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# Major and trace elements in aerosol of Central Antarctica (Dome C)

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# Contents

# Dissertation outline

## 1. Overview

Antarctica is one of the more remote area of the Planet (Bodhaine et al., 1992; Chown et al., 2012; Cressey, 2012), regarded as the ‘‘last of the wild’’ (Sanderson et al., 2002), under lower human impact than Arctic (Bennett et al., 2015) and other continents, owing to its geographical and natural barriers; such as a land mass quite completely covered by ice, entirely isolated from other continents, surrounded by Southern Ocean and isolated by Antarctic circumpolar current (ACC) and by the great distance from continental land masses (Bargagli, 2008). For this reason, it is regarded as the ideal archives of data for better understanding global processes (Bargagli, 2008; Suttie and Wolff, 1993). Thanks to its distance from anthropogenic and continental emission sources Antarctica is an excellent natural laboratory to study the biogeochemical cycles of natural elements and compounds and to investigate chemical transformation of species in the continent’s pristine atmosphere or after long-range transport from anthropogenic areas (Barbaro et al., 2017, 2016; Boucher et al., 2013).

A detailed knowledge of past climate is essential for a more complete understanding of temporal variability and of the forces that control future changes. As the continent most remote from direct human influence, Antarctica is an ideal location to study local-to-global scale climate change. Indeed, there is no other place in the world that can provide perspectives across a range of time scales greater than Antarctica, through the deciphering of proxies archived in ice and sedimentary records (SCAR 2017).

Though Antarctica is usually perceived as a remote and hostile place and as a symbol of the last great wilderness untouched by human disturbance, the Antarctic environment is no longer pristine and like other remote regions on Earth, it is not escaping the impact of local and global anthropogenic activities (UNEP, 2002; Bargagli, 2005; Bergstrom et al., 2006; Mayewski et al., 2017; Shaw et al., 2014).

Indeed, its wildness makes Antarctica more stressed and vulnerable to the increasing anthropogenic pressure of the last few years (IPCC 2007; Bargagli, 2008; Turner et al., 2009; SWIPA 2011; Convey et al., 2012). The vulnerability of the Antarctic continent is due to lack of functional redundancy in ecosystems and low temperatures that delay recovery from perturbances (Bennett et al., 2015). In the last few years, threats to the ecological integrity of Antarctica are accelerating because of a growing variety, intensity, and frequency of human activities and rapidly changing climates or forecasts for such change (Hughes and Convey, 2010; Hughes et al., 2013; Tin et al., 2014).

Rapid climate change affecting the polar regions will also have profound physical and ecological consequences for the rest of the Planet since the ice-covered Artic Ocean, the Antarctic continent, and the globally significant Antarctic circumpolar current play a key role in regulating the Earth's climate and ocean system (Convey et al., 2012). Cumulative effect of these many local changes is the global phenomenon of human influence on nature, a new geological epoch widely called the "anthropocene" (Steffen et al., 2004).

Aerosol plays an essential role in Earth's climate balance, due to its impact on the global radiative system, given to its chemical composition and physical properties (e.g. size, shape). Both the chemical and physical properties of aerosol are strictly connected to emission sources and lifetime in the atmosphere. Over recent decades, much work has been done to characterize aerosol emission sources and background aerosol populations across much of the globe (Boucher et al., 2013). However, due to the inaccessibility of the continent, the Antarctic aerosol population (particularly its sources and evolution) is still a subject of many open questions in atmospheric science. Improving our understanding of the processes that govern aerosol formation and evolution in Antarctica is important not only to our understanding of present day, but also to understanding the global climate history (Giordano et al., 2016).

The central Antarctic aerosol is characterized by weakly and episodically influenced by coarse sea-salt particles (occurring during windy conditions, especially in winter season) and insoluble crustal material because these particles, belonging to supra-micron equivalent diameter classes, undergo to a rapid scavenging by wet- and dry-deposition processes during the transport from their sources areas (Udisti et al., 2004). Conversely, sub-micron particles, favoured by subsidence processes from the free troposphere (Chaubey et al., 2011; Raes et al., 2000), usually linked to anthropogenic emission, can be transported far from continental areas reaching also the Antarctic plateau (Bodhaine et al., 1986; Shaw, 1988).

This study would also yield valuable information on the global transport of atmospheric particulate matter, interpreting the aerosol determinations evaluating the air masses back-trajectories (Rolph et al., 2017; Stein et al., 2015); and allows us to assess the contribution from human activities to the global background particulate matter (Maenhaut et al., 1979). Extensively, the present-day aerosol chemical characterization also improves the interpretation of changes in the past atmosphere revealed by the relationship with chemical stratigraphy of the European project for ice coring in Antarctica (EPICA) ice cores (Becagli et al., 2009; Udisti et al., 2004; Lambert et al., 2008).

Anthropogenic contamination of the Antarctic has been recognized since at least the 1960s (Murozumi et al., 1969). It has been widely demonstrated in seawater (Sañudo-Wilhelmy et al., 2002; Scarponi et al., 1995), snow and ice (Boutron and Patterson, 1987, 1983; Grotti et al., 2015; Van de Velde et al., 2005), glacial lakes (Ellis-Evans, 1996; Burgess and Kaup, 1997; Gasparon and Burgess, 2000; Goldsworthy et al., 2003) and organisms, (Bargagli, 2008; Bazzano et al., 2015; Grotti et al., 2008; Illuminati et al., 2016; Sanchez-Hernandez, 2000; Truzzi et al., 2008); the primary pathway of delivery of contaminants to Antarctica is via the atmosphere (Grotti et al., 2016). Beside the transport of contaminants from distant sources, the occurrence of significant local contamination has also been reported in relation with research station activities (Kennicutt et al., 1995; Negri et al., 2006; Wild et al., 2015), tourism (Amaro et al., 2015) or occasional incidents (Cripps and Shears, 1997). Today again, too little information on aerosol load, size and chemical composition of natural aerosols coming from remote areas such as oceanic and polar region are available (Hara et al., 2004; Jourdain and Legrand, 2002; Tuncel et al., 1989; Wagenbach et al., 1998). Therefore, a complete study of the Antarctic aerosol system is important to complete a global pattern of natural particles dynamics and persistent human impact growing in the Southern Hemisphere due to the development of industrial countries (Bargagli, 2008).

In particular PM10 fraction of the airborne particulate matter is considered a carrier of many harmful elements that can be deposited into human respiratory system (Malandrino et al., 2013a), contributing to adverse health effects and diseases like asthma, cardiopulmonary complications, lung cancer, even mortality ( Stone, 2000; Donaldson et al., 2002; Englert, 2004; Pope and Dockery, 2006). Urban particulate matter has been found to contain significantly high amounts of metals, which constitute a likely cause of the health-related effects of PM, as demonstrated by a number of studies (Burnett et al., 2000; Zelikoff et al., 2002; Zereini et al., 2005).

The association between particulate matter and adverse health effects (Alessandrini et al., 2013; Dockery et al., 2007) had led the governance to issue the Directive 1999/30/EC and, in recent years, the Directive 2008/50/CE and the Directive 2004/107/CE, that determined specific target values for the presence of PM10, PM2.5 and the concentrations of several chemical elements, namely arsenic, cadmium, nickel and lead, in PM10. These elements were specifically chosen as objects of the study because have an important role in the environmental impact studies and are typically associated to anthropogenic emissions (Bazzano et al., 2015; Cullen and Maldonado, 2013; Rosman et al., 1994; Toscano et al., 2005). Indeed, enrichment factors with respect to both mean crustal and seawater compositions have usually been attributed to inputs from human activity in Antarctica and/or elsewhere in the Southern Hemisphere by long-range transport (Hur et al., 2007; Mishra et al., 2004; Planchon et al., 2002). The above elements are among those released by the combustion of coal, oil and gasoline and by non-ferrous metal production (Pacyna and Pacyna, 2001). Other elements have been investigated to understand the natural (both crustal and marine) contribution sources to the aerosol amount. Usually, in Antarctica source determination is easier than in other sites because the paucity of sources one. Indeed, as reported in literature (Bazzano et al., 2015;

Illuminati et al., 2015; Toscano et al., 2005; this work) three main sources have been determined: crustal, marine and anthropic ones. Besides a few research stations, bases, and minor tourism activities, anthropogenic emission sources of aerosols and trace gases are rare in and around Antarctica (Shirsat and Graf, 2009). Antarctic aerosol is usually dominated by sea-salt particles, marine biogenic and volcanic emissions, and small amounts of soil dust (e.g. Arimoto et al., 2001; Wagenbach et al., 1998; Six et al., 2005). Most trace elements in Antarctic aerosol have a natural origin (e.g. Arimoto et al., 2008), however, especially in samples from the Antarctic Peninsula, high Cr, Cu, Ni, Pb, V and Zn enrichment factors with respect to both mean crustal and seawater compositions have usually been attributed to inputs from human activities in Antarctica and/or elsewhere in the Southern Hemisphere (Hur et al., 2007; Mishra et al., 2004; Planchon et al., 2002).

In the Antarctic plateau and in any other pristine environment, chemical composition of aerosol was investigated in order to understand transport pathways and troposphere chemical modifications. Under uncontaminated environmental conditions, it is possible to correctly distinguish between natural and anthropogenic factors (Fiebig et al., 2014). The study of elemental concentrations and the possible association between elements are employed as input to the study of source-apportionment in order to identify emission sources necessary to assess global strategies on climate change and management of air quality health strategies (Hopke et al., 1999; Watson et al., 2002). Combining information on chemical composition with temporal variation of abundances, wind patterns and the characteristics of potential sources can allow reliable assessment of particles origin (Contini et al., 2010) since an unanswered question in atmospheric science is the source and evolution of the Antarctic aerosol population (Giordano et al., 2016). Source apportionment determination is strictly site-specific, but to discriminate between possible origins, different markers have been selected. Aluminium and sodium are used here and in literature (Bazzano et al., 2015; Dick, 1991) respectively as reference elements to assess the contribution of crustal and marine components to the total mass of aerosol. To evaluate anthropic impact we had chosen elements with strong continental sources, like Pb and Zn. Every elements correlated to these markers create a cluster, to have been attributed the same emission source. To detect possible element associations, assessing their similarities and dissimilarities, and to infer, for each element/group of elements, on their main sources, and even their apportionment between the different sources, advanced multivariate statistical techniques, such as principal component analysis (PCA), hierarchical cluster analysis (HCA) and positive matrix factorization (PMF), have been applied (Bazzano et al., 2015; Cesari et al., 2016; Malandrino et al., 2016, 2013a, 2013b; Padoan et al., 2016; Toscano et al., 2005). Moreover, further support tools resulted to be very useful for environmental data interpretation: the analysis of local prevailing wind direction (wind rose), the pathway of air masses coming to the sampling site from remote areas (air masses back-trajectories), the crustal and marine enrichment factors.

## 2. Aim and objectives of the research activity during the Doctorate

In the scenario of global and local environmental changes, the objective of our study is to investigate the aerosol chemical composition collected in one of the more remote area of the continent: Dome C, the Italo-French Concordia station. Dome C is located in the Antarctic Plateau, at 3233 m a.s.l. about 1100 km from the coastline, so that, it is influenced by long-range transported Antarctic background aerosol (Udisti et al., 2004). This place offers one of the best location on the Earth for studying the processes controlling aerosol production, transport and composition of the background aerosol since it is isolated, both geographically and meteorologically, from the major sources of anthropogenic emissions of the Southern Hemisphere (Maenhaut et al., 1979; Zoller et al., 1974). The experimental design was thought to reach two main objectives: i) to investigate the impact of Concordia station on aerosol concentration, in accordance with one of the six priorities of the scientific committee on Antarctic research (SCAR) (Kennicutt et al., 2014), and ii) to determine the same metal concentration in a clean area, far from ~800 m the station, called Astrophysic Tent, under the hypothesis of no effect of the station. Here the "hypothesized background" of aerosol elemental concentration have been detected.

The knowledge of aerosol atmospheric composition is a fundamental aspect implicated in global climate and environmental changes. More in detail, the determination of major and trace elements allow to hypothesize local and/or remote emission sources implicated in micro and macro-scale air masses transport. In this scenario, the research activity has been developed in specific targets:

- ✓ The determination for the first time of the complete scenario of major and trace element concentrations in the area of Dome C (Antarctic Plateau) and their temporal evolution
- ✓ The determination of possible background atmospheric concentration of each elements
- ✓ The investigation about the impact of Concordia station on element aerosol concentrations, in accordance with one of the six priorities of the scientific committee on Antarctic research (SCAR) (Kennicutt et al., 2014)
- ✓ The hypothesis about the origin (either local or remote, primary and secondary) of the elements

As detailed objectives during the project has been continually defined the state of the art, addressed at identifying any data currently available related to element content in the Antarctic aerosol, either in Dome C or in other sites, since too little information are available on such remote areas. Moreover, given the low concentration of the elements in the Antarctic aerosol, the optimization of the analytical technique for the determination of accurate values has been another high challenging issue.

Until now, a complete elemental characterization scenario of the aerosol of Dome C is not available; only ionic composition of all year-round aerosol samples has been determined, related to 2004-2005 campaign (Becagli et al., 2009), in order to assess the seasonal load of marine, crustal and biogenic aerosol. The scarcity of data is due to the analytical difficulties, associated to the determination of trace and ultra-trace elemental concentrations, and to contamination problems.

This project has been developed in the framework of the scientific project the Italian national program for the research in Antarctica (PNRA), concerning a wide target related to air-snow relationship. This environmental aspect is relevant to the reconstruction of the changes occurred in the past atmosphere, and to estimate possible scenarios expected in the future. Indeed, it is possible to understand transport and scavenging processes and post-depositional transformation of the atmospheric aerosol components, through the analysis of chemical stratigraphy in ice cores (European project for ice coring in Antarctica, EPICA, Albert and Schultz, 2002). For this purpose, during the campaign, surface snow was sampled in the same sites where aerosol was collected, and in a transect between Concordia station and Astrophysic Tent. The present PhD project addresses aerosol characterization, while the snow and subsequent study of the relationship snow/aerosol is object of a research work in progress.

As first results, in Chapter 1 the total content of Cd, Pb and Cu in aerosol samples, collected at Dome C in Antarctica during the 2005-2006 summer campaign, has been determined. The choice of these specific metals is due to their possible implication with anthropic presence in the Antarctic continent. In particular, the potential effect of the Concordia station activities and the first hypotheses on other sources of such three elements have been made. In Chapter 2, the complete scenario of elemental composition of aerosol has been determined. It allowed the critical analysis of the achieved data and of the primary and secondary emission sources thanks to the employment of air masses back-trajectories pathways and advanced statistical tools (e.g. principal component analysis, hierarchical cluster analysis and positive matrix factorization).

## 3. Principal results of the research

The results, expressed in terms of atmospheric concentrations, showed that the major constituents (Na, Ca, Mg, Al, Fe) were present in the order of ~5 ng $m^{-3}$, while the trace elements values increased from a few units of pg $m^{-3}$ (Cd, Co, As, La), to a few tens of pg $m^{-3}$ (Pb, Mo, Ti), to hundreds of pg $m^{-3}$ (Cu, Mn, Ni, Zn). Statistical elaborations of the results, through PCA, HCA and PMF, showed a good agreement and highlighted three groupings of elements, clustered around recognized chemical tracers:

- Na, Ca, Mg mainly associated to a marine origin;
- Al, Fe, V, La, Ti, Ce, Co, Mo mainly associated to a crustal origin;
- Cd, Pb, Cu, Ni, Zn, As, mainly associated to the anthropic input;
- Mn was not univocally assigned, probably because multiple emission sources contribute to its atmospheric concentration.

The results underline a general high pollution in the first part of the season, particularly in the proximity of the station, in relation with the intense activity connected with the beginning of the expedition, including aircraft arrivals/departures. The effect of the station is lower, but undeniable, during the entire sampling period in samples collected close to the station.

Natural (both marine and crustal) factors prevail in samples collected by the two samplers located at the Astrophysic Tent, where aerosol atmospheric concentration is influenced also by air masses coming from remote sites (e.g. Southern Ocean and coastal areas not covered by ice).

Cluster analysis results agree quite well with PCA results in terms of the number of groupings and of their composition. The PMF was applied to model the source apportionment of each element. The results confirm the main sources highlighted by PCA and HCA for each element, with the exception of Mn, which appears almost equally associated to the crustal and anthropic origins, instead of the marine one.

A comparison with data available in the literature related to Antarctic plateau sites suggests that the background values measured in this work have a good agreement with other results related to major elements measured at Dome C during the summer campaigns 2004-2005 and 2006-2007. Concerning elemental aerosol determinations at South Pole from 1974 to 2003, they seem enriched in typical anthropic trace elements, such as Cd and As, while terrigenous elements, such as Fe and Mn, are quite higher at South Pole than at Dome C. As expected, in coastal areas (e.g. Terra Nova Bay, Bazzano et al., 2015) aerosol elemental concentrations are generally higher, due to the presence of sea-spray (marine source), terrigenous particles suspended in atmosphere from areas not covered by ice (crustal source), the influence of the station, the intense research activities and remote input from industrialized areas (anthropic source).

This work has opened new perspectives in understanding the major and trace element composition of the aerosol collected at the Antarctic Plateau, finding element associations deriving from either local or remote sources, reaching the most pristine area of the Planet. This aspect is considered fundamental, contributing to the knowledge of the atmospheric global circulation, in the view of estimating the climatic and environmental changes expected for the future.

## 4. Products

List of peer-reviewed papers from the research activities within the Doctorate:

- Illuminati, S., Annibaldi, A., Truzzi, C., Libani, G., Mantini, C., Scarponi, G., 2015. Determination of water-soluble, acid-extractable and inert fractions of Cd, Pb and Cu in Antarctic aerosol by square wave anodic stripping voltammetry after sequential extraction and microwave digestion, J. Electroanal. Chem. 755, 182–196
- Illuminati, S., Bau, S., Annibaldi, A., Mantini, C., Libani, G., Truzzi, C., Scarponi, G., 2016. Evolution of size-segregated aerosol mass concentration during the Antarctic summer at Northern Foothills, Victoria Land, Atmosph. Environ. 125, 212–221
- Truzzi, C., Annibaldi, A., Illuminati, S., Mantini, C., Scarponi, G., 2017. Chemical fractionation by sequential extraction of Cd, Pb, and Cu in Antarctic atmospheric particulate for the characterization of aerosol composition, sources, and summer evolution at Terra Nova Bay, Victoria Land, Air Qual Atmos Health 10, 783–7984

List of contributions to conferences within the Doctorate:

- EAC 2015 – Milan, 6-11/9/2015 «Determination of size-segregated aerosol mass concentration at Terra Nova Bay (Ross Sea, Antarctica)", Poster 1SPA_P010.
- EMEC 16 – Torino, 30 novembre – 3 dicembre 2015 «Chemical fractionation of Cd, Pb and Cu in Antarctic aerosol», P-ATMO-3
- XXVI Congresso della Divisione di Chimica Analitica - Giardini Naxos, 20 settembre 2016 «First measurements of trace metals in the atmospheric aerosol of central Antarctica at DomeC (Concordia station)», AMB-11
- XXVI Congresso Nazionale della Società di Chimica Italiana – Paestum, 10-14 settembre 2017 «Major and trace elements in the aerosol of Central Antarctica, Dome C (Italo-French Station "Concordia")», ANA-P027

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# Chapter 1

# FIRST MEASUREMENTS OF TRACE METALS AT DOME C (CENTRAL ANTARCTICA)

## Abstract

Knowledge of the chemical composition of the atmospheric aerosol in the Antarctic continent is an essential pre-requisite for the interpretation of data obtained from ice cores aimed at reconstructing the changes that occurred in the terrestrial atmosphere in the past and at estimating the climatic and environmental changes expected for the future. The aim of this work is to determine the total concentration of trace heavy metals Cd, Pb and Cu in aerosol samples collected at Dome C, a remote site on the Central Antarctic plateau, for which no data are available until now, in order to understand the seasonal summer evolution of metal contents in the aerosol, to find background values and to recognise possible metal sources. Eight Aerosol samples and six filter blanks were collected during the Austral Summer 2005-2006 using three PM10 high-volume impactors at two different locations: the first one was very close to the station (about 50 m downwind), while the other was in a “distant” site called “the Astrophysic Tent” (~800 m far from the station, upwind), where two samplers were installed very close to each other (sites called Astrophysic Tent 1 and 2). A differential weighing procedure was used on site to obtain the aerosol mass collected in each filter and then the aerosol atmospheric concentration was available for each sample. The availability of the aerosol mass in each sample allowed us to express metal results both in terms of mass fractions in the aerosol and in the usual way of atmospheric concentrations. Background metal mass fractions varied as follows: Cd ~1-2 μg $g^{-1}$, Pb ~100-130 μg $g^{-1}$, Cu ~0.2-1 mg $g^{-1}$. In terms of atmospheric concentrations, the values were Cd ~0.1-0.4 pg $m^{-3}$, Pb ~10-30 pg $m^{-3}$, Cu ~0.03-0.4 ng $m^{-3}$. The highest values were observed in the first part of the season, possibly in relation with the intense activity at Concordia station connected with the beginning of the expedition, including aircraft arrivals/departures. The effect of the wind direction was also observed. In particular, in the intermediate period of the campaign the wind direction reversed for several days with respect to the prevailing one, and the metal contents, in particular Cd, decreased at Concordia station and increased at Astrophysic Tent. Concerning Pb, practically, no differences are observed between samples collected near the station and those collected at the Astrophysic Tent if we consider the content expressed in mass fraction, while some reduction at the Astrophysic Tent is observed when we pass to the atmospheric concentration, due to the much lower aerosol content in this site than at the station. Relative high values are observed for Cu, especially at the beginning of the sampling

period. This result suggests that the human impact at Dome C (at least for Pb and Cu) influences, not only the zone very close to the station, but also the area in the neighborhood, including the "supposed clean" site of the Astrophysic Tent. About 800 m is not so far from the station, especially when the wind direction is the opposite of the prevailing one, leaving the site downwind of the station.

# 1. Introduction

Antarctica is a remote continent, characterized by lower direct human pressure than any other (Shaw et al., 2014). For this reason, it is considered as an excellent natural laboratory and the ideal place to study the natural bio-geochemical processes, and to better understand the impact of human activity on climatic and environmental changes. Important aspects are the biogeochemical cycles of natural elements and compounds, the transformation of chemical species in the pristine atmosphere, and the long-range transport of aerosol from continental areas (Barbaro et al., 2016).

Many researches on the aerosol chemistry in Antarctica (Artaxo et al., 1992; Asmi et al., 2010; Correia et al., 1998; Gadhavi and Jayaraman, 2004; Hillamo et al., 1998; Jourdain and Legrand, 2002; Kerminen et al., 2000; Chaubey et al., 2011; Rankin and Wolff, 2003; Shaw, 1988; Teinilä, et al., 2000; Teinilä et al., 2014; Tomasi et al., 2007; Wolff et al., 1998) deal with coastal sites (e.g. Halley, Terra Nova Bay, Dumont D'Urville, Aboa, Maitri, Newmayer and Antarctic Peninsula). As concerns the inland areas, few aerosol data are available (Becagli et al., 2009; Cunningham and Zoller 1981; Maenhaut et al. 1979) because of the extreme meteo-climatic condition existing in Central Antarctica and the difficulties in the analytical procedures concerning the management of extremely pure samples. Indeed, the available studies, suggest that aerosol has much lower concentration in inland sites than in coastal areas, which make the application of direct gravimetric methods highly challenging (Annibaldi et al., 2007; Artaxo et al., 1992, 1990; Gadhavi and Jayaraman, 2004; Mazzera et al., 2001; Teinilä et al., 2000; Truzzi et al., 2005).

An important study of Annibaldi et al., (2011), deals with aerosol samples collected in the area of Dome C (Italo-French station Concordia), East Antarctica during the Austral summer 2005-2006 in the frame of the Italian national program for research in Antarctica (PNRA). Aerosol atmospheric concentrations were measured by direct differential gravimetrical analysis. The observed values (reported in Table 1 and Figure 1) were the lowest ever observed in Antarctica. Data range is between 0.089-0.455 μg $m^{-3}$, mean value: 0.22 μg $m^{-3}$, expressed at "actual conditions" (temperature and pressure values at sampling site). These units instead of standard air were chosen in order to reconstruct the real load of aerosol components in the local atmosphere (Becagli, et al., 2009). Such data are the first ones in the literature dealing with an inland site of Antarctica based on the direct gravimetric method; the only comparable results are based on indirect measurements on the same site (Fattori et al., 2005; Udisti et al., 2012), and in other sites of inland Antarctica: South Pole, 1970-71 (Zoller et al., 1974); 1974-75 (Maenhaut et al., 1979; Maenhaut and Zoller, 1977); 1971-78; 1975-76; (Cunningham and Zoller, 1981); 1979-83; (Tuncel et al., 1989); 2000-01; 2003; (Arimoto et al., 2008, 2004) East Antarctic plateau, 1990-91 (de Mora et al., 1997).

These studies have shown that central Antarctica presents the lowest mass concentrations of aerosols on the Earth. Therefore, it can be considered the best place to study the background aerosol composition (Budhavant et al., 2015).

**Table 1.** PM 10 aerosol atmospheric concentration at Dome C during the summer 2005-06 (Annibaldi et al., 2011).

| Site | Sampling period | | Atmosph. aerosol conc. PM10 Mean±SD (µg m$^{-3}$ actual air) |
|---|---|---|---|
| Concordia | 1 | 7Dec-20Dec | 0,455±0,069 |
| | 2 | 20Dec-1Jan | 0,281±0,026 |
| | 3 | 1Jan-12Jan | 0,392±0,019 |
| Astrophysic T. 1 | 1 | 8Dec-20Dec | 0,106±0,008 |
| | 2 | 20Dec-1Jan | 0,189±0,016 |
| | 3 | 1Jan-13Jan | 0,089±0,013 |
| Astrophysic T. 2 | 1 | 8Dec-28Dec | 0,117±0,008 |
| | 2 | 28Dec-14Jan | 0,157±0,019 |

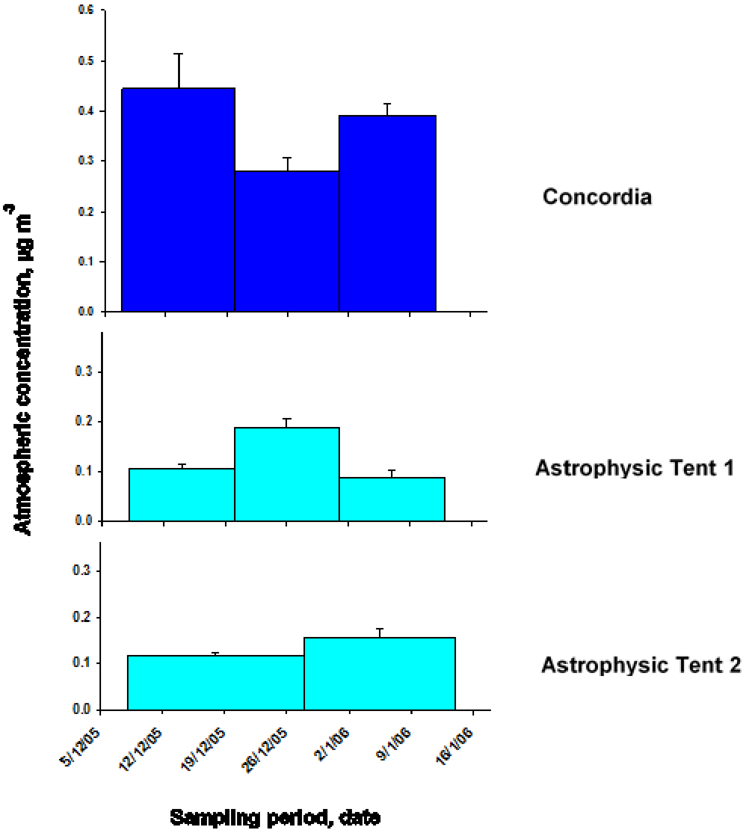

**Figure 1.** Temporal evolution of aerosol atmospheric concentration at Dome C, austral summer 2005-06 (Annibaldi et al., 2011).

The same aerosol samples presented above, collected at Dome C, are the object of the present study. Here we determined the aerosol trace metal concentrations, more specifically cadmium, lead and copper. These elements were chosen as object of the study, because typically associated to anthropogenic emissions (Bazzano et al., 2015; Cullen and Maldonado, 2013; Rosman et al., 1994; Toscano et al., 2005). Indeed, high enrichment factors with respect to mean crustal and seawater compositions have usually been attributed to inputs from human activities either local in Antarctica and/or remote in the Southern Hemisphere by long-range transport (Hur et al., 2007; Mishra et al., 2004; Planchon et al., 2002). The above elements are among those released by the combustion of coal, oil and gasoline and by non-ferrous metal production (Pacyna and Pacyna, 2001).

Cadmium is a high toxicity chemical element, present as trace element in the Earth's crust, it tends to be concentrated in sulphide, especially rich in zinc minerals (Cullen and Maldonado, 2013; Rudnick and Gao, 2003; Wedepohl, 1995). In the last 100 years, the increased presence of cadmium in Antarctica has been attributed to anthropic emissions (Cullen and Maldonado, 2013). Indeed, Antarctic ice recorded an increasing Cd deposition in response to long-range industrial emissions (Hong et al., 2004; Lee et al., 2008; Planchon et al., 2002; Wolff et al., 1999). However, the available literature supports also the hypothesis that cadmium could be associated to natural sources. In fact, the analyses of ice core from Dome C and Vostok (about 500 km far from Dome C), suggest that Cd could have had a volcanic source (e.g. from Mt. Erebus, Figure S3) during the cold and warm climatic ages (Gabrielli et al., 2005; Hong et al., 2004). It has been hypothesized that the volcano Erebus, emits especially during the summer, a sulphide and metal rich plume, and that its dispersion can reach the inland Antarctica, in particular the Central East Antarctica (Zreda-Gostynska et al., 1997). Moreover, Nriagu (1989) estimated that Cd of volcanic origin contributes to about 40-50% of the total annual emission.

As for lead, the low background atmospheric concentrations together with the well-known and often distinct isotopic characteristics of industrial sources, make this element an ideal tracer of industrial pollution (McConnell and Edwards, 2008; McConnell et al., 2002; R., 2001; Rosman et al., 1997, 1994, 1993; Sangster et al., 2000; Wolff and Suttie, 1994). Many authors have investigated about Pb as a pollutant also in Antarctica (Görlach and Boutron, 1992; Rosman et al., 1994; Wolff and Suttie, 1994). In particular, Boutron et al. (1988) have shown that in pre-industrial times, the total content of Pb in snow could have been explained by crustal (ca. two-thirds) and volcanic (ca. one-third) contributions. Marine contributions were evaluated as negligible. Higher concentrations of Pb were found in quite recent Antarctic snow (Boutron and Patterson, 1987; Dick, 1987; Wolff and Peel, 1985) cannot be attributed entirely to these sources, and the only explanation for this increase of Pb in the current Antarctic snowfall seems to be the input from anthropogenic pollution. The continental areas implicated in long-range transport of Pb, more intense during the spring season (Becagli, et al., 2009), are statistically shown to be mainly Australia and New Zealand and than South America (Rosman et al., 1994) and the southern Africa (McConnell et al., 2014). Recent studies of Pb in Antarctic ice have shown that concentrations first showed signs of anthropogenic emissions from the beginning of 20th century (McConnell et al., 2014). These concentrations decreased during the Second World War, then rose again since ~1950s in association with increasing trends in mining and smelting of non-ferrous metal ores in the consumption of leaded gasoline (Rosman et al., 1994; Wolff and Suttie, 1994; Barbante et al., 1997; Candelone et al., 1995). Such increasing emissions reached a maximum during the 1980s, due to the widespread use of motor vehicles and of leaded petrol. More recent concentrations in snow and firn during the 1990s and 2000s have decreased, coinciding with the phase-out of leaded petrol (Barbante et al., 1997; McConnell et al., 2014; Vallelonga et al., 2002).

Atmospheric copper concentration is too high to be explained in terms of normal crustal weathering processes. It is one of the most common pollutants of the environment and the source of contamination is reported to be of anthropogenic nature (Nriagu, 1979). Indeed, copper in Antarctica has been attributed to an anthropic origin, mainly connected to the local impact of the stations (Artaxo et al., 1992; Barbaro et al., 2016; Bazzano et al., 2015; Toscano et al., 2005). On the other hand, both mineralogical analyses and geochemical determinations (strontium and neodymium isotope ratios) carried out on the Dome C dust (Delmonte et al., 2008; Gaiero, 2007; Li et al., 2008) have demonstrated that copper has a predominant origin from Patagonian desert (Basile et al., 1997; Delmonte et al., 2002; Lunt and Valdes, 2001) and from the Tierra del Fuego (Gassó et al., 2010). Although dust deposition was more abundant in glacial times, recent studies in snow samples in Antarctic Peninsula and in East Antarctica (Lambert et al., 2008; Marino et al., 2008; Sala et al., 2008) indicate there have been recent depositions of dust in the last 100 years. Moreover, along the east coast of the Antarctic Peninsula there are many copper ores, copper-molybdenum porphyry deposits, while in minor amounts copper was also found in metamorphic and intrusive rocks of East Antarctica and Transantarctic Mountains not covered by ice (Congress Office of Technology Assessment, 1989; Rowley et al., 1975).

Currently, only the major elements in aerosol have been determined at Dome C, from 2004 to 2007 (Becagli, et al., 2009; Udisti et al., 2012) and more recently for the period 2011-12 and 2012-13 (Barbaro et al., 2017). As concerns the trace metal that are object of the present study, most data available on Antarctic aerosol mainly refer to coastal areas (Annibaldi et al., 2007; Bazzano et al., 2015; Toscano et al., 2005), and the only data dealing with inland sites are related to South Pole, starting from austral summer 1970 to 2003 (Table 2).

**Table 2**. Cadmium, lead and copper in literature data relative to inland sites of Antarctica.

| | | Metal atmospheric concentration, pg m$^{-3}$ | | | |
|---|---|---|---|---|---|
| Station/site | Period | Cd average±SD (min-max) | Pb average±SD (min-max) | Cu average±SD (min-max) | Reference |
| South Pole | Summer 1970-71 | - | 630±300<br>(<190-1200) | 36±19<br>(25-64) | (Zoller et al., 1974) |
| South Pole | Summer 1974-75 | < 15 | - | 29±17 | (Maenhaut and Zoller, 1977) |
| South Pole | Summer 1974-75 | ≤ 18 | 27±10<br>(Whatman filter)[a]<br>76±40<br>(Nucleopore filter)[b] | 29±17 | (Maenhaut et al., 1979) |
| South Pole | Summers 1971-78 | 49±38 | - | 59±47 | (Cunningham and Zoller, 1981) |
| | Winters 1975-76 | < 200 | - | 79±16 | |
| South Pole | Summers 1979-83 | 110±60 | - | 190±130 | (Tuncel et al., 1989) |
| | Winters 1979-83 | 50±40 | - | 130±80 | |
| South Pole | Nov2000-Jan2001 | - | <32[c] | - | (Arimoto et al., 2004) |
| South Pole | Nov2000-Jan2001 | - | 30±10 | - | (Arimoto et al., 2008) |
| South Pole | Nov-Dec 2003 | - | 180±40 | - | (Arimoto et al., 2008) |

(N) Nucleopore filters
(W) Whatman filter

The experimental design was planned in order to reach two main objectives: i) to establish background values of Cd, Pb and Cu in Dome C aerosol for the first time, ii) to investigate the impact of Concordia Station on the trace metal concentrations in the local aerosol concentration, in accordance with one of the six priorities recommended by the Scientific Committee on Antarctic Research (SCAR) (Kennicutt et al., 2014), and iii) to determine the metal concentrations in a clean area, under the hypothesis of no effect of the station. This last hypothesis has been supported by the prevailing wind direction during the sampling period, for which the site resulted upwind of the station in order to better understand local/remote sources of the atmospheric aerosol thanks to the knowledge of wind pathways (Budhavant et al., 2015; Chance et al., 2015; Illuminati et al., 2016; Udisti et al., 2012). The availability of background metal concentration in remote sites of Antarctica, poorly studied until now, is considered very important to investigate pollution in a global scale, considering the long-range transport from continental areas. No data on trace metal concentrations are available until now at Dome C, so this study can be considered a starting point for future research programmes.

## 2. Experimental part

### 2.1. The site

Eight samples of PM10-atmospheric aerosol were collected during the 2005-2006 austral summer campaign (from 7 December 2005 to 14 January 2006) at Dome C (Concordia Station)

(75°06′ S, 123° 21′ E), a remote site on the East Antarctic continental plateau at an altitude of 3233 m and more than 1000 km from the coastline, (see Figure 2 and Figure S1 of Supplementary Material). Sampling has been carried out using three PM10 high-volume impactors at two different sites: (i) immediately downwind of Concordia station (~50 m), and (ii) near the Astrophysic Tent (two samplers), the supposed "clean" site, ~800 m upwind of the Station.

The exposure time has been differentiated to comply with the requirements of trace elements determination; at Concordia station and at Astrophysic Tent 1 each sample was collected for about ten days, while at Astrophysic Tent 2 the sampling period was extended to about twenty days. The aerosol mass determination was carried out gravimetrically, by differential filter weighing, in the clean chemistry laboratory available at the station under controlled temperature (15,0±0,5 °C) and relative humidity (2,5%±0,5%) (Annibaldi et al., 2011; Truzzi et al., 2005). Each filter was reserved for our work and put into decontaminated LDPE bottles and stored frozen (–20 °C) until analysis. Blank filters ("field blanks") were also collected in the field, two for each sampler taken before and after the sampling program; they were not exposed to air flux, but were simply installed onto the switched-off samplers for few tens of minutes and then treated like samples.

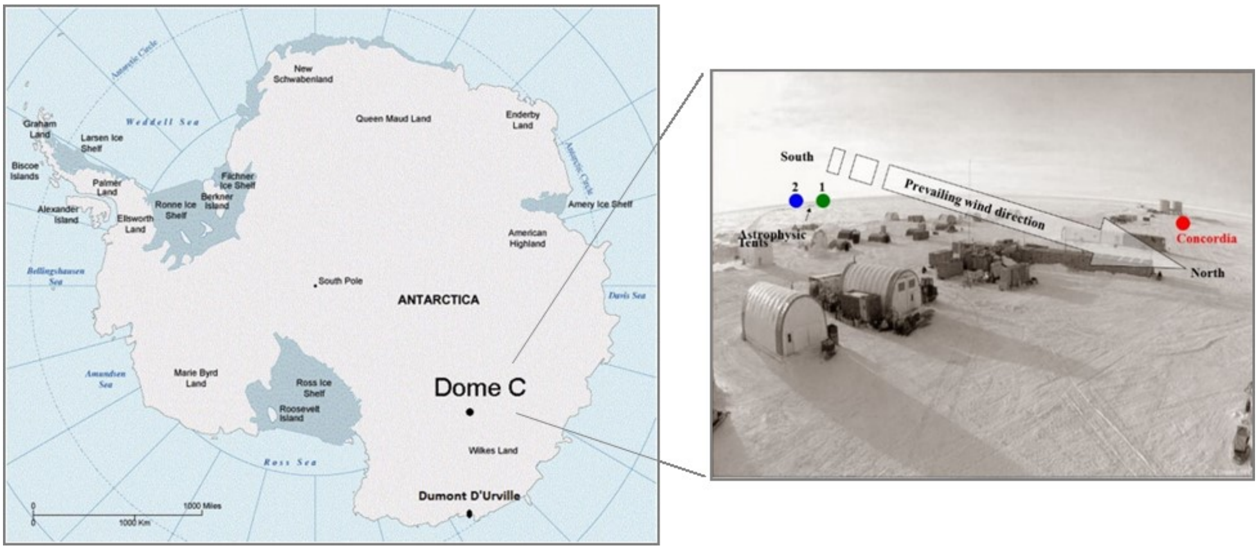

**Figure 2.** Map of Antarctica showing the location of Dome C (Concordia Station) and a picture showing the sampling sites and the prevailing wind direction related to the sampling period.

Meteorological parameters (air temperature, relative humidity, ambient pressure, wind speed and direction) were continuously registered at time intervals of 1h by the Automatic weather station (ASW) located close to the sampling sites at Concordia station. The mean values of these parameters are reported in Figure 3. During the sampling period the prevailing wind direction was, as expected, from South to North, except from December 27 to January 1 when was reversed. Average values were as follow: temperature -29 °C, pressure 656 hPa and a relative humidity 57%.

