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Baltic Sea Region
Baltic Slurry Acidification

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The effect of acidified slurry on soil based on leaching test data (2017–2018)

Valli Loide, Estonian Crop Research Institute

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EU STRATEGY FOR THE BALTIC SEA REGION
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Contents

Summary

Within the EU-project Baltic Slurry Acidification (BSA), leaching tests (micro) with organic fertilisers are performed where the pH is reduced through the addition of sulphuric acid. The trials took place from 2017 to 2018 in Estonia. This report is a summary of the results of these trials.

The leaching test within the BSA project started in 2017 and continued into 2018. The study was carried out in a greenhouse in four replicates of untreated and acidified pig and cattle slurry. In these trials, we used acidic soil *Gleyic Podzoluvisol* (sand 58.8%, label 32.9%, clay 8.3%, humus content 2.7%). Slurry (15 and 45 m^3 ha^{-1}) was used. The crops were cereals and grass during the first year and maize during the second year. Slurry, (15 m^3 ha^{-1}), was spread on the grass pots three times during the vegetation period.

The effect of the leaching of plant nutrients was applied with the slurry was determined by collecting drainage water from the soil and analysing the chemical composition of the water.

The effect of acidified slurry on ryegrass and maize yield was positive, increasing the yield by 40% and 20%, respectively.

The acidified slurry decreased the soil pH of 0.1 units after the use 45 m^3 ha^{-1} of liquid manure. A lesser amount of liquid manure (15 m^3 ha^{-1}) produced no significant acidification.

In the second year, in addition to the acidification of manure, a bacterial preparation was used as an alternative. The preparation was mixed with slurry before the manure was spread. The resulting crop yield was equal to the yield achieved by acidified slurry treatment, while the protein content was lower if the slurry was injected into the soil at a depth of 15 cm. At the same time, N leaching was higher when using a bacterial preparation than when using acidified slurry.

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When adding 45 m^3 ha^{-1} of manure, 225 kg N ha^{-1} and 159 kg S ha^{-1} were applied to the soil. Plants cannot use such amounts in a short time. Therefore, nutritional elements leach from the topsoil with water. Consequently, for environmental protection purposes, it is necessary to ensure that the nutrient amounts applied with slurry correspond to the needs of the plants.

Background

Within the EU-project Baltic Slurry Acidification, trials with slurry were performed in 2016–2018 in the countries around the Baltic Sea. In those trials, the pH of slurry was reduced through the addition of sulphuric acid, and the goal of the trials was to increase knowledge about the effect of slurry acidification on crop nutrient utilisation. In the present report, experiences and results from a leaching test performed in Estonian 2017 and 2018 are presented.

Aim

Acidification of slurry is one of the recommended treatments to reduce NH_3 emissions, with sulphuric acid proven to be the most appropriate substance for acidification. This study explains the impact of acidified slurry on soil and crop through a leaching test. Particular attention needs to be given to calcium-poor soils, which are more likely to suffer from impaired calcium due to SO_4-ion. Sulphate (S-SO_4) leaches readily from the soil.

Materials and methods

In this research, column leaching trials were performed in 2017 and 2018 with acidified and non-acidified slurry. The experiments were conducted in unheated, open greenhouses, aiming at simulating the leaching behaviour of nutrients during the water-soil interaction. In the trials we used an acidic soil *Gleyic Podzoluvisol* (sand 58.8%, silt 32.9, clay 8.3%, humus content 2.7%). Soil material was sourced from the top layer of the field. The basic agrochemical indicators of the test soil were (0–0.2 m): pH_{KCl} 5.5, the content of available calcium (Ca) 1390 mg kg^{-1}, phosphorus (P) 105, potassium (K) 102 and magnesium (Mg) 66 mg kg^{1}, in the Mehlich 3 extract, respectively (Mehlich, 1984); water-soluble sulphate 2.5 mg kg^{-1}.

