Analysis and dating of Pb, Cd, Cu, Zn sediment profiles from the Vitznau basin of Lake Lucerne (Switzerland)

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Lake sediments act as archives, where changing conditions can be traced for heavy metal cycling in the geosphere. Thus the increased emission of trace elements related to industrial activities is known to enhance significantly the total trace element concentrations in lake sediments as compared to natural background levels (Schaller et al. 1997, Lotter et al. 1997, Matschullat et al. 1987). In this respect we studied Pb, Zn, Cd and Cu metal concentration profiles of recent sediments in Lake Lucerne, Switzerland. The cores were recovered in the Vitznau basin, which is separated from the upper end of the lake by a vertical sill, which limits the exchange of water and particles (Aeschbach-Herig et al. 1996, van Senden et al. 1990). Only relatively small tributaries of its small catchment enter the Vitznau basin from its steep slopes. The impact of flood events to sedimentation should therefore be naturally small (Ambühl H. 1994, Bührer and Ambühl 1996). Based on former work (Lemcke 1992, Matta et al. 1997) and on historical sources (J. Doppmann, personal communication) the sediment cores could accurately be dated and could be used for precise calculation of the sedimentation rates for the Vitznau basin.

Material and Methods

Sampling site

At an altitude of 434 m a.s.l. Lake Lucerne is located in a complex geological environment of the central Swiss Alps. Its catchment comprises crystalline rocks of the Aar Massive, sandstones and limestones of the Helvetic Nappes, conglomerates, sandstone marls of the Molasse and glacial and proglacial deposits of the Quaternary. The analysed cores were recovered from the southern Vitznau basin at 138 m depth (N 206.8, E 675.6). The township of Vitznau lies at eastern slope of the basin, the nowadays closed quarry of Obermatt is situated at the southern slope of the lake, directly under the cliff of the Bürgenstock (fig.1).
Figure 1: The core sampling site. Squares and numbers relate to the Swiss km-spaced coordination system.

CORE RECOVERY AND SAMPLING

Two cores were recovered in October 1997 with an UVITEC gravity corer (Δ 6 cm) and a motorised winch fixed on a boat. After recovery, both cores (core 1: 35 cm; core 2: 44 cm length) were closed by air-tighten rubber stoppers. On core 1 the sedimentological analysis was performed, core 2 was dedicated to the chemical trace element analysis: it was sampled 4 h after coring by means of a piston driven by a graduated core crank pushing the sediment upward in the vertically adjusted core liner. 44 10 mm thick sediment disks were sampled. The outer 1 cm of the disks were eliminated, the unpolluted inner material was transferred in a clean polyethylene cup. The material in the cups was homogenised, weighted, lyophilised, and weighted again to obtain the dry weight.

TRACE ELEMENT ANALYSIS

100 mg sample material was heated at 110 °C during 48 h in a closed 60 ml Teflon savellex tube containing 3 ml conc. HNO₃ (70%, SDS subboiling grade) and 2 ml hydrogen peroxide (30%, Fluka puriss.). After opening and evaporation, 2 ml conc HCl (32%, SDS subboiling) were added, heated during 2 h and diluted to 100 ml after cooling. As expected a solid residue remained. For cross-comparison the selected samples #3 (core top), #17 (core body) and #32 (core bottom) suffered a second attack which differs from the principal protocol by a 1 ml addition of conc. HF (Merck suprapur). In these samples no solid residue was observed. Two blanks were additionally prepared, respectively with and without HF.
The sample preparation was performed in a clean room. Teflon savilex tubes and spatulas were cleaned by immersion in a concentrated HCl - HNO₃ solution during 20 minutes. Analysis were performed on the Fison VG Plasma Quad ICP-MS instrument. The masses 206 (²⁰⁶Pb), 207 (²⁰⁷Pb), 208 (²⁰⁸Pb), 111 (¹¹¹Cd), 65 (⁶⁵Cu), 63 (⁶³Cu), and 66 (⁶⁶Zn) were measured, individual isotopes were not calibrated.

