Natural mercury enrichment in a minerogenic fen—evaluation of sources and processes†

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Mercury (Hg) records in natural archives such as peat bogs are often used to evaluate anthropogenic or climatic influences on atmospheric Hg deposition. In this context, there is an ongoing discussion about natural sources or processes of Hg enrichment in natural archives. In the present study we estimated Hg fluxes from rock weathering, direct atmospheric deposition and from indirect atmospheric deposition in the catchment of a pristine minerogenic fen (GC2) located in the Magellanic Moorlands, southernmost Chile. The Hg record in the bog covers 11 174 cal. ^{14}C years and shows Hg concentrations of up to 570 µg kg^{-1} with an average of 268 µg kg^{-1}. Hg was found to be enriched in the peat by a factor of 81 if compared to the mean Hg concentrations in the rocks of the catchment (3.2 µg kg^{-1}). Hg and also Pb, Fe, and As were found to be enriched predominantly in goethite layers indicating high retention of these elements in the bog by iron oxyhydrates. It could also be demonstrated that the high peat decomposition rates in minerogenic bogs can increase the Hg concentrations in the minerogenic peat by a factor of approximately 2 at the same atmospheric Hg deposition rate if compared to ombrotrophic sites. This study has shown that Hg in minerogenic peat can be naturally enriched especially through the retention by autochthonous formed goethite and can be a solely internal process which does not require increased external Hg fluxes.

Introduction

In recent years increasing attention has been given to atmospheric deposition rates of mercury (Hg), as obtained from natural archives such as lacustrine sediments, peat bogs, and soils. The main reason for these investigations has been the evaluation of the anthropogenic impact on the global Hg cycle and the dispersion from industrial sources to pristine remote areas.

Besides investigations on the increased fluxes of Hg due to anthropogenic activity, there is an increasing interest in the evaluation of natural processes such as volcanic eruptions or climatic factors which may increase Hg deposition rates (e.g. refs. 1–5). The best archives for these studies concerning atmospheric deposition are those, which are only exposed to the atmosphere and not to soil erosion and surrounding ground and surface water systems. Several studies have shown raised bogs to fulfill these requirements and therefore to be excellent archives.[5–13] But for archives like fens, sediments, or soils, not to mention the deeper minerogenic part of raised bogs, non-atmospheric sources have to be taken into account. Hence, an accurate database about natural background levels and their variations are necessary to understand the relative importance of the globally dispersed Hg versus local sources.[14,15] One potential natural source of Hg might be weathering of bedrock. Roulet and Lucotte[16] have shown that high amounts of Hg in soils could be released through the weathering of Fe oxyhydrates. Moreover, fluxes of atmosphere-derived Hg from a catchment into natural sinks such as lakes or wetlands can enrich Hg in the sediments.[17–20] This process is also reported for other heavy metals such as U, Cu, and Ni.[21–23] There, the high amounts of organic material in the wetlands work as a filter and the most important process of metal retention is binding to humic acids which are ubiquitous in peat bogs.[23]

Furthermore, internal processes within the peat have to be taken into account. Recent results from Biester et al.[24] have shown that differences in peat humification and mass accumulation rates during peat evolution affect the calculation of Hg accumulation rates. Moreover, the role of early diagenetic processes is still not completely clarified. Fitzgerald et al.[15] hypothesise that Hg neither shows direct nor indirect enrichment in sediments affected by diagenesis. However, Hg is known to have a high adsorptive affinity to iron and manganese oxyhydroxides,[16,25–27] which are diagenetic influenced compounds. Moreover, Matty and Long[28] have shown that the reduction of iron and manganese oxides and also the humification of organic material lead to the release of mercury.

The aim of our study was the investigation of possible external and internal processes leading to Hg enrichments in a fen of southernmost Patagonia, Chile. For this, we considered three different external sources and pathways: direct atmospheric deposition, indirect atmospheric deposition within the catchment – called focusing, and weathering of Hg-bearing rocks within the catchment. To evaluate the direct atmospheric input we have used Hg data from a raised bog of the same area.[10] For internal processes we accounted Hg enrichment due to peat decomposition with consequential mass loss and diagenesis.

