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Evidence of human impact in Antarctic region by studying atmospheric aerosols

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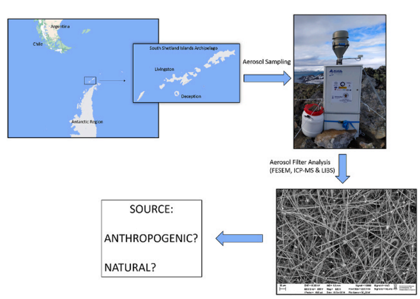
HIGHLIGHTS

- Antarctic atmospheric aerosols PM10 were analyzed by FESEM, LIBS and ICP-MS.
- All techniques showed great concentrations of crustal elements such as Fe, Al and Ti.
- Enrichment factors and correlations studies were performed pointing out an important human contribution of Ni and Cr.

GRAPHICAL ABSTRACT



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ABSTRACT

Air quality is a global concerning topic because of its great impact on the environment and health. Because of that, the study of atmospheric aerosols looking for harmful pollutants is rising, as well as the interest in the origin of the contaminants. Depending on the nature and size of the aerosols, some elements can be detected at a great distance from the emission source, even in Antarctica, where this study is conducted. Several samples of PM filters from 2018 to 2019 (Deception Island) and 2019–2020 (Livingston Island) campaigns have been analyzed by three powerful spectroscopic techniques: FESEM (Field Emission Scanning Electron Microscopy), LIBS (Laser Induced Breakdown Spectroscopy), and ICP-MS (Inductively Coupled Plasma Mass Spectrometry). These techniques have allowed us to find some heavy metals in the air of the Antarctic region (Al, Fe, Ti, Ni, Cr, and Mn). Deeper studies on ICP-MS results have confirmed those results and have also provided information on their

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potential sources. Thus, while Al, Fe, Ti and Mn concentrations can be explained by crustal origin, Ni and Cr presented high values only coherent with important human contribution. The results point out that the Antarctic region is no longer a clean and isolated environment from human pollution.

1. Introduction

During the past decades, human activities have negatively contributed to air pollution. Among others, exhaust from factories and industries, and emissions from motor engines of automobiles have led to high levels of harmful substances in air, such as nitrogen oxide, sulfur dioxide, volatile organic compounds (VOCs), dioxins, polycyclic aromatic hydrocarbons (PAHs), carbon dioxide or metals and their compounds, both inorganic and organic. A special issue to mention is Particulate Matter (PM), including most part of air pollutants (Bai et al.; Reche et al.; Ghorani-Azam et al., 2016). PM can present diverse composition, size, and chemical properties, and consequently, its impact can be very variable. When describing particle size, the term "aerodynamic equivalent diameter" (AED) is used. This concept is defined as the effective spherical diameter of a particle having the same falling velocity in air as a perfectly spherical particle of unit density (Henn, 1996). Two main groups raises from this classification, PM10 (coarse particles, $da = 10–2.5$ μm) and PM2.5 (fine particles, $da = 2.5$ μm of less) (Anderson et al., 2012). Depending on their *da*, some aerosols especially PM2.5 can be easily inhaled, and provoke several serious respiratory diseases, and also affect nervous and reproductive systems. Besides the severe effects on human health, all these substances play an important role in climate change locally and globally. The atmospheric chemistry is quite sensitive to small changes and is deeply modify by the presence of PM. PM components in the atmosphere usually remain for days or weeks during which they generally induce side chemical reactions and, therefore they can evolve into others chemically different forms (secondary aerosols) (Jimenez et al., 2009; Wang et al., 2016). Primary and secondary aerosols can travel really long distances based on their size, and therefore, some aerosols can be detected even thousands of kilometers away from their place of generation (Li et al., 2020).

