Czech University of Life Sciences in Prague

Faculty of Agrobiology, Food and Natural Recourses

Department of Agro-Environmental Chemistry and Plant Nutrition

Faculty of Agrobiology, Food and Natural Resources

Use of sulfur in plant production

Bachelor thesis

Tomáš Martínek

Sustainable use of natural resources

doc. Ing. Martin Kulhánek, Ph.D.

Declaration

I hereby declare that I have authored this bachelor's thesis carrying the name „Use of sulfur in plant production" independently under the guidance of my supervisor. Furthermore, I confirm that I have used only professional literature and other information sources that have been indicated in the thesis and listed in the bibliography at the end of the thesis. As the author of the bachelor's thesis, I further state that I have not infringed the copyrights of third parties in connection with its creation.

In Prague on 21.4.2023 ____________________________

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Use of Sulfur in Plant Production

Summary

The thesis shows the importance of sulfur in nature and in agriculture production. Sulfur is an essential nutrient for plant growth and development, playing a key role in root development, the absorption of nitrogen, chlorophyll production, and the functioning of enzyme systems. Together with nitrogen, phosphorus, and potassium, sulfur is one of the most important nutrients for plant life.

In the past, industrial emissions were a significant source of sulfur for plants but as they increased the acidity of the atmosphere and thus caused damage to human health as well as damaging plants, measures were taken to decrease sulfur emissions. This effort led to a decline in emissions and closely related to that, to decline in sulfur in soil. The deposits of sulfur from previous years declined by 50% between 1981-2007.

The amount of sulfur needed for agricultural soils varies based on factors such as type of plant, soil texture, and underground water levels. Additionally, soil analysis is recommended to determine the appropriate amount of sulfur fertilizer to use, as well as the appropriate time to apply it. Although sulfur fertilizers have positive effects on plant growth and protection, they also often increase soil acidity, which can lower the amount of soil bacteria and increase the solubility of, e.g., aluminum and manganese, which are toxic to plants.

Cost-benefit analysis is also an important factor to consider, when determining the amount of sulfur fertilizer to use. The overall benefits of using sulfur fertilizers, such as increased yield and higher quality of product, should be weighed against the costs of application of the fertilizers.

It is necessary to pay proper attention to sulfur usage and application as it is essential for optimal plant growth and yields. The role of sulfur in agriculture is vital, and it is important to continue research and development in this area to ensure sustainable and healthy crop production for the future.

Keywords: Sulfur, Organic S, Soil, S fractions, Sulfate

Content

1. Introduction

Sulfur is an essential macronutrient for plant growth and development. Together with nitrogen, phosphorus and potassium it is the most important nutrient for plants. It is a component of many key amino acids, such as cysteine and methionine, which are building blocks of proteins. Sulfur is also necessary for the synthesis of some vitamins and enzymes.

Although sulfur is the fourteenth most widely spread element on earth, it is not spread evenly all over the earth and lack of it in soil may be the crucial reason for low or even no growth of plants in given area. There are several reasons why the level of sulfur in soil is declining – it may be due to leaching, evaporation or use by plants growing on the soil. If the sulfur is not replenished, it´s level is gradually declining and thus negatively influencing plants.

Sulfur also plays a crucial role in photosynthesis, the process by which plants convert sunlight into energy. It is involved in the production of chlorophyll, the green pigment in plants that absorbs light energy. Without enough sulfur, plants cannot make enough chlorophyll, which can lead to low growth and thus reducing crop yields.

Overall, sulfur is important for plant growth and development, and its deficiency can negatively affect plant growth, yield, and quality.

2. Role of Sulphur in the plant nutrition

The role of sulfur was underestimated in the past years even though the role of sulfur is very important. The sulfur was actually identified as a limiting element in the plant's nutrition on a global scale, its role is similar to nitrogen as well as to phosphorus. It is known that in recent decades there has been a significant decrease in the mineral sulfur content in soils, due to:

- Decrease in sulfur inputs in atmospheric depositions
- Less application of ballast sulfur as a part of some fertilizers
- Cultivation of more powerful plant varieties with higher sulfur consumption

The atmospheric sulfur has been declining over past decades and in addition to that there was a decrease of usage of sulfur containing fertilizers. This decline was often more than 70% in the past 40 years (Kulhánek et al., 2020).

Sulfur is an essential element for plants and fundamental for many proteins. Some plants' enzyme systems could not function without it. The most important source of sulfur for plants is soil, to a lesser extent it is atmosphere (Ahmad & Abrol, 2003). The sulfur from atmosphere is also adsorbed by soil and afterward can be used by plants.

2.1. Importance of sulfur in the plant nutrition

It has been known for a very long time that sulfur is one of the basic building elements of plants. Sufficient content of sulfur enables better development of root and absorbing system of the plant, content of chlorophyll and number of nodules of legumes (Frazer, 1935)

Many authors (e.g., Tandon & Messick, 2007) rank importance of the elements as follows:

- Nitrogen
- Phosphorus
- Potassium
- Sulfur

Deficiency of the sulfur in plants cells increases their susceptibility to the stress factors – diseases, droughts, temperatures, pests, heavy metals and pathogens (Karamanos et al., 2006) (Ihsan et al., 2019).

Sulfur is a crucial microelement for plant nutrition, required for the biosynthesis of sulfolipides, antioxidants, cofactors, secondary metabolites, and amino acids that are strictly or conditionally essential for human nutrition (cysteine and methionine) (Tcherkez et al., 2019).

Sulfur is also essential for other nutrients to be processed and integrated by the plants. It supports protein formation, facilitates reactions that increase the content of sugar and fats in plants. It plays a significant role in the taste and smell of certain plants (garlic, onion, leek, mustard) (Karamanos et al., 2006).

Deficiency of sulfur can be observed in symptoms like chlorosis or necrosis mainly in younger leaves. There are other symptoms that are not that clearly visible but still damaging the plant (Nowak et al., 2015). Leaves do not have proper width and they seem to be long and narrow (Kulhánek et al., 2013). Signs of sulfur deficiency for particular plants are in Appendix 1.

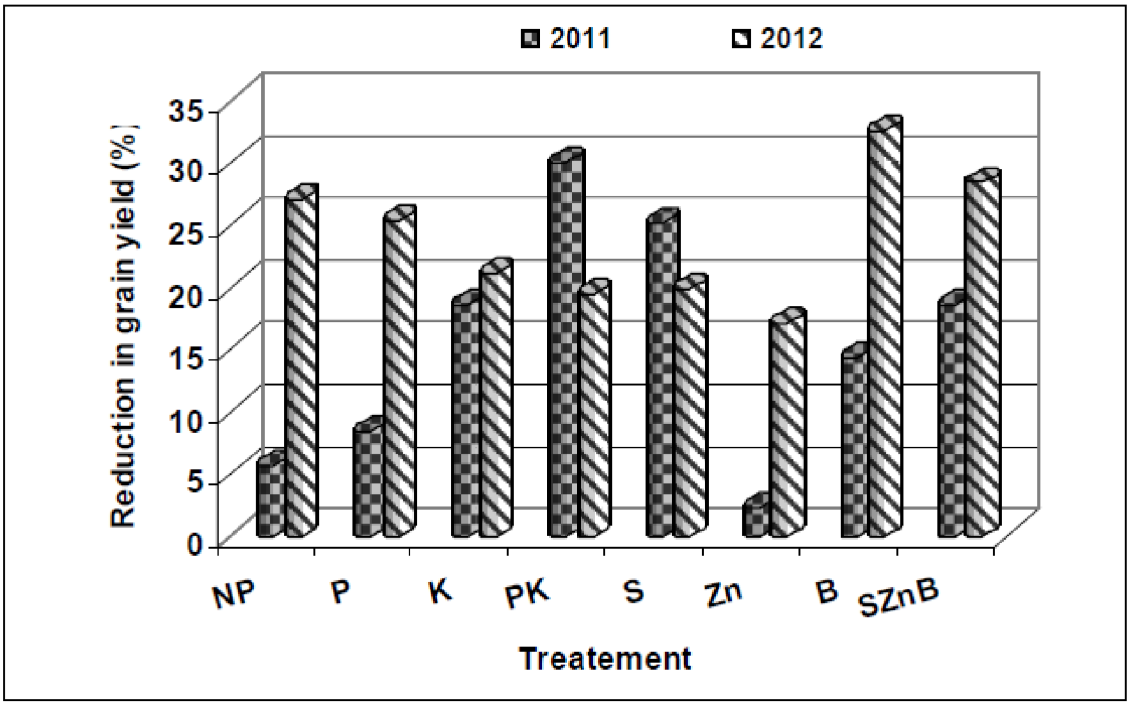
The importance of sulfur for the plant nutrition can be also documented by the fact that in certain cases (e.g., alfalfa) may even show a "sulfur hunger" and adding a sulfur fertilizer commonly increases yield by 50-100% (Frazer, 1935). This range may be obsolete because later research made by Tandon and Messick (2007) are showing different results (see Table 1). In any case, when sulfur fertilizer is used, there is often increase of yield. Sulfur fertilizer ($CaSO_4$) also greatly increases yields of cotton, which is just before blooming time showing the content of sulfur three times higher than that content of phosphorus (Frazer, 1935). Sufficient amount of sulfur fertilizers results in increased growth, greener plants, higher seed yields and quality (Ahmad & Abrol, 2003). Table 1. shows percentage yield increase for several species of plants in the case a sulfur fertilizer is applied.

