



GEOSCIENCES

Anthropogenic trace elements (Bi, Cd, Cr, Pb) concentrations in a West Antarctic ice core

FRANCIÉLE SCHWANCK, JEFFERSON C. SIMÕES, MICHAEL HANDLEY, PAUL A. MAYEWSKI & RONALDO BERNARDO

Abstract: Trace elements are emitted to the atmosphere from natural and anthropogenic sources. The increase in industrialization and mining occurring from the late 19th century released large quantities of toxic trace elements into the Earth's atmosphere. Here we investigate the variability of concentrations of bismuth, cadmium, chromium, and lead in two Mount Johns – MJ (79°55'28"S, 94°23'18"W, 2100 m a.s.l.) ice cores over 132 years (1883-2015). Trace element concentrations were determined using inductively coupled plasma mass spectrometry (CCI/UMaine). The data show evidence of pollution for these elements in Antarctica as early as the 1883. Several maxima concentrations were observed: first at the beginning of the 20th century and the last from 1970s to 1990s, with a clear decrease during recent years. Emissions occur from different anthropogenic sources and appear to be variable throughout the record. The main source of these elements is attributed to mining and smelting of non-ferrous metals in South America, Africa, and Australia. As well as a probable lead enrichment due to the use of fossil fuels. The MJ ice core record also reflects changes in atmospheric circulation and transport processes, probably associated with a strengthening of the westerlies.

Key words: Antarctica, anthropogenic emissions, ice core, transport.

INTRODUCTION

Trace elements are emitted to the atmosphere from natural sources including oceans, landmasses, volcanism, biomass burning, and biogenic activity (Nriagu 1989, Planchon et al. 2002, Dixon et al. 2013), and anthropogenic processes such as fossil fuel combustion, mining, ferrous and non-ferrous metal production, and waste incineration (Pacyna & Pacyna 2001, Eichler et al. 2014, Schwanck et al. 2016a).

These elements are ubiquitous throughout the environment, some are essential for life (e.g., Cu, Fe, and Zn), others are micronutrients (e.g., Se) and a few are considered toxic elements at any level (e.g., Cd, Hg, and Pb), meaning that continued emission could have future

implications for human health (Barbante et al. 2017).

Transport and deposition of trace elements occur in the aerosol phase. Primary aerosols can be generated by the dispersion of fine materials from the Earth's surface or windblown. In contrast, secondary aerosols are formed by chemical reactions and the condensation of atmospheric gases and vapors (McConnell & Edwards 2008). Both types are transported over long distances through the troposphere (Petit & Delmonte 2009) and sometimes through the stratosphere (Krinner et al. 2010), leading to deposition in remote areas such as Antarctica. The distance over which an aerosol particle is transported depend on its size, shape, mass, and other physical and chemical properties

(Barbante et al. 2017). Atmospheric lifetimes of most contaminants are short, the average varies from < 1 day for large particles ($> 10 \mu\text{m}$) to 2 – 4 weeks for smaller particles ($< 5 \mu\text{m}$) (Mahowald et al. 2011).

Impurities in snow and ice layers from polar regions provide a robust and well-preserved history of atmospheric circulation patterns (Dixon et al. 2011, Delmonte et al. 2017, Aarons et al. 2017). The chemical record of ice cores provides important information about cyclone activity (Hosking et al. 2017), wind intensity (Koffman et al. 2014), sea ice conditions (Criscitiello et al. 2014, Mezgec et al. 2017), and aridity and vegetation cover (McConnell et al. 2007). Past research demonstrates the extent and timing of global contamination by anthropogenic emissions (Hong et al. 2012, Tuohy et al. 2015, Potocki et al. 2016, Schwanck et al. 2016a). These studies reveal the history of human interferences in the environmental mobilization of these elements at regional and global scales.

In this paper, we present Bi, Cd, Cr, and Pb concentration records from 1883 to 2015, as obtained from two ice cores drilled on the Pine Island Glacier, West Antarctica. This region is mainly affected by the circumpolar westerly winds over the Southern Ocean and the permanent cyclone belt over the polar fronts (Hoskins & Hodges 2005). The concentration records are used to assess for the historical anthropogenic emissions of these elements from the South Hemisphere.

MATERIALS AND METHODS

Sampling site and ice-core characteristics

In December 2008 a 91.20 m long ice core was retrieved approximately 70 km from the nunatak Mount Johns – MJ ($79^{\circ}37'S$, $91^{\circ}14'W$), near Pine Island Glacier divide ($79^{\circ}55'28''S$, $94^{\circ}23'18''W$; elevation 2,122 m above sea level – a.s.l.) and in

2015 a second core (19.12 m) was drilled at the same site (Fig. 1). The ice thickness at the ice core site reaches 2,115 m (determined from the Bedmap 2 project data; Fretwell et al. 2013).

The drilling site was chosen due to its comparatively high accumulation rate (approximately 0.21 m water equivalent per year (w. eq. y^{-1})), which ensures seasonally preserved stratigraphic resolution (Schwanck et al. 2016b). This is a region of interest due to the pattern of atmospheric circulation, originating from the confluence of air masses from the Weddell, Amundsen, and Bellingshausen seas (Parish & Bromwich, 2007, Thoen et al. 2018).

Drilling of the first core was performed using the Fast-Electromechanical Lightweight Ice Coring System (FELICS) (Ginot et al. 2002). The second core was drilled using a Mark III auger (Kovacs Enterprises, Inc.) coupled with an electrical drive powered by a generator

Ice-core sections (1 m long, 8.5 cm diameter) were sealed in polyethylene bags and then stored in high-density Styrofoam boxes in the field and transported frozen to the Climate Change Institute (CCI), University of Maine for chemical analyses. For this study, only the upper part of the first ice core (0 – 45 m) was analyzed, the second ice core was fully analyzed. The timescale for both covers the period of 1883 – 2015 derived using a combination of annual layer counting and the identification of known volcanic eruptions (details in Schwanck et al. 2017).

Samples preparation and analytical procedures

Decontamination of the MJ ice cores was carried out in a certified cold room ISO 5 with temperature below -20°C (details in Schwanck et al. 2016a). The cores sections were melted using a continuous ice core melter system (details in Osterberg et al. 2006). Sampling resolution of

