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SHORT COMMUNICATIONS

Chalcophile Elements (Hg, Cd, Pb, and As) in Bottom Sediments of Water Bodies of the White Sea Catchment Area on the Kola Peninsula

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The north of European Russia including the Murmansk Region contains unique mineral resources. Many mining, processing, and smelting enterprises, the largest in Russia, are situated in the Murmansk Region, recovering annually millions of tons of rocks and ores to the surface, ejecting and discharging thousands of tons of contaminants, including highly toxic metal and organic compounds, into the atmosphere and water areas and streams.

Heavy metals, particularly highly toxic chalcophile elements (Hg, Cd, Pb, and As), are very dangerous for the environment and people. They can migrate in air and aquatic media over large distances owing to their geochemical properties, e.g., relatively low melting temperature, high ability to form organometallic compounds, etc. During the latest decades, these elements have become the main global contaminating agents. Although there are many contamination sources of chalcophile elements worldwide, including northern European Russia, the information on concentrations of these contaminants in the environment, particularly in water systems, is insufficient. This is primarily related to the very low contents of these elements in water, bottom sediments, and hydrobionts and some analytical problems in their determination.

Any water area is a good collector for contaminants of all types. Bottom sediments record information on variations of element fluxes in the biosphere with time [1, 2]. They are important sources of data on past climatic, geochemical, and environmental conditions within the whole catchment area and in individual water reservoirs, which allows the estimation of the present-day environmental state of air and water media. Lacustrine bottom sediments generally consist of material (1) of atmospheric precipitations, (2) transported from catchment area, and (3) synthesized in the water of the lake itself. Thus, the chemical composition of bottom sediments characterizes the specific features of both the lake and the surrounding catchment area. Moreover, the analysis of bottom sediment always includes information for a certain time interval, which depends on the thickness of the sediment layer analyzed and the sedimentation rate, whereas the water analysis characterizes water quality only at the moment of water sampling [3]. Chemical analyses can be coupled with radiometric dating (^{210}Pb, ^{14}C), and, thus estimates of water quality can be connected with certain historical events.

MATERIALS AND METHODS

To study the present-day state of surface water and the historical evolution of contamination of the White Sea catchment area on the Kola Peninsula with chalcophile elements we collected lacustrine bottom sediments with an open gravity-type corer with inner diameter of 44 mm and automatically closing diaphragm [4]. Sedimentary columns were then split into 1-cm layers. Concentrations of chalcophile elements in bottom sediments were determined in solutions by atomic absorption spectrophotometry after sample treatment in concentric nitric acid. The procedure of sampling and analysis of bottom sediments is described in detail in [3, 5, 6].

RESULTS AND DISCUSSION

Elevated contents and sedimentation rates of chalcophile elements in bottom sediments dated at the past century were found in study of the Russian and Norwegian lakes in Northern Fennoscandia [7]. Some of the higher Pb concentrations in bottom sediments are generally unrelated to emission of smelting plants, because they are dated at too early times, when industry was absent in Scandinavia. There are data for lacustrine bottom sediments from southern Sweden, which are indicative of atmospheric contamination with lead due to its intensive production and use in Europe since the times of ancient Greek and Roman civilizations [8]. It was noted that atmospheric precipitation of Pb increased

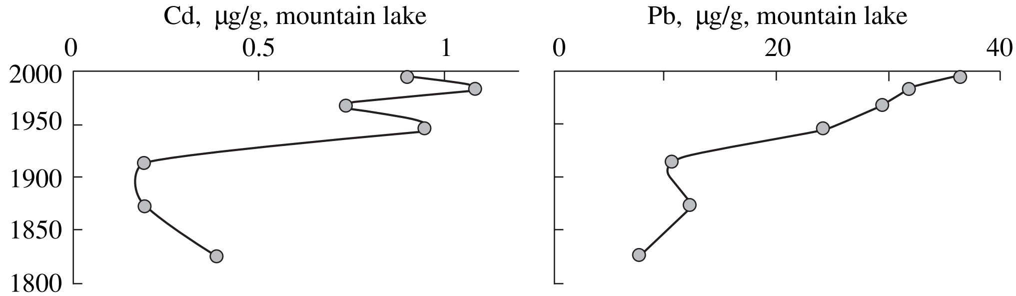

Fig. 1. Vertical distribution of Cd and Pb concentrations (μg/g of dry weight) in the dated bottom sediments of the mountain lake (Chunozero catchment area).

