluate the sea salt contribution to the total amount of sulphate, taking in account that ratios higher than 0.25 indicate that the seawater was the most preponderant emission source. This evaluation was done on all the different particle sizes. In all fractions values obtained ranged from a minimum of 0.5, found in the coarse fraction (particles diameter higher than 3 mm) to a maximum of 37 in the fine fraction (particles diameter lower than 0.49 mm). This wide range of SO_4^{2-} /Na^+ values highlighted that sulphate is not only produced by sea salt input [111]. As the main emission sources of nss- SO_4^{2-}, as well as MSA, it was proposed phytoplankton bloom in the oceans [103]. Both nss- SO_4^{2-} and MSA were mainly found in the fine fraction (< 0.49 mm) **Figure 27** and **Figure 28**. Furthermore, in aerosol data these two chemical species showed high correlation, with an R^2 value equal to 0.87. Ammonium was mostly distributed in the <0.49 mm fraction **Figure 27**, suggesting as first input source the ocean [117], [119], [118]

As mentioned in the first part of this dissertation of result, carboxylic acids with other water-soluble compounds represented below the 1% of the total amount of concentrations of all chemical species quantified **Figure 26**. Furthermore, carboxylic acids concentrations in samples collected during the 2014/2015 sampling campaign, this case of study, were 10 times lower compared to the ones found out in samples collected during the 2010/2011 sampling campaign [141]. Despite their low respective concentrations they were taken into account as important environmental markers to study in deep the emissions source, depending on their concentrations and particle size distribution [145]. The total mean concentration of carboxylic acids in these PM10 aerosol samples was 0.8 ± 0.5 ng m^{-3}. All the mean concentrations, with very low values, reported below are associated with a high standard deviation. The most concentrated carboxylic acid in the samples was the C_3-malonic acid which presented and average concentration of 0.2 ± 0.1 ng m^{-3}. After this analyte, C_4-succinic acid with an average concentration of 0.2 ± 0.1 ng m^{-3}, C_5-glutaric acid 0.1 ± 0.1 ng m^{-3}, C_2-oxalic acid 0.09 ± 0.08 ng m^{-3}, hC_4-malic acid 0.09 ± 0.06 ng m^{-3}, C_7-pimelic acid 0.04 ± 0.01 ng m^{-3}, C_6-adipic acid 0.04 ± 0.02 ng m^{-3}, C_2-glycolic acid (0.013 ± 0.009 ng m^{-3}). The particle size distribution of these species was mainly concentrated in the fine fraction, < 0.49 mm **Figure 29**.

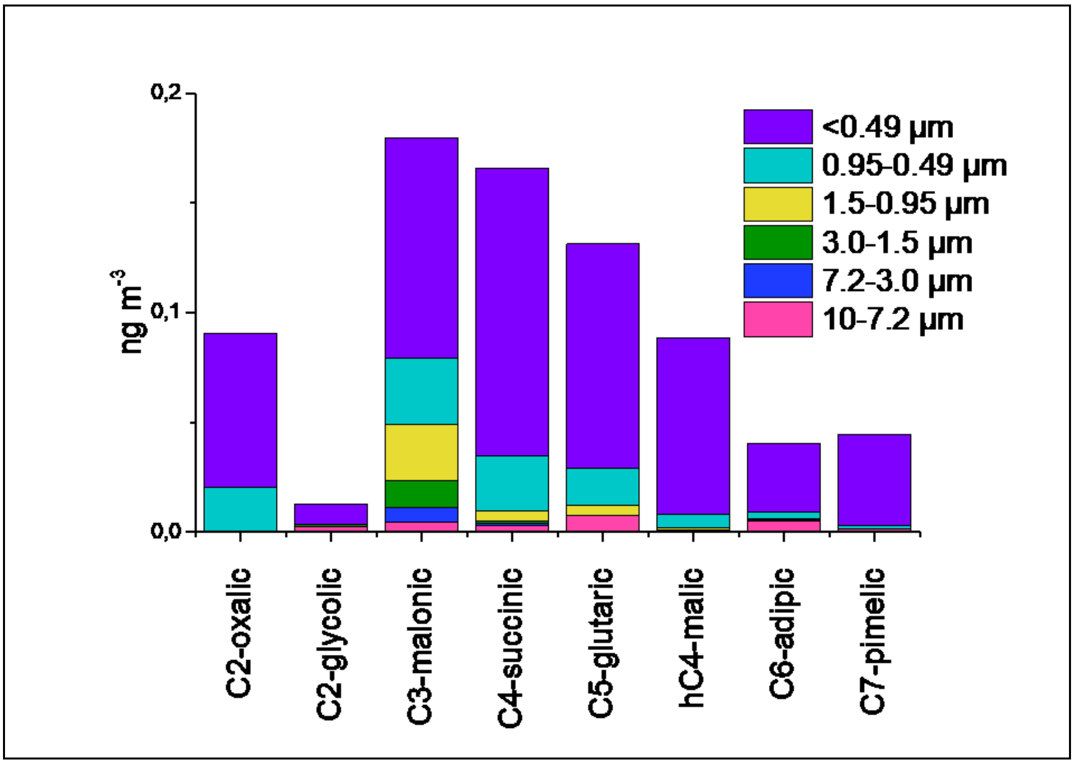


Figure 29. Particle size distribution of carboxylic acids in aerosol samples collected at Mario Zucchelli station, Antarctica, from the 6th November 2014 to the 13th January 2015.

This is due to the carboxylic acids nature of being secondary aerosol products in the atmosphere. C_2-oxalic acid showed different concentration values between samples coming from 2010/2011 sampling campaign and 2014/2015 sampling campaign. In the first case the mean concentration of this analyte was 3 ± 1 ng m^{-3}, while in the second case was 0.09 ± 0.08 ng m^{-3}. The explanation of this difference can be a different photochemical production of carboxylic acids once the alkenes were emitted by phytoplankton [135]. While, on one hand, the presence of C_2-oxalic acid in aerosol samples explain the happening of various oxidation/decomposition reaction in atmosphere, on the other hand the presence of long carboxylic acids chains suggests incomplete photochemical degradation of alkenes in the atmosphere. In this case of study the C_3-malonic acid /C_4-succinic acid ratio was used as indicator of enhanced photochemical production of diacids [138]. This because C_4-succinic acid can be degraded to C_3-malonic acid by decarboxylation reactions started by OH radicals [139]. This ratio in marine aerosol samples, coming from low-to mid-latitudes in the Northern Hemisphere range between 0.9 to 5.8 with a mean value of 2.3. These values compared to the ones found in the urban aerosol are three time higher [139]. These values suggested the photochemical production of C_3-malonic during the long range transport from continents to the marine atmosphere [139]. In samples collected during the 2014/2015 sampling campaign, the average value of the C_3-malonic acid /C_4-succinic acid ratio ranged between 0.8 and 2.3, accompanied by an average value of 1.45. These values suggested that the aerosol collected during the 204/2015 sampling campaign contained these chemical species underwent long range transport processes, where photochemical reactions took place. From the comparison between values obtained in 2014/2015 aerosol samples, over reported, and 2010/2011 aerosol samples (1.5), it was possible to observe that they are quite similar [141].

4.3.2 Sugar compounds

During the 2014/2015 austral summer, the sum of the mean concentrations of anhydrosugars, sugars alcohols, monosaccharides and disaccharides was equal to 0.7 ± 0.6 ng m^{-3}, representing the 0.1% of the total detected compounds. It is known that anhydrosugars, sugar alcohols, monosaccharides and disaccharides represent one of the major classes of water soluble organic compounds (WSOC) in the atmospheric aerosol [77]. Monosaccarides (MS) were the most concentrated family of sugar compounds, with a total PM10 concentration of 0.4 ± 0.4 ng m^{-3}. The glucose showed a concentration of 0.4 ± 0.3 ng m^{-3}, 48% of the total PM10 sugar concentration. During all the 2014/2015 austral summer, glucose concentration had an important temporal variability. In the same sampling site, glucose concentration, during the 2014/2015 sampling campaign was higher than the concentration during 2010/2011 sampling campaign, which was 84 ± 5 pg m^{-3} [75]. There was also a significant difference in the particle size distribution of glucose. In the 2010/2011 samples, glucose was mainly distributed in the fine fraction of the aerosol (< 1 mm) [75], while in 2014/2015 samples, 21% of the glucose was mostly concentrated in the fraction with a diameter > 3.0 mm **Figure 30**.

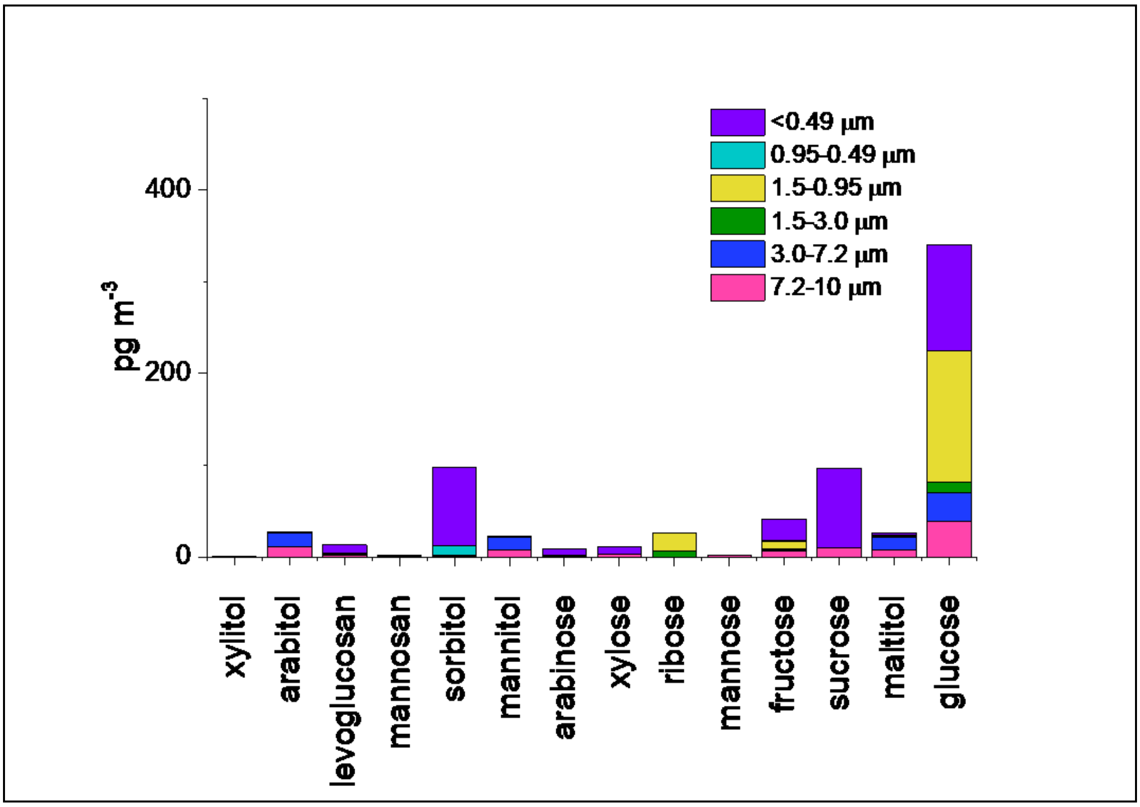


Figure 30. Particle size distribution of sugars in aerosol samples collected at Mario Zucchelli station, Antarctica, during the austral summer 2014-2015

The reason of glucose in the coarse fraction might be correlated to its emission source. The principal source of sugars distributed in this dimensional fraction, may be a biological degradation, such as the degradation of polysaccharides occurred during long range transport processes [146]. The biological degradation as source for sugars, seemed to be confirmed by the high concentration of sucrose, which present a concentration of 96 pg m^{-3} during the 2014/2015 sampling campaign. In 2010/2011 samples, sucrose presented a lower concentration equal to 3 pg m^{-3} [75]. In 2014/2015 samples, sugar alcohols, such as arabitol and mannitol, presented a mean concentration of 170 pg m^{-3} mostly concentrated on the coarse fraction (> 3 mm) **Figure 30**. In this case the distribution of the particles diameters confirmed the relation with primary biological particle such as fungal spores, as well [77], [5]. Among the anhydrosugars, in the 2014/2015 samples, levoglucosan was the most concentrated, 14 pg m^{-3}, follow by mannosan, which was also detected in some samples. The particle size distribution of levoglucosan was mainly concentrated in the fine fraction (< 0.49 μm) **Figure 30**. Levoglucosan is now completely recognized as a specific marker of the phenomena of biomass burning of the cellulose, so it may be found in Antarctic samples as a result of a long-range atmospheric transport [147].

4.3.3 Amino acids

In 2014/2015 aerosol samples, only ten L-amino acids (L-Ala, L-Asp, L-Arg, L-Glu, L-Leu, L-Phe, L-Pro, L-Tyr, L-Thr) and Glycine showed concentration higher than Method Quantification Limit (MQL) of the method used for this case of study. The mean total concentration of amino acids in 2014/2015 aerosol samples was equal to 0.04 ± 0.03 ng m^{-3} and was lower compared to the 2010/2011 amino acids mean total concentration 0.2 ± 0.1 ng m^{-3} [79]. The most abundant free amino acid was glycine, which represented the 60% of the total free amino acids, followed by L-glutamic acid,9%, L- arginine, 6%, L-Alanine, 6%, L-Leucine, 5%, L-Proline, 4%, L-Asparagine, 3%, L-Threonine, 3%, L-Tyrosine, 2%, and L-valine and L- Phenilalanine, 1%. Free amino acids were mainly distributed in the fine fraction of the aerosol (< 1 μm), suggesting a marine emission source, as proposed in previous studies [119], [148], [149], [150], **Figure 31**. Further investigations about aerosol-snow transfers are needed to apply free amino acids as markers of biological emissions.

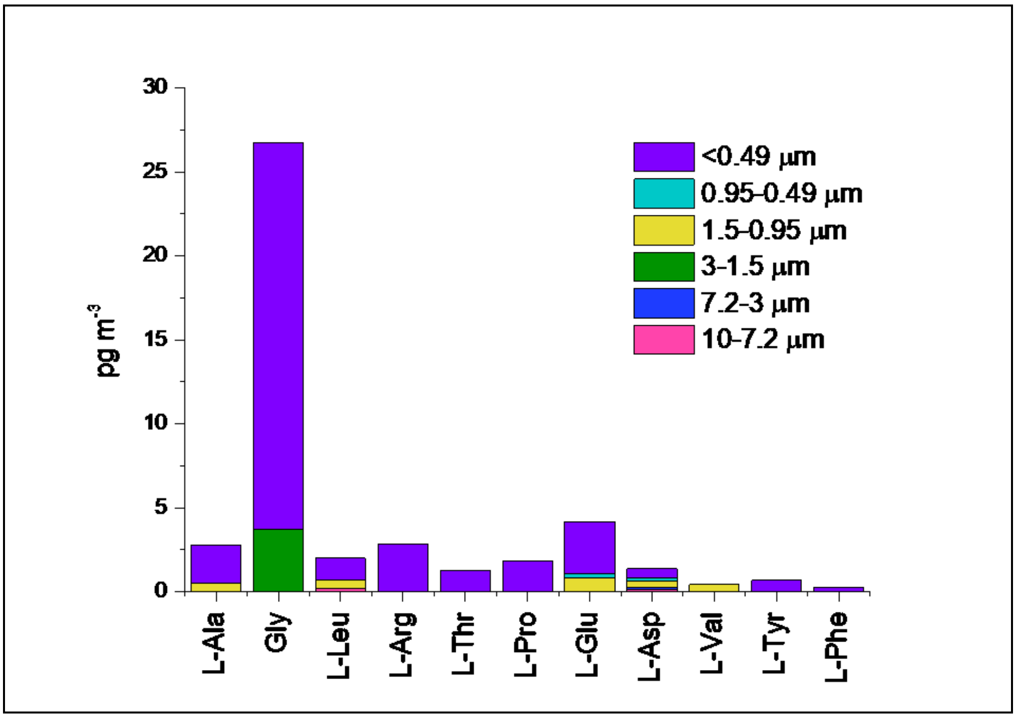


Figure 31. Particle size distribution of amino acids in the aerosol samples collected at Mario Zucchelli station, Antarctica, during the austral summer 2014-2015

4.3.4 Free phenolic compounds (PCs)

In 2014/2015 samples, 92% of the total concentration of free phenolic compounds were mainly found in the <0.49 µm fraction. PCs had a total mean concentration of 29 ± 12 pg m^{-3} **Figure 32**.

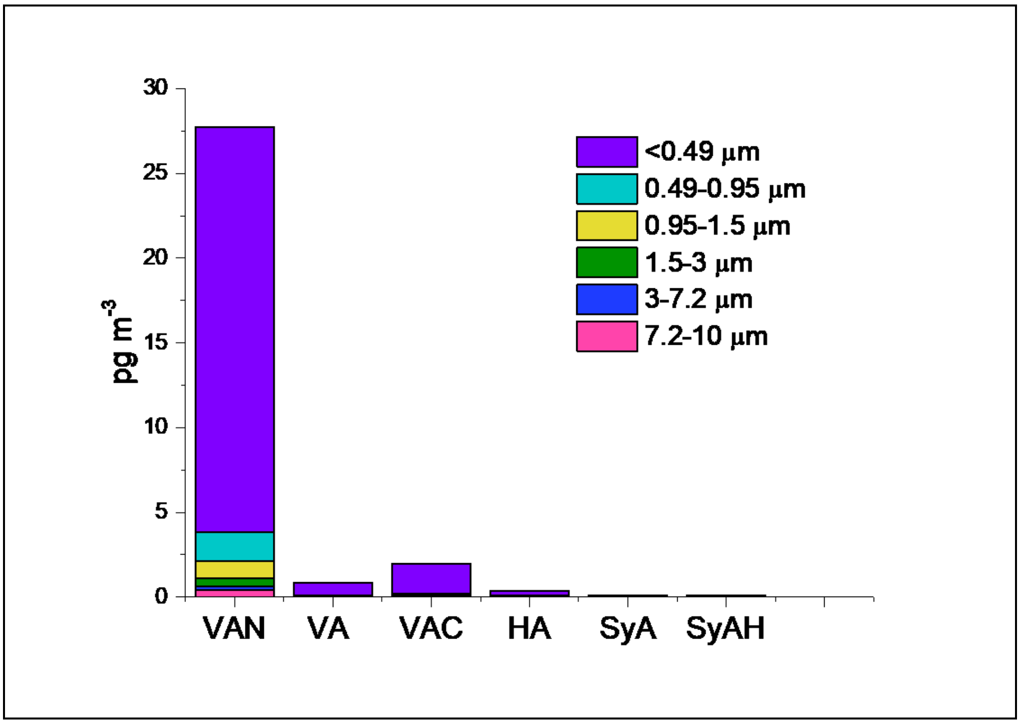


Figure 32. Particle size distribution of the phenolic compounds in aerosol samples collected at Mario Zucchelli station, Antarctica, during the austral summer 2014-2015

Vanillin (VAH) was the most abundant compound with a mean concentration of 0.02 ± 0.01 ng m^{-3}, representing 89% of the total PCs. Then acetovanillone (VAC) showed the second highest mean concentration, 2 ± 1 pg m^{-3} (7%), vanillic acid (VA), 0.8 ± 0.7 pg m^{-3} (3%). Among the syring compounds, traces of syringic acid (SyA), homovanillic acid (HA) and syringaldehyde (SyAH) were found. In the 2014/2015 aerosol samples, they represented 1% of the total concentration of PCs. In the 2010/2011 samples, PCs concentrations very similar were found [8]. O'Dowd and De Leeuw proposed ocean as the most probable local source of PCs through the ejection of fine particles, with a diameter lower than 1 mm, containing organic compounds [151]. In this case of study, the phenomenon of biomass burning was excluded as the main emission source of free phenolic compounds and in this case the marine emission was proposed as the main emission sources for these chemical compounds, as well. It was possible to exclude the biomass burning as main emission source through the simultaneous evaluation of PCs and levoglucosan, specific tracers of the pyrolysis of cellulose. The correlation between the sum of all PCs and levoglucosan was very low (R^2= 0.5). Also, the levoglucosan/VAH ratio and the levoglucosan/VA ratio were evaluated. The levoglucosan/VAH ratio had a value equal to 0.8 and the levoglucosan/VA had a value equal to 6.4, 100 times lower than those obtained for aerosol samples related to the biomass burning [152], [153], [154], [155], suggesting a different emission source for PCs [8].

4.3.5 Composition of surface snow samples

In order to evaluate exchanges between the atmosphere and the surface of the snow, surface snow samples were collected during the aerosol sampling. During the first sampling period there were no precipitation events. Starting from 8th to 11th January 2015, there was a snowfall event and during 10th, 12th and 13th of January 2015 fresh snow samples were collected. Samples collected at Mario Zucchelli station before the snow event showed a total mean concentration of water-soluble compounds equal to 66 $\mu g\ g^{-1}$. In 2014/2015 surface snow samples, the most abundant species were Na^+ with a total mean concentration of 22 $\mu g\ g^{-1}$, Mg^{2+} 22 $\mu g\ g^{-1}$, Cl^- 14 $\mu g\ g^{-1}$ and SO_4^{2-} 5 $\mu g\ g^{-1}$. These compounds may have been deposited on the superficial snow layer thanks to the dry deposition of marine aerosol. In samples collected after the snow event (from the 8th to the 11th of January), the total mean concentration of the water-soluble compounds showed a decrease, in fact it was 9 $\mu g\ g^{-1}$. This decrease was probably due to a dilution effect that the surface snow layer had with the deposit of the fresh snow **Figure 33**.

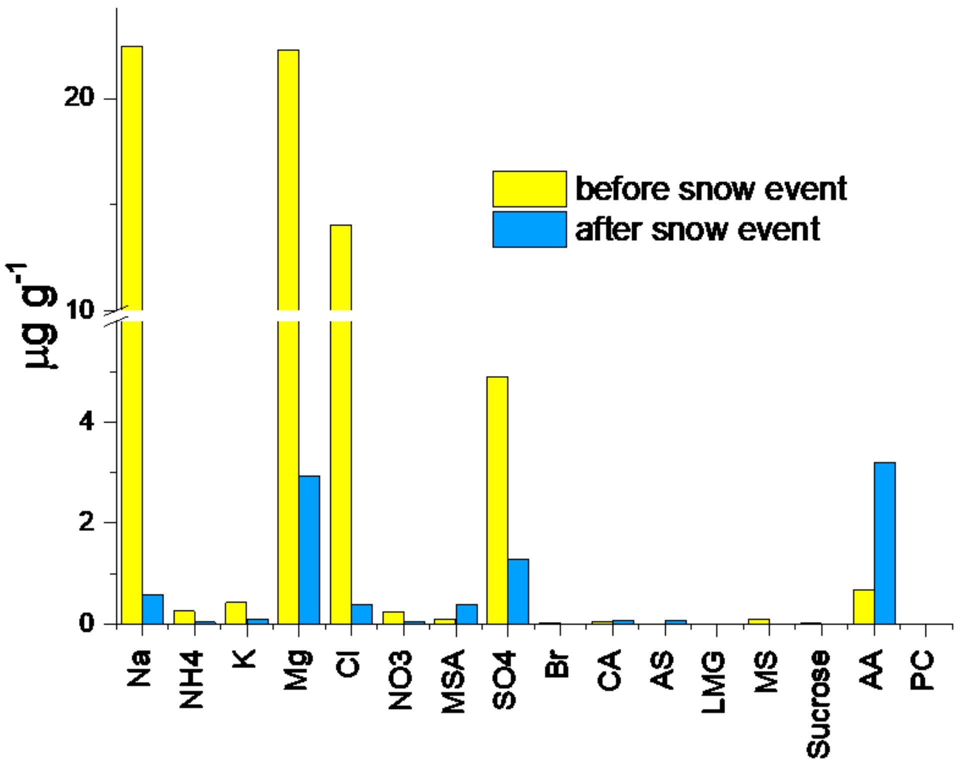


Figure 33. Composition of water-soluble compounds in surface snow collected at MZS during the austral summer 2014-2015. Comparison between the mean concentrations detected before the snow event, 9 January 2015, and after the snow event

The most abundant compounds were still Mg^{2+} with a mean concentration equal to 3 μg g^{-1}, SO_4^{2-} 1 μg g^{-1}, Na^+ 0.6 μg g^{-1} and Cl^- 0.4 μg g^{-1}. On the other hand, amino acids showed an increase after the snowfall: the amino acids total mean concentration in samples before the snowfall was equal to 0.6 μg g^{-1}, while after the snow event the total mean concentration was 3 μg g^{-1}. A possible source of free amino acids in fresh snow could be the degradation of proteinaceous material that fell with the snow. In 12th January samples, when the snowfall had ceased, was observed the major increase of amino acids compounds **Figure 34**.

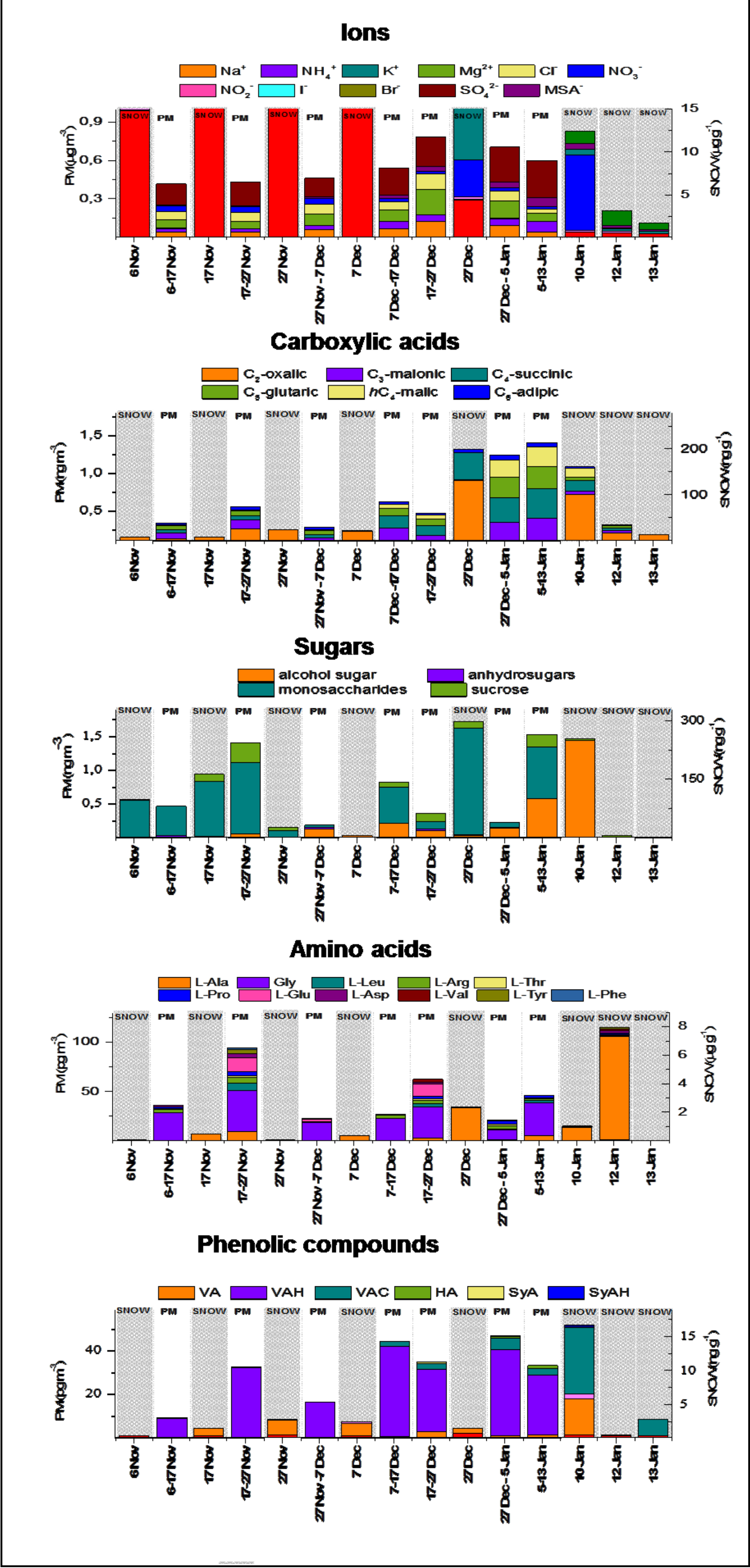
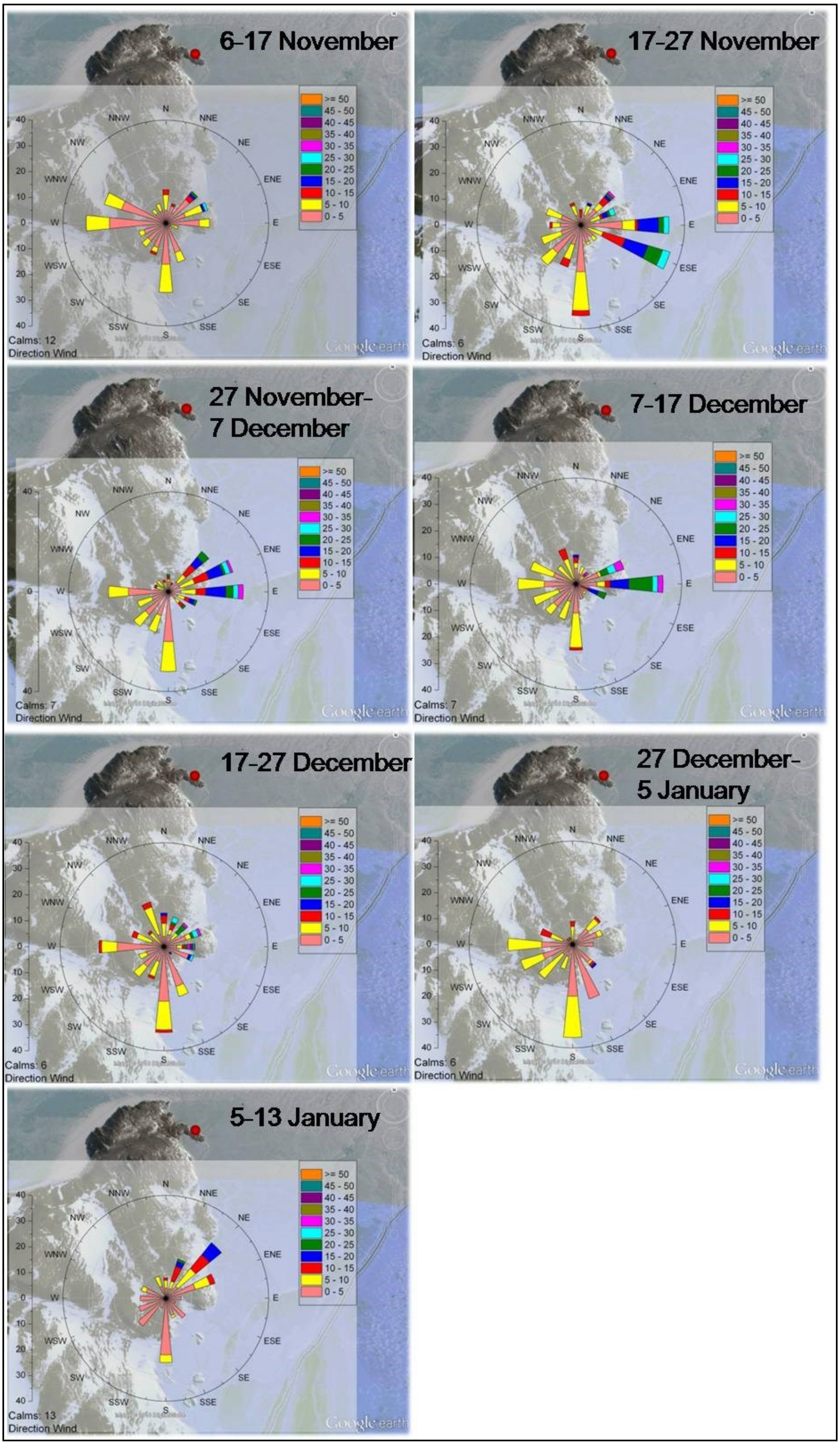


Figure 34. Concentration trends of each class of compounds investigated in aerosol samples (PM) and snow samples

On samples collected the day after, the 13th of January was observed an unclear decrease of amino acids. Certainly, further investigations are needed to completely and deeply understand the behavior of amino acids in the snowpack. Among the anhydrosugars, mannitol and arabitol showed increasing concentrations, confirming the deposition of biological material when snow events occurred. On the 27th of December, mannitol had a concentration equal to 3 ng g^{-1}, while its concentration during the 10th of January was equal to 241 ng g^{-1}, suggesting a deposition of primary biological material, such as airborne fungal spore [5].

