Dating and Heavy Metal Contents of Sediment Cores of a High-Alpine, Remote Lake: Jörisee (Switzerland)

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DATING AND HEAVY METAL CONTENTS OF SEDIMENT CORES OF A HIGH-ALPINE, REMOTE LAKE: JÖRISEE (SWITZERLAND)

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Sediment cores were collected at the MOLAR (MOuntain LAke Research) site Jörisee. The goal of the analysis was to date the sediment cores in order to correlate actual input conditions of nutrients and pollutants at this high-alpine, remote site, to historical situations. The sediment cores were dated by determining gamma rays of Pb-210 and Cs-137. The calculated sedimentation rate is 0.1 cm/year. Leaching techniques were used to investigate redox sensitive species. The results give evidence for post depositional recycling in case of Fe and Mn. In contrast, the heavy metals Pb, Zn, Cr and Ni are not affected by existing redox gradients. Sediment samples were leached with diluted nitric acid to determine anthropogenic input of Pb, Zn, Cr and Ni. Concentrations of these heavy metals reflect changes in the input conditions since the beginning of industrialization, which is the examined time period.

Keywords: High-alpine lake sediment; Pb-210 and Cs-137 dating; sedimentation rate; leaching; heavy metals; MOLAR

INTRODUCTION

Since the beginning of industrialization, anthropogenic activities had major impacts on the geochemical cycling of heavy metals. Both, global and regional cycles showed increased fluxes of metals between different environmental compartments [2]. Investigations of regional anthropogenic fluxes focused mainly on compartments near the sources [3]. However, it has been shown that remote envi-

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ronmental systems may have significant input of heavy metals [4]. Lead originating from automobile exhausts may be transported by atmospheric processes over significant distances [5].

The goal of our investigations was to determine the anthropogenic input of the heavy metals Pb, Zn, Cr and Ni in a remote alpine lake. Sediment samples from three cores of this lake were treated with different leaching procedures [6, 7] to evaluate the anthropogenic fraction of the heavy metals. In order to understand the historical input, a sedimentation rate was calculated using the decay of radio-activity of Pb-210 and Cs-137 [6]. The application of both methods should guarantee a precise and consistent determination of the sedimentation rate.

Our investigation area is the region of Jöriseen (2500 m.a.s.l.) in the Swiss Alps, which is one of the sites participating in the EU-program MOuntain LAke Research (MOLAR) [9]. In this program about 20 alpine remote lakes are studied in order to get chemical, biological, physical and meteorological data about such an extremely sensitive ecosystems. The Jöriseen area consists of about 25 alpine lakes formed during the retreat of the Jöri-glacier. The area and its characteristics are described elsewhere [1]. Our investigations are centered on Lake III [10]. This lake is fed by a subterranean glacial outlet and by bulk deposition and has a maximum depth of about 22 m. Sampling and analysis of bulk deposition, snow and lake water reflected this special input conditions [11].

EXPERIMENTAL

Bulk deposition and lake water were sampled in order to understand the actual conditions. Sediment cores were taken to evaluate the historic input of the heavy metals, which are the main interest of this work.

Equipment used for analytical procedures were pre-washed 5 times with Milli-Q water. In case of determination of heavy metals a solution of 5% HNO_3 (suprapur™, Merck) was used instead. Bulk deposition was collected in pre-washed PE vessels with a diameter of 10.5 cm and a height of 8 cm and changed weekly. Lake water was sampled in pre-washed PE bottles.

The first two sediment cores were taken during winter time (May 1997 core I and April 1998 core II) when the lake was frozen. A hole was digged into the ice cover and a plastic tube of a gravity corer (PE, 90 cm, diameter 8 cm) was driven into the sediment in order to obtain a sediment column (core I: 40 cm, core II: 60 cm length). A third sediment core, which was taken near the shore of the lake, was collected in summer, for which a plastic tube (PP, 20 cm, diameter 5 cm) was

driven into the sediment by hand. After the transport to the laboratory the cores were kept under a minimal original water column (5 cm) in a dark, cool (4°C) place. Subsequently, core I and core II were dissected into slices of 0.5 cm and 0.36 cm, respectively. The sediment material was transferred to PE tubes and lyophilized during one week.

Subsamples were measured by gamma spectroscopy (well type detector, ORTEC). The same amount (1 g for core I, 1.5 g for core II) of material from each slice was measured in order to get comparable measuring conditions. The relative changes of gamma counts on each line (Pb-210 47 keV, Cs-137 661 keV and 32 keV) were used to calculate deposition time for each sample. Following descriptions of radioactive decay [12] the exponential function (1) was used to fit the results of γ-spectroscopy.

$$A(t) = A_o \cdot e^{\left(\frac{\ln 2}{T_{1/2}} \cdot t\right)} \tag{1}$$

A: Activity, A_0 indicates the initial activity

$T_{1/2}$: half life of the examined radionuclide (in years), e.g. 22.3 or Pb-210

t: time elapsed since A_0 (in years)

Calculations of the sedimentation rate was performed by choosing an activity A and comparing its depth z_A with the depth $z_{A'}$ showing an activity of A/e. The sediment column between z_A and $z_{A'}$ was deposited during a time corresponding to $T_{1/2}$ of the element.

