A Holocene record of mercury accumulation in a pristine lake in Southernmost South America (53° S) – climatic and environmental drivers

Y.-M. Hermanns and H. Biester

Institute of Environmental Geology, Technical University of Braunschweig, Langer Kamp 19c, 38106 Braunschweig, Germany

Received: 26 May 2011 – Accepted: 19 June 2011 – Published: 8 July 2011

Correspondence to: Y.-M. Hermanns (y-m.hermanns@tu-bs.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

© Author(s) 2011. CC Attribution 3.0 License.
Abstract

Mercury accumulation in lake sediments has been extensively studied with regard to anthropogenic signals, but natural processes controlling mercury accumulation in the past and the influence of environmental and climatic changes are still poorly understood. In this study we present a 17 300 years old record of mercury accumulation in lake sediments in combination with a multi-proxy investigation of climatic and environmental changes in Southernmost Patagonia (53° S). Mercury accumulation in the remote pristine lake has been highly variable (up to a factor of 16), clearly exceeding the anthropogenic forcing of atmospheric mercury fluxes (factor of 3–5). Statistical data evaluation based on Principle Component Analysis reveals that the dominant driver of variations in mercury accumulation along with other organically bound elements (e.g. copper and yttrium) has been leaching of soluble organic complexes from catchment soils. This indicates that changes in precipitation rates and soils leaching are the most important climatic driver for short term variations in mercury in the lake’s sediments. In the long term, however, mercury accumulation rates remain relatively constant (29 µg m⁻² yr⁻¹). This reflects that mercury accumulation in the catchment soils through atmospheric deposition and bedrock weathering has been fairly constant, too. As carbon storage in the soils and transport into the lake have increased, Hg/C ratios in the soil OM decreased. Fluxes of Hg into the lake are therefore mainly determined by the amount of OM leached into the lake and its Hg/C ratio.

1 Introduction

Mercury (Hg) cycling between the atmosphere, terrestrial and aquatic systems, has been extensively studied during the past years, mainly due to its toxicity and potential bioaccumulation. Many studies focussed on past changes of Hg accumulation rates (Hg_AR) using lake sediments as natural archives (Fitzgerald et al., 1998; Lamborg et al., 2002; Yang et al., 2010). It has been shown, that Hg_AR increased globally by a factor
of about 3–5 due to the release of anthropogenic Hg into the atmosphere during the past 150 years (Fitzgerald et al., 1998; Lamborg et al., 2002; Biester et al., 2007; Yang et al., 2010). Despite recent efforts to reduce industrial emissions, vast amounts of Hg are stored in top soils providing a major source for future elevated Hg fluxes to aquatic systems.

Mercury is known for its affinity to bind to organic matter (OM) and it was postulated that the entire biogeochemical cycle of Hg is tightly coupled to that of OM (Meili, 1991). It was observed, that the amount of Hg transported from a catchment into adjacent aquatic systems is regulated by the amounts of terrestrial OM fluxes (Driscoll et al., 1995; Kolka et al., 1999; Ouellet et al., 2009; Teisserenc et al., 2010), at which several studies especially emphasize the role of terrestrial dissolved organic matter (DOM) as a complexing agent for Hg (Driscoll et al., 1995; Ouellet et al., 2009). Lake sediments provide archives to study such interrelations, since they offer chronological records of Hg accumulation as well as OM accumulation from different sources (aquatic as well as terrestrial). Moreover, Hg signals in lake sediments have been shown to be stable during sediment diagenesis (Gälmann et al., 2008; Rydberg et al., 2008; Feyte et al., 2011). Teisserenc et al. (2010) have shown that Hg variations in several Canadian boreal lake sediment records were mainly controlled by the amounts of humic material derived from catchment top-soils. Recent studies on sediments of Arctic lakes on the other hand found an interrelation between increasing rates of in lake productivity, caused by Arctic warming, and a rise in Hg_{AR} in the sediments (Outridge et al., 2005, 2007; Sanei and Godarzi, 2006; Stern et al., 2009). It was concluded, that increasing production of aquatic OM, especially algae, which provide large adsorption capacity, enforces scavenging and subsequent accumulation of Hg and other organic associated elements in the sediments. However, the causal relationship between both trends (enrichment of Hg and the increase in aquatic bioproductivity) is still under debate. Kirk et al. (2011) investigated a set of 14 lakes in the Canadian High and Subarctic and did not find a clear interrelation between both processes in all lakes.
Although suggesting different “carriers” of Hg into the sediments, both processes (scavenging due to aquatic productivity and terrestrial OM fluxes into the lake) are to a vast extent controlled by climatic conditions. Rainfall intensity and frequency for example controls the mobilization of soluble organic matter from soils (Inamdar et al., 2006), coevally enforcing fluxes of nutrients into lakes. Rising temperatures on the other hand have been shown to stimulate the microbial induced production of DOM (Xu and Saiers, 2010) as well as the aquatic productivity within lakes, e.g. in the Arctic (Smol et al., 2005). Long term records encompassing several thousand years of Hg accumulation during changing climatic conditions, however, have been rarely investigated so far. Yet, intense natural variations in Hg concentrations (HgC) and HgAR have been observed, which are comparable to the recent anthropogenic forcing of the atmospheric Hg cycle by a factor of 3–5 (Cannon et al., 2003; Hare et al., 2010).

We propose that studying Hg accumulation along with paleo-records of environmental and climatic changes is one of the key approaches to improve our understanding of the biogeochemical drivers of Hg transport in lake systems and their response to climate change. This is especially important concerning the large amounts of “anthropogenic” Hg, which has been emitted and accumulated in the environment (especially organic topsoils) since the industrial era.

