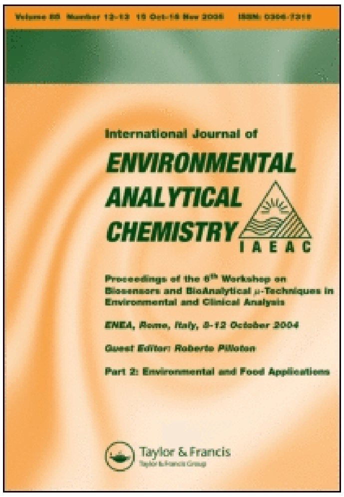

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THE CHANGING OCCURRENCE OF NATURAL AND MAN-DERIVED HEAVY METALS IN ANTARCTIC AND GREENLAND ANCIENT ICE AND RECENT SNOW

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A record of the past and recent changes in the large scale atmospheric cycles of Pb and other heavy metals can be found in the successive dated ice and snow layers stored in the Antarctic and Greenland ice caps. Deciphering these frozen archives has however been possible only when using sophisticated ultrasensitive and ultraclean analytical techniques. The available data have allowed to demonstrate that the atmospheric cycles of heavy metals have been highly dependent upon climate during pre-pollution times. During the last few centuries, they have been significantly altered by man. This is especially the case for Pb, whose concentrations were found to have strongly increased in Greenland ice and snow from several millennia ago to the mid 1960's, then to have decreased from the late 1960's to present.

KEYWORDS: Lead, heavy metals, Antarctica, Greenland, ice.

INTRODUCTION

There is presently an increasing interest in investigating the large scale biogeochemical atmospheric cycles of Pb, Cd, Hg and various other heavy metals. This is because human activities are emitting very large quantities of these toxic metals to the atmosphere[1] so that they have become a major ecological and health problem.

An unique way to assess these cycles is to study the occurrence of heavy metals in the successive dated snow and ice layers deposited in the large Antarctic and Greenland ice caps. Ancient ice, whose age can be up to several hundred thousand years, will indeed provide unique data on the past natural (pre-pollution) cycles of these metals, whose knowledge is mandatory for any proper assessment of recent changes. Once these natural references firmly established, the study of more recent ice and snow will allow to reconstruct the course of the increasing atmospheric pollution in both hemispheres.

Unfortunately, it is only recently that comprehensive although still very incomplete data became available: this is due to the fact that heavy metals concentrations in polar ice and snow are so low, down to the sub pg/g level, that the contamination and analytical problems are formidable[2,3].

We present here a short review which summarizes the key problems which are faced by investigators and rapidly overviews the main available results which are presently available.

FIELD SAMPLING AND LABORATORY ANALYSIS

Collection of ancient ice and recent snow

Ancient ice can be collected either by thermal or by electromechanical deep drilling (the deepest cores presently available are the 2,546 m soviet Vostok core from East Antarctica and the 3,028 m european GRIP core from central Greenland; both cover about 200,000 years). The outside of such deep cores is unfortunately always strongly contaminated for heavy metals, especially when the drilling hole is filled with a wall retaining fluid[4,5]. Fortunately, they can be decontaminated by chiselling successive veneers of ice in progression from the outside to the center of each core section, using sophisticated ultraclean procedures to prevent transfer of contamination from the dirty outside to the central parts.

To check the efficiency of these decontamination procedures, it is however mandatory to study in full details for each investigated heavy metal changes in concentrations from the outside to the center of each individual core section: it is only if a clear plateau of concentrations is observed in the central parts of a given core section (see Figure 1) that the

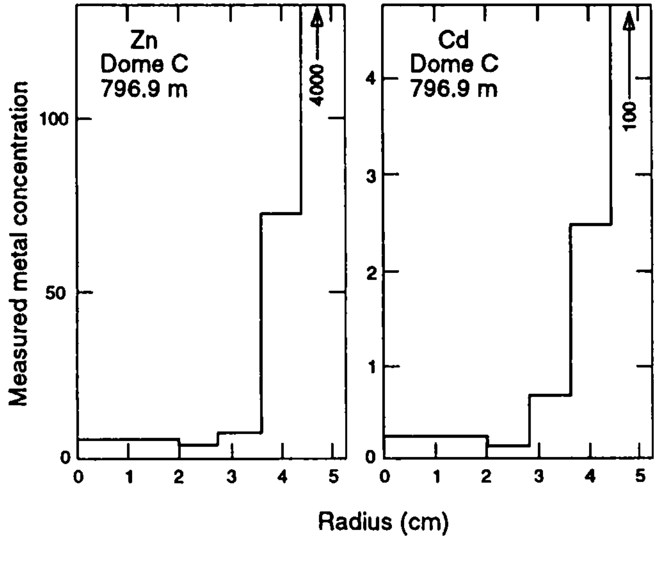

Figure 1 Changes in Zn and Cd concentrations from the outside to the center of a 10.5 cm in diameter section of the Dome C deep Antarctic ice core (depth 796.9 m, age 33,700 years). From refs. 5, 13.

concentrations measured in the center can be considered as representing the original genuine concentration in the ice.

