Isotopic analysis of snow from Dome C indicates changes in the source of atmospheric lead over the last fifty years in East Antarctica

Published version:

DOI:10.1016/j.chemosphere.2020.126858

Sources and recent trend of atmospheric lead over the last fifty years by isotopic measurements on snow from Dome C, East Antarctic Plateau

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Abstract

Lead (Pb) concentration and Pb isotope ratios have been determined in 109 snow pit samples collected at Dome C, in the East Antarctic Plateau, and corresponding to the period 1971-2017. The Pb concentration was 8.2 ± 1.0 pg g^{-1} (mean ± 95%-confidence interval), with a decreasing trend from early 1990s (the median Pb concentration halved from 9.0 pg g^{-1} in 1970-1980 to 4.4 pg g^{-1} in 2010-2017). The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios were 2.419 ± 0.003 and 1.158 ± 0.003 (mean and 95%-confidence interval), respectively. The temporal variations of Pb isotopic composition from 1970 to mid-1990s reflect the changes in the consumption of Pb-enriched gasoline in the Southern Hemisphere, whereas the subsequent increase of the Pb isotope ratios is ascribed to a shift toward the natural isotopic signature. Accordingly, the anthropogenic Pb decreased from 61 ± 3 % in 1980-1990 to 49 ± 10 % in 2010-2017. The measured ratios suggest that Australia has been a significant source of anthropogenic Pb to Antarctica, even in recent times. Differences and similarities among Pb content and its isotopic composition in various sites across Antarctica have been explored by principal component analysis, finding that the altitude and the distance from the coast significantly affect the Pb content but not its isotopic signature.

Keywords: lead; isotopic ratios; snow; Antarctica; pollution.

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1. Introduction

Lead (Pb) is a toxic trace element, whose natural biogeochemical cycle has been strongly affected by anthropogenic activities since ~5000 years ago (Weiss et al., 1999). In particular, Pb has been massively introduced into the atmosphere by mining and smelting activities, as well as by the use of leaded gasoline in the second half of the 1900s, before its phase-out at the end of the century (Oudijk, 2010). These anthropogenic inputs overlapped the natural occurrence of Pb, due to rock and soil dusts, ocean salt and volcanic emissions. Lead associated to fine particles can be transported over long distances by the atmospheric circulation, reaching the most pristine regions on Earth, like the Arctic and Antarctica. Here, it is accumulated in snow by dry and wet ~~precipitation~~deposition, so its determination in well-dated snow and ice samples can provide a proxy of historical changes of both natural and anthropogenic Pb in the atmosphere. In particular, the use of Pb isotope ratios for source assessment and to investigate transport pathways have been successfully applied in many polar studies (Ardini et al., 2019). In fact, Pb has four stable isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, and the last three are formed by radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively. The relative abundance of Pb isotopes in ores is, therefore, related both to the abundance of their parent nuclide at the moment of the ore formation and to the age of the rock. Consequently, there is a relatively large difference between the isotopic composition of Pb from various ore deposits (Sangster et al., 2000), so its isotopic signature can be an efficient tool for tracing sources of pollution and the movement of air-masses on a global scale (Bollhöfer and Rosman, 2001, 2000).

The first measurements of Pb isotopes in Antarctic snow were performed by Rosman et al. (1994), who analysed four surface snow blocks collected in 1983-84 along a transect from the Dumont d’Urville (DDU) station to a site 433 km inland and at the geographic South Pole, and in a single sample of ancient ice obtained at Dome C. The results highlighted the occurrence of anthropogenic Pb, even in samples containing 2.3 pg g^{-1} Pb, and indicated South America as a likely source of the anthropogenic Pb in Antarctic snow dated from the 1980s. Emission from

Australia was also proposed as an alternative explanation for a site 33 km from DDU, and the presence of significantly less radiogenic Pb in the snow adjacent to the DDU and Amundsen-Scott stations was ascribed to local contamination. Following various improvements in the analytical procedures (Chisholm et al., 1995, Vallelonga et al., 2002a), measurements of Pb isotopes were carried out on ice and snow from various locations, including Dome C (Rosman et al., 1999, Vallelonga et al., 2005, Vallelonga et al., 2010), Taylor Dome (Matsumoto and Hinkley, 2001), Law Dome (Vallelonga et al., 2002b), Coats Land (Planchon et al., 2003), Victoria Land (Van de Velde et al., 2005), Dome Fuji (Chang et al., 2016) and Dome A (Chang et al., 2016). Additionally, a composite record of semi-quantitative Pb isotopes data was reported for various sites across Antarctica (McConnell et al., 2014). Some of these studies (Rosman et al., 1999, Matsumoto and Hinkley, 2001, Vallelonga et al., 2005, 2010) discussed the Pb isotopic composition of old ice (~1-200 kyr before present) in relation to natural sources and climate changes. It was found that Pb isotopic compositions in Antarctic ice varied with changing climate, with lower ^{206}Pb/^{207}Pb ratios (and higher Pb concentration) during the glacial periods than in the Holocene and the other interglacial climate stages (Rosman et al., 1999, Vallelonga et al., 2005, 2010), although with a high level of variability (Vallelonga et al., 2010). Mineral dust and volcanism are the natural sources of Pb in this pre-industrial ice, and regional differences in the isotopic signature can be ascribed to different proportion of these sources (Vallelonga et al., 2005). For example, Pb from Dome C is generally less radiogenic than that from Taylor Dome, due to greater proportions of dust. In fact, dust accounts for 70% of Pb in Dome C ice (Vallelonga et al., 2005), but only a few percent in most samples from Taylor Dome, where the main source of Pb is represented by emissions from quiescent volcanoes (Matsumoto and Hinkley, 2001). Concerning the origin of the mineral dust, the southern part of South America was proposed as the major source of dust in interglacial periods, although a partial overlap with Australian potential source areas was observed (Vallelonga et al., 2010). Moreover, local sources were found to be non-trivial contributors (Vallelonga et al., 2010).