In this study we present a high resolution record of Hg accumulation in sediments of lake Hambre, South Patagonia, extending back to 17 300 cal yr BP. The data on Hg accumulation is combined with a multi-proxy investigation of climatic and environmental change, encompassing the transition from cold climates of the late Pleistocene towards the establishment of late Holocene climatic conditions. The comparison of HgAR with the sedimentary history of the lake will reveal the biogeochemical drivers of Hg accumulation in lake sediments and their relation to climate and environmental change.
2 Methods

2.1 Study site

Lake Hambre is located 50 km south of Punta Arenas next to the Strait of Magellan in Southernmost Patagonia (53° 36′ 13.19″ S, 70° 57′ 8.77″ W, Fig. 1). It is a small (surface area = 13 700 m²) and deep lake (depth = 17 m), with a catchment : lake ratio of 8. There are no inflows, but gullies in the catchment account for intermittent inflow during times of high precipitation. The lake is stratified at least once a year as noticed during the field campaign in March 2010. The geology surrounding the lake is dominated by schist. The lake is situated in the zone of subantarctic deciduous forest with *Nothofagus pumilio* and *Nothofagus antarctica* and numerous stumps all over the catchment account for clear-cutting of the forests, which happened about 100–200 yr ago. Before, there were no other disturbances due to anthropogenic activities. Precipitation is about 650–800 mm yr⁻¹ (Heusser et al., 2000) and the mean temperature is about 6.5 °C.

2.2 Sampling and analysis

A sediment core was recovered from the deepest part of the lake in 2008 using a 5 m long piston corer. Core sections were stored dark and cool (+4 °C) in the laboratory. After opening the core was photographed, described and sub-sampled for further geochemical analyses in 1 cm steps in the upper 470 cm and in 2 cm sections below. Bulk density was determined in 5 cm steps from 0–470 cm and in 10 cm from 470 cm to the bottom of the core using a plastic cylinder of known volume (3 ml). After correlation of overlapping core sections the total length of the record was 1414 cm.

The age depth model for the sediment record is based on 18 Accelerator Mass Spectrometry (AMS) ¹⁴C dates of terrestrial organic matter macro-fossils (leaves and wood, Table 1) as well as a Tephra layer of known age (Mt. Burney, 4250 cal yr BP, McCulloch and Davies, 2001). All ¹⁴C ages were calibrated with the Calib 6.0 software (Stuiver and Reimer, 1993; http://calib.qub.ac.uk/calib/) using the SHcal04 calibration curve.
(McCormac et al., 2004), except the four oldest ones. Here, the Northern Hemisphere calibration curve INTCAL09 (Reimer et al., 2010) was applied and 56 yr were added to every obtained calibrated age, to adjust them to the Southern Hemisphere ages (McCormac et al., 2004).

In addition plankton (>55 µm), terrestrial plants, rocks and soils were sampled to compare their chemical composition with that of the sediment.

Sediments and plant samples were freeze-dried, homogenized and analysed for Hg by CV-AAS after combustion of the sample and preconcentration of Hg by amalgamation using a DMA 80 Hg analyzer (milestone). Concentrations of carbon (C) and nitrogen (N) in the carbonate-free samples were determined by GC-TCD after thermal combustion in an elemental analyzer (Euro EA3000, Eurovector). Samples were analyzed for main and trace elements (Fe, Ti, Br, Ca, Sr, Y, Rb, Zr, Mn, Cu, Zn), using an energy-dispersive XRF miniprobe multi-element analyzer (EMMA, Cheburkin and Shotyk, 1996).

Principal component analysis (PCA) was applied to extract the geochemical signatures of the chemical composition of the sediment matrix and to get insights into the underlying factors accounting for them. The analysis was performed by means of the Z-scores transformation of the raw data (Z-score = (X_i - X_avg) / X_std, where X_i is a given value of a variable in a sample, X_avg is the average of that variable and X_std is its standard deviation). Z-scores allow keeping the relative variation of the original data while reducing all variables to a similar range of variation avoiding scaling effects.

The best solution was obtained with a varimax rotation, which is more restrictive with the variables associated to the principal components (i.e. maximizes the proportion of variance of the variables in the principal components). The square of the factor loadings was used as an estimation of the proportion of variance of each variable for each principal component.
3 Results and discussion

3.1 Geochronology

Radiocarbon dates used for the sediment chronology are shown in Table 1. For the calculation of the age model median values of the 2σ range were used. In addition the age of the Mt. Burney tephra (4250 cal yr BP, Mc Culloch and Davies, 2001; Stern, 2008) was included into the age depth model (Fig. 2). The model was obtained by fitting a two-order polynomial constrained to pass through the origin (Fig. 2). Figure 2 shows that all dates are well ordered. Three more tephra layers (Fig. 2, red triangles) are supposed to reflect known eruptions of the volcanoes Hudson, Mt. Burney and Reclus (Stern 2008). Here, model based predicted ages match those of the known eruptions.

3.2 Sedimentary history of Lake Hambre (bulk OM and inorganic geochemistry)

The sedimentary history of Lake Hambre reveals strong environmental and climatic changes during the past 17 300 yr, as indicated by organic as well as inorganic proxies (Figs. 3 and 4). Sedimentation rates increase from about 6 mm a\(^{-1}\) at the bottom of the core (17 300 cal yr BP) to about 13 mm a\(^{-1}\) at the top (∼ 100 cal yr BP). Three different sections can be distinguished, in the following referred to section I: 17 300–10 800 cal yr BP, section II: 10 800–5400 cal yr BP, and section III: 5400–100 cal yr BP.

The three sections differ strongly in their OM content, as indicated by organic carbon concentrations (C\(_C\)). Carbon concentrations and carbon accumulation rates (C\(_{AR}\)) are comparatively low in section I (C\(_C\): < 1–11 wt.-%, C\(_{AR}\): 4–35 g m\(^{-2}\) a\(^{-1}\)) and increase towards intermediate values in section II (C\(_C\): 8–22 wt.-%, C\(_{AR}\): 25–62 g m\(^{-2}\) a\(^{-1}\)). At about 5400 cal yr BP a sudden increase in C\(_C\) and C\(_{AR}\) is observed and above (section I) the sediment consists of OM almost exclusively (C\(_C\): 12–43 wt.-%, C\(_{AR}\): 33–119 g m\(^{-2}\) a\(^{-1}\), Figs. 3 and 4).
To estimate varying contributions of aquatic (algae) and terrestrial (vascular plants) OM we calculated C/N ratios of the OM and used them as a proxy to trace back the provenance of sedimentary OM. Algae usually have C/N ratios of 4–10, whereas terrestrial plants have C/N ratios of 20 and higher (Meyers and Terranes, 2001). C/N ratios in Lake Hambre sediments parallel records of $C_C$ and $C_{AR}$. They increase from median values of about 9 in section I towards intermediate values of 12 in section II and highest values of about 17 in section III. In combination with the concurrent rise in $C_{AR}$ the increasing C/N ratios hint to an increase in terrestrial OM fluxes into the lake from the late Pleistocene towards the late Holocene.

