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The history of metal pollution recorded in the sediments of Bohemian Forest lakes: Since the Bronze Age to the present

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Abstract

Chronology of metal pollution and the relative changes in the atmospheric input of pollutants into lake watersheds were studied in 0.3 to 1.3 m long sediment cores collected from Černé, Čertovo, Plešné and Prášilské Lake in 1987 and 1988. The ^{210}Pb and ^{14}C datings provide a reliable chronology of cores extending back to above 6500 BP (Prášilské Lake). The sediments have recorded both regional and local atmospheric pollution caused by smelting of metals, for Pb since about 2810 BP. Concentrations of Pb, Cu, Bi, and As increased during three periods of the 1st millennium AD (around 0 AD; 550 AD and 900 AD). The pollution produced by smelting was more pronounced in the 14th and 16th century AD, when concentrations of Pb exceeded natural by a factor of 7–8. These maxima of Pb, Bi, Sb and As resulted from pollution by metal smelting in the wider surroundings of the lakes and are unlike any previously reported. After a complex development during the Renaissance, the pollution peaked twice in 20th century: between 1900 and 1910 and from 1956 to 1978. Only last increase in the metal concentrations in the lake sediments was connected with emission from coal cumbustion and emission from mobile sources. A decrease in the metal deposition to the lake watersheds started in the 70's, earlier than did decrease in the deposition of sulphur compounds (1986).

Key words: Palaeolimnology, paleolimnology, lake, sediment, metal pollution, atmospheric transport, lead, copper, bismuth, Bohemian Forest, ancient smelting, heavy metal, archaeology of metallurgy.

Introduction

The profiles of lake sediments (NORTON & al. 1990, RENBERG & al. 1994, STEINBERG & al. 1984), peat (LEE & TALLIS 1973, SHOTYK & al.1998, VILE & al. 2000) and ice (HONG & al. 1994, HONG & al.1996) contain records concerning not only the past local and regional variations in the atmospheric deposition of some trace elements but also the changes in the vegetation and climate (BERGLUND & al. 1996, VESELÝ 1998). The changes that has occurred in lake watersheds and their surroundings can be studied by analysing the macrocomponents of dated sediment profiles, pollen, the residues of diatoms, by determining the isotopic composition and the trace element analysis of the sediments. The sediments of the Bohemian Forest lakes can also be a valuable source of such information, not only from the recent history (VESELÝ & al. 1993), but from the whole Holocene period, i.e., over approximately the last 11 500 years (BARD & al. 1993). Chemical analysis for some metals (especially lead) in sediment layers of various ages permits the obtaining of the chronology of the changes (CHARLES & NORTON 1986) and a comparison of the relative changes in the long-distance transport of these elements (i.e., in the atmospheric pollution). However, the anthropogenic metal fluxes into lake sediments mostly do not quantitatively correspond to their atmospheric deposition in lake watersheds (NRIAGU & WONG 1986, NORTON & al. 1986), for example due to focusing of sediment or early diagenesis.

The present work surveys results of the first study of the sediment profiles from the Bohemian Forest lakes. The work extended over almost ten years, with a few breaks. The results of the analyses of the Čertovo Lake sediments were summarised (VESELÝ & al. 1993) and the palynological analysis of a single profile from the Černé Lake was interpreted by the author (VESELÝ 1998). Preliminary information has also been provided on the long-range pollution of the sediments by metals transported in the atmosphere (VESELÝ 1997, VESELÝ 1988).

Methods

With the help of the divers from the Alfa Club in Tachov and using a home-made piston corer with a diameter of 0.06 m, three profiles were collected in the Černé Lake, two profiles in the Čertovo, Plešné and Prášilské Lakes each and one profile in the Popradské Lake in the High Tatras, Slovakia in 1987 and 1998. Immediately after the collection, the profiles were separated at the shore into a series of samples with thicknesses of 0.01, 0.02 and 0.05 m for the depths of up to 0.2, 0.4 m and deeper, respectively. In the Laboratories of the Czech Geological Survey, the water content was determined first by drying at 105°C and then the loss in weight on ignition (LOI, for 3 hrs. at 560°C) which is proportional to the organic matter content.

To determine the total metal concentrations, an amount of 250 mg of the dry sediment was mixed with 5 ml of HNO_3 (1: 1) in a teflon vessel, the liquid was evaporated, 3 ml of 70% $HClO_4$ and 2 ml of 40% HF were added, the mixture was evaporated to the appearance of perchloric acid fumes and then 2.5 ml of conc. HNO_3 were added. The residue was finally dissolved in 2 ml of hot conc. HCl and diluted with water. The metal concentrations were determined using flame atomic absorption spectroscopy (FAAS). Bi, Sb and As were determined in an acid leachate of lake sediment by the hydride technique (HG AAS).

Results

Dating

A dating of the sediment layers with a highest possible precision is at present a necessary condition for successful study of sedimentary profiles. Unfortunately, commercial radiocarbon dating (^{14}C) of small sediment samples was not available to the author at the end of the eighties and thus it was not clear how long time period is represented by the profiles collected and the interpretation of the results was delayed. During the nineties, one to three samples were dated of older parts of the profiles in the Černé, Plešné, Prášilské and Popradské lakes, using the ^{14}C method with AMS in the Rafter Radiocarbon Laboratory, New Zealand (a total of 9 data). Prior to the dating, components with differing isotopic composition (e.g. roots) were separated and the samples were subjected to a sequence of acid, alkaline and acid leaching. The precision of the sediment dating was checked by analysis of the alkaline leachate of organic compounds, plant remains and a leached sample of the Plešné Lake sediment. The following conventional radiocarbon ages (CRA) were obtained: 3637 ± 60 BP (NZA 9317) for the plant residues, 3560 ± 58 BP (NZA 9316) for leached sample and 3780 ± 73 BP for the alkali-soluble organic fraction (NZA 9343). The conversion of the CRA data to the calendar date (e.g. using the OxCal program – Stuiver & al. 1993) still has problems (KILIAN & al. 1995).

The youngest sedimentary layers (less than 150 years old) were dated by P.A. Appleby of the Liverpool University using the ^{210}Pb method (APPLEBY & al. 1988, ROBBINS & HERCHE 1993). An amount of about 50 mg of the thermally pretreated sample was analysed for ^{210}Pb by direct gamma spectroscopy, assuming that the unsupported ^{210}Pb is bound in the sediment at a constant rate (CRS calculation model). The ^{210}Pb dates were independently validated by ^{241}Am determination and by pollen stratigraphy in the Černé Lake sediment.

The age of the sediments between the layers dated by ^{14}C and ^{210}Pb was obtained by interpolation assuming a constant rate of mass deposition. The interpolation considered the depth compression of the sediments but disregarded possible erosion events, mudflows, hiatuses and the long-time trend in the matter accumulation rate. The latter is affected not only by land use or fire, but also, e.g., by climatic changes (BLAIS & al. 1998), has varied between 18 and 60 g $m^{-2}yr^{-1}$ and has generally been higher during the last two centuries. The correctness of the profile dating is, however, significantly supported by the relatively good agreement of the interpolated data with the known facts concerning the changes in the metal smelting during the Middle Ages (KOŘAN 1988) and elevated metal concentrations during the Roman times. The regional pollution observed in Greenland glaciers culminated around 0 AD or a few decades earlier (HONG & al. 1994, ROSMAN & al.1997, HONG & al. 1996), the local pollution with Pb culminated perhaps later in Britain (WEST & al.1997, LEE & TALLIS 1973). We assess the error in determination of the sample age at ≤ 15 years for sediments about one hundred years old and ≤ 200 years for 4000 years old sediments.

The Prášilské Lake profile comprised a period of ca. 6500 years in the 0.8 m long sediment column, that from Plešné Lake about 5000 years (1.2 m) similar to that from the Černé Lake I (1.15 m) in which the pollen spectrum was also analysed (VESELÝ 1998). Another Černé Lake profile (II), 1.35 m long, penetrated at a water depth of only 16 m even to sediments without organic compounds. The age of the oldest sediments in the longer profile from the Čertovo Lake can be estimated at 2800 to 3000 years; these sediments were originally assumed by us as coming from the Middle Ages because the radiocarbon dating was not available (VESELÝ & al. 1993).

