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# Trace elements in Bohemian Forest lakes

# Josef Veselý

Czech Geological Survey, Klárov 3, CZ-118 21 Prague 1, Czech Republic

# Abstract

The mean concentrations of 35 trace elements were determined in waters of 5 glacial and one man-made lake in the Bohemian Forest. Lakes situated on granite (Plešné and Žďarské) exhibit higher concentrations of Be, Li, Ti and U; lakes on gneiss higher concentrations of Ba, Cu and Co. The Mn and Be are mobilized from soils and rocks by acid atmospheric deposition, while direct atmospheric deposition enhances the concentrations of Pb and As. The level of the atmospheric deposition of Cu, Be, F and Zn decreased by ≤ 50 % in the 1990–1991 to 1998–1999 period and deposition of Pb was < 1/10 of the culminating Pb deposition, which occured around 1973. The concentrations of rare earth elements (REE), Y, Fe, As and V depended on concentrations of organic matter in the lake water. Bioaccumulation of Cu, Cd, Zn, and Pb by a factor of ~ 3x10<sup>5</sup> was observed in Černé Lake with the lowest DOC. The rather high ratios <sup>216</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb in anthropogenically unaffected sediments of Plešné Lake are connected with the higher concentrations of U in both the bedrock and sediment or higher radiogenic Pb in sediment. The substitution of V or As for P in freshwater algae is improbable in the Bohemian Forest lakes due to their low molar ratios of V/P (~ 1x 10<sup>-2</sup>) and As/P (~ 2x10<sup>-2</sup>). The trace element pollution seems to be a rather minor ecological problem in the lakes at present. Phosphorus is an exception and the study of the biogeochemical cycle of P remains to be the most serious problem.

#### Introduction

Acidification of Černé, Čertovo, Plešné and Prášilské lake waters and partial acidification of Laka Lake is a consequence of long-range atmospheric transport of S and N compounds and of the increase in the sulphate and nitrate concentrations in the lake water (Veselý 1996, Veselý & al.1998a). The processes in the Bohemian Forest catchment and lakes differ from those causing acidification in the Scandinavian and Canadian lakes in their intensity and in a high concentration of nitrates (Veselý & Majer 1992). The concentration of nitrates depends on N deposition and bioconsumption in the catchment and in the lake (Kopáček & al.1995). In the Bohemian Forest, the highest concentrations of NO<sub>3</sub> can be found in the deepest lakes, i.e., Černé and Čertovo lake where a considerable part of the lake water remains cool in hypolimnion all year round. E.g., Černé Lake has 37 % of the water volume deeper than 12.5 m, whereas the values for Plešné and Prášilské lakes are only about 10 % and 5 %, respectively. Relatively high concentration of NO<sub>3</sub> in Laka Lake is connected with a lower bioconsumption of N compounds in the lake due to a short residence time. On the contrary, the bioconsumption of N in the catchment of Žďárské Lake is practically complete and the NO<sub>3</sub> concentrations in the water are mostly negligible (Veselý & al. 1998a).

The bioconsumption of inorganic N in the Bohemian Forest lake waters is limited by a low concentration of phosphorus (Jírovec & Jírovcová 1937, Vrba & al. 1996); e.g., between 4.2 and 10.7 μgL<sup>-1</sup> in October 1993 (Κοράζεκ & al. 1995). Relatively low concentrations of P have been found also in the Bohemian Forest soils (Pelísek 1971) and thus a special attention is being paid to the P biochemical cycle (Κοράζεκ & al. 1998). In the literature it is pos-

sible to find information on inhibition of the growth and photosynthesis of algae and cyanobacteria due to substitution of P (orthophosphate –  $PO_4^{3}$ ) by As (arsenate –  $AsO_4^{3}$ ) (Planas & Healey 1978) or V (orthovanadate –  $VO_4^{3}$ ) (Nalewajko & al. 1995), caused by inability of algae to distinguish between these physically and chemically similar species. If the phosphate and vanadate are transported by the same system, then P-sufficient cells are less inhibited by V than P-deficient ones. Specific differences exist among variety of freshwater algae and cyanobacteria (Nalewajko & al.,1995) and the  $AsO_4^{3}$ /  $PO_4^{3}$  ratio is crucial in the regulation of the arsenate toxicity to the growth of phytoplankton species (Planas & Healey 1978).

