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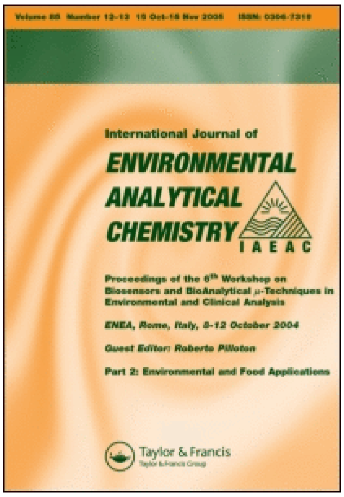

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RECENT DECREASE IN THE LEAD CONCENTRATION OF ANTARCTIC SNOW

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Differential Pulse Anodic Stripping Voltammetry (DPASV) was applied to determine the lead concentration in recent snow at two sites in the Victoria Land region, East Antarctica. Snow samples were collected during the 6th Italian Scientific Expedition to Antarctica (austral Summer 1990–91) along the wall of 2.5 m-deep hand-dug pits and by coring to a depth of about 11 m. The measurements revealed that lead content in Antarctic snow increased continuously from 1965 (about 3 pg/g) to the early 1980s (maximum about 8 pg/g), after which a marked, rapid decrease took place during the second half of 1980s, down to 2–4 pg/g in 1991. Estimates of the lead contributions from rocks and soils, volcanoes and the marine environment, together with analysis of statistical data on non-ferrous metal production and gasoline consumption, and the corresponding lead emissions into the atmosphere of the Southern Hemisphere, show that a net anthropogenic component is present and support the hypothesis that the trend observed in Antarctic snow may be related to lead consumption in gasoline, which firstly was on the rise, then declined owing to the increased use of unleaded gasoline.

Keywords: Lead; DPASV; snow; Victoria Land; Antarctica

INTRODUCTION

The massive use of lead in human activities for the manufacture of a variety of products, such as batteries, pigments, rolled and extruded items, cable sheaths and above all gasoline additives in the form of highly volatile alkyl lead compounds, causes large emissions of the metal into the environment and poses worrying ecological and health problems which demand an assessment of the consequent changes in the large-scale atmospheric cycles of this metal[1].

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The analytical investigation of polar ice caps (the earth's ice archives) has proved to be one of the most powerful ways of obtaining information on present, recent and past changes in the earth's atmosphere, including heavy metal changes[2,3].

The lead concentration vertical profile of the Greenland ice cap revealed that this metal is one of the earliest polluting substances of the Northern Hemisphere as used by the Greek and Roman civilizations, long before the Industrial Revolution[4]. In more recent periods the same profile clearly demonstrated the increase in large-scale pollution of the atmosphere from the Industrial Revolution, particularly after the Second World War and up to the late 1960s and the recent decrease mainly associated with the reduction in the use of lead in gasoline[5–9].

Recent studies have proved that even the remote Antarctic continent is significantly contaminated by lead, possibly due to the same anthropic sources[10–15], while a few data sets account for a possible, more recent, declining trend[14–16].

As a further contribution to the knowledge of recent changes of lead concentration in Antarctic snow, we present here new data obtained from samples collected at two sites in Victoria Land during the VI Italian Expedition to Antarctica (Summer 1990–91). Direct determination of lead in melted, decontaminated samples was carried out by Differential Pulse Anodic Stripping Voltammetry (DPASV), thus avoiding any long and contamination-prone enrichment procedure.

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EXPERIMENTAL

Laboratories and Chemicals

Both warm and cold (−20°C) clean chemistry laboratories were available with Class 100 vertical laminar flow areas. Wood benches with polypropylene shelves or Teflon coated stainless steel tables were installed in the laboratories. The cleaning of materials, handling of samples and instrumental measurements were carried out in the warm laboratory while the treatment and decontamination of frozen samples were performed in the cold laboratory. Researchers followed the clean room procedures strictly in both these clean environments.

Ultrapure water was obtained from Milli-Q or Alpha-Q systems (Millipore, MA, USA). NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) ultrapure HCl (32%) and HNO_3 (70%)[17] were used, respectively, for acidification of samples and for the final steps of the cleaning procedures of plastic items (see below). Analytical grade HNO_3 65% (Merck, Darmstadt, Germany) was used during the first step in the cleaning of materials. Saturated KCl solution (Suprapur KCl, Merck, ultrapure water) was further purified by passing it through Chelex 100 chelating resin (Bio-Rad, CA, USA). The 2.5 $\times 10^{-2}$ M $Hg(NO_3)_2$ solution was prepared by oxidation of hexadistilled Hg with concentrated ultrapure HNO_3 and diluting with ultrapure water. Nitrogen of chromatographic grade (purity >99.999%) was obtained through a nitrogen generator (Model NG 4000, Claind, Italy) or in high pressure cylinders (SIAD, Italy). Detergent powder from Alconox (NY, USA) was used.

Standard solutions (Pb: 10 μg/l; Al: 1, 5, 10 μg/l) were prepared through successive dilutions of AAS stock solutions (Titrisol, 1000 ppm, Merck). NASS-3 and NASS-4 open ocean seawater reference materials for trace metals were obtained from the National Research Council of Canada[18] and were used to check the analytical procedure for accuracy.

Cleaning of Materials

The PFA sample containers, the electrochemical cell components, Teflon and polyethylene bottles, and scrubbers, hammers and chisels used to decontaminate the pit walls and snow cores (see below) were acid cleaned following a five-step procedure previously described in detail[15].

Briefly items were cleaned as follows. Conventional chemical laboratory: immersion in detergent bath (40 °C, 10 days), rinsing with ultrapure water, immersion in 1:10 diluted HNO_3 analytical grade (40 °C, one week), repeated careful rinses with ultrapure water. Clean chemistry laboratory: immersion in 1:100 diluted ultrapure HNO_3 (35 °C, 15 days) rinsing and immersion in 1:1000 diluted ultrapure HNO_3, (35 °C, 20 days); finally, bottles are rinsed, filled with a 1:1000 diluted ultrapure HNO_3 fresh solution and stored inside double polyethylene bags, while scrubbers, knives and other items remain in the last bath until use.

Sampling and Datation

In January 1991, during the VI Italian Scientific Expedition to Antarctica, snow samples were collected at two sites in Victoria Land down to a depth of about 11 m (see Figure 1). The first site was located 40 km North-West of the Terra Nova Bay Station near the McCarthy Ridge (74° 32′ S – 162° 56′ E, elevation 700 m, 40 km from the sea, mean snow accumulation rate 27 g cm^{-2} y^{-1}[19]); the second was located 100 km North of the Station on the Styx Glacier plateau (73° 52′ S – 163° 42′ E, elevation 1700 m, 50 km from the sea, mean snow accumulation rate 16 g cm^{-2} y^{-1}[19]).