Table 1 Percent yield increase after sulfur fertilizing (Tandon & Messick, 2007)

Crop	**Percent Yield Increase**
Groundnut/peanut	32
Mustard	30
Wheat	25
Soybean	25
Sunflower	20
Rice (Paddy)	17

In the case of sulfur deficiency, plants show decreased yield and quality (Hawkesford, 1999). For example, deficiency of sulfur in the rice yield may be up to 25% - see Figure 1.

Figure 1 Percent reduction in grain yield in absence of different nutrients (Dash et al., 2015)



On the other side, excess of sulfur in the soil does not mean immediate problem for health of the plant due to series of metabolic processes which enables plant to store sulfur in metabolically inactive compartments. Because deficiency of sulfur poses substantially more often the problem than its excess does, the excess is therefore not so well researched. For the plant the bigger problem caused by sulfur represents increased acidity rather than excess of sulfur itself (Rennenberg, 2003).

2.2. Sulfur in environment

Sulfur is an abundant non-metallic element in the geosphere and occurs in various forms in nature. It is the fourteenth most abundant element in earth's crust. As one of the few elements in nature, it is also found in elementary form. The Earth's crust contains between 0,06 and 0,10% of sulfur (NASA, not dated). Sulfur also occurs as a compound with other elements in the form of sulfides, sulfates or organic forms, in sedimentary, metamorphic and igneous rocks or fossil fuels. Global sulfur resources are estimated at 5 billion tones in natural gas, oil, metallic sulfides, salt deposits and volcanic deposits, approximately 600 billion tones in coal and shale, and practically inexhaustible sources of sulphate in the form of gypsum or anhydrite (Kulhánek et al., 2020).

Sulfur in nature can usually be found in the form of elemental sulfur, which is most common and can be found in mineral deposits and in volcanic areas. It is yellow and crystalline and insoluble in water. Another forms are sulfides which are compounds containing sulfur and one or more metals usually found in mineral deposits (FeS, ZnS, CuS). Sulfates are yet another form of sulfur in nature. They consist of sulfur and oxygen, most common being calcium sulfate ($CaSO_4$) and magnesium sulfate ($MgSO_4$). Sulfur can be also found in organic compounds as a part of organic molecules like aminoacids, proteins and vitamins. These molecules are usually part of natural products such as garlic, onions and eggs (Frazer, 1935).

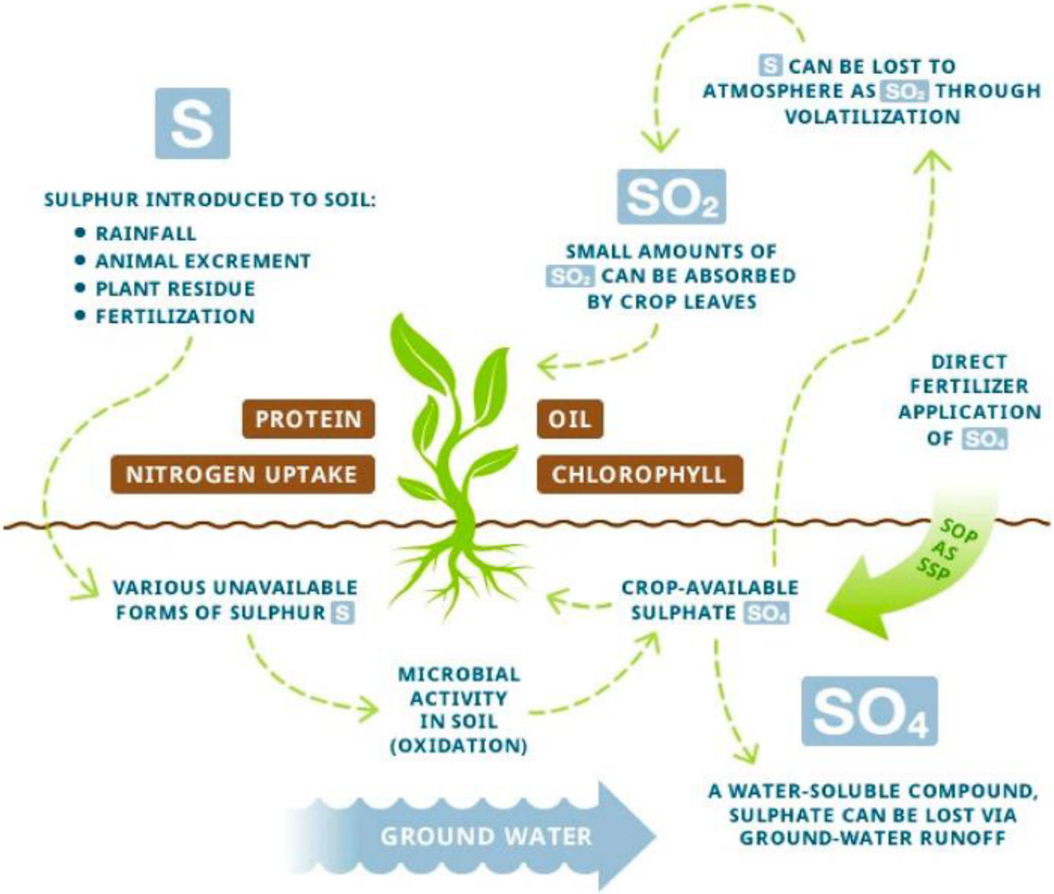
2.2.1. Sulfur cycle in nature

Picture 1 describes the overall sulfur cycle in nature. It is obvious that in the soils used for farming, the natural supply of sulfur (rainfall, animal excrements, plant residue, absorption from atmosphere) is insufficient because a great portion of sulfur is taken away in the form of crops. For example, 1 ton of canola will remove 7-10 kg of sulfur whereas 1 ton of wheat will remove 2 kg of sulfur and for lupins the amount is 2,5-4 kg (Ahmad & Abrol, 2003).

It is also important to mention that part of the sulfur in the soil is lost due to leaching. Obviously, it is necessary to replenish the negative balance of the sulfur back to the soil in the form of fertilizers.

