

# Liquid nitrogen-sulphur fertilizers – answer on sulphur deficiency in soil

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## Introduction

Liquid fertilizers are getting more often the alternative for solid fertilizers. Development of manufacturing processes and application of liquid fertilizers in agriculture started in 1970s [1]. At the beginning they were in fact nutrients dissolved in water, later they became a liquid slurry fertilizers. First liquid fertilizers were mainly with nitrogen, later products with more nutrients appeared.

Due to the fact, that every plant has its own requirement in case of nutrients supply, proper supplementation with respect to their needs are giving conditions to obtain bigger and higher quality of the crops [1, 3]. Nitrogen as a crop-creative factor in plant production is widely applied in agriculture in high amount. It is essential to building amino acids, which create proteins, it is a component of nucleic acids and it takes part in almost every biochemical reactions performed inside plant. In nitrogen fertilizers nitrogen can be present as  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  or in amid form ( $\text{NH}_2$ ). There are several factors which are important for effective farming of nitrogen such as its source, dosage, term of fertilization, its way, which adjust availability of nitrogen into farmed plant needs [4]. Loss of nitrogen delivered to soil with fertilizer are high, therefore it is applied every year, in small dosage preferably. Unfavourable feature of many nitrogen fertilizers is instant action, badly fitted to growth rhythm of the plant. This is a reason why it is necessary to fertilize using nitrogen agent a couple of times during vegetation. The highest demand on nitrogen can be observed during terms of intensive growth of green mass.

Speed of nitrogen fertilizer action depends on way of fertilization. Instant effect can be obtained using foliar feeding, because using that way, fertilizer is collected directly and used instantly. In general for foliar feeding every nitrogen form dissolved in water can be applied, but preferably it should be urea due to low burning abilities. In soil fertilization there is a variety of used agents, depending on action rate, which is dependent on nitrogen form: quick action (saltpetre), fairly quick action (ammonium-saltpetre), slow down action (ammonium), fairly slow action (amid), slow action (nitrogen in form of the compounds which are slightly soluble in water, coated fertilizers and ammonium-type with nitrification inhibitors) [3].

As a nitrogen source in fertilizers it is often to use urea [5]. In water it is easy soluble, and its granules has 46% of nitrogen in amid form, which in soil is changed into ammonium form, then nitrate form. Nitrate form is stopped by the soil, and thanks to its loss of the nitrogen due to the elution is small. Urea cause 2–4 times smaller salinity of the soil than other nitrogen forms and has influence on smaller accumulation of nitrates in plants. Biuret is toxic component for plants, which exists in urea, sometimes in excess. Due to that fact it is necessary to comply with permissible levels of biuret in fertilizers [3, 6]. Urea itself is universal fertilizer, it can be applied both before seeding and during vegetation, soil and foliar feed, it can be applied to every plant on different soils, except strongly acidic and basic soils or freshly calcified, in which urea transformation is highly limited.

Ability to creation by the urea many intermolecular connections (so called adducts) not only with organic compounds, but with inorganic as well, like salts, acids, hydrogen peroxide and sulphur trioxide, is known. Researches involving net adducts of urea with inorganic compounds were more developed in moment, in which it was proved, that some of them with success can be applied as fertilizers [7, 8]. Some of connections are existing only in solutions and it is not possible to obtain them in solid state, because they decompose during precipitate from solution [5, 9]. From urea adducts nitrogen is released gradually, in rate which can be adjusted to individual needs of specific plant [5, 9].

Plants for their proper growth need to deliver all nutrients. Sulphur – secondary nutrient in fertilizer provides effective collection and process nitrogen into crop. It supports protein formation, takes part in reaction, which has influence on increase content of sugars and fats in plants. It is present in volatile compounds and oils, which give significant taste and smell (garlic, onion, leek, mustard). Moreover, sulphur application increase plants resistance on action of pests, diseases and other factors, like drought, cold or heavy metals [10]. Pro ecological actions of chemical and energetic industry, which decreases sulphur emission to the atmosphere, decrease using of natural fertilizers and cultivation of plants with high crops and higher sulphur demand (rapeseed, onion, garlic, cabbages) – caused deficiency of sulphur in soil [10–14]. Additionally sulphur is easily washed from soil (30–70kg from ha), and crops take 15–60kg from ha by year [10, 13].