Samples from the sediment core material were leached with nitric acid according to the following procedure: 150 mg sample material was shaken with 10 mL of 3M HNO_3 during 24 hours. The leaching under reducing conditions was achieved by mixing about 500 mg of sample with 7.5 mL of a 0.04 M $NH_2OH*HCl$ in 25% acetic acid solution [13]. The solution was shaken and heated up to 95°C during 6 hours to dissolve the oxides present in the sediment. The samples of both leaching techniques were then centrifuged and analyzed directly by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, VARIAN, Liberty 150 AX Turbo) [14]. For higher sensitivity an ultrasonic nebulizing system (CETAC) was used. The error of the ICP-OES measurements performed with standards with the same matrix was determined to be around 10% for the discussed elements.

Total carbon concentrations (C_{tot}) were determined using an Elemental Analyzer (CARLO ERBA). The data were calibrated by the measurement of Tryptophan ($C_{11}O_2N_2H_{12}$), an internal standard used in our laboratory.

RESULTS AND DISCUSSION

Redox conditions

Many investigations showed that redox driven cycling of Fe and Mn can affect early diagenetic redistribution of trace elements such as Pb, Cr, Ni and Zn [4,15]. Furthermore Pb and Cr can themselves undergo a redox cycling. Leaching procedures under reducing conditions were performed with samples from the first 8 cm to study the distribution of oxides of Fe and Mn. The performed leaching shows no influence on other elements, which means that mainly Fe and Mn are participating in a biogeochemical cycle. Another possible influence of redox conditions was observed from 30 to 60 cm by correlating C_{tot} and Cr and Ni.

The redox-driven cycling of Fe and Mn in lakes is well documented in literature [16 – 19]. Decomposition of organic matter at the sediment surface can establish a redox gradient within the sediment, the water column or at the sediment-water interface. Gradients can be subject to temporal or spatial changes, often exhibiting typical seasonal patterns [20]. In case of lake III, oxygen profiles indicate that the point of zero oxygen moves into the sediment, which will lead to changing redox gradients in the sediment and enforce a cycling of Fe and Mn. Depending on their oxidation potential, the microbiota which are active and the amount of organic matter, Fe and Mn will show a peak of reprecipitates at a specific depth. The oxides which are present will be reduced and become soluble; so oxides from other parts of the sediment will diffuse through the sediment due to the redox gradient enforcement and precipitate as well [20]. In lake III oxygen was found in September to be zero at 3.75 cm in the sediment. This means that a peak of Fe and Mn leached under reducing conditions should be observed in the first few cm of the sediment core, what can effectively be seen in Figure 1.

As Fe is accumulating at the oxic/anoxic inter-phase a maximum of Fe is found at 2.2 cm, where the oxidation front is supposed to be during winter time. The Mn reprecipitates as oxide at 1.5 cm, above the Fe where we find higher oxidation potential in concordance with the involved redox potentials of Mn^{2+}/Mn^{4+} and Fe^{2+}/Fe^{3+}. This leads to the observed redox profile of Mn and Fe, which can be interpreted in terms of early diagenetic redistribution processes.

The total carbon content was measured in some samples of the sediment core. The results obtained are shown in Figure 2. The amount of carbon in the sediment core material was about 1.5 to 3.5 % of dry weight. The geology of the Jöriseen catchment area is free of calcareous rocks. For this reason and corollary patterns of C_{tot} and N_{tot}, we assume that the C_{tot} is essentially of organic origin.
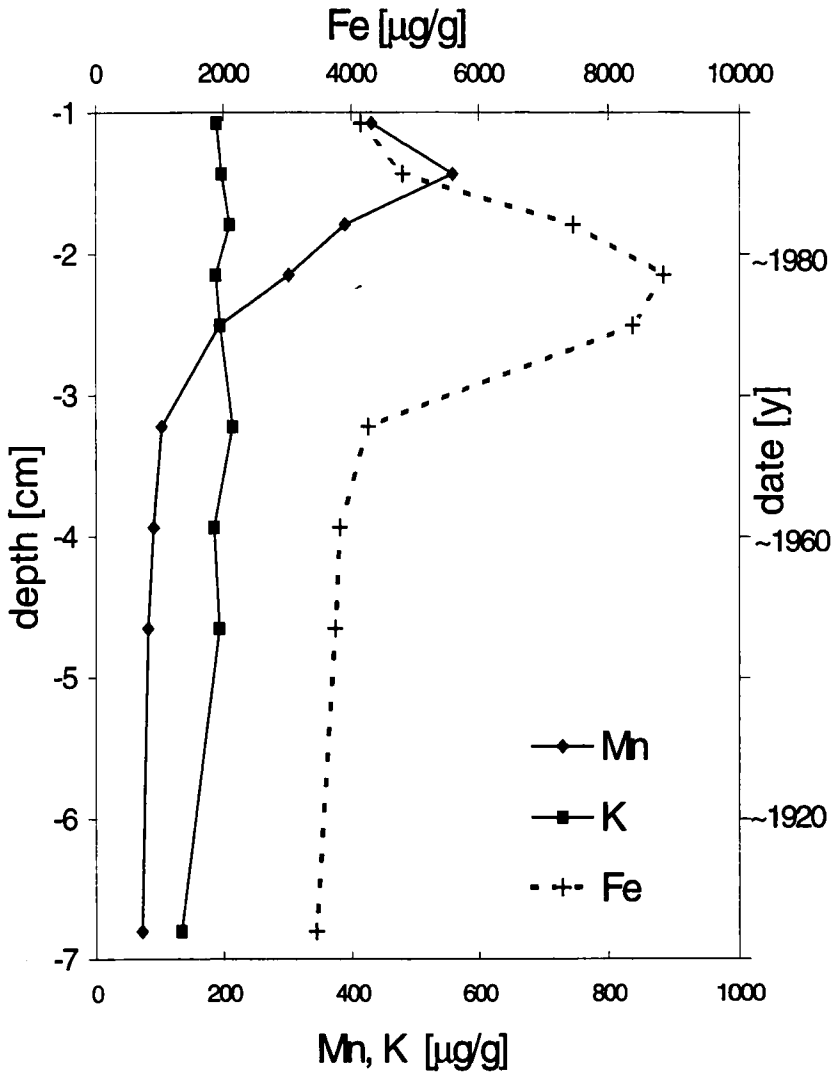
FIGURE 1 Profiles of Mn, Fe and K in core II. Concentrations were determined after leaching under reducing conditions of sediment samples