When using fertilizers, it is also necessary to have proper timing of the usage of fertilizers because in the areas for example with heavy rains or permeable soils, the fertilizers could be leached beyond the root zone and thus causing the sulfur deficiency despite the fact of applying the fertilizer in sufficient amount (Ahmad & Abrol, 2003)

Picture 1 Sulphur cycle and its interaction with crop (Ihsan et al., 2019)



2.2.2. Balance of sulfur cycle in the soil

Generally, it can be stated that sulfur cycle in the soil can be specified as follows:

Sulfur inputs:

- Emissions (either directly from atmosphere or washed down to soil)
- Mineral fertilizers
- Manure fertilizers

Sulfur outputs:

- Harvested crop
- Leaching from the soil
- Evaporation from the plants

Sulfur neutral:

- Closed sulfur cycle - Grown crops that grows (sulfur out) and then roots on the field (sulfur in)

Further description of sulfur balance

Emissions

As it is shown in the chapter 2.2.3.1. Sulfur emissions, the emissions are significantly decreasing (in the Czech Republic by some 90% in the period 1980-2004) (Vestreng et al., 2007), which had two effects:

1. Decrease of acidification of the soils
2. Decrease of sulfur supply from the emissions

Artificial fertilizers containing sulfur

The list of major fertilizers that are used in agriculture is mentioned in chapter 2.2.3.2. Sulfur fertilizers. Although there was a decline of use of sulfur fertilizers in previous 40 years (Kulhánek et al., 2020), it is relatively stable since 2010 (International Fertilizer Association, 2018).

Leaching from the soil

One of the major losses in the soil is caused by rain. Some studies show that sulfur is easily washed out from the soil in the amounts of 30-70 kg per hectare per year (Nowak et al., 2015). It is obvious that in the case the sulfur is not replaced either in the form of emissions or fertilizers, the overall level of sulfur in soil declines.

Harvested crops

This is the other major cause of losses of sulfur from the soil. The losses are reaching 15-60 kg per hectare per year depending on the type of plant (Karamanos et al., 2006).

Closed sulfur cycle

Part of the sulfur can return to soil in the form of residues. In the case of some crops, up to 85% of the sulfur from the above-plant plant residues is returned to soil by the decomposition (Kulhánek et al., 2020). Overall summary of sulfur cycle in soil is shown in Table 2.

Table 2 Summary of sulfur cycle

Action	**Amount**	**Units**
Harvested crops	Minus 15-60	kg per ha per year
Leaching	Minus 30-70	kg per ha per year
Evaporation from the plants	N/A	
Emissions	Plus 15	kg per ha per year
Total	**Minus 30-115**	**kg per ha per year**

The amount "total" in Table 2. represents the actual requirement of sulfur fertilizer in kilograms per hectare to be added every year to soil. Of course, it represents the average numbers dependent on type of plant, soil, management etc. Also, the figures used in the table are from different sources and different years, which may mean certain limitations for general use. However, mentioned facts are generally also confirming the necessity and importance to perform sulfur fertilizing in plant production.

2.2.3. Sulfur supply in the environment

The main sources of sulfur in the environment in the Czech Republic are emissions and mineral fertilizers (in case of agriculture). As will be made clear in the following chapters, both of these supplies are steadily declining on a long-term basis.

Due to effort to decrease sulfate pollution and acid rains, most European countries have reduced their emissions by more than 60% between 1990 and 2004, and one quarter have already achieved sulfur emission reductions higher than 80% (Vestreng et al., 2007). Input from emissions to the soils in the Czech Republic was 1,87 mil. of tons per year in 1990 meanwhile in 1998 it was 0,23 mil. tons per year (i.e., 15 kg/ha/year in 1998). This decline of atmospheric sulfur is thus increasing demand for higher input of fertilizers containing sulfur (Kulhánek et al., 2013).

The declining amount of atmospheric sulfur had a double impact. On one side, it was the fact that with declining emissions sulfur supply was also declining. On the other side, high sulfur in atmosphere (especially in the form of sulfates) was supplying sufficient amount of sulfur into soil. However, it was also causing "acid rains" that were damaging the plants by high acidity (low pH). Acid rains are defined as rains with pH lower that 5,6 and the major reason of the acidity are usually sulfates.

From Table 3 it can be seen, that plants can adsorb sulfites (SO_2) from the atmosphere for its own benefits, which can also result in increasing yield. On the other hand, the excess of sulfur in atmosphere damages plants and concentration over 1,5 mg/m^3 leads to depressions and necrosis of the plant (Richter, 2004a).

Table 3 Influence of atmospheric concentration of SO_2 on plant growth (Richter, 2004a)

	Concentration of SO_2 in mg/m^{-3}					**period of cultivation**
	0.0	0.2	0.5	1.0	1.5	
Plant	**amount of dry weight (g/plant)**					
Sunflower	70	103	103	113	100	15
Corn	100	110	118	111	107	13
Tobacco	31	41	43	54	46	9

2.2.3.1. Sulfur emissions

Sulfur emissions are declining on long term basis which is gradually increasing deficiency of sulfur in soil. It is expected that the trend will continue due to emission restrictions of SO_2 (Karamanos et al., 2006).

Table 4 a, b shows decline of sulfur emissions in the past years in the Czech Republic as well as a detailed view of the emissions of European countries (Vestreng et al., 2007). This table clearly shows that in the Czech Republic the emissions of sulfur declined by approx. 90% between the years 1980 and 2004. This fact, together with decline of use of mineral fertilizers containing sulfur, caused that accessible form of sulfur in the soil, in the past 40 years, declined by more than 70% (Kulhánek et al., 2020).

Table 4a Sulfur emissions Europe in th. tons (Vestreng et al., 2007)

Year	**1980**	**1985**	**1990**	**1995**	**2000**	**2004**
Austria	344	179	74	47	32	29
Belgium	828	400	361	262	171	154
Bosnia and Herzegovina	482	483	484	360	420	427
Bulgaria	2050	2314	2007	1477	918	929
Croatia	150	164	178	70	60	85
Cyprus	28	35	46	41	51	45
Czech Republic	2257	2277	1876	1090	264	227
Denmark	450	333	176	133	27	23
Estonia	287	254	274	117	96	90
Finland	584	382	259	95	74	83
France	3216	1496	1333	968	613	484
Georgia	230	273	43	6	7	5

Table 5b Sulfur emissions Europe in th. tons (Vestreng et al., 2007)

Year	**1980**	**1985**	**1990**	**1995**	**2000**	**2004**
Germany	7514	7732	5289	1708	630	559
Greece	400	500	487	536	493	537
Hungary	1633	1404	1011	705	486	240
Iceland	18	18	9	9	9	9
Ireland	222	140	186	161	131	71
Italy	3437	2045	1795	1320	755	496
Kazakhstan	639	575	651	528	506	425
Latvia	96	97	97	47	10	4
Lithuania	311	304	263	92	43	40
Luxembourg	26	26	26	7	4	4
Netherlands	490	258	189	127	72	66
Norway	136	91	53	34	27	25
Poland	4100	4300	3278	2381	1507	1286
Portugal	266	198	317	332	306	203
Republic of Moldova	308	282	175	94	13	15
Romania	1055	1255	1310	882	727	685
Russian Federation	7323	6350	6113	3101	2263	1858
Serbia and Montenegro	406	478	593	428	396	341
Slovakia	780	613	542	239	127	97
Slovenia	234	241	198	127	99	55
Spain	3024	2542	2103	1809	1479	1360
Sweden	491	266	117	79	52	47
Switzerland	116	76	42	28	19	17
TFYR of Macedonia	107	109	110	93	90	87
Turkey	1030	1345	1519	1397	2122	1792
Ukraine	3849	3463	3921	2342	1599	1145
United Kingdom	4838	3714	3699	2343	1173	833
Grand Total	**55340**	**48448**	**42896**	**26282**	**18263**	**15162**

The declining supply of sulfur from emissions is making use of sulfur fertilizers even more important. (Vestreng et al., 2007)

2.2.3.2. Sulfur fertilizers

There are different types of fertilizers used in agriculture. They can be generally divided into two groups:

A. Mineral fertilizers
B. Organic fertilizers

A. Mineral fertilizers

Table 5. shows basic types and percentage of sulfur in the mineral fertilizer's compound.

