

## Modelling Past Mercury Deposition from Peat Bogs – The Influence of Peat Structure and $^{210}\text{Pb}$ Mobility

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Historical records of mercury (Hg) accumulation in lake sediments and peat bogs are often used to estimate human impacts on the biogeochemical cycle of mercury. Atmospheric Hg loads are estimated to have increased 3–5-fold in modern times compared to background values, an estimate based largely on lake sediments. Recent studies of the Hg record in peat bogs, however, suggest a significantly higher modern increase, by as much as 30–100-fold. To evaluate the apparent difference between these two natural archives we compared literature data of modern and background Hg accumulation rates derived from globally distributed peat bogs and lake sediments and discuss reasons for the observed differences.

Median pre-industrial mercury accumulation rates in peat were about  $1 \mu\text{g m}^{-2} \text{yr}^{-1}$ , only varying within the range of  $0.6\text{--}1.7 \mu\text{g m}^{-2} \text{yr}^{-1}$  at most sites; lake sediments, when corrected for catchment size and sediment focusing, show background Hg accumulation rates that are 3–5-fold higher ( $3\text{--}3.5 \mu\text{g m}^{-2} \text{yr}^{-1}$ ) than peat. Modern mercury accumulation rates in bogs vary from 16 to  $184 \mu\text{g m}^{-2} \text{yr}^{-1}$  (median 59), which correspond to an average increase in the industrial age of 69-fold (9–410, median 38). In contrast to higher background accumulation rates, modern Hg accumulation rates (mean  $12 \mu\text{g m}^{-2} \text{yr}^{-1}$ ) in lake sediments increased on average by only 3.5-fold, which is ~10–20 times lower than in peat bogs. Direct measurements of modern wet Hg deposition rates ( $\sim 10 \mu\text{g m}^{-2} \text{yr}^{-1}$ ) gave values 6 (up to 18) times lower than in peat suggesting that recent Hg accumulation rates in peat bogs tend to overestimate deposition. Smearing of  $^{210}\text{Pb}$  used for dating and dynamics of mass loss in the uppermost peat layers are suggested to be the predominant reasons for the overestimation of modern Hg accumulation in many peat bogs. Similar strong increases in accumulation rates of other trace elements such as bromine or selenium in the uppermost peat sections which could not be explained by changes in atmospheric fluxes, confirm the general overestimation of trace element accumulation in peat due to  $^{210}\text{Pb}$  smearing. Mercury fluxes could be corrected for overestimation using accumulation rates of bromine or selenium assuming that deposition fluxes of these elements have been constant during the past 150 years. This results in corrected modern Hg accumulation rates, which are in line with those derived from lake sediments or direct Hg deposition measurements. The lower background Hg accumulation rates in peat as compared to sediments are assumed to be a result of non-quantitative Hg retention or release of Hg during peat decomposition.

## Use of organic sediments of Velke Darko to study climatic changes during 15,000 years (Protected Landscape Zdarske vrchy, Czech Republic)

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During the geological mapping of the Protected Landscape Area Žďárské vrchy (Zdarske vrchy) on a scale of 1:25 000 the research of organic sediments is being carried out. The geological mapping of the Quaternary sediments and the palynological investigation on the selected localities offers data on the Quaternary development of the territory and of a good condition of the contemporary ecosystems. The organic sediments on the map sheets were the subject of palynological investigation. Samples of the locality Velké Dářko (Velke Darko) were radiocarbon-dated too (Radiocarbon Laboratory Silesian Technical University, Gliwice, Poland). The results of the pollen analyses augment knowledge of the territory development and its state from the environmental quality point of view. They also indirectly draw attention to the water management importance of this area.

