



Trace metal contamination in Antarctic atmospheric deposition: insights from elemental and isotopic analysis of a snow pit at McCarthy Ridge, Victoria Land

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ABSTRACT

The study of chemical contamination in polar environments is fundamental for assessing recent and past atmospheric pollution on a global scale. To provide information on the occurrence, potential sources and temporal trends of trace metals in Antarctica, the concentration of Cd, Co, Cr, Cu, Pb, V, and Zn, along with Pb isotope ratios, were determined in 50 snow pit samples collected at McCarthy Ridge (Victoria Land, Antarctica), covering the period 2019–2021. The results highlighted an enrichment over the background levels by one order of magnitude (two orders for Zn), which was ascribed to the influence of both anthropogenic and natural sources. Pb isotopic data indicated that only $26 \pm 13\%$ of this contaminant in Victoria Land may be of anthropogenic origin, with a decreasing trend from $67 \pm 16\%$ during 1986–1994 and $38 \pm 22\%$ during the 2012–2015 period (computed from literature data). Finally, no regular seasonal pattern was identified, underscoring a high degree of complexity in the processes governing the atmospheric transport and deposition of trace metals in Antarctica at short temporal scales.

1. Introduction

Since snow precipitation efficiently removes airborne contaminants from the atmosphere (Rangel-Alvarado et al., 2022), the analysis of polar snow and ice represents a robust approach for assessing recent and past atmospheric pollution on a global scale (Wolff and Peel, 1985a; Gabrielli and Vallelonga, 2015) and for reconstructing historical changes in atmospheric composition and climate (Giorio et al., 2018; Raynaud et al., 2020). Snow pit samples can be collected at high vertical (time) resolution under strictly clean conditions and with minimal logistical requirements, making their analysis ideal for monitoring present-day pollution trends. In particular, records of trace metals have been obtained from snow pit samples collected across various Antarctic regions, including Victoria Land (Scarponi et al., 1997; Barbante et al., 1997a,b; Van de Velde et al., 2005; Han et al., 2022), Adélie Land (Görlach and Boutron, 1992), Coats Land (Planchon et al., 2002; Planchon et al., 2003), Princess Elizabeth Land (Hur et al., 2007), Marie Byrd Land (Kreutz and Koffman, 2011; Tuohy et al., 2015), the Antarctic

Peninsula (Hong et al., 2002), and the Antarctic Plateau (Chang et al., 2016; Bertinetti et al., 2020; Liu et al., 2021). Most of these studies have focused on Pb pollution, which is considered a paradigm of hemispheric-scale anthropogenic footprint on Antarctica (Bargagli, 2008). In fact, traces of this toxic element have been detected since the beginning of the industrial era and attributed primarily to mining and smelting of non-ferrous metal ores at Broken Hill (Australia), and to a lesser extent to coal combustion (Vallelonga et al., 2002; Planchon et al., 2003; Van de Velde et al., 2005; McConnell et al., 2014; Chang et al., 2016). The subsequent trend mirrored the rise and fall in the use of alkyl-Pb additives in gasoline across the Southern Hemisphere during the second half of the 20th century. However, anthropogenic Pb has remained persistent in Antarctica (McConnell et al., 2014; Chang et al., 2016; Bertinetti et al., 2020), due to legacy contamination and/or new sources, although a decline in the anthropogenic contribution has been suggested (Bertinetti et al., 2020; Liu et al., 2021). The sources of anthropogenic Pb in Antarctica in recent times remain a debated issue, with Australia and/or South America identified as

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Fig. 1. Map of Antarctica showing the locations of McCarthy Ridge and the other sampling sites referred to in the text (based on the Scientific Committee on Antarctic Research Antarctic Digital Database).

possible contributors, overlapping natural sources such as volcanic emissions and mineral dust. In this context, the precise measurements of Pb isotope ratios can provide valuable information on its geographic origin, the relative contribution of natural and anthropogenic sources and their evolution over time (Bollhöfer and Rosman, 2000; Komárek et al., 2008; Ardini et al., 2020).

Snow pit data for trace metals other than Pb are far fewer. Valuable records have been obtained by the analysis of dated snow samples collected in remote sites in Coats Land (Planchon et al., 2002), West Antarctic Ice Sheet Divide (Kreutz and Koffman, 2011), Lambert Glacier basin (Hur et al., 2007) and Dome A (Liu et al., 2021). The study by Planchon et al. (2002) covered the period from 1834 to 1990 and revealed pronounced enhancements in the last decades for several trace metals including Cr, Cu, Pb and Zn, attributed to emissions of trace metals to the atmosphere from human activities in Southern America,

Southern Africa and Australia, especially non-ferrous metal mining and smelting. Hur et al. (2007) investigated seasonal variations in trace metal depositions by analyzing snow samples collected at Lambert Glacier basin and dated between austral spring 1998 and summer 2002. The anthropogenic contribution was predominant for Cu and Pb; however, the depth profiles exhibited distinct seasonal patterns, which also differed from those observed for other metals and at other Antarctic sites, suggesting specific transport and deposition mechanisms. More recently, Liu et al. (2021) obtained a long-term record of trace metals at Dome A, on the Antarctic plateau, covering the period from 1950 to 2016. Despite a great variability in the annual concentration of all metals, the results indicated an enrichment of Cd, Cu and Pb in recent decades, likely due to anthropogenic activities in Australia and South America.