Outside contamination can, on the other hand, be kept to a minimum for surface or shallow depths samples: they can indeed be collected either by directly taking samples from the walls of clean hand dug pits or by using specially designed acid cleaned all plastic mechanical drills[6].

Ultraclean analytical techniques

By far, the most critical problem for the laboratory analysis of heavy metals in these very valuable samples is contamination. It can be overcome only if using specially designed positive pressure clean laboratories[7] and ultraclean analytical procedures. These include a careful choice of the containers which are to contact the samples (these containers must be made out of selected plastics such as conventional polyethylene or FEP teflon) and the use of sophisticated cleaning methods (by immersion in a succession of high purity heated acid baths[7]). In any case, it is essential to perform extensive blank determinations for each individual step of the whole analytical procedure.

Highly sensitive analytical techniques are mandatory. So far, the most sensitive technique for the measurement of heavy metals in Antarctic and Greenland ice and snow is the newly developed Laser Excited Atomic Fluorescence Spectrometry (LEAFS) technique[8,9]. The limit of detection is as low as about 5 fg for Pb and 0.5 fg for Cd (Figure 2). The ultimate sensitivity of this technique has allowed direct measurement of Pb, Cd and Bi in various samples without any preliminary preconcentration or extraction step using very small sample volumes. The other techniques (especially Isotope Dilution Mass Spectrometry[4,10] or Flameless Atomic Absorption Spectrometry[6,11]) are less sensitive: a preconcentration or extraction step is required.

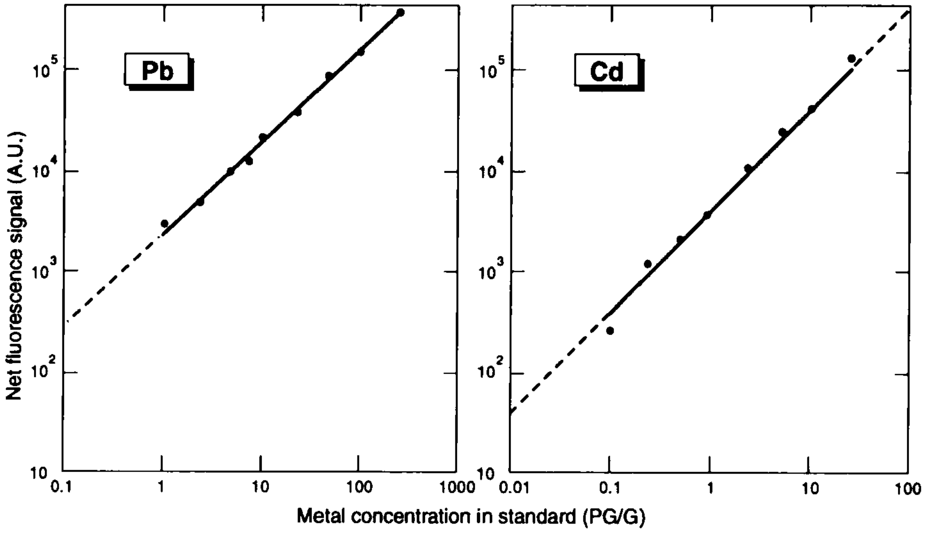

Figure 2 Laser Excited Atomic Fluorescence Spectrometry: calibration of the spectrometer for Pb and Cd using ultralow concentration standards (20 µl injections for Pb; 50 µl injections for Cd). From refs. 8,9.

MAIN AVAILABLE DATA

Natural changes in Antarctic ice during the last climatic cycle

Among the most interesting data which are now available are those recently obtained on the changes in heavy metals concentrations in ancient (pre-human activities) Antarctic ice during the full last climatic cycle (past 155,000 years). They were obtained from the analysis of various sections of the Dome C and Vostok deep Antarctic ice cores[5,10,12,13]. As shown in Figure 3, concentrations of Pb, Zn and Cd have varied widely, by up to two orders of magnitude, during the last climatic cycle. They were relatively high during the coldest glacial

