

CARLO BARBANTE (*/**), CLARA TURETTA (**), TANIA BELLOMI (*),
ANDREA GAMBARO (*/**), ROSSANO PIAZZA (*), IVO MORET (*/**)
& GIUSEPPE SCARPONI (***)

POSSIBLE SOURCES AND ORIGINS OF LEAD IN PRESENT-DAY EAST ANTARCTIC SNOW

ABSTRACT: BARBANTE C., TURETTA C., BELLOMI T., GAMBARO A., PIAZZA R., MORET I. & SCARPONI G., *Possible sources and origins of lead in present-day East Antarctic snow*. (IT ISSN 0391-9838, 1997).

New data obtained in our laboratory on the lead content of Victoria Land Antarctic snow (Hercules Névé) confirm the decreasing trend for the 1980s, as already observed in previous preliminary studies carried out at other sites. Comparison of the lead content trend in the snow of the Atlantic and Pacific sectors of East Antarctica with trends in the consumption of lead in gasoline in the different countries of the Southern Hemisphere show different clear relationships for the two areas. In particular, the location of the two concentration maxima of lead in the snow of the Atlantic and Pacific sectors, makes it possible to distinguish the geographical areas in which aerosols reaching Antarctica originate.

KEY WORDS: Lead, Snow, Victoria Land, Coats Land, Antarctica.

RIASSUNTO: BARBANTE C., TURETTA C., BELLOMI T., GAMBARO A., PIAZZA R., MORET I. & SCARPONI G., *Possibili origini del piombo nella neve recente dell'Antartide orientale*. (IT ISSN 0391-9838, 1997).

I nuovi dati ottenuti nel nostro laboratorio sul piombo contenuto nella neve antartica della Terra Vittoria (Hercules Névé) confermano l'esistenza di un andamento decrescente verificatosi negli anni '80, come era già stato osservato in alcuni studi preliminari condotti in altri siti. Il confronto tra gli andamenti temporali della concentrazione di piombo nella neve dei settori Atlantico e Pacifico dell'Antartide Orientale con quelli del consumo di piombo nella benzina in diversi paesi dell'emisfero sud, mostra differenti relazioni per i due settori, il che consente di discriminare le aree geografiche da cui hanno origine gli aerosol che raggiungono l'Antartide.

TERMINI CHIAVE: Piombo, Neve, Terra Vittoria, Terra di Coats, Antartide.

(*) Dipartimento di Scienze Ambientali, Università Ca' Foscari di Venezia, Dorsoduro 2137 - I-30123 Venezia, Italia.

(**) Centro di Studio sulla Chimica e le Tecnologie per l'Ambiente, Cnr, Venezia, Dorsoduro 2137 - I-30123 Venezia, Italia.

(***) Facoltà di Scienze Matematiche, Fisiche e Naturali, Università di Ancona, via Breccie Bianche - I-60131 Ancona.

This study was carried out in the framework of projects on «Glaciology and Paleoclimatology» and «Environmental Contamination» of the Italian Programme for Antarctic Research and financially supported by Enea through cooperation agreements with the Universities of Milan and Venice, respectively. The Authors are grateful to the members of the Italian technical staff for the excellent logistic support and to the researchers of the Environmental Contamination Group for the skilful sampling activity.

INTRODUCTION

Systematic research into Antarctic ice has recently been started to identify both the sources of aerosols reaching Antarctica and their respective geographical origins. The studies have taken into consideration current climatic conditions and those of the last glacial period (approximately the last 100,000 years; De Angelis & *alii*, 1992; Delmas & Petit, 1994; Gaudichet & *alii*, 1992; Grousset & *alii*, 1992; Murozumi & *alii*, 1969; Rosman & *alii*, 1994).

Some studies were based on variations in the isotopic composition of trace elements such as lead (Rosman & *alii*, 1994), or neodymium and strontium (Grousset & *alii*, 1992); others considered the mineralogical nature of the clays present in the dust enclosed within the ice and used global atmosphere circulation models (Gaudichet & *alii*, 1992); and still others exploited the spatial distribution of the concentration of certain major ions in surface snow (De Angelis & *alii*, 1992; Delmas & Petit, 1994).