Period prior to 1100 BC

More than 3700 to 4000 years ago, the concentrations of Cu and Cd (Fig. 1) and mostly also the concentrations of Zn and Ni (but not those of Co, Ag and Pb) were increased in the Plešné and Prášilské lakes. The natural concentrations of some elements, e.g., Cd or Be, probably decreased during the whole preceding Holocene period. These changes are attributed to changes in the climate and soil development (TAYLOR & BLUM 1995) and lake sediments from this period are especially suitable for a reconstruction of variations in the vegetation and climatic conditions. During the time covered by the collected profiles, the climate and the vegetation probably changed most at 2800 BP, from 3800 to 4000 BP and around 5100 years ago (VESELÝ 1998). For example, the change from a wetter climate to the drier, more continental one about 3800 years ago (KELTS 1997) is documented in the pollen spectrum of the Černé Lake sediments by the absence of Sphagnum in the 2nd millennium BC (VESELÝ 1998). At the end of the 3rd and at the beginning of the 2nd millennium BC, the MgO concentrations in the Plešné and Prášilské Lake sediments simultaneously increased (Fig. 2). At present, we analyze a 6 m long profile of the Plešné Lake sediments which should clarify the natural variations in the metal concentrations and the development of the vegetation in the lake surroundings.

The interpretation of the Černé and Čertovo lake profiles is complicated during this period by local erosion events (VESELÝ 1998) that were also observed by MICHLER (pers. commun.) and resulted from falls of large numbers of trees from the lake wall, high winds and mudflows in the lake with the bottom mean slope of 13°10′ (ŠVAMBERA 1938). Exogenic

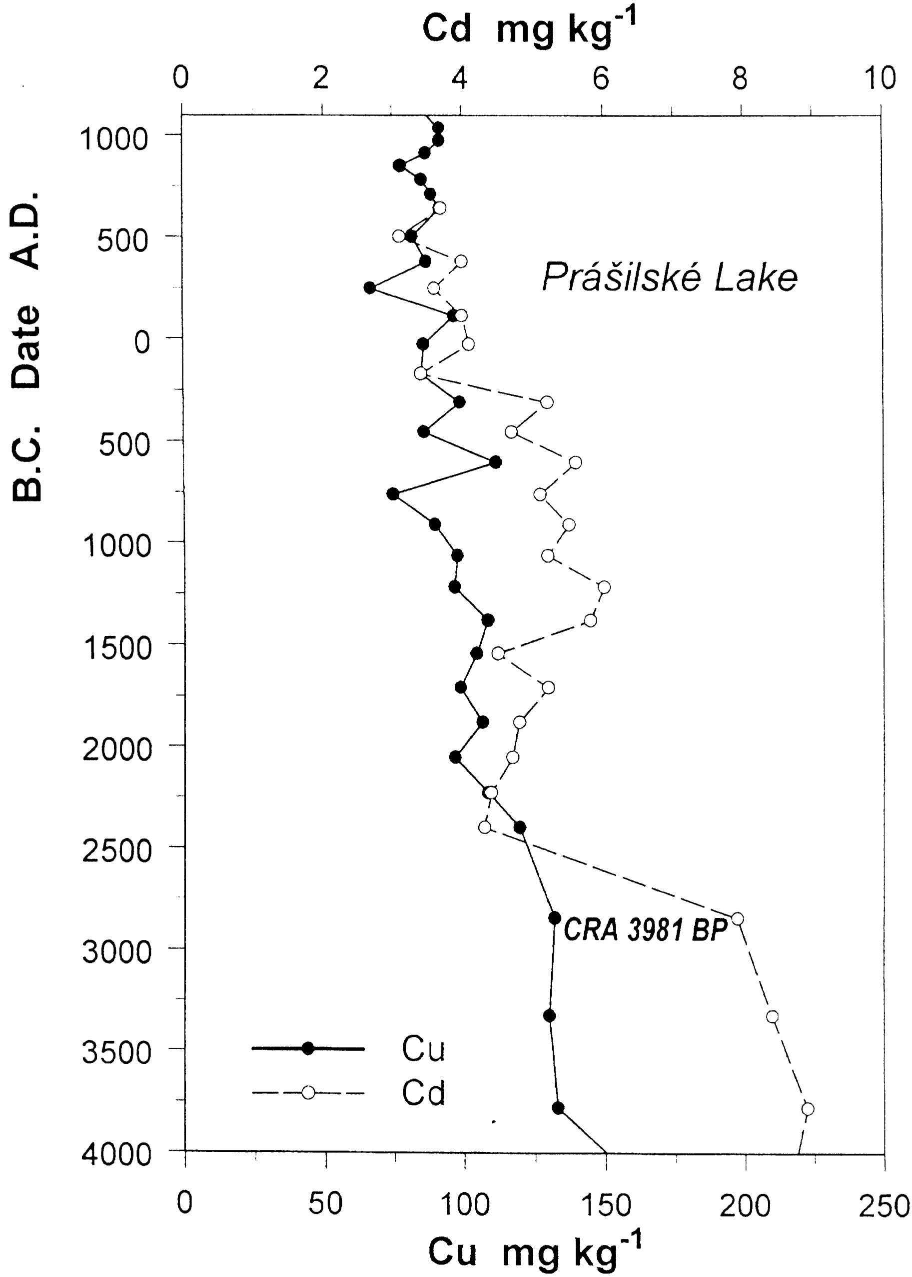

Fig. 1. – Concentrations of Cd and Cu in the Prášilské Lake – sience 4000 B.C. to 1000 A.D.