Below 20 cm an increase of organic matter can be detected (Figure 2), Corresponding to a black sediment layer [4]. We assume that the existence of this black layer refer to a colder period with smaller decomposition of organic matter (longer period of ice covering of the lake). Cr and Ni are enriched in the dark part
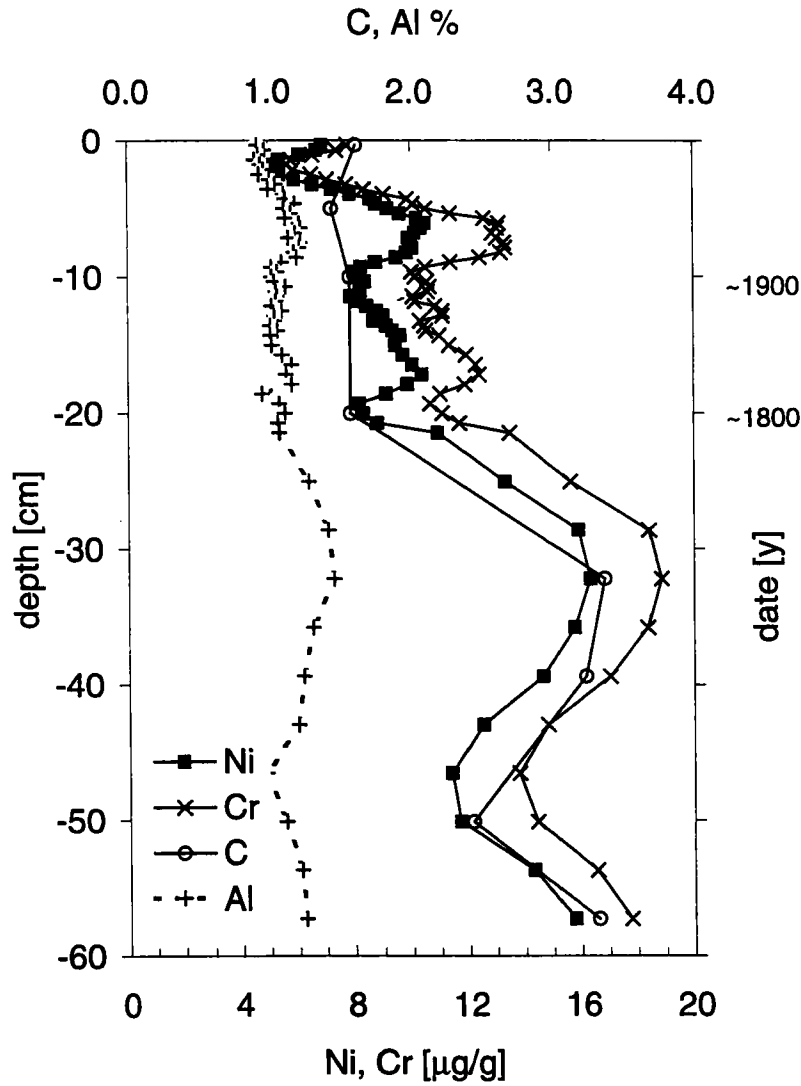
FIGURE 2 Cr, Ni, Al and C_{tot} determined in core II. The sediment samples were treated with acid leaching procedure for determination of Cr, Ni and Al. In case of C_{tot} a measurement on an elemental analyzer was performed

of the sediment. This may be due to other former redox situations in the lake, as the cycling of Cr in seasonally anoxic lakes is known [15]. Isotopic measurements of oxygen could give us some information in this direction. It is important to

keep those profiles in mind while interpreting the profiles of the measured heavy metals.

