Sulphur Balance in Agroecosystem

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Abstract

This field study shows how different crops and soil treatments with different nitrogen fertilization levels affect sulphur balance. Sulphur deposition, leaching through soil and water seepage, availability and uptake by crops, effects on crop yield and losses were investigated. The research was conducted on a field trial from 1996 to 2014 in temperate continental climate on Stagnosols. The soil was treated 10 times with mineral nitrogen fertilizers in an ascending doses from 0 to 300 kg N ha^{-1} and additional two 250 kg N ha^{-1} treatments, one with phosphogypsum and one with zeolite tuff and $CaCO_3$. Drainpipes and lysimeters were installed to collect water samples and measure the effects of N doses, amendments and precipitation on sulphur losses. Average annual sulphur losses were from 4.9 to 68.7 kg ha^{-}1 through drainage water, and from 1.5 to 24.9 kg ha^{-1} through lysimeter water. Depending on a crop, year and yield, average crop losses ranged from minimal 2.8 kg ha^{-1} in winter wheat up to 17.6 kg ha^{-1} in oilseed rape. Average total S content in soil varied from 882 to 1764 kg ha^{-1}. Overall agroecosystem S balance between input and output, calculated for all crops and all treatments was positive only in the treatment with phosphogypsum for winter wheat, corn and oilseed rape. Water shortage in 2011 caused positive S balance for soybean in other treatments too, not only in the treatment where phosphogypsum was applied.

Key words: phosphogypsum application, mineral nitrogen fertilization, crops, drainage and lysimeter water, soil, atmospheric deposition

Introduction

The presence of sulphur in the soil is in the form of organic compounds, sulphides (S^{-}), elemental sulphur (S^{0}) and sulphate (SO_4^{2-}). According to Isaac, Kerber (1971), a normal concentration range of total sulphur in soils is from 500 mg kg^{-1} to 4000 mg kg^{-1}. Total sulphur in mineral soils may range from < 20 mg kg^{-1} in sandy soils up to > 600 mg kg^{-1} in heavy texture soils. Organic soils may contain as much as 5000 mg kg^{-1} (Zgorelec et al., 2012). Most soils, however, contain between 100 and 500 mg kg^{-1} of sulphur. Elemental sulphur must be oxidized by soil bacteria to SO_4^{2-} before becoming plant available. Warm temperatures and good moisture and aeration are required for S-oxidizing bacteria to work. Sulphur oxidation is minimal at soil temperatures that are less than 10 °C. Even at 23 °C, sulphur oxidation rate is about 15 % of the oxidation taking place at 29 °C, therefore the peak rates of sulphur oxidation do not occur until late spring (Camberato et al., 2012). After sulphur is oxidized into sulphate, plants absorb it and it is converted into amino acids cysteine and methionine. These amino acids are the building blocks of sulphur based proteins and other key role compounds in multiple plant functions like photosynthesis, disease resistance and plant growth. Because of its important roles, optimizing the sulphur nutrition of crops is key to achieve top crop yields and quality. Since the early 1960s, the research on the response of crops to sulphur expanded over years and covered a large number of crops, soils and fertilizers. By 1990, it was clear that sulphur deficiencies were becoming increasingly important as evidenced not only by soil analyses but, more importantly, by the results of field research which documented effects of sulphur application to about 30 crops under various weather conditions and on various types of soil (Tandon, 2011). Sulphate leaching may be subject to considerable variations caused by differences of pH in the soil. Soils with lower pH value have better adsorption of sulphur. Eriksen et al. (2002) investigated sulphate leaching and S balance in organic cereal crop rotation. It was found that sulphate leaching was quantitatively the most important item of the S balance. On some treatments of nitrogen fertilization, FG was used. In the process of decomposition of raw phosphate with sulfuric acid which was used for phosphoric acid production, FG occurs as by-product. Vyshpolsky et al. (2010) conducted a two-year experiment on the plots of cotton on heavy clay with a 1% content of organic matter, and by applying FG the efficiency of irrigation was increased and water retention around the root system improved.

Given the fact that sulphur has been widely recognized as the fourth major plant nutrient after nitrogen, phosphorus and potassium and cannot do the job alone than it must work as a member of the plant nutrition team, assessment of the sulphur balance in this experiment is significant and gives an idea of the sulphur cycle in the soil-fertilizer-plant system. Sulphur addition with phosphogypsum, amelioration with zeolite tuff and $CaCO_3$ and fertilization with different nitrogen levels allows the role of sulphur and nitrogen to be monitored for growth, yield and crop quality, to be assessed the impact of pH on sulphur mobility and extraction, and of the plants, as well as sulphur adsorption from the soil. On the other hand, an anthropogenic impact through human influence on agriculture affects the ecosystem in general. Excessive accumulation of sulphur in the soil represents an environmental problem through its deposition on the soil and it's leaching in the lower layers of the soil which can lead to soil contamination. Therefore, it is important for us to explore the ecosystem, to have the agroecosystem and to implement management of plant nutrition, but in the same time to protect the ecosystem. Accordingly, the main goal was to determine sulphate losses and gains in a field experiment with a certain soil type and climate including different nitrogen fertilization doses and to valorise and determine an overall sulphur balance in agroecosystem (soil, planted crops, water and air deposition).