above background values more than 2600 years ago (at depth of 1.5–4 m in sedimentary columns). There is a notable increase in Pb precipitation about 2000 years ago and more significant increase about 1000 years ago. Lead precipitation significantly accelerated in the 19th, and, particularly, in the 20th century. The highest accumulation occurred in the 1970s. Prior to industrialization of the 19th century, Pb concentrations in lacustrine bottom sediments in southern Sweden had already increased by 10–30 times relative to background values because of atmospheric precipitations.

The rate of Pb accumulation in lacustrine bottom sediments in North America gradually increased from 1850–1875 until 1975 and has been decreasing since then [9]. A similar increase, but 50–75 years earlier, is observed for Europe. Anthropogenic lead has various sources including metallurgical and glass-making plants and the use of Pb tetraethyl as a knock-sedative dope to gasoline. The use of lead-free gasoline led to significant decrease of Pb precipitations in North America and Western Europe. Increases in Pb concentrations can be related to transboundary migration of lead from sources in North America and Southern Europe. The rate of head accumulation in northern Norway is lower than in the southern part of the country [10], as well as in the south of North America [9]. Small increase of Pb concentrations in bottom sediments in the eastern part of the Finnmark province in Norway could be related to the low rate of lacustrine sediment accumulation and very low background concentrations of Pb.

The age of layers accumulated during the past 200 years was determined for a bottom sediment column of a mountain lake in the Chunozero catchment area using ^{210}Pb chronology (Liverpool University, UK) [11] with CRS and CIC dating models [12]. Retrospective analysis of geochemical composition of bottom sediments revealed Cd and Pb accumulation in the 20th century (Fig. 1) despite low contents of these elements in water. Lead accumulation occurred since the end of the 19th century. During this period, the Kola North was an unreclaimed territory and the initial stage of Pb accumulation could be related to migration of contaminated air masses from industrial Europe. Variable Cd accumulation is observed with decrease of Cd concentrations at the end of the 19th century, its increase to 1930–1940s, new decrease in the mid 1970s, and elevated accumulation in the uppermost layer. Accumulation of Ni, Cu, and Co is noted since the 1940s and is ascribed to industrial development of the Kola region and initiation of processes for treatment of Cu–Ni ores in the town of Monchegorsk >20 km to the east of the mountain lake [13].

Increase of heavy metal concentrations, including those of chalcophile elements, affected the environmental state of the lake. The study of *Chironomidae* population in the mountain lake revealed three stages in its evolution [14]: (1) natural ontogenesis (prior to about 1945), (2) initial stage of the anthropogenic ontogenesis (about 1945–1982), and (3) anthropogenic ontogenesis (after about 1982).

Similar distribution of chalcophile element concentrations was found in bottom sediments of the Chunozero Lake, which is situated in the Laplandian State Biosphere Reserve and has suffered anthropogenic air contamination, generally by emission from the *Severonikel* plant. Because of the higher sedimentation rate in the Chunozero Lake, Pb concentrations notably increase at a depth of 15 cm (Fig. 2), whereas the concentration of this chalcophile element increases at depth of 5–6 cm in the bottom sediments of the mountain lake. This layer in the mountain lake corresponds to the end of 19th century.

