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Chalcophile elements Hg, Cd, Pb, As in Lake Umbozero, Murmansk Region, Russia

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ABSTRACT: Investigations of Lake Umbozero, the second largest and the deepest lake of the Murmansk Region, were carried out to detect and define biogeochemical patterns of distribution of the chalcophile elements (Hg, Cd, Pb, As) in water, sediments and organs and tissues of whitefishes. Lake Umbozero is affected by emissions and effluents from mining and metallurgical enterprises of the Murmansk Region, as well as air pollution of a global character. Surface and near-bottom maxima were found in the distributions of Pb and Cd in the water column. These two maxima appear to be associated with the cyclical growth of phytoplankton in surface water layers and with sedimentation of lifeless organisms and suspended particles in near-bottom layers. Average concentrations of Pb and Cd in the water column were more than the average value for water of lakes of the taiga zone. Pollution of Lake Umbozero led to higher concentrations of heavy metals in upper layers of sediments as compared to deeper layers. Among heavy metals, the highest factors of contamination were found for Cd and Pb. Pollution of the lake by chalcophile elements has also resulted in their accumulation in organs and tissues of whitefish. Values for concentration factors greater than unity were found for Cd in kidney (5.8) and for Hg in kidney, liver and muscle (3.6, 3.3 and 2.2, respectively) of whitefish.

Key words: Lake Umbozero, Murmansk Region, hydrochemistry, Sediments, Whitefish, Chalcophile elements, contamination

INTRODUCTION

The North of the European part of Russia, including the Murmansk Region, has unique mineral resources. The territory of the Murmansk Region has the largest mining, processing and metallurgical enterprises in the country, bringing to the Earth's surface millions of tons of rocks, as well as releasing into the atmosphere and dumping into reservoirs and rivers thousand of tons of polluting substances, including highly toxic metallic and organic compounds.Among polluting substances, heavy metals, in particular the highly toxic chalcophile elements (Hg, Cd, Pb, As), are extremely hazardous to the environment and to human health. They are capable of migrating significant distances in air and water environments due to their physical and chemical properties (for example, relatively low temperature of fusion, high ability to form metal organic complexes, etc.). These elements have, over recent decades, gained a reputation as global pollutants; yet, in spite of the many sources of chalcophile elements as pollutants in the world, including the Murmansk Region, there is insufficient information on the levels of contamination of the environment by these polluting substances, particularly in water systems.

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As is well known, elements can be divided into two categories based on their biological roles, i.e. essential (or biophilous), and non-essential. The first type of elements includes a large group of metals (such as Co, Cr, Cu, Zn, etc.) which are functionally necessary for living organisms in small concentrations; however, at high levels they become toxic by interfering with necessary biochemical functions (Moiseenko *et al.,* 2006). The non-essential category of elements includes chalcophile elements such as Pb, Cd, Hg and As, which are extremely toxic and represent a serious danger to living organisms.

Determination of the levels of chalcophile elements in the environment, including in biota, presents significant difficulties owing to the low concentrations of the elements to be measured and methodological requirements for specific analytical equipment. Therefore, until recently large-scale research on the distribution of chalcophile elements in fresh-water ecosystems of the Murmansk Region had not been carried out. There is some limited data on concentration levels of chalcophile elements (Hg, Cd, Pb, As) in water and sediments, obtained during the investigations of joint international scientific projects (e.g., Moiseenko *et al.,* 1997). However, recent development of an analytical instrument base has made it possible to carry out similar research in a more extensive manner.

The purpose of this research was to detect and define biogeochemical patterns of distribution of the chalcophile elements Hg, Cd, Pb and As in water and sediments as well as in organs and tissues of whitefish in Lake Umbozero, which is influenced by emissions and waste waters from the mining and metallurgical enterprises of the Murmansk Region.Lake Umbozero is the second-largest lake in the Murmansk Region: the surface area of the lake is 319.4 km^2, the area of the water mirror is 313.4 km^2, the longest length is 43.3 km and the greatest width is 12.0 km. The surface of the lake is 151.6 m above sea level. Based on a maximal depth of 115 m, the lake is one of the deepest lakes in the European part of Russia. In this respect it is surpassed only by Ladoga and Onega lakes (the two largest lakes in Europe). The southern part of the lake is shallower than the northern part. The total catchment area is 2130.8 km^2, and the lake is drained by the Umba River, which runs into the White Sea. The lake is located to the East of the Khibiny alkaline massif. The northern, rather narrow section of the lake lies between the Khibiny and Lovozero alkaline massifs. Here the width of the lake is 5-6 km. Two rivers (Tulijok and Moikvaltjok) enter the lake from the west at Postelnaya Bay. From the North flow the lacustrine-marsh Rivers Big and Small Chuda, Umbozerskaya, and Sura. The rivers Tavajok, Pargjok, Kuvtuaj and others flow down from the West of the Lovozero hills. The rivers Kitsa and Punche flow from the east of the lake at Sorvanov Island into Tuljiluht-Seida Bay. Sorvanov Island, the biggest in the lake, is in the southeast part of the lake, and has an area of about 2 km^2. The second-biggest island is the Big Elovy, located almost in the middle of the lake. The total area of all the islands does not exceed 6 km^2. A wide underwater ridge runs from the North in the direction of the longitudinal axis. Three small islands, Vysoky, Maly and Golodny, lay in the middle of this ridge (Krokhin, 1936; Richter, 1958, Alferovskaya, 1966).

Lake Umbozero is located to the East of the industrially developed centre of the Murmansk Region. Anthropogenic influences on the lake are much less than on Imandra Lake, which is the largest lake of the Kola Peninsula. A diagram (or chart) of Lake Umbozero showing locations of the water and sediment sampling stations is shown in Fig. 1. where the dark line also shows the expected direction of the water current.

Exploitation of the Koashva apatite-nepheline deposit since 1978 has caused the southwest part of Lake Umbozero to become polluted with suspended substances and nitrogenous compounds. In the “East” mine (on the south-western side of the lake), apatite-nepheline ore is mined. Effluent from the “East” mine enters the Vuonnemjok River, and flows through Kitchejavr and Kitchepahk lakes and then through the Umbolka River until draining into Lake Umbo-zero. In the first years of development of the mine a delay in the construction of cleaning installations caused huge amounts of suspended substances to enter the water system, resulting in siltation of the bottom of the southern part of Lake Umbozero. Installation of a cleaning system for the “East” mine and a decrease in levels of production has allowed a sharp reduction in discharge of polluted substances.An increased content of nitric compounds in the water system is an obvious