4.3.6 Aerosol-snow transfer processes of water-soluble compounds

In the **Figure 34** are shown concentrations of each class of compound investigated in aerosol and snow samples. Until 27th December 2014, aged snow samples were collected. Samples collected during 10th, 12th and 13th January 2015 contained fresh snow, collected directly after a snowfall which took place between 8th to 11th January 2015. In the second half of December, mostly in the 17 and 27 December samples, the PM_{10} concentration of the most important ions increased, having a maximum of their concentration during this same period **Figure 34**. The reason of this increase is probably due to seasonal reduction of the pack ice extent. In the end of the 2014/2015 sampling campaign a general decrease of concentrations was observed, and it was probably due to the abundant snowfall. Illuminati et al. [143] observed the same behaviour for the PM_{10} mass concentration, suggesting that the cause was the same. In aged snow samples, the ions the most concentrated were Na^+, Mg^{2+}, Cl^- and SO_4^{2-}. Furthermore, sea salt ions were found in the coarse fraction of the particulate matter **Figure 27**. These compounds could be removed from the atmosphere probably by the dry deposition of coarse particles. In fresh snow, from 10th to 13th of January, it was observed a general decrease in ions concentration, probably these ions were diluted by snowfall [156], **Figure 34**. This dilution process seemed to affect mostly the Mg^{2+} ion **Figure 34**. In 17th November snow sample, high concentrations of sea salt ions were observed. When this sample was collected the wind, direction was mainly from the East-South-East direction **Figure 35**.



6-17 November

17-27 November

27 November-7 December

7-17 December

17-27 December

27 December-5 January

5-13 January

Figure 35. Wind rose created with meteorological data collected near the sampling site, at AWS Eneide station of the PNRA (www.climantartide.it)

Presumably, the main source of sea salt compounds, found in these samples, was the dry deposition of biogenic material coming from areas with frost flowers. This is also confirmed by a negative correlation between sea salt compounds and nss-SO_4^{2-}, calculated in 17th November snow samples [110], [157], **Figure 36**.

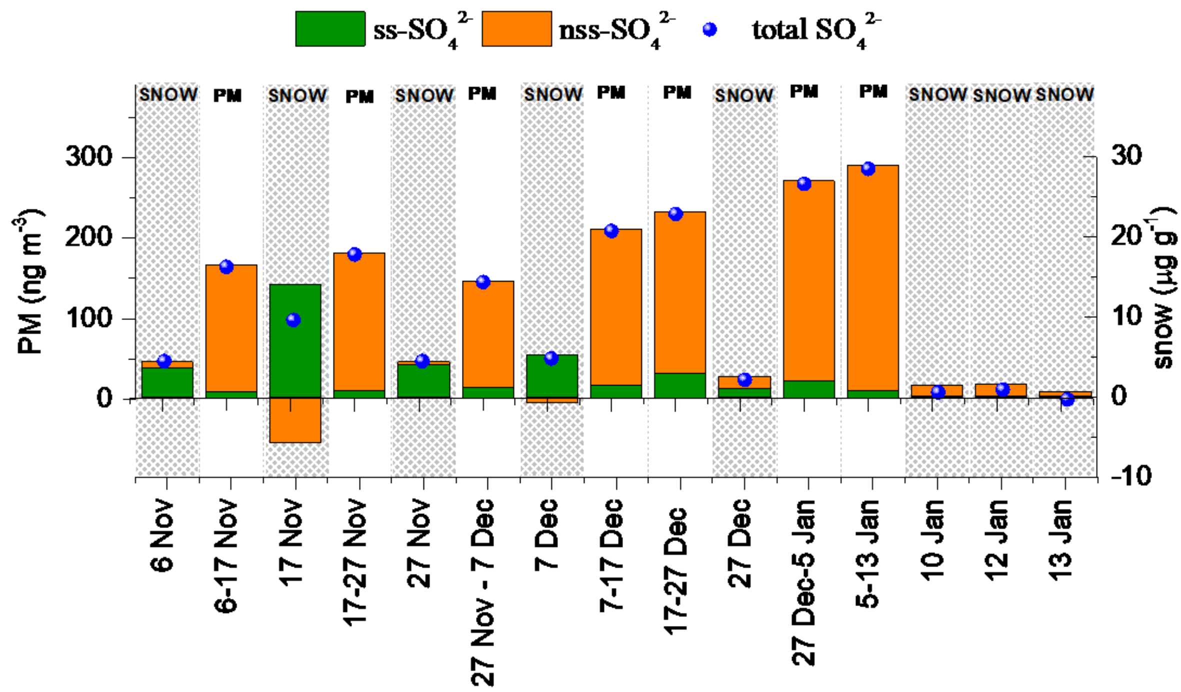


Figure 36. Trend of concentrations of sea-salt sulfate (ss-SO_4^{2-}), non-sea-salt sulfate (nss- SO_4^{2-}) and total sulfate (SO_4^{2-}) in 2014-2015 aerosol samples (PM) and 2014-2015 snow samples collected at Mario Zucchelli station

Nss-SO_4^{2-} concentration increased at the beginning of the Antarctic summer, **Figure 36**, and this is related with the phytoplankton bloom on the ocean surface, the biogenic source [113]. Samples collected before the snowfall (27th December sample), during the snowfall events (10th January sample) and after the snow events (12th and 13th January samples) presented a concentration of nss-SO_4^{2-} comparable and showed only a small decrease in the 13th January sample **Figure 37**.

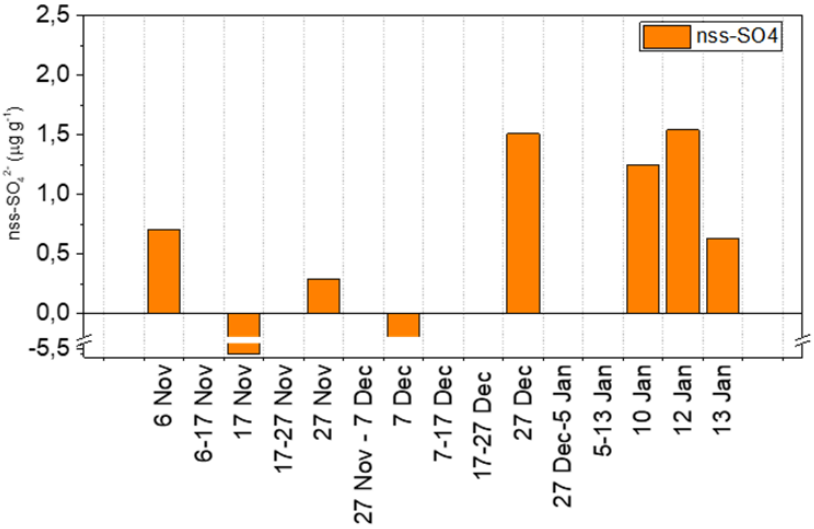


Figure 37. Trend of concentrations of non-sea-salt sulfate (nss-SO_4^{2-}) in 2014-2015 snow samples collected at Mario Zucchelli station

This decrease suggests that the wet deposition processes were negligible for this species and they also seem to be independent of the accumulation rate due to inefficient scavenging of nss-SO_4^{2-} aerosols by Antarctic snow [156]. In snow samples, among all carboxylic acids, C_2-oxalic was the most concentrated. In aerosol samples C_3-malonic, C_4-succinic and C_5-glutaric were the carboxylic acids the most concentrated **Figure 34**. Different evaporation rates, different particle size distributions, different emission sources and different snow chemistry are few of the several possible reasons for this different aerosol and snow composition of carboxylic acids. Carboxylic acids have a low volatility and a high polarity, so their evaporation from the snow surface is unlikely. Carboxylic acids with shorter chains, such as C_2 and C_3 diacids, can exist in the gas phase [158]; they could be also adsorbed on the surface of snowpack more than C_4 and C_5 acids due to their polarity. In snow samples, **Figure 34**, C_2-oxalic and C_3-malonic acids were the most abundant species, supporting the absorption of these species on the surface of the snow. Carboxylic acids are mainly distributed in the fine fraction, demonstrating that deposition velocities of each carboxylic acid may be similar **Figure 29**. Other reasons that could influence carboxylic acids concentrations on the snow surface, could be different emission sources and different snow chemistry. Carboxylic acids, as water soluble compounds, are strongly influenced by precipitation events. Focusing on snow samples and on the concentrations of carboxylic acids during the snowfall event (10th January sample) higher concentrations of carboxylic acids were observed, compared to samples collected after the snowfall events (12th and 13th Janaury samples) that present low dilution effects **Figure 34**. C_2-oxalic acid can be scavenged by both dry and wet deposition, it can be also generated by photochemical processes on the snow surface, as C_2-oxalic acid is the end-product of several photochemical reactions as suggested by Kawamura et al. [89]. Higher concentrations of C_2-oxalic acid were found before the snowfall event, in the aged samples. In the first period of the sampling campaign, monosaccharides sugars, such as glucose were the most concentrated in the atmosphere, while as Antarctic summer progressed, concentrations of sugar alcohols, such as mannitol and arabitol, increased with higher biological production. It was observed the same trend also in the snow composition. During the first period, monosaccharides were the most abundant species in snow samples, while sugar alcohols were scavenged from the air from the 27th December onwards. During snowfall, mannitol was the main compound scavenged to the surface-snow, but it underwent considerable dilution after the snow event **Figure 34**. In aerosol and snow samples, the main amino acids was glycine. Glycine is the amino acid with the highest stability [159]. Between the glycine concentrations in snow and aerosol samples, there was an unclear correlation **Figure 34**. When an increase of glycine in aged snow samples was observed, simultaneously a comparable decrease of glycine in aereosol samples happened. The decrease in aerosol samples ranged between 27th November and 7th December seemed to be related with an increase in the glycine concentration in the snow sample collected the 7th December **Figure 34** and **Figure 38**.

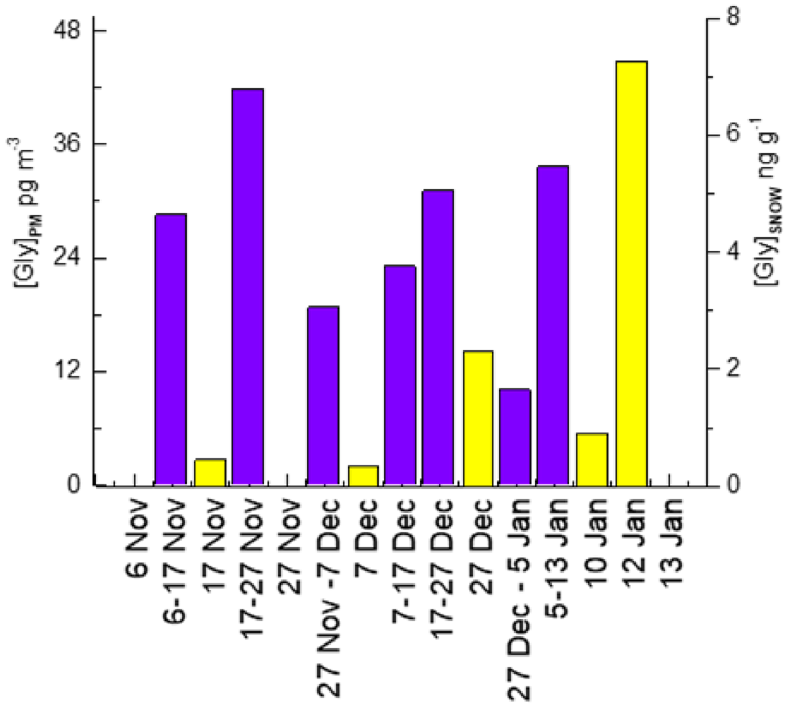


Figure 38. Trend of concentrations of glycine in 2014-2015 aerosol samples (PM) and 2014-2015 snow samples collected at Mario Zucchelli station

Higher aerosol concentrations of glycine are not related with an increase in glycine snow concentrations, so dry deposition seemed to be a negligible factor for the enrichment of glycine in the snow samples After the snowfall (8th and 11th January), the glycine concentration increased and this behaviour is probably due to a degradation of biological material in the snow surface, as it was observed in the 12th January snow samples **Figure 34**. Focusing on the free phenolic compounds, vanillin was the most concentrated compounds in the aerosol samples, while vanillic acid, its oxidation product, was the dominant species in the aged snow **Figure 34**. During the snow event, high concentrations of vanillin were observed along with other PCs. However, over the subsequent sampling days, it was noticed a large decrease of these compounds and this could be due to a dilution effect and to their semi-volatility, which influences the re-partition of these compounds between snow and the atmosphere, as well. After snowfall VA and SyA, the oxidized forms of VAH and SyAH, were the main PCs present.

4.4 Conclusions of this case of study

In this case of study aerosol and surface snow samples, collected from November 2014 to January 2015 at the coastal site of the Italian base, Mario Zucchelli station, were analysed. Ionic species, carboxylic acids, sugars, amino acids and free phenolic compounds were detected. In aerosol samples, the characterization of the water-soluble compounds showed that their account was of about 60% of the total PM_{10} mass concentration. Sea salt input and biogenic input were identified as the two predominant sources. The first one was characterised by high concentration of Na^+, Mg^{2+}, Cl^- and SO_4^{2-}; the second one was characterised by high contribution of amino acids, sugars and phenolic compounds. In this case of study, the investigation of the WSOC in aerosol samples was combined with the study of WSOC in surface snow and it was the first study in which amino acids and sugars were quantified. Ions were identified in the aerosol and they were mainly distributed in the coarse fraction of atmospheric aerosol. Ions were also the most abundant compounds in snow samples, suggesting that the main air-snow transfer process was the dry deposition. Sugars presented a similar composition in both aerosol and snow samples. In surface snow samples an increase in concentration of alcohol sugars, tracers of fungal spores in the atmosphere, was found, suggesting that they could also be markers for this source in climatic studies. Amino acids were an important component in the surface snow samples. In addition to aerosol input, amino acids could also originated from the decomposition of the biological material on the surface, as demonstrated by high concentrations of amino acids after snowfall. The reduction of temporal resolution of this and other study located in Antarctica is due to the low concentrations of water-soluble compounds in Antarctic aerosol, meaning aerosol has to be sampled for ten days to obtain concentrations above the detection limit. Further studies over subsequent Antarctic expeditions are essential to improve the sample numbers to have a full understand the applicability of these compounds in the study of ice cores for paleoclimatic investigations.

5 STUDY OF AIRBORNE PARTICULATE MATTER COMPOSITION IN SAMPLES (PM_1, $PM_{2.5}$ AND PM_{10}) COLLECTED AT SERNAGLIA DELLA BATTAGLIA

This chapter is based on preliminary results obtained during a six-month period abroad spent at Helmholtz Zentrum München (HMGU), Germany, from the 25.09.2018 to the 01.04.2018. The aim of my period abroad was twofold: firstly, to learn a new instrumentation the Gas Chromatography coupled to Time-Of-Flight Mass Spectrometry (GC-tof-MS) and secondly, the practical application of an analytical method developed in the laboratories of Comprehensive Molecular Analysis (CMA) at HMGU. The main purpose of this investigation was the characterisation of the airborne particulate matter of a rural area, valuating the application of a new wide range of environmental markers able to describe both natural and anthropogenic emissions. The analytical method is an in-situ derivatization direct thermal desorption, followed by gas chromatography time-of-flight mass spectrometry (IDTD-GC-TOFMS) for the determination of particle-bound non-polar and polar organic species in samples from ambient particulate matter [160]. *ARPAV (Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto) provided me* PM_1, $PM_{2.5}$ *and* PM_{10} *samples collected at Sernaglia della Battaglia, Treviso, Italy during several months in 2017.* PM_1, $PM_{2.5}$ *and* PM_{10} *samples were collected simultaneously using three different samplers one next to the other. It was decided to focus analyses on three different periods of the total sampling period in 2017: one period during winter, with a total amount of samples analysed equal to 21, one period during spring (n= 63) and one period during early summer (n= 15). Each* PM_1, $PM_{2.5}$ *and* PM_{10} *samples was analysed applying the IDTD-GC-TOFMS method. Seven main families of organic compounds were determined, each one composed by several chemical compounds, which are relevant environmental markers: acids, alkanes, alkanols, anhydro sugars, polycyclic aromatic hydrocarbon (PAH), oxidized polycyclic aromatic hydrocarbon (o-PAH), resin acids and triterpenoids. The respective compositions of* PM_1, $PM_{2.5}$ *and* PM_{10} *aerosol samples were investigated and discussed, taking into account the temporal variations during the three different periods investigated.*

5.1 Samples collection and processing

A simultaneous sampling campaign of PM_{10}, $PM_{2.5}$ and PM_1 aerosol were carried out in Sernaglia della Battaglia, a small city in the province of Treviso, in the region of Veneto in the north of Italy (lat. 45.8720, long12.1339). The sampling campaign started in December 2016 and lasted until July 2017**, Table 12**. The sampling sites are operated by the Regional Environmental Protection Agency (*ARPAV*, *Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto*). The PM_{10} samples were collected using a Tecora Charlie sequential module sentinel, with a nominal flow of 38.3 L/min. The $PM_{2.5}$ and PM_1 samples were collected using low-volume samplers Skypost Tecora set according to the European standard EN 12341:2014 protocol, with a nominal flow of 38.3 L/min. Samples were collected on quartz fibre filters (47 mm Ø, Whatman QMA, GE Healthcare, USA) over 24 hours, starting at midnight. As reported in EN 12341:2014 protocol, filters were conditioned for a period of at least 48 hours before and after being weighted in a conditioning chamber equipped with a control system for constant temperature and humidity, 20 ± 1 °C and of 50 ± 5% relative humidity, (Emerson S05KA Emerson Network Power — Piove di Sacco, Italy). An analytical balance (Sartorius series Genius, mod. SE2, Germany) with a sensitivity of 0.0001 mg was used to weight the PM mass (average of two measures). Samples were stored in clean Petri slides at a temperature of −20 °C to avoid sample degradation and losses of the more volatile compounds. Samples have been transported from ARPAV cold rooms, preserving the cold chain, to the Comprehensive Molecular Analytics (CMA), Helmholtz Zentrum in Munich, Germany. There, samples were stored again at -20 °C to preserve them from degradation. It was chosen to analyse three different sets of PM_{10}, $PM_{2.5}$ and PM_1, in order to investigate the aerosol composition during three different seasons of the 2017 year (winter, spring and late spring/summer period). The first set of aerosol samples was from 30.01 to 11.02 (winter); the second samples set was from 16.04 to 06.05 (spring) and the third samples set was from 12.06 to the 16.06 (early summer).

Table 12. List of aerosol samples collected at Sernaglia della Battaglia (TV), during the sampling campaign

	Date of sampling	PM_1	$PM_{2.5}$	PM_{10}
Sernaglia della Battaglia (TV)	**1st period**			
	30/01/2017	15QT201	15QT330	15QT182
	31/01/2017	15QT202	15QT331	
	01/02/2017	15QT147	15QT332	
	03/02/2017	15QT203	15QT248	
	05/02/2017	15QT253	15QT356	
	06/02/2017	15QT254	15QT357	
	07/02/2017	15QT335	15QT358	
	08/02/2017	15QT336	15QT359	15QT327
	11/02/2017	15QT382	15QT376	15QT289
	2nd period			
	16/04/2017	15QT751	15QT737	15QT744
	17/04/2017	15QT752	15QT738	15QT745
	18/04/2017	15QT753	15QT739	15QT746
	19/04/2017	15QT754	15QT740	15QT747
	20/04/2017	15QT755	15QT741	15QT748
	21/04/2017	15QT777	15QT784	15QT798
	22/04/2017	15QT778	15QT785	15QT799
	23/04/2017	15QT779	15QT786	15QT800
	24/04/2017	15QT780	15QT787	15QT801
	25/04/2017	15QT781	15QT788	15QT802
	26/04/2017	15QT782	15QT789	15QT803
	27/04/2017	15QT783	15QT790	15QT804
	28/04/2017	15QT805	15QT812	15QT819
	29/04/2017	15QT806	15QT813	15QT820
	30/04/2017	15QT807	15QT814	15QT821
	01/05/2017	15QT808	15QT815	15QT822
	02/05/2017	15QT809	15QT816	15QT823
	03/05/2017	15QT810	15QT817	15QT824
	04/05/2017	15QT811	15QT818	15QT825
	05/05/2017	15QT750	15QT881	15QT861
	06/05/2017	15QT868	15QT882	15QT862
	3rd period			
	12/06/2017	16QT065	16QT058	16QT079
	13/06/2017	16QT066	16QT059	16QT080
	14/06/2017	16QT067	16QT060	16QT081
	15/06/2017	16QT068	16QT061	16QT082
	16/06/2017	16QT131	16QT138	16QT124

Punches of quartz-fiber filters, from a minimum diameter of 3 mm, for the more loaded samples, to a maximum diameter of 10 mm, for the less loaded ones, were cut. On each punch were spiked two isotope-labelled internal standard mixtures. The first internal standard mixture was non-polar and it consisted of fifteen deuterated PAH, two deuterated o-PAH and four deuterated alkanes. The second internal standard mixture was polar and contained $^{13}C_6$-levoglucosan (Omicron Biochemicals, USA), $^{13}C_6$-vanillin (Larodan, Sweden) and D_{31}-palmitic acid (CIL, USA). Punches of samples were placed into goose-neck glass-liners for thermal desorption which were sealed with PTFE caps. For each sample a freshly deactivated GC liner was used. Each liner was previously deactivated putting it at 550 °C for a period of twelve hours then a derivatization of the glass surface with chlorotrimethylsilan (TMCS, Merck, Germany) was done for a further twelve hours. Then a small amount of glass wool was put above the goose-neck in order to prevent particles from the filter entering the capillary column. Before transfer liners entered the thermal injector unit, on quartz filters samples, in the glass-liner, 10μL of MSTFA (ThermoFisher, USA) were added, by a sampling robot.

5.2 Instrumental analysis

Aerosol samples were analyzed by an in-situ derivatization thermal desorption-gas chromatography and time-of-flight mass spectrometry (IDTD-GC-TOFMS). This methodology for the determination of non-polar and polar organic compounds was first developed by Orasche et al. [160]. The analytical method provides a first part with an in-situ derivatization and a thermal desorption of polar organic compounds directly from the particulate matter on the filters. The first step of the derivatization is the addition of the MSTFA directly on the punch of the filter. During the second step carrier gas is enriched with derivatization reagent by switching to a second pathway leading carrier gas over a cartridge filled with MSTFA to keep a surplus of MSTFA during the thermal desorption process. The second part of the analytical method, after the thermal desorption, is focused on the gas chromatography separation; starting from a T= 70 °C and heating up the GC oven to 130 °C at a rate of 80 °C min^{-1}. Then the rate is lowered to 8 °C min^{-1} until a temperature of 330 °C was reached followed by an isothermal time of 30 min. A Pegasus III TOFMS, with a Chroma TOF software package, LECO, USA, carries out the identification and quantification of target compounds. The data acquisition range was m/z 35 to 500 with an acquisition frequency of 25 spectra per second that is necessary for reliable peak deconvolution. With this method it is possible to determine simultaneously compounds such as acids, alkanes, anhydro sugars, alkanols, lignin dimers, lignin tracers, nitro-organic, PAHs, o-PAHs, polyols, resin acids and triterpenoids [161], [162], [163], [164].

5.3 Results

In PM_1, $PM_{2.5}$ and PM_{10} samples three different sampling periods during 2017 were investigated. The first set of samples were collected between 30.01.2017 and 11.02.2017; the second set was collected between 16.04.2017 and 06.05.2017 and the third set was collected between 12.06.2017 and 16.06.2017. Seven different families of chemical compounds were identified and quantified. 30 polycyclic aromatic hydrocarbons (PAH) and alkylated PAH, 14 alkanes, 10 oxidized polycyclic aromatic hydrocarbons (o-PAH), 3 anhydro sugars, 3 resin acids, 3 acids, 2 triterpenoids. **Table 13** fully describes names of chemical compounds analised.

Table 13. List of detected compounds and their respective chemical family of belonging

Family	Compounds			
PAH	Fluoranthene (FLU)	Acephenanthrylene (ACE)	Pyrene (PYR)	
	Benzo[c]phenanthrene	Benzo[ghi]fluoranthene	Benz[a]anthracene (BaA)	
	Cyclopenta[cd]pyrene	Chrysene (CRY)	Benzofluoranthenes (BbkF)	
	Benz[e]pyrene (BeP)	Benz[a]pyrene (BaP)	Perylene (PER)	
	Anthanthrene	Dibenz[ah]anthracene (DiBaA)	Indeno[1,2,3-cd]pyrene (IND)	
	Picene	Benzo[ghi]perylene (BaPy)	Coronene (COR)	
	Retene (RET)	PAH 302:1	PAH 302:2	
	1-Methyl-benz[a]anthracene	Naphtho[1,2-kb]fluoranthene	Dibenz[al]pyrene	
	Naphtho[2,3-b]fluoranthene	Dibenz[ae]pyrene	Naphtho[2,1-a]pyrene	
	Naphtho[2,3-a]pyrene	Dibenz[ai]pyrene	Dibenz[ah]pyrene	
O-PAH	1H-Phenalen-1-one	Xanthone		
	9,10-Anthracenedione (ANQ-DO)	Cyclopenta(def)phenanthrenone (CPPH-O)		
	1,8-Naphthalic anhydride (NAP-AN)	1,8-Naphthalaldehydic acid (NAP-AC)		
	11H-Benzo[a]fluoren-11-one (11HBaFone)	7H-Benzo[c]fluorene-7-one (11HBcFone)		
	11H-Benzo[b]fluoren-11-one (11HBbFone)	7H-Benzo[de]anthracen-7-one (11HBdeFone)		
Alkanes	Docosane (C_{22})	Tricosane (C_{23})		
	Tetracosane (C_{24})	Pentacosane (C_{25})		
	Hexacosane (C_{26})	Heptacosane (C_{27})		
	Octacosane (C_{28})	Nonacosane (C_{29})		
	Triacontane (C_{30})	Hentriacontane (C_{31})		
	Dotriacontane (C_{32})	Tritriacontane (C_{33})		
	Tetratriacontane (C_{34})	Pentatriacontane (C_{35})		
Anhydrous sugars	Galactosan (GAL)	Mannosan (MAN)	Levoglucosan (LEV)	
Resin acids	Isopimaric acid	Dehydroabietic acid, methyl ester	Dehydroabietic acid	
Acids	Stearic acid	Eicosanoic acid	Adipic acid	
Triterpenoids	α-sitosterol	Stigmasta-3,5-dien-7-one		

5.3.1 Results of PM_1 samples

PM_1 samples, anhydro sugars (the sum of levoglucosan, mannosan and galactosan) are the most concentrated compounds during the first and the second period, 30.01.2017-11.02.2017 and 16.04.2017- 06.05.2017, while during the third period, 12.06.2017-16.06.2017, acids are the class of compounds most present in aerosol samples **Figure 39**. During the first period, anhydro sugars showed a median concentration of 1113 ng/m^3, which in represented 85 % of the chemical markers investigated in the PM_1 samples. During the second period they showed a median concentration of 179 ng/m^3 which in represented 63% of the chemical markers investigated in the PM_1. During the third period they showed a median concentration of 26 ng/m^3 which in represented 27% of the chemical markers investigated in the PM1, exceeded by acids with a median concentration of 31 ng/m^3 which in represented 59% of the chemical markers investigated in PM_1. The trend of anhydro sugars showed a general decrease in concentrations through the spring and even more during early summer, highlighting a general bigger impact of these compounds during the colder period. This trend of decrease was common for every chemical compound here analysed, except for the acids and alkanes, whose concentration increased through spring and late spring/summer.

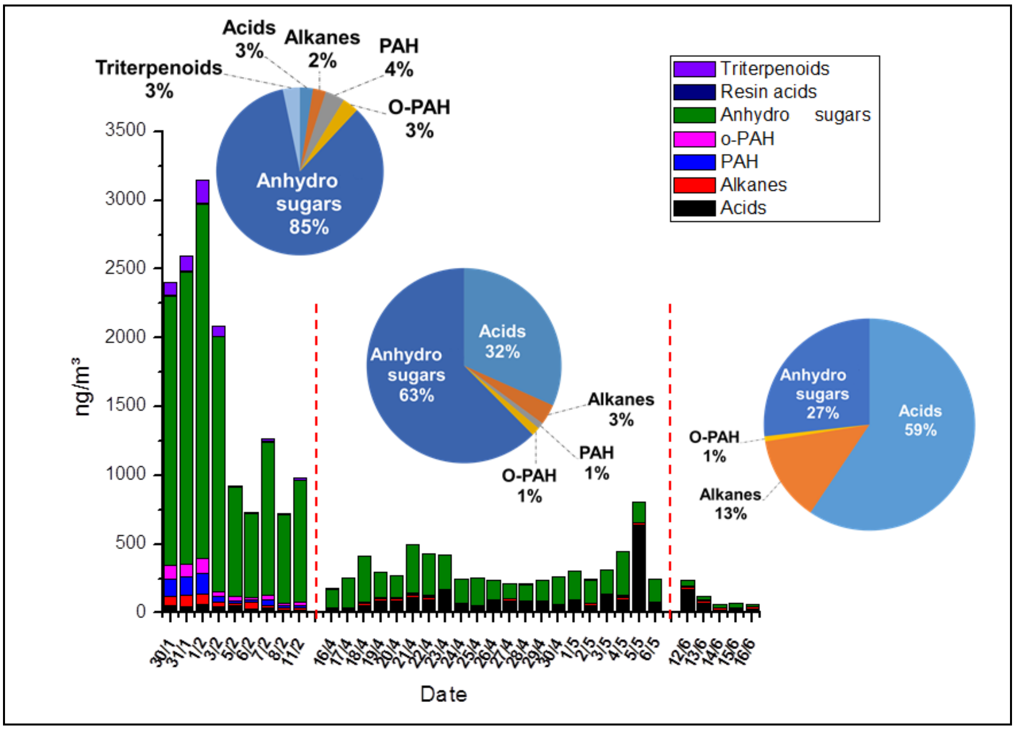


Figure 39. PM_1 samples composition of Sernaglia della Battaglia, during three different period 30.01- 11.02, 16.04- 06.05 and 12.06- 16.06. Dotted red lines highlight the three different periods of interest investigated in this case of study

In PM_1 samples, among the three anhydro sugars investigated, levoglucosan showed during all three periods the highest concentration. During the first period, levoglucosan showed a median concentration of 1083 ng/m^3, during the second period 162 ng/m^3 and during the third period 25.0 ng/m^3. Furthermore, levoglucosan and its isomers mannosan and galactosan showed the maximum of their concentrations during the same day, 1st February 2017. During this day, mannosan had the highest concentration equal to 169.4 ng/m^3 and galactosan equal to 45.6 ng/m^3, **Figure 40**.

Acids (the sum of adipic acid, eicosanoic acid and stearic acid) during the first period had a median concentration of 46.84 ng/m^3 which in represented 3% of the chemical markers investigated in PM_1 aerosol. During the second period acids had a median concentration of 79.6 ng/m^3 which in represented 32% of the chemical markers investigated in PM_1 aerosol. During the third period acids had a median concentration of 31.3 ng/m^3 which in represented 59% of the chemical markers investigated in PM_1 aerosol. Among the three acids investigated, stearic acid was the most concentrated, during all three periods of sampling, followed by the eicosanoic acid. Stearic acid and eicosanoic acid showed their maximum in concentration during the second period, precisely on the 5.05, with a concentration equal to 627 ng/m^3 and 12.4 ng/m^3 respectively, **Figure 40**.

Alkanes (the sum of docosane, tricosane, tetracosane, pentacosane, hexacosane, heptacosane, octacosane, nonacosane, triacontane, hentriacontane, dotriacontane, tritriacontane, tetratriacontane, pentatriacontane) during winter had a median concentration of 33.6 ng/m^3 which in represent 2% of the chemical markers investigated in PM_1. During spring alkanes had a median concentration of 9.96 ng/m^3 which in represented 3% of the chemical markers investigated in PM_1. During the early summer, alkanes had a median concentration of 13.14 ng/m^3 which in represented 13% of the chemical markers investigated in PM_1. The detailed composition of alkanes in PM_1 aerosol, showed a very homogenous distribution of almost all alkanes detected, **Figure 40**. During winter, spring and early summer tetracosane was the most concentrated alkane.

o-PAHs (the sum of 1H-phenalen-1-one, xanthone, 9,10-anthracenedione, cyclopenta (def) phenanthrenone, 1,8-naphthalic anhydride, 1,8-naphthalaldehydic acid, 11H-benzo [a] fluoren-11-one, 7H-benzo [c] fluorene-7-one, 11H-benzo [b] fluoren-11-one and 7H-benzo[de]anthracen-7-one) during the first period had a median concentration of 28.7 ng/m^3 which in represented 3% of the chemical markers investigated in PM_1. During the second period, o-PAHs had a median concentration of 3.88 ng/m^3, which in represented 1% of the chemical markers investigated in PM$_1$. During the third period o-PAH had a median concentration of 1.00 ng/m^3 which in represented 1% of the chemical markers investigated in PM$_1$. Among all o-PAHs, 1,8-naphthalaldehydic acid was the most concentrated compound, during all the three periods, **Figure 40**.