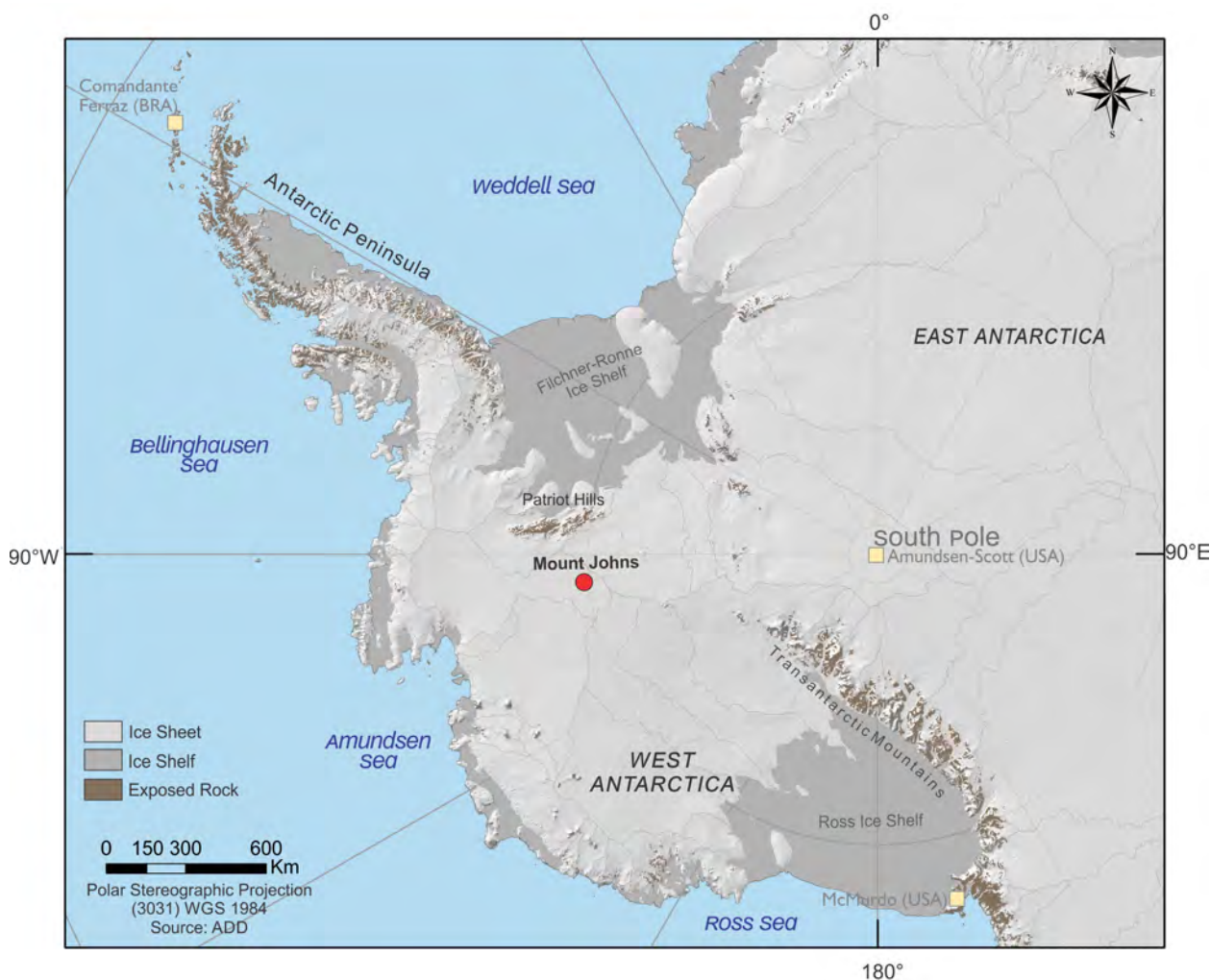


Figure 1. Map of West Antarctica showing the Mount Johns – MJ ice core site (79°55'28"S, 94°23'18"W).

the continuous record varied from 2 to 4 cm. The samples for trace elements analysis were collected into acid-cleaned (Optima HNO_3), low density polyethylene (LDPE) vials and acidified to 1 % with double-distilled HNO_3 . All samples handling were conducted in an ISO 5 clean room under a laminar flow High Efficiency Particle Air (HEPA) bench. Acidification time (at room temperature) was at least one month before analysis.

Concentrations of Bi, Cd, Cr, and Pb were determined by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) using a Thermo Electron Element 2 (CCI, United States). Working conditions and measurement

parameters are described in Schwanck et al. (2016a). Samples of de-ionized water, or "blanks", were prepared, treated, and analyzed using the same method applied to snow and ice samples. The Method Detection Limits (MDL) were defined as three times the standard deviation of blank samples (10 blank samples were used). Concentrations below the MDL were removed, which occurred in a few cases (minor than 1%).

Calculations of flux and enrichment factors

Flux was calculated by multiplying the elements concentrations in the ice (X_{ice}) by the meter water-equivalent (w. eq.) accumulation rate per

year for each sample. The annual deposition flux was estimated by Eq. (1).

$$\text{Flux} = X_{\text{ice}} \times w.\text{eq.} \quad (1)$$

A common approach for distinguishing between natural and anthropogenic sources for trace elements in the environment is to calculate a normalized enrichment factor for the element concentrations above uncontaminated background levels (Duce et al. 1975, Krachler et al. 2005). The calculation of the crustal enrichment factor (EF_C) is based on a conservative (lithogenic) element indicative of mineral matter, such as Al, Ba, Mn etc. (the enrichment factor was calculated using Al, Ba, and Mn concentrations and it is presented as the average of the calculated values, more information can be found in the Supplementary Material - Table SI), in addition to the reference element (e.g., Earth's Upper Continental Crust (UCC)), according to Eq. (2).

$$EF_C = \frac{X_{\text{ice}}/Y_{\text{ice}}}{X_{\text{ref}}/Y_{\text{ref}}}, \quad (2)$$

where X_{ice} is the trace element concentration in the sample, Y_{ice} is the chosen element concentration in the sample, and X_{ref} and Y_{ref} are the trace element and the chosen element concentrations in the reference material, respectively. UCC reference values were obtained from Wedepohl (1995). The interpretation of the enrichment factor is that an element with an enrichment factor value near unity has a probable source in the crustal material and elements with enrichment factor value larger than unity could be mainly of anthropogenic origin (Reimann & Caritat 2005).

Apart from assessing the upper crust, we also analyzed the sea salt spray effect on these trace element deposition at MJ site. Contributions from marine aerosols were estimated using the

ocean enrichment factor (EF_O) from the equation 3 (Osterberg 2007):

$$EF_O = \frac{X_{\text{ice}}/Na_{\text{ice}}}{X_{\text{ref}}/Na_{\text{ref}}}, \quad (3)$$

where X_{ice} is the trace element concentration in the sample, Na_{ice} is the Na concentration in the sample, and X_{ref} and Na_{ref} are the trace element and Na concentration in the reference material. Sodium is used as the reference element because it is the main sea salt constituent (Weller et al. 2008, Dixon et al. 2013). We used the mean composition of ocean water (Lide 2005) as a reference for the ocean elemental abundances.

HYSPLIT back-trajectory modeling and cluster analysis

To explore possible sources of the observed trace elements in aerosols, air mass backward trajectories were simulated for 1000 m above ground level over the drilling site. Trajectory simulations were made using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, developed by the NOAA Air Resources Laboratory (Draxler et al. 2010) in conjunction with the global reanalysis datasets from the National Centers for Environmental Prediction (NCEP) and the National Center for Atmospheric Research (NCAR), known as NCEP/NCAR reanalysis model (NCEP1) (Kalnay et al. 1996, Kistler et al. 2001).

Ten-day (240 hr), 3D back-trajectories were simulated from the MJ site at 00:00 UTC daily from January 1948 to January 2015 (a total of 24,406 trajectories). The ten-day simulation is an appropriate time-length when considering the average lifetime transport (10 days) of small size (0.1 – 2.5 μm) fractions of mineral dust and other aerosols, while transport of large particles (> 2.5 μm) is likely restricted to the first several days (Albani et al. 2012).

In order to obtain information about airflow patterns at the MJ site, a cluster analysis was applied to a database of individual trajectories (24,406 daily trajectories). The HYSPLIT model's cluster analysis algorithm groups trajectories by minimizing the spatial variability between trajectories within some defined number of clusters (Draxler 1999). For the trajectories presented here, it is determined that seven clusters are enough to capture seasonal variability during the 1948 to 2015 period.

RESULTS

Data presentation

Ice-core concentration and fluxes records of Bi, Cd, Cr, and Pb are presented in Fig. 2. Table I shows the summary statistics. The concentrations vary strongly with the season and show differences of about one order of magnitude between summer and winter values (Supplementary Material - Fig. S1 and Fig. S2). This behavior is attributed to different meteorological conditions within the seasons, as well as higher availability of these elements at source areas.

Concentrations of Cd, Cr, and Pb show similar trends, these elements present high concentrations in the first part of the record (1883 – 1935), remain at a low level for the period from 1935 to ~1965 and then increase between 1965 and 2008 with a decrease in recent years. This is different for Bi, increasing only after the mid-1970s.

The values of crustal enrichment factors for the measured trace elements are shown in the Fig. 3 and the oceanic enrichment factors are presented in the Fig. S3. The average EFC values are observed to be highly variable between elements, with the lowest mean value determined for Pb (13.11) and the highest

determined for Cd (550.27). The mean EFC values show a highly enriched content relative to oceanic water (> 5,000) for all elements, indicating a minor marine contribution. Overall, the mean values of EFC are relatively higher for Bi, Cd, Cr, and Pb (enriched elements, all higher than 10), reflecting an important contribution from anthropogenic sources.

In order, to understand the behavior of these trace elements we apply Principal component analysis (PCA). PCA is a multivariate statistical method that is frequently used to simplify large and complex datasets to identify potential species sources. In this study, Origin Pro 2019 for Windows (OriginLab Corporation, USA) was utilized for the analysis.

Trace elements that are continental dust markers (Al), marine spray markers (Na), as well as $\delta^{18}\text{O}$ (temperature marker) and accumulation data were added to the analysis aiming to find relationships.

