Elevated mercury accumulation in a peat bog of the Magellanic Moorlands, Chile (53°S) – an anthropogenic signal from the Southern Hemisphere

H. Biester [a,*], R. Kilian [b], C. Franzen [a], C. Woda [c], A. Mangini [c], H.F. Schöler [a]

[a] *Institute of Environmental Geochemistry, University of Heidelberg, INF 236, 69120 Heidelberg, Germany*
[b] *Department of Earth Sciences (FB VI), University of Trier, 54286 Trier, Germany*
[c] *Heidelberg Academy of Sciences, INF 229, 69120 Heidelberg, Germany*

Abstract

Increasing mercury deposition rates in the Northern Hemisphere recorded in natural archives such as peat bogs or lake sediments have been documented in numerous studies. However, data on atmospheric Hg deposition in the Southern Hemisphere dating back to pre-industrial times are rare. Here, we provide a continuous record of atmospheric Hg deposition in the Southern Hemisphere recorded by an ombrotrophic peat bog of the Magellanic Moorlands, Chile (53°S), extending back 3000 yr. Pre-industrial mercury accumulation rates range between 2.5 and 3.9 $\mu g/m^2/yr$. In the past 100 yr, Hg accumulation rates increased 18-fold from about 3 $\mu g/m^2/yr$ to a maximum of 62.5 $\mu g/m^2/yr$. If Hg accumulation rates were normalized to peat accumulation rates, maximum rates were 7.9 $\mu g/m^2/yr$, which is only 2.5 times the pre-industrial rates. Thus, Hg accumulation rates normalized to peat accumulation rates are more comparable to the three-fold net increase in atmospheric Hg concentrations estimated for the same period. We suggest that the increase in Hg accumulation rates in the Magellanic Moorlands within the past 100 yr is at least partly attributed to global dispersion of Hg derived from anthropogenic sources in the Northern Hemisphere. The finding that no increase of atmospheric deposition of Pb could be observed in the bog indicates the extraordinary long-range transport and ubiquitous dispersion of anthropogenic derived gaseous Hg compared to other metals. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Long-range transport of mercury emitted from anthropogenic sources such as coal burning, waste incineration or chlor-alkaline plants located at mid-latitudes and its deposition in remote areas has been documented in numerous studies [1–6]. Despite an ongoing discussion about the influence of geological sources on Hg records in peat and lake sediments [7,8], some of these studies have shown unambiguously that anthropogenic Hg

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* Corresponding author. Tel.: +49-6221-544819;
Fax: +49-6221-545228.
E-mail address: hbiester@ugc.uni-heidelberg.de (H. Biester).

emissions have increased relative to natural sources since the beginning of the industrial age. Mason et al. [2] have estimated that 70–80% of the present-day atmospheric Hg flux can be attributed to anthropogenic sources.

Gaseous metallic Hg is the predominant Hg species emitted from most natural and anthropogenic sources. That is why the atmosphere is the main pathway for the distribution of mercury at the Earth's surface. The residence time of Hg in the atmosphere is estimated to be at least 1 year [9]. In recent years increasing attention has been given to atmospheric deposition of Hg in remote areas, especially in sub-Arctic and Arctic regions. Increased Hg levels found in marine and lacustrine sediments [1,5] and in peat bogs [10] indicate increased fluxes of anthropogenic Hg from mid-latitudes to the Arctic. Besides transport of air masses from mid- to high latitudes increased deposition of Hg in Arctic regions is assumed to be also enhanced by light induced formation of reactive Hg species during polar sunrise [11].

Data on Hg dispersion in the Southern Hemisphere are generally sparse as compared to those available for the Northern Hemisphere. Fitzgerald et al. [13] showed that interhemispheric mixing allows Northern Hemispheric emission of Hg(0) to be transported to the atmosphere of the Southern Hemisphere. Slemr and Langer [4] documented an increase in Hg concentrations in the atmosphere over the Southern Hemisphere of 1.2% annually between 1977 and 1990. Lacerda et al. [12] provided a 30 000 yr record of Hg accumulation rates in lake sediments from Northern Brazil. They found an increase from background Hg accumulation rates of 0.7–2.6 $\mu g/m^2/yr$ before 1600 AD to a maximum of 10 $\mu g/m^2/yr$ which appears at about 1970 AD. They assigned this early increase to Hg emissions from Spanish silver mining from colonial times. The further increase in the 20th century was mostly attributed to gold mining in the Amazon region, where a total release of ca. 4000 tons of Hg within the past 30 yr has been estimated [12]. Fitzgerald et al. [13] reported recent accumulation rates of 11 $\mu g/m^2/yr$ for peat bogs in New Zealand. Sediment cores from Northern Brazil give evidence of ele-

vated Hg accumulation rates during colder climates in pre-anthropogenic times. There, Hg accumulation rates increased by a factor of up to 3 between 8500 and 12 000 BP and during the last glacial maximum at about 18 000 BP [12]. Vandal et al. [14] investigated mercury accumulation in ice cores from Antarctica and interpreted the variability of pre-anthropogenic Hg concentrations to be due to variations in biological productivity in the oceans.

In our study we have investigated the record of atmospheric Hg deposition in an ombrotrophic peat bog in the Magellanic Moorlands of Southern Chile (53°S) (Fig. 1). Several studies have shown that ombrotrophic peat bogs, receiving Hg exclusively from the atmosphere, are useful archives for records of atmospheric Hg deposition [15–19]. However, nearly all of the bogs investigated to date are located in the Northern Hemisphere and are built up in most cases by *Sphagnum* mosses.

The southernmost region of South America is characterized by narrow succession of climatic zones which are characterized by dryness on the east side and heavy rains and strong westerly winds driven all year long by the Antarctic circum polar vortex on the west side. A peculiarity of the bogs in the Magellanic Moorlands is that *Sphagnum* mosses are almost absent, which is assumed to be due to the high influx of sea spray. The bogs are so-called cushion bogs dominated by cushion plants such as *Donatia fascicularis*, *Astelia pumila* and different *Carex* species [20]. The Magellanic Moorlands are uninhabited so that there are no local anthropogenic sources of Hg. The sampling area is located within the Andes Mountains in the area of maximum annual precipitation (up to 10 000 mm/yr).

