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EFFECT OF SOIL FACTORS ON SULPHUR CHANGES AND AVAILABILITY FOR PLANTS

WPŁYW CZYNNIKÓW GLEBOWYCH NA PRZEMIANY I DOSTĘPNOŚĆ SIARKI DLA ROŚLIN

Abstract: The study presents the analysis of the effect of soil factors such as oxidation, reduction, immobilization, mineralization, leaching, ion competition, and water management on sulfur metabolism in soil and its availability to the crops. Sulfur is one of the nutrients that largely affects the quantity and quality of crop yields, and is also a component of many compounds, the lack of which causes some disturbances to the development of plants and diseases in humans and animals. Despite such a great importance, it was not subject to agricultural research until the early 80s, and was not taken into consideration when determining the fertilizing needs of plants. However, the situation has changed in recent years, when problems associated with sulfur deficiency in crop production began more and more to be emphasized. The absence of this component is to be expected especially at the lighter, usually acidic mineral soils, located away from industrial centers. Therefore, the transformation of sulfur in the soil and its availability to the crop becomes an important issue.

Keywords: sulfur forms, sulfur conversion in soil, sulfur migration, sulfur availability

Besides nitrogen, phosphorus, and potassium, sulfur belongs to a group of nutrients that play an important role in the metabolism of crops. Plants absorb sulfur mainly through their roots in the form of SO_4^{2-} ions. A certain amount of this element may also be uptaken through the leaves in the form of SO_2 [1, 2].

Sulfur absorbed by plants is relatively quickly built into organic compounds, in which it occurs in the reduced form. Cysteine, that is a product of this process, is the precursor of another sulfur-containing amino acid – methionine. Two cysteine molecules (R – SH) may also react with each other to form a disulfide bridge between them, thereby forming cystine. Disulfide bonds play an important role in reinforcing the structure of proteins, especially enzymes, and the ability of sulfur to make such bindings is one of the most important functions of this element [1, 3].

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Other significant sulfur compounds are also: lipoic acid, coenzyme A, biotin, and thiamin. In some plants, sulfur can be additionally present in the form of volatile compounds, an example of which may be allyl oil and its glycoside derivatives called mustard oils [4, 5].

Despite the importance of sulfur for plant growth and development, as well as the quality of harvested plant material, it has not been paid too much attention until recently. It was not the subject of interest in agricultural research, and was not taken into consideration when determining the fertilizing needs of crops. This was due to the fact that in most parts of the European continent, the sulfur balance was positive. On the positive balance of this component is largely influenced by SO_2 emitted into the atmosphere during the combustion of fuels, especially coal, brown coal and crude oil. The sulfur in this period was also introduced into the soil in large quantities with certain mineral fertilizers [6].

In recent years, various countries, including the Polish increasingly reach but some symptoms of sulfur deficiency in plant production have been recently observed in various countries, including Poland (Table 1) [7].

Table 1

Areas with sulfur deficiency in agricultural production [7]

Continent	Country
Africa	Burkina Faso, Cameroon, Central African Republic, Chad, Egypt, Ghana, Guinea, Côte d'Ivoire, Kenya, Mali, Malawi, Mozambique, Nigeria, Senegal, Tanzania, Togo, Uganda, Zaire, Zambia, Zimbabwe
North and South Americas	USA, Canada, Latin America, Argentina, Brazil, Chile, Colombia, Costa Rica, Dominican Republic, Salvador, Honduras, Mexico, Nicaragua, Panama, Puerto Rico, Venezuela, Windward Islands
Asia	Bangladesh, Burma, China, India, Indonesia, Lebanon, Malaysia, Pakistan, Philippines, Sri Lanka, Taiwan, Thailand
Europa	Belgium, Bulgaria, Denmark, Finland, France, Germany, Island, Ireland, Italy, Netherlands, Norway, Poland, Spain, Sweden, Great Britain, former USSR, former Yugoslavia
Oceania	Australia, Fiji, New Guinea, New Zealand, Solomon Islands

It resulted from a significant reduction in sulfur dioxide (IV) emissions into the atmosphere, decline of organic fertilization, and reduction in the consumption of mineral fertilizers containing sulfur [8, 9]. On the other hand, high demands of certain crops for this component, and remarkable leaching of sulfates make that in many cases the sulfur balance is negative [9, 10]. The absence of this component is to be expected especially on lighter, usually acidic, mineral soils located far away from industrial centers [3, 11]. Hence, the purpose of this paper based on the literature research, was to discussion of the soil factors affecting the metabolism and availability of sulfur for crops.

