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# Effect of Peat Decomposition and Mass Loss on Historic Mercury Records in Peat Bogs from Patagonia

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Ombrotrophic peat bogs have been widely used to evaluate long-term records of atmospheric mercury (Hg) deposition. One of the major aims of these investigations is the estimation of the increase in atmospheric Hg fluxes during the industrial age compared to preindustrial fluxes. Comparability of Hg accumulation rates calculated from density, peat accumulation rates, and Hg concentrations requires linearity between these parameters. Peat formation is a dynamic process accompanied by intense mass loss and alteration of the organic material. Our investigations on three peat cores from the Magellanic Moorlands, Chile, indicate that Hg concentrations in peat strongly depend on peat humification. Moreover, differences in mass accumulation rates during peat evolution are not compensated by linear changes in density, peat accumulation, or Hg concentrations. We suggest that Hg accumulation rates be normalized to carbon accumulation rates to achieve comparability of Hg accumulation rates derived from differently altered peat sections. Normalization to the carbon accumulation rates reduces Hg accumulation rates in less degraded peat sections in the upper peat layers by factors of more than 2. Our results suggest that the increase in Hg deposition rates during modern times derived from ombrotrophic peat bogs are potentially overestimated if Hg accumulation rates are not corrected for mass accumulation rates.

## Introduction

Numerous studies have shown that human activities have dramatically increased the atmospheric load of heavy metals and other trace elements. Historic atmospheric deposition of trace elements is often investigated in ombrotrophic peat bogs (see, e.g., refs *1*−*5*). Interpretations of metal records are usually based on differences in concentrations or accumulation rates. Metal concentrations or accumulation rates, however, depend strongly on physical properties such as density or accumulation rates of the material and on time-dependent biogeochemical alteration processes. Such biogeochemical processes could be changing sedimentation rates or diagenetic processes such as gravitational compaction or in situ migration of the metals as a result of species transformation during changing redox conditions (*5*−*8*). As a consequence, accumulation rates or concentrations of an element in different core sections of a peat core are only comparable when normalized to all chemico-physical changes that have a direct or indirect influence on the concentration or accumulation of an element.

The advantage of ombrotrophic peat bogs compared to sediment cores is that they receive all elements exclusively from the atmosphere; thus, they show no catchment effects. Compared to ice cores, which have a limited geographical distribution, peat bogs are found in nearly all latitudes if precipitation is sufficient. One disadvantage is that the formation of peat is controlled by rates of plant growth and climate-dependent humification processes that can vary widely (*9*). Most ombrotrophic bogs consist of two different layers called acrotelm and catotelm that differ in the extent of humification of the plant material, mass loss, and redox conditions (*10*−*12*). Humification is accompanied by an intense mass loss ($>$80%), which is highest in the acrotelm (*13*), and the loss of mass and rate of humification decrease exponentially with increasing depth of the peat profile (*14*). In the catotelm, the loss of carbon can reach 50% within 1700 years and up to 65% within 7500 years (*15*).

These findings indicate that humification processes and mass losses during the diagenesis of peat might have a strong influence on metal concentrations or accumulation rates, especially if the metal is bound directly to functional groups of the organic matter. Influences of peat humification on metal accumulation rates are assumed to be compensated by appropriate changes in the peat density or in the metal concentration. It is generally assumed that metal accumulation rates, peat accumulation rates, densities, and Hg concentrations change linearily during peat evolution, so that the metal accumulation rate will be constant through time, independent of peat evolution. Two arguments, however, make this assumption appear doubtful. First, mass loss during peat evolution is not linear. Second, the density of dry peat is $\sim$0.05−0.1 g cm$^{-3}$, which is a factor of 10−20 lower than that of water. As a result, the density in the water-saturated part of the bog is determined by the density of water and can therefore not be expected to increase linearily by compression, as water cannot be compressed.

Mercury is a volatile metal that is widely dispersed through the atmosphere from local emission sources to remote pristine areas (*16*). The influence of anthropogenic emission on the global Hg cycle has been demonstrated (*17*−*20*). Mercury is known to form stable complexes with humic acids by being preferably bound to reduced sulfur groups (*21*). Thus, concentrations or accumulation rates of Hg in ombrotrophic bogs are predestined to be influenced by peat humification processes. Several studies on Hg enrichment recorded in peat bogs have shown that Hg accumulation rates and also Hg concentrations are dependent on site location, climate, or influences from natural or anthropogenic sources (see, e.g., refs *2*, *7*, *22*−*26*). Variations in Hg concentrations or accumulation rates between bog sites are generally assumed to be due to varying atmospheric fluxes. However, the extent to which variations in Hg concentrations or Hg accumulation rates in ombrotrophic peat bogs can be caused by internal diagenetic processes such as the humification of organic matter is presently unclear. In this study, peat profiles from three pristine ombrotrophic bogs of the

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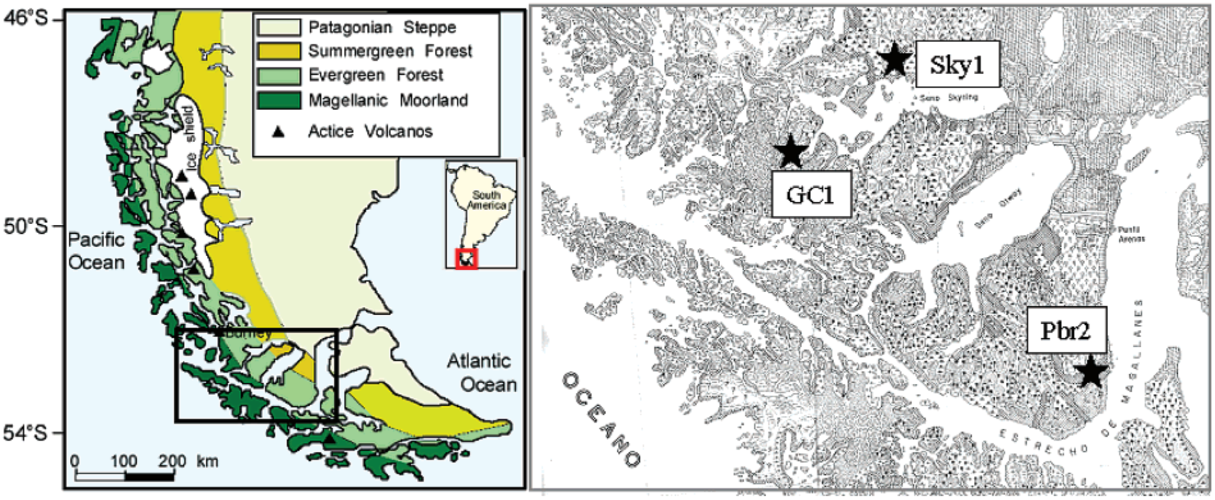

