

Assessment of Rosa Majalis Herrm-Fruits Contamination with Heavy Metals in Open-Pit Coal Mine Waste Dumps

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Abstract

The work studies heavy metals content in embryo-earths and Rosa majalis Herrm. Fruits in conditions of "Kedrovsky" open-pit coal mine waste dump in Kuzbass region, Russia. It has been experimentally proven that embryo-earths of the dump are characterized by significant fluctuations in heavy metal content - maximum values are typical for Mn and Fe (79.5 and 26.6 mg/kg), minimum values for Cd and Cu (0.134 and 0.27 mg/kg). It has been found that the content of biologically active elements, Cu and Zn, is below sufficient soils reserves. Comparison of results with hygienic standards did not reveal content of heavy metals in embryo-earths the dump more than MPC (APC). It has been found that the briar fruits accumulate more biophile metals (Mn, Fe, Zn, Cu); content of technogenic group elements (Pb, Cd, Cr, Ni, Co) is low - between 0.05 and 1.1 mg/kg. Calculation of biological motility rate (Bx) showed that briar fruits absorb more Cu (13.03) and Zn (4.82) from soil. For the majority of heavy metals (Pb, Cd, Mn, Ni, Fe and Cr) inhibition of biological absorption (Bx <1) has been detected with minimum for Pb. Hygienic assessment of Rosa majalis Herrm. fruits showed no excess in the content of heavy metals over MPC accepted for vegetative BAA, MPC based on generalized world information and regional background of ecologically pure areas of Kuzbass. The work accomplished proves safety of briar fruits grown at waste dumps of the Kedrovsky open-pit coal mine as far as ecotoxicants like heavy metals are concerned.

Keywords: open-pit coal mines, briar fruits, heavy metals, radionuclides

1. Introduction

Kuzbass is the center of the coal mining industry in Western Siberia. It has about 5 thousand industrial enterprises, including over 50 mines and open-pit coal mines. As a result of coal mining, the area of disturbed lands in the Kuzbass region exceeds 100 thousand hectares. In recent years about 20 thousand hectares have been rehabilitated, the rest of technogeneous land is subject to natural overgrowing due to drift of seeds from the surrounding areas.

At Kuzbass coal mines waste dumps, many medicinal herbs that are used in applied medicine grow, and local population collects and preserves them. However, wastes from coal production, i.e., dumps and terricones may be sources of high content of heavy metals.

HM hold a special place among the technogenic pollutants due to their wide occurrence and high toxicity. They are able to penetrate the biological cycle and cumulate in human body. In this regard, study of the resource potential of medicinal herbs growing at waste dumps of the Kuzbass coal mines and assessing their safety are actual.

Among brushwood at waste dumps of Kuzbass open-pit coal mines widespread is briar - Rosa majalis Herrm. of the Rose family (Rosaceae). Briar is a valuable forest improvement shrub and pharmacopoeial raw material that is used as a source of vitamins (State Register et al., 2008). Briar fruits contain ascorbic acid, carotenoids, flavonoids, catechins, carbohydrates, organic acids, vitamins B, K, P, E, polyunsaturated fatty acids, pectin, potassium, sodium, calcium, magnesium, phosphorus, iron, etc. (Andersson et al., 2012; Kumar et al., 2009; Zhang et al., 2013). Preparations made of briar fruits have a wide range of pharmacological action (Kirkeskov, et al., 2011; Muravyeva et al., 2002; Rein, et al., 2004; Schwager et al., 2011; Tumbas, et al., 2012; van der

Westhuizen, et al., 2008), they are used in preparing combined nutritional food and drinks (Perfilova 2010; Volobueva and Kozlova, 2011; Vossen, et al., 2012).

To assess the possibility of using medicinal raw materials grown in the technologically altered areas in medicine and in food production, research of their hygienic safety is needed. Important health safety indicators of medicinal raw material include content of heavy metals (HM).