Dating of the sediment cores

Sediment dating has to span ca. the last 150 years to be able to discuss trace metal profiles with respect to the industrialization. A prominent approach is the use of Pb-210 [12]. Its half-life of 22.3 years allows dating of sediments over the last 110–150 years. Source of Pb-210 is the natural decay of U-238 [12]. In case of Jörisee (lake III) we assume constant Pb-210 input [21]. A dating is possible over the timespan of about 5 to 7 half-lives, which gives a period of maximum 150 years backwards for Pb-210. As a control for this Pb-210 model assumptions, we determined Cs-137 ($T_{1/2}$ = 30.2 years) and Cs-134 ($T_{1/2}$ = 2.3 years). Both isotopes brought increased activity in 1986 (Chernobyl) and during the atomic bomb test series a higher Cs-137 is found. The maxima of Cs-137 input is estimated around 1963 and 1954 [21]. As more than 15 half-lives of Cs-134 have passed, this nuclide is not measurable anymore for this period.

As illustrated in Figure 3 in core I in the first 2.5 cm no decrease of Pb-210 radioactivity is observed. From 2.5 to 10 cm an exponential decrease is observed. Cs-137 shows a distinct peak at the depth of 2.5 cm. In the first 30 cm Ra-226 shows concordant patterns to Pb-210 (excepts the value at 5.5 cm). At a depth of 30 cm the Ra-226 activity is rising significantly.

The constant value of Pb-210 in the first 2.5 cm is due to the conditions in the upper most part of the sediment: In September 1997 the oxygen profile reached zero at a depth of 3.75 cm in the sediment. During winter the oxygen penetration depth may be shallower, due to consumption and inhibited mixing processes in the ice covered lake. A lower redox potential promotes early diagenetic remobilization of Pb in the first few centimeters of the sediment, smoothing the Pb-210 profile [5]. On the other hand smoothed profiles may indicate bioturbation. However, in this case it can be expected that mixing would blur also the Cs-137 signal. In contrast to Pb-210 the Cs-137 shows a very clear peak at 2.5 cm, which indicates that the mobility of lead should be the dominant factor leading to the observed distribution of its activity. Cs, like its homologue K is not very mobile [21]. The decay of the unsupported Pb-210 from 2.5 until 10.5 cm can be used to calculate a sedimentation rate of 0.1 ± 0.05 cm/year.

Pb-210 is a daughter of Ra-226. Therefore a proportional activity of Pb-210 (supported lead) is always found by measuring the γ-line of Ra-226. Below 25 cm, where the sediment core gets darker as well, a rising activity of Ra-226 was found. In order to obtain additional information about this behavior, a second sediment core was taken during winter season 97/98. (core II).
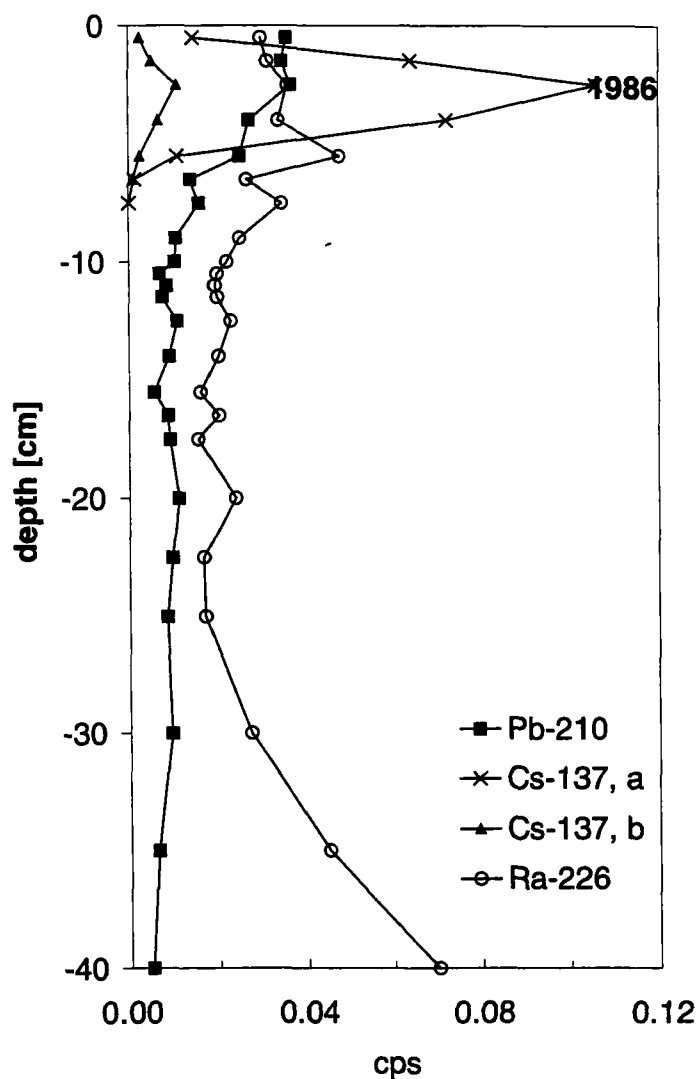
FIGURE 3 Analytical results for γ-spectroscopic measurements of sediment samples of core I. Cs-137 was measured at 661 (a) and 32 (b) [keV]. In case of Pb-210 and Ra-226, the lines 47 and 186 [keV] were used, respectively

The observed Cs-137 Peak at a depth of 2 − 2.5 cm is attributed to the reactor catastrophe of Chernobyl, in 1986. The fact that some Cs-134 was found additionally to the Cs-137 under the same peak emphasizes this interpretation. Based

on the Cs-137 peak a sedimentation rate of 0.15 ± 0.05 can be calculated, which is in quite good agreement with the sedimentation rate calculated for Pb-210. Many investigations showed two more Cs-137 peaks below the Chernobyl event. They were attributed to atmospheric bomb testing (maxima 1954 and 1963). In case of core I of Jörisee (lake III) however, no Cs-137 from the atmospheric bomb test can be clearly recognized in this sediment core due to the lower resolution of 0.5 cm per sample.

