Seasonal variations in aerosol compositions at Great Wall Station in Antarctica

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Abstract   High volume aerosol samplers at Great Wall Station in Antarctica were used to collect 73 aerosol samples between January 2012 and November 2013. The main ions in these aerosol samples, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, as well as methane sulfonic acid, were analyzed using ion chromatography. Trace metals in these samples, including Pb, Cu, Cd, V, Zn, Fe, and Al, were determined by inductively-coupled plasma mass spectrometry. Results showed that sea salt was the main component in aerosols at Great Wall Station. Most ions exhibited significant seasonal variations, with higher concentrations in summer and autumn than in winter and spring. Variations in ions and trace metals were related to several processes (or sources), including sea salt emission, secondary aerosol formation, and anthropogenic pollution from both local and distant sources. The sources of ions and trace metals were identified using enrichment factor, correlation, and factor analyses. Clearly, Na^+, K^+, Ca^{2+}, and Mg^{2+} were from marine sources, while Cu, Pb, Zn, and Cd were from anthropogenic pollution, and Al and V were mainly from crustal sources.

Keywords   Antarctica, Great Wall Station, aerosols, ions, trace metals, sea salt, seasonal variation, pollution, long-range transport

1 Introduction

Antarctica is the most pristine area on Earth, completely isolated from other continents by the Southern Ocean. Its unique geographical location has inspired much scientific interest in the status of its air, soil, water, ice, and biota, as a baseline for evaluation of various anthropogenic impacts worldwide. Much attention has been paid to the study of the chemical composition of its ambient aerosols, as well as its atmospheric cycles. Such studies provide basic information on their sources, and the pathways that determine baseline concentrations in the Antarctic atmosphere[1].

Despite the pristine environmental conditions of the

Antarctic, it has been demonstrated that sources from rocks, soil dusts, and oceanic particulates cannot fully account for the large amounts of trace metals present in its atmosphere. Comprehensive records in snow layers demonstrated that the natural patterns of occurrence of metals in the Antarctica have been greatly perturbed by diverse human activities in surrounding areas[2]. Many studies have characterized the chemical composition and atmospheric cycle of such aerosols in Antarctica[3-6]. However, their geographical distributions in this region are still largely unknown. The chemical compositions of its aerosols differ from one area to another, reflecting factors as diverse as wind regime, meteorological conditions, the balance between marine and continental sources, and the distance to other source regions (such as South America) for long-range transport of anthropogenic

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pollutants. Moreover, increasing human activities at many stations within Antarctica also influence the ambient atmospheric composition, at least at the local scale[7].

The Chinese Great Wall Station is located on Fildes Peninsula of King George Island in the South Shetland Islands. In recent years, there have been a large number of research and logistic personnel working at this station. As the number of tourists visiting the area also increases, they will cause greater environmental pressure on the region. To evaluate the influence of human activities on this unique environment, we undertook this study to identify metal and ionic pollution levels in aerosols, as well as their probable sources of origin at Great Wall Station. Here, we present the results of our aerosol composition measurements made at

Great Wall Station over an almost 2-year period, from January 2012 to November 2013.