Methods and material

Description of the sampling site

The Gran Campo Nevado study area is located in the Magellanic Moorlands in the southernmost part of Chile (Fig. 1). The area is characterized by fjords and glaciers and constantly strong western winds and extremely high precipitation rates of up to 9000 mm per year. The Magellanic
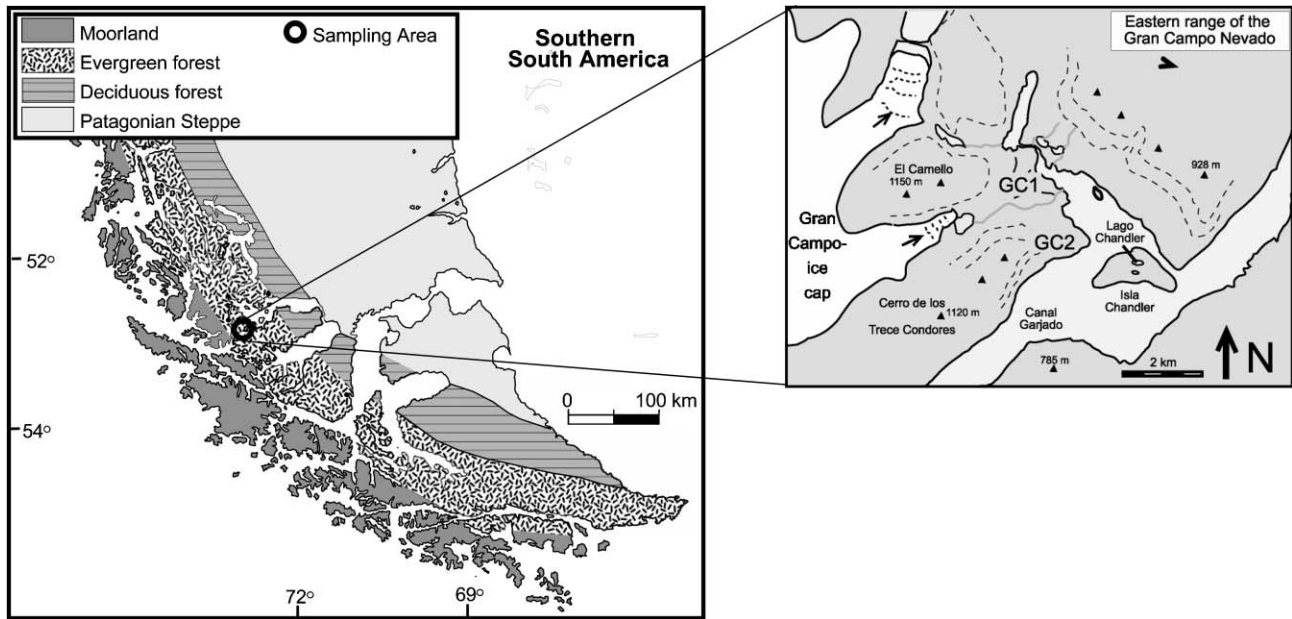
Fig. 1 Location of the sampling sites. GC1 sampling site of the ombrotrophic peat core. GC2 sampling site of the minerogenic peat core.

Moorlands are uninhabited and remote and the dominant westerly winds exclude influence from local or regional anthropogenic sources.

The fen (GC2) (S 52°48′36″/W 72°55′45″) is located in a basin between Roches Mountonées at a mountain slope in a height of about 70 m above sea level. The fen covers an area of about 120 × 80 m and has a maximum depth of approximately 2 m. The recent dominant plants are *Carex* species and the cushion plants *Donatia fascicularis* and *Astelia pumilia*. The peat is underlain by an approximately 70 cm layer of greyish clay. The fen is surrounded by different rocks, mainly phyllite and argillite, which have a total rock surface of about 100 000 m². However, approximately 50% of the catchment's surface area is wetland itself. An ombrotrophic peat bog (GC1) where direct atmospheric Hg fluxes were derived from is located at a distance of about 1 km in a straight-line to the GC2 fen. Further information on GC1 is given elsewhere.[10]

Sampling and sample preparation

Two peat cores were taken by means of a 10 × 10 × 200 cm stainless steel Wardenaar corer.[29] The length of the peat monoliths were about 190 cm, respectively. The cores were cut into 2 cm slices in the field using a serrated stainless steel bread knife. A layer of 1 cm was cut off from each side of the slices to avoid cross contamination attributed to smearing of material, especially from tephra layers. All samples were packed into polyethylene bags and stored deep frozen. Before analysis approximately half of each slice was freeze-dried and milled by means of a titanium plant mill.