These facts stimulated the study of further trace elements in the Bohemian Forest lake water. The concentrations of Be, Cd, Cu, F, Fe, Mn, Pb and Zn have been monitored since 1984 (Vesely & al. 1998b). This paper describes the mean concentrations of 35 elements in the water of the Bohemian Forest lakes, 27 of which for the first time. The concentrations obtained are compared with the mean concentrations of these elements in Norwegian lakes and in the filtered water of Czech rivers. The relative significance of the most important factors affecting the concentrations of trace elements in the lake water is discussed. Special attention is paid to the concentration of uranium in Plešné Lake caused by unusually high concentrations of U in lake sediments.

### Experimental

The water samples were collected in 100 ml PE bottles cleaned with 10 % HNO, for a minimum of 48 hours. The bottles were transported to the lake filled with distilled water acidified with HNO, to pH  $\approx$  1.5. The were rinsed 3 times by the lake water before sample collection and the samples were immediately acidified to a pH about 1.5 with 1 ml HNO<sub>3</sub>, purified by subboiling distillation. The samples were collected in July and October 1997 and 1998. The concentrations of trace elements were determined by ICP-MS in Analytica a.s.(J.Bendl) with the exception of Be, Fe, Pb, Cd, Mn, Zn, determined by AAS methods in Czech Geological Survey. The concentrations of Ge, Sb, Se, and Te were determined by the ICP-MS hydride method, which does not fully include the part of the element linked to organic matter and thus the final concentrations of the elements are lower. The repeated determination of trace elements in five blank samples showed that the level of the sample pollution caused by the analytical methods is safely under the detection limit for all the elements. The blank samples contained on average: 0.26 µgL<sup>-1</sup> Zn, 0.1 µgL<sup>-1</sup> Mn, 0.04 µgL<sup>-1</sup> Ni, 0.01 µgL<sup>-1</sup> Sb,  $0.02 \ \mu g L^{-1}$  Ba,  $0.002 \ \mu g L^{-1}$  La and Rb,  $0.002 \ \mu g L^{-1}$  U,  $0.001 \ \mu g L^{-1}$  Y and  $0.02 \ Sr \ \mu g L^{-1}$ . The only trace element present in the acid added at an unacceptably high concentration was P (the mean concentration in the blank samples was 45 μgL<sup>-1</sup>). The often discussed concentrations of Hg in the lake water was not determined because this would require a special type of sampling and determination, similar like determination of P. Isotopes of Pb were orientatively determined in an acid leachate of 9 Plešné and Prášilské lake sediment samples using the ICP -MS method at the Faculty of Sciences, Charles University, Prague (J. Košler).

#### Results

The observed medians for the waters of the Bohemian Forest lakes, together with the mean concentrations of trace elements in Norwegian lakes (Skjelkvåle & al. 1996) and the medians in filtered (0.4 µm Nuclepore) water of Czech rivers (Veselý & al. in press), are given in Table 1. Filtered river waters were selected because, unlike lake waters, river often contain considerable amounts of suspended particulate matter with high trace element concentrations.

Table 1. - Medians in the Bohemian Forest lakes in 1997 and 1998 (μgL<sup>-1</sup>).