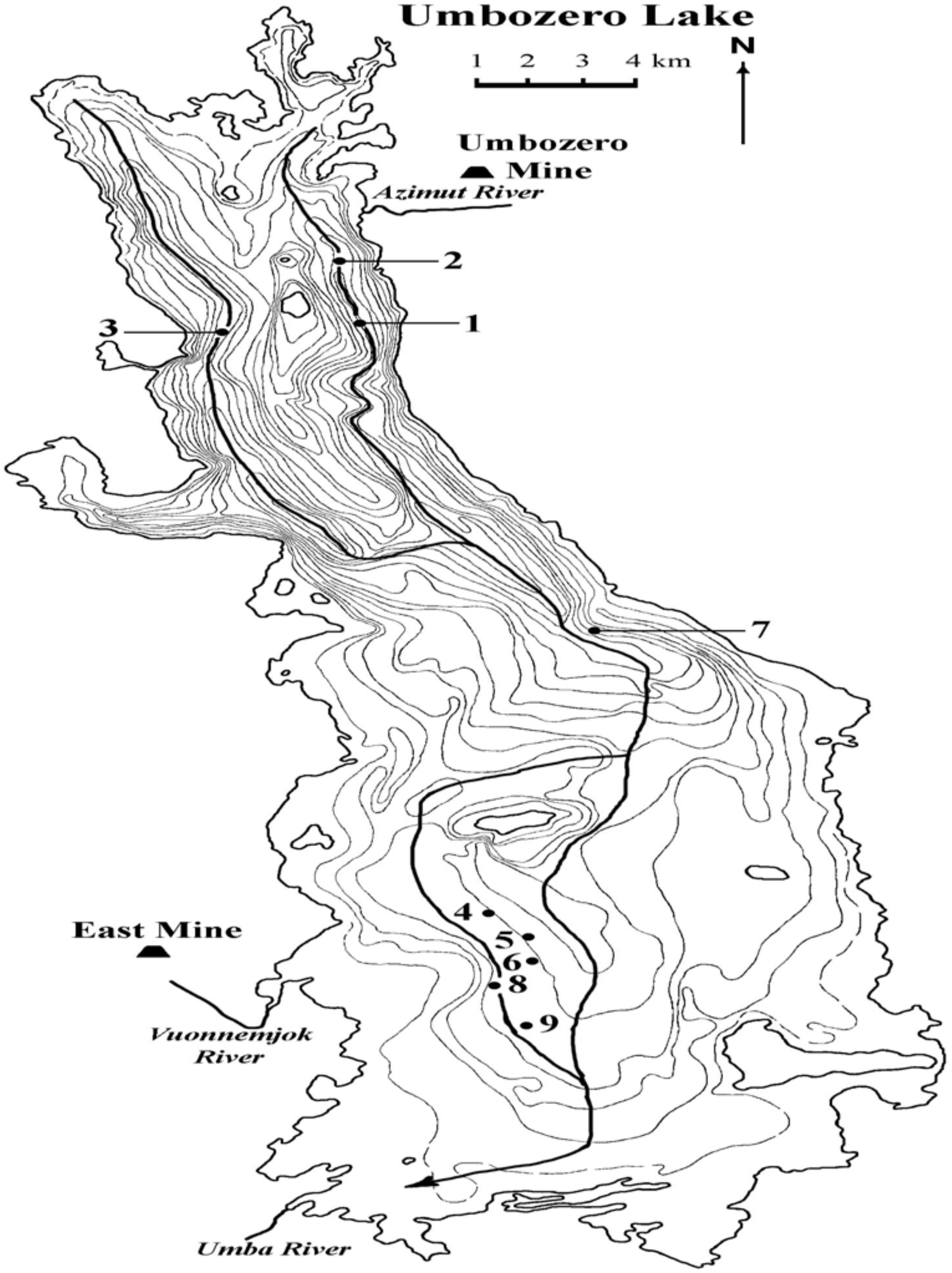

Fig. 1. The bathymetrical map of Lake Umbozero. 1-9 – stations for sampling of water and sediments. Solid line – expected direction of water current

consequence of conducting explosive works at the "East" mine. Domestic waste waters from the Koashva settlement enter the same surface water system, as well as the effluent from the "East" mine (Moiseenko and Yakovlev, 1990).Since the middle of the 1970's the northeast part of Lake Umbozero has been influence by waste effluents from the "Umbozero" mine of the Lovozero Company. The basic industrial mineral of the "Umbozero" mine (on the north-eastern side of the lake) is loparite – the ore of the rare-earth elements, as well as titan, niobium and tantalum. Sr, Y, Th are present as impurities. The components of the waste effluent besides these elements are also fluoride, hydrogen carbonate, and sodium. The primary recipient of the waste is the River Azimuth, receiving the mine waters pumped out onto the land and also into dumps in the industrial area. The polluting substances fluorine, suspended matter and mineral salts enter Lake Umbozero by this river (Moiseenko and Yakovlev, 1990).

MATERIALS & METHODS

In April and July 2005 a hydrochemical survey of Lake Umbozero was carried out, during which water samples from 9 stations and sediment cores from 5 stations were collected. In the samples, besides the basic ions and the main components (nutrients, organic matter), the concentrations of trace elements, including chalcophile elements, have been determined.The samples of water were collected by glass bathometer with a volume of 2 litres, transferred to plastic bottles of 1 litre volume and delivered to the chemical laboratory of the Institute of North Industrial Ecology Problems of the Kola Science Centre of the Russian Academy of Science.

Ten sediment cores at 5 stations (two from each station) in Lake Umbozero (Fig.1, Table 1) were collected by a gravity corer of an open type made from Plexiglas (internal diameter of 44 mm), with an automatically sealing diaphragm (Skogheim, 1979). This allowed transport of the sediment cores to the laboratory without breakage for further analyses. The sediment cores were vertically sectioned into 1 cm slices, placed in plastic boxes and stored at 4°C until further examined.

The sediment samples at the INEP laboratory were dried overnight at 105°Ñ and the water content was expressed as percent of wet sediment weight. The samples were then ignited for 4 h at 550°C for determination of the loss of weight on ignition as an indirect index of the organic matter content. The sediment was subsequently ground in a jasper mortar and homogenized. For metal analyses, ~0.4 g (dry wt.) was taken and digested in a Teflon® bomb for 4 h at 140°C with 4 ml concentrated nitric acid. The content of the bomb was cooled to room temperature. A 2-ml aliquot from the bomb was decanted into a 60-ml plastic bottle and diluted with deionised water to 20 ml and analysed as described below. For As and Hg analyses, samples of dried sediment from the second cores of each station were similarly treated and digested with concentrated nitric acid in the bomb and 2-ml aliquots were diluted and used for analysis as described below (see Table 1).

Concentrations of elements in water and sediment samples were determined by electro thermal atomic absorption spectrometry. The samples were analysed for As, Pb and Cd using AAnalyst-800 (Perkin-Elmer Corp) and the standard addition technique. Concentrations of Hg were determined using cold vapour atomic absorption spectrometry (Hg analyzer FIMS-100). Standard solutions with appropriate concentrations for each element were made from 1000 mg/L AAS stock standards (Merck, Darmstadt, Germany). Quality assurance for measurements was carried out using rigid intra-laboratory controls and verified annually by international inter-calibrations, which the analytical laboratory of INEP carries out with a number of the European laboratories within the framework of joint projects (Arnesen *et al.*, 1996; Makinen *et al.*, 1997; International Cooperative Programme, 2003; Intercomparison 0519, 2005). Limits of detection in water for Cd and Hg were 0.01 µg/L, for Pb were 0.04 µg/L and for As were 0.1 µg/L.

The sediment core from station 9 was dated by determining the Pb-210 content of the layers (Goldberg, 1963). The method used was slightly modified from the one presented in Häsänen (1977). Dating analysis was conducted in Laboratory of Radiochemistry of University of Helsinki. The technique of dating and results of the analysis were described in more detail in Jernström et al. (2008).To assess pollution by chalcophile elements, values for factor and degree of contamination were calculated according to the method suggested by Håkanson (1980). To describe the pollution of each element separately, the contamination factor (C_f^i) was determined by:

$$C_f^I = \frac{C_{0-1}^i}{C_n^i},$$

Table 1. Depth of lake, core length, collecting day and coordinates of the sediment sampling stations. The second cores were collected for As and Hg analyses

Stations	Depth, m	Core length, cm	Collecting day	Coordinate N	Coordinate E
3	54 m	21, 20 (As, Hg)	5.04.2005	67°48.614'	34°16.475'
4	21 m	26, 19 (As, Hg)	6.04.2005	67°37.447'	34°23.758'
6	34 m	23, 21 (As, Hg)	5.07.2005	67°36.871'	34°24.520'
8	20 m	10, 10 (As, Hg)	6.07.2005	67°35.728'	34°23.647'
9	19 m	15, 14 (As, Hg)	6.07.2005	67°35.245'	34°24.590'

where C_{0-1}^i is the content of substance i (i = chalcophile elements: Cd, Pb, As, Hg) in the superficial layer (0-1 cm) of the sediment core collected from the sampling station and C_n^i is the background value determined from the deepest part of the sediment core.A contamination factor (C_f^i) was calculated for each separate polluting element. If $C_{0-1}^I > C_n^i$, this element was considered to be polluting or enriched. If $C_{0-1}^i < C_n^i$, the element cannot be considered to be polluting for the station in question.In this approach, the following classification of values of contamination factor was used: $C_f^i < 1$ – low (low contamination of sediment by the element in question); $1 \leq C_f^i < 3$ – moderate; $3 \leq C_f^i < 6$ – considerable; and $C_f^i \geq 6$ – high contamination factor.The degree of contamination (C_d) was defined as the sum of all contamination factors (C_f^i) of chalcophile elements for that particular station:

$$C_d = \sum_{i=1}^{n} C_f^I = \sum_{i=1}^{n} \frac{C_{0-1}^i}{C_n^i}$$

This approach has allowed definition of a contamination factor (C_f^i) which characterizes the contamination of the given water area by separate chalcophile elements, and their total contribution on the basis of calculated degree of contamination (C_d), which determines the total pollution by the elements investigated.Similarly, the degree of contamination is composed of factors of contamination for separate elements, and the classification of values of C_d suggested by Håkanson (1980) was used, on the basis that C_d values were summed from the values of factors of contamination for n substances: $C_d < n$ – low; $n \leq C_d < 2n$ – moderate; $2n \leq C_d < 4n$ – considerable; $C_d \geq 4n$ – high (indicating serious anthropogenic pollution). Therefore, for four polluting toxic chalcophile elements the following classification of degree of contamination was accepted: $C_d < 4$ – low; $4 \leq C_d < 8$ – moderate; $8 \leq C_d < 16$ – considerable; $C_d \geq 16$ – high.Eight specimens of whitefish (*Coregonus lavaretus*) were collected on July 6, 2005, to the south of Sorvanov Island, from which organs and tissues (muscle, liver, kidneys, gills, skeleton) were taken for chemical analyses. In the collected samples, the concentrations of metals, including chalcophile elements (Cd, Pb, and Hg) were determined by atomic absorption spectrophotometer.The techniques of collection and the analyses of samples of organs and tissues of fish were described in detail previously (Kashulin, 2004; Kashulin *et al.*, 1999, 2005).To assess the degree of accumulation of chalcophile elements in organs and tissues of whitefish, the factor for biological accumulation was calculated as the ratio of the average concentration of the element in the organ to the average concentration of the element in the upper (0-1 cm) layer of sediment from Lake Umbozero (based on recalculation from dry weight).