In this study, a record of trace metals (Cd, Co, Cr, Cu, Pb, V, Zn) and

Pb isotope ratios was obtained from the analysis of 50 snow pit samples collected at McCarthy Ridge (Victoria Land, Antarctica) covering the period 2019–2021. The resulting data are presented and discussed with the aim of: (a) providing updated information on atmospheric trace metal pollution in recent years; (b) testing the hypothesis that this contamination is decreasing rather than reaching a ‘steady-state’ condition; and (c) assessing potential seasonal variations over the investigated time frame.

2. Experimental

2.1. Sample collection

The samples were collected on 28th November 2021 at McCarthy Ridge (Victoria Land, East Antarctica) (74.6516° S; 163.0590° E; elevation: 700 m a.s.l.; 40 km from the sea; Fig. 1), during the XXXVII expedition of the Italian National Antarctic Research Program (PNRA). The site is minimally affected by katabatic winds, ensuring that snow accumulation is less affected by wind-driven redistribution processes (Stenni et al., 2000).

Two parallel series (designated A and B), each consisting of 50 snow samples, were collected from the wall of a 150 cm-deep pit by horizontally inserting pre-cleaned 50 mL polypropylene graduated tubes at approximately 3 cm intervals. To minimize metal contamination, the pit was hand-dug, and the potentially contaminated surface layer (~10 cm) was removed using a pre-cleaned polypropylene scraper. Operators wore clean-room clothing, and all sampling operations were performed manually. After collection, tubes were individually sealed in polypropylene bags and stored at −20 °C until analysis.

2.2. Sample preparation and analysis

2.2.1. Trace metals

Ultratrace analysis of snow samples (series A) was performed using inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer Elan DRC II) following a procedure slightly modified from Grotti et al. (2008). Briefly, samples (~20 g) were allowed to melt inside their closed tubes, acidified with HNO₃ and HF to a final concentration of 0.5% (v/v) each, left to stand for 24 h, and then refrozen. Subsequently, samples were freeze-dried using the LIO-SPDGT system by 5 Pascal (Milan, Italy) coupled to a RV5 two-stage rotary pump by Edwards (Burgess Hill, UK). The process occurred at p~0.1 mbar and T ~ −50 °C and it lasted about 3 days.

Then, samples were redissolved in 200 µL of 0.05% HNO₃ solution, resulting in an approximately 100-fold preconcentration of analytes. The accurate preconcentration factors were determined by weighing each sample before and after the freeze-drying procedure. The preconcentrates were introduced at 20 µL min^{−1} into the ICP-MS spectrometer by the heated torch-integrated sample introduction system (Paredes et al., 2009; Grotti et al., 2013). All reagents used were of ultrapure grade quality and the sample preparation was carried out under a laminar flow work area. Procedural blanks were concomitantly prepared and analysed exactly as the snow samples, using 20.0 g of ultrapure water. The instrumental characteristics and operating parameters are reported in Table S1.

2.2.2. Lead isotope ratios

Lead isotopic analysis of snow samples (series B) was performed using the same preconcentration procedure applied for trace metal determination (section 2.2.1), and the resulting solutions were analysed by ICP-MS (PerkinElmer NexION 2000) according to Grotti et al. (2023). To maximize the preconcentration factor, freeze-dried samples were redissolved in 400 µL of 0.05% HNO₃ solution and introduced into the ICP-MS at a flow rate of 40 µL min^{−1} using a PFA-ST micro-nebulizer. Under these conditions, precise determination of the major Pb isotopes (²⁰⁸Pb, ²⁰⁷Pb, and ²⁰⁶Pb) was achieved in less than 8 min.

Instrumental mass bias was corrected by measuring a NIST SRM 981 standard solution (Pb concentration: 10 µg L^{−1}) every three samples and applying the bracketing external correction method (Vanhaecke et al., 2009). For each sample, twelve replicated measurements were performed with an integration time of 10 s each one, and raw data were corrected for the detector dead time (42 ns, determined according to Nelms et al., 2001). The instrumental characteristics and operating parameters are reported in Table S2.

