RELATIVE LEVELS OF NATURAL AND ANTHROPOGENIC LEAD
IN RECENT ANTARCTIC SNOW

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Abstract. Concentrations of lead have been measured by ultraclean isotope dilution mass spectrometry in large blocks of surface snow collected along a 433-km coast-interior axis in East Antarctica and near the geographic south pole. Slight contamination existed on the outside of the blocks, but concentration profiles from their exteriors to their interiors indicate that lead concentrations in the innermost parts of the blocks do represent the original concentrations in present-day Antarctic snow. Geographical variations of lead concentrations appear to be mainly due to local emissions from Dumont d'Urville and Amundsen Scott stations. The globally significant lead concentration in present-day Antarctic snow is found to be about 2 pg Pb/g. The corresponding value in Antarctic air is estimated to be about 7 pg Pb/m^3 STP, which is approximately fivefold larger than total natural lead contributed by soil dusts, volcanoes and sea salts. A tentative temporal curve of globally significant lead concentrations in Antarctic ice and snow for the last 13,000 years is given. It shows concentrations of about 0.4 pg Pb/g throughout most of the Holocene, with recent fivefold increases to about 2 pg Pb/g today. The general picture is then that four-fifths of total lead in the Antarctic troposphere today is anthropogenic.

1. Introduction

Detailed high-quality data have recently been obtained on the past variations of lead concentrations in the remote Antarctic tropospheric cell over the 155,000-to 3800-year B. P. time period from the analysis of the Dome C and Vostok deep Antarctic ice cores [Boutron and Patterson, 1986 ; Boutron et al., 1987]. These data show that natural background concentrations of lead have strongly varied in the Antarctic troposphere during the last 155,000 years. Lead concentrations in Antarctic ice were indeed high, up to about 30 pg Pb/g, during the end of the next to last ice age, which preceeded the last interglacial [Boutron et al., 1987], and during the last glacial maximum [Boutron and Patterson 1986]. They were on the other hand very low, down to about 0.3 pg Pb/g during the last interglacial, the first two thirds of the last ice age [Boutron et al., 1987], and the Holocene [Boutron and

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Patterson, 1986]. Soil dusts were shown to be the major source of natural lead. The volcanic contribution was found to be significant during low-lead time periods only and the contribution from sea salts always insignificant.

On the other hand, there are almost no reliable data on present-day tropospheric concentrations of lead in the Antarctic tropospheric cell. This cell is today the least-contaminated portion of the earth's troposphere with respect to industrial lead, which makes it of great interest for investigators studying relative emissions of industrial and natural lead to the troposphere. These present-day Antarctic tropospheric concentrations can be either measured directly on air filters or retrieved from concentrations recorded in surface snows combined with atmospheric scavenging ratios. Most corresponding data (see for instance Duce et al. [1975], Maenhaut et al. [1979], Peel and Wolff [1982], Boutron [1978, 1980,1981, 1982], Boutron and Lorius [1979], and Jaworowski et al. [1981]) have indeed been shown to be erroneous by up to several orders of magnitude because of improper control of lead contamination during field sampling and laboratory analysis [Patterson et al., 1985 ; Wolff and Peel, 1985b ; Dick and Peel, 1985 ; Boutron, 1986]. The only reliable data for Antarctic present-day air are now thought to be the few ones recently published by Dick and Peel [1985] and Dick [1987] for several locations in the Antarctic Peninsula and by Wagenbach [1987] and Wagenbach et al. [1987] for the Ekström ice shelf. For Antarctic recent snow the only reliable data appear to be those published for stake D55 in Adelie Land, East Antarctica, by Boutron and Patterson [1983] and those for a few locations in the Antarctic Peninsula published by Wolff and Peel [1985a]. But it is uncertain whether these few reliable data are significant for the entire Antarctic tropospheric cell or not, because local lead emissions from Antarctic scientific stations, traverse vehicles, and planes might have contaminated present-day Antarctic air and surface snow over very large areas within radii of hundreds of kilometers [Murozumi et al., 1969 ; Duce, 1972 ; Patterson, 1972].

This makes it difficult to estimate to what extent large-scale lead pollution has reached the remote Antarctic tropospheric cell today, and we still do not know the magnitude of the increase of lead concentrations during the last few millenia, if any. The increase factor was suggested to lie anywhere in the range of one to fortyfold by Wolff and Peel [1985a, b] ; a modest increase of up to sixfold was, however, thought to be the most likely [Peel, 1986].

We present here new data on the lead content of Antarctic surface snows. Contamination problems were minimized by collecting large-size blocks of snow under ultraclean conditions. These blocks were subsequently mechanically chiseled in an

TABLE 1. Sample Collection Sites Along the Dumont d'Urville-Stake D80 Trail
and at the Geographic South Pole

Location	Distance From Coast, km	Altitude m	Mean Annual Snow Accumulation Rate, g H_2O cm^{-2} yr^{-1}	Sampling Date
Stake D40	33	848	63[a]	Jan. 3, 1983
Stake D47	103	1500	26[a]	Jan. 5, 1983
Stake D80	433	2525	24[a]	Jan. 14, 1983
South Pole	1274	2880	8.5[b]	Jan. 18, 1984

(a) Pettre et al. [1986]
(b) Jouzel et al. [1983]

ultraclean laboratory in order to get the uncontaminated inner parts. Lead was determined by the ultraclean isotope dilution mass spectrometry (IDMS) technique.