RESULTS & DISCUSSION

In the water column, only Pb and Cd among the chalcophile elements were found in amounts exceeding the limit of detection for the analytical devices. The distribution of Pb in the water column during the pre-spring period under the ice in April, 2005 was determined, showing surface and subsurface maxima (Fig. 2). These maxima are probably connected to the beginning of phytoplankton activity when the sun's rays start to penetrate the ice at the beginning of spring. In the water samples collected in July, i.e. during intensive growth of phytoplankton, two maxima for Pb concentration – in surface and near-bottom layers– were seen (Fig. 2). These two maxima are probably associated with development of phytoplankton in upper layers of water and with sedimentation of lifeless organisms and suspended materials in near-bottom layers. Phytoplankton probably strongly sorbs Pb compounds as a result of biochemical functions. A rather high coefficient of correlation (r = 0.48, n = 42) between Pb concentrations and contents of organic material in the water column confirms this conclusion (Fig. 3). In total, the average Pb concentration in the water column of Lake Umbozero (0.45 ± 0.40 µg/L) appeared to be higher than the value for water of taiga zone lakes (< 0.1 µg/L) (Moiseenko *et al.*, 2006). The highest concentration of Pb (2.39 µg/L) was found in a near-bottom layer of station 9 in July, and the lowest (0.04 µg/L) at station 7 at a depth of 50 m, also in July.

similar situation is also seen for the distribution of total Cd in water columns of Lake Umbozero (Fig. 4) – the near-surface maximum is observed both in pre-spring and summer samples. Moreover, the increase in Cd concentration in near-bottom water layers during the summer period is marked (Fig. 4). In general, the average Cd concentration in the water column (0.085 ± 0.065 µg/L) appeared to be more than

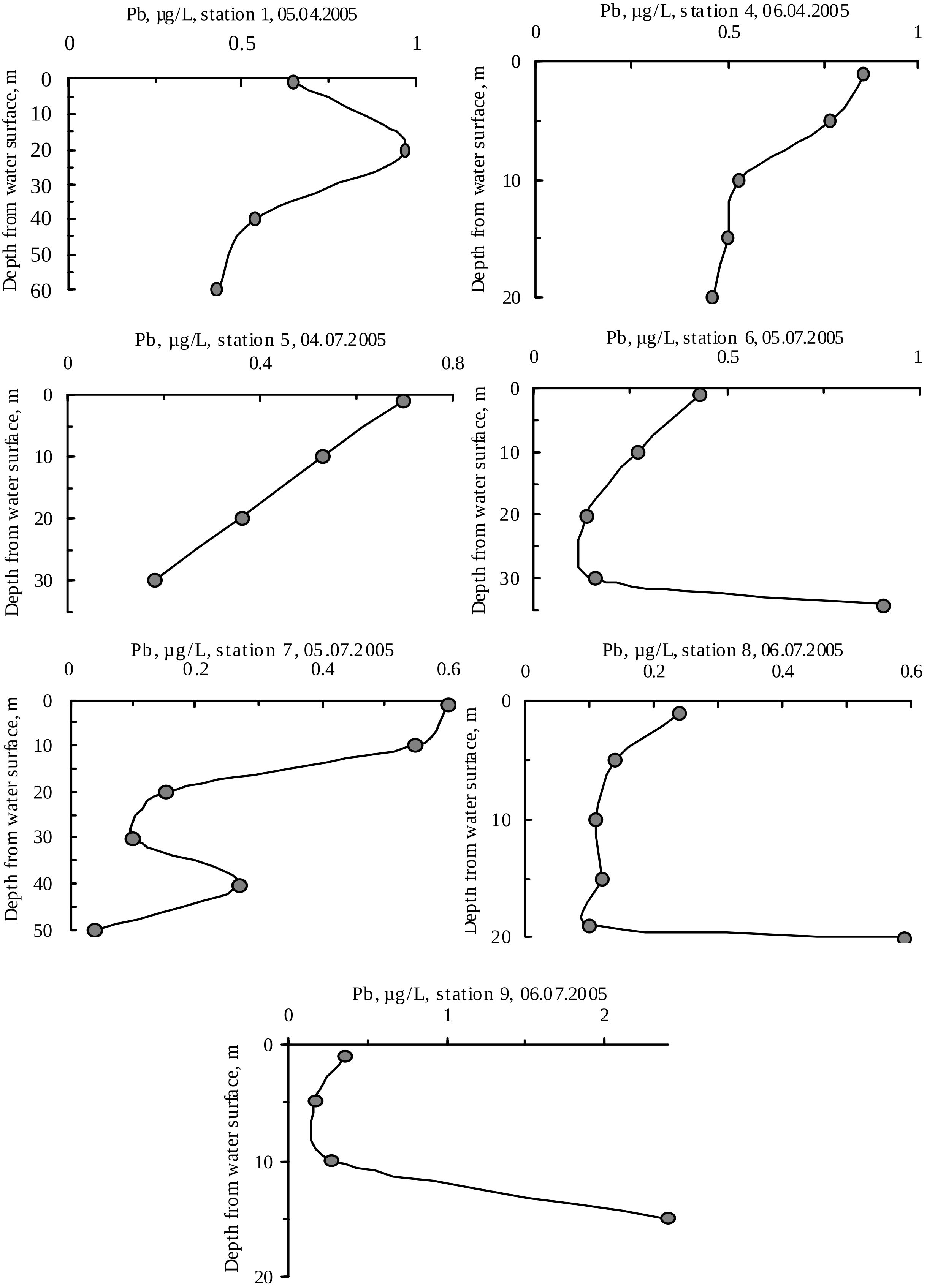

Fig. 2. Distribution of total concentration of Pb in water column of the sampling stations of Lake Umbozero (in µg/L)

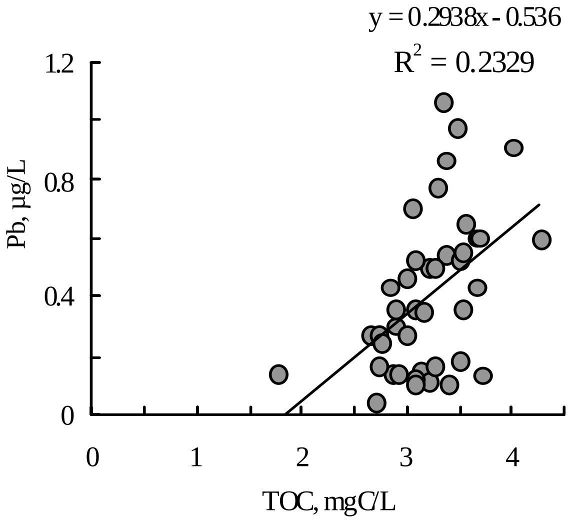

Fig. 3. Relationship between concentrations of Pb and total organic carbon (TOC) in water samples of Lake Umbozero

the average value for water of lakes of the taiga zone (0.04 ± 0.05 µg/L) (Moiseenko *et al.*, 2006). The highest Cd content (0.34 µg/L) was seen in a surface layer from station 6 in July, and the lowest (0.01 µg/L) at station 1 at a depth of 20 m in April.