The consideration of different tracers, however, has led to contrasting hypotheses concerning the geographical provenance of the aerosols reaching Antarctica.

In this paper we discuss the possibility of using measurements of Pb in Antarctic snow, in particular the depth profile for the last 30 years, to obtain information on the geographical origin of this toxic metal found in recent East Antarctic snow.

EXPERIMENTAL

In this study we update and discuss our data set on the Pb concentration trend in shallow snow samples of Victoria Land, adding new data from Hercules Névé (see below) to earlier results obtained on the Mc Carthy 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 (Piccardi & *alii*,

1994) and 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 (Piccardi & *alii*, 1994)).

During the austral summer 1993-1994 snow samples were collected in a high elevation plateau of Victoria Land, the Hercules Névé (73° 06' S, 165° 28' E, elevation 2960 m, 90 km from the sea, mean snow accumulation rate 17 g cm⁻² year⁻¹ (Piccardi & *alii*, 1995)), located 175 km N-NE of the Italian Station of Terra Nova Bay.

A 3 m-deep pit was dug and precleaned Teflon cylindrical containers were inserted horizontally along the decontaminated surfaces of the pit wall in order to gather samples. Another deeper sample (about 10 m) was also available from a snow core drilled at the same site and decontaminated in our clean cold laboratory (-20 °C) using a special chiseling procedure to discard the highly contaminated outer layers (Candelone & *alii*, 1994). The usual ultraclean procedures required in the clean room laboratory were adopted both in the field and in the laboratory. Researchers wore clean room garments, boot covers, and polyethylene gloves in order to reduce the possibility of snow contamination to a minimum (Barbante & *alii*, 1998; Scarponi & *alii*, 1994).

Differential Pulse Anodic Stripping Voltammetry (Dpasv) was used to analyze all the samples directly, without any preconcentration (Scarponi & *alii*, 1994). A polarographic analyzer (Model 384B) with a Ptfе electrochemical cell especially designed for ultratrace metal determination (Model Rotel 2), both from EG&G Instruments, were used. A rotating glassy carbon disk electrode (Rgcde) in which a thin mercury film (Tmfe) was electrolytically plated before each measurement was used as working electrode. A platinum wire auxiliary electrode and an Ag/Ag-Cl, KCl(sat) reference electrode were used.

Briefly, about 50 g of melted snow sample was acidified using 20 µl of concentrated HCl. Ultrapure acid (37%) from Nist (USA) was used (Paulsen & *alii*, 1988). A deposition potential of -0.930 V was applied to allow the simultaneous determination of Cd and Pb and after a 45-min deposition the usual differential pulsed anodic scan was applied and voltammogram registered (Scarponi & *alii*, 1994). Quantification was obtained by the multiple standard addition method.

A negligible blank contribution for the added acid had previously been experimentally verified (Barbante & *alii*, 1998; Scarponi & *alii*, 1994) in accordance with the certified purity of the acid (Paulsen & *alii*, 1988) and with literature data (Suttie & Wolff, 1992). For this reason, no blank correction was applied to instrumental results. Cylindrical containers used in the pit were shipped to Antarctica only if the lead concentration measured in the ultrapure water stored in them was comparable to that of the fresh ultrapure water (Barbante & *alii*, 1998; Scarponi & *alii*, 1994).

Considering that the analysis of samples by Dpasv is time- and sample-consuming, the precision of the measurements was estimated by pooling repetition data of a series of samples accumulated over time. This evaluation led to a pooled estimate of the relative standard deviation (Rsd) of 22% (Barbante & *alii*, 1998).