Other studies focussed on the Pb pollution history, well reconstructed by isotopic measurements on ice cores and snow dating back to the beginning of the industrial era (Vallelonga et al., 2002b, Planchon et al., 2003, Van de Velde et al., 2005, McConnell et al., 2014, Chang et al., 2016). Isotopic evidence of Pb pollution in Antarctica as early as the 1880-90s was first observed at Law Dome (Vallelonga et al., 2002b), Coats Land (Planchon et al., 2003) and Victoria Land (Van de Velde et al., 2005), and attributed to mining and smelting of non-ferrous metal ores at Broken Hill (Australia) and, at a minor extent, to coal combustion. The subsequent pollution events tracked by Pb isotopic ratios were linked to the rise and fall in the use of alkyl-Pb additives in gasoline in the Southern Hemisphere, which occurred in the second half of 20th century (Oudijk, 2010). These events were highlighted by an increase in the concentration and crustal enrichment of Pb (usually measured as Pb/Ba ratio) in the snow/ice, and a concomitant decrease in the ^{206}Pb/^{207}Pb ratios, with marked differences among the sites both in the timings of maxima and in the isotopic values. Concerning the sources of the anthropogenic Pb due to gasoline consumption, Vallelonga and co-workers (2002b) observed that the ^{206}Pb/^{207}Pb ratios measured at Law Dome in samples dated between 1950 and 1970 are compatible with inputs of alkyl-Pb from Australia and New Zealand, while the higher Pb isotopic ratios observed in the late 1970s and

1980s would suggest increased influence of gasoline Pb emissions from countries in the northern part of South America, such as Brazil. Similar conclusions were reported for Coats Land (Planchon et al., 2003) and Victoria Land (Van de Velde et al., 2005), explaining the differences among the sites by the substantial changes in the relative contributions of these two source regions. More recently, McConnell et al. (2014) analysed a composite record of semi-quantitative ^{206}Pb/^{207}Pb ratios across Antarctica (9 ice cores, collectively spanning from 1850-2010), suggesting that southern Australia was responsible for the introduction of Pb pollution into Antarctica at the end of the 19th century, remaining a significant source until (at least) 2010. Conversely, Chang et al. (2016) assigned to northern South America (Chile and Argentina) the origin of the Pb pollution in snow samples dated from mid-1980s to mid-1990s, collected at the central East Antarctic plateau (Dome Fuji and Dome A).

In this work, a record of Pb isotope ratios has been obtained by the analysis of 109 snow samples collected at Dome C and covering the period from 1970 to 2017. The obtained data are presented and discussed with the aim of: (a) providing updated information on the Pb pollution trend in the last fifty years (the more recent ones ends at 2010), especially to discriminate between "steady-state" and "decrease" trends in the last decade; (b) contributing to the source assessment of the atmospheric Pb reaching Antarctica, as a tracer of the mineral dust (Grouset and Biscaye 2005); (c) evaluating the anthropogenic-to-natural Pb ratio and its temporal variation, to be compared to similar estimations for other Antarctic sites.

2. Experimental

2.1 Sample collection

The samples were collected in December 2017 at Dome C, East Antarctic Plateau (elevation: 3233 m a.s.l.; 1100 km from the Adelie Land coast; Supporting Information, Figure S1), in a site (75.052° S; 123.580° E) 5-km far from the Italian-French Concordia station, and out from its influence according to the prevailing SSW wind direction. A continuous series of 109 snow samples was obtained from the wall of a 4-m-deep pit, by horizontally inserting 50 mL polypropylene graduated tubes, at about 3-cm intervals. In order to minimize Pb contamination, the snow pit was hand-dug and, after the digging, the potentially contaminated layer was removed by means of a pre-cleaned polypropylene scalpel. Operators wore clean room clothes and the tubes were inserted and removed manually. The sampling tubes had been previously acid-washed (0.05% HNO_3) and individually checked by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) measurements to exclude any significant Pb contamination. Immediately after the collection, the tubes were sealed inside polypropylene bags and stored at -20 °C until analysis. Field blanks were concomitantly collected and treated as the samples.

Sample dating was assigned on the basis of parallel measurements of non-sea-salt sulphates, using the well-identified large volcanic depositions from Mt. Pinatubo in 1992 (Castellano et al., 2005). The corresponding mean annual accumulation is about 8.4 cm yr^{-1} and the samples cover about fifty years (1971-2017).