Currently, HM content in Medicinal Raw Herbs (MRH) is still not standardized in Russia, so many researchers for MRH hygienic assessment use indicators adopted for vegetative nutritional supplement (Gravelle et al., 2008). This work is a continuation of the previously published studies in hygienic assessment of medicinal herbs growing on dumps of the Kuzbass open-pit coal mines (Neverova and Egorova, 2013; Egorova and Neverova, 2013; Egorova and Neverova, 2013a).

Research in this area will make it possible to assess the possibility in principle of introduction and industrial harvesting of MRH on dumps of the Kuzbass open-pit coal mines, will expand the variety of MRH harvested in the region, as well as will introduce the lands disturbed by coal mining into commercial use.

The goal of this work is assessment of briar (*Rosa majalis* Herrm.) fruits and adjacent embryo-earths with heavy metals at "Kedrovsky" coal mine waste dump.

2. Subject and Methods of Research

The research was performed at the Yuzhny waste dump of the Kedrovsky open-pit coal mine. The total area of the "Yuzhny" waste dump is 599.3 hectares and it has the altitude of 58 m, with plain-sloping terrain. Rocks that form dumps are mainly represented by sandstones (60%) with a considerable shares of siltstone (20%), and argillite (15%), loam and clay (5%).

Embryo-earths are mainly represented by heavy, moderately saturated clay loam (humus 3.5%) characterized by alkaline reaction of soil solution (pH of aqueous extract 7.1-7.7), low saturation with phosphorus and nitrogen (1.7-7.0) and content of exchangeable potassium little below normal (125 mg/kg). Objects of the study were samples of briar (*Rosa majalis* Herrm.) fruits and associated embryo-earths collected in years 2012 and 2013.

Raw material was procured during the period of full ripeness (early September), in dry sunny weather, according to the standard rules. The raw materials collected had no visible signs of damage. An average sample was prepared by quartering in accordance with GOST 24.027.0-80. Embryo-earths associated with the herbs were taken from the root layer (A 0-15 cm) using usual methods.

Elemental analysis of embryo-earths samples and MRH was performed using the atomic absorption method in air-acetylene flame in spectrophotometer AAS - 30 from Karl Ceis Jena (Germany) on the basis of the accredited test center of the "Kemerovsky" agrochemical service. For extracting HM from soil, ammonium acetate buffer was used with pH 4.8 in soil/solution ratio 1/10, time of extraction was 24 hours. Samples of plant raw materials were prepared by dry ashing followed by extraction with dilute nitric acid (1:1); time of extraction was 24 hours. To characterize availability of chemical elements for plants and extent of their use of mobile forms contained in embryo-earths, biological motility ratio (Bx) was calculated, i.e., the ratio of element concentration in the air-dry weight of the plant to the concentration of mobile forms of soil element. Analyses were performed in three replications; results were statistically processed using Statistica 6.0 software.

3. Research Results

Research results show that samples of dump embryo-earths are characterized by considerable fluctuations of elemental composition (Table 1). Maximum values are characterized by Mn and Fe (their contents 79.5 and 26.6mg/kg, respectively), minimum values for Cd and Cu (0.134 and 0.27 mg/kg, respectively). Low content level of dietary minerals was found, such as Cu and Zn - below soil sufficient saturation according to N. K. Krupsky - G.N. Alexandrova. Comparison of HM content in dump embryo-earths with hygienic standards showed no excess of MPC (APC) (GN 2.1.7.2041-06; Chuldzhiyan et al., 1988) (Table 1).