	Černé Lake	Čertovo Lake	Prášilské Lake	Plešné Lake	Laka Lake	Žďárské Lake	Norwegian lakes *	Czech rivers***
As	0.18	0.21	0.43	0.30	0.18	0.57	<0.05**	0.8
Ba	18.4	15.3	11.3	7.5	12.4	8.3	3.1	34.2
Be	0.19	0.10	0.06	0.33	0.05	0.41	< 0.01	< 0.02
Bi	0.02	0.02	0.04	0.03	0.04	0.05	0.02	
Cd	0.21	0.20	0.11	0.18	0.04	< 0.04	0.01**	0.04
Ce	0.12	0.15	0.31	0.36	0.24	0.73	0.21	0.20
Co	0.91	1.04	0.51	0.17	0.24	0.12	0.05	0.92
Cs	-	0.04	0.05	0.23	0.01	0.03	-	0.06
Cu	1.1	1.3	1.1	0.13	1.3	0.45	0.41	1.4
Eu	0.007	0.008	0.01	0.006	0.015	0.015	0.005	< 0.05
F	2.37	2	1.4	4.5	1.1	2.35	-	
Fe	90	131	103	70	140	400	61	190
Ga	0.02	0.01	0.01	0.02	0.02	0.03	0.12	0.09
Ge •	-	0.01	0.02	0.02	0.02	0.02	0.1	0.04
La	0.08	0.1	0.2	0.19	0.16	0.5	-	0.11
Li	-	0.7	0.6	1.9	0.46	1.1	0.17	5
Mn	38	31	32	41	17	25	3.4	79
Nd	0.06	0.06	0.13	0.09	0.09	0.37	0.15	0.07
Ni	2.3	1.6	1.3	1.0	1.1	1.3	0.33	3.4
Pb	1.1	1.2	0.89	1.1	0.62	0.57	0.18	0.37
Rb	2.54	1.66	1.85	3.1	1.27	1.85	0.49	4.21
Pr	-	0.02	0.05	0.04	0.03	0.11	0.04	0.02
Sb •	0.11	0.12	0.08	0.11	0.09	0.09	0.03	0.33
Se •	0.019	0.019	0.015	0.013	0.011	0.013	-	0.05
Sm	-	0.05	0.06	0.06	0.04	0.14	0.03	0.03
Sr	7.6	5.1	6	4.5	9.3	13.9	5.9	200
Te •	0.01	0.01	0.01	0.008	0.009	0.01	<0.006	-
Ti	0.97	4.7	3	5.1	3	6.2	4.9	11.4
Tl	-	0.011	0.013	0.02	0.007	0.006	-	0.016
U	0.01	0.01	0.02	0.46	0.02	0.21	0.04	0.45
V	0.06	0.12	0.08	0.08	0.15	0.28	0.1**	1.2
Y	0.45	0.26	0.8	0.31	0.59	0.75	0.09	0.12
Yb	0.02	0.02	0.05	0.02	0.04	0.06	0.01	0.03
Zn	13	10	9.7	11	3.2	2.2	1.7	8.2
Zr	0.03	0.05	0.04	0.06	0.05	0.14	<0.02	0.07
pН	4.71	4.41	4.81	4.78	5.36	5.90		7.67
DOC	1350	2560	4350	3130	3480	11600		5000

Six determinations in each lake. • = hydride method used; \* = Skjelkvåle & al. 1996 (n = 473); \*\* = Skjelkvåle & al. 1999 (n = 985, for As 520), \*\*\*= Veselý & al. (in press) (n= 119).

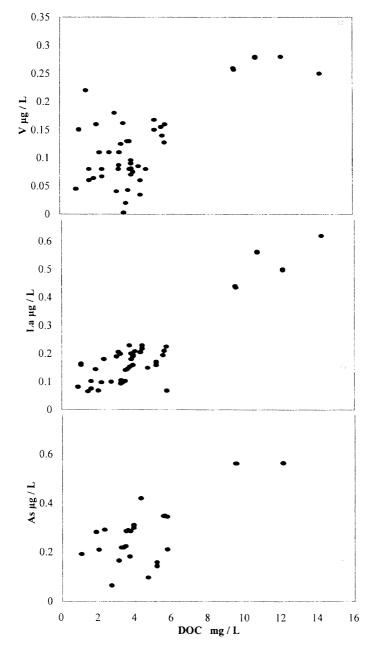


Fig.1. – Dependence of V, As and La concentrations on DOC in the Bohemian Forest lake waters (o = very acid tributary of the Černé Lake).

