

# conditions

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## Abstract

Using the INAA method, the ability of *Amaranthus tricolor* L. variety "Valentina" growing on soils with different degree of pollution to extract heavy metals was evaluated in the field experiments. It was found that amaranth of the studied variety characterized by the content of betacianin pigment, amaranthine, in the shoots and generative organ, is able to accumulate elements such as Mn, Fe and Ni from soils. The content of most of the studied elements decreases in the following order: leaves > inflorescences > stems. Under conditions of soil pollution with emissions from metallurgical plant, the phytoextraction of such elements as Mn, Fe, Co, Sb increases. The content of Fe and Mn in the leaves of A. tricolor var. "Valentina" exceeds the average data for vegetation from 7 to 17 times; the Co content exceeds the average data for vegetable from 4 to 7 times; the Sb content in the leaves exceeds the average data for vegetable from 10 to 23 times. Due to the fact that amaranth forms a sufficient biomass for the growing season, it can be recommended for phytoextraction of heavy metals from soils in case of polymetallic pollution.

Keywords amaranth

> Amaranthus tricolor soil pollution heavy metals transfer factor phytoremediation

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## Key findings

• The accumulation of elements by plants depends on the species and varietal characteristics. A number of plant substances capable of complex formation can contribute to the phytoextraction of elements from soils. In amaranth, such a substance can be the betacyanine pigment amaranthine. Amaranth varieties containing amaranthine accumulate toxic elements from the soil. The results of our experiment showed that *Amaranthus tricolor* var. "Valentina" on soils with varying degrees of anthropogenic pollution can actively extract Mn, Fe, Ni, Sb. This ability of red-colored amaranth varieties can be used for phytoremediation of contaminated soils from toxic elements, and should also be taken into account when grown for nutrition and processing on contaminated soils of agricultural lands.

• The maximum accumulation of toxic elements from soils among the studied aboveground organs was found in amaranth leaves. The minimum is in the stems.

## 1. Introduction

The problem of soil pollution by toxic elements, in particular, heavy metals (HMs), is acute all over the world and, in particular, in the regions with a high level of industrial development as well as in urban ecosystems [1, 2]. Accumulating in the soil, HMs are transferred through food chains and ultimately enter the body of plants, animals and humans. In addition, as a result of soil weathering during erosion, toxic elements can enter the body with inhaled particles of air aerosols and accumulate, subsequently causing a number of toxic effects, including teratogenic and carcinogenic. In this regard, it is necessary to



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carry out remediation of soils contaminated with toxic elements, which can be performed using mechanical, physicochemical and biological methods. Bioremediation has a number of advantages over the others listed: it is carried out in situ, is quite cheap and effective, and does not disturb the structure of the soil cover, but there is one drawback: it is stretched over time. Bioremediation can be carried out using bacteria, micromycetes, and plants. When selecting plants, one should take into account their accumulative properties and the ability to form sufficient biomass as well as resistance to toxic components of soil [3, 4]. Amaranth is a plant with C-4 type of photosynthesis, which is capable of forming a sufficiently large biomass in drought conditions, including physiological, which occurs against the background of disturbances in the structure and physicochemical properties of the soil, its salinization and acidification. In addition, amaranth is a valuable agricultural crop that contains a number of essential amino acids and at the same time belongs to vegetables, grains and oilseeds. In the genus amaranth there are many species and varieties used both in agricultural practice and in ornamental plant growing [5]. The most valuable varieties are those with the presence of the amaranthine - betacyanin pigment in the plant shoots [6]. Such varieties are capable of accumulating a number of HMs due to complexation with amarantine and the transfer of toxic elements into organometallic compounds [7]. This property can be used for the purposes of soil phytoremediation. Along with the traditional agricultural purpose of the sorghum Sorghum bicolor, amaranth Amaranthus spp. and the sunflower Helianthus annuus are widely studied as crops capable of absorbing and accumulating HMs from soils and used in experiments on phytoremediation of soils [8-13]. Amaranth is rarely used as a phytoremediate. There is information about the study of the accumulating ability of some of its species [11-14]. The accumulation capacity of Amaranthus hybridus and A. tricolor was shown in relation to three elements: iron, cadmium and chromium [11, 13, 14]. Expanding the list of species and varieties that have the ability to bioaccumulate HMs is fundamental in the development of measures for phytoremediation of soils. In this regard, we carried out this work to study the ability of A. tricolor of the Russian selection variety "Valentina" to absorb HMs from soils, including those with polyelement anomalies, in open ground conditions.