In the leaching study, plastic bottles were installed vertically upside down and with the bottom cut away (Photo 1, 2); 0.3-m high (diameter 0.12 m) bottles were filled with 1200 g of air-dried soil. The lower opening of the bottle was sealed with a filter paper. For soil analysis (without leaching), the experiment was duplicated using larger vessels and pots, containing 1350 g of air-dry soil. Crops were sown straight into the bottles

The test treatments are shown in Table 1. The experiment was conducted in four replications. The slurry was applied to the grass bottles 1–2 weeks after the cutting of grass. The slurry was acidified with H_2SO_4. The chemical composition of untreated and acidified slurries is presented in Table 2. The average temperature during the 5 days after slurry application time was: – 13.0 °C in 2017 (maximum 24.0 °C, minimum 2 °C) and 16.1 °C, 2018 (maximum 30.5 °C, minimum 1.8 °C).

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Table 1. Test treatments performed in 2017 and 2018.

Treatments, 2017		Treatments, 2018
Barley	Annual ryegrasses	Maize
1. Control (unfertilised)	1. Control (unfertilised)	1. Control (unfertilised)
2. 15 m^3 ha^{-1}PS (pig slurr 25.05	2. 15 m^3 ha^{-1}CS (cattle slurry)25.05	2.45 m^3 ha^{-1}PS+Bacter(14.05) 15 c (PSbac*)
3. 15 m^3ha^{-1}PAS (acidified)	3. 15 m^3ha^{-1}CAS (acidified)	3. 45 m^3 ha^{-1} PS 15cm (PS*)
4. 45 m^3ha^{-1}PS	4. 3x 15 m^3 ha^{-1}CS 25.05; 11.07;15.09	4. 45 m^3 ha^{-1}PS+Bacter 0 cm (PSbac)
5. 45 m^3ha^{-1}PAS	5. 3x 15 m^3ha^{-1}CAS	5. 45 m^3 ha^{-1}PS 0 cm (PS)
	6. 45 m^3ha^{-1}CS	6. 45 m^3 ha^{-1}PAS 0 cm (PAS)
	7. 45 m^3ha^{-1}CAS	

*-Slurry was injected into the soil at a depth 15 cm.

Table 2. The chemical composition of the slurry

Chemical composition	Pig slurry				Cattle slurry	
	Untreated slurry		Acidified slurry		Untreated slurry	Acidified slurry
	2017y	2018y	2017y	2018y	2017y	2017y
Total C, %	29.6	35.9	17	28.6	40.1	36.7
pH	7.6	8.2	6.3	6.04	7.9	5.0
Total N, kg m^3	2	5.1	2	5.0	3.8	3.8
NH_4, kg m^3	1.5	4.4	1.7	4.5	2.3	2.4
NO_3 kg m^3	-		-		-	-
Total P kg m^3	0.11	1.3	0.12	0.96	0.59	0.6
Total K kg m^3	1	2.2	1.1	2.1	2.2	2.3
Ca, kg m^3	0.15	1.5	0.16	1.1	0.112	0.146
S, %	0.002	0.032	0.110	0.310	0.029	0.257
DM, %	0.83	6.2	1.2	5.4	8.0	7.7
H_2 SO_4, l m^3	-	-	2.5	6.2	-	5.1

Methods:dry matter, gravimetria; N_{tot} – Kjeldahl method; pH - straight from the sample; NO_3-N – Foss Tecator AN 5232; NH_4-N – Foss Tecator AN 5226; P_{tot}, K_{tot}, Ca – wet ashes+ICP/OES[6];C_{tot}ISO 10694; 1995; S – PMK-JJ-4C.

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Photo 1. The lysimetric test for slurry (2017).