Two peat cores (GC1a, GC1c) were taken from an ombrotrophic peat bog and were analyzed for concentrations and accumulation rates of Hg and other metals. Additional parameters such as the content of ash or Ca and Sr were analyzed for the geochemical characterization of the peat. The aim of this study is to estimate the importance of anthropogenic influences on atmospheric Hg deposition in a remote, pristine sub-Antarctic area.
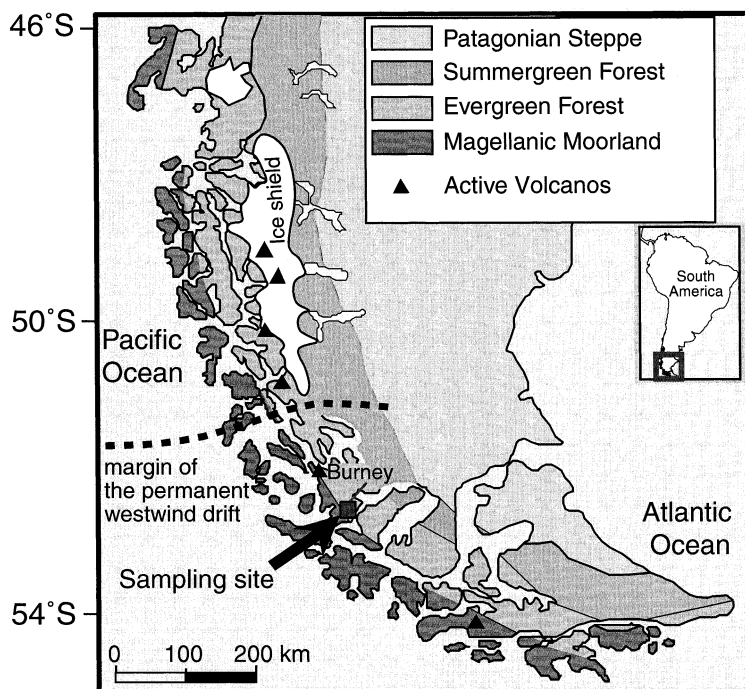
Fig. 1. Position of the sampling area near the Gran Campo Nevado Glacier in the Magellanic Moorlands, Chile.

2. Materials and methods

2.1. The Gran Campo (GC) bog

The GC bog is a raised bog situated on a former alluvial fan of the Gran Campo Nevado Glacier (52°47.443′S 72°56.616′W). The peat layer, which has a thickness of about 170 cm, is underlain by till. The growth of peat started approximately 3000 years ago after the fan was lifted above sea level due to isostatic rebound of the formerly glaciated areas. Today the surface of the bog is about 10 m above sea level. The vegetation is dominated by *D. fascicularis*, *A. pumila*, *Carex* species and *Nothofagus* trees in the drier parts of the bog. Hummocks and hollows, which are typical features of continental *Sphagnum* bogs, are absent in this bog.

2.2. Sampling

The two peat cores were taken using a $10 \times 10 \times 200$ cm stainless steel Wardenaar corer with a serrated cutting edge which allows cutting through the roots of the bog plants. The distance between the two cores was ca. 4 m. The length of each peat monolith was ca. 150 cm. In contrast to many *Sphagnum* bogs where a more or less thick layer of the upper part of the peat consists of poorly degraded plant material of low density, the layer of low degraded plant material in this cushion bog has a thickness of only several centimeters. Below this zone of living plants and the biologically active rooting zone the peat is typically highly degraded. Due to these characteristics, compression of the peat during sampling was comparatively low and did not exceed 10% of the total length of either core. A layer of ca. 1 cm was cut off from each side of the core to avoid contamination due to smearing of material from tephra layers. The cores were sectioned in the field into 2 cm thick slices (8×8 cm) using a serrated stainless steel bread knife and packed into polyethylene bags. All samples were stored deep-frozen before freeze-drying in the lab.

2.3. Determination of peat density

Bulk density was determined from three sub-samples, which were removed in the field from the fresh peat slices by means of an apple corer. To compensate for the compression of the peat when sub-sampling for density measurements with the apple corer, the thicknesses of the peat slices were determined prior to sampling of density samples. The volume of the peat cylinder for density measurements was then calculated based on the thickness of the peat slice, as this is more accurate than measuring the thickness of the peat cylinder after sampling. The dry weight of the peat cylinder was determined after freeze-drying. The standard deviation of the density measurements within a slice was in the range of 15–20%. A more detailed description and discussion of the measurement is given elsewhere [21]. Before analysis, half of each slice was freeze-dried and milled by means of a titanium plant mill. Milling was carried out in intervals < 15 s to avoid Hg losses caused by warming of the samples. The pH-value of the peat profile was determined directly in the field by inserting a glass combination pH electrode directly into the fresh peat monolith within the respective sections for ca. 3 min until equilibrium was obtained.

2.4. Mercury analysis

Mercury analyses were carried out in sub-samples of cores GC1A and GC1C. Mercury concentrations were determined using atomic absorption spectroscopy after thermal combustion of the freeze-dried samples (50–100 mg) and Hg pre-concentration on a single gold trap by means of an AMA 254 solid phase Hg-Analyzer (Leco). A detailed description of the method is given elsewhere [22]. Specific settings for analyses of the freeze-dried peat were 100 s for drying and 150 s for combustion. Standard reference materials (NIST 1515 apple leaves, 44 ± 4 µg/kg Hg, BCR 281 olive leaves, 20.5 ± 1.9 µg/kg Hg) were used for quality control.