The Žďárské vrchy Hills are situated at the borders of Bohemia and Moravia, in the highest part of the Českomoravská vysočina Highland. Peat-bogs mainly occur at the edge of the territory on the transition into the flat or undulating terrain of the rest of the Českomoravská vysočina Highland. The climatic conditions belong for their origin to the most favourable ones in our republic, because the annual course of the weather is uniform without bigger extremes both at rainfalls and temperatures. They belong among more humid territories of the state and these conditions create possibilities of formation and functioning of wetlands to peat-bogs. The territory of the Protected Landscape Area interferes in the northern part into the Železné hory Mts., in the western part in the Hornosázavská pahorkatina Upland, in the southern part into the Křižanovská vrchovina Highland. The bigger part of the territory belongs to the Hornosvratecká vrchovina Highland. The geomorphological under-whole the Žďárské vrchy Hills represents the culminating part of the whole territory and therefore the Protected Landscape Area bears particularly this name. The geographical situation of the Žďárské vrchy Hills and their environs demonstrates their important water management situation (Břízová 2006). Disturbance of the forest ecosystems and thus consequently of the peat-bogs function, how it is happening in the area, might have consequences, which appeared during the floods in 1997 and 2002.

The Velké Dářko locality is located in the vicinity of the Žďárské vrchy Hills. The surroundings of Velké Dářko are very important and interesting mainly from a geological, geomorphological and palaeoecological points of view. The results of the pollen analyses augment knowledge of the territory development and its state from the environmental quality point of view. They also indirectly draw attention to the water management importance of this area. The oldest palynological investigations come from the beginning of the pollen analysis introduction into the geology awareness and therefore it was necessary to carry out their revision namely from the Quaternary development point of view, and mainly on account of the Late Glacial, which is not mostly recorded in the old works. Their descriptions indicate that authors identically considered the Preboreal (10,250–9,100 B.P.) for the initial period of the origin, however, they mentioned that the lower ca 2 m in profiles were not analysed. In the research works quite different conditions at the development than it is in the peat-bogs of the border mountains of the Czech Republic are described. The spruce (*Picea*) forests with beech (*Fagus*) and fir (*Abies*) are taken for the final state of the Žďárské forests before human interference. Three radiocarbon data ( $^{14}\text{C}$ ) spring from this locality, too: 1. VD-D3/1/6.75–6.80 m, Gd-16468, **14,980 ± 310 B.P.**, 2. VD-D4/20/8.00–8.05 m, Gd-17454, **12,280 ± 360 B.P.** and 3. VD-D4/19/7.75–7.80 m, Gd-12974, **11,780 ± 150 B.P.** All measurements date the lower parts of the peat-bogs and confirm hypothesis that the origin is substantially earlier the Late Glacial (15,000/13,000–10,250 B.P.) than only the Preboreal (10,250–9,100 B.P.).

### References

Břízová, E. 2006. Findings of the organic sediments investigation at the geological mapping in the Protected Landscape Area Žďárské vrchy. In: Smolová, I. ed. Geomorfologické výzkumy v roce 2006. Olomouc. 22–25.

## Lake-sediment archives of preindustrial mercury pollution in the Andes

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Here we present the first records of preindustrial atmospheric mercury (Hg) pollution from lake-sediment cores in the Peruvian Andes. We targeted two regions, both hypothesized to have been major preindustrial sources of atmospheric Hg emissions: Huancavelica, the largest Hg deposit in the New World; and Cerro de Pasco, once the world's largest silver mine and foundation for the adoption of Hg amalgamation. At Huancavelica, intensive Hg mining first began ~1400 BC, predating the emergence of complex Andean societies. The earliest mining targeted cinnabar (HgS) for the production of vermilion, and generated local-scale cinnabar pollution. Following Inca conquest (~1450 AD), smelting was adopted at the mine, Hg pollution became widely circulated, and the deposition of matrix-bound phases of Hg predominated over cinnabar dust. The mine was seized by Spanish metallurgists in 1564 AD, and for the next ~300 year Hg extracted from Huancavelica was exported to silver mines throughout the Andes for use in Hg amalgamation. The sediment records capturing Hg emissions from Cerro de Pasco confirm widespread Hg pollution beginning with the deployment of amalgamation technology ~1600 AD. Our results provide the first evidence for intensive preindustrial Hg pollution associated with Hg mining and amalgamation, and place recent Hg enrichment in the Andes in a broader historical context.