Before subtraction Pb and Cu concentrations of the blanks were below 1.5 and 0.7% of the lowest and highest measured concentration, the corresponding Cd and Zn ratios were respectively below 5 and 1%.

Table 1 compares the trace element concentrations of the samples prepared with and without HF. When attacked with HF Pb, Cd and Zn total concentrations increase within —8 to 21%. Thus significant differences are recorded for these three metals depending from the attack protocol. Cu seems less affected. Effective total metal concentrations are thus possibly enhanced by 5 to about 15% as compared to concentrations presented below obtained from the HF less attack protocol.

<table>
<thead>
<tr>
<th></th>
<th>Pb mg/kg</th>
<th>Cd mg/kg</th>
<th>Cu mg/kg</th>
<th>Zn mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>#3 without HF</td>
<td>54.2</td>
<td>1.1</td>
<td>36.4</td>
<td>147.1</td>
</tr>
<tr>
<td>#3 with HF</td>
<td>68.9</td>
<td>1.29</td>
<td>36.4</td>
<td>172.8</td>
</tr>
<tr>
<td>loss (b/a -1)%</td>
<td>21</td>
<td>15</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>#17 w/o HF</td>
<td>66.4</td>
<td>1.29</td>
<td>43.5</td>
<td>160</td>
</tr>
<tr>
<td>#17 with HF</td>
<td>67.9</td>
<td>1.51</td>
<td>40.4</td>
<td>184.3</td>
</tr>
<tr>
<td>loss %</td>
<td>2</td>
<td>15</td>
<td>-8</td>
<td>13</td>
</tr>
<tr>
<td>#32 w/o HF</td>
<td>40.6</td>
<td>0.56</td>
<td>30.3</td>
<td>95</td>
</tr>
<tr>
<td>#32 with HF</td>
<td>38.7</td>
<td>0.52</td>
<td>32.8</td>
<td>95.4</td>
</tr>
<tr>
<td>loss %</td>
<td>-5</td>
<td>-8</td>
<td>8</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1: Comparison of sample attack results with and without HF.

Results

SEDIMENTOLOGICAL PROFILE

The simplified sedimentological profile recorded from core 1 is given in fig.2a. The top 3 cm are light grey-orange, the underlying section is dark grey showing black/light laminations, which represent annual laminae (varves). This section testifies the past eutrophication period of the lake (Ambühl, 1994). A homogeneous grey turbidite layer intercalates the dark section at 11 to 14 cm depth, followed by a 3 cm thick grey layer, embedded within two dark grey strata. The turbidite relates to a rock fall which occurred in three phases, with two smaller rock falls in 1962 and 1963 and a larger fall in August 1964 (Lemcke, 1992). Quarrying activities generated this rock slide from the Bürgenstock mountain at Obermatt. The location of the nowadays closed quarry is south of the Weggis village and of the sampling location. Thus not more than 700 m separates the rock fall impact location and the sampling site (fig.1). The rock fall...
transferred vast amounts of solid rocks into the lake and lead to the resuspension and consequent redeposition of 210'000 m$^3$ sediment material (Lemcke, 1992). Below the black, laminated section the sediment consists of homogeneous light grey sediment, with irregular bedding, including two black strata at 30 and 32 cm core depth.

**% DRY WEIGHT PROFILE**

The % dry weight ($W [%] =$ dry weight divided by total weight) profile of core 2 is given in fig. 2b. The $W$ values increase with depth, the values of the top and bottom samples are 7.9% and 35.9%, respectively. Two strong anomalies appear at 14 and 39 cm depth, characterised by high values of 26.3% and 52.4%, respectively, which point to two distinct accidental sediment input events. The upper anomaly relates to the turbidite of the 1962 to 64 rock fall; it is 6 cm thick (fig. 2b, 1.1.8 to 17.7 cm) and involves the six samples #13 to #18. The second anomaly is recorded at 38.7 to 40.7 cm depth and involves the two samples #40 and #41.