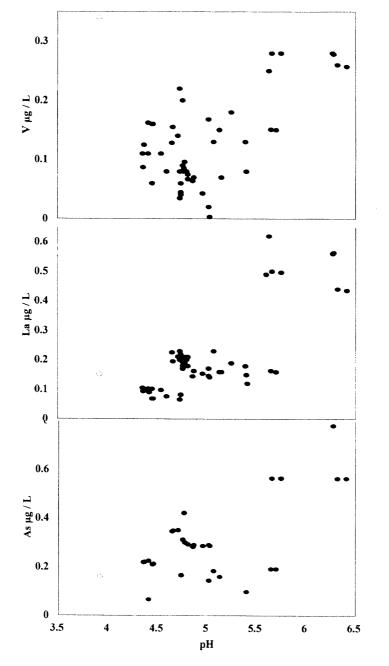


Fig.2. – Dependence of V, As and La concentrations on pH in the Bohemian Forest lake waters (o = very acid tributary of the Černé Lake).

Several natural differences were observed among the mean concentrations of trace elements in the individual Bohemian Forest lakes. Lakes on granite (Plešné and Žďárské) contain less Ba, Cu or Co and, on the contrary, more Be, Li, Ti and U. The higher concentrations of Cs and rather higher concentrations of Rb in Plešné Lake are probably caused by their higher concentrations in the bedrock (Rb 325 mg kg<sup>-1</sup>) and by higher concentrations of finely dispersed soil minerals in the lake water. This could be the cause of the turbidity of lake water that was repeatedly observed in the past. For example, on 24<sup>th</sup> August 1960, the water had a permanent, milky greenish, apparently inorganic turbidity (Procházková, pers. comm.).

The concentrations of the rare earth elements (Ce, La, Nd, Pr, Sm, Yb = REE), Y, As, Fe, V and Zn in the lake waters were considerably affected by the presence of organic matter (La, As and V, see Fig. 1). The highest mean concentrations of As and DOC in Žďárské Lake and the lowest concentrations in Černé Lake prove that As is bound to organic matter, although the concentrations of As are also affected by direct atmospheric deposition. The concentrations of La and As are closely correlated with both DOC and the pH (Fig.1 and 2). Concentrations of V are higher at higher DOC, minimal around pH 5.0 and thus the behaviour of V more reminds of the behaviour of phosphorus.

With low concentrations of organic matter in acidified lakes, bioaccumulation of trace elements in biota is more probable (IIVONEN & al. 1992) and has actually been observed from time to time during summers only in Černé Lake which has the lowest concentrations of organic matter. It can be observed as green surface spots measuring up to hundreds of m². It was observed, e.g., on 20th July 1998 not far from occasionally flowing strongly acidic tributary in the north-west corner of the lake, behind the place where there used to be a hotel. According to the analysis of dr. Hejzlar and dr. Komárková (HBÚ AV ČR, České Budějovice), algae *Carteria radiosa* (size 14–16 μm), *Chlamydomonas sp.* (10 and 14–16 μm), *Peridinium sp.* (24 μm) and *Chlorogonium sp.* (long about 30 μm) prevailed. Higher concentrations of Cd, Pb, Cu and Zn were observed in a sample of unfiltered water. If differences are recalculated between the concentrations in unfiltered and filtered water to undissolved matter caught by a filter 0.4 μm (31.3 mgL<sup>-1</sup>) then the particles separated contained 5.1 mg.kg<sup>-1</sup>

Table 2. – Stable lead isotopic ratios of Plešné and Prášilské Lake sediments.

	Age BP	<sup>206</sup> Pb/ <sup>207</sup> Pb	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb
Plešné Lake	>13 000 BP	1.490	23.41	39.91
Plešné Lake	10 050 BP	1.622	26.31	39.63
Plešné Lake	5 650 BP	1.394	21.79	38.30
Plešné Lake	1 970 BP	1.376	21.56	38.30
Plešné Lake	645 BP	1.223	18.92	37.64
Plešné Lake	405 BP	1.215	18.90	37.76
Prášilské Lake	1 590 BP	1.187	18.64	38.17
Prášilské Lake	560 BP	1.168	18.04	37.57
Prášilské Lake	- 38 BP	1.163	17.95	37.26

Anthropogenically unpolluted aerosol and upper continental crust have the following range of isotopic ratios: <sup>206</sup>Pb/<sup>207</sup>Pb 1.19 to 1.22, <sup>206</sup>Pb/<sup>204</sup>Pb 18.68 to 19.11 and <sup>208</sup>Pb/<sup>204</sup>Pb 38.58 to 39.47 (Weiss & al. 1999). Lead ores may have a significantly lower value and gasoline additives in Europe change <sup>206</sup>Pb/<sup>207</sup>Pb of 1.04 to 1.10. In contrast, higher values of <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb signify higher ratio of radiogenic to common lead.