Resin acids, isopimaric acid, dehydroabietic acid, methyl ester and dehydroabetic acid, were present in traces. Among the three resin acids, dehydroabetic acid was the most concentrated during all three different sampling periods. It showed its maximum during the winter with a median concentration equal to 4.23 ng/m^3 and its minimum concentration during the early summer with a median concentration equal to 0.1 ng/m^3 **Figure 40**

Triterpenoids (the sum of stigmasta-3,5-dien-7-one and α-sitosterol) showed an important weight only during winter, when they had a median value of 45.3 ng/m^3 which in represented 3% of the chemical markers investigated in PM$_1$ aerosol. Among the two triterpenoids, α-sitosterol was the most concentrated compound, **Figure 40**.

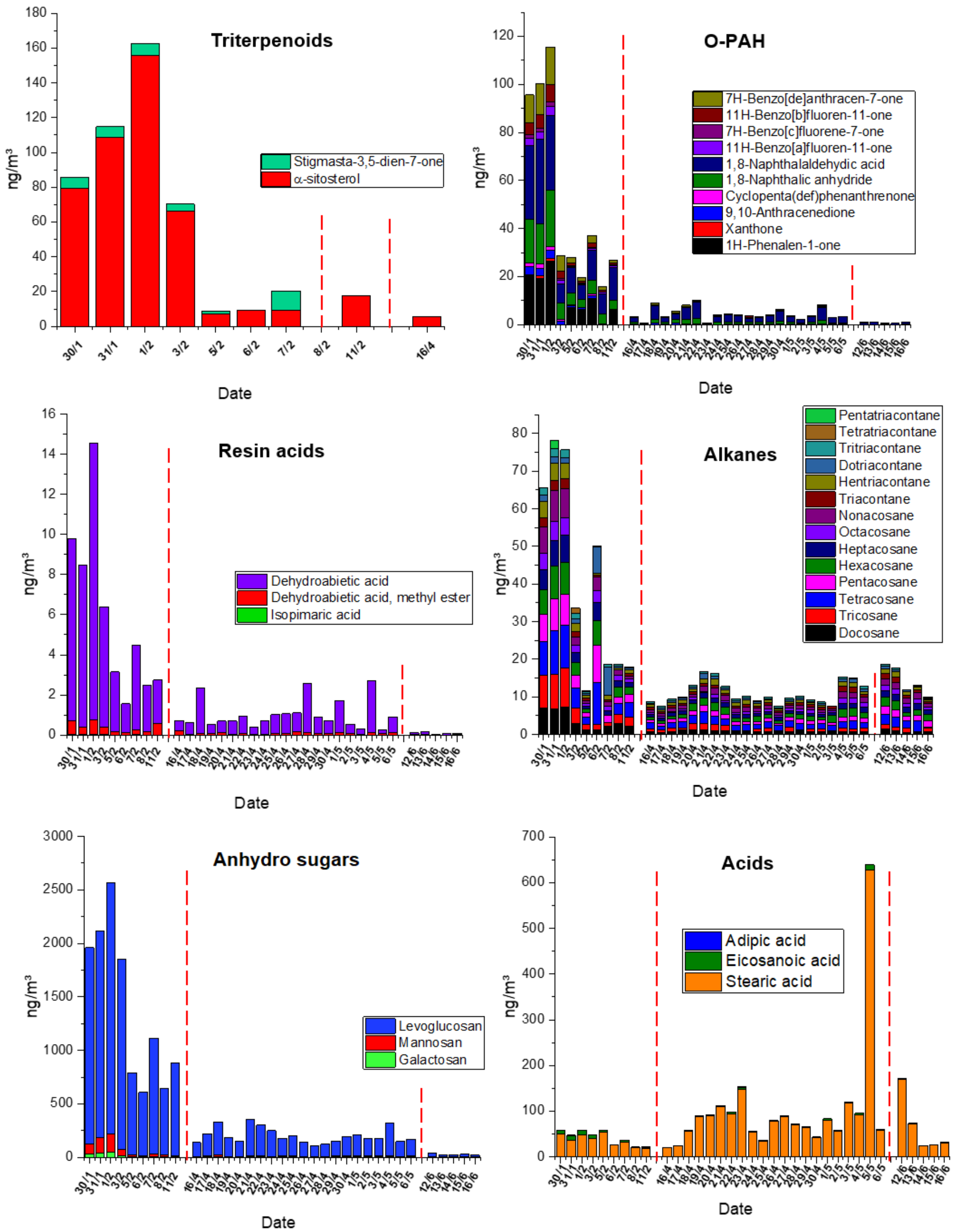


Figure 40. Detailed PM₁ composition for the three different periods investigated, A first period from 30.01- 11.02 a second period from 16.04 to 6.05 and a third period starting from the 12.06 until the 16.06. Dotted red lines highlight the three different periods of interest investigated in this case of study

To better visualize the PAHs results they were divided into two different groups. In the first one there are: PAH 302:1, PAH 302:2, (not identified PAH, m/z 302), 1-methyl-benz[a]anthracene, naphtho[1,2-kb]fluoranthene, dibenz[al]pyrene, naphtho[2,3-b]fluoranthene, dibenz[ae]pyrene, naphtho[2,1-a]pyrene, naphtho[2,3-a]pyrene, dibenz[ai]pyrene, dibenz[ah]pyrene. In the second group there are: fluoranthene, acephenanthrylene, pyrene, benzo[c]phenanthrene, benzo[ghi]fluoranthene, benz[a]anthracene, cyclopenta[cd]pyrene, chrysene, benzofluoranthenes, benz[e]pyrene, benz[a]pyrene, perylene, anthanthrene, dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene, picene, benzo[ghi]perylene, coronene and retene.

Polycyclic aromatic hydrocarbons, during winter showed a median concentration of 38.3 ng/m^3 which in represented 4% of the chemical markers investigated in PM$_1$. During spring, PAH had a median concentration of 2.72 ng/m^3 which in represented 1% of the chemical markers investigated in PM$_1$. During early summer, PAH were found only in a few traces, with a median concentration of 0.278 ng/m^3. In general PAHs decreased in spring and late spring/summer samples. The first group of PAHs was present only during the winter period. During this period, among this group of PAHs, Naphtho[1,2-kb] fluoranthene was the most concentrated with a median concentration of 2.78 ng/m^3. The second group of PAHs were quantified during all three sampling periods, with an important decrease during the spring and early summer periods. The sum of benzo[b/k] fluoranthene was the most concentrated analyte during the first and the second sampling periods. During the first period it had a median concentration of 7.51 ng/m^3 and during the second sampling period it had a median concentration of 0.758 ng/m^3. During early summer benz[e]pyrene, was the most concentrated analyte with a median concentration of 0.0538 ng/m^3, **Figure 41**.

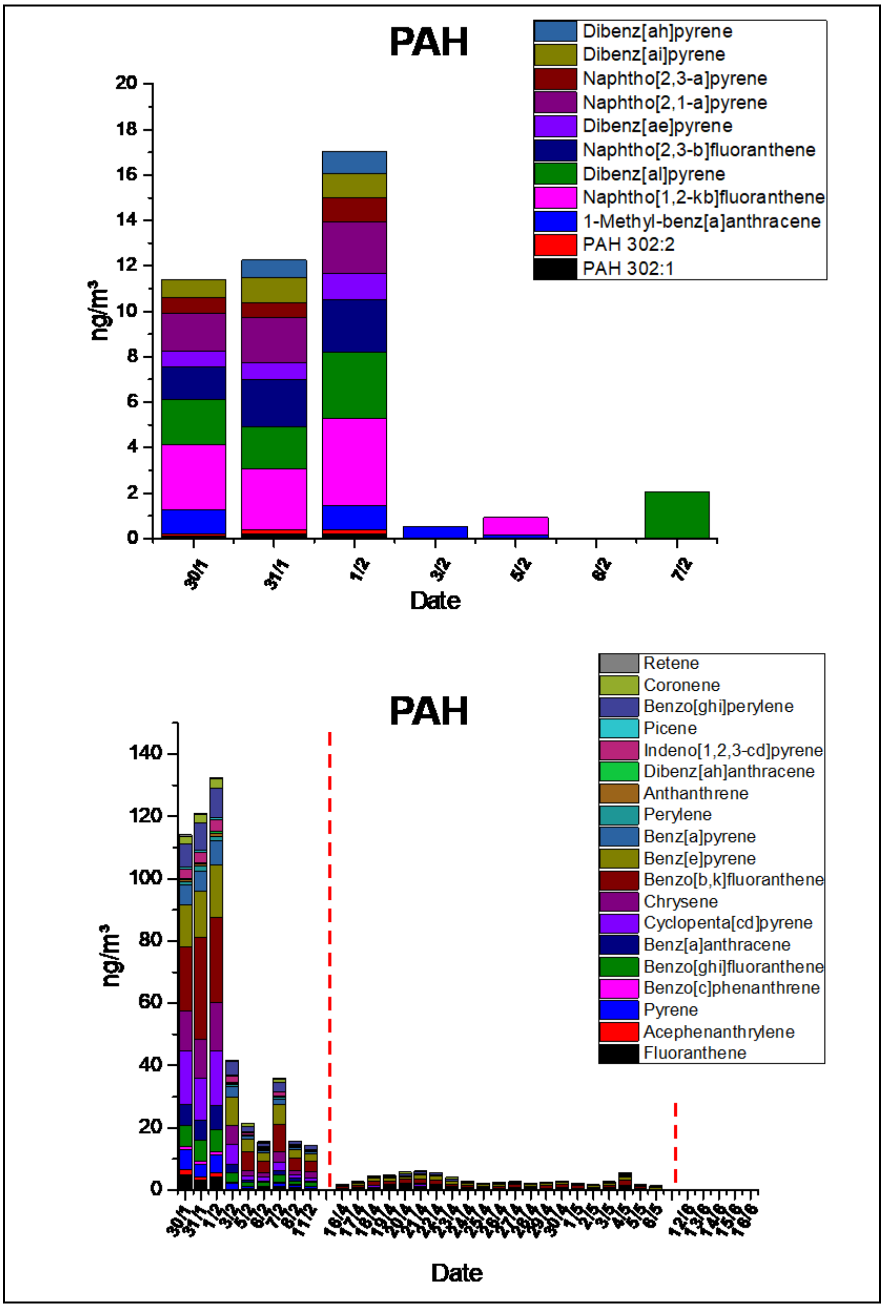


Figure 41. PAH composition of PM_1 samples. Dotted red lines highlight the three different periods of interest investigated in this case of study

5.3.2 Results of $PM_{2.5}$ samples

In $PM_{2.5}$ samples, during the first, 30.01- 11.02, and the second period, 16.04- 6.05, of sampling, anhydro sugars were the most concentrated compounds, while during the third period, 12.06- 16.06, $PM_{2.5}$ samples showed a higher concentrations of acids compounds than anhydro sugars, **Figure 42**. During the first period anhydro sugars showed a median concentration of 1448 ng/m^3 which in represented 82% of the chemical markers investigated in $PM_{2.5}$. During the second period anhydro sugars showed a median concentration of 209 ng/m^3 which in they represented 67% of the chemical markers investigated in $PM_{2.5}$. During the third period anhydro sugars showed a median concentration of 51.6 ng/m^3 which in represented 39% of the chemical markers investigated in $PM_{2.5}$. During the first period, anhydro sugars were followed by triterpenoids (median concentration of 43.7 ng/m^3), PAH (median concentration of 52.7 ng/m^3) and o-PAH (median concentration of 43.4 ng/m^3), with a respective total concentration of 4% of the chemical markers investigated in $PM_{2.5}$. Then, acids (median concentration of 46.8 ng/m^3), alkanes (median concentration of 26.1 ng/m^3) represented respectively the 3%. During the second period, acids (median concentration of 77.6 ng/m^3) represented 26% of the chemical markers investigated in $PM_{2.5}$, followed by alkanes (median concentration of 13.3 ng/m^3) 4%, o-PAH (median concentration of 4.91 ng/m^3) 2%, and PAH (median concentration of 3.30 ng/m^3) 1%. During the third period, acids (median concentration of 57.51 ng/m^3) represented 46% of the chemical markers investigated in $PM_{2.5}$, alkanes (median concentration of 18.2 ng/m^3) 14% and o-PAH (median concentration of 1.10 ng/m^3) 1%. All the chemical compounds, except for acids, showed higher concentrations during winter with a remarkable decrease during the spring and even more during the early summer sampling periods.

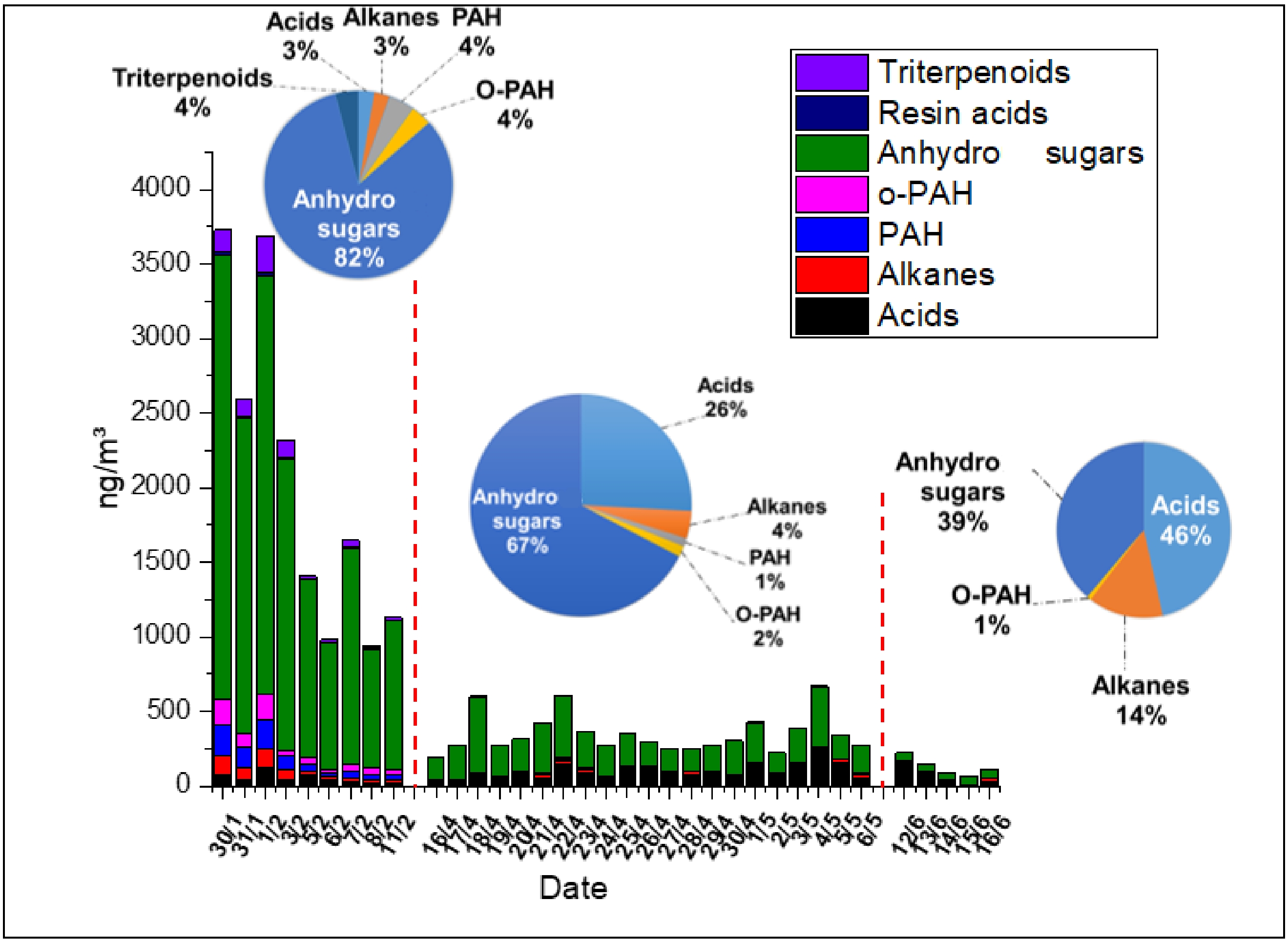


Figure 42. $PM_{2.5}$ samples composition of Sernaglia della Battaglia, during three different period 30.01- 11.02, 16.04- 06.05 and 12.06- 16.06. Dotted red lines highlight the three different periods of interest investigated in this case of study

In $PM_{2.5}$ samples, among three *anhydro sugars*, levoglucosan was the most concentrated during all three different sampling periods. During the first period, levoglusan showed a median concentration of 1408 ng/m^3 during the second period 196 ng/m^3 and during the third period 49.1 ng/m^3, **Figure 43**.

Among acids, stearic acid was the most concentrated, during all three different sampling periods. Stearic acid showed a median concentration of 37.7 ng/m^3 during winter, of 75.4 ng/m^3 during the spring and of 55.7 ng/m^3 during the early summer. Stearic acid was followed by eicosanoic acid while adipic acid was present only in traces **Figure 43**.

Among alkanes (docosane, tricosane, tetracosane, pentacosane, hexacosane, heptacosane, octacosane, nonacosane, triacontane, hentriacontane, dotriacontane, tritriacontane, tetratriacontane, pentatriacontane) during the first period, tricosane was the most concentrated alkane showing a median concentration of 4.21 ng/m^3. During the second period tetracosane was the most concentrated alkane showing a median concentration of 1.63 ng/m^3. During the third period, nonacosane was the most concentrated alkane showing a median concentration of 2.31 ng/m^3, **Figure 43**.

Among o-PAH, 1,8-naphthalaldehydic acid was the most concentrated during all the three different sampling periods. 1,8-naphthalaldehydic acid showed a median concentration of 18.2 ng/m^3 during winter, of 3.54 ng/m^3 during the spring and of 0.97 ng/m^3 during the early summer, **Figure 43**.

Among the investigated resin acids, isopimaric acid, dehydroabietic acid methyl ester and dehydroabietic acid, dehydroabietic acid was the most concentrated during all the three sampling periods. Dehydroabietic acid showed a median concentration of 5.86 ng/m^3 during winter, of 0.955 ng/m^3 during the spring and of 0.114 ng/m^3 during the early summer, **Figure 43**.

Triterpenoids were present only during winter and α-sitosterol was the most concentrated compound showed a median concentration of 38.8 ng/m^3, while stigmasta-3,5-dien-7-one showed a median concentration of 4.87 ng/m^3 **Figure 43** .

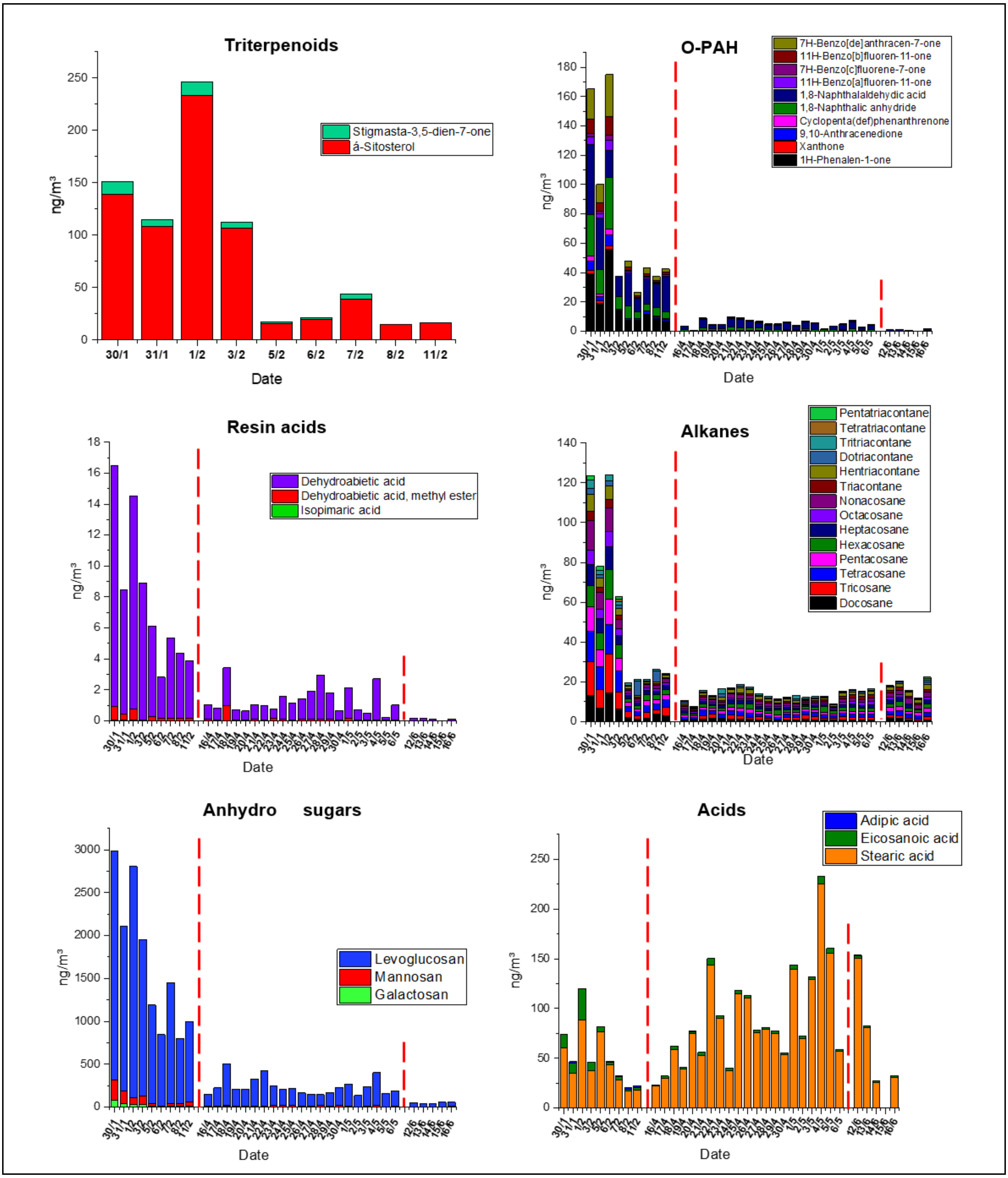


Figure 43. Detailed PM2.5 composition for the three different periods investigated. A first period from 30.01- 11.02 a second period from 16.04 to 6.05 and a third period starting from the 12.06 until the 16.06. Dotted red lines highlight the three different periods of interest investigated in this case of study

The first group of polycyclic aromatic hydrocarbons (PAHs), were present only during the first sampling period. During this period, naphtho[1,2-kb]fluoranthene showed a median concentration of 1.91 ng/m^3. The second group of PAHs was present during all the three sampling periods, with a remarkable decrease during spring and late spring/summer periods. Benzofluoranthenes was the most concentrated analyte during the first (median concentration of 12.5 ng/m^3) and the second periods (median concentration of 0.898 ng/m^3), while during the third period benz[e]pyrene, was the most concentrated analyte with a median concentration of 0.0831 ng/m^3 **Figure 44**.

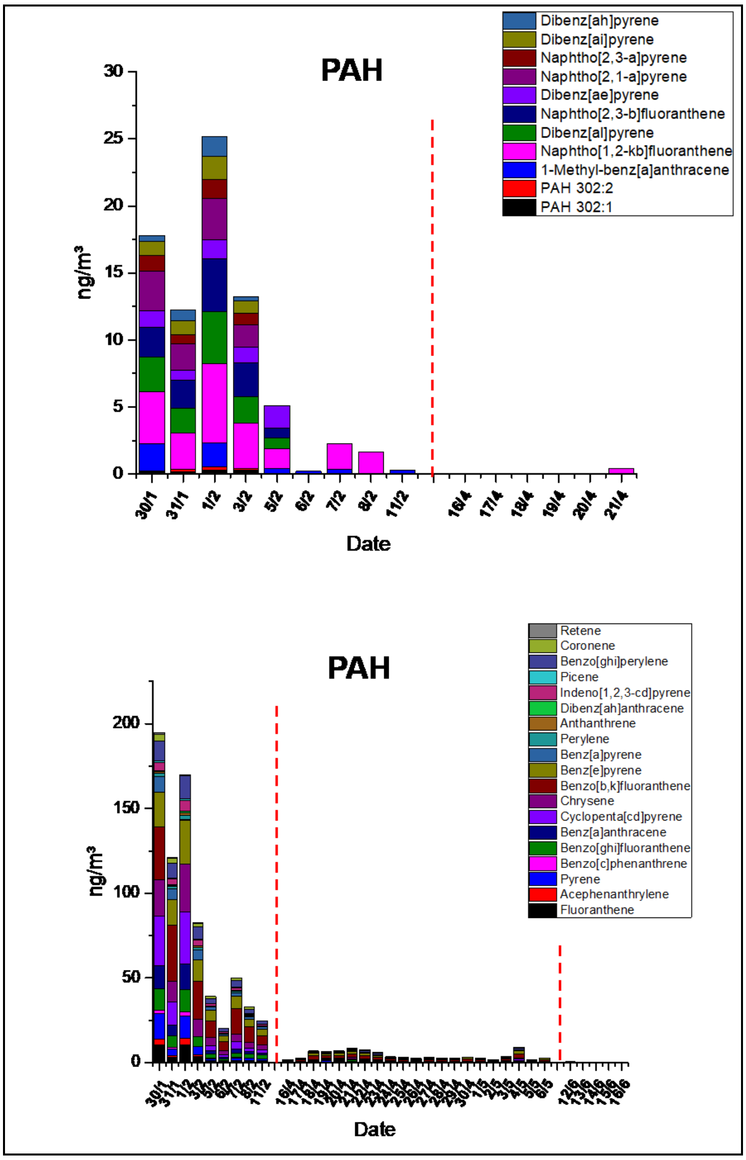


Figure 44. PAHs composition of PM$_{2.5}$ samples. Dotted red lines highlight the three different periods of interest investigated in this case of study

5.3.3 Results of PM_{10} samples

In PM_{10} samples, during the first, 30.01- 11.02, the second, 16.04- 6.05, and the third period of sampling, 12.06- 16.06, anhydro sugars were the most concentrated compounds. During the third period anhydro sugars concentrations are comparable to acids compounds concentration **Figure 45**. During winter anhydro sugars showed a median concentration of 1236 ng/m^3 which in represented 86% of the chemical markers investigated in PM_{10}. During spring they showed a median concentration of 211 ng/m^3 which in represented 67% of the chemical markers investigated in PM_{10} and during early summer they showed a median concentration of 60.2 ng/m^3 which in represented 45% of the chemical markers investigated in PM_{10}. Furthermore, during the first period, anhydro sugars were followed by PAH (median concentration of 32.7 ng/m^3) and alkanes (median concentration of 29.4 ng/m^3), with a respective total concentration which represented 4% of the chemical markers investigated in PM_{10}, and triterpenoids (median concentration of 35.1 ng/m^3) 3%, acids (median concentration of 29.4 ng/m^3) 2%, and resin acids (median concentration of 4.97 ng/m^3) 1%. During the second period, after anhydro sugars, acids (median concentration of 77.2 ng/m^3) represented 26% of the chemical markers investigated in PM_{10}, followed by alkanes (median concentration of 15.7 ng/m^3) 4%, o-PAH (median concentration of 5.68 ng/m^3) 2%, and PAH (median concentration of 3.57 ng/m^3) 1%. During the third period, acids (median concentration 41.7 ng/m^3) represented 25% of the chemical markers investigated in PM_{10} and alkanes (median concentration of 17.7 ng/m^3) 17%.

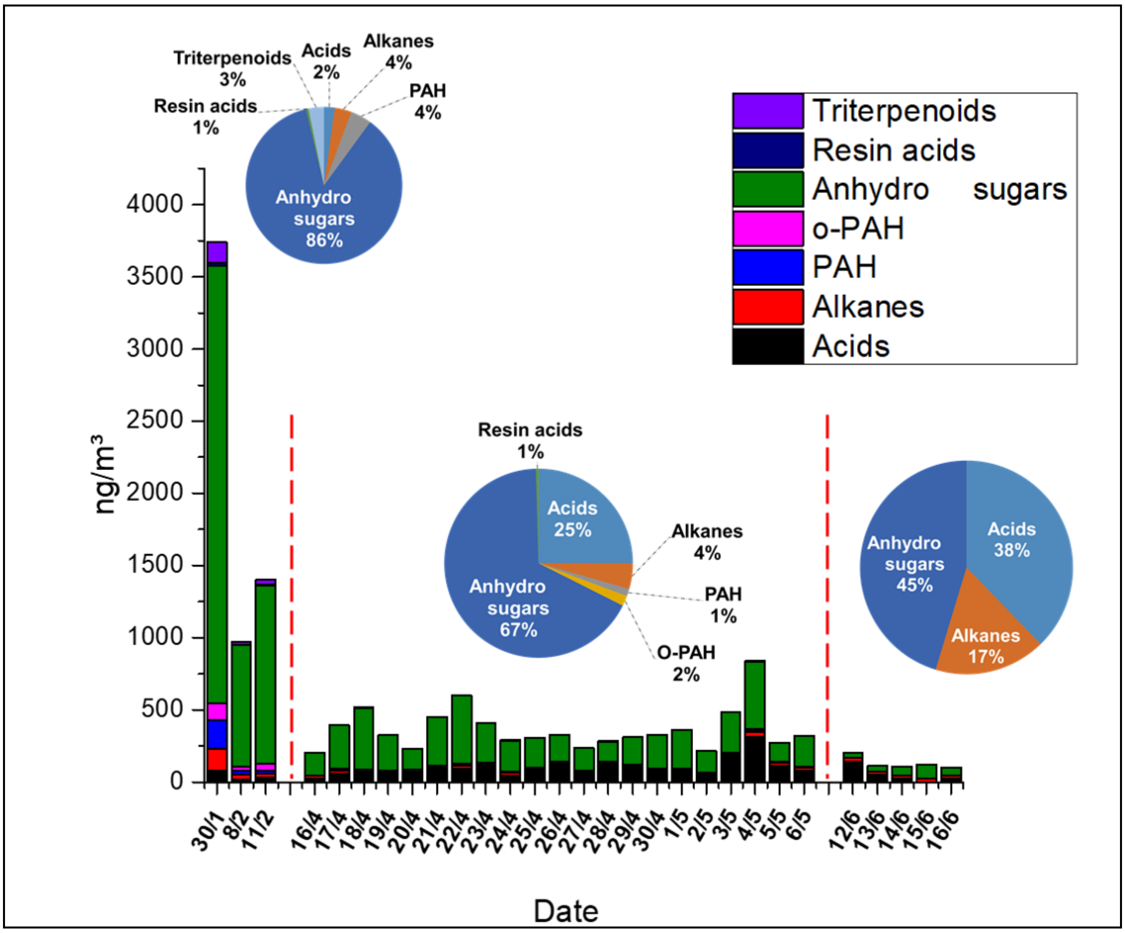


Figure 45. PM_{10} samples composition of Sernaglia della Battaglia, during three different period 30.01- 11.02, 16.04- 06.05 and 12.06- 16.06. Dotted red lines highlight the three different periods of interest investigated in this case of study

Among the investigated anhydro sugars, levoglucosan was the most concentrated during all the three different sampling periods, followed by mannosan and galactosan. During winter, levoglucosan showed a median concentration of 1168 ng/m^3. During the second period it showed a median concentration of 204 ng/m^3 and during the third sampling period of 51.5 ng/m^3, **Figure 46**.

Acids showed increasing concentrations during spring and early summer PM_{10} samples. Among all the investigated acids, stearic acids, was the most concentrated during all the three different sampling periods with a median concentration of 25.2 ng/m^3 during winter, of 73.4 ng/m^3, during spring and of 36.0 ng/m^3 , during early summer, **Figure 46**.

Alkanes have been mostly found in winter PM_{10} samples.

Among all the investigated alkanes, nonacosane showed the highest median concentration during winter, 2.95 ng/m^3 and during early summer, 3.73 ng/m^3, while during spring triacontane had the highest median concentration, 0.888 ng/m^3, **Figure 46**.

Among the investigated o-PAHs, 1,8-naphthalaldehydic acid was the most concentrated compound during all the three different sampling periods. During winter it showed a median concentration of 27.6 ng/m^3, during spring of 3.38 ng/m^3 and during early summer of 0.505 ng/m^3, **Figure 46**.

Among the three investigated resin acids, dehydroabietic acid was the most concentrated compound during all three sampling periods. During winter it showed a median concentration of 4.73 ng/m^3, during spring of 1.41 ng/m^3 and during early summer of 0.127 ng/m^3, **Figure 46**.

Triterpenoids were concentrated mostly during winter. α -sitosterol was the most concentrated compound with a median concentration of 32.2 ng/m^3, **Figure 46**.