LEAD IN ANTARCTIC SNOW

Together with well-known natural sources (such as marine, volcanic and rock and soil dust contributions) the principal sources of lead in Antarctic snow can at present be identified in modern non-ferrous metal production processes, coal and oil combustion and the massive use of leaded gasolines (Barbante & *alii*, 1998). The corresponding lead emissions are due mainly to this latter source, because of its considerably higher emission factor. About 75% of the lead used in gasoline is emitted as highly volatile compounds (Falchi & *alii*, 1992).

The long-distance anthropic contribution to the lead content of Antarctic snow has increased considerably over the last century, especially since leaded gasoline came into use on a large scale. The concentration of the metal, which stood at about 2 pg/g at the beginning of the century and was mainly attributed to the emissions from non-ferrous metal production activities (Barbante & *alii*, 1998; Wolff & Suttie, 1994), rose quickly (particularly from the 1950s) and reached about 8 pg/g during the 1970s (Görlach & Boutron, 1992; Wolff & Suttie, 1994). In more recent years there has fortunately been a rapid inversion in the trend. We have observed decreasing data for the snow deposited in Victoria Land (the Pacific sector of the Antarctic) over the last decade (Barbante & *alii*, 1998; Scarponi & *alii*, 1994; Scarponi & *alii*, 1997), and others have made similar observations in Coats Land (the Atlantic sector) since the mid-1970s (Wolff & Suttie, 1994).

The general trend observed has already been attributed (Rosman & *alii*, 1994; Wolff & Suttie, 1994) to the consumption of lead in gasoline in the countries of the Southern Hemisphere, which featured consistent and substantial growth until the introduction and increasingly widespread use of low-lead or «green» gasoline.

However, a more careful evaluation of available information, including new data presented here (tab. 1), shows that while we found that the highest values for lead content in Victoria Land snow occurred in the first half of the 1980s, the maximum for Coats Land (Wolff & Suttie, 1994) came in about 1975 (fig. 1).

In view of these findings it was decided to seek further evidence of a relationship between the concentration of

TABLE 1 - Average annual concentration of lead in Victoria Land snow from 1986 to 1991 (Hercules Névé, 1993-94 Campaign)

Depth (cm)	Datation ^a (year)	No. of samples	Average annual concentration of Pb (pg/g)	Min. - Max. (pg/g)
97-130	1991	5	2.5 (1.1) ^b	1.1 - 3.8
130-168	1990	7	3.9 (0.8)	3.0 - 5.1
168-201.5	1989	6	6.1 (2.3)	3.2 - 8.6
201.5-235	1988	6	5.8 (1.7)	3.7 - 8.2
235-269	1987	7	6.9 (4.2)	4.2 - 14.3
269-321	1986	6	8.4 (3.1)	4.8 - 12.7
937-974	1968	2	4.6 (1.0)	3.8 - 5.3

(a) Datation from Piccardi & *alii*, 1995.

(b) In brackets, Standard Deviation.

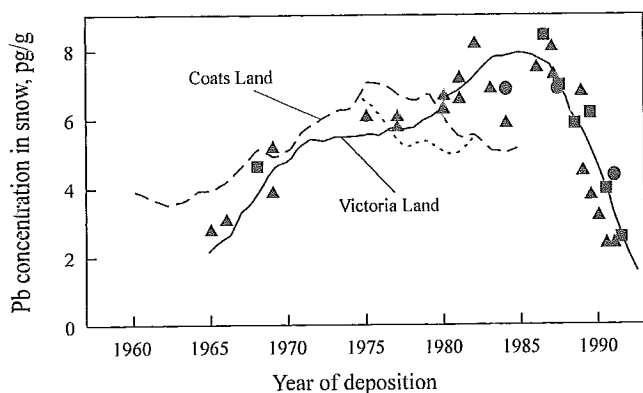


FIG. 1 - Temporal trends of lead concentration in Antarctic snow. (—) Victoria Land (● Mc Carthy Ridge (Barbante & alii, 1998), ▲ Styx Glacier plateau (Barbante & alii, 1998), ■ Hercules Nève, this work). (---) (·····) Coats Land (Wolff & Suttie, 1994).

lead in the snow of the two Antarctic regions mentioned and the consumption of lead in gasoline used in different parts of the Southern Hemisphere.

