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The study of mercury accumulation by plants depending on the chemical form of the element in the growing media

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ABSTRACT. The ability of plants to accumulate pollutants from natural and technogenic environments has found a wide application for cleaning up polluted areas. Most of the works published on this topic are related to the study of the plants efficiency to extract pollutants from polluted areas, including the intensification this process. However, much less attention is paid to the influence of chemical factors on the intensity of the elements accumulation as a function of their speciation. However, the chemical form of the element determines its migration pathways (mobility), bioavailability and toxicity. This issue is in the focus of the present work where the results of the study of mercury accumulation are discussed on the example of white mustard (*Sinápis álba*) depending on the chemical form of the element initially introduced into the growing matter. We have indicated that methylmercury is the most intensively accumulated species in comparison with mercury chloride and mercury sulfide.

***Keywords*:** mercury accumulation, elemental speciation, thermal evaporation technique.

1. Introduction

Intensive economic activity of mankind has led to the formation of many isolated storage zones of man-made materials that are dispersed and transformed in migration processes. The modern technologies allow using only a small part of mining rocks that are processed annually in the world, while the rest is accumulated as the waste, polluting the natural environment. Such areas represent a serious danger, which can be viewed as a challenge to modern humanity, in fact a 'chemical temporary bomb'. The problem of industrial waste disposal is especially important for the areas where mining industries previously functioned. When traditional technologies are used, a large amount of chemical reagents (acids, alkalis, solvents, etc.) will be required, and it is hardly possible to speak about the preservation of the natural environment. In contrast, phytotechnologies can be considered the most nature-friendly approaches (Yan et al., 2020). Some plants are known to accumulate one or more compounds and elements at a concentration level of 0.1-1% dry biomass, which makes this approach promising for the removal of toxic elements from polluted areas. In the articles published on this topic, the plants ability to extract pollutants is at the forefront, but the chemical aspect issues are very limited. The key question about the effect of the chemical form of an element in the growing medium on its accumulation by plant is insufficiently studied; however, this knowledge elucidates the essence of bioaccumulation phenomenon. As mercury refers to the most hazardous elements, the development of new approaches for mercury removal from polluted areas using bioaccumulation remains an actual issue of phytoremediation. The concept of the chemical form of an element is often substituted by a form of existence characterized by the binding of the element to the solid matter of the habitat, which usually specified using stepwise leaching, i.e. through the release of water-soluble compounds by the destruction of the material with the associated element (Hass and Fine, 2010; Chai et al., 2020; Huang et al., 2020). In one of the latest works, in a certain degree associated with the influence of the chemical form of mercury on the accumulation by plants the relationship between the extraction efficiency dependently on the form of its presence in technogenic environments, but the form the element existence does not allow to judge its toxicity, bioavailability and migration routes in nature. Although, frankly, it is worth noting in a few published

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works (Godbold, 1991; Ribeyre and Boudou, 1994; Wang, 2004), the authors of which assessed the effect of organic and inorganic mercury on the viability of macrophytes in laboratory experiments. It was shown that methylmercury had higher accumulation efficiency than Hg^{2+} reducing plant viability. Unfortunately, these studies did not receive further development. Currently, there are no data in the literature on the study of mercury accumulation from media containing various species of elements, especially considering their possible transformation during the growth process.

The scientific issue, at which this article is aimed, includes the study of relationship between the chemical forms of the element on the example of mercury and the efficiency of its accumulation by plants in relation to the mercury species typical of a real man-made object, Urskoe sulfide tailing dump (Kemerovo Region).

2. Materials and methods

2.1. Plant material

White mustard (*Sinápis álba*), annual plant, effective mercury accumulator, a green manure that improves the soil structure, changes acidity and enriches it in nitrogen, quickly sprout and bloom.

2.2. Planting medium

The lowland peat of the Siberian region with neutral acidity (pH 6.8) was used as a model medium for growing plants: this was due to the further perspective research on the phytoextraction of mercury from the materials of mining waste, the composition of which is represented by peat-bearing material that is in fact an organic-mineral mixture referred to as natural organic matter (Lazareva et al., 2019).

2.3. Reactants and materials

All chemicals used in research were not lower than analytical grade: mercury chloride, methylmercury chloride and mercury sulfide from Sigma-Aldrich (Australia), nitric acid, hydrochloric acid, oxygen peroxide, aluminum oxide, and sodium hydroxide from Reachem (Russia). Multi-elemental standard solutions for ICP-AES analysis were purchased from SKAT (Russia). Lowland peat of Charodey LLC (Russian Federation) was used as a growing medium.

2.4. Instrumentation

A RA-915+ mercury analyzer with Zeeman correction of nonselective absorption equipped with the RP-91C attachment (Lumex Instruments, Russia) and the RAPID data acquisition software (Lumex Instruments, Russia) was applied for the direct mercury determination in growing substrate and plants under study. For mercury speciation, a sample introduction system was modified with a thermocouple to control the temperature in the dosing unit and with a home-made adjustment to move the dosing unit inside the atomizer. LED lamps "Green power" LWL-2014-01CL ultraviolet lamp (Russia) was used to provide optimal conditions for the plants growth. An iCAP 6500 Duo atomic emission spectrometer with inductively coupled plasma (Thermo Fisher Scientific, USA) equipped with a special attachment for mercury cold vapor generation. A MARS 5 microwave system (CEM Corporation, USA) was used for mineralization of solid samples (peat and plants) before analysis.