Bulk density was determined from three subsamples of each slice, which were cut in the field from one of the cores using a stainless steel apple corer with a cross section of 2.9 cm². Rock samples were taken from exposures in the vicinity of the peat bogs. A sample of each rock type was crushed using a jaw breaker and pulverized in a disc-oscillating mill for 10 s. Additionally, pyrite crystals were separated from the phyllitic rocks and crushed in an agate mortar.

Metal analysis

Mercury concentrations were determined using atomic absorption spectroscopy after thermal combustion of the freeze-dried sample (approximately 50 mg) and Hg pre-concentration on a single gold trap using an AMA 254 solid phase Hg-Analyzer (LECO). Parameters of the Hg analysis were 70 s for drying, and 150 s for decomposition. The rock powder and the crushed pyrite crystals were analyzed for Hg using the same method as for the peat samples but with other parameters (drying time: 10 s, decomposition time: 400 s).

The standard reference materials NIST 1515, $44 \pm 4 \mu g \, kg^{-1}$ (apple leaves) and BCR 281, $20.5 \pm 1.9 \mu g \, kg^{-1}$ (olive leaves) and the non-certified in-lab reference P4 (minerogenic peat, $90 \pm 10 \mu g \, kg^{-1}$) were used for validating the Hg measurements.

Se, Br, Cu, Ti, and As in peat and Ti, Se, Br, Cu, As, Mn, Fe, and Pb in rock samples were determined directly in the solid material by means of an energy-dispersive miniprobe multi-element analyzer – EMMA-XRF.[30] Fe, Pb, and Mn in peat were determined by means of Flame-AAS after about 500 mg of each sample had been digested in *aqua regia* as the high concentrations of these elements in several peat sections cause strong interferences during EMMA-XRF measurements.

Determination of density, ash content, and crystalline components

For the determination of the peat density the peat cylinders were dried at 105 °C to constant weight. The dry weight and the known volume of the peat cylinders were used for the calculation of the density. For the determination of the ash content, about 500 mg of each sample were calcined at 550 °C for 3 h. Inorganic crystalline components in the peat were identified by means of X-ray diffraction (AXS-Bruker D-8; EVA, version 6).

Dating of peat sections

Five peat sections (38–40, 50–52, 116–118, 144–148, and 190–192 cm) were dated by means of ¹⁴C AMS using plant macrofossils which were obtained by sieving 2 g of the wet peat through a 1 mm meshed sieve to remove roots from the peat. ¹⁴C activity was determined in humic acid extracts and in the humic acid extraction residues. Conventional ¹⁴C-ages, defined after Stuiver and Polach[31] were calibrated using CALIB rev4.0, test version (data set 1).[32] All measurements were carried out at the Leibniz Laboratory Kiel, Germany.

Results and discussion

Characterization of the peat

Geochemical indicators such as the pH value, the ash content, or the concentrations of some typical elements such as Ca or Ti which can indicate influences of run-off, can be used to distinguish between minerogenic and ombrotrophic peat bogs.[9] The mean pH value was in the peat range from 4.6 to 6 and the average ash content was about 34% (min. 5%; max. 60%). In particular the high ash content in the peat clearly identifies the peat as being minerogenic. Ombrotrophic peat usually shows much lower ash content (1–5%) and lower pH values (<4). According to the high ash content, concentrations of lithogenic elements such as Ti and Zr (mean: 3672 and 50 mg kg^{-1}, respectively) and most other metals are much higher than that typically found in ombrotrophic sites confirming the minerogenic conditions in this bog.

Geochronology and peat accumulation

The ^{14}C-ages of the dated peat sections show that the profile spans the entire Holocene with basal date of 11 174 cal. ^{14}C years. The profile is marked by a 8 cm thick, coarse grained tephra layer at about −60 cm depth, which was identified as a Mt. Burney eruption at about 4250 BP.[33,34] The peat accumulation was more or less constant between 11 174 BP and the Mt. Burney eruption in 4250 BP and generally low (approximately 0.018 cm per year). After the eruption, the peat accumulation broke down for about 1500 years (0.005 cm per year) and subsequently rose again for the last 1000 years.

