Review

A Review of Atmospheric Aerosols in Antarctica: From Characterization to Data Processing

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Abstract: One of the major problems of the present era is air pollution, not only for its impact on climate change but also for the diseases provoked by this scourge. Among the most concerning air pollutants is particulate matter, since it can travel long distances and affect the entire globe. Antarctica is extremely sensitive to climate change and essential for regulating temperature and permitting life on Earth. Therefore, air quality studies in this region are extremely important. The aim of this review is to present the work conducted on the identification and detection of aerosols and particulate matter in the Antarctic region in the last 20 years. These studies revealed a large number of organic and inorganic species. Organochlorine pesticides or polychlorinated biphenyls represent almost 50% of the organic fraction detected in Antarctica. Furthermore, heavy metals such as Hg and Pb were also found in the region related to anthropogenic activities. To summarize, this work detailed different analytical techniques and data processing to help characterize Antarctic aerosols and their potential sources.

Keywords: particulate matter; POPs; long-range transport; air pollution; chemometrics; air mass back trajectories; Antarctica

1. Introduction

In last 50 years, atmospheric pollution established itself as a global issue and the major environmental threat to human health on Earth [1]. Although some natural phenomena such as sandstorms, volcanic activity, soil erosion, and the weathering of rocks are considered responsible for particulate matter (PM) in air, during the past few decades, human activities such as industry, burning of fossil fuels, vehicle exhaust, and smelting have been major factors that enhanced the level of carbon-based pollutants in air [2,3]. Volatile organic compounds (VOCs) are considered the most common form of air pollutants. Although they are generally produced by human activities such as air, road, and sea traffic, industry, and waste burning, vegetation also contributes as another source of hydrocarbon emissions [4]. For example, broad leaf trees and conifer plants are highly responsible for the release of terpene, semiterpene, and diterpene emissions [5]. Therefore, the combination of vegetation and the emissions from anthropogenic sources makes VOCs an outstanding problem for the environment. The problem becomes more difficult to understand when primary VOCs react with hydroxyl radicals ($\bullet$OH), ozone (O_3), and nitrate (NO_3^-) and produce secondary organic aerosols (SOA) or particulate-phase species in the atmosphere [6,7]. The

chemistry of such reactions is understandable to some extent in the troposphere. Still, the oxidation reactions become more complicated to recognize in the stratosphere, where other components such as ethane and acetylene become part of the game. This is a critical fact, since the secondary organic aerosols (SOAs) formed are also present in the troposphere. Therefore, they can be easily distributed around the globe [8].

One type of the most concerning organic pollutants is persistent organic compounds (POPs), which last a longer time in the atmosphere and have a significant resistivity to breaking down into other substances. For these reasons, they are considered more crucial for damaging human health [9]. In fact, the Stockholm Convention was held to make a global treat to protect human health and the environment from POPs because of their mentioned high persistency, toxicity, potential to bioaccumulate, and ability to undergo long-range transport [10].

Another class of important players of atmospheric chemistry is halogens. Tropospheric halogens are emitted from oceanic, terrestrial, and anthropogenic sources [11]. The oceanic source is very important, especially for bromine and chlorine. They are released as sea salt aerosols to become a part of the atmosphere [12]. Gaseous halogens are photolabile and, in daylight, form radicals that react rapidly with VOCs to synthesize haloalkanes. These compounds have a significant role in atmospheric chemistry, since they have a longer lifetime than that of VOCs [6,13].

A number of sulfur species are present both in the troposphere as well as the stratosphere. Among them, H_2S is the most abundant, followed by other organic sulfur gases such as dimethyl sulfide (DMS), carbonyl sulfide (COS), and carbon disulfide (CS_2), which are emitted from oceanic and volcanic sources [14]. Anthropogenic sulfur is mainly emitted as SO_2 from the combustion of coal and oil and used in industrial processes and biomass burning, and it is found higher than the natural emitted sulfur [15]. In the stratosphere, SO_2 has a longer lifetime (2 weeks) than in the troposphere (few days) [16], something related to their role in the atmospheric acid-base chemistry. SO_2 is an important precursor of many modified aerosols in the atmosphere. It is a well-known fact that SO_2 is the major contributor to acid rain, which is due to the formation of sulfuric acid by its reaction with water vapors or oxygen [15]. Due to its negative effect on human health, vegetation, aquatic life, and infrastructure, severe legislation has been imposed on sulfur emissions by international agencies. As a result, since 1990, European and North American SO_2 emissions have been reduced by 70–80% [17]. These attempts had no significant impact on global sulfur fluxes because of China's emissions, which are about 25% of the global SO_2 emissions. SO_2 can be transported large distances from China to other places, such as the Korean Peninsula, Japan, and the northwest Pacific Ocean [18].

As far as inorganic pollutants are concerned, heavy metals are very prominent in this class. Particulate matter generally contains nickel, chromium, lead, zinc, copper, mercury, arsenic, etc., which may have severe effects on human health [19]. For example, some metals such as iron, nickel, vanadium, chromium and copper can produce reactive oxygen species (ROS) in biological systems [20]. The special problem of metals is their non-degradability. They remain in the environment for a very long time [21]. Hg, As, and Pb mainly originate from anthropogenic sources such as mining operation and metallurgical processes employed for extraction of metals such as Cu, Ag, Zn, and Cr. Other potentially toxic anthropogenic elements (Ag, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Sr, Ti, V, and Zn) are typically present in gasoline and diesel fuels and gasoline and diesel engine exhausts [22]. Some of them were detected by our research group (Hf, Zr, As, Cu, Sn, Zn, and Pb). The presence of these elements was attributed to remote maritime traffic, local petrol combustion (generators or tourist cruises), and remote or local crust [23]. As has been observed in Antarctica, in other regions, and especially in industrialized areas [24], many possible sources of particulate matter can occur, including not only local sources but also remote ones. Due to the low size and weight of particulate matter, it can easily be transported across the entire planet by wind currents. This long-range transportation of pollutants around the globe is influenced by a number of favorable meteorological

conditions, such as temperature, the movement and direction of surface waters, air mass circulation, and wind speed [21]. There is solid evidence that pollutants, particularly POPs, can travel very far from their sources of emission [25]. The long-distance distribution of these anthropogenic contaminants has been revealed in different reports regarding air quality analysis conducted in Antarctica and the Arctic region. In the past, both regions were considered virgin zones since there was a certain isolation of its atmosphere with respect to the general planetary atmospheric circulation. In both places, aerosols mostly consist of harmless species such as Na^+, Mg^{2+}, and SO_4^{2-} ions [26,27] but are gradually getting polluted by dust- or smoke-related aerosols containing and VOCs [28,29].

The presence of air pollutants such as VOCs, sulfur species, and halogen-containing compounds (as well as their resulting radicals) emitted in urban areas due to man-made activities and mostly transported to the polar regions by wind is more crucial in the Antarctic atmosphere, since the ozone hole develops every year over Antarctica [30,31]. Ozone depletion due to halogen and related species is also observed in Europe, since previous studies on European air quality discovered that an almost 25% reduction in ozone concentration over Europe was due to halogen-related species [32].

The depletion of Antarctic ozone is mainly attributed to halogen-mediated reactions within polar stratospheric clouds under frigid temperatures and encircled by a polar vortex [33]. Moreover, although the Arctic and Antarctic climates are believed to be similar, temperatures colder than $-80\ °C$ at 70 mbar registered in Antarctica are probably responsible for the greatest differences found in ozone destruction between the hemispheres [34]. In addition to the Antarctic ozone hole, climate change is also dependent on aerosol interactions, since radiative forcing caused by aerosol–cloud interactions is about twice as large as that for CO_2 [35].

Studies in the Antarctic region are extremely necessary due to its unique temperature patterns and physical conditions. The extremely low temperatures of Antarctica facilitate the generation of a particular type of very cold, strong, and dry wind motion, known as katabatic winds [36]. The Polar Plateau always cools the air above it, and as a result, a collision between the different air masses generates a low-pressure belt that surrounds Antarctica with upward movements of air [37]. These air masses descend on Antarctica, feeding back on the katabatic system of wind described earlier. Consequently, a system is generated that is relatively isolated from the rest of the general planetary atmospheric circulation.

Interesting environmental investigations could be conducted in remote zones to access the anthropogenic pollution level. Here, an attempt is made to give a comprehensive view on the current state of knowledge and understanding concerning the level of organic and inorganic air pollutants and their effect on the climate of the Antarctic region. This review also reveals the attempts made in the recent past and reports the pollution level in the region. The special focus of this work is Antarctica because, as it is considered one of the least polluted places on Earth, it is ideal for measuring the spread of global pollutants. In addition, its special climate and prevailing winds make this region one of the final sinks for many pollutants, especially POPs [38–40] and heavy metals [41–43].
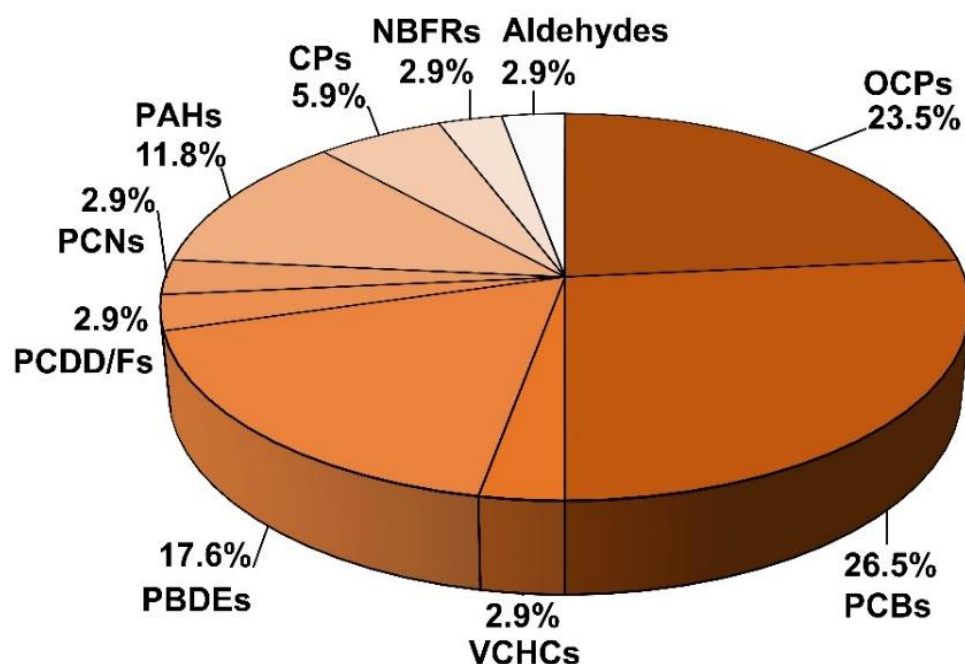
2. Different Types of Aerosols Detected in Antarctica

Antarctica is still a geographically isolated area, but its weather and climate are deeply linked with the climatic parameters of rest of the globe in terms of air mass, precipitation, etc. Several investigations have been conducted to measure and detect pollutants in the air from the Antarctic region. The transportation of particulate material over long distances to finally reach the Antarctic Peninsula has already been documented [44,45]. In the following section, for the reader's benefit and better understanding of the subject, the concerned pollutants have been divided according to their chemical nature into organic and inorganic compounds.