Figure 4 presents Pb-210 profiles determined in core II. Very similar to core I, the activity profile shows in the first few cm (0–3 cm) no decrease, as from 3 to 12 cm an exponential decrease is observed. We attribute the disturbed first 3 cm to Pb remobilization after deposition. From the exponential decrease observed between 3 and 12 cm depth a sedimentation rate of 0.1 ± 0.03 cm/year can be calculated, which is in very good agreement to results obtained for the first core. Based on the results of these two cores, we assume the sedimentation rate of 0.1 cm/year to be correct for the collected cores.

Figure 5 compares the gamma measurements of Cs-137 in cores I (1997) and II (1998) with the results from another core taken in lake III by the gamma-lab of Environmental Physics Department of the EAWAG (A. Lotter, 1995, unpublished data, core E). In core I only the Chernobyl peak can clearly be detected and the bomb peaks (about 1954 and 1963) are not very well visible. In contrast the bomb peaks were determined precisely in core II, but the 1986 marker is missing. To emphasize this interpretation it should be noted that under the bomb peaks no Cs-134 was found, while under the Chernobyl peak a small amount of Cs-134 was always measured.

Correlating this results with preliminary measurements done on core E it must be concluded that in core II the first 2 cm are missing. The real activities have been calculated and the amount of radioactivity corresponds to the one found in core E. Nevertheless, the dating by Cs-137 gave a sedimentation rate of 0.1 ± 0.05 cm/year for all cores (0.1 ± 0.02 for core II) which is in very good agreement with the Pb-210 dating. Compared to the Pb-210 inventory, the Ra-226 amount is again rising at about 25 cm up to 40 cm were it remains stable at a 4-fold higher value. This behavior is still open to interpretation.

Be-7 is often used to control if the complete sediment column is sampled. This can be determined by measuring Be-7. However, due to its short half-live of 53 days, Be-7 is no more measurable in a sediment which was deposited and laid at least 5 month under an ice cover. This is due to the stop of input of this cosmogenic produced radionuclide during the time period the lake is covered by ice. This assumption was confirmed by collecting a third core in summer time (August 1998). The first layer (0 – 0.6 cm) of this core showed a Be-7 peak (477 keV). The absence of Be-7 in cores that were taken in springtime (core I
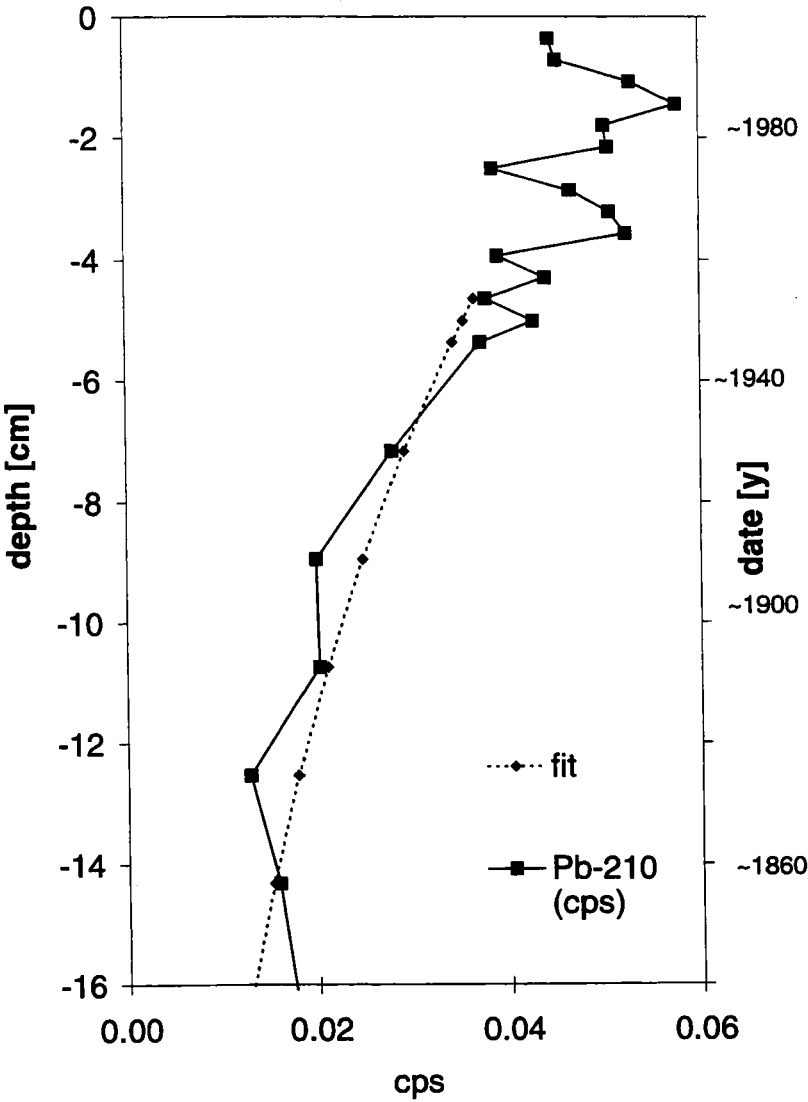
FIGURE 4 Pb-210 in sediment core II and exponential fit [······]. Calculations performed see text