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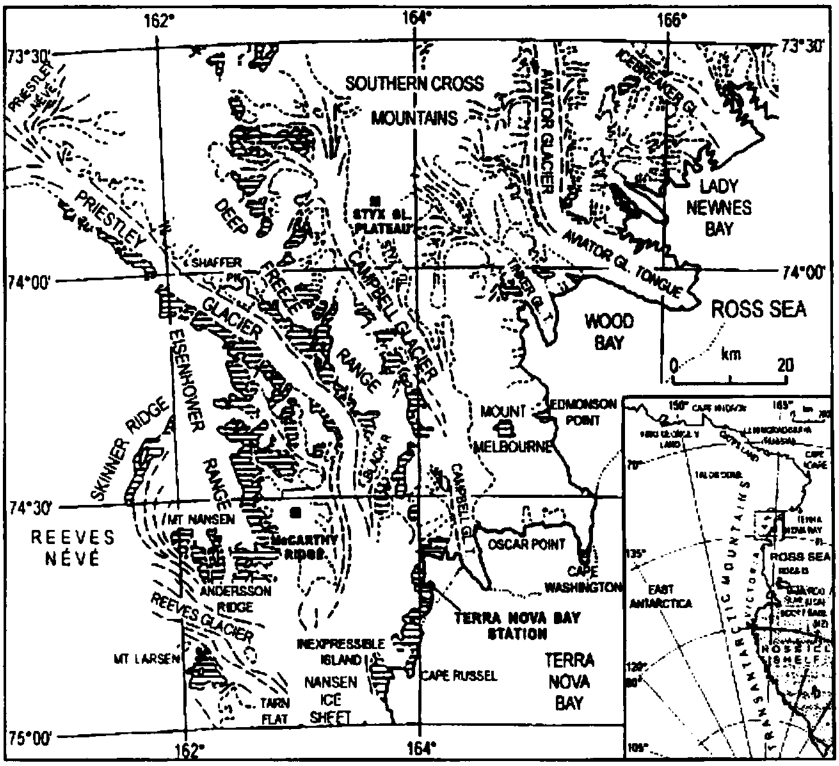

FIGURE 1 Locations of sampling sites on McCarthy Ridge and the Styx Glacier plateau (Victoria Land, East Antarctica). Ice-free area hatched.

Shallow samples were collected in 2.5-m deep hand-dug pits, inserting cylindrical containers horizontally in the carefully decontaminated upwind pit wall. After collection the containers were sealed inside double polyethylene bags and stored frozen (−20°C) until analysis. Pre-cleaned Teflon PFA containers with i.d. 11 cm, length 26 cm, capacity 2 litres (Savillex, MN, USA) were used. During the sampling operations researchers wore clean room garments, masks, polyethylene gloves and boot covers to prevent any contamination problem.

Deep samples were collected by means of a fibre-glass hand auger (i.d. 10.4 cm, length of the core barrel 127 cm, PICO, Polar Ice Coring Office, University of Nebraska-Lincoln, NB, USA). Snow core sections from 15 to 78 cm were obtained; they were sealed in two polyethylene bags and stored frozen (−20 °C) in rigid PVC tubes.

The age of the pit samples was estimated from the hydrogen peroxide deep profiles obtained in the same pits and already reported[19]. As usual[20] the H_2O_2

summer concentration maxima were used to reconstruct the age of snow layers. Each pit sample, considering the container diameter and the different thickness of the annual layers, spanned between 2 and 4 months. It is to be noted that the use of cylindrical samplers favours the snow layers in the central part of the cross section with respect to the upper and lower parts.

The age of the snow cores was estimated from the hydrogen peroxide and $\delta^{18}O$ vertical profiles measured in cores drilled at the same sites in the 1991–92 season[21] and considering the known snow accumulation during 1991 (41.0 cm and 29.5 cm of snow for McCarthy Ridge and Styx Glacier plateau, respectively)[22]. The uncertainty in datation was about 0.5 years. The analysed part of the snow core sections (usually 20 cm in length, see below) covers a period of about 4 months for McCarthy Ridge and from 4 to 10 months for the Styx Glacier plateau.

The depths at which analysed samples were collected and the corresponding estimated ages are reported below in Table I.

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Decontamination of Snow Cores

Despite the great care taken in the field to avoid contamination, the external layers of the snow cores are more or less contaminated by metal impurities due to the auger and the long storage period. For this reason a special decontamination procedure was carried out which enabled concentric layers of snow to be separated and lead concentration to be measured from the outside to centre in order to obtain radial concentration profiles.

Five snow core sections (McCarthy Ridge: 308–328 and 328–348 cm; Styx Glacier plateau: 668–688, 990–1010 and 1010–1030 cm) were decontaminated in the Laboratoire de Glaciologie et Geophysique de l'Environnement (LGGE), Grenoble, inside a laminar flow bench installed in a cold laboratory (−20°C) according to a procedure already described in detail[12]. Briefly, the snow core extremities are removed to prepare a 20-cm section with untouched surfaces; this section is inserted inside a 10.4 cm diameter polyethylene beaker. Then an ultra-clean polyethylene beaker (5.0 cm i.d.) is hammered longitudinally in the central part of the core and a series of 12 smaller polyethylene beakers (i.d. 1.0 cm) are hammered close to it. Finally the remaining external material is also collected. The procedure allows samples from three concentric layers to be obtained for each section, corresponding to the following ranges in radius: central core 0–2.5 cm, intermediate layer 2.5–3.5 cm, external layer 3.5–5.2 cm.

The remaining core sections were decontaminated in our cold, clean laboratory following the chiseling procedure already described in the literature[23]. Briefly, the snow core section is fixed on the Teflon holders of a clean polyeth-

Table I. Lead concentrations and estimated deposition period for samples collected on the McCarthy Ridge and Styx Glacier plateau

Depth[a] (cm)	Deposition period[b]	Pb concentration (pg/g) Measured values	Mean
		McCarthy Ridge	
5	S 1990-91	4.3, 5.1, 3.6	4.3[c]
200	W 1987	7.0, 7.0, 6.5	6.8[c]
308-328	1985	[d]*(213[e]) (11.8) (25.4)*	11.8[f]
328-348	1984	*(96, 100, 89)* (7.9) (4.6, 6.5)	6.8
		Styx Glacier plateau	
5	S 1990-91	53	53[f]
15	S 1990-91	2.1, 2.4, 2.3	2.3[c]
25	W 1990	2.6, 2.1, 2.2	2.3
48	S 1989-90	3.3, 2.6, 3.4, 3.0	3.1
70	W 1989	3.3, 4.6, 3.2	3.7
100	S 1988-89	7.0, 5.3, 7.8	6.7
150	S 1986-87	8.5, 7.2, 6.0	7.2
200	S 1985-86	13.8, 15.3, 9.7, 12.4	12.8[c, f]
133-153	1989	*(18)* (-[g]) (-) (4.5) (4.5, 3.8)	4.4
219-239	1987	*(112)* (-) *(17.8)* (9.2) (6.8, 6.7)	8.0
267-287	1986	*(170)* (-) *(31)* (9.1) (5.6, 5.8)	7.4
296-316	1984	*(374)* (-) *(33.8) (18.8)* (6.7, 5.0)	5.8
325-345	1983	*(389)* (-) *(27) (7.8)* (5.5, 6.1)	6.8
350-370	1982	*(164)* (-) *(12.1)* (8.8) (6.2, 8.5)	8.1
438-458	1981[h]	[h]*(202)* (-) *(13.8) (17.3)* (6.3, 7.9)	7.1
458-478	1981	(6.7, 6.3)	6.5
471-491	1980	*(509)* (-) *(17.3)* (7.0, 7.2) (5.6, 5.1)	6.2
491-511	1980	(6.1, 6.0)	6.6
597-614	1977	*(251, 222)* (-) *(13.4)* (6.5, 5.9) (5.4, 6.4)	6.0
614-631	1977	(3.8, 6.5)	5.7
668-688	1975	*(95, 82)* (5.0) (6.0, 7.4, 7.3)	6.0
850-867	1969	*(462)* (-) *(96) (32, 35)* (5.5, 4.7)	5.1
867-884	1969	(4.2, 3.4)	3.8
990-1010	1966	*(114, 123)* (2.3) (4.0, 3.2)	3.0
1010-1030	1965	*(122, 108)* (-) (2.6, 2.8)	2.7