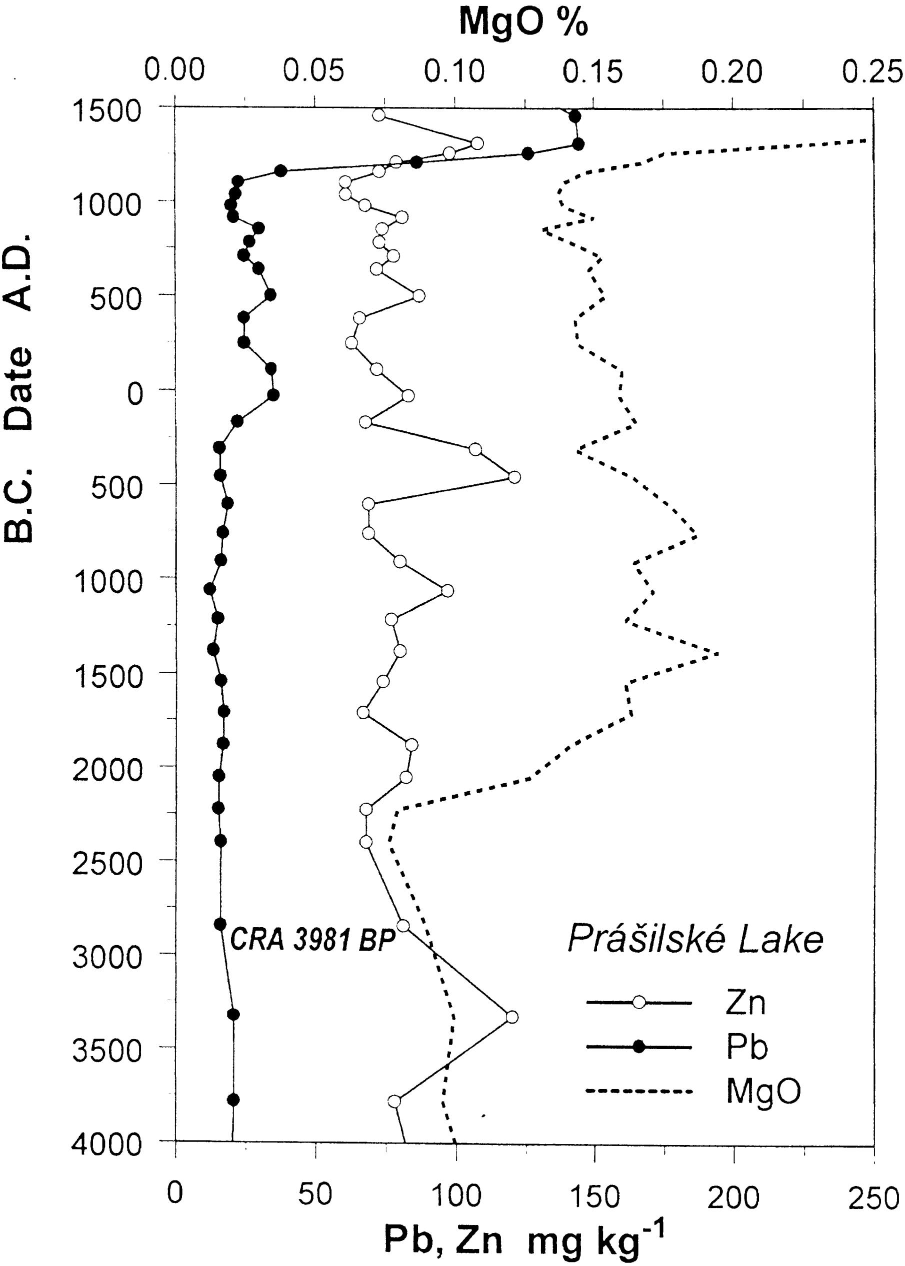

Fig. 2. – Concentrations of Pb, Zn and MgO in the Prášilské Lake, since 3000 B.C to the 1500 A.D.

effects caused occasional decreases in the organic matter concentration which amounted up to ca. 20% LOI at depths above 1 m, increases in flux of material (accumulation rate) into the sediments and complex changes in the trace element concentrations. The thickness of sediments rich in organic matter is usually between 2 and 3 m in the Bohemian Forest lakes.

Period between 1100 BC and 1000 AD

This period is primarily marked by an interesting increase in the Pb concentration around the turn of the eras in all the studied profiles (Fig. 3; VESELÝ 1997, VESELÝ 1998, LEE & TALLIS 1973). Two millennia ago, the Pb concentrations increased 3 to 5 times of the background values amounting to 11.2 ± 1.2 to 23.5 ± 4.6 mg kg^{-1} which corresponds to the reported crustal abundance of Pb (14.8 mg kg^{-1} - WEDEPOOL 1995). One profile from Černé Lake, the only one divided into 0.02 m slices in this section, exhibited yet an older, mild increase in the Pb concentration around the year 500 BC, i.e., at the time of flourishing Greek civilization (Fig. 3; VESELÝ 1998). The anthropogenic flux of Pb into the lake sediments was only about 0.1 mg $m^{-2}yr^{-1}$ that time, i.e., 5 to 10 times lower than around the year 0 AD when the annual metal production peaked at about 80 000 metric tons (HONG & al. 1994), and about 150 times lower than around 1970. The measured Pb concentrations begin to constantly exceed the background values in the 9th century BC (on average at 860 BC for 5 profiles), at a depth of 0.45 to 0.75 m. Around 350 BC, the Zn concentrations in the Prášilské Lake were by 40 mg kg^{-1} higher than for more than the following 1500 years (Fig. 2).

The Plešné Lake sediments contain, for natural causes, substantially less Cu than the other test sediments, except for that from the Popradské Lake that is also situated on granites. In addition to the Cu and Pb concentrations, Fig. 4 also gives the Cu/Al ratio that has been used to normalize the Cu concentrations in the Greenland ice (HONG & al. 1996). Normalization of the Cu concentrations to that of Al only made the assumed anthropogenic increase in the Cu concentrations more pronounced. Increases in the Cu concentrations have been observed for the time of the Roman empire, around 600 AD, in the 16th century AD and repeatedly in the industrial period. The Cu concentration increased from the original 15 mg kg^{-1} around 0 AD to 40 mg kg^{-1} in the 20th century. The Cu contamination 1900 and 1400 years ago increased the natural value by only about 4 mg kg^{-1} and thus could not be recorded in the lakes with Cu concentrations of 100 or more mg kg^{-1} (Černé, Prášilské, Čertovo). An increase in the Cu concentrations during the Roman times was observed about 100 years later than in the Greenland glaciers (HONG & al. 1996). An increase in the Cu concentration by about 3 mg kg^{-1} around 1100 BC in a single sample (Fig. 4) follows a long-term decrease in the Cu concentration and its anthropogenic origin is uncertain, although a somewhat increased concentration of Zn at the time was observed in the Prášilské Lake (Fig. 2).

All the studied profiles further exhibited a smaller increase in the Pb concentrations around 550 AD and in most of the lakes also around 900 AD (Figs. 2–4; VESELÝ 1998). In the Černé Lake, the relative increase in the Bi and As concentrations around the year 550 AD was even higher than that around the turn of the calendar (Fig. 5). However, this profile did not exhibit a Pb concentration peak in the 9th to 10th century AD, although the second profile from the Černé Lake (Fig. 3) indicated a pronounced increase in the Pb concentration in that time.

Period between 1000 AD and 1750 AD

All the studied profiles contained two or three pronounced Pb concentration peaks in the period from 300 to 800 years ago (Fig. 6; VESELÝ 1998). The Pb concentrations increased to 7 to 8 times the background value, i.e., the metal concentration in the sediments more than 3000 years old. It has been known that large quantities of silver were produced in the Bohemian territory since cca 1240 AD (KOŘAN 1988). However, silver itself is not much vola-