In this work, we present the results obtained from the analysis of aerosols in filters of the Antarctic region to finally understand the origin of the different detected elements. Antarctica is considered one of the cleanest and purest places on our planet but, although it seems to be isolated, some pollutants have been detected in the Antarctic region, such as metals, black carbon or microplastics (Marina-Montes et al., 2022). As well as previous works, some of these metals, especially those attributed to crustal sources have also been detected in this research performed during 2018/2019 and 2019/2020 Spanish Antarctic campaigns.

The present research is a multi-technique study where thorough measurements by Field Emission Scanning Electron Microscope (FESEM) were conducted. Electron microscopy has proved to be an ideal technique for characterization of individual particles. Morphology studies can play an important role, since they can give clues on the origin of these aerosols (Islam et al., 2019). However, Electron Microscopy become even more powerful by coupling an Energy Dispersive X-ray Spectrometer (EDS). Then, it can provide rewarding information not only on the composition, and the number and volume-size distribution, but also on potential sources, and atmospheric transformations (McMurry, 2000).

As complementary techniques, to confirm the chemical composition of PM found by FESEM, analysis by LIBS (Laser Induced Breakdown Spectroscopy) and ICP-MS (Inductively Coupled Plasma Mass Spectrometry) were also conducted. In recent years, an important number of researchers have reported LIBS-aerosols analysis and application, rising this "new" technique in air quality field (Marina-Montes et al., 2021). Although concern about the influence of the matrix in measurements is justified, there are some examples where the issue has been optimized. As a result, interesting research have been conducted (Redoglio et al., 2018; Anzano et al., 2021; Ji et al., 2021; Zhang et al., 2021). ICP-MS is still considered a reference analytical technique, even in the detection of some concerning pollutants such as microplastics (Bolea-Fernandez et al., 2020).

For all these reasons, we considered that the combination of these three robust techniques is suitable for identifying the chemical and structural composition of our aerosol samples.

2. Materials and methods

2.1. Site description and sampling

Atmospheric aerosol particles (PM10) were collected during the austral summer (from December 2018 to February 2019 and, from December 2019 to February 2020) in the surroundings of the Spanish Antarctic Research stations "Gabriel de Castilla" on Deception Island (62°58′09″S, 60°42′33″W) and "Juan Carlos I″ on Livingston Island (Queen Sofía Mount - 275 m high: 62°40′8.5″S, 60°22′50.1″W). Both islands are located approximately 120 km north of the Antarctic Peninsula and are part of the volcanic South Shetland Archipelago.

A total of 19 and 11 samples was collected in the austral summer (from December to March) of 2018–2019 (Deception Island: active volcanic island, during 24 h) and 2019–2020 (Livingston Island: non-active fumaroles, during 72 h), respectively. Circular quartz filter paper of 47 mm and 150 mm diameter (Pallflex) by a Derenda LVS 3.1 low volume sampler (2.3 m^3/h), and by a Digitel DHA-80 high-volume sampler (30.6 m^3/h), were respectively used. After 24 and 72 h, according to their size, filters were meticulously stored in sterile Petri dishes (47 mm) and aluminum foil (150 mm). Both kinds of filters were collected using sterile tweezers and nitrile globes.

PM filters were stabilized at 20 °C and 50% humidity for at least 2 days, then PM10 mass concentrations were obtained using standard gravimetric methods, EN 12341:1998 standard (CEN 1998), and a mean uncertainty of 1.2 μg/m^3 was determined. After determination of PM10 mass concentrations, several samples were randomly selected to be analyzed by Field emission scanning electron microscopy (FESEM), LIBS and ICP-MS to compare results.

2.2. FESEM measurements

FESEM measurements were carried out at the Institute of Materials Science of Aragon (ICMA) with a Carl Zeiss MERLIN™ Field Emission Scanning Electron Microscope. The chemical composition of the adsorbed PM on the filters was evaluated by energy-dispersive x-ray (EDS) analysis setup attached to the FESEM.