(a) Depths for samples collected in the pits measured at the center of the containers. Depths of the core samples refer to the final 20-cm segments analysed after decontamination.

(b) Estimated by seasonal variation of H_2O_2[19] (pit samples) or $\delta^{18}O$[21] (core samples); S= Summer, W= Winter.

(c) From Scarponi et al.[15]

(d) In parentheses, data ordered from outside to inside layers of snow cores.

(e) In italics, data from the external, contaminated layers not considered for the mean computation.

(f) Contaminated sample

(g) Sample not available for Pb determination (see the text).

(h) Adjacent segments of a core section, common data for external and intermediate layers.

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ylene speed lathe and successive veneers of snow are chiseled from outside to inside using clean chisels and collecting samples in clean polyethylene bottles. In this case five concentric sub-samples were obtained: the external veneer and three intermediate layers (thickness about 2.0 cm) and the inner core (radius 2.4 cm). The first intermediate layer was reserved for other measurements, thus a four-data radial concentration profile was obtained for each section (see below Table I). In the case of sections with lengths of at least 40 cm, two adjacent segments were chiseled together in a single procedure. This operation led to common samples of the external and intermediate layers, and two separate central cores. Segments of 20-cm length were generally obtained for analysis also in the chiseling procedure, with the only exception of two adjacent segments (17 cm) obtained from a section of insufficient length.

Analytical Instrumentation

The voltammetric system used to perform the lead measurements comprised a PTFE electrochemical cell especially designed[24] for ultratrace metal determinations (Model Rotel 2) and a Polarographic Analyzer (Model 384B), both from EG&G Instruments (Princeton, NJ, USA). The working electrode was a thin mercury film (TMFE) plated on a Rotating Glassy Carbon Disk Electrode (RGCDE). A platinum wire auxiliary electrode and an Ag/AgCl,KCl(sat.) reference electrode were used, both inserted in 2 mm i.d. FEP tubes, filled with saturated KCl/AgCl solution and plugged with porous Vycor tips. The voltammetric instrumentation was installed in a clean chemistry laboratory, under a laminar flow area.

A Perkin-Elmer graphite furnace atomic absorption spectrometer Model 5000 was used for the aluminium concentration measurements.

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Lead Measurements

Lead was measured by DPASV. This technique involves, for each determination, the preparation of a freshly formed thin mercury film electrode (TMFE) and the direct voltammetric analysis of the sample solution without any external preconcentration step. The procedure guarantees sufficient sensitivity and a minimum risk of sample contamination.

The TMFE is obtained by controlled potential electrolysis according to the following procedure. The glassy carbon electrode (RGCDE) is prepared by polishing the surface for 10–20 s using a filter paper and wetted γ-alumina (0.075 μm grain size) while the rotation rate is set to 1000 rpm. After repeated washings with ultrapure water and 1:200 diluted HCl, the plating solution (50 g ultrapure water, 200–300 μl ultrapure saturated KCl, 100 μl $Hg(NO_3)_2$ 2.5×10^{-2} M) is put into the electrochemical cell, purged with nitrogen flow for at least 20 min and the electrolytic deposition is carried out at a potential of -1.000 V, while the electrode is rotating at 4000 rpm. After a 20-min plating time rotation is stopped, a 30-s rest time is allowed to pass, the differential pulse potential scan is carried out in the positive direction (scan rate 10 mV s^{-1}, pulse height 50 mV, pulse frequency 5 s^{-1}, final potential -0.180 V) and the voltammogram is recorded. If the voltammogram shows a regular background line, a sufficiently low current (300–500 nA) and no peaks testifying for contamination, the analysis of the sample is begun, otherwise the film is destroyed using the polishing procedure and it is plated again.

The analysis is then carried out as follows. To about 50 g of melted snow sample (exact amount measured at the end of the analysis) 10–20 μl of ultrapure HCl are added as supporting electrolyte and the solution is purged with nitrogen flow (20 min at least). Electrode rotation is switched on (4000 rpm) and the metal deposition is carried out at a potential of between -0.900 to -0.930 V for 45 min. The electrode rotation is stopped and, after a 30-s equilibration time, the stripping voltammetric scan starts and the voltammogram is recorded. The following instrumental settings are used: scan rate 10 mV s^{-1}, pulse amplitude 50 mV, pulse frequency 5 s^{-1}, final potential -0.230 V. At the end of the scan the electrode is conditioned (to remove amalgamated metal completely) holding it at -0.200 V for 5 min with rotation at 4000 rpm. For quantification three subsequent spikes of the metal standard solution (10–20 μl each) are added and the voltammetric measurement is repeated after each addition. Finally the mass of the sample is precisely measured by weighing and a new polishing step is carried out to prepare the glassy carbon electrode for a new determination.

Typical voltammograms obtained for lead determination in a melted snow sample are shown in Figure 2 while the variation of lead peak current against deposition potential (the pseudopolarogram) is shown in Figure 3, where, for comparison, data obtained using KCl as supporting electrolyte are also reported. The half-wave potentials were -0.578 and -0.666 V, respectively in the HCl and KCl supporting electrolytes. As clearly appears from Figure 3, a better defined, steeper pseudopolarographic wave is obtained in the HCl solution, so this electrolyte was used throughout this work. Moreover the deposition potential applied (i.e. from -0.900 to -0.930 V) was selected to assure plateau conditions, but also to allow simultaneous determination of cadmium and lead. Linearity of the lead calibration plot was verified up to about 100 pg/g. In this work only lead results are considered.