Concentrations of Cd in the deepest parts of sediment cores of Lake Umbozero were generally less than the average value of the background concentration of Cd in sediments of Kola Peninsula lakes (Dauvalter, 1999). In the sediments of all sampling stations, there was an increase in Cd concentration in the upper parts of the cores (Fig. 5). Pollution of the lake by this element dates to the 1940's, i.e. prior to the beginning of current mining activity. The reason for this pollution could be the beginning of activity of "Severonickel" Company smelters (1938) in Monchegorsk, 50 km to the west of the lake. The lake was particularly intensively polluted in the last decade, which is possibly connected with mining activity and trans-boundary air pollution. Contamination factors for Cd were in the range of 4.5 to 8.4 (Table 2), i.e. values classified as of concern, considerable and high (Håkanson, 1980). The highest contamination factor values for Cd (classified as high) were seen in sediments of stations 8 and 9 (C_f^{Cd} = 8.4 and 8.3 respectively), situated close to the point of entry of effluent from the "East" mine of the "Apatite" Company (through the Vuonnemjok River). Contamination factors for Cd classified as "considerable" were observed at stations 3 and 4 of Lake Umbozero. However, the highest absolute value for Cd (0.51 µg/g) in superficial layers was observed at station 6 in the southern part of the lake. At the same station, the highest concentration of this element was registered in water – 0.34 µg/L. The negative correlation dependence of Cd concentration in layers of sediment cores with depth (Table 3) confirms the conclusion that there is an increase in Cd concentrations in near-surface present-day layers of sediments, and that this element is one of the basic polluting heavy metals. Concentrations of Cd in sediment profiles from the sampling stations have high coefficient of correlation values for all chalcophile elements investigated, and also for the content of organic material (Table 3). Hence, processes of migration and accumulation of this chalcophile element in lake sediments depend on the sorption properties of organic material.

The largest lake of the Murmansk Region, Imandra, receives effluent mainly from mines run by "Severonickel", "Apatite" and "Kovdor" Companies. The surface layers of the lake sediments have the maximum concentration of Cd in the Murmansk Region – 4.54 µg/g dry weight (Moiseenko *et al.*, 2002). Lake Kuetsjärvi, situated close to the "Pechenganickel" Company mine, also has a very high concentration of Cd in surface sediment layers – 3.14 µg/g dry weights (Dauvalter and Sandimirov, 2007). The concentrations of Cd in sediments of the above mentioned polluted lakes are an order of magnitude higher than in the Umbozero sediments.

The average background values for Pb concentrations for Kola Peninsula lakes (Dauvalter, 1999) is twice that found in the lower layers of the sediment cores from the sampling stations of Lake Umbozero. The Pb concentrations increase gradually toward the top of the lake, and are maximal in the uppermost layers (Fig. 6). This increase in Pb concentrations occurred at the beginning of the 20th century and is connected with trans-boundary transfer from industrial areas of Europe. Pollution rates for Pb, as well as Cd, have been maximal over the last decade, in spite of the removal of lead from gasoline in western countries. Contamination factors for Pb are also high, as are those for Cd, and are in the range of 5.5 to 11.9 (Table 1). The maximum contamination factor value for Pb was found in sediments of station 8, located close to the mouth of the River Vuonnemjok, through which waste waters enter

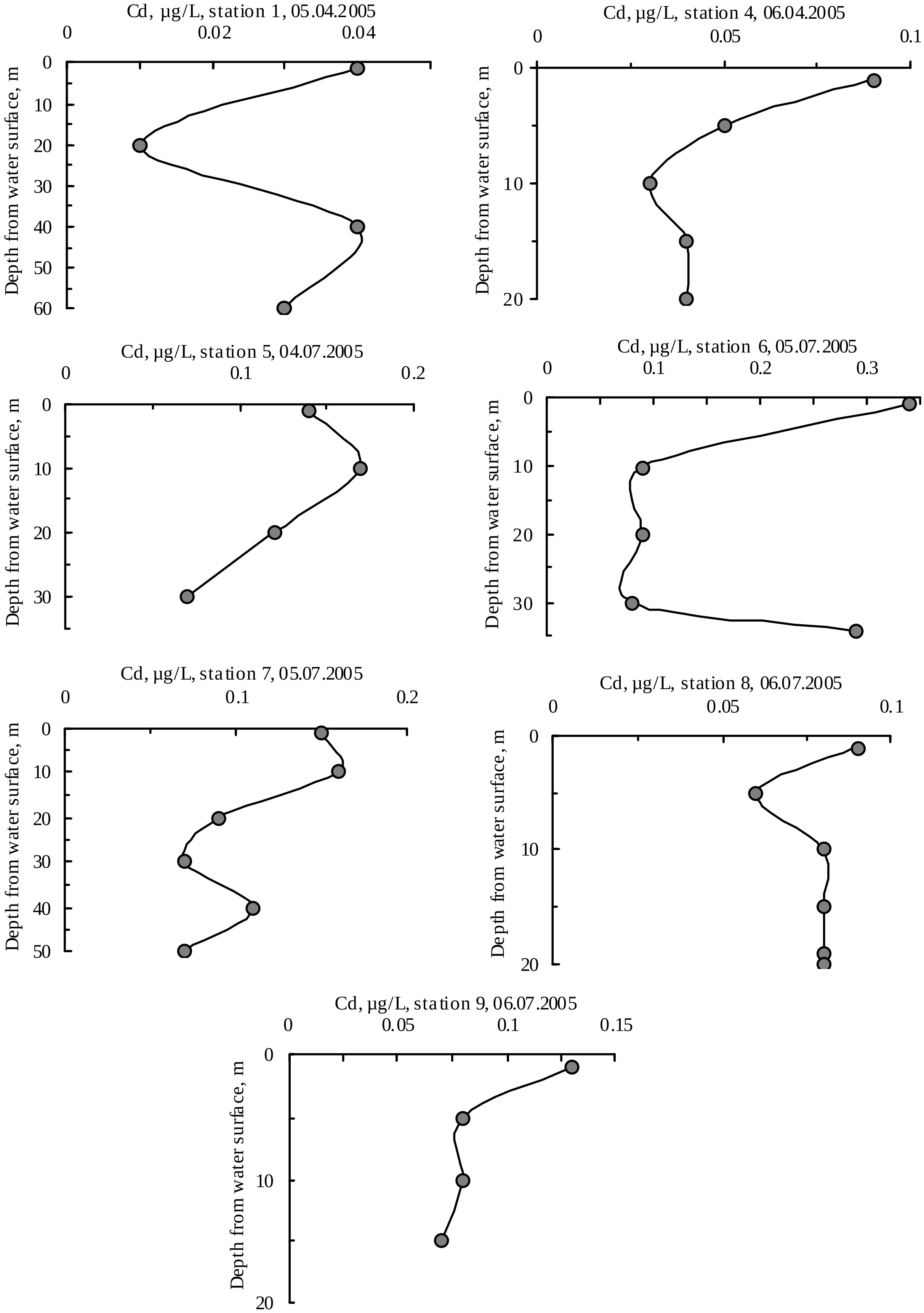

Fig. 4. Distribution of total concentration of Cd in water column of the sampling stations of Lake Umbozero (in µg/L)