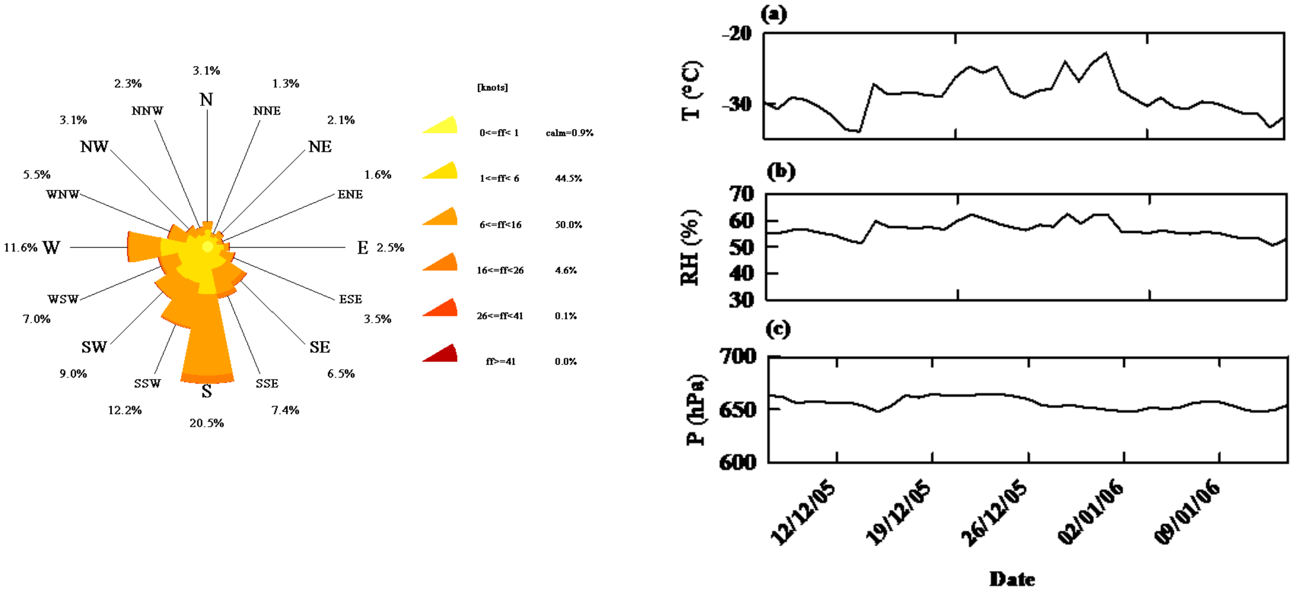

**Figure 3.** Wind rose and meteorological parameter variations at Dome C during the sampling period. The panels a), b) and c) show the day-to-day variation of air temperature (°C), relative humidity (%), pressure (hPa), respectively.

### 2.2. Laboratories, apparatus and general procedures

Clean room laboratories with areas in Class 5 (ISO 14644-1) (formerly Class 100, US Fed. Std. 209e) under laminar flow, were available both in Antarctica (Truzzi et al., 2005) and in Italy (Truzzi et al., 2002) for decontamination of materials, sample treatment, and sample analysis. The laboratory temperature is set at 20±1 °C during the winter and 23±1 °C during the summer. Clean-room garments, masks, and gloves were worn by the personnel, who strictly followed clean room procedures during all the most critical phase of treatments and sample analyses.

Aerosol samples (PM10) were collected using three teflon-coated (inner and outer), high-volume samplers (model TE-6070V-BL, from Tisch, Village of Cleves, OH, USA). Before aerosol collection, the samplers were cleaned inside and outside by repeated washing using ultrapure water (Milli-Q, Millipore, Bedford, MA). Afterwards they were calibrated in the field at the beginning upon installation, and at the end of the sampling period. Acid-cleaned (Annibaldi et al., 2007) 8×10 inch (20,3×25,4 cm) cellulose filters (Whatman 41, Cat. No. 1441-866, thickness 220 µm, ashes ≤0,007%, pore size 20-25 µm, basis weight 85 g m$^{-2}$), specifically prepared and tested for trace element determinations, were used. A Mettler Toledo (Greifensee, Switzerland), model AT261 computerized microbalance (readability 0,01 mg, repeatability SD = 0,015 mg) was used in Antarctica. Accuracy tests for the balance were obtained by two certified reference "weights (OIML class E1) of 10 mg (certified mass 0,0100005 g, 2SD = 0,0020 mg) and 100 mg (certified mass 0,0999979 g, 2SD = 0,0020 mg). A differential weighing procedure was carried out to determine aerosol mass directly from the difference between the mass of the exposed filters and their mass measured before exposure (Annibaldi et al., 2011). Conditioning (under a class 5 vertical cabinet) of filters and their weighing were carried out in a climatic cabinet for continuous temperature/humidity monitoring and control.

After gravimetric measurements, the filters were stored at -20 °C in acid-cleaned (Artaxo et al., 1990) 500 mL low density polyethylene bottles (LDPE) bottles (from Kartell, Italy) and transported frozen to Italy for subsequent analytical determinations of trace elements (Annibaldi et al., 2011).

A microwave (MW) accelerated reaction system MARS 5 (magnetron frequency 2450 MHz) from CEM (Matthews, NC, USA) was used for digestion of aerosol samples. MW vessels were 100-ml HP-500 plus in Teflon PFA (perfluoroalkoxy copolymer) from CEM.

The voltammetric instrumentation consisted of a Metrohm (Herisau, Switzerland) 746 VA Trace Analyser and a 747 VA Stand, equipped with a Teflon PFA (perfluoroalkoxycopolymer) cell and a three-electrode system, which includes an epoxy-impregnated graphite (Ultra Trace Graphite) rotating disk working electrode (to be used, after Hg deposition, as a rotating thin mercury film electrode, TMFE), an Ag/AgCl, KCl 3 mol $l^{-1}$ reference electrode (to which all potentials are referred throughout) and a glassy carbon rod counter electrode. It is used for Cd, Pb and Cu determinations.

Plastic containers used for storage of digested and not-digested sample solutions were of low-density polyethylene material. Variable-volume micropipettes and neutral tips were from Brand (Wertheim, Germany, Transferpette).

### *2.2.1. Reagents and standards*

The laboratory detergent solution for decontamination procedures was 1+100 diluted RSB-35 from Backer (Phillipsburg, NJ, USA). For decontamination procedure nitric acid (analytical grade, 65%, Carlo Erba, Cornaredo, Milano, IT) and hydrochloric acid (analytical grade, 37% Carlo Erba, Cornaredo, Milano, IT) were used, while all acids in contact with samples were of ultrapure grade, UpA, Romil, Cambridge, UK Ultrapure $HNO_3$ (70%), ultrapure HCl (34.5%), ultrapure HF (47-51%), ultrapure $H_2O_2$ (30%), all with impurities that, after dilution, were well below the detection limits. Ultrapure water was MIlli-Q from Millipore (Bedford, MA, USA). $Al_2O_3$ (superpure BDH, Poole, England), KCl (ultrapure, trace select Sigma-Aldrich, St. Louis, MO, USA), hexadistilled Hg (superpure Merck). Standard solutions of Cd, Pb and Cu were prepared every two weeks by direct dilution of AAS standards (Romil, Cambridge, UK) using acidified ultrapure water (2 mL ultrapure HCl in 1000 mL final solution). Research-grade nitrogen (purity ≥99.999%, Sol, Monza, IT) was used. The Certified Reference Materials routinely analysed, are: i) NIST 1648 and 1648a urban particulate reference material was from National Institute of Standards and Technology (NIST, Gaithersburg, USA); ii) NASS-6 (open ocean seawater) was from National Research Council of Canada (NRCC, Ontanio, Canada).

### *2.2.2. Decontamination procedures*

Description of the extensive decontamination procedures generally used in our laboratory for LDPE bottles and all other plastic material are reported elsewhere (Annibaldi et al., 2007; Truzzi et al., 2002). Briefly, a careful and prolonged washing procedure was applied to new containers with repeated treatments using, in sequence: tap water, deionised water and Milli-Q water (each washing repeated three times), diluted detergent solution to remove possible coarse residual, 1+10 diluted analytical grade $HNO_3$ in immersion for two weeks, 1+10 diluted superpure HCl in immersion for a week (this step is repeated two times) and finally 1+1000 diluted ultrapure HCl leaved inside for storage, until use.

A similar procedure was used for PFA microwave vessels. For both kinds of containers the cleaning procedure continued until values comparable to voltammetric instrumental blanks were reached.

Cellulose filters for aerosol collection were specifically prepared for trace element determinations. The filters were washed and decontaminated carefully with diluted HCl (Merck, Suprapure-grade), rinsed with Milli-Q water, dried under ISO Class 5 laminar flow cabinets and stored in acid-cleaned plastic bags until use in Antarctica.

## 2.3. Sample treatment

In Italy, an aliquot (1/8 or 1/12) of the original filters was cut in the clean room laboratory under laminar flux bench and then subjected to a MW assisted digestion previously set up for the subsequent voltammetric analysis (Illuminati et al., 2015). Mineralization was carried out mixing the filter aliquot inside a microwave vessel with 5 ml ultrapure $HNO_3$, 1 ml ultrapure $H_2O_2$ and 1 ml ultrapure HF to ensure total dissolution of the filter and complete oxidation of the organic matter, which interferes in the voltammetric measurements. Digestions were carried out using the “ramp to temperature” mode, with pressure limit constraints, in two steps. Vessels were left cool naturally to room temperature, then they were vented, opened and the solutions were diluted to 100 ml using ultrapure water and in this form subjected to voltammetric analysis.

## 2.4. Voltammetric analysis. General procedure

Detailed descriptions of the electrochemical pre-treatment of the graphite electrode, the thin mercury film electrode preparation and the overall procedure used for SWASV measurements in background subtraction mode have been reported in (Annibaldi et al., 2013, 2007, Illuminati et al., 2015, 2013; Truzzi et al., 2008).

For the voltammetric measurements the three metals were determined separately employing different deposition potentials set up in (Illuminati et al., 2015), while the deposition times varied, due to the metals involved and the concentrations detected, from 20 s to 45 min.

Quantification was achieved using the multiple standard addition method.

## 2.5. Quality control

During the work, repeated measurements of the laboratory blank were carried out with the electrochemical cell in optimal conditions (after the routine cleaning procedures). Blank measurements concerned: (1) the instrumental blank, obtained from measurements made on blank electrolytes (~0.022 mol $l^{-1}$ HCl; solution containing ~0.76 mol $l^{-1}$ $HNO_3$ and ~0.28 mol $l^{-1}$ HF); (2) the blank from LDPE bottles used for filters and MW digested solutions storage, measured on HCl solutions stored inside them for two days; (3) the blank from MW vessels used for digestion, measured on either HCl or $HNO_3/HF/H_2O_2$ solutions stored inside them for two days; (4) the blank from MW vessels after digestion with HCl solution or (5) after digestion with $HNO_3/HF/ H_2O_2$ solution.

The evaluation of the filter blanks is much more important than the laboratory blanks. In fact, due to the much greater mass of the filter with respect to the collected aerosol (a factor of ~400 is typical), the contribution of the cellulose material of the filters is expected to be significant, especially for Cd and Pb, even if analytes are present in it as trace impurities. For the present work the field blank filters, despite a quite instable matrix, have a very good repeatability. The mean values of total blanks obtained from all six filters are: Cd 10±1 ng $l^{-1}$, Pb 80±7 ng $l^{-1}$, Cu 0,36±0,02 μg $l^{-1}$ as reported in Table 3.

**Table 3.** Total blank obtained analysing field blank filters for Cd, Pb and Cu.

| Field blank filter | Metal concentration (mean±SD) | | |
|---|---|---|---|
| | Cd (ng l$^{-1}$) | Pb (ng l$^{-1}$) | Cu (µg l$^{-1}$) |
| Concordia blank 1 | 10,0±0,3<br>(n=3) | 84±5<br>(n=4) | 0,38$_8$±0,01$_8$<br>(n=5) |
| Concordia blank 2 | 9,4±0,8<br>(n=4) | 82±8<br>(n=4) | 0,33$_6$±0,03$_1$<br>(n=4) |
| Astrophysic T. 1 blank 1 | 10,1±1,0<br>(n=3) | 75±7<br>(n=3) | 0,34$_0$±0,02$_2$<br>(n=3) |
| Astrophysic T. 1 blank 2 | 9,4±1,8<br>(n=3) | 80±9<br>(n=3) | 0,40$_1$±0,02$_6$<br>(n=3) |
| Astrophysic T. 2 blank 1 | 10,7±0,3<br>(n=3) | 84±5<br>(n=3) | 0,34$_2$±0,01$_9$<br>(n=4) |
| Astrophysic T. 2 blank 2 | 10,0±1,8<br>(n=3) | 76±9<br>(n=4) | 0,37$_5$±0,03$_3$<br>(n=3) |
| Weighted mean±SD | 10±1 | 80±7 | 0,36±0,02 |

In our laboratory, accuracy of the voltammetric procedures for trace metal determinations in environmental samples is routinely tested using certified reference materials, see e.g. (Annibaldi et al., 2011, 2009, 2007; Dabek-Zlotorzynska et al., 2003; Illuminati et al., 2015, 2013, 2010; Karanasiou et al., 2005; Toscano et al., 2005; Truzzi et al., 2008). Concerning aerosol measurements, the NIST 1648 (NIST 1998) and 1648a (NIST 2012) urban particulate reference materials were used. Here 0.6 mg of NIST 1648a were subjected to the same treatment of the samples; after weighing they were totally mineralized by microwave digestion and analysed by SWASV technique. To verify a good accuracy even at low metal concentrations NASS-6 (NRCC 2010), seawater certified reference material, was analysed. The results of the systematic measurements carried out on reference materials during the work are showed in Table 4; results show that concentrations of Cd, Pb and Cu measured in the reference materials were in good agreement with certified reference values within the experimental errors, showing a good accuracy of all measurements.

**Table 4.** Accuracy tests on the NIST-1648a (NIST 2012) and NASS-6 (NRCC 2010) certified reference materials for atmospheric particulate matter and seawater, respectively.

| | Metal concentrations | | | | | |
|---|---|---|---|---|---|---|
| | NIST 1648a, mg kg$^{-1}$ [a] | | | NASS-6, ng l$^{-1}$ | | |
| | Cd | Pb | Cu | Cd | Pb | Cu |
| Experimental values | 79±7 | 0,68±0,032 | 619±37 | 30±4 | 6,0±0,4 | 270±46 |
| Certified values | 73,7±2,3 | 0,655±0,033 | 610±70 | 31±2 | 6±2 | 248±25 |
| Δ% | +7,2% | +3,5% | +1,5% | +4% | 0 | -9% |

[a] values for Pb are reported as percentage, %

### 2.6. Meteorological data and backward trajectories

In order to characterize the transport pathways of air masses arriving at Dome C, 5 days backward air trajectories were computed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) transport and dispersion model assessed via NOAA Air Resources Laboratory READY (Real-time Environmental Applications and Display sYstem), site http://www.arl.noaa.gov/ready/hysplit4.html, (Rolph, 2017; Stein et al., 2015). The meteorological data used for the calculations were the NCEP/GDAS 1 degree data. The vertical motion calculation method was selected to “Model vertical velocity”. The back trajectories were calculated for each day (arrival time 12 a.m.), with an extension of 5 days 6h interval time. Three arrival heights were selected (100 m, 500 m and 1000 m above ground level (a.g.l.)) to minimize ground friction and mixing air processes close to the soil.

The choice of 5 days was made due to the mean lifetime expected for aerosols in this region (Shaw, 1988) with respect to mid-latitudes. The residence time of aerosol is usually less than a week, depending on aerosol properties and meteorological conditions (Budhavant et al., 2015; Chance et al., 2015; Harris, 1992; Prospero et al., 1983).

WARNING: *Data and information on local meteorology were obtained from Operational Meterological Infrastructure of ENEA-UTA (www.enea.uta.it) through the “Meteo-Climatological Observatory” of PNRA (www.climanantartide.it).*

## 3. Results and discussion

The total content of metals in aerosol samples collected at Dome C during the 2005-2006 Antarctic summer campaign, is expressed both in terms of mass fractions and in atmospheric concentrations.

The first result represents the amount of metal present per unit mass of aerosol, while the second one is the amount of metal present per unit volume of air in particulate form, which is related to the metal mass fraction in the aerosol and to the aerosol atmospheric concentration. In fact, the data reported above on the aerosol atmospheric concentrations link the two ways of expressing metal concentration. Thus, we can discuss separately our results either in metal mass fractions, to understand the aerosol chemical composition, or its metal atmospheric concentrations, which are related to the total metal amount in the air.

Table 5 reports the metal mass fractions in the aerosol (blank subtracted); the values varied as follows (min-max): Cd 1,0-8,4 µg g$^{-1}$, Pb 96-470 µg g$^{-1}$, Cu 0,17-20 mg g$^{-1}$.

**Table 5.** Cd, Pb and Cu in Antarctic aerosol expressed as metal mass fraction, standard deviations in parenthesis (Dome C, Concordia station, austral summer 2005-06).

| Site | n. | Mass fraction (±SD) | | |
|---|---|---|---|---|
| | | (µg g$^{-1}$) | (µg g$^{-1}$) | (mg g$^{-1}$) |
| Concordia | 1 | 7,0±1,2 | 140±20 | 5,4±0,9 |
| | 2 | 1,4±0,4 | 110±10 | 3,9±0,6 |
| | 3 | 5,2±0,5 | 110±10 | 0,92±0,06 |
| Astrophysic T.1 | 1 | 6,6±1,6 | 470±60 | 20±2 |
| | 2 | 1,3± 0,4 | 120±10 | 1,06±0,14 |
| | 3 | 1,0±0,5 | 130±20 | 1,5±0,2 |
| Astrophysic T.2 | 1 | 8,4±1,0 | 200±30 | 0,88±0,28 |
| | 2 | 1,3±0,4 | 96±10 | 0,17±0,03 |

Table 6 reports the metal atmospheric concentrations; the values were in the following ranges: Cd 0,09-3,1 pg m$^{-3}$, Pb 12-62 pg m$^{-3}$, Cu 0,027-2,4 ng m$^{-3}$.

**Table 6.** Cd, Pb and Cu in Antarctic aerosol expressed as atmospheric concentration (Dome C, Concordia station, austral summer 2005-06).

| Site | n. | Atmospheric concentration (±SD) | | |
|---|---|---|---|---|
| | | Cd (pg m$^{-3}$) | Pb (pg m$^{-3}$) | Cu (ng m$^{-3}$) |
| Concordia | 1 | 3,1±0,4 | 62±7 | 2,4±0,3 |
| | 2 | 0,40±0,13 | 31±3 | 1,1±0,2 |
| | 3 | 2,0±0,2 | 44±6 | 0,36±0,04 |
| Astrophysic T.1 | 1 | 0,70±0,18 | 50±7 | 2,1±0,3 |
| | 2 | 0,25±0,09 | 23±2 | 0,2±0,03 |
| | 3 | 0,09±0,04 | 12±1 | 0,14±0,02 |
| Astrophysic T.2 | 1 | 0,98±0,14 | 24±4 | 0,10±0,03 |
| | 2 | 0,20±0,06 | 15±2 | 0,027±0,004 |

Figures 4 to 6 show graphically the metal profiles, for cadmium, lead and copper, respectively.

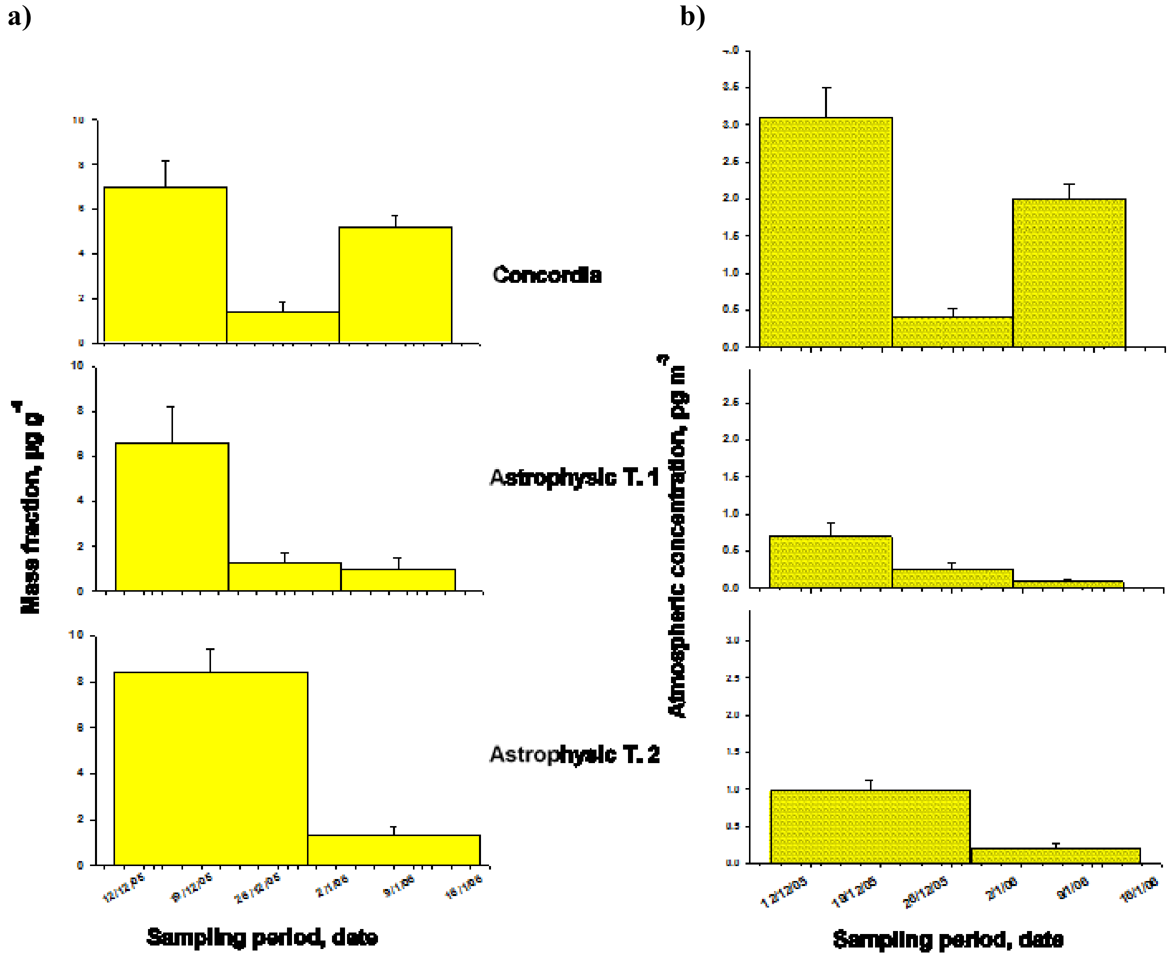

**Figure 4.** Seasonal trends of a) Cd mass fraction and b) Cd atmospheric concentration at Dome C during the 2005-06 austral summer.

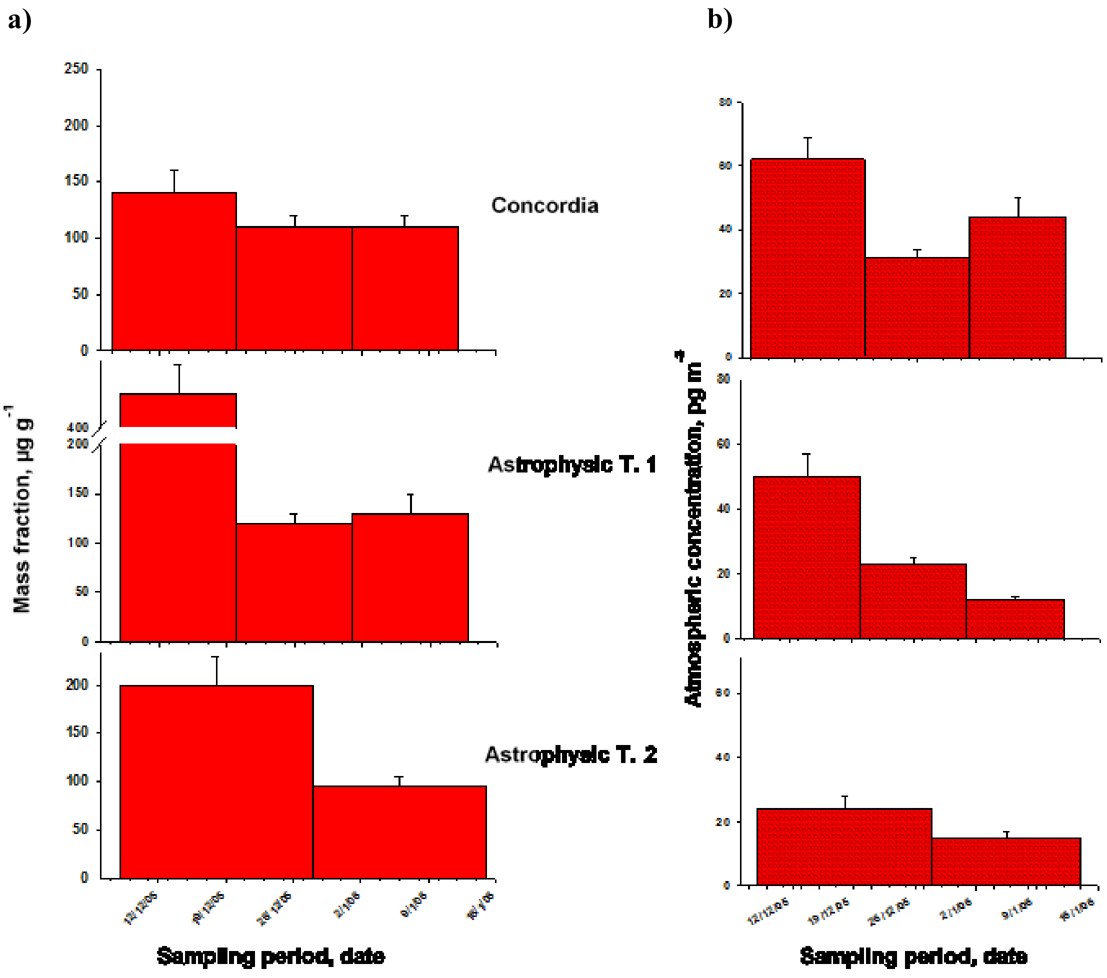

**Figure 5.** Seasonal trend of a) Pb mass fraction and b) Pb atmospheric concentration at Dome C during the 2005-06 austral summer.

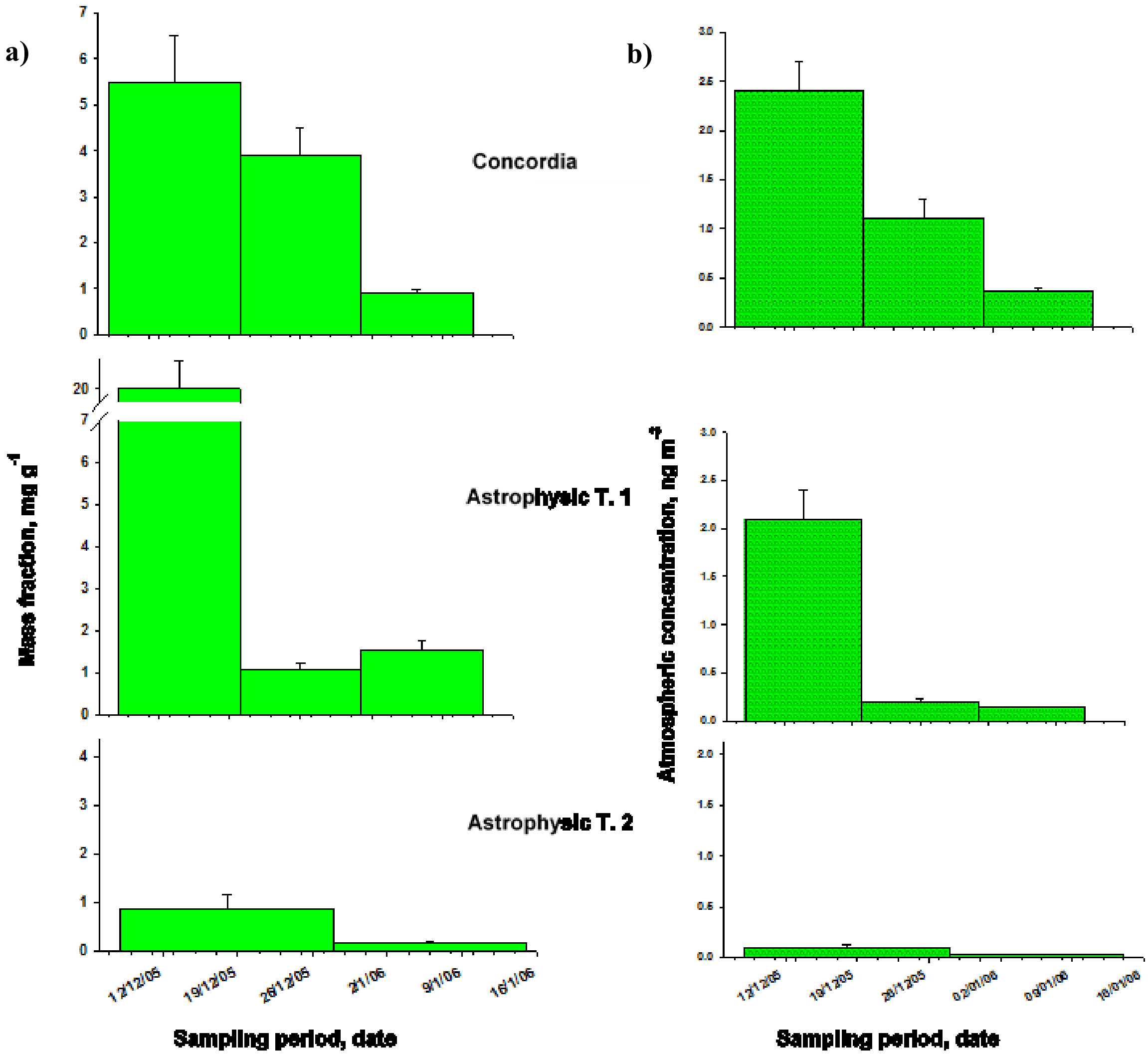

**Figure 6.** Seasonal trend of a) Cu mass fraction and b) Cu atmospheric concentration at Dome C during the 2005-06 austral summer.

A general analysis of data in Tables 5 and 6, and in Figures 4 to 6, suggests that the highest values were observed at the beginning of the expedition (corresponding to sample 1 for each site); this can be attributed to the intense activity at Concordia station, including aircraft arrivals/departures. A deeper understanding of the single metal profiles, needs also the information related to wind direction to evaluate impact of local sources (Fleming et al., 2012), classifying air patway in a simple way (Borbély-Kiss et al., 1999) and the consequent back-trajectories of the air masses (Figures S4, S5, S6.), a useful tool to speculate about remote origins of airborne particulate matter (Abdalmogith and Harrison, 2005; Borge et al., 2007; Buchanan et al., 2002; Nyanganyura et al., 2008). Indeed, this is necessary to provide evidence of long-range transport of aerosol particles to understand sources apportionments (Rose et al., 2012).

The analysis of air masses back trajectories were calculated at three elevations above ground level (i.e., 100 m, 500 m and 1000 m) in order to evaluate a complete scenario of air masses coming from remote areas revealing flying particles of different origins that could influence the sampling site. During the first sampling period (Figure S4), corresponding to the 7th to the 20st of December in this discussion (here the periods refer to the collections carried out with impactors located in the sites Concordia and Astrophysic Tent 1), the pictures suggest that the air masses originated and passed through inland of East Antarctica, coming mainly from the South, South-West during the main part of the period, with some contribution from coastal regions (see particle locations at 4-5 days before arrival on the 10th, 11th and 17th December. During the second sampling period (Figure S5), from the 21th of December to the 1st of January, air masses continued to come from South until 26th December when began to change direction and from 27th December to 1st January a complete inversion of wind direction was recorded. From the corresponding pictures, it is clearly visible a contribution of masses coming from East - North-East, carrying out particles from marine and coastal regions. During the last part of the season (2nd to 13th January), the major contribution of air masses came from South, South-West, flying across inland sites of Antarctica (Figure S6). A residual contribution from coastal sites was present in the 2nd and 3rd of January.

Figure 4 shows that Cd has the same trend for mass fraction and atmospheric concentration. At the beginning of the expedition, there are high levels of Cd, independently from the site; as previously reported, this is probably connected with intense station activities and use of logistic equipment for the arrival of the research expedition. The second samples of Concordia station and the Astrophysic Tent 1 correspond to the change in the wind direction discussed above: such change has an effect on cadmium concentration, which decreases at hypothesized background values of 1-1,5 $\mu g\ g^{-1}$ mass fraction and 0,1-0,4 $pg\ m^{-3}$ atmospheric concentration. At the end of the sampling period, when the wind again blew from the South, the Cd turned back to a relatively high value at the site Concordia.

Figure 5 shows Pb temporal trends. Concerning mass fraction, with the exception of the very high values of the first sampling period, there are no differences between samples collected near the station and those collected at the Astrophysic Tents, so is difficult to hypothesize a possible background level. Influence of wind direction is not observed in each site and in each sampling period. Indeed, considering atmospheric concentration the first samples at Concordia station and at Astrophyisic Tent 1 has high level of Pb like Cd, probably for the same reason; an high anthropic impact related to the station activities. When the wind direction changed, during the second sampling period, a low decrease in atmospheric concentration is observed at Concordia station. Even at Astrophysic Tent 1 Pb value decreases, but is not possible to understand if the wind from the North had an effect because of the too high level of Pb in the first sample. In the third sample, when the wind blew again from the South at Concordia station Pb turned back at high value, while at Astrophysic Tent Pb decrease at presumable background level of ~15 pg $m^{-3}$ atmospheric concentration.

Concerning Cu, data in Figure 6 highlight that very high values are observed for Cu, at the beginning of the sampling both at Concordia station and at Astrophysic Tent 1. These values tend to decrease in the second and third sample of each site during the period showing a different tendency if we consider Cd and Pb trend. In Astrophysic Tent we can probably obtain background level of aerosol, ~1 mg $g^{-1}$ in mass fraction and ~0,2 ng $m^{-3}$ in atmospheric concentration. Changing of wind direction discussed above, had no effect on metals concentrations considering both mass fraction and atmospheric concentration.

To better understand the relationship between metals, we also analysed their correlations. In a first step we had considered all sample in the same correlation matrix, independently from the sampling site, to have a general scenario of association between metals in the entire area of Dome C. The Table 7 reports the correlation coefficients calculated both for mass fraction and atmospheric concentration, while Figure 7 shows correlation plots.

The most significant correlation (r=0,93, r=0,87) is between lead and copper, both in mass fraction and in the atmospheric concentration. Cadmium and lead show high correlation only for the atmospheric concentration (r=0,83).

**Table 7.** Correlation coefficients between metal concentrations in all samples collected at Dome C, Concordia station, austral summer 2005-06.

| Metals | Mass fraction | Atmospheric concentration |
|---|---|---|
| Cd-Pb | 0,50 | 0,83 |
| Pb-Cu | 0,93 | 0,87 |
| Cd-Cu | 0,38 | 0,57 |

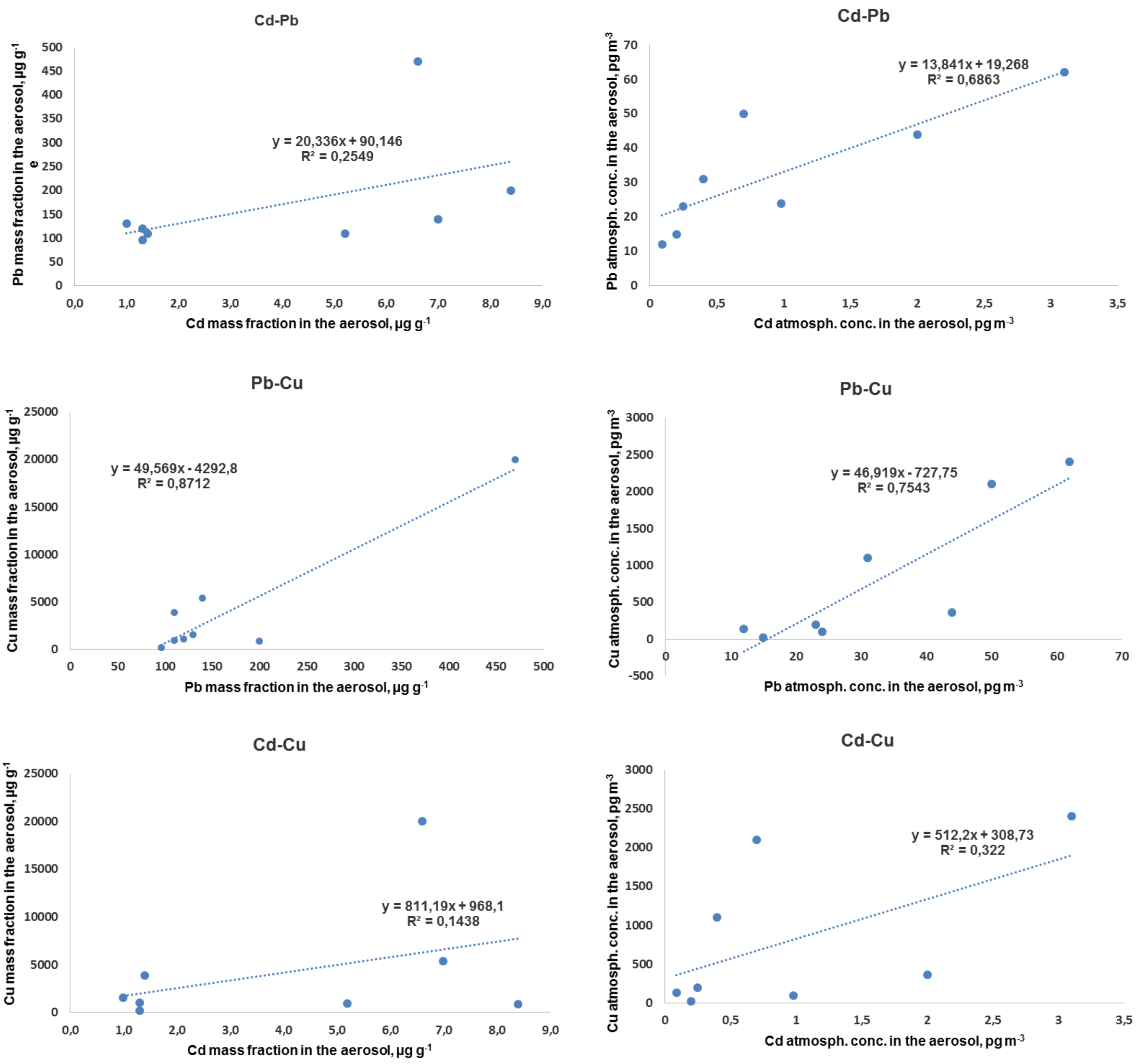

**Figure 7.** Correlation between metal concentration in the aerosol samples (mass fractions and atmospheric concentrations) - Dome C during austral summer 2005-06.

Despite eight samples are quite a low number, the available data have been separated in two series, in order to assess if metal correlation might change with the metal source. Indeed, the data reported above suggest that some of the samples are representative of a scenario where the base seems to be the main responsible for metal concentration in the aerosol (i.e. sample n. 1, 2 and 3 at Concordia station and the two samples n.1 at the Astrophysic Tents). On the other hand, other samples (i.e. sample n. 2 and 3 at Astrophysic Tent 1 and sample n. 2 at Astrophysic Tent 2) seem to be representative of a scenario classifiable as "background", where metal concentration in the aerosol could be affected by the general air masses circulation. Moreover, the sample 1 of the

Astrophysic Tent 2 has been included also in this last series, taking into account its relatively low level of metals, probably representative a borderline situation.

Table 8 shows the correlation coefficients between metals, both calculated for the mass fraction and the atmospheric concentration, within each series. Moreover, Figures 8 and 9 graphically represent such correlations, for the samples affected by the station activities and for the hypothesized background scenario, respectively.

Considering the first series, i.e. the one representative of the influence of the expedition logistics, it can be observed (Table 8 and Figure 8) that the most significant correlation (r=0,92) is between lead and copper, both in mass fraction and in the atmospheric concentration. Indeed, relatively low values of Pb correspond to relative low values of Cu, and vice versa. On the other hand, cadmium seems to be significantly correlated neither with copper nor with lead. Taking into account that all the samples in this series are considered as affected by the logistic of the expedition, the emissions of the various transports (snowcat, snowmobile, aircraft) and electrical power generator are supposed to be main responsible for metal enrichment in the aerosol. Consequently, it is expected to find the same correlation in the various fuel mixtures employed in such transport means.

Considering the second series, i.e. the one related to the hypothesized background, data in Table 8b and in Figure 9 evidence a high correlation between cadmium and lead (r=0,94), while copper seems not to be significantly correlated with any metal. As above reported, such samples are considered to be representative of the general air mass circulation. The high correlation between cadmium and lead could be explained by the same sources responsible for such metals enrichment in the atmospheric aerosol. Indeed, in the recent literature Cd is usually associated to an anthropogenic origin (Bazzano et al., 2015; Grotti et al., 2015, 2011; Toscano et al., 2005), while in crust it is present at a very low concentration (Cullen and Maldonado, 2013). Also a volcanic origin of Cd should be considered; indeed, Nriagu (1989) estimated that volcanic emissions contribute about 40% of Cd annually emitted. Similarly, also for Pb, the main source of enrichment is associated to industry, especially mining and smelting activities (McConnell et al., 2014) while in crust is present at low concentration, in particular associated with silicic volcanic materials (Congress Office of Technology Assessment, 1989).