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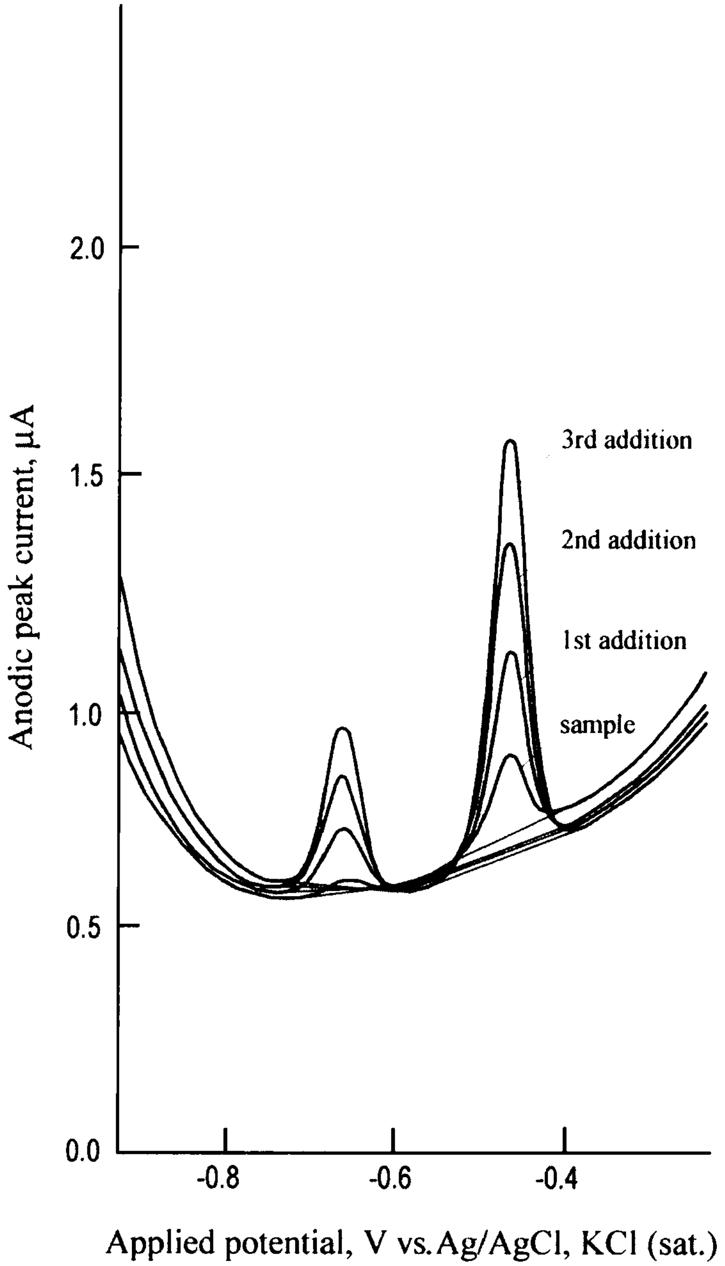

FIGURE 2 Voltammograms obtained in the analysis of one sample of the Styx Glacier plateau (depth 219–239 cm, central core). Additions: 20 µl Pb standard solution (10 µg/l); 10 µl Cd standard solution (20 µg/l).

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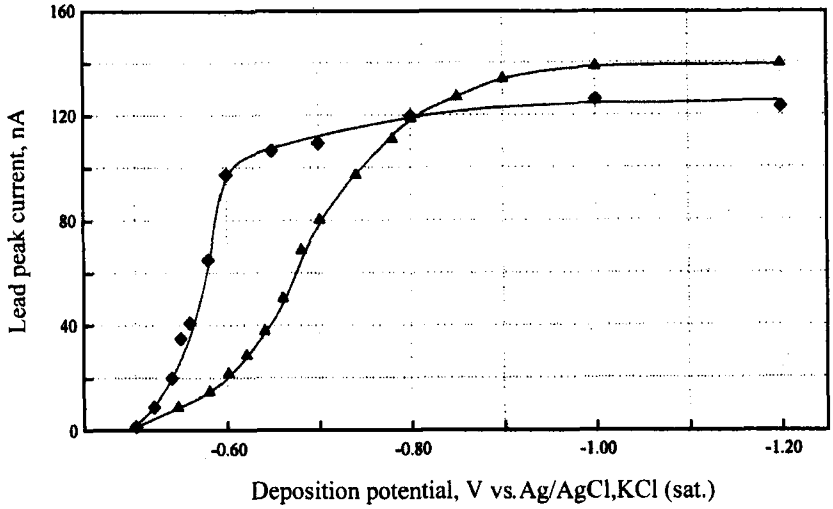

FIGURE 3 Pseudopolarograms of lead obtained from 50 g of melted snow to which 10 μl of HCl NIST (◆) or 20 μl of KCl saturated solution (▲) were added. Deposition time 40 min.

Analytical quality control of lead measurements was routinely carried out analysing the NASS-3 and NASS-4 seawater reference material for trace metals[18]. This material was selected because of the lack of one specific for snow and/or ice. Figure 4 shows a typical control chart obtained during the period of measurements carried out in this work. The mean values of all valid data obtained in the period of measurements, i.e. 39 (SD 5) and 13 (SD 2) ng/l, for

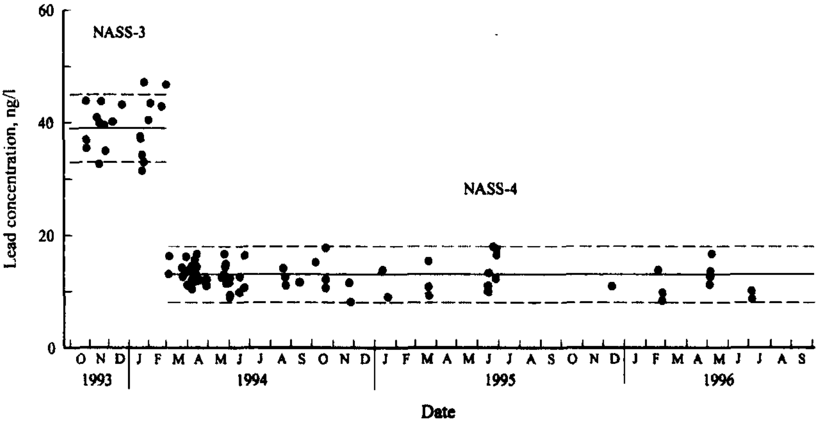

FIGURE 4 Control chart for lead measurements on NASS-3 and NASS-4[18] open ocean seawater reference material. (——) Mean, (----) 95% tolerance limit.

NASS-3 and NASS-4 respectively, are in good agreement with the certified values (see Figure 4). Routinely, if the measured value falls outside the 95% tolerance interval, analytical determinations are interrupted and a special check of the instrumentation is carried out with preparation of a new standard. It is to be noted that accuracy and precision of measurements in melted snow are expected to be better than in the more complex matrix of the reference sample.

No blank correction was applied to instrumental results owing to the ultra clean conditions adopted in all the analytical steps and the particular care taken for contamination control. A negligible blank contribution for the added acid was already experimentally verified[15] in accordance with the certified purity of the acid[17] and with literature data[25]. Containers used for pit sample collection were tested before shipping to Antarctica, verifying that the lead content of ultrapure water stored in them for few weeks was not significanly different from the blank value of fresh ultrapure water. PTFE cell cups and the electrode assembly of the electrochemical cell were periodically tested analysing acidified ultrapure water. Moreover a rough, but sensitive check of the comprehensive blank from the electrochemical cell is obtained routinely before each measurement in the context of the TMFE preparation and control (see above).