The first 6 PCA explain 96.77% of the total variance of our data (Table II). The first 2 principal components (PC1 and PC2), that explain 55.83 % of the total data variance are the most important in this analysis. PC1 is dominated by Cd, Cr, and Pb, representing 39.64% of the total variance, it indicates similar behavior for these elements. PC2 is dominated by Bi, $\delta^{18}\text{O}$, and accumulation, it represents 16.18% of the total variance, which may suggest that the Bi have a different source and its deposition is associated with higher accumulation rates. Cd, Cr, and Pb show a low relationship with crustal (Al) and marine (Na) transport, as well no variability associate to temperature and accumulation.

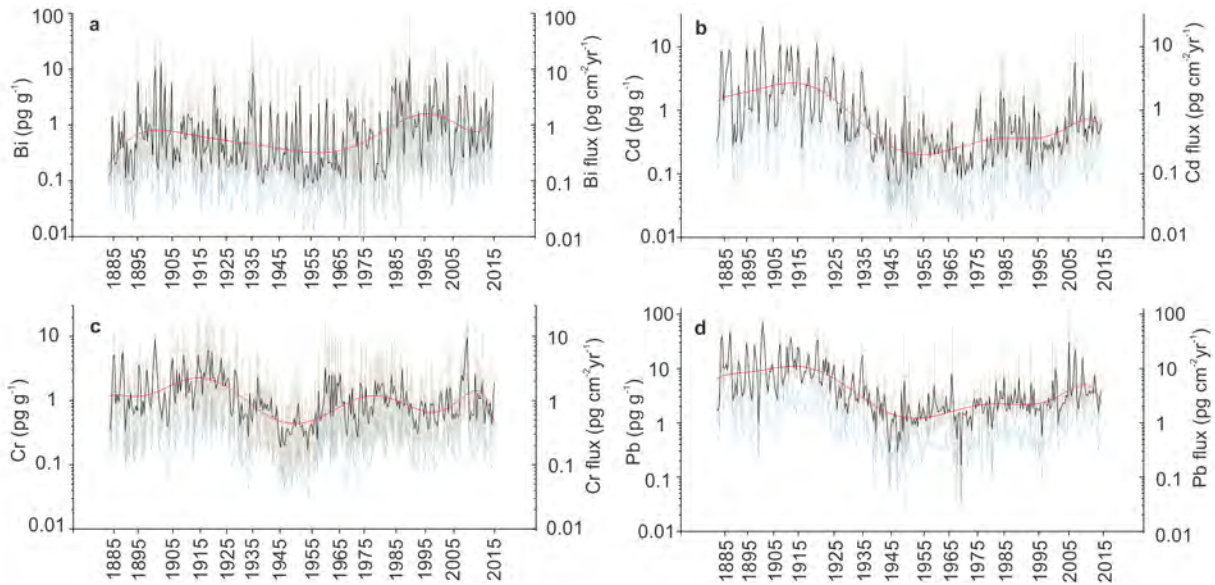


Figure 2. Ice-core concentration records of Bi, Cd, Cr, and Pb for the period of 1883 – 2015. The gray line is raw data and the black line is the 8-sample running average. The blue line represents the 8-sample running average for the flux and in red the trend line.

Table I. Statistical summary of Bi, Cd, Cr, and Pb concentrations (in pg g^{-1}) determined in MJ ice cores.

Elements	Mean	Median	Standard Deviation	Mean Uncertainty	Min	Max	MDL*
Bi	1.094	0.249	3.025	0.064	0.027	35.082	0.026
Cd	1.501	0.425	2.911	0.061	0.021	29.664	0.019
Cr	13.758	5.589	23.898	0.501	0.556	260.239	0.520
Pb	6.018	2.634	9.712	0.204	0.151	88.768	0.148

*Method Detection Limits.

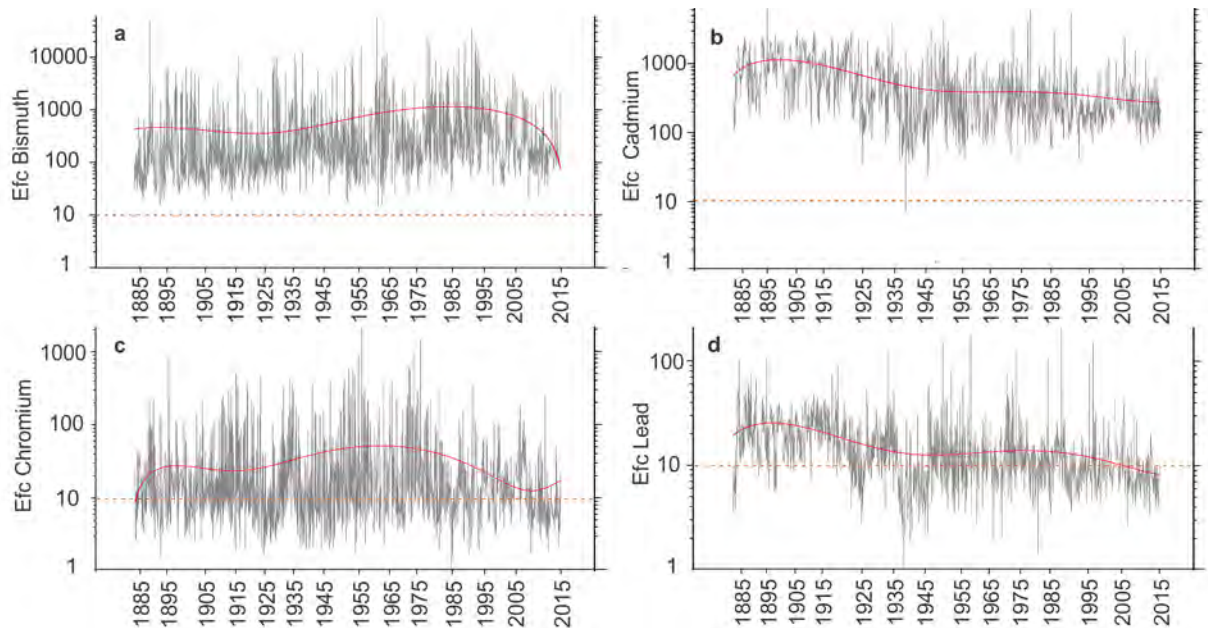


Figure 3. Ice-core crustal enrichment factor (Efc) records of Bi, Cd, Cr, and Pb for the period of 1883 – 2015. The red line is the trend line.

Table II. Principal Component Analysis (PCA) loadings for the trace element concentrations analyzed in MJ ice cores (PCA loadings > 0.3 or < -0.3 are shown in bold).

Elements	PC1	PC2	PC3	PC4	PC5	PC6
Bi	0.206	0.306	0.477	-0.648	0.462	0.005
Cd	0.517	0.023	-0.271	0.016	-0.069	-0.119
Cr	0.496	0.076	-0.222	0.068	0.132	-0.092
Pb	0.534	0.025	-0.214	0.000	-0.025	-0.077
Al	0.249	-0.282	0.393	0.569	0.452	0.404
Na	0.297	-0.100	0.433	-0.156	-0.726	0.384
d ¹⁸ O	0.039	0.605	0.405	0.468	-0.178	-0.465
Accumulation	-0.074	0.666	-0.313	0.083	0.019	0.667
Variance	39.64%	16.18%	12.02%	10.79%	9.48%	8.66%
Cumulative	39.64%	55.83%	67.84%	78.63%	88.11%	96.77%

DISCUSSION

Natural sources

Natural sources of Bi, Cd, Cr, and Pb include mineral dust and sea salt spray, volcanic emissions, forest fires, and direct biogenic emissions. To separate the natural and anthropogenic sources of these trace elements, we calculate the excess (Ex) elemental concentration. To determine Ex (i.e., the elemental contribution from sources other than mineral dust and ocean spray), we calculated the crustal and oceanic contribution and subtracted them from the raw concentrations.

Based upon the average Earth's crust composition, the proportion of the crustal input of trace element (TEc) can be estimated as follows:

$$TEc = Al_{ice} \times (TE_{crust} / Al_{crust}) \quad (4)$$

where TEc is the fraction of the crustal origin of the element, Al_{ice} is the Al concentration in the sample, and TE_{crust} and Al_{crust} are, respectively, the trace element and Al concentrations in

the reference material. The oceanic fraction was calculated using the same equation but substituting aluminum for sodium as the reference material.