2.2 Sample preparation and analysis

Lead isotopic analysis of snow samples was performed by ICP-MS using a previously reported method (Bazzano et al., 2014, Ardini et al., 2018). Briefly, the samples were allowed to melt in their closed tubes; subsequently, 20.0 g aliquots were acidified with 100 µL of HNO_3 and 100 µL of HF, left to stand for 24 h, and refrozen. Then, the samples were freeze-dried, redissolved in 200 µL of 0.05% HNO_3 solution and introduced into the ICP-MS spectrometer by using the heated torch-integrated sample introduction system (Paredes et al., 2009, Grotti et al., 2013). Therefore, the sample volumes were reduced from 20.0 to 0.200 mL, providing a 100-fold preconcentration of Pb. 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 instrument used (PerkinElmer Elan DRC II) was equipped with a dynamic reaction cell, placed between the ion optics and the mass analyser, which was pressurised with neon to improve the precision by collisional damping (Bandura et al., 2000). Instrumental mass bias was corrected ~~for~~ by measuring a NIST SRM 981 standard solution (Pb concentration: 5 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 (determined according to Nelms et al., 2001). Data are expressed as mean values and 95%-confidence intervals.

Lead concentration was estimated by comparing the ion intensity at m/z=208 measured in each sample to that measured in the bracketing NIST SRM 981 standard solutions.

Sea-salt sulphates were measured by ion chromatography in a parallel sequence of snow samples, at about 3-cm intervals, according to the procedure by Morganti et al. (2007).

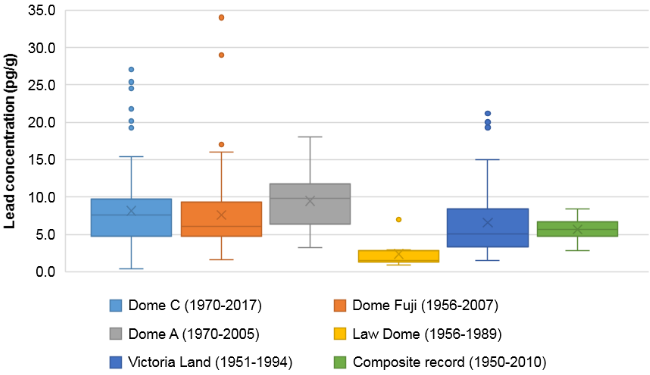
2.3. Analytical performances and quality control

The procedural blank of the procedure was 0.2±0.1 pg g^{-1} (n=4), resulting in a method detection limit of 0.3 pg g^{-1}, lower than the actual Pb concentration in the samples (Table S1). Field blanks were not significantly different from the procedural ones. Measurements of $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ isotopic ratios were characterized by an internal precision in the 0.2-1% range, at the concentration level of the analytical solutions (0.1-3 µg L^{-1}). The quality 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 ($^{208}Pb/^{207}Pb = 2.4087 \pm 0.0013$, $^{206}Pb/^{207}Pb = 1.1305 \pm 0.0005$, n=26) did not significantly differ from the reference ones ($^{208}Pb/^{207}Pb = 2.4078 \pm 0.0004$, $^{206}Pb/^{207}Pb = 1.1311 \pm 0.0001$), showing an external precision of 0.12% and an accuracy better than 0.05%.

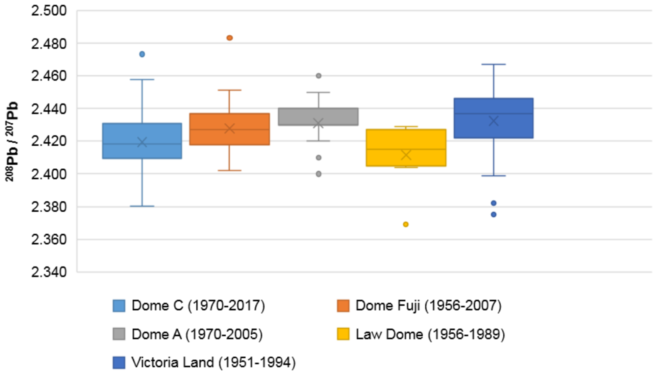
3. Results and discussion

3.1. Lead concentration

Lead concentration values are reported in Table S1 and compared to data obtained for other Antarctic sites and similar periods in Figure 1a. The Pb concentration in the snow samples from Dome C was 8.2 … higher than the mean value of … d dated 17th century (McConn



(a)



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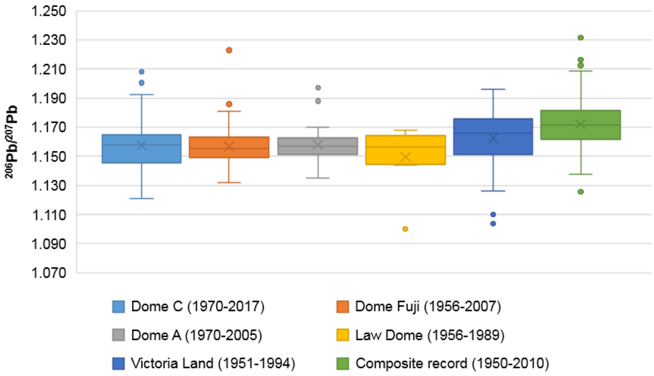

(c)