Table 6 Sulfur content in fertilizers (Kulhánek et al., 2013)

Fertilizer	Percentage of Sulfur
Ammonium sulfate	24
Ammonium thiosulfate	26
Elemental sulfur	>90
Gypsum (calcium sulfate)	19
Potassium magnesium sulfate	23
Potassium sulfate	18

- Ammonium Sulfate - this fertilizer has got an advantage that except of 24% sulfur also contains 21% of nitrogen. It is often used for alkaline soils and is lowering its pH balance. It has minimum hygroscopicity and high chemical stability.
- Ammonium thiosulfate - is a highly soluble fertilizer. It has a long-term effect because it is necessary for the soil microbes to convert it to sulfate (Kulhánek et al., 2013).
- Elemental Sulfur - is tested as a highly perspective mineral fertilizer, which is suitable for alkaline soils. The advantages are long-term availability of sulfur in soil, although the sulfur itself is not directly usable by the plants and it has to be converted (oxidized) into plant available form (sulfate). The best results are achieved when the sulfur is applied before planting. However, the disadvantage is that its use is significantly increasing the soil acidity.
- Calcium Sulfate - it has a long-term effect. The advantage of calcium sulfate is that it changes soil pH only slightly and in addition it is counteracting the toxic effects of aluminium on root development. The disadvantage of this fertilizer is that the sulfur is accessible for plants with difficulties. (Dick, 2018).

- Potassium magnesium sulfate - is an excellent source of magnesium and sulfur. It can be used on soils with low magnesium content.
- Potassium Sulfate - is an excellent source of potassium nutrition for plants, which together with sulfate makes it a good fertilizer. It is commonly used for some fruits, vegetables and tobacco.

B. Organic fertilizers

Organic fertilizers are either waste from livestock production or after-harvest remnants, which are also sources of sulfur. From table 6 can be seen that the best is chicken manure but it is important to mention that after harvest remnants are important source of sulfur as well.

Table 7 Content of sulfur in organic fertilizers and after-harvest remnants (Vojtěch, 2016)

Farmhouse fertilizers	Content of S in kg/t	After harvest remnants	Content of S in kg/t
Manure	1,0	straw cereal	1,5
Urea	0,1	straw legume	3,0
Pig and cattle manure	0,4	straw oilseed	2,0
Chicken Manure	0,8	beet tops	0,3
Dry Chicken Manure	4,0	potato stems	0,5

The positive effect of sulfur fertilization was proven by experiment where increased amount of sulfur was used as fertilizer, and it resulted in increased yield of rapeseed by up-to 25%. What is interesting is the fact that sulfur content in plants was not increased (Kulhánek et al., 2013).

Table 7 shows an overall increase of sulfur fertilizers, which increased by 21% in the period 2010-2018. This is positive trend as oppose to previous decline of usage of sulfur fertilizers. The increase of usage of sulfur fertilizers is enhancing supply of sulfur into soil but due to missing data, it is impossible to estimate whether the increase is sufficient to compensate declines of sulfur supply from emissions.

Table 8 Historical usage of sulfur fertilizers in the Czech Republic (International Fertilizer Association, 2018)

Year	Elemental Sulfur (Metric Tons)	Sulfate Fertilizers (Metric Tons)
2010	4,720	24,848
2011	4,907	28,821
2012	5,221	28,150
2013	5,086	29,508
2014	5,660	32,211
2015	5,653	30,124
2016	5,455	33,490
2017	5,881	33,193
2018	5,726	33,845

2.2.3.3. Impact of fertilizers on soil pH

One of the side effects of many fertilizers is that they are changing pH of soil. Soils get naturally acidified and this process is accelerated by agriculture. The speed of acidification depends on the type of soil, productivity and purpose of the land usage.

When plants are using nutrients from the soil, they tend to absorb positively charged nutrients (cations NH_4^+, K^+, Mg^{2+}, Na^+). The negatively charged anions are not absorbed at the same rate. This is balanced by hydrogen cations (H^+) that are excreted by roots to the soil. The result of the process is increasing alkalinity of the plant and increasing acidity of the soil. By removing the plant (harvest) the increased acidity remains on site.

It is therefore obvious that soils are getting acid naturally, meanwhile when adding fertilizers, the process is speeded up by both adding higher sources of cations and anions and removing the plants (harvest). Especially due to harvest, the plants do not re-enter the cycle. It means that by removing the alkaline part, logically the rest (soils) are increasing in acidity.

The major problem of the increased acidity of the soil is that it is causing higher solubility of the element's aluminium and manganese. These two elements, that are normally present in the soils became toxic for the plants in their soluble forms. From this point of view, it is not recommended for the acidity to be lower than 5,5 (Ahmad & Abrol, 2003).

Fertilizers influence the pH of soils. Table 8 shows the impact of fertilizers on soil pH measured by the amount of $CaCO_3$ needed for neutralization of the impact of use of fertilizer (Ahmad & Abrol, 2003).

Table 8 and Table 9 compare amounts of lime necessary to neutralize the effect of a fertilizer compared to sulfur fertilizer. It is also showing clearly that most of the fertilizers are having acidifying effect on soil, which means that without continuous adding of lime (or other neutralizing compound) the soil increases in acidity.

Table 9 Fertilizers and line needed for their neutralization (Ahmad & Abrol, 2003)

Fertilizer	**Lime required to neutralize fertilizer addition (kg $CaCO_3$/kg nutrient N, P, S) When amount the amount of nutrient leached is:**	
	0%	100%
Nitrogen fertilizers		
Ammonium Sulphate	3,6 (/kg N)	7,1 (/kg N)
Ammonium nitrate	0,0	3,6 (/kg N)
Urea	0,0	3,6 (/kg N)
DAP	1,8 (/kg N)	5,4 (/kg N)
Potassium nitrate	-3,6 (/kg N)	0,0
Sodium nitrate	-3,6 (/kg N)	0,0
Phosphorus fertilizers		
Single, double, triple superphosphate	0,0	-
Dicalcium phosphate	-1,6 (/kg P)	-
Rock phosphate (15.4% P)	-1,6 (/kg P)	-
Sulphur fertilizers		
Elemental sulfur	3,1 (/kg S)	-
Gypsum	0,0	-
Potassium Sulphate	0,0	-

As can be seen, elemental sulfur has very high lime requirement for neutralization of the increasing acidity. The same is valid for the ammonium sulfate meanwhile gypsum does not require any lime for neutralization.

Table 10 Influence of mineral fertilizers on pH of soil (Richter R., 2004b)

Fertilizers	Equivalent in kg to 100kg fertilizer	
	CaO	$CaC0_3$
Nitrogen lime	+ 63	+ 113
Calcium nitrate	+ 12	+ 22
Ammonium nitrate with cal. (25%)	- 10	- 17
Ammonium nitrate with cal. (27%)	- 15	- 27
Dam-390	- 29	- 52
Ammonium nitrate	- 33	- 60
Urea	- 46	- 82
Ammonium sulphate	- 63	- 112
Amofos	- 35	- 62
Fostim (8-24)	- 17	- 30
NPK 1 (12-19-19)	- 12	- 22
NPK 2A (11-11-14)	- 8	- 15
NPK NF (16-16-16)	- 7	- 12

Equivalent of acidity - shows the amount of CaO or $CaCO_3$ necessary for neutralization of the created acid reaction after the application of the fertilizers. The equivalent of alkalinity + shows the amount of alkaline active CaO, which the fertilizers add to the soil (Richter R., 2004b).

2.3. Sulfur in soil

Sulfur exists in soil in both organic and inorganic form. The sulfur can be converted from organic to inorganic and vice versa through mobilization, mineralization, immobilization, oxidation and reduction. The most mobile form of sulfur is sulfate anion $(SO_4)^{2-}$ meanwhile the organic form is little mobile (Kulhánek et al., 2020).