**FIGURE 1. Map of the study area and locations of sampling sites of three peat cores Pbr2, Sky1 and GC1 taken in the Magellanic Moorlands, Chile.**

Magellanic Moorlands, Chile, were analyzed for historic Hg concentrations and accumulation rates (Figure 1). To evaluate to which extent both parameters are influenced by peat humification processes, the Hg concentrations and accumulation rates in the peat were compared to carbon/nitrogen (C/N) ratios and the extent of mass loss as measures of peat degradation.

## Materials and Methods

**Characteristics of the Bogs and Geochronology.** The peat cores were taken from three bogs (GC1, Sky1, Pbr2) located in different climatic zones of the Magellanic Moorlands in southernmost Chile (Figure 1). The bogs show different trophic states in terms of availability of plant nutrients, as indicated by the different peat-forming plants. GC1 (52° 47.443′ S/72° 56.616′ W) is a cushion plant bog, which is typical for the super-humid study area. Cushion plants such as *Donatia fascicularis* and *Astelia pumilia* and some *Carex* species indicate a higher trophical level than *Sphagnum* bogs (*27*). The high supply of nutrients to this bog is attributed to the intense atmospheric deposition of sea-salt aerosols and the high precipitation rates (up to 8000 mm year$^{-1}$) in this area. *Sphagnum* mosses are mostly absent in the GC1 bog. Sky1 is a raised bog located in the transition zone between the extremely humid zone of the Magellanic Moorlands and the dry grasslands (52° 30.668′ S/72° 07.505′ W) (Figure 1). This bog is built up by cushion plants and *Sphagnum* moss. Because of the much lower precipitation rates at the Sky1 site (~1000 mm), the supply with nutrients is much lower than at the GC1 site allowing *Sphagnum* to grow. The Pbr2 bog (53° 38.281′ S/70° 58.029′ W) is a typical raised *Sphagnum* bog. Cushion plants are absent at this site, indicating that nutrient availability is generally low. All peat cores were sampled to the bottom of the bog. They differ in length and age range (Figure 2a−c) because of differences in altitude of the three sampling sites, which determine the beginning of peat growth after the last glaciation. As indicated by the ash record (Figure 3a−c), one or more tephra layers were found in all cores, which could be assigned to different eruptions of the volcanic Mts. Burney, Hudson, and Reclus, respectively, located in the southern Andes.

**Sampling and Sample Preparation.** All cores were taken at the highest elevation of the bogs, where hummocks and hollows and also trees were absent. The uppermost 2 m of the peat cores were sampled by means of a 10 × 10 × 200 cm stainless steel Wardenaar corer (*28*). Deeper sections were taken using a stainless steel Belarus corer with a 50 × 5 cm cylindric sample chamber. All cores were sectioned in the field and packed into polyethylene bags. GC1 was sectioned into 2-cm slices, whereas Sky1 and Pbr2 were sliced into 4-cm sections. A layer of about 1 cm was cut from each side of the core to avoid cross contamination due to smearing of material from the tephra layers. All samples were stored frozen. Half of each slice was freeze-dried and milled by means of a titanium centrifuge mill before analysis.

**Determination of Peat Bulk Density.** The bulk density of the GC1 core was determined from three subsamples, which were cut from the fresh peat slices in the field with an apple corer. Densities in sections from the uppermost 2 m of the Sky1 and the Pbr2 core were determined using a half slice of each section (5 × 8 × 4 cm). In deeper sections, those sampled with the Belarus corer, the density was derived from the whole sample, which was a half-cylinder with a thickness of 4 cm and a radius of 5 cm.

**Dating of Peat Samples.** The past 100 years were only dated in the GC1 core using $^{210}$Pb techniques. A detailed description of the dating techniques used here is given elsewhere (*26*). All other ages were obtained by $^{14}$C dating. 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, rev 4.0, test version 6 (data set 1). All ages are given as the means of the 1$\sigma$ values.

**Determination of Mercury, Carbon, Nitrogen, and Ash Concentrations.** Mercury concentrations were determined using atomic absorption spectrometry after thermal combustion of the freeze-dried samples (50−100 mg) and Hg preconcentration on a single gold trap by means of an AMA 254 soild-phase Hg analyzer (Leco). A detailed description of the method is given elsewhere (*29*). Standard reference materials (NIST 1515 apple leaves, 44 ± 4 $\mu$g kg$^{-1}$ Hg; BCR 281 olive leaves, 20.5 ± 1.9 $\mu$g kg$^{-1}$ Hg) were used for quality control. Relative standard deviation (RSD) of the determination of Hg in selected peat samples and reference materials range between 1.5 and 4.8% ($n = 4$). Results for the reference materials were always within the standard deviation of the certified value.

Carbon and nitrogen concentrations were determined by means of a C/N analyzer (Elementar) burning 10−20-mg sample aliquots in a tin capsule. Mean RSDs of the determination was 2.2% for C and 2.1% for N ($n = 3$). The ash content was determined from the weight loss of a ~2-g sample following ashing at 550 °C for 3 h.