2.5. Analysis of Pb, Ti, Fe, Mn, Ca, Sr and ash content

Analyses of Pb, Ti, Fe, Mn, Ca, Sr and the ash content in the peat were only performed for samples from the GC1A core. Peat samples (2–3 g) were dry ashed for 4 h at 550°C directly after freeze-drying. The ash content, calculated as wt%, provides an estimate of the amount of mineral matter in the peat. Concentrations of the metals were determined by means of an energy-

Table 1
Excess ^{210}Pb activity, ages of ^{210}Pb deposition calculated using the CRS model and ages of peat sections calculated using a constant sedimentation/constant flux model (CSCF) in the upper 18 cm of the GC1 peat core

Depth	[210]Pb excess activity	CRS model age	CSCF model age	Peat accumulation	Correction factor
[cm]	[dpm/g]	[yr]	[yr]	[cm/yr]	
0–2	7.18 ± 0.83	4	?		
2–4	11.00 ± 0.95	13	?	0.222	4.83
4–6	13.11 ± 0.74	26	32	0.154	3.35
6–8	11.64 ± 1.04	39	45	0.154	3.35
8–10	5.08 ± 0.54	46	58	0.286	6.2
10–12	4.55 ± 0.83	54	71	0.250	5.43
12–14	2.95 ± 0.81	60	84	0.333	7.23
14–16	1.86 ± 0.68	64	97	0.500	10.86
16–18	bld				
Pre-industrial mean				0.046	

Peat accumulation rates in pre-industrial highly decomposed peat sections and in low degraded peat sections of the upper 18 cm and correction factors for Hg accumulation rates in low degraded peat calculated based on ages obtained by using the CRS model.
bld = below limit of detection.

dispersive miniprobe multielement analyzer (EMMA), which is a small desk-top XRF system appropriate for the non-destructive determination of metals in peat. A description of the system and its application to metal analysis in peat is given elsewhere [23]. Sr, Ti, Fe and Mn were determined directly in the peat, whereas the concentration of Pb was below the detection limit of the EMMA, which was 0.4 µg/g. Pb was therefore determined in the ashed peat. Other studies have shown that there are no losses of Pb during ashing of peat samples [24].

2.6. Dating of peat samples

The chronology of peat accumulation was determined for the core GC1A. Ten samples representing the top 20 cm were dated using ^{210}Pb excess activity. Activity of ^{210}Pb was obtained by direct γ-spectroscopy [25] in 3 g samples of dried, milled peat. Supported ^{210}Pb was determined by direct measurement of ^{226}Ra or one of its radioactive daughters (^{214}Pb, ^{214}Bi) and subtracted from total ^{210}Pb to obtain unsupported (excess) ^{210}Pb activity [25]. Ages in the sections 0–18 cm were calculated using the constant rate of supply (CRS) model [26]. The unsupported ^{210}Pb activity and calculated model ages are given in Table 1.

Selected peat sections from deeper layers were dated by means of ^{14}C AMS using plant macrofossils which were obtained by sieving 2 g of the wet peat through a 1 mm meshed sieve to remove roots and pieces of wood. The activity of ^{14}C was determined in humic acid extracts and in the humic acid extraction residues. Conventional ^{14}C ages were calibrated using CALIB rev4.0, test version 6 (data set 1).

2.7. Calculation of metal accumulation rates

The calculated net accumulation rates of Hg and Pb are based on the average metal concentrations, the dry mass of peat and the time interval between two dated samples. Sections for calculating background Hg deposition rates were selected from those parts of the core where the variations in Hg concentrations and density were comparatively low.

Peat accumulation rates are usually higher in the uppermost part of peat cores, where the peat is only poorly degraded compared to deeper sections, where it is highly humified. We assume that the peat density, which shows only small variation throughout our core, does not entirely compensate for differences in peat accumulation between the acrotelm and the catotelm which are mainly due to intense mass losses (80–90%) in the acrotelm [27]. Due to these intense mass losses, long term peat accumulation in bogs is predominantly determined by peat decomposition and to a lesser extent by the extent of biomass production. The high accumulation rates of peat in the uppermost peat sections are therefore assumed to overestimate metal accumulation rates calculated for these sections. To compensate this, peat accumulation rates in the acrotelm were normalized to that of the catotelm (depth > 20 cm), assuming that low degraded peat from the acrotelm will show accumulation rates comparable to that of peat in the catotelm after undergoing further decomposition. Peat accumulation rates and correction factors are given in Table 1.