***Figure 1**. (a) Pb concentration, (b) ^{208}Pb/^{207}Pb and (c) ^{206}Pb/^{207}Pb values in recent snow from various Antarctic sites: Dome C (this work), Dome Fuji (Chang et al., 2016), Dome A (Chang et al., 2016), Law Dome (Vallelonga et al., 2002), Victoria Land (Van de Velde et al., 2005) and a composite Pb record from 16 ice cores across Antarctica (McConnell et al., 2014). See Figure S1 for locations.*

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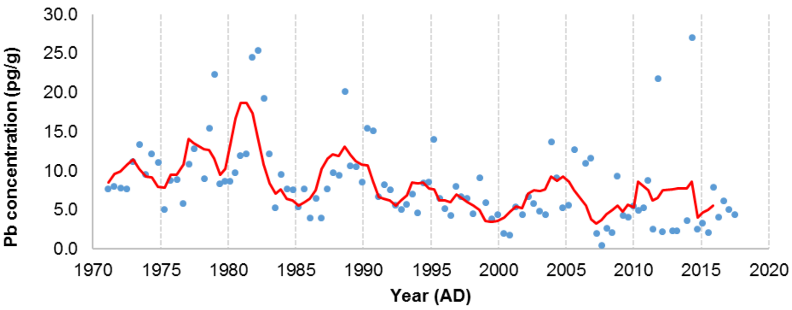
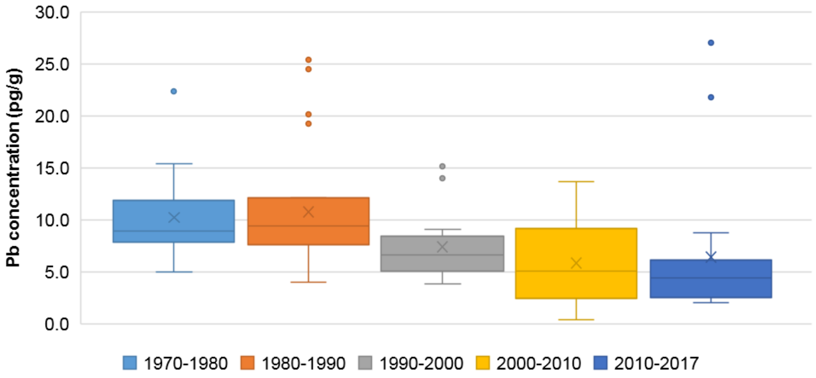
In fact, Pb in the pre-industrial ice largely derived from natural sources, such as crustal dust and volcanic activity (Matsumoto and Hinkley, 2001; Vallelonga et al., 2005). However, the occurring of industrial and mining activities in the Southern Hemisphere caused a significant increase of Pb inputs to Antarctica since the second half of the 19th century, leading to the values observed in recent snow. The Pb concentration in Dome C is in a good agreement with values found in other Antarctic sites, mainly at comparable altitude (see section 3.4), highlighting the homogeneity of the distribution of atmospheric Pb over Antarctica, as already observed (McConnell et al., 2014; Chang et al., 2016). The temporal trend of Pb concentration is illustrated in Figure 2.



(a)



(b)

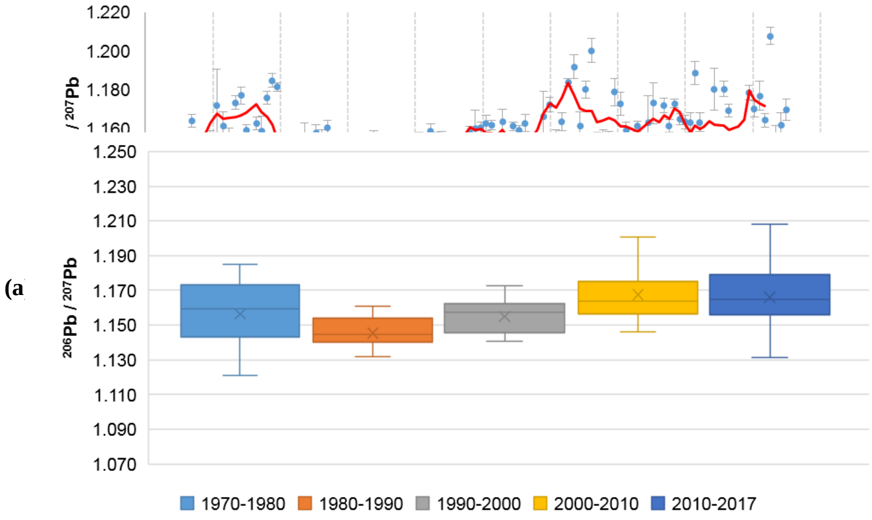
***Figure 2**. Temporal trend of Pb concentration in snow from Dome C. (a) single data and five-point running average; (b) boxplots of data grouped by decades.*