2.1. Organic Compounds

Table 1 reveals a summary concerning the research work carried out to access the presence and level of organic pollutants in the Antarctic region. Similarly, Figure 1 provides

insight into the relative weight of each pollutant family investigated in air quality studies conducted in the Antarctic region.

Figure 1. Relative abundance of each organic pollutant reported in Antarctic region from 2000 to 2021.

The large quantity of data collected by the scientists' work in various localities of the Antarctic region, given in above table and figure, reveals profound information and understanding regarding the major families of organic pollutants. What is still needed is a comparison of this data with those of urban areas in the civilized world and identification of their sources and mechanisms of transportation.

2.1.1. Organochlorine Pesticides (OCPs)

This class of compounds mainly consists of the highest concentrations of α, β, and γ isomers of hexachlorocyclohexane (HCH), chlordanes, and dichlorodiphenyltrichloroethane (DDT) compounds. Among these, HCH reached the highest levels in Antarctica, especially γ-HCH (22 pg/m^3, particulate + gaseous), followed by α-HCH and β-HCH (2.8 and 2.4 pg/m^3, respectively), whereas the chlordanes and DDT families were in the range of 0.04–0.90 pg/m^3 [46]. A serious study on pollution due to OCPs from 2011 to 2014 at King George Island was conducted [60], and a large amount of reliable data revealed a temporal profile of the area in those years (Figure 2). These data show that different isomers are present up to different levels of concentration. The concentrations of two isomers, α-HCH and β-HCH, were found to be higher than the total OCPs (90%) for each investigated year.

Table 1. Compilation of investigation studies on organic compounds carried out in the Antarctic atmosphere.

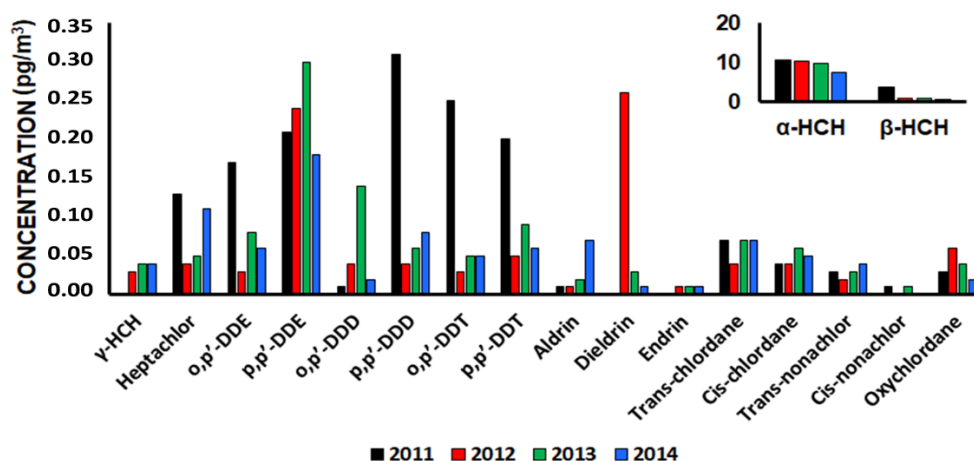| Sampling Location (within the Antarctic Region)	Study Period	Collected Phase	Sampling System	Target Compound Groups	Analysis Techniques	Reference
Signy Island, Antarctica (research station of the British Antarctic Survey)	From 5 December 1994 to 2 April 1995 (17 weeks)	Particulate matter Gaseous	Particles: high-volume sampler (glass fiber filter of 142 mm) Gas: PUF [1] (diameter: 100 mm, thickness: 50 mm, and 25 kg/m^3 density)	OCPs [2] and PCBs [3]	LRMS or HRMS [4]	[46]
King George Island	From 18 December 2004 to 5 December 2005	Gaseous	XAD resin-based passive air samplers	PCBs and OCPs	GC/MS	[47]
Northern Victoria Land (Terra Nova Bay)	From 4 November 2003 to 30 January 2004	Particulate matter Gaseous	Particles: high-volume active air sampler (quartz fiber filter) Gas: PUF (65-mm diameter and 75-mm height)	OCPs	GC/ECD [5]	[48]
Ross Sea Region (Northern Victoria Land)	Not defined (several Italian Antarctic Expeditions)	Gaseous	Modified diaphragm pump system and canisters	VCHCs [6]	CTI-GC–MS [7]	[49]
Three sites on the Barton Peninsula, King Sejong Station (King George Island)	August 2005–August 2006 (site 1), August 2006–August 2007 (site 2), and June 2008–June 2009 (site3)	Gaseous	XAD-2 resin-based passive air samplers	PCBs and OCPs	GC/HRMS	[50]
King George Island	From 8 December 2009 to 7 February 2010 (Austral summer)	Gaseous	PUF-based passive air samplers. Parameters: diameter of 14 cm, thickness of 1.35 cm, surface area of 365 cm^2, volume of 207 cm	PCBs and PBDEs [8]	HRMS	[51]
Terra Nova Bay	Austral summer 2009–2010	Particulate matter Gaseous	Particles: high-volume sampler (quartz fiber filter of 102 mm, porosity of 1 μm) Gas: PUF (65-mm diameter, 75-mm height)	PCDD/Fs [9], PCBs, PCNs [10], PBDEs, and PAHs [11]	GC/MS [12] (single quadrupole)	[52]
King George Island, Fildes Peninsula of Antarctica	From 16 January to 8 February 2013	Particulate matter Gaseous	Particles: high-volume sampler (glass fiber filter) Gas: PUF	CPs [13]	GC-MS/MS (triple quadrupole)	[53]
Palmer Peninsula (Palmer Station)	From 19 October to 11 November 2010	Particulate matter Gaseous	Particles: high-volume air sampler (glass fiber filter, 8 in × 10 in) Gas: PUF (7.8-cm diameter × 7.5 cm thick)	PCBs, OCPs and PBDEs	GC-MS/MS (triple quadrupole)	[54]

Table 1. *Cont.*

Sampling Location (within the Antarctic Region)	Study Period	Collected Phase	Sampling System	Target Compound Groups	Analysis Techniques	Reference
Terra Nova Bay (Mario Zucchelli Station)	From December 2010 to January 2011	Gaseous	PUF disk (14-cm diameter, 1.35 cm thick, surface area of 365 cm^2, mass of 4.40 g, volume of 207 cm^3, density of 21.3 mg/cm^3)	PCBs and OCPs	GC/MS	[55]
King George Island (Chinese Great Wall Station)	From January 2011 to January 2014	Particulate matter Gaseous	Particles: high-volume air sampler (glass fiber filter) Gas: PUF	PCBs and PBDEs	HRGC/HRMS [14]	[56]
Bransfield Strait	Austral summer of 2014	Particulate matter Gaseous	Particles: high-volume air sampler (glass fiber filter, rectangular, 250 × 200 mm) Gas: PUF (95-mm diameter and 50-mm height)	PAHs	GC/MS	[57]
Livingston Island (South Shetlands Archipelago)	From 1 December 2014 to March 1 2015	Gaseous	PUF (10 × 2 cm)	PAHs	GC/MS	[58]
Brazilian Comandante Ferraz Antarctic Station	Antarctic summer in 2012	Gaseous	Radiello passive samplers (impregnated with 2,4-dinitrophenyhydrazones)	Aldehydes	HPLC/UV [15]	[59]
King George Island (Chinese Great Wall Station)	From January 2011 to January 2014	Particulate matter Gaseous	Particles: high-volume air sampler (glass fiber filter) Gas: PUF	OCPs	HRMS	[60]
Fildes Peninsula (King George Island)	From December 2010 to January 2018	Gaseous	XAD-2 resin passive air samplers	PCBs, PBDEs and OCPs	HRGC-HRMS	[61]
Fildes Peninsula (King George Island)	Summers of 2013–2019	Particulate matter Gaseous	Particles: active high-volume sampler (glass fiber filter, rectangular, 250 × 200 mm) Gas: PUF (95-mm diameter and 50-mm height)	PAHs	GC/MS	[62]
King George Island (Chinese Great Wall Station)	From 2011 to 2018	Particulate matter Gaseous	Particles: high-volume active air sampler (glass fiber filter) Gas: PUF	NBFRs [16]	GC/MS	[63]

Table 1. *Cont.*

Sampling Location (within the Antarctic Region)	Study Period	Collected Phase	Sampling System	Target Compound Groups	Analysis Techniques	Reference
Wilkes Land (Casey Station)Dronning Maud Land (Troll Station)	From 2010 to 2015 Throughout 2013	Gaseous (Casey) Particulate matter and gaseous (Troll)	Gas: High flow-through passive air sampler (PUF, Casey) Particles: high-volume active sampling (glass fiber filters) Gas: PUF (Troll)	PBDEs	HRMS	[64]
King George Island (Chinese Great Wall Station)	From 2014 to 2018	Particulate matter Gaseous	Particles: active high-volume sampler (glass fiber filter, diameter: 102 mm) Gas: PUF (diameter: 2.5 in; 3 in high)	CPs	GC-MS/MS (QTOF, quadrupole time of flying)	[65]

Key: [1] PUF = polyurethane foam. [2] Organochlorine pesticides. [3] Polychlorinated biphenyls. [4] Low- or high-resolution mass spectrometry. [5] Gas chromatography equipped with electron capture detector. [6] Volatile chlorinated hydrocarbons. [7] Cryofocusing trap injector coupled to a gas chromatograph with mass spectrometric detection. [8] Polybrominated diphenyl ethers. [9] Polychlorinated dibenzodioxins and furans. [10] Polychlorinated naphthalene. [11] Polycyclic aromatic hydrocarbons. [12] Gas chromatography/mass spectrometry. [13] Chlorinated paraffins. [14] High-resolution gas chromatography coupled with high-resolution mass spectrometer. [15] High-performance pressure liquid chromatography with a UV detector. [16] Novel brominated flame retardants.