## A 250,000-year record of mercury accumulation in the Arctic

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There is increasing concern regarding the impact of anthropogenic mercury (Hg) deposition to arctic foodwebs and ecosystems. Lake-sediment cores collected from across the Arctic suggest a one- to four-fold increase in Hg deposition since 1850–1900 AD, and testify to the global nature of anthropogenic Hg pollution. Coupled to this recent increase in Hg pollution is the rapid warming of the Arctic. Yet little is known regarding the long-term natural variability of mercury deposition in the Arctic. Moreover, both modelling and lake-sediment studies suggest Hg-climate couplings exist at multiple timescales. Here we present a unique multi-proxy lacustrine-sediment record from Lake CF8 (located on the east coast of Baffin Island, Canada) to investigate natural Hg variability and Hg-climate couplings over millennial timescales. The lake record preserves four organic lake sediment units, which are separated by sands and record portions of the past three interglacial periods and one interstadial. Both Hg concentrations and total organic matter (TOM) are characterized by a progressively declining trend over the Holocene, the last interglacial (LIG), and previous interglacial (PIG) warm periods. These trends are in contrast to profiles of biogenic silica and Chl *a*, both of which record increases in within-lake primary production over the Holocene and the LIG. When considered alongside C:N ratios of TOM, the Lake CF8 sediment record suggests that temperature-mediated export of catchment-derived organic matter exerts a first-order control over Hg deposition. These results hold important implications for the future of mercury cycling in the Arctic given the recent trajectory of accelerated warming and anthropogenic Hg deposition.

## **Influence of peat decomposition on distribution of major and trace elements in peat**

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Peat bogs are widely used as geochemical archives to study historical changes in atmospheric deposition of trace elements. Recent studies hint at an important influence of climate and hydrology driven changes in peat decomposition and mass loss on the enrichment and release of organically bound elements (Hg, Br, I) in peatlands. However, this relationship has only been demonstrated for a small number of elements. Here, we investigated the historical distribution of Fe, Mn, Cr, Zr, Ti, Hg, Br, and I concentrations in four German peat bogs located in the lowland of northern Germany and the Harz Mountains and its relationship with peat decomposition patterns (C/N-ratios). Results indicate three different patterns of relationship between peat decomposition and element distribution. Concentrations of Hg, Br and I increase with increasing peat decomposition and mass loss due to the formation of stable organometal or organohalogen compounds. Concentrations of the conservative elements Ti and Zr also increase with increasing peat mass loss due to the low solubility of Ti and Zr species in peat. Although concentrations of Fe, Mn and Cr in peat are thought to be determined by changes in redox-conditions or varying input of mineral dust particles, enrichment or depletion of peat in all three elements were found to be mainly controlled by organic matter decomposition processes. Accordingly, highest concentrations of Fe, Mn and Cr were observed in less decomposed peat sections and decrease with increasing decomposition indicating that these elements are released from the peat during decomposition. In contrast to previous studies our results show that the trace element distribution in peatlands is predominately controlled by peat decomposition processes and to a minor extent by changes in atmospheric fluxes. Based on our observation we hypothesize that changes in climate and/or hydrology, especially bog wetness, will have strong influence on the fate of trace elements in peatland systems.

## Historical mercury deposition in the vicinity of Pb smelter as recorded in tree rings

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Tree rings have been used as geochemical archives of historical pollution in several studies on different tree species and for a number of different elements. In most works Pb and Cd concentrations in tree rings were investigated. Studies on past Hg pollution recorded in tree rings are rather rare. In this study tree rings from Norway spruce (*Picea abies* L.) were used to monitor historical Hg deposition in the Příbram area, central Czech Republic, affected by historical ore mining and smelting.

The Příbram smelter has been in operation for over 200 years. Historically it processed Pb-Ag ores mined in the area and at present produces Pb from scrap materials, mainly from car batteries. Mercury contamination in the Příbram region has been documented by number of studies, but precise information on Hg emissions from the smelter are unfortunately unknown. Dendrological cores were collected from three spruce trees (PB1, PB2 and PB3) in the close vicinity of the Pb smelter. The sampling sites were located approximately 0.5 km (PB1 and PB2) and 2.5 km (PB3) from the smelter stack.