2.2.3. Non-sea-salt sulphates

Sulphates (SO₄^{2−}) and sodium (Na⁺) concentrations were measured by ion chromatography (Thermo Scientific Dionex Aquion) on aliquots of snow samples (series A), after 10-fold dilution. The instrumental characteristics and operating parameters are reported in Table S3.

Non-sea-salt sulfates (nss-SO₄^{2−}) were calculated following Keene et al. (1986), using sodium as a seawater tracer:

$$\text{nssSO}_4^{2-} = \text{SO}_4^{2-} - 0.253 \text{ Na}^+ (1)$$

where 0.253 is the seawater sulphate-to-sodium mass ratio.

2.3. Analytical performances and quality control

For the determination of trace metals, limits of detection (LODs) were calculated from replicate analyses of ten procedural blanks, yielding values of 0.1, 0.4, 5.5, 6.3, 2.4, 0.7, and 26 pg g^{−1} for Cd, Co, Cr, Cu, Pb, V, and Zn, respectively. The accuracy of the method was assessed by the analysis of the certified reference material SRM 1640a from NIST. To match the analytical concentrations in the CRM solution with those expected in the samples, the CRM was diluted 20-fold. The analytical recoveries were in the 98–109% range and the precision was better than 10% (RSD, n = 6).

Measurements of ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁷Pb isotopic ratios were characterized by an internal precision ranging from 0.1% at 20 µg L^{−1} to 0.3% at 0.3 µg L^{−1}. The accuracy of the Pb isotopic measurements was systematically controlled at the beginning and the end of each analytical session, by the analysis of the reference material IRMM CRM 482, for which Pb isotopic data obtained by multi-collector ICP-MS are available (Cloquet et al., 2006). The mean measured values (²⁰⁸Pb/²⁰⁷Pb = 2.4066 ± 0.0032, ²⁰⁶Pb/²⁰⁷Pb = 1.1314 ± 0.0027, n = 13) did not significantly differ from the reference ones (²⁰⁸Pb/²⁰⁷Pb = 2.4078 ± 0.0004, ²⁰⁶Pb/²⁰⁷Pb = 1.1311 ± 0.0001), showing an external precision of 0.1–0.2% and an accuracy better than 0.05%.

Finally, ion chromatographic determinations of SO₄^{2−} and Na⁺ were characterized by a LOD of 3 ng/g and a precision better than 2%.

2.4. Data processing

Statistical analyses were performed using the open-source software R (R Core Team, 2014), with the additional package CAT (Leardi et al., 2026). Values below the LOD were replaced by one-half of the detection limit, representing the expected mean under a uniform distribution between zero and the LOD. The correlations between variables were evaluated by the Spearman rank correlation coefficient (ρ_s) and the comparison of data was performed using the Mann-Whitney test. Principal Component Analysis (PCA) was performed after data autoscaling. Time series were analysed using the Augmented Dickey–Fuller (ADF) test to assess stationarity, the Ljung–Box (LB) test to evaluate the presence of autocorrelation, and visual inspection of autocorrelation functions (ACF) to identify potential temporal structures. The anthropogenic contribution (%A) was obtained from isotopic data using two approaches. The first approach was based on the Euclidean distance of each data point from the anthropogenic and natural end-members:

$$\%A = \sqrt{\frac{(X_S - X_N)^2 + (Y_S - Y_N)^2}{(X_A - X_N)^2 + (Y_A - Y_N)^2}} * 100 \quad (2)$$

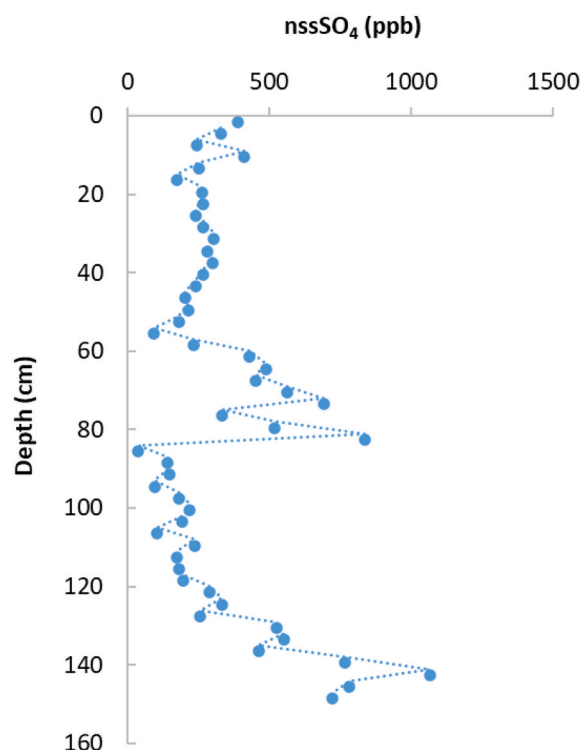


Fig. 2. Vertical profile of non-sea-salt sulphates in snow-pit at McCarthy Ridge, Victoria Land, Antarctica. Dotted line is the 2-period moving average.