2. Experimental Technique

2.1. Field Sampling

Three of the four sampling sites (see Table 1) were located in Adelie Land, East Antarctica, along a trail from the coastal French scientific station Dumont d'Urville (66°42'S, 139°57'E) to stake D80 (70°02'S, 134°50'E ; altitude, 2430 m ; distance from the sea, 433 km). At stakes D40 and D47 (see Table 1) the trail had not been occupied for 2 years. At stake D80 the trail had not been occupied for 10 years. The fourth site was 7.3 km from Amundsen Scott Station,near the geographic south pole. At each of these four sites we collected a large-size block (37 x 37 x 37 cm) of surface snow by pushing an acid-cleaned conventional polyethylene box vertically into the snow. The polyethylene boxes with polyethylene caps had been cleaned in a clean laboratory as follows : the interior was rinsed with chloroform to remove greases, then filled 3 days at room temperature with Merck Suprapur grade HNO_3 diluted 1:3 in purest water, then rinsed with this water, then filled 3 days with purest water, then dried. The outside was rinsed with chloroform, then wiped with an absorbent paper tissue moistened with HNO_3, then rinsed with purest water. Each box was then wrapped in double-sealed polyethylene bags and placed in a large thermally insulated plastic container.

At each of the three locations along the Adelie Land trail, the sampling site was selected about 500 m upwind of the stake, and no caterpillar vehicle was allowed to come to within this distance from the stake. Equipment was first brought about 50 m downwind of the exact sampling site using a hand-hauled sledge. Then operators dressed in full clean room clothing and walked to the sampling site. They put on plastic gloves and took the polyethylene box out of its polyethylene bags, then put on acid-cleaned plastic gloves. They walked an additional 10 m upwind. The large-size block was then taken by vertically pushing the polyethylene box into the snow upwind and away from the operator. The box was recovered by digging a shallow trench all around it, using an acid-cleaned polyethylene shovel, and breaking

the base of the block. It was then capped and placed in double-sealed polyethylene bags.

At the geographic south pole the sampling site was chosen 7.3 km of Amundsen Scott Station, along the 1°W meridian. The operators went to within about 300 m of the exact sampling site using a caterpillar vehicle. All the equipment was then brought to about 50 m downwind (a medium-speed wind was blowing during all the experiment) of the exact sampling site, using a wooden hand-hauled sledge. The sampling procedure was then similar to the one described in the previous paragraph.

The four snow blocks were transported frozen to the California Institute of Technology. Great precautions were taken not to allow any melting during transport.

At the geographic south pole the time period integrated by the block was determined by field stratigraphy : it integrates the entire year 1983 plus the end of 1982. At each of the three locations in Adelie Land, the time period integrated by the blocks can only be tentatively evaluated from the mean annual snow accumulation rates during the last decades (Table 1) : at stake D40, the block integrates about one fourth of a year ; at stakes D47 and D80, about half a year.

2.2. Mechanical Subsampling of Large-Size Blocks

Despite the unprecedented cleanliness of the field collection procedures described in previous section, we cleaned the snow blocks by mechanically chiseling several successive veneers of snow in progression from the outside to the interior of each block inside the ultraclean Caltech laboratory.

The chiseling procedure was as follows. The polyethylene box containing the snow was taken out of the double polyethylene bags in which it was packed and put inside a larger 208 L polyethylene tank, so that the upper edge of the snow box extended a few centimeters above the top of the tank (Figure 1a). The bottom of the tank had previously been filled with acid-cleaned polyethylene bags filled with crushed dry ice. Immediately after the snow box had been put inside the tank, additional acid-cleaned polyethylene bags filled with dry ice were put all around it (Figure 1a). The cap of the box was then removed and replaced with an acid-cleaned double-walled polyethylene cooling cap, filled with bags of dry ice (Figure 1a). The inside surface of this cap facing the snow was ultraclean.
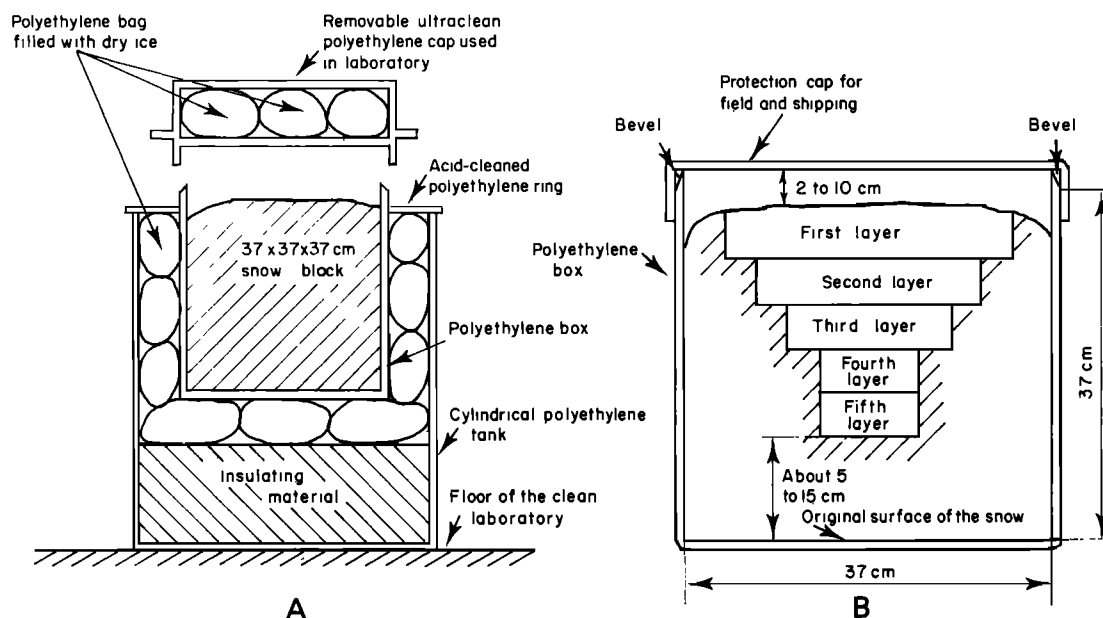
Fig. 1. Illustration of the way snow blocks were cooled and mechanically chiseled to obtain successive veneer layers (a) Cooling tank filled with dry ice, supported and chilled block of snow contained within its original field polyethylene box. The field protective cap was removed and replaced by a chilled ultraclean cap. An ultraclean polyethylene ring covered the dry ice and was attached to the cooling tank. The chilled cap was removed only while sampling a layer. (b) Removal of successive layers. Vertical chisel cuts were first made using several cooled stainless steel chisels, then the bottoms of the small cubes so obtained were cut and these cubes were removed with a stainless steel scoop. The original surface of the snow was at the bottom of the block in its laboratory-sampling configuration.