Mercury concentrations in tree rings are depicted in Fig. 1. All three tree cores showed similar trend in distribution of Hg concentrations. The concentrations increased since the 1960s with maxima (up to 8.4 ng.g<sup>-1</sup>) in the 1970s. Concentration maxima corresponded with reported peak of metallurgical production in the mid-1970s. Maximum net Hg accumulations between the 1960s and 1980s were observed also by Ettler et al. (2008) in peat cores from the vicinity of the Příbram smelter.

Significant decrease in Hg concentrations since the 1980s was recorded in the tree cores PB1 and PB3. The decrease was probably related to the improvement of flue-gas cleaning technologies launched in 1982. Local maximum in Hg concentration in the tree core PB2 in 1990 could be a result of radial movement of this element in the sapwood.

The present study showed that tree rings may provide a good document of the course in Hg deposition in the area affected by ore mining and Pb smelting. Nevertheless further investigation on Hg cycling in trees will be necessary to interpret satisfactorily the historical record of Hg in this archive.

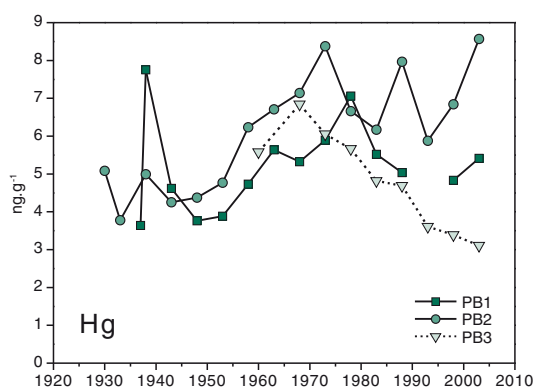


Figure 1. Mercury concentrations in tree rings of three spruce trees (PB1, PB2, PB3) in the vicinity of Pb smelter.

### References

Ettler, V., Navrátil, T., Mihaljevič, M., Rohovec, J., Zuna, M., Šebek, O., Strnad, L., Hojdová, M. 2008. Mercury deposition/accumulation rates in the vicinity of a lead smelter as recorded by a peat deposit. *Atmos Environ* 42: 5968–5977.

## The biomarker method: can a novel combination of organic chemical analysis and inverse modeling help reconstruct the past upper forest line in the Ecuadorian Andes?

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The higher parts of the Ecuadorian Andes consist of fragile ecosystems characterized by páramo grasslands and montane cloud forests. Natural climatic change and human interference (i.e. burning and clear-cutting) are believed to have dramatically lowered the UFL (upper forest line) in the area to the point that its natural position in the absence of disturbance is now uncertain. This is impeding our understanding of the response of the UFL to global climate change and hindering a correct strategy to reforest areas in the frame of Kyoto Protocol driven activities to fix carbon dioxide. An important cause of the uncertainty is that the traditional method of pollen analysis from peat or sediment deposits alone does not suffice to reconstruct shifts in the UFL. Reasons are the spatial uncertainty caused by wind-blown dispersal of pollen and the limited availability of peat or sediment deposits at all altitudes of interest. The RUFLE<sup>1</sup> program tackles this problem by combining traditional pollen and vegetation analyses with a novel biomarker approach. In the latter, plant species typical for specific vegetation zones are examined for the presence of biomarkers, defined as plant-specific (combinations of) organic chemical components. Our results show that the leaves and roots of the higher plants are responsible for the dominant biomass input in our study area in the Eastern Cordillera, Northern Ecuadorian Andes contain unique combinations of *n*-alkanes and *n*-alcohols in the carbon number range of C<sub>20</sub>-C<sub>36</sub>. Furthermore, we found these compounds to be well preserved in peat deposits and soils in chronological order for extended time periods (>6000 <sup>14</sup>C years B.P.). As such they offer great potential to serve as biomarkers for past vegetation dynamics, including UFL shifts. However, since there are unique combinations of otherwise ubiquitous *n*-alkanes, *n*-alcohols of various carbon chain-lengths that constitute our biomarkers, unraveling the mixed signal of various plants accumulated in soils and peat sediment over time poses a major challenge. To tackle this problem, we developed the VERHIB model that describes the accumulation of biomarkers in soils and peat sediments. By inversion the most likely vegetation composition leading to the mixed biomarker signal in the soil or peat sediment in question can be derived. Here we describe the results of the first application of the model in a peat core and several soil monoliths at various altitudes from our study area. Our results show that biomarker analysis using the VERHIB model can indeed serve as a new proxy to reconstruct historic vegetation compositions including the UFL in the Ecuadorian Andes, yielding information that is highly complementary to that which can be obtained through traditional pollen analysis. This is a significant breakthrough from a paleo-ecological point of view as it means an additional proxy is available to be used in combination with traditional pollen- and vegetation analysis. In addition, it is a very promising result from an applied point of view as the information gained will aid the Ecuadorian government in its strategic decisions concerning reforestation of possibly degraded natural areas.