2.3.1. Inorganic sulfur

Inorganic sources of sulfur are most common inputs in agriculture. The major sources of this type of sulfur in the Czech Republic are:

1. Emissions
2. Mineral fertilizers

The most important source of sulfur for plants are sulfates. Interestingly these compounds represent less than 5% of the total soil sulfur. This type of sulfur can be further divided to:

1. Sulfur in soil solution
2. Adsorbed sulfur

Meanwhile the sulfur in soil solution is relatively low (around 1 mg/l), adsorbed sulfur represents around 6 mg/kg in the Czech Republic (Kulhánek et al., 2020).

2.3.2. Organic sulfur

The content of organic sulfur in soil is usually 95-98% from total sulfur. As to form of organic compounds that contains sulfur, two basic types of compounds can be identified:

1. Sulfur indirectly bound to carbon with bond type C-O-S (ester sulfates) – this form of sulfur creates 30-70% of total content of organic sulfur in soil.
2. Sulfur directly bound to carbon with type of bond C-S (cysteine, methionine).
3. Other types of bonds (sulfonates, heterocyclic forms of sulfur) are less common.

Sulfur directly bound to carbon tends to be more stable, being an integral component of soil organic matter. As soil organic matter breaks down, the sulfur in the organic form mineralizes to sulfate-sulfur, which is the only form of sulfur that plant roots can absorb (Kulhánek et al., 2020).

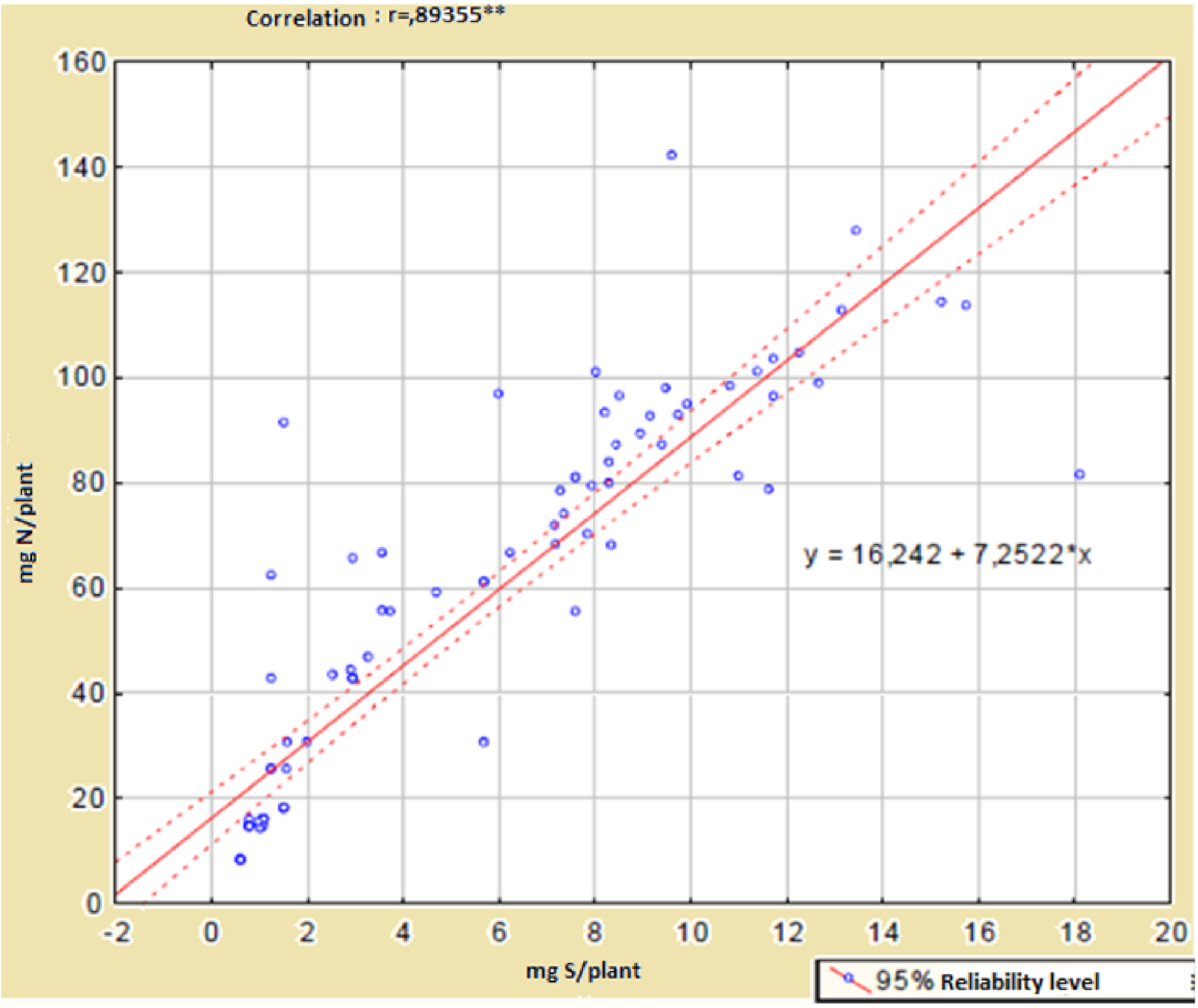
2.3.3. Mutual interaction of sulfur and other nutrients

The influence of sulfur is very closely related to the role of nitrogen in plants. The higher amount of sulfur causes a significant increase of nitrogen in the plants. The relationship between sulfur and nitrogen is not straightforward, though. The lack of sulfur will cause lower levels of nitrogen in the plants and on the other hand, excessive amounts of nitrogen in the plants may invoke external signs of sulfur deficiency. It is therefore important also to monitor N:S ratio, which should not exceed 19:1. For example in canola, sufficient level of sulfur is above 0.2% in young or recently matured leaves, however, if the N:S ratio is above 19:1, the plant exhibits signs of deficiency of sulfur even at concentration significantly higher than 0.2%. (Ahmad & Abrol, 2003).

In the case of other elements, the influence of sulfur is not always positive. For example, in apple tree tissues, the higher concentration of sulfur results in lower concentration of phosphorus and vice versa. It is than obvious that concentration of these elements are inversely influencing each other (Frazer, 1935)

Figure 2 clearly shows the importance of sulfur nitrogen interaction in the plant, on the top of that, increased sulfur also improves the quality of proteins generated by the plant (Hřivna, 2012).

Figure 2 Relation between intake of nitrogen and sulfur in process of vegetation (Hřivna, 2012)