**TRACE ELEMENT PROFILES**

The trace element profiles determined from core 2 are given in fig. 2c. For better graphic clarity the Pb, Cd, Cu and Zn concentrations have been multiplied by the scaling factors 1, 1.1, 75 and 0.4. This allows to compare the profiles in the bottom section between 31 and 44 cm depth (samples #32 to #44). This section is characterized by almost invariant metal concentrations, which indicate that during formation the sedi-
mentation rate and the metal input did not significantly vary with time. The mean Pb, Cd, Cu and Zn concentrations are there 37.9 ± 1.8, 0.53 ± 0.10, 33.0 ± 2.6, and 103.9 ± 5.5 mg/kg dry weight. The samples #40 and #41 are not considered in this calculation: Their metal concentrations are relatively low as they relate to a slide, occurring at the slopes of the Vitznau river (Lemcke, 1992). Another section situates between 17.5 to 31 cm and involves the samples #33 to #19. This section is characterized by exponentially increasing metal concentrations. The relative increase is highest for Cd, followed by Pb and Zn and is less pronounced for Cu. A next section situates between 17.5 and 10.7 cm is characterized by very low metal concentrations (#12 to #18). It relates to the rock fall, which occurred 1962 to 64. A comparison of fig.1b and 1c shows that the anomalies concord in W and in metal profiles, as anomalous low metal concentrations correspond to anomalous high W values.

The samples #13, #14 and #15 have constant and relatively low metal concentrations. These samples are thus supposed to be composed entirely from accidentally deposited material related to the rock fall. The top sample #12 concentrations situates halfway between those of the lower and upper samples #13 and #11 taken here as reference for ‘normally deposited’ and ‘foreign’ material. Thus about half of the sample material suggestively originates from the accidental event in sample #12. The two samples #16 and #17 at the lower end of the section seem to be composed both by approximately 75% of ‘normal’ and 25% from ‘foreign’ material, when compared to the lower #19 and upper #15, respectively. They both are related to the first and second rock fall (1962 and 1963). The subsequent samples #15 to #12 thus would then relate to the major fall of August 1964. The 4th and last section relates to the sediment deposited after the rock slide. The section involves the first 11 samples of the top 10.7 cm. The metal concentrations generally decrease in this section toward top.

**Core dating**

A mean sedimentation rate can be calculated from the dry weight data and the time which separates coring (1997) and the rock fall event in 1964. The calculation requires the precise determination of the lower depth limit, i.e. the depth at which normal sedimentation restarted after the 1962 to 1964 rock fall. Effectively, in this depth a 1 cm total sample thickness covers an approximate 4 year time-span of sedimentation, which is significant with respect to the considered total timespan of 34 years (1964 to 1997). Sample #12 situates at this lower limit and was found to be composed by half of ‘foreign’ material. It is thus considered to contribute only with the other half of its mass to normal sedimentation which started in 1964 (± 1 year precision). With this correction the sedimentation rate S

\[
S_{1964-1997} = \frac{1}{\sum_{#1 \text{ to } #12} (\rho \times \ell) / T} = 0.0405 \text{ [g cm}^{-2} \text{ y}^{-1}] \]

is calculated depending from \(\ell\) [cm], the sample thickness, \(T\), the time interval which equals 33 years and \(\rho_s\) [g cm\(^{-3}\)], the density of the dry material in the samples, rich in
organic material. \( \rho_i \) depends from the dry weight \( W_i \) [g/g], the density of the dry solid \( \rho_d \) and from \( \rho_{\text{H2O}} \) (both [g cm\(^{-3}\)])

\[
\rho_i = \frac{W_i}{W_i/\rho_d + (1-W_i)/\rho_{\text{H2O}}} \quad [\text{g cm}^3]
\]

\( \rho_d \) was set to 2.3 g cm\(^{-3}\), a typical value for hardwater lakes dominated by biogenic calcite (density 2.7 g cm\(^{-3}\)) and a small but substantial fraction of organic matter (density close to 1.0. \( \rho_{\text{H2O}} \equiv 1 \). \( i \) is the sample index.