Five successive veneer layers, each about 3 to 5 cm thick, were dug in sequence from the open top of the box (i.e., the side of the block which was initially the bottom side in Antarctica) (Figure 1b). The areas of the successive layers were chosen to decrease progressively from approximately 30 x 30 cm for the first layer to approximately 10 x 10 cm for the fourth layer. The size of the fifth layer, which was not analyzed for lead in the present work but was kept for subsequent analysis of the isotopic composition of lead, was the same as the size of the fourth layer. The bottom of the fourth layer was 9 - 18 cm from the original surface of the snow in Antarctica.

Each layer was dug by first cutting the vertical edges of small cubes in one horizontal layer, using stainless steel chisels, then scooping these cubes out in succession along the surface using a stainless steel scoop which cut and then collected each individual cube to be lifted out and dumped into a collection polyethylene beaker. The cooling polyethylene cap described above was removed only during the digging of each layer and was immediately put on top of the box before the next layer was dug. The stainless steel chisels and shovels were prechilled after cleaning and were replaced as they became warm with chilled substitutes to prevent melting. All such tools were recleaned and chilled before collecting the next successive layer in the snow block. The two investigators wore over their clean gowns and caps a large acid-cleaned polyethylene bag placed over the body

open side down, with slits cut for the eyes, the nose, and the arms. They wore thermal gloves and then shoulder-length polyethylene gloves. Over these gloves they wore fresh acid-cleaned polyethylene gloves, which were changed for each layer. Detailed cleaning procedures for the stainless steel chisels and scoops, the gloves,and the polyethylene beakers were similar to the ones described in detail by Boutron and Patterson [1983, 1986] and by Boutron et al. [1987].

2.3. Chemical Treatment and IDMS Analysis

Each layer from the blocks was analyzed separately for lead, using the ultraclean isotope dilution mass spectrometry technique [Patterson and Settle, 1976]. After melting overnight at room temperature (in the polyethylene beaker into which the small snow cubes were put from the snow block layers), a nonacidified 5-mL aliquot was taken for subsequent analysis of various anions by ion chromatography. Ultrapure HNO_3 was then added to make a 0.1% solution, and the acidified solution so obtained was allowed to sit for 2 hours. Acidified aliquots were then taken for subsequent analysis of other heavy metals by flameless atomic absorption spectrometry and of barium, potassium, and calcium by the IDMS technique.

The ^{208}Pb spike was added, and the solution was allowed to equilibrate for 2 hours. The pH was adjusted to 8-9 with ammonium hydroxide, then lead was extracted into 19.5 mL of $CHCl_3$ and 0.5 mL of Dithizone solution ($CHCl_3$)in a preconditioned 30-mL or 150-mL fluorinated ethylene propylene

TABLE 2. Measured Concentrations of Lead in Successive Layers of Surface Snow Blocks
From the Dumont d'Urville-Stake D80 trail and the Geographic South Pole.

Location	Measured Lead Concentrations in Snow Block,pg/g			
	layer 1	layer 2	layer 3	layer 4
Stake D40	10.5 (27-32 cm)	6.2 (24-27 cm)	6.5 (21-24 cm)	6.6 (18-21 cm)
Stake D47	24.4 (24-28 cm)	7.1 (19-24 cm)	9.9 (14-19 cm)	7.4 (10-14 cm)
Stake D80	6.9 (24-28 cm)	2.8 (19-24 cm)	2.3 (14-19 cm)	2.3 (10-14 cm)
South Pole	7.6 (18-21 cm)	5.5 (15-18 cm)	5.3 (12-15 cm)	6.3 (9-12 cm)

See Figure 1b which shows that for each block the first layer was taken from the original bottom of the block which was exposed in the laboratory. Depths of successive layer samples therefore approached the original snow surface. The fourth layer taken from near the center of the block was the closest to the original surface. Depth ranges from original snow surface are shown in parentheses.

(FEP) Teflon extraction funnel. The $CHCl_3$ solution layer was acid stripped in 5 mL of 5% HNO_3. This acid solution was washed with 5 mL of $CHCl_3$, then evaporated to dryness in a preconditioned FEP Teflon beaker. The residue was transferred to a rhenium filament, treated with H_3PO_4 and silica gel.

The filament was inserted into a 12-inch radius, single-focusing, solid source thermal ionization mass spectrometer. The $^{208}Pb/^{207}Pb$ ratio was measured to determine lead concentrations from the weights of the sample and spike and the $^{208}Pb/^{207}Pb$ ratio in them.

Contamination introduced by the mechanical chiseling of the successive snow layers was indirectly determined using an artificial core of frozen ultrapure water as a snow substitute, as previously described in detail by Boutron and Patterson [1983]. The chiseling was found to introduce about 10 pg of lead. Lead contamination introduced during melting of each snow layer and the chemical treatment to the final sample of isolated lead on the filament of the mass spectrometer source was determined from 7 to 11 separately measured contamination contributions from reagents and ware. It ranged from 20 to 90 pg Pb. The overall lead contamination ranged then from 30 to 100 pg Pb. When compared to the total lead content of the analyzed samples, this overall contamination ranged from 5 to 15%. The deviation of reported concentrations from true values is estimated to be of the order of ±10%.