Sulfur forms in soils

Sulfur makes up about 0.05 % of the Earth's crust and in terms of element prevalence, it ranks at the fifteenth place. Its content in the soil depends primarily on a bedrock, the quantity and quality of organic matter, soil acidity, water and climate conditions, as well as air pollution [9, 12, 13].

A constant lack of oxygen in swampy soils and wetlands precludes the possibility to form and accumulate sulfates. Therefore, the inorganic sulfur is found mainly in the form of sulfides and elemental sulfur. On the other hand, under conditions of water excess and oxygen deficit, accumulation of organic matter takes place, due to which the organic soil is clearly richer in sulfur than mineral soils [14].

In turn, in the moderately moist soils, in which aerobic processes of leaching over water evaporation dominate, there are conditions favoring the oxidation of sulfur compounds to sulfate forms that easily move to deeper soil layers, and even into the groundwater. Therefore, organic sulfur contained in the concentrated organic matter is a basic form of sulfur presence in the humus layers of humid and well ventilated soils, in which mineral sulfur compounds are not very stable [13, 15].

Sulfates, that often form a well-developed levels, such as gypsum levels in saline soils occurring in a steppe and semi-desert climate, predominate in dry climate soils, where evaporation much exceeds atmospheric precipitation [12].

Total sulfur content in Polish mineral soils ranges from 0.05 to 0.4 $gS \cdot kg^{-1}$ of soil, while in organic ones it may be up to 10 times higher (up to 4.5 $gS \cdot kg^{-1}$ of soil). It must be stressed that about 90–95 % of that amount of sulfur present in various organic combinations and only 5–10 % are minerals, which plants can directly use [11, 16].

Sulfur sources in arable soils

Undoubtedly minerals are the primary source of sulfur in the soil. The most important among them are: gypsum ($CaSO_4 \cdot 2H_2O$), ferrous sulfides (FeS and FeS_2), hydrotroilite ($FeS \cdot nH_2O$). Also sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and cobaltite (CoAsS) are found in soils at lower quantities. Under dry climate conditions, there can be found readily soluble sulfates, whereas in very dry – sodium alun ($NaAl(SO_4)_2 \cdot 12H_2O$) and tamarugite ($NaAl(SO_4)_2 \cdot 6H_2O$). The arable soils often contain sulfates of iron ($FeSO_4$), potassium (K_2SO_4), sodium (Na_2SO_4), magnesium ($MgSO_4$), as well as compounds with lower oxidation number such as sulfites, thiosulfates, pentathionates, and elemental sulfur [4, 12].

As it was previously indicated, an overwhelming amount of sulfur in the soil is present in organic forms. Much of the sulfur forms are part of the humus. Other organic compounds get into the soil along with the plant and animal remains, and micro-organisms. The most important are: amino acids (methionine and cysteine), peptides (glutathione), proteins, sulfolipids, and vitamins (thiamin and biotin) [3].

Considering agriculture, sulfur is also introduced into the soils along with some mineral fertilizers. The largest quantities of the element are transported with: ammonia sulfate (240 $kgS \cdot Mg^{-1}$ fertilizer), gypsum or phosphogypsum (180–190 $kgS \cdot Mg^{-1}$

fertilizer), magnesium sulfate (130 kgS · Mg^{-1} fertilizer), kieserite (220 kgS · Mg^{-1} fertilizer), and elemental sulfur [6].

A valuable source of this nutrient are also natural organic fertilizers, especially manure in which sulfur content oscillates around 0.3–0.6 kgS · Mg^{-1} fertilizer [19].

Sulfur can also penetrate the soils from the atmosphere. Sulfur oxide(IV), the main component of air pollution, can be absorbed on the soil surface in gaseous form and then dissolved and oxidized in the soil solution. It is referred to as dry deposition. Sulfur oxides can be also oxidized in the atmosphere to sulfuric acid and reach the soil with rain or other precipitation. This is wet subsidence that produces acid rains [2].