3. Results and discussion

Geochemical indicators such as the pH value of the peat, and the concentration of Ca, Sr, Ti, Zr or ash could be used to help distinguish between minerotrophic and ombrotrophic peat bogs (e.g. [28]). The distribution of these parameters in the GC1A core indicates that the uppermost 120 cm of the core GC1A are ombrotrophic, which means that all elements were exclusively supplied by atmospheric deposition. The mean pH-value of the peat was 3.7 (range 3.5–4.2), which is typical for ombrotrophic sites. The average ash content in the peat as an indication of the deposition of mineral matter was only 1.8%, which also indicates ombrotrophic conditions. Similarly, the continuously low concentrations of Ti and Zr above the tephra layer (Fig. 2b) are consistent with this interpretation. In the lowest part of the core concentrations of Ti, Zr, Fe, Mn and Pb are comparatively high, indicating supply of these elements from the underlying till (Fig. 2b–e). The beginning
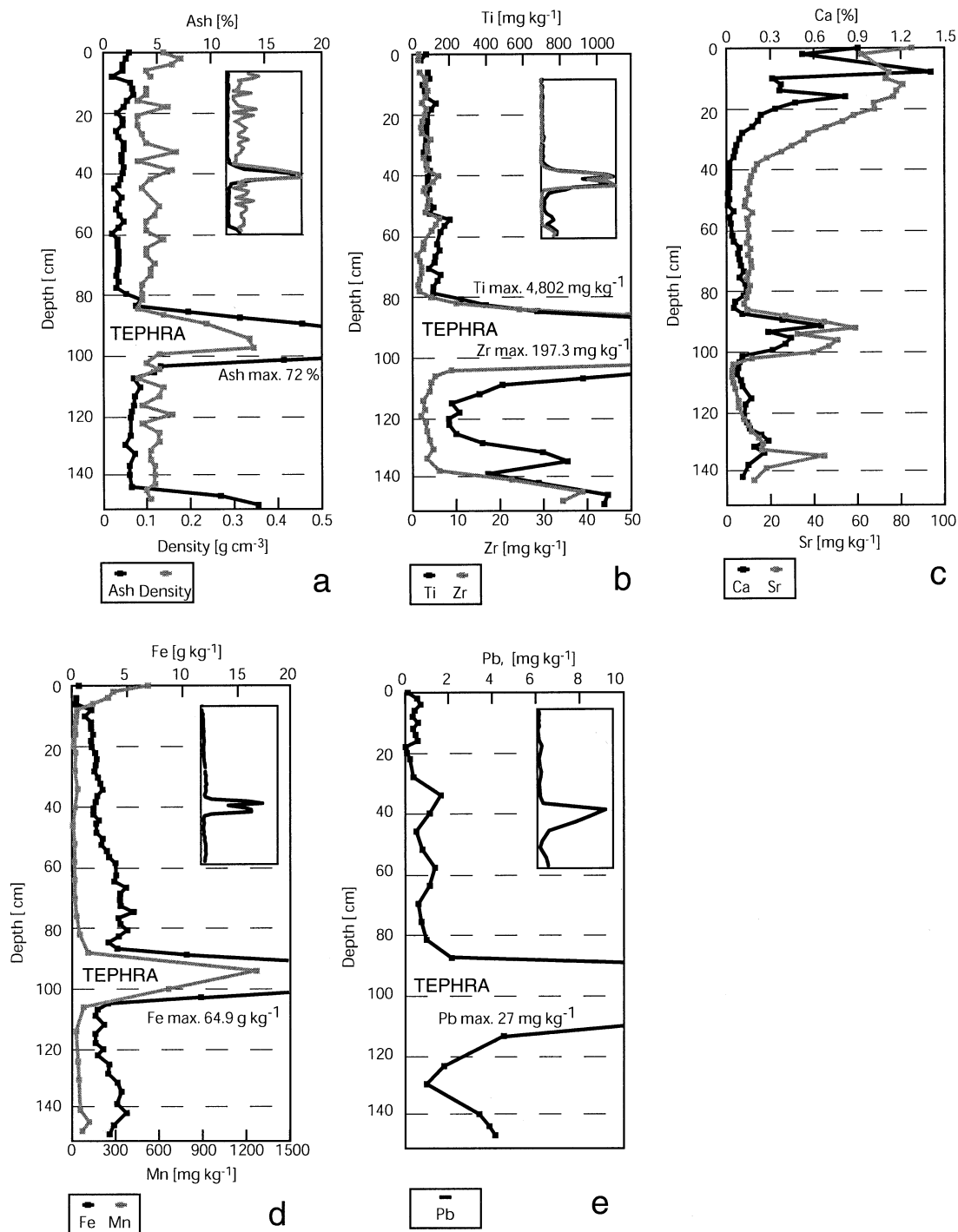
Fig. 2. (a) Records of the ash content (GC1a) and the variation of dry density (GC1) determined in peat cores from an ombro-trophic bog near the Gran Campo Nevado Glacier, Chile (53°S). (b) Records of Ti and Zr (GC1a, bulk samples); (c) of Ca and Sr (GC1a, bulk samples); (d) of Fe (GC1a, bulk samples) and Mn (analyzed in ashed samples referred to bulk samples); (e) of Pb (analyzed in ashed samples referred to bulk samples). Ashed peat samples were analyzed from each section (2 cm sections) in the upper 22 cm and in 6 cm intervals in deeper sections.

of the ombrotrophic part of the profile at about 120 cm is marked by the sharp decrease in Ti and Zr concentrations (Fig. 2b). Ca and Sr also show a typical decrease from the minerogenic into the ombrogenic part of the core (Fig. 2c). Here, Ca concentrations, which reflect in a sensitive way the influence of groundwater, do not exceed 0.15%. Such low Ca values are typically for ombrotrophic sites. However, Ca influx from surface- or groundwater was generally expected to be low as carbonate rocks do not occur in this area. Strontium concentrations show a distribution similar to Ca and were typically high due to the deposition of high amounts of sea spray. Both elements are known to be relatively mobile in peat but show a strong increase in the uppermost 40 cm of the core due to incorporation of these essential elements into the living plant layer and the roots (Fig. 2c). The enrichment of Mn and Zn (not depicted) in the uppermost 6 cm of the core also indicates that this section still contains fresh or poorly degraded plant material (Fig. 2d).

Both cores are marked by a 12 cm thick, coarse grained tephra layer at approximately 100 cm depth, which was identified as a Mt. Burney eruption at about 2000 BP [29]. In this mineral layer concentrations of ash, Ca, Sr and most metals are typically much higher than in the peat (Fig. 2a–e). The peat is dark brown and has only small-sized plant residues throughout the whole core, except the upper 20 cm, indicating that the plant material is strongly decomposed and humified below ca. 20 cm. This explains why the peat profile does not increase in density with depth.

3.1. Geochronology

Results of ^{14}C dating indicate that the GC1a core covers approximately 3000 radiocarbon years (Fig. 3a). The comparatively recent age of this bog can be attributed to the late uprise of the alluvial fan above sea level as a result of isostatic rebound of the South Patagonian landmass, and the simultaneous counter effect of sea-level rising. Excess activities of ^{210}Pb could be measured down to a depth of 16 cm, indicating that this core section covers approximately the past 100 yr. The highest excess activity of ^{210}Pb occurred in

the section 4–6 cm, decreasing more or less constantly down to a depth of 18 cm where no more unsupported ^{210}Pb activity could be detected (Fig. 3a). The increase in ^{210}Pb activity from the surface of the bog downward to 4–6 cm suggests that the ^{210}Pb is not entirely retained at the surface layer. We assume that the ^{210}Pb and also other atmospheric derived metals can move through the plant and root zone during changes of the water table and are finally accumulated in deeper sections where the peat becomes humified and dense, thereby restricting further migration. Accordingly, ^{210}Pb ages in our bog calculated by means of the CRS model give ages of ^{210}Pb deposition (or binding), not ages of peat accumulation. Due to the downward movement of ^{210}Pb in the uppermost peat sections the peat layers are always older than the ages of ^{210}Pb deposition. The ages of ^{210}Pb deposition calculated using the CRS model [26] suggest that the error resulting from the movement of the ^{210}Pb in the uppermost 5 cm of the core is in the range of about 30 yr (Table 1). This is the reason why only a maximum age of 64 yr was obtained for the deepest datable section instead of about 110 yr, which is the maximum age datable using ^{210}Pb. For comparison we have calculated ages based on the assumption that sedimentation rates and ^{210}Pb fluxes have been constant (CSCF model) within the sections 4–16 cm as indicated by the more or less constant decrease of unsupported ^{210}Pb activity in those sections. The mean sedimentation rate was then calculated based on the fitted exponential decrease of ^{210}Pb activity to 0.15 ± 0.2 cm yr^{-1}. Corresponding ages of the peat sections are given in Table 1.