3. Results

3.1. Character of the Data

Concentrations of lead measured in successive layers of the blocks are given in Table 2. As shown in Table 2, concentrations measured in the outside (first layer, see Figure 1b) of the blocks range from 6.9 to 24.4 pg Pb/g. For the blocks collected at stakes D47 and D80, they are about 3 times higher than the concentrations obtained in the next layers in the block, thus indicating that a significant contamination was present on the outside of these two blocks despite the cleanliness of the field collection procedure. For the blocks collected at stake D40 and at the south pole, concentrations measured in the outside (first) layer of the blocks are only slightly larger than the ones measured in subsequent layers, thus indicating that only small amounts of contamination were present on the outside of these two blocks. In all blocks, concentrations in layers 2, 3, and 4 are very close. The existence of this plateau of concentrations clearly indicates that these interior concentrations represent the original ones in the Antarctic snow.

The successive veneer layers correspond to different periods of the year. It is, however, difficult to identify clearly these time periods, since no detailed stratigraphic and stable isotope data are available for our blocks. Variations of lead concentrations from one layer to the next could then have been also related to short-term (seasonal) time variations of lead concentrations in Antarctic snows. There are presently no reliable data in the literature on seasonal variations of lead in Antarctic snow, ice, or air, but pronounced seasonal variations of other trace constituents have been detected in Antarctic snow and air (see, for instance Cunningham and Zoller [1981], Legrand and Delmas [1984], and Legrand [1985]). For Greenland and Arctic present-day snows it has been shown that there are pronounced seasonal variations for lead: the winter maximum [Murozumi et al., 1969; Mart, 1983] corresponds to periods when atmospheric conditions favor the input of pollutants from North America and Europe to the Arctic. The fact that we do not observe significant changes of lead concentrations from one layer to the next, except for the outside layer, might suggest that large seasonal variations of lead concentrations do not exist in Antarctic snows. The present data set is, however, much too small to arrive at any clear conclusion: what will be needed in the future to investigate

possible lead seasonal variations are high-quality lead depth profiles covering several years and preferentially measured at locations with sufficient snow accumulation rates.

3.2. Comparison With Data of Other Investigators

The lead content of surface snow along the Dumont d'Urville-stake D80 trail and at the south pole has already been extensively investigated by Boutron [1978, 1981, 1982]; the values obtained ranged from 14 to 184 pg Pb/g. Our values from this study are much lower, which confirms the conclusions of Boutron and Patterson [1983], Wolff and Peel [1985a, b], and Boutron [1986] that the lead values of Boutron [1978, 1981, 1982] were plagued by improper contamination control during field sampling, laboratory analysis, or both. Boutron and Patterson [1983] have published lead data for snow deposited during the last 2 centuries at stake D55 of the Dumont d'Urville-stake D80 trail (183 km from the coast). Our values are in good agreement with the concentrations (3.7 and 4.9 pg Pb/g) they got for the 1956-1966 snow layers. They are lower than the value (8.4 pg Pb/g) they got for the 1970-1973 layer; this value was thought to be unreliable because of slight preanalysis melting of the corresponding sample [Boutron and Patterson, 1983].

For other Antarctic areas the only published lead data for recent snow are those of Murozumi et al. [1969] for the New Byrd Station area in West Antarctica and of Landy and Peel [1981], Peel and Wolff [1982], and Wolff and Peel [1985a] for several locations in the Antarctic Peninsula. Only the lowest values given as less than the upper limits of 4 pg Pb/g reported by Murozumi et al. [1969] are comparable to the data we report in this study; their other reported values for recent snow (20 to 2000 pg Pb/g) are much higher. For the Antarctic Peninsula the values of Peel and Wolff [1982] for recent snow collected at Spaatz Island and at the Southern Palmer plateau (about 40 to 150 pg Pb/g) are much higher than the ones we report here. These values have already been questioned by their authors [Wolff and Peel, 1985 a, b]. Our values are on the other hand in excellent agreement with the data of Landy and Peel [1981] and Wolff and Peel [1985a]. The data of Wolff and Peel [1985a] were supported by careful determinations of outside-inside veneer curves and extensive blank determinations. The mean values they obtained for surface snow collected in February 1980 at three sites of the Southern Palmer plateau located about 150 km from the sea (6.9, 7.1, and 4.6 pg Pb/g, respectively) are in excellent agreement with our present data.

It must be emphasized that the snow accumulation rates are higher at the Antarctic Peninsula locations where Landy and Peel [1981], Peel and Wolff [1982] and Wolff and Peel [1985a] collected their samples (88 - 170 g H_2O cm^{-2} yr^{-1}) than at the four sampling sites of this study (see Table 1). These differences in snow accumulation rates could have resulted in differences of lead concentrations in the snow. It is, however, our feeling that it is unlikely that snow lead concentrations are strongly dependent on the accumulation rates. Recent measurements by

Dick and Peel [1985] and Dick [1987] of lead and other heavy metals on samples of aerosols and snow collected simultaneously in the Antarctic Peninsula indeed support the simple model of aerosol scavenging proposed by Junge [1977] and Shaw [1980], who consider that aerosol removal over polar ice sheets to be dominated by in-cloud processes. Similar measurements at remote uncontaminated areas with very low snow accumulation rates are, however, needed to accurately evaluate the impact of dry deposition in low-accumulation areas of central East Antarctica.