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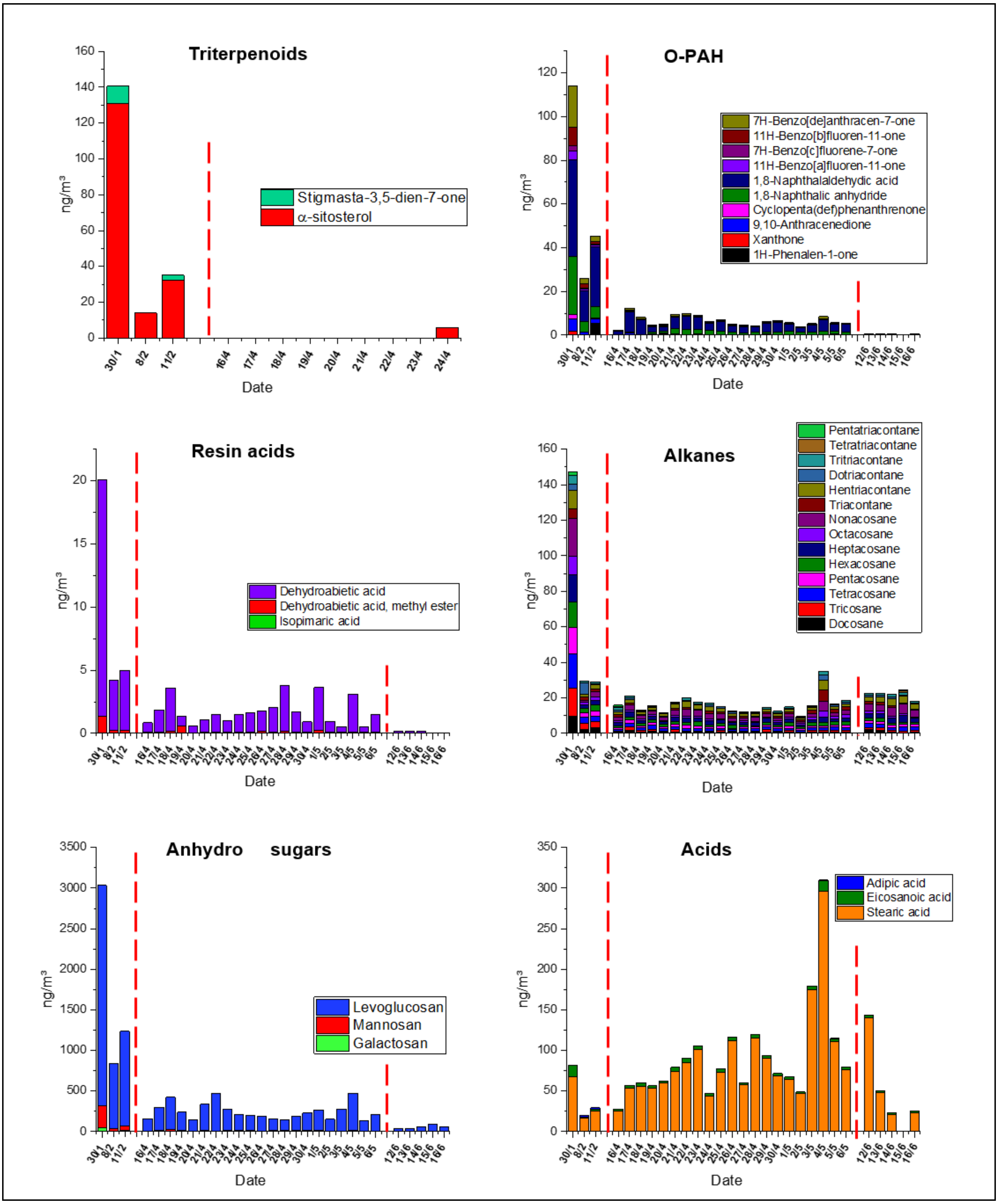

Figure 46. Detailed PM$_{10}$ composition for the three different periods investigated, A first period from 30.01- 11.02 a second period from 16.04 to 6.05 and a third period starting from 12.06 until 16.06. Dotted red lines highlight the three different periods of interest investigated in this case of study

The first group of polycyclic aromatic hydrocarbons (PAHs), were mostly present during winter and in few samples during spring and early summer. Naphtho[1,2-kb]fluoranthene was the most concentrated compound during all three periods. The second group of PAHs was present during winter, spring and summer, with a remarkable decrease during spring and early summer. Benzofluoranthenes was the most concentrated analyte during winter and spring periods with a respective median concentration of 7.44 ng/m^3 and 1.01 ng/m^3. During the early summer, benz[e]pyrene, was the most concentrated analyte with a median concentration of 0.0770 ng/m^3, **Figure 47**.

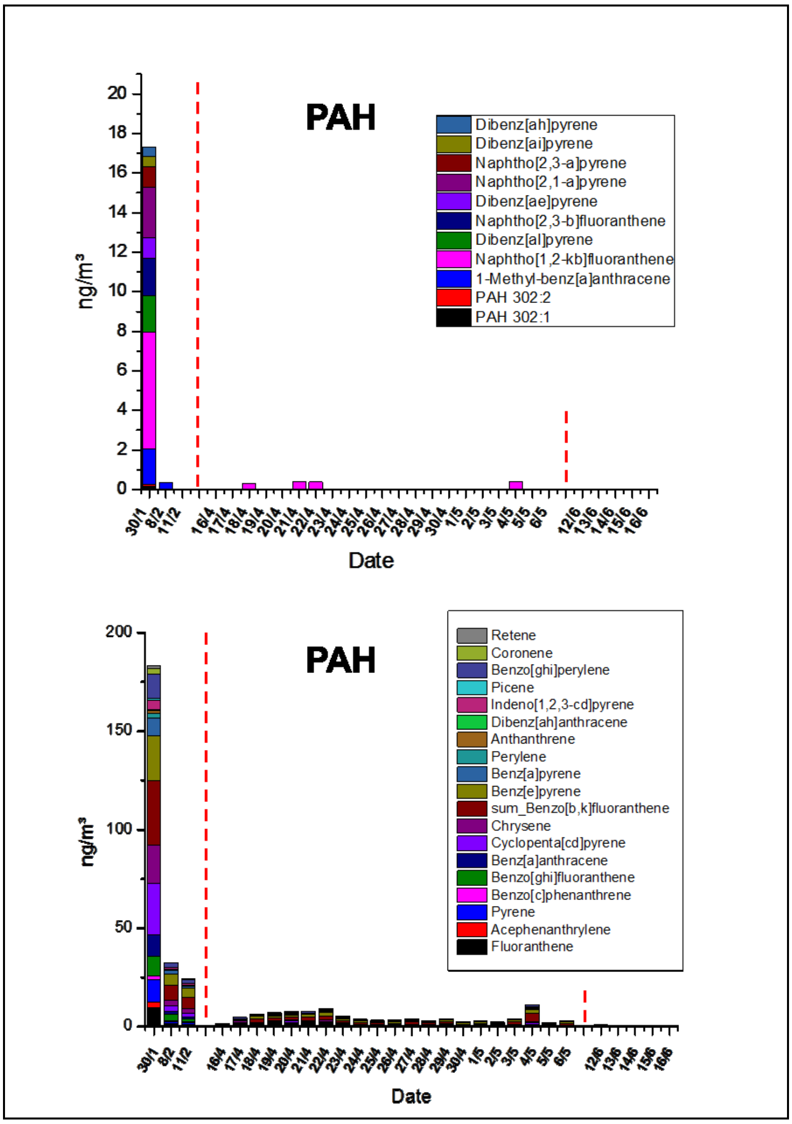

Figure 47. PAHs composition of PM$_{10}$ aerosol samples. Dotted red lines highlight the three different periods of interest investigated in this case of study

5.4 Discussion

5.4.1 Differences between the size classes

The seven groups of chemical compounds have been investigated in three different size fractions, PM_1, $PM_{2.5}$ and PM_{10}, during winter, spring and summer periods. Focusing on size classes, taking in account the median values for each group, **Figure 48**, the total of alkanes, PAH, o-PAH, resin acids and anhydro sugars are mostly concentrated on the PM_1 samples, in the fine fraction, highlighting a probable Secondary Organic Aerosol (SOA). PM_1 was the most concentrated fraction during winter, spring and early summer. Furthermore, PAH, o-PAH, triterpenoids, resin acids and anhydro sugars showed higher concentrations in $PM_{2.5}$ than in the PM_{10}, during winter, spring and early summer, confirming their higher distribution in the fine fraction. Alkanes showed a different trend, having, during the same periods, higher concentration in the PM_{10} than in $PM_{2.5}$. Acids showed a completely different trend, being mainly concentrated on the $PM_{2.5}$ samples, during winter, spring and early summer, PM_{10} as the second fraction more concentrated and showing lowest concentrations on PM_1, showing a higher distribution on the coarse fraction than the fine fraction.

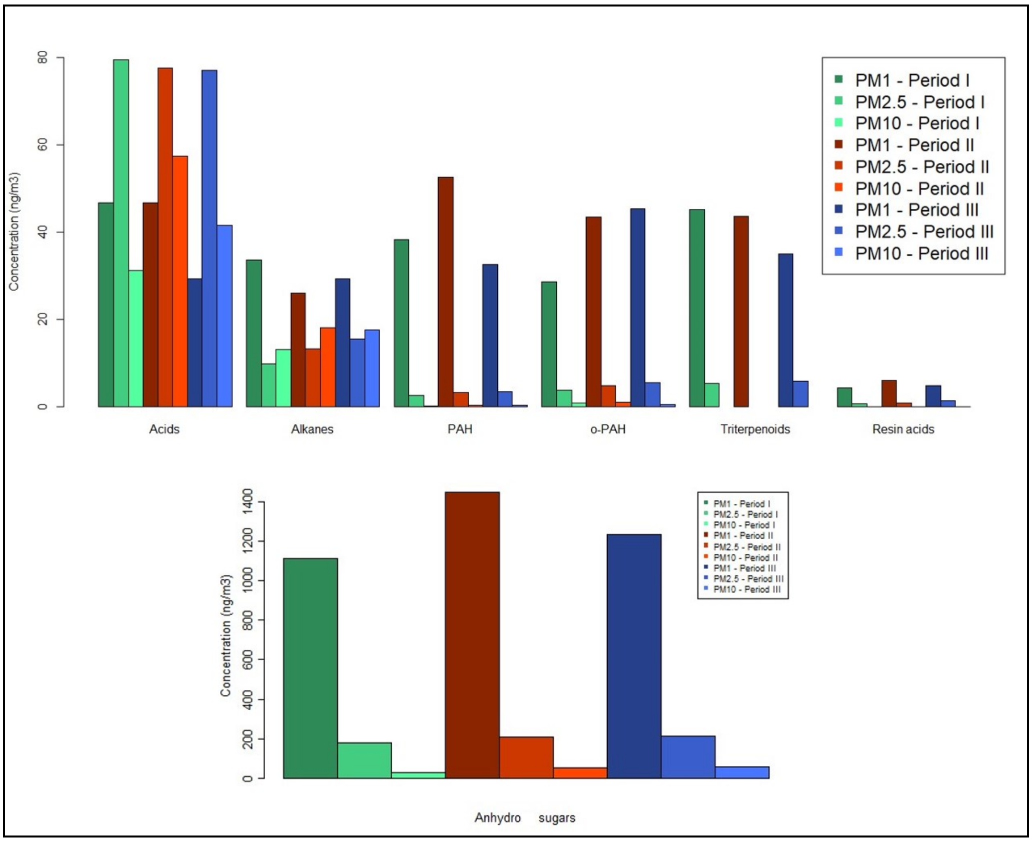

Figure 48. Difference between size classes

5.4.2 Markers of biomass burning

Levoglucosan and dehydroabietic acid were quantified in order to estimate the specific contribution of biomass burning sources [7]. Levoglucosan is considered specific marker for the biomass burning process. It is specifically formed during the pyrolysis process of cellulose. Although levoglucosan can degrade in the atmosphere by reacting with OH^- [165], NO_3^- and SO_4^{2-}, it is emitted in large quantities into smoke plumes, suggesting that enough remains to allow considering levoglucosan as a biomass burning tracer [166]. Furthermore it can derive from vegetation smoke, residential wood combustion, campfire burning and cigarette smoke [167].

Dehydroabietic acid is known as tracer of gymnosperm burning, it has been specifically found in plumes from burning of coniferous trees [74], [168], [21]. Tire abrasion may contribute to the atmospheric concentrations of dehydroabietic acid too [169].

As expected, both markers, with a quite similar temporal trend, showed higher concentration during winter than during spring and early summer, and they were mostly concentrated in the fine fraction, **Figure 49** . This indicates high emissions of smoke particles, associated with residential wood burning [170] and [171]. The ratio between levoglucosan, emitted by the burning of several types of cellulose containing biomass, and dehydroaboetic acid, only emitted by gymnosperm combustion, can be used to distinguish between different types of wood combustion contributions. Ratio values found in these samples are consistent with the composition of smoke emissions from residential wood burning in urban sites [171]. Statistical analysis, **Figure 52**, **Figure 53** and **Figure 54** on levoglucosan and dehydroabietic acid, highlighted a high correlation (R^2> 0.9) between this two variables, showing their same origin from biomass burning sources. Furthermore, statistical analysis, showed a high correlation (R^2> 0.7) also between levoglucosan, its isomers galactosan and mannosan, dehydroabietic acid methyl ester (partially formed by esterification of dehydroabietic acid with wood alcohol during the combustion) and dehydroabietic acid, showing an high similarity between chemical markers coming from the biomass burning processes.

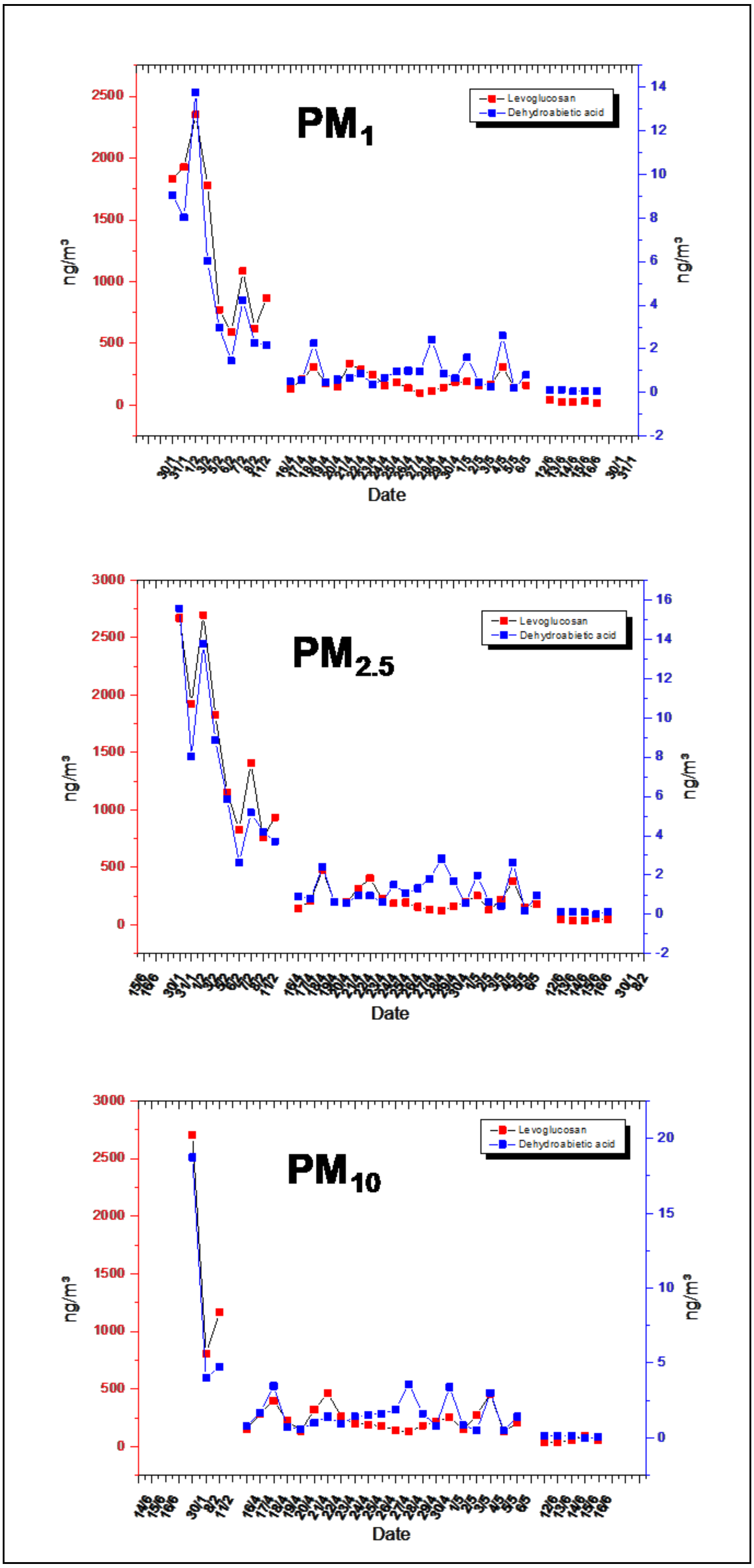

Figure 49. Levoglucosan and dehydroabietic acid temporal trend in PM$_1$, PM$_{2.5}$ and PM$_{10}$ aerosol samples

5.4.3 N- alkanes

N- alkanes are very useful compounds to track the origin and the changes of aerosol in the atmosphere. N- alkanes are markers both for anthropogenic and biogenic emissions. These two emissions sources can be differentiate by taking into account n- alkanes distribution with two parameters such as the carbon number maximum (C_{max}) and the carbon preference index (CPI) [170], [172], [173], [174] and [175].

In PM_1, $PM_{2.5}$ and PM_{10}, all n- alkanes showed higher concentration during colder period than warmer period. N- alkanes had their maximum concentration during the first sampling period, 30.01- 11.02, decreasing during the second sampling period, 16.04- 6.05 and the last sampling period, 12.06- 16.06.

The abundance distribution of different n- alkanes chains showed seasonal variations, highlighting changes in n- alkanes predominant emissions sources. During winter PM_1, $PM_{2.5}$ and PM_{10} showed higher concentrations in C_{22}- C_{29} alkanes, highlighting as a dominant emission source vehicle exhausted emissions, mostly from lubricating oil or fuel sources [164] and [175]. During spring and early summer, PM_1, $PM_{2.5}$ and PM_{10} showed a little shift of composition with lower concentrations of shorter chains C_{22} and C_{23} and higher concentrations of C_{24}- C_{31}, with the presence of heavier n- alkanes ($C> C_{27}$). These longer n- alkanes chains are typically emitted from plant waxes. They have been introduced into the aerosol atmosphere from plant abrasion or as products of incomplete biomass combustion [172], [167] and [176].

An important tool to indicate probable source is the Carbon Preference Index, CPI. CPI values are obtained by the ratio of the sum of odd carbon number of n- alkanes to the sum of even carbon number of n- alkanes. Lower CPI values, greater the anthropogenic inputs such as traffic, while CPI values greater than one implies a greater biogenic input [177].

In these PM_1, $PM_{2.5}$ and PM_{10} samples, CPI index (C_{22}-C_{35}) during all the three sampling periods was about 1, indicating that n- alkanes in this city are mainly of anthropogenic origin with a relatively minor contribution from higher plants, resulting in an aerosol characterised by fossil fuel. The CPI index for PM_1, $PM_{2.5}$ and PM_{10} showed a slight increase from the first period, 30.01- 11.02, through the second period, 16.04- 6.05 to the last period, 12.06-16.06 **Table 14**. This behaviour suggested a slight enrichment, but significant, in warmer period of biogenic emissions, remaining, however, an aerosol strongly characterized by anthropogenic emissions. Furthermore, differences in n- alkanes composition coupled to the minor changes in CPI suggested the impact of different gas-particle distribution with different temperatures.

Table 14. CPI index for PM_1, $PM_{2.5}$ and PM_{10} during three sampling periods

CPI INDEX		
30.01- 11.02	16.04- 6.05	12.06- 16.06
PM_1		
0.92	0.93	0.94
$PM_{2.5}$		
0.90	0.93	0.94
PM_{10}		
0.94	0.94	0.95

5.4.4 Iso- and anteiso- alkanes

In addition to n-alkanes, iso- and anteiso- alkanes, C_{29}- C_{33}, were usually evaluated as suitable tracers for particulate environmental emissions from tobacco smoke (ETS) both in the urban and rural environment, showing specific patterns in tobacco leaf waxes and partially survive in the cigarette combustion process [95], [178] and [179]. Furthermore, these chemical compounds had demonstrated to be sufficient specific and non-reactive character to be used as ETS tracers [178]. In these PM_1, $PM_{2.5}$ and PM_{10} samples, C_{29}-C_{33} have been quantified during winter, spring and early summer, mostly on the coarse fraction and ranging from 0.21 to 3.76 ng/m^3. Higher concentrations, in all three fractions, have been detected during winter than spring and summer. These data are consistent with levels usually found in rural outdoor samples, which usually show lower concentrations than those in the indoor aerosols [179].

5.4.5 PAH and O-PAH

Polycyclic aromatic hydrocarbon compounds (PAH) and oxided polycyclic aromatic hydrocarbon compounds (o-PAH) are produced by incomplete combustion of organic material due to anthropogenic emissions and wildfires [180]. These compounds come from traffic emissions, from the combustion of gas, fuel oil, wood or coal. Furthermore some of these PAHs compounds have been proved to be mutagenic and/or carcinogenic [181].Ten PAHs were discussed as main relevant source tracers: pyrene, fluoranthene, benz[a]anthracene, chrysene, benzofluoranthenes, benzo[e]pyrene, benzo[a]pyrene, indeno[cd]pyrene, benzo[ghi]perylene, coronene, markers of anthropogenic emissions. All PM_1, $PM_{2.5}$, PM_{10} analysed samples showed a strong seasonality. Higher PAHs concentrations were found during winter period, 30.01- 11.02, the coldest one **Figure 50**. This abundance during winter is mostly related with the increased emissions from primary sources such as motor vehicle traffic and domestic heating. Furthermore, higher concentration of PAHs were observed mainly in the heating season than in the non-heating season and they were mainly correlated with the increased emissions from primary sources such as domestic heating [181].

Furthermore, benzofluoranthenes, the most concentrated in PM_1, $PM_{2.5}$, PM_{10} during the first two sampling periods (30.01- 11.02 and 16.04- 6.05), suggested also a coal combustion origin, coming from coal burning for residential heating [182].

Furthermore, the benzo[e]pyrene/ benzo[ghi]perylene ratio (BGH/BEP) was investigated in all PM_1, $PM_{2.5}$, PM_{10} samples, during all the three sampling periods. For all PM_1, $PM_{2.5}$, PM_{10} samples, the BGH/BEP ratio showed higher values during the colder period, than the warmer periods. During winter sampling period the ratio, in PM_1, $PM_{2.5}$, PM_{10}, was equal to 2, while during the spring period it was equal to 3 and during the early summer period, it was equal to 4. Lower values during the colder period indicated increased influence of non-traffic sources [183] and [164].

Moreover, the oxidized polycyclic aromatic hydrocarbon compounds, o-PAH, were investigated because of their toxicological importance. In fact, they might be involved in the occurrence of oxidative stress: xanthone, 9,10anthracenedione, cyclopenta[def]phenanthrenone, benzo[a]fluorene11-one, benzo[b]fluorene-11-one, benz[de]anthracene-7-one [172], [9] and [184]. In PM_1, $PM_{2.5}$, PM_{10} aerosol samples o-PAHs were more concentrated during the colder period, 30.01- 11.02, than warmer periods, 16.04- 6.05 and 12.06- 16.06. The main reasons for the higher o-PAHs concentrations during the colder period were both the increased emissions from traffic and domestic heating. The hypothesis that o-PAHs, during the colder months, are mainly emitted from primary sources seems to be confirmed by the fact that during the colder months the photo degradation of PAHs is slowed by the less photochemical activity and lower ozone concentrations [164], [170], [174] and [175].

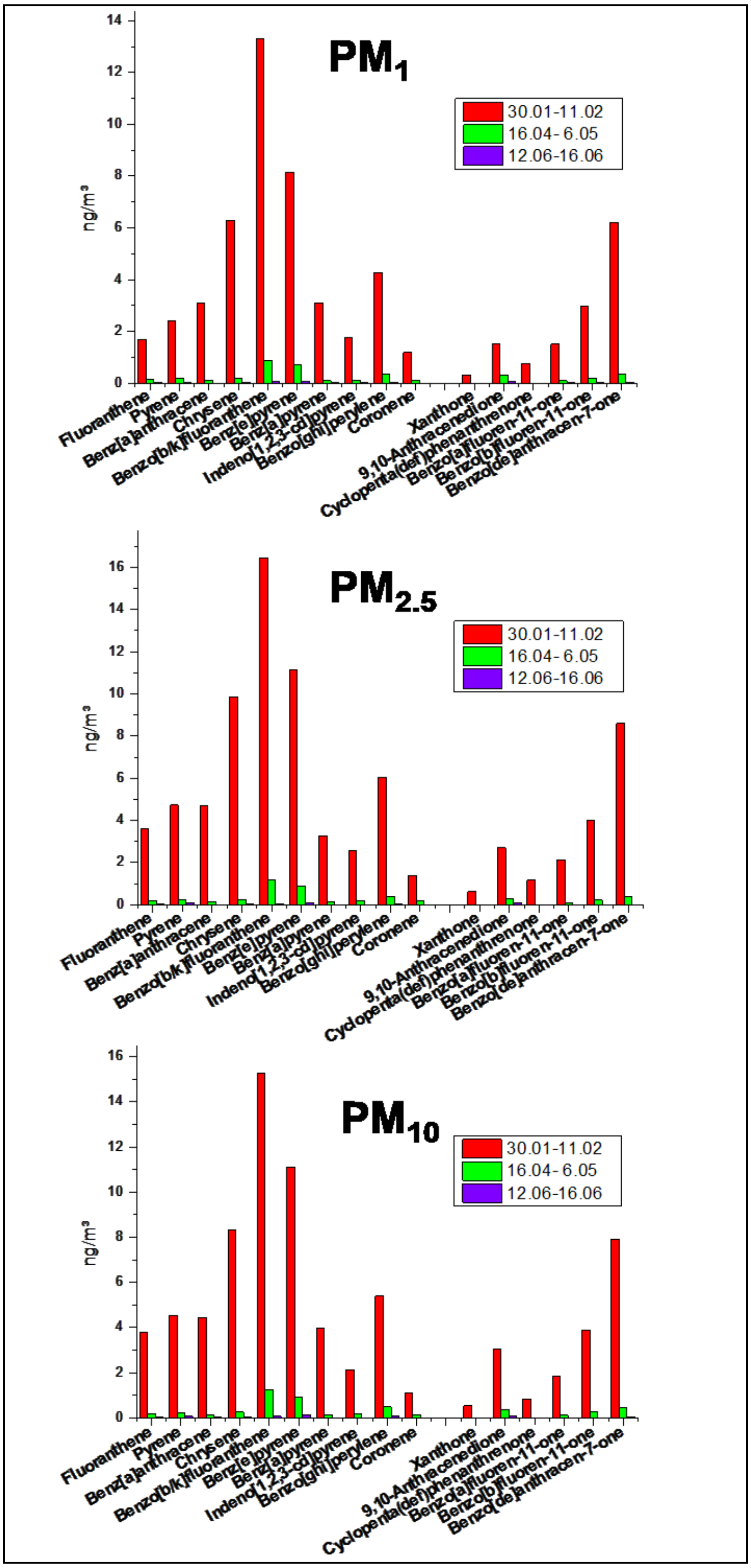

Figure 50. Trends of some PAHs and o-PAHs, the ones here discussed, in PM$_1$, PM$_{2.5}$ and PM$_{10}$ samples during the three different sampling periods

5.4.6 Short chains acid and fatty acids

Among the three investigated acids, the adipic acid ($C_{6:0}$) is a short- chain acid, while stearic acid ($C_{18:0}$) and eicosanoic acid ($C_{20:0}$) are long- chain acids. All samples showed higher concentration in stearic acid (C18:0) and eicosanoic acid (C20:0), long- chain acids, than adipic acid ($C_{6:0}$). Adipic acid ($C_{6:0}$) is an oxidation products from other organic compounds, can be considered as a Secondary Organic Compounds (SOA), reflecting the long-range transport of the aerosols [185]. Furthermore, adipic acid is a ozonolysis product of cyclohexene product of urban environment [186], [187]. Adipic acid concentrations, in PM_1, $PM_{2.5}$ and PM_{10}, were higher during warmer period than colder period highlighting a major contribution of SOA during spring and summer than winter.

Between the two long- chain acids, stearic acid ($C_{18:0}$) was the most concentrated acid during the three different sampling periods. Stearic acid, among the fatty acids homologs with C > C_{20}, are the most abundant components in the aereosol. They derive from terrestrial higher plant waxes and from anthropogenic sources, including the combustion of fossil fuels, wood and organic detritus and meat cooking. The higher amounts of stearic acid could be associated with the higher wax content in dead leaves and with wind abrasion. In fact it has been demonstrated that the fatty acid wax content in dead leaves is 5 times higher than that of green leaves [188] and [176].

5.4.7 Triterpenoids

Triterpenoids, α-sitosterol and stigmasta-3,5-dien-7-one, have been quantified in PM_1, $PM_{2.5}$ and PM_{10} samples, only during the first sampling period, 30.01- 11.02, related to a higher oils cooking usage during this period, being important components of different kind of oils. α-sitosterol has been mainly found in emissions from corn oil, olive oil and wheat germ oil [189]. Stigmasta-3,5-dien-7-one is one of the principal sterols in the plant foodstuffs and it has been found in soybean and rapeseed oils. In addition, stigmasta-3,5-dien-7-one has been found in oxidized soybean oils at a temperature between 30°C and 44 °C, up to 13 days [190]. The quantification of both α-sitosterol and stigmasta-3,5-dien-7-one explained an impact of cooking emission on our PM1, PM2.5 and PM10 samples only during the coldest period.

5.4.8 PCA

In general, the principal component analysis (PCA) is a widely used statistical technique which has the aim of reducing the dimensionality of a dataset with a large number of interrelated variables retaining, at the same time, as much as possible of the information (variance) present in a dataset. With a PCA analysis the initial dataset is transformed into a new set of variables, the principal components (PCs), which are uncorrelated (orthogonal to each other) and ordered so that the first few retain most of the variance present in the original variables. From a PCA analysis, two- or three-dimensions scores and loadings plots are obtained, for an easy visualization of relation between samples (scores) and between variables (loadings) and the study of their role in the analytical problem. Moreover, there is a quadrant correspondence between scores and loadings plot: samples in certain quadrant of scores plot are mostly explained by variables in the corresponding quadrant of loadings plot. PCA analyses have been applied to the present datasets of PM_1, $PM_{2.5}$ and PM_{10} aerosol samples to describe the samples and the chemical markers distribution through the three different sampling period. PCA analysis of three datesets well distinguish among the first sampling period, 30.01- 11.02, the second sampling period, 16.04- 6.05, and the third sampling period, 12.06- 16.06, in PM_1, $PM_{2.5}$ and PM_{10} aerosol samples **Figure 51**. The strong difference between the analyzed samples due to the seasonality is highlighted by this PCA: it is easily visualized how winter samples are well grouped together, and the distance of this group from the other samples is a proof of the showing different characteristics from the spring and summer samples. Furthermore, also spring samples and summer samples are well respectively related, grouped and discriminated, distancing spring samples from summer samples.

In the PCA of the PM_1 aerosol samples, PC1 represented 56% of the total variance, and PC2 represented 11%. In the PCA of the $PM_{2.5}$ aerosol samples, PC1 represented the 62% of the total variance, and PC2 represented 8%. In the PCA of the PM_{10} aerosol samples, PC1 represented 56% of the total variance, and PC2 represented 11%. During the winter period, 30.01- 11.02, some outliers were detected applying the Hotelling’s T2 analysis (a sort of multivariate extension of the univariate t-test) and they have been excluded from the dataset. The winter period shows, anyway, a great variability (samples are grouped, but their distance is still large, also compared to spring and summer groups). The “outliers” are samples which have an even greater variability, that could cover all the information carried by the other samples, therefore, it was decided to remove such outliers.