3.2. Accumulation of mercury

Relative standard deviations of Hg analyses of the reference materials and selected peat samples range between 1.5 and 3.1% for $n = 4$. Highest Hg concentrations occur in the uppermost 16 cm of the core, which cover the past 100 yr of peat accumulation. During this period Hg concentrations increased from 80 to 100 μg/kg to a maximum of 156 μg/kg (Fig. 3a). This corresponds to an 18-fold increase of uncorrected Hg accumulation rates from mean pre-industrial levels of
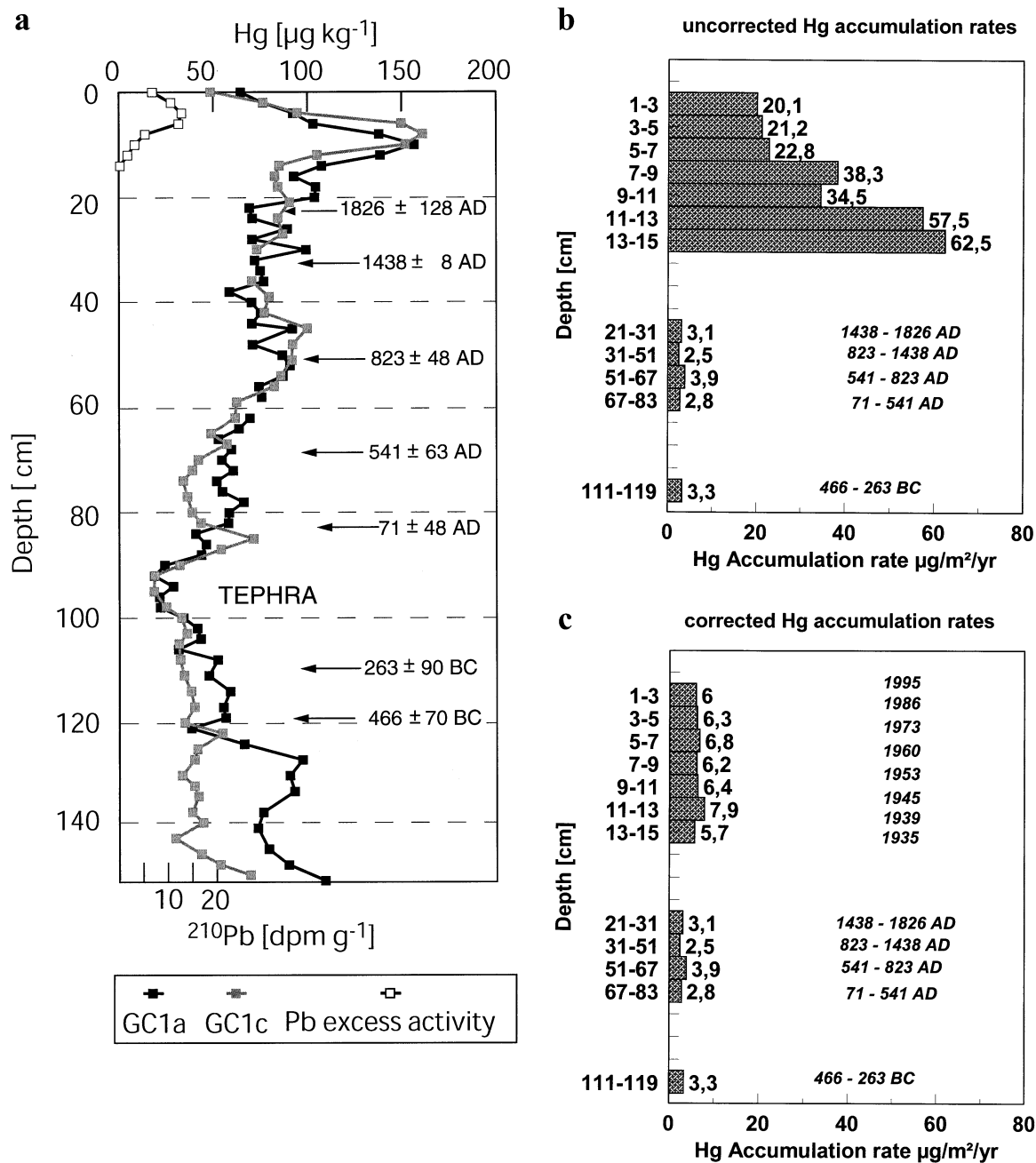
Fig. 3. (a) Records of Hg concentrations (GC1a and GC1c) in an ombrotrophic peat bog near the Gran Campo Nevado Glacier, Patagonia, Chile (53°S) and record of ^{210}Pb excess activity determined in the upper 20 cm. All other ages were obtained by means of ^{14}C AMS dating and are expressed as calibrated ^{14}C years (1σ-values). (b) Uncorrected net accumulation rates of Hg in selected sections of core GC1a calculated based on ^{210}Pb ages (CRS model) and (c) Hg accumulation rates corrected for differences in peat accumulation rates in high and low decomposed peat sections.

3.1 µg/m^2/yr to a maximum uncorrected rate of 62.5 µg/m^2/yr (range 20.1–62.5 µg/m^2/yr) during the past century (Fig. 3b). Hg accumulation rates decrease by factors between 3.4 and 11, ranging between 5 and 7.9 µg/m^2/yr if corrected for differences in peat accumulation (Fig. 3c). Accordingly, only a maximum increase of 2.5-fold is obtained in modern times compared to pre-industrial Hg accumulation rates when corrected accumulation rates were used.