Materials and Methods

This research was conducted from 1996 to 2014 in central part of Croatia in Popovaca (Figure 1) where intensive agriculture occurred. Selected location is on the border with Park of nature Lonjsko polje which has natural water retention and needs to be protected. According to Skoric (1986), the type of soil was plain, deep, district drained pseudogley (Stagnosols); deep, district pseudogley according to Husnjak (2014), and district Stagnosols according to FAO, WRB (2006). Excessive humidity was present in the upper part of profile, because of rainfall, and ground water occurred below 175 cm of depth. The soil was slightly porous throughout its depth, with mediocre capacity for water. Air capacity was very small. The soil was classified as acid (~ 4.5) (Zgorelec et al., 2013). The compaction of soil in the field trial was medium in arable and eluvial, and higher in deeper horizons. Because of these characteristics, drainage pipes were conducted on the surface. The characteristic of the area is continental climate with mean annual temperature of 10.7 °C and average rainfall of 865 mm (Zgorelec et al., 2013).

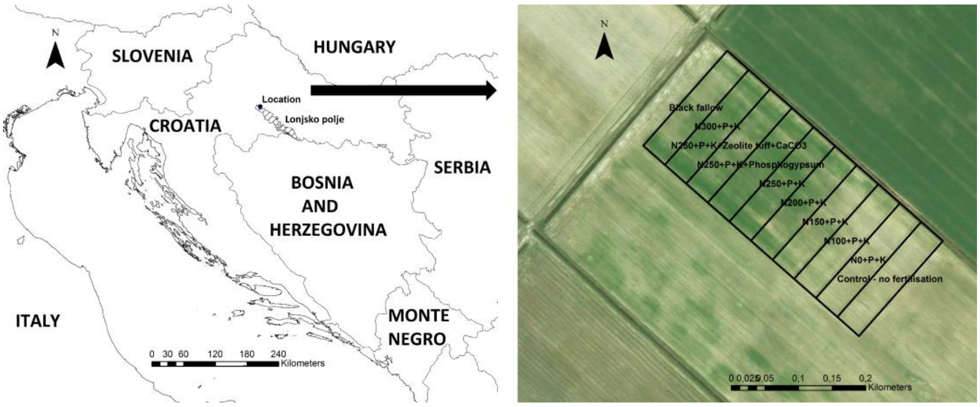


Figure 1. *Study location*

The trial consisted of 10 treatments with different mineral nitrogen doses. Table 1 presents treatments with different fertilization doses and application time during the experiment.

Table 1. *Fertilization (kg ha^{-1}) treatments and application time (per year)*

Treatment	Fertilization (kg ha^{-1})	Application period/year
I.	Control - no fertilization	-
II.	0 N + 120 P + 180 K	every year
III.	100 N + 120 P + 180 K	every year
IV.	150 N + 120 P + 180 K	every year
V.	200 N + 120 P + 180 K	every year
VI.	250 N + 120 P + 180 K	every year
VII.	250 N + 120 P + 180 K + **12 t ha^{-1} Phosphogypsum (FG)**	1996, 2002 and 2009
VIII.	250 N + 120 P + 180 K + **3 t ha^{-1} Zeolite tuff + $CaCO_3$ (+Dolomite)**	1996, 1999, 2002, 2009, (+2013)
IX.	300 N + 120 P + 180 K	every year
X.	Black fallow	-

All agro technical measures including tillage, herbicide applications etc. were identical in all trial treatments.

Soil samples were taken three times per year (2010), at the beginning of the growing season, during the growing season and immediately after the harvest of certain crops (winter wheat). Samples were taken from each treatment at surface horizon (0 – 30 cm). Total S in soil (kg ha^{-1}) was calculated from the measured concentration (mg kg^{-1}) of S in soil and soil bulk density (1.4 g cm^{-3}) determined in arable horizon (0-30 cm). The measurement for total S content in plant material started in 2006. The losses of total sulphur in kg ha^{-1} were calculated from measured concentration of total sulphur (mg kg^{-1}) in plants and from measured crop yield in kg ha^{-1}. Lysimeters and drainpipes were installed as described in Zgorelec et al. (2013); Vukovic et al. (2008) and Sestak et al. (2014). In drainage and lysimeter water, S-SO_4 concentration in water (mg L^{-1}) and drainage discharge (L day^{-1}) are taken to calculate sulphur losses in kg ha^{-1} (Figure 2 and Figure 3). Table 2 presents parameters determined in soil, plant material and water including determination methods.

Table 2. *Parameters determined in soil, plant material and water including determination methods*

SOIL	Sampling, transport and storage	Soil quality - Sampling - Guidance on sampling techniques	HRN ISO 10381-1 to 8 (2002-2006)
	drying/grinding/ sieving/homogenizing	Soil samples preparation for physical and chemical analysis	HRN ISO 11464:2006
	pH	Soil quality - Determination of pH in 0.01 M $CaCl_2$, 1 M KCl and H_2O at 1:2.5 (w/v) ratio	HRN ISO 10390:2004
	TS (% DM; g kg^{-1})	Soil quality - Determination of total sulphur with dry combustion method	HRN ISO 15178:2005
PLANT	sampling	Cereals and cereal products - sampling	ISO 24333:2009
	drying/grinding/ sieving/homogenizing	Sample preparation for analysis of inorganic chemical composition	modified HRN ISO 11464:2006
	TS (% DM; g kg^{-1})	Determination of total sulphur with dry combustion method	modified HRN ISO 15178:2005
WATER	F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-} and PO_4^{3-} (mg kg^{-1})	Water quality - Determination of fluorides, chlorides, nitrites, orthophosphates, bromides, nitrates and sulphates with ion liquid chromatography - part 1. Method for water with low contamination	HRN ISO 10304-1:1998

The crops grown in crop rotation are presented in Table 3. Considering that measurement of total S content in plant material started in 2006, the collected, analysed and taken into balance account data are marked with the bold text in Table 3.