Sulfur conversions in soils

Primary sulfur compounds and those that get into the soil from above described sources undergo a number of changes. Basic sulfur conversions in the soil can be divided into four phases: oxidation, reduction, immobilization, and mineralization. They are a combination of mutually dependent processes, the intensity of which is determined by a deficiency or complete lack of oxygen, soil pH, and contents of energy and nutritive components that affect the development of various groups of microorganisms [18, 19].

Oxidation. The processes of soil sulfur compounds oxidation can be carried out by soil microorganisms or occur during abiotic reactions. Sulfur bacteria oxidizing most of inorganic sulfur bindings in soils are the autotrophic organisms. They use the exothermic oxidation reactions of hydrogen sulfide, elemental sulfur, and other incompletely oxidized sulfur compounds as a source of energy required for the assimilation of carbon dioxide(IV). Heterotrophic organisms can also participate in the oxidation process. Although they do not carry out the full oxidation of reduced sulfur to sulfates, however they take part in particular stages of the process [13, 20].

The *Thiobacillus* genus bacteria are responsible for most of the reactions during oxidation of various mineral bindings of sulfur. They belong to the absolute aerobes with the exception of *T. denitryficans*, that is capable of oxidizing sulfur forms in anaerobic environment. Other species require appropriate soil pH and oxygen access for their development. Under low pH conditions *T. thiooxidans* and *T. ferrooxidans* prevail, while *T. thioparus* well develops near neutral pH values [13, 18, 20].

Compounds at different oxidation levels are a substrate for sulfur bacteria development, while sulfates are the final product. In the case of *T. thiooxidans*, elemental sulfur oxidation processes are as follows:

$$S^0 \rightarrow S_2O_3^{2-} \rightarrow S_4O_6^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-}$$

Each of these processes is a separate energy reaction, and the final product of one reaction is the starting point for the next one (depending on the environment) carried out by the same or other bacteria [4].

The sulfur compounds present at a lower oxidation state may also be oxidized by abiotic factors, which are often intertwined with reactions caused by microorganisms.

The abiotic reactions occur most often with iron participation and they tend to produce sulfates, basic ferrous sulfates, and sulfuric acid. These reactions are accompanied by a significant decrease in soil pH [18].

Reduction. Under anaerobic conditions, sulfates are reduced becoming acceptors of a hydrogen derived from microbial degradation of simple organic compounds. These reactions are usually carried out with the participation of numerous microorganisms of *Desulfovibrio* and *Spiryllum* genera. A common feature of these bacteria is the tolerance to high concentrations of salts and hydrogen sulfide, and that the optimal development of the majority of them occurs in an environment having a pH 5.5–9 range. In environments below pH 5, disappearance of these microorganisms activity is recorded [4].

The sulfate reduction process is carried out through a number of intermediate steps that are not separate reactions, as in the case of oxidation, and hydrogen sulfide is the only final product [18].

Iron is often involved in the processes of sulfate reduction; it substitute the alkaline cation combined with the sulfate ion thus causing its release and deposition in soil in the form of a suitable carbonate. Decaying organic matter is the source of carbon dioxide(IV) that is necessary to produce carbonate. In this type of soils, some increase in pH and a color change to dark brown or black, can be observed [21].

Immobilization and mineralization. Plants uptake sulfur in the form of sulfate ions and certain simple organic combinations. The same compounds are also a source of sulfur for most of heterotrophic microorganisms responsible for the organic substances degradation. Hence, biological immobilization prevents easily soluble sulfur bindings from leaching by rainwater and maintaining a supply of this nutrient in the soil. Under natural conditions, mineralization of organic residues and oxidation of mineral sulfur compounds to sulfates gradually launch the supply, enabling further development of microorganisms and plants. Thus, there is a dynamical balance between mineralization and biological immobilization [4, 14, 19, 22].

Human activities often affect the equilibrium of these processes. Irreversible removal of forage crops along with yields is one of the causes of the impoverishment in the soil sulfur reserves. The use of natural fertilizers poor in sulfur also can lead to competition between microorganisms and higher plants in relation to this nutrient. The degree of sulfur mineralization depends on carbon to sulfur ratio. If C:S ratio is less than 200, part of mineral sulfur compounds released is absorbed by microorganisms, while the remainder is available for higher plants. If the ratio C:S is greater than 400, immobilization of mineral sulfur bindings by a fast-growing heterotrophic organisms takes place. Thus, symptoms of sulfur deficit are very frequently observed at plants after adding a large amount of organic substances with low sulfur content, such as cereal straw, to the soil [4, 15, 17].

