Migration of heavy metals to the atmosphere in the process of transpiration

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For the first time, heavy metals were found in condensates of the transpiration excretion of macrophytes growing in sludge ponds of mining industry. Chemical analyses were made by AAS and ICP-MS methods. Lead and manganese were found in condensates of transpiration excretion of fluvial horsetail (*Equisetum fluviatile L.*) – 0.039 and 150 μg/(l·day) and common reed (*Phragmites australis L.*) – 0.14 and 48 μg/(l·day), respectively. The fact of the presence of heavy metals in transpiration was confirmed in laboratory for 7-day germs of spring wheat “Novosibirskaya-67” (*Triticum aestivum L.*) that were grown in sediment and water of tailings storage ponds. The following toxic elements and metals were found in wheat condensates: Cd (on average 0.087 μg/(l·day)), Pb (2.7), Hg (0.056), Sn (0.36), Cu (3.9), Zn (14), Fe (120), Mn (1.3). These elements penetrate into the atmosphere as a result of physiological processes in plants, rather than due to mechanical transport.

Introduction

One of the critical problems nowadays is the problem of the environmental effect of wastes from mining enterprises. Ore reduction, chemical processing, and other processes aimed at processing and concentration of ore favor the increase in lability of pollutants (metals – Cu, Zn, etc. and toxicants – Cd, Sn, As, Sb, etc.) above its natural value and penetration of pollutants into bottom sediment, soil, and biomass.[1,2]

There are many ways of pollutant migration into the environment from tailing storage ponds. Among them there are river water streams carrying solid substances, drain streams, aerosols, penetration of metals and toxicants into trophic chains, etc.[3–6] We consider the process of transpiration (evaporation of moisture from plant surface) as one of the possible ways of pollutant migration into the environment through the biological component of tailings storage ponds. The aim of this study is to determine whether metals and toxicants are present in transpiration excretion of plants. If yes, then there exists one more hard-to-control way of metal migration from sludge ponds to the environment, which can hardly be controlled, because plants make up an essential part of any biogeocenosis and roots of some plants penetrate deep into soil (down to several meters and even deeper).

Object and subject of the study

As an object of our study, we took tailings storage ponds (sludge ponds) of the Salair Ore Mining and Processing Enterprise (OMPE) in Kemerovo Region (Fig. 1). The sludge ponds contain wastes of cyanidation and flotation of barium sulfate-polymetallic ores and are made as so-called technogenic lakes – hard substance of wastes (mln. ton) covered with water. We have studied two of five ponds: sludge pond Dyukov Log (a well) and Settling tank. The former is not used at present. It consists of two related lakes: northern lake and southern lake, and wells, which are situated to the south from the first two lakes and lower by terrain. For the last 35 years no wastes were placed in it, but neutralization or conservation of tailings was not performed. The latter is an active sludge pond made as a back river intended for emergency discharges of the Lead-Zinc Concentrating Mill (LZCM).

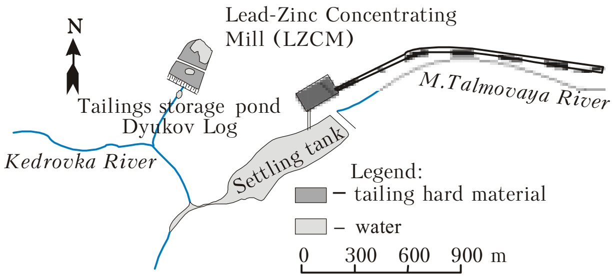

Fig. 1. Location of sludge ponds of the Salair Ore Mining and Processing Enterprise.

For a comparison of the processes proceeding in a polluted medium with natural processes, we studied plants from the background region upstream of Kedrovka River before the ingress of wastes in it. The concentration of metals (Cd, Pb, Cu, Zn, Fe, and Mn) in bottom sediment and water of the sludge ponds is several times higher than the background concentration.[7]

The sediment and water of the sludge ponds serve as a substrate for macrophytes forming vast bushes in them. As subjects of study, we took fluvial horsetail (*Equisetum fluviatile L.*), which is a hyperaccumulator,[8] in the Dyukov Log well and common reed (*Phragmites australis L.*), as a dominating plant, in the Settling tank.

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Methods used in the study

Method No. 1. To gather the condensate of transpiration excretion under the field conditions, a plant was placed in a plastic bottle so that it covered the whole part of the plant above the water. To do this, the above-water reed part was bended several times (Fig. 2). The bottleneck was closed by a polyethylene film, whose ends were fixed to the bottle with a Scotch tape. The bottle with the plant was fixed to a support placed near the plant so that the condensate was gathered in the bottle near the neck.

