Biological accumulation of zinc and copper in the «Soil-plant» system in the conditions of the south of Western Siberia

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Abstract. The purpose of the work was to study the intensity of biological accumulation of zinc and copper Tanacetum vulgare in the conditions of Western Siberia. Field experiments were carried out in the period 2012-2015 on meadow-chernozem soil of the southern forest-steppe of the Omsk region. The medicinal crop Tanacetum vulgare was chosen as an object of research. Copper and zinc fertilizers in acetate forms were applied in the background (N135P45K45). The content of mobile forms of Zn and Cu in soil and plant samples was determined by atomic absorption method. When zinc and copper fertilizers were applied, the content of mobile forms of Zn and Cu in the soil increased compared with the control and the ground. At the same time, application of micronutrient fertilizers did not lead to excess of MAC. The content of zinc in medicinal raw material Tanacetum vulgare changed from 25.3 to 48.0 mg/kg; of copper from 4.3 to 8.3 mg/kg after application of micronutrient fertilizers. The content of trace elements in medicinal raw material Tanacetum vulgare did not exceed MAL (Cu-30 mg/kg, Zn-50 mg/kg). To estimate the intensity of absorption of trace elements Tanacetum vulgare used coefficients of biological accumulation (CbaZn, CbaCu). According to values of coefficients of biological accumulation, Tanacetum vulgare intensively absorbed zinc (Cba = 4,59-16,8) and very intensively and intensively copper (Cba = 23,33-48,82). Thus, the studies showed that this crop is a copper concentrator, as CbaCu > CbaZn.

1. Introduction

Currently, in Russia and in the world there is an agrochemical problem associated with the exhaustion of reserves of plants of biophil macro and microelements in the soils of agricultural land [1]. To replenish their drawback, macro and micronutrient fertilizers are required [2, 3, 4]. Microelements have the ability to migrate from the soil into other adjacent media, including in the soil-plant system, therefore it is important to determine the coefficients of biological accumulation in crops capable of accumulating individual elements. This is especially important in the study of medicinal plants, which are sources not only biologically active substances, but also trace elements.

Tanacetum vulgare – a medicinal plant of a family of comprehensibles. It is widely used in the pharmaceutical industry and clinical trials confirmed its medicinal properties. Tanacetum vulgare has a choleretic, spasmyloytic, antihelminthic [5], antitumor [6], anti-inflammatory [7], antioxidant [8, 9] action; shows microbial activity [10] and antimalarial effect [11].

Despite the sufficient study of the biochemical composition of the Tanacetum vulgare L. [12, 13], only in single works there are data from the microelement analysis of the Tanacetum vulgare [14, 15, 16]. The question of its ability to accumulate trace elements, depending on the introduction into the
soil of various doses of micronutrient fertilizers, remains not studied. Meanwhile, it is known that many medicinal plants are concentrators of essential micronutrients and their complexes, enhancing the therapeutic effect of the main active substance [17]. Soil and hydrothermal conditions, certain concentrations and the ratio of chemical elements in the soil and plants and other factors affect the flow of trace elements in the plant. Therefore, from a practical point of view, in addition to the biochemical composition of plants, it is important to determine the intensity of accumulation of trace elements, the concentration coefficients and the migration of trace elements in the soil-plant system. Since the biological effects of trace elements in living systems are highly dependent on their concentration and therefore must be carefully controlled, especially if the culture is used in medicine, as in the case of Tanacetum vulgare.

The purpose of studies was to study the intensity of the biological accumulation of zinc and copper with the drug culture of Tanacetum vulgare in Western Siberia.