Table 3. *Cultivated crops during the experiment*

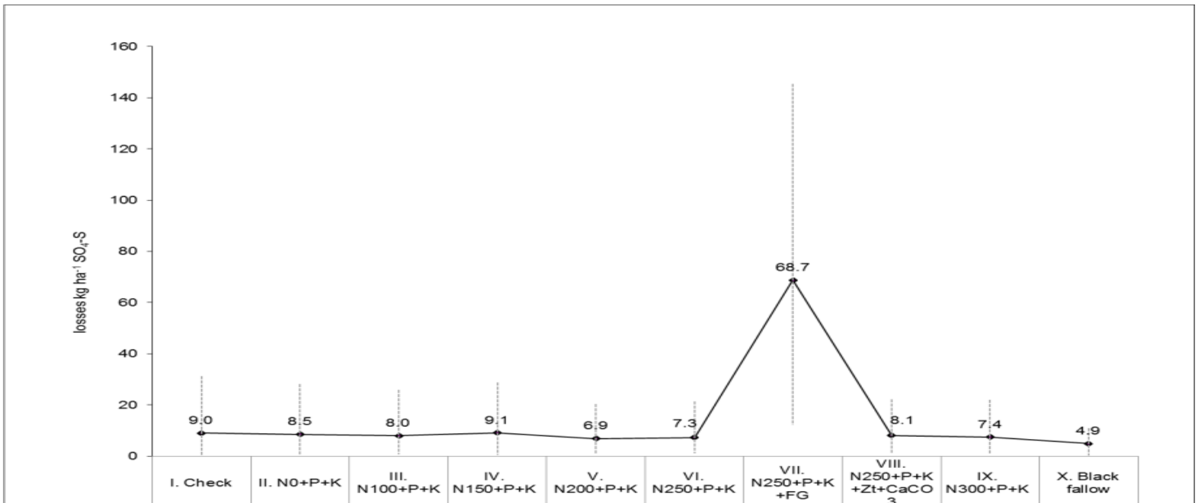
Crop	Vegetation year
Corn (Zea Mays L.)	1996, 1999, 2004, **2007**, **2013**
Oilseed rape (Brassica napus L.)	1998, 2001, **2009**
Soybean (Glycine L. max)	2002, 2005, **2011**
Winter wheat (Triticum aestivum L.)	1997, 2000, 2003, **2006**, **2008**, **2010**, **2012**

In this research, quality assessment and control were included. Analytical laboratory of Department of General Agronomy integrates Internal and External quality control. Internal quality control is carried out on a daily basis and involves checking the accuracy and repeatability of measurements by analysing the reference material (RM) and doing a minimum of three consecutive measurements. RM samples from different inter laboratory trials were used in the laboratory: ISE (International Soil analytical Exchange Programme organized by WEPAL [Wageningen Evaluating Programs for Analytical Laboratories, organized by Soil Chemistry and Chemical Soil Quality group, Department of Soil Quality of Wageningen University (WU), Netherlands]) for soil, IPE (International Plant analytical Exchange Programme organized by WEPAL) for plant and IFA (Water Proficiency Testing scheme organized by BOKU, Department for Agrobiotechnology, IFA-Tulln, Canter for Analytical Chemistry) for water. External quality control is performed once a year where it participates in various plant, soil and water field testing programs.

Results and Discussion

Drainage water

Figure 2 shows minimum, maximum and average annual SO_4-S losses through drainage water which are calculated for each treatment for the period between 1996 and 2014. If treatments VI, VII and VIII, to which the same doses of N, P and K were applied, are compared and if the fact that 335 kg ha^{-1} of S was annually applied through FG in treatment VII, is taken into consideration, the average loss was the highest in treatment with FG (VII), which is 9.4 times higher than the average loss in treatment VI leads to the conclusion that losses of S due to FG application were 61.4 kg ha^{-1}. Furthermore, we revealed that 18.3 % of applied S (in treatment VII) was drained, while the rest was adsorbed by the plant or the soil. Accordingly, Monaghan et al. (2000) investigated nutrient losses in drainage water where leaching losses of sulphate in the 0 N fertilizer treatment was 1.9 times higher (17 kg ha^{-1}) than in this research. In Riley et al. (2002) research, three years experiment recorded total S loss of 34.9 kg ha^{-1}.