Table 3. – Concentrations of Pb, As, Ba, Rb and Co at different depths of Plešné Lake on July 23<sup>th</sup>, 1997 (μg L<sup>-1</sup>).

areas produced	0 m	5m	10m	12.5 m	15 m
Pb	1.30	1.22	1.04	1.10	1.05
As	0.18	0.16	0.13	0.14	0.12
Ba	7.30	7.90	8.08	7.78	8.07
Rb	2.90	2.90	3.25	3.27	3.40
Co	0.17	0.17	0.21	0.22	0.22
V	0.08	0.05	0.08	0.11	0.13

**Table 4.** – Deposition to forest floor near Čertovo Lake (mg  $m^{-2} yr^{-1}$ ).

	Pb	Cd	Cu	Zn	F	Be	S
1980's	10	0.2	5	30	140	0.03	5700
1990	8	0.18	3	42	65	0.03	3000
1998-9	1.3	0.15	1.2	16	26	0.014	1250

1980's = data from Moldan (1991), average total atmospheric deposition in the Czechlands

Cd. 18 mg kg<sup>-1</sup> Pb, 49 mg kg<sup>-1</sup> Cu and 80 mg kg<sup>-1</sup> Zn. The concentrations of Pb, Cu and Zn on particles were 32 000 times higher than the mean concentrations in the water of epilimnion of Černé Lake, while this value was 23 000 for Cd. The strongly acidic (pH = 3.92) and temporarily flowing tributary probably brings increased concentrations of nutrients including phosphorus into the lake. It is evident from Fig.1 that the tributary (DOC 15.4 mg kg<sup>-1</sup>) contains also high concentrations of V, but not of As and La.

The concentrations of trace elements in the Bohemian Forest lakes are mostly higher, often substantially higher, than those in Norwegian lakes (Table 1). Only the concentrations of light REE, Ti and Sr are exceptional. Since higher mean concentration of Ge in Norwegian lakes can be caused by lower results provided by the hydride method used for waters of the Bohemian Forest lakes, the only element with higher mean concentrations in Norwegian lakes was Ga (compare 0.12  $\mu g L^{-1}$  and  $\leq 0.03~\mu g L^{-1}$  Ga ). On the contrary, the concentrations of Mn, Be, Cd, Zn in the strongly acidified Bohemian Forest lakes are approximately ten times higher than those in Norwegian lakes (Table 1). These elements are mostly or partially mobilized at low pH values of acid soil solutions from the soils and bedrock (Vesely & Majer 1996). For this reason, concentrations of Be and Cd were substantially higher in the Bohemian Forest lakes than in Czech river waters that have approximately neutral pH (Table 1).

#### Uranium in Plešné Lake

The concentrations of uranium in the water of Plešné Lake were about 40 times higher and in Žďárské Lake about 10 times higher than those in the Bohemian Forest lakes situated on gneiss (Table 1). About 10 years ago, we found unusually high, natural concentrations of U in two samples of the sediments from Plešné Lake (203 mg kg<sup>-1</sup> and 332 mg kg<sup>-1</sup>, depth 0.58 and 1.08 m, respectively). These concentrations were substantially higher than 6.2 mg kg<sup>-1</sup> the median concentration of U in the active sediments of Czech rivers (Veselý 1995).