As an indicator of changes in the fluxes of siliclastic material we use Zirconium concentrations and accumulation rates ($Zr_C$ and $Zr_{AR}$). Zr is a conservative element associated with minerals resistant against weathering. High $Zr_C$ and $Zr_{AR}$ therefore indicate periods of high siliclastic fluxes into the lake, e.g. caused by local soil erosion or atmospheric dust transport. In Lake Hambre median $Zr_C$ and $Zr_{AR}$ decrease from section I ($Zr_C$: 145 mg kg$^{-1}$, $Zr_{AR}$: 76 mg m$^{-2}$ a$^{-1}$) towards section III ($Zr_C$: 45 mg kg$^{-1}$, $Zr_{AR}$: 8 mg m$^{-2}$ a$^{-1}$) and mirror the trend of $C_C$ and $C_{AR}$ (Figs. 3 and 4), which indicates decreasing fluxes of siliclastic material into Lake Hambre during the past 17 300 yr. In the following this development as well as possible causes will be discussed more detailed.

### 3.2.1 Section I (17 300–10 800 cal yr BP)

The transition from glacial clays at the bottom of the core towards lake sedimentary material identifies the start of lake development following the Magellan glacier retreat at about 17 300 cal yr BP (Figs. 3 and 4; Heusser et al., 1995; McCulloch et al., 2000; McCulloch and Davies, 2001). $C_C$ and $C_{AR}$ are comparatively low (median $C_C$: 5 wt.-%, $C_{AR}$: 20 g m$^{-2}$ a$^{-1}$), showing a slightly increasing trend towards the transition to section II. Median C/N ratios of about 8 indicate algae as the predominant OM source and just a minor contribution of terrestrial OM during this time. Yet, $C_C$ and $C_{AR}$ generally parallel C/N ratios. This reveals a control of $C_{AR}$ by the amounts of terrestrial OM entering the lake. Here, the successive rise in terrestrial productivity (vegetation...
cover) and the development of a soils C pool after the retreat of the glacier caused an increase in terrestrial C fluxes into the lake probably due to both, a rise in direct erosion of bulk organic topsoils as well as leaching of DOM.

### 3.2.2 Section II (10 800–5400 cal yr BP)

The transition from section I to section II at about 10 800 cal yr BP is marked by a sharp increase in C_C and C_AR (~ factor 2) within decades. The abrupt rise corresponds to a decline in the accumulation of siliclastic material, as indicated by decreasing Zr_C and Zr_AR. This change in sedimentary conditions matches approximately the extensive warming pulse reported in McCulloch et al. (2000) at about 11 400 cal yr BP. Pollen analyses in a bog nearby document the spread of Nothofagus forests at the end of the younger Dryas (12 500 cal yr BP) and its dominance from about 11 000–10 500 cal yr BP until today (Heusser et al., 2000; Mc Culloch and Davies, 2001). Along with the increasing C/N ratios (from median values of about 8 towards mean values of about 12 in section II) this indicates that the increase in C_AR is mainly caused by enhanced fluxes of terrestrial OM into the lake. The temperature rise probably caused an increase in catchment productivity. As a consequence storage of OM in the topsoils increased as well as the turnover of OM in the soils, resulting in a subsequent increase in the release of bulk and dissolved OM.

Within section II, C_C and C_AR show almost cyclic variations (median C_C: 16 wt.-%, C_AR: 43 g m^{-2} a^{-1}). C/N ratios range from 9 to 16, slightly covarying with C_C and C_AR, which hints to a cyclic variation of terrestrial OM inputs. Villa-Martínez and Moreno (2007) detected similar oscillations in a pollen record from a small mire near Torres del Paine (Vega Ñandú). The period from 10 800 to 6800 cal yr BP was characterized by frequent transitions from shrubland to parkland, which the authors mainly attribute to strong rainfall variability during this period (Villa-Martínez and Moreno, 2007). A possible reason for the cyclic variations in C_C and C_AR are therefore varying precipitation patterns, enforcing terrestrial productivity and fluxes of bulk OM as well as DOM from soils during several wetter periods.
3.2.3 Section III (5400–100 cal yr BP)

At about 5400 cal yr BP there is a sharp increase in $C_{AR}$ up to a maximum of 126 g m$^{-2}$ a$^{-1}$. Both, $C_C$ and $C_{AR}$ are at their highest in section III (median $C_C$: 38 wt.-%, $C_{AR}$: 55 g m$^{-2}$ a$^{-1}$, Figs. 3 and 4) and the sediment almost exclusively consists of OM.

From 5400 cal yr BP until about 4250 cal yr BP there are remarkably strong variations in $C_C$ and $C_{AR}$, which clearly exceed those of older and younger sections. Figures 3 and 4 show that concentrations and accumulation rates of the other investigated trace elements as well increase in this period, showing a high variability.

In Fig. 5 the period from 6000 cal yr BP until 4250 cal yr BP is shown in detail. There are several $C_C$ minima (indicated by grey bars), which are accompanied by an increase in C/N ratios up to 20 and higher as well as comparatively high $Zr_C$. Comparison with soil characteristics in Table 3 shows that those C/N and $Zr$ maxima both match quite good the values of the catchment rocks and soils. This interrelation hints to a dilution of $C_C$ by sudden event-controlled fluxes of siliclastic material. Since soil erosion is mostly controlled by precipitation these layers indicate increasing rates of precipitation during this time.