The five-point running average shows concentration peaks in the late 1970s and in the early 1980s, as well as around 1990, in good agreement with the temporal trend observed at Dome Fuji (Chang et al., 2016). Moreover, the pattern is consistent with that reported for other Antarctic sites, with differences in the peaks position which can be attributed both to variations in the atmospheric processes (transport, deposition) and different contributions of anthropogenic and natural Pb from South America, Australia and local sources (Chang et al., 2016, Li et al., 2008, Van de Velde et al., 2005). From the early 1990s onward, a gradual decrease in the Pb concentration was observed, as highlighted by grouping data by decades (Figure 2b). For example, the median Pb concentration decreased from 9.0 pg g^{-1} in 1970-1980 to 4.4 pg g^{-1} in 2010-2017. This trend is in good agreement with the results by Chang et al. (2016), whereas McConnell et al. (2014) reported a persistent Pb concentration since 1980s, without a significant decreasing trend until 2010. By considering the global anthropogenic input to Antarctica, the observed decrease over the last decades can be ascribed to the reduction of Pb release into the environment after the ban of the Pb-enriched gasoline in many southernmost countries of the Southern Hemisphere (New Zeeland in 1996, Brazil in 1997, Argentina in 1998, Chile in 2001, Australia in 2002 and South Africa in 2006) and the reduction of emission of toxic elements from copper (Cu) production activities in Chile (Chang et al., 2016, McConnell et al., 2014). Nevertheless, the effect of anthropic activities on Antarctica environment continue to be evident, and even the Pb concentration in the more recent samples (2.1-7.9 pg g^{-1} in 2015-17) is still one order of magnitude higher than the natural background (0.2 pg g^{-1} in Holocene ice from Dome C (Vallelonga et al., 2010).

3.2. Temporal variation of Pb isotopic ratios

Lead isotopic ratios and their uncertainties are reported in Table S1. Values of $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ were 2.419 ± 0.003 and 1.158 ± 0.003 (mean and 95%-confidence interval, n=109), respectively. These values are significantly lower than the natural ratios measured at Dome C (2.478 and 1.210, respectively, Vallelonga et al., 2005), thereby highlighting the anthropogenic contribution to the Pb deposited in Antarctica over the last 50 years. Data are in good agreement with previous studies (Figure 1b,c). For example, the median value of the $^{206}Pb/^{207}Pb$ ratio (1.158) is very close to those reported for comparable periods at Fuji Dome (1.156, Chang et al., 2016), Dome A (1.157, Chang et al., 2016) and Law Dome (1.157, Vallelonga et al., 2002), and slightly lower than that obtained at Victoria Land (1.166, Van de Velde et al., 2005) and by the analysis of the composite record of semi-quantitative values (1.171, McConnell et al., 2014).

The temporal trend of $^{206}Pb/^{207}Pb$ ratio is displayed in Figure 3a (analogous trend was obtained for $^{208}Pb/^{207}Pb$, Figure S2).



(b)

***Figure 3**. Temporal trend of ^{206}Pb/^{207}Pb isotopic ratio in snow from Dome C. (a) single data with associated uncertainty and five-point running average; (b) boxplots of data grouped by decades.*

A sharp increase from the beginning to the end of 1970s may be observed, with the ratio changing from about 1.12 to 1.18. It was followed by an abrupt drop to less radiogenic values during the 1980s, concomitantly with the Pb concentration peaks in that very period (Figure 2a). From the end of 1980s, the Pb isotopic ratio raised again reaching the running average of 1.18 and then it has stabilized at a value of 1.167 ± 0.005 (mean and 95%-confidence interval, n=41) in 2000-2017 (Figure 3b). Similar temporal trends (Figure S3) were recorded at Dome Fuji and Dome A (Chang et al., 2017), as well as in certain ice cores analysed by McConnell et al. (2014), such as PIG2010 and B40, although the composite record did not show any variation in the ratio between 1970 and the end of 1990s.

The temporal trend from 1970s to the 2000 can be explained by considering the variations in the consumption of Pb-enriched gasoline in the various regions of the Southern Hemisphere. In fact, Bollhöfer and Rosman (2000) showed that marked differences existed in the Pb isotopic composition of the particulate airborne from different cities in the Southern Hemisphere, as a consequence of the local industrial activities and the different suppliers of the alkyl-Pb additives for the local gasoline. In particular, the two major alkyl-Pb suppliers were Associated Octel (UK), who mainly used Pb ores with low isotopic ratios (Broken Hill type ores, Australia, ^{208}Pb/^{207}Pb ≈ 2.315, ^{206}Pb/^{207}Pb ≈ 1.041, Sangster et al., 2000), and Ethyl Corp. (USA) who mainly used Pb ores with high isotopic ratios (Mississippi Valley type ores, USA, ^{208}Pb/^{207}Pb = 2.528-2.627, ^{206}Pb/^{207}Pb = 1.339-1.406, Sangster et al., 2000). As a consequence, the atmospheric particulate emitted from cites where the gasoline used was obtained by Broken Hill type ores (the southernmost regions of the Southern Hemisphere including Argentina, Chile, Australia and New Zealand) was characterized by lower Pb isotopic ratios than that from cities where the gasoline used was obtained by Mississippi Valley type ores (the north-central regions of South America, such as Brazil). Therefore, the abrupt rise of Pb isotope ratios in the first half of 1970s (Figure 3a) can be ascribed to the quickly increase of the consumption of gasoline in northern South America (mainly Brazil), characterized by more radiogenic isotopic values. On the other hand, since early 1980s, the consumption of Pb-enriched gasoline in Brazil significantly decreased, while it was unchanged in Argentina ~~and~~, Chile and Australia, where the gasoline (from Broken Hill type ores) was characterised by lower Pb isotopic ratios. This caused a decrease in the isotopic ratios measured in the samples dated 1980-1995. The following rise in the ratios can be explained in different ways. According to Chang et al. (2016), it could be ascribed to the Chilean Cu mining activity. In fact, the Pb ores of Chilean Andes have relatively high isotope ratios (^{208}Pb/^{207}Pb = 2.449-2.469, ^{206}Pb/^{207}Pb = 1.175-1.189; Puig, 1988) and the relative contribution of the mining activity in South America to the total Pb emission in the atmosphere increased after the phase-out of Pb-enriched gasoline. On the other hand, the increase in the Pb isotopic ratios after mid-1990s could also be due to a decrease of anthropogenic Pb compared to the natural one, which is characterized by more radiogenic values (^{208}Pb/^{207}Pb = 2.478, ^{206}Pb/^{207}Pb = 1.210; Vallelonga et al., 2005), as suggested by a concomitant decrease in the total Pb concentration (Figure 2). Finally, the Pb isotopic ratios after 2000 would seem to indicate that a rather stable situation has been reached, although dispersion of data was significantly higher compared to the previous decades, thereby indicating more pronounced inter-annual variations in the atmospheric transport of Pb to Antarctica.