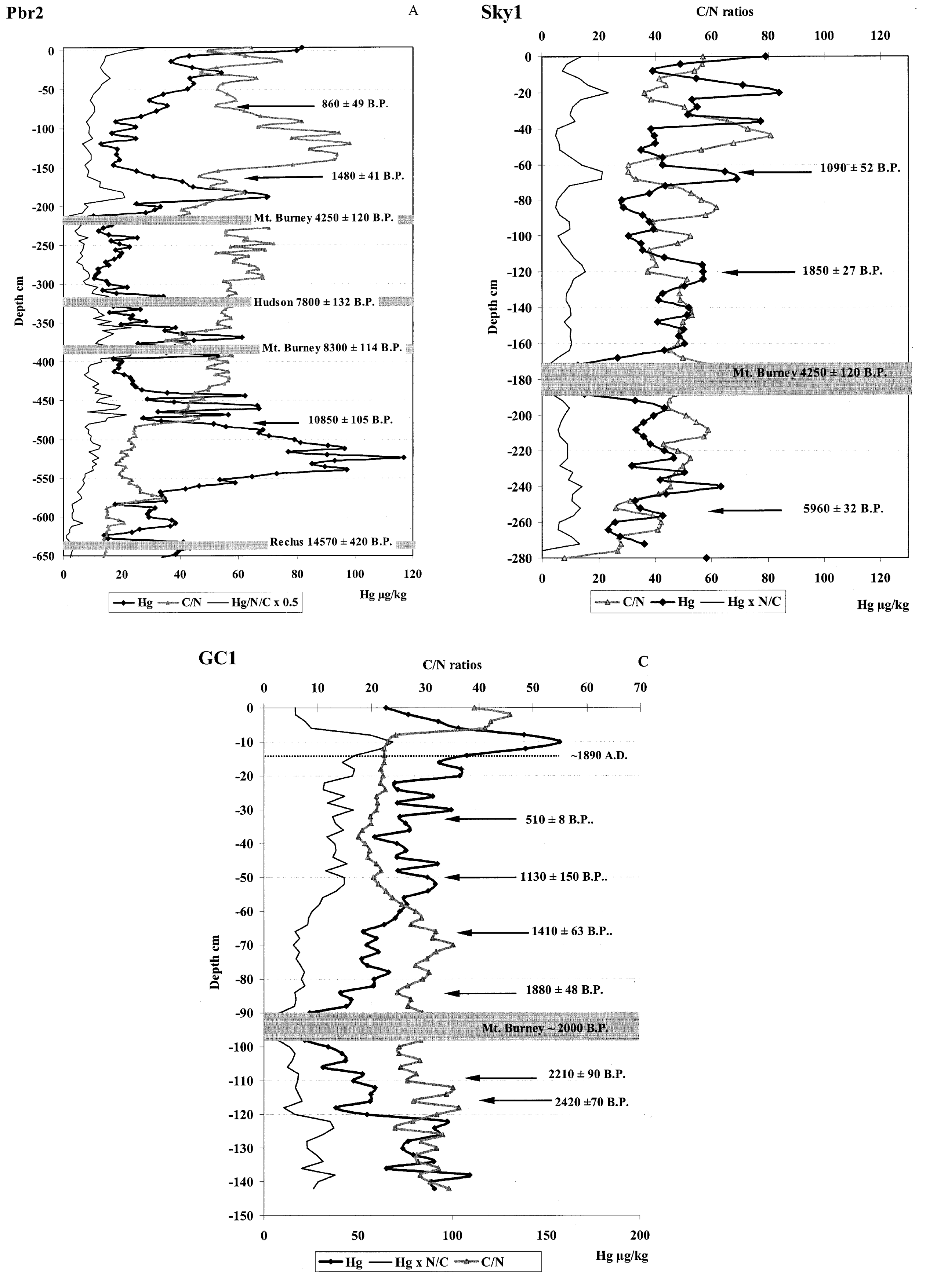

**FIGURE 2. Peat chronology, Hg concentrations, C/N ratios, and Hg/N ratios in cores from three ombrotrophic peat bogs [(A) Pbr2, (B) Sky1, and (C) GC1] taken in different climatic zones of the Magellanic Moorlands, Chile. The relative standard deviation (RSD) of the Hg determination in selected peat samples and reference materials ranges between 1.5 and 4.8% ($n = 4$). The mean RSDs of the C and N determinations were 2.2 and 2.1% ($n = 3$), respectively. Gray bars mark tephra layers.**