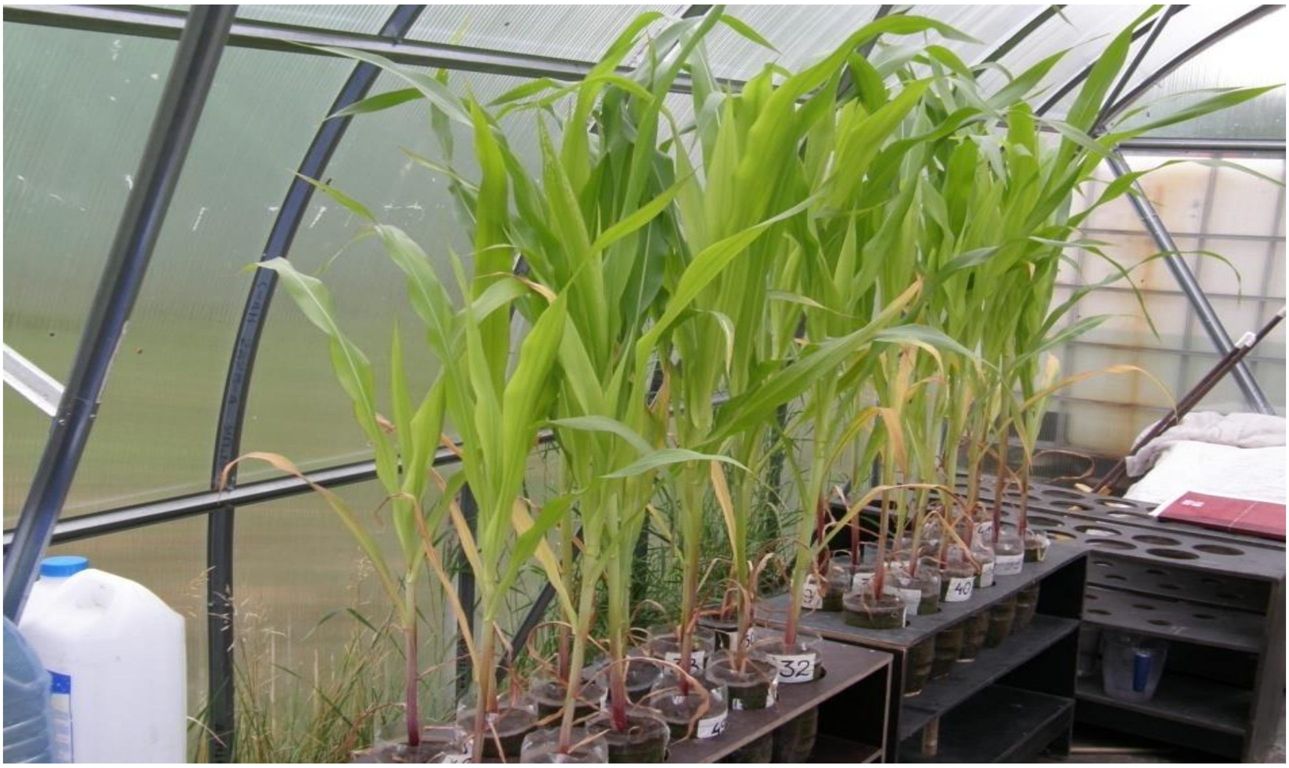

Photo 2. The lysimetric test for slurry (2018).

In 2018, to reduce emissions of N-NH_3, an alternative embodiment bacterium was used in the experiment. These consisted of the soil bacterium *Bacillus megaterium*, which is certified for use in both organic and conventional agriculture to fix N, release P, increase K susceptibility, protect against disease and to mineralise biomass. (BIOORG pro EMO - Effective Microorganisms).

The bacteria product was mixed with slurry (100 ml per m^3 of slurry) and applied to the soil surface in one treatment and another treatment was injected into the soil a depth 15 cm.

Filtrate collection - Bottles were dipped constantly with deionised water. Filtrate collection (100 ml) lasted for 2–3 days. The filtrate was collected after 15 and 30 days of the application of slurry to barley, and after 15, 30, 60, 90, 120 and 300 days for grass. In the maize trial, the filtrate was collected 12 and 30 days after that. The nutrients contents of the filtrate were determined – (P, Ca, K, Mg and SO_4). The methods of determination – were EVS-EN ISO 11885: 2009; N_{tot} - Method 4500-N, APHA, 998; NO_3-N - EVS-EN-ISO 13395; 1999 (CD column); and NH_4-N - Tecator Application Note ASN 140-02/90, 1990.

Yield – The crops included in the 2017 trials: barley and annual ryegrasses were both sown on the 17th of April. In 2018 maize, was sown on 30th of May. The maize had a lot of fresh matter, which was used in plant analysis and was also a strong nutrient consumer.