As regards precision, considering that the analysis of samples by DPASV is time- and sample-consuming, a pooled estimate of the relative standard deviation was calculated using repetition data obtained on samples collected in the pits. The RSD value was 21%.

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Aluminium Measurements

Aluminium measurements were carried out by GFAAS at a wave length of 309.3 nm following the operating procedures described in the literature[26]. 20 μl of sample were used for each determination and a three point calibration curve was used for the quantification.

RESULTS AND DISCUSSION

Changes in Lead Concentration During the Period 1965–1991

Table I reports the lead concentration results obtained in this work for the snow samples collected at the two sites of Victoria Land, together with previously reported, preliminary data[15]. In the case of snow cores, the radial concentration profile is reported, but only reliable data from the inner parts, are used to compute the mean sample concentration. In all cases but three consistent plateau

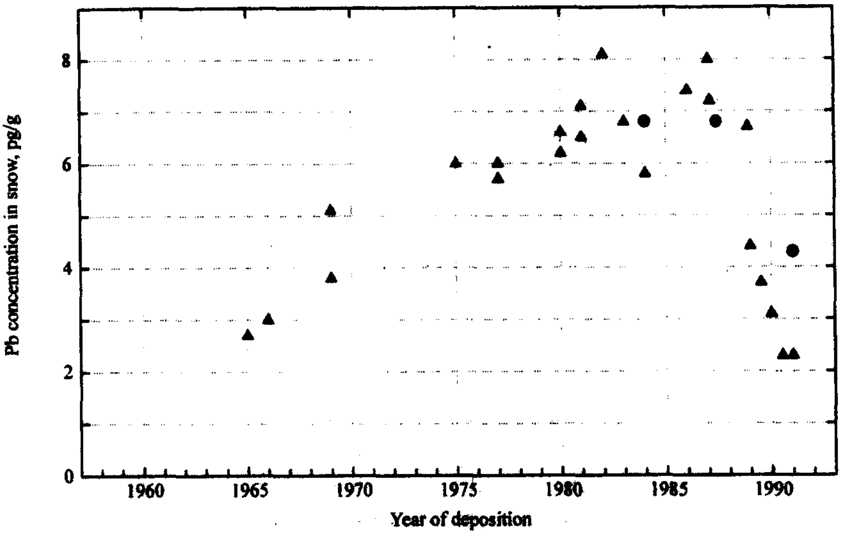

FIGURE 5 Temporal trend of lead concentration in Antarctic snow from Victoria Land for the period 1965–1991. (●) McCarthy Ridge, (▲) Styx Glacier plateau.

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values from two inner parts were obtained. This result indicates that contamination is approximately restricted to the external half of snow cores; moreover the radial concentration profiles (see Table I) show no apparent trend of external contamination along the 11-m core of the Styx Glacier plateau. As reported in the table only three core samples are considered contaminated, possibly during the collection and storage processes. The corresponding values are not considered for data interpretation.

The observed Pb concentration range (2.3–8.1 pg/g) appears in good agreement with reliable literature data referred to recent Antarctic snow, as verified at different sites (various sites in East Antarctica, 2.3–7.4 pg/g[10]; Dolleman Island, 1.0–8.8 pg/g[27]; Stake D55, 1.3–8.3 pg/g[12]; Coats Land, 0.8–9.0 pg/g[14]; values given as upper limits, and high values attributed to local contamination, not considered here).

Our data plotted against the year of deposition (Figure 5) show a very interesting pattern of Pb concentration in the period from 1965 to 1991. After a continuous increasing behaviour observed up to the mid-1980s, from 2.7 pg/g to a maximum of 8.1 pg/g, a net decreasing trend is observed down to 4.3 and 2.3 pg/g in McCarthy Ridge and Styx Glacier plateau, respectively, in 1991.

No clear seasonal structure is visible in the collected data (particularly from the Styx Glacier pit) possibly due to the very discontinuous sampling adopted, and the long period of time spanned by each sample collected.

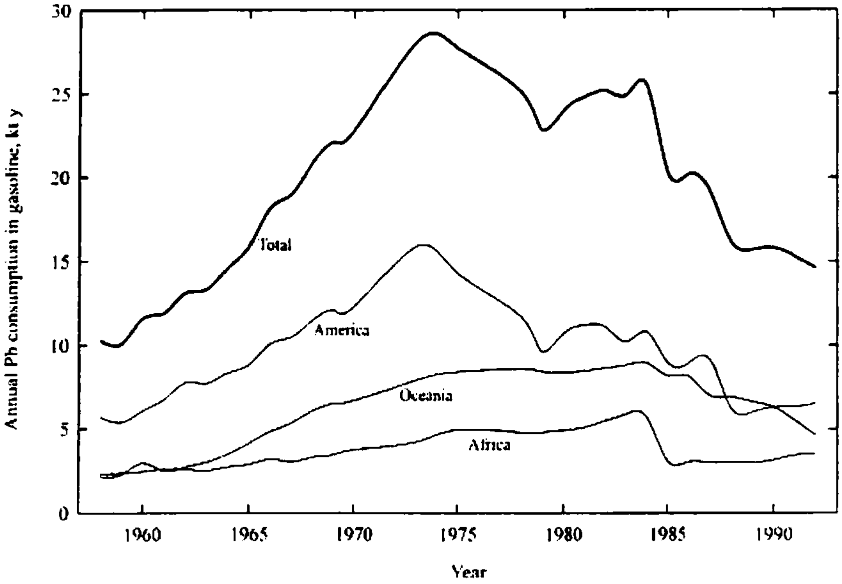

FIGURE 6 Annual consumption of lead in gasoline in the Southern Hemisphere Continents (south of Equator countries). Period 1958–1992. Data from Octel[38] and Fragomeni[39].

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The present results confirm and extend previous initial evidence[14–16] concerning the reversing trend occurring in the lead concentration of Antarctic snow within the last two decades. Moreover, considering also all the available data from the literature[12,14–16] one can conclude that the recent historical pattern of lead content in Antarctic snow, with a maximum located between the mid-1970s and mid-1980s, is quite similar, even if in a lower range of concentrations, to that already found in the Arctic (Central Greenland)[5]. Further discussion of the historical pattern in Antarctica will be found in the section on geographical origin (see below).

Natural Contributions

Present-day anthropic contribution to lead concentration in Antarctic snow superimposes on the natural background level arising from rock and soil windborne dust, volcanoes, sea-salt spray, forest fires, continental and marine biogenic particulates and volatiles. A rough estimation of the different natural contributions to the total lead concentration has been obtained using the global average of Pb/reference element mass ratios as known for the various sources, though there remains considerable uncertainty and a large variability. Similar procedures had already been attempted by other researchers in the field[10,12,14,27,28].