Table 1

Summary statistics for trace metal concentrations in snow pit samples collected at McCarthy Ridge (Victoria Land, Antarctica). Values in pg g^{-1} .

Statistics	Cd	Co	Cr	Cu	Pb	V	Zn
Mean	1.30	12.9	40.3	88.5	18.9	52.2	555
Median	1.12	4.4	22.7	55.5	7.8	18.3	497
Min	0.19	<0.4	<5.5	<6.3	<2.4	<0.7	32
Max	3.75	78.4	205	395	97.1	287	1455
SD	0.82	18.6	50.7	94.8	24.6	73.0	360
IQR	1.00	11.7	49.7	96.3	25.4	58.6	434
n	50	48	45	49	47	46	45

where X and Y are $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and subscripts S, A and N refer to the sample, anthropogenic end-member and natural end-member, respectively. The second approach was based on a binary isotopic mixing model, in which mixing proportions were estimated by projecting the sample composition onto the line defined by the two end-members.

$$\%A = \frac{(X_S - X_N)(X_A - X_N) + (Y_S - X_N)(Y_A - Y_N)}{(X_A - X_N)^2 + (Y_A - Y_N)^2} * 100 \quad (3)$$

Table 2

Lead isotopic ratios in snow pit samples collected at McCarthy Ridge (Victoria Land, Antarctica) and comparable studies across Antarctica.

Site	Time period	Median	IQR	Median	IQR	n	Reference	Analytical method
McCarthy Ridge	2019-2021	2.474	0.015	1.205	0.032	48	this work	A
Hercules Névé	1986-1994	2.431	0.022	1.160	0.021	38	Van de Velde et al. (2005)	B
Hercules Névé	2012-2015	2.458	0.042	1.190	0.052	40	Han et al. (2022)	C
Styx Glacier plateau	1872-1978	2.456	0.031	1.192	0.029	28	Van de Velde et al. (2005)	A
Dome A	1969-2004	2.430	0.010	1.157	0.011	40	Chang et al. (2016)	C
Dome C	1971-2017	2.418	0.021	1.158	0.019	109	Bertinetti et al. (2020)	A
Dome F	1956-2007	2.427	0.018	1.156	0.014	80	Chang et al. (2016)	C
Coats Land	1919-1990	2.410	0.016	1.139	0.020	77	Planchon et al. (2003)	B

Method: A) HF + HNO_3 ; ICP-MS; B) HNO_3 +silica gel + H_3PO_4 ; TIMS; C) HNO_3 +HF + H_3PO_4 ; TIMS.

3. Results

3.1. Snow pit dating

In the nss-SO_4^{2-} profile (Fig. 2), two maxima were identified at 80 cm and 145 cm depths. These peaks may be associated with the biogenic emission of dimethyl sulphide, which is oxidized in the atmosphere to form methanesulfonic acid and sulphate aerosols (Jongeblod et al., 2025). Since phytoplanktonic activity is enhanced during the summer, these nss-SO_4^{2-} peaks can be ascribed to depositions during the austral summers 2019/20 and 2020/21. This attribution was confirmed by the detection of sintered snow layers at depths corresponding to the late summer periods. Therefore, although precise dating was not possible due to the lack of additional proxies (e.g. $\delta^{18}\text{O}$), the snow-pit sequence was estimated to cover approximately two years. The resulting accumulation rate is $\sim 75 \text{ cm snow y}^{-1}$, corresponding to $250 \text{ kg m}^{-2} \text{ y}^{-1}$, in good agreement with the value previously reported for the same site ($260 \text{ kg m}^{-2} \text{ y}^{-1}$; Stenni et al., 2000). Finally, no volcanic stratospheric sulphur injections capable of affecting sulphate levels in Antarctica occurred in the decade preceding the sampling (Sigl et al., 2022).

3.2. Trace metal concentrations

Trace metal concentrations are reported in Table S4 and summarized in Table 1. Median concentrations were lowest for Cd, Co, and Pb (a few pg g^{-1}), higher for Cr, Cu, and V (tens of pg g^{-1}), and reached up to 0.5 ng g^{-1} for Zn. The levels measured for Cd and Pb are consistent with values reported in previous snow-pit studies across Antarctica (Table S5), whereas the concentrations of the remaining elements are significantly higher (Mann-Whitney test, $p < 0.05$). Due to the use of HF + HNO_3 mixture for particles dissolution, the obtained values can be considered as total concentrations. However, the differences with other studies can hardly be ascribed to the applied pre-treatment or quantification method, but they are likely the result of the specific features of the sampling site, as discussed below.