U concentrations affect stable lead isotope ratios. <sup>206</sup>Pb originates from disintegration of the

prevailing isotope <sup>238</sup>U, <sup>207</sup>Pb from dissociation of <sup>235</sup> U, the isotope <sup>208</sup>Pb results from the decay of <sup>232</sup>Th and <sup>204</sup>Pb is not radioactive. Isotopic ratios of <sup>206</sup>Pb/ <sup>207</sup>Pb, <sup>206</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/ <sup>204</sup>Pb in selected lake sediment samples are in Table 2. The <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb ratios in the sediments of Plešné Lake were higher than those known for anthropogenically unaffected aerosol and upper continental crust (Dunlap & al. 1999, Weiss & al. 1999) and substantially higher than the same ratios in the sediments of Prášilské Lake which are approximately of the same age. This is a result of the large difference in uranium concentrations. Higher U concentration in the catchment of Plešné Lake results in higher proportion of radiogenic vs. so-called common lead. The highest ratios of <sup>206</sup>Pb/<sup>207</sup>Pb (1.62) and <sup>206</sup>Pb/<sup>204</sup>Pb (26.31) were found in a sediment about 10 ka old. Consequently, the beginning of Holocene was the time when enhanced amounts of either radiogenic Pb or U were released from the Plesné Lake catchment. In addition, the decrease of values in Table 2 with time again illustrates anthropogenic pollution persisting for more than 2800 years in the Bohemian Forest (Vesely 2000).

The waters of Plešné Lake and Čertovo Lake ( the later with the catchment consisting of gneiss and quartzite) were analyzed for natural and artificial radionuclides in Immunotech a.s., Praha, in order to confirm or reject the suspicion of higher natural radioactivity in Plešné Lake. The volume activities of all the components analyzed in both water samples, i.e. <sup>226</sup>Ra, <sup>228</sup>Ac, <sup>214</sup>Pb, <sup>214</sup>Bi, <sup>208</sup>Tl, <sup>235</sup>U, <sup>40</sup>K and <sup>137</sup>Cs, were, however, lower than the limits of detection, i.e. 2.0; 0.7, 0.3; 0.4; 0.2; 1.0; 5.0 a 0.2 BqL<sup>-1</sup>, respectively.

# Direct atmospheric deposition of trace elements and changes in their concentrations with depth

It can be expected that elements whose significant source is direct atmospheric deposition will have higher concentrations in the surface lake water. The concentrations of As, Ba, Co, Pb, Rb and V at various depths of Plešné Lake on 23th July 1997 are given in Table 3. It is evident that the concentrations of Pb and As in surface water decrease with depth in epilimnion, while they are approximately constant in hypolimnion. On the contrary, the concentrations of Co, Ba and Rb were increasing with depth. This can be explained by different concentrations of the elements in precipitation water. While precipitation is an important source of Pb and As, soils and bedrocks are a major source of Rb, Ba and Co. Heavy raining decrease the concentrations of the latter elements in the epilimnion and increase those of the former elements. The concentrations of V seem to be affected by both atmospheric deposition and leaching of V from rock and soils, or by remobilization of the metal during so-called early diagenesis of the sediments.

The deposition of Be, Cd, Cu, F, Pb and Zn was measured at the forest floor near Čertovo Lake in 1990–1991 (Veselý & al. 1998b) and again in period 1998–1999 (Table 4). It is evident that the metal and F deposition decreased. The level of the deposition of Cu, Be, F and Zn decreased by more than 50 % in 8 years. The data for Be and Cd are only estimated because of a large number of samples with concentrations below the detection limits of the analytical methods. The deposition of Pb decreased after the mid–1970s (Veselý & al. 1998b, Veselý & al. 1993). At present it amounts to < 1/10 of the deposition level of Pb around 1973. Annual deposition of Pb into the Čertovo Lake catchment (to both soils and lake sediment) was around 6.4 kg in 1990–1991, but only about 0.6 kg in period 1998–1999.