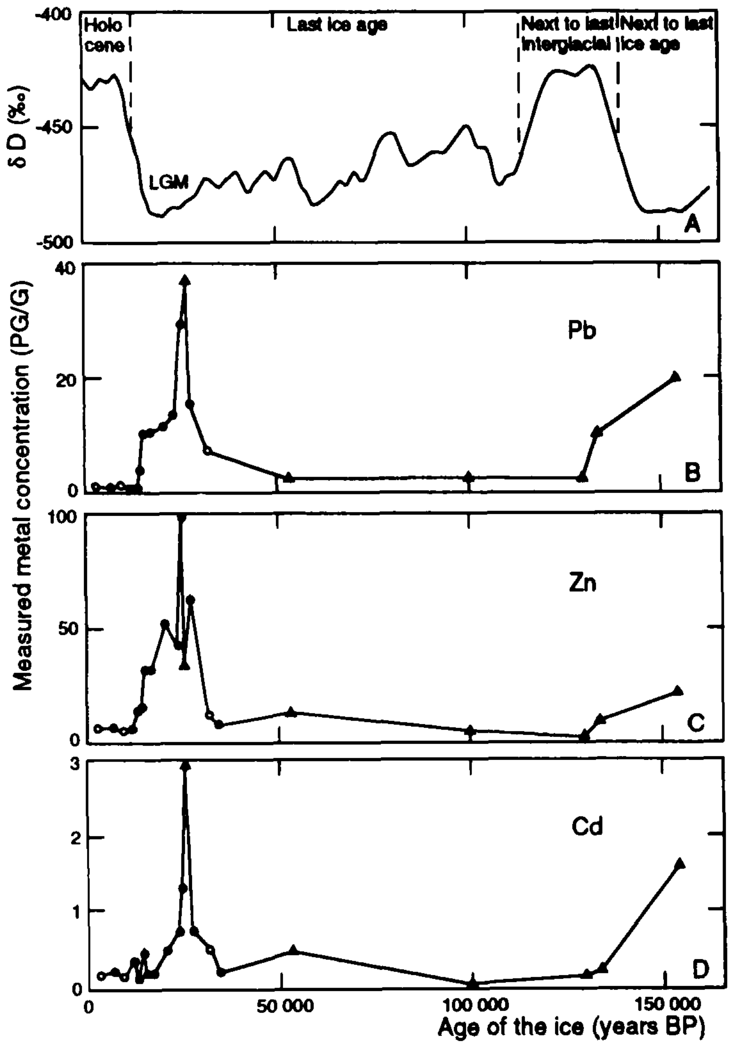

Figure 3 Past natural changes in Pb, Zn and Cd concentrations in Antarctic ice during the last 155,000 years (from refs. 5, 10, 12, 13). The successive climatic stages are shown at the top of the figure (changes in deuterium/hydrogen ratios expressed in δ D% versus SMOW). Open symbols indicate that the corresponding concentration value is given as an upper limit only (no plateau of concentrations on the outside-inside profile).

stages, especially during the Last Glacial Maximum (LGM) around 20,000 years BP. They were, on the other hand, much lower during the warmer periods (interglacials), especially during the Holocene. These natural (pre-pollution) changes can be accounted for mainly by changes in soil and rock dust fluxes to the atmosphere, which were greatly enhanced during the coldest time periods because of increased aridity, stronger winds and lower sea level.

Estimates of contributions from soil and rock dust, sea-salt spray, volcanic emissions and other possible natural sources[14] to the measured Pb, Zn and Cd concentrations in the ice confirm that during the peaks of the glacial periods, the large scale atmospheric fluxes of Pb, Cd and Zn were dominated by rock and soil dust. During warmer periods such as the Holocene, the other contributions, especially from volcanoes and possibly biogenic sources, become, on the other hand, significant.

These data have allowed major improvements in our present knowledge of the past natural (pre-pollution) large scale atmospheric cycles of several heavy metals, then providing a firm base against which to evaluate the recent changes of these fluxes by human activities.

Man induced changes during recent centuries

Of particular interest are the snow and ice layers deposited during the past few centuries, especially since the industrial revolution. They contain indeed very valuable archives of man induced changes of the large scale atmospheric cycles of heavy metals in the Northern Hemisphere (Greenland data) and in the Southern Hemisphere (Antarctic data).

Among the most interesting data which are now available are those obtained on the changes in Pb concentrations in Greenland ice and snow from several millennia ago to present[4,6,15]. As shown in Figure 4, Pb concentrations are documented to have massively increased by more than two orders of magnitude from several thousand years ago (when atmospheric Pb was totally natural in the Northern Hemisphere) to the mid 1960's. This clearly evidences that in the mid 1960's, more than 99% of Pb in the global atmosphere of the Northern Hemisphere was anthropogenic. The course of the increase was especially rapid after the 1930's, following the massive introduction of Pb alkyl additives in gasoline in the 1920's. From the late 1960's to present, a well pronounced decrease (by about 7.5 fold) is, on the other hand, observed, Figure 4. It is clearly the consequence of the very marked and rapid fall in the use of Pb alkyl additives in gasoline during the past twenty years, especially in North America, Japan and Europe. In United States for instance, the total consumption of Pb alkyl additives has decreased from about 250,000 tons/year in the late 1960's to about 10,000 tons/year in the late 1980's (J. O. Nriagu, personal communication).