Sulphur's metabolism in plants is strictly connected with nitrogen metabolism and insufficient amount of one cause stopping action of second. Deficiency 1 kg of sulphur in soil limits collection 10kg of nitrogen [12, 15, 16], sometimes even 15kg [13]. Symptoms of sulphur deficiency are intensified in case of high nitrogen fertilization levels. Many plant are able to collect nitrogen with higher amount than it is needed and they can store them in form of nitrates, nitrites and nitrosoamines [16]. They aren't dangerous for plants, but for people who eat them.

Insufficiency of sulphur in plant production became one of the serious problems of modern agriculture, specific in north Europe [13, 14, 16]. Due to the fact, that around 60% of soils in Poland have low sulphur content it is necessary to fertilize using this element [12]. The only one form which can be assimilated by plants is sulphate form [10, 13, 15, 16]. Plant collect it in form of the  $\text{SO}_4^{2-}$  with pH range between 4–7. Other forms of sulphur have to be oxidized to sulphates or reduced to sulphides before they will be used in biosynthesis reaction of sulphur aminoacids [4, 12, 13, 17]. Maximum of sulphur collection is present in early stages of plant vegetation, to the bloom stage [10].

Lack of certain nutrients is often observed straight on a field. Damaged leaves make possibility to observe reasons of nutrient insufficiency [10, 12]. Components like nitrogen, potassium and magnesium are mobile in plant, that means that they move good enough to younger leaves, so that symptoms of nutrients deficiencies would be present at older leaves. Plants seem to be faded, chlorosis can be observed. In other way deficiency of sulphur can be observed. It is collected mainly by the root system and it is transported upwards. Sulphur is relatively static in plant, so that symptoms like chlorosis or necrosis are mainly present at young leaves [12, 13]. Deficiency of

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sulphur in soils can be mainly seen in plants which need bigger amount of sulphur – Brassicaceae (rapeseed, cabbage), Fabaceae and some vegetables (leek, onion) [10]. Too small amount of sulphur cause characteristic and easily seen symptoms and hidden effects without symptoms, but with negative impact on crops [13].

### Nitrogen and nitrogen-sulphur liquid fertilizers RSM<sup>®</sup>, Pulaska<sup>®</sup> and RSM<sup>®</sup>S

During last year increase of interest about nitrogen and sulphur contain fertilizers is observed. In nitrogen liquid fertilizers applied nowadays in Poland are highly concentrated solutions saltpetre-urea RSM<sup>®</sup>, sell in three types (28%N, 30%N, 32%N) fitted to different transport and storage temperatures. (The most often we can buy RSM<sup>®</sup> with total nitrogen concentration at levels of 32%, nevertheless due to the best physicochemical characteristics it is preferable to use RSM<sup>®</sup> with 28% nitrogen content.) RSM<sup>®</sup> are produced from concentrated solutions of ammonium saltpetre and urea, collected from production installations. After mixing these two components water is added to obtain proper concentration and corrosion inhibitors, which are environmentally friendly, are added [4]. RSM<sup>®</sup> fertilizers contains three forms of nitrogen with suitable proportions, which secures constant intake during vegetation. Fertilizer acting is fast and long-lasting (liquid form improves nutrient assimilation by plants) [18].

Fertilizers with sulphur are wanted at the market and safe in usage. Sulphur in composition contain liquid fertilizers – Pulaska<sup>®</sup> and RSM<sup>®</sup>S. These innovative mineral fertilizers NS type are delivering at one application both nitrogen and sulphur. Pulaska<sup>®</sup> is liquid nitrogen fertilizer with addition of sulphur (in sulphate form), obtained by mixing solutions of urea and ammonium sulphate (from caprolactam installation). It contains nitrogen in two forms – amid and ammonium. It can be used for autonomic application in agriculture, but also together with liquid nitrogen fertilizers of RSM<sup>®</sup> type. RSM<sup>®</sup>S is liquid nitrogen fertilizer with addition of sulphur, obtained on a base RSM<sup>®</sup> and urea solution with ammonium sulphate. It is obtained by mixing RSM<sup>®</sup>32 with Pulaska<sup>®</sup> with ratio 1:1. Presence of three nitrogen compounds, which are urea, ammonium nitrate and ammonium sulphate allows to eliminate disadvantages both urea (nitrogen losses in ammonium form), and ammonium sulphate (acidic character of fertilizer) used as separate fertilizers. Both fertilizers – Pulaska<sup>®</sup> and RSM<sup>®</sup>S can be applied on every type of soils, under every plant and vegetables as well. In specific, they are recommended to use before seeding and during vegetation of rapeseed, corn and bulb plants. Thanks to sulphur concentration they increase collecting and usage of nitrogen present in fertilizer. These are soil fertilizers used by technique of bigdroplet spraying or flooding. Size of droplets >300um (bigdroplets) eliminates risk of burning plants and ability to washing away with wind. They should be stored in temperature higher than start of crystallization temperature [18].