2. Materials and methods
The studies were carried out on the meadow-chernozem soil of the experimental field of the Omsk GAU during 2012-2015. Objects of research were plants of the Tanacetum vulgare of the ordinary (first, second, third, fourth year of life) and a meadow-chernozem medium-humus heavy loam soil. The content of humus in the layer 0 ... 20 cm – 5.2%, nitrate nitrogen (aqueous exhaust) – 7 mg / kg of soil, movable phosphorus (by Chirikov) – 216, potassium – 419 mg / kg of soil, pH of an aqueous exhaust – 6.5-6.8. The provision of nitrate nitrogen before planting plants was low, phosphorus – medium and potassium – high. Field experience was laid in four-time repetition, options were systematically. Accounting area – 10 m². The predecessor is pure steam. The main soil processing is common to the zone. Planting of seedlings was carried out in the second decade of May. Echinacea planting scheme 70 cm x 15 cm. Fertilizers in the form of dry salts were manually introduced into the rows, followed by sealing into the soil at a depth of 15 cm three weeks after planting crops.

Micronutrient fertilizers were used as acetate forms on the background of N\textsubscript{135}P\textsubscript{45}K\textsubscript{45} (ammonia nitrate, simple superphosphate, potassium chloride). The doses of microelements were calculated on the basis of the content of movable forms Zn and Cu in the soil before landing and the maximum permissible concentration of Zn (23 mg / kg) and Cu (3 mg / kg) (SanPiN 1.2.3685-21). Zinc and copper fertilizers contributed to zinc and copper MPC shares: 0.25, 0.50, 0.75, 1.0.

In the course of the research, the aboveground part of Tanacetum vulgare plants was sampled and soil samples (0-30 cm layer) in each experiment variant:

1. Control
2. N\textsubscript{135}P\textsubscript{45}K\textsubscript{45} (Ground)
3. Zn\textsubscript{20} (0.25 MAC)
4. Zn\textsubscript{40} (0.5 MAC)
5. Zn\textsubscript{60} (0.75 MAC)
6. Zn\textsubscript{80} (1.0 MAC)
7. Cu\textsubscript{2,3} (0.25 MAC)
8. Cu\textsubscript{4,8} (0.5 MAC)
9. Cu\textsubscript{7,0} (0.75 MAC)
10. Cu\textsubscript{9,7} (1.0 MAC)

The content of moving forms Zn and Cu in soil samples and plants (grass) was determined by an atomic absorption method (extract: acetate-ammonium buffer, pH pH 4.8).

To establish the specifics of the culture (biological features) and the effects of various doses of micronutrient fertilizers (zinc and copper) on the intensity of accumulation of trace elements were calculated coefficients of biological accumulation ($C_{ba}$, equation 1) [18]:

$$C_{ba} = \frac{Cp}{Cn}$$

$Cp$ – content of the element in the plant, mg / kg;
$Cn$ – the content of the movable form of the element in the soil, mg / kg.
Mathematical processing of the field experiment data was performed according to B. A. Dospekhov using Microsoft Excel programs [19].

3. Results and discussion.
During the conducted studies, the content of moving forms of zinc and copper in meadow-chernozem soil was determined when making various doses of zinc and copper fertilizers under the plants of *Tanacetum vulgare* (Table 1).

The content of movable Zn in the soil when making zinc fertilizers was changed from 1.7-9.7 mg / kg, with copper from 2.0-4.2 mg / kg. The concentration of Cu in the soil increased slightly when making copper and zinc fertilizers (0.15-0.23 mg / kg). Micronutrient fertilizer application did not result in exceeding MAC.

Table 1. The content of trace elements in the soil and plants of *Tanacetum vulgare* L. (M±SEM, Omsk, Omsk region, on average for 2012-2015).