2.3. LIBS measurements

A Q-switched Nd:YAG laser (BrilliantQuantel, model Ultra CFR) with a wavelength of 1064 nm, was used for plasma creation. The pulse is characterized by 8 ns duration and 25 mJ as pulse energy. The light emitted by the plasma was collected by optic fibers connected to an Echelle spectrometer (Andor Mechelle ME5000, 195 mm focal length, F/7, l/Al 5000). The spectrometer has an intensified CCD detector (Andor iStar DH734, 1024 × 1024 pixels, 13,6 × 13,6 μm^2 by pixel, 18 mm of intensifier diameter). Before any measurement, the spectrometer and detector were properly calibrated with a mercury argon lamp. A total of 10 quartz filter paper of 47 mm were analyzed (9 samples and 1 blank) by focusing the laser beam on the middle of the filter. Each spectrum is the result of the accumulation of 6 measurements. To process the resulting spectra Andor MCD Software nv.4.1.0.0 was used.

2.4. ICP-MS studies

After PM10 mass concentrations were determined, a total of six filters (5 samples and 1 blank) were analyzed by IPC-MS (PerkinElmer Elan DRC-e). The chemical characterization of the samples was conducted according to the published analytical protocol (Querol et al., 1996). Then a small 3/16 section (~33.12 cm^2) of each filter was cut and digested with 2.5 mL of HNO_3 at 65%, 5 mL of HF at 40% to dissolve the potential aluminosilicates, carbonates, sulfur, etc., and finally 2.5 mL of 60% $HClO_4$ was added to dissolve organic matter. External calibration was conducted by using standard solutions (0.25, 0.5, 1, 2, 5 and 10 ppb as well as a HNO_3 5% blank). The minimum detectable concentration (MDC) obtained for most of the elements was in the range from 0.01 to 8.5 μg/g for ICP-MS..

3. Results and discussion

3.1. FESEM measurements

FESEM analysis allowed to identify several spherical (or near-spherical) and prismatic particles, enclosed on the filter surface. The detected spherical particles occur in a wide range of sizes, from about 1 to 5 μm of diameter (Fig. 2a). Nevertheless, prismatic particles were bigger, reaching up to 10 μm of diameter (Fig. 2a). The color of the particles allowed us also to distinguish two different population, those heavier than Si (used as internal reference) and others lighter than Si, greyish and with respectively.

In Fig. 2a, the 10 μm particle presented darker color than the other particles and even the filter fibers, for this reason, a bigger content in carbon and light elements can be assumed. Using EDS technique, we have been able to characterize the chemical composition of individually deposited aerosols, and as a consequence, carbon can be confirmed as the most abundant element in this particle (Fig. 2b). Additionally, the major elements detected in the smallest and whitest spherical particles are Na, O, Cl and Si. Besides the major elements, in some particles, some other elements have also been detected like Mg, Al, Ca, S, K, P, Fe and Ti (Fig. 3).

In terms of metals, although iron was detected in all the analyzed samples, Cr, Mn, and Ni were registered only in two samples. These three elements can be associated with fossil fuel combustion emissions, besides crustal emissions (Niemi et al., 2005; Cheng et al., 2008; Zhang et al., 2014; Goel et al., 2018).

The most representative and registered elements are collected in Table 1. These results indicated the analyzed aerosols were rich in oxygen and silicon. The presence of Si and O can be partially attributed to the quartz-based filter, but also to some crustal aerosols. Since Si is the second most abundant element in the Earth's crust, it can be easy found in atmospheric aerosols (Bzdek et al., 2014). Hence, Si is a very long-lasting element in air due to its incapability to form volatile species and its unique valence (+4) difficulties its reactivity (Savage et al., 2014). Although in the Antarctic regions, aerosols usually come from marine source (Barbaro et al., 2017), the registered concentrations of Na or Cl are less important than other elements like Al or Fe, typically attributed to crustal sources (Buck et al., 2006; Gao et al., 2020).

According to FESEM results, most of the detected metals can be explained by crustal factors and, since only a few traces of carbonated PM10 were registered (an indicator of fossil fuel burning), a minimal human contribution to Antarctic air quality can be inferred during 2018–2019 campaign. Nevertheless, some samples obtained during 2019–2020 Antarctic campaign (Fig. 4) started to show lead and other heavy metals in their composition, as it can be seen in Table 2.