### References

- Jansen, B. Nierop, K.G.J., Hageman, J.A., Cleef, A.M. & Verstraten, J.M. 2006. The straight chain lipid biomarker composition of plant species responsible for the dominant biomass production along two altitudinal transects in the Ecuadorian Andes. *Organic Geochemistry* 37: 1514-1536.
- Jansen, B. & Nierop, K.G.J. 2008. Methyl ketones in high altitude Ecuadorian Andosols confirm excellent conservation of plant-specific *n*-alkane patterns. *Organic Geochemistry* (in press).
- Tonneijck, F.H. & Jongmans, A.G. 2008. The influence of bioturbation on the vertical distribution of soil organic matter in volcanic ash soils: a case study in Northern Ecuador. *European Journal of Soil Science* (in press).
- Jansen, B., Van Loon, E.E., Hooghiemstra, H. & Verstraten, J.M. 2008. Analysis of plant biomarkers greatly improves reconstruction of palaeo-environments. *Geology* (submitted).

<sup>1</sup> RUFLE stands for Reconstruction of the Upper Forest Line in Ecuador.

## Spatial variability in Hg and Pb accumulation in the Chao de Lamoso bog (Xistral Mountains, NW Spain)

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Mercury and lead are heavy metals intensively investigated in peat cores, with the purpose of reconstructing past atmospheric pollution (i.e since prehistoric times, using long peat cores) and also of determining the timing of pollution since the start of the Industrial Revolution (using short peat cores). But most of the reconstructions rely on single peat cores and do not evaluate the within-bog spatial variability in metal accumulation. Recently, Bindler et al. (2004) analyzed Hg and Pb in multiple short cores from the same bog (Store Mosse, Sweden) and reached the conclusion that although general temporal trends were similar for all cores, single reconstructions didn't provide a representative flux for the bog as a whole. We have applied a similar approach to investigate the spatial variability in a blanket bog from NW Spain, Chao de Lamoso (CHL), where we collected 13 cores in a surface of 2 ha. Mercury was analyzed using a LECO-Altec AMA-254 analyzer and Pb using an EMMA-XRF analyzer (1996). The main results are synthesized in Table 1.

Maximum concentrations and total inventories of Hg and Pb in the CHL cores tend to be higher than those observed for Store Mosse (100–400 ng g<sup>-1</sup>, 85–340 ng cm<sup>-2</sup> for Hg; 70–200 µg g<sup>-1</sup>, 75–140 µg cm<sup>-2</sup> for Pb; Bindler et al., 2004). In the CHL cores concentrations and total inventories show similar ratios between maximum and minimum observed values: 2.4–2.4 fold for Hg and 1.6–1.7 fold for Pb. This variation is lower than that found in the Swedish bog (2 fold for Pb and 4 fold for Hg). The slopes of the relationship between Hg and Pb cumulative inventories also suggest differences in relative accumulation of both elements, and show a variation which is quite similar to that in Store Mosse (2.5x and 2.1x respectively).