Figure 2. Pollution profile of OCP congeners between 2011 and 2014 in the air of the Antarctic region (Wang et al. [60]).

As is clear from Figure 2, the rest of the species observed could not present such a sustainable temporal pattern. It is also evident that the concentration levels of compounds such as tetrachlorodiphenylethane (p,p′-DDD), α and β-HCH isomers, and dichlorodiphenyldichloroethylene (o,p′-DDE), reduced significantly in the prescribed period of research. However, o,p′-DDT, p,p′-DDT, and dieldrin exhibited an abrupt decline from the first to the second years (for the first compounds) and from the second to the third years for the last compound until 2014, whereas in the same period of time, o,p′-DDD and aldrin showed a significant rise in concentration. It is also clear from the profile that almost 50% of the OCPs (γ-HCH, p,p′-DDE, endrin, trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor, and oxychlordane) maintained their levels during the assessed period. Although a considerable temporal variation was observed in the concentrations of the OCP compounds, it can safely be concluded from the data that a global decline was substantiated between 2011 and January 2012. The overall concentration of total organochlorine pesticides (18 in number) progressively decreased over the period of three years (i.e., from 2012 to 2014).

It is astonishing that the concentration levels of endosulfan isomers were not frequently reported until 2010. However, studies conducted in 2016 determined the α-endosulfan levels at Palmer Station, which were found to be in the range of 1.1–3.4 pg/m^3 [54]. The values reported by this study reasonably agreed with the findings published for King George Island [50].

2.1.2. Polychlorinated Biphenyls (PCBs)

Numerous compounds included in the PCB family have been frequently estimated in the Antarctic atmosphere. It can be concluded from the data obtained that relatively lighter compounds were found in higher concentrations than those gaseous compounds with high molecular weights. A 1998 study revealed that the concentrations of the highest-estimated species pointed to PCBs 18, 28, 31, 47, 52, 66, 74, and 101, with mean minimum and maximum values of 1.5 and 17 pg/m^3, respectively, while the lowest ones were for PCBs 114, 128, 156, 167, 180, and 189, ranging between 0.02 and 0.34 pg/m^3 [46]. The total sum of the PCB concentrations (for 22 congeners in both particulate and gaseous phases) was calculated to be 57.05 pg/m^3. Assuming this level as an initial reference value, progressive diminishing PCB levels were observed in the following years.

Whereas the sum of the PCB concentrations (31 congeners in the gaseous phase) calculated in 2008 ranged between 2.10 and 8.07 pg/m^3 [47], reaching an abatement higher than 85% with regard to 1998, an interval from 1.66 to 6.50 pg/m^3 for the sum of the PCB levels (7 congeners in the gaseous phase) in 2009–2010 was found at King George Island. PCB sampling carried out at Terra Nova Bay over the same sampling period (2009–2010) showed a sum of the PCB levels (22 congeners) between 0.14 and 1.98 pg/m^3 in the gaseous

phase and 0.16 and 2.06 pg/m^3 in the dual-phase state (particulate + gaseous) [52]. In order to evaluate the PCB level trends determined at the same point, the work conducted by Wang revealed PCB data from 2011 to 2014 [56]. They observed a decrease in PCB concentrations (particle + gas) over the period of 3 years, with levels being an order of magnitude lower in 2012 and 2013 than in 2011.

2.1.3. Polycyclic Aromatic Hydrocarbons (PAHs)

Another interesting finding observed in the Antarctic atmosphere was that PAH concentrations in the gaseous phase were higher than those determined in the particulate phase. In this sense, the phenanthrene (three-ring PAH compound) was identified as the predominant PAH congener, which was found in the gaseous phase [58] and reached levels ranging between 7 and 45,318 pg/m^3 [52,62]. This fact was endorsed by Cao, who reported the prevailing phenanthrene concentration in both the gaseous phase as well as in particulate matter, reaching contributions of 40% and 54%, respectively, as the sum of the total PAHs [57]. This fact was also supported by another research group which collected gaseous and particulate PAHs simultaneously in Agra at a rural and a traffic-dominated site during the post-monsoon and winter seasons [66]. They revealed that 2–3-ring PAHs were dominant in the gaseous phase, while 4-, 5-, and 6-ring PAHs were dominant in the particle phase. In this regard, Figure 3 depicts the temporal PAH trend (dual phase: gas + particle) between the years 2013 and 2019.

Figure 3. Temporal profile of sum of gaseous and particulate PAHs from 2013 to 2019 in Antarctica (4-, 5-, and 6-ring PAHs are represented on the right axis). Own elaboration using pollution PAHs data from Na et al. [62].
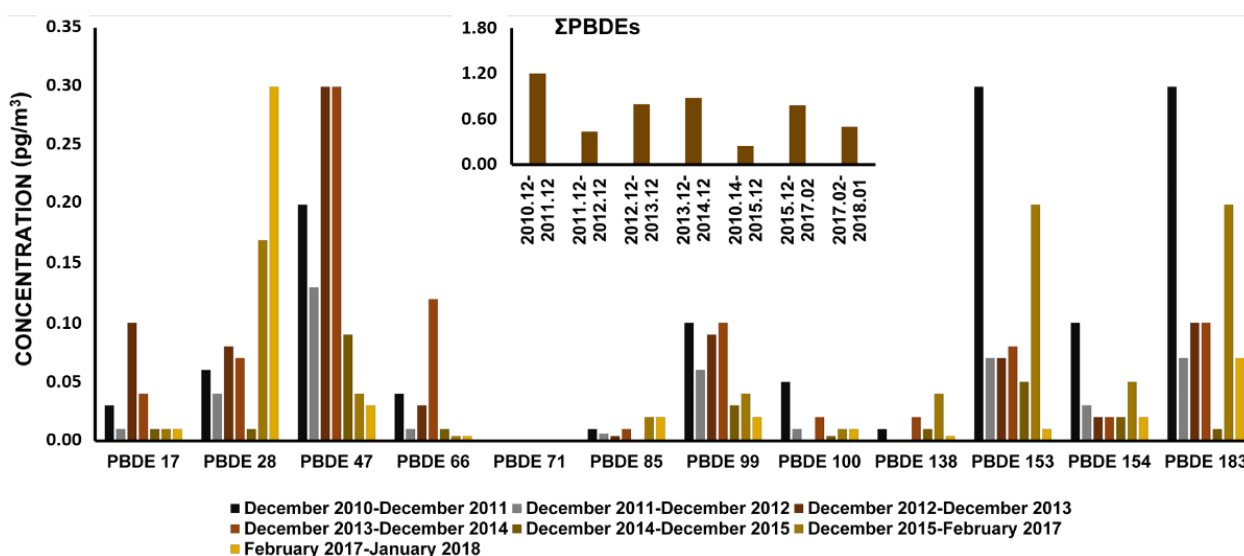
A clear downward trend in pollution levels due to PAHs is clear from Figure 3. A decline higher than 95% was observed for each category of PAH from 2013 to 2019, with the 3-ring PAH species found to have the maximum drop. According to the current European legislation on air quality standards for PAHs, benzo[a]pyrene (BaP), associated with particulate matter, is the one PAH congener with an annual average target value of 1 ng/m^3 (Directive 2004/107/EC). According to this, the measured BaP levels in the Antarctic region are below the annual average target value.

2.1.4. Polybrominated Diphenyl Ethers (PBDEs)

The first research work assessing the occurrence of PBDEs in the Antarctic atmosphere was brought to light by Li et al. [51]. They quantified 14 PBDE compounds, although several of them were not detected in any air samples (PBDE-85, PBDE-100, PBDE-138, PBDE-190, and PBDE-209) [51]. Nevertheless, PBDE-17, PBDE-28, and PBDE-183 were the predominant congeners, contributing on average 27%, 31%, and 19% of the total PBDE

concentration, which varied between 0.67 and 2.98 pg/m^3. In contrast to the previous studies, the atmospheric PBDE-47, PBDE-85, PBDE-99, and PBDE-100 levels in the particulate phase, together with PBDE-183, were evaluated at Terra Nova Bay and found to be the dominant congeners [52]. In the gaseous phase, PBDE concentrations ranged between 1.4 and 7.6 pg/m^3 [54], whereas concentration levels from 0.3 to 1.3 pg/m^3 for PBDEs were found in particulate matter.

　　Overall, a declining trend can be seen in the temporal profile of BPDE concentrations in the Antarctic atmosphere, although it quantitatively differed as a function of individual compounds (Figure 4). A decrease in concentration ranging between 0.006 (PBDE-138) and 0.29 pg/m^3 (PBDE-153) was observed from the previously reported pollution data [61]. Contrary to this, PBDE-28 showed a rising trend, with a notable increase of 0.24 pg/m^3 between late 2010 and early 2018. Similarly, a slight increase (0.01 pg/m^3) was observed in the concentration of PBDE-85.

Figure 4. Temporal profile of PBDE congeners between December 2010 and January 2018. Own elaboration using pollution PBDE data from Hao et al. [61] (study conducted at King George Island).

　　The concentration levels of various halogenated ethers also depend upon the sampling location. For example, the PBDE-47 levels found in the vicinity of the Casey and Troll stations were markedly different from each other. However, the mean average concentrations were found to be 4.9 and 760 fg/m^3 at the Casey and Troll stations, respectively [64].

　　Although enough work has been conducted in the Antarctic region to access the pollutants, relatively fewer studies have been performed to evaluate volatile chlorinated hydrocarbons (VCHCs), polychlorinated dibenzodioxins and furans (PCDD and Fs), polychlorinated naphthalenes (PCNs), chlorinated paraffins (PCs), novel brominated flame retardants (NBFRs), and aldehydes.

　　The levels of the VCHCs were measured for chloroform (CHCl$_3$), 1,1,1-trichloroethane (C$_2$H$_3$Cl$_3$), tetrachloromethane (CCl$_4$), 1,1,2-trichloroethylene (C$_2$HCl$_3$), and tetrachloroethylene (C$_2$Cl$_4$) at several different points in the Ross Sea region (Zoccolillo et al. [49]). The concentrations of the pollutants reported for CHCl$_3$ were in the range from 73 to 337 ng/m^3, in the range from 191 to 224 ng/m^3 for C$_2$H$_3$Cl$_3$, in the range from 648 to 843 ng/m^3 for CCl$_4$, in the range from 16 to 24 ng/m^3 for C$_2$HCl$_3$, and in the range from 32 to 75 ng/m^3 for C$_2$Cl$_4$.