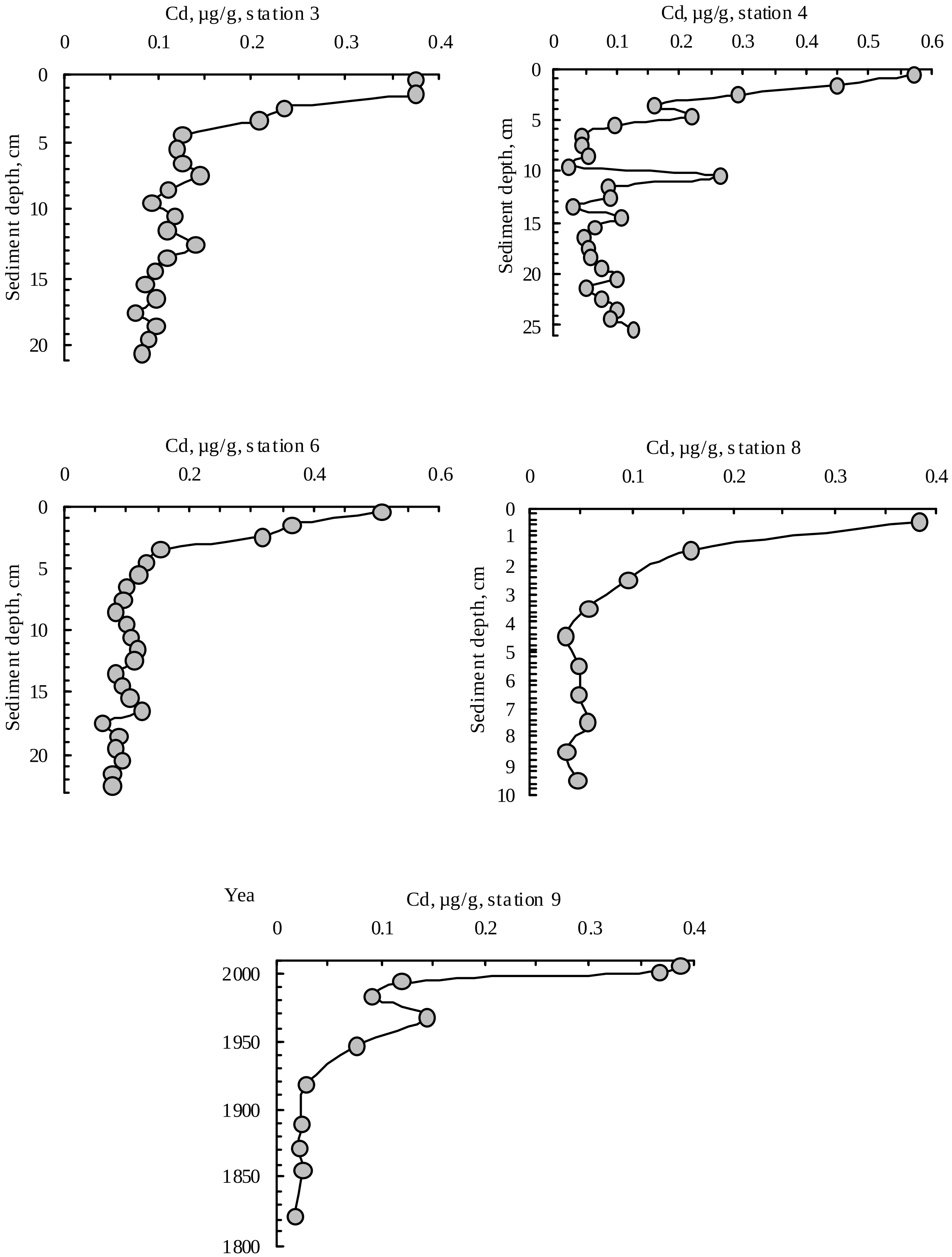

Fig. 5. Vertical distribution of Cd (µg/g dry weight) in the sediment cores of the sampling stations of Lake Umbozero (for station 9 in dating sediment core)

Table 2. Concentration of chalcophile elements (µg/g dry weight) in superficial (0-1 cm) and bottom layers of sediment cores, values for loss of weight at ignition (LOI, %) and values for factor (C_f) and degree (C_d) of contamination in Lake Umbozero

Station, depth, m	**Layer, cm**	**LOI, %**	**Cd**	**Pb**	**As**	**Hg**	**C_d**
Station 3	0-1	12.74	0.375	26.9	17.3	0.051	
54 m	20-21	9.61	0.084	4.1	4.3	0.016	
	Cf		**4.5**	**6.6**	**4.0**	**3.2**	**18.3**
Station 4	0-1	16.20	0.574	24.4	5.0	0.049	
21 m	25-26	11.63	0.127	3.7	1.1	0.014	
	Cf		**4.5**	**6.6**	**4.5**	**3.6**	**19.2**
Station 6	0-1	17.70	0.507	24.8	32.1	0.083	
34 m	22-23	12.18	0.077	4.5	6.9	0.020	
	Cf		**6.6**	**5.5**	**4.6**	**4.2**	**20.9**
Station 8	0-1	15.28	0.385	27.5	11.5	0.103	
20 m	9-10	6.60	0.046	2.3	5.8	0.018	
	Cf		**8.4**	**11.9**	**2.0**	**5.8**	**28.1**
Station 9	0-1	16.59	0.388	32.2	15.5	0.106	
19 m	14-15	8.61	0.047	3.6	7.1	0.018	
	Cf		**8.3**	**9.0**	**2.2**	**6.0**	**25.5**
Average	0-1	15.70	0.446	27.2	16.3	0.079	
contents	Background	9.73	0.076	3.6	5.0	0.017	

Table 3. Correlation coefficients amongst chalcophile elements, depth of sediment layers, and organic content (LOI) in sediment cores from Lake Umbozero

	Layer	**LOI**	**Cd**	**Pb**	**As**	**Hg**
Layer	1.00					
LOI	-0.13	1.00				
Cd	-0.52	0.66	1.00			
Pb	-0.63	0.67	0.88	1.00		
As	-0.38	0.17	0.36	0.39	1.00	
Hg	-0.57	0.51	0.74	0.82	0.29	1.00

the lake from the “East” mine of the “Apatite” Company. The maximum absolute concentration of Pb (32.2 µg/g) in superficial sediment layers was observed at station 9, where the highest concentration of this element in water (2.39 µg/L) was also found. A reliable negative correlation between Pb concentrations (as well as Cd) and sediment depth for the lake sampling stations (Table 3) was also established, suggesting the pollution of the superficial present-day sediments by this element. Therefore, it can be concluded that Pb is an important polluting heavy metal. Concentrations of Pb in sediment cores of the lake sampling stations have high values for correlation coefficients with all the examined chalcophile elements, and also with the content of organic material (Table 3). Therefore, the processes of migration and accumulation of this highly toxic chalcophile element in sediments depend on the sorption properties of organic material.

The surface layers of sediments of Lake Imandra have the maximum concentration of Pb in the Murmansk Region– 69.3 µg/g dry weight (Moiseenko *et al.*, 2002). Lake Kuetsjärvi also has high concentrations of Pb in surface sediment layers – 45.7 µg/g dry weight (Dauvalter and Sandimirov, 2007). The concentrations of Pb in sediments of the above mentioned polluted lakes are 2-3 times higher than in the Umbozero sediments.Concentrations of As in the deepest parts of sediment cores of Lake Umbozero were less than the average value for the background concentration of As in lake sediments of the Pechora River basin (Dauvalter, 1999). An increase in the concentration of As for all sampling stations was seen at the sediment surface, as was also found for Cd and Pb (Fig. 7). This increase dates to the end of the 19th century, when there was almost no economic activity in the territory of the Kola Peninsula. The amount of As in the sediment gradually increases and the maximal value is reached in the most recent years. The contamination factors for As in sediments of the

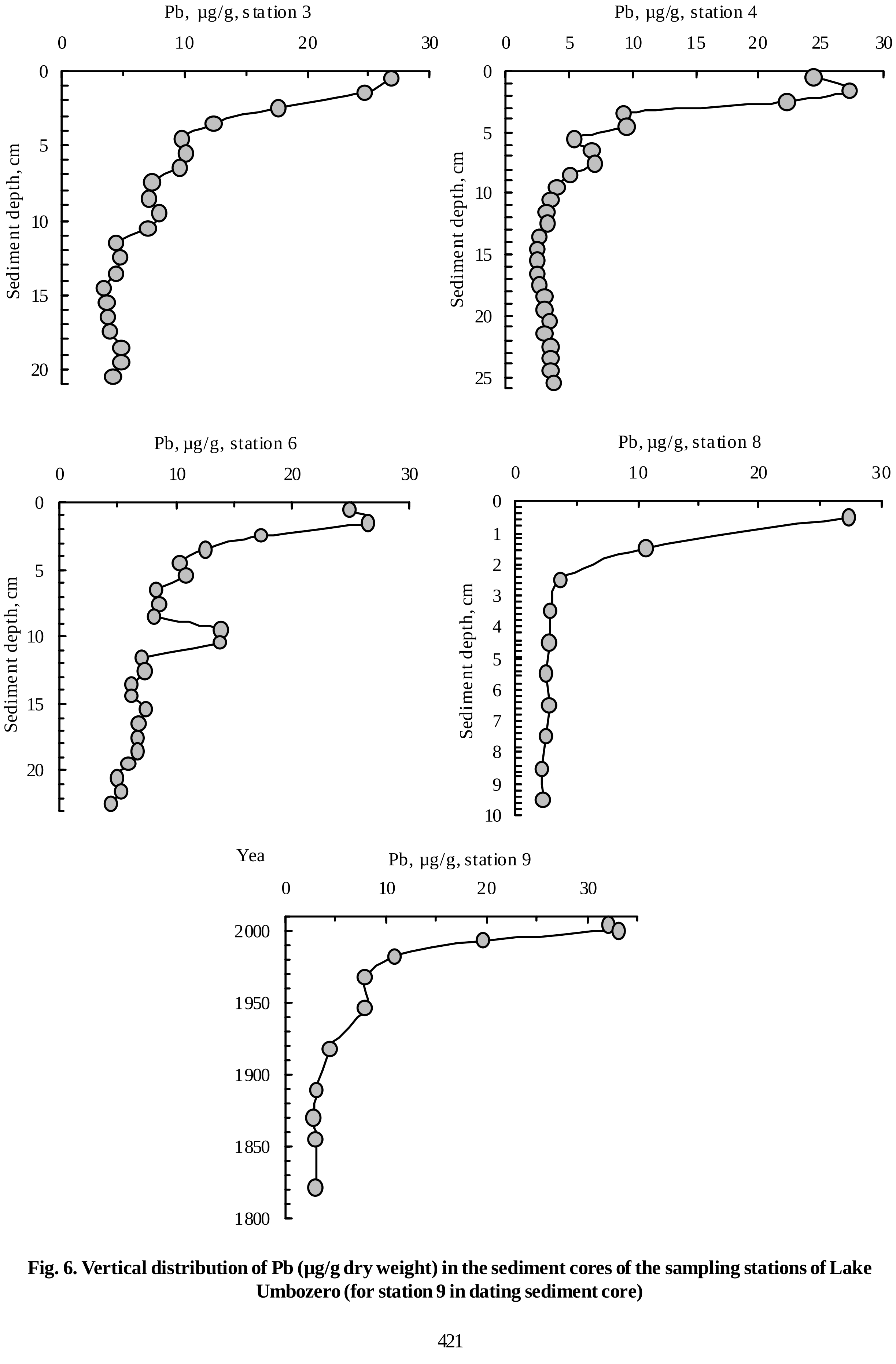

Fig. 6. Vertical distribution of Pb (µg/g dry weight) in the sediment cores of the sampling stations of Lake Umbozero (for station 9 in dating sediment core)

