Controlled release micronutrient fertilizers for precision agriculture

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Abstract:
Purpose: The purpose of the work was to present state-of-the-art in the topic of fertilizers with controlled release of micronutrients.
Methods: Four main types of fertilizers were selected and described: hardly soluble fertilizers, encapsulated fertilizers, fertilizers from bio-based resources and nanofertilizers.
Results: Precise fertilization techniques are the future of agriculture, in which nutrients are supplied in controlled way with minimized losses to the environment, caused by leaching to groundwater.
Conclusions: The challenge in elaboration of modern fertilizers designated for precision agriculture, is to match the kinetics of nutrients release to the plant's nutritional requirements. This has an impact not only on crop yield, but also on the environment, preventing micronutrients from entering surface waters and deeper soil layers.

Keywords: micronutrients, bioavailability, functional groups, uptake rate, biodegradability

1. Introduction

Agriculture produces crops that contain enough calories for the current population, however globally 1.5 billion people suffer from micronutrient deficits, often referred to as "*hidden hunger*" [1]. There are several aspects of malnutrition: providing the insufficient amount of calories (hunger) in the form of carbohydrates, fat or proteins and not supplying the required doses of nutrients (micronutrient hunger). While the first case is easily diagnosed, the second often gives unusual symptoms and is not correctly diagnosed. Preventively, there are no tests of the micronutrient status in human. Often it is not known that the diet lacks some selected microelement. To compensate for deficiencies of micronutrients in the diet, it is necessary to supplement them [2, 3]. Most often it takes place through dietary supplements (tablets, drinks - mainly mineral salts or chelates), but their bioavailability is low and they are of transit character (absorption lower than 10 %). Novel solutions are enriching food with microelements by the means of biofortification, important part of which is agronomic biofortification through specialized fertilization of crops with micronutrients. It is important to supplement micronutrient deficiencies in the diet, preferably in a bioavailable form - straight from plant material. For this reason, micronutrient fertilization is equally important as a macronutrient, for the sake of good crops quality in terms of nutritive properties.

2. Micronutrients for plants

Soil is the main source of nutrients. The demand for nutrients changes with the growth phase of the plant. Essential nutrients are compounds that affect the development cycle and plant metabolism. Microelements are partly organic compounds and are also responsible for energy storage, electron transport and enzyme activity. Due to the functions that they perform in the plant, they cannot be replaced with other components, they are essential for all plants.

At the beginning, chemical fertilizers included only macronutrients: nitrogen, phosphorus, and potassium. Due to the use of more intense production systems, native soils began to impoverish their micronutrient pools and micronutrient fertilizers became necessary [4]. Even though the total content of micronutrients in soil (zinc, copper, iron, manganese) seems sufficient, the levels of bioavailable forms – soluble in the soil solution - are insufficient to meet the need of crops. For instance, the available zinc for plants soils (extracted with diethylenetriamine pentaacetate (DTPA) is only 1% of the total zinc [5]. Micronutrients have stimulating effect on the growth of plants, play a key role in shaping the morphological and anatomical features of plants. They are often referred to as trace elements, because their content in dry matter does not exceed 0.01%. The deficiency of even one of the micronutrients may cause diseases and disturb proper vegetation of plants. The bioavailability of microelements depends on the pH and soil fertility, as well as the presence of other ions (synergism or antagonism).

The group of essential micronutrients includes elements such as boron, chlorine, copper, iron, manganese, molybdenum and zinc. Table 1 shows the influence of selected micronutrients on plant physiology.

Table 1. Role of micronutrients in growth and development of plants.

Micronutrient	Function	Deficiency symptoms	References
Iron	Occurs in the form of Fe^{2+}, Fe^{3+} or chelate ions. It participates in electron transfer as a component of oxidoreductive enzymes. It is an essential substrate for the synthesis of chlorophyll, participates in the process of photosynthesis and respiration, it is an essential microelement for the proper plant growth.	The most characteristic symptom of iron deficiency is chlorosis, mainly affecting young leaves. Chlorophyll disappears in young leaves, resulting in a change in the color of plant organs from green to white	[6]
Copper	Taken from the soil in the form of Cu^{2+} or chelates. Copper is a component of many important enzymes present in plants, increases plant resistance fungal and bacterial diseases.	Deficiency of copper in cereals causes whitening of leaves and ears and slowing down of maturation processes	[7]
Zinc	Affects the catalytic properties of enzymes, participates in the metabolism of carbohydrates and proteins. Zn is involved in gene transcription.	Insufficient amount of Zn^{2+} ions disturbs the synthesis of auxins - hormones responsible for plant growth and fruits size. In the initial phase there is mottled chlorosis on the leaves, and the	[8]