PM_1, $PM_{2.5}$ and PM_{10} samples from the winter are mostly explained by chemical compounds from combustion sources including fossil fuel emissions, short chains of n-alkanes and the most of PAHs, and biomass burning, levoglucosan (LEV) and dehydroabietic acid (high positive values of PC1), **Figure 52**, **Figure 53**, **Figure 54**. This is consistent with a higher contribution of anthropogenic emissions from domestic heating during the coldest period. PM_1, $PM_{2.5}$ and PM_{10} samples from spring, 16.04- 6.05, and from summer, 12.06- 16.06, are explained by the same chemical compounds too, but with an important role of acids, mainly stearic acids and longer n- alkanes chains, C29- C35 (negative values of PC1), indicating important biogenic sources and also highlighting the contribution of tracers for environmental tobacco smoke **Figure 52**, **Figure 53**, **Figure 54**. Anthracene dione (ANQ-DO), naphthalic anhydrid (NAP-AN) and naphthalaldehydic acid (NAP-AC, this one definitely a SOA compound) showed an high correlation in all samples (closeness in loading plot, at high positive values of PC1), showing a probable same origin as Secondary Organic Aaerosol (SOA) products. Furthermore in PM_{10} samples also adipic acid (a SOA compound) is quite close to anthracene dione (ANQ-DO), naphthalic anhydrid (NAP-AN) and naphthalaldehydic acid (NAP-AC), confirming the SOA nature of these compounds. Differently from adipic acid, that is quite distant, stearic and eicosanoic acids, long chain acids, are quite close in all samples loadings plots, showing similarity.

On the loadings plot of PM_1, $PM_{2.5}$ and PM_{10} samples (in particular for PM1), n-alkanes are distributed in three different groups: one group of n-alkanes with shorter chains, C22- C24 (high positive values of PC1), one with middle chains of n- alkanes, C25- C29 (high positive values of PC2), and one group of n-alkanes with longer chains, C30- C35 (negative values of PC1). N- alkanes with shorter carbon chains are close to the most of PAHs, o-PAHs, tracers of biomass burning and triterpenoids. PAHs are well grouped in PM_1, $PM_{2.5}$ and PM_{10} loadings plots, indicating a general similarity in anthropogenic emissions. O-PAHs are quite close to each other and also to PAHs a clear sign of the relation between PAHs and their oxidized forms and the similarity of emission sources **Figure 52**, **Figure 53**, **Figure 54**.

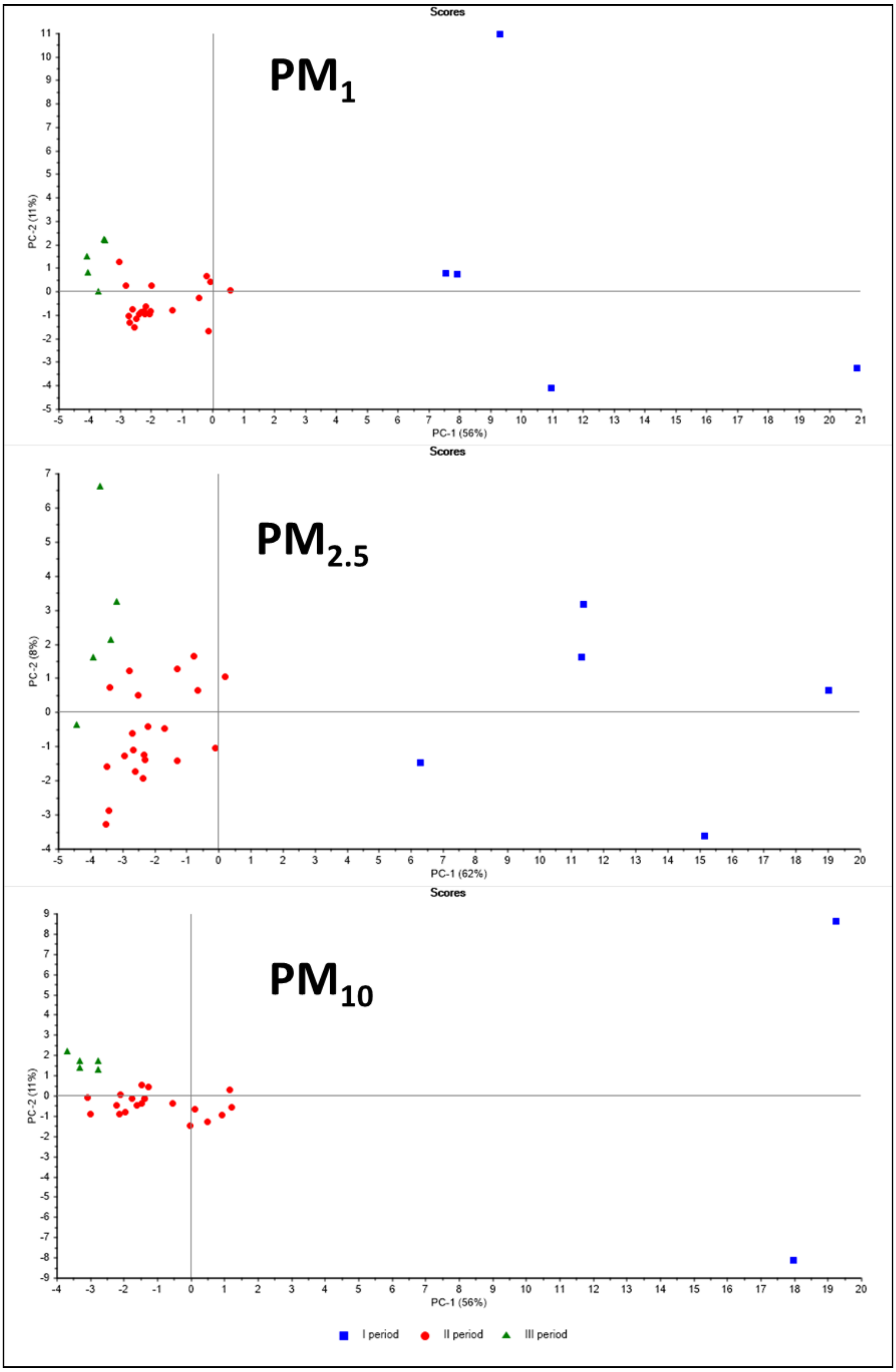

Figure 51. Scores plot from PCA of PM_1, $PM_{2.5}$ and PM_{10} aerosol analysis. The three different sampling period: in blue the first period, 30.01- 11.02, in red the second sampling period, 16.04- 6.05, and in green the third sampling period, 12.06- 16.06

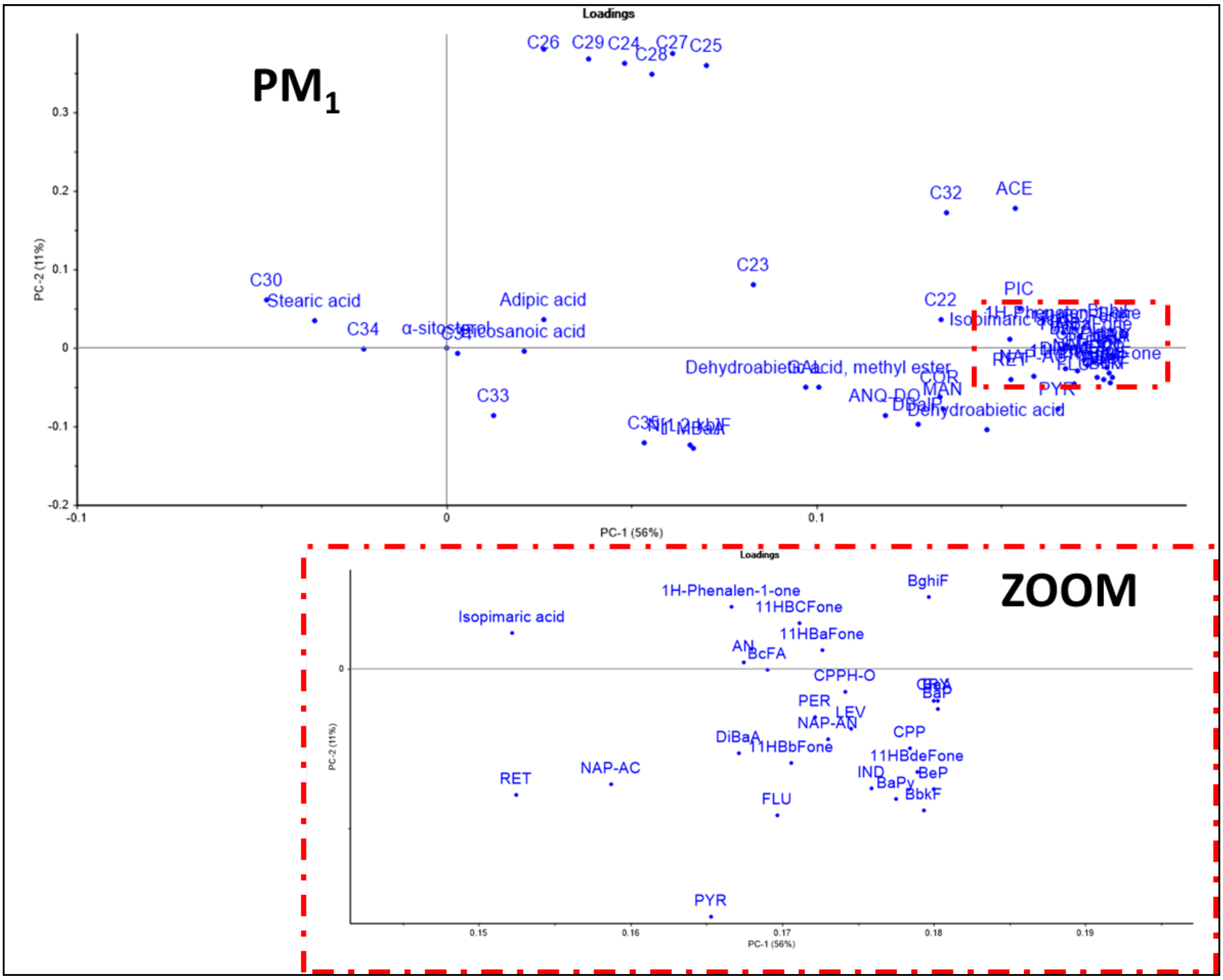

Figure 52. Loadings plot for PM₁ aerosol samples

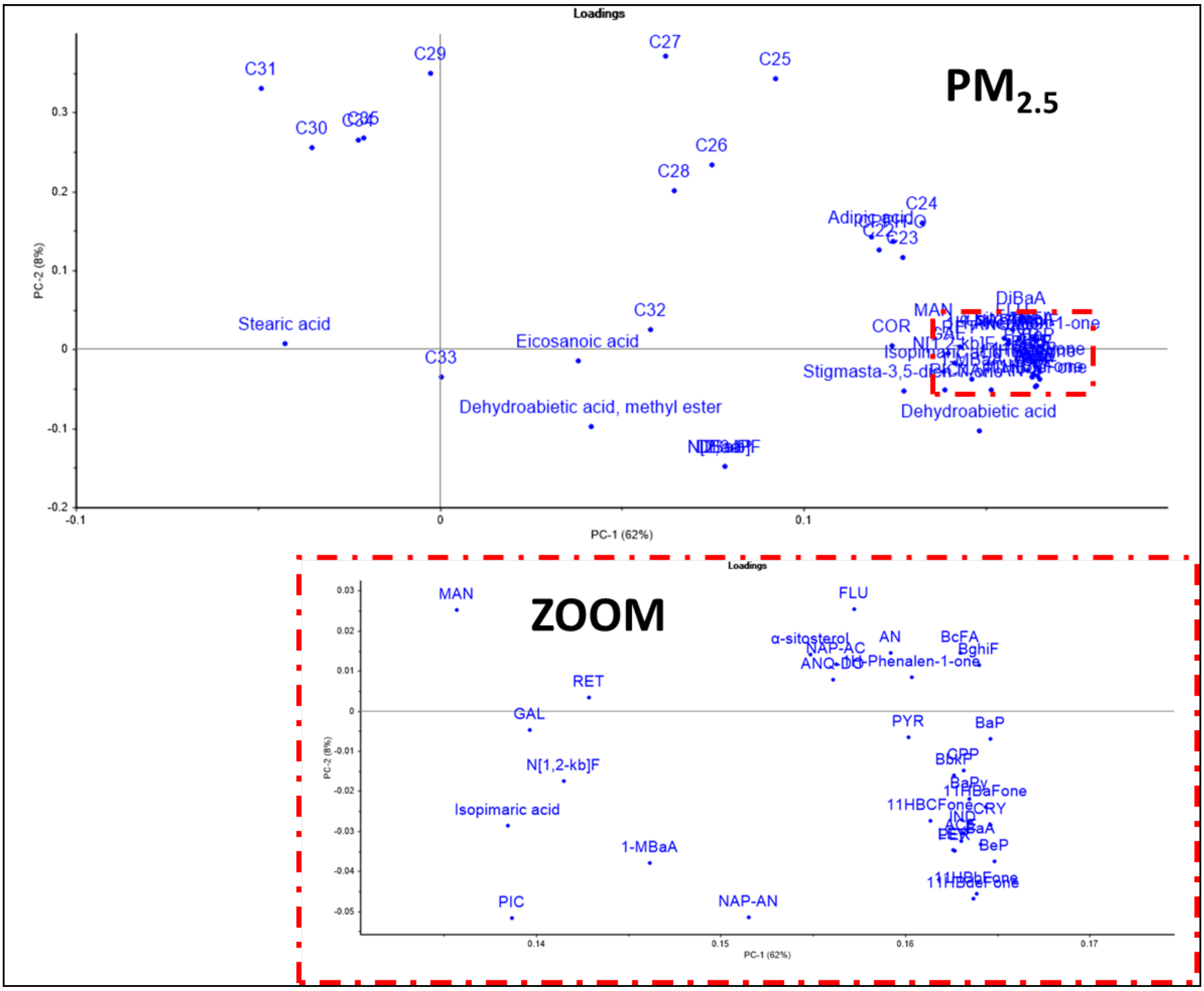

Figure 53. Loadings plot for $PM_{2.5}$ aerosol samples

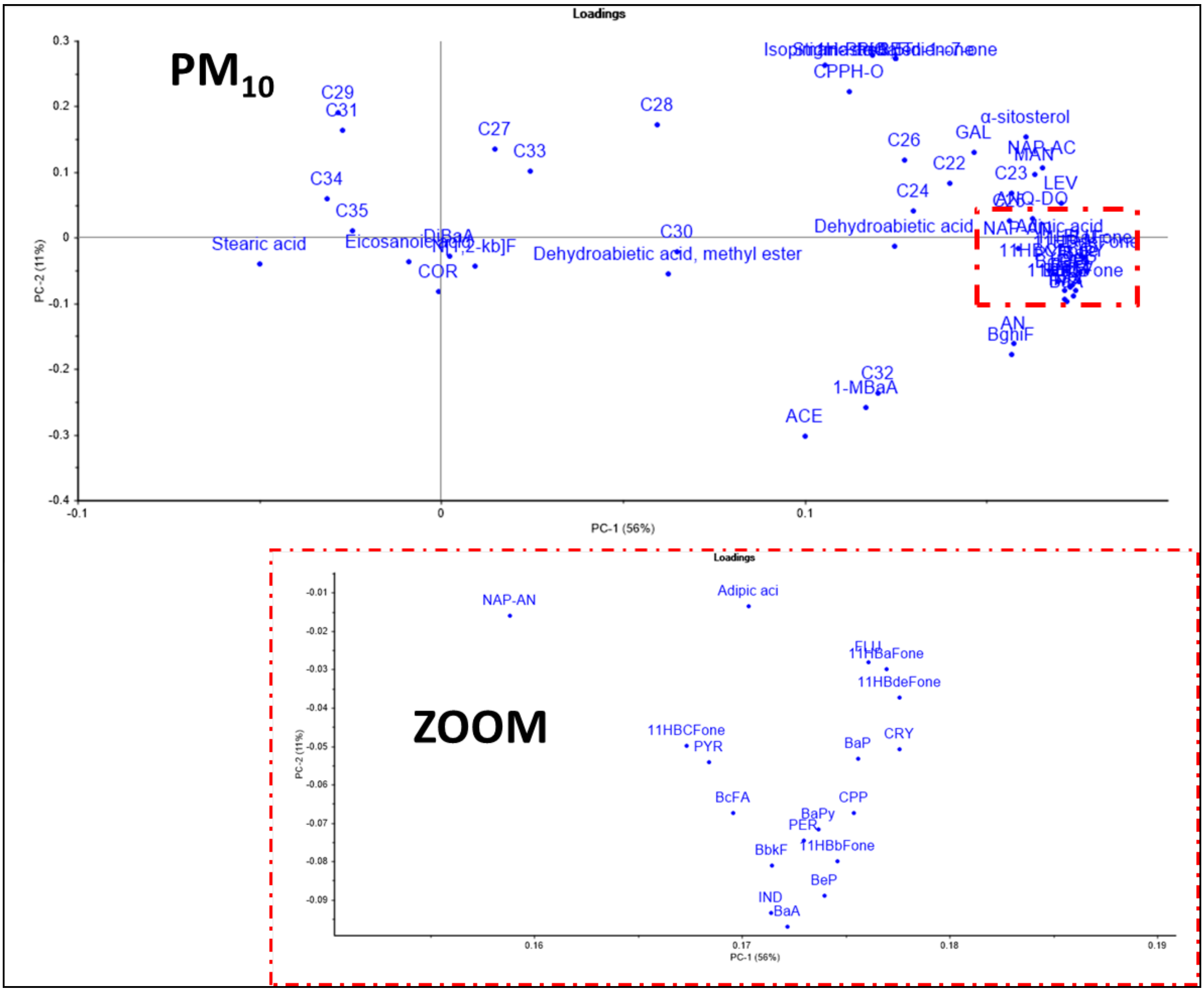

Figure 54. Loadings plot for PM_{10} aerosol samples

5.4.9 PCA and source identification

PCA was applied further to PM_1, $PM_{2.5}$ and PM_{10} samples dataset to describe the impact of source categories. From PCA three significant principal components (PCs) emerged, explaining the 73% of the variance contained in the PM_1 data, and the 76% of the variance contained in the $PM_{2.5}$ and PM_{10} data. PCA factors are easily distinguishable from others by sharp differences in factor loadings and can be interpreted as the marker species that primarily loaded the factor. The following results are consistent with the expectation that a factor is mainly loaded from multiple marker species for the same source type. In PM_1, $PM_{2.5}$ and PM_{10} samples, the main PC1 explains respectively the 56% in PM_1, the 62% in $PM_{2.5}$ and the 56% in PM_{10} samples of the total variance. PC1 contains almost all variables describing combustion sources, including fossil fuel emissions and biomass burning **Figure 55, Figure 56** and **Figure 57**. In this PC1, with positive loadings for all these variables, are present almost all PAHs, o-PAHs and markers of wood and biomass burning (levoglucosan (LEV), mannosan (MAN), galactosan (GAL), dehydroabietic acid and dehydroabietic acid methyl ester). So, PC1 explains for PM_1, $PM_{2.5}$ and PM_{10} samples those emission sources, characteristic of urban primary sources, such as vehicular emissions and emissions from residential heating and power plants.

PC2, in PM_1, $PM_{2.5}$ and PM_{10} samples, explained respectively the 11% in PM_1, the 8% in $PM_{2.5}$ and the 11% in PM_{10} of the total variance. PC2, mostly in PM_1 and $PM_{2.5}$ samples, shows positive loading on C_{24}- C_{31} alkanes. These PC2, explains mostly anthropogenic sources such as lubricating oil or fuel sources. Differently, PC2 on PM_{10} samples shows high positive loading on two PAHs, picene (PIC) (derivatives from brown coal) and retene (RET) (molecular marker of wood combustion), two o-PAHs, 1H-phenalen-1-one and cyclopenta(def)phenanthrenone (CPPH-O), one resin acid, isopimaric acid and one triterpenoid, stigmasta-3,5-dien-7-one. These variables describe quite well the PC2, their relevance had never been observed before, at the author's knowledge, and could be an important point to further, more, deeply studies, **Figure 55, Figure 56** and **Figure 57**.

PC3, in PM_1, $PM_{2.5}$ and PM_{10} samples explained respectively the 6% in PM_1, the 6% in $PM_{2.5}$ and the 9% in PM_{10} samples of the total variance. PC3 represents emissions from biogenic sources such as vegetative detritus and cooking. In fact, it shows strong positive loadings on long-chains n-alkanes C_{29}-C_{35} and fatty acids such as stearic and eicosanoic acids. PC3 contains also the contribution of tracers for environmental tobacco smoke cigarette markers, such as iso- and anteiso-alkanes (C_{29}- C_{33}). Furthermore, in PC3 on PM_1 and $PM_{2.5}$, with negative loading adipic acid, ANQ-DO, NAP-AC and NAP-AN are explained, representing Secondary Organic Aerosol formed by photochemical reactions in the atmosphere, **Figure 55, Figure 56** and **Figure 57**.

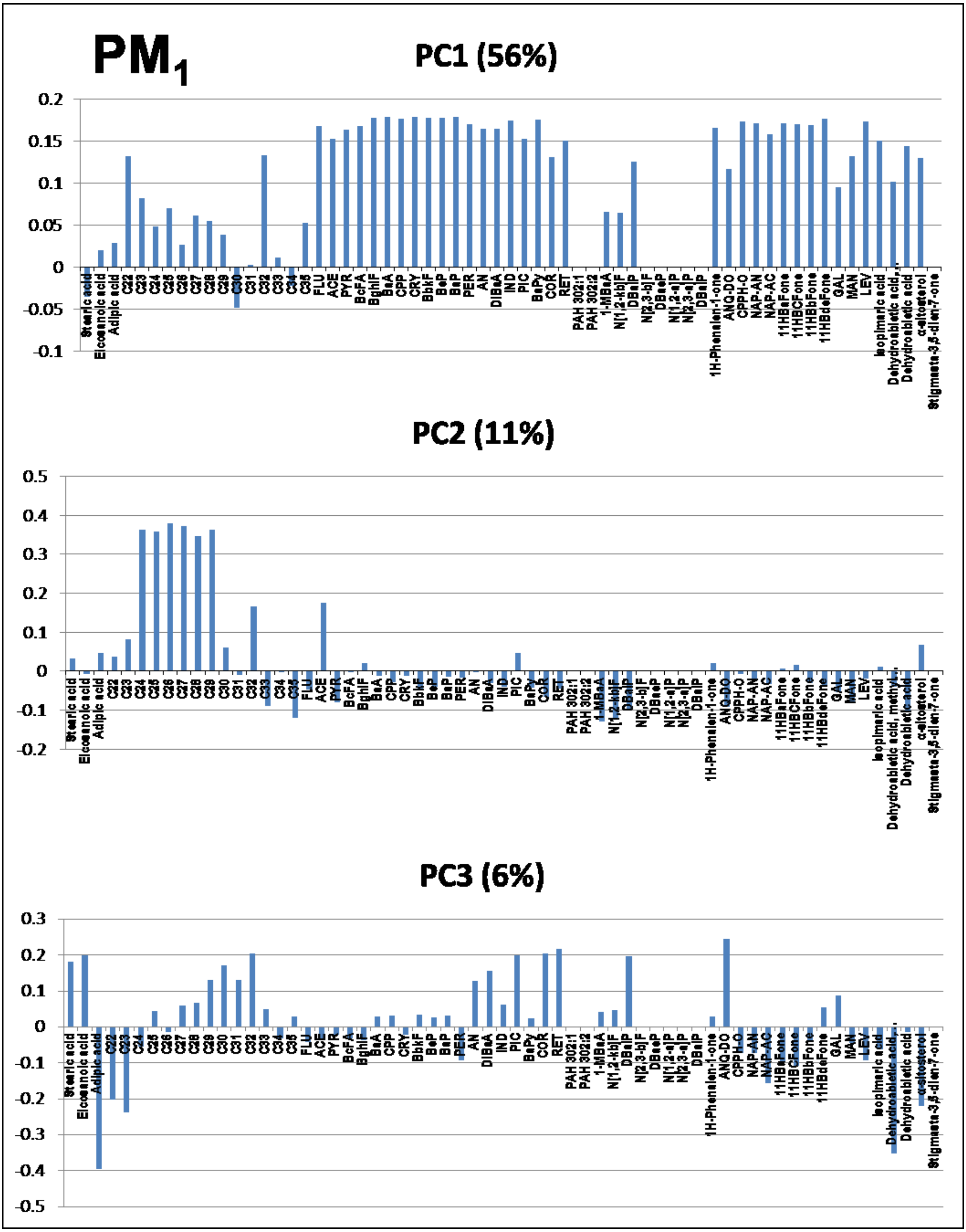

Figure 55. Loadings of the main 3 PCs emerged from PCA, in PM₁ samples

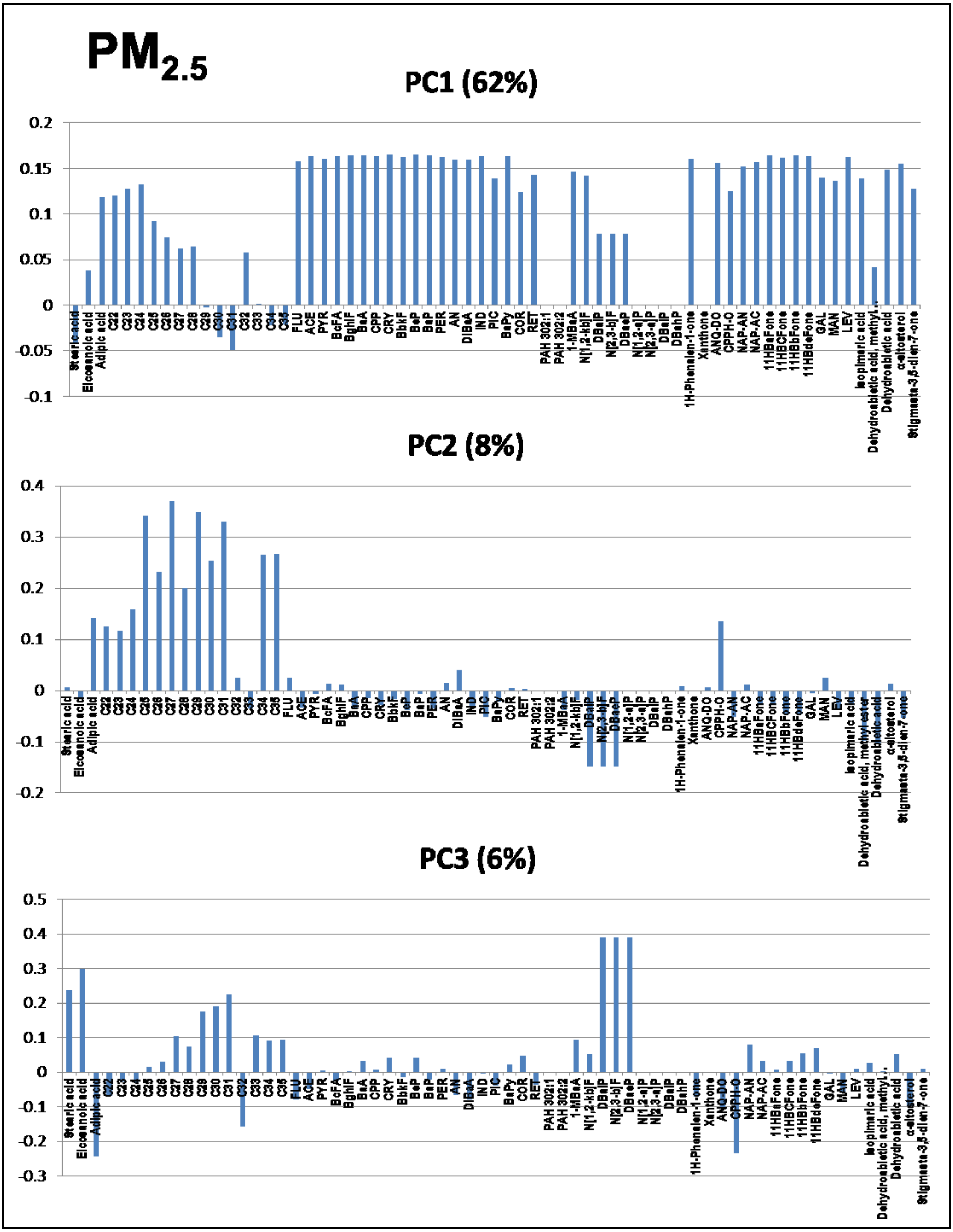

Figure 56. Loadings of the main 3 PCs emerged from PCA, in $PM_{2.5}$ samples

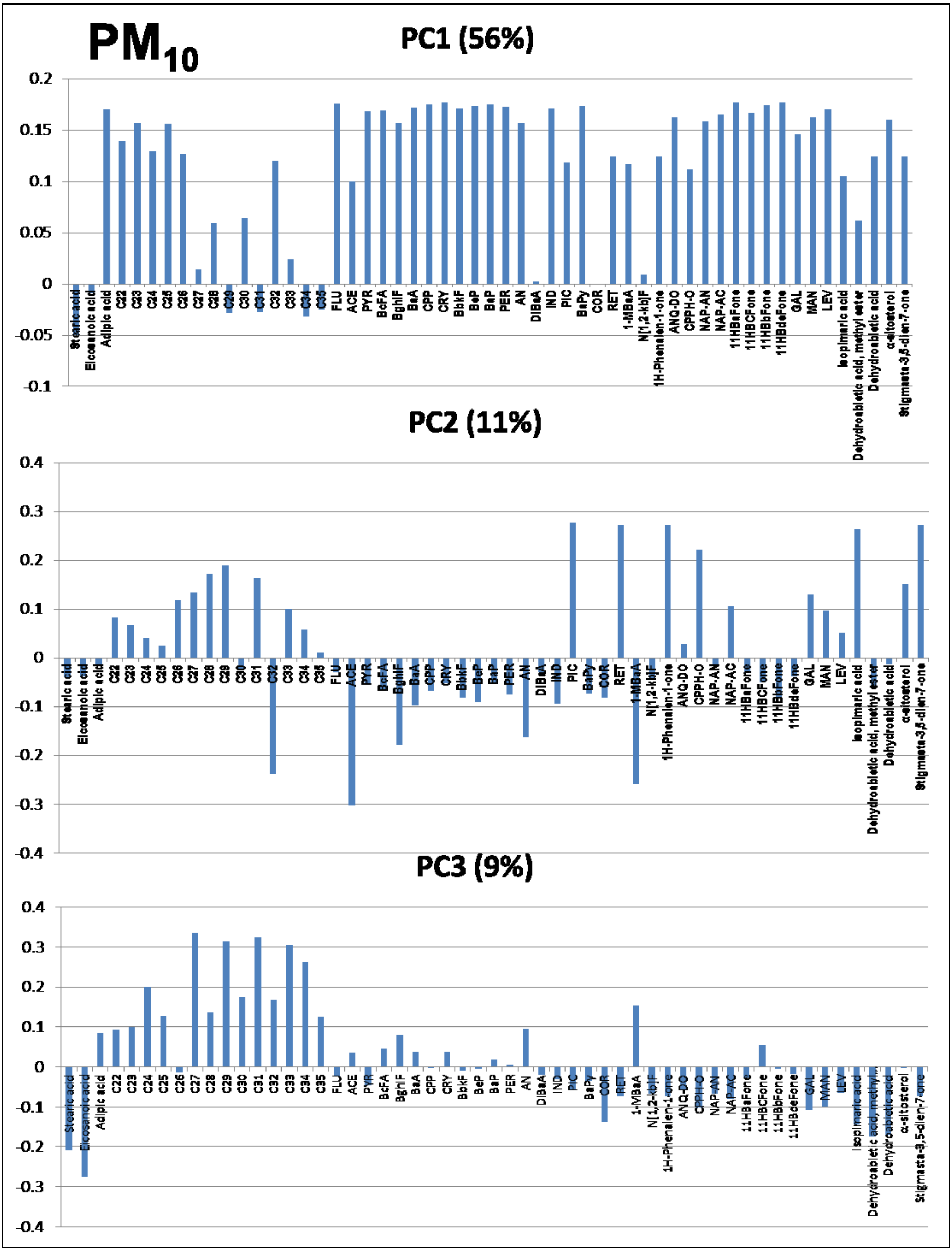

Figure 57. Loadings of the main 3 PCs emerged from PCA, in PM_{10} samples

5.5 Conclusion of this case of study

The chemical composition of PM_1, $PM_{2.5}$ and PM_{10} samples from Sernaglia della Battaglia were investigated. PM_1, $PM_{2.5}$ and PM_{10} samples were investigated during three different period of the 2017 year: during the winter, 30.01.2017- 11.02.2017, during the spring, 16.04.2017- 6.05.2017, and during early summer, 12.06.2017- 16.06.2017. Samples were analysed using IDTD–GC–TOFMS technique. The results confirmed that IDTD–GC–TOFMS is an analytical technique applicable to real atmospheric samples, providing a large dataset of different chemical markers in particulate samples. The distribution of several molecular markers compounds were determined during the three different periods. It was possible to identify different emission sources, discriminating between natural and anthropogenic emissions, and to study the temporal trend of these several environmental markers, showing the main changes during the year. An attentive discussion of each class of chemical tracers, allow to focus on the different emission sources and their respective roles. Furthermore, statistical analyses, through Principal Component Analysis (PCA), permitted a deeper discussion of the contribution of each class of chemical compound and the identification of the main factors representing different sources.