Imandra, the largest lake of the Kola Peninsula, is contaminated by waste discharge and atmospheric emission from the largest plants of the mining and metallurgical industries, i.e., *Severonikel* combine, OAO *Apatit,* and Olenegorsk mining and processing combine, as well as by domestic wastes of settlements within the catchment area of the lake. The lake has suffered intensive anthropogenic impact over more than 70 years, which has led to changes in the composition of the water and bottom sediments. The upper 10 cm of the sedimentary column of the Imandra Lake shows elevated contents of chalcophile elements (Fig. 3). Concentrations of Hg, Cd, Pb, and As in the uppermost layers of the bottom sediments exceed their background contents (in layers deeper than 10 cm) by 7, 5, 7, and 4 times, respectively.

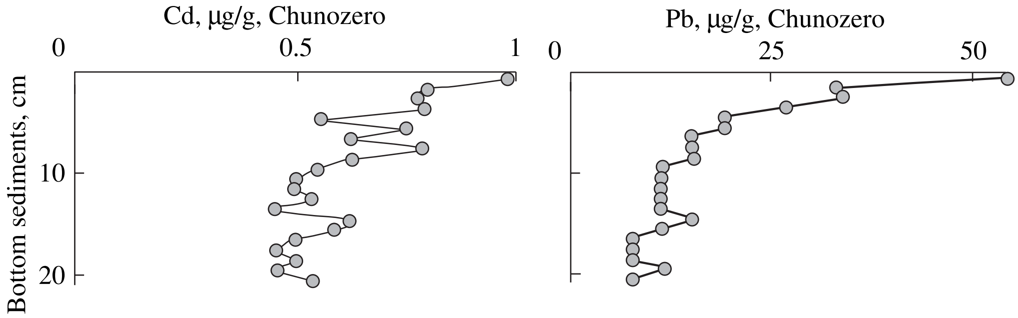

Fig. 2. Vertical distribution of chalcophile element concentrations (μg/g of dry weight) in bottom sediments of the Chunozero Lake.