Concentrations values along the snow pit were quite scattered, without a clear temporal trend, in agreement with previous investigations (Planchon et al., 2003; Liu et al., 2021). The application of time-series tests did not reveal significant temporal dependence or consistent seasonal patterns (ADF p-values < 0.01 ; LB p-values > 0.05 ; absence of clear periodic signals in the ACF). Trace metal concentrations were significantly correlated with each other ($\rho_s = 0.42-0.95$, $p < 0.05$), except for Cd, which showed significant correlations only with Cu and Zn (Table S6).

3.3. Lead isotopic ratios

Lead isotopic ratios are reported in Table S4 and compared to literature data from other snow pit studies in Table 2. The $^{208}\text{Pb}/^{207}\text{Pb}$ values ranged from 2.437 to 2.504, with a median of 2.474 and an interquartile range (IQR) of 0.015, indicating limited variability (0.6%) within the central portion of the dataset. The $^{206}\text{Pb}/^{207}\text{Pb}$ values ranged

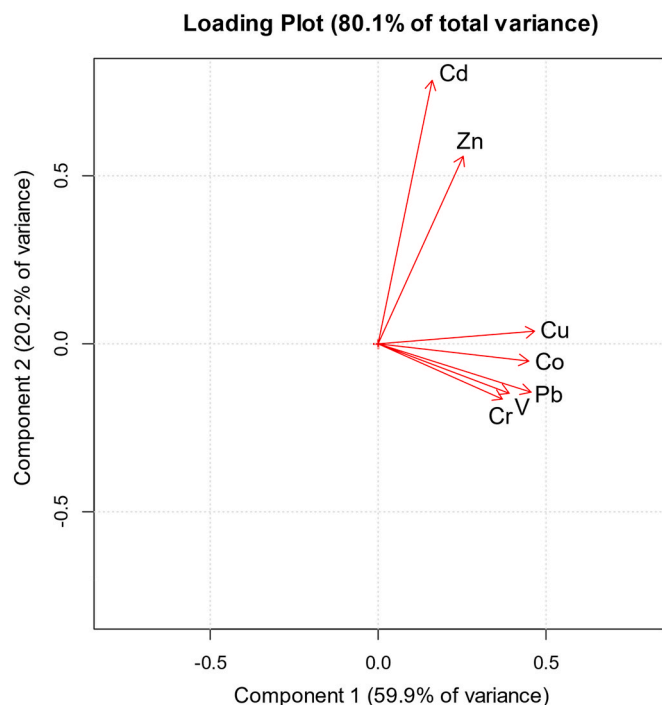


Fig. 3. Principal Component Analysis (loading plot).

from 1.176 to 1.257, with a median of 1.205 and an IQR of 0.032, reflecting a slightly broader spread (2.7%). Both isotope ratios displayed more radiogenic signatures relative to values reported for other locations and associated with earlier time series (Table 2). This trend is particularly clear when the comparison is restricted to the Victoria Land sites (McCarthy Ridge and Hercules N  v  ). For instance, the $^{208}\text{Pb}/^{207}\text{Pb}$ median increased from 1.160 in 1986–1994, to 1.190 in 2012–2015 and further to 1.205 in 2019–2021, reflecting a progressive shift toward more radiogenic signatures over time.