Concentration profiles of metals and arsenic in the bog

The Hg concentrations in the peat vary between 100 and 570 μg kg^{-1} with an average of 268 μg kg^{-1} (Fig. 2). Hg is enriched in several layers with highest concentrations in depths between 22 and 46 cm (with local maxima of 475 μg kg^{-1} in a depth of 24 cm and 543 μg kg^{-1} in 40 cm) and between 136 and 162 cm (with local maxima of 569 μg kg^{-1} in 142 cm and

571 μg kg^{-1} in 158 cm). Apart from the bottom and the top of the profile, lowest Hg concentrations are 200 μg kg^{-1} (RSD = 1.2 − 4%; $n = 3$).

The records of Fe, Pb, and As in the GC2 bog also show a layerwise enrichment in the peat and the highest Hg concentrations are partially associated with the enrichment of these elements (Fig. 3). The lithogenic elements Fe, Pb, and As are derived from the weathering of the basement or surrounding bedrock whereas other elements such as Hg or Br could also be derived from atmospheric deposition in the catchment.

Lithogenic elements such as Ti and Zr, show extreme enrichments in some sections of the core with maximum concentrations of 6460 mg kg^{-1} and 138 mg kg^{-1} (30 cm), respectively (data not depicted) indicating deposition of mineral matter in the bog.

Mercury sources and fluxes

The record of Hg concentrations determined in the GC2 peat correspond to deposition rates between 3.6 and 15.1 μg m^{-2} per year, with an average of 6.8 μg m^{-2} per year, which is twice as high as deposition rates determined in the ombrotrophic bog GC1 (3.4 μg m^{-2} per year).[10]

Mercury fluxes to the GC2 fen can be attributed to three major sources which are direct atmospheric deposition to the bog, fluxes of Hg from atmospheric deposition in the catchment of the fen (focusing) and fluxes of Hg released through weathering of the rocks in the catchment.

The part of Hg derived from direct atmospheric deposition to the GC2 fen could not be calculated directly from the Hg record in the GC2 peat but was indirectly obtained from the ombrotrophic peat bog (GC1) which is located in the same area about 1000 m distant from the GC2 fen (Fig. 1), so the same atmospheric inputs could be expected. This ombrotrophic peat bog derives all elements exclusively through atmospheric deposition. The average pre-industrial (3000 BP – ca. 1850 AD) rate of direct atmospheric Hg deposition in the Gran Campo Nevado area ranges between 2.5 and 3.9 μg m^{-2} per year with an average of 3.4 μg m^{-2} per year based on the Hg
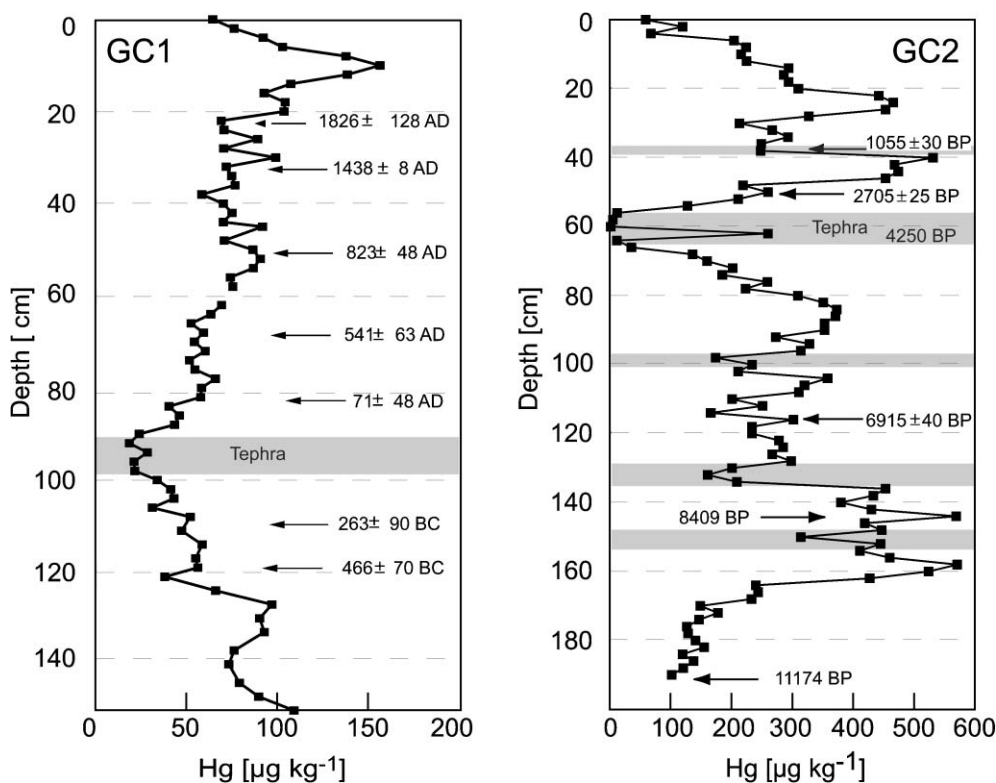