On the other hand, the presence of copper in the Antarctic atmospheric aerosol needs a separate discussion. Usually Cu is attributed to an anthropic origin (Artaxo et al., 1992; Barbaro et al., 2016; Bazzano et al., 2015); however, it may also have a natural origin. Indeed, as reported in the "Introduction" section, along the east coast of Antarctic Peninsula there are many copper ores also in rocks not covered by ice; moreover, dusts coming from Patagonia and Tierra del Fuego, rich in copper, have been demonstrated to have an influence on the metal enrichment of Antarctic aerosol

(Basile et al., 1997; Delmonte et al., 2002; Gassó et al., 2010; Lunt and Valdes, 2002). Moreover, as presented above, during the period 29 December – 1 of January, the air masses came from East coastal area, where are copper mineral occurences, as shown in Figure S2. Such scenario, together with the study on wind back trajectories, support the hypothesis that in the hypothesized background samples copper could have both an anthropic and a natural origin.

**Table 8.** Correlation coefficients between metal concentrations in samples affected by the station activities (a) and in the hypothesized background scenario (b) - (Dome C, Concordia station, austral summer 2005-06)

a)

| Metals | Mass Fraction | Atmospheric concentration |
|---|---|---|
| Cd-Pb | 0,37 | 0,72 |
| Pb-Cu | 0,92 | 0,82 |
| Cd-Cu | 0,11 | 0,32 |

b)

| Metals | Mass fraction | Atmospheric concentration |
|---|---|---|
| Cd-Pb | 0,94 | 0,73 |
| Pb-Cu | 0,28 | 0,37 |
| Cd-Cu | -0,07 | -0,12 |

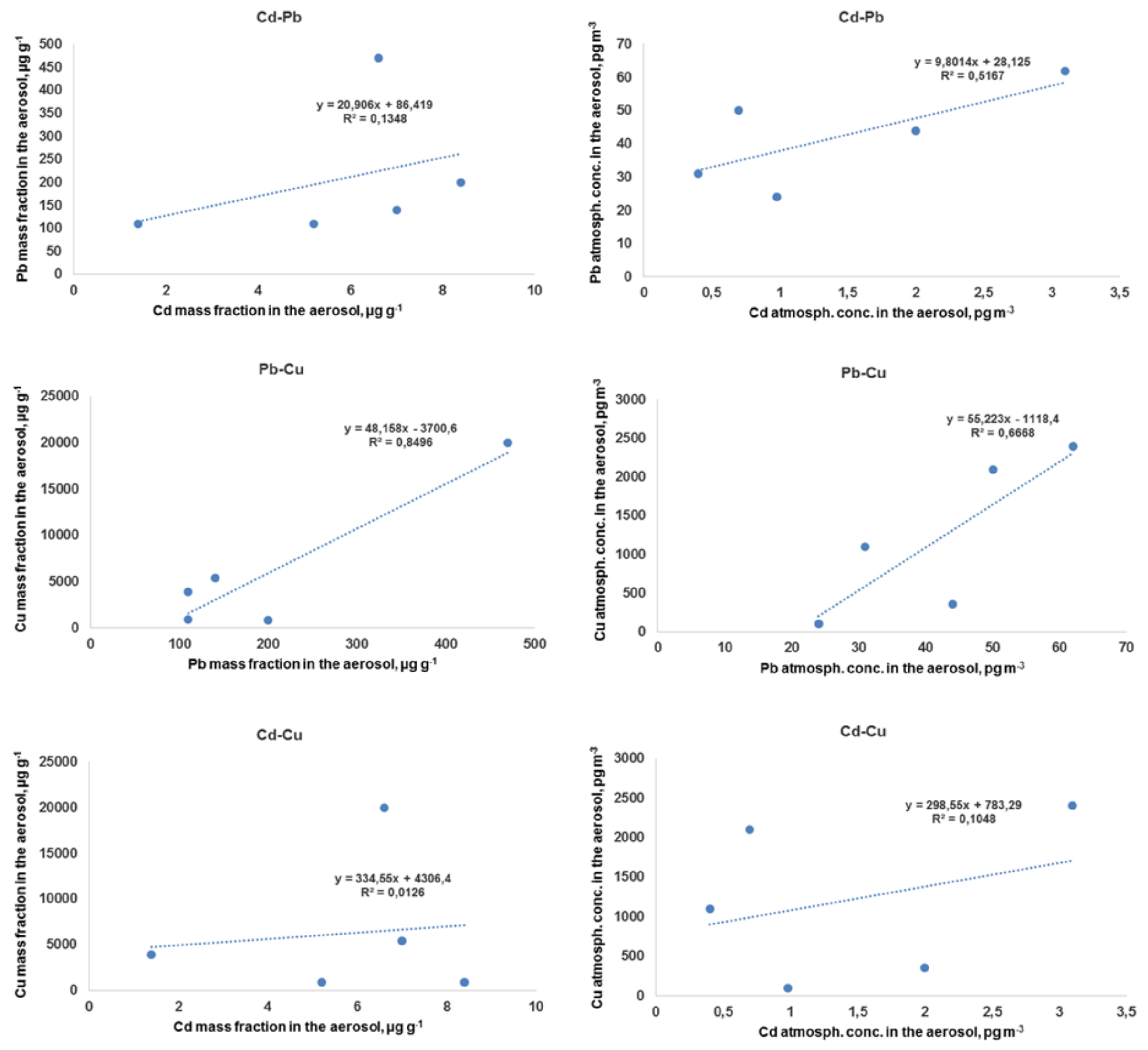

**Figure 8.** Correlation between metal concentration in the aerosol (mass fractions and atmospheric concentrations), within the data series representative of the base affected samples - Dome C during austral summer 2005-06.

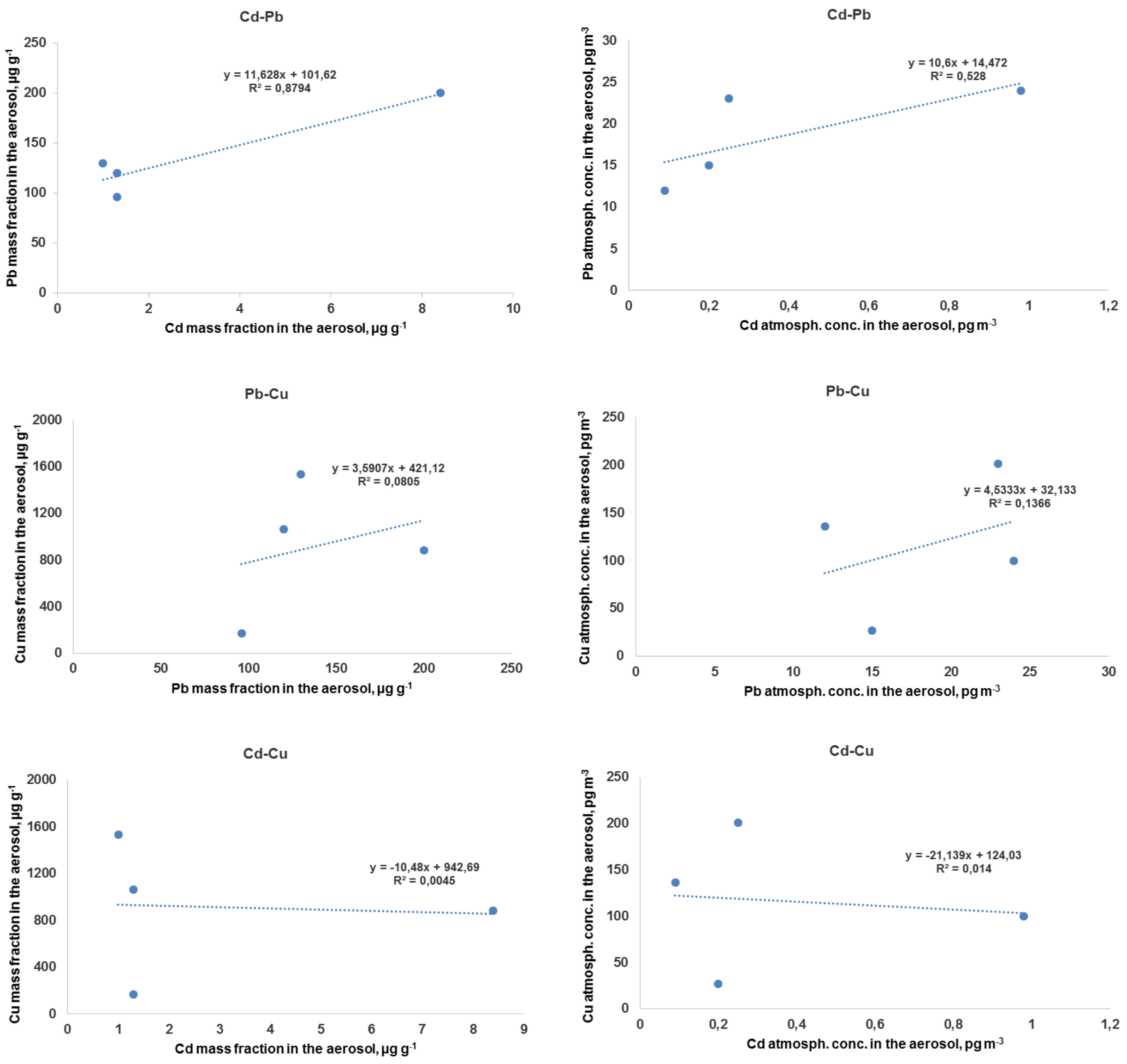

**Figure 9.** Correlation between metal concentration in the aerosol (mass fractions and atmospheric concentrations), within the data series representative of the hypothesized background samples - Dome C during austral summer 2005-06.

# 4. Conclusions

Aerosol metal concentrations have been determined for the first time at Dome C, East Antarctica. From the analysis of the samples, an anthropic impact has been revealed, both directly determined by the station activities (mainly due to the fuel for transports and electrical power generator), and originated from continental remote areas of the South America and Australia.

Although a general pollution of the sampling area was observed, the background metal concentrations have been determined at the Astrophysic Tents, when the wind blew from the South, as documented by wind rose analyses.

The study has been focused only on three metals, cadmium, lead and copper, as in previous scientific papers of our research group. Even if three metals are not enough to investigate the general aerosol chemical composition, these metals have an important role in the environmental impact studies, as widely documented in the “Introduction” section. This choice has been made also to improve the temporal record of our researches on such metals, determined in different sites (i.e. Faraglione Camp, Terra Nova Bay and Dome C) of Antarctica.

As future perspective, this analysis will be implemented with the determination of other metals, to better characterize the chemical composition of the Antarctic aerosol, and to define sources apportionment, only hypothesized until now. Indeed, in this work metal correlations have allowed us to suppose a discrimination between sources, considering two series of samples: the first one undoubtedly affected by the proximity of the station, and the second one unaffected by local anthropic impact, but influenced by long-range transport of remote continental particles. Also in this case, further work is needed where other elements are considered, in order to better discriminate about metal association and source apportionment.

Moreover, to better discriminate between sources should be analysed chemical fractionation by chemical sequential extraction of aerosol samples as set up by Illuminati et al. (2015). Three main fractions are identified as the main chemical compounds: water-soluble fraction contains water-soluble marine salts and ions – acid-extractable fraction contains mainly carbonates and sulphates ascribable to possible anthropogenic origin – inert fraction are oxides and silicates residual representing the possible contribution of the crustal dust.

The air-snow relationship is another aspect that should be considered in order to determine depositional fluxes of aerosol and of metals. This dynamic allows us to investigate if occur any chemical transformation of metals compounds after snow deposition and to reconstruct past climate changes.

To better discriminate the real origin of the pollution we should analyse the special mixture of fuel (called Jet-A1) employed in Antarctica, to characterize the combustible chemical profile. We expect the same metal ratio both in fuel and in aerosol samples.

## 5. References

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# Chapter 2

# MAJOR AND TRACE ELEMENTS IN THE AEROSOL OF CENTRAL ANTARCTICA, DOME C (ITALO-FRENCH STATION “CONCORDIA”)

## Abstract

The chemical characterization of aerosol is an essential aspect in the study of atmosphere, in order to reconstruct transport pathways and troposphere chemical modifications. In this scenario, major and trace elements (Al, As, Ca, Cd, Co, Cu, Fe, La, Mg, Mn, Mo, Na Ni, Pb, Ti, Zn) were determined for the first time in the aerosol collected at Dome C, Concordia Station, in the Antarctic Plateau, one of the cleanest area of the Earth. PM10 samples were collected during austral summer 2005-2006 using three high-volume samplers at two different locations: the first one was very close to the station (about 50 m downwind), while the other was quite far, in a site called “the Astrophysic Tent” (~800 m far from the station, upwind), with two samplers installed very close to each other (sites called Astrophysic Tent 1 and 2). The aims of this work were: i) to investigate the direct impact of the station on aerosol elemental concentration, ii) to hypothesize background concentrations of chemical constituent in a clean area and iii) to find possible association between elements, in order to determine local and remote influence of the emission sources. Elemental determinations were carried out by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS). Cd, Pb and Cu atmospheric concentrations, determined by square wave anodic stripping voltammetry (SWASV) previously discussed under Chapter 1, were added to the data matrix for a complete scenario. The results, expressed in terms of atmospheric concentrations, showed that the major constituents (Na, Ca, Mg, Al, Fe) were present in the order of ~5 ng $m^{-3}$, while the trace elements values increased from a few units of pg $m^{-3}$ (Cd, Co, As, La), to a few tens of pg $m^{-3}$ (Pb, Mo, Ti), to hundreds of pg $m^{-3}$ (Cu, Mn, Ni, Zn). In general, the highest element concentrations were observed around the beginning of the expedition, for each sampling site. This can be attributed to a high load in atmospheric concentration, probably determined by a general impact of the area connected to the intense activity at Concordia station. Conversely, very low values were observed subsequently, especially at the Astrophysic Tent. To acquire a deep knowledge of the chemical dynamics occurred in the sampling area, advanced statistical tools have been applied for data elaboration: principal component analysis (PCA), hierarchical cluster analysis (HCA) and positive

matrix factorization (PMF). Moreover, also the analysis of local prevailing wind direction (wind rose), the air masses back-trajectories, the coefficient correlation matrix and the crustal and marine enrichment factors (EFs) were taken into account for data interpretation. The analysis highlighted three groups of elements: Na. Ca and Mg appear to have mainly a marine origin; Al, Fe, V, La, Ti, Ce, Co, Mo seem all associated to a crustal source; Cd, Pb, Cu, Ni, Zn, As seem to be related to the local anthropic activity. Mn is not univocally determined, probably because multiple emission sources contribute to such atmospheric concentration. This work represents the first study of the aerosol elemental composition at Dome C, a remote site in the Antarctic Plateau. It contributes to understand the dynamics of the global atmospheric circulation, and elemental chemical transformations implicated in the environmental modifications and global climate changes.

# 1. Introduction

The Antarctic atmosphere is one of the cleanest in the planet (Chown et al., 2012; Cressey, 2012), thanks to Antarctic circumpolar current (ACC) that enhances the meteorological isolation of the continent. This feature makes Antarctica a valuable laboratory for monitoring and understanding the state of our global environment (Bodhaine et al., 1992) and offers a unique opportunity for studying background aerosol (Maenhaut et al., 1979; Maenhaut and Zoller, 1977; Zoller et al., 1974).

However, the anthropogenic impact in Antarctica is today undeniable, due to both the effect of a global atmospheric circulation and of local scientific expeditions (Bargagli, 2008, 2005; Bergstrom et al., 2006; Fattori et al., 2005; Murozumi et al., 1969; Suttie and Wolff, 1993). Human contamination in Antarctica has been widely demonstrated through snow (Grotti et al., 2015) and ice characterisation, both in the coastal area (Van de Velde et al., 2005) and in central Antarctica (Boutron and Patterson, 1987, 1983) in the seawater (Sañudo-Wilhelmy et al., 2002; Scarponi et al., 1995) in the glacial lakes located in the proximity of research stations (Ellis-Evans, 1996; Burgess and Kaup, 1997; Gasparon and Burgess, 2000; Goldsworthy et al., 2003), and in marine organisms (Sanchez-Hernandez, 2000; Bargagli, 2008; Grotti et al., 2008; S. Illuminati et al., 2016; Truzzi et al., 2008).

As concerns the aerosol characterisation, it has been widely applied in highly industrial/ anthropized areas, e.g. in the proximity of cities like Turin (Italy) (Malandrino et al., 2016, 2013a, 2013b; Padoan et al., 2016), Debrecen (Hungarian) (Borbély-Kiss et al., 1999), Boston (US) (Thurston and Spengler, 1985), Dhaka (Bangladesh) (Faridul Islam et al., 2015) and in rural sites (Hueglin et al., 2005), in order to monitor environmental quality and to protect the human health (Romanazzi et al., 2014; Wilson and Suh, 1997). More recently, it has also been applied in pristine remote regions, like Arctic and Antarctica (Bazzano et al., 2015a; Shevchenko et al., 2003; Udisti et al., 2016, 2012), to investigate transport pathways and troposphere chemical modifications.

Data dealing with aerosol characterisation are quite complex, since a high number of elements is determined for each sample. A first comparative analysis of the data allows to know the temporal evolution and any difference among sampling sites, for each element separately. However, the ambitious objective of the environmental research is to detect possible association among elements, to assess eventual similarities/dissimilarities among the analysed samples, for each element/group of elements to infer about the main emission source, and even its apportionment within the different potential sources. To support this critical data interpretation, advanced statistical tools are necessary. The widespread applied tools are based on multivariate statistical analysis, such as principal component analysis (PCA) (Bazzano et al., 2015b; Malandrino et al., 2016; Toscano et al., 2005; Truzzi et al., 2017), and hierarchical cluster analysis (HCA) (Contini et al., 2010; Malandrino et al., 2013a, 2013b; Padoan et al., 2016), that allows grouping elements considering their similarities: each group of elements around a recognized chemical marker can be attributed to the same main origin. To deepen the source apportionment of each element in the aerosol, an advanced multivariate statistical tool has been employed in the literature: the positive matrix factorization (PMF) (Viana et al., 2008). A unique feature of this statistical technique, is that PMF can discriminate between principal and secondary emission sources of each element, giving a more realistic modelling of the atmospheric composition at a receptor site. The application and the subsequent comparison of different statistical methods, together with the critical interpretation of air masses back-trajectories (Rolph et al., 2017; Stein et al., 2015) and of enrichment factors (EFs) (Annibaldi et al., 2007; Xu and Gao, 2014; Zoller et al., 1974), allow to validate the hypothesis about origin of each group of elements, that influence chemical atmospheric composition. This approach would solve the limitations of each models, by constructing a more robust scenario of aerosol atmospheric knowledge (Viana et al., 2008). This inter-comparison between methods is largely employed in literature, and it has been fitted also to Antarctic aerosol sampled in coastal areas (Bazzano et al., 2015b; Toscano et al., 2005; Truzzi et al., 2017). Indeed, the coastal area is the most studied as concerns the sources and evolution of the Antarctic aerosol population (Giordano et al., 2016; Hara et al., 2004; Jourdain and Legrand, 2002; Tuncel et al., 1989; Wagenbach et al., 1988). On the other hand, few data are available in the literature dealing with Antarctic inland sites (Table 1); most of the studies deal with major ionic compounds, (Becagli et al., 2009; Becagli et al., 2009, 2012; Fattori et al., 2005; Jourdain et al., 2008; Legrand et al., 2017; Udisti et al., 2012) while, few data are available for trace elements (Cunningham and Zoller, 1981; Maenhaut et al., 1979; Maenhaut and Zoller, 1977; Tuncel et al., 1989; Zoller et al., 1974) in inland sites different than Dome C (e. g. South Pole).

**Table 1.** Comparison between major and trace elements data in inland Antarctic aerosol

| **Sample site** | **Period** | **Major elements (ng $m^{-3}$)** | | | | | **Trace elements (pg $m^{-3}$)** | | | | | | | | | | | | | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Na | Ca | Mg | Fe | Al | Cu | Ni | Mn | Zn | Pb | Cd | Co | Mo | V | La | Ce | Ti | As | |
| South Pole | Summer 1974-75 | 3,3 | 0,49 | 0,72 | 0,62 | 0,82 | 29 | - | 13,3 | 33 | - | <15 | 0,49 | - | 1,33 | 0,45 | <4,1 | 100 | 7,1 (W)<br>31 (N) | (Maenhaut and Zoller, 1977) |
| South Pole | Summer 1974-75 | 3,3 | 0,49 | 0,72 | 0,62 | 0,82 | 29 | - | 13,3 | 33 | 27 (W)<br>76 (N) | ≤18 | 0,49 | - | 1,33 | 0,45 | <4,1 | 100 | 7,1 (W)<br>31 (N) | (Maenhaut et al., 1979) |
| South Pole | Summer 1970 - 71 | 7,2 | 0,05 | 1,0 | 0,84 | 0,57 | 36 | - | 10,3 | 30 | 630 | | 0,84 | - | 1,5 | 0,51 | 2,3 | - | - | (Zoller et al., 1974) |
| South Pole | Summer 1971-78 | 5,1±1,7 | 0,55±0,07 | 0,93±0,28 | 0,68±0,25 | 0,83±0,41 | 59±47 | - | 14±6 | 35±5 | - | 49±38 | - | - | 1,6±0,6 | 0,78±0,25 | 2,0±0,2 | 110±10 | 8,4±1,1 | (Cunningham and Zoller, 1981) |
| South Pole | Summer 1979-83 | 8,7±3,2 | 1,0±0,3 | 1,6±0,4 | 0,66±0,28 | 0,73±0,24 | 190±130 | - | 8,9±1,8 | 250±110 | - | 110±60 | 0,77±0,29 | 4,3±1,8 | 1,1±0,4 | 0,56±0,21 | 0,88±0,29 | 290±90 | 11±2 | (Tuncel et al., 1989) |
| South Pole | Dec 1998 - Jan 1999 | 45±5,9 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | (Arimoto et al., 2001) |
| South Pole | Nov 2000 - Jan 2001 | - | - | - | - | - | - | - | - | - | <32 | - | - | - | - | - | - | - | - | (Arimoto et al., 2004) |
| South Pole | Nov 2000 - Jan 2001 | 75,5±4,6 | - | - | 54,4±7,9 | 17,1±5,4 | - | - | - | 4010±1340 | 30±10 | - | - | - | - | - | - | - | - | (Arimoto et al., 2008) |
| South Pole | Nov - Dec 2003 | 9,9±1,5 | - | - | 7,7±1,7 | 3,40±0,66 | - | - | - | 880±260 | 180±40 | - | - | - | - | - | - | - | - | (Arimoto et al., 2008) |
| Concordia station | Jan 2006 - Jan 2007 | 2,4±2,3 summer<br>9,1±9,1 winter | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | (Jourdain et al., 2008) |
| Concordia station | Oct 2004 - Mar 2005 | 5,70±9,04 | 3,36±6,84 | 0,98±1,43 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | (Becagli et al., 2009) |
| Concordia station | Nov 2006 - Dec 2007 | 3,8±6,3 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | (Udisti et al., 2012) |
| Concordia station | 2006 - 15 | 42 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | (Legrand et al., 2017) |
| Dome Fuji | Dec 1997 - Apr 1998 | 10,11 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | (Hara et al., 2004) |

| **Sample site** | **Period** | **Major elements (ng $m^{-3}$)** | | | | | **Trace elements (pg $m^{-3}$)** | | | | | | | | | | | | | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Na | Ca | Mg | Fe | Al | Cu | Ni | Mn | Zn | Pb | Cd | Co | Mo | V | La | Ce | Ti | As | |
| Kohnen station | Feb 2003 - Dec 2005 | 24±25 | 1,3±5,7 | 3,9±4,0 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | (Weller and Wagenbach, 2007) |
| Dome C (background levels) | Dec 2005 – Jan 2006 | 6,4 | 1,5 | 2,0 | 0,12 | 0,71 | 27 | 19 | 2,4 | 59 | 12 | 0,1 | 0,26 | 1,5 | 1,4 | 0,61 | 0,47 | 18 | 0,7 | This study |

(N) Nucleopore filters
(W) Whatman filter

Until now, no data are available dealing with an exhaustive elemental characterization of Dome C aerosol, probably due to the difficulties of both sampling at such extreme meteorological conditions and preserving the uncontaminated nature of the samples. Therefore, the main goal of this study is to determine for the first time in the Antarctic Plateau, at Dome C - Concordia station, the concentration of major and trace elements such as Al, As, Ca, Cd, Ce, Co, Cu, Fe, La, Mg, Mn, Mo, Na Ni, Pb, Ti, V, Zn, by Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS), considering both mass fraction and atmospheric concentration.

The determination of elemental concentration allows us to observe a temporal trend of a great number of atmospheric elements, to identify background levels of chemicals in the aerosol of Dome C, never detected until now. Indeed, the measurements of background aerosol is frequently masked by locally generated particles (Tuncel et al., 1989); consequently, at the same time, it is important to investigate about the local impact generated by the scientific station activities (Kennicutt et al., 2014).

Advanced statistical tools have been applied to data matrix in order to acquire a deep knowledge of the aerosol chemical composition. More in details, firstly, crustal and marine enrichments factors have been calculated to discriminate between natural and anthropogenic elements, then, principal component analysis and hierarchical cluster analysis have been performed to find possible associations and the grade of similarities between elements in the particulate matter and between samples. Finally, as a deeper understanding of the source apportionment of each element and as confirm of the main association between species, positive matrix factorization was applied to data matrix.

This work will open new perspectives in understanding the elemental composition of the Antarctic Plateau aerosol, investigating about element associations coming from either local or remote source, reaching the most isolated area of the Planet. Moreover, this study contributes to the knowledge of the atmospheric global circulation, in the perspective of estimating the climatic and environmental changes expected for the future.

## 2. Experimental part

### 2.1. The site

The sampling activities of the present work were carried out during the 2005-2006 austral summer campaign (from 7 December 2005 to 14 January 2016) at Dome C (Concordia station) (75°06′ S, 123° 21′ E), a site on the East Antarctica continental plateau at an altitude of 3233 m and about 1000 km far from the coastline, so that the area is influenced by long-range transport of Antarctic background aerosol (Udisti et al., 2004). Eight aerosol samples were collected using three PM10 high-volume impactors at two different sites: (i) one, immediately downwind of Concordia station, and (ii) two near the Astrophysic Tent ~800 m upwind of the Station (Figure 1).

The exposure time has been differentiated; at Concordia station and at Astrophysic Tent 1 each sample was collected for ten days, while at Astrophysic Tent 2 the sampling period was extended to twenty days to ensure the trace metals determination. The aerosol concentrations were determined in accordance to Annibaldi et al., (2011) and Truzzi et al., (2005) as extensively exposed in the previous chapter. Each filter was reserved for our work and put into the decontaminated LDPE bottles and stored frozen (–20 °C) until analysis. Six blank filters (“field blanks”) were also collected in the field, for each sampler at both sampling sites, before and after the sampling exposure; they were treated like samples and subtracted to samples concentrations to better evaluate the contributions from handling, exposure and treatment of the filter and to establish baseline elemental concentrations.

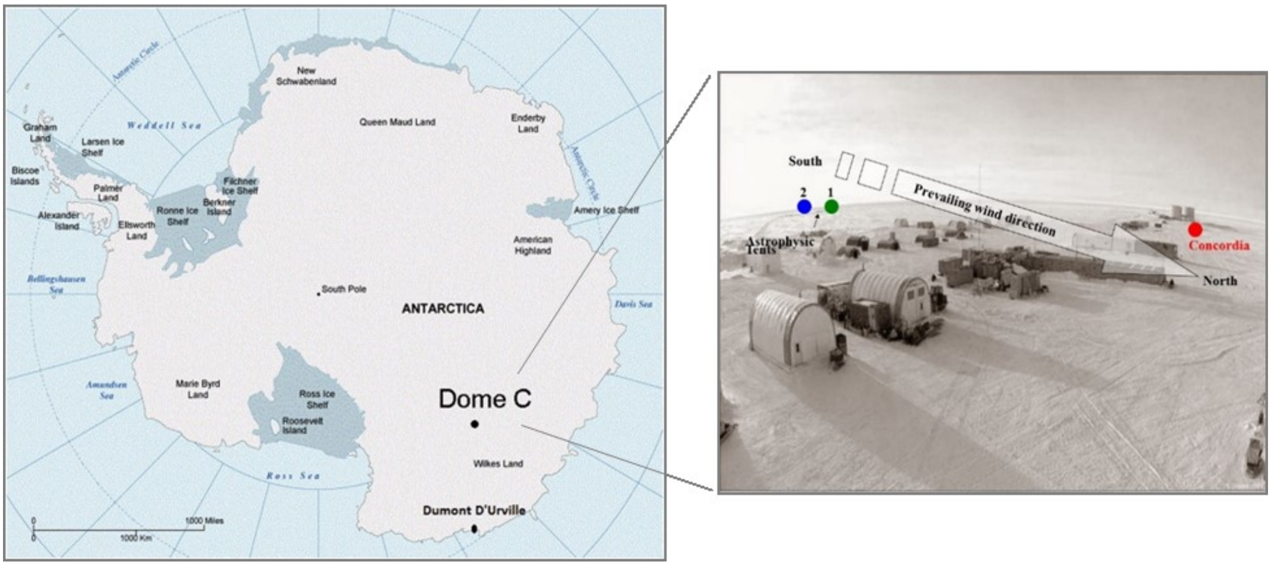


**Figure 1.** Map of Dome C (Concordia station and Astrophysic Tents) in Antarctica showing the sampling sites and the prevailing wind direction related to the sampling period.

Meteorological parameters (air temperature, relative humidity, ambient pressure, wind speed and direction) were continuously registered at time intervals of 1h by the Automatic weather station

(ASW) sited close to the sampling sites of the Concordia station. An average temperature of about -29 °C, a pressure of 656 hPa and a relative humidity of 57% were recorded. During the sampling period the prevailing wind direction was from South, except from December 27 to January 1 when was reversed.

## 2.2 Laboratories, apparatus and general procedures

Sample treatments, analysis and decontamination procedure are carried out in clean room laboratories with areas in Class 5 (ISO 14644-1) (formerly Class 100, US Fed. Std. 209e) under laminar flow, both in Antarctica (Truzzi et al., 2005) and in Italy (Truzzi et al., 2002). The laboratory temperature is set at 20±1 °C during the winter and 23±1 °C during the summer. Clean-room garments, masks, and gloves were worn by the personnel, who strictly followed contamination control procedures during all the most critical treatments and sample analysis phases.

To collect PM10-aerosol samples three teflon-coated (inner and outer), high-volume sampler (model TE-6070V-BL, from Tisch, Village of Cleves, OH, USA) were used. Before aerosol collection, the samplers were calibrated in the field upon installation and checked at the end of the sampling period, and were cleaned inside and outside by repeated washing using ultrapure water (Milli-Q, Millipore, Bedford, MA). Acid-cleaned (Annibaldi et al., 2007) 8×10 inch (20.3×25.4 cm) cellulose filters (Whatman 41, Cat. No. 1441-866, thickness 220 µm, ashes ≤0.007%, pore size 20-25 µm, basis weight 85 g $m^{-2}$), specifically prepared and tested for trace element determinations were used. A technical balance Mettler Toledo PB302 *(*capacity = 310 g; sensitivity = 0,2 g; accuracy = 1 mg; repeatability = 10 mg) was used to bring to volume standard solution under weight control. The micropipettes calibration was carried out using an analytical balance Mettler Toledo AB204 capacity = 210 g; sensitivity = 0,01 g; accuracy = 0,1 mg; repeatability = 0,1 mg).

The Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS, Element, Thermo Finnigan, NJ, USA) was employed to determine Al, As, Ca, Ce, Co, Fe, La, Mg, Mn, Mo, Na, Ni, Ti, V and Zn concentrations. Mass resolution and isotope selection were optimized for each element to ensure resolution of spectral interferences and maximize sensitivity (Malandrino et al., 2016).

Plastic containers used for storage of digested and not-digested sample solutions were of low-density polyethylene material. Variable-volume micropipettes and neutral tips were from Brand (Wertheim, Germany, Transferpette).

### 2.2.1. Reagents and standards

The laboratory detergent solution for decontamination procedures was 1+100 diluted RSB-35 from Backer (Phillipsburg, NJ, USA). For decontamination procedure nitric acid (analytical grade, 65%, Carlo Erba, Cornaredo, Milano, IT), chloridric acid (analytical grade, 37% Carlo Erba, Cornaredo, Milano, IT) were used, while all acids in contact with samples were of ultrapure grade: Ultrapure $HNO_3$ (70%, UpA, Romil, Cambridge, UK), ultrapure HCl (34.5%, UpA, Romil, Cambridge, UK), ultrapure HF (47-51%, UpA, Romil, Cambridge, UK), ultrapure $H_2O_2$ (30%, UpA, Romil, Cambridge, UK, with impurities that, after dilution, were well below the detection limits, ultrapure water was MIlli-Q from Millipore (Bedford, MA, USA). Standard solutions were prepared before every set of analyses by direct dilution of stock solution standards using $HNO_3$ 5% acidified ultrapure water. Table 2 reports the standard solutions for each metal.

**Table 2. Characteristics of standard solutions for the detected elements.**

| **Element** | **Type** | **Concentration ($mg\ l^{-1}$)** |
|---|---|---|
| Al | TraceCERT®solution | 1000 ± 4 |
| As | TraceCERT®solution | 1000 ± 4 |
| Ca | TraceCERT®solution | 10000 ± 20 |
| Co | TraceCERT®solution | 1000 ± 4 |
| Fe | TraceCERT®solution | 1000 ± 4 |
| Mg | TraceCERT®solution | 1001 ± 5 |
| Mn | TraceCERT®solution | 1004 ± 5 |
| Mo | Certipur®NISTsolution | 1000 ± 10 |
| Na | TraceCERT®solution | 1000 ± 4 |
| Ni | TraceCERT®solution | 1000 ± 4 |
| Ti | Titrisol®vial | 1,000 ±0,002 g |
| V | Aldrich®solution | 999± 10 |
| Zn | Aldrich®solution | 999 ± 10 |
| Rare Earth Elements | InorganicVentures CCS-1 | 100,0 ±0,8 |

*Note: "Rare earth" = Sc, Th, U, Ye, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. TraceCERT®= Fluka Analytical, Sigma-Aldrich.*

The Certified Reference Material NIST 1648 urban particulate reference material was from National Institute of Standards and Technology (NIST, 1998).

### 2.2.2. Decontamination procedures

Description of the extensive decontamination procedures generally used in our laboratory for LDPE bottles and all other plastic material are reported in (Annibaldi et al., 2007; Truzzi et al., 2002). Briefly, a careful and prolonged washing procedure was applied to new containers with repeated treatments using, in sequence: tap water, deionised water and Milli-Q water (each washing repeated three times), diluted detergent solution to remove possible coarse residual, 1+10 diluted analytical grade $HNO_3$ in immersion for two weeks, 1+10 diluted superpure HCl in immersion for a week (this step is repeated two times) and finally 1+1000 diluted ultrapure HCl in storage until use.

A similar procedure was used for PFA microwave vessels. For both kinds of containers, the cleaning procedure continue until values comparable to instrumental blanks were reached.

Cellulose filters for aerosol collection were specifically prepared for trace element determinations. The filters were washed and decontaminated carefully with diluted HCl (Merck, Suprapure-grade), rinsed with Milli-Q water, dried under ISO Class 5 laminar flow cabinets and stored in acid-cleaned plastic bags until use in Antarctica.

### *2.2.3. Sample treatments*

The filters weighing measures were achieved, after conditioning, in a climatic cabinet for continuous temperature/humidity monitoring (temperature 15.0±0.5 °C and relative humidity 2,5%±0.5%). After gravimetric measurements, the filters were stored at -20 °C in acid-cleaned (Artaxo et al., 1990) 500 mL low density polyethylene bottles (LDPE) (from Kartell, Italy) and transported frozen to Italy for subsequent analytical determinations of trace elements (Annibaldi et al., 2011).

As reported in the previous chapter a fraction of 1/8 or 1/12 of each filter was cut in the clean room laboratory under laminar flux bench and then subjected to a MW assisted digestion previously set up by (Illuminati et al., 2015). Mineralization was carried out mixing inside a microwave vessel 5 ml of ultrapure $HNO_3$, 1 ml of ultrapure $H_2O_2$ and 1 ml of ultrapure HF to ensure total dissolution of the filter and complete oxidation of the organic matter. Vessels were left cool naturally to room temperature, then they were vented, opened and the solutions were diluted to 100 mL using ultrapure water and in this form subjected to voltammetric analysis of Cd, Pb and Cu, as reported in previous chapter. The same solutions used for Cd, Pb and Cu determination are not suitable to be analysed by SF-ICP-MS because of the presence of dilute HF-acid, damaging for the instrument. For this reason, an aliquot of dilute digested solution was dehydrated naturally under laminar flux bench, and after complete evaporation, it was rehydrated with milli-Q water and 5% of $HNO_3$ acid of ultrapure grade.

The elemental contents were determined using Thermo-Finnigan Element 2 high resolution Sector Field Inductively Couple Plasma-Mass Spectrometry (SF-ICP-MS). Mass resolution and isotope selection were optimized for each element to ensure reduction of spectral interferences and maximize sensitivity. Before each set of analyses, to ensure operative parameters optimization, a monitoring procedure (tuning) was made, considering instrument's sensitivity and stability. To test instrumental resolution a solution of 1 $\mu g\ kg^{-1}$ of Li, In and U are used. Specifically these metals have different masses (about 7, 115 e 238 $g\ mol^{-1}$, respectively), and for this reason the solution is a good indicator of instrumental performance in the complete mass range.

A minimum of triplicate 180 s analyses, when working at low resolution, and quadruplicate when working at medium resolution, was conducted on each sample following a 60 s uptake and stabilization period. After each sample, proceeding the nebulizer system was rinsed for 2 min with 2% sub-boiling $HNO_3$, to eliminate carry-over. Sets of instrumental blanks and calibration verification checks were run at frequent intervals during the sequence (Malandrino et al., 2016). Analysis conditions are reported in Table 3.

**Table 3.** Instrumental and measurement parameters

| | | |
|---|---|---|
| **Plasma and sample introduction** | | |
| Power | 1.30 kW | |
| Plasma gas flow rate | 16.0 l min$^{-1}$ | |
| Auxiliary gas flow rate | 1.25 l min$^{-1}$ | |
| Carrier gas flow rate | 0.95 l min$^{-1}$ | |
| Sample uptake rate | 1 ml min$^{-1}$ | |
| Nebulizer | Concentric glass | |
| Spray Chamber | Scott double-pass | |
| **Measurement** | | |
| Scan mode | Electric | |
| Resolution [a] | 300 [b] | 4000 [c] |
| Points per peak | 10 [b] | 20 [c] |
| Dwell time | 10 ms [b] | 20 ms [c] |
| Scans per replicate | 10 [b] | 6 [c] |
| Replicates | 3 [b] | 3 [c] |

[a] Defined as M/ΔM, where M is the mass of the lightest of two adjacent peaks of similar intensity and ΔM is the mass differences between them (if the valley between the peaks drops to 10% of the peak height) or as the mass divided by the peak width at 5% of the peak height.

[b] low resolution

[c] medium resolution

Process blanks were incorporated into the dissolution and analytical procedure to assess metal contribution from the filters, MW vessels, Milli-Q water and purified acids used in this procedure. All signals for samples were obtained after subtraction of their appropriate process blank values. The relative standard deviation for all elements in each sample was always lower than 5% (Malandrino et al., 2016).

### *2.2.4. Quality control*

To ensure accuracy of data produced in metal determinations Certified Reference Material NIST 1648 urban particulate matter was analysed (NIST 1998). It is subjected to the same treatment of the samples; after weighing a mass of 1.7 ± 0.2 mg it was totally mineralized by microwave digestion it was dehydrated naturally under laminar flux bench, and after complete evaporation, it was rehydrated with milli-Q water and 5% of $HNO_3$ acid of ultrapure grade and analysed by SF-ICP-MS technique. Results, reported in Table 4, show a good accuracy.

**Table 4.** Accuracy tests on the NIST 1648 (NIST 1998) certified reference material for atmospheric particulate matter.

| | NIST 1648, metal concentrations | | | | | | |
|---|---|---|---|---|---|---|---|
| | % | | | mg kg$^{-1}$ | | | |
| | Al | Fe | Zn | As | Ni | Mn | V |
| Experimental values | 3,15 | 3,78 | 0,448 | 104 | 88 | 741 | 81 |
| Certified values | 3,42 | 3,91 | 0,476 | 115 | 82 | 686 | 127 |
| Δ% | -8% | -3% | -6% | -10% | 7% | 8% | -36% |

## 2.3 Numerical tools for data interpretation

### 2.3.1. Enrichment factors

Enrichment factors (EFs) are usually employed for a first interpretation of sources contributing to aerosol composition, giving a qualitative information about the origin of each element. They are calculated as a ratio between the concentration of the element in the sample and the concentration of the same element in the potential source (i.e. either crust or seawater). Before calculating the ratio, each concentration is normalized to the one of a reference element, usually considered as a marker of the source (Al for upper continental crust, and Na for seawater). The concentration of each element in upper crust and seawater have been fixed as reported in Wedepohl (1995) and Turekian (1968), respectively. EFs were calculated according to the following equations:

Equation 2.1

$$EF_{crust} = \frac{(X/Al)_{sample}}{(X/Al)_{crust}}$$

Equation 2.2

$$EF_{seawater} = \frac{(X/Na)_{sample}}{(X/Na)_{seawater}}$$

where X refers to the concentration of element of interest.