During these past twenty years, a clear decrease of Cd and Zn concentrations is also observed in Greenland snows[6]: it is attributed to the improvements in the control of the atmospheric emissions of these two metals in various countries of the Northern Hemisphere.

In Antarctica, Pb concentrations in present day snow are found to be about one order of magnitude higher than those in ice several thousand years old[16] (see Figure 5) which indicates that the large scale pollution of the atmosphere for Pb has reached even the most remote areas of the Southern Hemisphere.

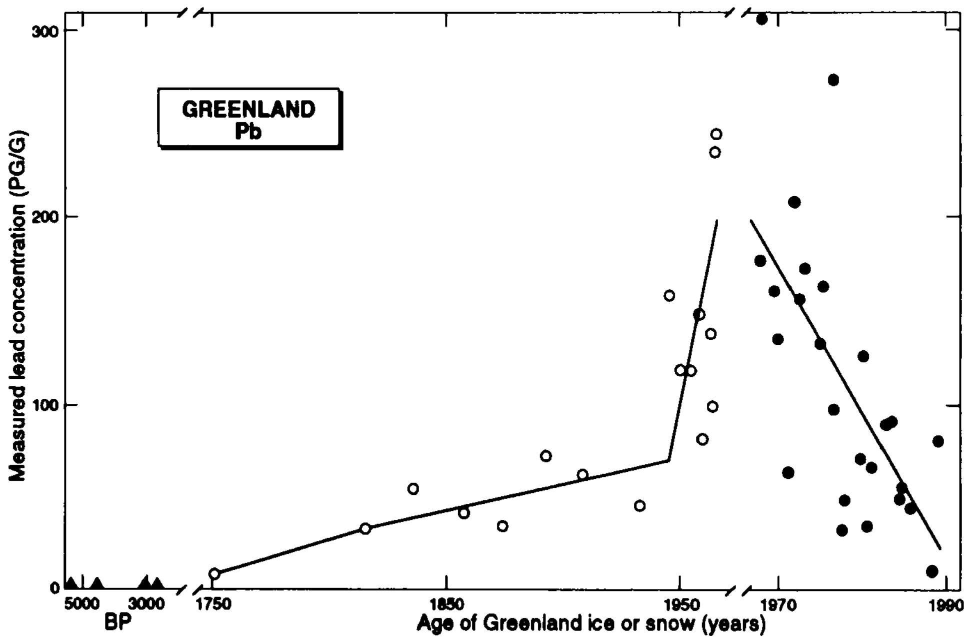

Figure 4 Changes in Pb concentrations in Greenland ice and snow from several millennia ago to present. From refs. 4, 6, 15.

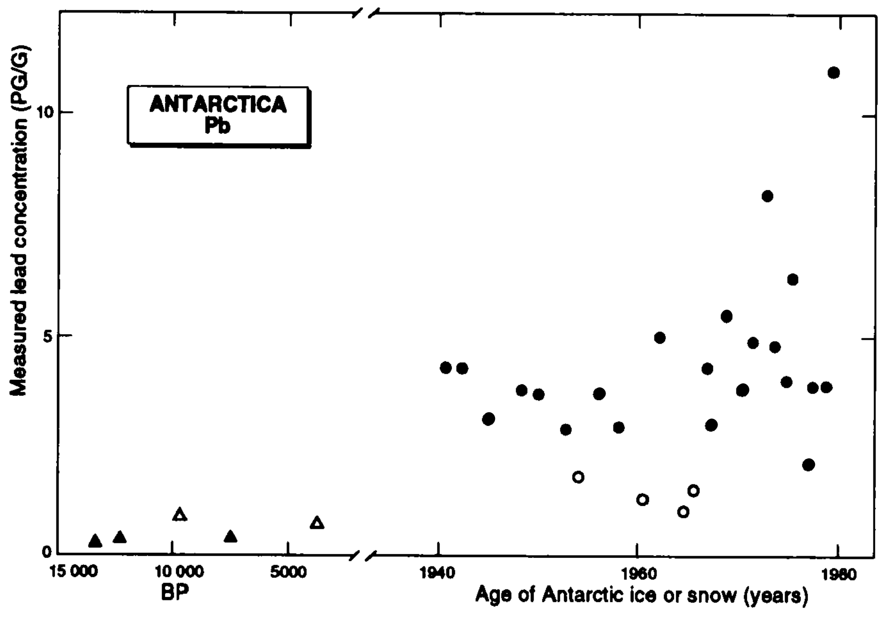

Figure 5 Changes in Pb concentrations in Antarctic ice and snow from several millennia ago to the late 1970's. From refs. 10, 16.

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