		obtained crops are underdeveloped	
Boron	Is a key component of cell walls. It regulates biochemical transformations of organic compounds, stimulates the incorporation of phosphorus into nucleic acid structures, and is responsible for the hormonal balance of plants, stimulates flowering and fruiting processes.	Growing on soils poor in boron leads to disturbances in the development of plants: the fruits are undersized and cracked, the leaves turn yellow and fall. Extremely sensitive to insufficient amount of boron in the substrate are beets, potatoes, rapeseed and fruit trees.	[9]
Manganese	Forms chelation bonds between the substrate and the protein. It stimulates the catalytic properties of enzymes involved in the breathing process. Takes part in the process of photosynthesis.	Most often the lack of manganese manifests itself in the form of chlorosis and in the next step browning and falling of the leaves	[10]
Molybdenum	Has oxidation-reduction properties that serve to bond atmospheric nitrogen as well as to convert nitrates into ammonia.	Molybdenum deficiency is most visible in legumes. This leads to a reduction in the amount of chlorophyll, drying of the tops of the stems and curling of the leaf edges	[11]

In addition to the listed minerals, other elements, such as sodium, silica, aluminum, vanadium or cobalt, favorably affect the growth and development processes of some species. Due to the possibility of substitution with other ingredients, their deficiency is not as harmful as in the case of micro and macroelements. The required dose of nutrients supplied to the plant allows for obtaining high and good quality crops. Both the deficiency and the excess of nutrients can be toxic to plants, the boundaries determining the proper growth of plants are difficult to specify and depend on the requirements of a specific species.

2.1. Micronutrient fertilizers

Fertilization is an effective way to regulate the content of minerals. In the case of deficiency of fertilizer nutrients, prevents the occurrence of disorders and diseases and keeps crop yield on desired level. It is, however, worth keeping moderation in the management of fertilizers, because their excessive exploitation leads to a decrease in the quality and health value of the yields obtained. When determining the dose of fertilizers, the need for plants should be taken into account but at the same time their amount should be reduced to the necessary minimum. Intense cultivation of crops gradually reduced micronutrients levels in soils. Information about the variability of different soil attributes within a field is essential in precision agriculture. On-the-go soil sensors can be used to measure mechanical, physical and chemical soil properties to improve the quality of soil-related information and on the basis of linking the level of nutrients in soil with the requirements of plant that is to be cultivated, can be useful in the future in the adaptation of the fertilizer doses tailored for a given soil and cultivated plant [12].

Micronutrient fertilization can be carried out in different ways by using a wide range of fertilizer formulations. Micronutrients can be applied in the form of aerosol on the leaves (foliar spray), on the soil as single salts or chelates or as admixtures for coating fertilizers with macro-nutrient fertilizer. Foliar sprays can be ineffective by low penetration of the leaves with thick waxy skins or washing off by rain. Direct application to the soil is ineffective because the salts are oxidized or precipitated as a result of reaction with soil components, which makes the micronutrients not available to the plants. For example, the formation of insoluble Zn and Mn phosphates in the vicinity of phosphorus-containing granules [13].

3. Controlled release micronutrient fertilizers

Among all the elements of the environment, soil is the mostly exposed to undesirable effects of excessive fertilization. Incorrect dosage and type of fertilizer can lead to the accumulation of salt in the soil solution, and consequently to increased acidification or salinity of the soil. In addition, over-fertilization increases the risk of heavy metal contamination by increasing their concentration in the soil. Farmers should undertake activities aimed not only at producing high and good quality crops, but also at protecting the environment by minimizing losses to groundwater and air. The conscious management of fertilizers is based on adjustment of doses to the needs of cultivated plant species. It should also take into account the assessment of soil quality (bioavailable form of macro and micronutrients), as well as adjusting the date of their application to weather conditions.