Several metals like Al, Fe, Mn, Sr and Ti have been used as crustal reference elements (Basha et al., 2010; Dai et al., 2015; Dongarrà et al., 2007; Yongming et al., 2006); we chose Al, since soil is considered to be the major source of Al in the aerosol (Wedepohl, 1995); and according to other authors who calculated EFs in Antarctica (Bazzano et al., 2015b; Dick, 1991). As concerns the marine marker, Na was chosen as reference element, because of its relevant abundance in seawater.

Indeed, as reported by Zoller et al., (1974), 98% of atmospheric sodium is attributable to sea spray, so this element has been chosen as marine marker.

### 2.3.2 Chemometric tools

The number of existing source apportionment techniques is relatively large, and it includes methods such as principal component analysis (PCA) (Thurston and Spengler, 1985), hierarchical cluster analysis (HCA) (Bridges, 1966), positive matrix factorization (PMF) (Paatero and Tapper, 1994), back-trajectory analysis (Rolph et al., 2017; Stein et al., 2015), and correlation matrix (Massart et al., 1997). These techniques require different degrees of knowledge about the number of sources at a given site, as well as of the source profiles ( Bruinen de Bruin et al., 2006; Schauer et al., 2006).

PCA and PMF are the most commonly used models requiring relatively little quantitative knowledge of sources and emission profiles, even though they do require initial qualitative knowledge of the sources present in the study area (Viana et al., 2008).

PCA is a technique that reduces the number of dimensions, summarising a set of multivariate data in few linear combinations of the variables (called principal components), without a significant loss of information (Otto, 1999). Results of PCA can be plotted to simplify the interpretation of the positive and negative correlations among variables (in this case the elements determined in aerosol samples), and the valuation of the behaviour of objects (aerosol samples) (Padoan et al., 2016).

Data elaboration was performed with UNISTAT 6.5.

HCA is an effective statistical method for the study of atmospheric aerosol composition, and can be used to confirm the groups of variables and samples obtained with PCA. The method groups data by similarity: objects with the maximum of similarity are arranged into a single group, or cluster, and the calculation is iteratively repeated. Data elaboration was performed with UNISTAT 6.5 setting the Euclidean distance and Ward's method.

Correlation coefficients measures the degree of association between two sets of data. They take on values ranging from –1 and +1 meaning complete negative or positive correlation respectively. A zero value means that the two data sets have no association. In this case, they are said to be uncorrelated. We calculate correlation matrix taking into account elemental atmospheric concentrations, using UNISTAT 6.5.

Positive matrix factorization is a multivariate factor analysis tool that operate decomposing a data matrix in two matrices following the equation:

Equation 2. 3

$$X = GF + E$$

where G represents a factor contribution, F a factor profile, and E the residual matrix. This model requires standard deviation matrix σ, creating a linkage with physical reality (Paatero and Tapper, 1994).

The mathematical algorithm has the constrain of positive factor loadings and scores, creating a more physically realistic solution (Reff et al., 2007); indeed sources do not emit negative amounts of elements in the atmosphere (Paatero and Tapper, 1994).

The model solves the previous equation minimizing the object function Q expressed as:

Equation 2.4

$$Q(E) = \sum_{i=1}^{m}\sum_{j=1}^{n}\frac{E_{ij}}{\sigma_{ij}}^{2}$$

The scaled model allows to optimize the result weighing the variables considering their importance.

To understand if the model correctly fits to the sampling data we have simulated different solutions, as reported in (Chen et al., 2017), firstly varying the number of factors from four to three, considering Q value as an important information about the quality of the fit (Equation 2.4). We have computed 20 runs and Q values were similar in each run. To choose the correct number of factor we have plotted Q/Qexp against the number of factors and we have chosen the point where the slope of the curve shows a marked change. Subsequently, we have considered that the best fitness for the model implicates the setting of species Mg, Al, Mn, Ni, Zn, As, Ce, Cd, Pb and Cu as "Weak" variables, when signal to noise ratio (S/N) was: $0.2<S/N<2$ (Paatero and Hopke, 2003). As the second step, we have investigated a possible rotational degree, varying the FPEAK parameter, but in the final solution, no rotation was applied because Q was too higher than Qexp. Another aspect that we have considered is the scaled residual analysis, as parameter to detect data anomalies, such as outliers (Juntto and Paatero, 1994). Data follow a normal distribution and the scaled residual frequency plot shows a random distribution with the totality of values located in the range -3, +3 (Juntto and Paatero, 1994).

The data elaboration was carried out using the model developed by Environmental Protection Agency (EPA), US, PMF Version 5.0.14.

### 2.3.3 Back trajectory analysis

In order to characterize the transport pathways of air masses arriving at Dome C, 5 days backward air trajectories were computed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) transport and dispersion model assessed via NOAA Air Resources Laboratory READY (Real-time Environmental Applications and Display sYstem), site http://www.arl.noaa.gov/ready/hysplit4.html, (Rolph et al., 2017; Stein et al., 2015). The meteorological data used for the calculations were the NCEP/GDAS 1 degree data. The vertical motion calculation method was selected to "Model vertical velocity". The back trajectories were calculated with 12h interval time for three arrival heights; 100 m, 500 m and 1000 m above ground level (a.g.l.) (Contini et al., 2010; Silvia Illuminati et al., 2016; Virkkula and Teinil, 2006) to minimize ground friction and mixing air processes close to the soil. We have chosen at least three level of trajectories to reduce error connected to a single observation (Abdalmogith and Harrison, 2005) and to simulate the air mass history, since the air particles arriving at observation site could have followed different trajectories (Fleming et al., 2012) staying inside Antarctic boundary layer (Argentini et al., 2005).

The choice of 5 days was made due to the mean lifetime expected for aerosols in this region (Shaw, 1988) with respect to mid-latitudes. The residence time of aerosol is usually less than a week, depending on aerosol properties and meteorological conditions (Budhavant et al., 2015; Chance et al., 2015; Harris, 1992; Prospero et al., 1983).

WARNING: *Data and information on local meteorology were obtained from Operational Meterological Infrastructure of ENEA-UTA (www.enea.uta.it) through the "Meteo-Climatological Observatory" of PNRA (www.climanantartide.it).*

## 3. Results and discussion

Figures 2-16 show the temporal trend of Al, As, Ca, Cd, Ce, Co, Cu, Fe, La, Mg, Mn, Mo, Na Ni, Pb, Ti, V, Zn collected during the 2005-2006 Antarctic summer campaign The data are reported in Table S1 and Table S2 of Supplementary Material. The data are discussed below, grouping elements showing a similar temporal trend and/or characterized by the same certain origin, as confirmed by literature

Data in Figures 2-16 are expressed, in terms of both mass fractions and atmospheric concentrations. The first one represents the amount of metal present per unit mass of aerosol, while the second one is the amount of metal present per unit volume of air in particulate form. Thus, we can better understand the aerosol chemical composition and its elemental enrichment related to the total amount of aerosol in the air.

Figures 2-6 represent the major elements: Na, Ca, Mg, Fe and Al.

Concerning Na, Ca and Mg, these elements have generally been connected to a common marine origin (Bazzano et al., 2015b; Becagli et al., 2009; Udisti et al., 2004). Indeed, they show the same tendency during the sampling period with relatively high values in the first part of the campaign, especially at Astrophysic Tent 2, while lower levels of each element are recorded at the end of the sampling period.

The concentrations of Na, Ca and Mg seem higher than literature data, as reported in Table 1; only the lowest levels, considered as possible background for Dome C, are comparable to literature data concerning Central Antarctica. The interpretation of such profiles can be supported by the back-trajectories elaborations reported in Figure S5, n: indeed, it seems that the presence of Na Ca and Mg in the aerosol is influenced by air flows coming from remote sites. In particular, when air masses came mainly from coastal areas passing through Southern Ocean, the highest concentrations are observed: this masses probably carried out sea spray particles rich in Na, Ca and Mg. On the other hand, during the third sampling period, the study of air masses back-trajectories suggests that only a little contribution came from the sea, with a consequent lower concentration of such elements in the aerosol.

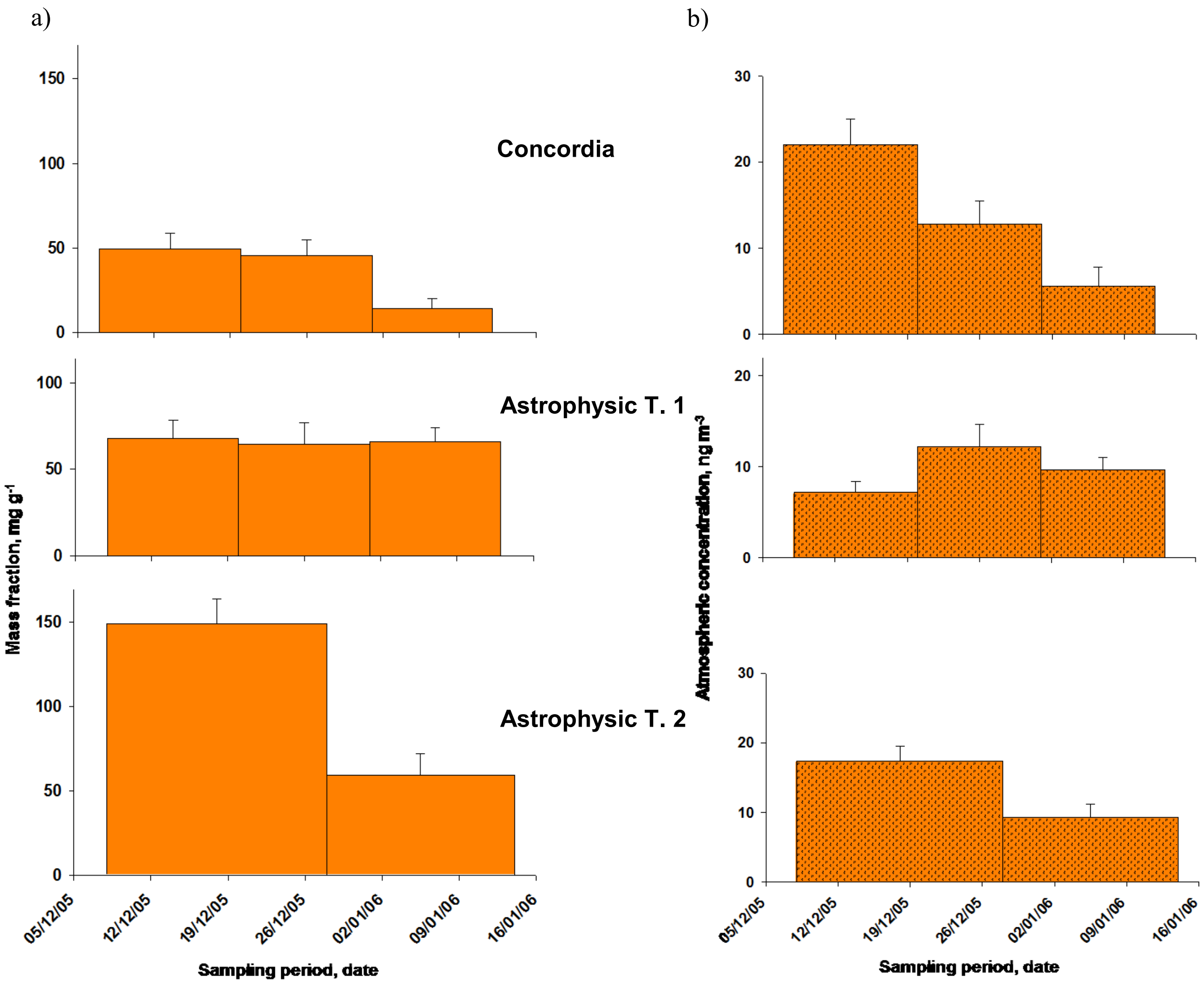


**Figure 2**. Seasonal trends of a) Na mass fraction and b) Na atmospheric concentration at Dome C during the 2005-06 austral summer.

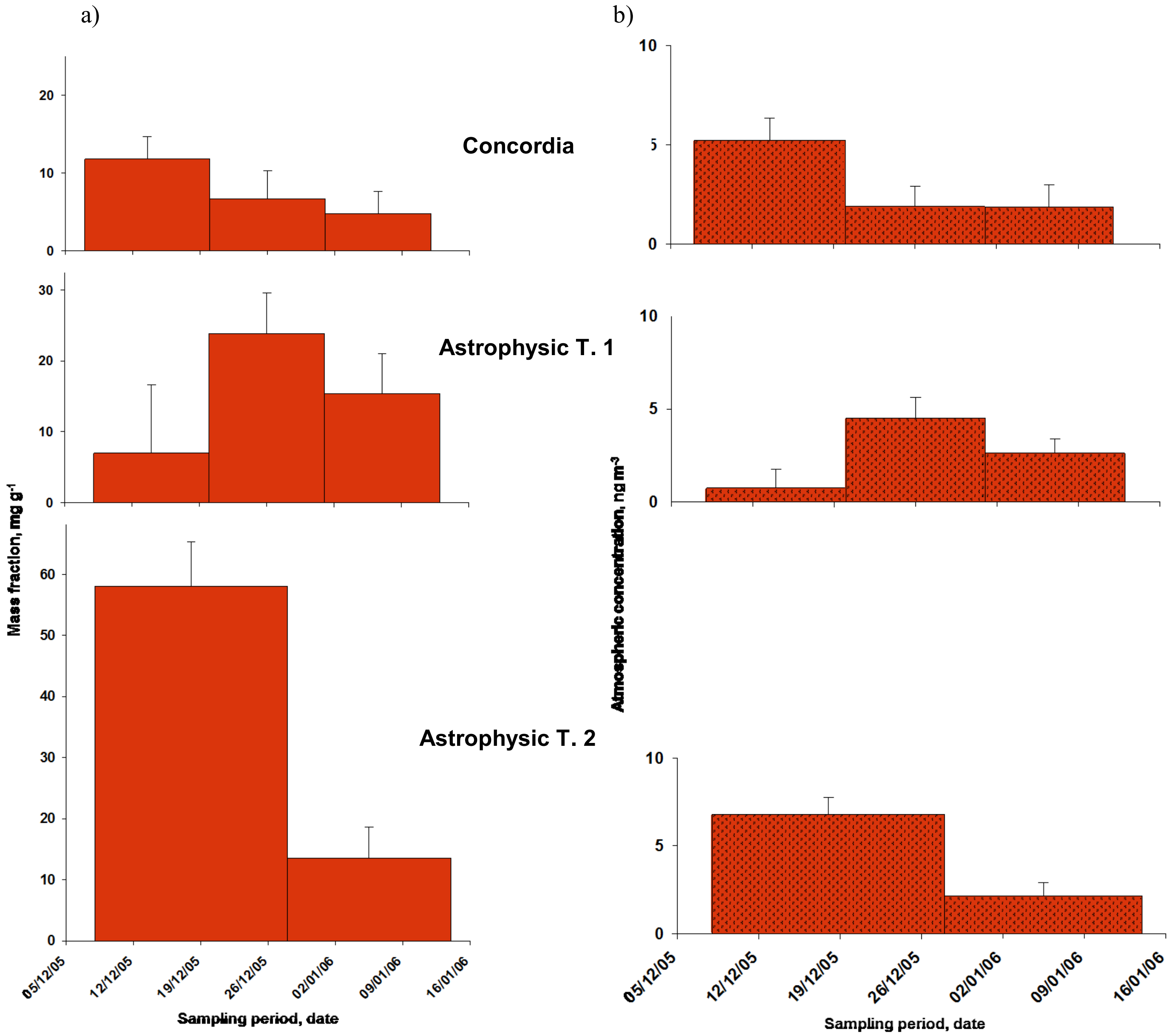


**Figure 3.** Seasonal trends of a) Ca mass fraction and b) Ca atmospheric concentration at Dome C during the 2005-06 austral summer.

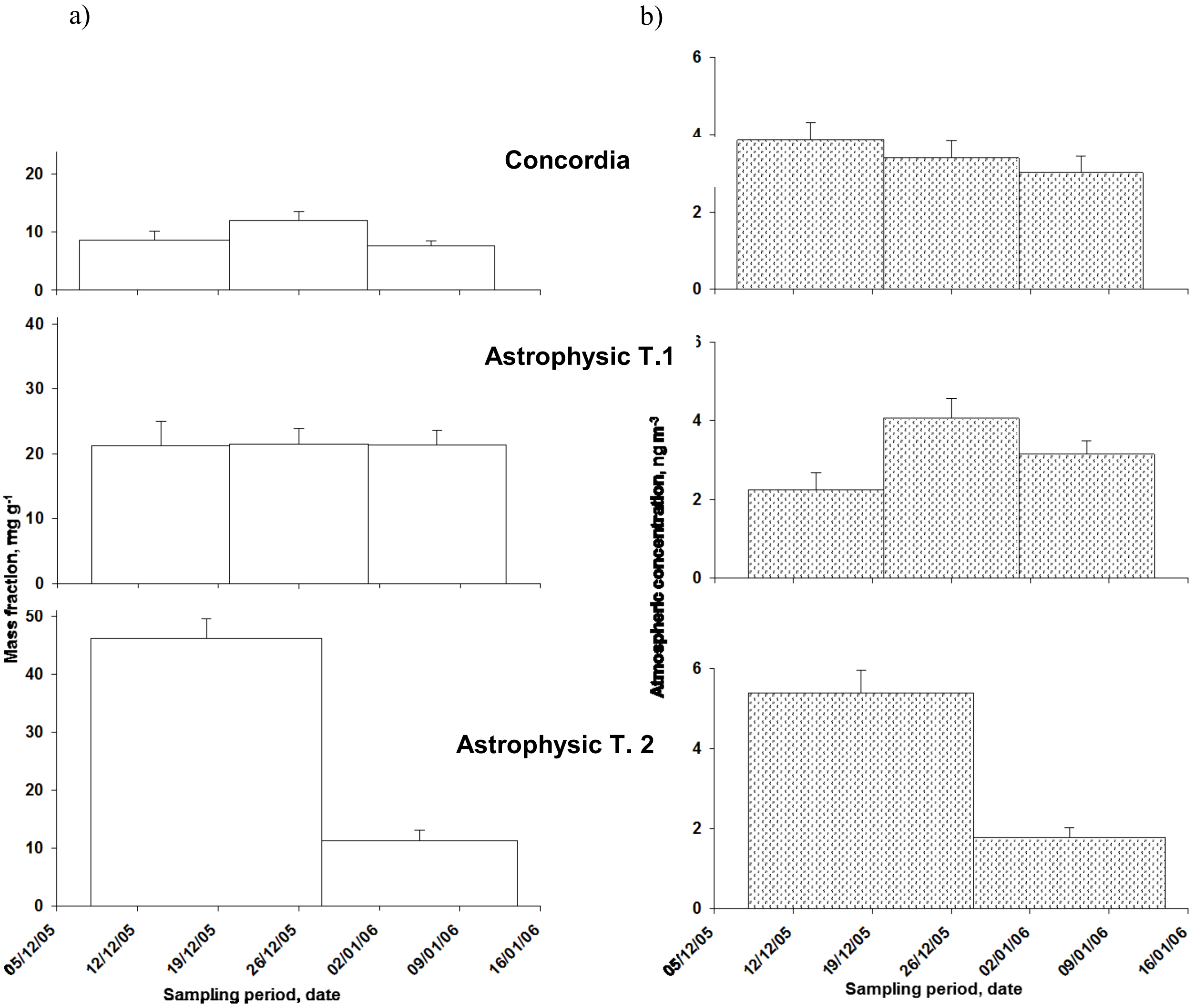


**Figure 4.** Seasonal trends of a) Mg mass fraction and b) Mg atmospheric concentration at Dome C during the 2005-06 austral summer.

Concerning Fe and Al (Figures 5-6), these two metals have a similar general trend: the highest values are observed for the first sample in all sites, and relatively low values are determined in the other samples. Such decrease of metal concentrations in both sites, suggests that wind direction and the exposure of the sampler either upwind or downwind have little effect on the metal amount in particulate matter.

The concentrations of both Fe and Al are enriched considering literature data concerning inland sites, (see Table 1) e.g. South Pole in seventies (Maenhaut et al., 1979; Maenhaut and Zoller, 1977; Zoller et al., 1974), while they are comparable to concentrations related to coastal sites, e.g. Coastal East Antarctica (Xu and Gao, 2014), Terra Nova Bay (Toscano et al., 2005; Bazzano et al., 2015b), Neumayer station (Weller et al., 2008) and Gipps Ice Rice (Dick, 1991). Indeed, Coastal East Antarctica, is rich in Fe mineral occurrences, as shown in Figure S2 on Supplementary Material. From the analysis of air masses back-trajectories, we observe that, in the pathways calculated for 9, 10 and 17 December (Figures S4 c,d,m), air blew from North, near Queen Mary Coast, the most extensive iron deposit in Antarctica: it seems plausible that Fe particles are transported toward Dome C. As concerns Al, it is usually not associated to Fe in rock and ores (U.S. Geological Survey, 19SS); furthermore, Antarctica does not have mineral occurrences rich in Al. On the other hand, Al is usually chosen as crustal marker in the determination of enrichment factor (Bazzano et al., 2015b; Toscano et al., 2005; Zoller et al., 1974), due to its general distribution in the upper Earth crust and in crustal dust, affecting primarily the aerosol metal composition. Probably, multiple emissions sources for Al in Dome C atmosphere can be hypothesized, so further advanced statistical analysis to validate this hypothesis is necessary.

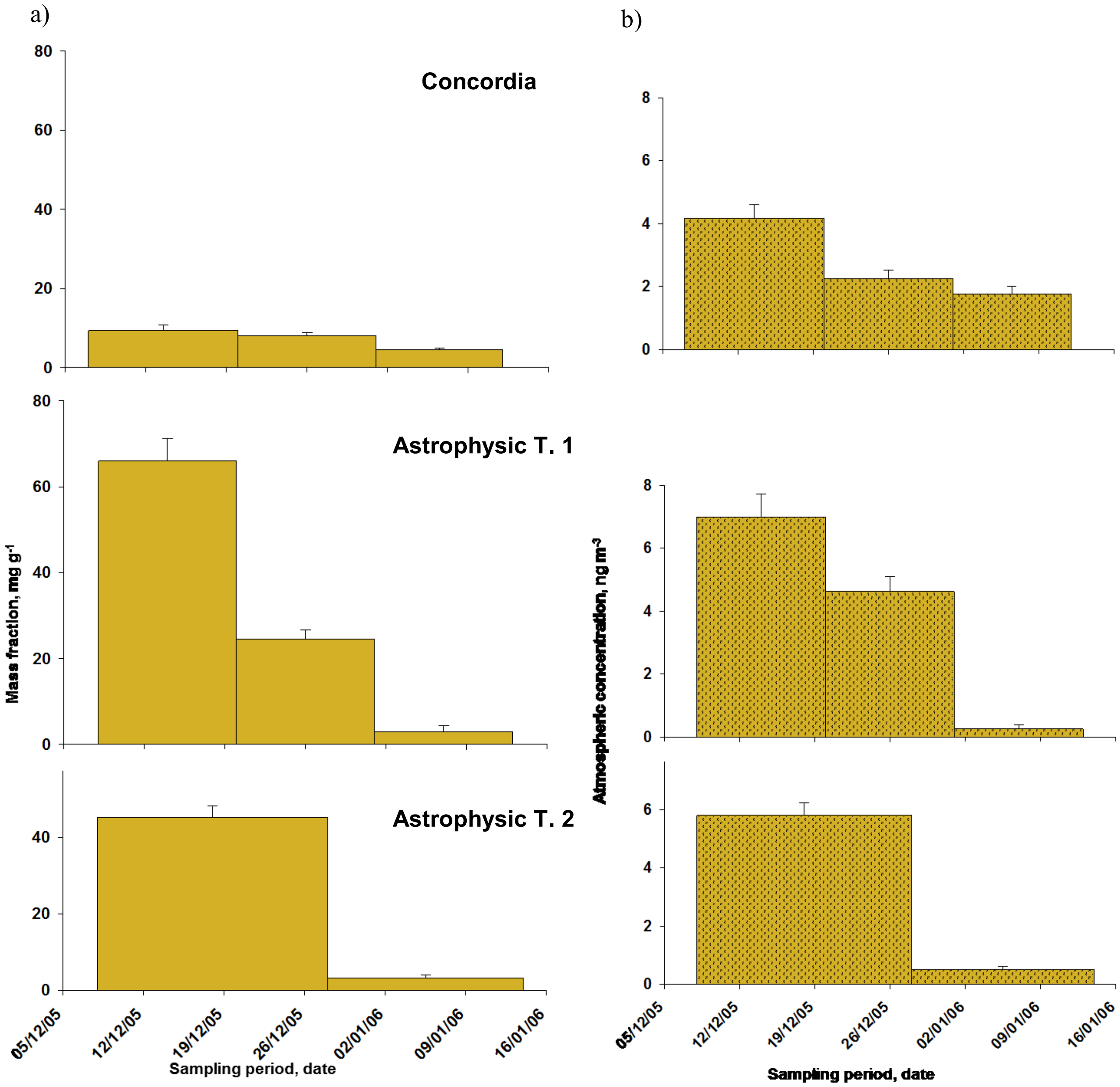


**Figure 5.** Seasonal trends of a) Fe mass fraction and b) Fe atmospheric concentration at Dome C during the 2005-06 austral summer.

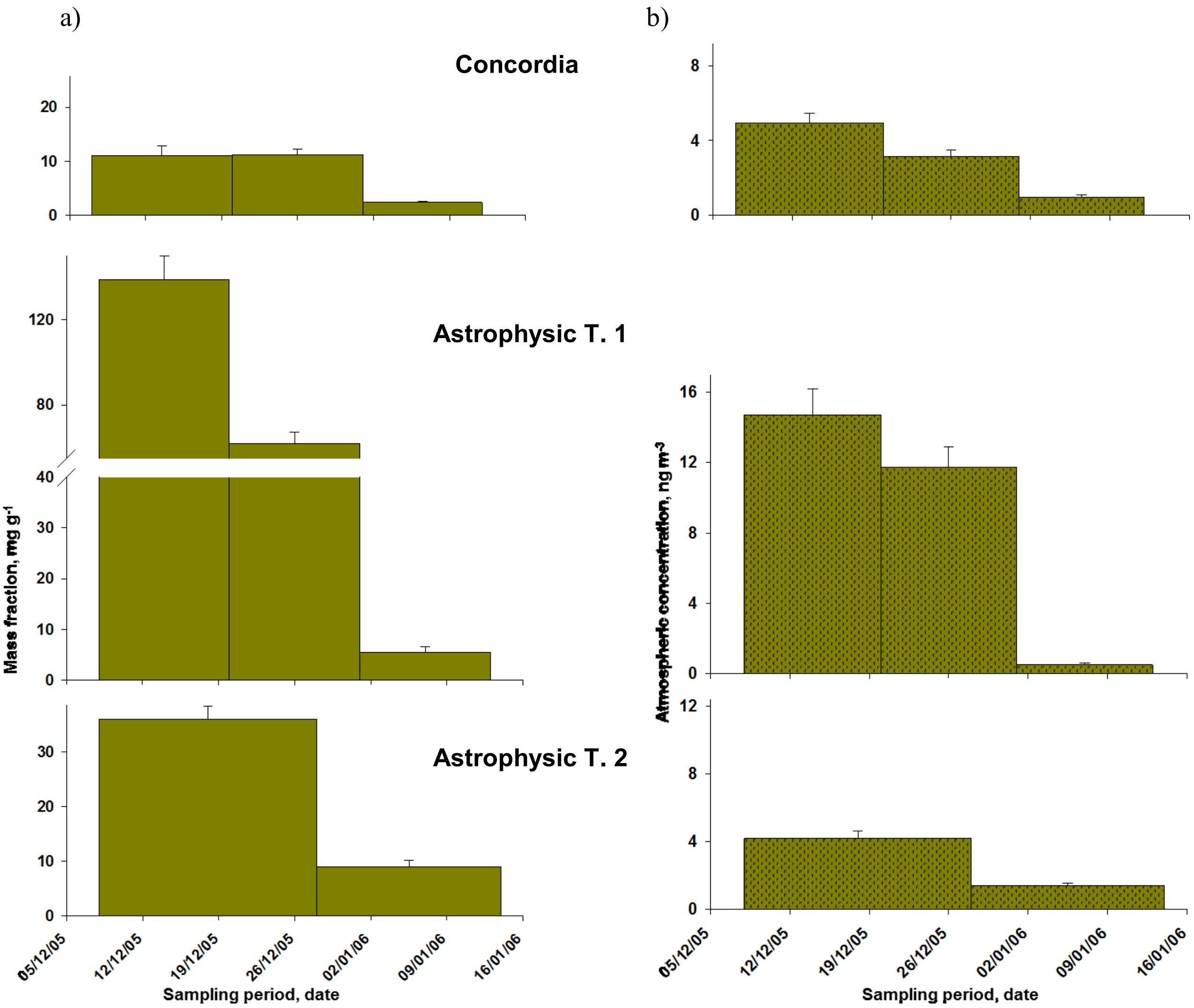


**Figure 6.** Seasonal trends of a) Al mass fraction and b) Al atmospheric concentration at Dome C during the 2005-06 austral summer.

Figures 7-16 show the summer trend of trace elements: Mn, Co, Ni, Zn, As, Mo, Ti, La Ce and V.

Mn and Co are discussed together because they are usually considered natural metals, originated by crustal dust (Bazzano et al., 2015b; Malandrino et al., 2016). These two metals are associated in mineral resources; in Antarctica, manganese and cobalt are quite rare, but some occurrences have been discovered at Dufek Massif, in the proximity of Transantarctic Mountains and at Adélie Coast (see Fig. S2). Mn and Co have general high values during the first sampling period in each site, with a progressive decrease in the second and the third sample, independently to the sampling site. This trend let us to hypothesize that wind direction in the site does not influence aerosol metal concentration; on the other hand, the analysis of air masses back-trajectories, can suggest a hypothesis on the source: indeed, during the period 29 December – 3 January (Figures S5 i-n, S6 a,b) air masses came from Adélie Coast, explaining the amount of Mn and Co in aerosol samples. Moreover, the atmospheric concentrations of these metals seem enriched in comparison with literature data reported in Table 1, in particular at the beginning of the campaign. This let us to suppose a possible additional source, connected to the beginning of the expedition, that contribute to such high elemental concentrations. The further statistical elaborations will clarify Mn and Co emission sources.

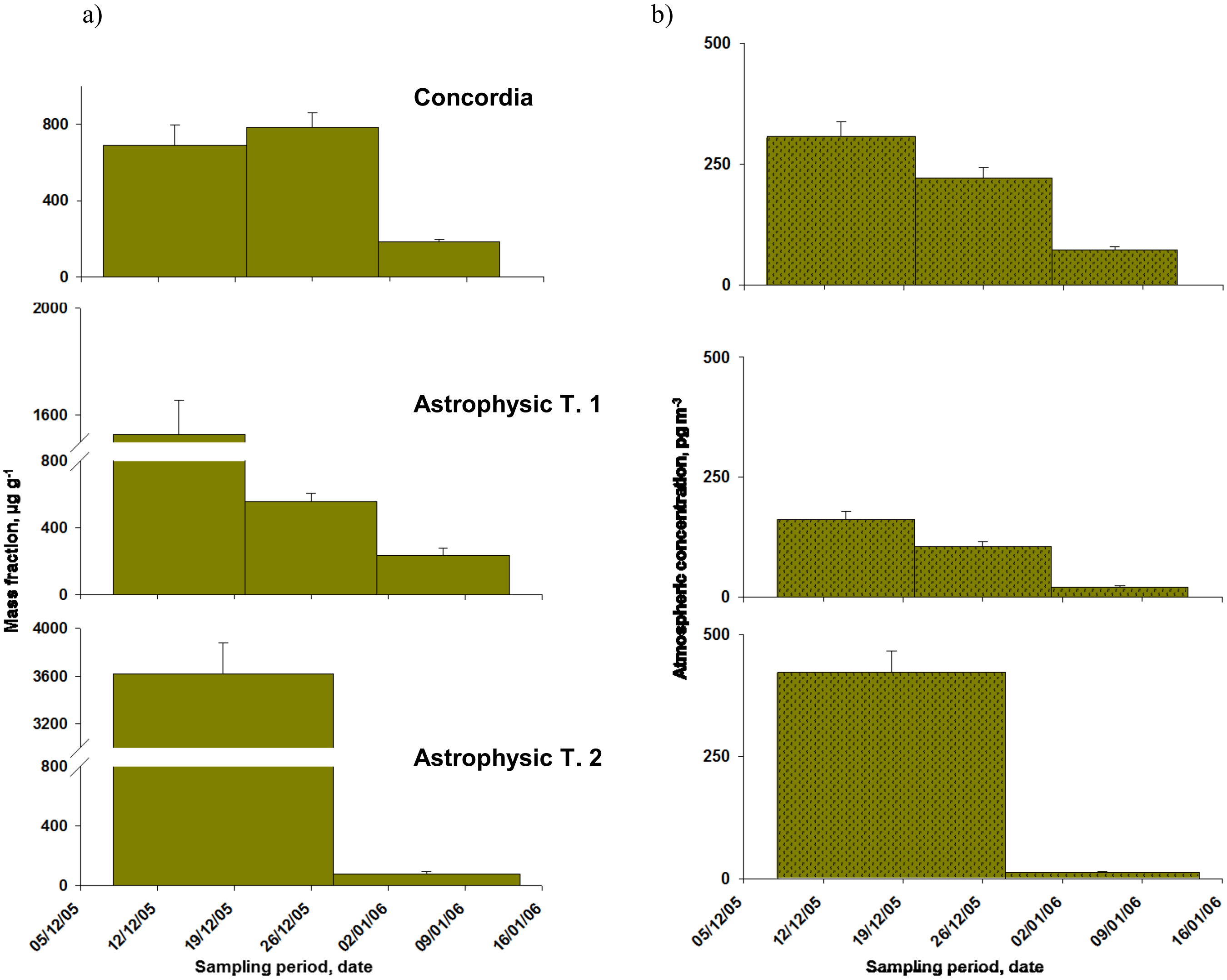


**Figure 7.** Seasonal trends of a) Mn mass fraction and b) Mn atmospheric concentration at Dome C during the 2005-06 austral summer.

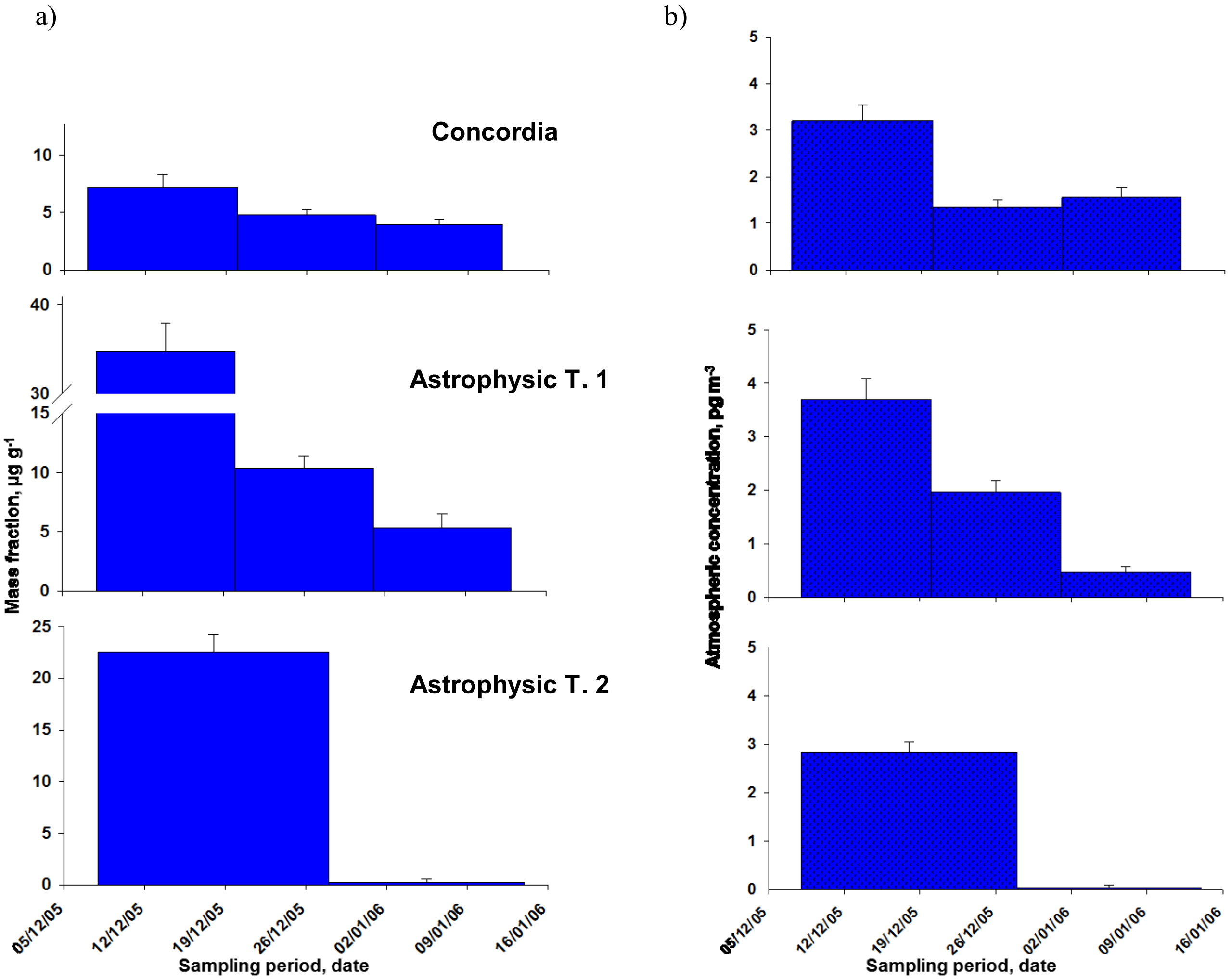


**Figure 8.** Seasonal trends of a) Co mass fraction and b) Co atmospheric concentration at Dome C during the 2005-06 austral summer.

Concerning Ni, this metal has a general decrease during the seasonal evolution: the highest values are generally observed during the first sampling period. A different trend is observed for nickel atmospheric concentration at the Astrophyisic Tent 1. Indeed, at the beginning of the season, Ni is about 300 pg m$^{-3}$ and during the second sampling period atmospheric concentration, it increases at about 400 pg m$^{-3}$ and then it decreases at 60 pg m$^{-3}$ during the third sampling. This evolution is similar to the trend observed for Cd and Pb presented in Chapter 1 and it may be attributed to the effect of wind direction: as reported in Materials and Method section, a change of the wind direction was observed during the second sampling period, and, as a consequence, the Astrophysic tents were impacted by the base. Consequently, nickel profile is very likely connected to the general pollution caused by the scientific expedition (e.g. intense handling of loads including aircraft arrivals/departures). Probably, there is also a natural source contribution: indeed during the period from 29 December to 1 January, the analysis of air masses back-trajectories shows a component coming from Adélie Coast, where Ni occurrences are present associated to Co (Fig. S5 i-n). A statistical support will be useful to highlight also the natural component of Ni present in the aerosol of Dome C.