Thus, although the Chao de Lamoso bog is located in a quite different climatic area (humid and temperate mid latitude), and closer to pollution sources than Store Mosse, the results still indicate a substantial spatial variability in Hg and Pb accumulation. Thus, in agreement with Bindler et al. (2004), these results also support the conclusion that multiple cores are necessary to provide representative data for a single bog.

Table 1. Mercury and Pb maximum concentrations (Hg<sub>max</sub> ng g<sup>-1</sup>, Pb<sub>max</sub> µg g<sup>-1</sup>), inventories (Hginv ng cm<sup>-2</sup>, Pb<sub>inv</sub> in µg cm<sup>-2</sup>, for a reference accumulated mass of 4 g cm<sup>-2</sup>) and slope of the Hg and Pb cumulative inventories relationship (Pb/Hg\*).

Core	Hg <sub>max</sub>	Pb <sub>max</sub>	Hginv	Pb <sub>inv</sub>	Pb/Hg*
CHL-01	142	74	370	167	0.455
CHL-02	224	106	639	244	0.406
CHL-03	144	95	443	288	0.661
CHL-04	338	122	540	190	0.359
CHL-05	148	85	386	171	0.462
CHL-06	300	85	807	202	0.260
CHL-07	295	75	860	219	0.260
CHL-08	181	96	536	194	0.371
CHL-09	146	96	420	217	0.547
CHL-10	214	84	561	262	0.466
CHL-11	181	77	593	235	0.403
CHL-12	170	111	448	237	0.543
CHL-13	242	79	622	207	0.330
Mx/Mn	2.4	1.6	2.3	1.7	2.5

### References

- Bindler, R., Klarqvist, M., Klaminder, J., Forster, J. 2004. Does within bog spatial variability of mercury and lead constrain reconstructions of absolute deposition rates from single peat records? The example of Store Moss, Sweden. *Global Biogeochem. Cycles* 18: 1–11.
- Cheburkin, A., Shotyk, W. 1996. An energy-dispersive miniprobe multi-element analyzer (EMMA) for direct analysis of Pb and other trace elements in peats. *Fresenius J. Anal. Chem.* 354: 688–691.



## Accumulation of trace metals in lakes with different catchment area and input of organic matter

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Many trace metals are shown to be enriched in the upper part of the sediments in several Norwegian lakes, due to long range atmospheric transport of pollutants (Rognerud and Fjeld, 2001). For the last decades, however, the aerial depositions of several trace metals and sulphate are shown to be reduced, indicating that the anthropogenic deposition of metals has decreased. At the same time, the colour and concentration of dissolved organic carbon (DOC) in surface waters of the boreal zone of Europe and North America have increased, possibly imposing a contrary effect with respect to metal accumulation, as DOC is an important transporting agent of metals.

In order to track long term development and recent changes in metal deposition of forest lakes located in a recreation area close to the city of Oslo, a paleolimnological study was conducted. Sediment cores from 5 lakes, differing in catchment area, retention time and DOC concentration (Table 1), were sectioned and subject to analyses of organic carbon, total S, total N, dry matter, radio-caesium and several trace metals (e.g. Hg, Cd, Cu, Zn, Pb).

Table 1. Lake water characteristics of 5 lakes in Oslo Østmark, Norway, subject to sediment sampling in March 2008. Total organic carbon (TOC), pH and conductivity were measured during the autumn circulation period in Nov. 2008.

Lake	TOC (mg L <sup>-1</sup> )	Conductivity (mS cm <sup>-2</sup> )	pH	Lake surface area (km <sup>2</sup> )	Catchment area (km <sup>2</sup> )
Lutvann	1.9	5.8	6.7	0.43	1.73
Krokvann S	3.4	3.1	6.7	0.23	1.36
Forfoten	8.5	2.6	6.3	0.098	3.47
Solbergvann	16.5	3.3	6.1	0.013	0.12
Bonntjern	16.6	2.8	5.8	0.005	3.44

Generally, the upper layers of the sediments had elevated concentration of trace metals compared to deeper layers. For some elements a small reduction in the uppermost layer was observed. Factors influencing both long term and recent accumulation of trace metals will be further discussed, with a particular focus on the impact of organic carbon and sulphur.