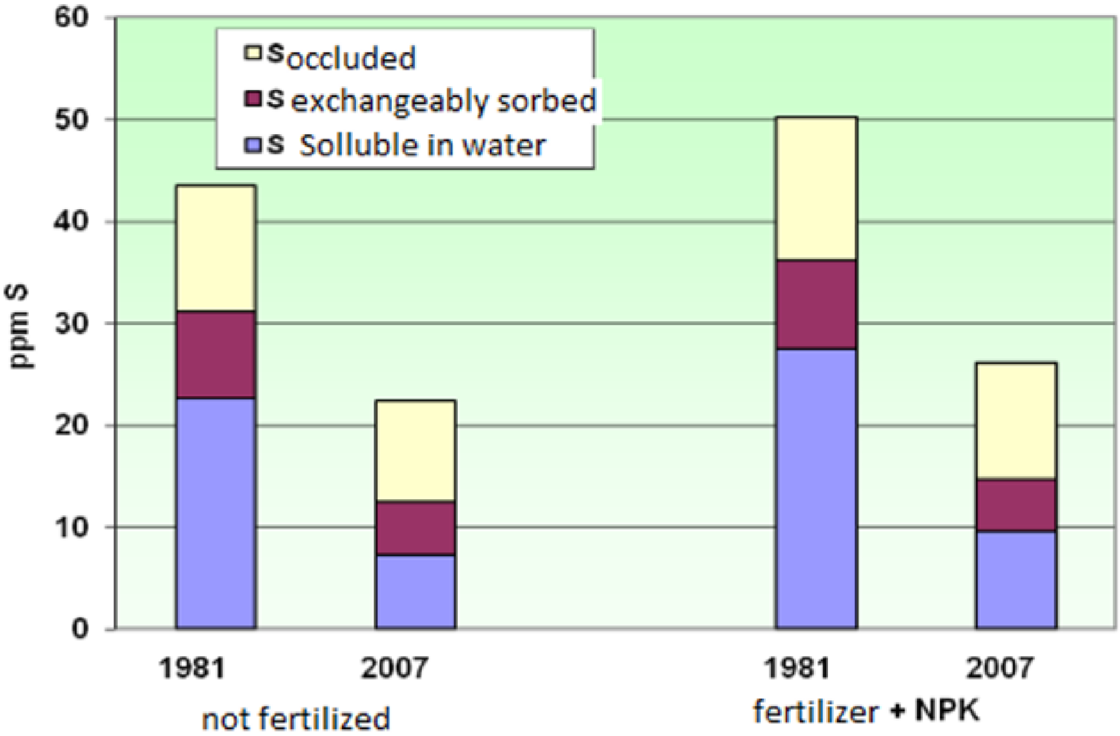


Availability of sulfur for plants depends on soil organic matter due to C:S ratio. If this ratio is less than 200:1 there is an accumulation of sulfur while immobilization happens when ratio is more than 400:1 (Kulhánek et al., 2020).

2.3.4. Content of sulfur in soil

As it was already mentioned, level of sulfur in soils in Czech Republic is declining. Figure 3 clearly shows the content of sulfur in soil decreased from 1981 to 2007. This decrease can be observed in both, fertilized and non-fertilized soils (Kulhánek et al., 2013).

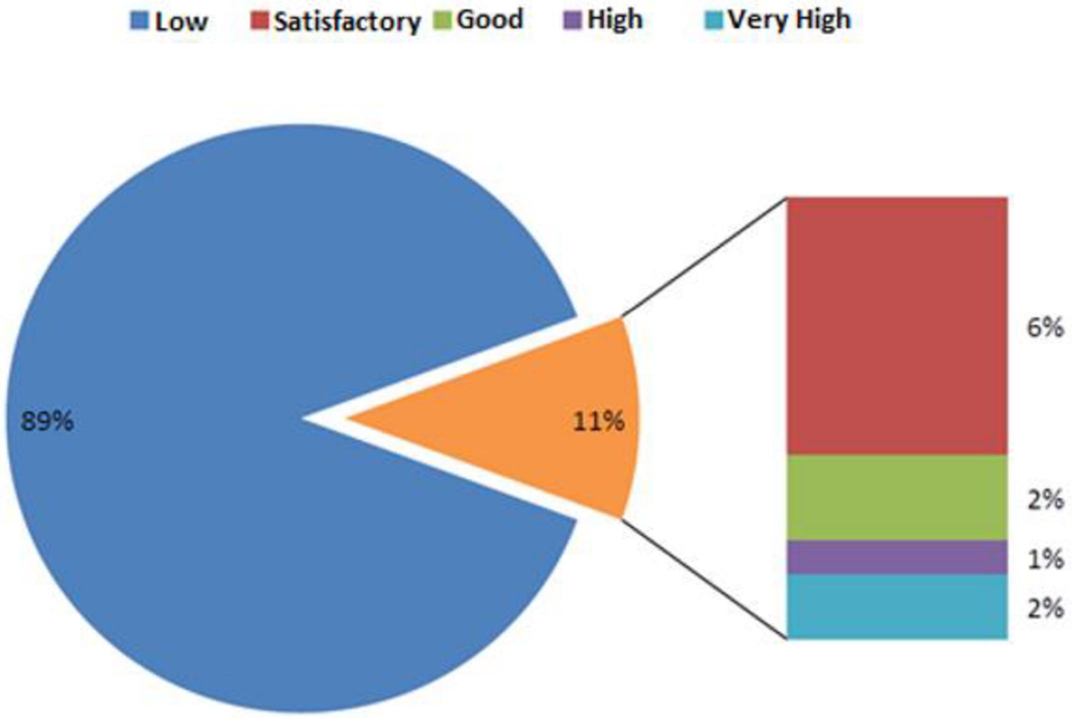
Figure 3 Comparison of mineral fractions in soil in years 1981 and 2007 (Vaněk, et al., 2012)



Research carried out on non-fertilized soils showed that there was a 50% decline of sulfur content in soils in the years 1981-2007. This is strongly supporting the argument that decline of emissions leads to decline of sulfur level in soils (Vaněk, et al., 2012).

Research carried out in 2014 showed that the amount of sulfur in soil in the Czech Republic is generally very low. Figure 4 shows that altogether 89% of the soils has got low sulfur level, 6% is satisfactory in S and the remaining 5% is good or above (Vojtěch, 2016).

Figure 4 Content of sulfur in soil 2014 (Vojtěch, 2016)



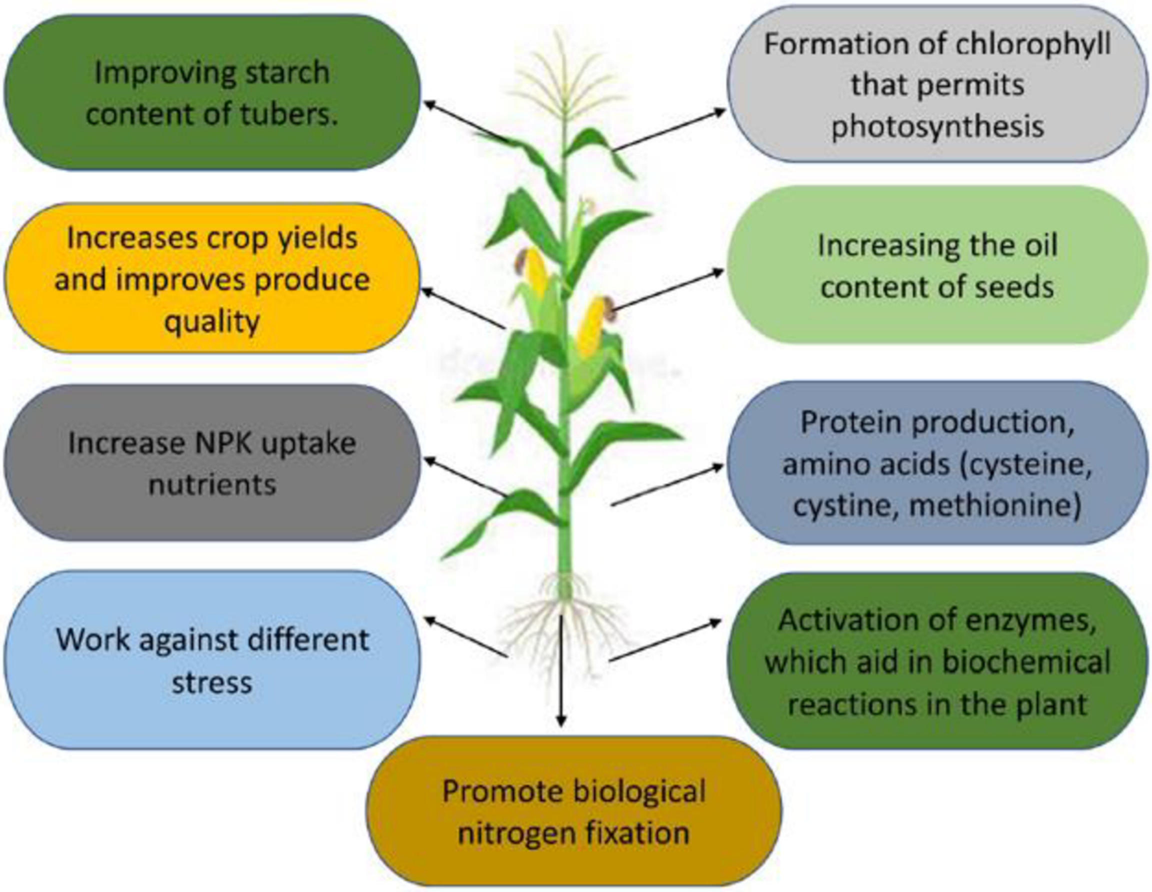
2.4. Sulfur in plant

Major part of sulfur is acquired by plants through roots, in certain cases (especially higher plants) the plants are able to assimilate sulfur also from atmosphere through the stomates. These plants can absorb up to 30% of sulfur (in the form of sulfur dioxide) from air and store 75-90% in leaves (Kulhánek et al., 2020).