2.5. Experiment description

2.5.1. Preparation of the media for planting

The peat sample was divided into four portions (2.5 kg each). Solutions (suspensions) of the studied mercury species were introduced into the peat as follows: spraying a certain volume of mercury chloride ($HgCl_2$) solution (C = 310 ppb) and methylmercury chloride CH_3HgCl (C = 330 ppb), constantly stirring in a volume until the concentration of mercury in the peat was at the level of ~2 ppm (as mercury). In the case of mercury sulfide, HgS (C = 310 ppb), a suspension of mercury sulfide was also introduced into the peat with constant stirring. Then the peat samples were analyzed for the total mercury concentration using a RA-915+ direct analyzer to clarify an exact concentration of the element.

2.5.2. Planting

The peat samples weighing 0.50 kg with a layer thickness of 10 cm were placed in containers. Overall, five containers were prepared with various forms of mercury, and five containers were not seeded.

After 30, 60 and 90 days of the start of experiment, the total mercury concentrations and its species contents were determined in growing media. The accumulation abilities of the plant relative to their species were evaluated using bioaccumulation factor: $BCF = C_{pl}/C_{med}$, where C_{pl} and C_{med} are mercury concentrations in plant and peat, respectively (Arnot and Gobas, 2006). Mercury speciation in the peat material was performed according to our approach proposed previously based on the dilution of the samples with aluminum oxide to unify the analysis procedure and prevent the matrix effect (Shuvaeva et al., 2008).

3. Results and discussion

To study the efficiency of mercury accumulation by plants, we refined the total concentration of the element in the peat samples after introducing various species using the TR-ETA-AAS technique. Obviously, after the completion of the mercury species introduction into the peat substance, the results differed slightly from the calculated ones, which was due to their uneven distribution in the sample.

The results of mercury distribution in the studied plant and bioaccumulation factors (BCF) for each chemical form of mercury in temporal dynamics are presented in Table and in Fig. 1*A*.

Table. Mercury concentrations in parts of white mustard and BCF values for the plants grown in various substrates, n = 3

Experiment duration, days	Mercury concentration			BCF
	Roots	Upper part	The whole plant	
Mercury chloride, $HgCl_2$, 1.9 ± 0.2 ppm				
30	N/d	N/d	0.7 ± 0.3	**0.4**
60	3.9 ± 1.1	0.5 ± 0.2	2.2 ± 0.8	**1.2**
90	11.4 ± 5.5	7.4 ± 2.1	9.4 ± 2.3	**4.9**
Methylmercury chloride, CH3HgCl, 1.2 ±0.1 ppm				
30	N/d	N/d	1.9 ± 0.3	**1.6**
60	11.8 ± 6.0	4.2 ± 1.1	8 ± 2	**6.7**
90	30.2 ± 9.1	11.6 ± 0.4	20.9 ± 5.1	**17.4**
Mercury sulfide, HgS, 1. 4±0.3 ppm				
30	N/d	N/d	1.4 ± 0.7	**1**
60	4.3 ± 0.5	0.6 ± 0.1	2.5 ± 0.2	**1.8**
90	13 ± 7.1	3.4 ±1.8	9.9 ± 2.5	**7.1**

It was obvious that the plants extracted mercury most intensively from the environment containing methylmercury chloride: BCF values within 90 days of the experiment increased from 1.6 to 17.4.

However, it was surprising that the element was extracted more intensively from a medium containing insoluble mercury sulfide compared to that containing mercury chloride. As an explanation for this effect, we can assume that mercury sulfide was oxidized to sulfate in the growing medium, which was confirmed by the data on translocation factor (TF) for mercury sulfide in the plant (Fig. 1*B*) assessed as the ratio of element concentrations in the upper (green) part of the plant to that in the root. In evaluating the efficiency of element accumulation by plants, the value of the translocation factor (TF) is often taken into account: the more TF, the more the plant is able to accumulate the element and, hence, the higher its accumulation capacity. A plant is considered an effective accumulator if TF > 1.

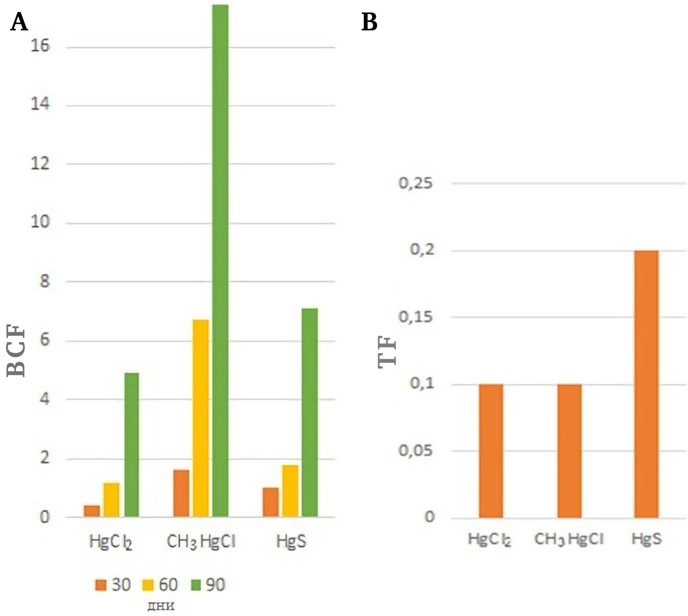

Fig.1. Factors of bioconcentration (*A*) and translocation (*B*) of the studied plant depending on mercury speciation in growing media.

4. Conclusions

In summary, the study indicates that in the process of growth in media containing various forms of mercury, namely, mercury chloride, etc. white mustard extracts accumulate methylmercury chloride most efficiently. At the same time, the translocation factor for mercury sulfide is higher than for other forms, which suggests the transformation of mercury forms in the media during plant growth. This issue is important for a deeper understanding of the essence of the bioaccumulation phenomenon.

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Conflict of interest

Authors declare no conflict of interest.

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