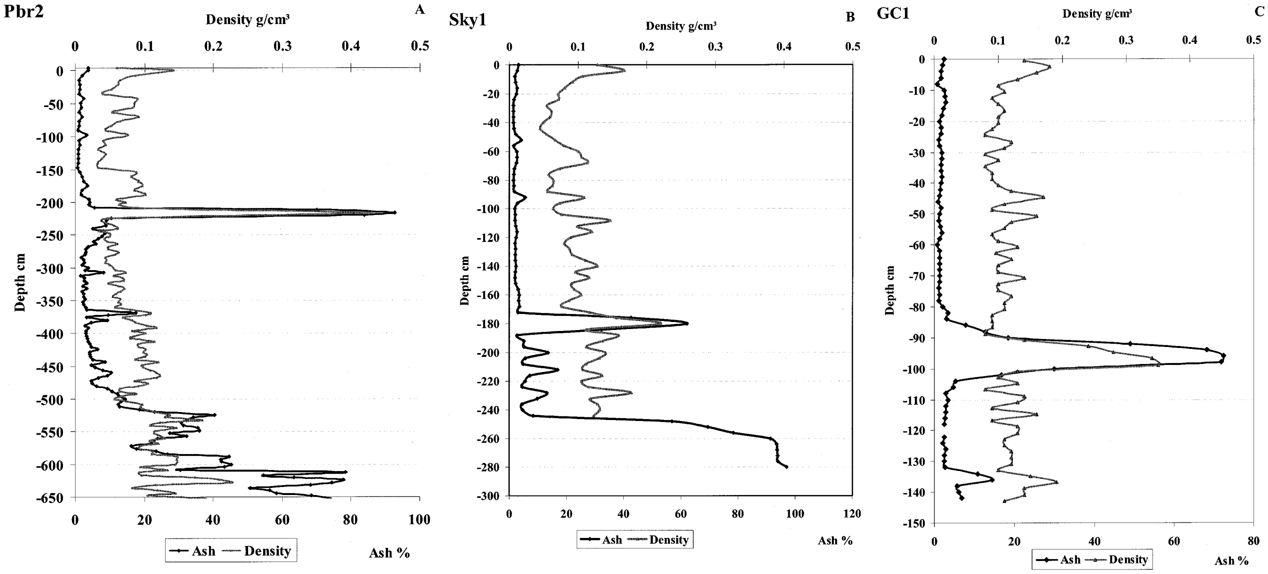

**FIGURE 3. Ash content and density in three ombrotrophic peat cores [(A) Pbr2, (B) Sky1, and (C) GC1] taken in different climatic zones of the Magellanic Moorlands, Chile.**

## Results and Discussion

**Ombrotrophic Nature of the Bogs.** The low ash contents (<4%) (Figure 3b), low pH's (<4), and low calcium concentrations (data not shown) in all three bogs indicate their ombrotrophic character, which means that all elements were supplied exclusively by atmospheric deposition. All three cores show minerogenic conditions in their deepest part, as indicated by the high ash contents (Figure 3a−c) and increased element concentrations (data not shown). A more detailed description of the geochemical composition of the GC1 cushion plant bog regarding its ombrothrophic nature is given elsewhere (*26*).

**Mercury Concentrations.** The Pbr2 core shows the lowest Hg concentrations of the three bogs, ranging between 3.2 and 81.7 $\mu g^{-1}$ kg (mean 29.2 $\mu g\ kg^{-1}$) in the ombrotrophic part of the core (Figure 2a). The Hg concentrations increase strongly in the sections 147−216 cm, 316−324 cm, and 364−372 cm. The record of ash (Figure 3a) and the chronology of the bog (Figure 2a) indicate that those Hg enrichments appear above three tephra layers that could be assigned to two eruptions of Mt. Burney [8300 BP (I) and 4250 BP (II) (*31*)] and one eruption of Hudson volcano [7800 BP (*30*)]. Mercury concentrations also increase from approximately −10 cm to the top of the core. This increase is assumed to be due to the increase in atmospheric Hg concentration during the industrial age and could also be observed in the other cores (Figure 2a−c). A more detailed discussion of anthropogenic influences on the deposition of Hg in this area is found elsewhere (*26*).

In the minerogenic part of the Pbr2 core (480−580 cm), the Hg concentrations increase significantly up to 116 $\mu g\ kg^{-1}$, which we attribute to Hg from rock weathering. Previous studies have shown that minerogenic bogs can be strongly enriched in Hg derived from rock weathering and atmospheric deposition in the catchment as a result of the high retention of Hg in peat (*32*).

In the Sky1 core (Figure 2b), the Hg concentrations are higher and more variable than those in Pbr2. The mercury concentrations vary between 9.5 and 84 $\mu g\ kg^{-1}$, with a mean of 43 $\mu g\ kg^{-1}$ (Figure 2b). The largest variation in Hg concentration (disregarding the tephra layer) appears in the upper 100 cm of the core, where the concentration varies by a factor of up to 2.5. The ash record of the Sky1 core shows the Mt. Burney (II) tephra layer at a depth of 190 cm (Figure 3b). A slight increase in the ash content at 96 cm probably indicates deposition of volcanic ash from another but later Mt. Burney eruption (~2000 BP). In contrast to Pbr2, no increase in Hg concentrations could be observed above the tephra layers in Sky1. Moreover, the Hg concentrations do not generally increase in the minerogenic section (240−280 cm) of Sky1 (Figure 2b). The basal layer underlying this bog consists of clay of glacial origin, which is an unlikely source of Hg.

In the GC1 core, the Hg concentrations are the highest of the three cores, varying between 19 and 157 $\mu g\ kg^{-1}$ with a mean of 71 $\mu g\ kg^{-1}$ (Figure 2c). The core also shows a Mt. Burney tephra layer at 90 cm, which was dated to 2000 BP (*26*). Similarly to Sky1, the Hg concentrations do not increase above the tephra layer as it was observed in Pbr2 (Figure 2a). The average Hg concentrations in GC1 increase slightly at 1410 BP (70 cm) from 58 to 77 $\mu g\ kg^{-1}$ (55 cm). A high Hg peak (156 $\mu g\ kg^{-1}$) is found in the uppermost 15 cm, which was dated to cover the past 100 years and was suggested to reflect the increase in atmospheric Hg concentrations during the industrial age (*26*). The differences in Hg concentrations between GC1 and the other two bogs is assumed to be related to the high precipitation rates at the GC1 site, which are at least 5 times higher than those at the Sky1 and Pbr2 sites.