2.4.1. Sulfur as one basic building stone of plants

It seems that one of the mechanisms how sulfur is acting in plants is that sulfur is facilitating release of phosphorus from older parts of the plant to enable its use in the growing younger tissue of the plant (Frazer, 1935). Picture 2 shows the major role of sulfur in the proper functioning of plants.

Picture 2 Role of Sulphur in plant growth and development (Narayan et al., 2022)



2.4.2. Sulfur content in plants

Different plants contain different amounts of sulfur. The content of the sulfur in the plants is not dependent only on the type of plant but also on the part of the life cycle of the plant.

The optimal content of sulfur in plant for ideal growth is between 0,1-0,5% in dry-matter. The peak of sulfur assimilation, in the form of sulfate, by plants is around 4 pH and decreases with higher pH (Kulhánek et al., 2013). It was also found that the older the tissue of the plant, the higher was the sulfur content (Frazer, 1935).

Table 10 shows that the plants contain different amounts of sulfur (in dry weight). It is then necessary to keep in mind that this is representing the amount of sulfur that is taken away from the soil due to the harvest (Grime, 2016).

Table 11 Sulfur content in plant species (Grime, 2016)

Plant Species	Sulfur Content (Dry Weight)
Soybean	1.5%
Alfalfa	1.2%
Mustard	0.9%
Broccoli	0.6%
Onion	0.5%
Garlic	0.4%
Tomato	0.3%
Wheat	0.2%
Rice	0.1%
Corn	0.1%

2.4.3. Sulfur requirements of plants

The different plants require different amounts of sulfur in soil to prosper and give optimum yield. As can be read from table 11, the plant requiring highest addition of sulfur is rape (80 kg of sulfur per hectare per year) meanwhile for example poppy seed, barley or oat require only 25 kg per hectare per year (Vojtěch, 2016).

Table 12 Amount of sulfur required by plants (Vojtěch, 2016)

Plant	S/kg/1t production	industrial yield t/ha	necessary supply S/kg/ha
wheat	3,3	9,0	30,0
winter rye	4,2	6,0	25,0
winter barley	3,1	8,0	25,0
triticale	3,6	7,0	25,0
spring barley	3,8	6,5	25,0
oat	3,8	6,5	25,0
corn grain	3,3	9,0	30,0
winter rape	20,0	4,0	80,0
sunflower	13,0	3,0	39,0
poppy	17,0	1,5	25,0
sugar beet	0,8	55,0	40,0
potatoes	0,8	40,0	30,0
fodder beet	0,5	80,0	40,0
pea	6,3	4,0	25,0
corn silage	0,6	55,0	30,0
fodder beet	3,0	10,0	30,0

Different species of plants are having not only different requirements on sulfur, but they have also different susceptibility to the deficiency of sulfur. This example can be seen in table 12.

Table 13 Susceptibility of plants to sulfur deficiency (Ahmad & Abrol, 2003)

High susceptibility	**Moderate susceptibility**	**Low susceptibility**
Canola Lucerne	Clovers Grasses Lupins	Wheat Oats Barley

The probability of sulfur deficiency depends on many criteria. One of the major criteria is plant species as it is shown in Table 13.

Table 14 Probability of sulfur deficit (Baranyk & Fábry, 2007)

Parameter	**Probability of deficit**				
	Low		-	High	
Plant species	grasses	Sugar beet	potatoes	cereals	oil rape
total income of S (kg/ha)	<10	10-20	20-30	15-40	40-100
The border concentration of Sulphur deficit (% dry weight)	0,10-0,12	0,17-0,21	0,17-0,21	0,12	<0,35
Critical amount for maximum yield	<0,30	0,35-0,40	0,40	0,40	0,65

This is showing basic demand on the presence of sulfur where it is obvious that oilseed rape requires substantially more sulfur than grasses. All species of plants have got critical concentration of sulfur in dry matter that ensures maximum yield. If the concentration of sulfur declines to (or go under) the border amount, the plant starts to show symptoms of sulfur deficiency.

The other parameters that are influencing probability of sulfur deficit are:

- Soil texture
- Climatic conditions

- Level of underground water

Table 14 shows the probability of sulfur deficiency in correlation with these parameters. The clay type of soil is substantially decreasing probability of sulfur deficit meanwhile a sand type of soil is causing high deficiency, the major reason is leaching.

Table 15 Probability of sulfur deficiency (Baranyk & Fábry, 2007)

Parametr	**Probability of deficit**	
	Low	High
Soil texture	clay	sand
climatic conditions	Low amount of precipitation in winter period	High amount of precipitation in winter period
	<200mm - 300mm - 400mm - 500mm - >500mm	
	Low amount of precipitation in summer period	High amount of precipitation in summer period
Level of underground water	High level of underground water (<1,5m underground)	Low level of underground water (>2,5 - 3m underground)

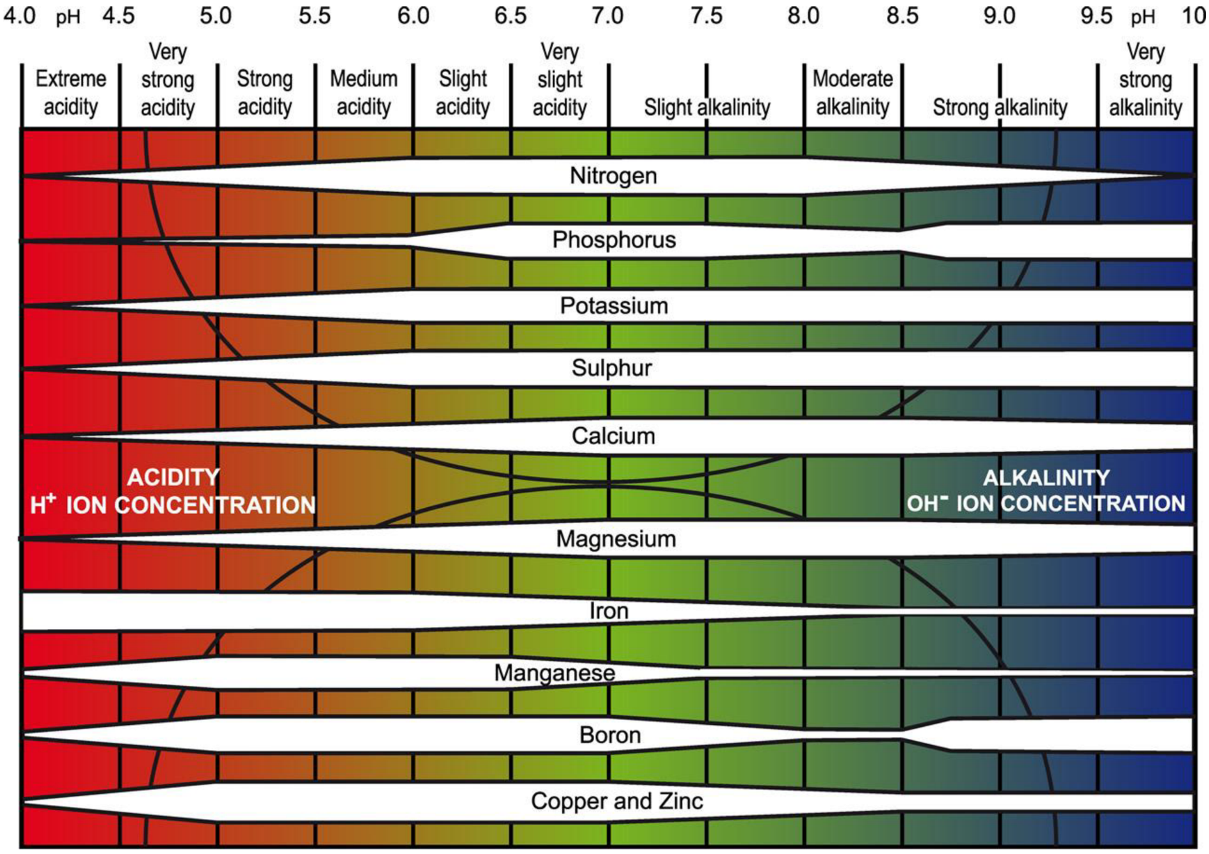
Similar effects have got too much rain both in summer and winter. They are also the reason for sulfur to be leached from the soil and thus causing the sulfur deficit. The similar effect has underground water levels – the lower the underground water levels the higher probability of sulfur deficiency.