Commentato [b2]: Fino a qua non emerge il contributo dell'Australia sui rapporti isotopici, mentre dopo se ne afferma l'importanza.

3.3. Anthropogenic and natural Pb sources

In order to assess the contribution of possible anthropogenic and natural sources, Pb isotopic data were displayed in a three-isotope plot and compared to reference values (Figure 4). All the measured Pb isotopic ratios are scattered along a straight line (R^2 = 0.764), resulting from the mixing of at least two sources. However, the assessment of these sources is not trivial, because of the temporal variation mentioned above and the co-linearity of the isotopic data (Ellam, 2010). According to previous studies on Antarctic snow and atmospheric particulate (Van de Velde et al., 2005, Bazzano et al., 2015a,b), the measured Pb isotopic ratios may be interpreted according to a two-terms mixing model, with a natural and an anthropogenic end-member.

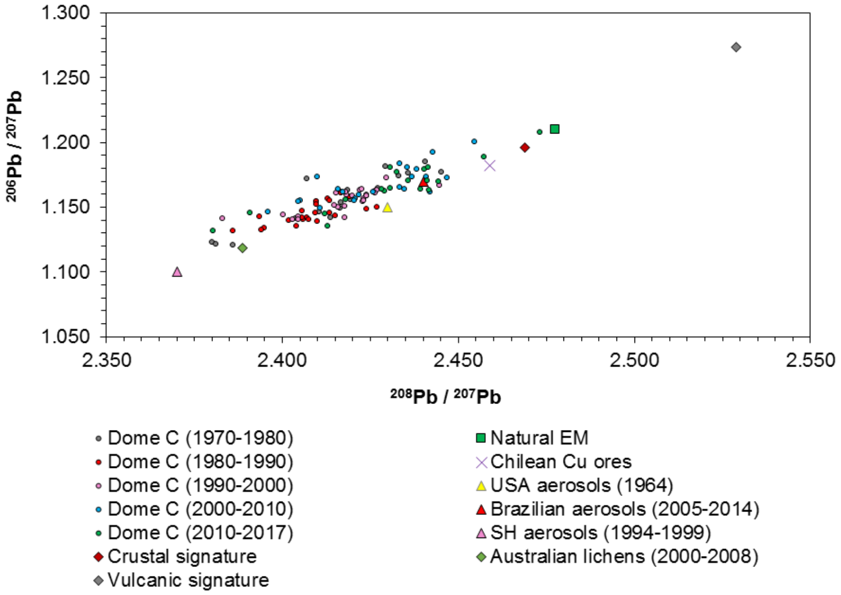


***Figure 4**. Three-isotope plot of Pb isotopic ratios in Antarctic snow from Dome C, differentiated by sample age. Possible natural and anthropogenic sources are also showed (see text for references).*

In particular, the natural end-member (^{208}Pb/^{207}Pb = 2.478, ^{206}Pb/^{207}Pb = 1.210) was computed by averaging data obtained by the analysis of 30 ice core samples from Dome C and dated 6.9 to 217 kyr before present (Vallelonga et al., 2005). Considering the Pb isotopic signatures of volcanic (^{208}Pb/^{207}Pb = 2.529, ^{206}Pb/^{207}Pb = 1.274; Van de Velde et al., 2005) and crustal (^{208}Pb/^{207}Pb = 2.469, ^{206}Pb/^{207}Pb = 1.196; Rosman et al., 1999) sources and applying a simple binary mixture model, the relative contribution of these sources to the composition of the natural end-member would result 17% and 83%, respectively. This result highlights the major contribution of dust at Dome C compared to other Antarctic sites (e.g. Taylor Dome, see Matsumoto and Hinkley, 2001), as pointed out by Vallelonga et al., (2005).