Table 1. HM content in embryo-earths and briar fruits at "Kedrovsky" coal mine waste dump

Elements	Content of elements, mg/kg					
	Embryo-earths		Briar fruits	Vegetative materials		
	Mobile form	MPC, APC *		RB*	MPC for BAA**	MPC, world generalized ***
Pb	2.183±0.037	6.0	0.439±0.035	1.18	6.0	5-10
Cd	0.134±0.034	APC 1.0	0.051±0.004	0.21	1.0	0.05-0.2
Cu	0.270±0.017	3.0	3.517±0.230	6.94	-	5-30
Zn	0.990±0.053	23.0	4.771±0.085	9.96	-	27-150
Mn	79.467±3.753	140-500	30.693±0.303	21.58	-	20-300
Ni	1.877±0.094	4.0	1.100±0.047	1.98	-	-
Co	0.757±0.072	5.0	0.897±0.014	2.15	-	-
Fe	26.060±0.552	-	9.507±0.309	104.51	-	-
Cr	1.277±0.054	6.0	1.020±0.015	4.08	-	-

Notes: APC* is roughly allowable concentration. RF*- regional background - relatively clean zone (Egorova, 2010, Popov, 1995), MPC for BAA** (SanPin 2.3.2.1078-01. 2002), MPC, world generalized *** (Parkhomenko and Ermokhin, 2005).

It has been experimentally found that briar fruits accumulate more biophile metals - Mn (30.693mg/kg), Fe (9.507 mg/kg), Zn (4.771mg/kg) and Cu (3.517 mg/kg). Content of technogenic group elements in briar fruits (Pb, Cd, Cr, Ni, Co) is characterized by low values within 0.05-1.1 mg/kg.

Calculations of biological motility coefficients (Bx) showed that briar fruits accumulate more Cu (13.03) and Zn (4.82) from soil. For the majority of heavy metals (Pb, Cd, Mn, Ni, Fe and Cr), inhibition of biological absorption (Bx < 1) was detected with a minimum of Pb (Figure 1).

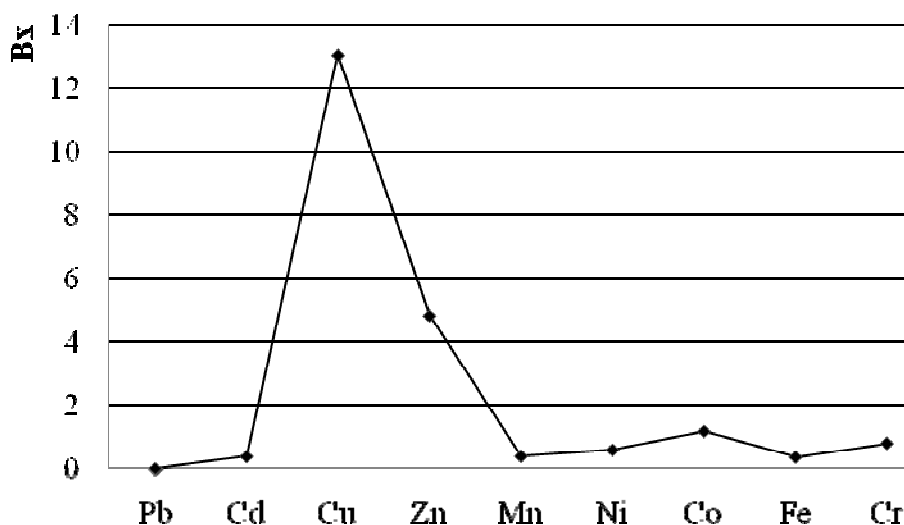


Figure 1. Biological motility coefficients (Bx) for *Rosa majalis* Herrm., growing at waste dumps

Inverse relationship has been found between the content of mobile forms of Cu and Zn in embryo-earths and the

coefficients and their biological motility (Bx) -predominantly low values of mobile forms of these HMs in embryo-earths correspond to high indicators Bx (Table 1, Figure 1). This confirms existence of complex and apparently determined by plants' specie specificity mechanisms in plants for selective absorption and accumulation of chemical elements by various organs.

Hygienic assessment of *Rosa majalis* Herrm. fruits showed no excess in heavy metals content over the MPC accepted for vegetative BAA, MPC based on generalized world information and regional background of ecologically pure areas of Kuzbass.

