The level of chemical elements in red and white clover

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Abstract. The work was carried out in the period from 2012 to 2018 on the basis of apiaries in the South of the Tyumen region, laboratory studies were performed at the Department of anatomy and physiology and in the clinical and diagnostic laboratory Of the Institute of biotechnology and veterinary medicine of the state agrarian University of the Northern TRANS-Urals, as well as in the laboratory of the Novosibirsk Institute of soil science and Agrochemistry SB RAS. The research material was flowers of white and red clover, samples of which were collected in apiaries. The number of the following chemical elements was determined in flower samples: Pb, Co, Ti, Mn, Zr, Zn, Cu, F, Ba, Sr, Ga, Mo, Sn, Sc, Yb, Be, As. The results of the study showed that red and white clover flowers growing under the same conditions showed different storage capacity for chemical elements. Since, in the flowers, the amounts of many minerals: Pb, Co, Mn, Zr, Zn, Cu, Ba, Mo, Sn, Sc and Be, were at different levels. To the rest of the trace elements As, Yb, P, Ti, Ga and Sr, the flowers of these plants showed the same cumulative properties.

1. Introduction
Determining the level of chemical elements in biological objects is the most important component of the biogeochemical indication of the environment.

Cells and tissues of living organisms consist of elementary particles, bioelements, which are factors in the change in the physico-chemical state of the colloid and thereby directly affect the structure of the cell. Metals and non-metals have toxic and antitoxic effects on living tissues and organs. They act as catalysts for biochemical reactions, and play a role in maintaining turgor and protoplasm permeability. They are centers of electrical and radioactive phenomena in the cell [1, 2].

But increasing anthropogenic environmental pollution contributes to the accumulation of large amounts of trace elements in soil and plants, and their further promotion along the food chain into the body of bees, beekeeping products and the human body. Therefore, determining the level of minerals in the flowers of honey plants is a priority [3]. In the Tyumen region, good honey plants include white and red clover, which are an easily accessible fodder resource for bees on meadow lands and generally where there are their arrays or thickets [4, 5].

2. Materials and research methods
The work was carried out on the basis of apiaries in the south of the Tyumen region, at the Department of Anatomy and Physiology, and in the clinical diagnostic laboratory of the Institute of Biotechnology and Veterinary Medicine of the State Agricultural University of the Northern Trans-Urals, as well as in the laboratory of the Novosibirsk Institute of Soil Science and Agricultural Chemistry of the SB RAS.
The research material was white and red clover flowers, samples of which were collected in apiaries in the Chernaya Rechka village of the Tyumen Region. 50 samples of red and white clover flowers were selected. In the flower samples, the amount of the following chemical elements was determined: Pb, Co, Ti, Mn, Zr, Zn, Cu, P, Ba, Sr, Ga, Mo, Sn, Sc, Yb, Be, As.

The level of minerals in the flower samples was established by the method intended for the simultaneous quantitative atomic emission spectrographic determination of 19 elements and a separate determination of Cd, As in beekeeping products with preliminary mineralization of the initial product. The work was carried out according to the “Definitions of trace elements in natural environments (Novosibirsk, 1994) [6]. The directly analyzed material was ash of flowers; the method of dry mineralization was used, according to GOST 26929-86 [7].

3. Research results

The level of chemicals in plants mainly depends on the state of the environment, especially on the chemical composition of the soil on which the plant grows and on the cumulative properties of the plants.

As a result of the research, it was revealed that the flowers of red and white clover exhibit different accumulative properties to individual trace elements (figure 1.)

It was found that the arsenic content in the colors of white and red clover differs slightly: its level in the colors of red clover was 0.02 ± 0.001 mg / kg, in the colors of white - 0.018 ± 0.0001 mg / kg. Arsenic as a trace element is important for some life forms: inhibits oxidative processes; reduces the production of thyroid-stimulating hormones; increases the synthesis of proteins, globulins. But in large quantities, it is carcinogen.