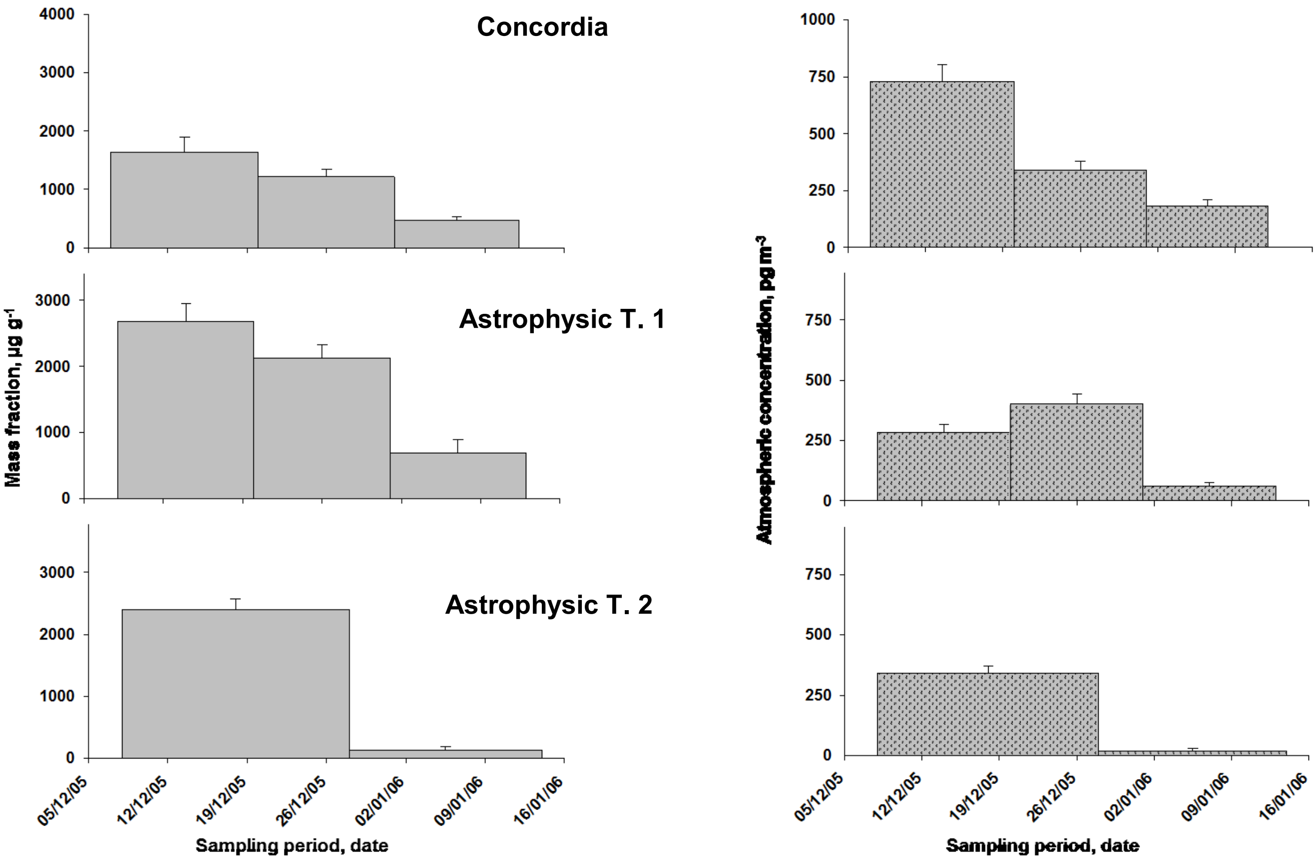

a)
b)

**Figure 9.** Seasonal trends of a) Ni mass fraction and b) Ni atmospheric concentration at Dome C during the 2005-06 austral summer.

Zn (Figure 10) has a mean atmospheric concentration higher than literature data, as reported in Table 1; probably only the final samples of Astrophysic Tent 1 and 2 represent the background level of Zn at Dome C (mean value 60 pg m$^{-3}$, see Table 1 in the Introduction section). This period is characterized by air masses coming from South and South-West (see Figures S6 l-o), carrying clean air from the plateau, an extended area totally covered by ice, depleted of metals. The other samples have a metal concentration quite constant, independently from the site. This probably represents a general pollution of the area, extended not only near the station but also in the supposed clean area of the Astrophysic Tents.

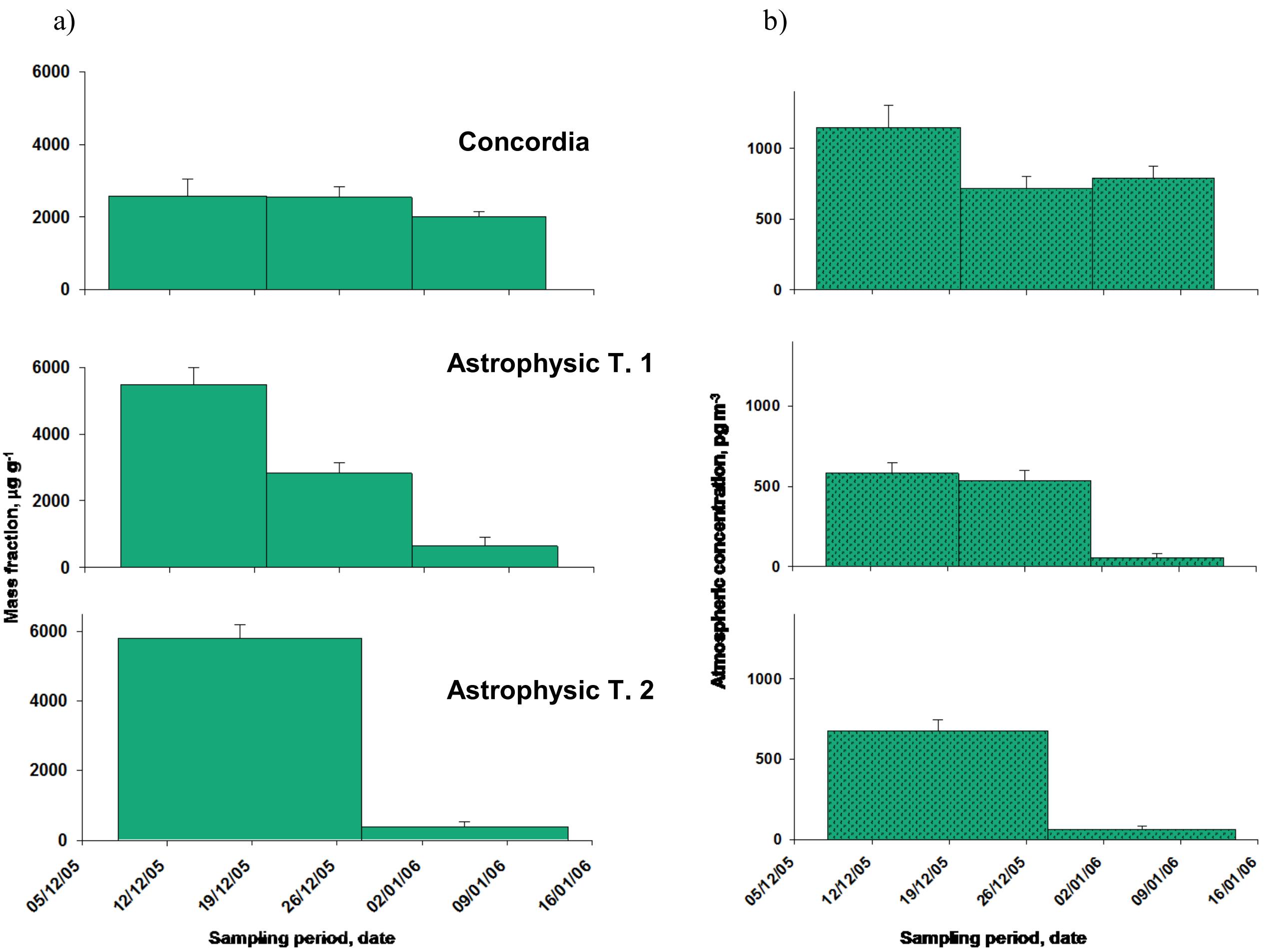


**Figure 10.** Seasonal trends of a) Zn mass fraction and b) Zn atmospheric concentration at Dome C during the 2005-06 austral summer.

The average As atmospheric concentration (Figure 11) has comparable values with literature data (Maenhaut et al., 1979; Maenhaut and Zoller, 1977). As is usually associated with anthropic activities, in particular in relationship with fossil fuel combustion processes (Malandrino et al., 2016), especially in highly anthropized areas. It shows a temporal decrease during the entire sampling period, probably connected with the general pollution in the area, more intense at the beginning of the expedition and in progressive reduction during the seasonal evolution.

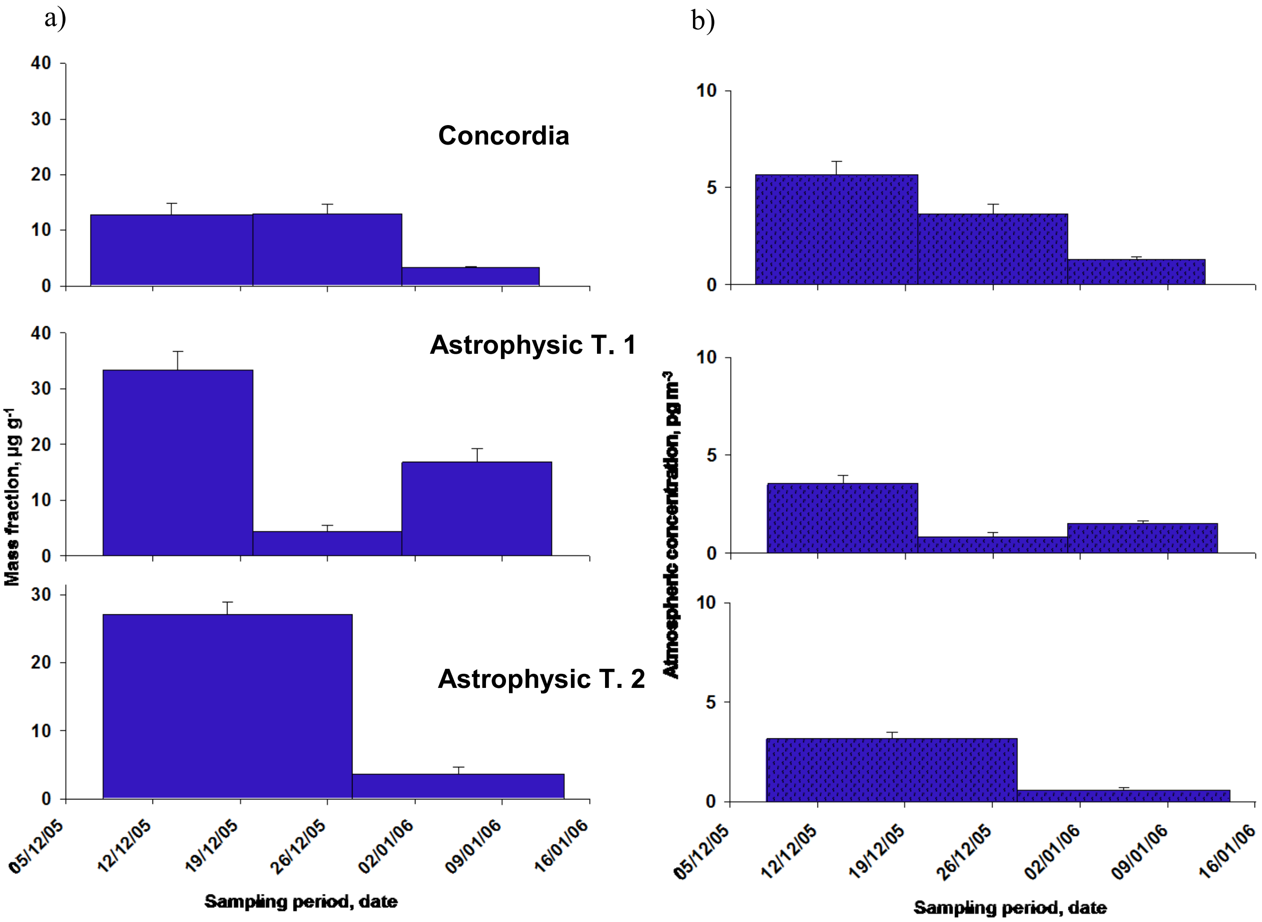


**Figure 11.** Seasonal trends of a) As mass fraction and b) As atmospheric concentration at Dome C during the 2005-06 austral summer.

Figure 12 shows the temporal trend of Mo. The atmospheric concentrations are higher than literature data (Bazzano et al., 2015b), except background values determined at Astrophysic Tents during the final period of the expedition (1,5 pg m$^{-3}$, as reported in Table 1). For this reason, we can suppose that the aerosol of Dome C is generally enriched of this metal. The seasonal evolution reports the highest concentration at the beginning of the sampling period independently from the site, followed by a gradual decrease, more evident at Astrophysic Tents than at Concordia. As previously observed for Co and Ni, this seasonal evolution might be influenced by air masses back-trajectories. In particular, during the first sampling period, air masses came mainly from South, but brief inversion of their direction are reported the 9th, 10th and 17th December (see Figures S4 c,d,m), when they came from North, passing through Queen Mary Coast: this area is characterised by porphyry copper deposits, containing also molybdenum. During the second sampling period, from the 29th of December to the 1st January, air masses came from Adélie Coast (Figure S5 i-n), a site rich in porphyritic intrusions of copper and molybdenum. Both in natural and anthropic source Mo is associated with Cu, as reported in Figure S2 and by Bazzano et al., (2015b) and Malandrino et al., (2016). Also in this case the statistical analysis could support in the source apportionment of molybdenum.

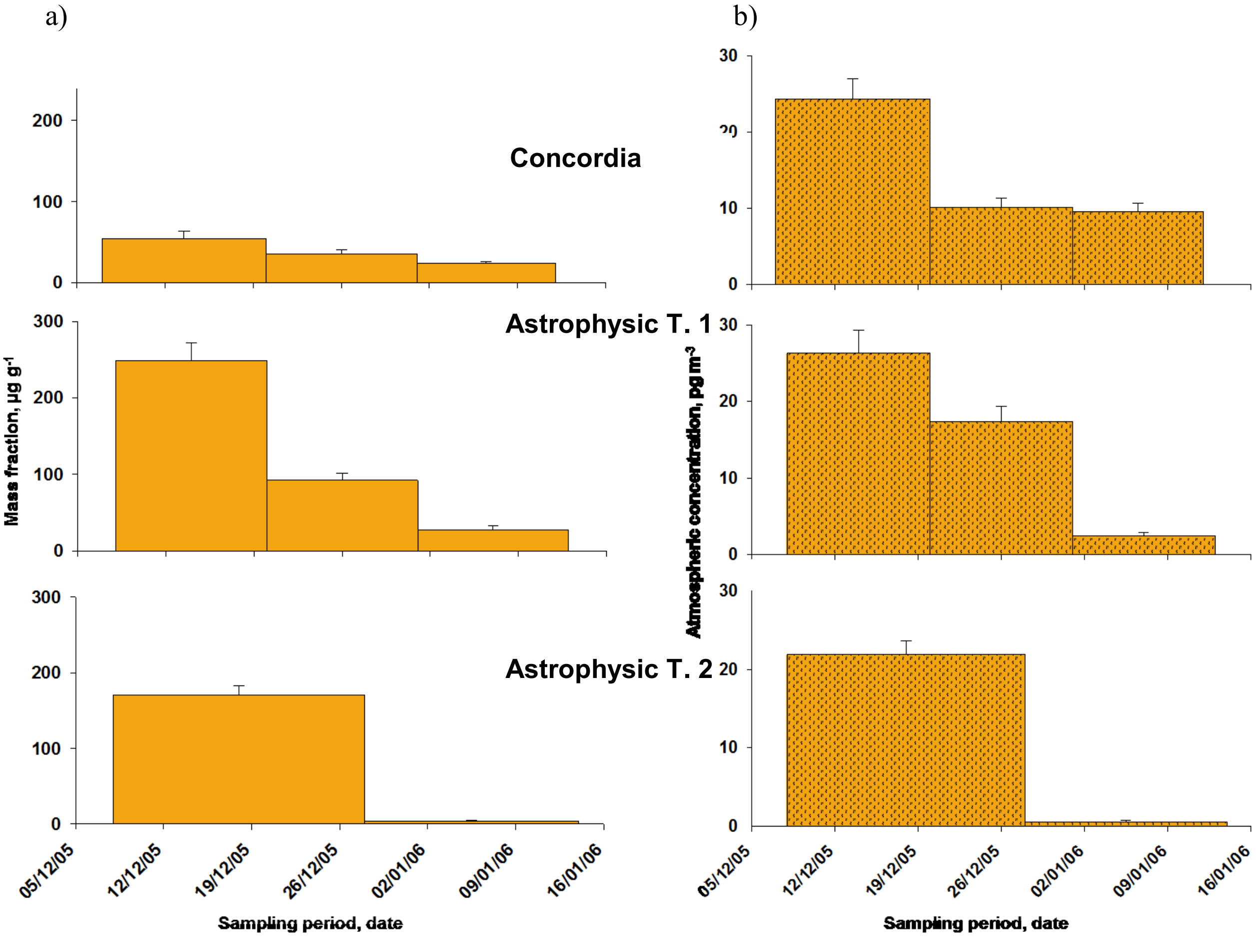


**Figure 12.** Seasonal trends of a) Mo mass fraction and b) Mo atmospheric concentration at Dome C during the 2005-06 austral summer.

As shown in Figure 13, Ti has a different trend than other metals, while it has a similar temporal evolution of Cd, as reported in Chapter 1. The highest values are observed at the beginning of the season in each site, more elevated at Astrophysic Tents than at Concordia station. When the wind reversed from the prevailing direction respect to the station (i.e. from North respect to the usual direction from South), metal concentrations decrease at Concordia and increase at Astrophysic Tent 1. The effect of the wind is visible only at Concordia station where, during the third sampling period, metal concentrations increase again, while at Astrophysic Tent concentrations decrease at hypotesized background level lower than 20 pg m$^{-3}$, as reported in Table 1. Tipically, in the literature Ti is considered a possible geogenic element (Bazzano et al., 2015b; Malandrino et al., 2016; Marino et al., 2004): the statistical elaboration of data will support this hypothesis.

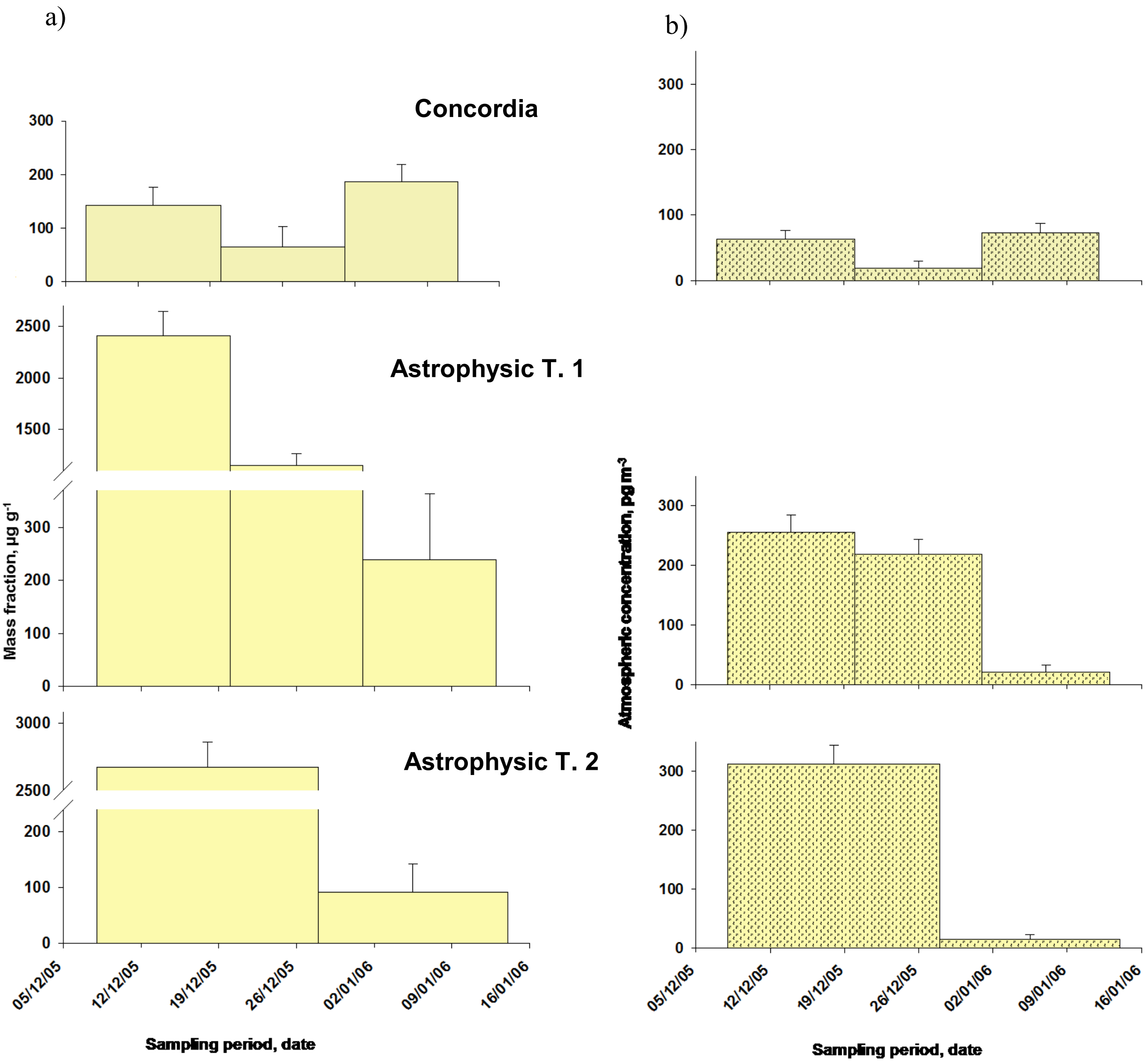


**Figure 13.** Seasonal trends of a) Ti mass fraction and b) Ti atmospheric concentration at Dome C during the 2005-06 austral summer.

Figure 14 reports the summer evolution of La. The highest metal concentrations have been determined during the first sampling, more elevated at Astrophysic Tents, while at Concordia station no relevant variations in metal content are observed. During the second and the third part of the season, concentrations tend to decrease at values comparable to literature data (Maenhaut et al., 1979; Maenhaut and Zoller, 1977; Weller et al., 2008; Zoller et al., 1974). The effect of wind is not evident; therefore, the concentrations seems to be more influenced by air masses back trajectories. Usually, considering literature data, lanthanum has an origin attributable to mineral dust (Weller et al., 2008) but we have scarse information about a certain emission source. So, to determine definite source of La, the applying of statistical tools to data matrix is necessary.

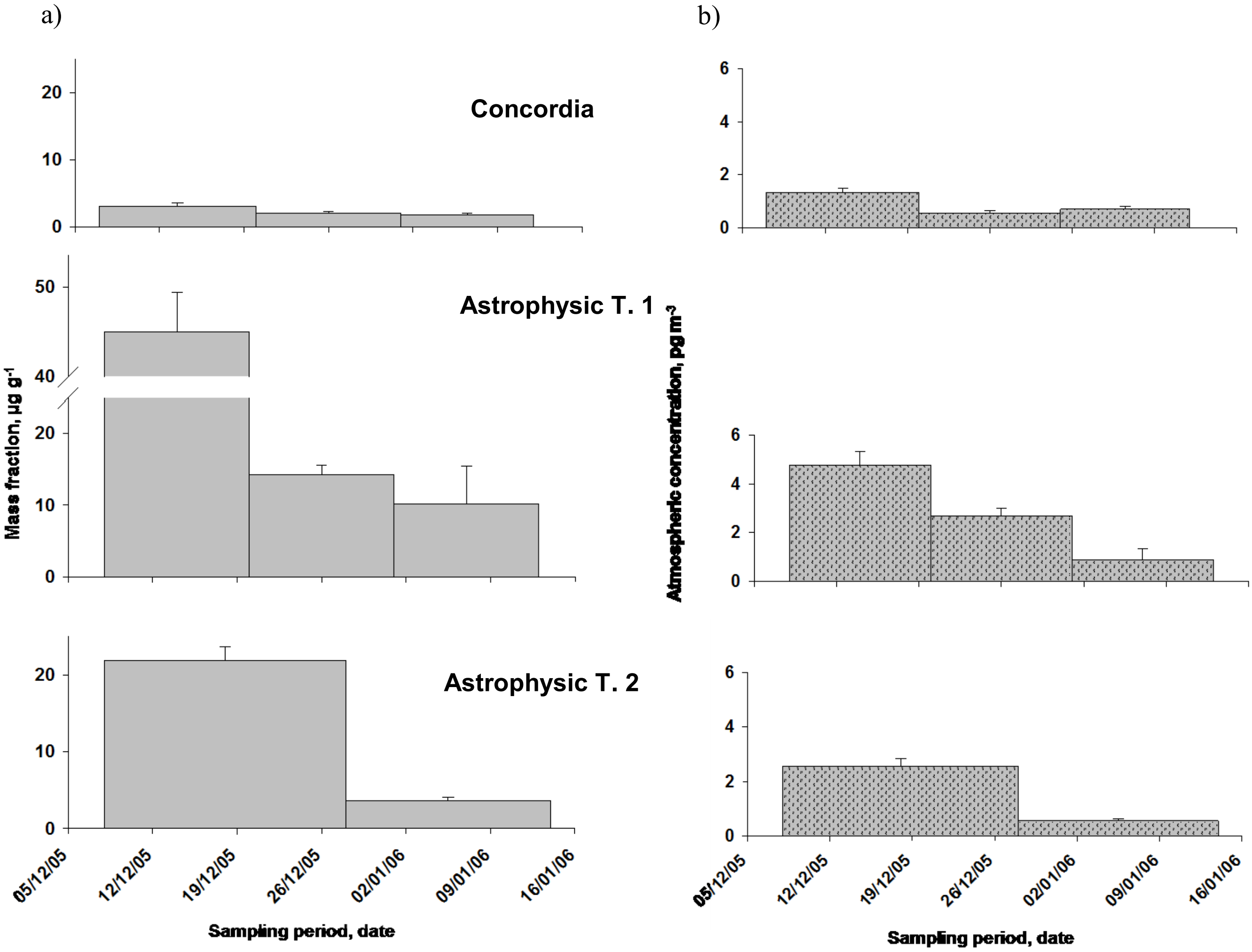


**Figure 14.** Seasonal trends of a) La mass fraction and b) La atmospheric concentration at Dome C during the 2005-06 austral summer.

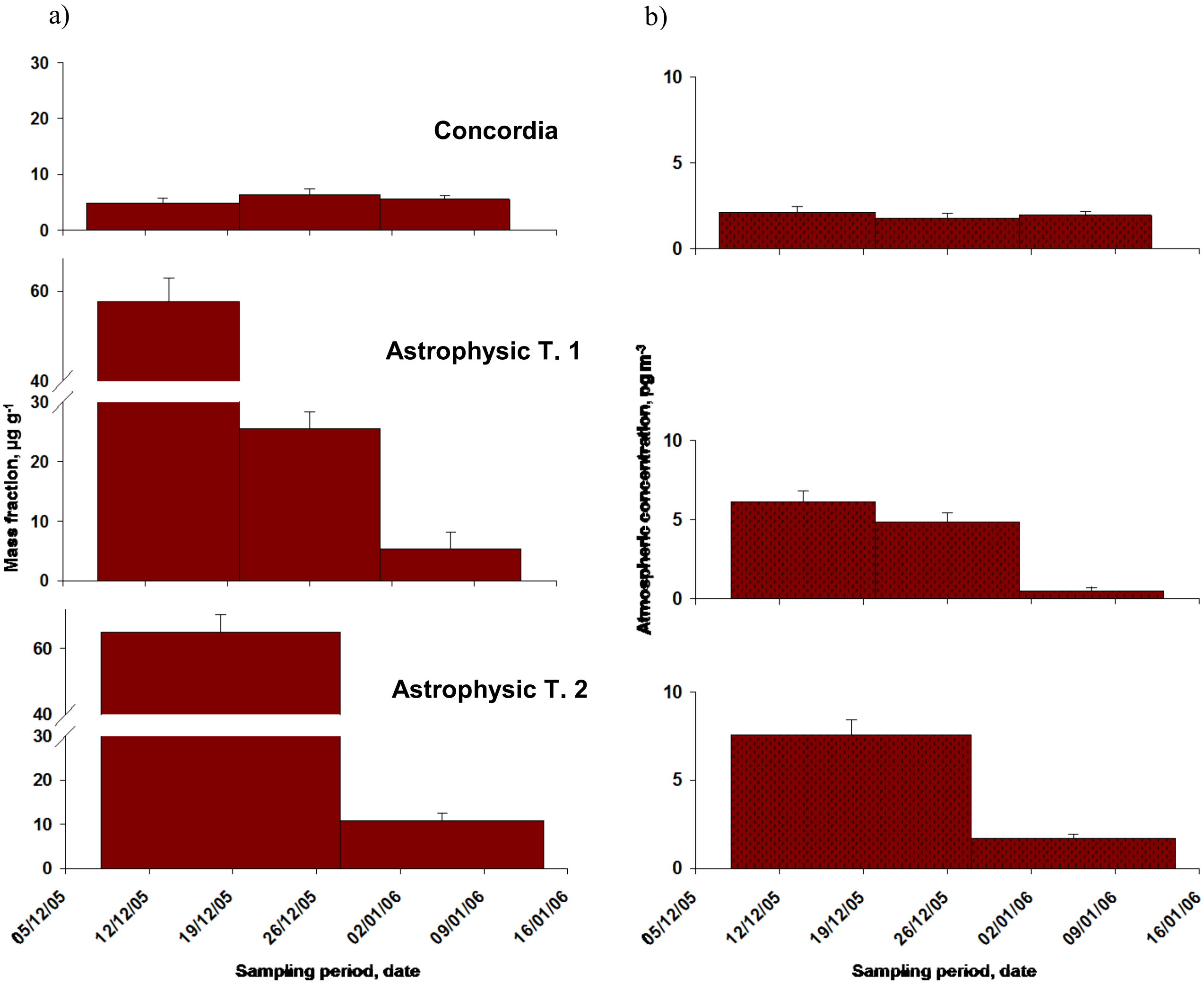


**Figure 15.** Seasonal trends of a) Ce mass fraction and b) Ce atmospheric concentration at Dome C during the 2005-06 austral summer.

Figures 15-16 reported Ce and V trend. at Concordia station We can observe quite a constant level during all the sampling period, both in mass fraction and in atmospheric concentration. Conversely, a general decrease both in mass fraction and in atmospheric concentration is observed at the Astrophysic Tents, where, probably, the background level of 0.47 pg $m^{-3}$ for Ce and 1.4 pg $m^{-3}$ for V (as reported in Table 1), are reached at the end of the campaign. Literature data report a crustal dust prevailing origin for Ce (Weller et al., 2008); as concerns V, it is a typical crustal element in Antarctic environment (Toscano et al., 2005), while it has a probably anthropic origin in urban areas, being a fossil fuel combustion marker (Becagli et al., 2012). The applying of statistical tools will probably highlight a certain origin of these elements.

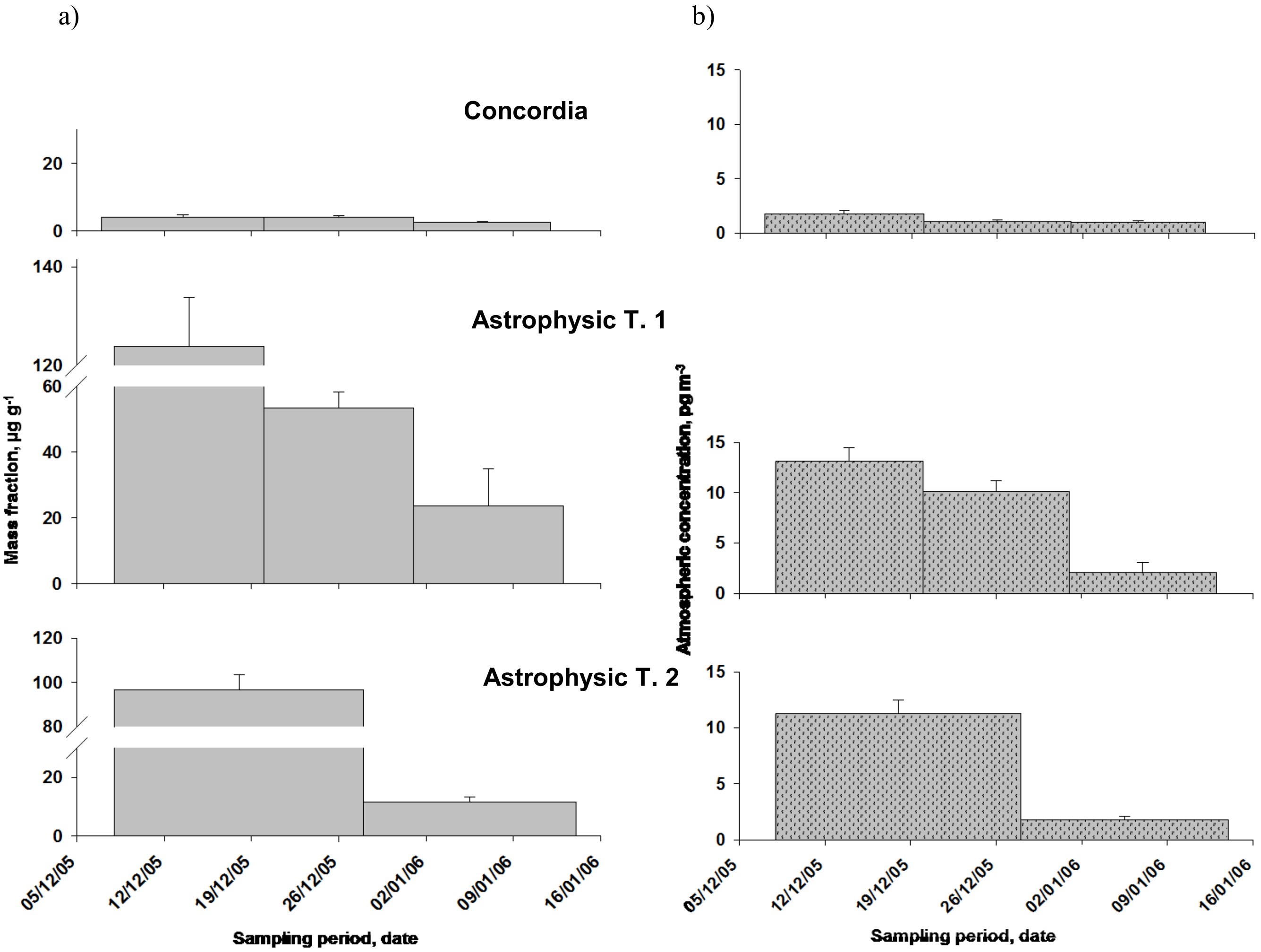


**Figure 16.** Seasonal trends of a) V mass fraction and b) V atmospheric concentration at Dome C during the 2005-06 austral summer.

In order to better understand the possible associations between elements, to assess their origin and their source apportionment, we have applied typical tools employed in environmental analysis, such as the estimation of enrichment factors, principal component analysis, hierarchical cluster analysis and positive matrix factorization. Data of Cap 1 related to Cd, Pb and Cu atmospheric concentrations have also been merged with the other elements to create a complete scenario of atmospheric aerosol composition at Dome C.

### 3.1 Enrichment factors

The estimation of two enrichment factors (EFs), i.e. crustal EF and marine EF (Paragraph 2.3.1 in Materials and Methods section), is used in this work to achieve a first indication on the main sources (marine, crustal, anthropic) of the considered elements. However, some caution should be taken when interpreting the results, taking into account the wide variation of elemental concentration in the upper crust (Contini et al., 2010; Wedepohl, 1995) and in seawater, in particular in the Antarctic region.

It is usually assumed that if the estimated value for the EF of the element is lower than 10, this element has the same origin as the EF (i.e. either crustal or marine) (Gao et al., 2002; Gharaibeh et al., 2010; Kaya and Tuncel, 1997). If both EFs are lower than 10, both sources, crustal and marine, contribute to the presence of that element in the atmospheric aerosol. Conversely, when both EFs are higher than 10, the aerosol is considered as “enriched” of that element: in this case, an additional emission source is hypothesized for that element, mainly attributable to an anthropogenic origin.

Figures 17-20 show the estimated values of the two EFs for each element. In order to have a complete scenario, we have estimated the EFs considering an average value of each element independently of the sampling site (“Dome C” EFs, Figure 17), and specific values for each sample (Figures 18-20), to better discriminate among different locations and different wind exposure.

Data in Figure 17 suggest that three different groups of elements are established: a cluster of elements, including Ce, V, Fe, La, Co, Mn and Ti, characterized by crustal origin. The elements Ca and Mg are probably both in marine and crustal sources, and finally Cu, Pb, Cd, Mo, As, Zn and Ni seem to be attributable to an additional source. These elements are usually associated in Antarctica to an anthropic origin (Bazzano et al., 2015b; Planchon et al., 2002; Wolff et al., 1999; Wolff and Suttie, 1994), so it seems plausible a direct effect of the base and of the intense handling of loads in the area of the station.

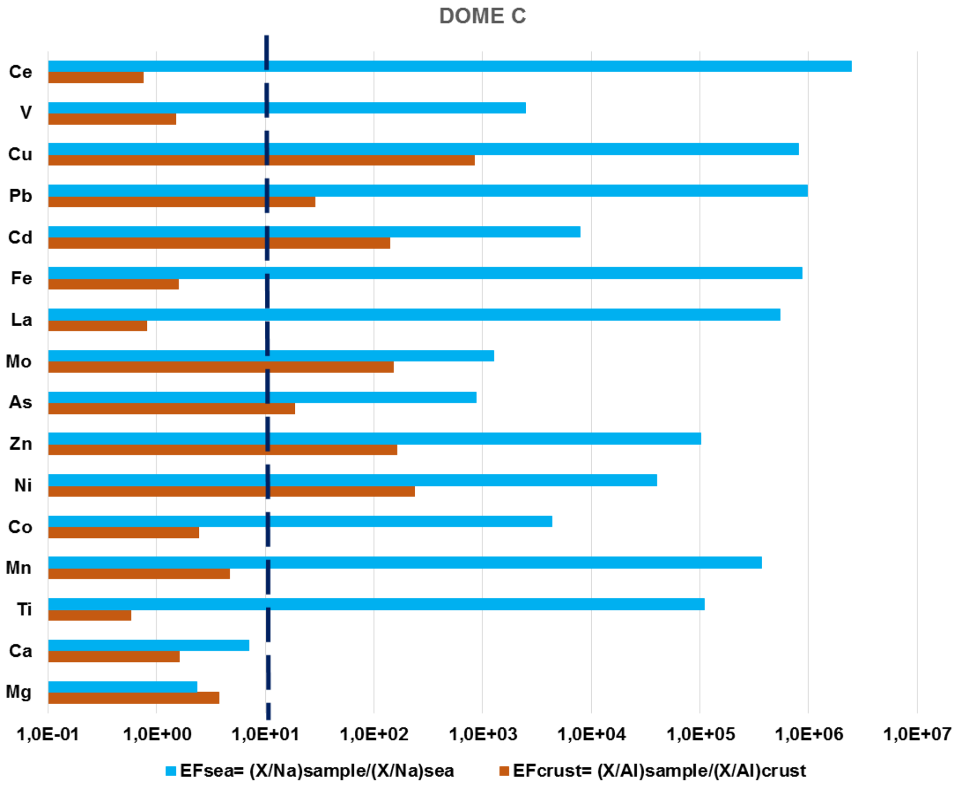
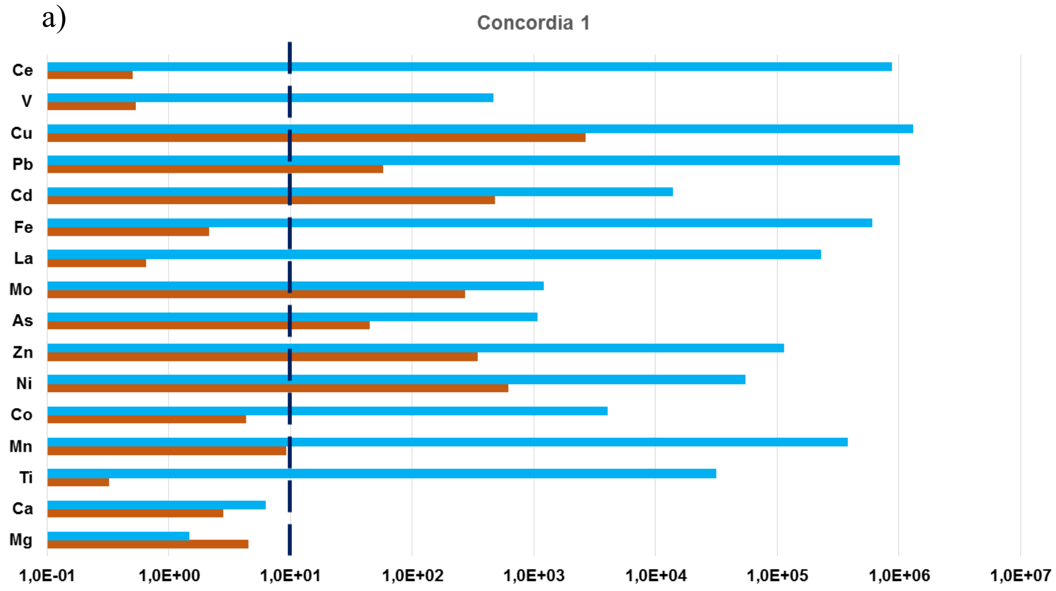


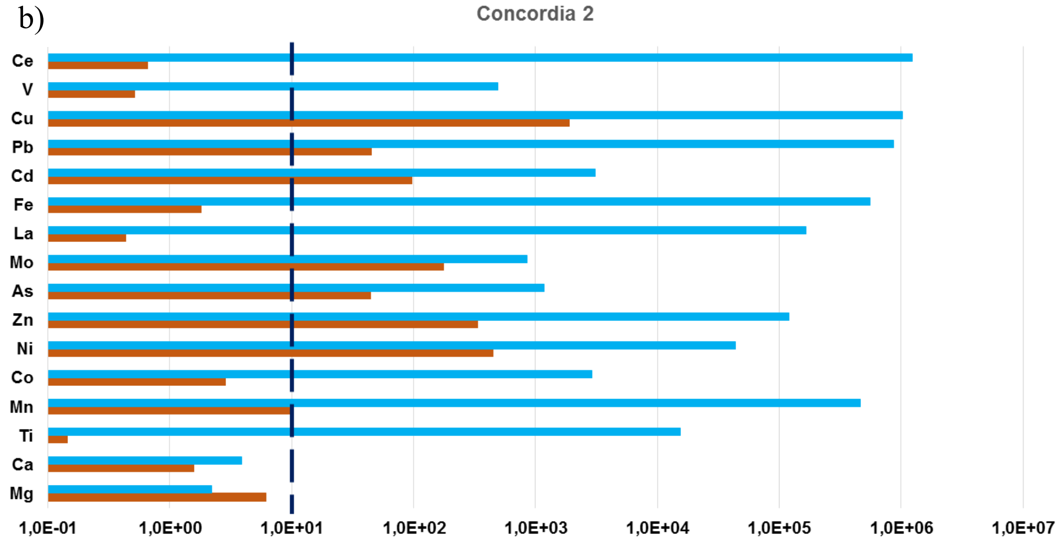
**Figure 17.** Enrichment Factors in the sampling area of Dome C, summer campaign 2005 – 2006.