Lake Umbozero stations were in the range of 2.0 to 4.6 (Table 2), i.e. of concern to moderate and considerable (Håkanson, 1980), and the highest values were found not only at stations located close to the mouth of the River Vuonnemjok, but also in the northern part of the lake, which was affected by effluent from the "Umbozero" mine. Just as for concentrations of Cd and Pb, concentrations of As in sediment cores of the sampling stations have high correlation coefficients with all examined chalcophile elements, and also with the amount of organic material (Table 3).

The surface layers of sediments of Lake Kuetsjärvi have a high concentration of As – 86 µg/g dry weight (Dauvalter and Sandimirov, 2007), which is 3-10 times higher than that of the Umbozero sediments.Concentrations of Hg in the deepest parts of the sediment cores of the sampling stations were on average 5 times less than the average background concentration of Hg in sediments of Kola Peninsula lakes (Dauvalter, 1999). At all sampling stations of Lake Umbozero there is, as for the other chalcophile elements studied, an increasing concentration gradient on moving toward the surface from the bottom of the core (Fig. 8). The beginning of the contamination by Hg dates to the end of the 19th century, but the most intensive pollution dates from the initiation of mining operations on the coast of the lake.Contamination factors for Hg of sediments were in the range of 3.2 to 6.0 (Table 2), i.e. of concern to considerable (Håkanson, 1980). The highest Hg contamination factors were found in sediments of stations 8 and 9 (C_f^{Hg} = 5.8 and 6.0 respectively), located close to the mouth of the River Vuonnemjok (Table 1). A negative correlation between Hg concentrations and depth of sediment layers was observed (Table 3), confirming the increase in Hg concentrations toward the sediment surface. Therefore, it is possible to conclude that Hg, due to its extreme toxicity along with high concentrations in sediment, is one of the most important of the polluting heavy metals in Lake Umbozero. High correlation coefficient values for Hg in sediment cores of the sampling stations with all of the investigated chalcophile elements, as well as with the contents of organic material, were also observed (Table 3). Therefore, the processes of migration and accumulation of this chalcophile element in the sediments of Lake Umbozero depend on the sorption properties of organic material.

The surface layers of sediments of Lake Imandra have the maximum concentration of Hg in the Murmansk Region – 2.89 µg/g dry weight (Moiseenko *et al.*, 2002). Lake Kuetsjärvi also has high concentrations of Hg in surface sediment layers – 0.50 µg/g dry weight (Dauvalter and Sandimirov, 2007). The concentrations of Hg in sediments of the above mentioned lakes are 5-50 times higher than in the Umbozero sediments.According to our investigations of the sediments of Lake Umbozero, the lake is subjected to anthropogenic influences, especially the mines ("East" and "Umbozero") located on the lake shores. This influence causes an increase in concentrations of elements such as heavy metals in superficial sediment layers. Of the metals examined, the highest contamination factors were observed for Cd and Pb, i.e. metals that have been of great concern to scientists in recent decades. Ecologists have been particularly concerned as they have become aware of mechanisms by which global weather patterns cause world-wide pollutants to accumulate in the Arctic and Subarctic zones of the Northern Hemisphere (Norton *et al.*, 1990, 1992; Pacyna and pacyna, 2001). Contamination factors for Cd and Pb reach 8.4 and 11.9 (at station 8), respectively.

Mercury and arsenic are also of concern as global pollutants. Concentrations of Hg increased in superficial sediment layers in practically all of the sampling stations. Contamination factors for Hg were in the range of 3.2 to 6.0. Mercury is an extremely toxic metal; therefore even these contamination factor values can have a significant negative impact on vital functions of aquatic organisms. Arsenic showed moderate to considerable contamination of sediments of the sampling stations. Contamination factors of As were in the range of 2.0 to 4.6.The highest degree of contamination, calculated as the sum of the contamination factors of the 4 elements (Cd, Pb, Hg and As), was seen at station 8, where a value of 28.1 was found (Table 2). According to Håkanson (1980) all stations of Lake Umbozero were characterized as highly polluted by the four investigated chalcophile elements.Therefore, it is possible to conclude that Lake Umbozero is subject to intensive global influences, and also polluted by effluent from the mines that causes an increase in the concentration of the highly toxic chalcophile elements Cd, Pb, Hg and As in superficial sediment layers of the lake.

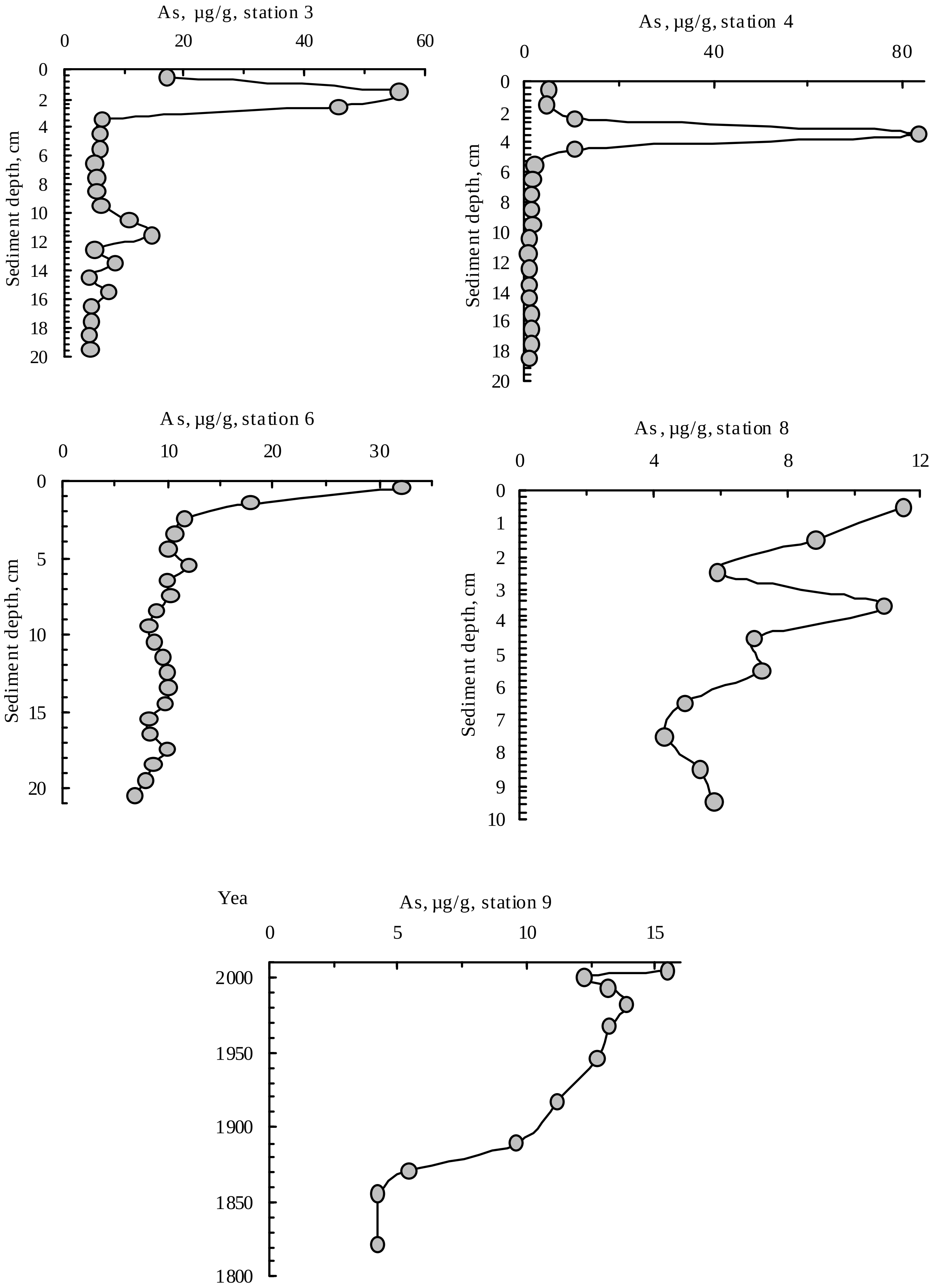

Fig. 7. Vertical distribution of As (µg/g dry weight) in the sediment cores of the sampling stations of Lake Umbozero (for station 9 in dating sediment core)