and II) is no indication of in/completeness of recovering since the ice cover stops the input of this nuclide during wintertime (from November to April the lake is permanently covered by ice).
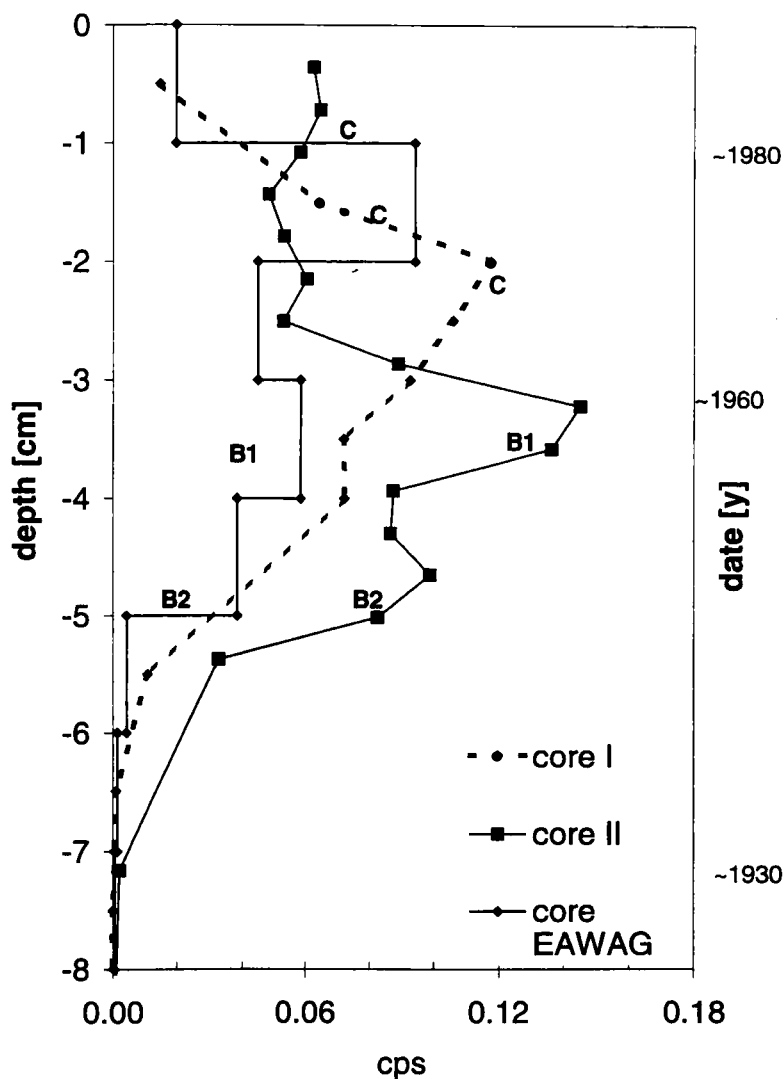
FIGURE 5 Comparison of Cs-137 in different cores. For core I 1g material was measured, for core II 1.5 g. The third core was analyzed by A. Lueck and A. Zwyssig of the EAWAG. (C = Chernobyl, 1986, B1 = bomb tests maximum, about 1963, B2 = bomb tests second maximum, about 1954)

The discussion above showed clearly that sedimentation rates calculated by two different methods in two different cores agree well within the range of 10%. We therefore use a rate of 0.1 cm/year for further discussion. The comparison of

core I, core II and core E indicates moreover that the sedimentation is homogenous in the deepest part of the lake.

Heavy metal profiles

In actual bulk deposition the loads of major cations, anions and of heavy metals were estimated from measurements in 1996 and 1997. Results presented in Table I show loads in decreasing order for both ions and heavy metals. The measured heavy metals show a much smaller input than in the Swiss Midlands [11]. The input reduction was about a factor of 20 for Zn, of 40 for Pb and even of 100 for Cd.

The actual concentrations of those species in lake water are found to be mainly corresponding to the deposition. The range of concentration for the measured ions and heavy metals in 1996 and 1997 are presented in Table II. For nutrient source parameters as for P_{tot}, NO_3^- and NH_4^+ a nutrient like profile was found during summer time, during biological activity. For comparison, data of other MOLAR lakes are included [22]: Gossenköllesee (Austria), which is very similar to Jörisee, Hagelsee, another Swiss lake which has a calcium-rich geologic catchment and Øvre Neådalsvatn, a Norwegian lake, which has a similar geologic setting as lake Jöri but is influenced by sea-salt due to its geographical location.

Jörisee (lake III) shows the same characteristics as other lakes in the same situation (far away from civilization, high-alpine and crystalline catchment). The actual conditions show that the Jöriseen are not heavily polluted and that lake III is an oligotrophic ecosystem and not (yet) acidified. To determine the anthropogenically influenced input of heavy metals we choose core II, since the resolution is better than in core I. Figure 6 shows the results of Mn and Zn measurements. For the first 15 cm we can use the determined sedimentation rate of 0.1 cm/year.