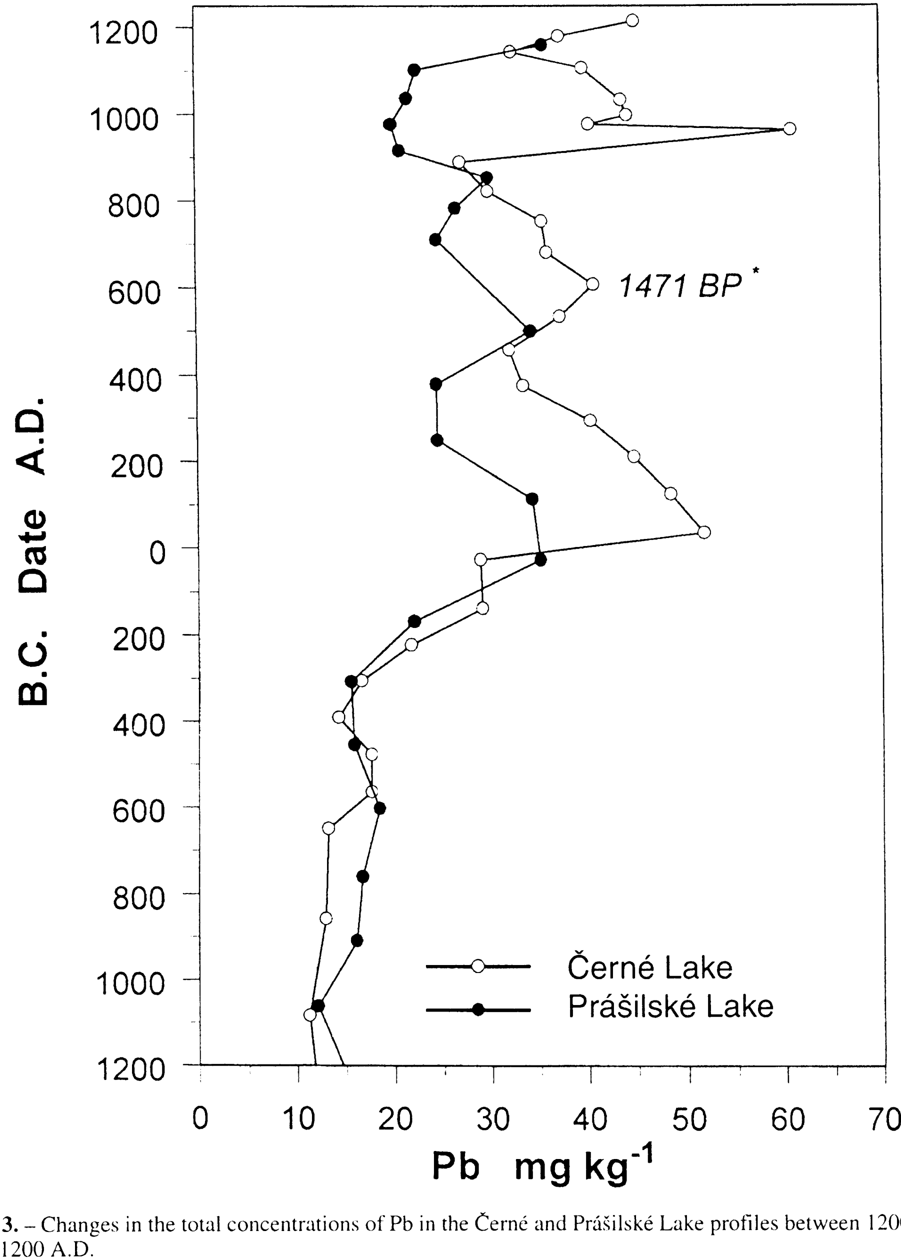

Fig. 3. – Changes in the total concentrations of Pb in the Černé and Prášilské Lake profiles between 1200 B.C. and 1200 A.D.
Pollution by Pb in Roman times, around 600 A.D. and probably also around 500 B.C. and 900 A.D. are demonstrated. * = reservoir corrected radiocarbon age (VESELÝ 1998).

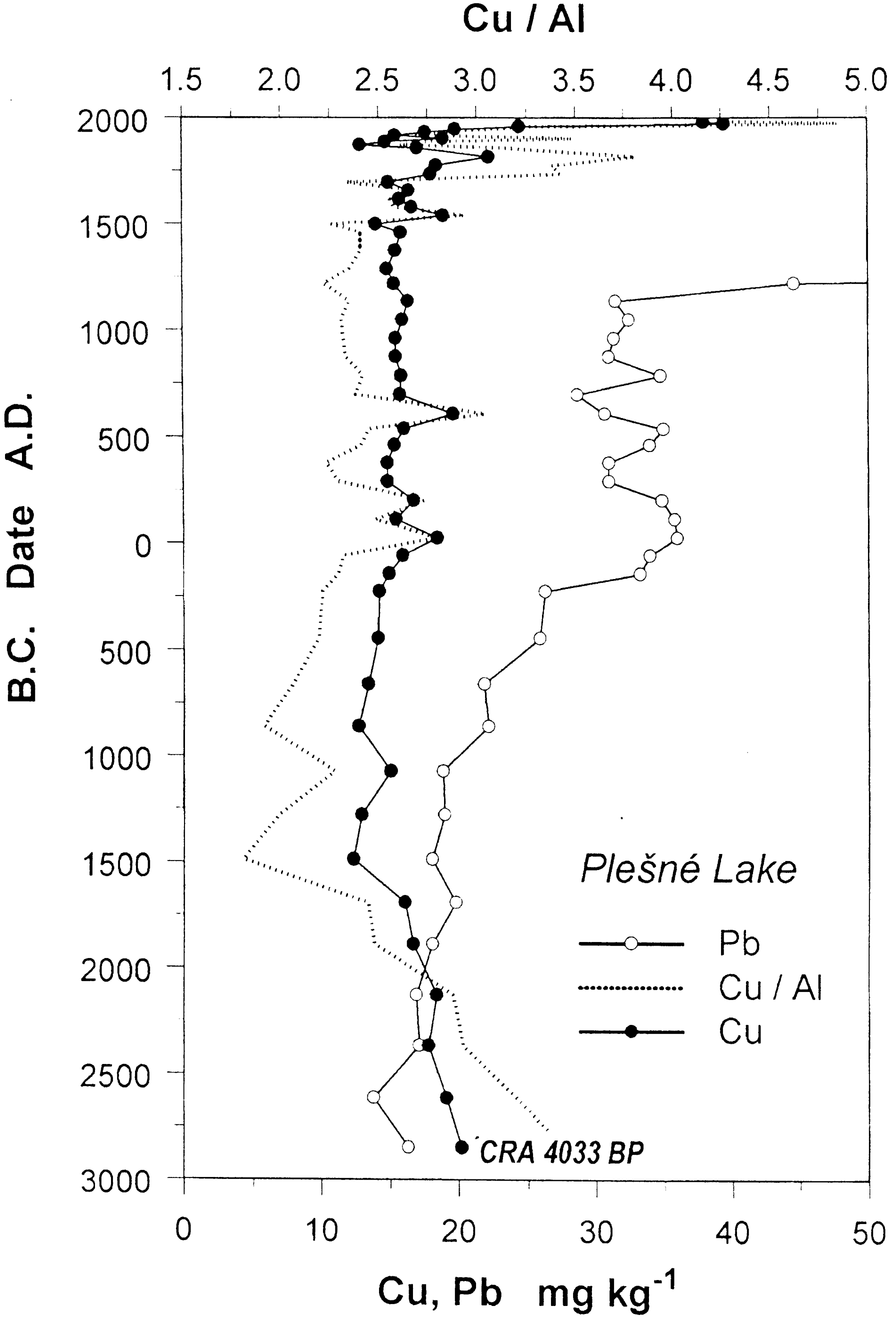

Fig. 4. – Concentrations of Cu and Pb and the Cu /Al ratio in the Plešné Lake sediments. Anthropogenic pollution by Cu is demonstrated.

tilized but lead, which was used in the production of the silver metal at 8 to 14 over-supply (HOLUB pers. commun.) volatilizes more readily and thus forms pronounced anomalies in the lake sediments. Other metals were also present in the silver ores treated and thus readily volatilizing elements, primarily As, Bi and Sb (MAJER 1986, SHOTYK & al. 1996, HOLUB 1997), were also deposited in the Bohemian Forest lake sediments (Fig.5; VESELÝ 1997). Although concentrations of Pb and As, Bi and Sb in sediment of the 20th century and in the Middle Ages are comparable, mediaeval Pb accumulation rates were approximately one fifth due to lower mass accumulation rate. Imissions of Cu, Zn, Cd, and especially Co, V and Be, were insignificant in the Bohemian Forest during the Middle Ages, compared to their natural flux into the sediments.

The changes in the Pb concentration in the Plešné Lake sediments at the end of the Middle Ages differ from those that occurred in the other lake (for the Černé Lake see VESELÝ 1998) in that the first peak is higher than the second one that is, in addition, separated into two smaller peaks (Fig. 6). The mediaeval accumulation of Pb possibly peaked somewhat earlier in the watershed of this lake than in the watersheds of the other Bohemian lakes. This time shift might be connected with the production of silver at Jihlava (PLUSKAL & VOSÁHLO 1998) or with production outside the Bohemian Kingdom, whereas the smaller intensity of the second peak might be caused by the longer distance of the Plešné Lake from Jáchymov and the German Freiberg, from where most of the metals were probably transported by air in the 16th century. If the second maximum in the Plešné Lake sediments (Fig. 6) corresponds to the production of Ag at Jáchymov (Ore Mts.), then the dating of the lake sediments within this time period exhibits a positive error of ca. 70 years.

This increase in the Pb (and also Sb, Bi and As) concentrations has not been observed in the sediments of the Popradské Lake in the High Tatras (Slovakia), at a distance of 500 km to the east (Fig. 7). The Pb concentration in the Popradské Lake sediments increased smoothly for about 700 years, up to the 20th century, in spite of the fact that Kremnica and Banská Štiavnica produced about 10% of the European silver at that time and further smelters were in the 15th century in the vicinity of the Polish Krakow. The differences in the changes in the Pb concentrations between the Popradské Lake and the Bohemian Forest Lakes may be explained by combined effects of different distance from the principal sources of anthropogenic pollution and the higher location of the Popradské Lake (1494 m a.s.l.).