### References

Rognerud, S. and Fjeld, E. (2001). Trace element contamination of Norwegian lake sediments. *Ambio* 30:11-19.

## Chironomid-inferred Holocene summer temperature at Plešné lake, the Bohemian Forest, Czech Republic

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A number of regional chironomid-based inference models of mean July air temperature has been developed and successfully used for reconstruction of Late-glacial climate fluctuations (Brooks, 2006). Even though the Holocene time period records relatively small temperature variability that is often within the prediction errors of inference models (Broecker, 2001), the Holocene paleotemperature reconstruction in the Swiss Alps (Heiri et al., 2003) suggested that the chironomid-inferred models is able to reflect also smaller climatic signals.

In co-operation with dr. Heiri from the Utrecht University in Netherlands, we used the transfer function developed for the Swiss Alps (Heiri et al., 2003). The inferred July air temperature varied from 10.6 to 14.0°C. The oldest samples coinciding with the period of Preboreal (10.3–9 cal ka BP), produced a temperature range of 10.6–12.2°C and showed decreasing trend. The temperature inferred for Boreal interval (9–8 cal ka BP) varied between 11.4–12.4°C with an increasing tendency reversing around 8 cal ka BP. The reconstructed temperature for the followed period of the Late Holocene demonstrates increasing trend with a reverse in period of 3–2 cal ka BP and exhibits large fluctuations overall (Fig.1).

The quantitative temperature reconstruction from Plešné lake does not follow the common trend of the maximum temperature recorded in the early Holocene and subsequent cooling, as was documented by chironomid records from other sites throughout much of the northern hemisphere (Larocque & Hall, 2004).

Over the period ca. 6–5 cal ka BP, the greatest afforestation took place in the catchment of Plešné lake, and the climax forest has become a source of organic matter for the lake. Since ca. 2 cal ka BP, the pollen analysis (Jankovská, 2006) showed a first distinct human impact on the original vegetation. The high organic matter input and human activities

near the lake probably has led to the oxygen deficiency or anoxia in the lake. Decreasing trends of Mn:Fe molar ration (Koining et al., 2003) in the sediment from Plešné lake suggest the oxygen depletion could be the explanatory factor that has overridden the effects of temperature on chironomid community.

### References

- Broecker, W.S. 2001. Was the medieval Warm Period Global? *Science* 261: 1497–1499.
- Heiri, O., Lotter, A.F., Hausmann, S. & Kienast, F. 2003. A chironomid-based Holocene summer air temperature reconstruction from the Swiss Alps. *The Holocene* 13: 477–484.
- Larocque, I., & Hall, R.I. 2004. Holocene temperature estimates and chironomid community composition in the Abisko valley, northern Sweden. *Quaternary Sci Rev* 23: 2453–2465.
- Jankovská, V. 2006. Late Glacial and Holocene history of Plešné Lake and its surrounding landscape based on pollen and palaeoalgalogical analyses. *Biologia, Bratislava* 61: Suppl. 20: S371–S385.
- Koining, K.A., Shotyk, W., Lotter, A.F., Ohlendorf, C. & Sturm, M. 2003. 9000 years of geochemical evolution of lithogenic major and trace elements in the sediment of an alpine lake – the role of climate, vegetation, and land-use history. *Journal of Paleolimnology* 30, 307–320.