Concerning the anthropogenic end-member, according to the major variations in the sources discussed above (section 3.2), three periods have been considered: 1970-1980, 1980-2000 and

2000-2017. For the first decade, van de Velde et al. (2005) used the isotopic signature reported in gasoline and aerosol in the Los Angeles Basin the early 1970s (Chow and Johnstone, 1965), considered to be representative of gasoline alkyl-Pb additives consumed in the Southern Hemisphere between 1951 and 1981. However, these values resulted to be too radiogenic to explain the ratios found in our 1970-1980 samples (Figure 4) and, for the lack of other reference data for that period, we could not set a reliable anthropogenic end-member for those samples. For the period 1980-2000, the mean Pb isotopic signature reported by Bollhoffer and Rosman (2000) for urban aerosols in various Southern Hemisphere cities over the period 1994-1999 was used, according to van den Velde et al. (2005). Finally, for the 2000-2017 samples, the anthropogenic signature was deduced from the isotopic composition of Australian lichens and fungi collected between 2000 and 2008 (Wu et al., 2016). In fact, the Pb isotopic signatures of both the Chilean Cu ores and of the atmospheric particulate collected in Brazilian cities between 2005 and 2014 (average ^{208}Pb/^{207}Pb = 2.44, ^{206}Pb/^{207}Pb =1.17; Mirlean et al., 2005, Gemeiner et al, 2017, Gioia et al., 2017, Khondoker et al., 2018) were more radiogenic than that measured in the most of the Antarctic snow samples dated 2010-2017 (Figure 4). More likely, these values can be ascribed to inputs from the Australian regions, as suggested by many authors (Revel-Rolland et al., 2006, Li et al., 2008, McConnell et al., 2014). In fact, Australian regions have preserved low values of Pb isotopic ratios even after the ban of Pb-enriched gasoline in 2002 (Wu et al., 2016), and they could have contributed to lowering the Pb isotopic ratios of the atmospheric particulate reaching Antarctica, respect to the Chilean Cu ore or the natural signature. A possible major influence from South Australia was also suggested by measurements of ^{87}Sr/^{86}Sr isotope ratio in surface snow samples collected at Dome C on 2006 and 2010 (Bazzano et al., 2017).

Using these natural and anthropogenic end-members, the proportion of anthropogenic Pb deposited at Dome C was computed. The result is illustrated in Figure 5, where data are grouped by decade. The estimated percentage of anthropogenic Pb was 54 ± 3 % (mean ± 95%-confidence interval, n=89), slightly decreasing from 61 ± 3 % in 1980-1990 to 49 ± 10 % in 2010-2017.

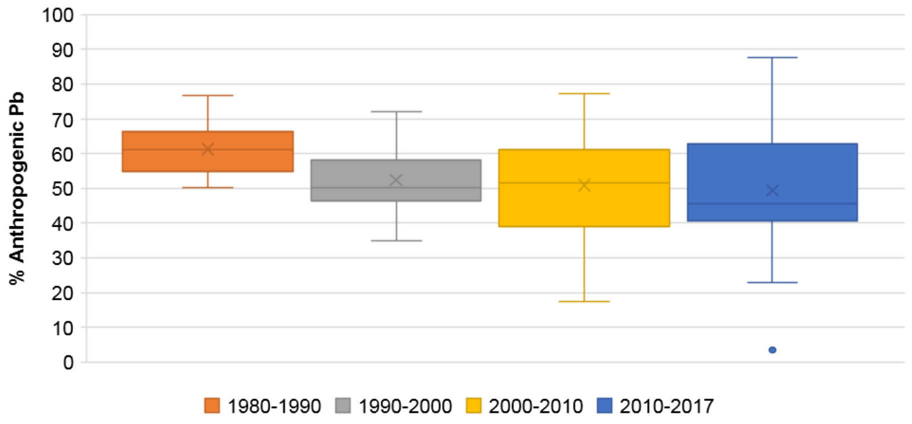
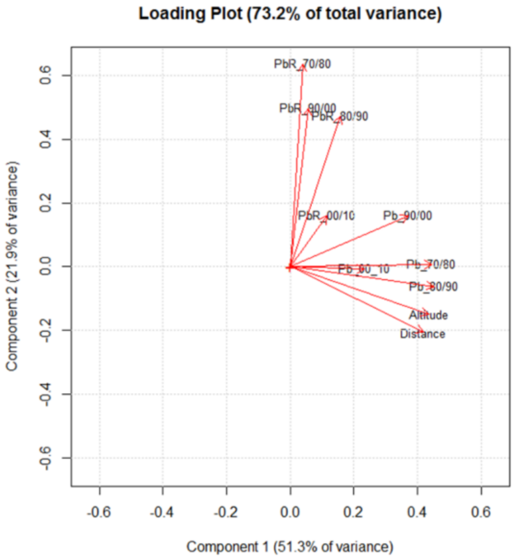


Figure 5. *Estimated percentages of anthropogenic Pb, grouped by decades.*

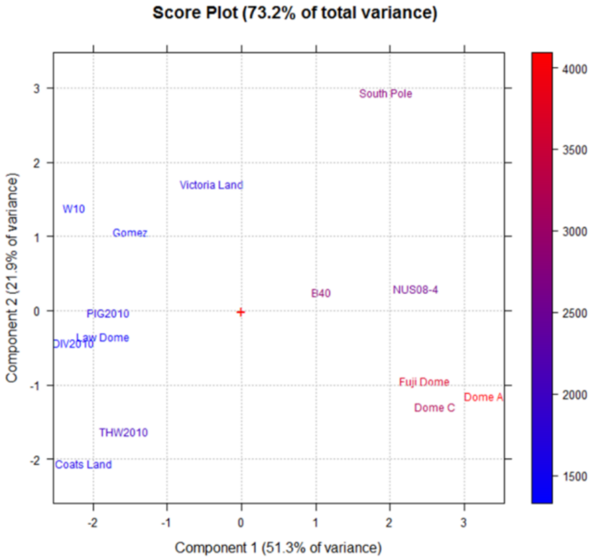
These data are in good with the estimations by van den Velde et al. (2005), who calculated an anthropogenic Pb contribution of ≈ 60% in the Hercules Neve (Victoria Land) snow samples dated between 1986 and 1994. On the other hand, our estimation is in contrast with Chang and co-workers (2016), who reported that more than 90% of the Pb in the snow from the Antarctic Plateau (Dome A and Dome Fuji) is of anthropogenic origin.