The extent to which atmospheric Hg accumulation rates have been increased due to anthropogenic emissions to ombrotrophic bogs at various sites in the Northern Hemisphere varies from none [16] to a factor of more than 10 [18] depending on distance of the bogs to emission sources and meteorological conditions. Lindqvist et al. [30] reported modern Hg fluxes of 2–35 µg/m^2/yr for different regions in the Nordic countries. Mason et al. [2] estimated an average value of 16 µg/ m^2/yr for the Northern Hemisphere using data from several locations within North America, Asia and Europe. Moreover, they calculated that atmospheric Hg emissions during the 19th and 20th centuries have increased by a factor of 4.5 due to anthropogenic activity. Attributed to deposition of much of the emitted Hg near the emission sources and retention of Hg in soils, the net increase of the atmospheric Hg burden has only tripled [2]. The 2.6-times increase in net atmospheric Hg accumulation rates recorded in our peat bog is thus comparable to the inferred increase in atmospheric Hg fluxes for the Northern Hemisphere.

In the uppermost 8 cm of the cores Hg concentrations decrease from more than 100 to ∼65 µg/ kg, which is assumed to be mostly attributed to a low retention of Hg by the fresh or poorly degraded cushion plants and their roots in the uppermost 4 cm (Fig. 3a). If the section 4–6 cm is defined as the present accumulation zone of Hg (according to the record of unsupported ^{210}Pb excess activity), the highest Hg accumulation rates would have occurred around 1940. After the maximum, Hg accumulation rates decrease from 7.9 µg/m^2/yr to values between 6.2 and 6.8 µg/m^2/ yr (Fig. 3c). This trend of decreasing Hg accumulation rates in the upper section may reflect a trend of decreasing atmospheric Hg emissions from anthropogenic sources in the Northern Hemisphere in the past decades attributed to Hg emission prevention [6]. In Southeast Brazil the highest Hg accumulation rates in industrial times were reported to occur in the 1960s and 1970s. There, the maximum (uncorrected) accumulation rates were followed by a strong decrease from 80– 130 µg/m^2/yr to 20–30 µg/m^2/yr in the 1990s [12]. The recent increase in Hg emissions of 2.7–4.5%/ yr [28] from sources in the Southern Hemisphere are probably too low in terms of absolute quantities of Hg released to have a visible effect on the Hg deposition at the GC site.

We suggest that the increase in Hg deposition in the investigated bog must be attributed to anthropogenic emissions. We do not know any natural source or effect which could have produced such a strong increase in Hg concentrations in the upper part of an ombrotrophic peat bog. The coupling of Hg enrichment to redox processes of Fe and Mn compounds in sediments has been demonstrated and discussed in other studies [31]. The distribution of Fe and Mn in the peat profile do not give any indications that the distribution of Hg is related to that of Fe or Mn or any other element in the peat (Fig. 2d). Due to the remote location of the site it is reasonable that all atmospheric Hg deposited there was subject to long distance transport. It is so far not clear to which extent sources in the Northern and Southern Hemisphere, respectively, contribute to the anthropogenic Hg load which is transported to the remote south of South America. Mercury emissions from sources in the Northern Hemisphere account for more than 90% of total global emitted Hg from anthropogenic sources [32] and about 50% of the anthropogenic emissions appear to enter the global atmospheric Hg cycle [2]. Given the remote location of the Patagonian bog, the lack of any local or regional Hg sources, the extent of open ocean surrounding the region and the direction of the predominant wind systems, the peat bog at GC appears to record the changes in atmospheric Hg emission of the Northern Hemisphere. We conclude that Hg concentrations in the atmosphere at this latitude are primarily the result of intense atmospheric mixing and predom-

inantly reflect changes of atmospheric Hg concentrations on a global scale.

Since 540 AD Hg concentrations have increased from 40–60 μg/kg to 80–100 μg/kg (Fig. 3a). However, the calculated Hg accumulation rates do not show a continuous increase in the same period (Fig. 3b). Martinez-Cortizas et al. [19] observed an increase in Hg accumulation rates to a Spanish peat bog starting at about 1500 yr ago, which they assigned to the use of Hg in the first metallurgical revolution during the Islamic period. Lacerda et al. [12] also reported an increase of Hg accumulation in Northern Brazil during the Colonial period due to the use of Hg to extract silver and gold from soils and sediments. The absence of a comparable signal in the GC1 bog is probably due to its remote location.

Pre-industrial Hg accumulation rates of the GC1 peat (mean 3.1 μg/m^2/yr) are similar to those reported for sites in the Northern Hemisphere where values vary between 1.5 and 8 μg/m^2/yr with a mean of 3.3 ± 1.1 μg/m^2/yr [2,19]. They are also comparable to those reported for sites in Northern Brazil (0.7–2.6 μg/m^2/yr) [12]. These pre-industrial fluxes seem to be comparatively high considering the smaller landmass in the Southern Hemisphere, especially in the southernmost regions, compared to the Northern Hemisphere. However, we assume that the high precipitation rates are an important factor controlling Hg deposition at the GC site, and must be important at other sites also. In addition, the strong westerly winds produce high amounts of sea-salt aerosols in the atmosphere over South Patagonia. It is known from other studies that sea-salt aerosols, especially the high concentrations of chloride and bromide, can produce a significant percentage of reactive gaseous Hg (Hg(II)) through oxidation of Hg(0) in the marine boundary layer [33]. Hg(II) dissolved in rain droplets is more easily removed from the atmosphere by precipitation than gaseous Hg(0). The influence of other natural sources on the deposition of Hg to the GC-site is not yet known. Several studies have shown that there is a link between biological productivity and Hg evasion from the oceans, especially in sub-polar and polar areas [14,34]. The global contribution of

sea-salt aerosols to atmospheric Hg is estimated to be in the range of 20–40 tons/yr [35]. Similar fluxes have been estimated for atmospheric Hg emissions from volcanoes [36]. However, all those factors are considered to have been more or less constant throughout the past 3000 yr and neither of these could have produced a 2.5- or even 18-fold increase in Hg accumulation rates in the past 100 yr.