The cobalt (Co) content in the colors of red clover (84.5 ± 3.44 mg / kg) is almost 20% higher than in the colors of white (67.7 ± 6.7 mg / kg). Cobalt is important for all life forms: affects the growth and development of the body; one of the main components of vitamin B12; participates in the process of hematopoiesis, stimulates the formation of red blood cells and hemoglobin; has a neurophysiological effect; affects all types of metabolism; participates in the breakdown of carbohydrates; is carcinogen.

The level of tin (Sn) in the colors of red clover (46.5 ± 3.7 mg / kg) is 22% higher than in the colors of white clover (36.1 ± 1.7 mg / kg). Tin is a toxic element, with an excess of it, phenomena such as headache, vomiting, photophobia, abdominal pain, dehydration and urinary retention occur.

Scandium (SC) is a low-toxic carcinogen. Its content in the colors of red clover was 144.0 ± 4.35 mg / kg, which is 14 more than in of white clover 130.1 ± 5.6 mg / kg.

![Figure 1. The level of Pb, Ga, Be, Yb, Mo, Sc, Sn, Co and As in the flowers of white clover (Trifolium repens) and red clover (Trifolium rubens) (mg / kg).](image-url)
Molybdenum (Mo) is a silver-white soft metal that is not found in its free form. It retains fluoride in the body. Molybdenum stimulates the activity of enzymes in plants and animals, provides the synthesis of ascorbic acid and normal respiration of tissues. In the colors of red clover, its content was 39.2 ± 0.98 mg / kg, white clover 27.0 ± 0.25 mg / kg, which is 12.0 less than the first.

Ytterbium (Yb) is a rare earth metal. It is the colors a low toxic element. A significant difference between Yb levels in the color samples of red clover (38.1 ± 1.45 mg / kg) and white (37.3 ± 5.67 mg / kg) was not observed.

Beryllium (Be) is present in the tissues of many plants and animals. The level of Be in the samples of flowers of red clover was 15.5 ± 0.62 mg / kg, of white clover - 17.3 ± 0.78 mg / kg, which is approximately 1.83 mg more than in samples of red clover.

Gallium (Ga) is a low-toxic element, the amount of Ga in the samples was at different levels, so in the colors of red clover - 65.0 ± 2.34 mg / g, white -64.3 ± 1.07 mg / kg.

The lead (Pb) content in the samples was also different, so in the colors of red clover - 75.5 ± 3.45 mg / kg, white - 67.7 ± 4.43 mg / kg, which is 7.8 less than in the colors of white clover. Lead is a toxic element that adversely affects the body of animals and insects. The danger of lead is determined by its significant toxicity and ability to accumulate in the body. The high intake of lead in the body of bees reduces the quantitative indicators of potassium and magnesium, ions, which are the predominant cations in hemolymph. In response to environmental pollution by heavy metals, the activation of biochemical reactions in the body is noted, contributing to their adaptation to pollution.

Salts of phosphoric acid are part of all cells and intercellular fluids, various proteins, lipids, carbohydrates, coenzymes and other metabolic products. The phosphorylation process is of great importance for the absorption and metabolism of a number of substances. Phosphoric acid is involved in the metabolism of proteins, fats, carbohydrates and vitamins. In addition, salts of phosphoric acid serve as a buffer system while maintaining acid-base balance in tissues. The average content of this microelement was 4.28 ± 0.001 mg / kg in the samples of red clover flowers, and 4.65 ± 0.001 mg / kg in the samples of white clover flowers. As you know, phosphorus is an important element in the body of bees, is part of the cuticle and organs of movement, therefore, it is necessary for the normal functioning of the body (figure 2).

![Figure 2. The level of P, B, Ba and Sr in the flowers of white clover (Trifolium repens) and red clover (Trifolium rubens) (mg/kg).](image-url)
The boron level (B) of red clover flowers was 0.73 ± 0.32 mg / kg, of white -0.51 ± 0.32 mg / kg, which is 0.22 less than the first. Sufficient supply of plants with boron increases the intensity of photosynthesis, improves carbohydrate and protein metabolism, activates the activity of enzymes, and positively affects the processes of cell division.