2 Sampling and analyses

Aerosol samples were collected from January 2012 to November 2013 at the Chinese Great Wall Station (62°12′59″S, 58°57′52″W) (Figure 1), located on the northern tip of the Antarctic Peninsula. In our study, a high volume aerosol sampler was used for sampling, without any wind direction controls. The sampler was placed on the ground, near the seashore, approximately 1000 m from the power generator for the Great Wall Station. Sample collection time was about 10 d, giving a sampling volume of ca. 9000 m^3.
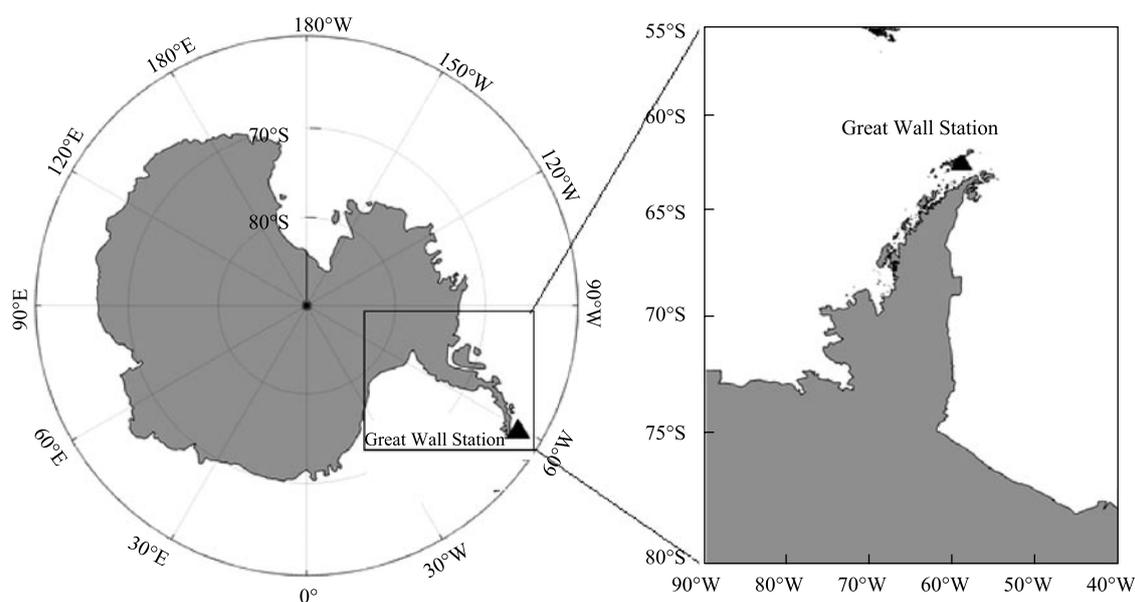

Figure 1 Location of the Chinese Great Wall Station in Antarctica.

All ions were analyzed using ion chromatography (Dionex ICS-2500; Thermo Scientific, CA, USA), with detection limits of about 10 ng·gL^{-1}. The analysis of ionic constituents was made following their filter extraction in deionized water. Cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH^{4+}, were analyzed using a guard (CG12A) and an analytical column (CS12A). Anions, such as F^-, Cl^-, NO_3^-, SO_4^{2-}, and MSA were analyzed using a guard (AG18) and an analytical column (AS18).

To analyze trace metals, the filter samples were extracted in an acid solution, as described below. First, the filter was cut with glass shears, and placed into a polytetrafluoroethylene crucible, containing ultra-pure hydrofluoric and nitric acids. The sample was leached in this acid solution overnight. The sample was nitrated on an electric hot plate, before being diluted to constant volume with 2% HNO_3. These extractants were analyzed using inductively-coupled plasma mass spectrometry (XXX) with detection limits ranging from 1–20 ppt.

3 Results and discussion

3.1 Chemical composition of aerosols at Great Wall Station

Percentage compositions of all major ions in the aerosol samples from Great Wall Station are presented in Figure 2. Ion concentrations in sequential order were $Cl^- > Na^+ > SO_4^{2-} > Mg^{2+} > Ca^{2+} > K^+ > NO_3^- > NH_4^+ > MSA > F^-$. Average concentrations for each ion are listed in Table 1. Clearly, the most abundant ions were Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, and Ca^{2+}; these five ions contributed 91.3% to the total ion mass. In particular, the contributions of Na^+ and Cl^- were as high as 79.3%.

The results of our study indicate strong enrichment (Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, and Ca^{2+}) and depletion (NO_3^-, NH_4^+, MSA, and F^-) of specific ions. The relative enrichment in Na^+ (and Cl^-) in our samples reflects the substantial input from oceanic sources at this coastal location. Sea salt clearly is a major

contributor to the total particulate matter in the Antarctic atmosphere, and is the most abundant aerosol at this site.
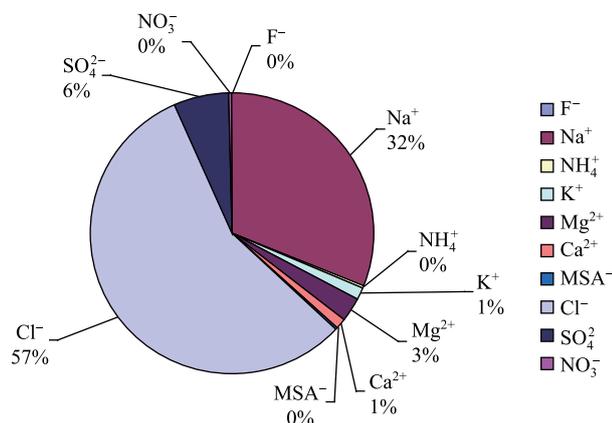

Figure 2 Average percentage compositions of ions in aerosol samples from Great Wall Station.