Figure 18 a), b), c) shows the EFs estimated for the three samples collected in the proximity of the station. For each sample, we can observe a similar trend as observed for the average values (Figure 17), without relevant change during the campaign. Indeed, Ce, V, Fe, La, Co, Mn and Ti are the elements mainly characterized by a crustal emission source; Ca and Mg seem to be associated to both crustal and marine source, except Mg in the sample Concordia 3 that has a prevailing marine origin; all the other elements, i.e. Cu, Pb, Cd, Mo, As, Zn and Ni, have EFs higher than 10, so they probably confirm the anthropic impact in the Antarctic aerosol.

a)



b)



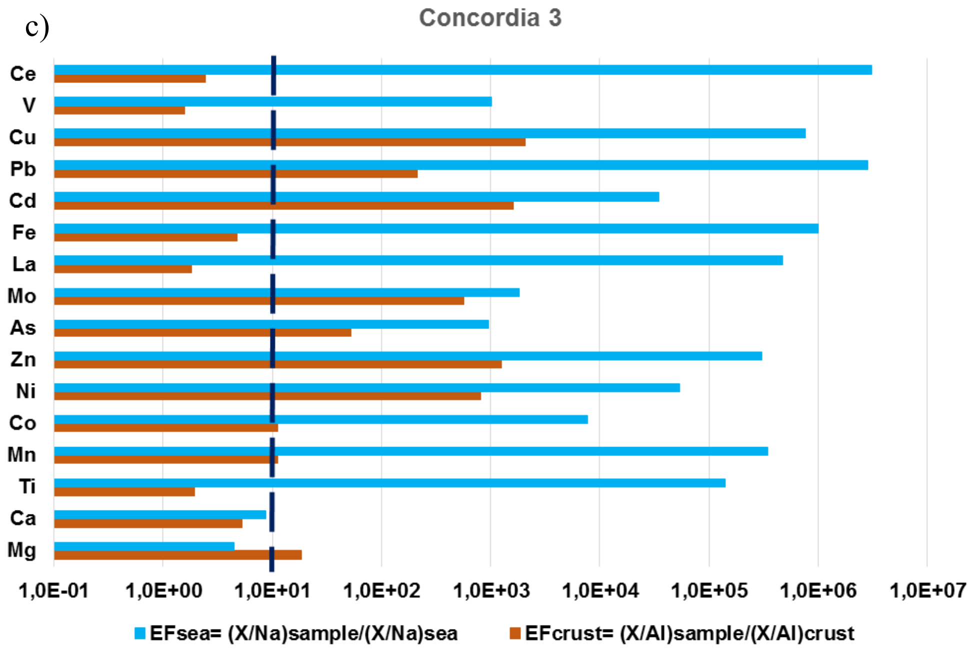
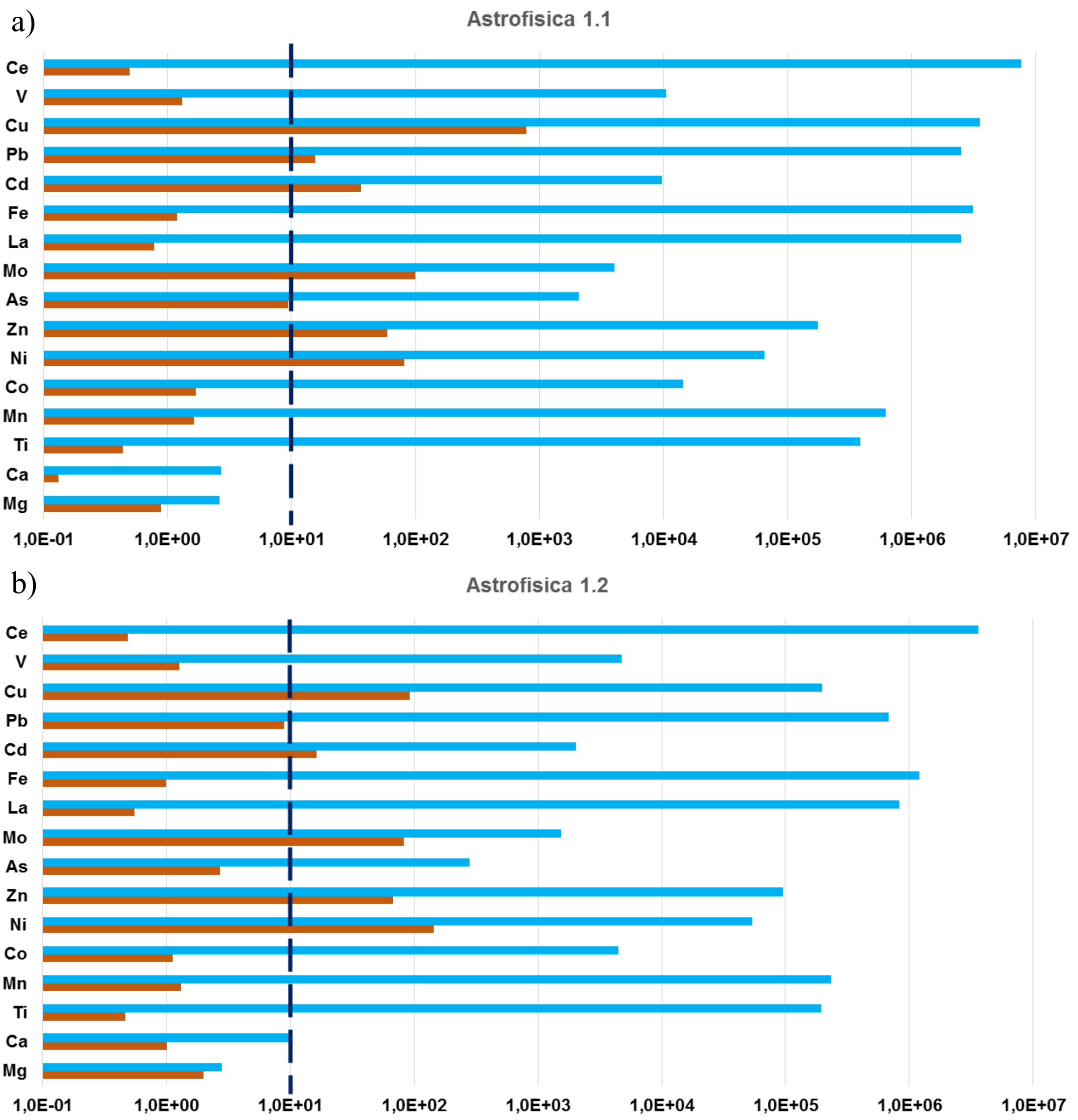


**Figure 18.** Enrichment Factors at Concordia station, a) sample Concordia 1, 7.12.2005 – 20.12.2005, b) sample Concordia 2, 20.12.2005 – 01.01.2006, c) sample Concordia 3, 01.01.2006 – 12.01.2006.

Figure 19 a), b), c) reports the scenario of EFs at the Astrophysic Tent 1. Most of EFs confirm the previous observations (Figure 17 and Figure 18), excluding As and Pb, usually with an anthropic origin, that in some samples seem compatible with a crustal origin. Also in the case of the EFs at the Astrophysic Tent 2 (Figure 19), most of EFs confirm the previous observations (Figure 17 and Figure 18). In the case an outlier behaviour is sown by the element Mn, that seems to have an anthropic origin rather than a crustal one as observed in most samples.

As in Concordia station, also in both the Astrophysic Tents, many elements seem to have an anthropic source during the entire campaign. This is an indication of a general pollution, not only near the station (Concordia) but also in a more remote site (the Astrophysic Tent 1).



a) Astrofisica 1.1

b) Astrofisica 1.2

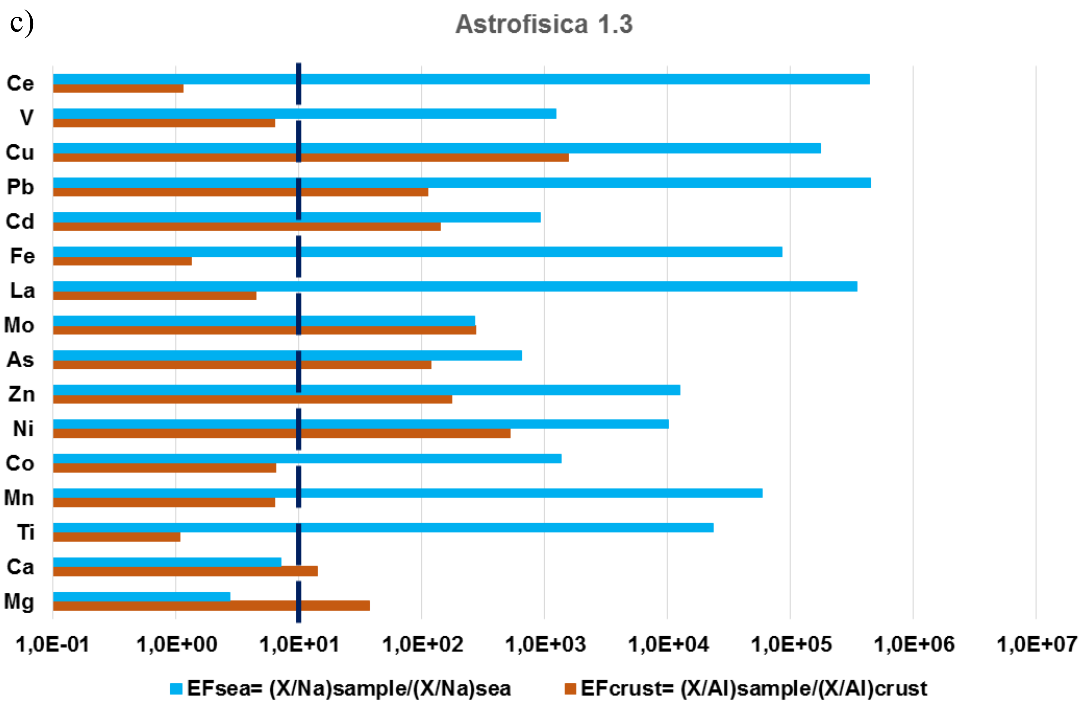
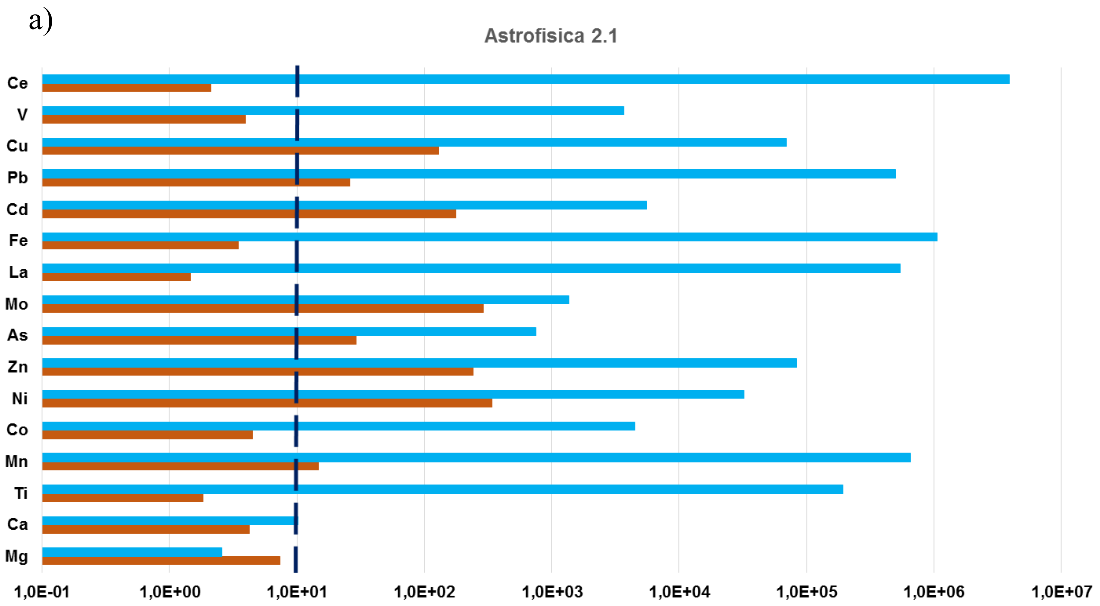


**Figure 19.** Enrichment Factors Astrophysic Tent 1 a) sample Astrophysic Tent 1.1, 8.12.2005 – 20.12.2005, b) sample Astrophysic Tent 1.2, 20.12.2005 – 01.01.2006, c) sample Astrophysic Tent 1.3, 01.01.2006 – 13.01.2006.



b)

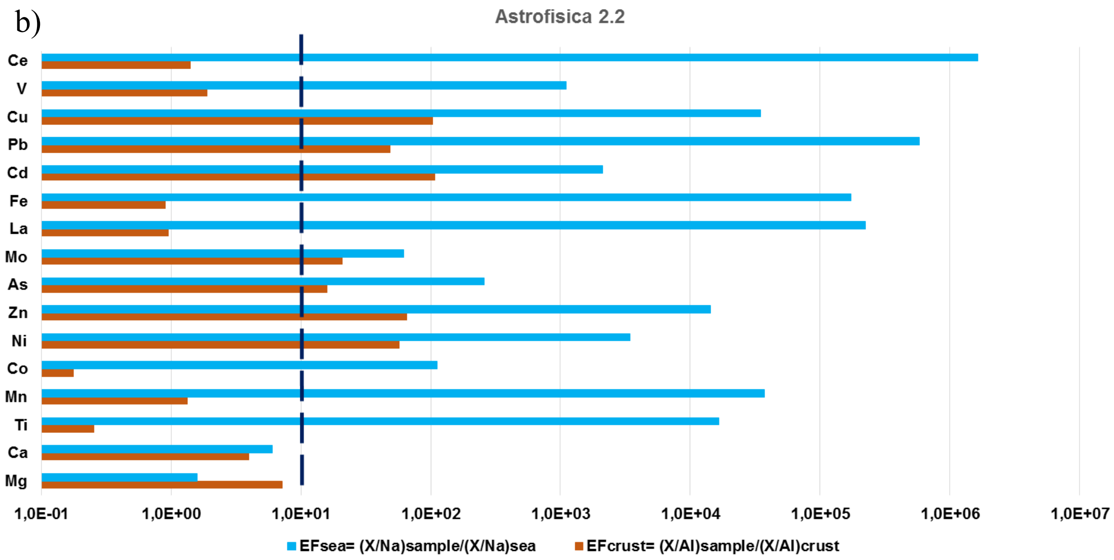


**Figure 20.** Enrichment Factors Astrophysic Tent 2 a) sample Astrophysic Tent 2.1, 8.12.2005 – 28.12.2005, b) sample Astrophysic Tent 2.2, 28.12.2005 – 14.01.2006.

### 3.2 Principal component analysis

Principal component analysis is a well-established method for aerosol analysis, after its first application to aerosol source apportionment (Thurston and Spengler, 1985). The strength of this multivariate technique is that it is based on the evolution of data collected in a specific site, and an a priori knowledge of classifying objects into classes (sources) is not required (Abollino et al., 2011; Malandrino et al., 2013b).

The aerosol atmospheric concentration standardized data matrix was subjected to PCA using the element concentrations as variables and the samples as objects, in order to represent the data structure in a smaller number of dimensions. This permits us to observe the object groupings (Toscano et al., 2005), to explore possible correlations between variables and similarities among samples (Bazzano et al., 2015b).

The PCA results reported in Table S6 indicate that the first three principal components explain about 92% of the data variance.

The scores and loadings plots of the first three principal components, for all the samples, are reported in Figures 21 and 22, while Table S7-S8 reports the numerical values of scores and loadings.

Concerning the first two components, they explain 76% of the total variance of the data. The score plot (Figure 21 a) shows the objects arranged according to a temporal trend. Indeed, the first samples of each site have positive values in the first principal component, the samples of intermediate period are grouped in the central part of the plot and the samples of the third period of sampling have common negative score in the first principal component.

Figure 21 b) reports the loading plot, component 1 vs. component 2. We can observe that all elements are grouped on the first principal component, representing the total elemental load at the beginning of the expedition, when the aerosol atmospheric concentrations are higher (Annibaldi et al., 2011).

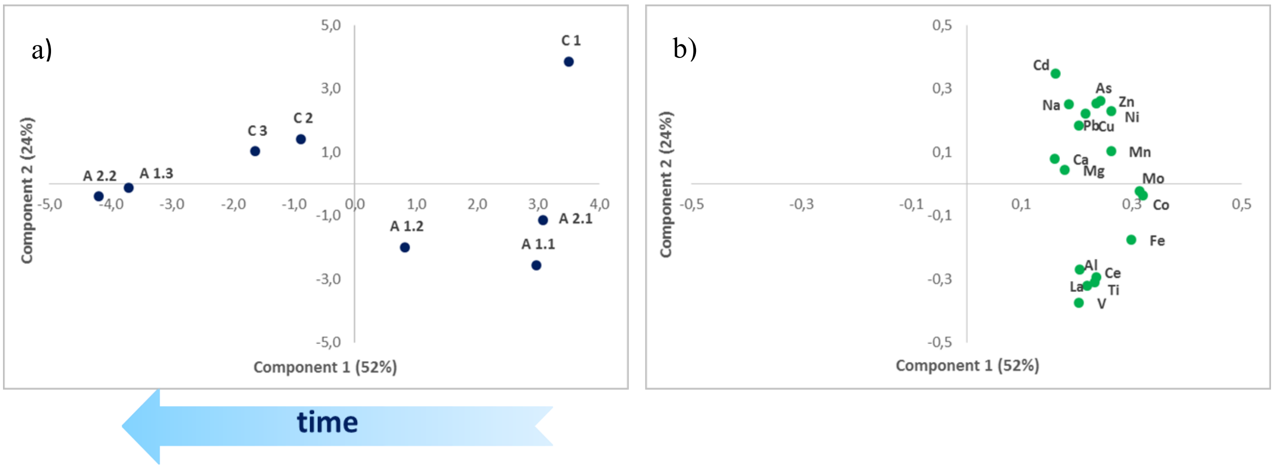


**Figure 21.** Scores a) and loadings b) plots on PC1-PC2 for aerosol samples collected at Dome C during the summer 2005-06.

Figure 22 reports the score (a) and loading (b) plots related to the component 2 vs. component 3. Concerning the score plot, we can observe a grouping of the objects according to the values calculated for the component 2 (PC2): the three sample collected at Concordia station have positive values of the PC2, all the other samples of Astrophysic Tents have negative values of the PC2.

If we consider the loading plot, we can identify different elements grouped around a tracer. Ca and Mg group with Na, one of a major element of seawater composition (Turekian, 1968); consequently these elements could be ascribable to a marine origin. Moreover, the marine group are positive correlated with component 3. Ti, La, V, Ce, Fe are grouped around Al, a typical crustal marker; therefore, all these elements are probably associated in a terrigenous origin. Also Co and Mo are included in the group of crustal elements, but because of their loadings lower than other variables of the group, we might hypothesize that they are emitted in the Antarctic atmosphere by another minor source. As concerns the anthropic marker, such role is usually attributed in the literature to Cd, Pb, Cu, Zn, As and Ni (Pacyna and Pacyna, 2001). These elements seem well grouped together on component 2. We can also observe how component 2 discriminates anthropic grouping (positive high values) to crustal one (negative high values). Such grouping of the elements according to the three different sources marine crustal and anthropic is in agreement with literature data dealing with Antarctic studies (Bazzano et al., 2015b; Truzzi et al., 2017).

Mn is not clearly associated to any of the three group of elements presented above, probably because of multiple source apportionment that contribute to its atmospheric concentration.

A comparative analysis of Figure 22 a) and b) suggests how the variables influences some objects; indeed, the anthropic component influences all samples collected at Concordia station, while the marine variables seem to influence mainly the Astrophysic Tents, in particular the objects A 1.3, A 2.1 and A 2.2., related to the second part of the sampling period. Finally, the crustal elements influence mainly the first two samples collected at the Astrophysic Tent 1 (e.g. A 1.1 and A 1.2).

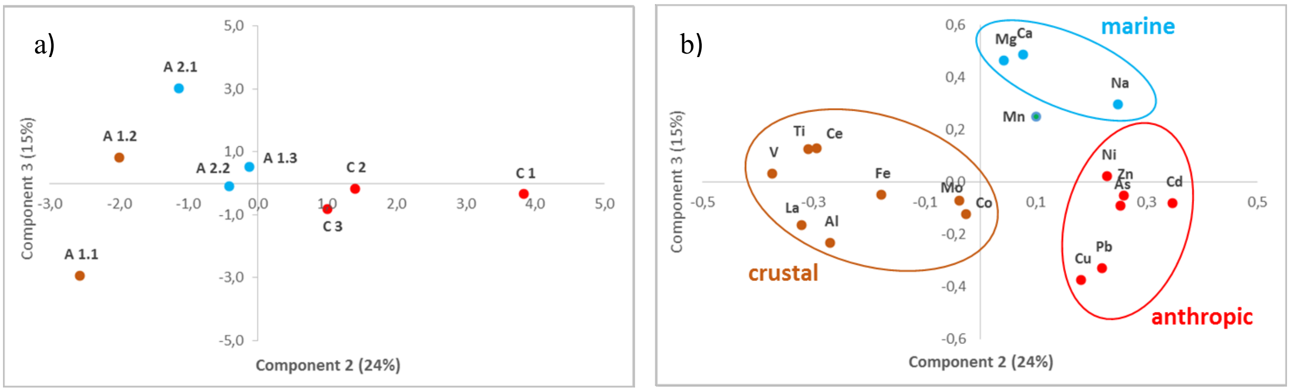


**Figure 22.** Scores a) and loadings b) plots on PC2-PC3 for aerosol samples collected at Dome C during the summer 2005-06.

To support the interpretation of the emission sources that contribute to the atmospheric aerosol of Dome C, we carried out a Varimax rotation. The number of factors was selected taking into account the eigenvalue higher than one: consequently we have considered only the first three factors, in order to increase the weight of higher loadings and to decrease the weights of lower ones (Abollino et al., 2011). The three prominent factors were oriented orthogonally in the plots, as reported in Figure 23. In details, we can observe in Figure 23 b) how Factor 1 represents crustal elements, Factor 2 well groups anthropic elements, while in Figure 23 d) the plot represents Factor 1 against Factor 3, grouping the marine elements. Considering the object plot (Figure 23 a), the Factor 1, representing crustal elements, influences mainly the object A 1.1, the Factor 2 contributed to high score of C 1, corresponding to the beginning of the expedition, when the anthropic activities have been more intense, and finally marine elements influences the sample A 2.1, as reported in Figure 23 c).

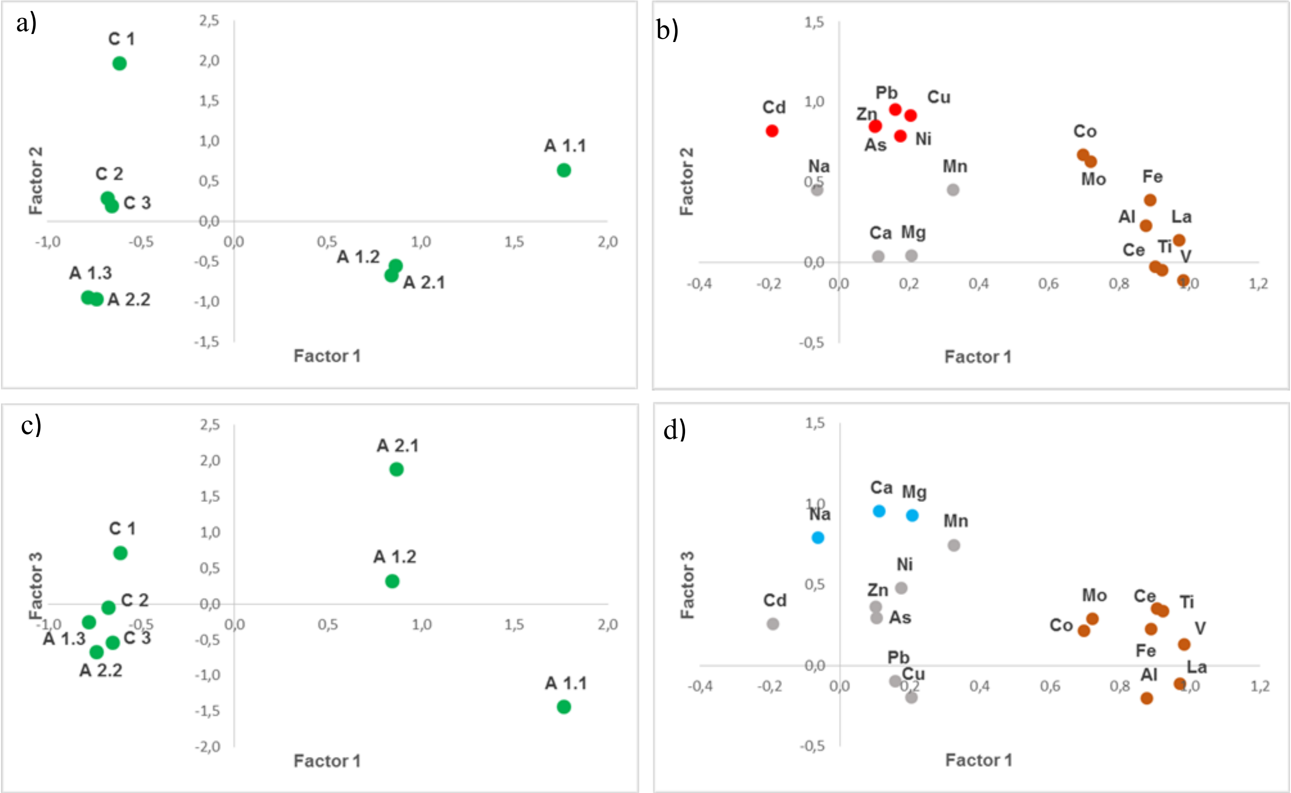


**Figure 23.** The plots related to Varimax rotation; a), c) plot of objects, b), d) plots of variables, underlying the three groups of elements.

We can observe that statistical and qualitative analysis substantially confirmed the source assessment based on PCA, EF values and air masses back trajectories.

### 3.3 Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) is an effective statistical method for the qualitative study of atmospheric aerosol composition. It can be used to highlight possible similarities between variables, which indicate common sources of atmospheric particulate matter (Padoan et al., 2016). HCA is usually employed to confirm the groups of variables obtained with PCA (Contini et al., 2010; Dongarrà et al., 2007; Miranda et al., 1996). Data elaboration has been applied on elemental atmospheric concentrations of aerosol, data was standardized and analysis has been performed with Unistat 6.5 software package applying Ward's method of agglomeration and Euclidean distance as the measurement of similarity.

The dendrogram reported in Figure 24 shows the following three clusters:

- The first cluster observable is characterised by elements such as Na, Mn, Mg and Ca, well correlated each other even in PCA, and not linked with other clusters. In this group Mn is also included, that in PCA has not a clear affinity to any group of elements. Given the presence of Na as marine marker, this cluster has been attributable to a marine origin.

- The second group encloses the variables Ni, Zn, Cd, Pb, Cu and As, linked at a similar level of dissimilarity. This cluster represents the anthropic component of the aerosol, due to the presence of the typical markers as Cd and Pb.
- The third group is characterized by more elements such as V, La, Al, Ti, Ce, Co, Mo and Fe, linked at different level of dissimilarity; in particular, V, La, Al, Ti and Ce have quite similar dissimilarity, while Co, Fe and Mo have a major distance from these elements. This cluster is characterized principally by a terrigenous origin due to the presence of Al, a major element of the Earth crust.

The results obtained from hierarchical cluster analysis are in a good accordance to ones obtained by PCA, EFs and correlation matrix (reported on Supplementary Materials), confirming our hypotheses about the three main sources affecting the aerosol composition at Dome

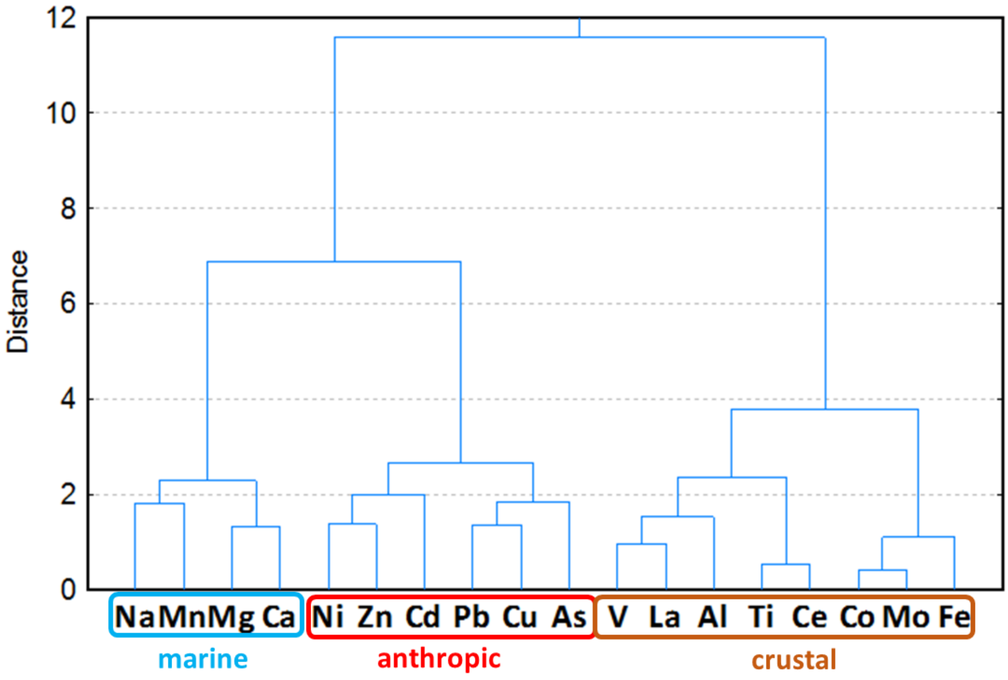


**Figure 248.** Dendrogram of hierarchical cluster analysis.

### 3.4 Positive matrix factorization

Positive matrix factorization is a multivariate factor analysis tool that decomposes a matrix of aerosol data into two matrices: factor contributions and factor profiles. These factor profiles need to be interpreted by the user to identify the source types that may be contributing to the samples using measured source profile information and emissions (Paatero, 1997; Paatero and Tapper, 1994).

Source apportionment on Antarctic aerosols is typically confined to a limited number of sources due to scarce numbers of contributions in a remote continent. Indeed, in our analysis we have identify only three main factors as emission sources that influence the sampling site: a marine contribution that reaches Antarctic plateau, crustal particles coming from areas not covered by ice and a component connected to local human presence near the sampling area or possibly coming from remote continents, reaching Antarctica through the global air masses circulation.

Figure 25 reports the results of the PMF, showing the normalized percentage contribution for each element according to atmospheric concentrations detected during the entire sampling period.

Every variable shows a prevailing factor contribution that allow us to create grouping characterized by the same predominant origin. Indeed, Na, Mg and Ca seem to have the same prevalent factor, ascribable to a marine origin, as just recognized by other statistical tools results (e.g. PCA and HCA), for Al, Ti, V, Mn, Co, Mo, La, Ce and Fe a common factor linked to crustal origin prevails, given the presence of Al as marker. Finally, the anthropogenic factor seems prevailing for Ni, Zn, As, Cd, Pb and Cu.

Despite the limited number of available samples that increase the uncertainty of the analysis, the factor profile reported in Figure 25 substantially confirm the source assessment previously identified by other multivariate statistical analysis tools, such as EFs, PCA, HCA.

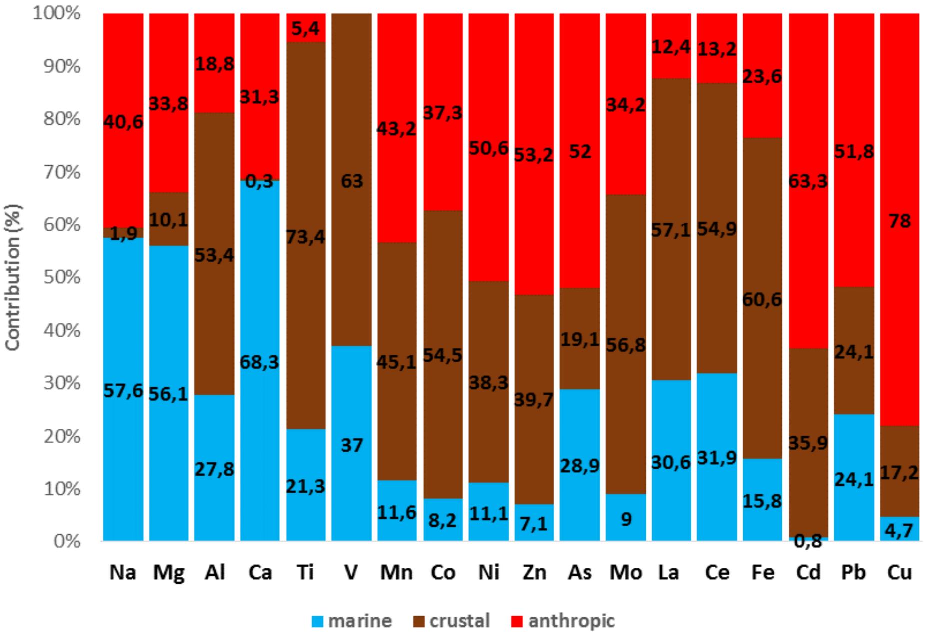


**Figure 25.** Factor profiles from Positive Matrix Factorisation (PMF) analysis. Values are expressed as percentage contribution of each factor.

Moreover, the PMF allows to evaluate not only the prevailing emission source like the other tools for data interpretation, but also the secondary ones: indeed, the elements in the aerosol are distributed in percentage into all the three factors (i.e. the three sources). This aspect overcome the limits of other statistical tools, creating a model that create a more realistic pathway of aerosol chemical composition. Regarding our samples, this aspect may support the interpretation, overcoming the conflicting classification of Mn highlighted by PCA, HCA, EFs: indeed, it has a quite equal contribution of crustal (45%) and anthropic (43%) factor.

Figure 26 reports the factor contribution in each sample, as a further output of the PMF analysis. Also in this case, it is important not to forget the quite high uncertainty level associated to the analysis due to the low number of samples. However, we can observe a prevailing anthropic impact in the proximity of the station, corresponding to the samples C 1, C 2 and C3, and a prevailing natural (marine and crustal) contribution in the aerosol sampled at the Astrophysic tents.

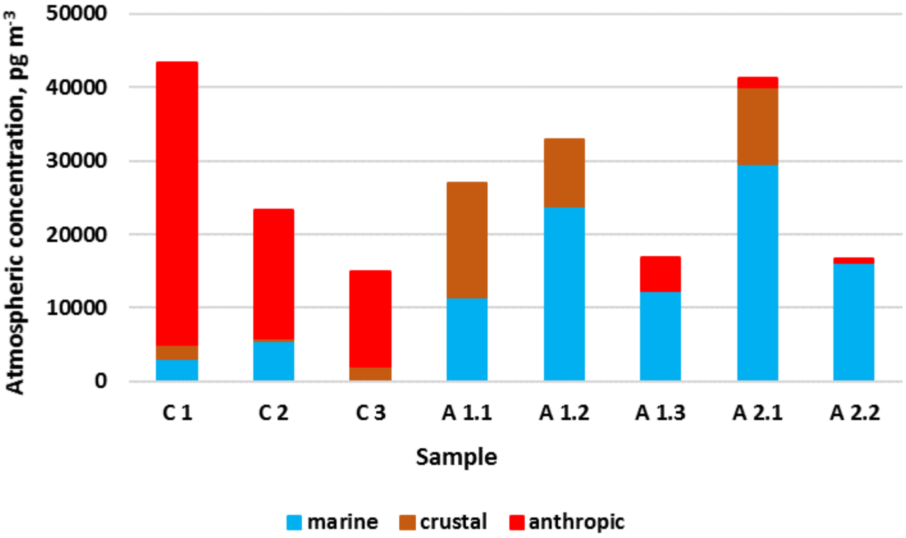


**Figure 26.** Factor contributions of each sample collected at Dome C during 2005-2006 summer campaign.

## 4. Conclusions

Aerosol chemical concentration has been determined, for the first time, at Dome C, Antarctic Plateau, in order to know the major and trace elemental composition of the aerosol during the austral summer 2005-06. Data analysis allowed to hypothesize background level of major and trace elements in the aerosol never determine before at Dome C. Their amount and the complexity of the results needed the employment of statistical tools and the support of air masses back-trajectories and the measurements of enrichment factors, to find possible associations and similarities between elements. This critical approach allowed us to validate the hypothesis of main provenance of each group of elements in order to reconstruct the local and remote emission sources. As higher purpose of our work we have tried to interpret also source apportionment in secondary sources affecting the aerosol atmospheric composition at the receptor site.

The multivariate statistical analysis allows to identify three main groups of elements according to recognized chemical tracer:

- Na, Ca, Mg associated in a marine origin;
- Al, Fe, V, La, Ti, Ce, Co, Mo associated in crustal origin;
- Cd, Pb, Cu, Ni, Zn, As, typical anthropic elements;
- Mn is not univocally determined, probably because multiple emission sources contribute to such atmospheric concentrations.

The analysis of the results and the temporal trend observed underline a general high pollution determined by the station activities, more intense at the beginning of the scientific expedition, including aircraft arrivals/departures. The impact of the base tends to decrease during the proceeding of the season, partially affecting all the samples collected near the station (e.g. samples C 2, C 3). Conversely, at Astrophysic Tent, prevails a natural (both crustal and marine) component of aerosol, as reveals the analysis of air masses back-trajectories coming from remote sites of Southern Ocean and other coastal areas not covered by ice.

This work has opened new perspectives in understanding the elemental composition of the Antarctic Plateau aerosol, investigating about element associations coming from either local or remote sources, reaching the most pristine area of the Planet. This aspect is considered a fundamental contribution to the knowledge of the atmospheric global circulation, in the view of estimating the climatic and environmental changes expected for the future.

In the perspective of deeper knowledge of aerosol chemical composition, should be useful to analyse chemical fractionation obtained by chemical sequential extraction of aerosol samples as set up by Illuminati et al. (2015). Indeed, every fractions are ascribable to a class of chemical compounds and this a valid instrument for the identification of emission sources, applying as a confirm of source apportionment obtained by PMF model.

Finally, to investigate about chemical transformations occurring at the receptor site, also air-snow relationship should be considered. This aspect might open a new perspective in the knowledge of depositional fluxes of aerosol compound and their natural chemical transformation expected for the future.