The lowest Hg concentrations in the peat core were found in the tephra layer (90–100 cm) which decrease from ca. 60 μg/kg in the peat to ca. 20 μg/kg in the tephra (Fig. 3a). It is not surprising that the tephra itself does not contain elevated Hg concentrations because of the high temperatures occurring during volcanic eruptions. Moreover, gases such as Hg emitted from volcanoes are to a large extent injected high into the stratosphere and are more likely to be deposited far from the volcano. The Mt. Burney volcano is only about 70 km away from the GC site. Thus, if volcanic emissions of Hg were locally important, they would certainly be seen in this peat profile. Due to the absence of a Hg signal which could be assigned to the Mt. Burney eruption we concluded that the amount of emitted Hg during this volcanic eruption is probably too low or too widely dispersed to produce a significant increase in Hg concentrations in the GC1 peat.

Pb is enriched in many peat bogs from the Northern Hemisphere due to anthropogenic emissions [37,38], but does not show any visible increase in concentrations or accumulation rates in the GC peat bog during the past 2000 yr (Fig. 2e). Transport and deposition of lead of anthropogenic origin to Antarctica has been shown in several studies [39,40]. Modern deposition rates of Pb to Antarctica were reported to be about 0.2 μg/m^2/yr [40]. More recent data indicate values between 0.64 and 2.73 μg/m^2/yr [41]. Pb fluxes from the atmosphere in the South Pacific region were estimated to be 20.7 μg/m^2/yr for the South Pacific Easterlies and 99.5 μg/m^2/yr for the South Pacific Westerlies [40]. Pb-isotopic data clearly indicate that most atmospheric lead in the South Pacific is of anthropogenic origin from sources in the Southern Hemisphere [40]. The influence of Pb emissions from the Northern Hemisphere is unim-

portant for the South Pacific because the interhemispheric transport of lead in both the troposphere and the ocean currents is minimal [40]. Pre-industrial Pb accumulation rates in the GC1 bog range between 27 and 66 µg/m^2/yr (mean 36.9 µg/m^2/yr). Mean corrected Pb accumulation rates in the past 100 yr were 32.9 µg/m^2/yr, which is in the range of pre-industrial accumulation rates. The study area is probably too remote from anthropogenic sources to show a Pb signal of anthropogenic origin. Pb fluxes of anthropogenic origin at the GC1 site are assumed to be more comparable to those found in Antarctica and are therefore too low to be detectable at the given background fluxes at the GC1 site. The absence of an anthropogenic Pb signal in the GC1 peat emphasizes the global dispersion of gaseous Hg as compared to Pb, which is dispersed on a hemispheric scale only.

3.3. Conclusions

Mercury accumulation rates in peat cores from the Magellanic Moorlands implicate an 18-fold increase in Hg deposition rates within the industrial age. Regarding the estimated three-fold increase of global atmospheric Hg concentrations in the same period and the absence of local Hg sources, this value is suggested to be overestimated. Mercury accumulation rates normalized to peat accumulation rates reveal only a 2.5-fold increase, which is comparable to the increase in atmospheric Hg concentrations. According to the generally observed increase of Hg emissions from anthropogenic sources within this period, this observation gives strong indication that the increase in Hg accumulation, even at this remote site, is attributed to anthropogenic emissions and long-range atmospheric transport. Other metals emitted from anthropogenic sources such as Pb, which are known to be transported in a particle bound form, do not show an increase in our bog during the industrial age. These findings emphasize the global dispersion of gaseous mercury if compared to other metals and confirms interhemispheric exchange of anthropogenic Hg. Earlier influences of Hg emissions from anthropogenic sources such as gold and silver mining in northern South America

could not be detected in the Magellanic Moorland peat.

References

[1] AMAP, Arctic Pollution Issues: A State of the Arctic Environment Report (1998).

[2] R.P. Mason, W.F. Fitzgerald, F.M.M. Morel, The biogeochemical cycling of elemental mercury: anthropogenic influences, Geochim. Cosmochim. Acta 58 (1994) 3191–3198.

[3] J.O. Nriagu, J.M. Pacyna, Quantitative assessment of worldwide contamination of air, water and soils by trace metals, Nature 333 (1988) 134–139.

[4] F. Slemr, E. Langer, Increase in global atmospheric concentrations of mercury inferred from measurements over the Atlantic Ocean, Nature 355 (1992) 434–437.

[5] M.H. Hermanson, Anthropogenic mercury deposition to arctic lake sediments, Water Air Soil Pollut. 101 (1998) 309–321.

[6] J.M. Pacyna, G.J. Keeler, Sources of mercury in the Arctic, Water Air Soil Pollut. 80 (1995) 621–632.

[7] P.E. Rasmussen, Current methods of estimating atmospheric fluxes in remote areas, Environ. Sci. Technol. 28 (1994) 2233–2241.

[8] W.F. Fitzgerald, D.R. Engstrom, R.P. Mason, E.A. Nater, The case of atmospheric mercury contamination in remote areas, Environ. Sci. Technol. 32/1 (1998) 1–7.

[9] W.F. Fitzgerald, Is mercury increasing in the atmosphere? The need for an atmospheric mercury network (AMNET), Water Air Soil Pollut. 80 (1995) 245–254.

[10] E. Steinnes, E.M. Andersson, Atmospheric deposition of mercury in Norway: Temporal and spatial trends, Water Air Soil Pollut. 56 (1991) 391–404.

[11] W.H. Schroeder, K.G. Anlauf, L.A. Barrie, J.Y. Lu, A. Steffen, D.R. Schneeberger, T. Berg, Arctic springtime depletion of mercury, Nature 394 (1998) 331–332.

[12] L.D. Lacerda, M.G. Ribeiro, R.C. Cordeiro, A. Sifeddine, B. Turcq, Atmospheric mercury deposition over Brazil during the past 30,000 years, Environ. Biodivers. 51 (1999) 363–371.

[13] W.F. Fitzgerald, C.H. Lamborg, A.W.H. Damman, J.M. Benoit, P.H. Balcom, Contemporary and historical Eolian depositional fluxes of mercury: Archival records in ombrothrophic bogs and lake sediments from Nova Scotia and New Zealand, Abstracts of the Fifth International Conference on Mercury as a Global Pollutant, Rio de Janeiro, Brazil, 1999, p. 551.

[14] G.M. Vandal, W.F. Fitzgerald, C.F. Boutron, J.P. Candelone, Variations in mercury deposition to Antarctica over the past 34,000 years, Nature 362 (1993) 621–623.