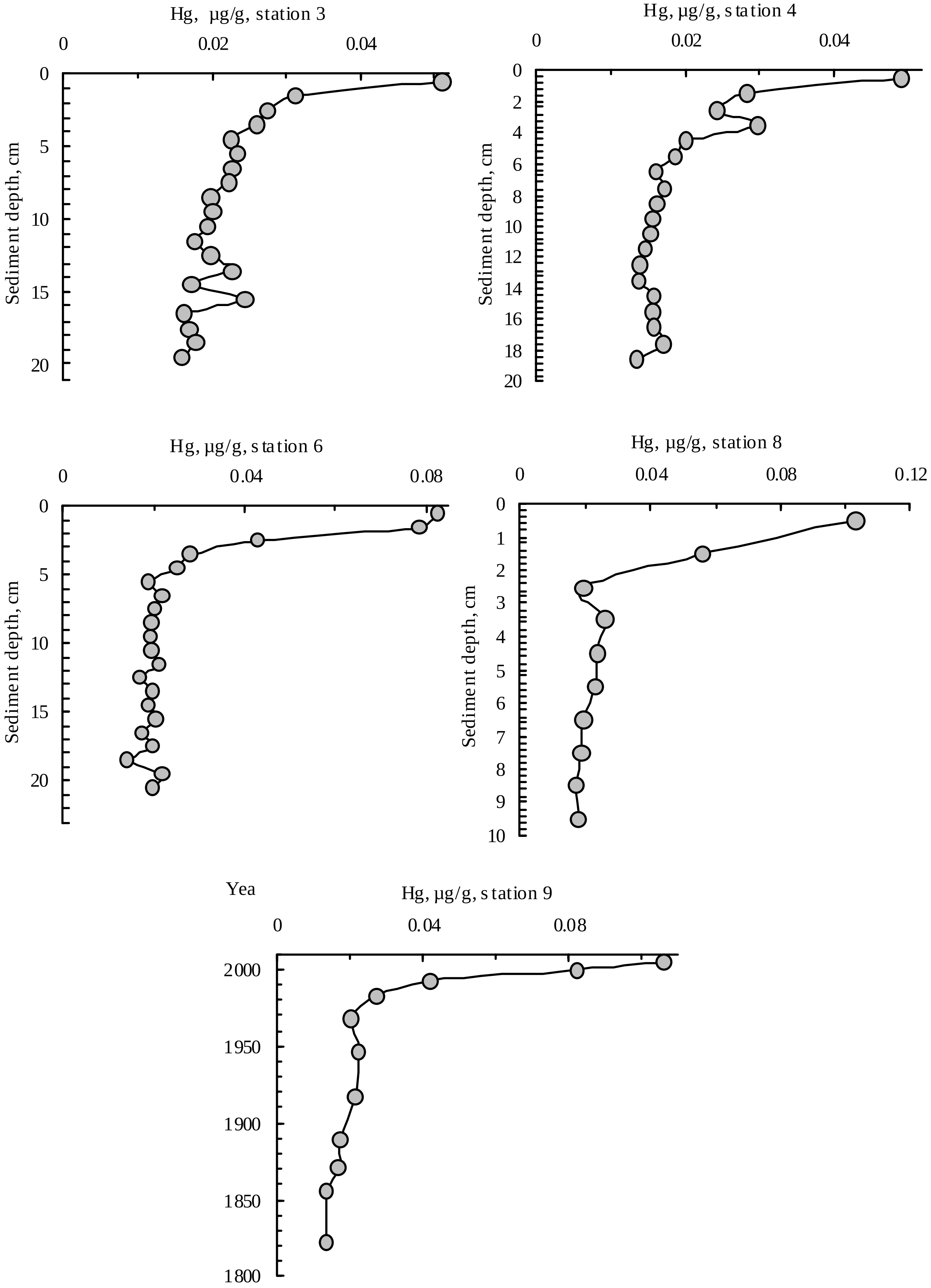

Fig. 8. Vertical distribution of Hg (µg/g dry weight) in the sediment cores of the sampling stations of Lake Umbozero (for station 9 in dating sediment core)

Heavy metals are able to accumulate in living organisms to higher concentrations than in the environment. The concentration of heavy metals in tissues of fishes reflects the dynamics of changes of these elements in the environment and can be used for monitoring environmental contamination, and can also provide an explanation for observed abnormalities in individuals and in the population as a whole in polluted lakes (Kashulin, 2004; Kashulin *et al.,* 1999, 2005). The amount of metals in organs and tissues of fishes depends on geochemical conditions of a particular location, with generative and plastic exchange as well as other factors (Wicklund and Ruun, 1988). Absorption and accumulation of heavy metals by fishes depends on the chemical and physical processes occurring in the water and on the sediment surface in a lake (Iivonen *et al.,* 1992). For example, an increase in the concentration of Ca in water reduces absorption of some heavy metals by animals, and complex agents can reduce or increase bioavailability of metals. Seasonal changes also influence the amount and availability of metals.Results of the chemical analyses of the chalcophile elements in organs and tissues (muscle, liver, kidneys, gills, skeleton) of whitefish (*Coregonus lavaretus*) and comparison with the average contents of these elements in the superficial sediment layer are shown in Fig. 9 and Table 4.Based on their ability to accumulate Cd, the organs and tissues of whitefish in Lake Umbozero can be arranged in the following order (Fig. 9. Table 4):

Kidneys > liver > gills > skeleton > muscle

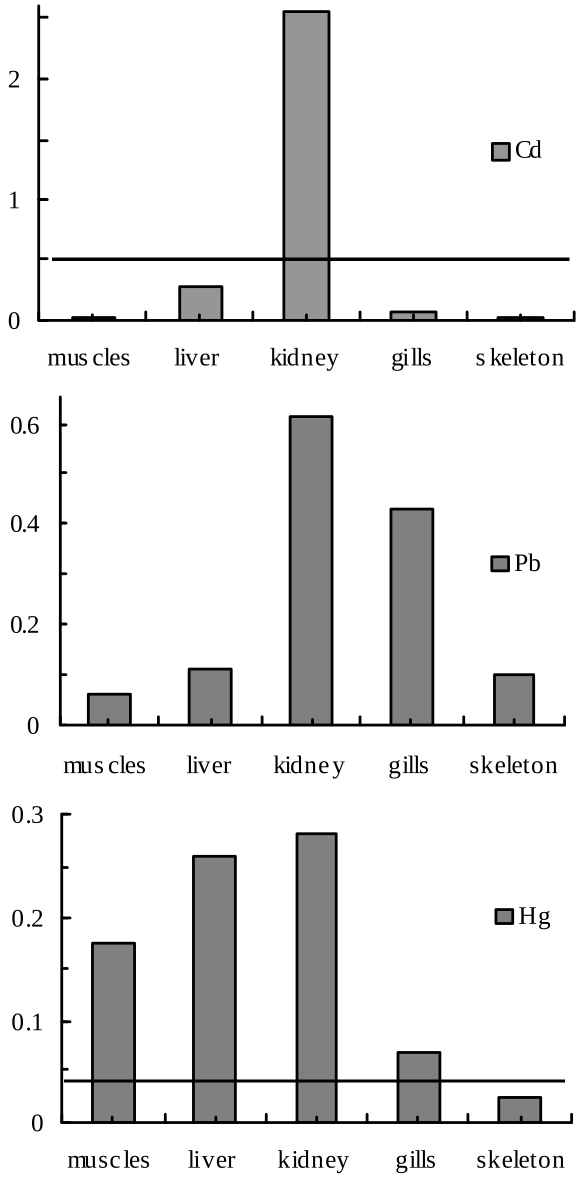

Fig. 9. Accumulation of chalcophile elements (in µg/g dry weight) in organs of whitefish of Lake Umbozero in 2005. The average values from 8 specimens of whitefish are shown in bar graphs with straight lines showing the average content (in µg/g dry weight) of Cd and Hg in the superficial layer (0-1 cm) of the sediment cores; this value for Pb is equal to 27 µg/g