Most of the aerosol at this site is composed of sea salt particles, sulfates, and nitrates. The sulfate aerosol particle size distributions ranged from 0.1 μm to 1.0 μm, having sizes with great influence on the solar radiation budget. Additionally, with hydration of the sulfate ion, these aerosols act as cloud condensation nuclei (CCN), also affecting climate. The sulfate at this site has two sources; one is from sea salt, i.e., sea-salt SO_4^{2-} (SS-SO_4^{2-}), while the other one is derived from emissions from both human activities and marine biota, known as non-sea-salt SO_4^{2-} (NSS-SO_4^{2-}). The relationship between these components is given by: NSS-$SO_4^{2-} = [SO_4^{2-}]_{Total} - [Na^+] \times 0.252$, where 0.252 is the SO_4^{2-}/Na^+ mass ratio in seawater. Significant positive correlations between the secondary aerosol ions NO_3^-, NH_4^+ and NSS-SO_4^{2-} suggest that NH_4^+ mainly exists as NH_4NO_3, NH_4HSO_4 and $(NH_4)_2SO_4$. Previous studies indicate that reactions that generate NH_4^+ in the atmospheric particulate are:

$$NH_{3(g)} + HNO_{3(g)} \rightarrow NH_4NO_3, \tag{1}$$

$$NH_3 + H_2SO_4 \rightarrow (NH_4)HSO_4, \tag{2}$$

$$NH_3 + (NH_4)HSO_4 \rightarrow (NH_4)_2SO_4. \tag{3}$$

NO_3^- is mainly formed through reaction (1). Its reaction on the surface of sea salt particles gives:

$$HNO_3 + NaCl \rightarrow NaNO_3. \tag{4}$$
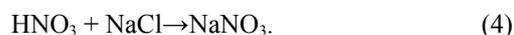
Reaction (4) produces additional NO_3^- and NH_4^+ is produced

through reactions (1), (2), and (3).

The results of our metal element analysis show that metals of crustal origin (such as Al, Zn) are more abundant than those derived from anthropogenic sources (Table 2). By comparing their absolute magnitudes, metal element concentrations at this site can be grouped into two categories: (i) those with high concentrations (above 1.00 ng·m^{-3}), including Al, and Zn; and (ii) those with low concentrations (below 1.00 ng·m^{-3}), including Pb, Cu, Zn, Cd, V, and Cr. In comparison with studies elsewhere in Antarctica, we found that metal concentrations at Great Wall Station are generally comparable to or lower than those at other stations. Clearly, the atmospheric environment at Great Wall Station is clean, with little pollution. However, the concentrations of Zn, and Al measured at Great Wall Station are relatively high (5.34 and 73.99 ng·m^{-3}). Such Zn levels are 3–4 times higher than at McMurdo Station in Antarctica, while Al levels area a factor eight higher than at Comandante Ferraz in Antarctica. As Dick and Peel[8] pointed out, there is some possibility of contamination during sample treatment, and some of the results shown in Table 1 are suspected to reflect such Zn and Al contamination. Although our values are lower than those suspected to have contamination, they still tend to be much higher than previous studies[9]. Despite the relative low concentrations of trace metals (like Pb, Cu, Cd, V, and Cr), the increase in human activities during the summer season at Great Wall Station may play an important role in contributing to aerosols of anthropogenic origin. During the summer, there are 80 researchers living at Great Wall Station that use 200 tons of oil. In addition, remobilization of surface dusts and fine-grained substances from coastal bedrock also mainly occurs during summer.

3.2 Seasonal variations of aerosols at Great Wall Station

Figure 3 shows the seasonal and monthly variations of atmospheric Cl^-, NO_3^-, SO_4^{2-}, Na^+, Ca^{2+}, K^+, Mg^{2+}, NH_4^+, and MSA over the study period. The concentrations of Cl^-, SO_4^{2-}, Na^+, Ca^{2+}, K^+, and Mg^{2+} show similar seasonal patterns, with peak concentrations occurring in autumn. This peak is attributed to seawater spray, caused by big waves and high wind speeds. Peaks were also observed in Cl^-, and Na^+ at the other coastal Antarctic locations from December to February[11]. The seasonal variation in NO_3^- was consistent