4. Discussion

4.1. Geographical Variations of Lead Concentrations

Variations of lead concentrations measured in the innermost (fourth) layer of the blocks as a function of the distance from the coast are shown as solid circles and a solid curve in Figure 2. Lead concentrations are found to be minimum (2.3 pg Pb/g) at stake D80, 433 km from the coast. They increase about threefold, to 7 pg Pb/g, when going from stake D80 to stakes D47 and D40 (103 and 33 km from the coast, respectively). They also increase about threefold when going from stake D80 to the south pole (1274 km from the coast).

These geographical variations cannot be explained by geographical variations in lead contributions by windblown soil dusts, volcanoes, and sea salts, since total contributions of lead from these natural sources is found to be very small (less than 0.5 pg Pb/g; see section 4.3.) and not to display significant geographical variations (open circles and dashed curve in Figure 2).

As already discussed in section 3.2., it is likely that differences in snow accumulation rates cannot result in large differences of lead concentrations. Should such an effect be predominant, one should moreover have observed an increase of lead concentrations when going from stake D40 (63 g H_2O cm^{-2} yr^{-1}) to stake D80 (24 g H_2O cm^{-2} yr^{-1}), which is not what is observed. Further investigations on dry-deposition rates of lead in East Antarctica will, however, obviously need to be done in the future to confirm that the higher lead concentrations at the south pole, when compared with the data for stake D80, are not significantly linked with differences of snow accumulation rates (8.5 g H_2O cm^{-2} yr^{-1} at the south pole, 24 g H_2O cm^{-2} yr^{-1} at stake D80).

Another explanation could be that these geographical variations are at least partially linked with short-term (seasonal) variations of lead concentrations in Antarctic snows, since the analyzed snow layers do not correspond to the same time periods at the different sampling sites (see section 2.1). This explanation is thought to be unlikely, since we do not observe significant changes of lead concentrations from one layer to the next in the snow blocks (Table 2). However, it cannot entirely be ruled out until detailed high-quality lead depth profiles covering several years become available in the literature.

The innermost (fourth) layer of the three blocks collected along the Dumont d'Urville-stake D80 trail corresponds to snow layers which were
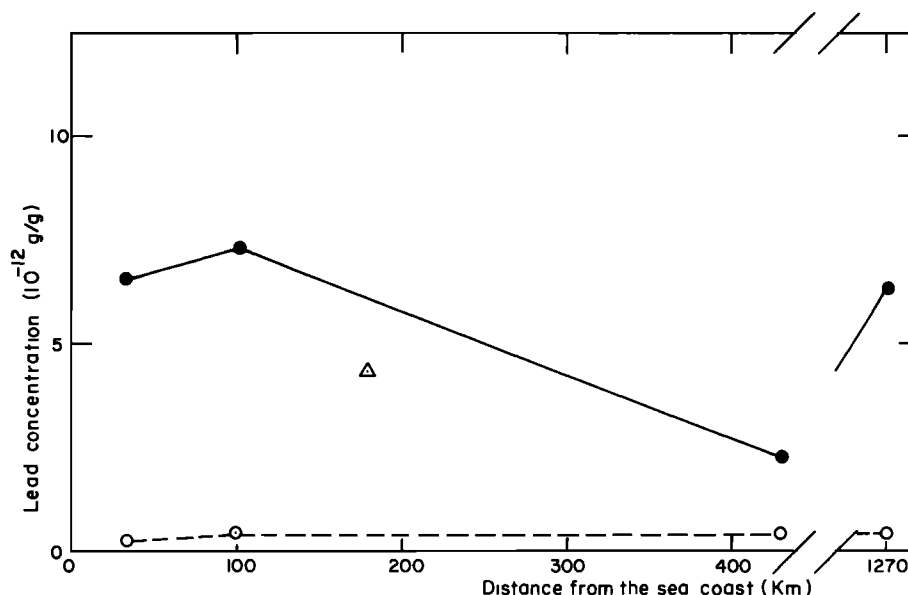
Fig. 2. Variations of lead concentrations in the innermost (fourth) layer of the snow blocks as a function of the distance to the sea coast (solid points and solid curve, data from this study). Mean lead concentration in the 1956-1966 snow layers at stake D55 of the Dumont d'Urville-stake D80 trail, 183 km from the coast, is shown as an open triangle, data from Boutron and Patterson [1983]. Total lead contributions from soil dusts, volcanoes,and the oceans (see Table 3) are shown as open circles on a dashed curve.

originally 10-21 cm below the snow surface in Antarctica (Table 2). It is therefore unlikely that it was contaminated by logistical operations (caterpillar vehicles, etc.) during the field party during which the blocks were collected. If such contamination occurred by penetration of contaminated air through the permeable surface snow layers, then concentrations would have decreased with depth, which is not what is observed (see Table 2). It is also unlikely that the innermost layer was contaminated by logistical operations during previous field parties along the Dumont d'Urville-stake D80 trail. The trail had not been occupied for 2 years at stakes D40 and D47 and for 10 years at stake D80, which corresponds to snow layers approximately 2, 1, and 5 m deep, respectively, at the time our blocks were collected.