Because micronutrients are toxic in higher doses, excessive fertilization may lead to pollution of the environment, by leaching to groundwater. For this reason, it is significant to supply them in a precise way to the plant, so the quantity lost would be minimal. This is the scope of interest of ‘precision agriculture’ that is defined as “techniques that monitor and optimize production processes …thereby conceivably increasing yields and outputs and improving the efficiency and effectiveness of inputs” [14]. Thanks to precision agricultural methodology, heterogeneity of farms can be achieved - which is often associated with uncertainty and management risks - and used to optimize farms in terms of food production and biodiversity protection [15].

The basic problem of traditional fertilizers is the rate of release of mineral substances into the soil. The nutrients penetrate it quickly enough that the plants are unable to take the total amount. It is estimated that the bioavailability of supplied components does not exceed 50%. The remaining part penetrates deep into the soil, accumulating or leaching into groundwater, causes eutrophication of water reservoirs. Therefore, it is necessary to fertilize further to meet the plant's nutritional requirements. Taking into account the economic and ecological aspects of the use of fertilizers, it is necessary to reduce their amount discharged to the environment and at the same time increase the efficiency of fertilization. Such requirements can be met by fertilizers, in which the process of nutrients release is slowed down and the rate is adjusted to the nutritional needs of plants. They include SRF (*Slow-Release Fertilizers*) and CRF (*Controlled-Release Fertilizers*). CRF provide nutrients in a regular and continuous manner to plants at a sufficient level to ensure healthy growth without many applications. The problem of losses of nutrients and root damage caused by high salt concentrations is reduced [16].

The life cycle of such a fertilizer, must be the best suited to the nutritional needs of plants, at a given stage of its growth and development. The process of releasing nutrients from coated granules takes place in stages, it starts when the fertilizer is introduced into the soil. There are several types of controlled release fertilizers, including hardly soluble fertilizers, encapsulated fertilizers, fertilizers based on biological materials (including hydrogel structures) and nanofertilizers.

3.1. Fertilizers with lower solubility

Products with a slowed-down release of nutrients are characterized by low solubility, making it harder to leach out of the soil. The oldest example of CRF’s are compounds containing low solubility nutrients, for instance, double phosphates that contain macro and micronutrients with the general formula $M(II)M(I)PO_4.XH_2O$ ([M(II)]: Mg, Fe, Zn, Mn, Cu, Co and M(I): NH_4, K, T1, Rb]. Metal ammonium phosphates have low solubility in water. It is possible to synthesize struvite particles with controlled diameters for Cu (II) adsorption [17].

An important group of fertilizers are hydrolysed fertilizers, in which nutrients are released by cutting bonds, eg metaphosphates, glass phosphates (glass frits). Phosphate glasses and metaphosphates have been used as slow release sources of microelements. Glassy phosphates are made from melts (temperatures between 800 and 1400°C), metaphosphates are obtained at temperatures below fusion (<500°C) [18, 19]. The short-chain polyphosphates as carriers of micronutrients were developed as a way to avoid problems with the production of glassy phosphates and the very low solubility of micronutrient metaphosphates [19]. The controlled release microelement fertilizer was obtained by incorporating molybdenum into the long-chain polyphosphate structure. Tests on plants have shown a significant increase in yield, an increased amount of nitrogen in biomass at a relatively low dose of fertilizer [20]. Multielemental fertilizer, incorporating zinc, iron, manganese, and copper in crystalline polyphosphate showed low solubility in water, but it was well soluble in organic acids, which suggests good accessibility for plants. Higher yields were obtained, potato tubers had a much higher content of vitamin C [21]. Co-granulation of boron with mono-ammonium phosphate also allowed to obtain a fertilizer with low solubility [22]. Polymeric phosphate structure displays a fertilizer containing iron and magnesium. Experiments have shown that this fertilizer increases yield by almost 50% [23].

3.2. Fertilizers with external coating

Due to the need to improve CRF fertilizers, coated fertilizers have been proposed. These are granules coated with a special coating, inside which there are readily available forms of nutrients [24]. Diffusion of these substances occurs with slower rate than in the case of traditional fertilizers, because the coating is a physical barrier that hinders their transport. The release of nutrients from coated fertilizer is controlled by diffusion through the material of the coating. Coating materials should be cheap, easily degraded in soil to environmentally friendly products and the products of degradation should not be toxic to plants. From the historical perspective, the first CRFs were made of synthetic and non-biodegradable polymer matrices that contaminated the soil due to non-degraded polymer residues. Currently, research focuses on CRF based on a biodegradable polymer - coatings that allow the release of nutrients from fertilizers without transferring toxic substances to the soil, which can be completely degraded after the end of the release process [16].