The period after the year 1750

This period is characterised by anthropogenic effects on not only the trace metal concentrations in the lake sediments but also on sedimentation of macrocomponents, i.e., organic substances, clay minerals and rock detrite. As can be seen in Fig. 8, the MgO concentrations in the Plešné Lake sediments primarily increased in the first half of the 19th century (i.e., at the time of maximal utilization of the lake water for transport of timber by the Schwarzenberg canal), and around 1955. The long-term decrease in the CaO concentration changed around 1950 into a rapid decrease due to strong acidification of the lake and its watershed. Similar general tendencies were also observed in the Prášilské Lake sediments, but the decrease in the CaO concentration and an increase in the MgO concentration in the 19th century were more complicated. Exogenic effects caused greater changes in the main component concentrations in the Černé (VESELÝ 1998) and Čertovo (VESELÝ & al. 1993) lakes. As the macrocomponents of the sediments have differing background concentrations and differing affinities to trace elements, the interpretation of the metal concentrations in these profiles is difficult.

This period is best recorded in the profiles from the Plešné and Prášilské lakes with unusually high and relatively stable contents of organic substances (around 69.2 ± 1.2 and 59.4

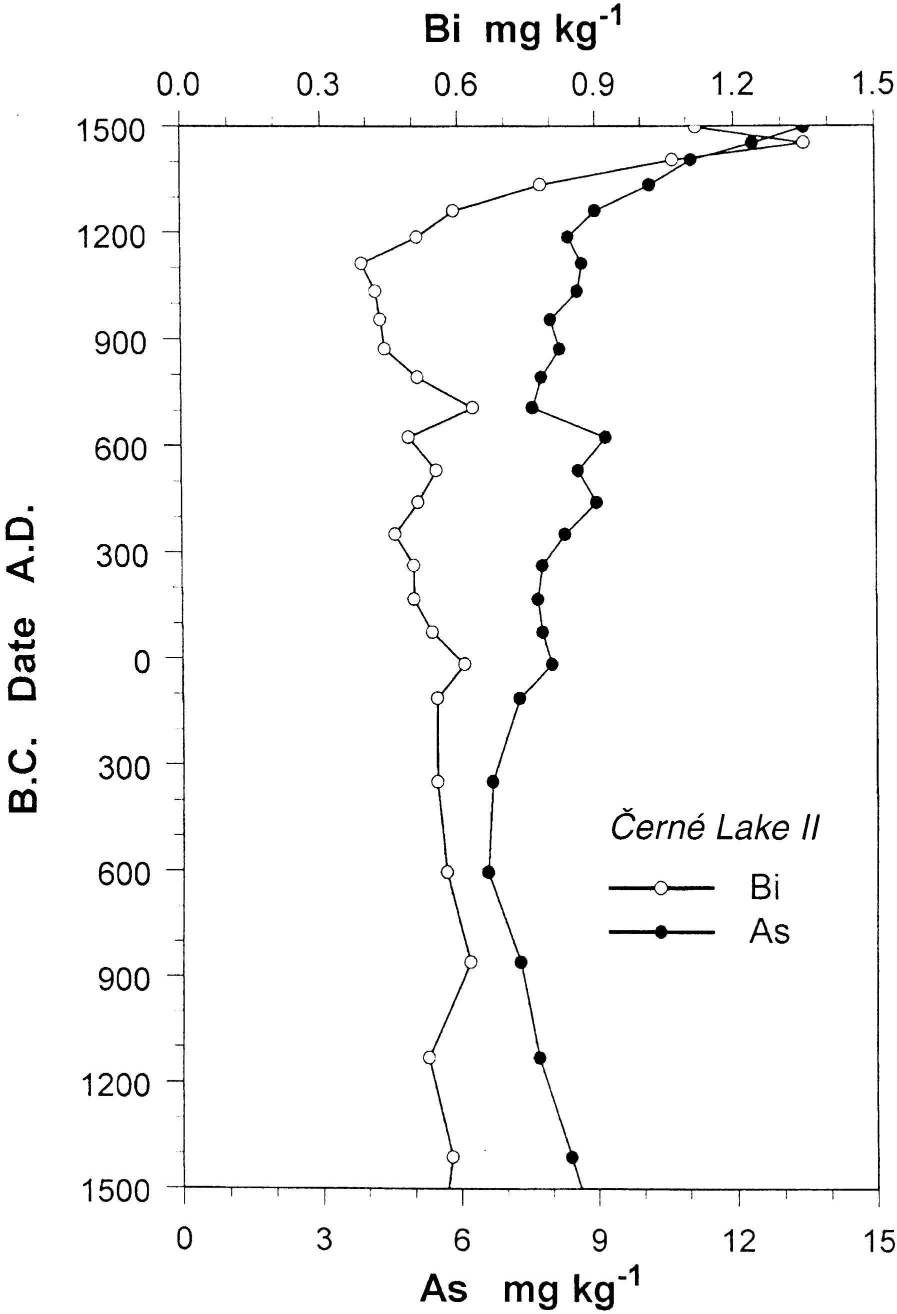

Fig. 5. – Concentrations of Bi and As in the Černé Lake sediment – between 1500 B.C. and 1500 A.D. Other metals were also present in the silver and lead ores treated and thus deposited in the Bohemian Forest lake sediment.

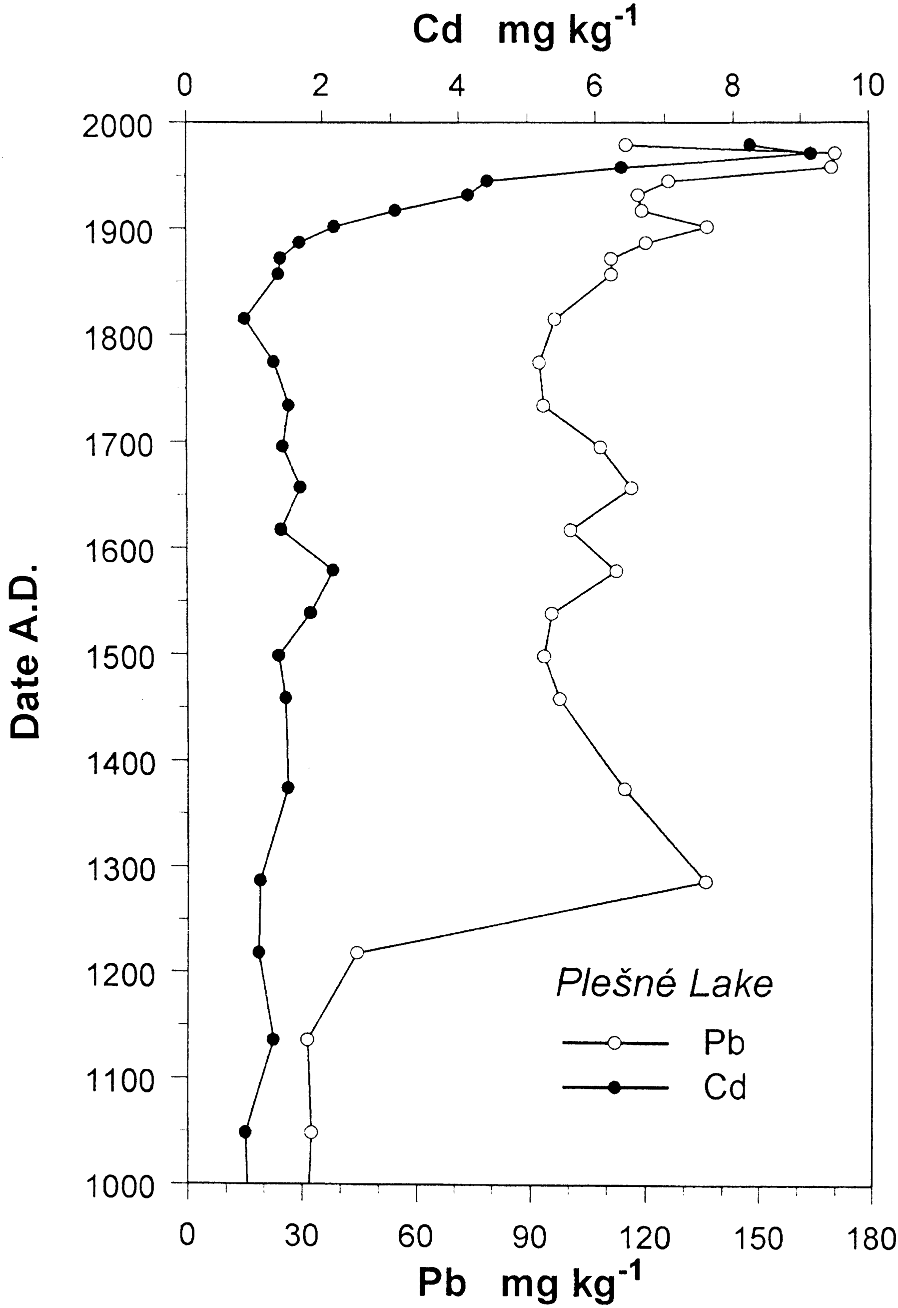

Fig. 6. – Concentrations of Pb and Cd in the Plešné Lake profile – last millennium.
Four or five peaks of Pb concentrations were observed. The Middle Ages concentrations of Pb are comparable with modern Pb concentrations.