**Influences of Volcanic Eruptions.** In all three cores, the Hg concentrations were found to be lowest in the tephra layers, indicating that the tephra contains only very small amounts of Hg. Volcanic emissions are suggested to be an important natural source of atmospheric Hg. The increasing Hg concentrations above the tephra layers in the Pbr2 core might imply that the volcanic eruptions caused increased Hg deposition to this bog. However, the fact that such enrichment is absent in the other two bogs indicates that other sources or processes must have caused the Hg enrichments above the tephra layers in the Pbr2 bog. The Hg enrichment above the Mt. Burney II tephra layer in the Pbr2 core covers about 2800 years (Figure 2a). A volcanic eruption, however, is only a short event and would not last longer than several weeks or months. Even if the eruptions are accompanied by high Hg emissions, a Hg signal from such an eruption should cover no more than 2 years because the residence time of Hg in the atmosphere is 1−2 years (*18*). Global mercury emissions from volcanoes have been estimated to be less than 100 tons per year (see, e.g., ref *33*). We

**TABLE 1. Changes in Density, Peat Accumulation Rates, Carbon and Mercury Concentrations, Carbon and Mercury Accumulation Rates, and Mass Loss Correction Factors (MLCFs) in Peat Cores Taken at Three Different Sites (Pbr2, Sky1, GC1) in the Magellanic Moorlands, Chile**

| core | section (cm) | age[a] (years) | peat accum. (cm year$^{-1}$) | density (median) (g cm$^{-3}$) | carbon concn (median) (%) | carbon accum. (g m$^{-2}$ year$^{-1}$) | Hg conc. (median) ($\mu$g kg$^{-1}$) | Hg accum. ($\mu$g m$^{-2}$ year$^{-1}$) | MLCF[b] |
|---|---|---|---|---|---|---|---|---|---|
| Pbr2 | 0–63 | 860 | 0.057 | 0.074 (0.064) | 53.2 (51.9) | 28.8 | 48.5 (43.2) | 2.63 | 0.48 |
| | 63–147 | 620 | 0.133 | 0.05 (0.043) | 51.3 (50.2) | 34.8 | 22.5 (19.1) | 1.5 | 0.39 |
| | 147–216 | 2770 | 0.025 | 0.078 (0.084) | 56.7 (54.8) | 11.01 | 37 (31.2) | 0.72 | 1.24 |
| | 216–480 | 6600 | 0.036 | 0.075 (0.069) | 45.7 (45.4) | 13.7 | 26.9 (22.5) | 0.81 | reference |
| Sky1 | 0–68 | 1090 | 0.062 | 0.084 (0.075) | 44.6 (45) | 23.3 | 54.8 (52.5) | 2.85 | 0.65 |
| | 68–120 | 760 | 0.069 | 0.086 (0.075) | 46.7 (48) | 27.5 | 39.2 (38.1) | 2.3 | 0.55 |
| | 120–244 | 4110 | 0.026 | 0.113 (0.111) | 44.3 (50) | 15.1 | 39.5 (42.6) | 1.2 | reference |
| GC1 | 4–18 | 110 | 0.127 | 0.11 | 45.3 | 64.6 | 122.8 (107.7) | 17.2 | 0.43 |
| | 32–120 | 1910 | 0.046 | 0.12 (0.11) | 51.2 (46.9) | 27.5 | 67.7 (59.8) | 3.4 | reference |

[a] Calibrated radiocarbon years. [b] Calculation of MLCFs is based on the differences in carbon accumulation rates between less degraded peat sections and a reference section for highly decomposed peat.

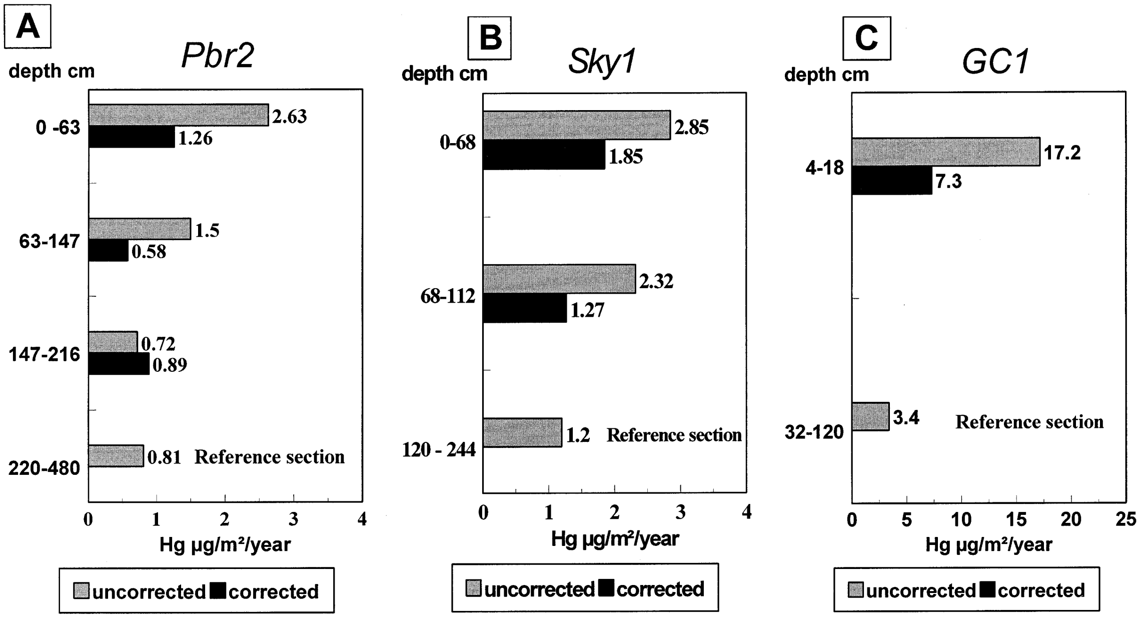

**FIGURE 4. Mercury accumulation rates in three ombrotrophic peat cores [(A) Pbr2, (B) Sky1, and (C) GC1] before and after correction for mass losses occurring during peat decomposition. Corrected Hg accumulation rates were obtained by normalizing the carbon accumulation rates in less degraded peat sections to that of a reference section of highly decomposed peat.**

assume that the amount of Hg emitted from a single volcano or the time resolution of our bogs is too low to produce a clear Hg signal of a volcanic source located so far away (70–150 km). The record of Hg accumulation rates calculated for the Pbr2 core (Table 1) shows that the strong Hg enrichment above the Mt. Burney (II) tephra layer is unlikely to be due to an increase in Hg deposition, as the Hg accumulation rate of 0.89 $\mu$g m$^{-2}$ year$^{-1}$ is only slightly higher than the mean Hg accumulation rate determined for older peat sections (Figure 4a). We will show later that the increase in Hg accumulation above the tephra layers in this core is a result of increased peat humification.