Several other climatic records support our hypothesis of a climatic shift at about 5400 cal yr BP. Although the potential drivers are still under debate, reviews of a broad set of environmental archives from all over the world clearly reveal a major global climatic change between 5000 and 5600 cal yr BP (Magny and Haas, 2004; Thompson et al., 2006). At a regional level Mc Culloch and Davies (2001) proposed comparatively humid conditions at Puerto del Hambre from about 4420 cal yr BP until present, based on pollen records as well as the low degree of peat humification in a peat bog next to lake Hambre. However, their peat record is interrupted by a marine incursion between about 9200 and 4420 cal yr BP and it is not possible to estimate weather the increase in precipitation was a successive one starting already before the marine transgression, or if there was an abrupt rise as indicated in Lake Hambre at about 5400 cal yr BP.
A review of a multiplicity of palynological records south of 50° S by Markgraf (1993) rather confirms the latter hypothesis, since it documents a shift towards substantially wetter conditions in the mid and high-latitudes about 4900–5300 cal yr BP, after a short period of drier and warmer conditions before (recalibrated dates from Markgraf, 1993). Pollen data from Heusser (1995, 1998) as well as a seismic record farther east (Lake Fagnano; Waldmann et al., 2010; Moy et al., 2011) also stated a shift towards an increase in humidity during the late Holocene. Moreover, they propose warmer summer temperatures between 7000 and 5000 cal yr BP as indicated by an increase in aquatic bioproductivity during the same period. The timing of that climate change coincides with the northward shift of the Southern Hemisphere Westerly core zone as stated by Lamy et al. (2010) resulting in a general decrease in precipitation rates west of the Andes. Although the position of the Westerly core zone through time and its effect on precipitation patterns east of the Andes are still under debate (Lamy et al., 2010; Markgraf et al., 2003; Waldmann et al., 2010; Moy et al., 2011), proxy records from archives east of the Andes clearly point towards a rise in precipitation rates, starting at about 4900–5500 cal yr BP.

Above the Mt. Burney tephra C_C and C_AR as well as C/N ratios remain comparatively high and variable indicating a mixture of aquatic and terrestrial OM (Figs. 3 and 4). This agrees with observations during our field campaign in 2010. An intense plankton bloom was observed as well as high amounts of algae debris in the sediment. Additionally, numerous intact leaves and macroscopic fibrous remains of vascular plants in section I hint to a substantial contribution of terrestrial OM and a relative low level of degradation after sediment burial.

3.3 Mercury concentrations and accumulation rates

Mercury concentrations (Fig. 3) show an increasing trend from the bottom towards the top of the core. Median Hg_C range from 68 µg kg⁻¹ in section I to 104 µg kg⁻¹ in section II and highest values of about 186 µg kg⁻¹ in section III. Minimum (26 µg kg⁻¹) and maximum values (528 µg kg⁻¹) differ by a factor of 20. Accumulation rates of Hg vary...
from 10 to 157 µg m\(^{-2}\) yr\(^{-1}\) (factor of 16, median Hg\(_C\): 31 µg m\(^{-2}\) yr\(^{-1}\)), which clearly exceeds the anthropogenic forcing of the atmospheric Hg cycling as extracted from lake sediment studies (factor of 3–5; Fitzgerald et al., 1998; Lamborg et al., 2002; Biester et al., 2007; Yang et al., 2010). Although highly variable, Hg\(_{AR}\) do not show a significant long-term trend throughout the core (median of 29 µg m\(^{-2}\) yr\(^{-1}\) in section I versus median of 32 µg m\(^{-2}\) yr\(^{-1}\) in section III, Fig. 4). The largest increase in Hg\(_C\) and Hg\(_{AR}\) and the most striking short term variations (factor of 14) appear at 5500 cal yr BP lasting about 1000 yr up to the tephra of the Mt. Burney eruption 4250 cal yr BP.

In several studies variations in pre-industrial Hg accumulation rates in lake sediments have been at least partly attributed to changes in atmospheric Hg fluxes or changing rates of siliclastic fluxes, either due to dust deposition or soil erosion (Cannon et al., 2003; Fitzgerald et al., 2005; Phillips et al., 2011; Yang et al., 2010). Recent open field wet Hg deposition rates as measured in Swedish catchments, are in the range of about 4 to 7 µg m\(^{-2}\) yr\(^{-1}\) (Lee et al., 2000; Regnell et al., 2009). Moreover Hg accumulation rates obtained from a peat bog about 1 km distant from Lake Hambre suggest that mean atmospheric Hg fluxes throughout the Holocene were below 4 µg m\(^{-2}\) yr\(^{-1}\) (Biester et al., 2003), which is about eight times less than median Hg accumulation in Lake Hambre. Along with the particular strong variations in both, Hg\(_C\) and Hg\(_{AR}\), this fact contradicts changes in atmospheric fluxes alone to be the main driver of Hg accumulation and its variation in Lake Hambre and points towards a significant supply of Hg from the catchment.

Mercury concentrations in the local rocks and soils range from 23–57 µg kg\(^{-1}\) (Table 3). Given the fact that Hg\(_C\) in the sediments, especially in section II (mean: 104 µg kg\(^{-1}\)) and III (mean: 186 µg kg\(^{-1}\)) are two- to eightfold higher than in the catchment soils, erosion of siliclastic material does not seem to play a significant role for the Hg\(_C\) and Hg\(_{AR}\) as well.

Tephra layers in the Lake Hambre sediment record indicate several volcanic eruptions during the past 17 300 yr. Since volcanos are known to be an important natural sources of Hg (Nriagu and Becker, 2003) a potential influence of Hg emissions due to
volcanic activity has to be considered. Farther north, in the Nahuel Huapi National Park (40°–41° S) Ribeiro Guevara et al. (2010) found a clear interrelation between increases in HgC in the sediments of the studied lakes and volcanic activity as indicated by several tephra layers. The most striking Hg enrichment in the lake Hambre sediment core appears below the 4250 year old Mt. Burney tephra, starting at about 5500 cal yr BP. However, the residence time of Hg in the atmosphere is about 1–2 yr (Schroeder and Munthe, 1998), whereas the period of high and variable Hg concentrations lasted for more than 1000 years. Moreover, peat records about 3 and 150 km distant from Lake Hambre do not show any comparable Hg enrichments (Biester et al., 2003). This indicates that other processes than volcanic Hg emissions must have caused the Hg the pronounced Hg enrichments in Lake Hambre sediments between 5500 and 4250 BP.

In studies investigating natural mechanisms controlling the sedimentation of Hg in lakes two concepts considering OM as the main driver have been discussed during the past years. It was suggested that OM from catchment soils acts as an important transport vector for Hg into lakes and rivers (Driscoll et al., 1995; Ouellet et al., 2009; Regnell et al., 2009; Selvendrian et al., 2009), mainly due to the complexation of Hg by DOM. Teisserenc et al. (2010) explained most of the Hg variation in their sediment cores by varying inputs of humified OM derived from the catchment soils. Several studies in Arctic and Subarctic lakes on the other hand reveal a control of Hg accumulation in lake sediments by changes in aquatic bioproductivity and scavenging by algae material (Outridge et al., 2005, 2007; Sanei and Goodarzi, 2006; Stern et al, 2009).