Table 1 A comparison of atmospheric concentrations of various metal elements measured in this study and with other locations in Antarctica

Site	Cu/ (ng·m^{-3})	Pb/ (ng·m^{-3})	Zn/ (ng·m^{-3})	Cd/ (ng·m^{-3})	Cr/ (ng·m^{-3})	V/ (ng·m^{-3})	Al/ (ng·m^{-3})	Reference
Great Wall Station	0.13	0.25	5.23	0.01	0.08	0.03	73.99	This study
Zhongshan Station	1.28	0.56	8.35	0.07	0.77	0.58	38.9	[10]
McMurdo Station	0.19	0.85	1.52	/	0.14	0.36	181	[9]
Comandante Ferraz	0.82	0.65	5.50	/	0.57	/	8.81	[8]

with NH_4^+, with both peak values occurring in summer and autumn. Their elevated concentrations reflect high-altitude transport from continents (or local source activities). The reactions on the surfaces of particle via reactions (1) and (4) would produce HNO_3, while reaction (4) would dominate the production of $NO_3^{-[12]}$.

The concentrations of MSA exhibited a strong seasonal cycle, with peak values occurring in summer, and minima occurring in winter. From April to October, in the austral winter, atmospheric MSA concentrations were very low. At this time, the heavy coverage of sea ice around Antarctica would result in extremely low phytoplankton activities in the ocean, with very few dimethyl sulfide (DMS) emissions. Because DMS is primarily oxidized to MSA in the atmosphere, this results in low MSA levels. From the November to March, with increasing air temperature and melting of sea ice, the phytoplankton activities in the ocean also increase. Subsequently, DMS sea-air fluxes would be enhanced, leading to relative high MSA concentrations in the atmosphere. Previous studies found that early spring blooms of phytoplankton commonly occur in polynyas; hence, the high MSA concentrations are likely related such blooms[13-14].

If we compare our results across seasons, then peak concentrations differed greatly among metals. Monthly and seasonal variations in all metals are compared in Figure 4. We observed that in the six main metals, maximum concentrations occurred during spring (Cu, Cd and Zn), summer (V and Cr), or autumn (Pb) at our study site. Previous studies of anthropogenic components in aerosols at different sites in Antarctic showed similar seasonal patterns[15]. Generally, anthropogenic components (Pb and Cu) in aerosol samples peaked during spring/summer at remote sites in West Antarctica[16]. The sources and pathways of certain metals (e.g., metals of crustal origin) should exhibit similar temporal patterns in this environment. In contrast, the increase in human activities during the summer at various locations near the Great Wall Station will enhance contamination, elevating metals of anthropogenic origin. In addition to local sources, input from South America may also be important during the summer (and autumn). This is because long-distant wind transport of aerosols is from the NW (South America) during these seasons.
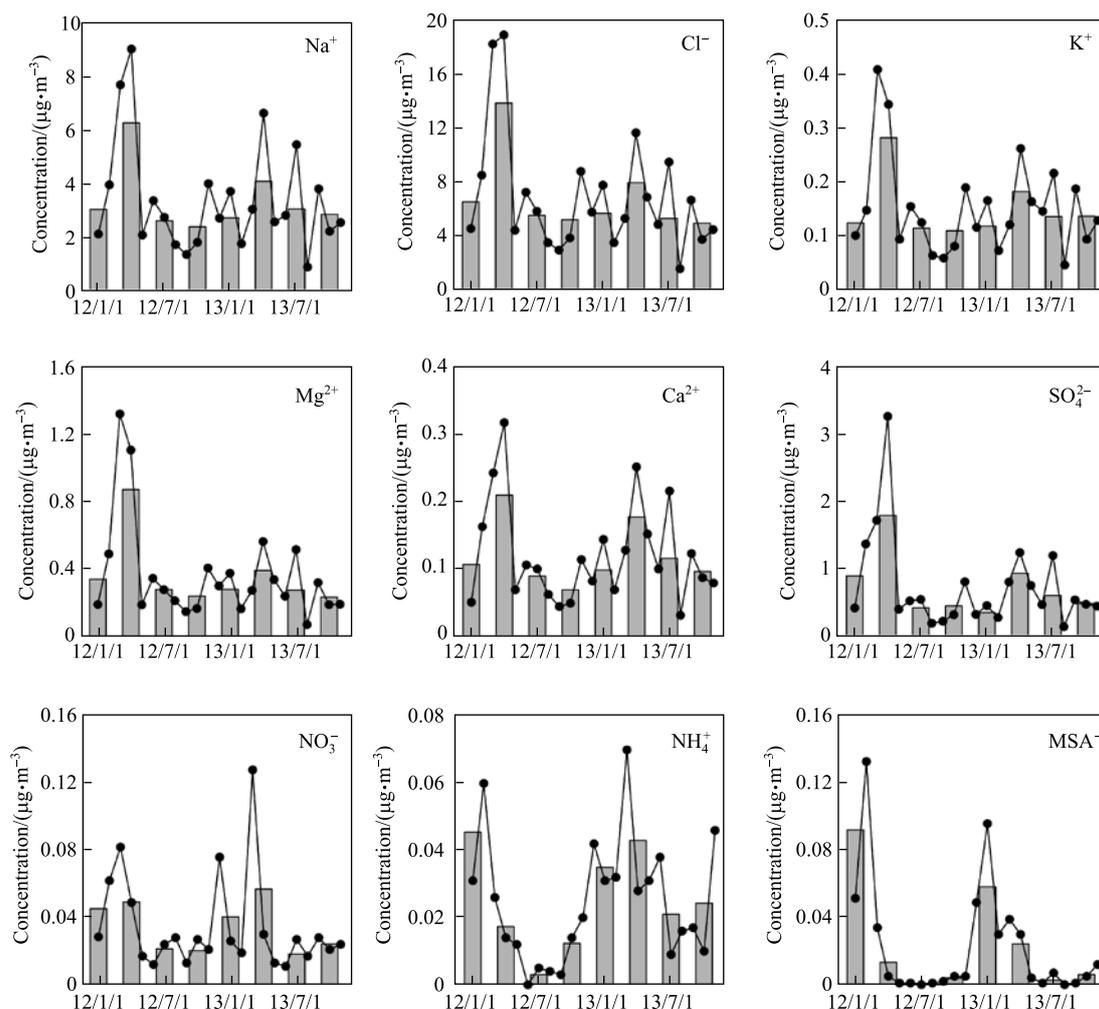