**Natural Sources and Processes of Hg Enrichment in Peat.** Preanthropogenic Hg enrichments in ombrotrophic peat bogs have been explained by external sources or processes only. Cold climates combined with increased biological production have been suggested to increase Hg emissions from the oceans, especially in high latitudes (*34*). The enrichment of metals in ombrotrophic peat due to internal processes such as humification or mass loss has been widely ignored. Many characteristics of peat such as density or accumulation rate could be altered by the decomposition of organic material through humification or mineralization. The humification of peat is largely an abiotic process. Decomposition by microorganisms is limited because of the lack of nutrients in the peat and the low pH (*9*). The C/N ratios in peat are an indicator of the degree of humification, where low C/N ratios indicate high peat humification and vice versa. Here, we used C/N ratios to examine the relationship between Hg concentration and peat humification.

**Connection between Hg Concentration and Peat Humification.** Figure 2a–c shows the record of C/N ratios compared to that of Hg concentrations in the three investigated bogs. These plots show that Hg enrichments in core sections dated to preanthropogenic times correspond to comparatively low C/N ratios, which indicate higher peat decomposition. The low C/N ratios found above the tephra layers in the Pbr2 core provide a strong indication that the increased peat humification is related to the deposition of the tephra (Figure 2a). We suggest that, as a result of nutrient-rich mineral deposition, the peat bog reached a higher trophic level, which allowed for enhanced microbial activity and more intense mineralization of the peat. The higher decomposition of the peat was accompanied by an increased loss of mass. Because of this mass loss, the peat accumulation rate decreased from a mean rate in the catotelm of 0.036 to 0.025

cm year$^{-1}$ in the section 147−216 cm (Table 1). McCulloch and Davies (*35*) investigated a peat core from Puerto del Hambre near the Pbr2 site and interpreted the higher peat humification above the 4250 BP tephra layer as a result of drier climatic conditions during which the bog became dry. If a bog falls dry, peat humification increases when the upper peat layers become aerated. Regardless, our data clearly indicate that the enrichment of Hg in this section is connected to the humification process expressed by the low C/N ratios. Comparable results were obtained for halogenes (TOX) in these cores (*36*).

The GC1 and the Sky1 profiles, however, do not show any increase in Hg concentrations, nor do they show increased peat humification above the tephra layers (Figure 2b,c), which argues against the theory that climatic changes caused the increased peat humification in section 147−216 cm of Pbr2 as stated by McCulloch and Davies (*35*). The absence of a Hg peak above the tephra layers and the fact that GC1 and Sky1 are located even closer to the Mt. Burney volcano than Pbr2 confirm that the Hg enrichments in Pbr2 are not directly attributable to Hg emissions from the volcanoes.

We assume that the different trophic levels of the two different kinds of peat bogs are the reasons for the absence or the occurrence of Hg enrichments due to increased peat decomposition. Again, GC1 and Sky1 are cushion-plant-dominated bogs with higher trophical levels and higher supplies of nutrients (sea spray) compared to the Pbr2 bog, which is an oligotrophic *Sphagnum* bog that is poor in nutrients. For that reason, the cushion-plant bog GC1 and the mixed-plant bog Sky1 show generally lower mean C/N ratios than the Pbr2 peat (27, 47, and 57, respectively) according to the more intense peat humification in the GC1 and Sky1 bogs (Figure 2a−c). Because of the generally high peat humification rates in GC1 and Sky1, we assume that the deposition of tephra does not further increase the humification of the peat by supplying additional nutrients, which could, in turn, increase Hg concentrations. The large difference in peat humification between the three bogs is shown by the observation that even the highest C/N ratio in GC1 is still lower than the lowest C/N ratio in Pbr2. These data indicate that the Hg enrichment above the tephra layers in Pbr2 is solely an internal process related to increased peat decomposition.

The C/N ratios in Sky1 vary widely, especially in the upper 1 m of the core, which corresponds to varying Hg concentrations (Figure 2b). As in Pbr2, the C/N ratios are inversely related to the Hg concentrations. The reasons for the different peat humification rates in this bog are unknown. As Sky1 is located in the transition zone between wet and comparatively dry climates (Figure 1), changing precipitation rates and temporary drying of the bog might have caused the differences in peat humification.

The GC1 core shows generally low variations in C/N values compared to Pbr2 and Sky1 (Figure 2c). However, even for GC1, the C/N ratios run inversely to the Hg concentrations. Here, the Hg concentrations decrease from about 160 $\mu$g kg$^{-1}$ at 10 cm to 65 $\mu$g kg$^{-1}$ in the uppermost 2 cm. Such a decrease in Hg concentrations might be interpreted as decreasing Hg concentrations in the atmosphere as a result of Hg emission control in the industrialized nations during recent decades. However, the increase of the C/N ratios in this section provides a strong indication that the low Hg concentrations can be attributed to low peat humification in the uppermost peat sections and to generally low Hg retention in the less degraded plant material (Figure 2c). This indicates that atmosphere-derived Hg is not retained initially on the bog surface but in the section where the plant material becomes humified.

These findings suggest that the concentrations of elements that undergo enrichment during peat humification are only comparable when normalized to the same degree of humification. Linear corrections of the Hg concentration records for C/N or N/C ratios (nitrogen is the more varying component) were found to have only a minor effect, indicating that this parameter alone does not entirely compensate for all humification effects (Figure 2a−c).