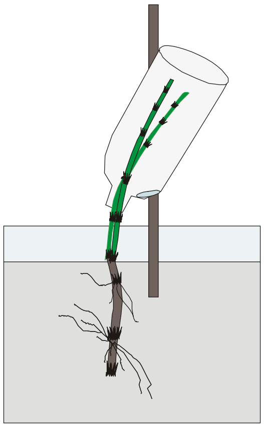

Fig. 2. Collecting the condensate of transpiration excretion of plants under field conditions (method No. 1).

Condensate samples were collected in 24 h, along with collecting control samples, which were used to estimate the amounts of elements coming to a sample from a bottle surface and from the plant surface.

However, this method has some disadvantages: (1) the condensate contacts with bottle walls for 24 h, so ingress of pollutants from the walls to the condensate is possible; 2) ingress of particles formed as plant integuments die is possible; (3) ingress of dust and aerosol of non-plant origin from air is also possible.

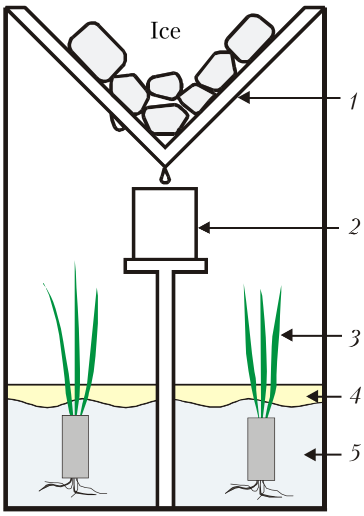

Fig. 3. Collecting the condensate of transpiration excretion of plants under laboratory conditions (method No. 2).

Method No. 2. Disadvantages of the field method No. 1 cast some doubt on the fact of ingress of metals and toxicants into the atmosphere with transpiration, even in the case that they were detected in the condensate. Therefore, it was decided to conduct laboratory studies using 7-day germs of spring wheat "Novosibirskaya-67" (*Triticum aestivum L.*). The experiment was conducted in a clean room (class A) on young wheat germs, and this excluded the presence of phytogenic and non-phytogenic aerosol, because integuments do not die at the early stage of vegetation. We have developed a specialized setup for collecting the condensate of transpiration excretion, which practically excluded the possibility of ingress of uncontrolled pollutants into the condensate, see Fig. 3.

The laboratory setup for collecting transpiration excretion is based on the principle of production of super-pure water by the method of subboiler distillation. The setup consists of a polyethylene breaker 20 cm in diameter, on which a fluoroplastic funnel *1* is placed (see Fig. 3). At the center of the breaker, a small 50-ml fluoroplastic breaker *2* is placed on a support so that drops of the condensate generated on the inner surface of the funnel fall in it. From the outside, the funnel was filled with ice for more intense generation of the condensate. The polyethylene breaker was filled with sediment and water from the surge ponds, and 7-days wheat germs *3* grown in the technogenic biotope were planted in it. The condensate of transpiration excretion was gathered for 24 h. To exclude evaporation from the open water surface, it was covered by a vegetable oil layer *4*. For 3 days, three samples of the condensate have been obtained. On the third day, germs started to die likely because of oxygen deficit, since control germs in the polluted medium, but in the open air and without oil on the water surface continued to grow.

The "purity" of the experiment was checked by conducting a control experiment with wheat germs grown in the unpolluted medium. In this case, no metals and toxicants were found in the condensate collected with the same setup.

The concentration of elements in the condensate samples collected in field experiments was determined by the method of atomic absorption spectrometry (AAS) with plasma and electrothermal atomization on Perkin Elmer model 3030 and the method of inductively coupled plasma mass spectroscopy (ICP-MS) on Finnigan MAT ELEMENT. In the wheat condensate, the concentration of elements was determined only by the ICP-MS method, because it was lower than the detection limit of the AAS method with both plasma and electrothermal atomization.

To estimate the concentrations of elements in the condensate of wheat transpiration excretion by the ICP-MS method, we used a semiquantitative method based on device calibration against Merck standard 10090a977c. The calibration curve of the spectrometer sensitivity as a function of mass for In, Ba, Lu, and U is shown in Fig. 4. The analytical signal for the determined elements at the concentration equal to 1 ppb was estimated by the calibration curve assuming the linear mass dependence of the sensitivity (cps/ppb). The concentrations of the elements in the samples were calculated from the values of the analytical signal and the calibration curve.

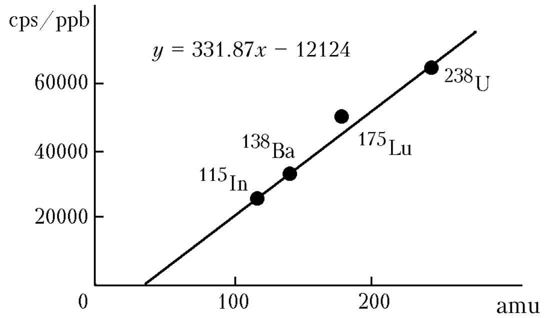

Fig. 4. Calibration curve of the sensitivity (cps/ppb) as a function of mass (amu) for 10090a977c standard.