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# Supplementary material

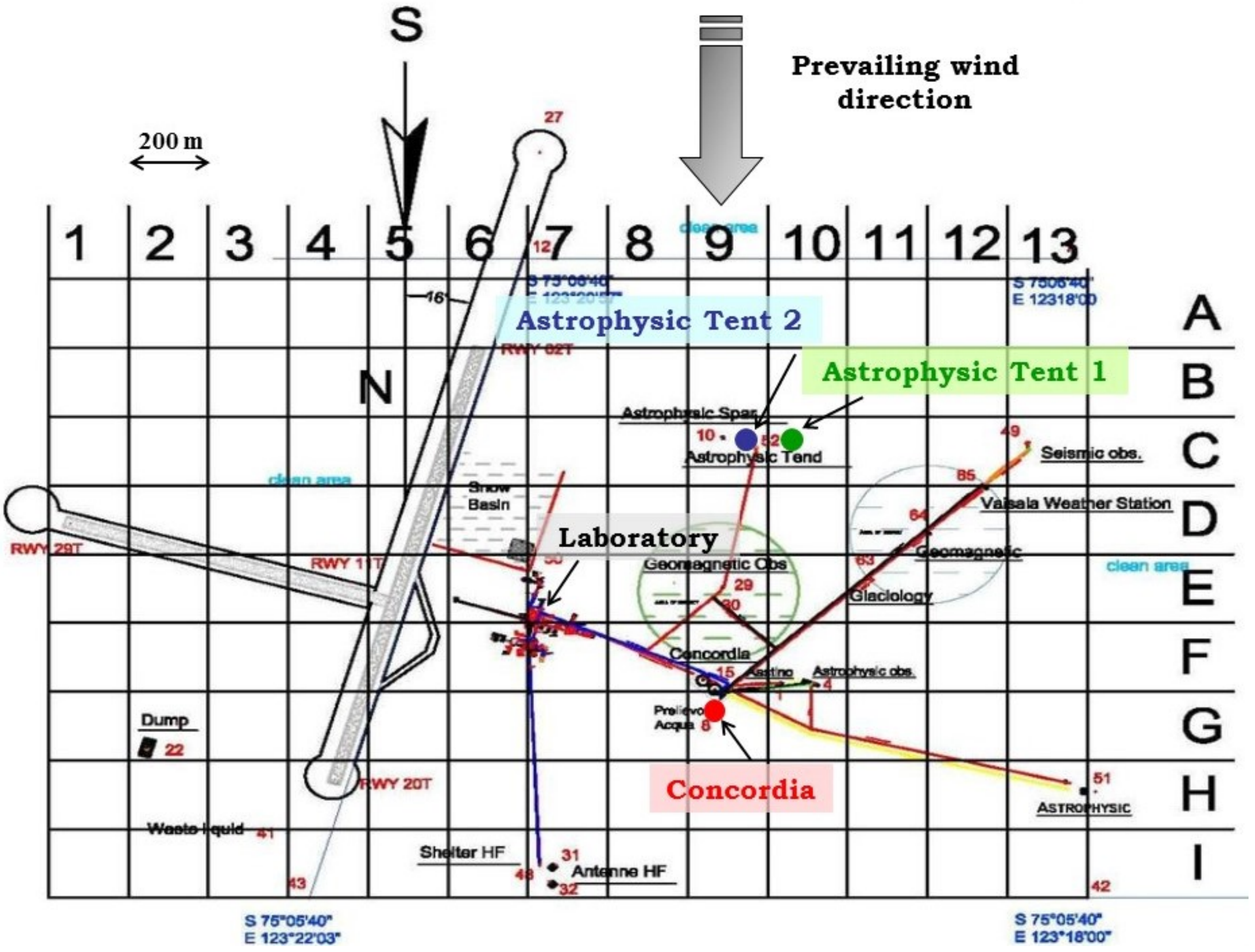


**Figure S1.** Map of the sampling area. In the figure the locations of aerosol sampling are shown.

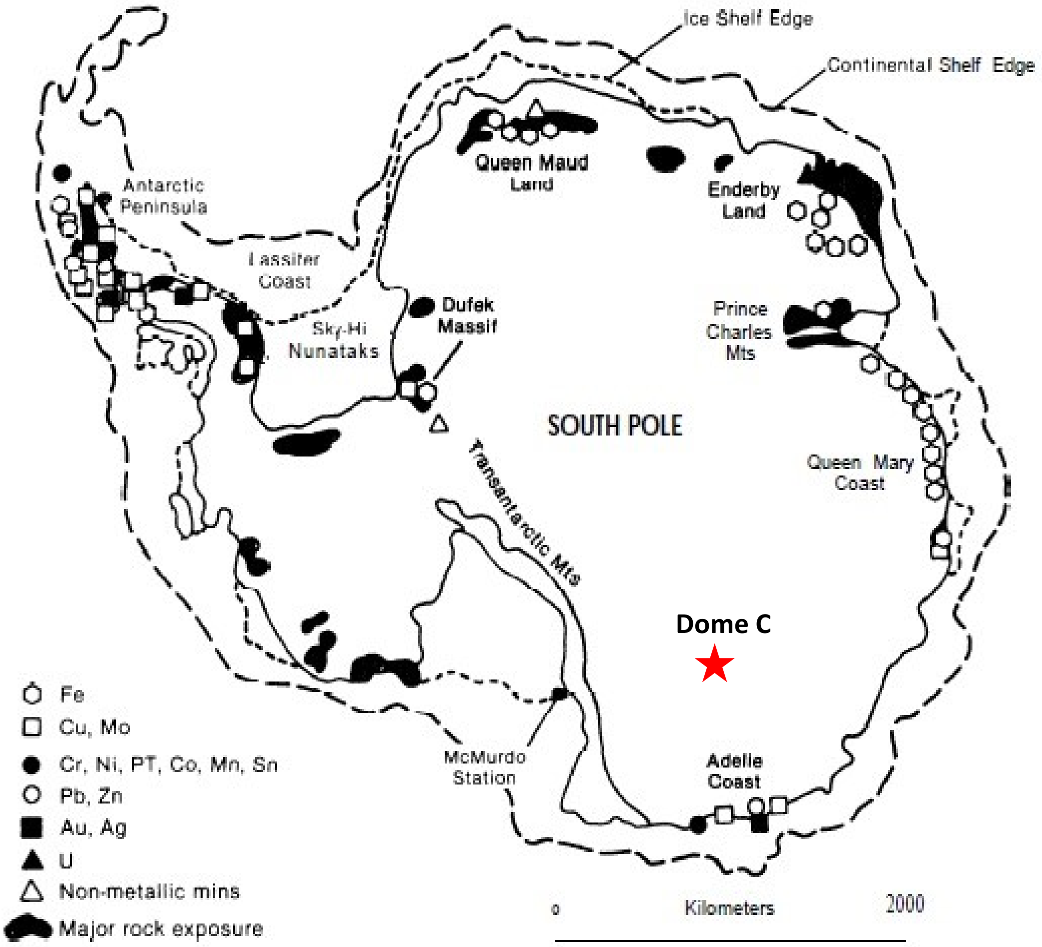


**Figure S2.** Antarctica mineral occurrences. Sources, U.S. Geological Survey, 19SS

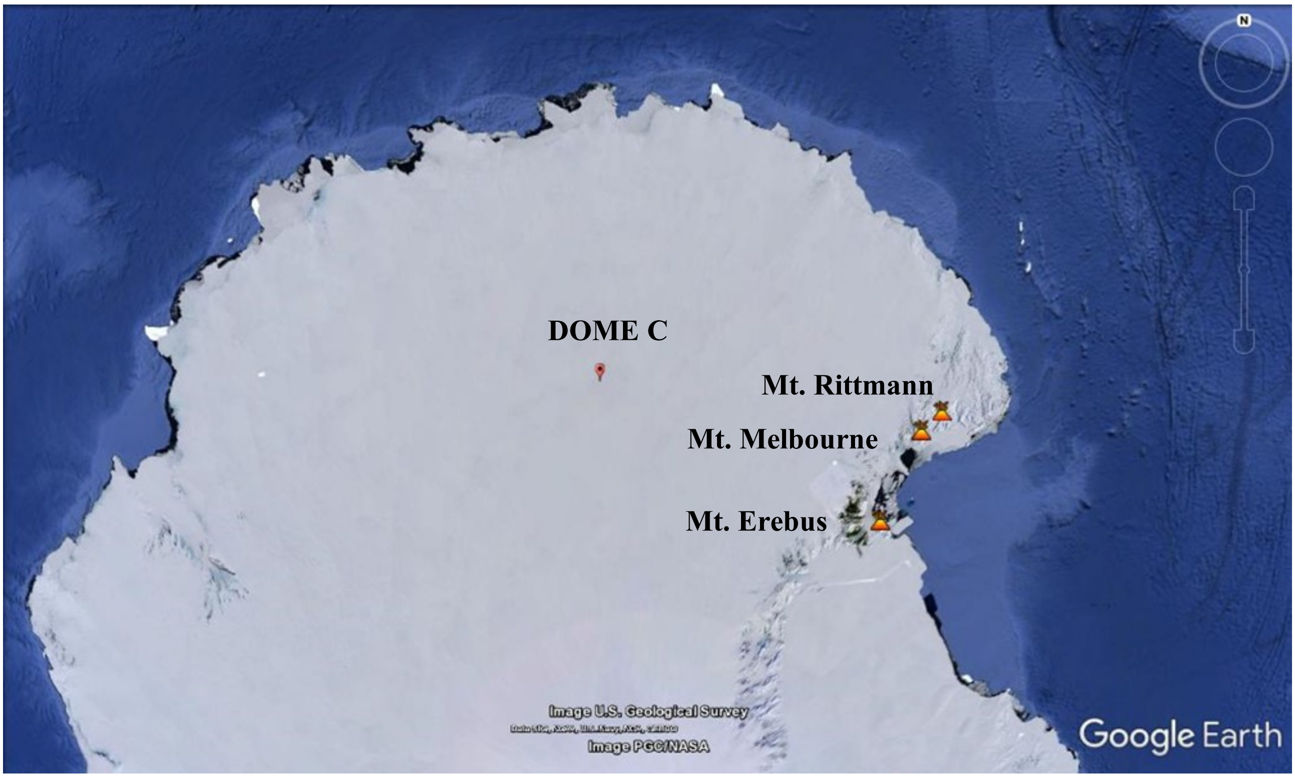
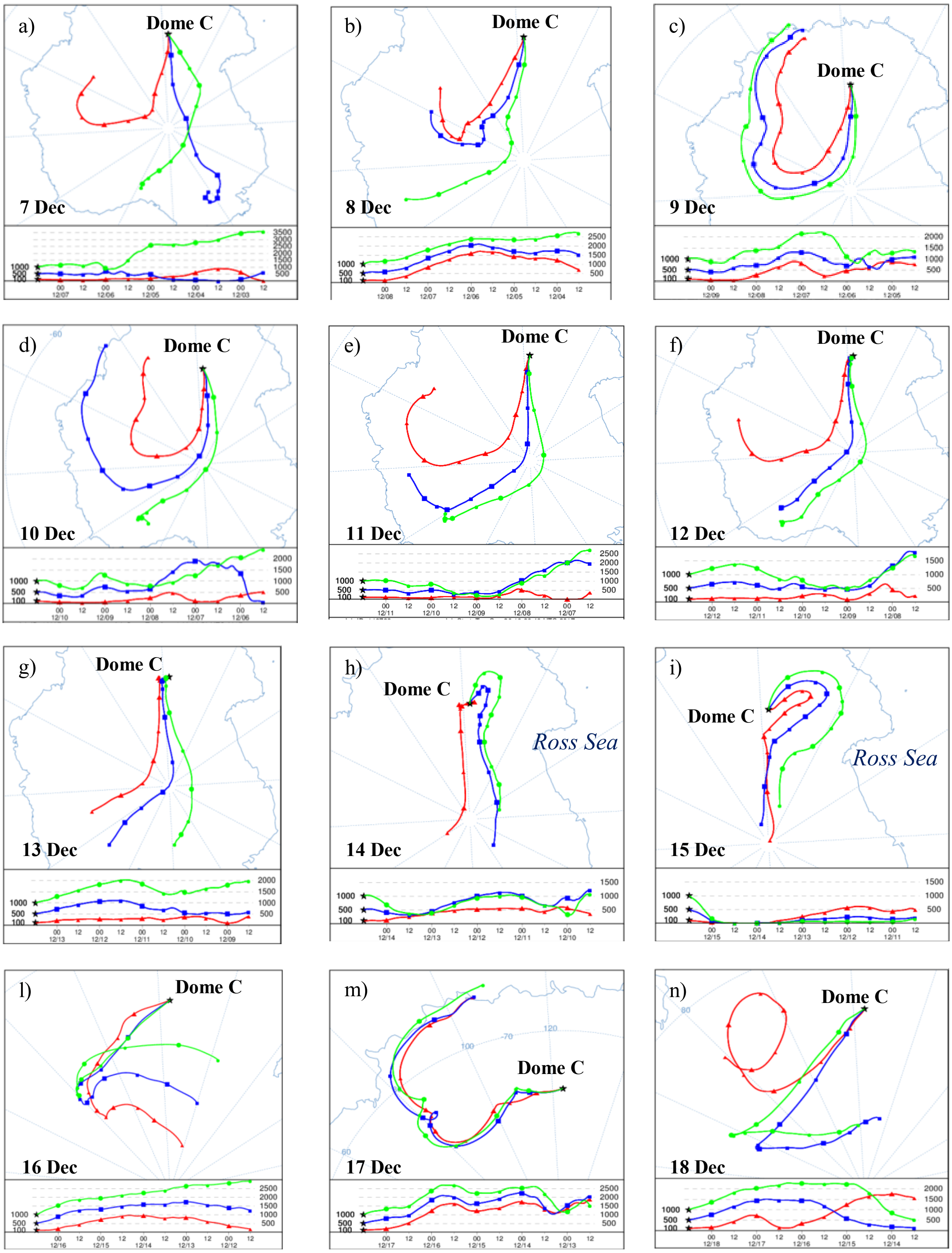
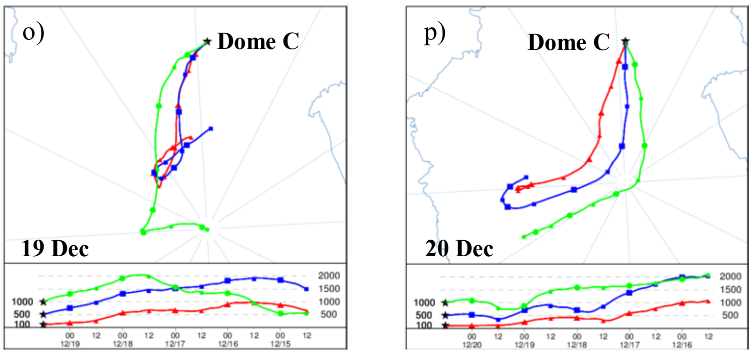


**Figure S3.** Map showing the area of Dome C and the volcanoes Melbourne and Rittmann and Erebus. From Google Earth, access March 16, 2017.


a)
Dome C
7 Dec
b)
Dome C
8 Dec
c)
Dome C
9 Dec
d)
Dome C
10 Dec
e)
Dome C
11 Dec
f)
Dome C
12 Dec
g)
Dome C
13 Dec
h)
Dome C
Ross Sea
14 Dec
i)
Dome C
Ross Sea
15 Dec
l)
Dome C
16 Dec
m)
Dome C
17 Dec
n)
Dome C
18 Dec



**Figures S4.** NOAA Hysplit five-days backward trajectories run for arrival heights of 100 m, 500 m and 1000 m a.g.l. at 12 a.m. of each day recorded at Dome C during the summer 2005-2006. Period corresponding to sample 1 at Concordia station (7th to 20th December 2005).

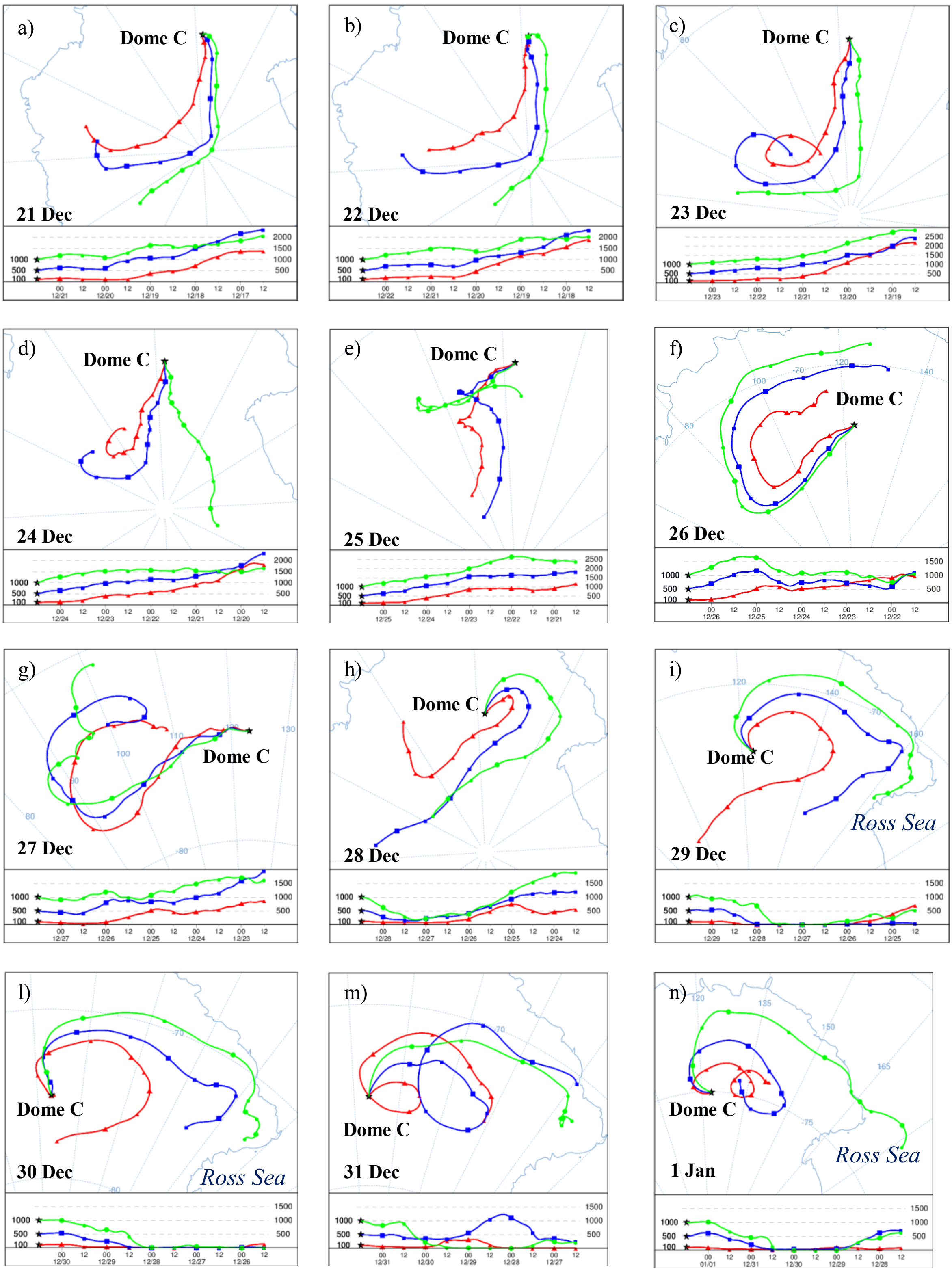
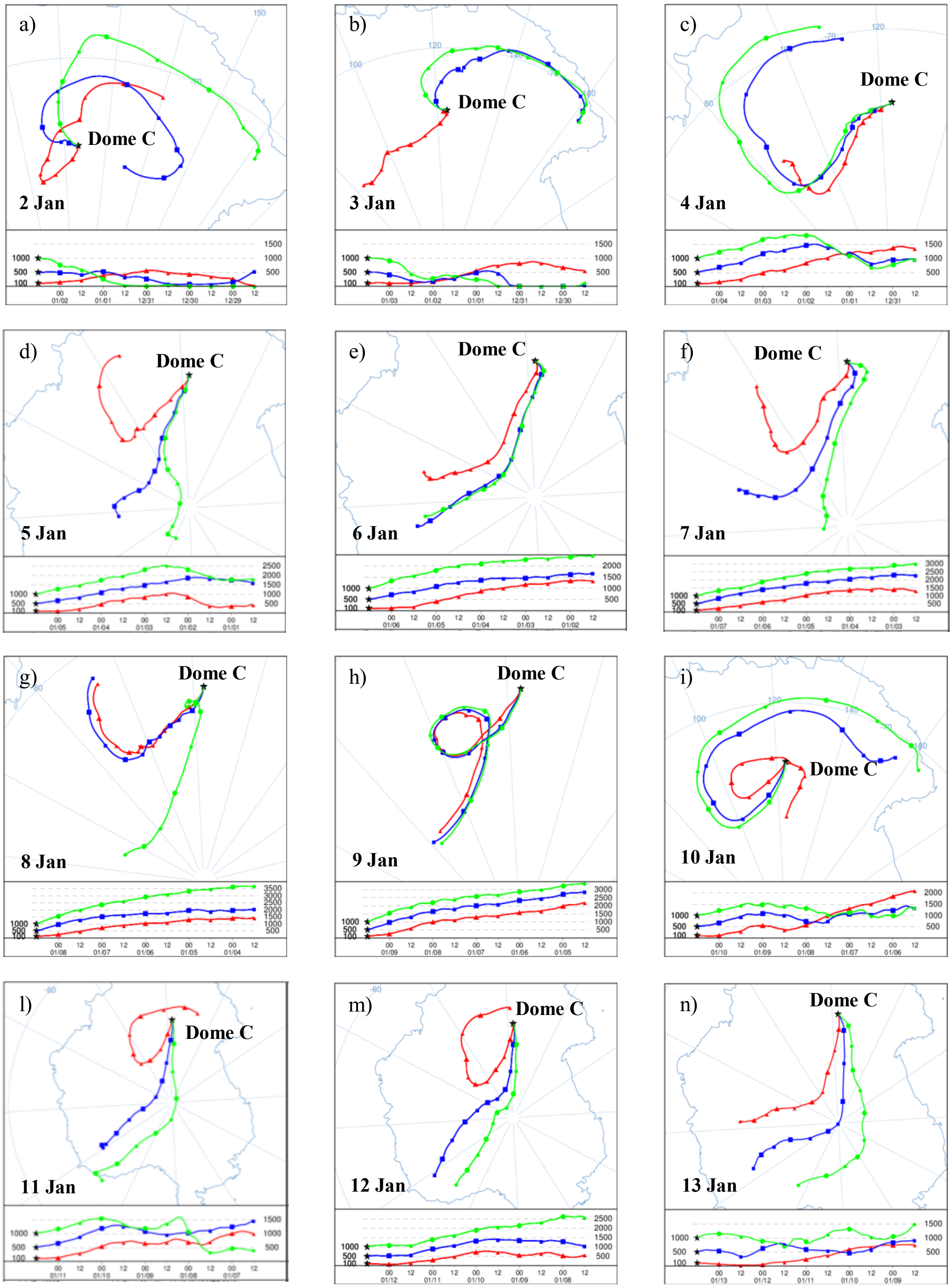


**Figure S5.** NOAA Hysplit five-days backward trajectories run for arrival heights of 100 m, 500 m and 1000 m a.g.l. at 12 a.m. of each day recorded at Dome C during the summer 2005-2006. Period corresponding to sample 2 at Concordia station (21th December 2005 to 1st January 2006).


a)
Dome C
2 Jan
b)
Dome C
3 Jan
c)
Dome C
4 Jan
d)
Dome C
5 Jan
e)
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6 Jan
f)
Dome C
7 Jan
g)
Dome C
8 Jan
h)
Dome C
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11 Jan
m)
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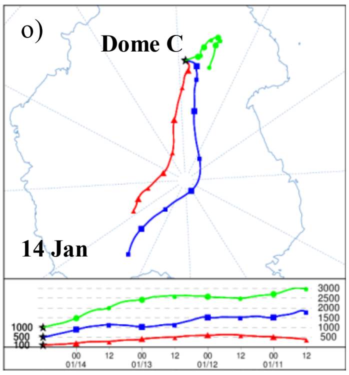
12 Jan
n)
Dome C
13 Jan



**Figures S6.** NOAA Hysplit five-days backward trajectories run for arrival heights of 100 m, 500 m and 1000 m a.g.l. at 12 a.m. of each day recorded at Dome C during the summer 2005-2006. Period corresponding to sample 3 at Concordia station (2nd to 14th January 2006).

**Table S1.** Major and trace elements in Antarctic aerosol expressed as metal mass fraction, standard deviations in parenthesis (Dome C, Concordia station, austral summer 2005-06).

| Site | n. | Major elements (mg g $^{-1}$) | | | | | Trace elements (µg g$^{-1}$) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Na | Mg | Al | Ca | Fe | Ti | Mn | Co | Ni | Zn | As | Mo | La | Ce | V |
| Concordia | 1 | 50±9 | 8,7±1,4 | 11,1±1,8 | 11,8±1,8 | 9,4±1,5 | 143±33 | 689±108 | 7,2±1,2 | 1637±257 | 2576±467 | 12,7±2,2 | 54,6±8,9 | 3,0±0,5 | 4,8±0,9 | 4,0±0,8 |
| | 2 | 46±9 | 12,0±1,5 | 11,2±1,1 | 6,7±3,6 | 8,0±0,9 | 65±38 | 783±76 | 4,8±0,6 | 1214±129 | 2539±285 | 12,9±1,7 | 35,7±4,4 | 2,0±0,3 | 6,28±1,06 | 3,9±0,5 |
| | 3 | 14±6 | 7,7±0,9 | 2,4±0,3 | 4,8±2,8 | 4,5±0,5 | 187±32 | 183±12 | 4,0±0,4 | 468±59 | 2011±138 | 3,2±0,2 | 24,3±2,2 | 1,8±0,2 | 5,5±0,7 | 2,6±0,3 |
| Astrophysic T.1 | 1 | 68±11 | 21,2±3,7 | 138±11 | 7,0±9,7 | 66±5 | 2408±232 | 1529±127 | 34,8±3,1 | 2680±273 | 5485±497 | 33,4±3,2 | 249±23 | 44,9±4,5 | 55,7±5,3 | 123±10 |
| | 2 | 65±13 | 21,5±2,4 | 62,1±5,3 | 23,8±5,8 | 24,5±2,2 | 1154±116 | 557±48 | 10,3±1,0 | 2125±199 | 2825±305 | 4,4±1,1 | 92,2±9,0 | 14,2±1,4 | 25,6±2,8 | 53,5±4,8 |
| | 3 | 66±8 | 21,3±2,2 | 5,5±1,2 | 15,4±5,6 | 2,9±1,5 | 238±124 | 235±41 | 5,3±1,2 | 680±204 | 638±275 | 16,8±2,5 | 27,0±6,4 | 10,2±5,3 | 5,3±2,8 | 23,5±11,5 |
| Astrophysic T.2 | 1 | 149±15 | 46,2±3,4 | 36,0±2,4 | 58,1±7,2 | 45±3 | 2672±187 | 3621±256 | 22,6±1,6 | 2403±169 | 5804±401 | 27,1±1,9 | 170±12 | 21,9±1,8 | 64,9±5,3 | 96,8±7,0 |
| | 2 | 59±13 | 11,3±1,8 | 9,0±1,1 | 13,6±5,0 | 3,2±0,7 | 91±50 | 81±13 | 0,24±0,33 | 124±64 | 394±135 | 3,7±1,0 | 3,4±1,7 | 3,6±0,5 | 10,7±1,9 | 11,6±1,7 |

**Table S2.** Major and trace elements in Antarctic aerosol expressed as metal atmospheric concentration, standard deviations in parenthesis (Dome C, Concordia station, austral summer 2005-06).

| Site | n. | Major elements (ng m$^{-3}$) | | | | | Trace elements (pg m$^{-3}$) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Na | Mg | Al | Ca | Fe | Ti | Mn | Co | Ni | Zn | As | Mo | La | Ce | V |
| Concordia | 1 | 22±3 | 3,9±0,5 | 5,0±0,5 | 5,2±1,1 | 4,2±0,4 | 64±13 | 306±32 | 3,2±0,4 | 728±75 | 1146±156 | 5,6±0,7 | 24±3 | 1,3±0,2 | 2,1±0,3 | 1,8±0,3 |
| | 2 | 13±3 | 3,4±0,4 | 3,2±0,3 | 1,9±1,0 | 2,3±0,3 | 18±11 | 220±23 | 1,3±0,2 | 341±39 | 714±85 | 3,6±0,5 | 10±1 | 0,6±0,1 | 1,8±0,3 | 1,1±0,2 |
| | 3 | 6±2 | 3,0±0,4 | 0,94±0,13 | 1,9±1,1 | 1,8±0,2 | 73±14 | 72±8 | 1,6±0,2 | 184±28 | 786±83 | 1,3±0,1 | 9,5±1,2 | 0,7±0,1 | 1,9±0,2 | 1,0±0,1 |
| Astrophysic T.1 | 1 | 7±1 | 2,3±0,4 | 15±1 | 0,74±1,03 | 7,0±0,7 | 256±29 | 162±17 | 3,7±0,4 | 284±34 | 582±64 | 3,5±0,4 | 26±3 | 4,8±0,6 | 6,1±0,7 | 13±1 |
| | 2 | 12±2 | 4,1±0,5 | 12±1 | 4,5±1,1 | 4,6±0,5 | 218±25 | 105±11 | 2,0±0,2 | 402±43 | 534±64 | 0,8±0,2 | 17±2 | 2,7±0,3 | 4,8±0,6 | 10±1 |
| | 3 | 10±1 | 3,2±0,3 | 0,49±0,09 | 2,6±0,8 | 0,26±0,13 | 21±11 | 21±3 | 0,47±0,11 | 60±17 | 57±24 | 1,5±0,2 | 2,4±0,5 | 0,9±0,5 | 0,5±0,2 | 2±1 |
| Astrophysic T.2 | 1 | 17±2 | 5,4±0,6 | 4,2±0,4 | 6,8±1,0 | 5,8±0,4 | 312±32 | 422±44 | 2,8±0,2 | 343±28 | 677±69 | 3,2±0,3 | 22±2 | 2,6±0,3 | 7,6±0,8 | 11±1 |
| | 2 | 9±2 | 1,8±0,3 | 1,4±0,2 | 2,1±0,8 | 0,5±0,1 | 14±8 | 13±2 | 0,04±0,05 | 19±10 | 62±21 | 0,6±0,2 | 0,5±0,3 | 0,6±0,1 | 1,7±0,3 | 2,0±0,2 |

**Table S3.** Mean values of filter blank for each element, referred to 1/8 filter and a dilution to 100 ml

| | | |
|---|---|---|
| Major elements (µg 100 ml$^{-1}$) | Na | 23,87±4,82 |
| | Ca | 11,66±2,48 |
| | Mg | 5,89±0,62 |
| | Fe | 1,54±0,32 |
| | Al | 0,62±0,19 |
| Trace elements (ng 100 ml$^{-1}$) | Ni | 360±30 |
| | Zn | 400±60 |
| | As | b.d.l. |
| | Ti | 198±27 |
| | Mn | 32,8±4,7 |
| | Co | 0,98±0,17 |
| | Mo | 6,5±0,9 |
| | V | 0,9±0,2 |
| | La | 0,3±0,1 |
| | Ce | 0,8±0,6 |

## ERICHMENT FACTOR

**Table S4.** Crustal enrichment factor

| | Mg | Ca | Ti | Mn | Co | Ni | Zn | As | Mo | La | Fe | Cd | Pb | Cu | V | Ce |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C.1 | 4 | 3 | 0 | 9 | 4 | 614 | 345 | 44 | 272 | 1 | 2 | 476 | 57 | 2631 | 1 | 1 |
| C.2 | 6 | 2 | 0 | 10 | 3 | 451 | 337 | 45 | 176 | 0 | 2 | 96 | 45 | 1892 | 1 | 1 |
| C.3 | 18 | 5 | 2 | 11 | 11 | 815 | 1252 | 53 | 562 | 2 | 5 | 1619 | 214 | 2079 | 2 | 2 |
| A 1.1 | 1 | 0 | 0 | 2 | 2 | 80 | 59 | 9 | 99 | 1 | 1 | 36 | 15 | 773 | 1 | 0 |
| A 1.2 | 2 | 1 | 0 | 1 | 1 | 143 | 68 | 3 | 82 | 1 | 1 | 16 | 9 | 92 | 1 | 0 |
| A 1.3 | 37 | 14 | 1 | 6 | 7 | 516 | 173 | 119 | 272 | 4 | 1 | 140 | 112 | 1555 | 6 | 1 |
| A 2.1 | 7 | 4 | 2 | 15 | 4 | 340 | 240 | 29 | 288 | 1 | 3 | 177 | 26 | 129 | 4 | 2 |
| A 2.2 | 7 | 4 | 0 | 1 | 0 | 57 | 65 | 16 | 21 | 1 | 1 | 108 | 48 | 104 | 2 | 1 |

**Table S5**. Marine enrichment factors

| | Mg | Ca | Ti | Mn | Co | Ni | Zn | As | Mo | La | Fe | Cd | Pb | Cu | V | Ce |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C.1 | 1 | 6 | 31257 | 375493 | 4016 | 54082 | 112302 | 1064 | 1191 | 225973 | 601362 | 13813 | 1012947 | 1307028 | 462 | 866436 |
| C.2 | 2 | 4 | 15448 | 463539 | 2900 | 43571 | 120314 | 1179 | 847 | 164983 | 559091 | 3066 | 871164 | 1030409 | 492 | 1239617 |
| C.3 | 4 | 9 | 140877 | 344990 | 7707 | 53515 | 303350 | 947 | 1833 | 470958 | 997661 | 34976 | 2821379 | 769467 | 1010 | 3114534 |
| A 1.1 | 3 | 3 | 383992 | 609528 | 14214 | 64760 | 174939 | 2048 | 3965 | 2471683 | 3095135 | 9564 | 2504772 | 3506680 | 10397 | 7663015 |
| A 1.2 | 3 | 10 | 192804 | 232519 | 4444 | 53797 | 94397 | 280 | 1540 | 820624 | 1201890 | 2010 | 678044 | 196534 | 4705 | 3560590 |
| A 1.3 | 3 | 7 | 23563 | 58200 | 1356 | 10198 | 12621 | 641 | 267 | 346471 | 84340 | 911 | 445409 | 173215 | 1226 | 439400 |
| A 2.1 | 3 | 10 | 193276 | 654871 | 4491 | 32225 | 83969 | 755 | 1358 | 546478 | 1060065 | 5525 | 496158 | 68911 | 3684 | 3913297 |
| A 2.2 | 2 | 6 | 16636 | 37004 | 111 | 3418 | 14343 | 257 | 62 | 223749 | 173595 | 2109 | 579979 | 34799 | 1110 | 1629508 |

## PRINCIPAL COMPONENT ANALYSIS

**Table S6.** Variance table

| Component | Eigenvalue | Cumulative Variance | Percent | Cumulative |
|---|---|---|---|---|
| 1 | 9,4456 | 9,4456 | 0,5248 | 0,5248 |
| 2 | 4,2580 | 13,7036 | 0,2366 | 0,7613 |
| 3 | 2,7775 | 16,4810 | 0,1543 | 0,9156 |
| 4 | 0,6904 | 17,1714 | 0,0384 | 0,9540 |
| 5 | 0,4531 | 17,6245 | 0,0252 | 0,9791 |
| 6 | 0,2598 | 17,8843 | 0,0144 | 0,9936 |
| 7 | 0,1157 | 18,0000 | 0,0064 | 1,0000 |

**Table S7.** Scores of the first three components

|  | Component 1 | Component 2 | Component 3 |
|---|---|---|---|
| C 1 | 3,5113 | 3,8403 | -0,3468 |
| C 2 | -0,8723 | 1,3987 | -0,1720 |
| C 3 | -1,6294 | 1,0081 | -0,8136 |
| A 1.1 | 2,9786 | -2,5648 | -2,9300 |
| A 1.2 | 0,8239 | -2,0041 | 0,8258 |
| A 1.3 | -3,7035 | -0,1214 | 0,5119 |
| A 2.1 | 3,0853 | -1,1416 | 3,0155 |
| A 2.2 | -4,1938 | -0,4153 | -0,0908 |

**Table S8.** Loadings of the first three components

| Element | Component 1 | Compnent 2 | Component 3 |
|---|---|---|---|
| Na | 0,1870 | 0,2490 | 0,2954 |
| Mg | 0,1790 | 0,0429 | 0,4632 |
| Al | 0,2067 | -0,2705 | -0,2319 |
| Ca | 0,1608 | 0,0778 | 0,4865 |
| Ti | 0,2329 | -0,3102 | 0,1265 |
| V | 0,2043 | -0,3750 | 0,0310 |
| Mn | 0,2632 | 0,1024 | 0,2470 |
| Co | 0,3153 | -0,0250 | -0,1213 |
| Ni | 0,2643 | 0,2288 | 0,0233 |
| Zn | 0,2446 | 0,2594 | -0,0509 |
| As | 0,2371 | 0,2529 | -0,0895 |
| Mo | 0,3217 | -0,0377 | -0,0707 |

| Element | Component 1 | Compnent 2 | Component 3 |
|---|---|---|---|
| La | 0,2206 | -0,3217 | -0,1654 |
| Ce | 0,2363 | -0,2947 | 0,1295 |
| Fe | 0,3009 | -0,1779 | -0,0490 |
| Cd | 0,1628 | 0,3469 | -0,0791 |
| Pb | 0,2163 | 0,2203 | -0,3278 |
| Cu | 0,2050 | 0,1818 | -0,3724 |

## VARIMAX ROTATION

**Table S9.** Factor scores

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| C 1 | -0,6138 | 1,9789 | 0,7207 |
| C 2 | -0,6799 | 0,2926 | -0,0523 |
| C 3 | -0,6565 | 0,1967 | -0,5370 |
| A 1.1 | 1,7641 | 0,6439 | -1,4313 |
| A 1.2 | 0,8434 | -0,6669 | 0,3233 |
| A 1.3 | -0,7824 | -0,9372 | -0,2437 |
| A 2.1 | 0,8646 | -0,5481 | 1,8815 |
| A 2.2 | -0,7396 | -0,9600 | -0,6611 |

**Table S10.** Rotated factor matrix

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| Na | -0,0620 | 0,4561 | 0,7905 |
| Mg | 0,2069 | 0,0459 | 0,9282 |
| Al | 0,8776 | 0,2293 | -0,2049 |
| Ca | 0,1119 | 0,0376 | 0,9557 |
| Ti | 0,9231 | -0,0467 | 0,3351 |
| V | 0,9833 | -0,1122 | 0,1277 |
| Mn | 0,3266 | 0,4518 | 0,7469 |
| Co | 0,6977 | 0,6711 | 0,2126 |
| Ni | 0,1769 | 0,7888 | 0,4805 |
| Zn | 0,1041 | 0,8471 | 0,3611 |
| As | 0,1063 | 0,8538 | 0,2917 |
| Mo | 0,7206 | 0,6282 | 0,2889 |
| La | 0,9717 | 0,1390 | -0,1141 |
| Ce | 0,9055 | -0,0225 | 0,3512 |
| Fe | 0,8901 | 0,3904 | 0,2275 |
| Cd | -0,1902 | 0,8234 | 0,2568 |
| Pb | 0,1600 | 0,9547 | -0,0998 |
| Cu | 0,2048 | 0,9175 | -0,1979 |

## HIERARCHICAL CLUSTER ANALYSIS

**Table S11.** Cluster

| | Cases | Percentage | Within SSQ | Average Distance | Minimum | Maximum |
|---|---|---|---|---|---|---|
| Cluster 1 | 4 | 22,22% | 5,0014 | 1,1136 | 0,9613 | 1,2226 |
| Cluster 2 | 8 | 44,44% | 9,0656 | 1,0342 | 0,4998 | 1,3642 |
| Cluster 3 | 6 | 33,33% | 8,8108 | 1,2011 | 0,9577 | 1,4089 |

**Table S12.** Cluster centroids

| | Cluster 1 | Cluster 2 | Cluster 3 | Overall |
|---|---|---|---|---|
| C 1 | 1,0609 | 0,0551 | 1,7719 | 0,8509 |
| C 2 | -0,0250 | -0,5897 | 0,1530 | -0,2166 |
| C 3 | -0,6981 | -0,5770 | 0,0911 | -0,3812 |
| A 1.1 | -0,7771 | 1,4621 | 0,4417 | 0,6244 |
| A 1.2 | 0,2157 | 0,6397 | -0,4054 | 0,1971 |
| A 1.3 | -0,4763 | -0,9436 | -0,9536 | -0,8431 |
| A 2.1 | 1,5775 | 0,9107 | -0,0554 | 0,7368 |
| A 2.2 | -0,8776 | -0,9574 | -1,0432 | -0,9683 |

**Table S13.** Distance between centroids

| | Cluster 1 | Cluster 2 | Cluster 3 |
|---|---|---|---|
| Cluster 1 | 0,0000 | 2,6848 | 2,4400 |
| Cluster 2 | 2,6848 | 0,0000 | 2,6494 |
| Cluster 3 | 2,4400 | 2,6494 | 0,0000 |

## CORRELATION MATRIX

Correlation analysis is a bivariate technique for the measurement of the degree of association between two variables. The correlation matrix between variables was calculated in order to study the relationship between elements in atmospheric particulate matter. The values of correlation coefficients are useful in order to make hypotheses on the sources emitting these elements in the atmosphere.

The Table S16 reports correlation matrix between elements and in bold are reported higher correlation coefficients between elements. We can observe three main group with high correlation:

- Na, Ca, Mg
- Mo, Co, Al, La, Ti, Fe, V, Ce
- Zn, Ni, Cd, Pb, Cu

These groups show a high accordance with the three main groups of elements just determined in PCA and HCA.