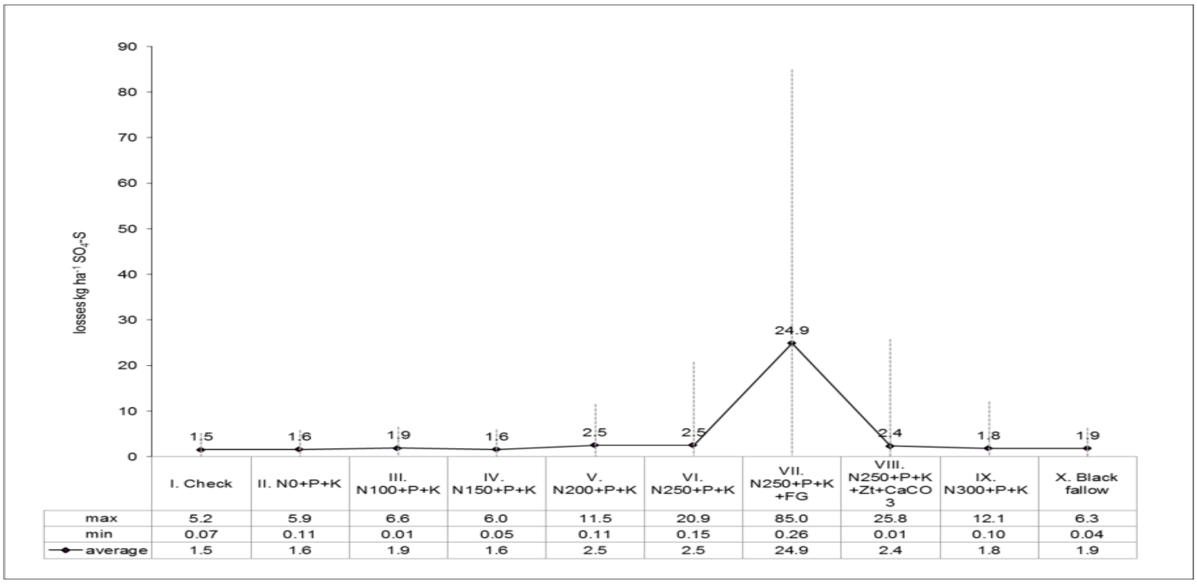


	I. Check	II. N0+P+K	III. N100+P+K	IV. N150+P+K	V. N200+P+K	VI. N250+P+K	VII. N250+P+K +FG	VIII. N250+P+K +Zt+CaCO3	IX. N300+P+K	X. Black fallow
max	31.2	28.1	25.8	28.8	20.3	21.4	145.5	22.2	22.0	10.9
min	0.2	0.4	0.6	0.4	0.9	1.0	12.2	0.8	0.9	0.2
average	9.0	8.5	8.0	9.1	6.9	7.3	68.7	8.1	7.4	4.9

Figure 2. *Average annual SO_4-S losses through drainage water (from 1996 to 2014); n=151*

Lysimeter water

Figure 3 shows minimum, maximum and average annual SO_4-S losses through lysimeters water which were calculated for each treatment for the period from 1996 to 2014. If treatments VI, VII and VIII, to which the same doses of N, P and K were applied, are compared and if the fact that 335 kg ha^{-1} of S was applied annually through FG in treatment VII, is taken into consideration, the average loss was the highest in treatment with FG (VII), which is 9.7 times higher than the average loss in treatment VI meaning that the input of S to water due to FG was 22.4 kg ha^{-1}. The conclusion is that 6.7 % of applied S gets lost through lysimeter water, while the rest is adsorbed in the soil and/or the plant. Eriksen, Askegaard (2000) found that sulphate leaching from an organic dairy crop rotation, on sandy soil was 20 kg ha^{-1} – average of 4 years, equivalent to 60 % of total sulphur input. In this research, average S loss by lysimeter water calculated for all treatments except treatment VII was 2.0 kg ha^{-1}.



	I. Check	II. N0+P+K	III. N100+P+K	IV. N150+P+K	V. N200+P+K	VI. N250+P+K	VII. N250+P+K +FG	VIII. N250+P+K +Zt+CaCO3	IX. N300+P+K	X. Black fallow
max	5.2	5.9	6.6	6.0	11.5	20.9	85.0	25.8	12.1	6.3
min	0.07	0.11	0.01	0.05	0.11	0.15	0.26	0.01	0.10	0.04
average	1.5	1.6	1.9	1.6	2.5	2.5	24.9	2.4	1.8	1.9

Figure 3. *Average annual SO_4-S losses through lysimeter water (from 1996 to 2014); n=124*