**Peat Humification and Hg Accumulation Rates.** In the literature, interpretations of Hg records in peat bogs are usually based on Hg concentrations and Hg accumulation rates as well. However, the records of Hg concentrations in our bog samples have shown that changes in Hg concentrations in peat can be independent of external fluxes. Accordingly, only Hg accumulation rates can give true indication of changes in Hg fluxes to a bog. Mercury accumulation rates in peat are calculated on the basis of age, peat accumulation, density, and mean Hg concentration of a peat section. The use of these parameters to compare Hg accumulation rates in different peat layers assumes that the relationships among them are always linear. The problem of calculating accumulation rates of an element based on this linearity is that peat decay is accompanied by an intense mass loss, which is assumed to decrease exponentially with increasing depth and age of the bog (*14*).

Because most of the peat consists of organic material that is about 50% carbon, concentrations and accumulation rates of carbon are suggested to reflect changes in peat humification and related mass losses in bogs. Table 1 shows peat accumulation rates in different sections of the three cores compared to their densities and carbon accumulation rates and concentrations. All three cores show a distinct increase in peat accumulation in their upper parts. This increase in peat accumulation marks the transition between high-humified (HHP) and low-humified (LHP) peat. The rates of C and Hg accumulation both show a strong increase in the same LHP sections compared to the values found in the HHP sections (Table 1). To compare accumulation rates and concentrations of C and Hg in LHP with those of HHP, we set the mean peat accumulation rate, the mean density, and the mean carbon concentration in the deeper sections of catotelm as reference values (sections containing tephra layers were excluded from this calculation). The assumption for this calculation is the observation that humification and mass-loss processes in the catotelm become slow in the HHP sections when compared to the LHP sections (*15*). Moreover, we assume that peat from the low-humified sections will show the same properties as HHP after undergoing the same evolution.

Reference values of mean accumulation rates of peat, C, and Hg in HHP in Pbr2 were calculated from the 216−480 cm section (reference section). The peat above the Mt. Burney II tephra (147−216 cm) was seen as a special case because of its minerogenic properties and was excluded from the calculation of reference values. In the Pbr2 63−147 cm section, the Hg accumulation rates increase 2-fold, whereas the mean Hg concentrations decrease only 1.2-fold compared to the reference section (Table 1). In the same section, peat accumulation rates increase by a factor of 3.7, whereas the mean density decreases by only a factor of 1.5. A similar situation was observed for carbon, which shows a 2.7-fold increase in accumulation rates whereas C concentrations increase only 1.1-fold. Additionally, the C/N ratios increase from 53.8 to 77.5, indicating comparatively low peat humification in this section.

A comparable situation was found in the other two cores. In Sky1, the Hg accumulation rates increase by a factor of about 2 and peat accumulation rates by a factor of 2.7 between the reference section (120−244 cm) and the 68−120 cm section, whereas the mean Hg concentration does not change, and the mean density decreases by only a factor of 1.3 (Table 1). Similar changes were found in all dated LHP sections in

Pbr2 and Sky1, when compared to the values found in their HHP reference section.

In the upper 16 cm (4−18 cm) of the GC1 core, the Hg accumulation rates increase by a factor of 5 from 3.4 to 17.2 $\mu$g m$^{-2}$ year$^{-1}$, whereas peat accumulation rates increase by a factor of 2.8. The mean density does not change much in this section, but the mean Hg concentration increases by a factor of more than 2. In this case, the increase in Hg accumulation in the uppermost part of the GC1 core could not be explained by higher peat humification as it is not correlated with low C/N ratios. The GC1 core might show an increase of atmospheric Hg related to anthropogenic sources as mentioned above (*26*). These results show that the changes in peat accumulation rates, densities, carbon concentrations, and accumulation rates in peat cores are nonlinear during humification (Table 1).

Assigning the 2-fold increase in preindustrial Hg accumulation rates observed in the Sky1 and Pbr2 cores solely to external factors would mean that atmospheric Hg concentrations in the atmosphere of the Southern Hemisphere must have increased to the same extent. There are some arguments that make the conclusion of a 2-fold increase in atmospheric Hg concentrations in preindustrial times appear questionable. A colder climate that could have increased Hg deposition rates through higher biological production in the oceans as proposed by Vandal et al. (*34*) can be excluded, as a colder climate would have decreased the peat accumulation. Climatic changes such as increased precipitation could not increase Hg deposition rates to such a large extent, given that a large portion of atmosphere-derived Hg in soils can be due to dry deposition. No other natural process has been reported that can reconcile such a large increase in atmospheric Hg concentrations.

We conclude that the high peat accumulation rates in the LHP sections led to an overestimation of Hg accumulation rates. The comparison of peat accumulation rates and C/N ratios shows that high peat accumulation rates are in most cases accompanied by low peat decomposition. From this observation, we also conclude that the changes in peat and Hg accumulation rates between LHP and HHP in our bogs are due to the mass loss occurring during peat decay. The carbon accumulation rates and C/N ratios in the three bogs show that both parameters become more or less constant in the ombrotrophic part of the catotelm, indicating that the humification process and the related mass loss has become slow (Table 1).

Because changes in peat humification affect the concentrations and accumulation rates of Hg in peat, we suggest that all parameters affected by humification processes should be normalized to the same degree of humification. In this way, accumulation rates of Hg calculated for different sections of a peat core can be compared consistently. The data in Table 1 indicate that the peat accumulation rate has the strongest effect on the calculation of Hg accumulation rates and is, therefore, the most important parameter to be normalized. Normalizing the peat accumulation rates in a peat core means that climatically related differences in biomass production are neglected. The total mass loss of the plant material in the acrotelm can exceed 90% (*13*). Thus, the accumulation of peat in the catotelm is determined predominately by mass loss during humification and only to a small extent by climatically induced variation of biomass production. Accordingly, peat accumulation rates in LHP sections have to be normalized to that in HHP sections to correct for mass loss.