3.4 Mercury accumulation and lake sedimentary history

The sedimentation history of Lake Hambre as well as the Hg record clearly show three phases of different sedimentation characteristics, whose transitions seem to be affected by major changes in sedimentary conditions attributed to the development of catchment soils and vegetation. At a first step the three sections are examined separately, before addressing the long term trends. As a tool to identify the different processes affecting Lake Hambre sedimentation in general and especially to account for
those controlling Hg accumulation, we applied PCA. This statistical technique provides a reduction of the multiproxy dataset (concentration records) to principle components, which reflect the different environmental processes controlling Lake Hambre sedimentation. Moreover it allows an estimation of the degree at which such biogeochemical processes influence the variation of a distinct element.

In Table 2 results of the PCA for sections I–III are shown separately. Tephra layers as well as the sections with the highest Hg variations directly below the Mt. Burney tephra (5400–4250 cal yr BP) are not included in the calculation of the principal biogeochemical components.

In all three sections at most four components explain > 75 % of the total variance of all elements. The major part of the Hg variance (> 60 %) is explained by one principle component in each section (Table 2, in italics). This indicates that in each section one environmental process solely accounts for the major proportion of the Hg variation in the sediments.

3.4.1 Section I (17 300–10 800 cal yr BP)

In section I most of the Hg variance (61 %) is explained by the second principal component (PC 2), which likewise explains most of the variance of Cu and Y (74 % and 66 %, respectively). Besides dust deposition, which should have affected other dust related elements as well (e.g., Zr), Cu and Y unlike Hg do not have a known atmospheric source. Therefore, the variation of Hg, Cu and Y has to be controlled by fluxes from the catchment soils into the lake. In Table 3 concentrations of Hg, Cu, Y and Zr in the catchment soils are compared to mean values in the sediments of section I. Zr is given for comparison, because it is held in very stable minerals resistant against weathering and further mobilization in the sediments and therefore ideally suited as a tracer of the erosion of siliclastic material. While ZrC in the local rocks and soils match the concentrations in the sediments, Hg, Cu and Y are enriched by a factor of 1.2–3.0 in the sediments (Table 3). Moreover, Zr has no significant loading on PC 2, which indicates that another process than soil erosion has caused the similarities in the variation of
Hg, Cu and Y concentrations in Lake Hambre sediments. Cu, similar to Hg, is known to interact strongly with DOM in soils (Bergkvist, 1989). Hence a high production and release of DOM from soils favours the release of Cu and Hg. Y on the other hand is mostly held in minerals like Monazite or Zircon, which are mostly resistant against weathering. Therefore, Y has been traditionally assumed to be immobile and was, similar to Zr, used as a geochemical tracer for mineral matter fluxes in previous studies (Murad, 1978). However, Haraguchi et al. (1998) have shown that transport of Y in natural waters occurs mainly bound to large organic molecules. Due to the covariance of Hg, Cu and Y we propose, that part of the Y, probably held in comparatively unstable ferro-magnesium silicates, is released during weathering in local rocks and soils and subsequently complexed by DOM. Accordingly we conclude that PC 2 represents the export of DOM and associated complexed trace elements from the catchment soils.

Although we assume leaching of terrestrial DOM as the main driver for the variation in Hg, Cu and Y concentrations, there is no significant loading on the C/N ratios in PC 2, which are used as a proxy for different OM sources (aquatic versus terrestrial) in this study. The lack of such a covariance is probably due to the small amounts C transported into the lake as DOM in contrast to bulk organic matter. It is obvious, that an increase in DOM supply to the lake will not alter the C/N ratios of the sediment. Instead, most of the variance of the C/N ratios is explained by PC 1, which represents the long-term increase in terrestrial OM accumulation (high positive loadings on C and C/N ratios) versus a decrease in mineral matter accumulation (high negative loading on Zr, Table 2, Figs. 3 and 4), due to the development of the catchment vegetation and organic rich top-soils after the retreat of the glacier.

Principle Component 1, moreover, explained an additional amount of about 18 % of the Hg variance. Hg derived either from the atmosphere or from weathering of the bedrocks is bound to the OM in the organic topsoils and accumulates. Accordingly, erosion of bulk topsoil material transports an increasing amount of OM and organically bound trace metals into the lake. The proportion of siliclastic material on the other hand decreased, as indicated by the high negative loading of Zr in PC 1.
3.4.2 Section II (10 800–5400 cal yr BP)

In section II most of the Hg variance (66%) is explained by PC 1 (Table 2), which explains a total of 31% of the overall data variation. PC 1 represents the comparatively short-term (about millennial) cyclic variation of OM in the sediment, as indicated by high positive loadings of carbon. Nitrogen, Hg, Cu, Y, Br and Zn have high loadings on PC 1 as well (Table 2). The fact, that most of the C variation is explained by PC 1 in Section II, suggest that PC 1 rather represents a mixture of bulk OM and DOM fluxes into the sediments. However, C/N ratios do not indicate unequivocally, to which extent the cyclic variation of the OM associated elements is driven by either terrestrial OM fluxes or changes in aquatic productivity and related scavenging effects. Since the variations in OM in Lake Hambre act on a millenial scale, a leading control by scavenging appears rather questionable. Without an enhanced additional supply of Hg from the catchment soils or the atmosphere, a depletion of Hg in the water column would inhibit an increase in $Hg_{AR}$, during several high productive years in series. We conclude that terrestrial DOM fluxes are the main driver for the variations of Hg, Cu and Y as well as Br and Zn accumulation in this section. Those variable fluxes are probably caused by a cyclic variation of the frequency and intensity of precipitation events, leaching large amounts of DOM out of the catchment soils, which have been produced in between.