All PM_1, $PM_{2.5}$ and PM_{10} samples showed higher concentrations of all chemical compounds during winter than spring and summer, highlighting the greater impact of emission sources during the coldest period of sampling. During winter, PM_1, $PM_{2.5}$ and PM_{10} samples were mostly characterized by chemical compounds from combustion sources including fossil fuel emissions, short chains of n- alkanes and the most of PAHs and o-PAHs and biomass burning markers, levoglucosan and dehydroabietic acid. During spring and early summer, PM_1, $PM_{2.5}$ and PM_{10} samples are explained by the same chemical compounds too, but with an important role of acids, mainly stearic acids and longer n- alkanes chains, C_{29}- C_{35}, indicating a more important role of biogenic sources and also highlighting the contribution of tracers for environmental tobacco smoke.

CONCLUSION

Through the three studies conducted in this PhD thesis it has been possible to demonstrate widely the applicability of a wide range of environmental markers in analytical studies with the aim of environmental characterization of aerosol. It has been demonstrated that environmental markers can characterize different areas; remote areas, such as Antarctica, strongly characterized by natural inputs, and rural areas, such as Sernaglia della Battaglia, characterized by both natural inputs and anthropic inputs. A first case of study, entirely focused on one remote area, Antarctica, permitted the investigation of the chemical composition and particle size distribution of Antarctic aerosol, in two different sampling sites. One coastal site, on Victoria Land near the Italian Mario Zucchelli Station, during the 26th sampling campaign, and over the Antarctic plateau at Concordia Station, during two consecutive campaigns, the 27th sampling campaign and the 28th sampling campaign. Sea salt input, Na^+, Mg^{2+} and SO_4^{2-} characterized the aerosol collected in the coastal site. It was differentiated between ss-SO_4^{2-} and nss-SO_4^{2-}. Furthermore, in MZS samples the species more concentrated were found in the coarse fraction, because they are primary species. DC samples confirmed that aerosol over the Antarctic plateau was characterized by high concentration of anion species such as, nss-SO_4^{2-}, MSA acid and NO_3^-. The determined ionic species were mainly distributed in the fine fraction due to the atmospheric processes of long-range transport.

The second case study, focused on the remote area of Antarctica allowed to concentrate completely on a single sampling site, on the coast of Antarctica.

In this case, a wider range of environmental markers has been applied, allowing a deeper and more precise characterization of the coastal aerosol through the evaluation of different emission sources. In this second case of study were analysed aerosol and surface snow samples, collected from November 2014 to January 2015 at the coastal site of the Italian base, Mario Zucchelli station. A wide range of environmental markers were detected: ionic species, carboxylic acids, sugars, amino acids and free phenolic compounds. In aerosol samples, the characterization of the water-soluble compounds showed that their account was of about 60% of the total PM_{10} mass concentration, identifying as two predominant sources, sea salt and biogenic input. The first one was characterised by high concentration of Na^+, Mg^{2+}, Cl^- and SO_4^{2-}; the second one was characterised by high contribution of amino acids, sugars and phenolic compounds. Furthermore, in this case of study, the investigation of the WSOC in aerosol samples was combined with the study of WSOC in surface snow and it was the first study in which amino acids and sugars were quantified. Ions were identified in the aerosol and they were mainly distributed in the coarse fraction of atmospheric aerosol. Ions were also the most abundant compounds in snow samples, suggesting that the main air-snow transfer process was the dry deposition. Sugars presented a similar composition in both aerosol and snow samples. In surface snow samples an increase in concentration of alcohol sugars, tracers of fungal spores in the atmosphere, was found, suggesting that they could also be markers for this source in climatic studies. Amino acids were an important component in the surface snow samples. In addition to aerosol input, amino acids could also be originated from the decomposition of the biological material on the surface, as demonstrated by high concentrations of amino acids after snowfall.

The third and last case study, set in the rural area of Sernaglia della Battaglia, showed the change of the investigated area for the characterization of an aerosol with both natural and anthropogenic inputs. Furthermore, the application of a new and wide set of environmental markers allowed to discriminate between natural and anthropogenic sources. PM_1, $PM_{2.5}$ and PM_{10} aerosol samples from Sernaglia della Battaglia were investigated during three different period of the 2017 year: during the winter period, 30.01- 11.02, during the spring period, 16.04- 6.05, and during late spring/summer period, 12.06- 16.06. Samples were analysed using IDTD–GC–TOFMS technique. The distribution of several molecular markers compounds were determined during the three different periods. It was possible to identify different emission sources, discriminating between natural and anthropogenic emissions, and to study the temporal trend of these several environmental markers, showing the main changes during the year. During the first sampling period, 30.01- 11.02, PM1, PM2.5 and PM10 aerosol samples were mostly characterized by chemical compounds from combustion sources including fossil fuel emissions, short chains of n-alkanes and the most of PAHs, and biomass burning, levoglucosan and dehydroabietic acid. During the second sampling period, 16.04- 6.05, and the third sampling period, 12.06- 16.06, PM1, PM2.5 and PM10 aerosol samples are explained by the same chemical compounds too, but with an important role of acids, mainly stearic acids and longer n- alkanes chains, C29- C35 (negative values of PC1), indicating important biogenic sources and also highlighting the contribution of tracers for environmental tobacco smoke.

To sum up, the general conclusion of this PhD thesis is the great utility of environmental markers as a research tool: it was demonstrated that they can indicate the sources from which they were emitted and the chemical transformations they have undergone, allowing the environmental characterization of extremely different places all over the world. The prospects arising from this research are many, but I would like to focus mainly on two: firstly the identification of an increasing number of environmental markers which can explain in a more detailed way the environment. Secondly, the application of the environmental markers in a greater number of areas around the world, to validate their universal application.

LIST OF TABLES

LIST OF FIGURES

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Particle size distribution of inorganic and organic ions in coastal and inland Antarctic aerosol

This work was financially supported by the Italian National Program of Antarctic Research (PNRA) through the project ‘Studio delle sorgenti e dei processi di trasferimento dell’ aerosol atmosferico antartico’ (no. 2009/A2.11). The research was also supported by the National Research Council of Italy (Consiglio Nazionale delle Ricerche, CNR). The authors thank ELGA LabWater for providing the Pure-Laboratory Option-R and Ultra Analytic, which produced the ultrapure water used in these experiments.

Aerosol and snow transfer processes: An investigation on the behavior of water-soluble organic compounds and ionic species

Data and information on local meteorology were obtained from Operational Meteorological Infrastructure of ENEA-UTA (www.enea.uta.it) through the “Meteo-Climatological Observatory” of PNRA (www.climantartide.it). This work was financially supported by the Italian “Programma Nazionale di Ricerche in Antartide” (PNRA) through the project (PdR2013/AZ3.04) “Air-snow exchanges and relationships for trace elements and organic compounds of climatic interest”. The research was also supported by the National Research Council of Italy (Consiglio Nazionale delle Ricerche, CNR). The authors also acknowledge Elga Lab Water (High Wycombe, UK) for providing the ultrapure water systems. In conclusion we would like to thank Dr. Silvia Illuminati (Polytechnic University of Marche e Ancona, Italy) for her help and cooperation during the sampling activities in Antarctica.

Study of aerosol composition in samples (pm1, pm2.5 and pm10) collected at sernaglia della battaglia

PM_1, $PM_{2.5}$ and PM_{10} aerosol samples were provided by ARPAV (Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto). in-situ derivatization direct thermal desorption gas chromatography time-of-flight mass spectrometry (IDTD-GC-TOFMS) analysis were performed in CMA, Helmholtz Zentrum, laboratories, in Munich, Germany.

APPENDIX

Scientific Publications and Conferences Contributions

2018

Paper published on a scientific journal

Stoycheva, Stella; Marchese, Dayton; Paul, Cameron; Padoan, Sara; Juhmani, Abdulsalam; Linkov, Igor: Multi-criteria decision analysis framework for sustainable manufacturing in automotive industry, JOURNAL OF CLEANER PRODUCTION, vol. 187, pp. 257-272 (ISSN 0959-6526)

Abstract of the Acts of the Congress

Gambaro, Andrea; Barbaro, Elena; Feltracco, Matteo; Padoan, Sara; Zangrando, Roberta; Contini, Daniele; Barbante, Carlo: Caratterizzazione dimensionale dei composti solubili in acqua nella frazione ultrafine, fine e grossolana dell'aerosol urbano , PM2018, IAS - Italian Aerosol Society, Congress: VIII Convegno Nazionale sul Particolato Atmosferico - PM2018, 23 - 25 May 2018

Abstract of the Acts of the Congress

Sara, Padoan; Elena, Barbaro; Matteo, Feltracco; Roberta, Zangrando; Carlo, Barbante; Andrea, Gambaro: Characterization of Ionic Composition in the Submicron Fraction of Urban Aerosol, ACTS of the XXVI SCI NATIONAL CONGRESS, Volume II, Division of Environmental Chemistry and Cultural Heritage, Division of Analytical Chemistry, Italian Chemical Company, Congress: XXVI Congresso Nazionale della Società Chimica Italiana, 11-14 September 2017 (ISBN 9788886208802)

2017

Paper published on a scientific journal

Barbaro, Elena; Zangrando, Roberta; Padoan, Sara; Karroca, Ornela; Toscano, Giuseppa; Cairns, Warren R.L.; Barbante, Carlo; Gambaro, Andrea: Aerosol and snow transfer processes: An investigation on the behavior of water-soluble organic compounds and ionic species, CHEMOSPHERE vol. 183, pp. 132-138 (ISSN 0045-6535)

Paper published on a scientific journal

Barbaro, Elena; Padoan, Sara; Kirchgeorg, Torben; Zangrando, Roberta; Toscano, Giuseppa; Barbante, Carlo; Gambaro, Andrea: Particle size distribution of inorganic and organic ions in coastal and inland Antarctic aerosol, ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH INTERNATIONAL" vol. 24, pp. 2724-2733 (ISSN 0944-1344)

Abstract in Acts of the Congress

- Padoan, Sara; Barbaro, Elena; Zangrando, Roberta; Capodaglio, Gabriele; Barbante, Carlo; Gambaro, Andrea: Determination of ionic compounds in Antarctic samples using ion-chromatography coupled to mass spectrometry, Book of Abstracts, YISAC 2017, Congress: YISAC 2017, 28-30 June 2017

2016

Poster in Acts of the Congress

Barbaro, Elena; Padoan, Sara; Kirchgeorg, Torben; Zangrando, Roberta; Karroca, Ornela; Gambaro, Andrea: Water-soluble compounds as indicators of the study of atmosphere-snow exchanges in the Antarctic, PM2016, VII Convegno Nazionale sul Particolato Atmosferico, 17-20 May 2016

Poster in Acts of the Congress

Padoan, S.; Barbaro, E.; Zangrando, R.; Karroca, O.; Barbante, C.; Gambaro, A. Methoxyphenols in Arctic seawater, Italian Chemical Company, Congress: XXVI Congresso della Divisione di Chimica Analitica della Società Chimica Italiana, 18-22 September 2016 (ISBN 978-88-86208-91-8)
Pubblicazioni:

Curriculum Vitae

PERSONAL INFORMATION

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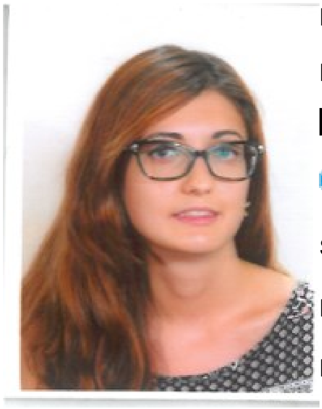

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Date of birth 25/11/1991

Nationality Italian

WORK EXPERIENCE AND TRAINING

From September 25th 2017
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PhD Internship as researcher at HelmholtzZentrum München

HelmholtzZentrum München, Munich, Germany

- Chemical analyses with gas chromatograph combined with mass spectrometry (GC-tof-MS)
- Chemical analyses on carbon OC and EC

From September 19th 2016
to January 31st 2017

Master’s Degree Internship as researcher at Ca’ Foscari University of Venice

University laboratory of analytical chemistry, Ca’ Foscari University of Venice

- Support as lecturer in the analytical chemistry laboratory
- Research in the analytical chemistry laboratory

From June 30th
to July 14th 2016

BANSIC 2016 Oceanographic Research Campaign on board of the “N/O Minerva Uno” in collaboration with IAMC/CNR

“N/O Minerva Uno”, Sicilian Channel, Italy

- Water sampling with a rosette sampler equipped with 12 Niskin bottles

From December 9th 2014
to July 31st 2015

Training

Laboratory of Analytic and Environmental Chemistry, Ca’ Foscari University of Venice, Italy

- Chemical analyses with ion chromatograph combined with mass spectrometry (IC-MS)

From January 7th 2013
to July 31st 2013

Training

Laboratory of Analytic Chemistry, University of Bologna, Italy

- Chemical analyses with polarography

EDUCATION

From September 15th 2015
to September 2018
(expected term)

PhD in Environmental Sciences

Ca' Foscari University of Venice

From September 2013
to July 2015

Master's Degree in Sustainable Chemistry and Technologies

Ca' Foscari University of Venice

Master's Degree thesis: "Study of ionic compounds in samples from the Antarctic through ion chromatograph combined with mass spectrometry"
Thesis advisor: Mr. Andrea Gambaro
Thesis Co-Advisors: Mrs. Elena Barbaro and Mr. Torben Kirchgeorg

From September 2010
to July 2013

Bachelor's Degree in Chemistry and Materials Chemistry

University of Bologna

Bachelor's Degree thesis: "Study on toxic metals in cosmetics through analytical voltammetry"
Thesis advisor: Mr. Clinio Locatelli
Thesis Co-Advisor: Mrs. Dora Melucci

From September 2005
to July 2010

Scientific High School Diploma

"Enrico Fermi" Scientific High School, Bologna, Italy

PERSONAL SKILLS

Mother tongue: Italian

Other language(s)	UNDERSTANDING		SPEAKING		WRITING
	Listening	Reading	Spoken interaction	Spoken production	
English	C1	C1	C1	C1	C1
	OXSET C1, Oxford School of English (June, 2018)				
French	B2	B2	B2	B2	B2

	DELF B2, Alliance Française (2009)
	Levels: A1/A2: Basic user - B1/B2: Independent user - C1/C2 Proficient user Common European Framework of Reference for Languages
Communication skills	Good communication and interpersonal skills developed during the university career. Constructive attitude and adaptability to multicultural environments.
Organisational / managerial skills	Extremely developed cooperation skills focused on obtaining the team goals. Ability acquired during both my university, training career and the six months abroad period in Germany.
Job-related skills	Knowledge of analytical techniques of separation, ion and liquid chromatography techniques combined with electrical conductivity and mass spectrometry. Knowledge of analytical techniques of separation, gas chromatography combined with mass spectrometry. Knowledge of analytical techniques of separation, thin-layer chromatography, extraction, crystallization and distillation. Knowledge of analytical techniques of titration. Polarography usage. Basic knowledge of inorganic and organic synthesis.
Digital skills	Good knowledge of: - *Microsoft Windows operating system* - *Microsoft Office applications* - *Browser Web* - *ChemOffice 8.0 (Chromatography Data System)* - *Origin* - *The Unscrambler* - *R* - *QGIS*
Other skills	Classical music: piano playing (3 years experience); Traditional and ethnic cooking; Photography
Driving licence	Car driving license

Scientific Publications

2018

Paper published on a scientific journal

- Stoycheva, Stella; Marchese, Dayton; Paul, Cameron; Padoan, Sara; Juhmani, Abdulsalam; Linkov, Igor: *Multi-criteria decision analysis framework for sustainable manufacturing in automotive industry*, JOURNAL OF CLEANER PRODUCTION, vol. 187, pp. 257-272 (ISSN 0959-6526)

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Abstract of the Acts of the Congress

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- Barbaro, Elena; Zangrando, Roberta; Padoan, Sara; Karroca, Ornela; Toscano, Giuseppa; Cairns, Warren R.L.; Barbante, Carlo; Gambaro, Andrea: *Aerosol and snow transfer processes: An investigation on the behavior of water-soluble organic compounds and ionic species*, CHEMOSPHERE vol. 183, pp. 132-138 (ISSN 0045-6535)

Paper published on a scientific journal

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Abstract in Acts of the Congress

- Padoan, Sara; Barbaro, Elena; Zangrando, Roberta; Capodaglio, Gabriele; Barbante, Carlo; Gambaro, Andrea: *Determination of ionic compounds in Antarctic samples using ion-chromatography coupled to mass spectrometry*, Book of Abstracts, YISAC 2017, Congress: YISAC 2017, 28-30 June 2017

2016

Poster in Acts of the Congress

- Barbaro, Elena; Padoan, Sara; Kirchgeorg, Torben; Zangrando, Roberta; Karroca, Ornela; Gambaro, Andrea: *Water-soluble compounds as indicators of the study of atmosphere-snow exchanges in the Antarctic*, PM2016, VII Convegno Nazionale sul Particolato Atmosferico, 17-20 May 2016

Poster in Acts of the Congress

- Padoan, S.; Barbaro, E.; Zangrando, R.; Karroca, O.; Barbante, C.; Gambaro, A. *Methoxyphenols in Arctic seawater,* Italian Chemical Company, Congress: XXVI Congresso della Divisione di Chimica Analitica della Società Chimica Italiana, 18-22 September 2016 (ISBN 978-88-86208-91-8)

In compliance with the Italian legislative Decree no. 196 dated 30/06/2003, I hereby authorize you to use and process my personal details contained in this document.

Sara Padoan

Publications

Post- print versions of:

1) Particle size distribution of inorganic and organic ions in coastal and inland Antarctic aerosol

2) Aerosol and snow transfer processes: An investigation on the behavior of water-soluble organic compounds and ionic species

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RESEARCH ARTICLE

Particle size distribution of inorganic and organic ions in coastal and inland Antarctic aerosol

Elena Barbaro[1,2] · Sara Padoan[1] · Torben Kirchgeorg[1] · Roberta Zangrando[2] · Giuseppa Toscano[1,2] · Carlo Barbante[1,2] · Andrea Gambaro[1,2]

Received: 30 June 2016 / Accepted: 2 November 2016 / Published online: 10 November 2016

Abstract The concentration and particle-size distribution of ionic species in Antarctic aerosol samples were determined to investigate their potential sources, chemical evolution, and transport. We analyzed aerosol samples collected at two different Antarctic sites: a coastal site near Victoria Land close to the Italian Research Base "Mario Zucchelli", and another site located on the Antarctic plateau, close to Italian-French Concordia Research Station. We investigated anionic compounds using ion-chromatography coupled to mass spectrometry, and cationic species through capillary ion chromatography with conductometry. Aerosol collected close to the coast was mainly characterized by sea salt species such as Na^+, Mg^{2+}, and SO_4^{2-}. These species represented a percentage of 88% of the total sum of all detected ionic species in the aerosol samples from the coastal site. These species were mainly distributed in the coarse fraction, confirming the presence of primary aerosol near the ocean source. Aerosol collected over the Antarctic plateau was characterized by high acidity, with nss-SO_4^{2-}, NO_3^-, and methanesulfonic acid as the most abundant species. These species were mainly distributed in the <0.49 μm fraction, and they had a behavior of a typical secondary aerosol, where several chemical and physical processes occurred.

Keywords Aerosol · Antarctica · Ions · Carboxylic acids · Particle size distribution · Sea spray

Introduction

It is widely recognized that the study of climate change also requires the complete investigation of the chemical composition and physical features of atmospheric aerosol particles (Fiore et al. 2015). Aerosol can interfere with solar radiation by scattering and absorption, influencing the radiation energy balance of the earth system (IPCC 2007). Determining sources and emission of particles to the atmosphere is crucial, to better understanding their impact on climate change. Some chemical markers can describe chemical, physical, or biological processes in the atmosphere. Their presence and concentration could give us some useful information about origin of aerosol and atmospheric long-range transport processes. Several studies investigated different ions in the Antarctic atmosphere (Fattori et al. 2005; Kawamura et al. 1996b; Minikin et al. 1998; Preunkert et al. 2008; Teinila et al. 2000; Udisti et al. 2012). Sea spray emitted by bubble bursting is the main source of aerosol in the coastal areas and salt crystals influence the climatic conditions, contributing to the formation of cloud condensation nuclei and altering the albedo and the optical properties of the aerosol (Udisti et al. 2012). Some cationic species, such as sodium, magnesium, or potassium, derive mainly from this sea-air exchange (Udisti et al. 2012), while ammonium originates mainly from the decomposition of organic matter(Weller et al. 2008). Some anions, such as nitrate and sulfate, are part of important biogeochemical cycles and

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are able to participate in numerous reactions that influence the chemistry of the atmosphere.

Carboxylic acids (CA) may have different emission sources to the atmosphere. Some organic acids can be produced by photochemical reactions of oxidation of anthropogenic organic pollutants(Mochida et al. 2007). Once emitted in the atmosphere, CA precursors undergo oxidation or photochemical reactions or react with strong oxidants, e.g., ozone (Kawamura et al. 1996a).

The main aim of this study is to compare the composition and concentration of ionic compounds in the aerosol collected at an Antarctic coastal site in the vicinity of the Mario Zucchelli Station (MZS) and at an inland site close to Dome C (DC) in order to investigate different sources of aerosols and to understand possible chemical transformation processes during long range atmospheric transport.

Highly sensitive analytical methods were used to simultaneously determine several ionic compounds and CA in aerosols samples collected during three different Antarctic expeditions: the first, that occurred from November 2010 to January 2011, at MZS; two consecutive campaigns took at DC during the XXVII Italian Antarctic expedition from December 2011 to January 2012 (DC27) and during the XXVIII Italian Antarctic expedition from December 2012 to January 2013 (DC28). We investigated the nitrogen cycle components (nitrite (NO_2^-), nitrate (NO_3^-), and ammonium (NH_4^+)), two components of the sulfur cycle (sulfate (SO_4^{2-}) and methanesulfonic acid (MSA)), seven ions (chloride (Cl^-), sodium (Na^+), phosphate (PO_4^{3-}), bromide (Br^-), iodide (I^-), potassium (K^+), and magnesium (Mg^+)), and 13 CA (C_2-oxalic, C_2-acetic, C_2-glycolic, C_3-malonic, C_4-succinic, *h*C_4-malic, *cis-us*C_4-maleic, *trans-us*C_4-fumaric, C_5-glutaric, C_6-adipic, C_7-pimelic, αC_7-benzoic, and C_8-suberic acids).

Experimental section

Material and methods

Ultra pure water (18.2 MΩ cm, 0.01 TOC) was produced using a PURELAB flex ultra system (Elga, High Wycombe, UK). The multi anion standard solution for ion chromatography(Cl^- 10 mg L^{-1}; NO_3^- 20 mg L^{-1}; Br^- 20 mg L^{-1}; PO_4^{3-} 30 mg L^{-1}; SO_4^{2-} 20 mg L^{-1}) and single standard solutions (all 1000 mg L^{-1}) of I^-, NO_2^-, and CA (C_2-oxalic, C_2-acetic, C_2-glycolic, and C_3-malonic) were obtained from Sigma Aldrich. Standard solutions of other compounds (MSA, *cis-us*C_4-maleic, *trans-us*C_4-fumaric, hC_4-malic, C_4-succinic, C_5-glutaric, C_6-adipic, C_7-pimelic, αC_7-benzoic, C8-suberic) purchased from Sigma Aldrich, were prepared from the solid standard solved in ultrapure water. The multi cation standard solution for ion chromatography (K^+, Li^+, Mg^+, Na^+, and NH_4^+) at the concentration of 100 mg L^{-1} was obtained from Sigma Aldrich.

Sample collection and processing

Aerosol samples (*n* = 14) were collected during three different Antarctic campaigns. Five samples were collected from 29 November 2010 to 23 January 2011 at Campo Faraglione (74° 42′ S–164° 06′ E), about 3 km south of the Italian research base MZS. Four samples were collected over the Antarctic plateau (75° 06′ S–123° 20′ E), near the Italian-French scientific base Concordia station (DC), from 19 December 2011 to 28 January 2012 (DC27) and from 7 December 2012 to 26 January 2013 (DC28). Concordia station is located at Dome C (DC), Antarctica's fourth highest dome (3233 m above sea level), about 1200 km from the Southern Ocean. The two sampling sites are shown in Fig. 1.

A multi-stage Andersen impactor (TE-6000 series, Tisch Environmental Inc.) was used to collect aerosol samples on six pre-combusted (4 h at 400 °C in a muffle furnace) quartz fiber filters. The sampler accumulated particles with 10.0–7.2 μm, 7.2–3.0 μm, 3.0–1.5 μm, 1.5–0.95 μm, and 0.95–0.49 μm on slotted filters and <0.49 μm particle cut-off diameters on backup filter. The frequency of sampling was every 10 days with a total air volume of ~15,000 m^3 per sample. Blank samples were obtained using filters installed on the sampler with the air pump switched off. Samples and blanks were wrapped in a double layer of aluminum foil and stored at −20 °C until analysis.

During sample preparation, the filters were handled under a laminar flow bench (class 100), where they were broken into small pieces and placed in polyethylene tubes, using steel tweezers. All materials were previously cleaned with ultrapure water by sonication for 30 min at room temperature. Slotted

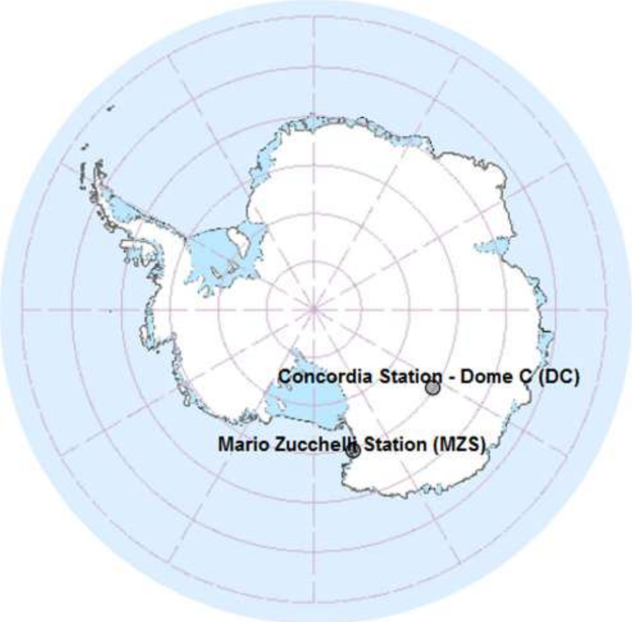

Fig. 1. Aerosol samplers were located near Mario Zucchelli Station (MZS, 74° 42′ S–164° 06′ E) and near Concordia Station (DC; 75° 06′ S–123° 20′ E; 3233 m above sea level)

filters were ultrasonically extracted for 30 min with 7 mL of ultra-pure water, while backup filters with 15 mL of ultra-pure water. Extracts were filtrated through a 0.45 μm PTFE filter (ThermoFisher) to remove residues before the analysis.

Instrumental analysis

Anion determination was performed using an IC (ThermoScientific™ Dionex™ ICS-5000, Waltham, US) equipped with an anionic exchange column (Dionex Ion Pac AS 11 2 × 250 mm) and a guard column (Dionex Ion Pac AG11 2 × 50 mm). Sodium hydroxide (NaOH), used as mobile phase, was produced by an eluent generator (Dionex ICS 5000EG, Thermo Scientific). The gradient with a 0.25 mL min^{-1} flow rate was 0 min, 0.5 mM; 0–3.5 min gradient from 0.5 to 5 mM; 3.5–5 min gradient from 5 to 10 mM; 5–25 min gradient from 10 to 38 mM; 25–30 min, column cleaning with 38 mM; 30–35 min; equilibration at 0.5 mM. The injection volume was 100 μL. A suppressor (ASRS 500, 2 mm, Thermo Scientific) removed NaOH before entering the MS source. The IC was coupled to a single quadrupole mass spectrometer (MSQ Plus™, Thermo Scientific ™) with an electrospray source (ESI) that operated in negative mode with a temperature of 500 °C and a needle voltage of 2.5 kV. Selected ion monitoring(SIM) was used for detection. Mass to charge ratios of [M-H]$^-$, compound-specific cone voltage, and acquisition time are provided in Table 1.

To determine cationic species, a capillary ion chromatograph (Thermo Scientific Dionex ICS-5000), equipped with a capillary cation exchange column (Dionex IonPac CS19-4 μm, 0.4 × 250 mm), a guard column (Dionex Ion Pac CG19-4 μm, 0.4 × 50 mm) was used. Methanesulfonic acid was used as mobile phase and was produced by an eluent generator (Dionex ICS 5000EG, Thermo Scientific). The gradient was 0–17.3 min; 1.5 mM; 17.3–21.9 min gradient from 1.5 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}. A suppressor (CCES 300, Thermo Scientific) removed MSA before entering the conductibility detector. Chromeleon 6.8 Chromatography data system was used for data acquisition and elaboration.

Quality control

The analytical procedure was validated through measurement of procedural blanks, recoveries, errors, and repeatability. Trueness and repeatability were evaluated by analyzing cleaned quartz fiber slotted filters (*n* = 3) and quartz fiber backup filters (*n* = 3) spiked with a known quantity of multi-ion standard solution. Seven and fifteen microgram of the anionic standard solution was added on cleaned slotted filters and on backup filters, respectively. The analytical method was validated for almost all of the anions. Repeatability, based on relative standard deviation (RSD) of the three replicates,

Table 1. Summary of mass to charge ratio (m/z) of [M-H]$^-$, instrumental parameters for each compound

Compounds	[M-H]$^-$	Cone (V)	Time range (min)
Inorganic ions			
Cl^-	35	90	5.00–8.00
NO_2^-	46	100	5.00–7.50
NO_3^-	62	70	7.00–10.00
Br^-	79	40	7.00–9.50
PO_4^{3-}, SO_4^{2-}	97	60	10.00–20.00
I^-	127	40	15.00–20.00
Organic acids			
C_2-acetic	59	40	3.00–6.00
C_2-glycolic	75	40	3.50–5.50
C_2-oxalic	89	100	11.00–14.00
MSA	95	40	3.50–6.00
C_3-malonic	103	70	9.00–12.00
cis-usC_4-maleic, trans-usC_4-fumaric	115	40	10.00–15.00
C_4-succinic	117	30	8.00–12.00
αC_7-benzoic	121	40	8.00–11.50
C_5-glutaric	131	100	8.00–12.00
hC_4-malic	133	40	8.50–11.00
C_6-adipic	145	50	8.00–11.00
C_7-pimelic	159	40	8.00–12.00
C_8-suberic	173	40	9.00–14.00

which was always below 10%. Percent errors ranged between −9 and 10% (Table S1).

For the cation method, a known amount (14 μg on slotted filters and 30 μg on backup filters) of the cationic standard solution was spiked. The analytical method was validated for almost the all of the cations with repeatability always below 10%. The accuracy of quantification demonstrated errors below ±10% (Table S2). We determined the instrumental detection limits (LOD) and the quantification limits (LOQ) for each compound (Table 2) by evaluating the signal-to-noise ratio of three and ten times, respectively, of a known absolute amount of the target compound(Bliesner 2006). The method detection limits (MDL) and method quantification limits (MQL) of the analytical procedure were determined as three and ten times the standard deviation of the average value of the field blank. They are also reported in Table 2. The MDL values reported in the present paper were similar to those reported by Morganti et al. (Morganti et al. 2007).

Results

Figure 2 shows the comparison between mean concentrations of anionic and cationic species in the aerosol samples collected at MZS during the 26th campaign and those determined in the samples collected at DC during the 27th campaign (DC 27) and during the 28th campaign (DC28). The ionic concentrations of the first sample (from 29 November to 9 December 2010) collected at MZS were excluded from the calculation of the mean values because they differ from the four next samples of the same campaign. The concentrations of chloride, nitrate, and CA were between 3 and 10 times higher than those of the other four samples of the same campaign (Fig. S1).