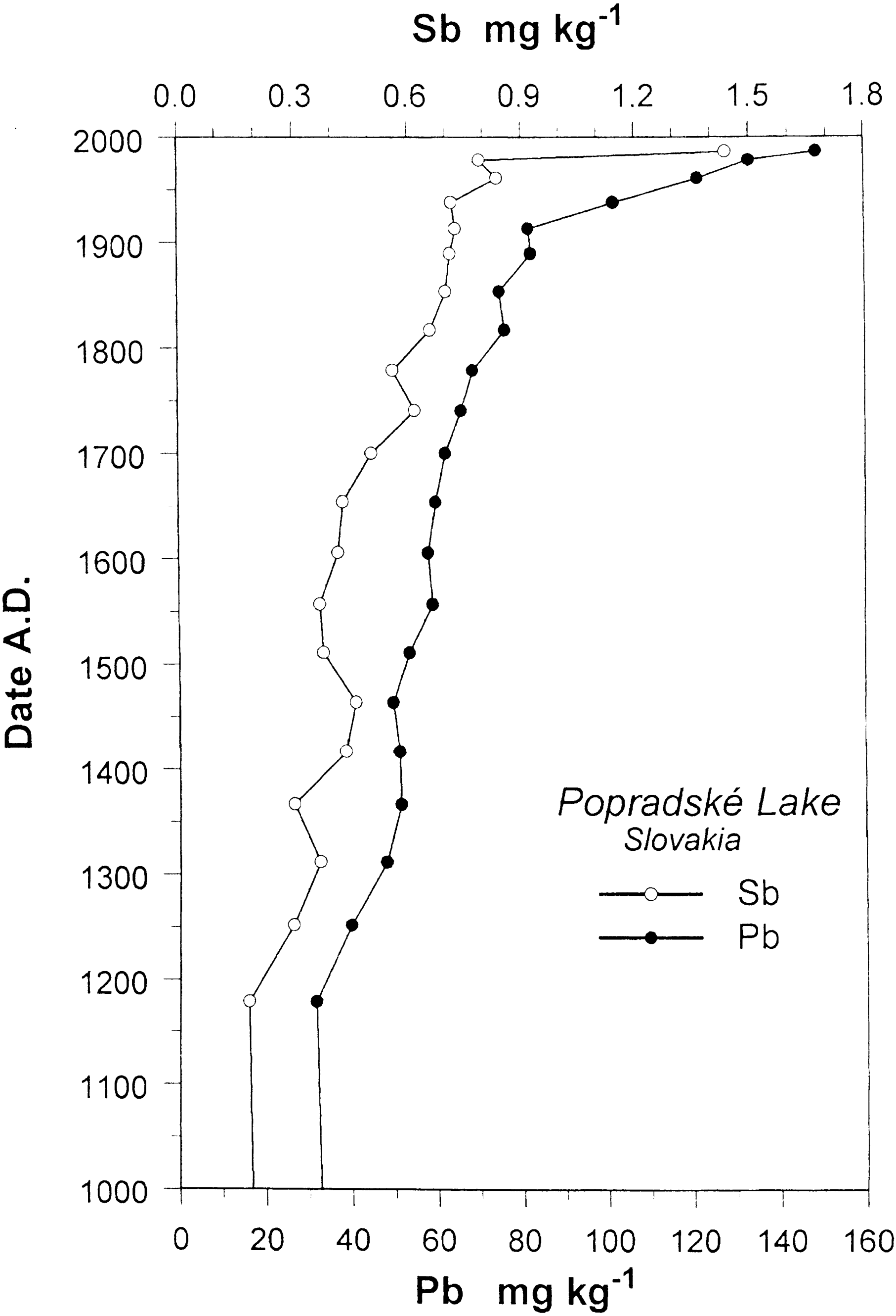

Fig. 7. – Concentrations of Pb and Sb in the Popradské Lake (Slovakia) sediment profile – last millennium. Gradual increase of Pb and Sb in the High Tatras lake in 500 km distance substantially restrict territory for possible the Middle Ages and early Renaissance pollution sources.