The excess trace element (Ex) is then obtained as follows:

$$Ex = TE_{total} - (TE_{crust} + TE_{oceanic}) \quad (5)$$

Sea-salt spray was considered a negligible source of the four trace elements, with the values ranging from less than 1% of the measured concentrations. Furthermore, we cannot exclude an impact from mineral dust on the Bi, Cr, and Pb concentration records. These trace elements present 14.10%, 24.43%, and 26.69% respectively of their total concentration being from crustal origin. For the trace element Cd, the crustal influence is the ~1.08%. We acknowledge that Cd may have an additional contribution from biogenic processes, but due to a lack of data, we will not address this issue here.

Volcanic emissions (from quiescent degassing and explosive eruptions) could contribute significantly to the natural emission

of trace elements (Mather et al. 2012). However, due to the occasional occurrence in our data (affecting specific years) we chose not to address this aspect in this paper. Fig. 4 shows the excess concentration for the trace elements analyzed.

Anthropogenic sources

The major anthropogenic sources emitted to the atmosphere include fossil fuel combustion, non-ferrous metals production (especially Cu smelting), iron and steel production, vehicular traffic, waste incineration, cement production, and biomass burning (Pacyna & Pacyna 2001).

The best solution for assessing the emission of trace metals from smelters is to measure these emissions. However, such measurements are largely lacking in South American and African countries (Pacyna & Pacyna 2001). In order to quantify the sources affecting the inputs of the measured elements, we used historical records of the non-ferrous metal mining in South America (Argentina, Bolivia, Brazil, Chile, Colombia, Ecuador, Peru, and Venezuela), Africa (Algeria, Angola, Cameroon, Congo, Egypt, Kenya,

Madagascar, Morocco, Mozambique, Namibia, Nigeria, South Africa, Sudan, Tanzania, Tunisia, Uganda, Zambia, and Zimbabwe), and Oceania (Australia, New Zealand, New Caledonia, and Papua New Guinea) as a surrogate for the emission rates. These historical records were obtained from international and national mineral statistical yearbooks (<https://www.usgs.gov/centers/nmic/minerals-yearbook-metals-and-minerals>). Fig. 5 shows the annual production in tons of Pb in the Southern Hemisphere, as well as the excess concentration measured for Pb, for the period between 1883 – 2015 (annual production for Bi, Cd, and Cr are in the Figures S4, S5, and S6).

The production of Bi and Pb (mainly in South America and Oceania) increased after 1884 reaching a maximum by 1918 with a temporary low during the Great Depression (1931) and again just after the end of World War II (1948). Production increased after 1960 and remained high until the present for Pb and decreases considerably for Bi in the last decade. The historical production data for Cd starts

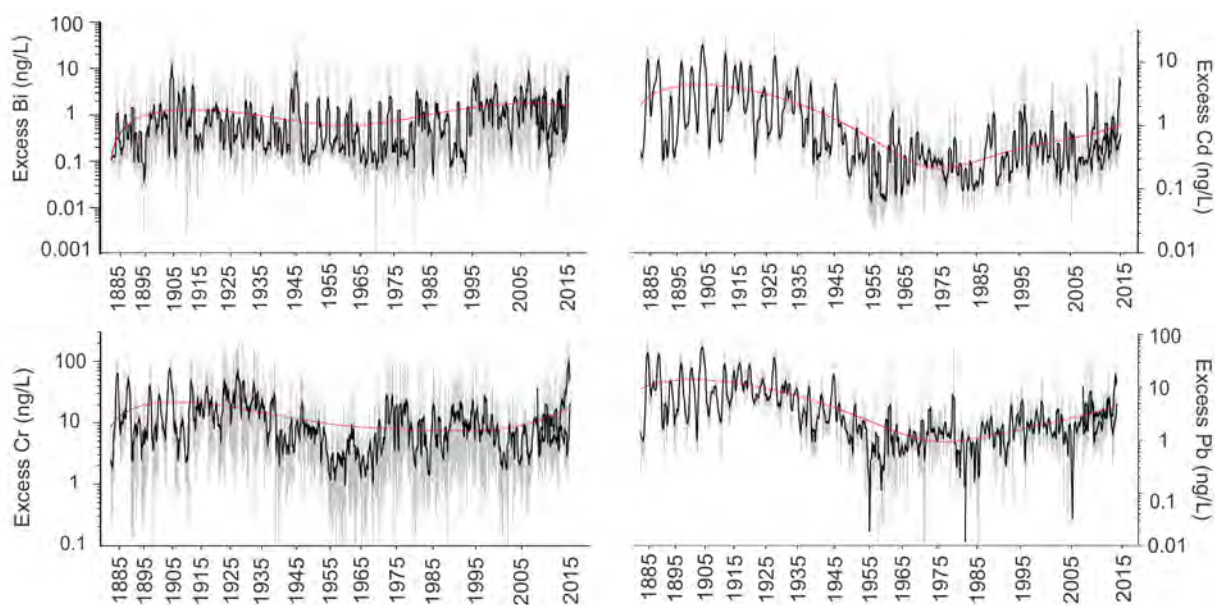


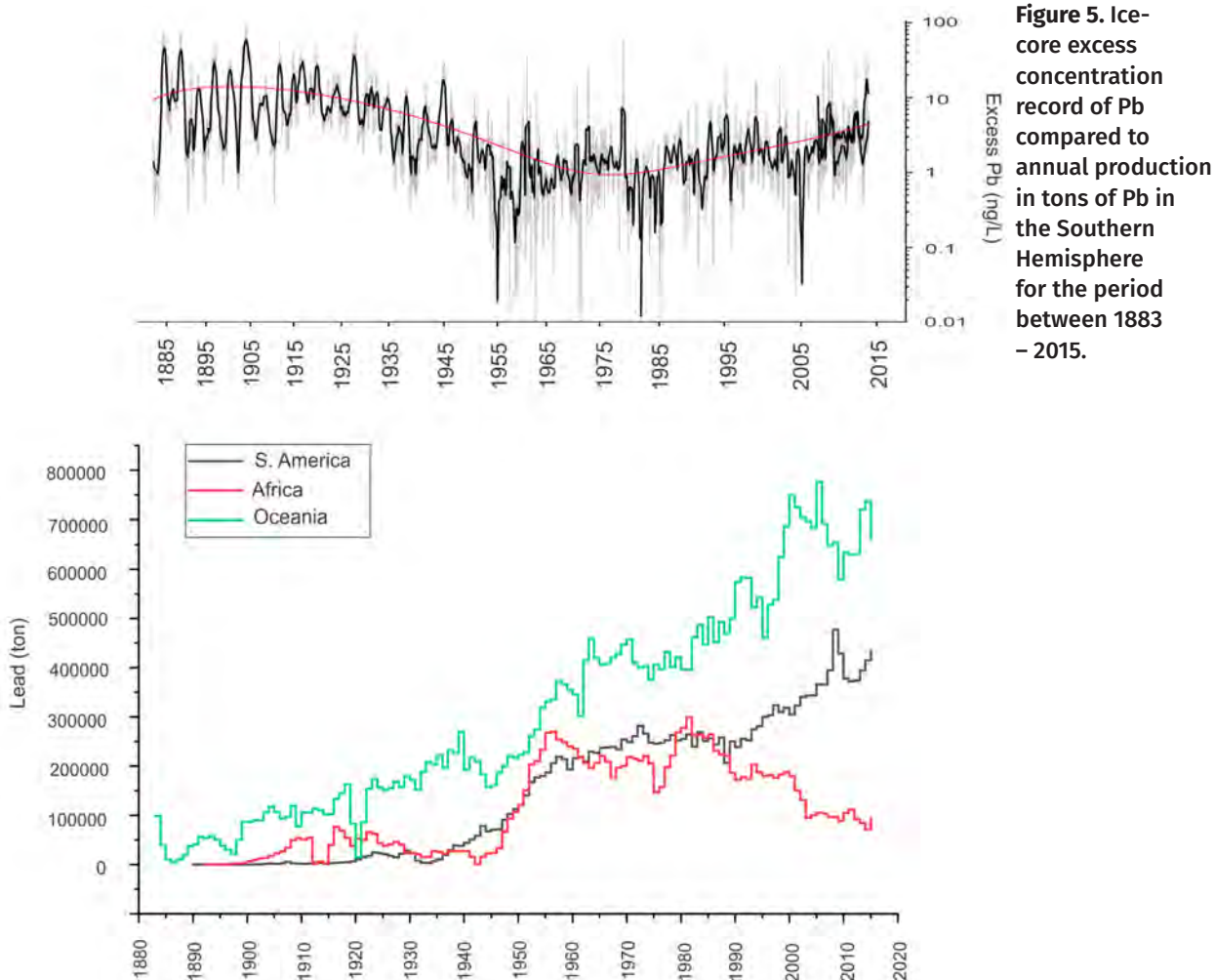
Figure 4. Ice-core excess concentration records of Bi, Cd, Cr, and Pb for the period of 1883 – 2015. The gray line is raw data, and the black line is the 8-sample running average. The red line represents the trend line.

around 1920 and shows different production peaks for the different continents analyzed. The Cr production is significant only for production on the African continent and has increased considerably since 1945.