Lead contribution from rock and soil dust was estimated from the average Al concentration measured in five of the samples analysed for lead, i.e. 0.68 ng/g (SD 0.37 ng/g). Combining this value with the Pb/Al mass ratio in bulk crustal material (9.5×10^{-5})[29], an average contribution of 0.065 pg/g of lead was calculated.

Lead input from volcanic sources was estimated from the Pb/S mass ratio in volcanic emissions ($\sim 7 \times 10^{-5}$[30,31]) and from sulphate concentration measured in samples collected in the same pits dug at the two sites[19], considering that sulphur originating from volcanic emissions has been estimated to be about 12% of S in non-sea-salt sulphate (excess sulphate) in the global atmosphere[31]. Using the mean values of the excess sulphate data[19], i.e. 82 ng/g for McCarthy Ridge and 36 ng/g for the Styx Glacier plateau, average volcanic contributions for lead of 0.2 and 0.1 pg/g were obtained for the two sites.

Lead contribution originating from sea-salt spray was estimated from marine Na concentration in snow and the Pb/Na mass ratio in the sea-derived aerosol which is obtained from the Pb/Na ratio in seawater (i.e. 5.8×10^{-10}: average Pb in Terra Nova Bay, 6.4 ng/l[32], Na in seawater, 11.015 g/l[33]) multiplied by the enrichment factor for sea-derived aerosol relative to bulk seawater (i.e. 100[28,34]). Marine Na was obtained from chloride measurements carried out in the same sites (average chloride concentrations: 1250 and 670 ng/g for McCarthy Ridge and Styx Glacier plateau, respectively[19]), using the Cl/Na mass ratio in seawater of 1.80[33] and considering that chloride in snow of Antarctic costal areas is mainly of marine origin. Contributions of lead from marine aerosol were calculated as 0.04 and 0.02 pg/g for McCarthy Ridge and Styx Glacier plateau, respectively.

From our data it is not possible to calculate the other natural contributions coming from forest fires, continental and marine biogenic particulates and volatiles, but looking at the corresponding fluxes to the atmosphere compared to those of the other sources considered above[30], they are certainly negligible.

In conclusion our estimates led to a total natural contribution of 0.2–0.3 pg/g of lead, with a large margin of uncertainty. However the present result is comparable with other estimates reported in the literature, i.e. 0.25–0.47 pg/g for various sites of East Antarctica[10] and <0.8 pg/g for Coats Land[14].

Anthropic Contributions: Indication of a “Gasoline” Contribution

Comparing the lead concentration observed in our samples with the above estimation for the overall natural contribution, a significant excess ranging from about 2 to 7.8 pg/g is obtained, which in principle can be attributed to local and/or remote anthropogenic sources.

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Local contamination, mainly imputable to research stations, has been proved to account for only a few per cent of the total fall-out of lead to the Antarctic continent, and to be restricted to areas very close to the stations[35]. Other local human activities, such as logistic and scientific flights can contribute to a wider dispersion of lead-rich aerosols, but these contributions remain very difficult to estimate. For such reasons, considering also that in the Victoria Land area there are no scientific stations other than the small Italian one, which has only been operating, on a relatively small scale, since 1985, we can reasonably exclude any significant local anthropic contribution to the lead content in snow.

The remote anthropic contribution can be attributed to aerosols originating mainly from southern hemisphere countries, as interhemispheric exchanges are practically prevented[36]. Major sources can be identified with modern non-ferrous metal production processes and the use of leaded gasolines.

Table II reports statistical data for both non-ferrous metal production[37] and the consumption of lead as a gasoline additive[38,39] in southern hemisphere countries. Data refer to selected years of the past three decades and countries are grouped according to the relevant continents. From these data the corresponding lead emissions to the atmosphere are estimated for each source using the average values of emission factors reported in the literature[40,41]. Slight reductions in emission from non-ferrous metal production processes which may have occurred during the last decade are not considered in the computations.

Note that although the amount of lead and other metals involved in non-ferrous metal production is of about two orders of magnitude higher than the lead amount used in gasoline, the corresponding lead emissions are highly in favor of the latter source, due to its considerably higher emission factor. Indeed modern car engines emit, as volatile halogeno-lead compounds, about 75% of the lead present in gasoline[41].

Finally, even if the real end-effect onto Antarctic snow should account for a, possibly different, long-range transport coefficient for the emitted lead by the two types of sources considered, the overall balance at the emission level shows a clear prevalence of the gasoline lead source, at least for the period of time considered here.

A crucial clue to identification of the lead source which caused the characteristic behaviour here observed in Antarctic snow, lies in consideration and comparison of the temporal trends of the two kinds of emissions.

Data reported in Table II show that in this period lead emissions from metal production processes underwent a slight, fairly continuous increase, while emissions from gasoline consumption expanded rapidly during the 1960s and early 1970s, after which there was a net decrease due to policy initiatives taken in

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TABLE II Lead sources from non-ferrous metal production and Pb consumption in gasoline from the Southern Hemisphere continents. Annual production/consumption and estimated Pb emissions into the atmosphere for selected years from 1962 to 1992.

Source	*Metal production*[a] *or consumption*[b] *(kt* y^{-1}*)*					*Pb emitted*[c] *(kt* y^{-1}*)*				
	1962	*1970*	*1978*	*1985*	*1992*	*1962*	*1970*	*1978*	*1985*	*1992*
					Pb mining					
America S.E.[d]	210.7	227.8	237.4	256	216	0.16	0.17	0.18	0.19	0.16
Africa S.E.	151.3	174.7	133.6	162	102	0.11	0.13	0.10	0.12	0.08
Oceania	376	459.4	418.8	498	575	0.28	0.34	0.31	0.37	0.43
Total	738	861.9	789.8	916	893	0.55	0.65	0.59	0.69	0.67
					Pb production					
America S.E.	106.5	130.0	154.9	193.8	176	0.59	0.72	0.85	1.07	0.97
Africa S.E.	82.7	112.7	75.8	81.3	64	0.45	0.62	0.42	0.45	0.35
Oceania	208.1	214.2	243.2	226.1	232	1.14	1.18	1.34	1.24	1.28
Total	397.3	456.9	473.9	501.2	472	2.19	2.51	2.61	2.76	2.60
					Cu in Cu-Ni production					
America S.E.	710.3	830.8	1246.4	1335.9	1669	1.39	1.62	2.43	2.61	3.25
Africa S.E.	921.6	1268.2	1326.8	1245.5	771	1.80	2.47	2.59	2.43	1.50
Oceania	87.8	111.6	167.8	167.7	314	0.17	0.22	0.33	0.33	0.61
Total	1719.7	2210.6	2741.0	2749.1	2754	3.35	4.31	5.34	5.36	5.37
					Zn in Zn-Cd production					
America S.E.	60.2	105.3	148.1	311.7	339	0.11	0.19	0.27	0.58	0.63
Africa S.E.	136.9	144.1	146.0	180.8	109	0.25	0.27	0.27	0.33	0.20
Oceania	170.6	260.6	290.1	288.7	332	0.32	0.48	0.54	0.53	0.61
Total	367.7	510.0	584.2	781.2	780	0.68	0.94	1.08	1.45	1.44
Total sum[e]						6.77	8.41	9.62	10.25	10.08