3.2. LIBS measurements

To better elucidate and characterized the filter samples, we conducted analyses using additional techniques. LIBS spectroscopy is a powerful and useful technique that allows detecting and quantifying any element in a sample. This fact implies a great advantage compared to XRF (X-ray fluorescence), which cannot detect light elements ($Z < 11$) (Pathak et al., 2012), or ICP-MS. Besides, LIBS technique does not require any sample preparation and it is nondestructive. For a better understanding, previous measurements of blank filter were performed and compared to different selected filters of the Antarctic campaign 2018–2019. During the analyses of the blank filter Si, O, Ar and H spectral lines were detected. These lines are inherent in the composition of the filter (Si and O) and the measurement conditions since Ar is used to perform the analysis in a controlled atmosphere. In addition, some residual signals of C, Ca, Na and Mg were registered but in a much less concentration than in the used filters with PM. The resulting spectra found for the different samples were very similar, changing only the intensity of the peaks or the related intensity between ones and others. In Table 3, the most relevant and assigned spectral bands are collected.

In Fig. 5, a LIBS spectrum is presented with some of the more important spectral lines assigned. LIBS spectrum is like a fingerprint since every element present in the filter exhibits a line in the same wavelength regardless of the sample. Additionally, LIBS analyses were needed due to their low detection limit and their capacity to detect some elements that, for example, ICP-MS cannot. The identification of each element was performed carefully since each element can arise different

Fig. 1. Map of the investigated Antarctic region with an index with Livingston and Deception islands locations.

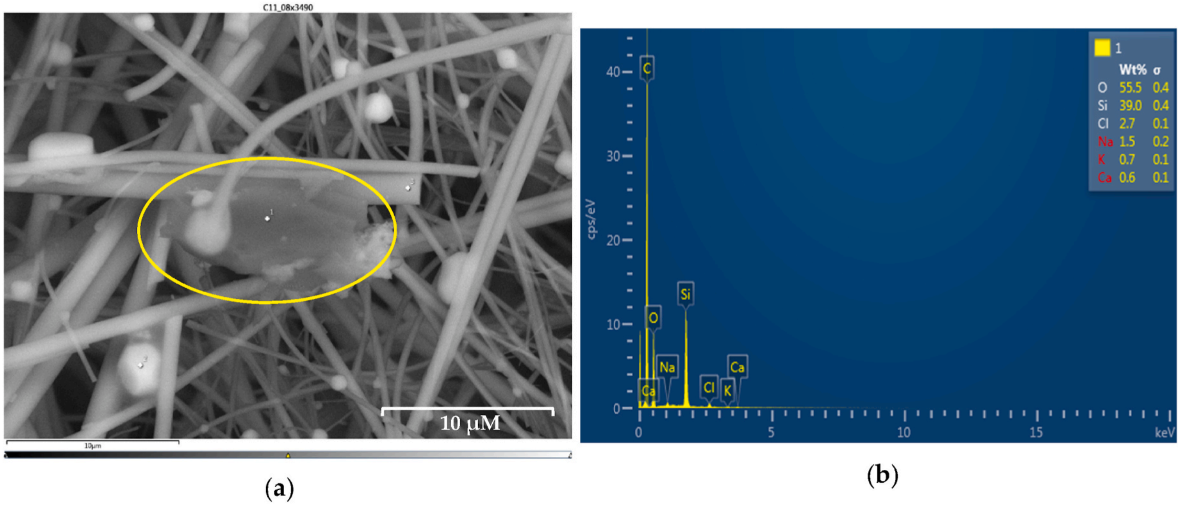

Fig. 2. FESEM images of stack Antarctic PM10 on 150 mm quartz microfiber filters (**a**) at 3490× magnification and (**b**). Elemental composition of 10 μM particle (highlight with a circle).