Results

In the field experiments, we have obtained the condensate of transpiration excretion of fluvial horsetail and common reed (method No. 1). The obtained solutions of the condensates were colorless, transparent, and containing no suspended matter. This is an indirect proof of the fact that they did not include phytogenic aerosols that are formed as integuments die.

From the results of AAS and ICP-MS analyses, the following elements were detected in the condensates of transpiration excretion: Cd, Pb, Mn, Fe, Cu, and Zn (Table 1). Table 1 also gives the results of analysis of control samples: CS-1 – water washout from bottle walls and CS-2 – water washout from plant surface. In general, the results of AAS and ICP-MS analyses agree well. The concentration of Pb and Fe in the condensate proved to be lower than the detection limit of the AAS method, and therefore it was determined only by the ICP-MS method. The results of analysis of the control samples by the ICP-MS method showed that the concentrations of Cd, Cu, and Zn are comparable with and sometimes even higher than those in the condensate. The concentration of Fe in the condensate is roughly twice as high as that in the control samples. Only the content of Pb and Mn in the condensate is far (one to two orders of magnitude) higher than that in the control samples.

Later, under the laboratory conditions, the fact of the presence of heavy metals in plant transpiration was confirmed by studying 7-day wheat germs. The condensate of wheat transpiration excretion was sampled by the method No. 2, which allowed us to exclude many hampering factors. The condensate was sampled for 3 days: WT-1 for the first day, WT-2 for the second day, and WT-3 for the third day. At the third day, the germs begin to die because of anoxia. The concentration of elements in the samples was determined by a semiquantitative method with the help of the ICP-MS method. It was found that the concentrate of transpiration excretion of wheat germs contained the same elements as transpiration excretion of fluvial horsetail and common reed, namely, Cd, Pb, Mn, Fe, Cu, Zn, as well as Hg and Sn (see Table. 2).

Table 1. Concentration of elements in the condensate of transpiration excretion of macrophytes growing in sludge ponds of the Salair OMPE, in μg/(l·day)

Element	Fluvial horsetail				Common reed			
	Condensate		CS-1	CS-2	Condensate		CS-1	CS-2
	AAS	ICP-MS			AAS	ICP-MS		
Cd	0.058	0.120	0.051	0.052	0.072	0.18	0.12	0.14
Pb	< 1.4	0.039	0.0060	0.012	< 1.4	0.14	0.0040	0.0080
Mn	110	150	1.4	0.93	43	48	5.7	6.5
Fe	< 290	11	8.7	7.1	< 290	11	6.6	6.8
Cu	68	37	86	230	180	59	93	36
Zn	120	58	230	240	36	29	54	44

Table 2. Concentration of elements in the condensate of transpiration excretion of wheat germs, in μg/(l·day). Spring wheat "Novosibirskaya-67"

Element	WT-1	WT-2	WT-3
Cd	0.081	0.093	0.0049
Sn	0.50	0.22	0.0099
Hg	0.078	0.034	0.00086
Pb	2.4	3.0	0.14
Mn	1.1	1.4	0.023
Fe	130	110	not found
Cu	2.8	5.0	0.22
Zn	23	5.4	1.6

In the process of study, it was revealed that evaporation of heavy metals at transpiration occurs as a result of physiological processes in plants. In the condensate of dying wheat germs, the concentration decreases by 1–3 orders of magnitude as compared to that in the living plants (see Table 2) with the intensity of transpiration no less than in alive germs. The volume of the condensate collected from dying and normally functioning wheat germs was the same.

In spite of a relatively low content of pollutants in transpiration excretion (in the condensates collected for one day, the concentration of elements is lower than in the surface water), they present a severe hazard, because the amount of water transpired by bushes of aquatic plants can several times exceed the amount of water evaporated from the open water surface.[9] The amount of water transpired, in particular, by reed bushes is, on the average, twice as large as that evaporated from the open water surface.

If plantations are rather large (in our case, they occupy up to 40% of the area of technogenic lakes), then transpiration excretion aerosols can contribute significantly to atmospheric pollution. Besides, such aerosols (particle size about 0.1 μm) can be transported to very long distances. It should be also remembered that these aerosols contain such highly toxic elements as Cd, Sn, Hg, and Pb, which significantly worsen the situation.

Conclusions

Because of the use of the highly sensitive method – inductively coupled plasma mass spectroscopy – metals and toxicants have been found for the first time in the condensate of transpiration excretion of aquatic and land plants. Such elements as Pb and Mn were found in the condensate of fluvial horsetail and common reed, and Cd, Pb, Mn, Fe, Cu, Zn, as well as Sn and Hg were detected in the condensate of spring wheat "Novosibirskaya-67." It was established that metals and toxicants come into the atmosphere as a result of transpiration excretion due to physiological processes in plants.

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