## 2. Object and Methods

For the study, a variety of red-leaves amaranth of the *Amaranthus tricolor* L. var. "Valentina" of the Federal State Budgetary Scientific Institution "Federal Scientific Vegetable Center" (VNIISSOK) selection was taken (Figure 1). The content of amaranthine – betacyanine pigment in the leaves of this variety averages at 0.43 mg/g and can vary depending on the phase of development and the chemical composition of the soil, as well as climatic conditions. Amaranth

seeds were sown in open ground in small farms of the Tula region located within the city of Tula (in the zone of influence of emissions from the Kosogorskiy metallurgical plant), Kireevskiy and Plavskiy districts to a depth of 0.5 cm. The characteristics of soils of small farms are presented in Table 1. Soils of the first sampling point (Tula) were contaminated with such elements as Cr, Mn, Fe, Ni, Zn; soils of the Kireevskiy district small farm - Cr, Fe, Ni and Plavskiy - Fe, Ni, Zn. The plant nutrition area in the experiment was 0.15 m<sup>2</sup>. The vegetation period of the plants was 4 months. At the end of the growing season (before frost), plant shoots were divided into leaves, stem and inflorescence, washed in running water, then double washed in distilled water, dried under natural conditions (in the shade), packed in envelopes and sent to FLNP JINR for the subsequent neutron activation analysis.



Figure 1 Amaranthus tricolor var. "Valentina" generative plants.

Table 1 The pH values and content of elements in soils (mg/kg).

Paramete	r Tula	Kireevskiy district	Plavskiy district	MPC* [18-20]					
рН	7.1	6.8	7.2	-					
V	70±12	68±12	63±12	150					
Cr	75±7	75±7	58±5	-					
Mn	1500±67	676±39	625±38	1500					
Fe	23760±642	27340±738	23150±625	-					
Со	9.9±0.8	11.7±0.9	9.7±0.7	-					
Ni	27.7±5.2	33.8±6.3	24.3±4.9	20-80					
Zn	139±7	85±4	148±6	55-200					
As	6.1±0.6	5.8±0.6	4.7±0.5	2-10					
Sr	169±10	100±7	113±7	-					
Мо	0.46±0.05	0.20±0.06	0.23±0.07	-					
Sb	0.65±0.07	0.53±0.06	0.93±0.09	4.5					
Cs	2.9±0.4	3.6±0.5	3.1±0.4	-					
MDC	averaged of the merimum remainsible concentration								

\* MPC – exceeded the maximum permissible concentration

X-ray spectral analysis of the soil samples was carried out in the laboratory of chemical analytical research of the Geological Institute of the Russian Academy of Sciences (GIN RAS) using a sequential wave XRF spectrometer "S4 Pioneer" Bruker AXS [15].

The results were processed using the "S4 Spectra Plus" software package. Using this method, the concentration in the soil of Al, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Mo, Ba, Pb, and Th was determined. The following standard reference materials were used as comparators: SCHT-1,2, IAEA Soil-7. GBW-07404, 07405.

Instrumental epithermal neutron activation analysis (EINAA) was carried out at a pulsed fast reactor IBR-2 of the Frank Laboratory of Neutron Physics, JINR, Dubna, Russia. A total of 42 elements were determined. To determine elements with short lived isotopes (Cl, V, I, Mg, Al, and Mn) samples were irradiated for 3 min and measured for 20 min. To determine elements with long lived isotopes: Na, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, W, Th, and U, the cadmium-screened channel 1 was used. Samples were irradiated for 4 days, re-packed, and measured twice using HP germanium detectors after 4 and 20 days of decay, respectively. The NAA data processing and determination of element concentrations were performed using software developed in FLNP JINR [16, 17].

The quality control of EINAA results was provided by using certified reference materials: 1570a (Spinach Leaves) and 1575a (Pine Needles). The experimentally measured contents were in good agreement with the recommended values. The uncertainties in elemental determinations of Na, K, Cl, As, Sr, Fe, Pb were in the range of 5–10%; and uncertainty for V, Ni, Cu, Se, Mo, Cd, Sb was 30%.

#### 3. Results and discussion

The results of the study showed that the accumulation of V in the stems of amaranth var. "Valentina" was

0.06–0.49 mg/kg of dry weight (DW) and was the highest in a small farm in Tula. Leaves accumulated 2 times more V than stems: 0.90–1.11 mg/kg DW (Table 2). The V content in the inflorescences was 0.45–0.64 mg/kg DW. This fact is associated with the presence of aerosol particles of vanadium in the atmospheric air (there is a factory for the production of vanadium in the city) and their possible absorption through the stomata and epidermis of the leaves, as well as the covering tissues of the stem, that is, not only absorption and accumulation of the element through the root system of the plant from soils, but also foliar absorption from atmospheric deposition.

The Cr content was 0.5 mg/kg DW in the stems, 0.87–0.97 mg/kg in inflorescences, and 1.26–1.44 mg/kg DW in leaves, which was 4 times higher than the average data for vegetable crops, and also exceeded the maximum permissible concentration (MPC) for agricultural crops (5.0 times in inflorescences and 6.5 times in leaves) (Table 2).