| Variant            | Content in soil, mg / kg | Content in plants, mg / kg |
|--------------------|--------------------------|-----------------------------|
|                    | Zn          | Cu                  | Zn         | Cu                  |
| Control            | 1.0 ± 0.34 | 0.10 ± 0.007        | 17.3 ± 2.89 | 4.2 ± 0.32         |
| N133P35K35 (Ground)| 1.1 ± 0.33 | 0.13 ± 0.005        | 17.0 ± 2.96 | 4.4 ± 0.27         |
| Zn30 (0,25 MAC)    | 1.7 ± 0.26** | 0.15 ± 0.002*     | 25.8 ± 1.03 | 5.7 ± 0.01        |
| Zn40 (0,5 MAC)     | 6.2 ± 0.24** | 0.17 ± 0.0001**    | 28.3 ± 0.48 | 6.5 ± 0.19        |
| Zn60 (0,75 MAC)    | 8.5 ± 0.50** | 0.20 ± 0.003**     | 39.7 ± 2.01 | 7.7 ± 0.45        |
| Zn80 (1,0 MAC)     | 9.7 ± 0.63** | 0.17 ± 0.0001**    | 48.0 ± 3.83 | 8.3 ± 0.58        |
| Cu2,3 (0,25 MAC)   | 2.0 ± 0.23** | 0.17 ± 0.0001**    | 25.3 ± 1.14 | 4.3 ± 0.30        |
| Cu4,8 (0,5 MAC)    | 2.2 ± 0.21** | 0.18 ± 0.001**     | 29.3 ± 0.27 | 4.5 ± 0.25        |
| Cu7,0 (0,75 MAC)   | 3.8 ± 0.03** | 0.21 ± 0.004**     | 33.7 ± 0.70 | 4.9 ± 0.16        |
| Cu9,7 (1,0 MAC)    | 4.2 ± 0.02** | 0.23 ± 0.006**     | 40.7 ± 2.23 | 6.0 ± 0.08        |
| MAC [20]           | 23          | 3                   | -          | -                   |
| MAL [21]           | -           | -                   | 50         | 30                  |

Note: * is significantly relative to the control at the significance level p≤0.05; ″ is reliable relative to the background at significance level p≤0.05.

In our studies zinc and copper according to the degree of mobility can be positioned in the following series Zn > Cu. This tendency of changes in the degree of zinc and copper mobility is associated with the fact that Cu forms more strong specific bonds with the components of the soil absorbing complex (MAC) and humic acids than Zn, which binds to nonspecific and becoming more movable [22].

To identify the peculiarities of accumulation of trace elements in drug raw materials, the content of Zn and Cu was studied. In the plant plants, the zinc content was more compared to copper (Table 1). These data are consistent with research [14], in which the authors note that zinc (besides Fe, Mn and Ca) in *Tanacetum vulgare* plants are present in significantly large concentrations, and in the grass, the concentration of Zn in comparison with Cu above. As can be seen from Table 1, the zinc and copper content in medicinal raw material of the *Tanacetum vulgare* does not exceed the MAL (maximum allowable level), which is for Cu – 30 mg/kg, for Zn – 50 mg/kg.
In the works of many researchers [23-27] showed that between the chemical composition of plants, on the one hand, and the medium Habitat, on the other, there is an undoubted communication [28].

The chemical composition of plants directly depends on the chemical composition of the soil on which they grow, but does not repeat it, since the plants selectively absorb and accumulate the elements they need, in accordance with their physiological and biochemical needs [29].

A quantitative indicator of the transition of chemical elements, especially in mobile plant-accessible forms, from soil to plant is the biogeochemical indicator, the accumulation factor, which is the ratio of the content of the element in plants to its content in the soil. The accumulation factor is close to the biological absorption coefficient proposed by A. I. Perelman [30], which is the ratio of the content of the element in the ash of plants to its clade in the earth's crust. In this case, biological absorption is a physiological process, and accumulation, both the result of absorption and internal redistribution of chemical elements, that is, the accumulation factor is the accumulative strategy of the plant [31].

A. Y. Kovalevsky [32] proposes a series of biological accumulation of chemical elements depending on the value of $C_{ba}$ to divide into 5 groups. Thus, if $C_{ba} = 30-300$ – an element of very intensive absorption, $C_{ba} = 3-30$ – intensive absorption, $C_{ba} = 0.3-3$ – average absorption, $C_{ba} = 0.03$-0.3 – weak absorption and $C_{ba} = 0.03$ – very weak absorption.

Since the value of $C_{ba}$ is a quantitative indicator of transfer of chemical elements from soil to the plant, therefore, to estimate the intensity of microelement intake into the plant organism we calculated and analyzed coefficients of biological accumulation of Zn and Cu by medicinal plants (Table 2).

The studies showed that trace elements (Zn and Cu) have different degrees of biological accumulation by plants, the intensity of which is determined primarily by the species-specific accumulation of chemical elements by plants and the presence of functional barriers at the boundaries root-stem, stem-leaf, stem-reproductive organs [33] (Table 2).