GEOGRAPHICAL ORIGINS

The statistical data on the consumption of lead in gasoline used in the Austral Hemisphere (fig. 2) show a temporal trend that in general reflects that of lead in Antarctic snow (cf. fig. 1).

If the data are broken down for the various continents however, consumption trends provide an interesting lead to identification of the geographical origins of the aerosol. Figures relating to South America, thanks to action undertaken mainly in Brazil, with the introduction in the market of alcohol fuels, show that the consumption of gasoline lead (and hence emission of Pb into the atmosphere) be-

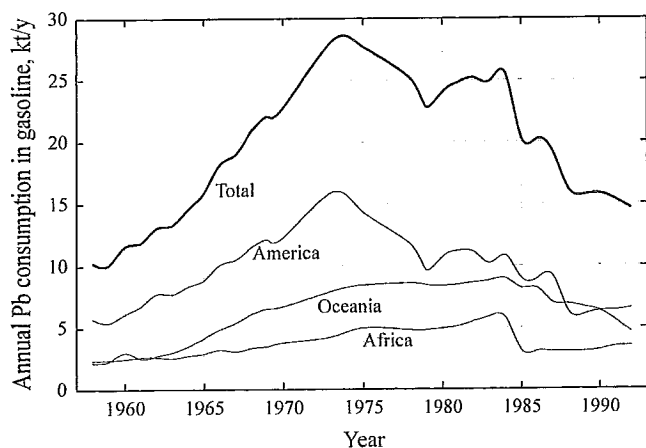


FIG. 2. Annual consumption of lead in gasoline in the countries of the Southern Hemisphere (south of the Equator), 1958-92. Data from Ocelt (1984-1994) and Fragomeni (1995, Personal communication).

gan to fall approximately 10 years before the countries of Oceania (Australia mainly, and New Zealand).

Our data (see fig. 1) show that the temporal trend in the concentration of lead in the snow of Victoria Land bears a clear relation to the consumption pattern of lead in gasoline used in Oceania (corr. 0.88, $p < 0.000001$), while the lead content of Coats Land snow, as reported by other researchers (Wolff & Suttie, 1994) (see fig. 1), compares well with lead consumption in South America (corr. 0.90, $p < 0.000001$).

It is worth noting that comparable maxima in the lead concentration in the snow were observed in the two sectors of Antarctica (see fig. 1), despite much larger emissions in South America than Oceania. This reflects the fact that the main South American emissions occur much further north (Brazil) compared to the Oceania emissions (Southern Australia).

Given these relationships, it can be hypothesized that while the Pacific sector of the Antarctic continent is subject to the influence of aerosols originating in Australia, the Atlantic sector is more directly affected by aerosols from South America.

CONCLUSIONS

The results obtained in this study and the relationships observed make it possible: (1) to confirm that the introduction of low-lead gasoline has been reflected in a considerable reduction in the concentration of lead also in Antarctic snows, and (2) to hypothesize that, in present-day climatic conditions, the aerosols reaching the Pacific and Atlantic sectors of Eastern Antarctica for the most part originate respectively in Oceania and South America.

It is useful to note that the results of this work agree with the Gaudichet et al.'s model predictions that South American emissions would be most relevant in Coats Land and those of Oceania in Victoria Land (based on the figure in their paper) (Gaudichet & alii, 1992). Conversely our findings do not confirm the possibility of aerosols of South American origin reaching Victoria Land as suggested by lead isotopic signatures in Antarctica snow (Rosman & alii, 1994).

Our findings for lead could be extended to other aerosols, if the source areas and the relative strengths are similar.