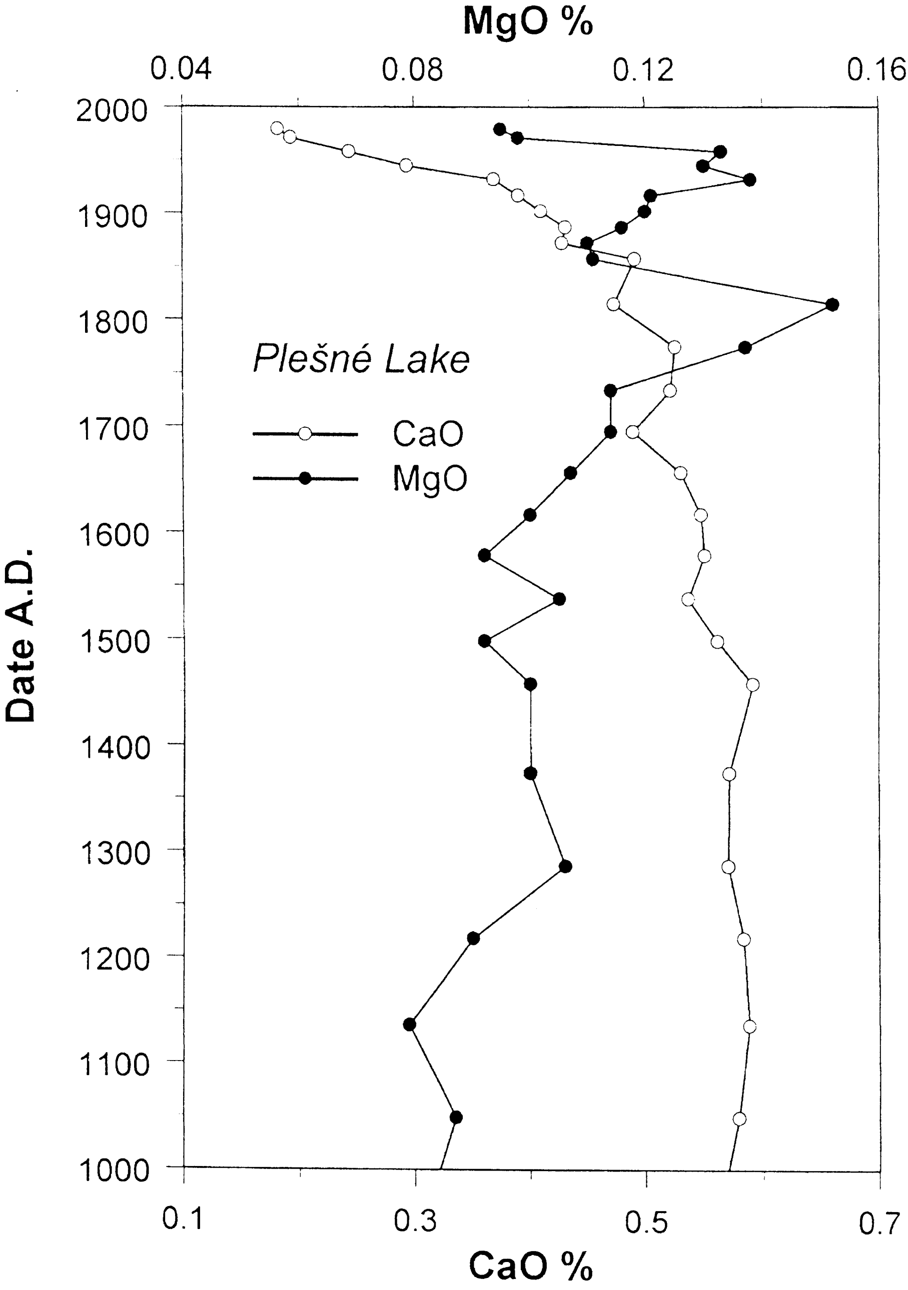

Fig. 8. – Concentration of CaO and MgO in the Plešné Lake sediments – last millennium. Concentrations of MgO gradually increased during the last millennium and peaked in the first half of the 19th century (lake water was used for the transport of timber by the Schwarzenberg canal) and around 1955, due to erosion connected with the fence instalation in the watershed. The long-term decrease in the CaO concentration changed around 1950 into a rapid decrease due to strong acidification of the lake and its watershed.

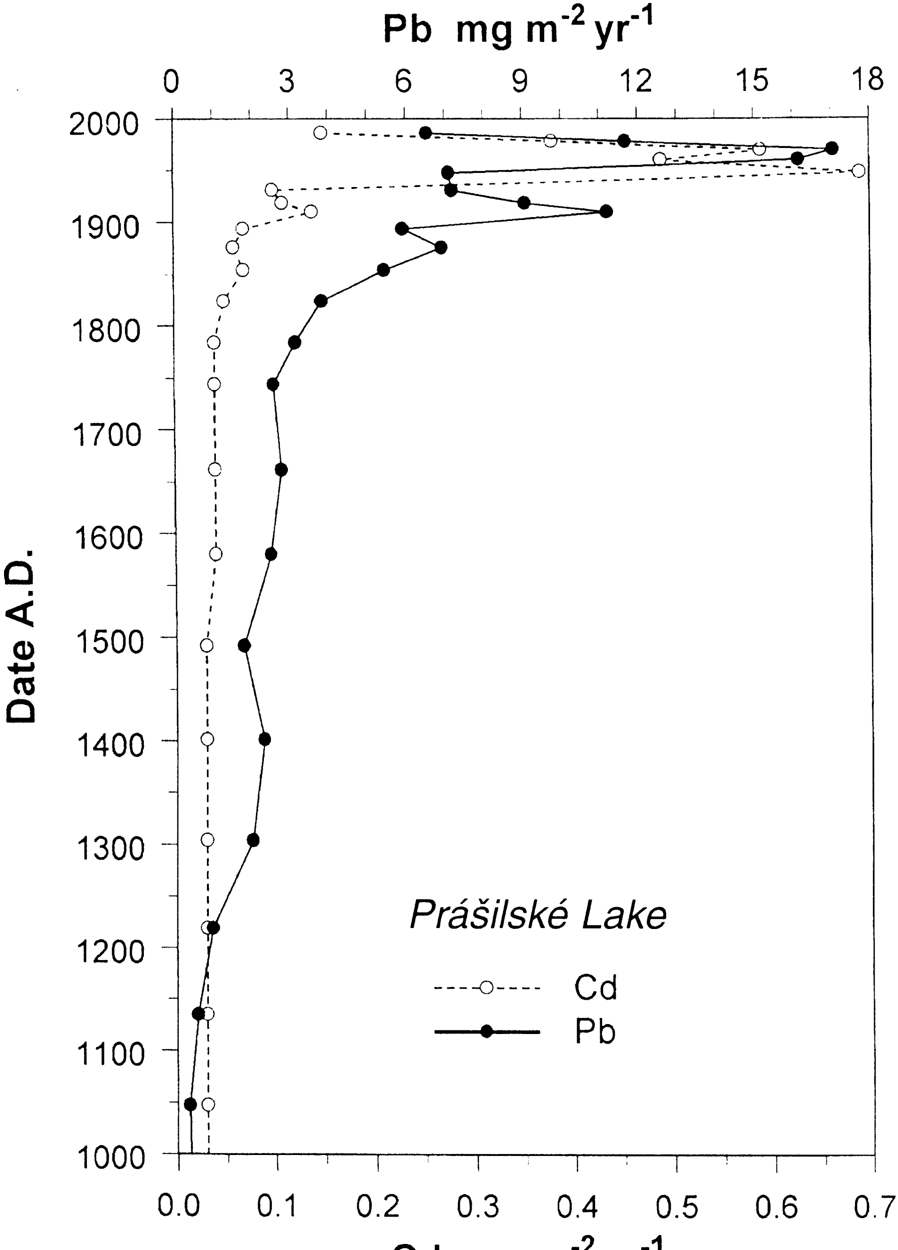

Fig. 9. – Fluxes of Pb and Cd to Prášilské Lake sediments after 1000 A.D.
Two peaks in accumulation rates of Pb and Cd in the 20[th] century and the difference between mediaeval and modern flux to sediment is demonstrated.

± 2.7 % LOI for the former and latter, respectively, prior to 1800 AD). The metal accumulation in the Prášilské Lake sediments (e.g., Pb, Zn and Cu) culminated at least twice during the last 250 years, at 1910 ± 7 and at 1967 ± 11 (Fig. 9). The last increase in the metal deposition into the Plešné Lake also occurred in the second half of the sixties (1966 ± 9), but the increase in the beginning of the 20th century appeared a little early than with the Prášilské Lake (1900 ± 7). Fig. 9 indicates that accumulation of Pb into the sediments of the Prášilské Lake was about 11 mg $m^{-2} yr^{-1}$ ca. 100 years ago and about 17 mg $m^{-2}yr^{-1}$ around the year 1967. The smaller increase in the Pb accumulation rate into the Prášilské Lake in the 19th century (see Fig. 9) is probably connected with increase of the mass accumulation rate at that time (VESELÝ 1994).

The short-time increase in the Cd accumulation in the Prášilské Lake, up to 0.7 mg $m^{-2}yr^{-1}$ around 1950 (Fig. 9) was caused by dissolution of the wire fences erected in the lake watersheds along the state border, separating the western and eastern Europe. In view of the substantially lower background concentration of Cd, the effect of zinc-covered wire mesh was more pronounced in the Cd concentration than in those of Zn and Fe. Contamination of the lake with Cd from the fuel tank discarded from an allied plane at the end of the II. World War is less probable. The tank was recovered from the lake during our collection of the sediments in 1987.

In the second half of the sixties, the accumulation of most of the test metals (Pb, Cd, Zn, Co, Cu, V) into the lake sediments culminated and the seventies and especially eighties of the 20th century witnessed a decrease in the atmospheric deposition into the lake watersheds (Fig. 9; VESELÝ & al. 1998) which continued, according to direct measurements of deposition, during the nineties (VESELÝ 2000). For example, the atmospheric deposition of Pb into the lake watersheds was 1.3 mg $m^{-2} yr^{-1}$ in period 1998–1999, while in the years 1990–1991 was around 8 mg $m^{-2} yr^{-1}$. This was only a few per cent of the Pb deposition in 1973 when the highest value was probably attained in the Bohemian Forest (VESELÝ & al.1993).