Accordingly a second mean sedimentation rate \( S_{1962-1674} \) can be calculated for the timespan within the two events 1962 and 1674 and the respective samples #19 to #39. This rate \( S_{1962-1674} \) becomes 0.025 g cm\(^{-2}\) y\(^{-1}\). This rate is significantly lower than the first rate. Among others this significant difference may relate to the deposition of organic material in the timespan of eutrophication of the lake, which started in 1954.

**Discussion**

The dated profiles given in fig. 3 allow to assess the evolution of metal concentrations with time. From 1770 to 1800 the metal concentrations are constant and then increase exponentially. The Cu maxima (56.3 mg/kg, #20 dated 1948 to 1955) and the Cd and Zn maxima (1.94 and 213 mg/kg, respectively both in #19 dated 1959 to 1962) are very close and occur all within a 14 year time-span. It has to be noticed that this period precedes the rock fall event, thus an eventual maximal input concentration within the years 1963/64 of Cd and Zn is not observable. The Pb maxima occur later within the 1974 to 1977 time-span (#9). The top sample is particularly enriched with Pb, this anomaly was not further considered.

The observed variations relate to the timescale of industrial development. Thus before 1800 the constant concentrations are considered to represent the natural background concentrations. After this date the impact related to the increasing industrial activity becomes discernible from the background. The later decrease of these metal concentrations in the second half of this century testifies the successful efforts of society and industries to limit the diffusive emission of these heavy metals in the aquatic and atmospheric environment. The relatively late decrease of Pb concentrations relates to the substitution of Pb-tetraethylene in gasoline products. In Switzerland unleaded gasoline dominated the market from 1985 on. The estimated lead emissions from gasoline reached their peak in 1970 with 1200 t yr\(^{-1}\), were almost constant until 1980 (1100 t yr\(^{-1}\)) and decreased to 510 t yr\(^{-1}\) in 1984 and about 290 t yr\(^{-1}\) in 1990 (Moor et al., 1996).

Metal concentrations of accidentally deposited material relate to their origin. Thus the metal concentrations of the 1964 rock fall depositions are very close to those found in the bottom core section and thus compare to the pre-industrial background concentrations. This material thus suggestively relates to resuspended deep sediment layers of pre-industrial times. The relatively increased metal concentrations in the samples #17 and #18 then relates to a weaker impact with a higher relative content of more recent and
consequently polluted material. Instead, the metal concentrations of the 1674 slide of the Vitznau stream are caused by high quantities of external fine particles which entered in the lake. Their metal concentrations thus naturally do not compare the lake sediment concentrations.

Summary and Conclusions

Metal concentrations in the sediments increase from 1800 up to the years 1950 to 1970 and actually decrease from the 70ies onward. This work thus confirms that sediment profiles can be used as tracers of anthropogenic development: emissions increase in a first time related to increasing industrial production, and then decrease again, due to the efforts of the post-industrial society to limit the diffusive emission of heavy metals. However, the actual metal input concentrations are still higher than the original background concentrations. This work further confirms that trace elements can be used as precise tracers of sediment mixing conditions and further may help to determine the origin of foreign material deposited in particular sedimentation events.

Acknowledgments: We acknowledge M. Doppmann Joseph, schoolteacher in Weggis, for his information relative to the chronic of the church of Weggis. Carole Jacquemot, graduate student, and Jean Amossé, professor at the University of Grenoble 1, are respectively acknowledged for performing and guiding the ICP-MS analysis work. Financial support provided from the FAUST founds of the "Observatoire des Sciences de l'Univers de Grenoble" (University of Grenoble I, OSUG).

References


Abstract: Two parallel sediment cores were recovered in the Vitznau basin of Lake Lucerne, Switzerland, were analysed for % dry weight and for Pb, Cd, Cu, Zn. The dry weight and the four metal profiles show two anomalies at 12 cm and at 39 cm core depth pointing to anomalous sedimentation events. The first anomaly (at 12 cm) can be related to the rock fall of the Bürgenstock at Obermatt which occurred in two phases in 1963 and 1964. The second anomaly (at 39 cm) is related to the slide of the Vitznau river in 1674. The mean sedimentation rates, obtained from these two events and the dry weight profiles are $S_{1997-1964} = 0.041 \, \text{g cm}^{-2} \, \text{y}^{-1}$ and $S_{1962-1674} = 0.025 \, \text{g cm}^{-2} \, \text{y}^{-1}$. The difference in the rates is supposedly primarily due to the deposition of organic matter related to eutrophication which started in 1954.