Table 2. Instrumental detection limit (LOD) and quantification limit (LOQ) and method detection limit (MDL) and method quantification limit (MQL) for each anions in both slotted and backup filters

			Slotted filters			Backup filters		
Ionic compounds	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	Blank (pg m^{-3})	MDL (pg m^{-3})	MQL (pg m^{-3})	Blank (pg m^{-3})	MDL (pg m^{-3})	MQL (pg m^{-3})
Cl^-	11	37	46	29	292	51	32	318
Br^-	3	10	4	3	26	3	1	8
I^-	5	16	1	0.1	1	1	0.1	1
NO_2^-	11	37	5	1	15	4	2	15
NO_3^-	8	25	336	13	129	362	7	67
MSA	0.4	1	46	5	48	47	13	127
SO_4^{2-}	2	6	444	110	1103	870	206	2058
PO_4^{3-}	9	30	28	0.5	5	166	5	45
C_2-oxalic acid	1	4	34	1	12	32	11	110
C_2-glycolic acid	1	5	6	3	26	6	2	19
C_2-acetic acid	13	44	129	7	75	188	39	385
C_3-malonic acid	1	3	3	1	6	5	2	16
cis-usC_4-maleic	1	3	2	1	5	5	1	6
trans-usC_4-fumaric	4	13	3	1	8	9	3	31
C_4-succinic acid	1	3	4	1	12	7	3	30
αC_7-benzoic acid	2	7	9	0.3	3	10	2	15
C_5-glutaric acid	1	5	1	0.4	4	1	2	19
hC_4-malic acid	1	3	2	1	13	1	1	11
C_6-adipic acid	1	4	4	1	12	4	2	22
C_7-pimelic acid	1	2	3	1	11	3	2	20
C_8-suberic acid	3	9	4	1	7	7	2	18
Li^+	0.1	0.3	1	1	3	1	1	2
Na^+	0.4	1.3	51	42	139	112	119	398
NH_4^+	0.2	0.9	13	4	13	10	2	8
K^+	4	14	170	31	103	304	134	448
Mg^+	1	3	24	38	125	15	22	74

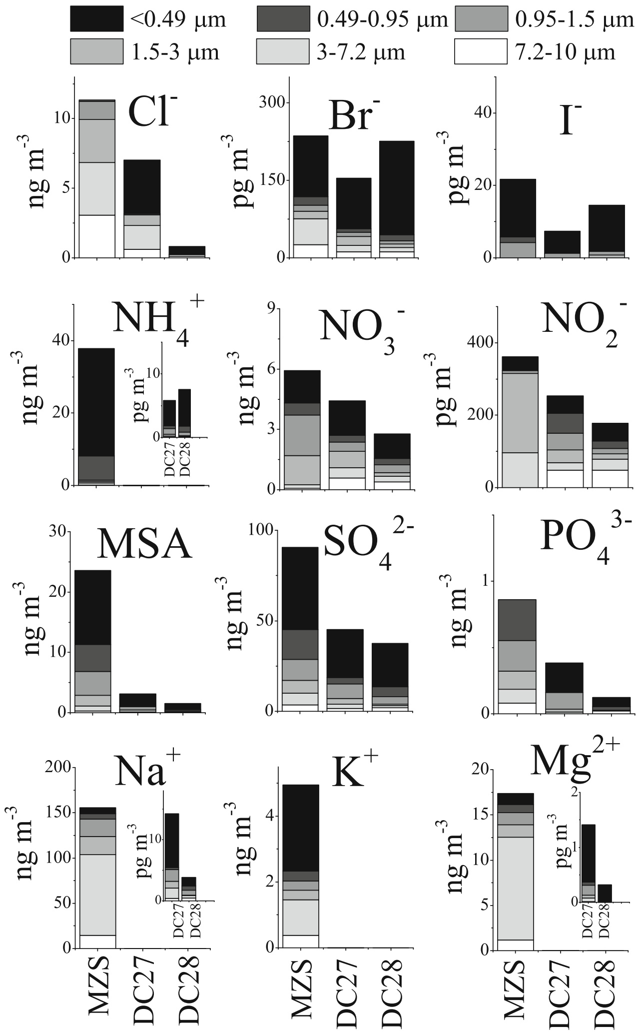

Fig. 2. Average concentrations of major ions and relative particle size-distribution of aerosol samples collected at Mario Zucchelli Station (MZS) during the austral summer 2010–2011 and at Concordia Station, Dome C (DC27 and DC28) during two consecutive austral summers 2011–2012 and 2012–2013

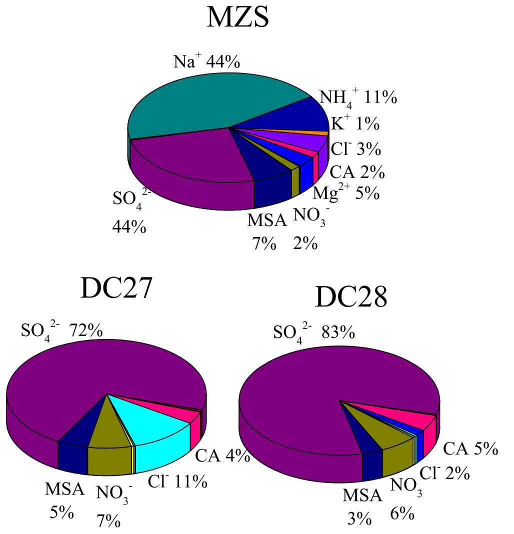

Fig. 3. Percentage of ionic species on the samples collected at MZS during the austral summer 2010–2011 and over Antarctic plateau at Dome C during the austral summer 2011–2012 (DC27) and during the austral summer 2012–2013 (DC28)

These high concentrations were probably due to a local biomass burning event as demonstrated by our previous studies on biomass burning markers, conducted on the same samples (Barbaro et al. 2015a; Zangrando et al. 2016).

The most abundant species found in the aerosol samples collected at MZS were Na^+ (113 ng m^{-3}as mean concentration; 45% of the total sum of all detected ionic species), SO_4^{2-} (90 ng m^{-3}, 26%), NH_4^+ (38 ng m^{-3}, 11%), MSA (24 ng m^{-3}, 7%), and Mg^{2+} (17 ng m^{-3}, 5%). Figure 3 shows the percentage of ionic species of the samples collected at MZS and at DC, demonstrating that SO_4^{2-} was the main ionic compound on the aerosol samples collected over the plateau (DC) in both campaigns (45 and 37 ng m^{-3}, 72 and 83%, respectively). During DC27, higher percentages and concentrations of Cl^- were 11% and 7 ng m^{-3}, while during DC28 Cl^- percentage and concentration were 2% and 0.8 ng m^{-3}. The ionic composition of aerosol samples collected over the plateau (DC) was characterized by high percentage of anionic species (SO_4^{2-}, NO_3^-, Cl^-, MSA, and CA) while aerosol samples collected near the coast (MZS) indicated a high contribution of cationic species, as demonstrated by a high percentage of Na^+ and Mg^{2+} (Fig. 3). The concentration values of major ions on the MZS and DC samples were very similar to those reported by Fattori et al. (Fattori et al. 2005).

The composition of CA was quite similar between the samples collected at MZS and those sampled at DC (Fig. 4). The most abundant compound was C_2-oxalic acid, which had a mean PM_{10} concentration of 2.7 ng m^{-3} at MZS, while the mean values of the DC samples were 1.5 and 1.2 ng m^{-3}, respectively. The second most abundant CA was C_2-acetic acid, which had a higher concentration at MZS (2.6 ng m^{-3}) compared to DC (0.7 and 0.6 ng m^{-3}, respectively), while other CA demonstrated negligible concentrations. Our values of CA were comparable to those reported in literature from a different Antarctic site (Kawamura et al. 1996b) and from the Southern Ocean (Wang et al. 2006).

Discussion

The composition and particle size distribution of ionic species can be used to define aerosol sources and chemical and physical processes occurring during long range atmospheric transport. Aerosol samples collected at MZS were dominated by sea spray input, represented by high contents of Na^+, Mg^{2+}, and SO_4^{2-} (Hillamo et al. 1998; Wyputta 1997). Na^+ and Mg^{2+} were mainly distributed in the coarse fraction, with higher concentrations in the first four stages (0.95–1.5 μm, 1.5–3 μm, 3–7.2 μm, and 7.2–10 μm) (Fig. 2). The

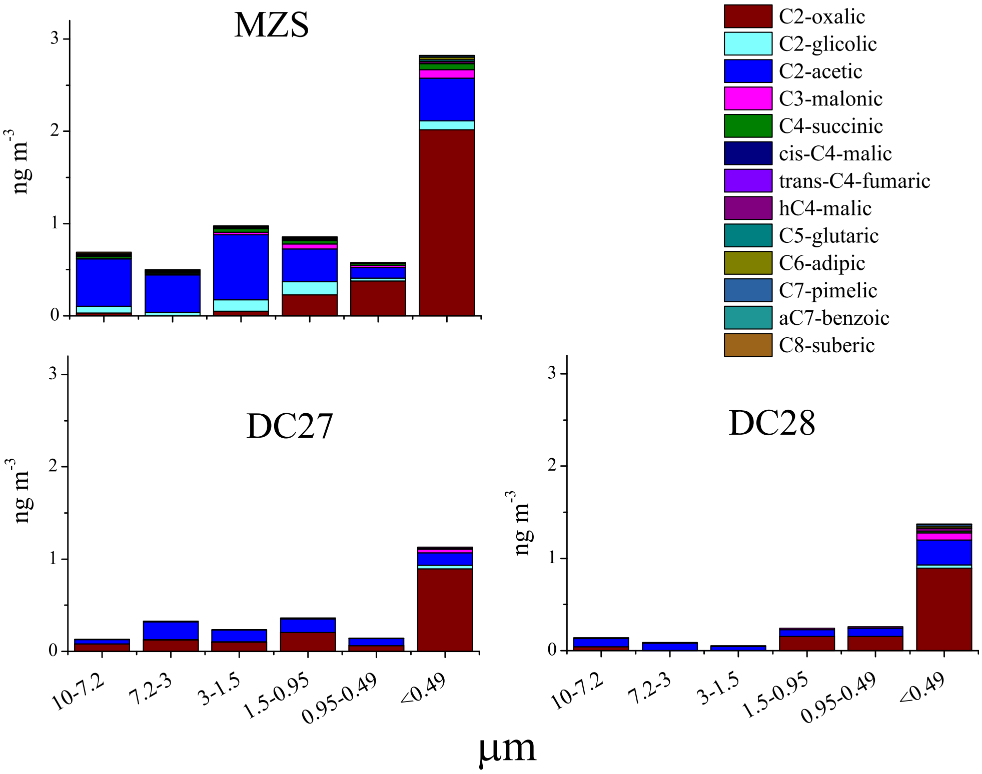

Fig. 4. Particle size distribution of the mean concentration of carboxylic acids on the aerosol samples collected at MZS and over the Antarctic plateau (DC 27 and DC28)

concentration of these species in the aerosol samples collected over the plateau (DC) were 10^4 times lower than those of MZS with an evident change in the particle size distribution: DC aerosol was characterized by Na^+ and Mg^{2+} mainly distributed in the <0.49 μm fraction. Fine particles of sea salt aerosol are less affected by the removal processes and eventually can move over Antarctica, where some air mass mixes down toward the surface (Cunningham and Zoller 1981).

The mean concentration of sea-salt particle mass in MZS samples was 505 ng m^{-3}, assuming that the original sea salt mass is equal to 3.248 times the sodium mass (Smith and Kalber 1974). This value was similar to those reported in other studies at coastal Antarctic stations, such as Halley Bay (160 ng m^{-3}) and at Neumayer (580 ng m^{-3}) while our mean concentration was lower than values reported at Aboa (2100 ng m^{-3}) and at Dumont d'Urville (DDU) (2100 ng m^{-3}) (Kerminen et al. 2000; Wolfenbarger and Seinfeld 1990). The contribution of sea-salt particle mass was up to one order of magnitude lower in the aerosol samples collected at DC, with mean values of 46 and 12 pg m^{-3} for DC27 and DC28, respectively. The difference between samples collected at the coastal (MZS) and internal (DC27 and DC28) stations suggests that fresh oceanic emissions were the main source of aerosol at the coastal base, while a depletion of sea salt particles occurred during the long range atmospheric transport over the Antarctic plateau.

Calculations based on the observed total sulfate, total sodium concentrations, and the Na^+/SO_4^{2-} ratio in bulk seawater show that non-sea salt sulfate (nss-SO_4^{2-}) represented >90% of the total sulfate in the fine fraction (<0.49 and 0.49–0.95 μm) of the samples collected at MZS. Sea salt sulfate (ss-SO_4^{2-}) was the only form of sulfate on the 3–7.2 μm and 7.2–10 μm fractions of MZS samples (Fig. S2), according to the other markers of sea salt input, Na^+ and Mg^{2+}. Negative nss-SO_4^{2-}, observed on 3–7.2 μm fraction (Fig. S2) of MZS samples along with high salt concentrations, may suggest that air masses originate from frost flowers (Wolff et al. 2003). The sea salt contribution to the sulfate concentration was negligible over the plateau, because nss-SO_4^{2-} was the single species of sulfate presented in aerosol samples collected at DC and it was mainly distributed in the <0.49 fraction (Fig. S2). The main source of nss-SO_4^{2-} was marine biogenic sulfur produced by marine phytoplankton in the oceans.

The contribution of sea salt to sulfate concentrations was evaluated using SO_4^{2-} to Na^+ ratio (Fig. S3). Ratios higher than a seawater value of 0.25 were calculated in the <3 μm fractions of aerosol collected at MZS during 2010–2011 austral summer, while minor or similar ratios were found in 3–7.2 μm and 7.2–10 μm fractions. This particle size distribution of SO_4^{2-} to Na^+ ratio was comparable to previous results obtained at the coastal station of DDU (Jourdain and Legrand 2002). The SO_4^{2-} to Na^+ ratios were always higher than the seawater value in the samples collected at DC during the austral summer 2011–2012 and 2012–2013, confirming that sea-salt contribution in sulfate concentration was negligible over the Antarctic plateau. Jourdain et al. (2008) found high value of SO_4^{2-} to Na^+ ratio in the samples collected at DC in March, suggesting a heterogeneous conversion of SO_2 on sea-salt aerosol.

Dimethyl sulfide (DMS) was emitted in the atmosphere, where it was oxidized mainly to either MSA or SO_2, which is further oxidized to SO_4^{2-}. In the polar summer, the contribution of non-biogenic sulfate (i.e., long-range-transported sulfur-containing species) was less than 10% of the total nss-SO_4^{2-} amount (Minikin et al. 1998). MSA and nss-SO_4^{2-} showed high concentrations on the <0.49 μm fraction of MZS and DC samples with decreasing concentrations over the plateau, far from the ocean source. A strong correlation between MSA and nss-SO_4^{2-} ($r^2 = 0.78$) underline the same biogenic source (Fattori et al. 2005). Several studies (deMora et al. 1997; Jourdain and Legrand 2001, 2002; Jourdain et al. 2008; Kerminen et al. 2000; Legrand et al. 1992) investigated MSA to nss-SO_4^{2-} ratio (R) in Antarctic aerosol samples in order to disentangle marine biogenic emissions versus other sulfur sources and to trace back the latitude of marine source regions influencing nss-SO_4^{2-} and MSA at a given site (i.e., high ratios suggesting high-latitude marine sources). Our value of R was 0.3 ± 0.1 in the MZS samples, comparable to data reported in literature for samples collected at coastal Antarctica (Jourdain and Legrand 2001, 2002; Kerminen et al. 2000; Legrand and Pasteur 1998). This mean ratios decreased to 0.08 ± 0.02 and 0.04 ± 0.01 for our aerosol samples collected over the Antarctic plateau (DC27 and DC28, respectively) due to distance of marine sources and longer atmospheric lifetime of nss-sulfate aerosol with respect to the one of MSA (Minikin et al. 1998).

Ammonium was mainly distributed in the <0.49 μm fraction of both MZS and DC samples (Fig. 2), but with lower concentrations at DC compared to MZS. This distribution suggests that the main source of NH_4^+ was probably the ocean (Jickells et al. 2003; Johnson and Bell 2008; O'Dowd et al. 2004) or the emission of seabirds and penguin colonies or soils exposed to these colonies (Blackall et al. 2007; Legrand et al. 1998; Schmale et al. 2013). Due to the distance from this potential source, significantly lower ammonium concentration was observed in the DC samples.

Nitrate in aerosol samples collected near the coast was mainly found in the >1 μm fraction (63%). Although its similar particle size distribution compared to sea salt does not reveal a marine source. The transport of nitrate to Antarctica provably involves gaseous compounds or particulate nitrate transferred back to the gas-phase prior to arrive at the lower Antarctic troposphere (Kerminen et al. 2000). The main formation pathway was the interaction of nitric acid or other reactive nitrogen compounds with sea-salt particles in the Antarctic atmosphere (Teinila et al. 2000). Indeed, nitrate is produced via the atmospheric oxidation of gaseous nitrogen oxides to nitric acid. The main sources of nitrogen oxide are nitrification in soils, biomass burning, fossil fuel, and oxidation of atmospheric nitrogen by lightning strikes (Legrand and Delmas 1986; Legrand and Kirchner 1990). Nitric acid tends to condense onto existing particles such as sea salt or mineral particles, because it has a high saturation vapor pressure. Nitrate aerosol particles have a formation pathway completely different from MSA or nss-SO_4^{2-}, that nucleate and originate new particles (Rankin and Wolff 2003).

Nitric acid may react with some species that are condensed on the same particles. An important example of these reactions is the chloride depletion. This is the reaction of sea salt particles, containing NaCl, with NO_3^-, SO_4^{2-}, and other organic acids to release HCl (Zhuang et al. 1999). The evaluation of chloride depletion allows us to estimate the amount of nitrate and sulfate formed on sea salt particles. The percentage of chloride depletion (%Cl_{dep}) in sea-salt aerosols is defined as ($[Cl_{ss}][Cl_{meas}]/[Cl_{ss}]100\%$, where $[Cl_{ss}] = 1.174\ [Na^+_{meas}]$ and $[Cl_{meas}]$ and $[Na^+_{meas}]$ are the measured Cl− and Na^+ equivalent concentrations(Yao et al. 2003). The percentage of chloride depletion ranged from 87 to 98% during the sampling period at MZS, near the marine source. Chloride depletion in the MZS samples was also evaluated by considering the particle size distribution. The highest values were observed in the fine fraction (<0.49 μm), where the highest concentration of sulfate was observed.

Chloride in the DC samples was mainly distributed in the fine fraction. The correlation with Na^+ was disappeared due to an extra-sea spray contribution to the Cl^- concentration. The main source of chloride in the aerosol over the Antarctic plateau was the air masses originating from the ocean that transport fine particles, containing NaCl and HCl adsorbed on the particle surface (Traversi et al. 2009). Another possible source could be a slow reemission of HCl into the atmosphere from the snow layer, where NaCl and HCl were deposited (Becagli et al. 2012). Figure 2 shows that the particle size distributions of chloride in the DC campaigns were quite different: in the first samplings (DC27), chloride was also detected on the coarse fraction, while during DC 28 it was detected only in the fine fraction (<0.49 μm). Considering the backward trajectories of air masses calculated for the same sampling periods by Barbaro et al. (2015b), we can establish that during DC27 air masses arrived at Dome C in about 36 h while in the austral summer 2012–2013 (DC28) air masses took 4 to 7 days to reach the site. This may suggest that the time of the long-range transport processes is a key factor in the life duration of coarse particles and in the aerosol composition over the Antarctic plateau.

Despite their environmental and climatic importance (Spolaor et al. 2014, Spolaor et al. 2013), data regarding Br^- and I^- in Antarctic aerosol are not often available due to their low concentrations. Iodide is correlated with phytoplankton's emissions, because it is present in the underside of sea ice (Saiz-Lopez et al. 2007). Br^- and I^- represented a low percentage of the total ionic content: 0.07% on the MZS samples and

0.2 and 0.5% on DC27 and DC28 samples, respectively. Bromide has a concentration 10 times higher than iodide at both sampling sites (Fig. 2). Both halogens were mainly distributed in the 0.49 μm fraction, and the particle size distribution was very similar at MZS and DC. Our bromide concentrations were very similar to values reported by Legrand et al. (2016) in bulk aerosol samples at Concordia Station (DC) and DDU. The main sources of bromide were biogenic emission such as phytoplankton (Hara 2004) or frost flowers (Rankin 2002). The relationship between bromide and sodium in aerosol collected at MZS had a R^2 value of 0.923 with a mean slope of 0.004, suggesting that sea salt was the main source of bromide in our aerosol samples collected at MZS during the austral summer 2010–2011. A depletion of bromide relative to sodium was observed in our summer MZS samples because the bromide to sodium mass-based ratio was lower (mean 2×10^{-3}) than the seawater value (6.25×10^{-3}). This process is commonly observed at remote marine sites of the Southern Hemisphere (Sander et al. 2003).

As suggested by Legrand et al. (2016), the bromine depletion factor (DF) was calculated in our MZS samples in order to evaluate the fraction of bromine lost from aerosol to the gas phase. DF is defined as 1- $([Br^-]/[Na^+])_{aerosol}/([Br^-]/[Na^+])_{reference}$, where $([Br^-]/[Na^+])_{reference}$ is the ratio value obtained by considering that sea-salt aerosol comes from open ocean (i.e., 6.25×10^{-3}). A mean DF value of 0.6 was obtained from our MZS samples, values higher than 0.49, 0.31, and 0.21 were reported by Legrand et al. (2016) in bulk aerosol at DDU for November, December, and January, respectively. Evaluating the depletion of bromide respect to particle size distribution (Fig. S4), the bromide to sodium mass-based ratio was lower than seawater value in coarse particles (>0.95 μm) while exceeded the seawater value in fine particles (<0.49 μm). These results show the same trend as reported by Legrand et al. (2016) in coastal Antarctic aerosol. The correlations between bromide and sodium in the samples collected over the Antarctic plateau were completely different during our two consecutive campaigns, DC27 and DC28. As previously described for chloride concentrations, the atmospheric transport time of aerosol over the Antarctic plateau was probably a critical factor for aerosol concentrations obtained at DC. In fact, during DC 27 when the air masses arrived over the plateau in about 3 h, the correlation between bromide and sodium had a R^2 of 0.96, while during DC28 the correlation was very poor ($R^2 = 0.005$) because air masses took 4 to 7 days to reach the site.

CA with low molecular weight (C_2-C_8) was also investigated in this study, as they can provide information about the sources and formation of organic aerosol. Figure 4 shows the comparison of particle size distributions between samples collected at MZS and those sampled at DC during two consecutive campaigns (DC27 and DC28). The most abundant CA in both sampling sites was C_2-oxalic acid, the end-product of various oxidation/decomposition reactions in the atmosphere (Kawamura and Sakaguchi 1999). Photochemical production of alkenes released by phytoplankton produced mainly these compounds (Xu et al. 2013). All acids, except for C_2-acetic acid, were mainly distributed in the fine fraction (<0.49 μm) due to their nature of secondary aerosol products in the atmosphere. This is different to the results from Jourdain and Legrand (Jourdain and Legrand 2002). They reported that C_2-oxalic acid was mainly distributed in 10 μm fraction of aerosol collected at DDU, where an evident contribution by ornithogenic (guano-enriched soils) is present.

C_2-acetic acid has a different behavior than other acids, because it is concentrated in the coarse fraction. Due to its high vapor pressure, C_2-acetic acid is emitted as secondary product in the gas phase and is then absorbed onto coarse particles, such as sea salt (Matsumoto et al. 1998). The concentration of C_2-acetic acid in the coarse fraction of the DC samples is lower probably due to the reduction of sea salt particles, where the organic acid adsorbs. This confirms its secondary behavior. The presence of C_2-acetic acid mainly in the gas-phase was confirmed by Legrand et al. (2012). They gas-phase concentrations at DDU of 10^5 times higher compared to our concentrations in the particulate fraction at MZS during the same sampling campaign. However, these concentrations were strongly influenced by the guano decomposition in the large penguin colonies at DDU.

To investigate the potential sources of CA in Antarctic aerosols, we used C_3-malonic to C_4-succinic ratio as indicator of enhanced photochemical production of diacids (Kawamura and Ikushima 1993). Indeed, C_4-succinic acid can be degraded to C_3-malonic acid by decarboxylation reactions activated by OH radicals (Fu et al. 2013). The mean C_3 to C_4 ratio calculated for MZS samples was 1.5, which is very similar to ratios calculated for marine areas (Fu et al. 2013). Mean ratio values of 5 and 6, calculated for DC27 and DC28 samples, suggest that malonic acid (C_3) was photochemically produced during long-range atmospheric transport over the Antarctic plateau (Fu et al. 2013).

To compare the acidity of aerosols between the coastal and inland site, the ionic balance was evaluated considering the ionic concentrations in terms of equivalent of fine (<0.95 μm) and coarse (>0.95 μm) fraction of aerosol samples collected at MZS and DC (Fig. S5). An important anion deficit was observed in the MZS samples in both fractions. In order to neutralize the MZS aerosol on the coarse fraction, other anionic species were necessary but we did not identify them. A explanation about the occurrence of these unknown anionic species (X^-) present in the MZS aerosol could be carbonate originating from the ice-free areas near the sampling site. The hypothesis of a local source of this unknown anionic species (X^-) is also supported by particle size distribution: the higher concentration of X^- was present in the coarse fraction. Anionic deficit in the fine fraction could be due to the presence of other organic compounds emitted by the ocean nearby. An opposite situation was observed in DC samples (Fig. S5), where a deficit of cations relative to the measured anions was observed. This deficit was due to a significant concentration of hydrogen cations present in the aqueous solution associated with the aerosols (Traversi et al. 2009).

Conclusions

We investigated the particle size distribution of Antarctic aerosol was investigated, comparing aerosol samples from two different sites: a coastal site on Victoria Land near the Italian Mario Zucchelli Station and two consecutive campaigns carried out over the Antarctic plateau at Concordia Station.

Antarctica is an isolated system that allows investigating natural sources of aerosol and processes of chemical and physical transformation during long-range transport. Aerosol collected near the coast was characterized by sea salt input with Na+, Mg^{2+}, and SO_4^{2-} as the main species. The study of sulfate concentrations allowed us to differentiate between sea salt sulfate and non-sea salt sulfate. The former species was mainly distributed in the coarse fraction, because it is a primary species, while the latter species is a secondary marine biogenic compound that characterizes the <0.49 μm fraction.

Two consecutive sampling campaigns confirmed that aerosol over the plateau presents high concentrations of anionic species such as non-sea salt sulfate, methanesulfonic acid, and nitrate. The presence of these compounds, produced by chemical reactions in the atmosphere, was coupled with the high acidity of this inland aerosol. The determined ionic species were mainly distributed in the fine fraction due to the atmospheric processes of long range transport.

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Aerosol and snow transfer processes: An investigation on the behavior of water-soluble organic compounds and ionic species

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HIGHLIGHTS

- The air-snow transfer processes were evaluated using water soluble compounds.
- This is the first study about amino acids and sugar concentration in surface snow.
- Water soluble organic fractions of Antarctic aerosol and snow were investigated.

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ABSTRACT

The concentrations of water-soluble compounds (ions, carboxylic acids, amino acids, sugars, phenolic compounds) in aerosol and snow have been determined at the coastal Italian base "Mario Zucchelli" (Antarctica) during the 2014–2015 austral summer. The main aim of this research was to investigate the air-snow transfer processes of a number of classes of chemical compounds and investigate their potential as tracers for specific sources.

The composition and particle size distribution of Antarctic aerosol was measured, and water-soluble compounds accounted for 66% of the PM_{10} total mass concentration. The major ions Na^+, Mg^{2+}, Cl^- and SO_4^{2-} made up 99% of the total water soluble compound concentration indicating that sea spray input was the main source of aerosol. These ionic species were found mainly in the coarse fraction of the aerosol resulting in enhanced deposition, as reflected by the snow composition.

Biogenic sources were identified using chemical markers such as carboxylic acids, amino acids, sugars and phenolic compounds. This study describes the first characterization of amino acids and sugar concentrations in surface snow. High concentrations of amino acids were found after a snowfall event, their presence is probably due to the degradation of biological material scavenged during the snow event. Alcohol sugars increased in concentration after the snow event, suggesting a deposition of primary biological particles, such as airborne fungal spores.

1. Introduction

Chemical markers provide unique information on the sources of aerosol and the chemical processes that took place during atmospheric transport. Their applicability to paleoclimatic studies of ice cores from polar regions, offers exceptional potential to evaluate the role and influence of aerosol in anthropogenic and natural forcing of climate change.

Several studies have been conducted to evaluate the relationships between the concentrations of some markers in air and snow. So far, only the relationship between ionic compounds and carboxylic acids has been investigated since they are the most easily detectable in most matrices. Wolff et al. (1998) determined the most abundant ionic compounds in the aerosol, fresh snow and firn cores from three coastal Antarctic stations and highlighted the difficulties in studying processes in an area where environmental conditions change frequently. Investigations on the depositional fluxes of non-sea salt sulfate and methanesulfonic acid allowed an assessment of the spatial variation of marine biogenic sulfur (Minikin et al., 1998) to be made.

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At Dome C on the Antarctic plateau, it was demonstrated that nitrate and chloride can be caught by the surface snow through dry deposition and adsorption processes (Udisti et al., 2004). The interactions of carboxylic acid at the air-snow interface has been studied in the Arctic (Narukawa et al., 2002), and underlined the compositional difference between aerosol and snow samples.

Ionic species such as Na$^+$, Mg^{2+}, Cl$^-$ and SO$_4^{2-}$ are the most abundant compounds in Antarctic aerosol (Udisti et al., 2012) because the main source of aerosol in polar regions is fine sea spray emitted by bubble bursting because they are distant from any anthropogenic or continental emission sources.

Carboxylic acids (CA) may have different emission sources to the atmosphere (Kawamura et al., 1996a). Some anthropogenic organic pollutants that act as CA precursors, once emitted into the atmosphere they can undergo photochemical reactions or react with strong oxidants, such as ozone (Kawamura et al., 1996b). It is thought that the main natural source for CA is photochemical reactions after the release of alkenes by phytoplankton (Xu et al., 2013).

Several organic compound classes, such as sugars and amino acids, are emitted from biogenic sources into the atmosphere. Bioaerosol (bacteria, fungi, viruses, pollen, cell debris) contains primary saccharides such as glucose and sucrose (Medeiros et al., 2006). Arabitol and mannitol can be used as tracers for airborne fungal spores (Bauer et al., 2008), and are also the main carbohydrates in lichens and bacteria (Medeiros et al., 2006).

Levoglucosan, the most abundant anhydrosugar, is a specific atmospheric tracer of biomass burning (Simoneit and Elias, 2001). Some studies have demonstrated that the composition of phenolic compounds (PC) in atmospheric aerosol is linked to the type of vegetation that was burned (Simoneit, 2002), although Zangrando et al. (2016) have suggested that these compounds may have an additional marine source. A possible correlation between primary marine production and amino acids has also been identified (Barbaro et al., 2015b).

The main aim of this study was to investigate the behavior of water-soluble compounds during aerosol-snow transfer processes. Aerosol and snow samples were collected at Faraglione Camp, about 3 km from the Italian station “Mario Zucchelli”, called MZS (Terra Nova Bay, Antarctica) during the 2014–2015 austral summer. Our research focused on several classes of compounds, such as ionic species (Cl$^-$, Br$^-$, I$^-$, NO$_2^-$ NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$, methanesulfonate (MSA), NH$_4^+$, Na$^+$, Mg^{2+}, K$^+$), CA (C$_2$-oxalic, C$_2$-glycolic,C$_3$-malonic, C$_4$-succinic, *h*C$_4$-malic, *cis-us*C$_4$-maleic, *trans-us*C$_4$-fumaric, C$_5$-glutaric, C$_6$-adipic, C$_7$-pimelic, *a*C$_7$-benzoic, C$_8$-suberic), sugars (monosaccharides, disaccharides, alcohol sugars and anhydrosugars), amino acids (AA) and PC (vanillin, syringyl and coumaryl compounds). This is the first study of potential relationships between sugars, AA and PC in aerosol and snow samples from the same site.

2. Material and methods

2.1. Collection and processing of aerosol samples

Aerosol samples (n = 7) were collected using a multi-stage Andersen impactor (TE-6070, Tisch Environmental Inc., Cleves, OH, USA) placed at Campo Faraglione (74° 41′ S, 164° 06′ E), 3 km south of the Italian MZS (Victoria Land, Antarctica) from the 6th of November 2014 to the 13th of January 2015.

Aerosol samples were collected on six pre-combusted (4 h at 400 °C in a muffle furnace) quartz fiber filters with different cut-offs: the sampler accumulated particles with the following size fractions: 10.0–7.2 μm, 7.2–3.0 μm, 3.0–1.5 μm, 1.5–0.95 μm, 0.95–0.49 μm on slotted filters and the <0.49 μm particle size on a backup filter at an average sampling airflow of 1.1 m^3 min^{-1}. Samples were collected for 10 days, as previous tests showed that this exposure time was necessary to quantify species at very low concentrations (Barbaro et al., 2015a, 2015b, 2016, 2017; Zangrando et al., 2016). Further sampling details are available in Table S2. 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, following the same procedure used for installation and removal of the sample filters. Samples and blanks were wrapped in a double layer of aluminum foil and stored at −20 °C until analysis.