　　As far as PCDD and furans were concerned, only a few compounds out of the 17 with the most potential could be detected and evaluated by Piazza et al. [52]. They reported the presence of 1,2,3,4,6,7,8-HpCDD (in the dual-phase state), OCDD (in the gaseous phase), and 2,3,4,7,8-PeCDF (in the gaseous phase). The concentrations were found in the order of fg/m^3. The compound found at the highest level was 1,2,3,4,6,7,8-HpCDD. In this work, PCNs were

also studied in the Antarctic atmosphere. For a total of 5 congeners checked, only PCN-52 and -67 were detected in some samples at levels of 1–9 fg/m^3 and 3 fg/m^3, respectively.

In 2013, research performed between 16 January and 8 February at King George Island reported higher PC levels in the gaseous than particulate phases, reaching means of 17.3 and 2.5 pg/m^3, respectively. In particular, the short-chain chlorinated paraffin (SCPC) concentrations were found to be 3.5 and 2.4 times higher (gas and particle phases, respectively) than those of the medium-chain chlorinated paraffins (MCCPs). Average concentrations of 13.5 and 3.8 pg/m^3 (gas phase) and 1.7 and 0.7 pg/m^3 (particle phase) were found for the SCPCs and MCCPs, respectively [53]. Another study conducted from 2014 to 2018 at King George Island revealed the presence of PCs in the ambient air of Antarctica in the range of 71.4–4230 pg/m^3, with a rising trend during the investigated period [65].

The first research work regarding the assessment of NBFRs was reported in 2020, when Zhao et al. [63]. quantified the NBFRs (12 congeners) in both the particulate and gaseous phases at King George Island from 2011 to 2018 [63]. A total concentration ranging from 0.27 to 3.0 pg/m^3 was reported in this study, detecting decabromodiphenyl ethane as the prevailing compound. Within the respected temporal frame, an increasing trend was reported with a mean sum of PBDE concentrations within an interval of 1–15 pg/m^3, except for the years 2012 and 2013 (lower than 1 pg/m^3).

As the researchers and associated staff mostly worked indoors except for collecting samples from various sites in the Antarctic region, a study related to evaluating indoor aldehyde levels using radiello samplers at the Brazilian Comandante Ferraz Antarctic Station was also conducted [59]. They reported an average sum of aldehyde concentrations of 177 μg/m^3, dominated by acrolein, acetaldehyde, formaldehyde, and hexanaldehyde. Those compounds were found to constitute almost 80% of the total aldehydes.

Although enough research has been conducted on various pollutants in the Antarctic region by different groups, a large number of organic aerosols have still not been touched. There is a need to explore compounds in the atmosphere further at different locations in Antarctica. In addition, the sources of these pollutants must be located as well as the mechanism through which they are transported over long distances. A system of constant monitoring of pollutants should be installed to obtain annual data without any breaks. Such information shall be of great help for the future prediction of global climate change as well as to save the aquatic life in that part of the globe.

2.2. Bioaerosols

Bioaerosols represent an important fraction of organic aerosols, which are generally produced by plants and animals as well as by biological activities. These aerosols consist of living and dead microorganisms (bacteria, fungi, viruses, etc.), dispersal units (fungal spores or plant pollen), or byproducts of biological activities [67]. The biosphere releases these particles into the atmosphere where they can be easily shifted from one layer to another, particularly due to their light weight and small size (between 0.001 and 100 μm). Although this natural transport is essential for the reproduction and spread of some organisms, they also play an important role during their transport in atmospheric chemistry. Therefore, they are capable of affecting the climate, biosphere, and human health significantly in a certain region.

In the atmosphere, biological airborne particles constantly undergo chemical and physical modifications, consequently modifying the chemistry and composition of the atmosphere. For example, they can act as cloud condensation nuclei, serve as ice-nucleating particles, or absorb or reflect incoming sunlight [68]. Similarly, airborne microorganisms can interact with other pollutants, such as by altering OH radical production via H_2O_2 degradation [69].

Another possibility of transfer is that the microorganisms are deposited on the Earth's surface by dry and wet deposition processes [70], but due to atmospheric transport, they can reach any place on the globe, even on the Antarctic continent [71]. That aside, the air is

not the only way for microorganisms to be present in the atmosphere of Antarctica, as the oceans are also an important source of microorganisms where, by the rupturing of bubbles, they can become airborne [72,73].

There are a few studies indicating the presence of pollen species from South America which were transported to the Antarctic region. According to a research report, about 90% of the atmospheric aerosols of Antarctica are expected to be of a local origin [74], which suggests a limited exchange of airborne microbes in that region. An important local source of bioaerosols in the Antarctic region is penguin colonies. In fact, the global warming process has modified the disposition of ice, consequently affecting the movement and foraging activity of such colonies. In contrast, other studies have pointed out that additional sources are required to fully understand the transportation of detected microorganisms [75,76].

There are several methods for identifying and estimating bioaerosols, such as cultivation, spectroscopy, microscopy, DNA and RNA analysis, X-ray microscopy and spectroscopy, chemical tracers, optical and mass spectrometry, and fluorescence detection [77]. Nowadays, DNA sequencing is the most widely used method, especially through the use of quantitative polymerase chain reactions. This powerful technique provides highly accurate and absolute concentrations of microorganisms and permits quantifying the individual species, genera, or groups of fungi, bacteria, or archaea [78,79]. Alternatively, many biological compounds with intrinsic fluorescence (or many existing fluorescent stains) are well-established for their specific binding to various biological molecules. These two aspects make fluorescence microscopy an easy and robust technique for locating intracellular components [80]. Aside from that, fluorescence microscopy enables us to create a unique sample-specific fingerprint.

2.3. Inorganic Compounds

Metals are natural components of all ecosystems. Most of them are found in the Earth's crust, but they are continually moving. Like water, metals participate in different geochemical cycles that make the concentrations of metals stable. Some natural phenomena also contribute to certain metal concentrations in the atmosphere, such as at Deception Island, where volcanic eruptions are an important source of mercury [81]. Aside from the inherent danger of gaseous Hg, Antarctica's climate conditions seem to favor methyl-Hg formation, and as a consequence, Antarctic waters present the highest Me-Hg concentrations observed in open waters [82].

However, the major sources are human activities which have provoked a deep alteration in atmosphere composition because of fuel burning and mineral consumption. During some industrial processes, fuel combustion, mining operations, or other activities, some trace metals can be evaporated and become a part of the atmosphere. Consequently, they are transported through air masses within different ecosystems, generating a great impact on several geochemical cycles not only at local scale but also on the global scale [83].

The chemistry of metals, especially heavy metals, is quite different from other components of airborne PM since they are not easily degraded, and for this reason, they can become persistent contaminants that accumulate in soil and sediments. Although there are a few heavy metals, such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn), that are considered essential micronutrients for the human body, their excess can be a health risk and cause certain problems and diseases in the body [84]. Consequently, there has been increasing concern about the effect of these metals on ecology and global human health.

Antarctica is still considered a neat and clean environment. However, the effects of human activities are now visible in the atmosphere of Antarctica. The initial hunting, fishing, and exploration activities which took place in last three centuries have been replaced by research and tourism, generating an important impact on the local terrestrial and marine ecosystems and the composition of its air [85]. In principle, non-crustal metals should be found in the atmosphere of Antarctica. Nevertheless, several studies (summarized in Table 2) have reported not only that there are metals present in the atmosphere, but their

concentration levels are also increasing in Antarctica. These metals could only be generated by anthropogenic sources.

Some of these elements detected in the Antarctica atmosphere were expected, as they form part of the Earth's crust. Therefore, in order to know the contribution of the human factor and to understand the ratio of natural and anthropogenic origins of the pollutants, enrichment factor analysis (EF) was carried out. These studies permitted us to establish a potential human contribution, since it is the observed metal/normalizer ratio in the sample divided by the metal/normalizer ratio reported for a reference material. As the reference materials, aluminum, titanium, and iron were used. According to previously reported studies [93], calculated EF values below 5 have a crustal origin, whereas values higher than 10 correspond to supplementary sources, such as a human origin.

Based on the EF results performed during several Antarctic campaigns at different locations, the rise in concentration of some metals can be safely attributed to anthropogenic sources. Marina-Montes et al. [23] established severe enrichment in the concentration of Pb but also a significant rise in the Hf, Sn, Zr, As, Zn, Cu, and V levels on Deception Island [23]. These results agreed well with those obtained in previous investigations on trace metals in Antarctic aerosols conducted in Terra Nova Bay [88], where the human contributions for the metals Cu, Zn, Cr, Pb, and Bi were of high levels.

This field of research still needs some work to be carried out to discover the origins of these aerosols. For example, by calculating the Pearson coefficient between metals, a relationship can be derived, and consequently, the source can be established. In this regard, the studies of Marina-Montes et al. [43]. suggest potential sources for V and As, Zr and Hf, and a few other metals [43]. That aside, by this analysis, one can confirm the crustal origin of inorganic pollutants. The correlation between two or more metals can also point out the specific human activity responsible for this pollution, such as metallurgical operations, industry, or even smoke from biomass burning in South America. A number of studies using various techniques have been conducted to trace the possible origins of the pollutants. Among them, air mass backward trajectories can be calculated through isotopic analysis.

Isotopic analyses are based on the fact that the different components of air, water, or land present a unique chemical profile that allows one to identify and trace them all around the globe. The stable isotopes can be taken as a distinctive chemical signature of the concerned element within the polluting material. Carbon isotopes have been used in studies on air pollution since the 1980s to fully characterize the biomass burning and fuel-related emissions [96]. The two most known and stable isotopes of carbon are ^{12}C, with a natural abundance of 98.89%, and ^{13}C (abundance: 1.11%). Such a ratio, which also occurs in other elements, is sensitive to the chemical structure and the environment [97]. These slight alterations are termed "fractionation", and this factor permits tracking of the pollutants. The known isotopes of some elements are given in Table 3.

Table 2. Compilation of investigation studies (from 2001) on metal traces carried out in the air of Antarctica.