[15] P. Pheiffer-Madsen, Peat bog records of atmospheric mercury deposition, Nature 293 (1981) 127.

[16] A. Jensen, A. Jensen, Historical deposition rates of mercury in Scandinavia estimated by dating and measurements of mercury in cores of peat bogs, Water Air Soil Pollut. 56 (1991) 769–778.

[17] J.M. Benoit, W.F. Fitzgerald, A.W.H. Damman, Historical atmospheric mercury deposition in the mid-continental U.S. as recorded in an ombrogenic peat bog, in: J. Huckabee, C. Watras (Eds.), Mercury Pollution: Integration and Synthesis, Lewis Publishers, Chelsea, MI, 1994, pp. 187–202.

[18] S.A. Norton, G.C. Evans, J.S. Kahl, Comparision of Hg and Pb fluxes to hummocks and hollows of ombrotrophic Big Heath bog and to nearby Sargent Mt. Pond, Maine, USA, Water Air Soil Pollut. 100 (1997) 271–286.

[19] A. Martinez-Cortizas, X. Pontvedra-Pombal, E. Garcia-Rodeja, J.C. Novoa-Munoz, W. Shotyk, Mercury in a Spanish peat bog: Archive of Climate change and atmospheric metal deposition, Science 284 (1999) 939–942.

[20] B. Ruthsatz, C. Villagran, Vegetation pattern and soil nurients of a Magellanic moorland on the Cordillera de Piuchué, Chiloé Island, Chile, Rev. Chil. Hist. Nat. 64 (1991) 461–478.

[21] F. Roos, A. Martinez-Cortizas, M.E. Goodsite, H. Biester, W. Shotyk, An analytical protocol for the determination of mercury concentrations in solid peat samples, Sci. Tot. Environ. 292 (2001) 129–139.

[22] G.E.M. Hall, P. Pelchat, Evaluation of a direct solid sampling atomic absorption spectrometer for the trace determination of mercury in geological samples, Analyst 122 (1997) 924–924.

[23] W. Shotyk, A.K. Cheburkin, P.G. Appleby, A. Fankhauser, J.D. Kramers, Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland, Earth Planet. Sci. Lett. 145 (1996) E1–E7.

[24] D. Weiss, A.K. Cheburkin, W. Shotyk, M. Gloor, Determination of Pb in the ash fraction of plants and peats using the Energy-dispersive Miniprobe Multielement Analyzer (EMMA), Analyst 123 (1998) 2097–2102.

[25] A. Bollhöfer, A. Mangini, A. Lenhard, M. Wessels, F. Giovanoli, B. Schwarz, High-resolution ^{210}Pb dating of Lake Constance sediments: Stable lead in Lake Constance, Environ. Geol. 24 (1994) 267–274.

[26] P.G. Appleby, F. Oldfield, The calculation of ^{210}Pb dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment, Catena 5 (1978) 1–8.

[27] A.J. Francez, H. Vasander, Peat accumulation and peat decomposition after human disturbance in French and Finnish mire, Acta Oecol. 16 (1995) 599–608.

[28] W. Shotyk, Peat bogs archives of atmospheric metal deposition: geochemical assessment of peat profiles, natural variations in metal concentrations and metal enrichment factors, Environ. Rev. 4 (1996) 149–183.

[29] C. Stern, Tefrochronolgia de Magallanes: Nuevos datos e implicaciones, Ans. Int. Pat. Ser. Cs. Punta Arenas (Chile) 18 (1992) 139–146.

[30] O. Lindqvist, K. Johansson, M. Aastrup, A. Andersson, L. Brinkmark, G. Hovsenius, L. Håkanson, A. Iverfeldt, M. Meili, B. Timm, Mercury in the Swedish environment – Recent research on causes, consequences and corrective methods, Water Air Soil Pollut. 55 (1991) 261 pp.

[31] J.M. Matty, D.T. Long, Early diagenesis of mercury in the Laurentian Great Lakes, J. Great Lakes Res. 21 (1995) 574–586.

[32] N. Pirrone, G. Keeler, J.O. Nriagu, Regional differences in worldwide emissions of mercury to the atmosphere, Atmos. Environ. 30 (1996) 2981–2987.

[33] I.M Hedgecock, L. Forlano, N. Pirrone, Mercury, sunshine and sea-salt aerosol: Is it a recipe for cycling in the marine boundary layer?, Proceedings of the 11th Conference on Heavy Metals in the Environment, Ann Arbor, MI, USA, 2000, Contrib. 1005.

[34] J.P. Kim, W.F. Fitzgerald, Sea–air partitioning of mercury over the equatorial Pacific Ocean, Science 231 (1986) 1131–1133.

[35] J.O. Nriagu, A global assessment of natural sources of atmospheric trace metals, Nature 338 (1989) 47–49.

[36] W.F. Fitzgerald, Mercury emissions from volcanos, Abstracts of the Fourth International Conference on Mercury as a Global Pollutant, Hamburg, Germany, 1996, p. 87.

[37] H. Kempter, M. Görres, B. Frenzel, Ti and Pb concentrations in rainwater-fed bogs in Europe as indicators of past anthropogenic activities, Water Air Soil Pollut. 100 (1997) 367–377.

[38] W. Shotyk, D. Weiss, P.G. Appleby, A.K. Cheburkin, R. Frei, M. Gloor, J.D. Kramers, S. Reese, W.O. VanDer-Knaap, History of atmospheric lead deposition since 12,370 ^{14}C yr BP from a peat bog, Jura Mountains, Switzerland, Science 281 (1998) 1635–1640.

[39] A.R. Flegal, C.C. Patterson, Vertical concentration profiles of lead in the Central Pacific at 15 °N and 20 °S, Earth Planet. Sci. Lett. 64 (1983) 19–32.

[40] A.R. Flegal, H. Maring, S. Niemeyer, Anthropogenic lead in Antarctic sea water, Nature (1993) 242–244.

[41] D. Qin, P.A. Mayewski, B.W. Lyons, J. Sun, S. Hou, Lead pollution in Antarctic surface snow revealed along the route of the International Trans-Antarctic Expedition, Ann. Glaciol. 29 (1999) 94–98.