The principal components 2, 3 and 4 probably reflect changes in soil erosion and/or grain size effects. Although changes in soil erosion seem to have affected the C/N ratios by a higher supply of terrestrial plant material, as indicated by moderate to high factor loadings in PC 2 and 3 (0.30 and −0.76), this process does not play a significant role for the accumulation of Hg. Figures 2 and 3 show that in contrast to section I, there is no further long term change in the accumulation of organic or siliclastic material (as indicated by C or Zr, Table 2, Figs. 3 and 4) in section II.
3.4.3 Section III (5400–100 cal yr BP)

Section III starts with an abrupt increase in Hg, Cu and Y accumulation rates, which remain high, but variable (factor of 14) for more than 1000 years until the eruption of Mt. Burney 4250 cal yr BP. It has been argued, that volcanic gaseous emissions are not a likely cause for this enrichment. Several erosion events (indicated by high Zr$_{C}$ and low C$_{C}$ along with high C/N ratios, Fig. 5), have been detected in the sediment and indicate an increase in the intensity and frequency of precipitation in the period from 5500–4250 cal yr BP. We propose that increasing rates of precipitation as well as some individual storm events flushed vast amounts of soluble OM out of the soils. Several previous studies have shown that the release of DOM from soils is to a great extent controlled by extreme precipitation events (Inamdar et al., 2006; Raymond and Syers, 2010). Those increased DOM fluxes coevally resulted in an increase in the transport of Hg, Cu and Y out of the soils, which are complexed by the soluble OM. Total C$_{C}$ instead increased to a lesser extent, since bulk OM fluxes into the lake are rather controlled by the erosion of bulk organic topsoil material than leaching of DOM.

However, the strong short term variations of Hg, Cu and Y concentrations and accumulation rates during the period from 5500–4250 cal yr BP cannot be explained by DOM leaching. In Fig. 5, the concentration records of Hg, Cu and Y are compared to those of Zr, C and C/N. The minima in Hg, Cu and Y clearly coincide with maxima in Zr$_{C}$ and C/N ratios (Fig. 5), which already have been shown to indicate distinct erosion events. We conclude that besides the overall increase in Hg, Cu and Y concentrations due to a rise in DOM leaching on one hand, the increase in precipitation frequency and intensity caused several distinct erosion events transporting siliclastic material into the lake, which diluted the Hg, Cu and Y concentrations in the sediment on the other hand.

Above the Mt. Burney tephra Hg, Cu and Y accumulation rates decrease, whereas terrestrial bulk OM fluxes as indicated by C$_{AR}$ remain high. A possible explanation is a decrease in the frequency and intensity in local precipitation events and the subsequent establishment of a new equilibrium of DOM production and mobilization along
with complexed trace metals in the catchment soils. While the production and the export of OM is higher in section III than in section II, the supply of trace metals from weathering or atmospheric fluxes remains constant. Consistently, the loading of the soil OM (solid as well as soluble) with trace elements decreases. This concept of changing trace element to carbon ratios of the terrestrial OM was established by Meili (1991) before. With respect to Hg he postulated that a comparatively constant atmospheric Hg deposition will result in different soil Hg/C ratios, depending on the “biodilution” by different amounts of soil C present or produced during the same period. When the OM pool in the soils is not in steady state, but changing with time, while atmospheric Hg deposition remains constant, Hg/C ratios will therefore change also.

Comparable to sections I and II Cu and Y show high loadings on the same Principle Component (PC 4) in the period between 4250 cal yr BP and 100 cal yr BP. About 72% of the Hg variance in this section is explained by PC 4, which as in section I and II reflects the export of DOM and associated trace elements into the lake.

3.5 Long-term changes in mercury accumulation

Our data indicates that the accumulation of Hg in the sediments of all three sections is tightly coupled to fluxes of terrestrial DOM acting as a carrier for complexed metals, such as Hg, Cu and Y. However, on a long term scale there is no clear interrelation between C, Hg, Y and Cu accumulation. While C accumulation rates increase towards the top of the core Hg\textsubscript{AR} remain stable and Y\textsubscript{AR} as well as Cu\textsubscript{AR} decrease. To study this in detail, we calculated enrichment/depletion factors for the accumulation of C, Zr, Hg, Cu and Y (Table 4), which represent the magnitude of the increase or decrease of the accumulation rates from the late Pleistocene (section I) to the Late Holocene (section III).

Accumulation rates of C increased by a factor of 2.8 from section I to section III. This is mainly due to the long-term increase in the catchment productivity and the subsequent rise in bulk, as well as dissolved terrestrial OM fluxes into the lake as indicated by the increase in C/N ratios (Fig. 3).
In contrast $\text{Zr}_{\text{AR}}$, indicating siliclastic fluxes into the lake, decrease strongly (factor of 11.4), which we mainly attribute to the development of a protective vegetation cover in the catchment. The mean concentrations of Zr in the late Pleistocene sediments (143 mg kg$^{-1}$) match those of the surrounding rocks (147 mg kg$^{-1}$, Table 3), which confirms that fluxes of siliclastic material dominate the sedimentation process during this period.

Copper and Y accumulation rates decrease in line with $\text{Zr}_{\text{AR}}$ from section I to section III. This reflects that Cu and Y are partly retained in stable minerals and transported into the lake via the erosion of siliclastic material. The decrease in siliclastic fluxes consistently leads to a decrease in Cu and Y fluxes, also. In contrast to Zr, however, Cu and Y decrease to a lesser extent (factor of 11.4 (Zr) versus a factor of 3.1 (Cu) and 3.4 (Y), respectively, Table 4). We suggest that this is due to the additional supply of DOM associated Cu and Y into the lake, which counteracts the decreasing rates of siliclastic fluxes. The enrichment of Cu and Y in the sediments compared to the rocks and soils in the catchment (Table 3) confirms this hypothesis.