2.4.4. Impact of pH of soil on plants

Acidity of the soil has a significant impact on fertility. High acidity (pH lower than 5,5) decreases the number of useful bacteria (such as *Rhizobia*, *Azotobacter chroococum* and nitrification bacteria), which are essential for biochemical reactions in the soil. On the contrary it enables growth of less desirable microorganisms (fungus and molds). In addition, mineralization processes are slowed down and synthetic processes lead to origination of lower quality humus (development of more fulvic acids). High acidity of soil also leads into dilution of aluminium and heavy metals which are harmful for both plants and humans. High acidity has also a negative impact on the effectiveness of some fertilizers (Richter, 2004b).

Picture 3 shows the capability of plants to utilize particular elements and use them effectively for their metabolism related to pH value. It seems that for most elements the optimum pH is between 6-7. However, the optimum pH varies from plant to plant.

Picture 3 How soil pH affects availability of plant nutrients (Soil Science Society of America, 2011)



The influence of pH is very significant in plant nutrition. This can be documented by the case of apple tree tissues where under normal circumstances higher sulfur content causes lower phosphorus content but when acid phosphate is added, the content of both sulfur and phosphorus significantly increases (Frazer, 1935)

Although it seems obvious that ensuring excess of sulfur in the soil is clearly an imperative, it is necessary to consider, that excess of sulfur in the soil also increases the acidity of the soil that is than adversely influencing plants and thus the yield of the crop (Richter, 2004b).

Optimal acidity of soil differs from plant to plant. Table 15 shows optimum pH for different plant species.

Table 16 Demands of certain plants on the soil reaction (Baier & Baierová, 1985)

Plant	pH/KCl
winter rye	4,8 - 7,1
winter wheat	6,0 - 7,2
spring barley	6,2 -7,5
oats	4,7 - 7,3
potatoes	4,7 - 6,2
sugar beat	6,7 - 7,4
maize	5,5 - 6,8
field peas	5,7 - 7,0
common bean	6,0 - 6,6
winter rape	6,0 - 7,5
poppy	6,3 - 7,2
sunflower	5,7 - 6,2
meadow clover	5,4 - 6,7
lucerne	6,7 - 7,8

Plant	pH/KCl
meadow grasses	5,3 - 6,2
ryegrass	6,7 - 7,1
lettuce	5,7 - 6,8
carrot	5,2 - 6,7
red beetroot	6,5 - 7,1
kale	6,4 - 7,0
cabbage	7,0 - 8,4
onion	6,8 - 8,5
cucumbers	5,7 - 7,5
tomatoes	6,0 - 6,9
stone fruit	6,2 - 8,0
kernels	6,0 - 8,0
berries	5,5 - 7,0
strawberry	4,5 - 6,5

2.5. Economics of the usage of sulfur fertilizers

The economics of usage of sulfur fertilizers depend on several factors such as what type of crop is grown, soil conditions and local market prices of both sulfur fertilizers and crops being produced.

In general, sulfur is an essential nutrient, and its sufficiency leads to increased yields and quality of the crop. It brings major economic effect especially in plants that are sensitive to sulfur fertilizers such as rape. Although it increases the yield of the plant generally this increase may be so low that overall economic effect may be low or even negative (increased yield would not pay-off the cost of fertilizer). In such cases it would require economic analysis to be carried out annually to properly evaluate whether it is making economic sense to employ sulfur fertilizer (Brealy & Myers, 1991).

3. Conclusion

Sulfur plays important role in plant production. It has many different effects, both positive and negative, ranging from increased plant health and yields to decreased pH. It belongs together with nitrogen, phosphorus and potassium to the group of the most important nutrients for plant life. Deficiency of sulfur causes necrosis of younger plant parts and chlorosis and increases susceptibility to stress factors and diseases.

In the past, there was a significant supply of sulfur for the plants via emissions (mainly industrial ones). Due to impact on plants and human health, measures were taken which decreased sulfur emissions more than ten times since 1981. This of course means that supply of sulfur is not sufficient and the soil deposits from previous times are declining.

Due to processes of harvest, leaching, evaporation from the plants and soil, the amount of sulfur is decreasing and it is only partly compensated by atmosphere emissions. The calculated overall balance of sulfur during a year on farmed soil is usually 30-115 kg per hectare per year. This is the amount that needs to be added back to soil mainly in form of sulfur fertilizer.

Most sulfur fertilizers are increasing the acidity of soil (decreasing pH). Proper management has to be taken with regard to the increase of acidity to decide which fertilizer to use and how much lime to add to counteract the increased acidity.

From my point of view, the role of sulfur in agriculture is very important, and it is necessary to pay proper attention to its usage and application.

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Apendixes

Apendix 1 Sulfur deficiency symptoms in economically important plants (Narayan et al., 2022)

Plants	**Symptoms**
Wheat	Yellowing of the plant, more prominent between the veins.
Rice	Yellowish leaf sheath and leaf blade. Reduced plant height and number of tillers. Fewer panicles, shorter and fewer grains.
Maize	The initial stage, yellowing between the veins in younger leaves. Later, reddening at the base of the stem and along the leaf margins.
Chickpea	Plants appear erect, premature drying, and withering of young leaves.
Sunflower	Leaves and flowers become pale. Plants are smaller with shorter internodes. Reduced number and size of leaves.
Tomato	Small plant height and lighter green. Yellowing in various plant parts. In the severe deficiency, petioles and stems show a clear reddening.
Groundnut	Small Plant height. A "V" shaped petiole appearance. New leaves, the area around the main vein may be pale. Seed maturity delayed.
Sugarcane	Younger leaves become yellowish-green colors. Older leaves show a faint purplish tinge. Stems are thinner and taper toward the tip.
Tea	Sulfur deficient bushes turn yellow, reduce in leaf size, short internodes, the entire plant appears shrunken. Leaves curl up and their edges and tips turn brown.
Pea	Chlorosis in young leaves. Flowering and yield are reduced.
Tobacco	Young leaves are uniformly pale-yellow green. Leaves are smaller and internodes are shorter.
Banana	Young leaves show chlorosis. Severe sulfur deficient conditions lead to chlorosis in between the veins. Retracted growth and small fruits are produced.
Green gram	Stunted plants growth reduced branching and flowering, and pods have shrunken seeds.
Cotton	Persistent yellowing of new leaves and reddening of the petiole.
Potato	Evident inward curling of youngest leaves, substantial yellowing of the stems, overall yellowing of the plants
Coffee	Young leaves show yellow color, mature leaves show chlorosis of mature, small leaves size. Interveinal tissue looks like a mottled appearance.
Rubber	The entire leaf surface turns yellowish-green color, reduced in size, with typical brown necrotic spots at the tips of the leaves.

List of figures