**Calculation of Mass Loss Compensation Factors.** We propose a calculation of mass loss compensation factors (MLCFs) based on the mass balance of carbon in the bog because the accumulation of carbon predominately determines the accumulation of peat. The MLCF normalizes all peat accumulation rates to the same degree of humification and mass loss by referring the carbon accumulation rates of individual peat sections to that of a reference section of highly humified peat. The ratio between the carbon accumulation rate of the reference section and that of an LHP section gives the MLCF (eq 1)

$$\mathrm{MLCF} = \frac{\dfrac{P_{\mathrm{ref}}\rho_{\mathrm{ref}}\mathrm{cC}_{\mathrm{ref}}}{t_{\mathrm{ref}}}}{\dfrac{P_{\mathrm{i}}\rho_{\mathrm{i}}\mathrm{cC}_{\mathrm{i}}}{t_{\mathrm{i}}}} = \frac{\mathrm{aC}_{\mathrm{ref}}}{\mathrm{aC}_{\mathrm{i}}} \qquad (1)$$

where $P_{\mathrm{ref}}$ is the peat accumulation of the reference section, $\rho_{\mathrm{ref}}$ is the mean density of the reference section, $\mathrm{cC}_{\mathrm{ref}}$ is the mean carbon concentration of the reference section, $t_{\mathrm{ref}}$ is the age of the reference section, $P_{\mathrm{i}}$ is the peat accumulation of the LHP section, $\rho_{\mathrm{i}}$ is the mean density of the LHP section, $\mathrm{cC}_{\mathrm{i}}$ is the mean carbon concentration of the LHP section, $t_{\mathrm{i}}$ is the age of the LHP section, $\mathrm{aC}_{\mathrm{ref}}$ is the carbon accumulation rate of the reference section, and $\mathrm{aC}_{\mathrm{i}}$ is the carbon accumulation rate of the LHP section.

This factor must be calculated separately for each dated LHP section. Uncorrected Hg accumulation rates multiplied by the MLCF give the corrected Hg accumulation rates. This calculation considers only the loss of the bulk mass, which is mostly carbon and oxygen, and changes in density but neglects the behavior of other elements. Accordingly, this calculation is valid only for element that are known to be mostly immobile in the bog, as is assumed for Hg (Hg reemission rates from buried peat are assumed to be low). Other elements might be released from the organic matter during humification and, therefore, depleted in sections of increased humification. The consequence of normalizing peat accumulation based on averages derived from a reference section in HHP is that the Hg accumulation rates in sections of high peat decomposition where peat accumulation rates are lower than in the reference section will increase through the mass loss correction. However, it is clear that this increase is not due to higher Hg deposition rates, but rather shows how differences in humification can affect Hg accumulation rates and the difficulty in obtaining an estimation of true atmospheric fluxes. The 147−216 cm section above the Mt. Burney II tephra in the Pbr2 core represents a special case. Here, the peat accumulation rate is distinctly lower than in the reference section because of the higher peat decomposition and mass losses. As a consequence, the correction for mass loss based on carbon accumulation increases the Hg accumulation rate from 0.72 to 0.89 $\mu$g m$^{-2}$ year$^{-1}$, which is an overestimation.

Figure 4a−c illustrates the Hg accumulation rates in the three cores before and after correction for mass losses. The correction leads to a decrease in Hg accumulation rates of between 35 and 61% with a mean of 51%, where the highest decrease is observed in the 63−147 cm section of the Pbr2 core. Nevertheless, all three cores still show an increase in Hg accumulation rates in the uppermost dated sections by factors between 1.6 and 2.2 as compared to their reference sections in the catotelm. The increase in atmospheric Hg in the industrial age was calculated to be a factor of about 3 compared to preindustrial levels (*18*). The past 100 years were only dated in the GC1 core, where the $^{210}$Pb activity was sufficiently high because of the high precipitation rates at this site. The Sky1 core shows a $^{210}$Pb activity below the detection limit. $^{210}$Pb activity in the Pbr2 core has not yet been determined. The uncorrected average Hg accumulation rate in the past 110 years (upper 18 cm) derived from the GC1 core indicate a 5-fold increase if compared to preindustrial dated core sections (Figure 4c). This is nearly a factor of 2 higher than the reported 3-fold net increase of atmospheric Hg concentrations in the same period. The corrected values, however, indicate a maximum increase by a factor of 2.2, which is more similar to the reported net increase in atmospheric Hg (*18*). In Sky1 and Pbr2, the Hg accumulation rates increased by only a factor of ~1.6 during the past 850−1100 years. Because of the large time span covered by the uppermost dated section in these cores, the stronger increase in Hg deposition expected for the past 120 years is assumed to be averaged out.

This study has shown that records of concentrations and accumulation rates of Hg in peat bogs are strongly influenced by biochemical alteration of the peat during humification. As a result of the strong binding of Hg to humic substances, the Hg concentrations in peat were found to increase as a result of mass losses during humification. Mercury concentrations were found to increase drastically above tephra layers in oligotrophic *Sphagnum* bogs as a result of high peat degradation induced by high nutrient supply from the tephras. Accordingly, the variations in Hg concentrations in peat do not necessarily reflect the variations in external Hg fluxes to the bog, and the use of Hg concentrations to interpret changes in atmospheric Hg fluxes is questionable. Moreover, less degraded peat sections in ombrotrophic peat bogs tend to overestimate Hg accumulation rates when compared to more degraded peat sections, which have lost considerable amounts of mass. Normalization of Hg accumulation rates to rates of carbon accumulation reduces Hg accumulation rates in less degraded peat in the upper peat sections by factors of more than 2. Our results suggest that the increases in modern times in Hg deposition rates derived from ombrotrophic peat bogs are potentially overestimated if the Hg accumulation rates are not corrected for mass accumulation rates. There are strong indications that the accumulation rates of other metals should also be normalized to mass accumulation rates to provide comparable results.

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