Barley was harvested on the 4th July 2017. The yield (whole plant) was determined by dry matter content and protein content. Two cuts were made from the grass on the 5th July and 30th August 2017 and from maize on the 25th July 2018, which was used to determine the dry matter, protein and P contents.

Soil - At the end of the experiment, the soil chemical composition was determined: pH_{KCl}, P; K, Ca; Mg - Mehlich 3 extraction; water-soluble SO_4, total-N Kjeldahl.

2017, Results and Discussion

The effect of acidified slurry on barley and ryegrass yield

The yield, protein content and protein yield are shown in Table 3. For barley, the highest yields were obtained in treatments with 15 m^3 of 45 m^3 ha^{-1} acidified pig slurry. The largest grass yields were on a treatment 3 x 15 m^3 and 45 m^3 ha^{-1} of acidified cattle slurry. The highest protein yields were obtained in treatments with two acidified slurries. It was also observed that the P content was higher in plants grown in the acidified slurry.

Table 3. The effect of acidified slurry on barley and ryegrass yield and protein content

Treatments	Barley			Ryegrass			
	Yield, g/ bottle	Prot., %	Yield protein, g	Yield, g/bottle	Prot., %	P ,%	Yield protein, g/bottle
1. Control	3.35	9.8	3.28	0.73	7.8	-	0.85
2. 15 m^3 ha^{-1} PS/CS	3.36	10.2	3.43	0.82	8.5	-	0.70
3. 3x 15 m^3 ha^{-1}CS	-	-	-	1.31	8.5	-	1.11
4. 15 m^3 ha^{-1}PAS/CAS	3.68	9.6	3.53	0.98	7.8	-	1.06
5. 3x 15 m^3 ha^{-1}PAS/CAS	-	-	-	1.35	7.8	-	1.05
6. 45 m^3 ha^{-1}PS/CS	3.08	10.2	3.41	1.02	8.6	0.161	0.88
7. 45 m^3 ha^{-1}PAS/CAS	3.63	10.2	3.70	1.43	9.1	0.194	1.30
LSD 95%	0.30	0.36	0.19	0.25	0.5		0.18

*Red – statistically significant negative effect
Green – statistically significant positive effect

The effect of acidified pig slurry on the leaching of elements in the soil under barley crop

The quantities of leached elements were small (Table 4) and did not significantly affect soil properties (Table 5), with the exception of S. The main leaching element was sulphur, followed by calcium, potassium and phosphorus. Using acidified pig slurry resulted in an increase of S, Ca, and K leaching, and decrease of P leaching. A larger amount of acidified slurry (45 m^3 ha^{-1}) also reduced leaching of N compared to the non-acidified slurry (Table 4). Due to the acidified slurry, the soil SO_4 content increased significantly, as well as the acidity of the soil.

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Table 4. Leaching of elements from the soil treated with pig slurry (45 m^3 ha^{-1}) under barley crop (the sum of three measurements over 90 days)

Treatments	Elemental content in leachate, mg l^{-1}				
	Ca	SO_4	P	K	N_{tot}
Control	27.4	17.7	0.460	16.5	6.7
15 m^3PS	24.8	15.7	0.403	15.8	7.7
15 m^3PAS	37.0*	66.4	0.306	16.4	6.7
45 m^3PS	29.3	16.0	0.376	16.2	6.7
45 m^3PAS	70.3	170.5	0.255	19.8	4,8
LSD 95%	23.3	83.1	0.100	2.0	1.3

*Red– statistically significant negative effect; Green – statistically significant positive effect

Table 5. The effect of pig slurry treatment on the soil under the barley crop

Treatments	Elemental content in soil, mg kg^{-1}						
	pH_{KCl}	Ca	SO_4	N_{-tot}	P	K	Mg
1. Control	5.00	1146	2.3	0.180	97	79	67
2. 15 m^3 ha^{-1}PS	4.97	1151	2.5	0.183	99	79	64
3. 15 m^3 ha^{-1} PAS	4.93	1138	5.2	0.183	98	79	65
4. 45 m^3 ha^{-1}PS	4,93	1097?	2.7	0.187	97	79	65
5. 45 m^3 ha^{-1}PAS	4.90	1141	14.5	0.183	98	79	66
LSD 95%	0.05	27	6.5	0.003	1.2	0	1.6