Figure 3 Seasonal and the monthly variations in atmospheric Cl^-, NO_3^-, SO_4^{2-}, Na^+, Ca^{2+}, K^+, Mg^{2+}, NH_4^+, and methane sulfonic acid (MSA) over the study period. The points and bars denote monthly values and seasonal averages, respectively.
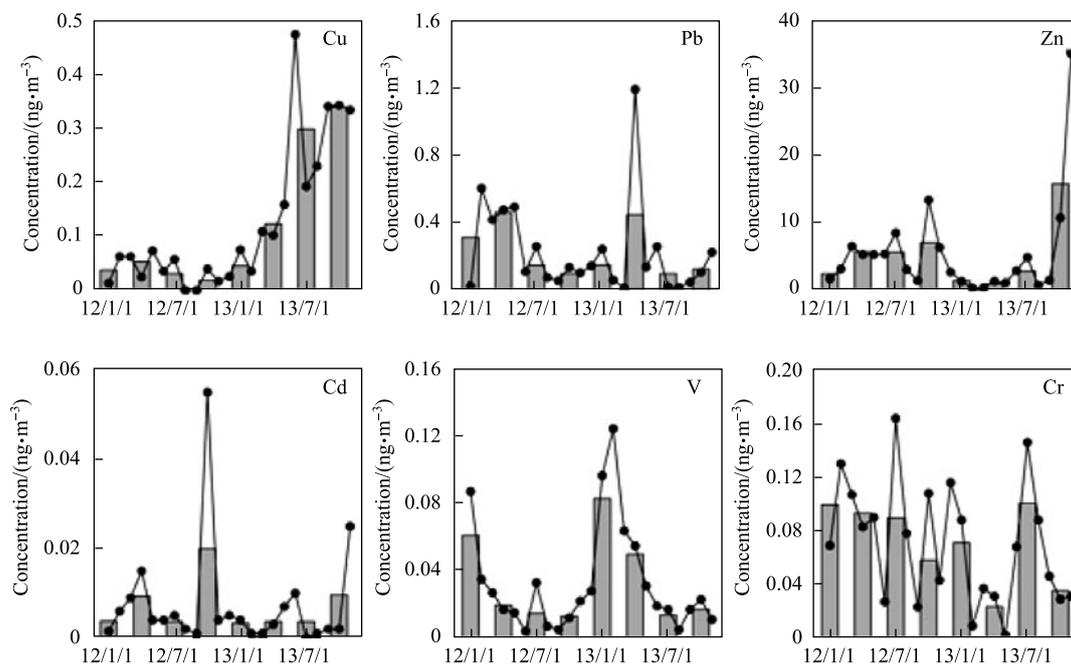
Figure 4 Seasonal and the monthly variations in atmospheric Cu, Pb, Zn, Cd, V, and Cr over the study period. The points and bars denote monthly values and seasonal averages, respectively.