Fig. 2 Record of Hg concentrations and geochronology in the GC1 and GC2 peat cores.
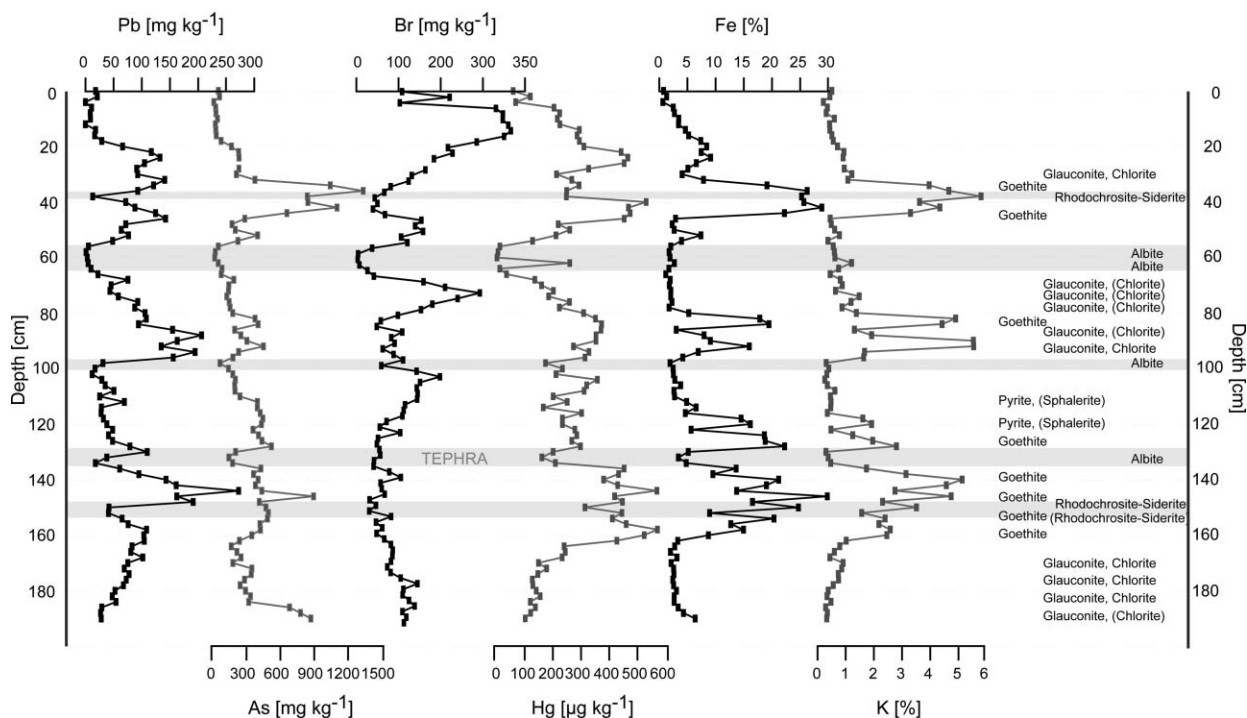
Fig. 3 Records of Pb, As, Br, Hg, Fe, and K concentrations, and mineral phases in the GC2 peat core.

record in the GC1 bog. A detailed description of the geochemistry of the GC1 bog is given elsewhere.[10]

Direct atmospheric Hg deposition does therefore contribute about 50% (3.4 μg m^{-2} per year) of the total Hg accumulation rate (6.8 μg m^{-2} per year) in the GC2 fen. This calculation assumes that the atmospheric Hg deposition rate between 11 000 and 3 000 BP – which is not covered by the GC1 Hg record – is more or less the same as that between 3000 BP and 1850 AD.