*Red– statistically significant negative effect
Green – statistically significant positive effect

The effect of acidified cattle slurry on the leaching of elements in the soil under ryegrass

That the effect of slurry acidification on the leaching of the elements and its dynamics was different for different elements (Table 6, Fig. 1). The use of acidified slurry resulted in higher S and Ca excretion 2 months after slurry application. The K content was the highest in leachate at the last fertilized that was collected after the last (third) slurry application. The P content in the leachate, decreased with the use of acidified slurry at a later stage, while the use of non-acidified slurry increased the amount of water–soluble P in the leachate. With the use of acidified slurry, the leaching of Mg increased, and leaching of N_{tot} decreased. Statistically, the leaching of Ca, S, K and Mg from the grassland trial soils increased as a result of acidification of 45 m^3 and 3 x 15 m^3 ha^{-1} cattle slurry but leaching of P and N_{tot} decreased (Table 6).

Table 6. Leaching of elements from the soil treated with cattle slurry from grassland (sum of six measurements for 300 days)

Treatments	Elemental content in leachate, mg l^{-1}					
	Ca	SO_4	P	K	Mg	N_{tot}
Control	31.6	18.1	1.64	34.7	0.94	7.96
15 m^3 ha^{-1}CS	27.8	18.3	1.44	35.5	0.71	8.65
15 m^3 ha^{-1}CAS	53.0	140.4	1.25	45.1	1.45	6.50
3x 15 m^3 ha^{-1}CS	35.0	21.9	2.06	47.7	1.09	8.00
3x 15 m^3 ha^{-1}CAS	142.3	424.6	1.13	61.9	4.15	6.12
45 m^3 ha^{-1}CS	29.5	20.7	1.72	41.8	0.92	6.71
45 m^3 ha^{-1}CAS	154.1	423.1	1.25	58.0	2.10	4.87
LSD 95%	51.6	176.3	0.30	9.7	1.12	0.74

*Red – statistically significant negative effect, Green – statistically significant positive effect

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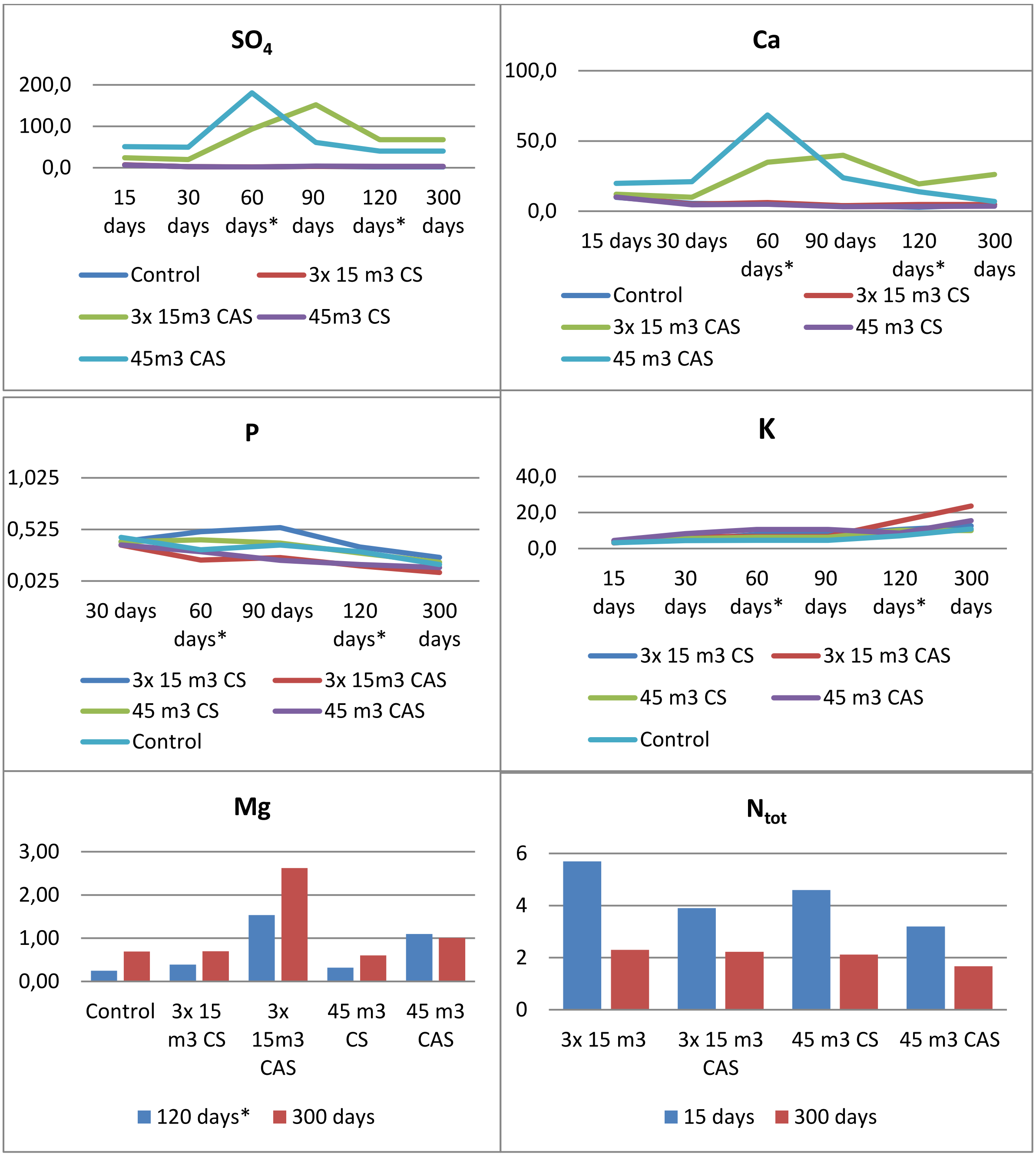