The accumulation of another soil pollutant, Mn, was minimal in the stems of amaranth (9–23 mg/kg DW), intermediate in inflorescences (53–75 mg/kg DW) and reached a maximum in leaves (115–228 mg/kg DW). The extraction of this element by leaves can be associated with both long-distance transport of substances through the plant, and with foliar absorption of an element from atmospheric deposition.

The transfer factor of Mn from soils to leaves was 0.12–0.33 mg/kg DW, that is, the period of removal of this element from soils during phytoremediation measures will average from 3 to 9 years.

The Co content in the amaranth organs was within the limits of normal regulation and amounted to 0.07–0.12 mg/kg DW in the stems, 0.13–0.29 mg/kg DW in inflorescences and 0.19–0.31 mg/kg DW in leaves. At the same time, with polymetallic soil pollution, the content of Co in the organs decreases (Table 2).

Table 2 The content of elements in the organs of A. tricolor var. "Valentina" (mg/kg DW).

Plant organ	Sampling point	v	Cr	Mn	Fe	Co	Ni	Zn	As	Sb
Inflorescence	Tula	0.64	0.91	75	486	0.13	0.61	58	0.064	0.156
	Kyreevskiy dis- trict	0.64	0.87	61	631	0.20	2.84	55	0.280	0.056
	Plavskiy district	0.45	0.97	53	286	0.29	2.62	54	0.280	0.016
Leaves	Tula	1.19	1.26	182	783	0.19	1.01	52	0.280	0.046
	Kyreevskiy dis- trict	0.90	1.44	228	403	0.34	2.09	66	0.169	0.025
	Plavskiy district	1.11	1.28	115	450	0.31	1.64	64	0.041	0.020
Stem	Tula	0.49	0.5	23	117	0.07	0.3	29	0.280	0.009
	Kyreevskiy dis- trict	0.06	0.5	15	69	0.08	1.38	30	0.280	0.003
	Plavskiy district	0.06	0.5	9	81	0.12	0.3	26	0.280	0.003
Average data for vegetable [21]		-	0.32	13	57	0.05	0.6	7	0.021	<0.002
Need (daily intake)/toxic dose, mg/day [22]			<u>0.05-0.2</u> 200	<u>3.7</u> 10-20*	<u>6-40</u> 200	<u>0.04-0.3</u> 500	0.005	<u>6-30</u> 150-600	0.05	0.05
MPC [23]		-	0.2	-	-	-	0.5	5-10	0.2	0.3

The Ni content in amaranth was 0.3–1.4 mg/kg DW in stems, 0.61–2.84 mg/kg DW in inflorescences and 1.01–2.09 mg/kg DW in leaves.

The content of elements in inflorescences and leaves exceeded the MPC of Ni for agricultural crops by 1.2–5.6 times, and it was maximal in Kireevskiy district, where the content of all elements in soils was maximal (Tables 1, 2).

The Zn content in the aboveground organs of amaranth was within the average for plants, but higher than for vegetable crops, and higher than the MPC for agricultural crops. It ranged from 26–30 mg/kg DW in stems to 52–66 mg/kg DW in leaves.

Considering that the consumption of amaranth per day usually does not exceed 200 g, the accumulation of zinc in organs during soil contamination is not critical. The dependence of the Zn content in the shoots of amaranth with the content of the element in soils was not revealed.

The As content in the region soils varied from 0.041 to 0.280 mg/kg DW and was higher in the amaranth stems and inflorescences (Table 2). The As content in the organs of the studied amaranth variety was up to 10 times higher than the average for vegetable crops and slightly higher than the MPC for vegetable crops [23]. The transfer factor for the element was 0.009–0.59, i.e. arsenic appears to be a highly toxic element for amaranth and is poorly accumulated by the plant.

The Sb content of in amaranth organs was in the range of data averaged over plants, but higher than the data for vegetable crops; however, it does not exceed the MPC.

#### 4. Conclusions

During the study, it was revealed that *Amaranthus tricolor* variety "Valentina" is capable to accumulate such heavy metals as Mn, Fe, and Ni from soils in quantities exceeding toxic doses for plants and humans. Therefore, the use of amaranth of this variety as a vegetable crop in conditions of soil contamination with these elements is not recommended. However, amaranth of the studied variety, as a plant that accumulates sufficient biomass during the growing season due to a special pathway of photosynthesis (C-4), can be used as a phytoremediant in soil contamination with the above elements. The content of elements in the aboveground organs of amaranth decreases in the following order: leaves > inflorescences > stems. This is partly due to the foliar uptake of elements from atmospheric deposition.

## Supplementary materials

No supplementary materials are available.

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#### **Conflict of interest**

The authors declare no conflict of interest.

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