In this context it should be mentioned that Hg concentrations alone are of minor importance for the evaluation of Hg records in peat bogs. A process that can lead to an increase in Hg concentrations in minerogenic peat bogs is a higher peat decomposition rate as compared to ombrotrophic bogs. The higher decomposition of the organic material, leads to the enrichment of several elements, especially those which are bound to organic matter such as sulfur, nitrogen and many metals including Hg, which is known to be tightly bound to reduced sulfur groups of humic acids.[35] Accordingly, the mean calculated Hg concentration in the GC2 fen which corresponds to an atmospheric Hg deposition rate of 3.4 μg m^{-2} a^{-1} is 130 μg kg^{-1} which is a factor of about two higher than the mean Hg concentration of 63 μg kg^{-1} in the ombrotrophic GC1 bog, clearly indicating the causal relationship between peat decomposition and Hg enrichment.

The fact that 50% of the total Hg is derived directly from the atmosphere entails that the other 50% are contributed by the two other sources and pathways - indirect atmospheric deposition and weathering of rocks. With the current data, it is not possible to calculate the exact proportion of these two sources. However, the direct atmospheric deposition staying the same over at least the last three thousand years implies that the indirect atmospheric depositions stay the same too and that there are no dramatic climatic variations which would result in a change of weathering rates.

To evaluate whether there is a Hg contribution from rock weathering, we have analyzed different types of bedrocks within the catchment. Two types of rocks exist in the surrounding area: phyllite and argillite, with phyllite being the dominant one. It mainly consists of quartz and feldspar and contains, just as the argilites, pyrite-crystals.

The pyrite crystals of the phyllite show Hg concentrations of 20 ± 1 μg kg^{-1} ($n = 5$). The total rock contained 3.15 ± 0.2 μg kg^{-1} ($n = 4$). The argilites, which contain more pyrite than the phyllites, show total Hg concentrations of 8.5 ± 1 μg kg^{-1} ($n = 3$). Hence, we consider, that most of the Hg contained in the rocks is associated with pyrite. During weathering of the rocks the pyrite is oxidized and reacts to goethite due to the interaction with oxygen-rich waters. Together with other weathering products like *e.g.* clays (glauconite) and chlorite the goethite is transported to the bog. An indication for this process being probable is the occurence of goethite (FeOOH), pyrite (FeS$_2$), glauconite (KMg(Fe,Al)$_3$(SiO$_3$)$_6$·3H$_2$O), and chlorite ((Mg,Fe)$_3$(Al,Si)$_4$O$_{10}$(OH)$_8$·(Mg,Fe,Al)$_3$ (OH)$_6$) as inorganic components within the peat profile (Fig. 3).

While goethite can be formed during the transport or even after deposition of the elements in the peat, the other iron containing phases (glauconite and chlorite) are already formed during weathering rather than after deposition of the elements. The good correlation between K and Fe (correlation coefficient, Fe–K: $r^2 = 0.84$) emphasises the elements originating from the same mineral forming one weathering product (glauconite). Mercury shows a similar trend, but does not correlate with the other elements as well (Fe–Hg: $r^2 = 0.57$). The sections of Hg enrichment are not as distinctive as those of K and Fe, but rather blurred. The relatively low correlation coefficient between Fe and Hg may be influenced by several factors but the spatial coincidence of Fe and Hg peaks is a strong argument for particulate import of Hg into the fen.

Table 1 shows the element enrichment factors in the peat calculated from mean element concentrations in the peat and the rocks occurring in the catchment of the bog. Calculation of mean element concentrations in the rocks is based on a ratio of 30:1 for the occurrence of phyllite and argilites in the catchment.