When comparing measured trace element excess-concentrations with mining production historical data in the Southern Hemisphere, some similarities were observed. The correlation analysis between the production data and the measured concentrations also showed that the records are related to each other (Table SII). Concentrations of Cd, Cr, and Pb present high levels in the first part of the record (1883 – 1935), remained on a low level in the period from 1935 to 1965, and increase from 1965 to

2008, and decrease in recent years. The decline of excess-concentrations around the 1940s and 1950s suggests that there was a weakening in anthropogenic inputs to the remote Antarctic during that period. There are evidences of a decline in the corresponding emissions due to the economic recession and World War II (Planchon et al. 2003).

There is no doubt that increase in Pb concentrations in Antarctica after 1960 was a consequence of the great rise in the use of leaded gasoline in the southern hemispheric continents (Barbante et al. 1997). However, our data does not demonstrate this. Although excess-concentrations increased after 1960, it does not reflect the use of leaded gasoline as



data from other Antarctic places, as examples, records from Law Dome, East Antarctica (Vallelonga et al. 2002), and Coats Land, West Antarctica (Planchon et al. 2003). However, we cannot disregard the contribution of these emissions to the measured concentrations.

The trace element record shows a better fit with the production record in the first period (1883 – 1950) than in the second period (1950 – 2015), since 1950 onwards the mineral production of these elements has increased considerably, while the excess-concentration level in the MJ samples has decreased when compared to the first period of the profile. This suggests there have been changes in either the sources for these elements or the atmospheric transport or atmospheric circulation efficiency was large enough to significantly change the recorded concentrations. McConnell et al. (2014) showed similarities between multi-decadal ENSO variability and lead flux during the industrial era (post-1890) indicate that changes in long-range transport in addition to emissions may contribute to the observed variations in lead deposition over Antarctica.

Atmospheric transport to Mount Johns ice core site

The HYSPLIT model was used to simulate backward trajectories over the drilling site. The simulation aimed to explore possible sources for the observed trace elements and understand the transport of these elements to the MJ area. The trajectories were clustered over austral summer (December–January), fall (March–May), winter (June–August), and spring (September–November) months (Fig. 6). For the simulations presented here, we suggest that seven clusters are enough to capture seasonal variability during the period.

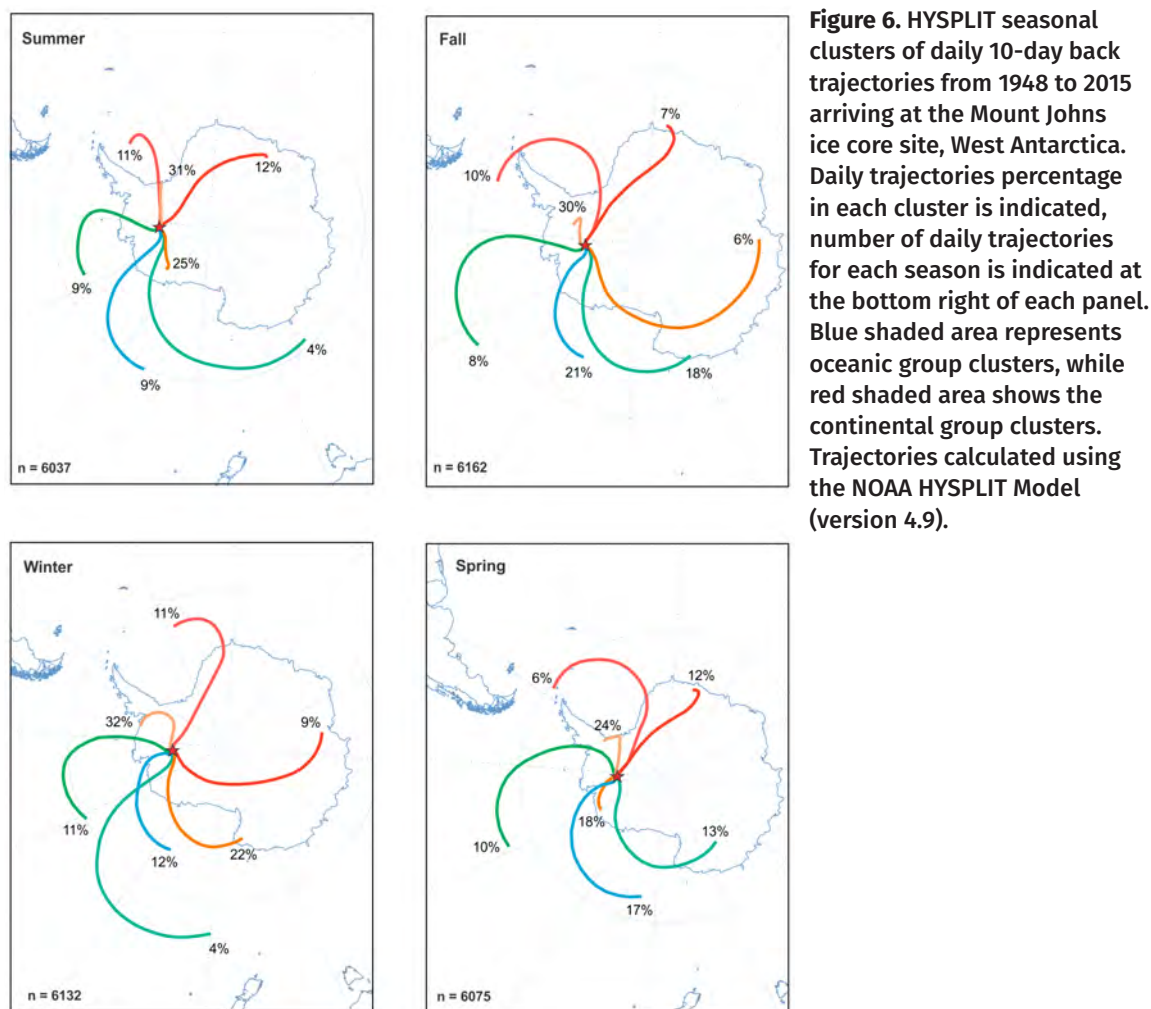
The back-trajectory analysis shows distinct seasonality, with strong westerly transport

in the fall/winter months and a secondary northeasterly transport in the summer. The MJ site receives most air masses from the Amundsen Sea, and less frequently, from the Weddell Sea. During warm periods, the trajectories present slow-moving (short lines) transport and are more locally influenced than in cold periods.

It is possible to identify three clusters with dominant westerly flow patterns ranging from fast (long lines) to slow-moving (short lines) depending on the season; one cluster includes fast-moving trajectories with strong cyclonic curvature around the Ross Ice Shelf (whole year); a group with northeasterly direction, and two continental grouping that contains mainly katabatic flow paths from the interior.

We also applied the cluster analysis in two 10-years periods (1948 – 1957 and 1998 – 2007) to investigate the transport variation (Fig. 7). For the first period (1948 – 1957), the trajectories are shorter and start close to the continent in all seasons. During this period less long-distance transport occurs, since the trajectories start on the Antarctic coast, which can be seen in the blue dots (each one is a starting point). During the second period (1998 – 2007), and especially during the winter season, the trajectories begin far from Antarctica and many of them over continental areas of South America and Oceania, a long-distance transport responsible for a greater remobilization and transport of aerosols and dust from these areas, as well as the transport of pollutants. This pattern was also identified by Neff & Bertler (2015), which showed that the West Antarctica is dominated by New Zealand and Patagonia air masses, while in interior East Antarctica, source contributions are limited and highly mixed.