*- Before the sample was taken, 2 and 3 times the slurry was applied 15 m3 ha^{-1}.

Figure 1. The dynamics of leached nutrient content in the leachate, mg l^{-1}.

Soil properties were significantly affected by the use of 45 m^3 of the slurry. Acidified slurry decreased the soil 0.1 pH_{KCl} units, which was also correlated (r = 0.768) with soil S content (Table 7). The second most influential element was K, which increased in the leachate when slurry was used. Due to the acidified slurry, the increase of content in soil was somewhat lower due to leaching of K.

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Table 7. The effect of acidified cattle slurry on the soil grassland after leaching of elements

Treatments	Elemental content in soil, mg kg^{-1}						
	pH_{KCl}	P	K	Ca	Mg	SO_4	N_{tot}
Control	5.0	93	93	1177	54	2.6	0.19
15 m^3 ha^{-1}CS	5.0	91	99	1170	53	2.2	0.18
15 m^3 ha^{-1}AS	5.0	92	95	1182	54	5.0	0.19
3x 15 m^3 ha^{-1}CS	5.0	100?	123	1219	64	2.6	0.20
3x 15 m^3 ha^{-1}CAS	5.0	96	116	1209	64	10.0	0.19
45 m^3 ha^{-1}CS	5.0	94	115	1203	58	2.5	0.19
45 m^3 ha^{-1}CAS	4.9*	95	107	1179	58	6.2	0.19
LSD 95%	0.03	3	11	17	4	2.6	0.01

*Red – statistically significant negative effect,
Green – statistically significant positive effect

The effect of acidified slurry on the soil

Leaching depends on rainfall. Figures 2 and 3 show data on abundant rainfall (leaching) and low (evaporation) rainfall. Depending on the amount of precipitation, the S content (Fig. 2) of the soil increased significantly with 45 m^3 of acidified slurry (70–80 kg S ha^{-1}). Each subsequent fertilisation further increased the S accumulation. The high content of S in the soil causes soil contamination and acidification. Besides, this is indirectly responsible for mobilisation of phytotoxic chemicals, such as aluminium and some trace element (Komarnisky et al., 2003). Plants use 30–50 kg ha^{-1} of S. The application of 45 m^3 ha^{-1} of acidified slurry, which reaches 70–80 kg of S ha^{-1} into the soil, increased the acidity of soil by 0.1 pH_{KCl} units, which requires 0.2–0.4 t ha^{-1} $CaCO_3$ to neutralise, depending on soil type (Loide, 2008). On the other hand, the content of available Ca (Fig. 3) was somewhat higher in the case of lower rainfall, as leaching of Ca slurry was strongly influenced by the as acidification of slurry.