The most likely explanation for the geographical variations shown in Figure 2 is that they are linked with local emissions of anthropogenic lead from both Amundsen Scott station at the south pole and Dumont d'Urville station at the coast. Such a local contamination effect has already been suggested by Murozumi et al. [1969] and Patterson [1972] for New Byrd station in West Antarctica; by Duce [1972], Warren and Wiscombe [1980], and Boutron [1982] for Amundsen Scott Station; and by Murozumi et al. [1969] and Mayewski et al. [1987] for Camp Century and Dye 3 stations in Greenland. For instance, Murozumi et al. [1969] collected 1965 winter snow in West Antarctica uncontaminated by artifact lead introduced during field collection at two sites along a staked trail from New Byrd station on which leaded gasoline-fueled vehicles had been used the previous summer. Each of the sites was 1 km upwind and normal to the trail. The snow layer

related to those summer activities was below the sampled 1965 winter layer. They also collected a sample from the latter layer in an area beyond the staked trail. They found 2000 pg Pb/g at a distance 35 km from New Byrd station, 900 pg Pb/g at a distance 125 km from New Byrd station, and 10 pg Pb/g 90 km beyond the end of the staked trail in virgin snow. The two extremely high values were attributed to the use of snowmobiles burning leaded gasoline at and in the vicinity of New Byrd station. Murozumi et al. [1969] also sampled surface snow in the 1965 spring layer at various distances from Camp Century in Greenland, and they found 270 pg Pb/g at a distance 1 km from the station, 200 pg Pb/g at a distance 45 km from the station in virgin snow, and 190 pg Pb/g at a distance 80 km from the station in virgin snow. The geographical variations shown in Figure 2 accord with these earlier observations of local contamination effects and strongly suggest that local lead emissions from both Amundsen Scott and Dumont d'Urville stations have contaminated widespread areas surrounding them within radii of hundreds of kilometers and that this effect declines with distance from the stations. The only snow block useful for globally significant purposes is then thought to be the one collected at stake D80, 433 km from coastal Dumont d'Urville station, in which the lead concentration is 2.3 pg Pb/g.

This interpretation will obviously need to be substantiated in the future by studying in more detail the geographical variations of lead concentrations along the Dumont d'Urville station-stake D80 axis, in the Amundsen Scott station area, and near other Antarctic stations. It will also be mandatory to build up an inventory of lead emissions by Antarctic stations from data

on usage of diesel fuel, jet fuel, and gasoline at these stations. Such an inventory is not yet available, but simple preliminary calculations from present usage of gasoline at Amundsen Scott station (J.T.Lynch, personal communication, 1987) and lead content of this gasoline (1.1 g/L) conclusively show that the excess of lead above that contributed by soil dusts, volcanoes and the oceans (5.9 pg Pb/g; see section 4.3. and Table 3) we observe 7.3 km from Amundsen Scott station can be quantitatively accounted for by local lead emissions.

4.2. Globally Significant Present-Day Lead Levels in Antarctic Air

The significance of a few human-monitored, event samples of Antarctic air collected for lead concentration measurements is greatly enhanced by relating them to a properly selected snow sample which integrates tropospheric lead concentrations over long time periods. It is possible to collect samples from air masses on an event basis so chosen as to exclude meteorological regimes which might contaminate the samples with local Pb emissions. Such samples might contain lead concentrations which reflect those in widespread air masses, if proper care is also taken to exclude artifact contamination during collection and analysis. But meteorological restraints limit the number of such samples which can be collected during long time intervals. The significance of these limited samples is therefore reduced in computing annual means from them. Concentrations of tropospheric lead can be integrated over long time intervals within samples of recent snow, but snows deposited during acceptable meteorological regimes may become contaminated by local lead emissions if the sampling sites are within several hundred kilometers of support stations or frequently traveled trails. Therefore it is a matter of proper site selection, not meteorological regime selection, which determines the scientific appropriateness of a surface snow-sampling site.

In previous sections, we have seen that the only snow block useful for evaluation of globally significant Antarctic tropospheric lead concentrations is probably the one collected at stake D80. The corresponding lead value (2.3 pg Pb/g) can be combined with an independently measured scavenging ratio of 0.3 obtained from the ratio (pg Pb/g precipitation) / (pg Pb/m³ air STP) [Patterson and Settle, 1987a] to yield a calculated value of 7 pg Pb/m³ Antarctic air STP.

This value can be compared with the few reliable direct measurements of lead concentrations in Antarctic air which have been recently made by Dick and Peel [1985], Dick [1987], Wagenbach [1987], and Wagenbach et al. [1987]. Dick and Peel [1985] obtained only an upper limit (< 8.5 pg Pb/m³ STP, range < 4 to < 18 pg Pb/m³ STP) for a few weeks summer period at two sites on the west side of the Antarctic Peninsula (Beethoven Peninsula and Crescent Scarp). Using improved procedures, Dick [1987] got a mean value of 5.0 pg Pb/m³ STP (range 1.4-10.4 pg Pb/m³ STP) for a few weeks summer period at Gipps Ice Rise on the east side of the Antarctic Peninsula. Finally, Wagenbach [1987] and Wagenbach et al. [1987] obtained a preliminary average concentration value

of about 10 pg Pb/m³ STP (range 3-15 pg Pb/m³ STP) near Georg Von Neumayer station on the Ekström Ice Shelf for a 2-year sampling time period. Our calculated value of 7 pg Pb/m³ STP is in good agreement with these direct air measurements, despite the fact that the air lead values were obtained at other locations than where our 2.3 pg Pb/g was measured and that they may apply to different time periods. It seems therefore reasonable to consider that this 7 pg Pb/m³ STP value is globally significant.

On the other hand, our calculated value is much lower than the summer values previously published by Maenhaut et al. [1979] (27-76 pg Pb/m³ STP at the south pole) and by Peel and Wolff [1982] (mean 184 pg Pb/m³ STP in the Antarctic Peninsula). These earlier values had already been questioned [Boutron and Patterson, 1983; Dick and Peel, 1985; Wolff and Peel, 1985b]. They were probably plagued by improper control of contamination during field sampling, laboratory analysis, or both.