Barium (Ba) displaces Ca and P from the bones; in excess, it is a weak mutagen and toxic. Rodenticides are especially toxic [2]. The level of barium in the colors of red clover was 3.05 ± 0.32 mg / kg, and in the colors of white clover 4.3 ± 0.43 mg / kg, which is 1.25 higher than in the samples of flowers of red clover.

Strontium (Sr) is found in all organs and tissues of animals. Deposition of this element in tissues proceeds parallel to calcium deposition [2]. The amount of strontium in the colors of red clover and white clover was the same (2.6 ± 0.12 and mg / kg, respectively, 2.6 ± 0.24 mg / kg).

Copper is a part of protein compounds and enzymes. Copper is a catalyst that accelerates the oxidation of ascorbic acid. It contributes to the implementation of physiological processes such as pigmentation and keratization, the formation of myelin, collagen, elastin [2]. Its content in the colors of red clover was 2.55 ± 0.57 mg / kg, and in the colors of white clover 1.35 ± 0.28 mg / kg, which is 1.20 mg less than in the colors of red clover.

The level of manganese (Mn) in the colors of red clover is 0.266 higher than in the colors of clover white. Manganese is found in all organs and tissues of animals. It is part of some enzymes and enhances their activity. Manganese plays an important role in the metabolism of proteins, carbohydrates and fats.

Titanium (Ti) is a low toxic element. The titanium level in the colors of red (27.15 ± 1.24 mg / kg) white clover (27.33 ± 2.21 mg / kg) is not significantly different (figure 3).

Zinc is important for all life forms, is a catalyst for cellular processes, participates in the exchange of nucleic acids and the formation of their helical structure, is part of many enzymes, is necessary for the formation of proteins from amino acids, affects reproductive function, participates in the formation of bone and cartilage tissue, promotes tissue repair, stimulates the functioning of the immune system. Its content in the colors of red clover was 1.61 ± 0.31 mg / kg, in white 2.24 ± 0.21 mg / kg.

The zirconium content in the colors of red clover was 2.58 ± 0.21 mg / kg, white clover - 3.05 ± 0.26 mg / kg. Zirconium is not toxic; it is found in the blood, bone and muscle tissue of animals. Zirconium, as a metal, has anti-allergic properties, and also contributes to the rapid healing of open wounds.

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**Figure 3.** The level of Cu, Mn, Ti, Zn and Zr in the flowers of white clover (Trifolium repens) and red clover (Trifolium rubens) (mg / kg).
4. Conclusion

Cells and tissues of living organisms consist of elementary particles, bioelements, which are factors in the change of the physicochemical state. They create osmotic pressure and directly affect the structure of the cell.

The amount of trace elements in plants largely depends on the state of the environment, mainly on the level of chemicals in the soil on which these plants grow, and of course on the cumulative properties of plants.

Thus, the researches showed that red and white clover flowers growing under the same conditions showed different accumulative abilities for chemical elements. Since, in the flowers, the amounts of many minerals: Pb, Co, Mn, Zr, Zn, Cu, Ba, Mo, Sn, Sc and Be, were at different levels. The flowers of red and white clover showed high accumulative properties for scandium, the content of which in the colors of red clover was $144.0 \pm 4.35 \text{ mg} / \text{ kg}$, and in the colors of white clover $130.1 \pm 5.6 \text{ mg} / \text{ kg}$. The cobalt (Co) content in the colors of red clover ($84.5 \pm 3.44 \text{ mg} / \text{ kg}$) was almost 20% higher than in the colors of white ($67.7 \pm 6.7 \text{ mg} / \text{ kg}$).

For the remaining trace elements As, Yb, P, Ti, Ga and Sr, the flowers of these plants showed the same cumulative properties.

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