Sampling Location (within the Antarctic Region)	Study Period	Collected Phase	Sampling System	Target Compound Groups	Analysis Techniques	Ref.
Terra Nova Bay	2000–2001 austral summer	Particulate Matter PM10	Cellulose filters	Cd, Pb, and Cu	SWASV [1]	[86]
McMurdo Station	1995–1996 and 1996–1997 austral summers	Particulate Matter PM10	Quartz fiber filter and Teflon filters	Pb and Zn	XRF [2]	[87]
King George Island	From January 2000 to December 2001	Particulate Matter PM10	TFE Teflon filter	Bi, Cd, Co, Cr, Cu, Ni, V, and Zn	ICP-MS [3]	[44]
Terra Nova Bay	From November 2000 to February 2001 and from November 2001 to February 2002	Particulate Matter PM10	Cellulose filters	Li, Pb, Cd, U, Ba, Bi, Cs, Rb, Tl, Sr, Al, V, Fe, Cu, Mn, Zn, Co, and Ag	ICP-SFMS [4]	[88]
Terra Nova Bay	From mid-November 2000 to mid-February 2001	Particulate Matter PM10	Cellulose filters	Cd, Pb, and Cu	SWASV	[89]
Chinese Zhongshan Station	From February 2005 to November 2008	Particulate Matter PM10	Paper filters	Al, V, Cr, Fe, Cu, Zn, and Pb	ICP-MS	[90]
Deception Island	From December 2016 to February 2017	Particulate Matter PM10	Quartz microfiber filter papers	Hf, Zr, V, As, Ti, Mn, Cu, Sn, Zn, and Pb	ICP-MS	[43]
Larsemann Hills	From December 2009 to February 2010	PM10 and PM2.5	Glass microfiber filter and Teflon microfiber filters	Na, K, Ca, Mg, Fe, Al, Sr, Sb, Zn, Mn, Cu, and Pb	AAS [5]	[91]
Terra Nova Bay	From November 2017 to January 2018	Particulate Matter PM10	Cellulose filters	Hg	Direct Mercury Analyzer®	[92]
Dome C (Concordia Station)	From December 2005 to 14 January 2006	Particulate Matter PM10	Cellulose filters	Cd, Pb, and Cu	Voltammetric determinations	[41]
Terra Nova Bay	From 29 November 2010 to 23 January 2011	Particulate Matter PM10	Cellulose filters	Cr, Cu, Mo, and Pb	ICP-AES [6] ICP-MS	[93]
Deception Island	From December 2016 to February 2017	Particulate Matter PM10	Quartz microfiber filters	Al, Ca, Fe, K, Mg, Na, P, S, Cu, Pb, Sr, Ti, Zn, Hf, Zr, V, As, Ti, Mn, Sn, and Cr	ICP-AES ICP-MS	[23]
Deception Island	From December 2016 to February 2017	Particulate Matter PM10	Quartz microfiber filters	Al, Ca, Fe, K, Mg, Na, P, S, Cu, Pb, Sr, Ti, Zn, and Cr	ICP-AES ICP-MS	[94]
Neumayer station	From March 1999 to December 2003	Aerosol	Cellulose filters	Li, Na, K, Mg, Ca, Sr, Al, La, Ce, Nd, and Se	ICP-QMS [7]	[95]

[1] Ultrasensitive square wave anodic stripping voltammetric. [2] X-ray fluorescence. [3] Inductively coupled plasma mass spectrometry. [4] Inductively coupled plasma sector field mass spectrometry. [5] Atomic absorption spectrometry. [6] Inductively coupled plasma atomic emission spectrometry. [7] Inductively coupled plasma quadrupole mass spectrometry.

Table 3. Average terrestrial abundances (%) of the stable isotopes of major elements of interest in ecological studies [98].

H	C	N	O	Mg	S	Cl	K	Ca	Fe	Cu	Zn
^{1}H (99.985)	^{12}C (98.89)	^{14}N (99.63)	^{16}O 99.759)	^{24}Mg (78.70)	^{32}S (95.02)	^{35}Cl (75.53)	^{39}K (93.10)	^{40}Ca (96.97)	^{54}Fe (5.82)	^{63}Cu (69.09)	^{64}Zn (48.89)
^{2}H (0.015)	^{13}C (1.11)	^{15}N (0.37)	^{17}O (0.037)	^{25}Mg (1.13)	^{33}S (0.75)	^{37}Cl (24.47)	^{40}K (0.0118)	^{42}Ca (0.64)	^{56}Fe (91.66)	^{65}Cu (30.91)	^{66}Zn (27.81)
				^{26}Mg (11.17)	^{34}S (4.21)		^{41}K (6.88)	^{43}Ca (0.145)	^{57}Fe (2.19)		^{67}Zn (4.11)
					^{36}S (0.02)			^{44}Ca (2.06)	^{58}Fe (0.33)		^{68}Zn (18.57)
								^{46}Ca (0.033)			^{70}Zn (0.62)
								^{48}Ca (0.18)			

This useful tool for identifying pollutants can be applied to inorganic samples by using the nonconventional stable isotope signatures of metals Schleicher et al., 2020 [97]. In fact, the determination of metals associated with particulate matter, such as Al (crustal marker), Na (marine marker), or Pb, may provide useful information about the possible sources and the possible enrichment of elements compared with their natural levels. In Antarctica, a number of efforts have been made to estimate the anthropogenic contributions to the concentrations of some elements by isotopic analysis, such as lead Bertinetti et al. [97] McConnell et al. [97] and sulfur Pruett et al. [97], and a few researchers also employed some traditional isotopes for this work on oxygen, carbon, and hydrogen Brook and Buizert [97].

3. Analytical Techniques to Identify and Quantify Atmospheric Aerosols

Since the impacts of all these species on the environment and climate are not yet fully understood [99], a complete investigation of the aerosol chemical complexity is needed to help better understand the reactions and the mixing states of these particles in the atmosphere [100]. These investigations are particularly relevant in Antarctica, which acts as a global thermostat driving the Earth's climate.

3.1. Analytical Techniques for Organic Aerosols (OAs)

As was explained previously, particulate matter mostly consists of organic compounds. Polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs released from incomplete combustion and vehicular exhaust are found in high quantities in PM. Organic aerosols also contain a wide spectrum of olefins, aldehydes, ketones, nitro-compounds, quinones, etc. [101]. The detection of this incredibly large variety of compounds present in the samples of particulate matter becomes extremely difficult due to the vast diversity in their physico-chemical properties [102]. For these reasons, analytical methods with high chemical and time resolutions are required for comprehensive characterization.

The most widely used analytical technique for determining organic aerosols is gas chromatography (GC). Nevertheless, conventional one-dimensional GC is usually limited by poor separation in complex OA samples, resulting in co-elution of several compounds and unresolved complex mixtures [103]. Therefore, two-dimensional gas chromatography (GC-GC) is preferred with a higher chemical resolution, higher peak capacity, and structured chromatograms [104].

The combination of different chemical separation methods and various advanced detection techniques opened a new horizon for characterizing the organic fractions of particulate materials. GC-MS provides full molecular separation and a corresponding mass spectra of compounds, allowing several data processing methods, including target

analysis, group-type analysis, and non-target analysis [105]. For example, a combination of non-discriminating thermal desorption and pyrolysis with comprehensive GC-GC and time-of-flight mass spectrometry (TOF-MS) was applied, with a detailed PM organic chemical composition level obtained [106].

There are multiple options for the separation system based on the chemical properties of the organic components [107]. If the nature of organic component does not allow for detection or being determined by direct GC-MS, the pollutants can be analyzed after derivatization or also by modifying the column parameters or diferent detectors. As an alternative to GC-MS, and related to those compounds that are thermally labile and have low vapor pressure or highly polar functional groups, liquid chromatography-mass spectrometry (LC-MS) or LC-MS-MS can be used [108]. The second one is usually employed for detecting select oxygenated PAHs in PM$_{2.5}$.

Size exclusion chromatography (SEC) and supercritical fluid chromatography (SFC) can also be used to separate organic components, taking advantage of their hydrophilic properties and molecular weights. SEC offers the possibility to tune the solvent properties of supercritical fluids to match with those of the analytes. In fact, multi-technique analysis can be performed to combine and gain all the advantages of its method. For example, the separation and characterization of n-alkanes, hopanes, steranes, PAHs, oxy-PAHs, n-alkanals, and n-alkan-2-ones (Shimmo et al. [109]) as well as a few more polar compounds such as n-alkan-2-ones, n-alkanes, oxy-PAHs, and quinines was achieved by coupling SFC with LC-GC-MS [109].

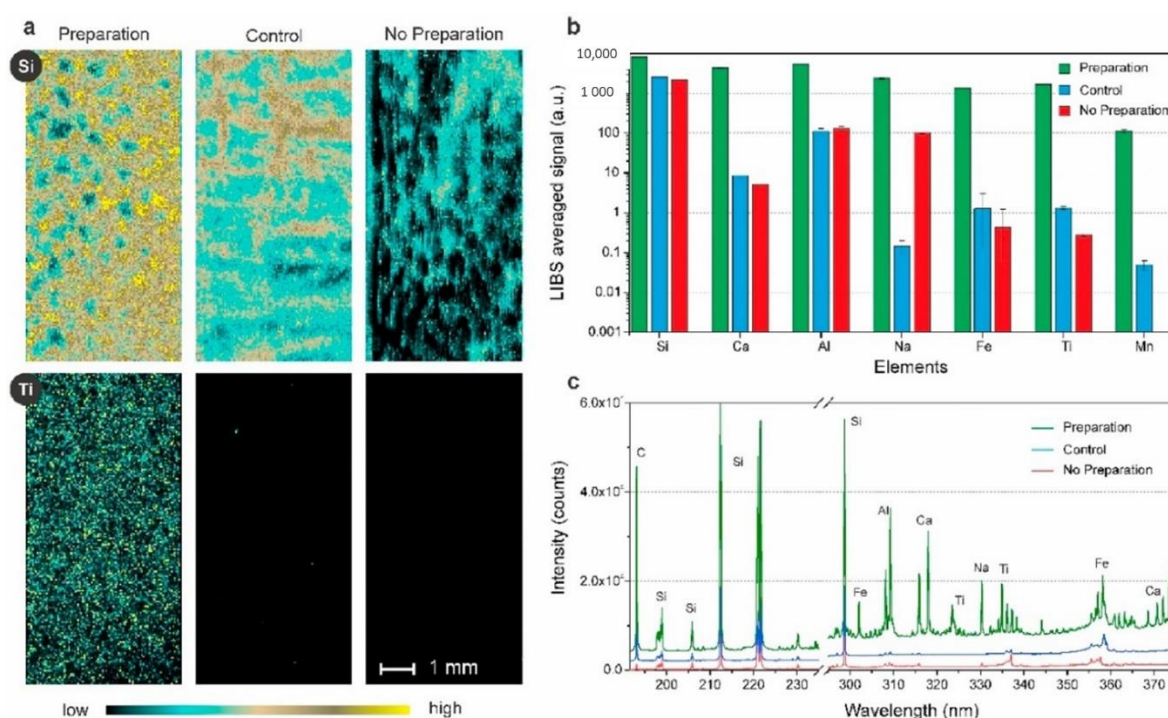### 3.2. Analytical Techniques for Inorganic Aerosols