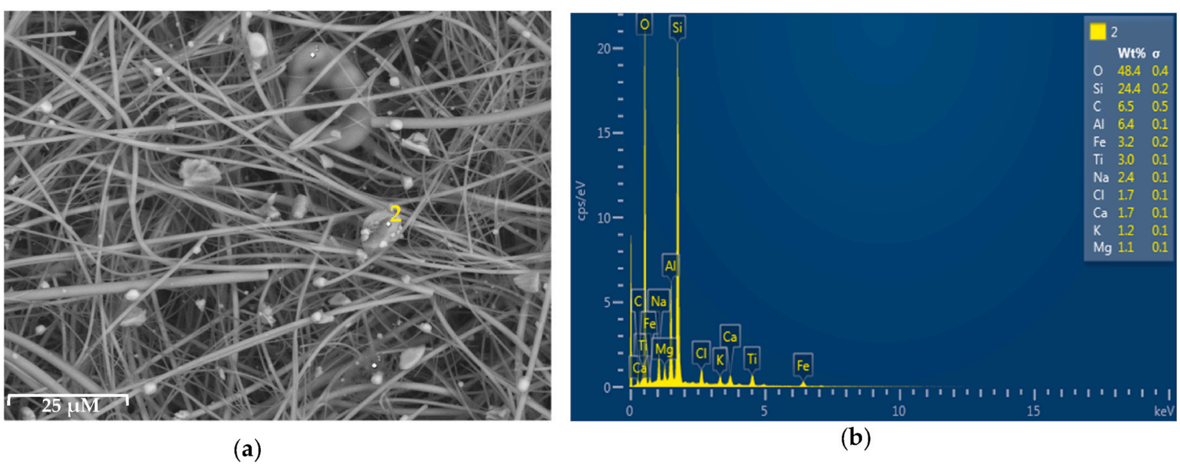

Fig. 3. (a) FESEM images of stack Antarctic PM10 on 150 mm quartz microfiber filters at 1000× magnification and, (**b**) EDS spectrum of point 2.

Table 1
Abundance (%) of the major elements detected on Antarctic PM10 on quartz microfiber filters from 2018 to 2019 campaign.

Elements	O	Si	Al	Fe	Ca	Na	Mg	K	Ti	Cl
Abundance of elements	45.67	26.34	6.97	8.35	4.82	2.06	2.66	0.86	1.65	0.60
	52.54	23.97	7.56	2.04	2.88	2.06	2.12	2.09	0.50	3.89
	50.74	25.81	6.02	6.76	2.92	3.05	1.75	0.93	1.36	0.67
	47.20	28.05	7.23	7.01	3.76	2.29	1.99	0.76	1.35	0.35
	54.29	24.23	6.33	5.77	3.24	2.07	2.09	0.48	1.33	0.17
	42.85	24.57	5.46	10.82	7.16	1.73	3.58	0.64	2.57	0.26
	52.07	22.71	6.28	5.36	4.01	3.74	2.98	0.35	0.83	1.68
Abundance average	49.34	25.10	6.55	6.59	4.11	2.43	2.45	0.87	1.37	1.09

lines in a very congested spectral zone, as it can be seen for Si, Ti and Mn. However, it can be also an advantage since each element can be found in different lines. Elements such as Fe and Ti present many signals, whereas K and Cl have very few lines. Intensity and number of lines are crucial to proper identification, which has been conducted according to NIST database (Kramida et al., 2021). The identified elements by LIBS are in good accordance with those detected FESEM studies.

3.3. ICP-MS studies

As it was done with LIBS spectroscopy, ICP-MS studies were also carried out as a quality reference analysis. ICP-MS is considered the reference technique for trace element determination in atmospheric aerosol particles because of its versatility, small sample volume requirement, high sensibility, and short analysis time.

Firstly, the determination of filter blank composition was evaluated to be able to properly analyze and compare the results from filter samples. In Table 4, the average results of some representative samples are collected. As it can be seen, more elements were even detected than LIBS measurements, but also some metals that were found in FESEM analysis.