RSM<sup>®</sup>, Pulaska<sup>®</sup> and RSM<sup>®</sup>S fertilizers are compared in Table 1. They are fertilizers of high quality, signed by „WE fertilizer” symbol [6]. From agricultural point of view nitrogen-sulphur fertilizer production based on urea and ammonium sulphate is profitable, because using mixture of RSM<sup>®</sup> and Pulaska<sup>®</sup> fertilizers admits to fit fertilizer formula directly to nutrient needs of plants [4, 17].

In years 2008–2009 research was made, which primary purpose was comparison between effects of fertilization using solid fertilizers and liquid nitrogen fertilizers and liquid nitrogen-sulphur fertilizers (applied were urea, urea+S, RSM<sup>®</sup> and RSM<sup>®</sup>S) and their influence on size and quality of winter rapeseed [17]. Maximum crop of winter rapeseed and fat crop in seeds was obtained using RSM<sup>®</sup>S. In years 2009–2012 field tests including effects of fertilization using solid and liquid nitrogen and liquid nitrogen-sulphur fertilizers (applied were urea, urea+S, RSM<sup>®</sup> and RSM<sup>®</sup>S) and their influence on size of corn's crop were made [4]. Maximum crop was obtained again using RSM<sup>®</sup>S.

Table 1

Characteristic of liquid fertilizer type RSM<sup>®</sup>, Pulaska<sup>®</sup> and RSM<sup>®</sup>S

	RSM <sup>®</sup> 28	RSM <sup>®</sup> 30	RSM <sup>®</sup> 32	Pulaska <sup>®</sup>	RSM <sup>®</sup> S
Total nitrogen content	28%(±0.6)	30%(±0.6)	32%(±0.6)	20%(±0.6)	26%(±0.6)
Content of nitrogen in ammonium and nitrate summed	14%(±0.6)	15%(±0.6)	16%(±0.6)		
Nitrogen from ammonium content				5.3%(±0.6)	6.6%(±0.6)
Nitrogen from amid content	complementary	complementary	complementary	complementary	15.2%(±0.6)
Nitrogen from nitrate content				-	complementary
Sulphur content	-	-	-	6%(±0.36), 15% of SO <sub>3</sub>	3%(±0.36), 7.5% of SO <sub>3</sub>
Density in 20°C	1.28(±0.01) kg/dm <sup>3</sup>	1.30(±0.01) kg/dm <sup>3</sup>	1.32(±0.01) kg/dm <sup>3</sup>	approx. 1.25kg/dm <sup>3</sup>	approx. 1.28kg/dm <sup>3</sup>
Crystallization temperature	(-17)°C	(-9)°C	0°C	2°C	(-7)°C
pH	7(±0.5)	7(±0.5)	7(±0.5)	approx. 6.0	approx. 6.0
Biuret content, no more than	0.5%	0.5%	0.5%	0.38%	0.5%

### Ammonium thiosulfate – source of nitrogen and sulphur in liquid fertilizers

Thiosulphate ion S<sub>2</sub>O<sub>3</sub><sup>2-</sup> is structural analog of sulphate, in which one atom of oxygen is replaced by sulphur. This is why it contains sulphur on two different oxidation state: S<sup>6+</sup> and S<sup>2-</sup>. Chemical behaviour of thiosulphate is dominated by the activity of sulphide atom of sulphur, from which it has its reductive and complexing abilities [19].

Sulphur present in thiosulphate is decomposed in soil on sulphate and colloidal sulphur. Sulphates are easy digestible and also easy washed from soil. Colloidal sulphur with help of microorganisms is converted into sulphates during vegetation period of plants and it becomes a source of quick digestible sulphur [20]. Thiosulphates in application with urea or RSM<sup>®</sup> are also inhibitors of urease which cause nitrogen losses by ammonium evaporation [21]. If ratio N:S 7:1 is used, it is possible to attain around 50% reduction of nitrogen losses [22]. Thanks to ability to create complex ions with many metals, with zinc in particular, and due to lowering pH of soil thiosulphates make easy digestion of some of microelements [23]. They also support action of pesticides. As well as, it is known, that they have antifungal abilities [20].

Thiosulphates are characterised by high water solubility, definitely bigger than sulphates what allows to obtain fertilizers with higher nutrient content [24]. (For example in 0°C solubility of ammonium sulphate is 70.2g/100ml of water, while for ammonium thiosulphate 135g/100ml; at 20°C it is 75.1g/100ml and 173g/100ml respectively [25]).