Before 1800 the metal profiles are constant and these concentrations are considered to represent pre-industrial geochemical background concentrations: 37.9 ± 1.8 mg/kg for Pb, 0.53 ± 0.10 mg/kg for Cd, 33.0 ± 2.6 mg/kg for Cu, and 103.9 ± 5.5 mg/kg for Zn. From 1800 up to 1950 all four metal concentrations increase exponentially and decrease from 1970 onwards to recent days. We consider these curves as related to the increasing diffusive emission of heavy metals in the environment during industrial development and the subsequent efforts of the post-industrial society to limit this pollution. Maximum measured metal concentrations increased by 3.5 (Pb), 3.8 (Cd), 1.7 (Cu) and 2.0 (Zn) times relative to natural background concentrations. The relative late decrease of Pb concentration in the profiles, starting around 1975, relates to the ban of leaded gasoline in Switzerland. Actual metal concentrations are still far above the natural background levels.

Key-words: trace elements, Pb, Cd, Cu, Zn, pollution, diffusive pollution, lake, lake Lucern, sediment, core, societal development, historical archives

Résumé: Analyse et datation de profils en Pb, Cd, Cu, Zn de sédiments lacustres provenant du lac des Quatre cantons, Suisse (bassin de Vitznau). Deux carottes parallèles de sédiments lacustres provenant du bassin de la Vitznau (lac des Quatre Cantons, Suisse) ont été échantillonnées et analysées en teneurs d’eau et en Pb, Cd, Cu et Zn. Les cinq profils sont caractérisés par deux anomalies à 12 et à 39 cm de profondeur. La première anomalie à 12 cm est liée aux éboulements successifs du flanc nord du ‘Bürgenstock’ situé à Obermatt qui a eu lieu en trois phases en 1963 et 1964. La deuxième anomalie (39 cm) est corrélée au glissement de terrain de la rivière Vitznau de 1674.

Les deux taux de sédimentation moyens obtenus pour les périodes séparant ces deux événements sont de $S_{1997-1964} = 0.041 \, \text{g cm}^{-2} \, \text{y}^{-1}$ et $S_{1962-1674} = 0.025 \, \text{g cm}^{-2} \, \text{y}^{-1}$. L’élévation du taux moyen plus récent témoigne de l’excès de matière organique déposée en liaison avec l’eutrophisation du bassin débutant en 1954.

Les profils de métaux sont constants avant 1800, les concentrations respectives caractérisent ainsi le fond géochimique préindustriel: 37.9 ± 1.8 mg/kg de Pb, 0.53 ± 0.10 mg/kg de Cd, 33.0 ± 2.6 mg/kg de Cu, et 103.9 ± 5.5 mg/kg de Zn. De 1800 à 1950 les quatre concentrations croissent conjointement de façon exponentielle, suivi d’une diminution marquée à partir de 1965 qui perdure jusqu’à nos jours. Ces courbes témoignent donc de l’accroissement de l’émission diffusive des métaux de la société industrielle en phase de développement et de la diminution de cette même pollution dans le cadre des efforts entrepris dans ce sens par la société post-industrielle. Les concentrations maximales sont 3.5 (Pb), 3.8 (Cd), 1.7 (Cu) et 2.0 (Zn) fois celles du fond géochimique. La diminution relativement tardive du Pb à partir de 1975 est liée à la substitution de combustibles plombés. Les concentrations actuelles sont loin d’avoir atteint les seuils préindustriels.

Mots-clés: éléments trace, métaux lourds, Pb, Cd, Cu, Zn, pollution, pollution diffusive, lac, lacustre, sédiment, lac des Quatre cantons, Suisse, développement industriel