REFERENCES

- BARBANTE C., TURETTA C., CAPODAGLIO G. & SCARPONI G. (1998) - Recent decrease in the lead content of Antarctic snow. *Int. Journ. Environ. Anal. Chem.*, in press.
- CANDELONE J.P., HONG S. & BOUTRON C.F. (1994) - An improved method for decontaminating polar snow and ice cores for heavy metals analysis. *Anal. Chim. Acta*, 299, 9-16.
- DE ANGELIS M., BARKOV N.I. & PETROV V.N. (1992) - Sources of continental dust over Antarctica during the last glacial cycle. *Journ. Atmosph. Chem.*, 14, 233-244.
- DELMAS R.J. & PETIT J.R. (1994) - Present Antarctic aerosol composition: a memory of ice age atmospheric dust? *Geophys. Res. Lett.*, 21, 879-882.

- FALCHI P., GIDLOW D.A. & SEARLE G.R. (1992) - *How to obtain rapid improvements in air quality*. Società Italiana Additivi per Carburanti s.r.l.
- FRAGOMENI A.S. (1995) Personal communication - *Lead consumption in gasoline in Brazil*. Petrobras Research and Development Centre, Rio de Janeiro, Brazil.
- GAUDICHET A., DE ANGELIS M., JOUSSAUME S., PETIT J.R., KOROTKEVITCH Y.S. & PETROV V.N. (1992) - *Comments on the origin of dust in East Antarctica for present and ice age conditions*. Journ. Atmosph. Chem., 14, 129-142.
- GÖRLACH U. & BOUTRON C.F. (1992) - *Variations in heavy metals concentrations in Antarctic snows from 1940 to 1980*. Journ. Atmos. Chem., 14, 205-222.
- GROUSSET F.E., BISCAYE P.E., REVEL M., PETIT J.R., PYE K., JOUSSAUME S. & JOUZEL J. (1992) - *Antarctic (Dome C) ice-core dust at 18 k.y. B.P.: Isotopic constraints on origin*. Earth Planet. Sc. Lett., 111, 175-182.
- MUROZUMI M., CHOW T.J. & PATTERSON C.C. (1969) - *Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata*. Geochim. Cosmochim. Acta, 33, 1247-1294.
- OCTEL. (1984-1994) - *Worldwide Gasoline Survey*. The Associated Octel Company Ltd., London, U.K., 1984-1994, various issues.
- PAULSEN P.J., BEARY E.S., BUSHEE D.S. & MOODY J.R. (1988) - *Inductively coupled plasma mass spectrometric analysis of ultrapur acids*. Anal. Chem., 60, 971-975.
- PICCARDI G., BARBOLANI E., BECAGLI S., TRAVERSI R. & UDISTI R. (1995) - *Ruolo della stagionalità e dell'altitudine su fenomeni di frazionamento atmosferico e sulla identificazione di fonti secondarie nelle precipitazioni nevose in Antartide* «4° Convegno Nazionale Contaminazione Ambientale», 53-62, Venezia, 6-7 Dicembre 1995.
- PICCARDI G., UDISTI R. & CASELLA F. (1994) - *Seasonal trend and chemical composition of snow at Terra Nova Bay (Antarctica)*. Int. Journ. Environ. Anal. Chem., 55, 219-234.
- ROSMAN K.J.R., CHISHOLM W., BOUTRON C.F., CANDELONE J.P. & PATTERSON C.C. (1994) - *Anthropogenic lead isotopes in Antarctica*. Geophys. Res. Lett., 21, 2669-2672.
- SCARPONI G., BARBANTE C. & CESCONE P. (1994) - *Differential pulse anodic stripping voltammetry for ultratrace determination of cadmium and lead in Antarctic snow*. Analisis, 22, M47-M50.
- SCARPONI G., BARBANTE C., TURETTA C., GAMBARO A. & CESCONE P. (1997) - *Chemical contamination of Antarctic snow: the case of lead*. Microchem. Journ., 55, 24-32.
- SUTTIE E.D. & WOLFF E.W. (1992) - *Seasonal input of heavy metals to Antarctic snow*. Tellus, 44B, 351-357.
- WOLFF E.W. & SUTTIE E.D. (1994) - *Antarctic snow record of southern hemisphere lead pollution*. Geophys. Res. Lett., 21, 781-784.