4. Discussion

The fact of more substantial accumulation of biophile metals by briar fruits - Mn, Fe, Zn and Cu that we established is consistent with the results obtained by E.P. Pavlova (2009) who studied *Rosa acicularis* and *R. Davurica* fruits in the Republic of Buryatia and the Trans-Baikal region. This pattern was noted for fruits of other plants. In particular, M. Lavinia et al. (2012) established the regularity of biophile metal accumulation in fruits of *Hippophae rhamnoides* L. in the row: Fe > Mn > Zn > Cu; Ružica J. Micić et al. (2013) found higher contents of Fe, Zn, Mn, Cu in fruits of red and white mulberry. Increased need for biophile metals in plants is obviously related to their participation in vital biochemical processes that determine normal growth and development.

Some researchers note that fruits of plants, unlike other morphological groups of raw materials (grass, leaves, flowers), accumulate heavy metals in much smaller quantities, and attribute this fact to the presence of scarfskin membrane of the fruits, from which in rainy season dust settled is washed away (Gravelle 2005; Strekalova, 2007). Peter Andráš et al. (2010) comparing certain types of plant tissues showed that the highest concentrations of heavy metals are found in roots, and the lowest - in flowers, seeds and fruits.

Literature states that concentration of heavy metals in plant fruits exceeds the maximum allowable safe level. In particular, Saeed Akhtar et al. (2010) in varieties of Pakistani mangoes found Fe, Zn, Ni, Cr, Cd, Pb above safety limits set by the World Health Organization (WHO). Motylyova (2000), T.V. Sennovskaya (2004) recorded excess of maximum permissible concentration (MPC) of heavy metals in fruits and berries grown under increasing anthropogenic load. With that, contamination of fruits and berries can also be observed in cases where content of heavy metals in the soil is below MPC.

There is information that heavy metals accumulation depends on varietal characteristics of plants, in particular W. Letchamo et al. (2002) observed difference in the ability to accumulate heavy metals by buckthorn fruits depending on their variety. E.T. Egoshina (2008) notes that in technological areas of the Kirov region, accumulation of heavy metals above MPC by different parts of plants was observed. So, in fruits of *R. majalis* that grows in the mud lagoon of non-ferrous metals processing plant, lead content in fruits 7.8 times exceeds MPC. This author also notes that the process of lead accumulation in different organs of plants depends on particular species of plants. S.M.

5. Conclusion

The study established that embryo-earths of the dump are characterized by significant fluctuations in heavy metal content - maximum values are typical for Mn and Fe (79.5 and 26.6 mg/kg), minimum values for Cd and Cu (0.134 and 0.27 mg/kg). Content level of such dietary minerals as Cu and Zn was found below soil sufficient saturation according to N. K. Krupsky - G.N. Alexandrova. Comparison of HM content in dump embryo-earths to hygienic standards showed no excess of MPC (APC).

It has been found that the briar fruits accumulate more biophile metals - Mn (30.693 mg/kg), Fe (9.507 mg/kg), Zn (4.771 mg/kg), Cu (3.517 mg/kg); content of technogenic group elements (Pb, Cd, Cr, Ni, Co) is low and ranges between 0.05 and 1.1 mg/kg with the minimum for Cd and the maximum for Ni. Calculations of biological mobility coefficients (Bx) showed that briar fruits accumulate more Cu (13.03) and Zn (4.82) from soil. For the majority of heavy metals (Pb, Cd, Mn, Ni, Fe and Cr) inhibition of biological absorption ($Bx < 1$) has been detected with minimum for Pb. Inverse relationship has been found between the content of mobile forms of Cu and Zn in embryo-earths and the coefficients and their biological motility (Bx) -predominantly low values of mobile forms of these HMs in embryo-earths correspond to high indicators Bx, which fact confirms the existence of the mechanism for separate adsorption of heavy metals in plants. Hygienic assessment of *Rosa majalis* Herrm. fruits showed no excess in the content of heavy metals over MPC accepted for vegetative BAA, MPC based on generalized world information and regional background of ecologically pure areas of Kuzbass.

So it has been experimentally proven that briar fruits grown at waste dump of the Kedrovsky open pit coal mine is ecologically safe as far as ecotoxicants like heavy metals are concerned.

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