One of the materials used to make the CRF coating is sulfur, because it is cheap and easily biodegradable. As a result of coating urea granules with molten sulfur, SCU (*Sulfur Coated Urea*) fertilizers are obtained. Such granules can be coated with wax, polyolefins or resins were also used in the coating process (*Polymer-coated sulfur-coated urea,* PCSCU). The additional layer of organic polymer increases the control over the release of nutrients [25] and can be used not only for the formation of urea-based fertilizers, but also in the production of multi-component NPK enriched with microelements. PCSCU is currently the largest group of controlled release fertilizers on the market.

Polymer-coated fertilizers (PCF) is a group of fertilizers with an external layer of various polymer and polymer composite materials acting as semipermeable membrane for releasing of selected compounds over prolonged period. Microcapsules containing microelement ions (Fe^{3+}), coated with three different polymer layers (ethyl cellulose, glycerol mono stearate and Compritol 888 ATO), released the ferric ions in a slowed manner for a period of 7 days [24]. Biodegradable coatings (based on agar, gelatin and palm stearin) containing microelements, surrounding urea granules reduce nitrogen losses and contribute to the improvement of nutrient content in the soil. Such structures allow for a slow release of nutrients because microelement ions such as Cu and Zn inhibit nitrogen (in the form of NH_3) release from the granules [26]. Another study investigated the effect of adding fertilizers P, K and micronutrients on the release of urea through a polymer membrane (polystyrene). The addition, saturated aqueous solutions of phosphate salts reduced the permeability of the coating to urea, while potassium salts increased its release. According to the assumed model of mass transfer, two mechanisms with the opposite effect can be considered [27].

3.3. Fertilizers based on biological materials

Controlled release fertilizers are very popular, but the coatings used so far have not been environmentally friendly. New solutions are still being sought to improve this technology. A promising alternative to commonly used fertilizers may be biological materials that have a natural ability to bind ions of micronutrients. In the development of slow-release fertilizers, it was hypothesized that functional groups, including hydroxyl, amino, phosphate have an affinity for metal cations containing microelements, forming metal complexes [17]. This makes binding of micronutrient cations to bio-based material by biosorption an interesting method to produce CRF. Such fertilizers would supply micronutrients on the biodegradable carrier. Biomass based fertilizers are characterized by a higher bioavailability and slowed release to the soil. This bio-based fertilizer is fully biodegradable, which reduces the negative impact of fertilizers on the environment [28]. Comparison of the efficiency of fertilizer produced by biosorption technology with conventional fertilizers have shown that they are easily absorbed by plants and are characterized by a gradation of release. The obtained crop fertilized with zinc was higher compared to plants fertilized with conventional fertilizers - inorganic salt and chelates [28].

Increasing the sorption capacity of biological materials is most easily achieved by fragmentation of the material. Such fragmented material is unfortunately difficult to handle (problems with separation from the solution), so it is important that such material should be immobilized in larger structures. An example may be the immobilization of biosorbents in a polymer matrix. The enrichment of biomass with valuable micronutrients and its subsequent immobilization in the gel structure gives the possibility to create composites (**Fig**. 1.) that release substances gradually, adapting to the nutritional needs of plants. An additional advantage is the use of post-extraction biomass, which can be a source for creating new functional materials, and waste recycling minimizes production costs. As the immobilizing matrix, biopolymers, i.e. alginate or chitosan, are used, which are widely available, and their production costs are small. Biopolymer capsules are used not only in agriculture, they are also used as drug carriers in the pharmaceutical or medical industry. Biopolymer material is biocompatible, biodegradable and non-toxic, and thus does not pose a threat to the environment.