**Table S14.** Correlation matrix of atmospheric concentrations of samples collected at Dome C during summer campaign 2005 – 06.

| | **Na** | **Mg** | **Al** | **Ca** | **Ti** | **Mn** | **Co** | **Ni** | **Zn** | **As** | **Mo** | **La** | **Fe** | **Cd** | **Pb** | **Cu** | **V** | **Ce** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Na** | **1** | 0.66777 | -0.02933 | **0.81041** | 0.12421 | 0.76399 | 0.39470 | 0.79147 | 0.54330 | 0.68534 | 0.46572 | -0.05815 | 0.29949 | 0.48588 | 0.27152 | 0.34383 | 0.00635 | 0.16952 |
| **Mg** | | **1** | 0.00623 | **0.87719** | 0.50904 | 0.76052 | 0.38896 | 0.53130 | 0.45713 | 0.31279 | 0.45216 | 0.09671 | 0.40698 | 0.23011 | -0.00362 | -0.12675 | 0.30734 | 0.48363 |
| **Al** | | | **1** | -0.05153 | 0.68412 | 0.15656 | 0.68509 | 0.36197 | 0.20401 | 0.19161 | 0.72155 | **0.90732** | **0.81972** | -0.10212 | 0.34130 | 0.45640 | **0.81255** | 0.65867 |
| **Ca** | | | | **1** | 0.42195 | 0.69116 | 0.30256 | 0.54121 | 0.34967 | 0.26794 | 0.38924 | 0.02510 | 0.32299 | 0.31521 | -0.03303 | -0.13213 | 0.23949 | 0.41540 |
| **Ti** | | | | | **1** | 0.52913 | 0.70208 | 0.24881 | 0.21396 | 0.11589 | 0.73570 | **0.84550** | **0.88015** | -0.05238 | 0.10991 | 0.03804 | **0.95217** | **0.98028** |
| **Mn** | | | | | | **1** | 0.69279 | 0.69413 | 0.67788 | 0.74684 | 0.71849 | 0.28000 | 0.65139 | 0.43364 | 0.38949 | 0.36137 | 0.35979 | 0.59924 |
| **Co** | | | | | | | **1** | 0.72210 | 0.72353 | 0.70704 | **0.98842** | 0.75318 | **0.92820** | 0.51127 | 0.74852 | 0.70302 | 0.63845 | 0.69657 |
| **Ni** | | | | | | | | **1** | **0.86633** | 0.78632 | 0.76675 | 0.22300 | 0.57079 | 0.68162 | 0.70429 | 0.67918 | 0.14643 | 0.25778 |
| **Zn** | | | | | | | | | **1** | 0.74239 | 0.71357 | 0.13001 | 0.51441 | **0.82410** | **0.84569** | 0.63860 | 0.03098 | 0.23375 |
| **As** | | | | | | | | | | **1** | 0.68334 | 0.21184 | 0.49657 | 0.61846 | 0.73100 | **0.84315** | 0.05418 | 0.17233 |
| **Mo** | | | | | | | | | | | **1** | 0.75758 | **0.94992** | 0.46866 | 0.69143 | 0.66174 | 0.67583 | 0.73371 |
| **La** | | | | | | | | | | | | **1** | **0.88556** | -0.09957 | 0.28701 | 0.37397 | **0.93441** | **0.81535** |
| **Fe** | | | | | | | | | | | | | **1** | 0.20478 | 0.49320 | 0.49332 | **0.85804** | **0.88813** |
| **Cd** | | | | | | | | | | | | | | **1** | **0.82846** | 0.56747 | -0.24554 | -0.05983 |
| **Pb** | | | | | | | | | | | | | | | **1** | **0.86848** | 0.03193 | 0.11661 |
| **Cu** | | | | | | | | | | | | | | | | **1** | 0.08474 | 0.06679 |
| **V** | | | | | | | | | | | | | | | | | **1** | **0.931386** |
| **Ce** | | | | | | | | | | | | | | | | | | **1** |

## POSITIVE MATRIX FACTORIZATION

**Table S15.** Statistic results of positive matrix factorization

| Species | Category | $r^2$ | Intercept | Intercept SE | Slope | Slope SE | SE | Normal residual |
|---|---|---|---|---|---|---|---|---|
| Na | Strong | 0,99693 | -379,01292 | 306,66214 | 1,03624 | 0,02347 | 337,79955 | Yes |
| Mg | Weak | 0,55783 | 93,56963 | 1155,20891 | 0,90250 | 0,32803 | 971,63041 | Yes |
| Al | Weak | 0,66410 | 1270,93928 | 704,13188 | 0,33914 | 0,09847 | 1368,44779 | Yes |
| Ca | Strong | 0,82355 | 1185,32744 | 462,49708 | 0,65256 | 0,12331 | 671,21807 | Yes |
| Ti | Strong | 0,93043 | 0,82288 | 17,76198 | 0,95869 | 0,10702 | 34,05993 | Yes |
| V | Strong | 0,99285 | -0,08336 | 0,24466 | 0,98014 | 0,03395 | 0,46958 | Yes |
| Mn | Weak | 0,56479 | 49,71057 | 29,09834 | 0,38077 | 0,13645 | 52,04698 | Yes |
| Co | Strong | 0,98388 | -0,00564 | 0,11643 | 0,99529 | 0,05201 | 0,17757 | Yes |
| Ni | Weak | 0,87442 | 43,19178 | 43,55963 | 0,77934 | 0,12057 | 71,01955 | Yes |
| Zn | Weak | 0,84324 | -18,64048 | 114,31497 | 0,97740 | 0,17204 | 166,29456 | Yes |
| As | Weak | 0,78751 | 0,48318 | 0,41599 | 0,65155 | 0,13817 | 0,64351 | Yes |
| Mo | Strong | 0,99692 | 0,01683 | 0,38133 | 0,99889 | 0,02265 | 0,59290 | Yes |
| La | Strong | 0,85594 | 0,17612 | 0,29927 | 0,79651 | 0,13340 | 0,52414 | Yes |
| Ce | Weak | 0,92426 | 0,03361 | 0,46254 | 0,97230 | 0,11363 | 0,75986 | Yes |
| Fe | Strong | 0,99394 | 6,99147 | 128,19935 | 0,99773 | 0,03179 | 208,52768 | Yes |
| Cd | Weak | 0,73864 | 0,23617 | 0,16696 | 0,49663 | 0,12060 | 0,33858 | Yes |
| Pb | Weak | 0,61671 | 2,88817 | 9,21020 | 0,78193 | 0,25166 | 11,80367 | Yes |
| Cu | Weak | 0,52022 | 124,44655 | 133,75560 | 0,28357 | 0,11117 | 281,61630 | Yes |

## ELEMENTAL MEASUREMENTS ON SOLUTIONS

The samples A 2.1 and A 2.2 have reported two different values on the first column: the first is related to a 1/12 of filter and the second one is reported to 1/8, as all other samples.

**Table S16.** Na measurements on solution (subtracted blank 238,7±48,2 µg 100 ml$^{-1}$)

| Sample | Concentration on 6 ml solution µg l$^{-1}$ | Concentration on 100 ml µg l$^{-1}$ | Concentration on 100 ml blank subtracted µg l$^{-1}$ | Aerosol mass mg | Mass fraction mg g$^{-1}$ | Actual air volume m$^{3}$ | Atmospheric conc. ng m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 1347,22±39,20 | 808,33±23,52 | 569,63±53,63 | 9,20±1,43 | 50±9 | 20683±2068 | 22±3 |
| C 2 | 934,27±56,01 | 560,56±33,61 | 321,86±58,76 | 5,65±0,52 | 46±9 | 20103±2010 | 13±3 |
| C 3 | 607,79±8,75 | 364,68±5,25 | 125,98±48,49 | 7,04±0,42 | 14±1 | 17958±1796 | 6±2 |
| A 1.1 | 688,39±39,41 | 413,03±23,65 | 174,33±53,69 | 2,06±0,16 | 68±11 | 19413±1943 | 7±1 |
| A 1.2 | 446,01±12,24 | 535,21±14,69 | 296,51±50,39 | 3,67±0,31 | 65±12 | 19428±1943 | 12±2 |
| A 1.3 | 25232,70±648,48 | 15139,62±389,09 | 14900,92±392,06 | 1,78±0,26 | 66±8 | 20037±2004 | 10±1 |
| A 2.1 | 528,65±12,45 – 792,98±18,67 | 951,57±22,41 | 712,87±53,15 | 3,82±0,25 | 149±15 | 32752±3275 | 17±2 |
| A 2.2 | 623,72±31,72 – 935,58±47,57 | 561,35±28,54 | 322,65±56,02 | 4,35±0,52 | 59±13 | 27727±2773 | 9±2 |

**Table S17.** Mg measurements on solution (subtracted blank 58,9±6,2 µg 100 ml$^{-1}$)

| Sample | Concentration on 6 ml solution µg l$^{-1}$ | Concentration on 100 ml µg l$^{-1}$ | Concentration on 100 ml blank subtracted µg l$^{-1}$ | Aerosol mass mg | Mass fraction mg g$^{-1}$ | Actual air volume m$^3$ | Atmospheric conc. ng m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 264,54±2,76 | 158,73±1,66 | 99,85±6,38 | 9,20±1,43 | 8,7±1,5 | 20683±2068 | 3,9±0,5 |
| C 2 | 240,20±6,81 | 144,12±4,09 | 85,25±7,39 | 5,65±0,52 | 12,1±1,5 | 20103±2010 | 3,4±0,4 |
| C 3 | 210,93±3,63 | 126,56±2,18 | 67,69±6,53 | 7,04±0,42 | 7,7±0,9 | 17958±1796 | 3,0±0,4 |
| A 1.1 | 189,20±10,05 | 113,52±6,03 | 54,65±8,62 | 2,06±0,16 | 21,2±3,7 | 19413±1943 | 2,3±0,4 |
| A 1.2 | 131,26±3,05 | 157,52±3,66 | 98,64±7,17 | 3,67±0,31 | 21,5±2,4 | 19428±1943 | 4,1±0,5 |
| A 1.3 | 280,34±4,64 | 168,21±2,78 | 109,33±6,76 | 1,78±0,26 | 21,4±2,2 | 20037±2004 | 3,2±0,3 |
| A 2.1 | 155,25±2,03 – 232,87±3,05 | 279,44±3,66 | 220,57±7,17 | 3,82±0,25 | 46,2±3,4 | 32752±3275 | 5,4±0,6 |
| A 2.2 | 133,57±2,97 – 200,36±4,46 | 120,22±2,67 | 61,34±6,72 | 4,35±0,52 | 11,3±1,8 | 27727±2773 | 1,8±0,3 |

**Table S18.** Al measurements on solution (subtracted blank 6,2±1,9 μg 100 ml$^{-1}$)

| Sample | Concentration on 6 ml solution μg l$^{-1}$ | Concentration on 100 ml μg l$^{-1}$ | Concentration on 100 ml blank subtracted μg l$^{-1}$ | Aerosol mass mg | Mass fraction mg g$^{-1}$ | Actual air volume m$^3$ | Atmospheric conc. ng m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 223,24±6,81 | 133,94±4,09 | 127,74±4,52 | 9,20±1,43 | 11,1±1,8 | 20683±2068 | 4,9±0,5 |
| C 2 | 142,24±1,56 | 85,34±0,94 | 79,14±2,15 | 5,65±0,52 | 11,2±1,1 | 20103±2010 | 3,1±0,3 |
| C 3 | 45,43±1,39 | 27,26±0,83 | 21,05±2,10 | 7,04±0,42 | 2,4±0,3 | 17958±1796 | 0,9±0,1 |
| A 1.1 | 605,60±7,27 | 363,36±4,36 | 357,16±4,77 | 2,06±0,16 | 138,7±10,9 | 19413±1943 | 14,7±1,5 |
| A 1.2 | 242,39±3,64 | 290,87±4,36 | 284,66±4,77 | 3,67±0,31 | 62,1±5,3 | 19428±1943 | 11,7±1,2 |
| A 1.3 | 30,69±0,34 | 18,42±0,20 | 12,21±1,94 | 1,78±0,26 | 5,5±1,2 | 20037±2004 | 0,5±0,1 |
| A 2.1 | 98,94±0,78 – 148,42±1,17 | 178,10±1,41 | 171,89±2,39 | 3,82±0,25 | 36,0±2,4 | 32752±3275 | 4,2±0,4 |
| A 2.2 | 61,20±0,85 – 91,81±1,28 | 55,08±0,77 | 48,88±2,08 | 4,35±0,52 | 9,0±1,1 | 27727±2773 | 1,4±0,2 |

**Table S19.** Ca measurements on solution (subtracted blank 116,6±24,8 μg 100 $ml^{-1}$)

| Sample | Concentration on 6 ml solution μg $l^{-1}$ | Concentration on 100 ml μg $l^{-1}$ | Concentration on 100 ml blank subtracted μg $l^{-1}$ | Aerosol mass mg | Mass fraction mg $g^{-1}$ | Actual air volume $m^3$ | Atmospheric conc. ng $m^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 419,85±12,60 | 251,91±7,56 | 135,31±25,95 | 9,20±1,43 | 11,8±2,9 | 20683±2068 | 5,2±1,1 |
| C 2 | 273,22±3,88 | 163,93±2,33 | 47,33±24,93 | 5,65±0,52 | 6,7±3,6 | 20103±2010 | 1,9±1,0 |
| C 3 | 264,42±2,70 | 158,65±1,62 | 42,05±24,87 | 7,04±0,42 | 4,8±2,8 | 17958±1796 | 1,9±1,1 |
| A 1.1 | 224,28±2,58 | 134,57±1,55 | 17,97±24,87 | 2,06±0,16 | 7,0±9,7 | 19413±1943 | 0,7±1,0 |
| A 1.2 | 188,21±2,22 | 225,85±2,67 | 109,25±24,96 | 3,67±0,31 | 23,8±5,8 | 19428±1943 | 4,5±1,1 |
| A 1.3 | 989,97±21,78 | 593,98±13,07 | 477,38±28,05 | 1,78±0,26 | 15,4±5,6 | 20037±2004 | 2,6±0,8 |
| A 2.1 | 218,88±8,49 – 328,32±14,74 | 393,98±15,29 | 277,38±29,15 | 3,82±0,25 | 58,1±7,2 | 32752±3275 | 6,8±1,0 |
| A 2.2 | 211,54±8,76 – 317,31±13,14 | 190,38±7,88 | 73,78±26,04 | 4,35±0,52 | 13,6±5,1 | 27727±2773 | 2,1±0,8 |

**Table S20.** Fe measurements on solution (subtracted blank 15,4±3,2 μg 100 ml$^{-1}$)

| Sample | Concentration on 6 ml solution μg l$^{-1}$ | Concentration on 100 ml μg l$^{-1}$ | Concentration on 100 ml blank subtracted μg l$^{-1}$ | Aerosol mass mg | Mass fraction mg g$^{-1}$ | Actual air volume m$^3$ | Atmospheric conc. ng m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 205,45±3,94 | 123,27±2,37 | 107,85±3,97 | 9,20±1,43 | 9,4±1,5 | 20683±2068 | 4,2±0,4 |
| C 2 | 120,13±2,38 | 72,08±1,43 | 56,66±3,49 | 5,65±0,52 | 8,0±0,9 | 20103±2010 | 2,3±0,3 |
| C 3 | 91,67±1,86 | 55,00±1,12 | 39,58±3,37 | 7,04±0,42 | 4,5±0,5 | 17958±1796 | 1,8±0,2 |
| A 1.1 | 308,89±3,61 | 185,34±2,17 | 169,92±3,85 | 2,06±0,16 | 66,0±5,3 | 19413±1943 | 7,0±0,7 |
| A 1.2 | 106,36±0,58 | 127,63±0,70 | 112,21±3,26 | 3,67±0,31 | 24,5±2,2 | 19428±1943 | 4,6±0,5 |
| A 1.3 | 36,44±0,70 | 21,87±0,42 | 6,45±3,21 | 1,78±0,26 | 2,9±1,5 | 20037±2004 | 0,3±0,1 |
| A 2.1 | 605,48±2,79 – 908,22±4,18 | 1089,86±5,01 | 1074,44±5,94 | 3,82±0,25 | 45,2±2,9 | 32752±3275 | 5,8±0,4 |
| A 2.2 | 36,72±0,91 – 55,09±1,37 | 33,05±0,82 | 14,64±3,29 | 4,35±0,52 | 3,2±0,7 | 27727±2773 | 0,5±0,1 |

**TableS21.** Ti measurements on solution (subtracted blank 1,98±0,27 µg 100 ml$^{-1}$)

| Sample | Concentration on 6 ml solution µg l$^{-1}$ | Concentration on 100 ml µg l$^{-1}$ | Concentration on 100 ml blank subtracted µg l$^{-1}$ | Aerosol mass mg | Mass fraction µg g$^{-1}$ | Actual air volume m$^3$ | Atmospheric conc. pg m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 6,04±0,16 | 3,62±0,10 | 1,65±0,28 | 9,20±1,43 | 143,4±33,1 | 20683±2068 | 63,8±12,6 |
| C 2 | 4,06±0,07 | 2,44±0,04 | 0,46±0,27 | 5,65±0,52 | 65,2±38,4 | 20103±2010 | 18,3±10,8 |
| C 3 | 6,03±0,02 | 3,62±0,01 | 1,64±0,26 | 7,04±0,42 | 186,8±32,1 | 17958±1796 | 73,23±13,9 |
| A 1.1 | 13,63±0,39 | 8,18±0,24 | 6,20±0,35 | 2,06±0,16 | 2407,8±232,1 | 19413±1943 | 255,51±29,4 |
| A 1.2 | 6,06±0,09 | 7,27±0,11 | 5,29±0,29 | 3,67±0,31 | 1154,1±115,9 | 19428±1943 | 218,0±24,8 |
| A 1.3 | 1,43±0,02 | 0,86±0,01 | 0,53±0,27 | 1,78±0,26 | 238,2±124,1 | 20037±2004 | 21,2±10,8 |
| A 2.1 | 8,19±0,09 – 12,28±0,14 | 14,73±0,17 | 12,76±0,31 | 3,82±0,25 | 2671,9±186,7 | 32752±3275 | 311,6±32,1 |
| A 2.2 | 2,75±0,03 – 4,12±0,05 | 2,47±0,03 | 0,50±0,27 | 4,35±0,52 | 91,4±50,2 | 27727±2773 | 14,3±7,8 |

**Table S22.** Mn measurements on solution (subtracted blank 0,328±0,047 µg 100 ml$^{-1}$)

| Sample | Concentration on 6 ml solution µg l$^{-1}$ | Concentration on 100 ml µg l$^{-1}$ | Concentration on 100 ml blank subtracted µg l$^{-1}$ | Aerosol mass mg | Mass fraction µg g$^{-1}$ | Actual air volume m$^3$ | Atmospheric conc. pg m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 13,75±0,32 | 8,25±0,19 | 7,92±0,20 | 9,20±1,43 | 688,9±108,5 | 20683±2068 | 306,4±31,6 |
| C 2 | 9,76±0,29 | 5,85±0,17 | 5,53±0,18 | 5,65±0,52 | 782,5±76,4 | 20103±2010 | 219,9±23,1 |
| C 3 | 3,23±0,04 | 1,94±0,02 | 1,61±0,05 | 7,04±0,42 | 183,0±12,4 | 17958±1796 | 71,7±7,5 |
| A 1.1 | 7,11±0,17 | 4,26±0,10 | 3,94±0,11 | 2,06±0,16 | 1528,8±126,8 | 19413±1943 | 162,2±16,9 |
| A 1.2 | 2,40±0,01 | 2,88±0,01 | 2,55±0,05 | 3,67±0,31 | 556,7±48,2 | 19428±1943 | 105,2±10,7 |
| A 1.3 | 1,42±0,01 | 0,85±0,01 | 0,52±0,05 | 1,78±0,26 | 235,3±40,5 | 20037±2004 | 20,9±2,8 |
| A 2.1 | 9,79±0,26 – 14,68±0,39 | 17,62±0,47 | 17,29±0,47 | 3,82±0,25 | 3621,3±256,4 | 32752±3275 | 422,36±43,8 |
| A 2.2 | 0,86±0,01 – 1,28±0,01 | 0,77±0,01 | 0,44±0,05 | 4,35±0,52 | 81,3±13,1 | 27727±2773 | 12,8±1,9 |

**Table S23.** Co measurements on solution (subtracted blank 9,82±1,70 ng 100 $ml^{-1}$)

| Sample | Concentration on 6 ml solution µg $l^{-1}$ | Concentration on 100 ml µg $l^{-1}$ | Concentration on 100 ml blank subtracted µg $l^{-1}$ | Aerosol mass mg | Mass fraction µg $g^{-1}$ | Actual air volume $m^3$ | Atmospheric conc. pg $m^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 0,15±0,01 | 0,092±0,003 | 0,083±0,004 | 9,20±1,43 | 7,18±1,16 | 20683±2068 | 3,20±0,35 |
| C 2 | 0,073±0,002 | 0,044±0,001 | 0,034±0,002 | 5,65±0,52 | 4,77±0,52 | 20103±2010 | 1,34±0,16 |
| C 3 | 0,075±0,004 | 0,045±0,002 | 0,035±0,003 | 7,04±0,42 | 3,99±0,41 | 17958±1796 | 1,56±0,20 |
| A 1.1 | 0,17±0,01 | 0,099±0,004 | 0,090±0,004 | 2,06±0,16 | 34,76±3,13 | 19413±1943 | 3,69±0,40 |
| A 1.2 | 0,048±0,002 | 0,057±0,002 | 0,048±0,003 | 3,67±0,31 | 10,37±1,05 | 19428±1943 | 1,96±0,22 |
| A 1.3 | 0,036±0,001 | 0,022±0,001 | 0,012±0,002 | 1,78±0,26 | 5,34±1,16 | 20037±2004 | 0,47±0,09 |
| A 2.1 | 0,83±0,06 – 1,25±0,09 | 1,50±0,11 | 1,487±0,108 | 3,82±0,25 | 22,57±1,65 | 32752±3275 | 2,82±0,23 |
| A 2.2 | 0,012±0,001 – 0,019±0,001 | 0,011±0,001 | 0,001±0,002 | 4,35±0,52 | 0,24±0,33 | 27727±2773 | 0,037±0,05 |

**Table S24.** Ni measurements on solution (subtracted blank 3,62±0,34 μg 100 $ml^{-1}$)

| Sample | Concentration on 6 ml solution μg $l^{-1}$ | Concentration on 100 ml μg $l^{-1}$ | Concentration on 100 ml blank subtracted μg $l^{-1}$ | Aerosol mass mg | Mass fraction μg $g^{-1}$ | Actual air volume $m^3$ | Atmospheric conc. pg $m^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 37,42±0,47 | 22,45±0,28 | 18,83±0,44 | 9,20±1,43 | 1637±257 | 20683±2068 | 728±75 |
| C 2 | 20,33±0,50 | 12,20±0,30 | 8,57±0,45 | 5,65±0,52 | 1214±129 | 20103±2010 | 341±39 |
| C 3 | 12,91±0,52 | 7,75±0,31 | 4,12±0,46 | 7,04±0,42 | 468±59 | 17958±1796 | 184±28 |
| A 1.1 | 17,54±0,51 | 10,53±0,30 | 6,90±0,45 | 2,06±0,16 | 2680±273 | 19413±1943 | 284±34 |
| A 1.2 | 11,14±0,18 | 13,37±0,21 | 9,75±0,40 | 3,67±0,31 | 2125±199 | 19428±1943 | 401±43 |
| A 1.3 | 8,56±0,35 | 5,14±0,21 | 1,51±0,40 | 1,78±0,26 | 680±204 | 20037±2004 | 60±17 |
| A 2.1 | 68,17±1,85 - 102,26±2,78 | 122,71±3,33 | 119,09±3,35 | 3,82±0,25 | 2403±169 | 32752±3275 | 343±28 |
| A 2.2 | 1,80±0,09 - 2,71±0,14 | 1,62±0,08 | 0,67±0,34 | 4,35±0,52 | 124±64 | 27727±2773 | 19±10 |

**Table S25.** Zn measurements on solution (subtracted blank 4,01±0,57 µg 100 ml$^{-1}$)

| Sample | Concentration on 6 ml solution µg l$^{-1}$ | Concentration on 100 ml µg l$^{-1}$ | Concentration on 100 ml blank subtracted µg l$^{-1}$ | Aerosol mass mg | Mass fraction µg g$^{-1}$ | Actual air volume m$^{3}$ | Atmospheric conc. pg m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 56,06±4,45 | 33,63±2,67 | 29,62±2,73 | 9,20±1,43 | 2576±465 | 20683±2068 | 1146±156 |
| C 2 | 36,58±1,67 | 21,95±1,00 | 17,93±1,15 | 5,65±0,52 | 2539±285 | 20103±2010 | 714±85 |
| C 3 | 36,19±0,33 | 21,71±0,20 | 17,70±0,60 | 7,04±0,42 | 2011±138 | 17958±1796 | 788±83 |
| A 1.1 | 30,23±0,56 | 18,14±0,34 | 14,12±0,66 | 2,06±0,16 | 5485±497 | 19413±1943 | 582±64 |
| A 1.2 | 14,15±0,55 | 16,97±0,66 | 12,96±0,87 | 3,67±0,31 | 2825±305 | 19428±1943 | 534±64 |
| A 1.3 | 9,06 (0,15) | 5,43±0,09 | 1,42 ±0,58 | 1,78±0,26 | 638±275 | 20037±2004 | 57±24 |
| A 2.1 | 17,63±0,13 – 26,44±0,19 | 31,73±0,23 | 27,71±0,61 | 3,82±0,25 | 5804±401 | 32752±3275 | 677±69 |
| A 2.2 | 6,84±0,43 – 10,26±0,65 | 6,16±0,39 | 2,14±0,69 | 4,35±0,52 | 394 ±135 | 27727±2773 | 62±21 |

**Table S26.** As measurements on solution. Blank below detection limit

| Sample | Concentration on 6 ml solution µg l$^{-1}$ | Concentration on 100 ml ng l$^{-1}$ | Aerosol mass mg | Mass fraction µg g$^{-1}$ | Actual air volume m$^{3}$ | Atmospheric conc. pg m$^{-3}$ |
|---|---|---|---|---|---|---|
| C 1 | 0,24±0,02 | 14,6±1,2 | 9,20±1,43 | 12,68±2,22 | 20683±2068 | 5,64±0,72 |
| C 2 | 0,15±0,01 | 9,1±0,9 | 5,65±0,52 | 12,93±1,73 | 20103±2010 | 3,63±0,51 |
| C 3 | 0,048±0,001 | 2,9±0,1 | 7,04±0,42 | 3,27±0,21 | 17958±1796 | 1,28±0,13 |
| A 1.1 | 0,14±0,01 | 8,6±0,5 | 2,06±0,16 | 33,39±3,22 | 19413±1943 | 3,54±0,41 |
| A 1.2 | 0,0032±0,0008 | 2,0±0,5 | 3,67±0,31 | 4,36±1,14 | 19428±1943 | 0,82±0,22 |
| A 1.3 | 0,062±0,001 | 3,7±0,1 | 1,78±0,26 | 16,85±2,48 | 20037±2004 | 1,50±0,15 |
| A 2.1 | 0,072±0,001 - 0,108±0,002 | 13,0±0,3 | 3,82±0,25 | 27,15±1,88 | 32752±3275 | 3,17±0,32 |
| A 2.2 | 0,0021±0,0005 - 0,0032±0,0008 | 2,0±0,5 | 4,35±0,52 | 3,68±1,01 | 27727±2773 | 0,58±0,15 |

**Table S27.** Mo measurements on solution (subtracted blank 0,065±0,009 µg 100 ml$^{-1}$)

| Sample | Concentration on 6 ml solution µg l$^{-1}$ | Concentration on 100 ml µg l$^{-1}$ | Concentration on 100 ml blank subtracted µg l$^{-1}$ | Aerosol mass mg | Mass fraction µg g$^{-1}$ | Actual air volume m$^{3}$ | Atmospheric conc. pg m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 1,16±0,05 | 0,69±0,03 | 0,63±0,03 | 9,20±1,43 | 54,6±8,9 | 20683±2068 | 24,3±2,7 |
| C 2 | 0,53±0,03 | 0,32±0,02 | 0,25±0,02 | 5,65±0,52 | 35,7±4,4 | 20103±2010 | 10,0±1,3 |
| C 3 | 0,47±0,02 | 0,28±0,01 | 0,21±0,01 | 7,04±0,42 | 24,3±2,2 | 17958±1796 | 9,5±1,2 |
| A 1.1 | 1,18±0,05 | 0,71±0,03 | 0,64±0,03 | 2,06±0,16 | 248,6±23,0 | 19413±1943 | 26,4±3,0 |
| A 1.2 | 0,41±0,02 | 0,49±0,02 | 0,42±0,02 | 3,67±0,31 | 92,2±9,0 | 19428±1943 | 17,4±1,9 |
| A 1.3 | 0,21±0,01 | 0,13±0,01 | 0,06±0,01 | 1,78±0,26 | 27,0±6,5 | 20037±2004 | 2,4±0,5 |
| A 2.1 | 2,90±0,10 – 4,36±0,16 | 5,23±0,19 | 5,16±0,19 | 3,82±0,25 | 170,4±12,3 | 32752±3275 | 21,9±1,8 |
| A 2.2 | 0,04±0,001 – 0,06±0,002 | 0,036±0,001 | 0,02±0,01 | 4,35±0,52 | 3,4±1,7 | 27727±2773 | 0,5±0,3 |

**Table S28.** La measurements on solution (subtracted blank 0,003±0,001 μg 100 $ml^{-1}$)

| Sample | Concentration on 6 ml solution μg $l^{-1}$ | Concentration on 100 ml μg $l^{-1}$ | Concentration on 100 ml blank subtracted μg $l^{-1}$ | Aerosol mass mg | Mass fraction μg $g^{-1}$ | Actual air volume $m^3$ | Atmospheric conc. pg $m^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 0,062±0,004 | 0,037±0,003 | 0,035±0,003 | 9,20±1,43 | 3,0±0,5 | 20683±2068 | 1,3±0,2 |
| C 2 | 0,028±0,002 | 0,017±0,001 | 0,014±0,002 | 5,65±0,52 | 2,0±0,3 | 20103±2010 | 0,6±0,1 |
| C 3 | 0,031±0,003 | 0,019±0,002 | 0,016±0,002 | 7,04±0,42 | 1,8±0,2 | 17958±1796 | 0,7±0,1 |
| A 1.1 | 0,197±0,012 | 0,118±0,007 | 0,116±0,007 | 2,06±0,16 | 44,9±4,5 | 19413±1943 | 4,8±0,6 |
| A 1.2 | 0,057±0,002 | 0,068±0,003 | 0,065±0,003 | 3,67±0,31 | 14,2±1,4 | 19428±1943 | 2,7±0,3 |
| A 1.3 | 0,00037±0,0003 | 0,0022±0,0002 | 0,002±0,001 | 1,78±0,26 | 10,2±5,3 | 20037±2004 | 0,9±0,5 |
| A 2.1 | 0,060±0,003 – 0,089±0,004 | 0,1073±0,0047 | 0,105±0,005 | 3,82±0,25 | 21,9±1,8 | 32752±3275 | 2,6±0,3 |
| A 2.2 | 0,025±0,001 – 0,0368±0,001 | 0,0221±0,0009 | 0,019±0,001 | 4,35±0,52 | 3,6±0,5 | 27727±2773 | 0,6±0,1 |

**Table S29.** Ce measurements on solution (subtracted blank 8,2±5,9 ng 100 ml$^{-1}$)

| Sample | Concentration on 6 ml solution µg l$^{-1}$ | Concentration on 100 ml µg l$^{-1}$ | Concentration on 100 ml blank subtracted µg l$^{-1}$ | Aerosol mass mg | Mass fraction µg g$^{-1}$ | Actual air volume m$^3$ | Atmospheric conc. pg m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 0,105±0,005 | 0,063±0,003 | 0,05±0,01 | 9,20±1,43 | 4,8±0,9 | 20683±2068 | 2,1±0,3 |
| C 2 | 0,088±0,003 | 0,053±0,002 | 0,04±0,01 | 5,65±0,52 | 6,3±1,1 | 20103±2010 | 1,8±0,3 |
| C 3 | 1,523±0,044 | 0,91±0,03 | 0,91±0,03 | 7,04±0,42 | 5,5±0,7 | 17958±1796 | 1,9±0,2 |
| A 1.1 | 0,261±0,007 | 0,157±0,004 | 0,15±0,01 | 2,06±0,16 | 57,7±5,3 | 19413±1943 | 6,1±0,7 |
| A 1.2 | 0,105±0,004 | 0,13±0,01 | 0,12±0,01 | 3,67±0,31 | 25,6±2,8 | 19428±1943 | 4,8±0,6 |
| A 1.3 | 0,009±0,001 | 0,0052±0,0004 | 0,012±0,006 | 1,78±0,26 | 5,3±2,8 | 20037±2004 | 0,47±0,24 |
| A 2.1 | 0,177±0,008 – 0,27±0,01 | 0,32±0,01 | 0,31±0,01 | 3,82±0,25 | 64,9±5,3 | 32752±3275 | 7,6±0,8 |
| A 2.2 | 0,074±0,005 – 0,111±0,007 | 0,067±0,004 | 0,06±0,01 | 4,35±0,52 | 10,7±1,9 | 27727±2773 | 1,7±0,3 |

**Table S30.** V measurements on solution (subtracted blank 9,4±2,3 ng 100 ml$^{-1}$)

| Sample | Concentration on 6 ml solution $\mu g\ l^{-1}$ | Concentration on 100 ml $\mu g\ l^{-1}$ | Concentration on 100 ml blank subtracted $\mu g\ l^{-1}$ | Aerosol mass mg | Mass fraction $\mu g\ g^{-1}$ | Actual air volume $m^3$ | Atmospheric conc. pg $m^{-3}$ |
|---|---|---|---|---|---|---|---|
| C 1 | 0,09±0,01 | 0,056±0,005 | 0,046±0,005 | 9,20±1,43 | 4,0±0,8 | 20683±2068 | 1,8±0,3 |
| C 2 | 0,062±0,003 | 0,037±0,002 | 0,028±0,003 | 5,65±0,52 | 3,9±0,5 | 20103±2010 | 1,1±0,2 |
| C 3 | 0,0529±0,0005 | 0,0318±0,0003 | 0,022±0,002 | 7,04±0,42 | 2,5±0,3 | 17958±1796 | 1,0±0,1 |
| A 1.1 | 0,55±0,01 | 0,328±0,005 | 0,319±0,005 | 2,06±0,16 | 123,9±9,9 | 19413±1943 | 13,1±1,3 |
| A 1.2 | 0,21±0,01 | 0,255±0,007 | 0,245±0,008 | 3,67±0,31 | 53,5±4,8 | 19428±1943 | 10,1±1,1 |
| A 1.3 | 0,024±0,001 | 0,015±0,001 | 0,005±0,002 | 1,78±0,26 | 23,5±11,5 | 20037±2004 | 2,1±1,0 |
| A 2.1 | 0,26±0,01 – 0,39±0,01 | 0,471±0,014 | 0,462±0,014 | 3,82±0,25 | 96,8±7,0 | 32752±3275 | 11,3±1,2 |
| A 2.2 | 0,080±0,005 – 0,121±0,008 | 0,072±0,005 | 0,063±0,005 | 4,35±0,52 | 11,6±1,7 | 27727±2773 | 1,8±0,2 |

**Table S31.** Cd measurements on solution (subtracted blank 0,1±0,01 μg 100 $ml^{-1}$)

| Sample | Concentration on 100 ml ng $l^{-1}$ | Concentration on 100 ml blank subtracted ng $l^{-1}$ | Aerosol mass mg | Mass fraction μg $g^{-1}$ | Actual air volume $m^3$ | Atmospheric conc. pg $m^{-3}$ |
|---|---|---|---|---|---|---|
| C 1 | 90±6 | 80±6 | 9,20±1,43 | 7,0±1,2 | 20683±2068 | 3,1±0,4 |
| C 2 | 20±3 | 10±3 | 5,65±0,52 | 1,4±0,4 | 20103±2010 | 0,40±0.13 |
| C 3 | 56±3 | 46±3 | 7,04±0,42 | 5,2±0,5 | 17958±1796 | 2,0±0,2 |
| A 1.1 | 27±4 | 17±4 | 2,06±0,16 | 6,6±1,6 | 19413±1943 | 0,70±0,18 |
| A 1.2 | 16±2 | 6±2 | 3,67±0,31 | 1,3±0,4 | 19428±1943 | 0,25±0,09 |
| A 1.3 | 12,2±0,7 | 2,2±1 | 1,78±0,26 | 1,0±0,5 | 20037±2004 | 0,09±0,04 |
| A 2.1 | 33±3 - 50±4 | 27±3 - 40±4 | 3,82±0,25 | 8,4±1,0 | 32752±3275 | 0,98±0,14 |
| A 2.2 | 11±1 - 17±2 | 5±1 - 7±2 | 4,35±0,52 | 1,3±0,4 | 27727±2773 | 0,20±0,06 |

**Table S32.** Pb measurements on solution (subtracted blank 0,8±0,07 µg 100 ml$^{-1}$)

| Sample | Concentration on 100 ml µg l$^{-1}$ | Concentration on 100 ml blank subtracted ng l$^{-1}$ | Aerosol mass mg | Mass fraction µg g$^{-1}$ | Actual air volume m$^{3}$ | Atmospheric conc. pg m$^{-3}$ |
|---|---|---|---|---|---|---|
| C 1 | 1,7±0,1 | 1600±100 | 9,20±1,43 | 140±20 | 20683±2068 | 62±7 |
| C 2 | 0,86±0,04 | 780±40 | 5,65±0,52 | 110±10 | 20103±2010 | 31±3 |
| C 3 | 1,1±1 | 990±100 | 7,04±0,42 | 110±10 | 17958±1796 | 44±6 |
| A 1.1 | 1,3±0,1 | 1220±120 | 2,06±0,16 | 470±60 | 19413±1943 | 50±7 |
| A 1.2 | 0,65±0,02 | 570±20 | 3,67±0,31 | 120±10 | 19428±1943 | 23±2 |
| A 1.3 | 0,375±0,002 | 295±7 | 1,78±0,26 | 130±20 | 20037±2004 | 12±1 |
| A 2.1 | 0,7±0,7 - 1,1±1 | 653±80 - 980±120 | 3,82±0,25 | 200±30 | 32752±3275 | 24±4 |
| A 2.2 | 0,40±0,03 - 0,60±0,05 | 347±33 - 520±50 | 4,35±0,52 | 96±10 | 27727±2773 | 15±2 |

**Table S33.** Cu measurements on solution (subtracted blank 3,6±0,2 μg 100 $ml^{-1}$)

| Sample | Concentration on 100 ml μg $l^{-1}$ | Concentration on 100 ml blank subtracted μg $l^{-1}$ | Aerosol mass mg | Mass fraction μg $g^{-1}$ | Actual air volume $m^3$ | Atmospheric conc. pg $m^{-3}$ |
|---|---|---|---|---|---|---|
| C 1 | 63±5 | 62±5 | 9,20±1,43 | 5,4±0,9 | 20683±2068 | 2,4±0,3 |
| C 2 | 28±3 | 28±3 | 5,65±0,52 | 3,9±0,6 | 20103±2010 | 1,1±0,2 |
| C 3 | 8,5±0,1 | 8,1±0,1 | 7,04±0,42 | 0,92±0,06 | 17958±1796 | 0,36±0,04 |
| A 1.1 | 52±4 | 52±4 | 2,06±0,16 | 20±2 | 19413±1943 | 2,1±0,03 |
| A 1.2 | 22±2 | 22±2 | 3,67±0,31 | 1,06±0,14 | 19428±1943 | 0,2±0,03 |
| A 1.3 | 9,9±0,8 | 9,5±0,8 | 1,78±0,26 | 1,5±0,2 | 20037±2004 | 0,14±0,02 |
| A 2.1 | 3,1±0,9 - 4,6±1,3 | 2,8±0,9 - 4,2±1,3 | 3,82±0,25 | 0,88±0,28 | 32752±3275 | 0,10±0,03 |
| A 2.2 | 0,88±0,10 - 1,32±0,1 | 0,63±0,07 - 0,94±0,11 | 4,35±0,52 | 0,17±0,03 | 27727±2773 | 0,027±0,004 |

ERROR PROPAGATION

$$mass\ fraction \times \sqrt{\left(\frac{SD_{sample-blank}}{sample - blank}\right)^2 + \left(\frac{SD_{aerosol\ mass}}{aerosol\ mass}\right)^2}$$

# Acronyms

ACC Antarctic circumpolar current

ASW Automatic weather station

EFs Enrichment factors

EPA Environmental protection agency

EPICA European project for ice coring in Antarctica

HCA Hierarchical cluster analysis

PC Principal component

PCA Principal component analysis

PM Particulate matter

PMF Positive matrix factorization

PNRA National program for the research in Antarctica

SCAR Scientific committee on Antarctic research

SF-ICP-MS Sector field inductively couple plasma mass spectrometry

TMFE Thin mercury film elecrode