Losses of sulphur through crop yields

It is well established that sulphur application not only increases crop yield but also improves crop quality. It improves crop quality in many ways, some of which are: increasing the oil content of seeds, improving nutritional quality of forages by providing a balanced NS ratio, increasing crude protein content, and improving baking quality of wheat (Tandon, 2011). A balanced NS ratio is important because of nitrogen use efficiency, plant vigour, water use efficiency, phosphate use, carbohydrate production and utilization, the rate of grain fill, maturity and many other plant factors. It primarily reflects the complementary relationship that nitrogen and sulphur have in producing plant proteins. On a higher nitrogen fertilization level, the plant uptake of sulphur was higher, because on a high nitrogen level in the soil, sulphur in the soil becomes more mobile, and the plant can easily take it (synergism). The importance of concurrent NS management in wheat was described in Salvagiotti et al. (2009) research. In this research, the highest level of nitrogen fertilizers was applied in treatment IX with 300N + 120P + 180K kg ha^{-1}. Losses through yield were calculated by sulphur content in crop yield. The lowest S losses were observed in winter wheat at treatment with 0N + 120P + 180K kg ha^{-1} (II), and the highest in oilseed rape at treatment with 250N + 120P + 180K kg ha^{-1} + zeolite tuff + $CaCO_3$ (VIII) (Figure 4). The sulphur requirements of different crops vary widely. It is reported by Beeson (1941) that legumes utilize large amounts of sulphur for growth, while cereals and similar crops generally have less requirements of sulphur. The author also revealed that sulphur content in wheat (grain/straw) ranged from 1.7 g kg^{-1} to as high as 4.5 g kg^{-1} in sweet clover. In this research, sulphur was also associated with a higher biological N fixation by legumes. The trend of increase in S content in grain due to rising mineral N content in the soil was noticed in Figure 4. For example, in soybean, the application of sulphur increased the number of nodules/plant and nodule weight (Gupta, Dubey 1998; Tiwari, Gupta 2006). Whenever the sulphur status of growing plants drops below the critical level which is different for different cultures, the visual symptoms of sulphur deficiency start appearing on the plant, generally in leaves. In many ways, sulphur deficiency symptoms resemble those of N in the early stages in that the leaves become pale-yellow or light green. The appearance of such symptoms itself indicates a serious condition because crop yields can decrease even without the appearance of such symptoms as a result of hidden hunger (Tandon, 2011). In Figure 4 losses of total sulphur through different crop yield are shown respectively (winter wheat, corn, soybean and oilseed rape).

Table 4. *Average sulphur content (g kg^{-1}), annual average yield (t ha^{-1}) and losses of S through yield for all treatments (kg ha^{-1})*

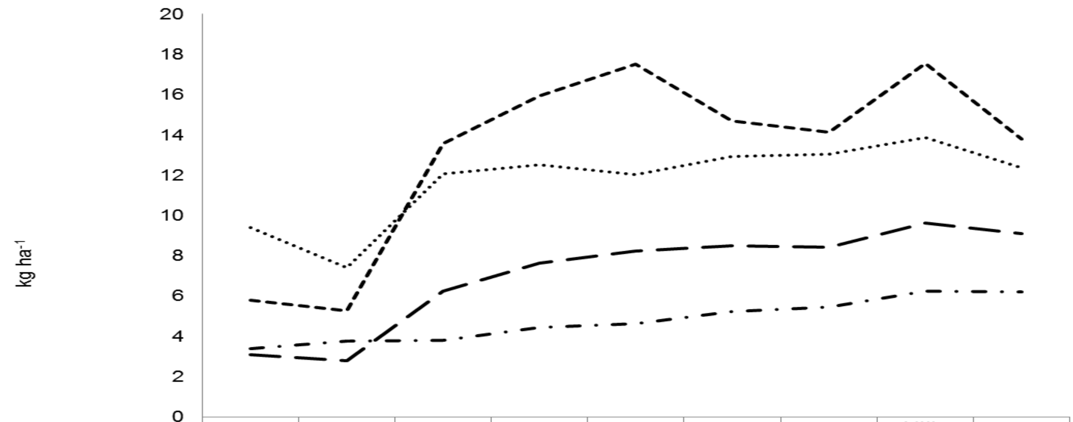
	Winter wheat n=144	**Corn n=72**	**Soybean n=36**	**Oilseed rape n=36**
Average sulphur content in yield, g kg^{-1}	2.0	1.8	1.7	4.9
Annual average yield, t ha^{-1}	3.2	6.7	2.7	2.6
Average losses of S through yield, kg ha^{-1}	6.4	12.1	4.6	12.7

In Table 4, average sulphur content in yield, annual average yield and losses of S through yield were calculated for all treatments and all years. Table 4 clearly shows higher S content in oilseed rape than in other crops, while losses of S in oilseed rape were similar to corn, because of higher yield of corn.Sulphur removal by corn, winter wheat, oilseed rape and soybean are presented on Figure 4. Average losses of S through winter wheat yield (Table 4) is in consistence with Beeson's (1941) meaning that harvesting crops with lower percentage of sulphur content may result in annually removal of 6 kg ha^{-1} of sulphur. Sulphur deficiency significantly effects the production and quality of winter wheat (McGrath, 2003; Györi, 2005). Without adequate sulphur, crops cannot reach their full potential in terms of yield, quality or protein content; nor can they make efficient use of applied nitrogen (Sahota, 2006). Eriksen et al. (2002) reported that sulphur output by winter wheat uptake could be up to 4 kg ha^{-1} depending on year and soil type.

According to this research, in Camberato, Casteel (2017) research about 11 kg S ha^{-1} is removed by corn. The research of sulphur application to corn and soybean crops in Iowa revealed that the combined S supply from soil profile, sulphate, atmospheric deposition, crop residue and organic matter mineralization fulfil corn requirements for sulphur (Sawyer et al., 2002).

For soybean, sulphur requirement is higher especially than in many other crops (Akter et al., 2013). Considering that fact, losses in this research are low compared with other investigated crops (corn, winter wheat and oilseed rape). Received losses can be attributed to yield, which was considerably lower in 2011 due to the intense drought. In Lamond (1997) research, sulphur removal by soybean grain was 13 kg ha^{-1}.

In Eriksen, Mortensen (1999) research, removal of S by oilseed rape was 3.6 and 3.0 kg ha^{-1}, respectively. Oilseed rape has a high demand for sulphur compared with cereals, with approximately 16 kg of sulphur required to produce each tone of seed (HGCA, 1998). Consequently, oilseed rape is particularly sensitive to any shortfall in sulphur supply.