Discussion

The beginning of the discernible production of Pb and Cu was caused by the discovery of a new technology of Pb-Ag smelting from galenite and Ag cupellation, about 5 000 years ago (BUDD 1992) and by the beginning of sulphidic ore smelting about 4 500 years ago (HONG & al. 1996). The metal production increased during the Copper, Bronze and Iron Ages. The long-range atmospheric transport of Pb induced by people was so weak before 1000 BC in the Bohemian Forest that it cannot be distinguished from the natural variations and the changes caused by anthropogenic utilization of the landscape. Further research should clarify the cause of the irregularly observed increases in the Cu, Zn and Cd concentrations at ≥ 3 100 years ago which cannot be unambiguously attributed to anthropogenic effects, although e.g., WEST & al. (1997) reported an increase in the Cu and Zn concentrations in Britain at about 1600 BC. Unfortunately, Cu and Zn have a relatively large natural variability in lake sediment. The oldest anthropogenic increases observed at present are those in Swiss peatbogs about 3 200 years ago (SHOTYK & al. 1998), with a substantially lower background value for the Pb concentration (WEISS & al. 1997).

During the Hallstadt period (named according to an excavation place near Salzburg, Austria, which is only ca. 150 km far from the Bohemian Forest lakes), the intensity of anthropogenic Pb immissions was already unambiguously differentiable from the natural flux of Pb into the sediments amounting to 0.25 to 0.40 mg $m^{-2}yr^{-1}$. During the following period, the Greek production of Pb and Ag increased, being stimulated by the beginning of mintage (ca. 650 BC) and was assessed at about 600 000 tones of Pb between the years 600 BC and 100

AD (see ROMAN & al.,1997), i.e., at about one tenth of the later „Roman„ production (HONG & al. 1994). During the peak of the Roman power, the contamination of Silva Gabreta (the Roman name of the Bohemian Forest) with lead was quite perceptible. The Pb/Ag was produced in open-air furnaces with no control on emission rates. The extent of lead use in the antique Rome has even caused speculations about connections with the decline of the imperium (NRIAGU 1983). In our estimation, about 20 tones of anthropogenic Pb could deposit annually on the Bohemian territory around the year 0 AD, i.e., about 0.5% of the lead emitted (HONG & al. 1994).

As this contamination of the Bohemian Forest by lead is accompanied by pollution with Bi, As and Sb, it is evident that it stems from metal smelting, especially in the distant south of Spain and Balkans (37 and 27% of the Pb production at that time – NRIAGU 1983). For example, around 70% of lead was transported into the Greenland ice from southern Spain between the years 366 BC and 35 AD (ROSMAN & al. 1997). British sources might contribute somewhat later (0 – 400 AD – WEST & al. 1997, LEE & TALLIS 1973) and possibly also smaller, but substantially closer, sources, e.g. in southern Bavaria (KEMPTER & al. 1997). In this connection it is interesting that the pollen spectrum of the Černé Lake sediment exhibits a sudden and short-lived decrease in the beech content in Roman time (VESELÝ 1998). The beech charcoal was preferred for smelting, as it yielded higher temperatures. Therefore, the slight shift of the centre of the „Roman„ peak of Pb to the first centuries AD (e.g. Černé Lake, Fig.3) need not necessarily stem from imprecision of the profile dating.

Approximately at the same time, about 2300 tones of Cu were also emitted annually into the atmosphere which definitely was reflected in the increase of the Cu concentration in the Plešné Lake. Such an increase is probably reported for the first time in lake sediment, because the Cu/Al ratio was used for the contamination of the Greenland ice (HONG & al. 1996). The Cu/Al ratio just makes the changes in the Cu concentration also in the Plešné Lake sediments more pronounced.

The increase in the Pb concentrations during the 6th and during the 8th to 10th centuries was observed also by MARTÍNEZ-CORTIZAS & al. (1997) in a peatbog in distant southwestern Spain. CAMARERO & al. (1998) observed an increase in the immission of Pb into the sediments of the Redó Lake in Pyrenees that is located at a high altitude (2240 m), at ca. 660 AD, but they did not record an increase in the Pb concentration during the time of the Roman empire. An increase in the Pb concentration between 800 and 1300 AD was observed by KEMPTER & al. (1997). The sources of contamination in 6th and perhaps during 8th to 10th century AD are, so far, only speculative and their identification would also clarify the origin of Ag used for denar minting in Bavaria (especially in Regensburg) and by the Czech princes Boleslav I and II in the 10th century (PETRÁŇ 1998). Contributions of emissions from Harz in lower Saxony are probable (KLAPPAUF & al. 1992, MATSCHULLAT & al. 1997, KEMPTER & al. 1997). Among the Czech localities, Manín, now part of Kutná Hora, can be one of the sources.

The long-term, exceptionally large production of about 1/3 of the European silver in the Bohemian Kingdom at the end of the Middle Ages definitely strongly participated in the relatively strong pollution of the Bohemian Forest with Pb, Bi and As 700 years ago. The silver was first produced at Jihlava and its surroundings, later at Kutná Hora and in the 16th century at Jáchymov, Příbram, Rudolfov, Nážlovské (Stříbrné) Hory and at a number of other places. Considerable amounts of lead were used during the Ag production (KOŘAN 1981) and the lead for these purposes was mostly imported from Poland, Harz and Karnten, because small amounts of galenite mined at the town of Stříbro were primarily used for pottery glazing (KOŘAN 1981). At town Kutná Hora alone, 65 km to the east of Prague, up to 20 tones of Ag were produced annually just around the year 1300 which respond to emission of 200 to 250 tuns of Pb (HOLUB, pers. commun.). The Kjelnárka stream contaminated the Elbe river even at that time (VESELÝ & GÜRTLEROVÁ 1996). The local Pb immissions in the Bohemian Forest were complemented to an unknown extent from sources outside the Bohemian Kingdom. An increase in the Pb concentration was also observed at the end of the Middle Ages in the Greenland ice (after 1200 AD – ROSMAN & al. 1997) and a weak increase around 1290 AD in Swiss peatbogs (SHOTYK & al. 1998). However, these increases were much less pronounced than those in the Bohemian Forest lake sediments and the Pb pollution of that time is probably mainly Bohemian origin.

Emissions of metals from Kutná Hora, Jáchymov and other places were definitely accompanied by increased emissions of acidifying sulphur compounds, with a contribution of smelters producing tin (BOUZEK & al. 1989) and iron. Ores were also baked in the Bohemian Forest (e.g. close to Velhartice) and the pyrite was treated e.g. at the vitriol smelter near Strážov (HOFMANN 1980). There exists first evidence on decreases in the pH in sensitive lakes during the preindustrial time, on the basis of analyses of the diatom residues, e.g., in the sediments of the Herrenwieser See in Black Forest, Germany (JÜTTNER & al. 1997). Similar conclusions follow from analyses of diatoms carried out by D.F. Charles (unpubl. res.) in the Prášilské Lake sediments collected by J.Hruška.

Atmospheric deposition of metals into the lake watersheds experienced a complex development during the Renaissance and peaked twice during the 20th century, at its beginning and in the second half of the sixties. An increased pollution with Pb at the beginning of the century peaked between 1900 and 1910, it was recently also observed in the Swiss peatbogs (SHOTYK & al. 1997) and in Greenland snow and ice (CALDELONE & al 1995). We assume that this was also connected to metal smelting as (i) annual production of silver culminated at 30 to 45 metric tuns in Bohemia, (ii) we can see no reason for limited coal combustion after 1920 mentioned by WEISS & al.(1999). A local peak of emissions from coal combustion at the beginning of the 20th century is improbable in the Bohemian Forest because this is an area rich in timber and without coal deposits whose use was introduced slowly.

The last peak of the metal deposition was mainly caused by emissions of power plant ashes. Because this was primarily an emission of particles, the sediments contain even maximum concentrations of elements that would normally be difficult to transport through the atmosphere (e.g., Ag). The emissions of ashes were decreased by installation of separators in the coal power stations substantially earlier that the suppression of sulphur emissions that has been observed in the Bohemian Forest from the half of 1986 (VESELÝ 1990). Around 1970, lead was already primarily emitted from mobile sources (NRIAGU & PACYNA 1988). In the then West Germany, the concentration of Pb in the car fuel began to be limited in 1973, in Czechoslovakia in 1982. Our previous results indicated that contamination of the Bohemian Forest with lead already decreased since the second half of the seventies (VESELÝ & al. 1993) and in 1998 was by more than 90% lower than in 1973.

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