In order to understand the meteorological variable that most affects this ice core record, we also show the 2m-temperature and 250hPa U-wind and V-wind anomalies for the two



periods (Fig. 8). The solutions were found using NCEP/NCAR reanalysis (ClimateReanalyzer.org). With this analysis, it was possible to identify that temperature was not a decisive factor in transport variability, since the drilling site is located in an area that is not yet directly affected by large-scale warming (blue area – Fig. 8a). This can be confirmed by the stable isotope record (Fig. S7) which has low variability compared to records from the Antarctic Peninsula and the coastal region of WAIS. However, when looking at the 250-hPa circulation (i.e., jet stream), it is evident that there has been a strengthening and contraction of the jet stream around Antarctica (U-winds; Fig. 8b) as well as increased poleward transport (V-winds; Fig. 8c) between the two

periods. Several studies have shown that the westerlies in the Southern Hemisphere have increased in speed and shifted toward Antarctica over the last few decades through the combined influence of an increase in greenhouse gases and stratospheric ozone depletion (Mayewski et al. 2015, Goyal et al. 2021). Since the 1950s, the SAM (Southern Annular Mode) has trended toward increasing positive polarity (i.e., increasingly low pressure over Antarctica), characterized by a strengthening polar vortex and intensification of the westerly winds (Thompson & Solomon 2002, Fogt & Marshall 2020). After 1965, the MJ record peaks at times that are consistent with positive SAM, but the two records do not correlate (Table SIII). This likely reflects the fact that the MJ site

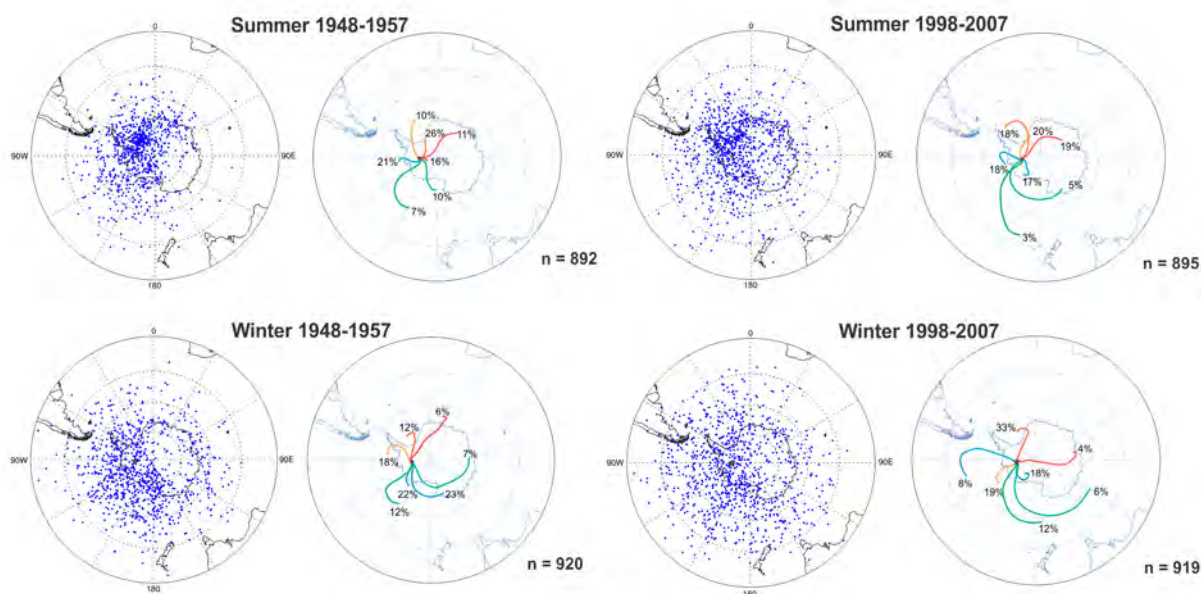


Figure 7. HYSPLIT seasonal cluster analysis in two 10-year periods (1948 – 1957 and 1998 – 2007) of air masses trajectories arriving at the Mount Johns ice core site, West Antarctica.

is influenced almost exclusively by cyclonic systems and onshore winds in the Amundsen-Bellinghousen Sea region, whereas the SAM indices represent zonal and seasonal averages in sea-level pressure.

Based on these finds, it is possible to state that the transport of these four elements depend on long distance transport and occurs preferentially during winter. It also reflects changes in atmospheric circulation, probably associated with a strengthening and contraction of the westerlies. This may explain the difference between the concentrations measured in Antarctica and the historical data on mineral production, the latter shows a continuous increase in production while the concentration profiles show variations along the record.

Environmental laws and air pollution control

Public awareness of the toxicity of many pollutants grew during the 1990s. Recognition of the health effects led to development of cross-industry regulation and health and safety

procedures in some countries (OECD/ECLAC 2005, OECD 2007).

Between the many environmental reforms of the early 1990s, South American countries (Argentina, Brazil, Chile, Colombia, and Venezuela) introduced for the first time environmental constitutional amendments and national environmental laws (Table SIV), along with government agencies to oversee environmental management (Hochstetler 2002). Similarly, in Australia and New Zealand, a variety of amendments to existing environmental and safety policies, along with new laws were passed to tighten regulations of pollutant emissions (McLaughlin et al. 2000).

It is discernible a reduction in the concentration's values in the MJ ice core in recent years (Fig. 9), what can be relate to a decrease in anthropogenic emissions reaching Antarctica. Although it cannot be said with certainty it is possible that the introduced policies along with public awareness successfully achieved an important reduction in atmospheric emission of heavy metals.

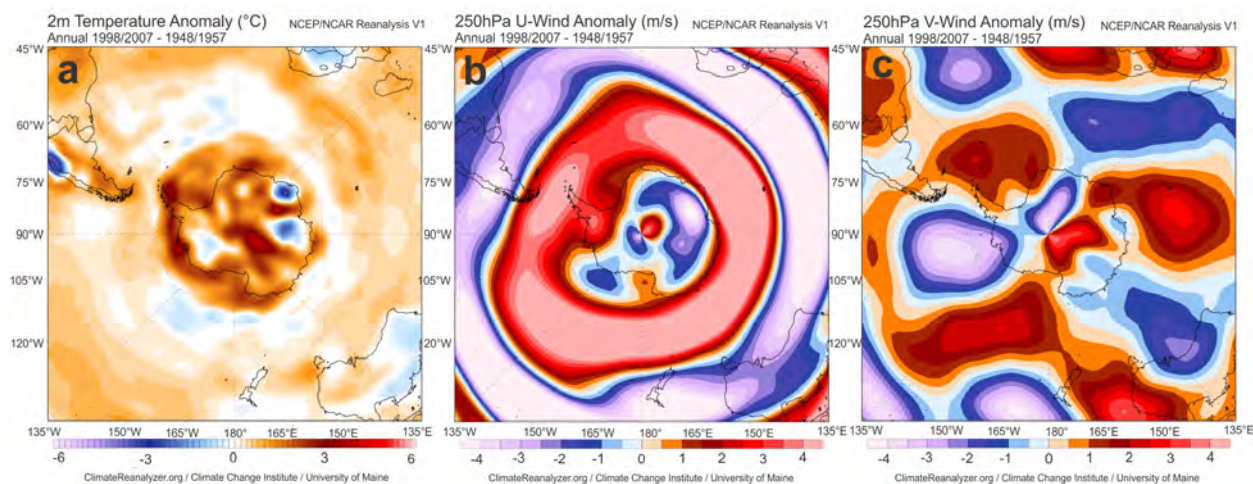


Figure 8. Meteorological variables simulations for the two 10-years periods (1948 – 1957 and 1998 – 2007). a) 2m-temperature anomaly, b) 250hPa U-wind anomaly, and c) 250hPa V-wind anomaly. The solutions were made using NCEP/NCAR reanalysis (ClimateReanalyser.org).