	I. Control	II. N0+P+K	III. N100+P +K	IV. N150+P +K	V. N200+P +K	VI. N250+P +K	VII. N250+P +K+FG	VIII. N250+P +K+Zt+ CaCO3	IX. N300+P +K
corn; n=8	9.4	7.4	12.1	12.5	12.0	12.9	13.0	13.9	12.4
winter wheat; n=16	3.1	2.8	6.3	7.6	8.2	8.5	8.4	9.6	9.1
oilseed rape; n=4	5.8	5.3	13.6	16.0	17.5	14.7	14.1	17.6	13.8
soybean; n=4	3.4	3.8	3.8	4.5	4.6	5.2	5.5	6.2	6.2

Figure 4. *Losses of sulphur through crops yield/grain (corn, n=8; winter wheat, n=16; oilseed rape, n=4; soybean, n=4)*

Sulphur content in soil

The main source of S for plants originates from soil. According to Yang et al. (2007), Kotkova et al. (2008), and Förster et al. (2009), the total soil S content depends on fertilizer types applied (mineral or organic manure), and changes in soils have been found to be proportional to the amount of organic residues added. As it is written in the introduction, a normal concentration range of total S content in soils could range from 2 100 kg ha^{-1} to 16 800 kg ha^{-1}, while in this study the range was from 882 kg ha^{-1} in control treatment (I), to 1764 kg ha^{-1} in 250 kg N ha^{-1} on FG variant (VII) (Figure 5), in soil layer 0 – 30 cm. In total, 36 000 kg FG ha^{-1} was applied three times every six years, i.e. 12 000 kg FG ha^{-1} per dose, on treatment VII. Accordingly, the S content that was applied in this study for a total period was 6 698 kg S ha^{-1}, or 335 kg S ha^{-1} per year. If we compare treatments VI and VII, on which were applied the same doses of NPK but they differ in FG, we observed 462 kg ha^{-1} more S in the soil on treatment VII with FG than on treatment VI without FG. Considering that FG contains S, it can be added through the FG application where the exact concentration of S must be determined according to its leaching tendency. In a long-term field experiment conducted by Yang et al. (2007), total S ranged from 1392 kg ha^{-1} in the control without fertilizer application to 1808 kg ha^{-1} in the treatment with farmyard manure. In the plots receiving either NK or NPKS fertilizers for more than 80 years, no significant accumulation of total S, as compared with the control, could be detected.