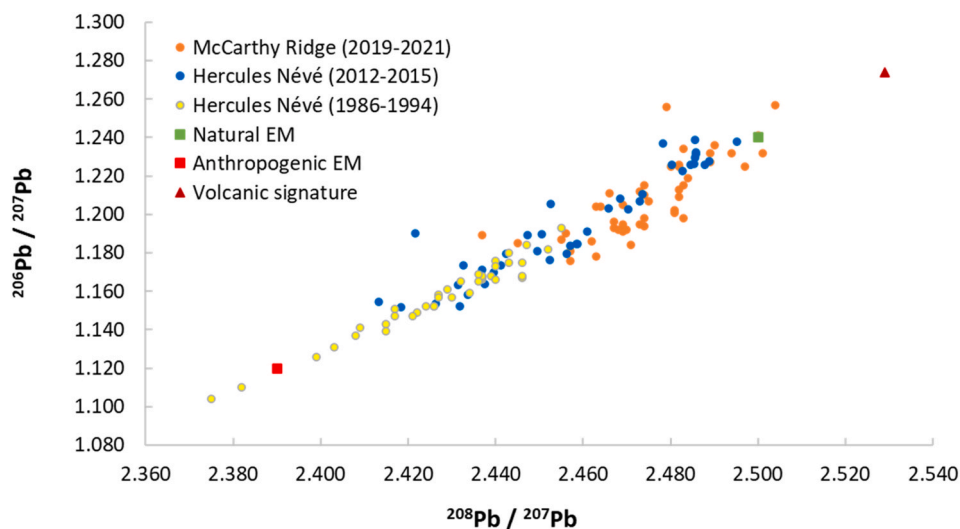


Fig. 4. Three-isotope plot of Pb isotopic ratios measured in snow-pit samples collected at McCarthy Ridge (this work) and Hercules N  v   (Van de Velde et al., 2005; Han et al., 2022), Victoria Land, Antarctica. Volcanic, natural and anthropogenic signatures are also shown (Matsumoto and Hinkley, 2001; Van de Velde et al. 2005).

4. Discussion

4.1. Natural and anthropogenic contributions to trace metals in Antarctic snow

It is well established that concentrations of trace elements in recent Antarctic snow, although at the few-ppt level at the most pristine sites, substantially exceed their natural background, estimated through ultra-clean analyses of ancient ice samples: $\sim 0.1 \text{ pg g}^{-1}$ for Cd and Co, $\sim 0.4 \text{ pg g}^{-1}$ for Pb, $\sim 2\text{--}3 \text{ pg g}^{-1}$ for Cr, Cu, V and $\sim 5 \text{ pg g}^{-1}$ for Zn (Wolff and Peel, 1985b; Boutron et al., 1988; Batifol et al., 1989; Boutron and G  rlach, 1990). Based on these background values, the samples analysed in this work were one order of magnitude higher for Cd, Co, Cr, Cu, Pb, V, whereas the enrichment for Zn was two orders of magnitude. The result highlights a likely effect of the global atmospheric contamination but, for some element, it could also be related to the geographical and geological features of the area. For example, van de Velde et al. (2005) reported natural Pb concentrations of 2.2 pg g^{-1} in old Styx Glacier samples (Victoria Land), attributed to stronger local crustal and volcanic inputs than at Coats Land and Law Dome, where the background Pb level of $\sim 0.4 \text{ pg g}^{-1}$ had been measured. Similarly, Matsumoto and Hinkley (2001) reported mean concentrations of Pb and Cd in ancient ice at Taylor Dome as high as 9.7 and 0.76 pg g^{-1} , respectively, ascribed to emissions from quiescent degassing of volcanoes.

To gain insights into the sources of trace metals, PCA was applied, and the resulting loading plot is shown in Fig. 3. The analysis suggests a common source for Co, Cr, Cu, Pb, and V, whereas Cd and Zn exhibit a different behaviour, indicating distinct sources or pathways.

McCarthy Ridge is located in the foothills of the Transantarctic Mountains in Victoria Land, where a significant natural contribution from crustal material is plausible and it could account for the relatively high concentrations of lithogenic elements such as Co, Cr, Cu, V and Zn. In addition, the site is also in proximity to quiescent volcanic centres of the McMurdo Volcanic Group; therefore, diffuse volcanic degassing can represent an additional natural source of trace metals, particularly with respect to chalcophile elements like Cd, Cu, Pb and Zn (Landy and Peel, 1981; Zreda-Gostynska et al., 1997; Matsumoto and Hinkley, 2001; Vallelonga et al., 2010; Edmonds et al., 2022). The McCarthy Ridge site is located approximately 40 km inland from the coast, potentially allowing for some influence from marine inputs. Planchon et al. (2002) suggested that sea-salt spray could represent a significant source of Cd, Cu, V and Zn in Antarctic snow from Coats Land, despite the site being