These results were useful not only to corroborate the detected elements by previous techniques, but also for a complete study of the

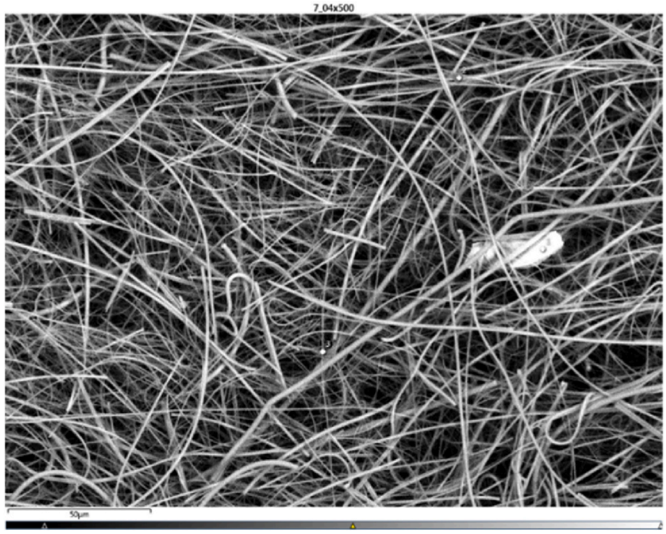

Fig. 4. FESEM images of stack Antarctic PM10 on 150 mm quartz microfiber filters at 500× magnification.

Table 2
Abundance (%) of the major elements detected on Antarctic PM10 on quartz microfiber filters from 2019 to 2020 campaign.

Elements	Ca	Ti	Cr	Mn	Fe	Ni	Pb
Abundance of elements	–	–	0.75	0.63	62.76	0.33	0.22
	–	–	–	–	–	0.14	0.12
	0.54	7.49	1.75	0.93	1.85	0.03	0.02
	0.18	2.50	0.83	0.52	32.30	0.17	0.12

Table 3
Spectral lines of the Antarctic PM10 on quartz microfiber filters from 2018 to 2019 campaign.

Species	Lines Wavelength (nm)
Fe I	217.2, 218.6, 344.1, 374.5, 457.6
Fe II	260.7, 261.4, 274.0
Si I	252.6, 288.2
Mn II	320.6, 403.1
Ti I	321.6, 375.3
Na I	589.0, 589.6
Al I	394.4
Ca I	422.7
Ca II	393.2, 396.8
Mg I	280.3, 517.2
K I	766.5, 769.9
H I	656.3
O I	777.4

potential sources of metals and the relationship among them. For this propose, multivariate analyses were conducted to examine the operating mechanisms in the evolution of aerosol constituents at our Antarctic location. As it was mentioned, Al, Fe and Ti are likely from crustal sources, something that was confirmed by these studies. A strong correlation was observed between them using Pearson coefficient analysis ($r = 0.73$ *p-value* $= 0.0005$ Al/Ti, $r = 0.63$ *p-value* $= 0.0006$ Fe/Ti) so the same terrestrial origin was pointed for these three metals.

No evidence of other significant relationships among the other found transition metals were exposed, therefore different sources were attributed.

Once we clearly determined that Titanium is crustal, we can establish it as a reference metal to calculate the crustal enrichment factor (EFc) (Chen et al., 2021; Ediagbonya and Ajayi, 2021). Through this analysis, we evaluate the impact of natural and anthropogenic sources on the study area.