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TABLE II *continued*

Source	*Metal production*[a] *or consumption*[b] *(kt* y^{-1}*)*					*Pb emitted*[c] *(kt* y^{-1}*)*				
	1962	*1970*	*1978*	*1985*	*1992*	*1962*	*1970*	*1978*	*1985*	*1992*
					Pb from gasoline consumption					
America S.E.	7.75	12.33	11.74	8.98	6.53	5.81	9.25	8.81	6.74	4.90
Africa S.E.	2.57	3.60	4.72	2.95	3.43	1.92	2.70	3.54	2.22	2.57
Oceania	2.75	6.71	8.60	8.16	4.63	2.07	5.03	6.45	6.12	3.47
Total	13.07	22.64	25.07	20.09	14.59	9.80	16.98	18.80	15.07	10.94

a) From United Nations Statistical Yearbook[37].

b) From Octel[38] and Fragomeni[39].

c) Emission data for non-ferrous metal production calculated from average values of emission factor ranges reported by Nriagu et al.[40] (in g t^{-1} metal produced): Pb mining, 750; Pb production, 5500; Cu-Ni production, 1950; Zn-Cd production, 1850. Emission data for gasoline calculated from the fraction of Pb emitted of 0.75 g g^{-1} metal consumed[41].

d) S.E. = south of Equator.

e) For Pb mining and production of metals displayed.

some southern hemisphere countries to limit the emission of the toxic metal into the atmosphere.

The complete data set of annual consumption of lead in gasoline is displayed in Figure 6 and comparison with Figure 5 shows a close relationship between lead concentration in Antarctic snow and lead consumption in gasoline (corr 0.57, $p = 0.02$) when annual mean Pb concentrations are used. Conversely no correlation is obtained when the total sum of lead emissions from the non-ferrous metal production is considered. These results represent a further contribution in favour of the hypothesis[13,14] that most of the lead present in recent Antarctic snow originates from the consumption of leaded gasoline and confirms, as already verified in the northern hemisphere[5–9], that initiatives taken to lower the emission of lead into the atmosphere, are also reflected in a marked decrease of lead spread in the Antarctic.

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Geographical Origin

The problem of the geographical provenance of aerosols reaching Antarctica for both present and past climatic conditions has been already debated with contrasting results[13,42–47]. Here an attempt to identify the geographical origin of the lead detected in our samples has been carried out by comparing separately the temporal trend reported in the literature for Coats Land (Atlantic sector of East Antarctica)[14] and that here obtained for Victoria Land (Pacific sector) respectively with the gasoline lead consumption data in South America and in Oceania (Figure 7). Consistent literature data from Adelie Land (Pacific sector)[12] are also displayed on the same figure.

This comparison shows, in the first case, that the lead concentration decrease in Coats Land started in 1975, approximately corresponding to the sharp reduction of lead use in Brazil's gasoline, which had previously contributed highly to the total lead emission of South America[39]. This behaviour reflects a fairly good relationship between lead content in the snow of Coats Land (annual mean values) and lead consumption in the gasoline of the Southern Hemisphere countries of South America (corr 0.47, $p = 0.01$). Conversely the lead concentration trend in Victoria Land seems to reflect more closely the variation in gasoline lead consumption in Australia and New Zealand, which showed a rapid increase from 1960 to 1975, a sort of plateau in 1975–1985, with a maximum in 1984, and then continuously decreased. In fact correlation between the lead data of the present work (annual mean values) and gasoline lead consumption using only data from Oceania is significantly improved (corr 0.80, $p = 0.0002$) with respect to the value obtained above using all Southern Hemisphere data (corr 0.57, $p = 0.02$).

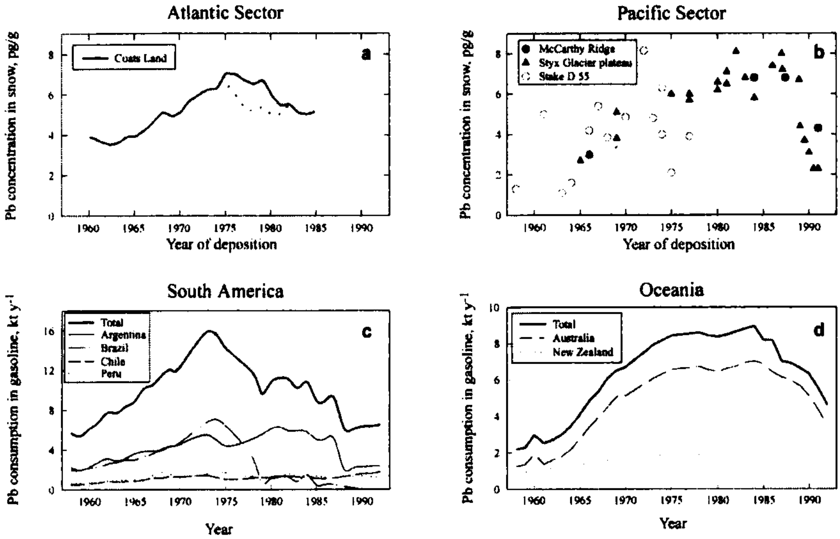

FIGURE 7 Comparison of the temporal trends of lead concentration in the snow of (a) the Atlantic sector of Antarctica (Coats Land[14]), and (b) the Pacific sector (Victoria Land, present data, and Adelie Land, Stake D 55[12]), respectively with the gasoline lead consumption in (c) South America and (d) Oceania[38,39].

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These different behaviours suggest that, under the present-day climatic conditions, South America and Oceania are the predominant source areas for aerosols reaching Atlantic and Pacific sectors of Antarctica, respectively. It is expected that more defined and detailed patterns will soon be available for lead in snow in the two Antarctic sectors. However, further, possibly conclusive, contributions with respect to the present hypothesis could be obtained from new data from, e.g., isotopic measurements and rare earth element determinations or other tracers.

CONCLUSIONS

DPASV confirmed its potential in terms of the extremely high sensitivity which allows the direct determination of lead in Antarctic snow, down to the low pg/g level, to be carried out without any sample preconcentration. This feature, together with the easy transportability of the instrumentation, is continuously exploited by us to make on-site measurements during Italian expeditions to Antarctica, where a clean chemistry laboratory is available at the permanent summer station of Terra Nova Bay.

The new data obtained in this work confirm that lead concentration in the snow of Victoria Land decreased markedly during the second half of the 1980s. The concomitant reduction of lead consumption as gasoline additive in Southern Hemisphere countries, particularly Australia and New Zealand, led us to hypothesize that this source was prevailing in the past three decades and that the origin of aerosols reaching the Pacific sector of Antarctica is presumably Oceania.

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References

[1] V. Thomas and T. Spiro, In: *Industrial ecology and global change* (R. Socolow, C. Andrews, F. Berkhout and V. Thomas, eds., Cambridge University Press, Cambridge, UK, 1994) pp. 297–318.