#### Discussion

The concentrations of trace elements in lake waters result from a number of factors and processes affecting both the input of the elements into the lake and their output by outflow or sedimentation. The results indicate four especially significant factors: (i) the accessibility of element in rocks and soils of the catchment, (ii) the intensity of acid deposition, (iii) the direct atmospheric deposition of the element, and (iv) the content of organic matter in water. Several centuries of anthropogenic influence on lakes through atmospheric deposition could not obscure natural effects of the bedrock and soils on the concentrations of trace elements in lake waters. The higher concentrations of U, Be and Li in Plešné Lake is linked to a higher speed of their leaching from the soils and rocks of the catchment. However, the accessibility of an element is not only a function of its total contents in the bedrock and soil of the catchment, but also a function of its binding in various rock minerals with different speeds of weathering. The individual elements also have different capabilities of binding in secondary minerals and affinities to the solids phase – they exhibit various values of distribution (partition) coefficients. The distribution coefficient (i.e. the ratio of the element content in the solids present in water to element concentration in the water) is, e.g. for U, the highest around pH 6 and decreases both at lower and higher pH values (VESELY & al. in press). Soluble carbonate complexes of U are formed at pH > 6, in an acid environment U is bound to organic matter, present in the sediments of Plešné Lake at an unusually high concentration (around 70 %). The rather high ratios <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb in the lake sediment are connected with the higher concentrations of U in the catchment. However, the volume activities including the activity of <sup>235</sup>U were under the limit in the waters of Plešné and Čertovo lakes  $(U < 1.0 \text{ BqL}^{-1})$ . An influence of the differences in the radioactivity of lake water on biodiversity in the lakes has not been proved.

Acidification of lakes and their catchments is a cause of the relatively high concentrations of Mn and Be, the source of which in a mountainous terrain is nearly exclusively a mobilization from the lake catchments. Their concentrations in precipitation are negligibly low. Unlike Be, Mn and Fe are mobilized from peat and sediments after the reduction to Mn <sup>2+</sup> and Mn is intensively washed from the foliage (Skrivan & al. 1996). Mn <sup>2+</sup> is mostly present in water as the free ion and its concentrations are inversely related to the pH (Vesely & Majer 1996), while Fe is usually bound to organic matter in water. The substantial difference in the concentrations of Be, Mn, Zn and Cd in the Czech and Norwegian lakes may approximately represent a difference in the intensity of acid deposition. Leaching of soils by strong acid deposition can decrease the accessibility of these elements in soils and possibly can gradually decrease their concentrations in very acidified waters (Vesely & Majer 1996). Zn and Cd are also mobilized by acids, but they also partially enter the catchment through direct atmospheric deposition.

Anthropogenic atmospheric deposition of Pb into lake catchments has existed with varying intensity in the Bohemian Forest for at least 2800 years (Vesely 1997, Vesely 2000). While the contamination by metals was originally caused by smelting of metals, the last maximum of trace element deposition (around 1970) was caused by emissions of power station ashes and, in the case of Pb, even by emissions from mobile sources. Although the present deposition of trace elements is already low (comparable with level before 200 years and still decreasing – Porkert, 1998), the effect of direct atmospheric deposition on the concentrations of Pb and As in lake waters was still evident in 1997 and 1998.

Organic matter is associated in lake waters with, e.g. REE, As, Fe, Pb, and V in the form of colloids (Vesely & al. in press), with the particles smaller than 0.4 – 0.45  $\mu$ m. Phosphorus is also associated with organic matter (Kopacek & al. 1995). In lowlands of Finland and

Sweden, lake waters contain high concentrations of organic matter and high concentrations of Fe (Skjelkvåle & al. 1999) and further elements bound to organic matter. Higher concentrations of organic matter probably limit bioaccumulation of trace elements which is connected with ligands of recent biological origin. These specific ligands are present at low concentrations (1–300 nM) and thus represent only a tiny fraction of DOC (Xue & Sigg 1999). The increase observed in the concentrations of Cu, Pb and Zn through bioaccumulation by a factor of  $3x10^5$  is important and requires a toxicological study. The concentrations of As are lower and those of V substantially lower than those of P in lake waters (Vrba & al. 1996, Kopácek, pers. comm.). While the concentrations of V are comparable with those in Norwegian lakes, the As concentrations in the Bohemian Forest lakes are higher owing to a higher atmospheric deposition of As in the Czech Republic.

The concentrations of V are only partially anthropogenically affected. The capability of V and As to substitute phosphorus in lake algae is considered improbable, due to the low molar ratios of their total concentrations ( $V/P = 5x10^{-3}$  to  $1.5x10^{-2}$ ; As/P =  $1.2x10^{-2}$  to  $2.8x10^{-2}$ ). Studies of the biochemical cycles of P, so far the only trace element well-known to affect the life of lake waters, remain a priority.

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