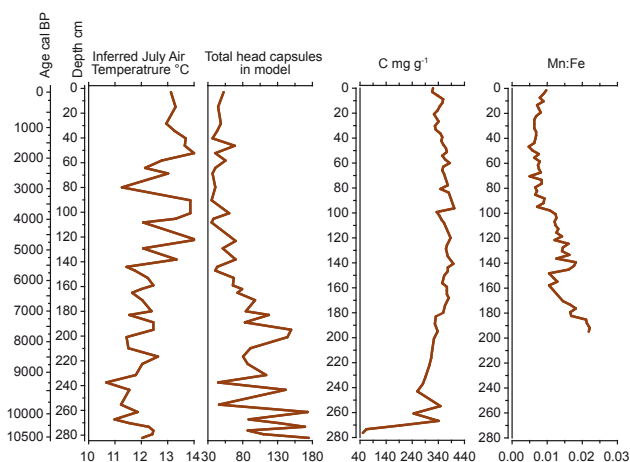


Fig. 1. Chironomid-July air inferred temperature, organic Carbon (C) and Mn:Fe molar ration in the sediment of the Plešné lake.

## Investigating the role of humic acids from ombrotrophic peat in the accumulation of Pb and Hg along a Swiss bog profile

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Peat bogs are often used as archives of atmospheric deposition of Hg and Pb, but the possible mechanisms by which bogs are able to preserve a historical record of either elements have undergone limited investigation. Here we compare the abundance of Hg and Pb in peat and its corresponding humic acids (HA) fraction, in an effort to understand the extent to which humification may contribute to the accumulation of these two environmentally significant metals. For this study, a new peat core was collected from a Swiss bog (Etang de la Gruère) which has been the subject of studies of Hg and Pb in the past. Both bulk peat and HA samples were characterized using several molecular spectroscopic methods (Ft-IR, UV-Vis, Fluorescence) and elemental analysis (CHNS). In addition to Hg and Pb, a variety of other trace metals (including Ti and Zr) and non-metals (e.g., Br) were measured also, for comparison.

Lead and Hg are two “soft” cations that show a strong affinity for the organic ligands, and tend to form inner-sphere complexes. Although both are considered quite immobile along peat profiles, our data underlined completely different behaviours: Hg showed a similar trend both in peat and corresponding HA ( $R^2 = 0.84$ ,  $p < 0.001$ ), and highest concentrations in the latter fraction, while Pb, although abundant in bulk peat, was almost undetectable in the HA molecules. In detail, ca. 66% of the total Hg present in peat was strongly bound by the HA fraction, while this percentage averaged around 3% for Pb, thus suggesting that the latter element could be preferentially bound to the humin, non-humic substances and/or associated to mineral particles. In fact, while Hg is present in the atmosphere mainly in the form of a gas ( $\text{Hg}^0$ ), but can be readily washed out once it has been oxidized to the ionic form ( $\text{Hg}^{2+}$ ), Pb, in the studied bog, seems to behave similarly to Ti and Zr. Since the latter ones are known to be associated almost exclusively with dense accessory minerals (such as rutile and zircon) which are resistant to chemical reaction, even at the low pH (4) which is typical of ombrotrophic bogs, the absence of these elements in HA suggests that, during humification, the mineral phases bearing these elements are unaffected, and therefore that these metals are not available for chemical reaction. Thus, basing on the observed similarity among Pb, Ti and Zr, we assume that Pb which is deposited on the surface of the bog, whether derived from natural or anthropogenic processes, could be present in minerals or aerosols which become preserved in the peat, possibly via the formation of protective organic coatings. As a consequence, very little Pb is labile, and available for incorporation into HA molecules.

Even though Br has different chemical features, it seemed to behave similarly to Hg showing higher concentrations in HA rather than in corresponding bulk peat samples (ca. 40% of total Br in peat was found in the HA fraction). In addition, Br and Hg trends in HA were significantly correlated ( $R^2 = 0.78$ ,  $p < 0.001$ ). Further, data clearly showed that the magnitude of changes in Br and Hg concentrations along the studied profile cannot be attributed to the different degree of peat humification, as resulted from both the HA extraction yield and the C/N ratio. In fact, higher Br and Hg concentrations were found in the upper layers, where a lower humification degree and higher C/N ratios occur. Consequently, because the zone of elevated Br and Hg concentrations seen in the surface layers of the Swiss peat core corresponds to the decades of greatest industrialization, the accumulation of these elements is probably the result of both natural processes as well as anthropogenic inputs, with the latter clearly dominant during the past few centuries.