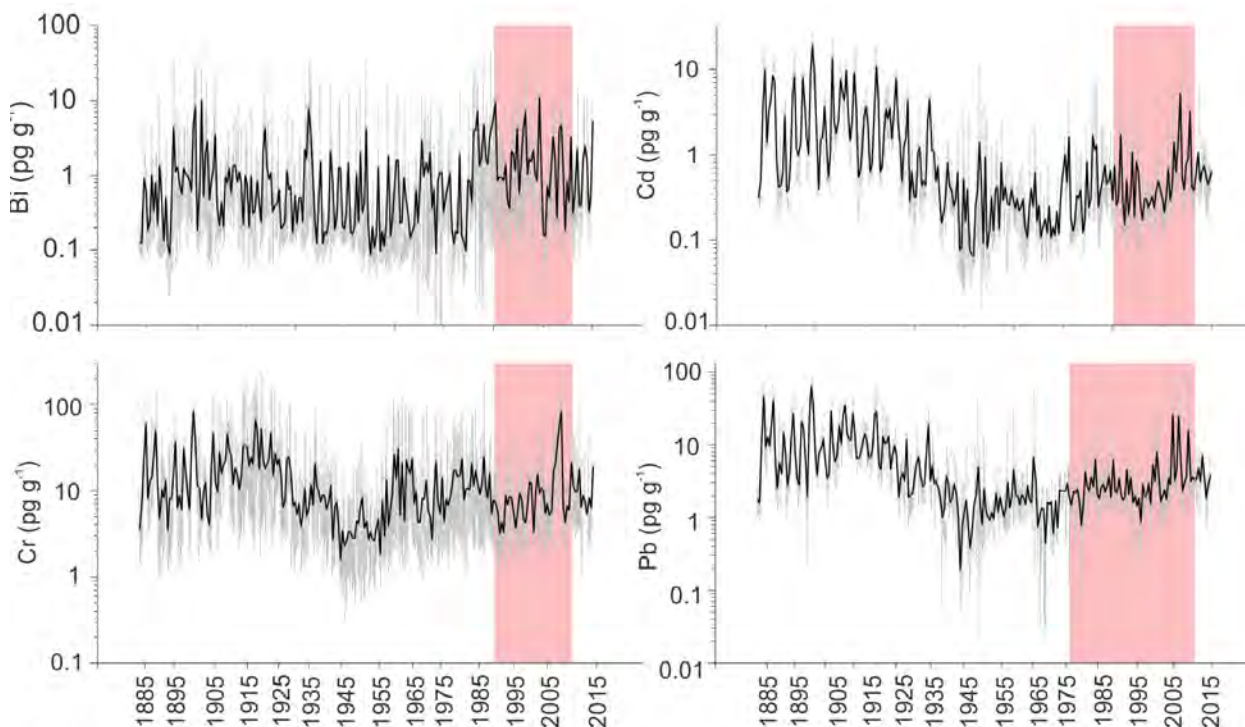


Figure 9. Trace elements concentration (Bi, Cd, Cr, and Pb) measured in the Mount Johns ice core (Antarctica) from 1883 to 2015. The shadow marks the period of introduction of environmental regulations in South America, Oceania, and Africa. For Pb, the shaded part is larger because it includes the regulations for vehicle emission standards in Australia (1976).

CONCLUSIONS

Atmospheric concentrations of trace elements are influenced by natural and anthropogenic processes. Most anthropogenic sources have

increased since the late 19th century becoming a worldwide issue for humans and the environment. The MJ ice core record reflects changes in emissions as well as atmospheric circulation and transport processes. Bismuth,

cadmium, chromium, and lead concentrations on MJ area are heavily influenced by anthropogenic emissions, mainly mining, and smelting of non-ferrous metals, as well as vehicular traffic (lead). The record's variability demonstrates close interplay between transport fluxes and environmental changes (mainly associated with a strengthening and contraction of the westerlies). Last, the introduction of environmental laws could have contributed to declining concentrations observed in Mount Johns in recent years.

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REFERENCES

AARONS SM ET AL. 2017. Dust composition changes from Taylor Glacier (East Antarctica) during the last glacial-interglacial transition: A multi-proxy approach. *Quaternary Sci Rev* 162: 60-71.

ALBANI S, MAHOWALD NM, DELMONTE B, MAGGI V & WINCKLER G. 2012. Comparing modeled and observed changes in mineral dust transport and deposition to Antarctica between the Last Glacial Maximum and current climates. *Clim Dynam* 38(9-10): 1731-1755.

BARBANTE C, BELLOMI T, MEZZADRI G, CESCO P, SCARPONI G, MOREL C, JAY S, VAN DE VELDE K, FERRARI C & BOUTRON CF. 1997. Direct determination of heavy metals at picogram per gram levels in Greenland and Antarctic snow by Double Focusing Inductively Coupled Plasma Mass Spectrometry. *J Anal Atom Spectrom* 12: 925-931.

BARBANTE C, SPOLAOR A, CAIRNS WRL & BOUTRON C. 2017. Man's footprint on the Arctic environment as revealed by analysis of ice and snow. *Earth-Sci Rev* 168: 218-231.

CRISCITIELLO AS, DAS SB, KARNAUSKAS KB, EVANS MJ, FREY KE, JOUGHIN I, STEIG EJ, MCCONNELL JR & MEDLEY B. 2014. Tropical Pacific influence on the source and transport of marine aerosols to West Antarctica. *J Climate* 27: 1343-1363.

DELMONTE B ET AL. 2017. Causes of dust size variability in central East Antarctica (Dome B): Atmospheric transport from expanded South American sources during Marine Isotope Stage 2. *Quaternary Sci Rev* 168: 55-68.

DIXON DA, MAYEWSKI PA, GOODWIN ID, MARSHALL GJ, FREEMAN R, MAASCH KA & SNEED SB. 2011. An ice-proxy for northerly air mass incursions into West Antarctica. *Int J Climatol* 32: 1455-1465.

DIXON DA, MAYEWSKI PA, KOROTKIKH E, SNEED SB, HANDLEY MJ, INTRONE DS & SCAMBOS TA. 2013. Variations in snow and firn chemistry along US ITASE traverses and the effect of surface glazing. *The Cryosphere* 7: 515-535.

DRAXLER RR. 1999. HYSPLIT4 user's guide, technical memorandum. NOAA, Silver Spring, Maryland, 46 p.

DRAXLER RR, GINOX P & STEIN AF. 2010. An empirically derived emission algorithm for wind-blown dust. *J Geophys Res - Atmos* 115(D16212).

DUCE RA, HOFFMAN GL & ZOLLER WH. 1975. Atmospheric trace metals at remote northern and southern hemisphere sites: pollution or natural? *Science* 187: 59-61.

EICHLER A, TOBLER L, EYRIKH S, MALYGINA N, PAPINA T & SCHWIKOWSKI M. 2014. Ice-core based assessment of historical anthropogenic heavy metal (Cd, Cu, Sb, Zn) emissions in the Soviet Union. *Environ Sci & Technology* 48: 2635-2642.

FOGT RL & MARSHALL GJ. 2020. The Southern Annular Mode: variability, trends, and climate impacts across the Southern Hemisphere. *Wiley Interdiscip Rev Clim Change* 11: 1-24.

FRETWELL P ET AL. 2013. Bedmap2: improved ice bed, surface and thickness datasets for Antarctica. *The Cryosphere* 7: 375-393.

GINOT P, STAMPFLI F, STAMPFLI D, SCHWIKOWSKI M & GÄGGELER HW. 2002. FELICS, a new ice core drilling system for high-altitude glaciers. *Memoirs of National Institute of Polar Research, Special Issue* 56: 38-48.

GOYAL R, GUPTA AS, JUCKER M & ENGLAND MH. 2021. Historical and projected changes in the Southern Hemisphere surface westerlies. *Geophys Res Lett* 48: 1-13.

HOCHSTETLER K. 2002. After the boomerang: Environmental movements and politics in the La Plata River Basin. *Global Environ Polit* 2: 35-57.