**Table 2. Biological accumulation coefficients Zn and Cu plants of *Tanacetum vulgare* L.**

(Omsk, Omsk region, on average for 2012-2015).

| Variant | Biological accumulation coefficients |
|---------|-----------------------------------|
|         | Zn                                 | Cu            |
| Control | 16.80**                            | 35.00*        |
| N<sub>135</sub>P<sub>45</sub>K<sub>55</sub> (Ground) | 16.04**          | 33.85*        |
| Zn<sub>20</sub> (0.25 MAC) | 15.00**            | 38.00*        |
| Zn<sub>40</sub> (0.5 MAC) | 4.59**             | 38.24*        |
| Zn<sub>60</sub> (0.75 MAC) | 4.70**             | 38.50*        |
| Zn<sub>80</sub> (1.0 MAC) | 4.95**             | 48.82*        |
| Cu<sub>2.3</sub> (0.25 MAC) | 12.65**            | 25.29**       |
| Cu<sub>4.8</sub> (0.5 MAC) | 13.32**            | 25.00**       |
| Cu<sub>7.0</sub> (0.75 MAC) | 8.87**             | 23.33**       |
| Cu<sub>9.7</sub> (1.0 MAC) | 9.69**             | 26.09**       |

Intensity of biological absorption of microelements (A.Y. Kovalevsky [32])

- very high absorption ($C_{ba} = 30-300$)*
- high absorption ($C_{ba} = 3-30$)**
- average absorption ($C_{ba} = 0.3-3$)***
*Tanacetum vulgare*, according to the values of biological accumulation coefficients, is intensively absorbed zinc ($C_{ba} = 4.59$-$16.8$) and very intense and intensively copper ($C_{ba} = 23.33$-$48.82$). It should be noted that with increasing doses of zinc and copper fertilizers, the values of zinc accumulation coefficients are reduced, which indicates the existence of the regulation mechanisms that prevent the excess accumulation of this metal in plants. That is, on the one hand, plants can actively resist the redundant entry of toxic elements, and on the other - selectively accumulate essential elements. The inverse situation is noted on copper. Thus, with an increase in doses of zinc fertilizers, the coefficient of copper accumulation increases ($C_{ba} = 38.00$-$48.82$), i.e. the plants begin to be very intensively accumulated copper. The $C_{ba}$ Cu is higher when in the soil of zinc fertilizers ($C_{ba} = 38.00$-$48.82$), in comparison with copper ($C_{ba} = 23.33$-$26.09$).

Based on the values of the $C_{ba}$ of the considered microelements, an empirical series of their accumulation was constructed, which for plants of the *Tanacetum vulgare* has the form: Cu $>$ Zn, that is *Tanacetum vulgare* was mostly absorbed by copper (Table 2). Our data is consistent with research G.G. Buckunova et al. [14], which note that on the intensity of absorption, the elements are located in the following sequence: Pb $>$ Mn $>$ Fe $>$ Cu $>$ Cd $>$ Zn. D.S. Elagina et al. [34] in their studies found that the copper content in the planting plants is higher even in the territories where the content available for copper plants was low, that is *Tanacetum vulgare* is a concentrator of this metal.

**Conclusion**

The results of the study of the content of trace elements in soil and vegetable samples of the *Tanacetum vulgare* cultivated in the conditions of the south of Western Siberia allow us to make the following conclusions:

1. The content of moving forms of zinc and copper when making various doses of micronutrient fertilizers is within the limits of agrochemical, biogeochemical and hygienic standards, does not exceed the MAC. Mobility of these forms of trace elements in soils is very low, which is why their disadvantages are noted.

2. The deficiency of essential trace elements in the soil led to the lack of these elements in plants, exceeding the MAL was not observed, even when making micronutrient fertilizers into the soil.

3. The plants of the matches of the ordinary when introduced into the soil of microfertilizers are characterized by intense and very intense accumulation of zinc and copper. At the same time, the degree of PIRM absorbs copper from the soil.

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