The high variation of enrichment factors reflects the different retention of the elements by the peat and the different phases (aqueous or solid) by which the elements are transported to the bog. Enrichment factors of lithogenic elements were found to be between 4 (Fe) and 30 (As). Much higher enrichment was found for Br (85) which is mostly derived from atmospheric washout and deposition of sea-salt aerosols.[36] Mercury shows

Table 1 Mean enrichment factors of Hg, Br, Fe, As, Pb, and Cu in the GC2 fen compared to mean concentrations in rocks in the catchment of the fen

	Hg/μg kg^{-1}	Br/mg kg^{-1}	Fe (%)	As/mg kg^{-1}	Pb/mg kg^{-1}	Cu (%)
Means in peat	268	120	7.87	308.1	72.6	34.6
Means in rocks	3.32	1.41	1.82	10.4	6.29	1.95
Enrichment factor	80.7	85.1	4.32	29.7	11.5	17.8

an enrichment of about 81 which is similar to the value found for Br, indicating, that the largest part must come from atmospheric deposition (Table 1).

Further indications that the Hg input due to rock weathering is relatively low are the weathering rates. Using typical weathering rates of rocks found in the literature,[37,38] of which all range between 5 and 15 μm per year, maximal Hg input could be approximately 1.2 μg m^{-2} per year, which is 25% of the total Hg input. In fact, the real Hg input due to rock weathering is even much lower because most of the weathering products, including Hg, will already be retained within the catchment of the fen.

Hence, at least 25% of the total Hg input is due to fluxes of Hg from atmospheric deposition within the catchment of the fen.

Reasons for the layer-wise enrichments

As mentioned above K, Fe, As, Pb, and Hg show similar trends of concentration within the profile (Fig. 2 and 3). These elements are all enriched in particular layers and not throughout the profile. But as stated above, it is improbable that these peaks are a result of changes in elemental deposition rates but are rather due to internal processes. Fe and As are known for showing diagenetic-caused enrichments due to changing redox conditions.[39,40] However, the fact that K and Pb, which do not show this effect, are also enriched in the same sections, is an indication against the theory of redox dependent enrichments but hints to deposition of crystalline components. The determination of the crystalline phases showed that most

sections, where K, Fe, and As are enriched, mainly consist of glauconite and chlorite as minerals (Fig. 3 and 4). On closer examination of the K/Fe-enrichments it becomes apparent, that there are some sections in which Fe is more enriched relative to K. The distribution of the mineral phases in the core shows that in these sections only goethite occurs (Fig. 3). The goethite generally occurs in different sections than glauconite and chlorite. The reason for that is that goethite is at least partly not immediately formed during the weathering process but later on during the transport in the fluid phase or even only after the deposition of the Fe in the bog. This is confirmed by goethite concretions found within the fen, which have been formed along roots of *Carex* (Fig. 4). The formation of these tube-like concretions indicates that Fe^{2+} formed in the anoxic zone has been oxidized by oxygenated water transported downwards along the roots or due to oxidation processes in the root/peat contact zone. The fact, that goethite could also be detected in the reducing part of the profile could be explained by the metastability of goethite.

The question about early diagenetic processes as a cause for Hg enrichments comprises two different cases. On the one hand there is the direct Hg enrichment due to a variation of the redox state, as observed for other elements such as Fe, Mn, U, or As.[39,40] On the other hand an indirect dependency due to the adsorption of Hg on early diagenetic formed Mn- or Fe-oxyhydroxides. Whereas the direct Hg enrichment is seen to be unlikely[15] the redox dependent release or adsorption of Hg on diagenetic formed Mn- and Fe-oxyhydroxides has not yet been completely solved. Fitzgerald[15] stated that Hg peaks are independent from Fe or Mn enrichments. Hence, they
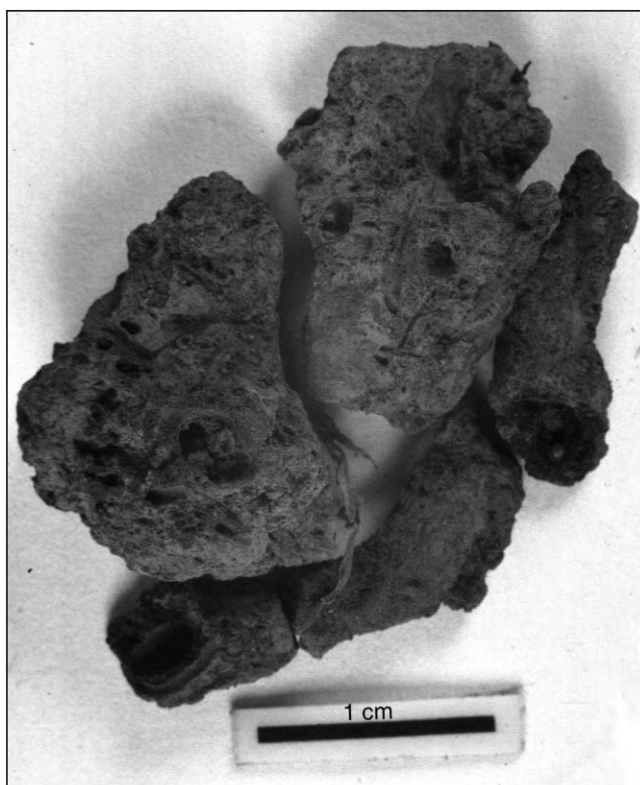