- HONG S, SOYOL-ERDENE T-O, HWANG HJ, HONG SB, HUR S & MOTOYAMA H. 2012. Evidence of global-scale As, Mo, Sb, and Tl atmospheric pollution in the Antarctic snow. *Environ Sci & Technology* 46(21): 11550-11557.
- HOSKING JS, FOGT R, THOMAS ER, MOOSAVI V, PHILLIPS T, COGGINS J & REUSCH D. 2017. Accumulation in coastal West Antarctic ice core records and the role of cyclone activity. *Geophys Res Lett* 44: 9084-9092.
- HOSKING JS & HODGES KI. 2005. A new perspective on Southern Hemisphere storm tracks. *J Climate* 18: 4108-4129.
- KALNAY E ET AL. 1996. The NCEP/NCAR 40-year reanalysis project. *BAMS* 77(3): 437-472.
- KISTLER R ET AL. 2001. The NCEP-NCAR 50-year reanalysis: Monthly means CD-ROM and documentation. *BAMS* 82: 247-268.
- KOFFMAN BG, HANDLEY MJ, OSTERBERG EC, WELLS ML & KREUTZ KJ. 2014. Dependence of ice-core relative trace-element concentration on acidification. *J Glaciol* 60(219): 103-112.
- KRACHLER M, ZHENG J, FISHER D & SHOTYK W. 2005. Analytical procedures for improved trace element detection limits in polar ice from Arctic Canada using ICP-SMS. *Anal Chim Acta* 530: 291-298.
- KRINNER G, PETIT J-R & DELMONTE B. 2010. Altitude of atmospheric tracer transport towards Antarctica in present and glacial climate. *Quaternary Sci Rev* 29: 274-284.
- LIDE DR. 2005. Abundance of elements in the Earth's crust and in the sea. In: Lide DR (Ed). *CRC Handbook of Chemistry and Physics*, Internet Version 2005. Boca Raton, CRC Press.
- MAHOWALD N, WARD DS, KLOSTER S, FLANNER MG, HEALD CL, HEAVENS NG, HESS PG, LAMARQUE J-F & CHUANG PY. 2011. Aerosol impacts on climate and biogeochemistry. *Annu Rev Env Resour* 36: 45-74.
- MATHER TA ET AL. 2012. Halogens and trace metal emissions from the ongoing 2008 summit eruption of Kilauea volcano, Hawaii. *Geochim Cosmochim Acta* 83: 292-323.
- MAYEWSKI PA ET AL. 2015. Potential for Southern Hemisphere climate surprises. *J Quat Sci* 30(5): 391-395.
- MCCONNELL JR, ARISTARAIN AJ, BANTA JR, EDWARDS PR & SIMÕES JC. 2007. 20th-Century doubling in dust archived in an Antarctic Peninsula ice core parallels climate change and desertification in South America. *PNAS* 104(14): 5743-5748.
- MCCONNELL JR & EDWARDS R. 2008. Coal burning leaves toxic heavy metal legacy in the Arctic. *PNAS* 105(34): 12140-12144.
- MCCONNELL JR ET AL. 2014. Antarctic-wide array of high-resolution ice core records reveals pervasive lead pollution began in 1889 and persists today. *Sci Rep* 4(5848): 1-5.
- MCLAUGHLIN MJ, HAMON RE, MCLAREN RG, SPEIR TW & ROGERS SL. 2000. Review: A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Aust J Soil Res* 38: 1037-1086.
- MEZGEC K ET AL. 2017. Holocene sea ice variability driven by wind and polynya efficiency in the Ross Sea. *Nat Commun* 8(1334).
- NEFF PD & BERTLER NAN. 2015. Trajectory modeling of modern dust transport to the Southern Ocean and Antarctica. *J Geophys Res - Atmos* 120: 1-20.
- NRIAGU JO. 1989. A global assessment of natural sources of atmospheric trace metals. *Nature* 338: 47-49.
- OECD/ECLAC. 2005. *OECD Environmental Performance Reviews: Chile 2005*. OECD Publishing.
- OECD. 2007. *OECD Environmental Performance Reviews: Australia 2007*. OECD Publishing.
- OSTERBERG EC. 2007. North Pacific late Holocene climate variability and atmospheric composition. Ph.D. Thesis. University Maine, USA, 161 p.
- OSTERBERG EC, HANDLEY MJ, SNEED SB, MAYEWSKI PA & KREUTZ KJ. 2006. Continuous ice core melter system with discrete sampling for major ion, trace element, and stable isotope analyses. *Environ Sci & Technology* 40: 3355-3361.
- PACZYNA JM & PACZYNA EG. 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ Rev* 9: 269-298.
- PARISH TR & BROMWICH DH. 2007. Reexamination of the near-surface airflow over the Antarctic continent and implications on atmospheric circulations at high southern latitudes. *Mon Weather Rev* 135: 1961-1973.
- PETIT JR & DELMONTE B. 2009. A model for large glacial-interglacial climate-induced changes in dust and sea salt concentrations in deep ice cores (central Antarctica): paleoclimatic implications and prospects for refining ice core chronologies. *Tellus* 61B: 768-790.
- PLANCHON FAM, BOUTRON CF, BARBANTE C, COZZI G, GASPARI V, WOLFF EW, FERRARI CP & CESCO P. 2002. Changes in heavy metals in Antarctic snow from Coats Land since the

mid-19th to the late-20th century. *Earth Planet Sci Lett* 200: 207-222.

PLANCHON FAM, VAN DE VELDE K, ROSMAN KJR, WOLFF EW, FERRARI CP & BOUTRON CF. 2003. One hundred fifty-year record of lead isotopes in Antarctic snow from Coats Land. *Geochim Cosmochim Acta* 67(4): 693-708.

POTOCKI M, MAYEWSKI PA, KURBATOV AV, SIMÕES JC, DIXON DA, GOODWIN I, CARLETON AM, HANDLEY MJ, JAÑA R & KOROTKIKH EV. 2016. Recent increase in Antarctic Peninsula ice core uranium concentrations. *Atmos Environ* 140: 381-385.

REIMANN C & DE CARITAT P. 2005. Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. *Sci Total Environ* 337: 91-107.

SCHWANCK F, SIMÕES JC, HANDLEY M, MAYEWSKI PA, AUGER JD, BERNARDO RT & AQUINO FE. 2017. A 125-year record of climate and chemistry variability at the Pine Island Glacier ice divide, Antarctica. *The Cryosphere* 11: 1537-1552.

SCHWANCK F, SIMÕES JC, HANDLEY M, MAYEWSKI PA, BERNARDO RT & AQUINO FE. 2016a. Anomalously high arsenic concentration in a West Antarctic ice core and its relationship to copper mining in Chile. *Atmos Environ* 125: 257-264.

SCHWANCK F, SIMÕES JC, HANDLEY M, MAYEWSKI PA, BERNARDO RT & AQUINO FE. 2016b. Drilling, processing and first results for Mount Johns ice core in West Antarctica Ice Sheet. *Braz J Geol* 46(1): 29-40.

THOEN IU, SIMÕES JC, LINDAU FGL & SNEED SB. 2018. Ionic content in an ice core from the West Antarctic Ice Sheet: 1882-2008 A.D. *Braz J Geol* 48(4): 853-865.

THOMPSON DWJ & SOLOMON S. 2002. Interpretation of recent Southern Hemisphere climate change. *Science* 296(3): 895-899.

TUOHY A, BERTLER N, NEFF P, EDWARDS R, EMANUELSSON D, BEERS T & MAYEWSKI PA. 2015. Transport and deposition of heavy metals in the Ross Sea Region, Antarctica. *J Geophys Res - Atmos* 120(20): 10996-11011.

VALLELONGA P, VAN DE VELDE K, CANDELONE J-P, MORGAN VI, BOUTRON CF & ROSMAN KJR. 2002. The lead pollution history of Law Dome, Antarctica, from isotopic measurements on ice cores: 1500 AD to 1989 AD. *Earth Planet Sci Lett* 204: 291-306.

WEDEPOHL KH. 1995. The composition of the continental crust. *Geochim Cosmochim Acta* 59(7): 1217-1232.

WELLER R, WOLTJEN J, PIEL C, RESENBERG R, WAGENBACH D, KONIG-LANGLO G & KRIEWS M. 2008. Seasonal variability

of crustal and marine trace elements in the aerosol at Neumayer station, Antarctica. *Tellus* 60B: 742-752.

SUPPLEMENTARY MATERIAL

Tables S1 - SIV

Figures S1 - S7

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FRANCIÉLE SCHWANCK¹

<https://orcid.org/0000-0003-1046-8080>

JEFFERSON C. SIMÕES^{1,2}

<https://orcid.org/0000-0001-5555-3401>

MICHAEL HANDLEY²

<https://orcid.org/0000-0001-6712-9843>

PAUL A. MAYEWSKI²

<https://orcid.org/0000-0002-3360-763X>

RONALDO BERNARDO¹

<https://orcid.org/0000-0002-1143-7916>

¹Universidade Federal do Rio Grande do Sul/UFRGS, Instituto de Geociências, Centro Polar e Climático, Av. Bento Gonçalves, 9500, 90650-001 Porto Alegre, RS, Brazil

²Climate Change Institute, University of Maine, Orono, ME 04469, USA

Correspondence to: **Franciéle Schwanck**

E-mail: schwanck.carlos@ufrgs.br

Author contributions

Franciéle Schwanck led the production of this manuscript, with written contributions from Jefferson Cardia Simões and Paul A. Mayewski. Ronaldo Bernardo contributed to sampling melting and preparation and Michael Handley realized the ICP-SMS analysis.