[2] C.F. Boutron, *Environ. Rev.*, **3**, 1–28 (1995).

[3] H. Oeschger and C.C. Langway Jr, Eds. *The environmental record in glaciers and ice sheets* (Wiley, Chichester, UK, 1989) pp. 400.

[4] S. Hong, J.P. Candelone, C.C. Patterson and C.F. Boutron, *Science*, **265**, 1841–1843 (1994).

[5] C.F. Boutron, U. Görlach, J.P. Candelone, M.A. Bolshov and R.J. Delmas, *Nature*, **353**, 153–156 (1991).

[6] K.J.R. Rosman, W. Chisholm, C.F. Boutron, J.P. Candelone and S. Hong, *Geochim. Cosmochim. Acta*, **58**, 3265–3269 (1994).

[7] R. Lobinski, C.F. Boutron, J.P. Candelone, S. Hong, J. Szpunar-Lobinska and F.C. Adams, *Environ. Sci. Technol.*, **28**, 1459–1466 (1994).

[8] R. Lobinski, C.F. Boutron, J.P. Candelone, S. Hong, J. Szpunar-Lobinska and F.C. Adams, *Environ. Sci. Technol.*, **28**, 1467–1471 (1994).

[9] J.P. Candelone, S. Hong, C. Pellone and C.F. Boutron, *J. Geophys. Res.*, **100**, 16605–16616 (1995).

[10] C.F. Boutron and C.C. Patterson, *J. Geophys. Res.*, **92**, 8454–8464 (1987).

[11] C.F. Boutron and C.C. Patterson, *Geochim. Cosmochim. Acta*, **47**, 1355–1368 (1983).

[12] U. Görlach and C.F. Boutron, *J. Atmos. Chem.*, **14**, 205–222 (1992).

[13] K.J.R. Rosman, W. Chisholm, C.F. Boutron, J.P. Candelone and C.C. Patterson, *Geophys. Res. Lett.*, **21**, 2669–2672 (1994).

[14] E.W. Wolff and E.D. Suttie, *Geophys. Res. Lett.*, **21**, 781–784 (1994).

[15] G. Scarponi, C. Barbante and P. Cescon, *Analusis*, **22**, M47–M50 (1994).

[16] G. Scarponi, C. Barbante and C. Turetta, *Terra Antartica Reports*, **1**, 103–106 (1997).

[17] P.J. Paulsen, E.S. Beary, D.S. Bushee and J.R. Moody, *Anal. Chem.*, **60**, 971–975 (1988).

[18] NASS-3, NASS-4, Open Ocean Seawater Reference Material for Trace Metals (1990, 1992). National Research Council of Canada, MACSP, Ottawa, Canada K1A 0R6.

[19] G. Piccardi, R. Udisti and F. Casella, *Intern. J. Environ. Anal. Chem.*, **55**, 219–234 (1994).

[20] A. Neftel, P. Jacob and D. Klockow, *Nature*, **311**, 43–45 (1984).

[21] E. Barbolani, M. Dini, M. Frerrotti, V. Maggi, G. Piccardi, F. Serra, B. Stenni and R. Udisti, *Terra Antartica Reports*, **1**, 65–70 (1997).

[22] G. Piccardi, E. Barbolani, S. Becagli, R. Traversi and R. Udisti, In: *Proceedings of 4th National Congress on Environmental Contamination* (Venice, December 6–7 1995). pp. 53–62.

[23] J.P. Candelone, S. Hong and C.F. Boutron, *Anal. Chim. Acta*, **299**, 9–16 (1994).

[24] L. Mart, H.W. Nürnberg and P. Valenta, *Fresenius Z. Anal. Chem.*, **300**, 350–362 (1980).

[25] E.D. Suttie and E.W. Wolff, *Atmos. Environ.*, **27A**, 1833–1841 (1993).

[26] C.F. Boutron and S. Martin, *Anal. Chem.*, **51**, 140–145 (1979).

[27] E.D. Suttie and E.W. Wolff, *Tellus*, **44B**, 351–357 (1992).

[28] C.F. Boutron and C.C. Patterson, *Nature*, **323**, 222–225 (1986).

[29] S.R. Taylor and S.M. McLennan *The continental crust: its composition and evolution. An examination of the geochemical record preserved in sedimentary rocks* (Blackwell Scientific Publications, Oxford, UK, 1985), 300 pp.

[30] J.O. Nriagu, *Nature*, **338**, 47–49 (1989).

[31] C.C. Patterson and D.M. Settle, *Geochim. Cosmochim. Acta*, **51**, 675–681 (1987); Erratum, **52**, 245 (1988).

[32] G. Scarponi, G. Capodaglio, G. Toscano, C. Barbante and P. Cescon, *Microchem. J.*, **51**, 214–230 (1995).

[33] T.R.S. Wilson, In: *Marine electrochemistry* (M. Whitfield and D. Jagner, eds., Wiley, Chichester, UK, 1981) pp. 145–185.

[34] C.P. Weisel, R.A. Duce, J.L. Fasching and R.W. Heaton, *J. Geophys. Res.*, **89**, 11607–11618 (1984).

[35] C.F. Boutron and E.W. Wolff, *Atmos. Environ.*, **23**, 1669–1675 (1989).

[36] D. Wagenbach, In: *Chemical exchange between the atmosphere and polar snow* (E. W. Wolff and R. C. Bales, eds., Springer, Berlin, 1996) pp. 173–199.

[37] U.N. (1965–1992). *United Nations Statistical Yearbook* (U.N., New York).

[38] Octel (1984–1994). *Worldwide Gasoline Survey*. The Associated Octel Company Ltd., London, U.K., various issues.

[39] A.S. Fragomeni, *Lead consumption in gasoline in Brazil*. Petrobras Research and Development Centre, Rio de Janeiro, Brazil. Personal communication (1995).

[40] J.O. Nriagu and J.M. Pacyna, *Nature*, **333**, 134–139 (1988).

[41] P. Falchi, D.A. Gidlow and G.R. Searle, *How to obtain rapid improvements in air quality*. (Società Italiana Additivi per Carburanti s.r.l., Milan, 1992).

[42] S. Joussaume and J. Jouzel, *J. Geophys. Res.*, **98**, 2767–2805 (1993).

[43] F.E. Grousset, P.E. Biscaye, M. Revel, J.R. Petit, K. Pye, S. Joussaume and J. Jouzel, *Earth Planet. Sci. Lett.*, **111**, 175–182 (1992).

[44] A. Gaudichet, M. De Angelis, S. Joussaume, J.R. Petit, Y.S. Korotkevitch and V.N. Petrov, *J. Atmosph. Chem.*, **14**, 129–142 (1992).

[45] M. De Angelis, N.I. Barkov and V.N. Petrov, *Nature*, **325**, 318–321 (1987).

[46] M. De Angelis, N.I. Barkov and V.N. Petrov, *J. Atmosph. Chem.*, **14**, 233–244 (1992).

[47] R.J. Delmas and J.R. Petit, *Geophys. Res. Lett.*, **21**, 879–882 (1994).

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