A similar order of ability to accumulate Cd in organs and tissues, which is not species dependent, has been noted previously (Moiseenko *et al.,* 2006). These researchers also noted that the contents of Cd in kidneys of all species of fish exceed the concentration in liver by a factor of two. In the kidneys of the Lake Umbozero whitefish, the average content of Cd is almost an order of magnitude greater than in liver, is almost 50 times greater than in gills, is more than 200 times greater than in skeleton, and is more than 250 greater than in muscle (Table 4). The concentration of Cd in whitefish muscle does not exceed the permissible concentration in fish products – 0.1 µg/g of wet weight (Harmful chemical substances…, 1988). The highest factor of biological accumulation for Cd, found in kidneys, was 5.8, and therefore, the concentration of this element in kidneys is almost 6 times more than in the lake surface sediment layer.Based on their ability to accumulate Pb, the organs and tissues of whitefish in Lake Umbozero can be arranged in the following order (Fig. 9. Table 4):

Kidney > gills > liver = skeleton > muscle

Moiseenko et al. (2006) found a different order for relative accumulation of Pb in whitefish:

Liver e" kidney > gills > skeleton e" muscle

Table 4. Concentrations of chalcophile elements in organs (µg/g dry weight) of whitefish of Lake Umbozero and the factor of biological accumulation (FBA) calculated as the ratio of the average values in organs of whitefish to the average concentration (µg/g dry weight) of the element in the superficial (0-1 cm) layer of sediment cores

Organs	Value	Cd	Pb	Hg
muscles	Average	0.010	0.062	0.175
	Minimum	0.001	0.004	0.065
	Maximum	0.029	0.210	0.486
	Standard deviation	0.010	0.068	0.131
	FBA (muscle / sediments)	0.02	0.002	**2.23**
liver	Average	0.274	0.110	0.261
	Minimum	0.123	0.061	0.217
	Maximum	0.443	0.165	0.321
	Standard deviation	0.117	0.036	0.040
	FBA (liver / sediments)	0.61	0.004	**3.32**
kidney	Average	2.569	0.610	0.283
	Minimum	1.676	0.136	0.213
	Maximum	4.616	3.435	0.411
	Standard deviation	0.893	1.143	0.064
	FBA (kidney / sediments)	**5.77**	0.02	**3.61**
gills	Average	0.058	0.429	0.069
	Minimum	0.046	0.240	0.049
	Maximum	0.073	0.581	0.101
	Standard deviation	0.009	0.121	0.017
	FBA (gill / sediments)	0.13	0.02	0.88
skeleton	Average	0.012	0.104	0.025
	Minimum	0.006	0.042	0.019
	Maximum	0.016	0.171	0.036
	Standard deviation	0.004	0.042	0.006
	FBA (skeleton / sediments)	0.03	0.004	0.32

They also suggested that Ca accompanies Pb accumulation; therefore, significant accumulation of Pb in gills and bone tissue can be expected, as was found in whitefish of Lake Umbozero. In the kidneys of whitefish, the average content of Pb exceeds by almost 1.5 times the concentration of this element in gills, by 5 times the concentration in liver and skeleton, and by almost an order of magnitude that in muscle (Table 4). The content of Pb in muscle of whitefish of Umbozero Lake does not exceed the permissible concentration in fish products – 1 µg/g of wet weight (Harmful chemical substances…, 1988). The factor of biological accumulation of Pb was highest for kidneys – 0.022, therefore, the concentrations of this element in kidneys was almost 50 times less than the average concentrations in surface sediments.Based on their ability to accumulate Hg, the organs and tissues of whitefish in Lake Umbozero can be arranged in the following order (Fig. 9, Table 4):

Kidney > liver > muscle > gills > skeleton

In Moiseenko et al. (2006) a different order of Hg accumulation in organs and tissues of whitefish was found:

Liver e” muscle e” kidney e” gills e” skeleton

They also noticed that Hg accumulation is greatest in liver and muscle; therefore, these organs are recommended for assessment of pollution of bodies of water by mercury. However, the amount of metals accumulated in organs results from the complex processes of their absorption, distribution in the organism, biotransformation of metal organic compounds, accumulation and removal. The process of detoxification ends with the removal of heavy metals from the organism or their deposition as inert compounds in some tissues (skeleton, for example). Various metals are distributed in an organism according to different patterns. Their concentrations in an organ at the moment of sampling and ratio of their concentrations in different organs reflect a difference between the amount of the metal absorbed (loading) and the amount of metal removed from the organism. It is thought that heavy metals in fish are removed primarily by the kidneys (low-molecular weight compounds) and/or by bile (complex metal organic compounds) (Kashulin *et al.*, 1999). Studies of seasonal fluctuations in levels of metals (Pb, Cd) in liver and kidney of Arctic char from high-mountain

Austrian lake have shown that concentrations of metals in liver were the lowest at the end of winter and increased during the summer, reaching a maximum level by the end of August to the beginning of September. It has been shown that the progressive increase in concentrations of metals in liver coincides with the period of increase in temperatures during the summer. During the winter, removal of metals exceeds absorption, resulting in a net decrease in the concentration of metals in liver and kidney. However, the fish is not capable of eliminating the metals completely each winter, leading to an annual step-by-step accumulation of metallic pollutants during the lifetime of the organism. Although both absorption and removal of metals takes place all during the year, Koch et al. (1996) believe that the majority of the annual absorption occurs during the summer. If the summer accumulation is taken as 100%, the fish removes more than 80% of accumulated Pb annually. The increase in concentration of metals in the kidney occurs several weeks later than in the liver. In contrast to metals in the liver, their metabolism in kidney is a consequence of redistribution of the absorbed metal inside the organism.

According to our results, kidney has the highest levels of accumulation of Hg of the organs and tissues of whitefish of Lake Umbozero. On average, the amount of Hg in kidney was 10% greater than in liver, 1.6 times greater than in muscle, 4 times greater than in gills, and 11 times greater than in skeleton (Table 4). These results demonstrate that at the moment of sampling (the beginning of July), the process of removal of the metal from the fish accelerates. The amount of Hg in muscle of whitefish of Lake Umbozero does not exceed the permissible concentration for fish products – 0.5 µg/g of wet weight (Harmful chemical substances…, 1988). The factor of biological accumulation of Hg was the highest for kidney (3.6), and somewhat lower for liver (3.3), and for muscle (2.2); therefore the concentrations of Hg in these organs are 2-4 times more than the average Hg concentrations in the surface sediment layers of the lake.

CONCLUSION

The investigations of the concentration of chalcophile elements in water and sediment, and in organs and tissues of fish of Lake Umbozero have shown obvious pollution by these toxic elements. Measurements of the metal content of dated sediments revealed that pollution by chalcophile elements started at the end of the 19th and the beginning of the 20th centuries, i.e. long before mines on the lake watershed began operating in the 1970's. The highest accumulation of chalcophile elements in surface layers of sediments was seen in the southern part of the lake, where there is a sharp reduction in the current flow, so that the polluting substances originating from the Umbozero mine on the northern part of the lake precipitate.The relatively high concentrations of chalcophile elements in bottom layers of the water column of some sampling stations also suggest the presence of deep-water currents. The most polluted southern sites of the lake are also close to the mouth of the Vuonnemjok River, bearing polluted waters from the "East" mine. Thus, our data suggests that Lake Umbozero is subject to pollution first of all from the effluents of the "East" and "Umbozero" mines, and secondly from air pollution of a global character. The former conclusion is supported by the sharp increase in concentration of these elements in the layers dating from the 1980's and 1990's, which is presumably associated with the initiation of mining operations in the area. The latter conclusion is suggested by the fact that the first evidence of pollution of chalcophile elements comes from sediments dated to the end of the 19th and beginning of the 20th centuries. This pollution has also caused these toxic metals to accumulate in organs and tissues of fish. Cadmium in kidney and mercury in kidney, liver and muscle have accumulated to the greatest extent, in comparison to the concentration of these elements in the 1-cm surface layer of the lake sediments. Nonetheless, the pollution of Lake Umbozero by chalcophile elements is an order of magnitude lower than in the largest lake of the Murmansk Region, Imandra, and in lakes of the northwest part of the Murmansk Region which receive the major part of the water effluent and air pollution from the largest metallurgical and mining enterprises – "Severonickel" (in Monchegorsk) and "Pechengsnickel" (in Nickel and Zapolyarny) Companies.

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