Mn shows a peak at 1.5 cm which intensity is threefold higher than the background concentration of 200 µg/g sample. From 3 cm to 20 cm there is no change observed in the Mn profile. Zn shows a similar behavior from 3 to 20 cm. From 3 to 0 cm a slight decrease is observed. Pb shows a completely different pattern. The concentration stays stable at 20 µg/g sample from 20 to 12 cm. From this point (about 1880) an increase is observed with a maximum at 3.5 cm at 50 µg/g sample. Around 6 cm there may be a decrease/increase. In the first 2 cm a decrease back to concentrations about 35 µg/g sample is observed.

Mn shows clearly the influence of the redox conditions in the lake [23]. Leaching under acid and reducing conditions result in the same amount and the same profile of measurable Mn. In the deeper part (after about 200 years) Mn and Zn show the same behavior. Zn seems to have the same profile structure as Al,

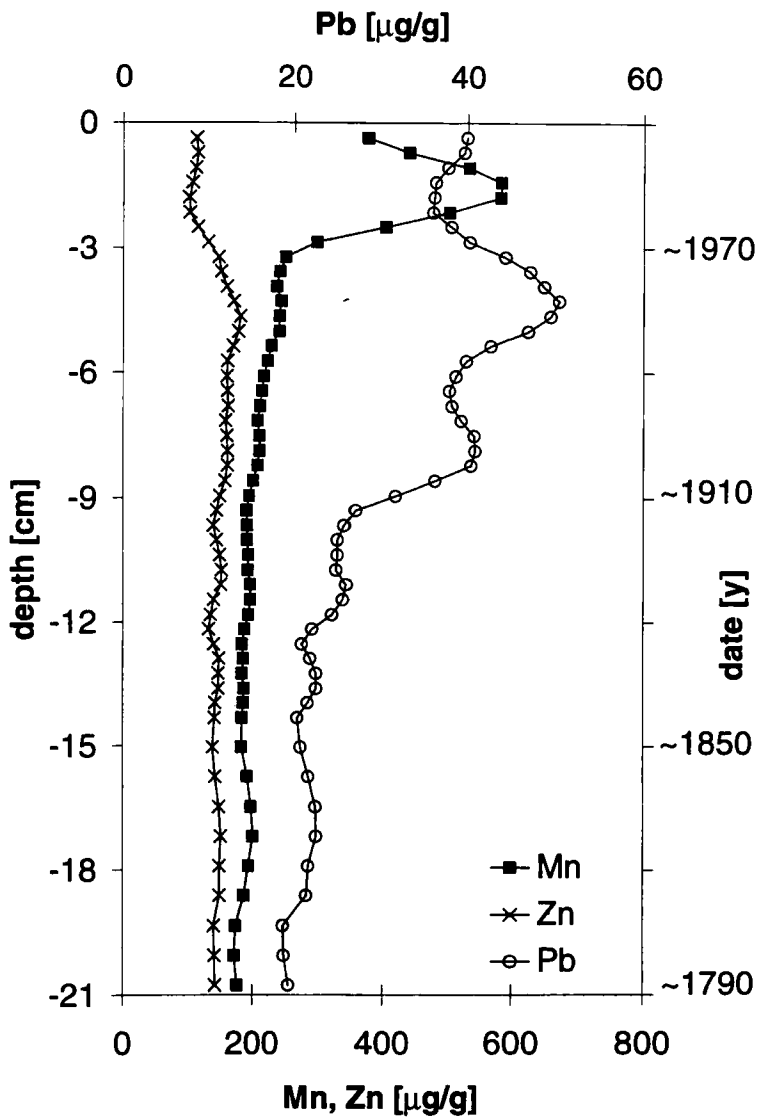FIGURE 6 Mn, Zn and Pb in sediment core II, running means of acid leaching

which can be used as an indicator for geogenic inputs. As the Al profile does not show any large changes, we can assume that our leaching procedure dissolves a representative part of the geogenic Al. A distinct influence from industrialization can not be determined. The observed decrease of Zn, a rather volatile element in

waste incineration, can not be only due to restrictions in emission enforced in the last few years. A similar behavior is observed [4] at other Swiss oligotrophic alpine lakes as well. The different patterns of Mn and Zn profiles indicates that Zn is not coupled to the Mn cycling in the sediment core [13].

For Pb an anthropogenic effect can be observed, which is due to the long range transport properties of lead in aerosols to higher regions, as shown in Figure 4. The lead input shows a large increase starting at 12 cm, which correlates with the beginning of industrialization [2]. In the top 3 cm of this core an expected decrease correlated to the increased use of nonleaded fuel can be observed. Early diagenetic processes have mixed the 2 first cm of the core and hence blur the decrease. The slight decrease/increase which is observed at 10 cm could indicate a weakened economy due to the first world war.