Along with organic compounds, trace elements are also found in particular matter. Sometimes these elements are deposited over organic aerosols. The determination of these compounds requires different techniques, depending upon the sample and nature of the inorganic compounds present. The chemical compositions of aerosols can be determined with high accuracy by various analytical techniques, such as aerosol mass spectrometry (AMS) [110], inductively coupled plasma mass spectrometry (ICP-MS) [43,94], inductively coupled plasma atomic emission spectrometry (ICP-AES) [23], scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) [111], Raman spectroscopy (RS) [100,112], and laser-induced breakdown spectroscopy (LIBS) [113]. Accurate measurements and characterization of aerosols require the collection of representative samples in the field as well as their subsequent analysis in a laboratory. In the field, including Antarctica, aerosols are normally collected on quartz fiber filters through volume samplers for no less than 24 h of sampling. The filters are then taken to a laboratory, where they can be analyzed using different analytical techniques. Some of these analytical techniques used for the determination and characterization of metal-containing aerosols are ICP-MS, Raman spectroscopy, SEM-EDX, and LIBS.

3.2.1. Analysis of Inorganic Compounds Using LIBS

LIBS is based on atomic emission spectroscopy, which aims to provide qualitative as well as quantitative results of samples without or with minimal sample preparation and destruction [114]. This technique has been implemented in multiple fields, such as biology [115], geology [116,117], industry [118,119], archaeology [120,121], and the planetary field [122]. This popular analytical technique employs an energy laser pulse directed over the sample surface to produce vaporization of the sample. The produced plasma light on the surface contains highly relevant information on the elements present in the sample, taken from a spectrometer. The atomic spectra produced are considered the chemical "fingerprint", and the spectral intensity of each line is converted to the concentrations of the elements present [123].

The use of LIBS for the characterization of aerosols has been broadly implemented in the last few years [124,125]. However, our group working on the analysis of aerosols in Antarctica modified the classical LIBS analysis and used an innovative method based

on micro-LIBS for the characterization of Antarctic aerosols collected on filters [113]. Our modified method, equipped with an optical design and multi-elemental scanning imaging capability, allowed a close look into the elemental aerosol composition deposited on the filters (Figure 5a). The novel technique provided a high LOD up to the ppm level and a lateral resolution of approximately 40 μm with the maximum operating speed (100 Hz). By comparison with classical LIBS, our new protocol has distinctive advantages over the traditional technique. By using the modified method, more elemental signals were obtained (Figure 5b,c) when the operating resolution was optimized (40 μm). Secondly, when the spatial distribution of the PM collected and characterized through the new protocol was studied, it was found to be adequately representative. Thirdly, the ICP-LIBS calibration curves were equally useful for quantitative measurements, and finally, the new protocol allowed us to obtain the spectra of the same "exotic" elements, such as Ni, Zn, Cr, Ba, Cu, and P. Based on the results obtained in our studies, we concluded that micro-LIBS is an interesting and promising technique for analysing the atmospheric aerosols on filters.

Figure 5. (**a**) Distribution imaging of Si and Ti in an Antarctic PM filter sample following the preparation protocol and no preparation. The control sample was prepared following the preparation protocol. (**b**) Average LIBS signal associated with some elements for the three different scenarios (preparation, control, and no preparation). (**c**) Average LIBS spectrum of the three scenarios in two spectral ranges (180–253 nm and 290–379 nm) [113].

3.2.2. Analysis of Inorganic Compounds Using ICP-MS and ICP-AES

As far as plasma-conjugative techniques are concerned, although ICP-MS and ICP-AES are both destructive, they are considered the most common analytical methods used for characterizing atmospheric aerosols in filters. The sample preparation in both techniques is similar and consists of liquid extraction in water or an acid solution [126]. Sample treatment is cumbersome and laborious in both techniques, and the detection limits are relatively low compared with other techniques. The main difference between the two emission-based techniques is that ICP-AES is less sensitive and detects fewer elements than ICP-MS [127]. Therefore, ICP-MS is usually employed for the trace elemental analysis of atmospheric aerosols, while ICP-AES is used for major elements. The sample preparation for both ICP-MS and ICP-AES consists of acid digestion of a portion of the filter [128].

After obtaining the clear solution of the sample, it is aspirated to the argon plasma in the form of very fine droplets. In the case of ICP-MS, the ions of the elements present in the sample solution are taken to a mass spectrometer for further analysis [126]. Contrarily, in ICP-AES, the elements in the aerosol droplets are vaporized, atomized, and ionized. Then, by using optical spectrometry, the photons emitted by the atoms are analyzed. Since ICP-MS and ICP-AES are classical techniques for aerosol characterization, and several studies are available in the literature about the subject, in the following, we shall focus first on Antarctic aerosol studies during the period from 2011 to 2021 and second on the work by our team conducted in the Antarctic atmosphere.

For more than 4 years, (February 2005–November 2008), the aerosol composition was studied after collection through filters and analyzed by ICP-MS in the surroundings of the Chinese Antarctic station "Zhongshan" [90]. This investigation revealed crustal and anthropogenic pollution sources, as well as marine sources in the coastal regions of East Antarctica. Nearly similar results were found in the same area and over the Southern Ocean in a study performed during the austral summer of 2010–2011. A few more studies in which shipboard sampling of aerosols was performed also found analogous results [129]. Over the western Antarctic Peninsula on Anvers Island (Palmer Station) during the austral summer of 2016–2017, Fan et al. [130] characterized the trace elements in aerosols through sector field ICP-MS [130]. They concluded that elements such as Al, P, Ti, V, Mn, and Ce were derived from crustal sources (mineral dust), while Ni, Cu, Zn, and Pb came from anthropogenic sources and Na, K, and Ca came from some marine sources.

Our team performed several studies to analyze Antarctic aerosols collected on filters and used ICP-MS and ICP-AES for characterization of the metal components at Spanish Antarctic research stations "Gabriel de Castilla" (Deception Island) and "Juan Carlos I" (Livingston Island) in the South Shetland Islands [23,43,94,113]. These investigations confirmed the presence of anthropogenic pollutants in the air of the islands, as reported by previous investigations. When the results obtained using the ICP-MS and ICP-AES techniques were subjected to statistical methods, and the polar contour maps and air mass backward trajectories were also considered, it became possible to locate the local and distant origins of particulate matter.

3.2.3. Analysis of Inorganic Compounds Using Raman Spectroscopy and SEM-EDX

Raman spectroscopy (RS) is a rapid and non-destructive analytical technique generally employed in PM characterization [131–134]. This method is ideal for characterizing individual particles and identifying their sources [100]. The technique is based on the vibrational and rotational transitions through which molecules inelastically scatter or absorb light, offering picogram sensitivity at a $\geq$1-μm diameter scale for single particles [135]. RS provides the chemical, physical, and structural information of a single aerosol particle.
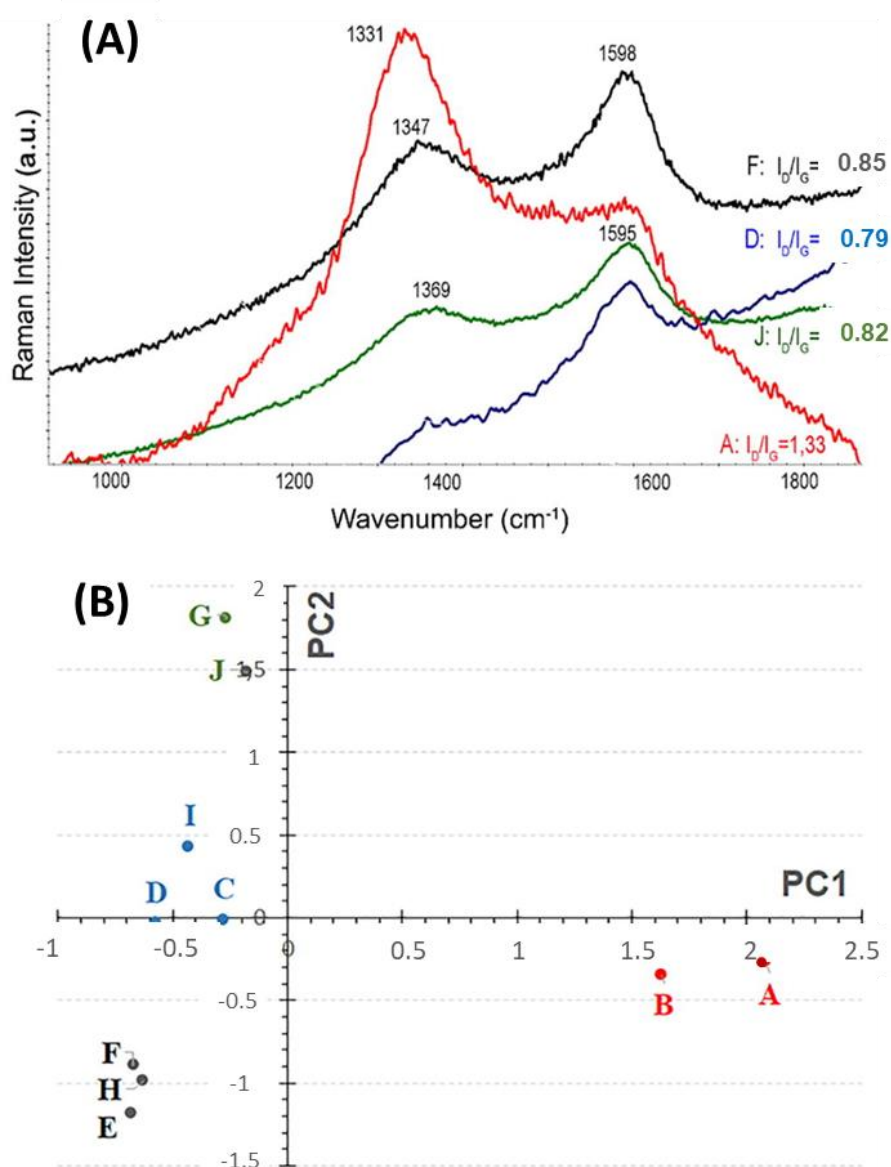
SEM combined with X-ray emission is a non-destructive technique for elemental characterization which allows analyzing and characterizing even a single aerosol particle. The technique is based on the detection and spectroscopic analysis of secondary radiation (X-rays) emitted when a high-intensity incident electron beam interacts with the sample. By using SEM and X-ray emission spectroscopy, it is possible to obtain information about the multiple properties of individual particles, such as the morphology, size, and elemental composition.