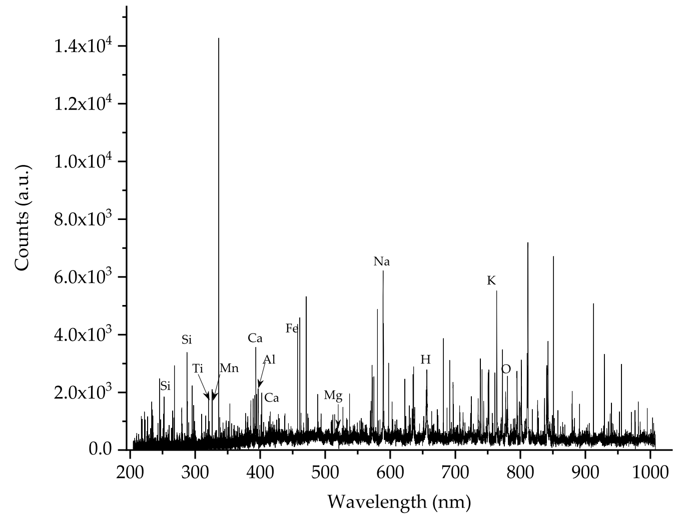

Fig. 5. Average LIBS spectrum of circular quartz filter paper of 47 mm of Antarctic campaign 2018–2019.

$$\mathrm{EFc} = \frac{\left(\frac{X}{Ref}\right)\ aerosol\ sample}{\left(\frac{X}{Ref}\right)\ crustal\ mean} \quad (1)$$

where X is the concentration of the element under study and Ref is the concentration in the continental crust used as reference (Winchester et al., 1981), in this case, titanium. According to previous works, those calculated EFc values below 5 are attributed to a crustal origin, whereas higher values than 10 correspond to a severe enrichment, and therefore, supplementary sources have to be considered (Bazzano et al., 2015).

ICP-MS analyses and also, FESEM and LIBS measurements, detected some concentrations of Ni, Cr and Mn, besides other lighter elements. EFc calculated values showed that, except for Mn (EFc = 8.9) which seems to be still crustal, Ni and Cr values (EFc = 266.5 and 293.8, respectively) can be only explained by an important anthropogenic contribution. Additionally, during the correlation studies performed, Ni and Cr did not show a clear relationship between them, so different sources are operating.

4. Conclusions

Three powerful analysis techniques such as FESEM, LIBS spectroscopy, and ICP-MS were used for a complete chemical and morphological characterization of PM10 from the Antarctic region. These techniques allowed to establish different concentrations of major elements such as Na, Mg, K, Ca, Al, Fe, and Ti. Additionally, other elements have been detected as Cr, Ni and Mn, but in a lower concentration than the previous ones, and only in a few samples from 2018 to 2019 campaign. Multivariate analyses based on ICP-MS results were conducted to determine the potential sources of each metal. In this manner, we can confirm that Fe, Ti, Al and also Mn, proceed from natural and local sources, while Ni and Cr were found in severe enrichment coherent with anthropogenic factors. Pearson analysis showed no direct correlation between these two metals, so the origin is different for each other. Only a few carbonated particles were detected by FESEM, coherent with the local human activities. As a consequence of the presented results, it can be reasonably concluded that a human impact is already visible in the Antarctic air.

Author contributions statement

Elisa Abás: Writing-original draft, Methodology, Formal analysis.; **César Marina-Montés**: Writing-original draft, Methodology, Formal

Table 4
Composition (μg/g) of the Antarctic PM10 on quartz microfiber filters from 2018 to 2019 campaign by ICP-MS.

Na	Mg	Si	K	Ca	Ti	Cr	Mn	Fe	Ni
1497,18	142,86	1840,46	63,57	10,334,40	32,16	40,69	3,26	503,56	12,45

analysis.; **Mariano Laguna**: Supervision.; **Roberto Lasheras**: Methodology.; **Patricia Rivas**: Formal analysis.; **Pablo Peribañez**: LIBS analysis. **Javier del Valle**: Sample acquisition.; **Miguel Escudero**: Methodology.; **Abrahan Velásquez**: Formal analysis.; **Jorge O. Cáceres**: Supervision.; **Luis Vicente Pérez-Arribas**: Methodology.; **Jesús Anzano**: Project administration, Funding acquisition, Supervision. All authors have read and agreed to the published version of the manuscript.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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