Although S is increasingly considered to be an important element in fertilisers and is referred to as 'the fourth macro element', it must be remembered that excessive amounts of S can be toxic to plants, soil and water (Skwierawska et al., 2008). In their research Skwierawska et al. (2008). the effect of S fertilisers on the soil, reporting that after 3-year use of NPK mineral fertilizers with 120 kg of SO_4-S ha^{-1}, the soil pH decreased in the

0–40 cm layer from 5.30 to 4.36; the S-SO_4 content however, increased from 4.8 to 12.5, and in the 40–80 cm soil layer from 3.3 to 9.2 mg kg^{-1}.

To protect freshwater organisms in British Columbia, a water quality guideline of 33 mg S/l (100 mg SO_4/l) for dissolved sulphate is also recommended (Singleton, 2000). This guideline is a maximum concentration that should not be exceeded in any case.

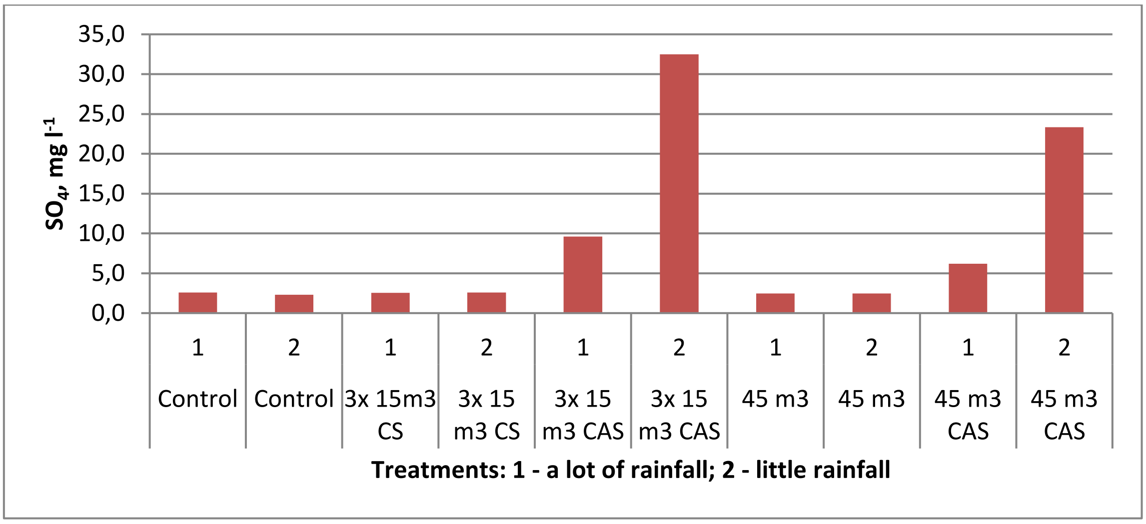

Figure 2. The effect of precipitation (conditional) and of acidified cattle slurry on S content in the soil.