However, the use of a unique individual technique cannot encompass all of the information. As Raman scattering does not give information about surface morphology, and SEM-EDX fails to provide knowledge about elemental composition [136], both complementary techniques are generally employed simultaneously to find the complete picture and specifically characterize size-segregated atmospheric particles [137,138]. Such a combination allows for obtaining a complete elemental, morphological, and physical analysis of individual particles [136].

Our scientific team combined RS with SEM-EDX to study single aerosol particles collected on filters from Antarctica [112]. From these studies, it was concluded that black carbon (BC) particles were formed by amorphous carbon, which is a combination of

crystalline graphite and a non-graphite element. The I_D/I_G ratio peaks provided the relative amount of the edge relative to the volume of the crystals; therefore, the I_D/I_G ratio was an indicator of the degree of BC disorder. The D peak was attributed to the graphite breaking down near the edges of the crystal, while the G peak was due to the E2g mode of bulk crystalline graphite. As shown in Figure 6, the results from this study revealed the presence in the Antarctic air of different black carbon particles with different I_D/I_G ratios. Principal component analysis (PCA), shown in Figure 6B, confirmed the four different BC particles and their potential sources. In addition, various organic compounds such as polystyrene and bacteria were also found in the Antarctic atmosphere. The analytical results revealed that a number of exotic minerals (polyhalite, arcanite, nitre, ammonium nitrate, NPK fertilizer, etc.) and natural PM (sea salts, silicates, iron oxides, etc.) were also present in the material trapped in the filters.

Figure 6. Ref. [112]. (**A**) Two-peak fitting results from Raman spectra of four BC particles (A, D, F, and J) from different Antarctic aerosol samples. (**B**) Scores from statistical analysis from Raman spectra of BC particles from PCA of two PCs (group 1: A and B; group 2: C, D, and I; group 3: G and J; group 4: F, H, and E).

4. Modeling of Air Mass Back Trajectories

Once the concentration level of a given pollutant was determined, it was then essential to establish its geographical origin. As mentioned in the introduction, atmospheric pollutants can travel long distances far from their sources, as air masses flow under existing weather conditions. In order to determine the origins of the air masses and the pollutants that are present in them at a given location within a specific period of time, one can use back trajectory modeling. As stated by Fleming et al. [139], "a modelled trajectory is an estimate of the transport pathway of an infinitesimally small air parcel and an estimate of the centre line of an advected air mass subject to vertical and horizontal dispersion". Therefore, back trajectories (time-reversed) can be used to track the pathways and histories of particles arriving at a location of interest. Consequently, they provide useful information about the origins of pollution emissions, as well as the chronology of both local and long-distance transport and the effect of the latter in the air mass composition, which may be modified by physical and chemical processes occurring within the atmospheric flow. The analysis of back trajectories also allows the study of seasonal and long-distance trends for contaminants.

The very notion of air mass back trajectory is linked with the Lagrangian specification of the flow field (that is, the one that uses a moving frame of reference that follows the average atmospheric motion). The most popular models used in this field, such as FLEXPART [140], HYSPLIT [141], LAGRANTO [142], and NAME [143], compute trajectories by following a "kinematic Lagrangian" scheme [144]. In this approach, the position of a hypothetical massless air particle as a function of time is governed by a Eulerian velocity field. This implies that a discrete velocity field has to be interpolated for every time step and position by solving the advection-diffusion equation over a fixed three-dimensional grid [145]. Such a solution needs the input of the previously recorded meteorological data, which are usually obtained from direct measurements or numerical simulations.

As mentioned above, back trajectory calculations are commonly used to elucidate the source–receptor relationships for pollutants. However, steady flow solutions to the equation of the motion of air parcels cannot take their turbulent mixing into account. Going beyond this approximation opposes the so-called Lagrangian particle dispersion models, which statistically incorporate the effects of turbulence on the evolution of computed magnitudes to provide a more realistic description of the atmospheric flow [146].

It should also be kept in mind that atmospheric chemical species, when transported long distances, experience specific changes during travel. They can be transformed into new species, decompose, or be deposited on some available surface. Consequently, these processes must also be considered for a correct interpretation of atmospheric pollution measurements [139].

In recent years, back trajectories have been employed to trace the sources of atmospheric aerosols present in many different geographical areas [147–154]. In Table 4, all such scientific studies have been compiled that were published between 2019 and 2021. As can be seen in the table, intensive fieldwork at different Antarctic locations has been conducted which covers a wide scope of topics within the area of atmospheric aerosols, including the production of marine aerosols and bioaerosols [155–157], the interaction between aerosols and clouds [35,158,159], and the monitoring of tracing and heavy metals in the Antarctic atmosphere [92,130,160].

Table 4 provides different examples of models of back trajectories employed in different studies. Under specific conditions, they can precisely locate the distant origin of a certain pollutant detected in Antarctica [161]. The back trajectory models can only provide plausible hypotheses regarding the location of the pollutant and its possible route of transport [23,41,42]. However, a detailed study of air mass history can confirm a local origin for some anthropogenic aerosols [160]. Finally, some other authors used back trajectories to estimate the average time spent by air masses traveling over different areas, such as land, ice zones, or open ocean, in order to ensure that their recorded measurements solely originated from natural sources [35,162].

Table 4. Compilation of recent studies on atmospheric aerosols in the Antarctic region that use back trajectories or dispersion models.

Topic	Sampling Site	Trajectory or Dispersion Model	Ref.
Carbonaceous, water-soluble species and trace metals in PM_{10} aerosols	Bharati Station, East Antarctica.	HYSPLIT [a]	[160]
Submicron organic aerosols	Ship cruise round the Antarctic Peninsula, South Orkney Islands, and South Georgia Island.	HYSPLIT [a]	[155]
Biogenic organic aerosols	Palmer Station, Anvers Island, western Antarctic Peninsula.	HYSPLIT [a]	[156]
Record of near-surface ozone (O_3) and O_3 enhancement events	Kunlun Station, Dome A, East Antarctica	HYSPLIT [a]	[163]
Concentrations, particle size distributions, and dry deposition fluxes of aerosol trace elements	Palmer Station, Anvers Island, western Antarctic Peninsula	HYSPLIT [a]	[130]
Particle size distributions and solubility of aerosol iron (Fe)	Palmer Station, Anvers Island, western Antarctic Peninsula	HYSPLIT [a]	[164]
Photochemical reactions of aerosols	Criosfera 1 Research Module, West Antarctica	HYSPLIT [a]	[157]
Characterization of stratospheric smoke particles	Marambio Station, Marambio Island, Antarctic Peninsula	HYSPLIT [a]	[161]
Seasonal features and origins of carbonaceous aerosols	Syowa Station, Ongul Island, East Antarctica	HYSPLIT [a]	[165]
Characterization of aerosol number size distributions	Syowa Station, Ongul Island, East Antarctica	HYSPLIT [a]	[159]
Cloud condensation nuclei (CCN) measurements	Princess Elisabeth Station, Dronning Maud Land, East Antarctica	HYSPLIT [a], NAME [b]	[166]
Ionic species concentrations in PM_{10} and $PM_{2.5}$ aerosols	King Sejong Station, King George Island, Antarctic Peninsula	HYSPLIT [a]	[167]
Seasonal evolution of particulate mercury (Hg) in atmospheric aerosols	Faraglione Camp, Terra Nova Bay, East Antarctica	HYSPLIT [a]	[92]
Determination of cadmium (Cd), lead (Pb), and copper (Cu) in atmospheric aerosols	Concordia Station, Dome C, East Antarctica	HYSPLIT [a]	[41]
Observation of new particle formation events	King Sejong Station, King George Island, Antarctic Peninsula	HYSPLIT [a]	[158]
Annual variability of aerosol size distributions	Halley Station, Brunt Ice Shelf, East Antarctica	HYSPLIT [a]	[162]
Transport pathways of heavy metals in atmospheric aerosols	Gabriel de Castilla Station, Deception Island, Antarctic Peninsula	HYSPLIT [a]	[43]
Local and remote sources of airborne suspended particulate matter	Gabriel de Castilla Station, Deception Island, Antarctic Peninsula	HYSPLIT [a]	[23]
In situ measurements of tropospheric isoprene	Ship cruise around the Antarctic Peninsula	HYSPLIT [a], NAME [b]	[168]
Study of aerosol–cloud interaction	Ship cruise all the way around Antarctica	LAGRANTO [c]	[35]
Summer aerosol measurements over the East Antarctic seasonal ice zone	Ship cruise from Australia to the East Antarctic seasonal sea ice zone	HYSPLIT [a]	[169]
Seasonal evolution of the chemical compositions of atmospheric aerosols	Faraglione Camp, Terra Nova kBay, East Antarctica	HYSPLIT [a]	[42]
Characterization of the chemical compositions of atmospheric aerosols	Zhongshan Station, Prydz Bay, East Antarctica	HYSPLIT [a]	[90]
Distributions of water-soluble ions in size-aggregated aerosols	Ship cruise from Australia to coastal Antarctica	HYSPLIT [a]	[170]
Characterization of marine aerosols	Ship cruise around the Antarctic Peninsula	HYSPLIT [a]	[171]

[a] See [141]. [b] See [143]. [c] See [142].

5. Chemometrics and Data Processing Methods

In order to control and monitor the environmental systems and predict a true picture of the future, a large quantity of very complex types of data regarding aerosols and PM, including diverse natural and anthropogenic processes, needed to be properly managed and processed [172]. One way to extract information from these large sets is using different chemometric and statistical techniques. These tools are very suitable as a great help for obtaining environmental information from the chemical analytical data or relating the chemical data to the environmental data beyond univariate analysis, allowing one to identify the interrelationship of environmental drivers, sources of contamination, and their potential impact on the environment. Generally, chemometrics applied to environmental analysis cover different stages, including sampling, experimental design, optimization of experimental conditions, signal processing, and data analysis. Presently, there is a large variety of chemometric methods that can be applied to environmental analysis, including atmospheric studies [173–177]. These techniques are mainly focused first on identifying the sources of pollution and second on the impact of air pollutants on certain rural or urban areas and on the population, as well as the flora and fauna residing there.