The small Hg depletion factor of 1.1 (Table 4) shows that Hg accumulation remains almost constant in a long term. In contrast we propose that DOM fluxes into the lake have increased from section I towards section III along with the increase in bulk OM fluxes. Due to the strong coupling of short term DOM and Hg fluxes into the lake a similar increase in Hg might be suggested. We attributed the lack of such an interrelation to a decrease in the Hg/C ratio of the terrestrial OM due to the rise in terrestrial OM production and storage in the top-soils accompanied by a comparatively constant supply of Hg by atmospheric deposition and weathering. Hence, an increase in DOM export out of the catchment soils does not result in a simultaneous rise in Hg fluxes. We conclude that Hg accumulation in the catchment soils due to atmospheric deposition and bedrock weathering is in balance with the export of organically bound Hg from the catchment soils.
4 Conclusions

Our investigation of lake Hambre sediments reveal that natural mercury accumulation rates have been highly variable within periods of hundreds of years. Covariant distributions of Hg, Cu and Y which are independent from patterns of mineral matter erosion suggest leaching of Hg organic complexes from catchment soils as the major pathway of Hg to the lake. Accordingly changes in local precipitation rates are likely to be the main driver for changes in Hg accumulation in the lake. Despite a large increase in terrestrial bulk organic matter fluxes to the lake throughout the Holocene average long term Hg accumulation rates remained relative constant (29 µg m\(^{-2}\) yr\(^{-1}\)). This long-term constant Hg accumulation in the lake reflects that Hg accumulation in catchment soils by atmospheric deposition and bedrock weathering have been fairly constant, too. As carbon storage in the soils and transport into the lake have increased, Hg/C ratios in the soil OM decreased. Fluxes of Hg into the lake are therefore mainly determined by the amount of OM leached into the lake and its Hg/C ratio.

Acknowledgements. Financial support was provided by the German Science Foundation (BI 734/10-1). For providing the sediment core and their support during sample preparation we are very grateful to R. Kilian, H. Arz and J. Kaiser. We thank C. R. Cardoza (Instituto de la Patagonia, Universidad de Magallanes) and P. Cid-Agüero (Dirección de Programas Antárticos, Universidad de Magallanes) for logistic support during the field campaigns.

References


A Holocene Southern Hemispheric lake mercury record

Y.-M. Hermanns and H. Biester

--- | --- | --- | ---
Title Page | Abstract | Introduction | Conclusions | References | Tables | Figures


McCulloch, R. D. and Davies, S. J.: Late glacial and Holocene paleoenvironmental changes in
Regnell, O., Watras, C. J., Troedsson, B., Helgee, A., and Hammar, T.: Mercury in a boreal forest stream – role of historical mercury pollution, TOC, temperature and water discharge,
A Holocene Southern Hemispheric lake mercury record

Y.-M. Hermanns and H. Biester


6578


Table 1. Radiocarbon dating of Lake Hambre sediments performed on Nothofagus leaves and wood samples. Ages in italics were calculated with the Northern Hemisphere Calibration Curve INTCAL09 and 56 yr were added according to McCormac et al. (2004).

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Calibration data set</th>
<th>Sample material</th>
<th>LAB ID</th>
<th>depth (cm)</th>
<th>$^{14}$C yr BP BP</th>
<th>cal yr BP BP</th>
<th>$2\sigma$ range (cal yr BP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>73 893</td>
<td>67–68</td>
<td>235 ± 15</td>
<td>193</td>
<td>298–152*</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>73 894</td>
<td>92–93</td>
<td>945 ± 20</td>
<td>801</td>
<td>904–741*</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>79 254</td>
<td>136–137</td>
<td>1205 ± 15</td>
<td>1047</td>
<td>1168–980*</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>79 255</td>
<td>152–153</td>
<td>1220 ± 15</td>
<td>1080</td>
<td>1171–1037*</td>
</tr>
<tr>
<td>WHOI, Woods Hole</td>
<td>SHcal04</td>
<td>leave</td>
<td>74 832</td>
<td>200</td>
<td>1870 ± 30</td>
<td>1755</td>
<td>1862–1626*</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>79 256</td>
<td>255–256</td>
<td>2045 ± 15</td>
<td>1939</td>
<td>1993–1886*</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>73 895</td>
<td>325–326</td>
<td>2575 ± 15</td>
<td>2593</td>
<td>2740–2492*</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>79 257</td>
<td>412–413</td>
<td>3105 ± 15</td>
<td>3281</td>
<td>3354–3171*</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>79 258</td>
<td>554–556</td>
<td>4520 ± 15</td>
<td>5169</td>
<td>5286–4974</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>73 896</td>
<td>632–634</td>
<td>5510 ± 15</td>
<td>6250</td>
<td>6300–6209</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>79 259</td>
<td>722–724</td>
<td>6425 ± 15</td>
<td>7300</td>
<td>7417–7253</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>79 260</td>
<td>804–806</td>
<td>7370 ± 20</td>
<td>8109</td>
<td>8182–8032</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>SHcal04</td>
<td>leave</td>
<td>79 261</td>
<td>926–928</td>
<td>8745 ± 20</td>
<td>9625</td>
<td>9730–9548</td>
</tr>
<tr>
<td>WHOI, Woods Hole</td>
<td>SHcal04</td>
<td>wood</td>
<td>73 016</td>
<td>1054</td>
<td>9360 ± 45</td>
<td>10 504</td>
<td>10 656–10 297</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>INTCAL09</td>
<td>wood</td>
<td>79 262</td>
<td>1162–1164</td>
<td>10 595 ± 25</td>
<td>12 622</td>
<td>12 697–12 579</td>
</tr>
<tr>
<td>Keck, Irvine</td>
<td>INTCAL09</td>
<td>wood</td>
<td>79 263</td>
<td>1228–1230</td>
<td>12 525 ± 25</td>
<td>14 778</td>
<td>15 157–14 474</td>
</tr>
<tr>
<td>WHOI, Woods Hole</td>
<td>INTCAL09</td>
<td>wood</td>
<td>69 372</td>
<td>1374–1376</td>
<td>13 500 ± 60</td>
<td>16 730</td>
<td>16 944–16 439</td>
</tr>
</tbody>
</table>
Table 2. Varimax rotated factor matrices for the transformed (Z-scores) geochemical datasets of section I, II and III of Lake Hambre sediments. Significant (> 0.4 and < −0.4) factor loadings are designated in bold, Principle Components explaining most (> 60 %) of the Hg's variance are designated in italics.