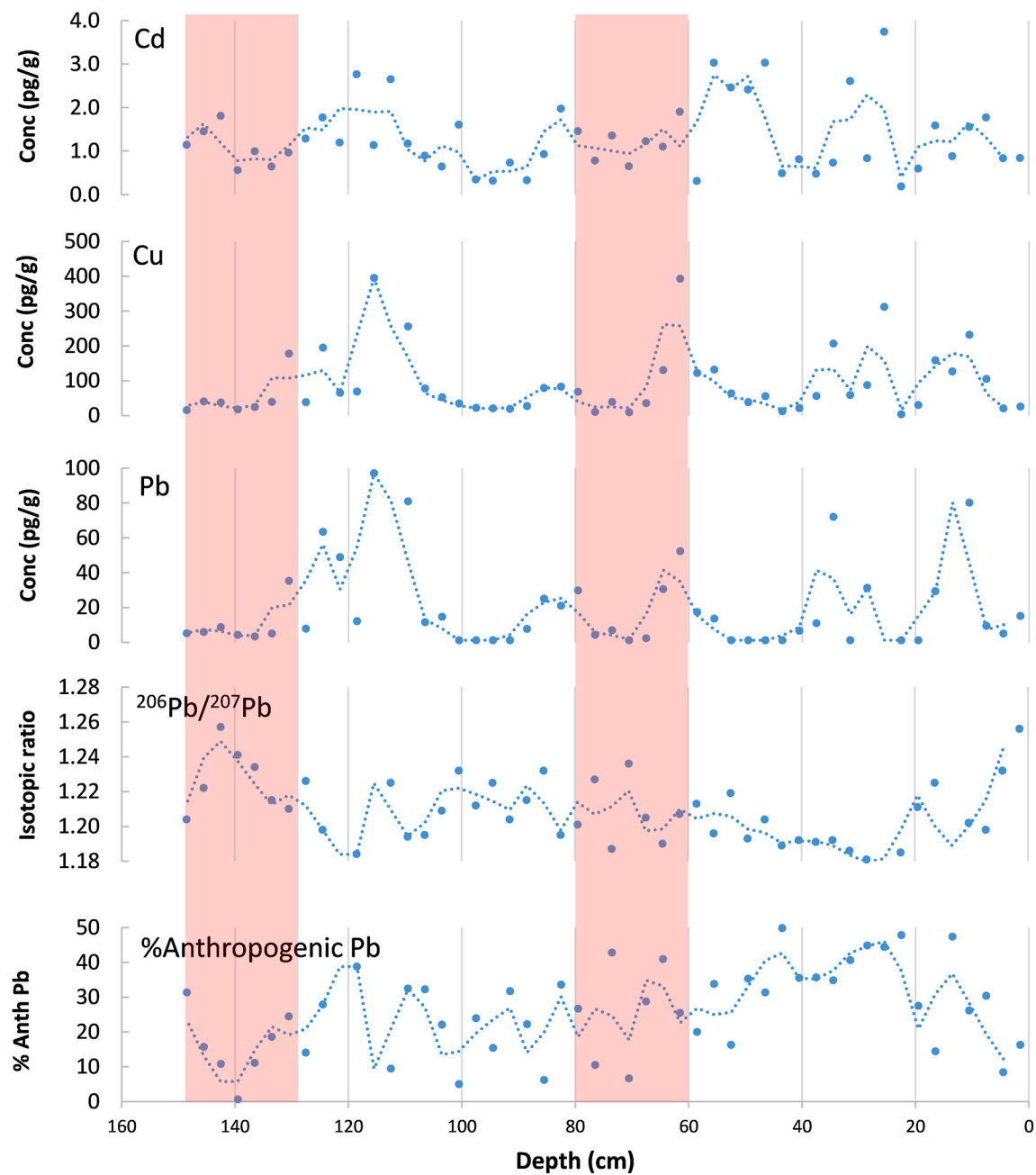


Fig. 5. Depth profile of Cd, Cu, Pb concentrations, $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic ratio and estimated anthropogenic contribution at McCarthy Ridge, Victoria Land, Antarctica. Dotted line is the 2-period moving average. Coloured bands indicate the summer periods.

located approximately 200 km from the coast. In contrast, estimates for surface snow collected at Terra Nova Bay indicated that a substantial marine contribution ($\sim 50\%$) was limited to Cd (Grotti et al., 2011), which could explain its unique behaviour. Finally, discrepancies with former investigations in coastal sites could be also ascribed to differences in altitude of the sampling locations; in fact, it has been found that altitude can affect elemental concentration of deposited particulate matter more than the distance from the coast (Bertinetti et al., 2020).

In addition to natural sources, several studies have shown that the occurrence of trace metals in Antarctic snow is also influenced by anthropogenic inputs, mainly through long-range atmospheric transport (e.g. Planchon et al., 2002; Van de Velde et al., 2005; Hur et al., 2007; Liu et al., 2021). However, distinguishing between natural and anthropogenic contributions is not straightforward. In the case of Pb, precise measurements of its isotopic composition represent a valuable tool to

address this issue. Moreover, due to its correlation with Co, Cr, Cu and V, the information about its origin can be extended to these elements. Isotopic data obtained in this study are plotted in a three-isotope plot together with literature values (Fig. 4). Values lie on a straight line, following the same isotopic mixing line of data previously reported for Hercules N  v   (Van de Velde et al., 2005; Han et al., 2022). This trend is commonly interpreted as resulting from the mixing of particles derived from natural and anthropogenic sources that are thoroughly mixed in the atmosphere. In particular, the local natural signature was set at $^{208}\text{Pb}/^{207}\text{Pb} = 2.50$ and $^{206}\text{Pb}/^{207}\text{Pb} = 1.24$, based on the values measured in old ice samples from the Styx glacier and Taylor Dome, corresponding to pre-industrial Pb deposited in Victoria Land (Van de Velde et al. 2005; Matsumoto and Hinkley, 2001). The anthropogenic end-member was defined using the less radiogenic Pb isotopic composition that dominates the contemporary Southern Hemisphere