3.3 Element enrichment factors for trace metal sources

Element enrichment factors (*EF*s) are calculated by normalizing data with respect to a reference metal; they are commonly used to determine sources. Here, they are defined as the ratio of a given element or compound in marine aerosol to the ratio at its source, as shown:

$$EF_I = (X_I / X_R)_{air} / (X_I / X_R)_{sou}. \qquad (5)$$

In formula (5), EF_I is the enrichment factor of metal *I*, while *R* is the reference metal element. Likewise, $(X_I / X_R)_{air}$ is the concentration ratio of element *I* and element *R* in marine aerosol, while $(X_I / X_R)_{sou}$ ratio is the concentration ratio of element *I* and element *R* in source compounds. If an *EF* value is less than 3–5, then element *I* and element *R* have a common source. While if an *EF* value is significantly larger than 3, then element *I* has a larger enrichment relative to element *R*, and its sources will be different. In aerosol studies, Na is commonly used as an indicator for marine sea salt sources, while Al is used as an indicator for crustal sources.

According to the average concentrations of the trace metals in aerosols at Great Wall Station, the *EF* of each metal element was calculated using formula (5) (Table 2). Clearly, *EF*s of Cu, Pb, Cd, Zn, Cr, and V were to 4–9 orders of magnitude more than for marine sources, having *EF*s significantly higher than 1. Therefore, these metals did not originate from a marine source. Similarly, the *EF*s of Cu, Pb, Cd, and Zn were much higher than 1, indicating that Cu, Pb, Cd, Zn, Cr, and V were not derived from crustal sources.

Table 2 Enrichment factors (*EF*s) of metal elements in aerosols from Great Wall Station

*EF*s	Cu	Pb	Zn	Cd	Cr	V	Na	Al
EF (marine source, Na)	2.61×10^8	2.19×10^9	1.55×10^9	1.43×10^8	7.46×10^5	3.59×10^4	1	2.46×10^7
EF (crustal source, Al)	5.74×10^3	1.56×10^4	6.87×10^3	4.30×10^3	3.46×10^3	1.38×10^3	20.3	1

3.4 Correlations analysis for trace metals

Correlation analyses are used to evaluate relationships between components. In general, a good relationship occurs between compounds that have a common source in the atmosphere. Thus, correlation coefficients between metal elements were analyzed to identify their sources. Pearson's correlation coefficient can be used to evaluate the linear correlation between two variables.

Strong positive correlations were found between Na and K, as well as Mg and Ca (Table 3), indicating these metal elements were mainly from sea salt. No significant correlation was found between Na and other trace metals, confirming that Pb, Cu, Zn, Cd, V, Cr, and Al were not from a marine source. Poor correlations found between Pb, Cu, Zn, Cd, Cr, and Al indicate that neither do they come from a crustal source. A

Table 3 Correlations among atmospheric metal elements at Great Wall Station

Metal	Na	K	Mg	Ca	Pb	Cu	Cd	V	Zn	Cr	Al
Na	1										
K	0.959	1									
Mg	0.944	0.973	1								
Ca	0.941	0.857	0.877	1							
Pb	0.316	0.110	0.265	0.141	1						
Cu	0.013	0.021	0.224	0.013	0.006	1					
Cd	0.024	0.032	0.173	0.010	0.134	0.114	1				
V	0.016	0.011	0.010	0.010	0.310	0.110	0.063	1			
Zn	0.034	0.118	0.141	0.006	0.009	0.130	0.442	0.316	1		
Cr	0.072	0.110	0.245	0.114	0.300	0.194	0.190	0.332	0.010	1	
Al	0.014	0.031	0.141	0.008	0.173	0.005	0.164	0.498	0.010	0.089	1

slight positive correlation found between V and Al suggests that V may be partly derived from the crust. Good correlations existed between V, and Pb, Zn, and Cd. Such correlations are characteristic of pollutants in the atmosphere; thus, Pb, Zn, and Cd were possibly derived from contamination. Very likely, pollutants and mineral dust have undergone mixing during long-distance transport. Given the complicated sources and atmospheric transport processes involved in dispersal of atmospheric metal elements, it is difficult to distinguish their sources purely on a correlation analysis.