Fig. 4 Limonite/goethite tubes formed around *Carex* roots in the upper 20 cm of the GC2 peat bog.

conclude that there is no correlation between those elements. On the other hand, Matty and Long[28] show that the release of Hg from sediments could be coupled to the decomposition of organic matter and the reduction of Mn and Fe oxides. They also presume that these diagenetic-caused Hg fluxes are slight within organic-rich sediments with low decomposition rates.

Nevertheless, it is known that Hg has a high capability of being adsorbed onto the surface of Fe and Mn oxyhydroxides.[16,25–27] The records of Hg- and Fe-phases in the GC2 fen clearly show that there is a correlation between the Hg enrichments and the occurrence of the goethite layers. In environments where peaty soils occur, Hg is preferently transported as a soluble Hg-fulvo-acid-complex[41–43] which is also known to be effectively sorbed on goethite surfaces.[44]

These observations suggest two different explanations for the enrichment of Hg in the peat. First: under the assumption that the Hg fluxes to the peat are constant (otherwise they have to vary by a factor of more than 2 which is not reasonable) the retention of Hg in the goethite layers must be much more effective than in sections where only humified peat and no goethite occurs. Second: Hg is at least partly released and becomes mobile during the decomposition of the organic matter – as proposed by Matty and Long[28] – and is then readsorbed on freshly formed goethite.

One third explanation for the enrichment of Hg has to be considered. Enrichments might result from different peat decomposition rates at different times.[24] This would result in higher metal concentrations during periods of higher peat decomposition (or lower mass accumulation rates). Higher peat decomposition might for example occur during dry periods in which the water table and consequently the boundary between acrotelm and catotelm sinks, resulting in the decomposition of older material. This process would also explain the varying element and crystalline concentrations and the occurrence of the goethite layers because goethite is only being formed under oxic conditions.

If the enrichment of Hg is only due to a more effective sorption on goethite (compared to peat), it has to be considered that this means that the retention of Hg in the goethite free peat layers is less than 50% of all Hg transported through the bog. In this case the true Hg fluxes to the bog must not be calculated based on average Hg concentrations but on those of the Hg enriched goethite layers. The observations concerning the different Hg sources has shown that such high fluxes are not realistic. Accordingly, internal processes are suggested to be the main cause of the Hg enrichment in the peat.

Conclusions

This study has shown that mercury can be strongly enriched in minerogenic peat by natural processes. The lower peat accumulation rates in minerogenic peat were found to be a major factor for elevated Hg concentrations in minerogenic peat if compared to ombrotrophic sites, resulting in an enrichment factor of 2 for this case. Furthermore, there are additional Hg sources besides the direct atmospheric deposition, which accounts for approximately 50% of the total Hg input. The other 50% is due to fluxes from atmospheric deposition in the catchment of the fen and fluxes of Hg released through weathering of the rocks in the catchment, the latter amounting to only 25% at an outside estimate. Highest concentrations of Hg and also of Pb and As were associated with autochthonous formed goethite layers indicating effective retention of those elements by Fe-oxyhydroxides. Thus, the potential natural enrichment of Hg as a result of increased peat decomposition and/or retention by Fe-oxyhydroxides from run-off has to be taken into account if Hg enrichments in the minerogenic part of peat bogs are assigned to changes in atmospheric deposition rates attributed to anthropogenic emissions or climatic effects.

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