Correlation among all measured elements were calculated. The data were divided in three parts. A first part, chosen between 0–8 cm which is influenced by different redox conditions and oxidation of C_{org} in the sediment column insure that all redox phenomena are included. Selecting a narrower range, e.g. 0–6 cm does not change the main information. A second part between 8–15 cm (only influenced by anthropogenic changes including the beginning of the industrialization and former diagenesis) and the a third part between 15–60 cm were chosen. In the first part (0–8 cm) Al is strongly correlated with Zn, Ni and also with Cr (which is furthermore correlated with K and Ni). These metals, which are mainly released to the atmosphere by mankind, do not show any anthropogenic increase. This may be due to a high natural background which makes it impossible to see small anthropogenic changes. Pb is not correlated with any of these elements. This may indicate the anthropogenic influence of its consumption, which increased drastically with industrialization.

In the second part (8–15 cm) a medium correlation of Al with Cr and Zn was found. The only strong correlation was found between Pb and Mn, which would indicate that during former diagenetic processes Pb was coupled with the Mn cycle. Zn as an element related to the industrialization process was correlated with other heavy metals like Cr and Pb. Ni, which is also an industrially produced pollutant, did not show a clear correlation with Zn. This means that the anthropogenic influenced aerosols containing Ni are not transported in a large enough amount to the elevation of Jörisee [2] at about 2,500 m. a.s.l.

The last part shows again the same correlation among Al, Cr and Ni. These elements show no anthropogenic influence over the whole column. A correlation between Mn and Fe is observed as well. In this part no anthropogenic influences could be observed. This third part corresponds to the time more than 150 years ago, this observation seems to be reasonable.

TABLE I Loads of summer deposition (mean of bulk deposition sampled at lake II in 1996 and 1997)

	Ca^{2+}	Na^+	K^+	Mg^{2+}	NH_4^{2+}	SO_4^{2-}	NO_3^{2-}	Cl^-	Zn	Pb	Cd
Loads of deposition (mean n=57)	2.0 mg/m²d	0.5 mg/m²d	0.5 mg/m²d	0.2 mg/m²d	0.4 mgN/ m²d	2.2 mg/m²d	0.6 mgN/ m²d	0.1 mg/m²d	2.3 µg/m²d	0.3 µg/m²d	0.4 ng/m²d

TABLE II Lake water concentrations of lake Jöri III (mean 1996 and 1997) and for comparison data of other MOIAR lakes [21]

	Jörisee	*Gossenköllesee*	*Hagelsee*	*Øvre Neådalsvatn*
pH	7.03	6.76	8.11	6.22
Ca^{2+} (μeq/l)	128	142	1225	32
Na^+ (μeq/l)	18	15	21	44
K^+ (μeq/l)	9	5	14	4
Mg^{2+} (μeq/l)	27	18	205	14
NH_4^+ (μeq/l)	1	1	4	0
SO_4^{2-} (μeq/l)	56	58	252	17
NO_3^- (μeq/l)	17	19	12	2
Cl^- (μeq/l)	3	3	18	47
Zn (ng/g)	7	–	–	–
Pb (ng/g)	0.5	–	–	–
Cd (ng/g)	0.01	–	–	–

In Table III a mean value of the concentrations of the measured elements over the whole sediment column (0–60 cm) are presented in decreasing order to give an idea about the range of concentrations found in the leaching solutions.

TABLE III Mean values of leachable (3M HNO_3) contents over the whole sediment core (0 –60 cm). All values in μg/g

Element	*Fe*	*Al*	*K*	*Mg*	*Ca*
	13'150	11'060	3'350	3'300	2'120
Mn	Zn	Pb	Cr	Ni	Cd
236	150	30.0	11.5	9.5	0.3

CONCLUSIONS

Leaching under reducing conditions showed that the elements Mn and Fe undergo a biogeochemical cycling. The oxic/anoxic inter-phase is located a few cm in the sediment column, peaks of Fe and Mn oxides are found at 2.2 cm and 1.5 cm depth, respectively. The total carbon content of the sediment core material is mainly organic matter and varies from 1.5 to 3.5 % of dry weight. At

a depth of about 25 cm the core gets darker and the Cr and Ni amounts are elevated. This may indicate changing redox conditions or changes in temperature in former times.

Both dating methods with Cs-137 and Pb-210 gave in good agreement a sedimentation rate of 0.1 ± 0.03 cm/year for core II. This indicates, that the sediment is deposited homogeneously in the deepest part of the lake.

The Pb profile shows the influence of industrialization and use of leaded fuel. Due to the increased use of non-leaded fuel for the last 20 years even a decrease is visible. Zn, Cr and Ni do not show any clear anthropogenic influence due to the high geogenic background. The measured elements Al, Cr, Ni, K and Zn are correlated in the first approximately 8 cm (influenced by redox conditions in the sediment column) and do not show any "industrialization-like" profile. In the second part of the sediment, which corresponds to the beginning of the industrialization up to 1930 (8–15 cm) Zn an indicator element related to the industrialization process is correlated with other heavy metals like Cr and Pb. Ni another industrially produced pollutant does not show a clear correlation with Zn. This may be due to the less important production of Ni or to a less efficient transport of Ni containing aerosols to the Jöriseen due to a lower volatility compared to Zn. In the lowest part of the sediment core, which was deposited more than 150 years ago, no anthropogenic influence can be seen.

The presented analysis performed on sediment cores, lake water and bulk deposition sampling from Jörisee does show that the lake is not heavily influenced by anthropogenic emissions or acidity since beginning of industrialization. This confirms the choice of Jörisee as an uncontaminated lake to take part in the MOLAR program.

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