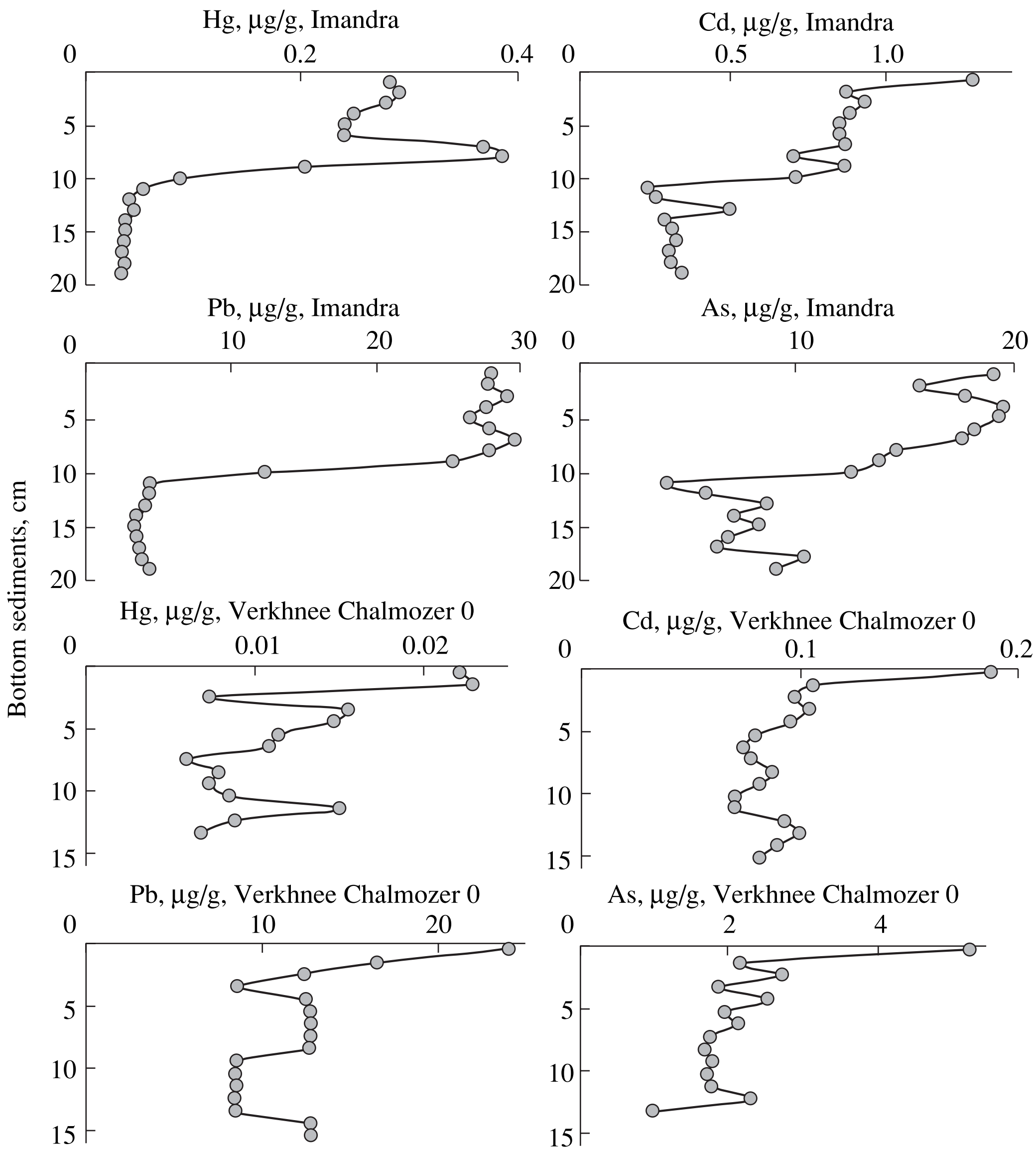

Fig. 3. Vertical distribution of chalcophile element concentrations (μg/g of dry weight) in bottom sediments of the Imandra and Verkhnee Chalmozero lakes.

The Verkhnee Chalmozero Lake, a part of the Pirenga lakes system and situated within the catchment area of the Imandra Lake, suffers generally from the impact of air pollution, although it also gains wastes from the Kovdor mining and processing combine through the Kovdora and Ena rivers. Increase of chalcophile element concentrations in the Verkhnee Chalmozero Lake is found only in the upper 1–2-cm layer of bottom sediments (Fig. 3), probably because of the lower sedimentation rate in this lake as compared with the other above-mentioned lakes. Concentrations of Hg, Cd, Pb, and As in the uppermost layers of bottom sediments increased by 3.3, 2.3, 1.9, and 5.4 times, respectively.

CONCLUSIONS

Studies of the chemical composition of lacustrine bottom sediments in the catchment area of the White Sea on the Kola Peninsula have revealed that concentrations of chalcophile elements (Hg, Cd, Pb, and As) increase in all lakes examined, regardless of contamination sources, i.e., atmospheric pollution or wastes discharged from industrial enterprises. During the latest decades, these elements have become the main global contaminating agents. The thickness of the contaminated layer depends on the sedimentation rate and varies from 1 to 15 cm. Lead concentrations increased since the end of the 19th century until the beginning of industrial activity on the Kola Peninsula. The initial stage of Pb accumulation could be related to the migration of contaminated air masses from industrial Europe. Notable increase in Cd contents is observed in the 1930–1940s with its accumulation in the uppermost layer. Elevated contents of chalcophile elements in the bottom sediments of Imandra, the largest lake of the Kola Peninsula, are found in the upper 10 cm of the sedimentary column. Concentrations of Hg, Cd, Pb, and As in the uppermost layers of bottom sediments exceed their background contents by 7, 5, 7, and 4 times, respectively.

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