3.4. Regional variations

Antarctica covers an area of $14\text{x}10^6$ km^2, wider than Europe and U.S. However, its position in the globe, that keeps it in the centre of the atmospheric transport processes, and its morphological characteristics (e.g. a flat plateau covering a large portion of east Antarctica), make it possible to have analogies among places also very far from each other. Using the data by McConnell et al. (2014), Chang et al. (2016), Planchon et al. (2003), Van de Velde et al. (2005), Vallelonga et al. (2002) and this work, the sampling sites were compared by applying a principal component analysis (PCA). Lead concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios were averaged by grouping the samples by decades and the mean values in each decade were considered as variables, along with altitude and distance from the coast, while the different sites were set as objects. After autoscaling of data, two principal components (PCs) were obtained, collectively explaining 73.2% of the total variance of data.



(a)



(b)

***Figure 6**. Principal component analysis results: (a) loading plot; (b) score plot. The sites name are colored according their altitude in agree with the chromatic scale shown on the side.*

The loading plot (Figure 6a) shows that Pb concentration, altitude and distance are strongly correlated between each other, directly loading on the first PC, whereas Pb isotopic ratios load on the second PC and are uncorrelated with the total Pb concentration, altitude and distance. The correlation of Pb concentration with altitude was statistically significant and decreased with time (from r=0.910, p<0.0001 in 1970-1980 to r=0.661, p=0.01 in 2000-2010). Considering the temporal trend of Pb concentration discussed above (Figure 2b), this would indicate that the effect of the altitude is stronger when the amount of Pb is high. The correlation with the distance was also significant (r=0.911-0.646, p<0.05), except for the 2000-2010 decade. Similarities and differences among the sites are highlighted in the score plot (Figure 6b). Dome C, Dome A and Dome Fuji, located on the East Antarctic plateau above 3000 m a.s.l., show a high similarity, although they are distant about one thousand kilometres from each other. Similarly, the other sites are grouped according to the altitude and the distance from the coast. For instance, Law Dome and Gomez are close in the score plot, although they are on opposite sides of the continent. By looking at the score and loading plots together, it can be deduced that the sites at high altitude are differentiated from the others because of a higher Pb concentration. This result is in good agreement with the increase in the fallout flux of anthropogenic elements in the Antarctic plateau above 3500 m a.s.l. reported by Ikegawa et al. (1999), reflecting the polar stratospheric precipitation or long-range tropospheric transport from the Southern Hemisphere.

Finally, Dome C, Dome A, Dome Fuji, Law Dome and Coats Land are characterised by similar scores on the second PC, mainly affected by the ^{206}Pb/^{207}Pb ratios, confirming their similar isotopic composition.

Commentato [b3]: Law Dome sembra essere diverso dal gruppo DomeC-DomeA-DomeFuji sulla PC2. Ci sarebbe il sito chiamato THW2010, che è simile a Coats Land

Conclusion

This study has presented an updated record of Pb concentration and isotopic ratios in snow samples from the East Antarctic Plateau, providing new insights into the possible sources and the temporal trend of Pb atmospheric deposition over the last fifty years. Isotopic data for samples dated from 1970 to mid-1990s reflected the well-known changes in the consumption of Pb-enriched gasoline in the Southern Hemisphere, whereas the subsequent increase of the Pb isotope ratios is here ascribed to a shift toward the natural isotopic signature, in agreement with the concomitant decrease of total Pb concentration. According to our estimation, the contribution of anthropogenic Pb was 61 ± 3 % in 1980-1990 samples (in excellent agreement with van den Velde et al. 2005), and decreased to 49 ± 10 % in 2010-2017. Moreover, the measured Pb isotopic ratios suggest that Australia has been a significant anthropogenic source over the last fifty years, as indicated by previous measurements of $^{87}Sr/^{86}Sr$ isotope ratio (Bazzano et al., 2017). However, for a better assessment of the sources of atmospheric Pb to Antarctica, there is still the need of additional analytical data, including precise measurements of $^{20X}Pb/^{204}Pb$ ratios using multi-collector ICP-MS (Bazzano et al., 2015b) and more detailed isotopic values for Australian and Southern America potential source areas (Vallelonga et al., 2010). Finally, principal component analysis of data for various sites across Antarctica highlighted that the altitude and the distance from the coast significantly affect the Pb concentration, but not its isotopic signature.

Acknowledgments

This work has been funded by the Italian National Program of Research in Antarctica (projects PNRA14_00091, PNRA16_00252). The authors wish to thank Giulio Esposito, Andrea Spolaor, Alessandro Baù, Marco Buttu, Matthias Jaggi, Angelo Domesi and the PNRA logistic staff for their help in the field work.

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