<table>
<thead>
<tr>
<th></th>
<th>Section I</th>
<th></th>
<th>Section II</th>
<th></th>
<th>Section III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC1</td>
<td>PC2</td>
<td>PC3</td>
<td>PC1</td>
<td>PC2</td>
</tr>
<tr>
<td>Hg</td>
<td>0.42</td>
<td>0.78</td>
<td>−0.16</td>
<td>Hg</td>
<td>0.81</td>
</tr>
<tr>
<td>N</td>
<td>0.85</td>
<td>0.33</td>
<td>−0.02</td>
<td>N</td>
<td>0.86</td>
</tr>
<tr>
<td>C</td>
<td>0.94</td>
<td>0.22</td>
<td>−0.06</td>
<td>C</td>
<td>0.78</td>
</tr>
<tr>
<td>C/N</td>
<td>0.74</td>
<td>0.10</td>
<td>−0.19</td>
<td>C/N</td>
<td>−0.06</td>
</tr>
<tr>
<td>Cu</td>
<td>0.10</td>
<td>0.86</td>
<td>0.17</td>
<td>Cu</td>
<td>0.69</td>
</tr>
<tr>
<td>Y</td>
<td>0.32</td>
<td>0.81</td>
<td>−0.20</td>
<td>Y</td>
<td>0.50</td>
</tr>
<tr>
<td>Br</td>
<td>0.86</td>
<td>0.31</td>
<td>0.08</td>
<td>Br</td>
<td>0.85</td>
</tr>
<tr>
<td>Ca</td>
<td>−0.05</td>
<td>−0.18</td>
<td>0.80</td>
<td>Ca</td>
<td>0.11</td>
</tr>
<tr>
<td>Ti</td>
<td>0.05</td>
<td>0.01</td>
<td>0.96</td>
<td>Ti</td>
<td>0.09</td>
</tr>
<tr>
<td>Mn</td>
<td>0.76</td>
<td>0.02</td>
<td>0.13</td>
<td>Mn</td>
<td>0.09</td>
</tr>
<tr>
<td>Fe</td>
<td>0.40</td>
<td>0.32</td>
<td>0.71</td>
<td>Fe</td>
<td>0.22</td>
</tr>
<tr>
<td>Zn</td>
<td>0.61</td>
<td>0.36</td>
<td>0.19</td>
<td>Zn</td>
<td>0.52</td>
</tr>
<tr>
<td>Rb</td>
<td>−0.45</td>
<td>−0.09</td>
<td>0.62</td>
<td>Rb</td>
<td>−0.25</td>
</tr>
<tr>
<td>Sr</td>
<td>−0.79</td>
<td>−0.41</td>
<td>0.15</td>
<td>Sr</td>
<td>−0.11</td>
</tr>
<tr>
<td>Zr</td>
<td>−0.86</td>
<td>−0.19</td>
<td>0.01</td>
<td>Zr</td>
<td>−0.13</td>
</tr>
</tbody>
</table>
Table 3. Concentrations of Hg, Cu, Y and Zr and C/N ratios in rocks and soils of the Lake Hambre catchment as well as in Lake Hambre sediments of the late Pleistocene (section I).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (cm)</th>
<th>Hg (µg kg(^{-1}))</th>
<th>Cu (mg kg(^{-1}))</th>
<th>Y (mg kg(^{-1}))</th>
<th>Zr (mg kg(^{-1}))</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schist</td>
<td>–</td>
<td>23</td>
<td>26</td>
<td>17</td>
<td>147</td>
<td>–</td>
</tr>
<tr>
<td>HB soil 1</td>
<td>0–10</td>
<td>57</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>32</td>
</tr>
<tr>
<td>HB soil 1</td>
<td>10–15</td>
<td>32</td>
<td>12</td>
<td>12</td>
<td>142</td>
<td>20</td>
</tr>
<tr>
<td>HB soil 1</td>
<td>&gt; 15</td>
<td>27</td>
<td>25</td>
<td>14</td>
<td>149</td>
<td>38</td>
</tr>
<tr>
<td>HB soil 2</td>
<td>0–10</td>
<td>49</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>24</td>
</tr>
<tr>
<td>HB soil 2</td>
<td>&gt; 10</td>
<td>42</td>
<td>22</td>
<td>21</td>
<td>146</td>
<td>45</td>
</tr>
<tr>
<td>Sediment section I</td>
<td>–</td>
<td>68</td>
<td>39</td>
<td>25</td>
<td>143</td>
<td>8</td>
</tr>
</tbody>
</table>
**Table 4.** Mean accumulation rates of C, Zr, Hg, Cu and Y in section I and III and resulting enrichment/depletion factors.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Zr</th>
<th>Hg</th>
<th>Cu</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean accumulation rate section III (µg m(^{-2}) yr(^{-1}))</td>
<td>56.6</td>
<td>6.5</td>
<td>28.9</td>
<td>8.9</td>
<td>4.8</td>
</tr>
<tr>
<td>Mean accumulation rate section I (µg m(^{-2}) yr(^{-1}))</td>
<td>20.0</td>
<td>74.5</td>
<td>31.5</td>
<td>27.6</td>
<td>16.3</td>
</tr>
<tr>
<td>Enrichment (+)/depletion (−) factor</td>
<td>2.8 (+)</td>
<td>11.5 (−)</td>
<td>1.1 (−)</td>
<td>3.1 (−)</td>
<td>3.4 (−)</td>
</tr>
</tbody>
</table>
Fig. 1. Map of Southern South America with location of Lake Hambre.
Fig. 2. Age depth model (2 polynominal) of the Lake Hambre sediment core. Black circles represent calibrated $^{14}$C ages. Error bars indicate 2 sigma uncertainties. The yellow triangle represents the tephra of the Mt. Burney eruption 4250 cal yr BP (McCulloch and Davies, 2001; Stern, 2008), which was included in the model. Red triangles represent tephra layers, which are assumed to reflect the indicated eruptions of the volcanoes Hudson, Mt. Burney and Reclus (Stern, 2008).
**Fig. 3.** Concentrations records of C, Hg, Cu, Y and Zr in Lake Hambre sediments as well as the record of the C/N ratios. Grey dashed bars indicate tephra layers of four known volcanic eruptions (McCulloch and Davies, 2001; Stern, 2008).
Fig. 4. Accumulation rates of C, Hg, Cu, Y and Zr in Lake Hambre sediments as well as the record of the C/N ratios. Grey dashed bars indicate tephra layers of four known volcanic eruptions (McCulloch and Davies, 2001; Stern, 2008).
Fig. 5. Highly variable concentration records of C, Hg, Cu, Y, and Zr between 6000 and 4250 cal yr BP. Grey bars indicate soil erosion events indicated by high C/N ratios, high Zr concentrations and a dilution of organo-associated elements (Hg, Cu and Y).