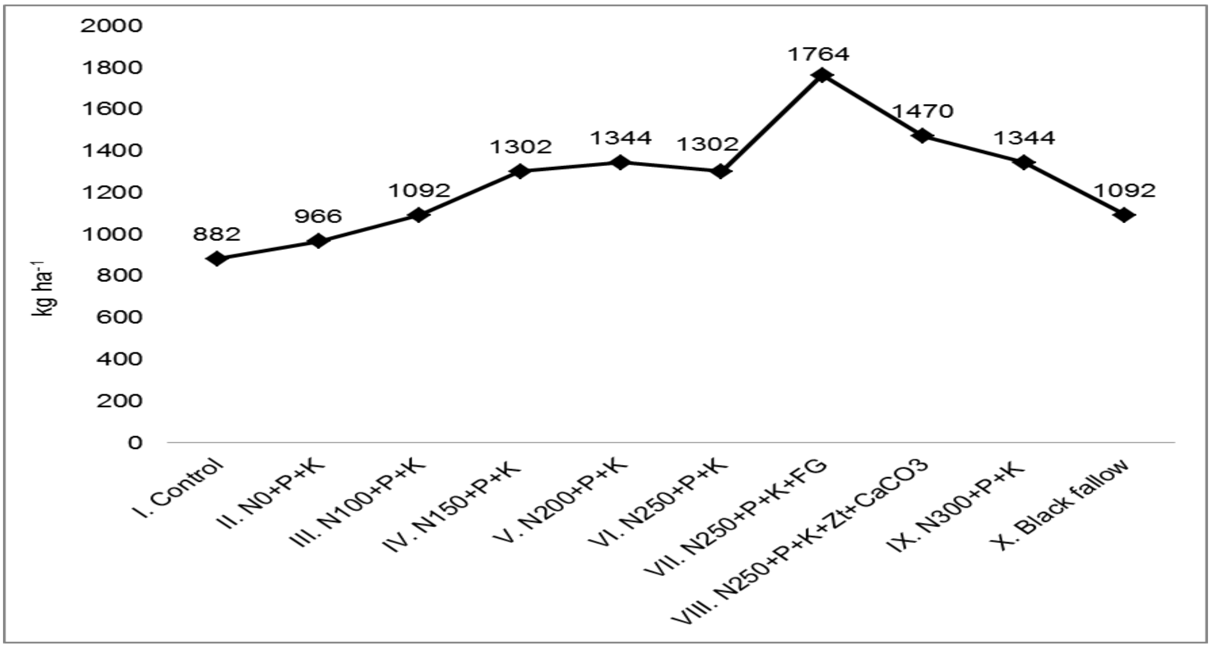


Figure 5. *Average sulphur content in soil*

Sulphur wet deposition through trial period

Deposition of sulphur compounds is considered a major environmental issue (pollutant) – especially in Europe, where its effects were first observed (Walaszek, 2013). Due to technological development in industry and switching fuels from coal to oil and gas, emissions of oxidized sulphur dropped by 45 % over the last few decades. The removal of pollutants from the atmosphere can occur in one of two ways: by wet deposition or dry deposition (Fagerli, 2008; Giannitrapani, 2006). Erisman et al. (2005) estimated that about 80 % of pollutants deposited in Europe are subject to wet deposition. Wet deposition is a process of washing out pollutants from the air by precipitation or cloud droplets (Walaszek, 2013) and may cause natural vegetation damage (Bytnerowicz et al., 2007), soil and water acidification (Sullivan et al., 2005; Zhao et al., 2009) and water eutrophication (Camargo, Alonso 2006). As it stands in Hu et al. (2005) current inputs of S from atmospheric deposition are less than 10 kg ha^{-1} in most Western European countries. Annual wet deposition of $S-SO_4^{2-}$ at measuring station Bilogora, which is the nearest to the field trial ranged from 2.6 kg $S-SO_4^{2-}$ ha^{-1} in 2011 to 10.6 kg $S-SO_4^{2-}$ ha^{-1} in 2001 (Statistical Yearbook of Republic of Croatia, 2001 - 2015) and shown on Figure 6. An average deposition through this study was 6.0 $S-SO_4^{2-}ha^{-1}$. Jian et al. (2014) studied atmospheric wet deposition of sulphur in developing and developed areas of South-eastern China and found S deposition in range of 56.02 – 59.06 kg ha^{-1} per year, respectively, surpassing their corresponding critical loads in China which is incomparably higher than in this research. Knights et al. (2000) reported that large S inputs from atmospheric deposition and from sulfate fertilizer did not accumulate as organic and inorganic S in arable soils, but organic S obviously increased after FYM supply.

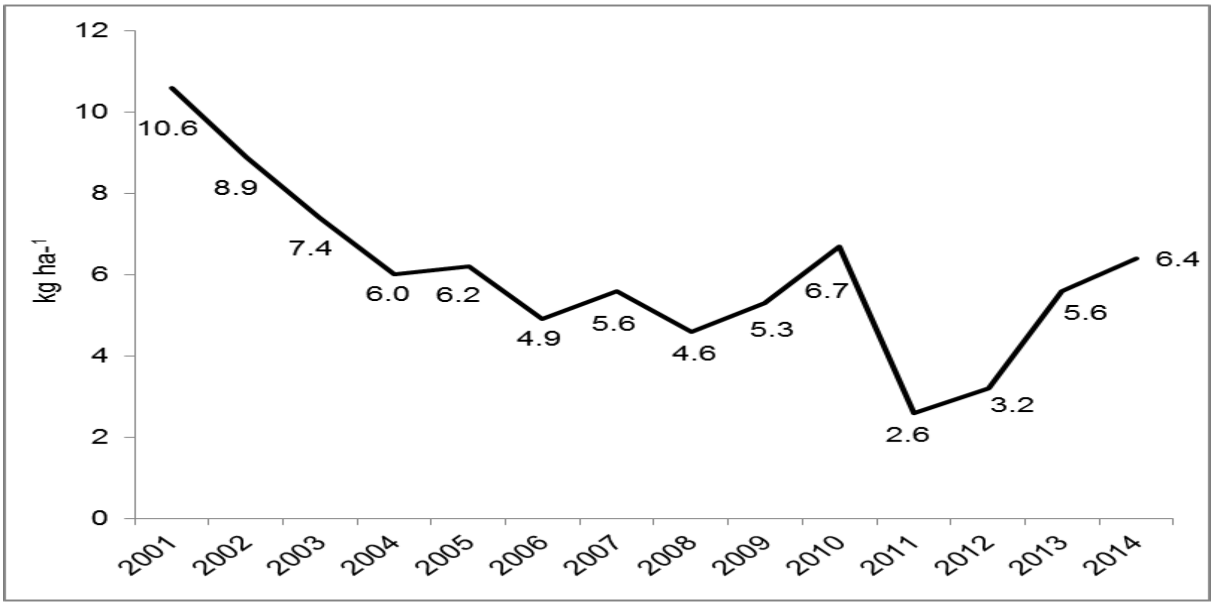


Figure 6. *Annual wet deposition of S-SO_4 from 2001 to 2014 (Source: Statistical Yearbook of Republic of Croatia; 2001 - 2015)*

Sulphur balance through trial period

Sulphur balance for all investigated crops is shown in Table 5. Volatilization from crops or soil was ignored as the amount of sulphur emitted from these sources was considered insignificant (Janzen, Ellert 1998). The input from atmospheric wet deposition was in average 6.0 kg ha^{-1} of S-SO_4. The following year, an average sulphur balance was calculated for specific crops: winter wheat – 2006, 2008, 2010, 2012; corn – 2007, 2013; soybean – 2011; oilseed rape – 2009. The results of average losses of drainage water, lysimeter water and removal through yield as output were shown for every year that was taken in calculation. The average wet deposition and FG application were taken as input value of sulphur. The overall sulphur balance was negative, except in treatment where FG was applied.