The process of sulfur compounds mineralization can exert a significant impact on the nitrogen to sulfur ratio in decaying material. It is assumed that if N:S ratio in decaying plants amounts to about 14.2:1, sulfates immobilization occurs only to a small extent under such conditions. Introducing organic residues into the soil with a high value of N:S ratio may cause substantially greater sulfur than nitrogen immobilization [23].

Migration of sulfur compounds within the soil profile

The amount of sulfur in the form directly accessible to plants is determined by movement of the component into the deeper soil layers. Migration of sulfur compounds within the soil profile depends on several factors such as chemical properties and pH value of the environment, nature of the component bindings, redox conditions, presence of organic matter, and soil microflora composition [24–26]. The fact that sulfates are highly mobile in the substrate and are not absorbed at above pH 6 indicates that their contents in soil are closely related to water management. The water management, as a factor affecting the amount of sulfates available for plant, was paid too little attention until recently. The model calculations conducted by Schnug [27] suggest that rapeseed can cover up to 50 % of its sulfur demands from this source

Sulfates are very readily leached out of the soil profile. Annual sulfur loss due to this process can reach from 13 up to 141 $kgS \cdot ha^{-1}$ [3].

Sulfate leaching beyond the soil profile is partially mitigated by non-specific sorption of anions. Hydrated aluminum and iron oxides, as well as kaolinite present in the soil profile plays an important role. There is also a strong correlation between pH and sulfate sorption. The maximum sorption takes place at a pH in the range from 2 to 4, which is consistent with properties of the main sorbents, *ie* hydrated oxides of aluminum and iron. It needs to be mentioned that hydrated iron oxides retain significantly less sulfates than aluminum ones under the same conditions [28, 29].

Influence of different factors on sulfur availability for plants

The content of sulfur in the soil and its availability to plants is much influenced by other ions present in the environment, in particular phosphates, molybdates, arsenates, thiocyanates, and oxalates. Considering inorganic ions, phosphates have the greatest reducing effect on sulfate absorption, while oxalates can be quoted as organic ions. Additionally, OH^- and HCO_3^- ions present in the soil solution, like phosphates, make the sulfate sorption is diminished [29, 30].

The influence of various anions on sulfate sorption results most probably from the following reasons:

– competition for "sites of exchange";

– ability of anions to form chelates with iron and aluminum; these compounds durably block the active centers within the sorption complex of the soil;

– precipitation reactions [1].

Transformations of sulfur have a large impact on the content of available forms of this nutrient in the soil. These forms are primarily sulfates, the content of which is constantly changing. Differentiation amounts of sulfates in soil results from the soil pH, microbial processes, atmospheric deposit, discharge of sulfur along with crops, soil fertilization, and changes in water management [12].

Influence of sulfur on the properties of arable soils

The oxidation of sulfur compounds in the soil, can contribute to an increase in acidification of soil, providing at the same time disadvantageous conditions are often quite toxic to most plants. Sulphated soil degradation factor is not only acidic but also an accompanying nutrient deficiency and excess phytotoxic elements such as aluminum and heavy metals [12, 27].

Under the influence of long-term contamination of the soil with sulfur are also subject to adverse changes in their sorption properties is reduced because the sum of the content of alkaline cations, mainly due to loss of exchangeable calcium and magnesium [12].

Sulphation is attributed to the significant impact on the mineralogical composition of soils. This is due to the fact that in an acidic environment there is a higher rate of weathering of rocks and minerals. In these processes there is not only the release of substantial amounts of aluminum and other elements, but also to changes in the mineral composition by decomposition and transformation of minerals such as carbonates in that dolomite. Contamination of soil sulfur so they deteriorate the basic parameters of fertility, including a reduction in the amount of soil humus and causes changes in the content of digestible components, in particular phosphorus, potassium, magnesium and molybdenum. Generally, states that as a result of acidification of soil sulfur compounds content of available forms of these elements is reduced [3, 12].

Excess sulfur in the soil environment also creates unfavorable conditions for the life of many organisms. The soils contaminated with sulfur followed by a decrease in the number of bacteria and actinomycetes, and at pH 3.0 or below these micro-organisms are no longer present. In such conditions, only the presence of fungi found [12].