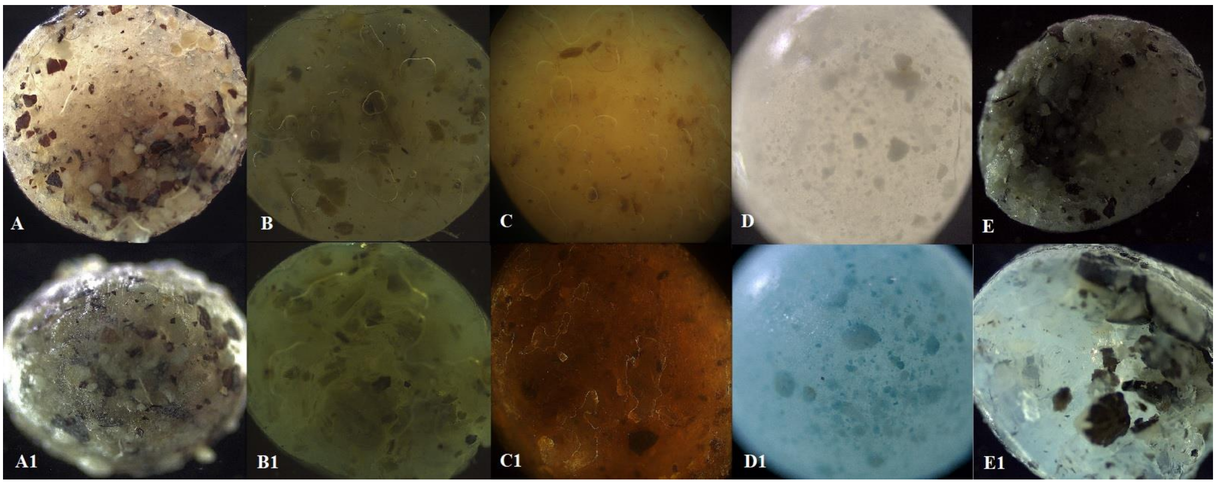

Fig. 1. Immobilized biomass in a polymer matrix as eco-friendly fertilizers produced by biosorption: A – rapeseed meal post extraction residues, B – alfalfa post extraction residues, C – goldenrod post extraction residues, D – eggshells, E - blackcurrant post extraction residues, lower line with number 1 – capsules enriched with Cu^{2+}

A potential matrix for the controlled release of nutrients can also be an interpenetrating network (IPN) based on xanthan gum. Such a hydrogel contains trapped water in its network, which can contribute to maintaining long-term soil moisture. The closure of nutrients in the hydrogel (bio-based fertilizer extracted from vermicompost) allowed long-term fertilization and resulted in the accelerated growth of shoots and roots [29].

3.4. Nanofertilizers

Nanotechnology can improve the bioavailability of micronutrients to plants. Nano-micronutrient preparations can be sprayed on plants or can be delivered to the soil for root intake, to improve the health and vigor of the soil. For instance, Fe deficiency is a common problem in plants growing mainly in high pH and calcareous soils. The foliar application of Fe compounds in nanoparticle technology can be a solution to this problem. The concentrations of the iron nano-oxide solution are low and consequently the doses - in the range of 0.01% -0.04% [4]. Fertilizers based on nanomaterials require a matrix in which they could be thoroughly dispersed. An example of such a medium can be a synthetic material based on starch-PVA, which can serve as a carrier of microelements. Nanofertilizer by gradual release of micronutrients from carbon nanofibers dispersed in the polymer improved growth chickpeas. The presence of starch in the mixture increased the biodegradability of PVA [30]. The use of ZnO nanoparticles can affect the flowering period, for example, decrease in onion 12-14 days [31]. Cu nanoparticles have the potential to increase wheat growth and yield. Their presence affected the content of chlorophyll, leaf area and other parameters [32]. Chitosan nanoparticles can be used as a delivery system for agrochemicals (including micronutrients) for plants, stimulating growth of plants, moreover chitosan nanoparticles possess antimicrobial activity [33].

4. Conclusions

The future of agriculture are precision techniques, whereby nutrients are supplied to the plant itself with minimization of losses and dissipation to the environment. Nutrients should be supplied to the site from which a plant would take them up and at the rate the plant needs them. Kinetics of nutrients release should be thus adjusted to plant requirements and kinetics of uptake by the plant. This opens the door for smart controlled release fertilizers. This property can be achieved in different ways: by using insoluble compounds, biodegradable coatings or binding micronutrients to functional groups by biosorption, also in biopolymeric structures.

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