atmosphere ($^{206}\text{Pb}/^{207}\text{Pb} = 1.12$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.39$), reflecting the persistence of legacy anthropogenic Pb (Bertinetti et al., 2020; Han et al., 2022; Vecchio et al., 2025). Based on the Euclidean distance of each data point from the defined isotopic end-members (equation (2)), the anthropogenic Pb contribution was estimated to be $26 \pm 13\%$. Applying the same computation to the literature data for the Hercules Névé, the anthropogenic Pb contribution resulted $38 \pm 22\%$ for the 2012–2015 period and $67 \pm 16\%$ for the 1986–1994 period. The estimations based on a binary isotopic mixing model (equation (3)) were nearly identical because the samples lie close to the mixing line.

Together, these results clearly indicate a temporal decrease in the fraction of anthropogenic Pb deposited onto Antarctic snow, consistent with the declining trend previously documented for the East Antarctic Plateau (Bertinetti et al., 2020) and the low crustal enrichment factors (<10) reported for surface snow at Terra Nova Bay during 2000–2005 (Grotti et al., 2011). This result can be ascribed to the phase-out of leaded gasoline in the Southern Hemisphere, which determined a shift of Pb ratios towards the natural signature. However, Han et al. (2022) suggested that Pb pollution in Antarctica has not significantly decreased based on the dominance of non-crustal Pb, and the observed increase in radiogenic Pb isotope ratios was interpreted as a shift in anthropogenic sources, from leaded gasoline emissions to industrial activities in northern South America.

4.2. Seasonal trends of trace metals and Pb isotopic signature

Depth profiles of selected trace metals, $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and Pb anthropogenic fraction derived from the analysis of the snow-pit series are shown in Fig. 5. Pb and Cu (together with Co, Cr, V, and Zn) exhibited similar variability, as indicated by their significant correlations (Table S6), whereas Cd showed a distinct behaviour. Interestingly, the Pb isotopic signature - and the inferred anthropogenic contribution - varied independently of Pb concentration, consistent with observations by Van de Velde et al. (2005). The application of time-series tests did not reveal significant temporal trends, in agreement with snow-pit studies from Hercules Névé (Van de Velde et al., 2005) and Coats Land (Planchon et al., 2003). Although the short period of investigation (two years) limits the statistical power of the analysis, the lack of a clear temporal trend highlights the complex variability of the processes governing the atmospheric transport and deposition of trace metals in Antarctica. According to Van de Velde et al. (2005), such variability could result from the vertical transport of anthropogenic aerosols into the mid-troposphere, variations in transport pathways from different continents to Antarctica, and air-mass mixing within the Antarctic circumpolar vortex.

5. Conclusion

The concentrations of trace metals measured in the snow pit samples collected at McCarthy Ridge exceeded the background levels typically reported in comparable environmental studies, suggesting a possible influence of anthropogenic inputs. However, considering the specific characteristics of the study site, the observed enrichment may also be explained by natural processes, including crustal and volcanic sources, as well as marine contributions in the case of Cd. Accordingly, based on the Pb isotopic data, it was estimated that only $26 \pm 13\%$ of this metal - and potentially of other correlated elements - may be of anthropogenic origin. This proportion is lower than similar estimates obtained using isotopic data for Victoria Land but referred to earlier periods, suggesting a temporal decrease in the fraction of anthropogenic Pb deposited onto Antarctic snow. Finally, the absence of a well-defined seasonal pattern suggested that the processes governing the atmospheric transport and deposition of trace metals in Antarctica are complex and likely influenced by multiple factors. Overall, this study demonstrated that trace metals are still present in the Antarctic environment at levels exceeding the natural background, but their sources are not fully defined yet. In

particular, it is necessary to disentangle the potential anthropogenic sources by enlarging the number of chemical proxies (e.g. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios), expanding the database of isotopic values for potential source areas, and applying multi-sources regression models.

CRedit authorship contribution statement

Francisco Ardini: Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Alessia Chiaro:** Investigation. **Matilde Mataloni:** Writing – review & editing, Investigation. **Elisa Cerri:** Writing – review & editing, Investigation. **Marco Vecchiato:** Investigation. **Marco Grotti:** Writing – original draft, Supervision, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Francisco Ardini reports financial support was provided by Ministry of Education and Research. Marco Grotti reports financial support was provided by Ministry of Education and Research. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2026.128765>.

Data availability

Data will be made available on request.

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