Summary and conclusions

It has been well known since years that sulfur plays an important role in the growth and development of plants. Given the quantitative requirements of plants for this component, it is usually ranked at fourth place after nitrogen, potassium, and phosphorus.

Sulfur plays a specific role in the metabolism of plants. It is a component of many important compounds, the lack of which causes interference with plant growth and disease in humans and animals.

Despite its importance, until the early 80s of this century sulfur in European countries not received much attention. It was not the subject of interest in agricultural research, and it was not taken into account in determining fertilizer needs of plants. This was due to the fact that in most parts of the continent sulfur balance was positive. On the positive balance of this component in Poland is largely influenced by SO_2 emitted into the atmosphere during the combustion of fuels, especially coal, brown coal and crude oil (Table 2). The sulfur in the 80s was also introduced into the soil in large quantities with certain mineral fertilizers.

Table 2

Total emission of sulphur dioxide in Poland in years of 1975–2006 [3]

Years	SO_2 [$kg \cdot ha^{-1}$]	Years	SO_2 [$kg \cdot ha^{-1}$]
1975	99.8	1997	69.9
1980	132.1	1998	60.8
1985	127.2	1999	55.1
1990	102.6	2000	48.4
1991	95.8	2001	50.1
1992	90.2	2002	46.7
1993	87.1	2003	44.1
1994	84.6	2004	39.8
1995	74.9	2005	39.2
1996	75.7	2006	38.3

Lowering the sulfur deposit from the atmosphere and decrease the amount of input of mineral fertilizers led to a deficiency of this nutrient. The deficit of sulfur in the environment plant growth takes place mainly in the countries of Western and Northern Europe. However, many facts indicate that in some parts of Polish, the sulfur balance in the soil can be negative. The absence of this component is expected mainly on lighter, usually acidic, mineral soils located far away from industrial centers. Hence, to identify the factors affecting the metabolism of sulfur in the soil and its availability to plants becomes an important issue.

Sulfur is in fact a nutrient that has a big impact on the amount and quality of the yield of crops [31]. Deficiency of this component is limited primarily protein synthesis, causing further disturbances in the metabolism of sugars, in the case of oilseeds, the lack of sulfur leads to a reduced fat content. A suitable degree of sulfur supply of plants is also important for cereals. Sulfur deficiency decreases because the quality of wheat flour by the deterioration of its baking value. The beneficial effects of sulfur on the quality of the yield was also observed in the case of vegetables, where it increased carotene content and contribute to improving the flavor of onions and garlic. Bearing in mind these elements primarily must ensure is that the sulfur in the soil was in the forms and quantities to satisfy the nutritional needs of crops.

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WPŁYW CZYNNIKÓW GLEBOWYCH NA PRZEMIANY I DOSTĘPNOŚĆ SIARKI DLA ROŚLIN

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Abstrakt: W pracy przeanalizowano wpływ czynników glebowych, takich jak utlenianie, redukcja, immobilizacja, mineralizacja, wymywanie, konkurencja jonowa oraz gospodarka wodna na przemiany siarki w glebie i jej dostępność dla roślin uprawnych. Siarka jest jednym ze składników pokarmowych, który w dużej mierze wpływa na wielkość i jakość plonów roślin uprawnych, jest również składnikiem wielu związków, których brak powoduje zakłócenia w rozwoju roślin oraz schorzenia u ludzi i zwierzą. Pomimo tak dużego znaczenia aż do początku lat 80. nie była ona przedmiotem badań rolniczych, a także nie brano jej pod uwagę przy ustalaniu potrzeb nawozowych roślin. Sytuacja jednak zmieniła się w ciągu ostatnich lat, kiedy to coraz częściej zaczęto podkreślać problemy związane z deficytem siarki w produkcji roślinnej. Braku tego składnika należy się spodziewać przede wszystkim na lżejszych, zwykle zakwaszonych glebach mineralnych, usytuowanych z daleka od ośrodków przemysłowych. Stąd ważnym zagadnieniem stają się przemiany siarki w glebie i jej dostępność dla roślin uprawnych.

Słowa kluczowe: formy siarki, przemiany siarki w glebie, migracja siarki, dostępność siarki