The pre-analytical protocol to determine the ionic species (Cl$^-$, NO$_3^-$, NO$_2^-$, SO$_4^{2-}$, MSA, I$^-$, Br$^-$, PO$_4^{3-}$, Na$^+$, NH$_4^+$, Mg$^+$, K$^+$) and 12 CA (C$_2$-oxalic, C$_2$-glycolic, C$_3$-malonic, C$_4$-succinic, *h*C$_4$-malic, *cis-us*C$_4$-maleic, *trans-us*C$_4$-fumaric, C$_5$-glutaric, C$_6$-adipic, C$_7$-pimelic, αC$_7$-benzoic, C$_8$-suberic acids, Table S1) is described elsewhere (Barbaro et al., 2016). A quarter of each sample filter was broken into small pieces and placed into polyethylene tubes, using steel tweezers. All materials were previously cleaned by sonication with ultrapure water for 30 min at room temperature, and all sample handling was carried out under a class 100 laminar flow hood. Slotted filters were ultrasonicated for 30 min in 7 mL of ultrapure water, while backup filters were extracted with 15 mL of ultrapure water. Extracts were filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter (ThermoFisher) to remove solid residues before analysis.

Half of each sample filter was used to determine AA, sugars and PC using a previously described method (Barbaro et al., 2015a, 2015b; Zangrando et al., 2016), where filter subsamples were spiked with a ^{13}C-labelled internal standard mix (AA, PC and levoglucosan), ultrasonicated twice for 15 min in ultrapure water, and filtered through a 0.45-μm PTFE filter before analysis.

2.2. Collection and processing of snow samples

Surface snow samples (n = 8) were collected about 30 m from the aerosol sampling site. Snow samples were collected at 10-days intervals, when aerosol filter changing occurred (6 November, 17 November, 27 November, 7 December, 27 December 2014). Three consecutive snow samplings (10, 12 and 13 January 2015) were also performed during a snowfall event that lasted from the 8th to 11th of January 2015. Surface snow samples (ca. 1 cm in depth) were collected in 2-L polyethylene bottles, previously cleaned with ultrapure water and methanol. The samples were melted in an ISO 4 clean room and aliquoted into pre-cleaned vials prior to determination of ionic species and organic compounds. Before analysis for sugars, AA and PC the melted aliquots were spiked with a ^{13}C-labelled internal standard mix.

2.3. Instrumental analysis

The quantification of all anions and CA was performed using an ion chromatograph (Thermo Scientific Dionex TM 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 quadrupole mass spectrometer (MSQ PlusTM, ThermoScientific, Bremen, Germany). The ion chromatograph was equipped with a capillary system to simultaneously determine cations using a conductivity detector. Cations were separated using an Ion Pac CS19 − 4 mm capillary cation-exchange column (0.4 × 250 mm) equipped with an Ion Pac CG19 − 4 mm guard column (0.4 × 50 mm). Further details about the methods for anion and cation determinations are reported by Barbaro et al. (2016).

Quantifications of the AA were obtained using high-performance liquid chromatography with a chiral column coupled with tandem mass spectrometry for detection (HPLC-MS/MS) (Barbaro et al., 2014). PC were analyzed using reverse-phase chromatography coupled with tandem mass spectrometry (Zangrando et al., 2013), whereas sugars were determined using ion chromatography coupled with mass spectrometry (IC-MS) (Barbaro et al., 2015a).

3. Results

3.1. *PM$_{10}$ composition and particle size distribution*

The mean aerosol concentration of all water-soluble compounds (ions, sugars, CA, AA, PC) in PM$_{10}$ aerosol samples, obtained from the sum of different size-segregated fractions, was 0.6 ± 0.1 μg m^{-3}. This total concentration of analyzed compounds represented 66 ± 20% of the PM$_{10}$ total mass concentrations as determined in other samples taken in parallel (Illuminati et al., 2016).

3.1.1. *Ionic compounds in PM$_{10}$*

The mean composition of PM$_{10}$ aerosol samples showed that inorganic ions were the main species collected on the filters (Fig. S1). The most abundant, SO_4^{2-} represented 38% (214 ± 53 ng m^{-3}) of the total concentration of the analyzed compounds. Mg^{2+} (0.10 ± 0.05 μg m^{-3}, 17%) had higher concentrations than Cl^- (0.07 ± 0.03 μg m^{-3}, 13%) and Na^+ (0.07 ± 0.03 μg m^{-3}, 11%). NH_4^+ was present at 8% (0.05 ± 0.02 μg m^{-3}), while NO_3^- was 6% (0.03 ± 0.02 μg m^{-3}) and MSA 5% (0.03 ± 0.01 μg m^{-3}). Other quantified species represented 1% of the total.

The aerosol composition and the particle size distribution of ionic species can be used to define sources. Aerosol collected at the coastal base MZS has a characteristic sea salt input, indicated by the high content of Na^+, Mg^{2+} and SO_4^{2-} (Hillamo et al., 1998). Mg^{2+}, Na^+ and Cl^- were mainly in the coarse fraction (>1 μm) (Fig. S2). Two different sources of SO_4^{2-}can be recognized by distinguishing between non-sea salt sulfate (nss-SO_4^{2-}) and sea salt sulfate (ss-SO_4^{2-}). Ss-SO_4^{2-} was mainly distributed on particles with a diameter above 1 μm (Fig. S3), and is calculated against other markers of sea salt input, such as Na^+ and Mg^{2+}. In the 2014–2015 samples, the contribution of sea salt to sulfate concentrations was determined using the SO_4^{2-} to Na^+ ratio, ratios higher than the seawater value of 0.25 are indicative of seawater plus other sources. The values calculated in all fractions, ranged by 0.5 in the coarse fraction (diameter above 3 μm) to 37 in the <0.49 μm fraction. These values suggest inputs of sulfate not just from sea salt particles (Jourdain and Legrand, 2002). The main source of nss-SO_4^{2-}, as well as MSA, is emission by phytoplankton bloom in the oceans (Fattori et al., 2005). These two species were mainly distributed on the <0.49 μm fraction (Figs. S2 and S3) and showed high correlation ($R^2 = 0.87$) in the aerosol data. Ammonium was mainly distributed in the <0.49 μm fraction (Fig. S2), suggesting that its main source was the ocean (Jickells et al., 2003; O'Dowd et al., 2004; Johnson and Bell, 2008). The ionic composition, concentration and particle size distributions were similar to data obtained from the same sampling site during the austral summer of 2010–11 (Barbaro et al., 2017).

3.1.2. *Carboxylic acids (CA) in PM$_{10}$*

Although the other water soluble organic compounds (WSOC) quantified in the present research were below 1% of the total concentration of all the determined chemical species (Fig. S1), they may provide useful information based on their composition and particle size distributions. CA are major contributors to organic aerosol mass (Sempere and Kawamura, 2003). The total mean concentration of CA in our PM$_{10}$ samples was 0.8 ± 0.5 ng m^{-3}, the mean concentrations reported are associated with a high standard deviations due to the very low concentrations in Antarctic samples.

The CA detected in our samples were C$_3$-malonic acid (with an average concentration of 0.2 ± 0.1 ng m^{-3}), C$_4$-succinic acid (0.2 ± 0.1 ng m^{-3}), C$_5$-glutaric acid (0.1 ± 0.1 ng m^{-3}), C$_2$-oxalic acid (0.09 ± 0.08 ng m^{-3}), *h*C$_4$-malic acid (0.09 ± 0.06 ng m^{-3}), C$_7$-pimelic acid (0.04 ± 0.01 ng m^{-3}), C$_6$-adipic acid (0.04 ± 0.02 ng m^{-3}), and C$_2$-glycolic acid (0.013 ± 0.009 ng m^{-3}). These compounds were mainly distributed in the <0.49 μm fractions (Fig. S4) due to their nature of being secondary aerosol products in the atmosphere. The concentrations of CA determined in the 2014–2015 campaign were 10 times lower than those found during the austral summer of 2010–2011 (Barbaro et al., 2017). The main difference resides in the concentrations of C$_2$-oxalic acid: in the aerosol samples from 2010 to 2011, the mean concentration was 3 ± 1 ng m^{-3}, whilst in the 2014–2015 samples the mean concentration was 0.09 ± 0.08 pg m^{-3}. This difference can be explained by differences in the photochemical production of CA after the release of alkenes by phytoplankton (Xu et al., 2013). C$_2$-oxalic acid is an end-product of various oxidation/decomposition reactions in the atmosphere (Kawamura and Sakaguchi, 1999), whereas the presence of long chain CA suggests incomplete photochemical degradation of alkenes in the atmosphere. The C$_3$-malonic/C$_4$-succinic ratio can be used as an indicator of enhanced photochemical production of diacids (Kawamura and Ikushima, 1993), as C$_4$-succinic acid can be degraded to C$_3$-malonic acid by decarboxylation reactions activated by OH radicals (Fu et al., 2013). The C3/C4 ratios in the marine aerosols collected at low-to mid-latitudes in the Northern Hemisphere vary between 0.9 and 5.8 with an average of 2.3, which were about three times higher than those found in urban aerosol (Fu et al., 2013). These values suggested that C$_3$-malonic acid is photochemically produced during long range transport from continents to the marine atmosphere (Fu et al., 2013). The mean C$_3$/C$_4$ ratio calculated in the 2014/2015 Antarctic samples ranged between 0.8 and 2.3 with an average value of 1.45, suggesting that aerosol contained these species underwent long range transport processes, where photochemical degradation occurred. These ratio values were very similar to the ratios obtained in the 2010-11 Antarctic samples (C$_3$/C$_4$ ratio of 1.5) (Barbaro et al., 2017).

3.1.3. *Sugars in PM$_{10}$*

Anhydrosugars, sugar alcohols, monosaccharides and disaccharides are among the major classes of WSOC in atmospheric aerosol (Yttri et al., 2007). The sum of the mean concentrations of all sugars in PM$_{10}$ samples collected during the austral summer 2014–2015 was 0.7 ± 0.6 ng m^{-3} and sugars represented 0.1% of the total detected compounds. The most abundant class of sugars were monosaccharides (MS), with a total mean PM$_{10}$ concentration of 0.4 ± 0.4 ng m^{-3}, while glucose represented 48% of the total PM$_{10}$ sugar concentration. The concentration of glucose in the 2014–2015 samples (0.4 ± 0.3 ng m^{-3}) showed considerable temporal variability and was higher than the mean concentrations found during the austral summer 2010–2011 campaign at the same sampling site (84 ± 5 pg m^{-3}) (Barbaro et al., 2015a). The difference between these two sampling campaigns can be explained by the particle size distribution of glucose. During 2010–2011, glucose was essentially found in the aerosol fine fraction (<1 μm) only (Barbaro et al., 2015a), while during 2014–2015, 21% of glucose was found in the >3.0 μm fraction (Fig. S5). The additional occurrence of glucose in the coarse particles (>1 μm) may be due to degradation of polysaccharides occurred during long range transport processes (Leck et al., 2013). Biological degradation, as a source of sugars, is also indicated by the higher mean concentration of sucrose (96 pg m^{-3}) in the 2014–2015 samples compared to the mean concentration (3 pg m^{-3}) in the 2010–2011 samples (Barbaro et al., 2015a). Sugar alcohols, such as mannitol and arabitol, had a mean concentration of 170 pg m^{-3} in the 2014–2015 samples and were mainly found in the coarse fraction (>3 μm) (Fig. S5). This particle size distribution confirms the association with primary biological particles such as airborne fungal spores (Yttri et al., 2007; Bauer et al., 2008).

The main anhydrosugar present in 2014–2015 was levoglucosan (14 pg m^{-3}), mannosan was also detected in a few samples. Levoglucosan was mainly found in the <0.49 μm fraction (Fig. S5), suggesting long-range atmospheric transport from sites where biomass burning occurred. Indeed, levoglucosan is now recognized as a specific biomarker of cellulose combustion (Kuo et al., 2011).

3.1.4. *Free amino acids (AA) in PM_{10}*

The composition and particle size distribution of AA were evaluated to investigate their use as possible tracers of primary biological matter as suggested in previous studies (Barbaro et al., 2015b). Since further investigations about their aerosol behavior and aerosol-snow transfer processes are necessary before applying these compounds as tracers in climate studies.

Ten L-AA (L-Ala, L-Asp, L-Arg, L-Glu, L-Leu, L-Phe, L-Pro, L-Tyr, L-Thr) and Gly were detected in the aerosol samples collected at MZS in 2014–2015. The mean total concentration of free AA (0.04 ± 0.03 ng m^{-3}) was lower than those found in 2010–2011 (0.2 ± 0.1 ng m^{-3}) (Barbaro et al., 2015b). Gly was the most abundant compound (60% of the total free AA), while other percentages of AA were homogenously distributed (9% for L-Glu; 6% for L-Arg and L-Ala; 5% for L-Leu; 4% for L-Pro; 3% for L-Asp and L-Thr; and 2% for Tyr; 1% for L-Val and L-Phe).

A marine source of free AA was suggested by particle size distribution mostly in the fine fraction (<1 μm) of our samples (Fig. S6), confirming suggestions from previous studies (O'Dowd et al., 2004; Keene et al., 2007; Facchini et al., 2008; Modini et al., 2010).

3.1.5. *Phenolic compounds (PC) in PM_{10}*

PC can derive from lignin combustion and the presence of these compounds in atmospheric aerosol may indicate which types of plants were burned (Simoneit, 2002). Previous studies of these compounds in Antarctic aerosol (Zangrando et al., 2016) demonstrated that PC had a bad correlation with levoglucosan, specific tracers of biomass burning, suggesting the existence of sources of PC. Further studies of PC were suggested to fully understand their applicability as environmental markers.

The <0.49 μm fraction of aerosol samples from 2014 to 2015 contained 92% of the total PC concentrations with a total mean concentration of 29 ± 12 pg m^{-3} (Fig. S7). Vanillin (VAH) was the most abundant compound (89%, 0.02 ± 0.01 ng m^{-3}), while the mean concentration of acetovanillone (VAC) was 2 ± 1 pg m^{-3} (7%), and that of vanillic acid (VA) 0.8 ± 0.7 pg m^{-3} (3%). Traces of syringic acid (SyA), homovanillic acid (HA) and syringaldehyde (SyAH) represented 1% of the total concentration of PC in the aerosol samples collected in 2014–2015. The concentrations were similar in 2010–2011 (Zangrando et al., 2016), where the ocean was suggested as a possible local source of PC by ejecting fine particles (<1 μm) containing organic compounds into the atmosphere (O'Dowd and De Leeuw, 2007). For the 2014–2015 samples evaluated in the present research, the same source can also be suggested and biomass burning can be excluded as the main source of PC. This affirmation can be confirmed by comparing PC concentrations with those of levoglucosan, specific tracers of pyrolysis of cellulose. The correlation coefficient between the sum of PCs and levoglucosan was 0.5, while the ratios of levoglucosan/VAH and levoglucosan/VA were 0.8 and 6.4 respectively. These ratios were 100 times lower than those obtained for aerosol samples affected by biomass burning (Graham et al., 2002; Ward et al., 2006, 2011; Fu et al., 2010), suggesting another natural source for PC (Zangrando et al., 2016).

3.2. *Composition of surface snow*

Superficial snow samples were collected during aerosol sampling to investigate exchanges between the atmosphere and the snow layer. The first sampling period had no precipitation events, while the three samples collected on the 10, 12 and 13 of January 2015 were fresh snow from snowfall that lasted from the 8 to 11January 2015.

Aged snow collected before the snow event at MZS had a total mean concentration of water-soluble compounds of 66 μg g^{-1}, with Na^+ (22 μg g^{-1}), Mg^{2+} (22 μg g^{-1}), Cl^- (14 μg g^{-1}) andSO_4^{2-} (5 μg g^{-1}) as the most abundant species. Dry deposition of marine aerosol was the most plausible source of these compounds on the superficial snow layer. After the snow event (8–11 January), the total concentration of water-soluble species decreased from 66 μg g^{-1} to 9 μg g^{-1}, probably due to dilution effects (Fig. S8). Mg^{2+} (3 μg g^{-1}), SO_4^{2-} (1 μg g^{-1}), Na^+ (0.6 μg g^{-1}) and Cl^- (0.4 μg g^{-1}) were still the most abundant compounds. In contrast, an increase in AA concentration occurred, with concentrations varying from 0.6 μg g^{-1} before the snow event to 3 μg g^{-1} after snowfall. Degradation of proteinaceous material that fell with the snow could be a possible source of free AA in fresh snow, as this increase was observed in the 12 January samples, when the snowfall had ceased (Fig. 1). An unclear decrease in AA was found on the following sampling day (13 January) and further investigations are needed to understand the behavior of these species in the snowpack.

The deposition of biological material with snowfall was also confirmed by an increase in the concentration of AS such as mannitol and arabitol. Mannitol had a concentration of 3 ng g^{-1} on 27 December, while its concentration was 241 ng g^{-1} on 10 January, suggesting a deposition of primary biological particles, such as airborne fungal spores (Bauer et al., 2008).

4. Discussion

4.1. *Exchange between atmosphere and snow of water-soluble compounds*

Fig. 1 shows the concentrations of analyte in aerosol and snow samples. Aged snow was collected until 27 December 2014, while the samples of 10, 12 and 13 January 2015 were fresh snow after snowfall between the 8 to 11 of January 2015.

The PM_{10} concentration of major ions increased and peaked in the second half of December (17–27 December sample, Fig. 1), probably due to seasonal reduction of the pack ice extent. At the end of the field campaign a decrease in concentration was observed, caused by abundant snowfall. The same behavior was observed for the PM_{10} mass concentration (Illuminati et al., 2016), suggesting the same cause.

The main ions found in aged snow samples were Na^+, Mg^{2+}, Cl^- and SO_4^{2-}, and sea salt ions were also found in the coarse fraction of particulate matter (Fig. S2). Dry deposition of coarse particles was probably the main process that removed these compounds from the atmosphere. These ions were diluted by snowfall (Kreutz and Mayewski, 1999) as demonstrated by a decrease in ion concentration in fresh snow samples from 10 to 13 January (Fig. 1). In particular, Mg^{2+} seems to be the ion most affected by this dilution process (zoom on Fig. 1).

High concentrations of sea salt ions were observed in the 17 November snow sample, when the wind direction was mainly from

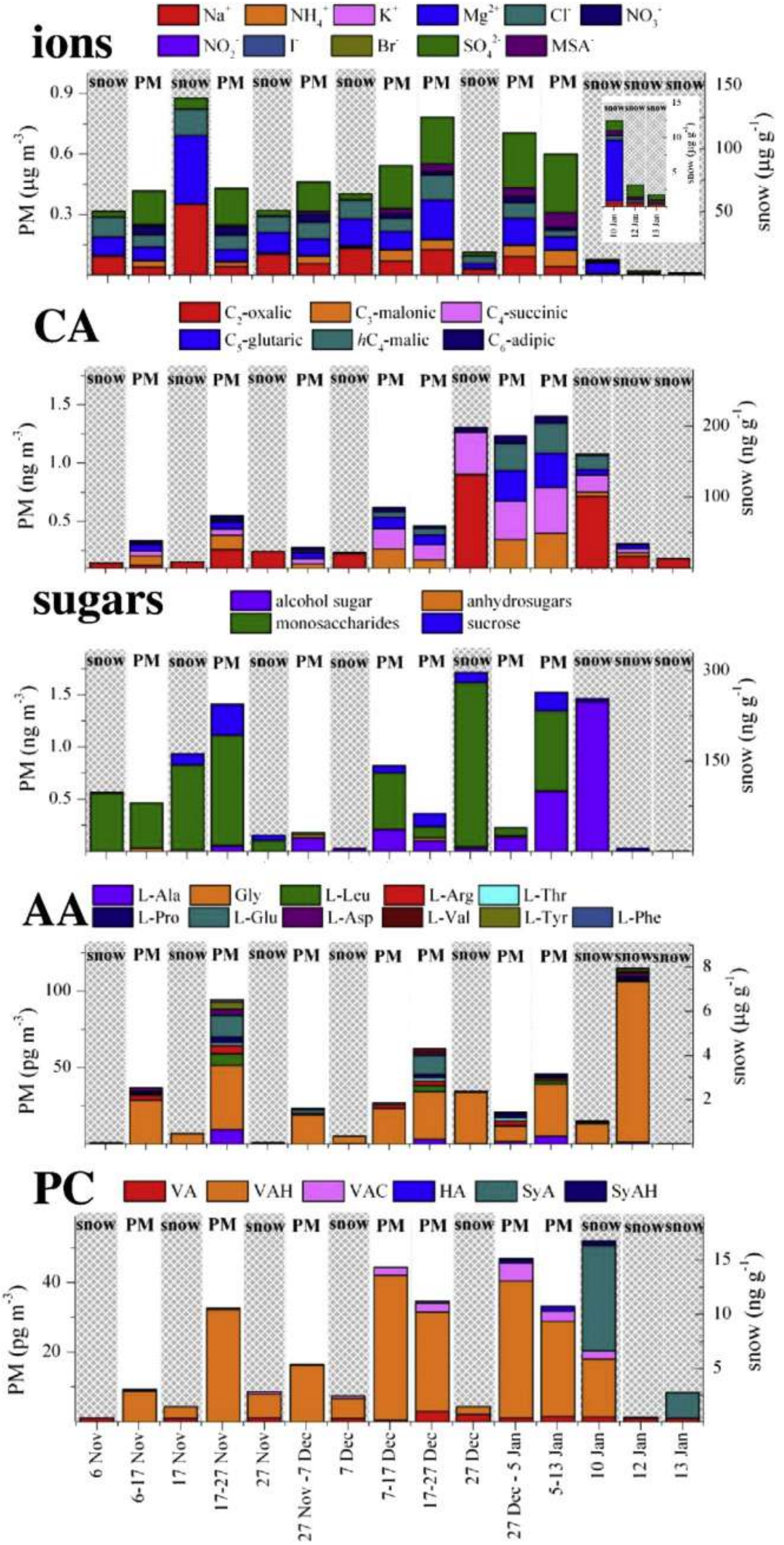

Fig. 1. Concentration trends of each class of compounds investigated in aerosol samples (PM) and snow samples. CA: carboxylic acids; AA: amino acids; PC: phenolic compounds.

the East-South-East direction (Fig. S9). The main source of these sea salt compounds presumed to be dry deposition of material coming from areas with frost flowers as a negative nss-SO_4^{2-} value (Fig. S10) was calculated for the 17 November snow samples (Wolff et al., 2003; Kaspari et al., 2005).

Nss-SO_4^{2-} concentrations increased at the beginning of the Antarctic summer (Fig. S10) because its biogenic source is phytoplankton blooms on the ocean surface (Minikin et al., 1998). The concentration of nss-SO_4^{2-}before (sample of 27 December), during (snow sample of 10 January) and after the snow fall event of the 10th of January (snow samples of 12 and 13 January) are comparable and show only a small decrease in the 13 January sample (Fig. S11). This observation suggests that wet deposition processes are negligible for this species, and seem to be independent of the accumulation rate due to inefficient scavenging of nss-SO_4^{2-}aerosols by Antarctic snow (Kreutz and Mayewski, 1999).

C_2-oxalic acid was the main CA found in snow samples, while C_3-malonic, C_4-succinic and C_5-glutaric were the main CA in aerosol samples (Fig. 1). There are several possible reasons for this difference between aerosol and snow samples, such as: different evaporation rates, different particle size distributions, or different sources and snow chemistry. CA evaporation from the snow surface is unlikely due to their low volatility and high polarity. Low chain CA, such as C2 and C3 diacids can exist in the gas phase (Baboukas et al., 2000) but they should be adsorbed onto the snowpack surface more than C4 and C5 acids due to their polarity. The results in Fig. 1 support absorption on the snow surface because C_2-oxalic and C_3-malonic were the most abundant species in the snow samples. Deposition velocities of each CA should be similar because they are mainly distributed in the fine fraction (Fig. S4). Differences in their sources and/or snow chemistry are other factors that could influence the concentrations of CAs on the snow surface. Since CAs are water soluble, they are strongly influenced by precipitation events. We can observe higher concentrations of these compounds during snowfall (10 January snow sample) and low dilution effects after that event (12–13 January samples) (Fig. 1). Because C_2-oxalic acid is the end-product of several photochemical reactions (Kawamura et al., 1996a), it can be scavenged by both dry and wet deposition, as well as be generated by photochemical processes at the snow surface. In fact, higher concentrations of C_2-oxalic acid were found before snowfall in aged snow.

MS such as glucose were the main sugars present in the atmosphere in the first period of sampling campaign, while the concentration of sugar alcohols, such as mannitol and arabitol, increased as the Antarctic summer progressed with increased biological production. This atmospheric trend is also reflected in the snow composition; MS were the most abundant species in the snow samples during the first period, while sugar alcohols were scavenged from the air from 27 December onwards. During snowfall, mannitol was the main compound scavenged to the surface snow, but it underwent considerable dilution after the snow event (Fig. 1).

The main AA detected in aerosol and snow samples was glycine, the most stable of this compound class in the atmosphere (McGregor and Anastasio, 2001). An unclear correlation between the snow and aerosol concentration of glycine is shown in Fig. 1. The observation of an increase in glycine concentration in aged snow was comparable with a decrease in aerosol concentration: for example the decrease in aerosol samples between 27 November –7 December seems to be associated with an increase in the Gly concentration in 7 December snow sample (Fig. 1, Fig. S12). Dry deposition seems to be a negligible factor for the glycine in the snow because higher aerosol concentrations of Gly are not matched to an increase in snow concentrations for this amino acid. The glycine concentration increased after snowfall (8–11 January), probably due to consecutive degradation of biological material at the snow surface, as seen in the 12 January snow sample (Fig. 1).

For PC, VAH was the dominant species in the aerosol samples while its oxidation product, VA, was significantly present in aged snow (Fig. 1). During snowfall, high concentrations of VAH were observed along with other PCs. However, a large decrease in these compounds was found over the subsequent sampling days. This behavior could be due both to a dilution effect and their semi-volatility, which influences the re-partition of these compounds between snow and the atmosphere. After snowfall VA and SyA, the oxidized forms of VAH and SyAH, were the main PCs present.

5. Conclusion

Ionic species, CA, sugars, AA and PC were detected in aerosol and surface snow samples collected at the coastal Italian base in Antarctica from November 2014 to January 2015. Characterization of water-soluble compounds in the aerosol showed that they accounted for about 66% of the PM_{10} mass concentration. From this two predominant sources were identified: 1) sea salt input, characterized by high concentrations Na^+, Mg^{2+}, Cl^- and SO_4^{2-}; 2) biogenic input, suggested by the presence of organic compounds, such as AA, sugars and PC. This study on the WSOC aerosol composition was aimed at improving our understanding of the AA, sugars and PCin Antarctic aerosol, a topic that remains poorly studied.

This information was combined with the study of WSOC in surface snow, and is the first to quantify AA and sugars in this matrix. Ions that were mainly distributed in the coarse fraction of atmospheric aerosol, were also the most abundant compounds in snow samples, suggesting that the main air-snow transfer process was dry deposition. The composition of sugars in the snow reflected their aerosol composition. An increase in concentration of alcohol sugars, that are tracers of fungal spores in the atmosphere, was also found in surface snow, suggesting that they could also be markers for this source in climatic studies. AA were an important component of surface snow, but in addition to aerosol input, another possible source could be the decomposition of biological material on the surface, as demonstrated by high concentrations of AA after snowfall.

Investigation of the concentrations of water-soluble compounds in aerosol samples in Antarctica is hampered by their low concentrations, meaning aerosol has to be sampled for 10 days to obtain concentrations above the detection limits. This dramatically reduces the temporal resolution of any study. For this reason, further studies over subsequent Antarctic expeditions will be essential to improve the sample numbers so we can fully understand the applicability of these compounds in the study of ice cores for paleoclimatic investigations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2017.05.098.

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PhD Thesis Abstract

Student: Sara Padoan badge number: 848711

PhD: PhD in environmental Sciences

Cycle: XXXI

Thesis title: Environmental Markers in Remote Areas and Urban Sites. Investigation of the Contribution of Natural and Anthropogenic Sources

Abstract: the study of aerosol composition is fundamental to highlight the quality of the air and its environmental impact, distinguishing between the natural and the anthropogenic components. In particular the investigation of several important environmental markers, in the aerosol, allow the investigation of their potential sources, their chemical evolutions and their transport mechanisms. The aim of this PhD Thesis was to study the large applicability of a wide range of different environmental markers in very different environments and validate their use as a research tool. On the one hand, two studies focused on environmental markers in one remote area, Antarctica, that, thanks to its geographical position, is a perfect open-air laboratory, optimal for studying those emission sources exclusively natural. On the other hand, one study focused on environmental markers in one urban site, Sernaglia della Battaglia, province of Treviso, Italy. This medium-sized village was proposed as an ideal place for the study of environmental markers which can discriminate between natural and anthropic markers. In Antarctica, the first study focused on ionic species in two different sampling sites: one coastal site, near the scientific base "Mario Zucchelli" and one inland site, near the research base "Concordia". The results of this study highlighted that aerosol collected close to the coast was mainly a primary aerosol characterized by sea salt input species such as Na^+,Mg^{2+}, and SO_4^{2-}, while inland samples showed a secondary aerosol with high concentrations of anionic species: non-sea salt sulfate, methanesulfonic acid and nitrate. The second study in Antarctica focused only on the coastal site nearby the scientific base "Mario Zucchelli", adding to the ionic species further environmental markers, such as sugars, phenolic compounds and amino acids. The most concentrated environmental markers were glucose between sugars, vanillin among the phenolic compounds and glycine among the amino acids. The third study completely focused on samples from the rural environment of Sernaglia della Battaglia presented the quantification of a wide range of new environmental indicators, able to discriminate between natural and anthropogenic emissions. It was therefore possible to highlight the strong impact of anthropogenic emissions, in this case above all emissions for domestic heating, and to follow the evolution of these distributions during three different sampling periods.

Student signature

Sara Pado

Estratto per riassunto della tesi di dottorato

Studente: Sara Padoan matricola: 848711

Dottorato: Dottorato in Scienze Ambientali

Ciclo: XXXI

Titolo di Tesi: Environmental Markers in Remote Areas and Urban Sites. Investigation of the Contribution of Natural and Anthropogenic Sources

Abstract: lo studio dell'aerosol è essenziale per conoscere la qualità dell'aria e il suo impatto ambientale, discriminando tra la componente naturale e quella antropica. In particolare, l'indagine di numerosi importanti *markers* ambientali, all'interno dell'aerosol, consente di indagare le loro potenziali sorgenti, le loro evoluzioni chimiche e i loro meccanismi di trasporto. Lo scopo di questa tesi di dottorato è stato quello di studiare l'ampia applicabilità di una vasta gamma di *markers* ambientali in ambienti estremamente diversi e validarne il loro utilizzo come strumento di ricerca. Da un lato, due studi si sono concentrati su *markers* ambientali in un' area remota, l'Antartide, che, grazie alla sua posizione geografica, è un perfetto laboratorio a cielo aperto, ottimale per studiare quelle sorgenti di emissione esclusivamente naturali. Dall'altro lato, uno studio si è concentrato sui *markers* ambientali in un sito urbano, Sernaglia della Battaglia, in provincia di Treviso, Italia. Questo paese di medie dimensioni si propone come luogo ideale per la discriminazione tra *markers* ambientali di origine naturale o antropica. In Antartide la prima indagine si è concentrata sulle specie ioniche in due diversi siti di campionamento: uno costiero, vicino alla base scientifica "Mario Zucchelli" e uno interno, vicino alla base di ricerca "Concordia". I risultati di questo studio hanno evidenziato che l'aerosol costiero era principalmente un aerosol primario, principalmente caratterizzato da specie marine come Na^+, Mg^{2+} e SO_4^{2-}, mentre i campioni provenienti dal sito di campionamento interno hanno mostrato un aerosol secondario con alte concentrazioni di specie anioniche: SO_4^{2-} non di sale marino, MSA e NO_3^-. Il secondo studio in Antartide si è concentrato sul sito costiero di Mario Zucchelli, aggiungendo alle specie ioniche ulteriori *markers* ambientali, come zuccheri, composti fenolici e amminoacidi. I *markers* ambientali più concentrati sono risultati il glucosio tra gli zuccheri, la vanillina tra i composti fenolici e la glicina tra gli amino acidi. Il terzo studio completamente incentrato su campioni provenienti dall'ambiente rurale di Sernaglia della Battaglia ha presentato la quantificazione di una vasta gamma di nuovi indicatori ambientali, in grado di discriminare tra emissioni naturali e antropogeniche. È stato, quindi, possibile evidenziare il forte impatto delle emissioni antropogeniche, in questo caso soprattutto emissioni per il riscaldamento domestico, e seguire l'evoluzione di queste distribuzioni durante tre diversi periodi di campionamento.

Firma dello studente

Sara Pado

Università
Ca'Foscari
Venezia

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Io sottoscritto SARA PADOAN

natA. a BOLOGNA (prov. BO) il 25.11.1991

residente a BOLOGNA in VIA C. BARUZZI n. 10

Matricola (se posseduta) 848711 Autore della tesi di dottorato dal titolo:

ENVIRONMENTAL MARKERS IN REMOTE AREAS AND URBAN SITES: INVESTIGATION OF THE CONTRIBUTION OF NATURAL AND ANTHROPOGENIC SOURCES.

Dottorato di ricerca in SCIENZE AMBIENTALI

(in cotutela con ....)

Ciclo XXXI

Anno di conseguimento del titolo 2019

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