Table 5 summarizes the different chemometric methods that are usually applied to atmospheric studies and aerosol analysis, and most of them are related to multivariate analysis (PCA and HCA). The main objective of these methods is the grouping and classification of variables (in the case of the air quality and assessment of the environmental pollution, sampling points, days, etc.) as well as the model relationships. This permits one to establish some correlations between different parameters and, at the same time, find correlations between the amounts of several pollutants [178]. Principal component analysis (PCA) is one such method that is based on data reduction that considers the correlation between the data. This is possible because in all datasets, only a few variables can be considered significant. PCA has been extensively employed in environmental analysis because this chemometric method is very useful in data interpretation.

Thus, PCA has been used together with other multivariate techniques such as cluster analysis [179–182]. Cluster analysis (CA) represents a group of methods that is used to arrange the objects (i.e., samples) according to the similarity of their features. It depends on the mathematical method or algorithm and is considered one of the most popular methods of data handling in environmental analysis. The clusters obtained can be arranged hierarchically or non-hierarchically, and this technique is termed hierarchical cluster analysis (HCA). This is based on building a hierarchy of clusters by aggregating objects according to the resemblance of their features. As a result, a hierarchical graph called a "dendrogram" is obtained. This dendrogram permits one to determine the ideal number of clusters in which the objects can be classified. This technique is quite useful in the chemical and physical characterization of airborne particles collected on a filter. Thus, Morozzi used HCA for the identification of Sahara dust events in the southern Iberia Peninsula [183]. The parameters included in the hierarchical classification were the color and semi-quantitative data of iron oxides. Siepka used HCA and PCA in combination with Raman micro-spectrometry to determine the quantitative molecular compositions of atmospheric aerosols and obtained impressive results [179].

Table 5. Chemometric methods recently applied to atmospheric studies and aerosol analysis.

Name	Acronym	Function or Utility	Ref.
Principal Component Analysis	PCA	Pattern recognition, classification, and exploration of main pollution sources. Search for similarities between samples, sampling points, sampling days, etc. and, in general, data interpretation.	[94] [184] [185] [186] [23] [43] [181] [187] [182] [188] [179] [189] [180]
Cluster Analysis or Hierarchical Cluster Analysis	CA or HCA	Patter recognition and classification of samples, pollutants, sources, etc. Useful in chemical and physical characterization of airborne particles.	[190] [191] [192] [193] [183] [181] [182] [188] [179] [189] [180]
Correlation or Regression Analysis and Canonical Correlation Analysis	CCA	Search of relationships between pollutants and source exploration.	[190] [194] [23] [43] [183]
Partial Least Squares and Unfolded Partial Least Squares	PLS and U-PLS	Prediction and construction of mathematical predictive models. Especially useful when there are many factors with high collinearity.	[195] [186] [196] [189] [197]
Factor Analysis and Parallel Factor Analysis	FA and PARAFAC	Receptor modeling, searching of hidden patterns, and source apportionment.	[198] [195] [187]
Positive Matrix Factorization	PMF	Source identification of pollutants.	[199] [200]

Another chemometric tool frequently used in environmental analysis is correlation analysis. This is mainly used to identify the relationship between pollutants and other variables that affect air quality. This technique is also very useful for understanding the nature of aerosols, identifying the most influential factors, and predicting the sources of chemical components [190].

These relationships between variables can be visualized in a multivariate mode by the graphs obtained through PCA. From these plots, information about the correlation of the variables can be inferred easily. For example, the smaller the angle between two vectors representing a given pair of variables, the higher the correlation between them will be (positive correlation). On the other hand, uncorrelated features are usually orthogonal with each other. Finally, when the vectors represent a pair of variables in opposite directions, this means that those factors which promote the appearance of one variable will favor the disappearance of the other and vice versa (negative correlation) [178].

The correlation between a pair of variables can be estimated and quantified in bivariate analysis using a linear regression method. In these cases, the strength of the relationship is determined by the correlation coefficient (Pearson, Kendall, or Sperman). They all assume values in the range from -1 to $+1$, where values close to ±1 indicate the strongest possible agreement and zero (0) is the strongest possible disagreement. A positive correlation means that an increase in one variable leads to an increase in the other. However, a negative correlation indicates that when one variable increases, the other decreases and vice versa. The analysis of correlations in multivariate mode, through loading analysis, and in bivariate mode was used by Cáceres [94] and by Marina-Montes [23,43] when they analyzed the atmospheric aerosols in the Antarctic region. Correlation analysis can also be used to model the correlations between two datasets rather than between a pair of single variables. This type of analysis is termed canonical correlation analysis (CCA). This method of analysis can be used for linear relationships that could exist between two datasets, with each containing multiple variables [201]. One set may contain variables classified as predictor or independent variables, while the other dataset of variables has the response or dependent variables. Canonical correlation analysis (CCA), along with principal component analysis (PCA), was used to detect the relationships between meteorology and air pollutant concentrations by Binaku [190] in a multivariate statistical analysis of air quality in Chicago, IL, USA.

In environmental studies, several independent and dependent variables may be operative. In these cases, controllable variables or easy-to-measure variables (factors) can predict or explain the behavior of other variables (responses). Generally, observable variables (factors) and responses are arranged in two different matrices. The relationship between both matrices can be established by means of regression methods, also known as multivariate regression methods. The most popular multivariate regression methods include multiple linear regression (MLR), principal component regression (PCR), and partial least squares (PLS) [176]. Multiple linear regression (MLR) helps to obtain a mathematical model of the linear relationship between the factors and the variables. Basically, it is a multivariate extension of the classical linear regression of one variable. If the factors are few in number, and collinearity is not significant, then the relationship between the factor and responses is well known, and MLR would be adequate. However, if one or more of these conditions breaks down, then MLR may be inefficient. One alternative is to use "soft models" based on biased parameter estimations, as in PCR and PLS. The principal advantage of PLS is its ability to build predictive models when the factors are numerous and highly collinear. There are other statistical methods which can be derived from PLS, such as genetic algorithms-partial least squares (GA-PLS), moving window-partial least squares (MW-PLS), uninformative variable elimination-partial least squares (UVE-PLS), and many more [176,202]. Thus, Elcoroaristizabal et al. [195] proposed a method based on the combination of excitation-emission fluorescence matrices (EEMs) and second-order algorithms to identify several PAHs in extracts of aerosol samples. By using unfolded partial least squares coupled with residual bilinearization (U-PLS/RBL), they obtained good results when the sample matrices were moderately complex [195]. Wyche et al. [189] used positive least squares discriminant analysis (PLS-DA) in studying organic reactivity and secondary concomitant organic aerosol formation [189]. Other applications of PLS in atmospheric studies are shown in Table 5.

Factor analysis (FA) can be defined as a statistical method that converts a mass of data into smaller datasets to look for hidden patterns. In other words, the aim of FA is to express the features by means of a small number of common factors. For example, it is possible that variations in six observed variables (six air pollutants of a big city) mainly reflect the changes in two unobserved (latent) variables (such as traffic and wind direction). In FA, each factor is associated with a hidden variable which is not directly measurable and not included in the measured dataset. Like PCA, factor analysis is particularly useful for the elimination of variable collinearity. PARAFAC is the acronym of parallel factor analysis, and it can be considered general terminology of PCA which arranges the dataset in higher-order arrays of data, usually as thee-way data or data cube structures [187,198].

Finally, another chemometric tool used in environmental evaluation data is positive matrix factorization (PMF). This tool was developed by Paatero [203]. Since then, PMF has been widely used for source identification of anthropogenic pollutants in different media such as air, water, and soil [204]. Basically, PMF is a multivariate factor analysis technique used for the chemometric evaluation and modeling of environmental datasets which overcomes the limitations of PCA by using experimental uncertainties in data matrix analysis and constraining the solutions to nonnegative values. In PM analysis, PMF has recently been used by Masiol et al. [200] to investigate the chemical speciation of particulate matter with sizes less than 2.5 μm ($PM_{2.5}$) collected at three sites in the Venice area of eastern Po Valley (Italy). A number of other studies also used PMF to investigate the different aspects related to environmental analysis [199].

6. Conclusions

This review highlights the latest advances in atmospheric research in Antarctica, both in the detection of organic and inorganic compounds and the principal analytical techniques used. These studies were focused on the importance of the statistical methods employed in the analysis of atmospheric data and highlighted the significance of contour maps and back trajectory calculations, which provide a broader view of understanding how they influence other parameters such as wind speed and direction. Moreover, the feedback analyses allow clear determination of the anthropogenic effect on PM in Antarctica. In the studies which were conducted in previous years and referenced in this review, the presence of anthropogenic pollutants is clearly evidenced. These pollutants consist of a vast range of compounds having different natures and chemistries, such as organic and inorganic aerosols. Among organic aerosols, the species frequently detected in the Antarctic region are organo-chlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). Something quite concerning and interesting is the detection of heavy metals in Antarctic air samples, since they are persistent contaminants that accumulate in the soil, sediment, fauna, and organisms as well. There are some very effective techniques for identifying and quantifying the different pollutants and species, but it is crucial to improve the detection limits. Although a large number of studies have been conducted to measure the air quality in Antarctica, the results reported vary significantly. This is probably due to the fact that studies were conducted at different locations and times of the year. Although an adequate quantity of data is available regarding the estimation of various pollutants, there is still a lot of research work required to find out the origins of the pollutants, their transportation to Antarctica, and the transformations that occur through the journey. Only then can the effectiveness of emission control strategies worldwide be achieved. In this respect, the modeling of air mass back trajectories can be used as a powerful tool that can help to elucidate the source of a given pollutant. By using these trajectories, one can determine whether pollutants originate from inside or outside of Antarctica and, moreover, whether they are of natural or anthropogenic origins. Additionally, chemometrics and other statistical tools are an important aid in environmental analysis, especially in those cases where it is necessary to process a large amount of environmental data. Among the techniques used in aerosol analysis, clustering and classification techniques such as PCA, CA, and HCA are the most useful methods and are employed by many workers. Since there is still a lot of missing information before full comprehension of the potential effects of Antarctic aerosols on both the climate and ecosystems, futher research on these topics is needed.

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