This level of about 7 pg Pb/m³ STP of lead in the Antarctic air cell is about 1/100 of that observed in the Greenland atmosphere [Davidson et al., 1985], which is an unexpectedly small ratio. A difference of only about twentyfold would be expected from the observed global pattern of differences in atmospheric lead concentrations between the five other major meridional circulation cells [Patterson and Settle, 1987a]. Lead concentrations are about 2000 pg Pb/m³ STP in the combined North Pacific and North Atlantic regions of the northern hemisphere westerlies meridional circulation cell [Settle and Patterson, 1982], indicating that sufficient industrial lead emitted to the westerlies from North America, Europe, and Japan leaks across the circumpolar convergence barrier into the north polar cell to maintain about a 1:6 ratio across that barrier in oceanic regions. Other differences in oceanic regions in atmospheric lead concentrations measured across meridional cell boundaries are fivefold between the North Pacific westerlies (1000 pg Pb/m³ STP) and easterlies (200 pg Pb/m³ STP), sevenfold between the equatorial Pacific easterlies north (200 pg Pb/m³ STP) and South (30 pg Pb/m³ STP), and fivefold between the South Pacific easterlies (30 pg Pb/m³ STP) and westerlies (160 pg Pb/m³ STP).

These relations suggest that a level of about 30 pg Pb/m³ STP should prevail in the Antarctic, should mixing factors be about uniform. But the observed concentrations and calculated value inferred from precipitation data indicate a level of about 7 pg Pb/m³ which suggests that the south circumpolar convergence may be a more effective barrier to tropospheric mixing than are other meridional cell convergences. An alternative explanation is however that the Greenland values published by Davidson et al. [1985] might be erroneously too high because of improper contamination control during field sampling, as already suggested by Wolff and Peel [1987].

4.3. Lead Contribution From Soil Dusts, Volcanoes, and the Oceans

Aluminium, non-sea-salt sulfate and sodium have not yet been determined in the snow blocks. But values of these constituents have already been obtained for the four locations where our snow

TABLE 3. Antarctic Present Day Surface Snow: Evaluation of Relative Contributions of Soil Dusts, Volcanoes, and the Oceans to Measured Lead Concentrations.

Location	Al,[a] ng/g	Na,[b] ng/g	SO_4,[b] ng/g	SO_4 excess,[b] ng/g	Calculated Lead Contribution, pg/g				Measured lead,[f] pg/g
					Soil Dusts[c]	Volcanoes[d]	Oceans[e]	Total	
Stake D40	1.23	61	30	15	0.20	0.05	0.00028	0.25	6.6
Stake D47	1.75	21	29	24	0.30	0.08	0.00010	0.38	7.4
Stake D80	2.0	17	29	25	0.35	0.08	0.00008	0.43	2.3
South Pole	2.0	16	60	56	0.35	0.18	0.00004	0.47	6.3

(a) From Boutron [1981]: mean concentration for the 0-40 cm snow layer (collected in summer 1972-1973) multiplied by 2.5, see text. At the South Pole, 0-40 cm snow layer collected in summer 1973-1974

(b) Legrand and Delmas [1985] and M. Legrand (personal communication 1986), mean concentration for the 0-40 cm snow layer collected in summer 1982-1983 (i.e., during the same field party as the snow blocks)

(c) Calculated from Al values: soil dusts $Pb = 1.7 \times 10^{-4}$ Al [Patterson and Settle, 1987a]

(d) Calculated from SO_4 values: volcanic $Pb = 0.32 \times 10^{-5}$ excess SO_4 [Boutron and Patterson, 1986; Patterson and Settle, 1987a, b]. The fraction of excess SO_4 estimated to be volcanic is about 13 % [Boutron and Patterson, 1986]

(e) Calculated from Na values: oceanic $Pb = 0.46 \times 10^{-8}$ Na [Boutron and Patterson, 1986]

(f) Measured concentration in the fourth layer of the blocks (see Table 2).

blocks were collected [Boutron, 1978, 1981, 1982; Legrand and Delmas, 1985; M. Legrand, personal communication, 1986], which can be used to calculate the relative natural contributions of soil dusts, volcanoes and the oceans to the measured lead concentrations (see Table 3). The surface samples which were analyzed by Legrand and Delmas [1985] and M. Legrand (personal communication, 1986) were collected during the same field parties as our snow blocks, within short distances, and the depth intervals were about the same. The non-sea-salt sulfate and sodium values given in Table 3 are then probably very close to the actual ones in the blocks. The surface samples which were analyzed for aluminium by Boutron [1978, 1981, 1982] were, on the other hand, collected about 10 years before our snow blocks, so that the actual aluminium concentrations in the blocks might be slightly different because of temporal variability [Boutron, 1982].

Boutron [1978, 1981, 1982] measured aluminium by flameless atomic absorption spectrometry after preconcentrating the samples by slow evaporation, without adding acids. Recent comparative measurements of aluminium by instrumental neutron activation analysis have consistently shown that the aluminium concentration values of Boutron [1978, 1981, 1982] are probably systematically too low by a factor of about 2.5, because of losses of aluminosilicate materials by sedimentation after the melting of the sample and of incomplete solubilization of these materials during the preconcentration step. In Table 3, we have therefore multiplied the aluminium values of Boutron [1978, 1981, 1982] by 2.5.

Total lead contribution from soil dusts, volcanoes, and the oceans is found to range from 0.25 to 0.47 pg Pb/g (see Table 3 and Figure 2, dashed line and open circle points). At stake D80, these contributions comprise only about 1/5 of measured lead; and about 1/25, 1/20, and 1/15, at stake D40, stake D47, and the south pole, respectively. These excesses are in strong contrast with the situation which prevailed several millenia ago when soil dusts and volcanic aerosols accounted for all lead in preindustrial ice layers [Boutron and Patterson, 1986; Boutron et al., 1987]. At stakes D40 and D47 and at the south pole, part of this present-day excess of lead probably originates from local contamination by Dumont d'Urville and Amundsen Scott stations, as discussed in section 4.1. But at stake D80 the observed fivefold excess is thought to represent the present-day level of lead in the Antarctic tropospheric air cell.