Table 5 Average sulphur S-SO_4 (kg ha^{-1}) balance per crop

Variants	Sulphur content in soil (2010) 0-30 cm	Winter wheat,n=4						Corn, n=2					
		Input		Output				Input		Output			
		Wet dep.	Phosphogypsum	Lysimeter	Drainage	Removal through yield	**Balance**	Wet dep.	Phosphogypsum	Lysimeter	Drainage	Removal through yield	**Balance**
I	882	6.0	-	2.1	2.9	3.1	-2.1	6.0	-	8.0	5.4	9.4	-16.9
II	996	6.0	-	4.3	2.5	2.8	-3.6	6.0	-	12.6	4.5	7.4	-18.4
III	1092	6.0	-	4.1	2.8	6.3	-7.1	6.0	-	17.1	6.5	12.1	-29.7
IV	1302	6.0	-	4.2	2.8	7.6	-8.7	6.0	-	13.2	5.8	12.5	-25.5
V	1344	6.0	-	5.0	2.3	8.2	-9.6	6.0	-	20.9	5.9	12.0	-32.8
VI	1302	6.0	-	7.3	2.6	8.5	-12.4	6.0	-	22.3	6.3	12.9	-35.5
VII	1764	6.0	335.0	54.4	29.4	8.4	248.8	6.0	335.0	251.3	68.1	13.0	8.6
VIII	1470	6.0	-	4.6	4.2	9.6	-12.5	6.0	-	14.7	7.0	13.9	-29.5
IX	1344	6.0	-	3.5	1.7	9.1	-8.3	6.0	-	10.9	5.2	12.4	-22.5
X	1092	6.0	-	4.4	2.1	-	-0.5	6.0	-	7.8	5.8	-	-7.6

Variants	Soybean, n=1 (2011)						Oilseed rape, n=1					
	Input		Output				Input		Output			
	Wet dep.	Phosphogypsum	Lysimeter	Drainage	Removal through yield	**Balance**	Wet dep.	Phosphogypsum	Lysimeter	Drainage	Removal through yield	**Balance**
I	6.0	-	-	-	3.4	2.6	6.0	-	3.5	4.8	5.8	-8.1
II	6.0	-	-	-	3.8	2.2	6.0	-	4.2	4.4	5.3	-7.9
III	6.0	-	-	-	3.8	2.2	6.0	-	8.0	3.9	13.6	-19.5
IV	6.0	-	-	-	4.5	1.5	6.0	-	5.0	4.2	16.0	-19.2
V	6.0	-	-	-	4.6	1.4	6.0	-	6.9	3.3	17.5	-21.8
VI	6.0	-	-	-	5.2	0.8	6.0	-	7.1	3.7	14.7	-19.5
VII	6.0	335.0	-	-	5.5	335.5	6.0	335.0	54.7	34.6	14.1	237.6
VIII	6.0	-	-	-	6.2	-0.2	6.0	-	4.5	4.8	17.6	-20.9
IX	6.0	-	-	-	6.2	-0.2	6.0	-	4.5	1.6	13.8	-13.9
X	6.0	-	-	-	-	6.0	6.0	-	4.4	3.4	-	-1.8

Considering this, the lowest value of sulphur balance was determined in corn in treatment VI, with the difference between input and output of sulphur: -35.5 kg ha-1 S-SO4, while the highest level was determined for soybean in treatment VII, where the difference between input and output of sulphur was 335.5 kg ha-1 S-SO4. These could be explained because of high water shortage in 2011, when precipitation was 44 % below average (Zgorelec et al., 2015), and as a result, there was no lysimeter or drainage leaching. Crops with low crop density (corn) had the highest losses through drainage (68.1 kg ha-1– VII) and lysimeter (251.3 kg ha-1– VII) water in comparison to crops a with high crop density (winter wheat, soybean, oilseed rape).

Sulphur balance was analysed in the research of sulphate leaching in an organic crop rotation on sandy soil in Denmark, from 1994 to 1998. Considerable sulphate leaching occurred in the organic crop rotation, and it was equivalent to 60 % of the total input. The conclusion was that immediate sulphur deficiency may not occur, but negative sulphur balance must be expected in the long period (Eriksen, Askegaard 2000). A net negative total sulphur balance of 60 kg ha^{-1} for sorghum, 54 kg ha^{-1} for rice and 68 kg ha^{-1} for sugarcane, especially from non-sulphur applied plots were observed (Singh, 2014) in an experiment on sulphur balance in soils influenced by sulphur carriers and crops in India.

Conclusions

In this research, sulphur addition with FG, amelioration with zeolite tuff and $CaCO_3$ and fertilization with different nitrogen levels addresses important issues related to plant nutrition in especially intensive agriculture on less quality soil and the protection of the environment from pollution. Global S balance in the examined agroecosystem is in deficit except in the FG treatment. The results show that S application through FG is an acceptable and necessary measure for preventing soil degradation (in soils where S balance is in deficit in combination with calcification if soil pH is low). In this study S application resulted in 7.0 % increase of S soil amount, with losses of 6.7 % through lysimeter water, and 18.3 % through drainage water. Long-term FG application could be beneficial however it is necessary to determine the optimal dose of FG for each soil type, climatic conditions and crop, and to find sustainable amount that would increase sulphur content in soil and minimize S leaching because excessive FG application can lead to excessive accumulation of S in soil, which could risk surface water and groundwater loads.

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