3.5 Factor analysis of atmospheric metal element sources

Factor analysis is a multivariate statistical method, which uses a relatively small number of representative factors to explain relationships between variables. In aerosol science, factor analysis is used to apportion sources. Here, we analyzed the factors (aerosol source) of variables (elements) to evaluate their source contributions[17].

Specifically, we analyzed all 73 aerosol samples collected at Great Wall Station in our source apportionment study. We carried out a sample correlation matrix factor analysis, using principal components with eigenvalues greater than 1.4. Eigenvalues, variance contribution rates, and the cumulative variance contribution rate are shown in Table 4. The cumulative variance contribution rate for the first three factors was 62.35%. Therefore, these three factors provide an adequate description of the metal element sources in this study. Our results show that the first factor has greatest loadings of Na, K, Mg, and Ca, the second factor has greatest loadings of Cu, Pb, Zn, and Cd, while the first three factors in Al are also loaded in V. The first factor is clearly related to marine sources, while the second factor is related to pollution, and the third to crustal sources. From the above analysis, we conclude that atmospheric trace metal elements at the Great Wall Station are influenced by three main factors, specifically marine, crustal, and pollution aerosol sources.

Table 4 Eigenvalues, contribution rates of variance, and cumulative contribution rates of variance of metal elements in the atmosphere at Great Wall Station

Factor	Eigenvalues	Contribution rates	Cumulative contribution rates
F_1	3.826	34.783	34.783
F_2	1.604	14.584	49.367
F_3	1.428	12.979	62.346
F_4	1.154	10.489	72.835
F_5	0.956	8.691	81.526
F_6	0.786	7.145	88.671
F_7	0.593	5.393	94.065
F_8	0.429	3.904	97.969
F_9	0.183	1.662	99.631
F_{10}	0.026	0.235	99.866
F_{11}	0.015	0.134	100.000

Using the factor analysis eigenvalue formula for sources of metal elements (CM):

$$CM = \frac{\lambda_1}{\lambda_1 + \lambda_2 + \lambda_3} F_1 + \frac{\lambda_2}{\lambda_1 + \lambda_2 + \lambda_3} F_2 + \frac{\lambda_3}{\lambda_1 + \lambda_2 + \lambda_3} F_3, \quad (6)$$

where F_1 is the marine factor, F_2 is the pollution factor, and F_3 is the crustal factor, we can obtain the following relationship at our study site:

$$CM = 0.387 F_1 + 0.311 F_2 + 0.302 F_3. \quad (7)$$

Here, the marine factor is the most prominent, while pollution and crustal factors have a similar influence. The impact of the crust is only slightly larger than pollution at this site. Thus, anthropogenic pollution at the Great Wall Station plays an important role in contributing metals to the

atmosphere. However, metals concentrations are not only derived from air pollution, but also from crustal sources.

4 Conclusions

The concentrations of aerosol components were measured at Great Wall Station, off the Antarctic Peninsula, to characterize their compositions and seasonal variations. High concentrations of several species (like Na^+, K^+, Ca^{2+}, and Mg^{2+}) were attributed to oceanic input. Very high *EF* values (above 100) for a few anthropogenic metals (Cu, Pb, Zn, and Cd) indicated the important role of local anthropogenic processes at this remote location. When compared across seasons, most atmospheric ions had highest concentrations in summer and autumn, with lower concentrations in winter and spring. The increase in some oceanic species during summer and autumn reflects an increase in sea-salt aerosol formation at these times. Variations in atmospheric trace metals were related to anthropogenic pollution and crustal material derived from both local and distant sources. The enhanced concentrations of some metals and ions in summer may indicate contributions from local sources related to the human activities at Great Wall Station at those times. Correlation analysis and factor analysis identified three strongly correlated groups, namely, crustal metals, sea salt, and anthropogenic pollutants, whereby Na^+, K^+, Ca^{2+}, and Mg^{2+} are from marine sources, Cu, Pb, Zn, and Cd are mainly from pollution , while Al, V are mainly from crustal sources.

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