4.4. Time Variations of Lead in Antarctic Ice and Snow Since the Beginning of Holocene

These variations can tentatively be estimated from the data of Boutron and Patterson [1983, 1986] and of this study. For the 13000-3800 years B.P. period, Boutron and Patterson [1986] have obtained lead concentrations in the 0.32- 0.94 pg Pb/g range, without any time trend. The two highest values they got, 0.76 and 0.94 pg Pb/g, were, however, given as upper limits only. The mean lead concentration during this time period was then probably about 0.4 pg Pb/g (Figure 3). For the subsequent 3600 years, i.e., until the
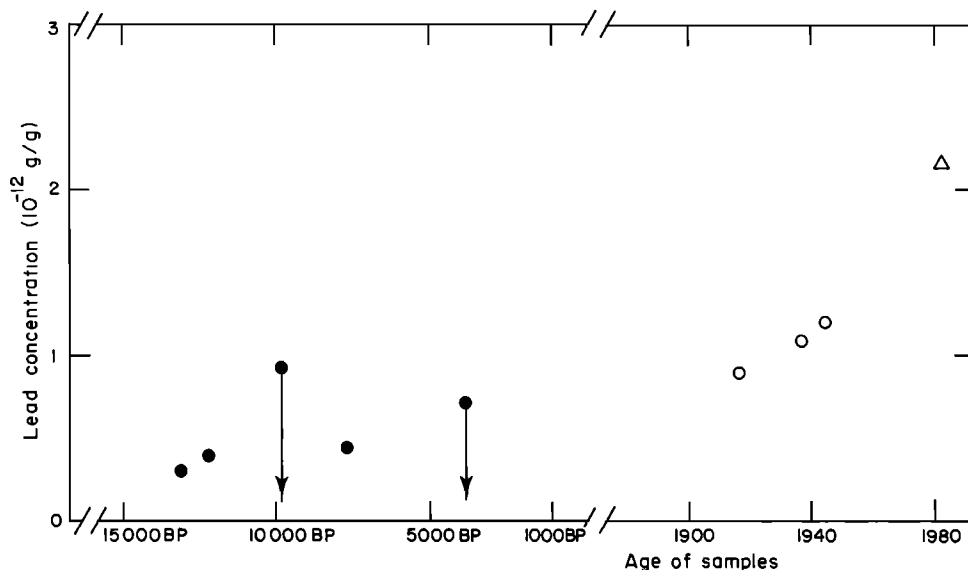
Fig. 3. Tentative temporal curve of lead concentrations in Antarctic ice and snow from the beginning of Holocene to present day. Solid circle points indicate concentrations measured in five sections of the Dome C deep-ice core, data from Boutron and Patterson [1986] ; downward arrows indicate that the corresponding solid point is given as an upper limit only. Open circles indicate concentrations measured in three snow core sections collected at stake D55 of the Dumont d'Urville-stake D80 trail, data from Boutron and Patterson [1983], see text. Open triangle shows concentration in present-day surface snow at stake D80, data from this study.

beginning of the industrial period 2 centuries ago, no data are presently available, but the upper limits obtained by Ng and Patterson [1981] for two sections, 2010 and 1490 years old, of the Byrd deep-ice core, <2.2 pg Pb/g and <1.4 pg Pb/g, respectively, suggest that lead concentrations remained very low.

For the last 2 centuries the best available data are those of Boutron and Patterson [1983], which extend from 1973 back to 1801. They were obtained by analyzing small-diameter snow cores collected at stake D55 of the Dumont d'Urville-stake D80 trail (183 km from the coast) using an all-plastic acid-cleaned auger. Lead concentrations measured in the innermost parts of the analyzed snow core sections ranged from 0.9 to 9.5 pg Pb/g. Lead concentration profiles across the core diameters were performed for part of the analyzed sections only. They showed that for at least part of the sections, variable amounts of artifact lead contamination had been transported to their interiors by light inadvertent melting during transport. Lead concentrations measured in centers of these core sections should then be considered as upper limits only. The innermost parts of three sections, whose ages ranged from 1917 to 1947, showed, however, singularly low lead concentrations (0.9, 1.1 and 1.2 pg Pb/g). Unfortunately no cross-core profiles were performed for these three sections. In the light of the new data of Boutron and Patterson [1986], we think that these three concentration values probably were the only reliable data in the data set of Boutron and Patterson [1983]. Lead concentrations in Antarctic snows probably were then still very low, about 1 pg Pb/g, in the 1940s (Figure 3).

According to this study, lead concentrations increased then to present-day values of about 2.3 pg Pb/g (Figure 3). If this preliminary temporal curve is correct, then lead concentrations have increased about 2.5 times from early Holocene times to the 1940s, and subsequently increased again about 2.5 times from the 1940s to the present day (Figure 3). This estimated overall approximate fivefold increase is much smaller than the~200-fold increase which is observed in Greenland snow and ice [Murozumi et al., 1969; Ng and Patterson, 1981]. For Greenland, lead concentration increased from less than 1 pg Pb/g several millenia ago to about 50 pg Pb/g in the 1930s [Murozumi et al., 1969], i.e., at least a fiftyfold increase. Subsequently, they increased to about 200 pg Pb/g for present day snow, i.e., an additional fourfold rapid increase during the last few decades which was attributed to the acceleration of the manufacture and burning of leaded gasoline during and after World War II [Settle and Patterson, 1980].

This preliminary temporal curve will of course need to be confirmed in the future by new data. There is especially an urgent need for a new and detailed time series to cover the past few hundred years.

The general picture is that the Antarctic tropospheric cell is today the least contaminated on earth with respect to anthropogenic lead. But only about one-fifth of total lead today in Antarctic air is natural, and about four-fifths is anthropogenic.

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