Ammonium thiosulphate liquid fertilizer formula 12-0-0 (26%S) or its mixtures with RSM<sup>®</sup> fertilizer are used for many years with success in for example USA [20]. 60% solution of ammonium thiosulphate (ATS) is excellent source of sulphur for liquid fertilization; it is compatible with another liquid fertilizers and pesticides [24]. This is uniquely precious thanks to connection of seeding, hydration, fertilization and pesticide application into one agrochemical operation ability, what causes lowering costs of plant production.

Using ammonium thiosulphate as sulphur ingredient in fertilizer it is possible to obtain much more attractive compositions of liquid fertilizers. For example, mixing RSM<sup>®</sup>32 with ATS in 1:4 weight ratio one may obtain N(S) 15(20) [24]. Lack of domestic production of ammonium thiosulphate (ATS) is an obstacle in starting production of fertilizers of these type.

In application of ammonium thiosulphate as liquid fertilizer element it should be noted, that pH of solutions should not be lower than 6, because of the ATS decomposition in these conditions. According to researches [16] it was stated, that in these conditions speed of urea hydrolysis is high enough to rapid pH increase in solution and one should not be afraid of serious decomposition of  $S_2O_3^{2-}$  ions. Our own researches stated [24], that thiosulphates solutions are stable in alkali conditions, but rapid acidification/lowering pH below 6 causes precipitation of atomic colloidal sulphur.

### Summary

Considerable deficiency of sulphur in soils would still increase due to emission restriction of  $SO_2$  and many other factors. According to fact, sulphur is essential element of growth and plant functioning its deficiency can cause serious economic problems. Simultaneously delivering proper amount of sulphur to plants has also ecological role, because its deficiency limits usage of nitrogen in fertilizers, what in consequence cause losses of that element.

Liquid fertilizing, which allows deliverance of easy digestible nutrient and combining irrigation, fertilization and plant protection into one agrotechnical operation is consistent with good agricultural practise. Union integrated agricultural plant production system has as a purpose obtaining high and healthy crops with limited usage of fertilizers and pesticides and minimal negative impact on natural environment. Due to the fact, that deficiency of sulphur in plants' cells increase their susceptibility on stress factors – diseases, droughts, temperatures, pathogens – application of fertilizers containing sulphur is agrotechnical operation improving health of plants and quality of products, then, fulfils sustainable agriculture and integral plant production assumptions.

Fertilizers Pulaska® and RSM®S are modern, long-operating liquid nitrogen-sulphur fertilizers. In its composition they have different forms of nitrogen, in particular RSM®S, which contains nitrogen in three different states and easy-accessible sulphate sulphur. Presence of that forms in one fertilizer allows to satisfy needs of every plant in respect to sulphur and nitrogen, and proper proportions guarantees constant access to nutrients during whole vegetation process. Due to the sulphur presence both fertilizers increase immunity on diseases and pests, and way of fertilization – spraying – satisfy even distribution of nutrients, what influence significantly effectiveness of fertilization and decrease nitrogen losses. Liquid form of fertilizers allows high efficiency also in case of too low humidity in soil and gives opportunity to use pesticides simultaneously. High effectiveness of liquid nitrogen-sulphur fertilizers is shown in field tests.

Another type of liquid fertilizers are thiosulphates solutions. Ammonium thiosulphate (ATS) as fertilizer containing nitrogen and sulphur is known for very long time. ATS solution with composition 12–0–26(S) belongs to liquid fertilizers with high sulphur content. Advantage of thiosulphates in liquid fertilization aspect is higher solubility in water than the others, cheaper sulphur sources, sulphates for example. It allows obtaining fertilizers with higher concentration of nutrients. Additionally thiosulphates decrease nitrogen losses due to inhibition of urease and nitrification processes. Liquid fertilizer allowing elastic approach to fertilizing (fitting fertilizer composition to plant needs) has to be compatible with other components, that means it has to have good miscibility, has constant composition or lack of sliming precipitation creation. 60% ammonium thiosulphate solution with 12% of nitrogen and 26% of sulphur mixes in every ratio with RSM® solution. It gives lot of opportunities of liquid, multicomponent fertilizers with high amount of digestible sulphur creation.

Nowadays in Poland ammonium thiosulphate, which is hard to reach and expensive, as nitrogen fertilizer solution N(S) is applied mainly in fruit-farming for thinning out fruit trees. Domestic production of mixtures of ammonium thiosulphate with liquid nitrogen fertilizers of RSM® type would be reasonable in Poland.

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