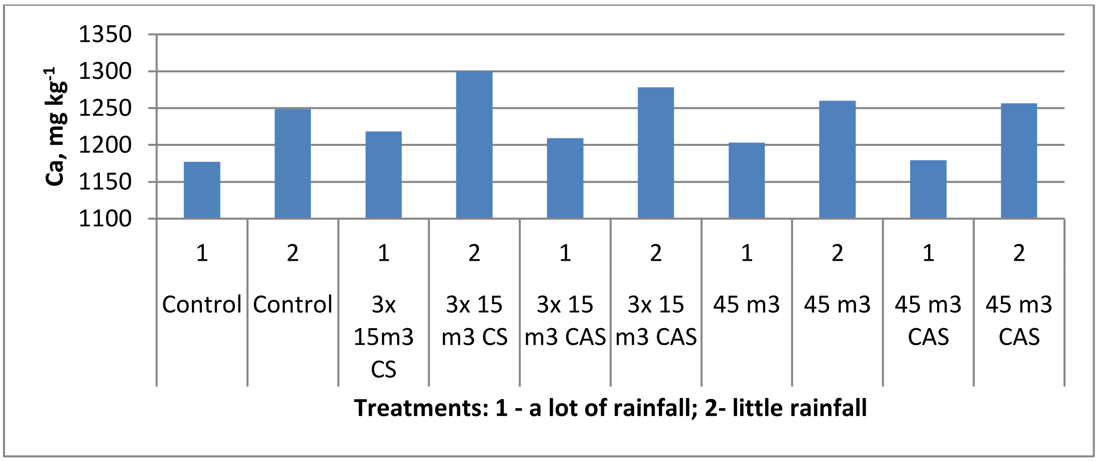

Figure 3. The effect of precipitation (conditional) and use of acidified cattle slurry on Ca in soil.

For crops with a high S requirement such as winter oilseed rape, a fertiliser application of 50 kg S/ha is the upper recommendation, even for high-yielding crops. Knights et al. (2000) measured up to 40 mg l^{-1} sulphate-S in drainage from 75 cm depth following long-term applications of 52 kg S/ha/yr on the experiment. In lysimeters, after autumn application of 50 kg S ha^{-1} in sulphate form (which is not a recommended practice), the water draining at 60 cm depth contained a maximum of almost 50 mg l^{-1} S-SO_4 (Riley et al. 2002). Both of these examples are from the UK, with high potential for leaching. Although the concentrations in water following sulphur fertiliser use do not exceed the drinking water quality level, this illustrates the need to be vigilant. If the lower guideline above is more generally adopted to protect natural systems, extremely high applications of S, as well in excess of crop demands, are to be discouraged. Because sulphate is highly leachable, S applications should be timed to coincide with the phase of high demand by crops, which usually means in spring rather than in autumn (McGrath et al. 2003).

In our experiment, less P leached from the soil treated with acidified slurry, while in plants there was more P than in other variants (Table 3, 4, 6). Gądor and Motowicka-Terelak (1986), in their research, also found that the presence of free sulphur acid in S-rich soils creates favourable conditions for the release of phosphorus from compounds that are hardly soluble. Skwierawska et al., (2008) found that P mobilisation and migration increased with 120 kg S-SO_4 mineral fertilisers. As a result, the soil P content in the topsoil increased from 38.8 to 49.2 and in the subsoil from 36.7 to 49.9 mg kg^{-1} throughout 3 years. The available references contain diverse interpretation of the influence of S on the dynamics of available P in soil. The differences stem from changes in soil pH, competition among sulphate ions, mineralisation of P organic forms (Jaggi et al. 2005) as well as liberation of Al and Fe ions, which bind fewer phosphate ions by reacting with sulphates. Besides, the presence of free sulphur acid in S-rich soils creates favourable conditions for the release of P from compounds that are hardly soluble (Gądor and Motowicka-Terelak 1986).

Skwierawska et al (2008) also emphasised that clear-cut changes only occurred after 3 years of using S-SO_4 fertiliser. In our experiment, 70–80 kg S ha^{-1} was transferred to soil with 45 m^3 of slurry, which exceeds the need for multiple plants, especially in the autumn. Based on waterproofing, it is recommended not to exceed 50 kg of S-SO_4 ha^{-1} per year, although it is better not to exceed 30 kg. Oilseed rape consumes 40–50 kg ha^{-1} of S-SO_4, and other crops consume 20–30 kg ha^{-1}. Therefore, the use of acidified slurry should be done carefully, because an excessive portion of used S-SO_4 cannot be absorbed by plants and endangers groundwater and drinking water quality.

WHO report (2004) says: "The existing data do not identify a level of sulphate in drinking-water that is likely to cause adverse human health effects. The data from the liquid diet piglet study and from tap water studies with human volunteers indicate a laxative effect at concentrations of 1000–1200 mg/litre, but no increase in diarrhoea, dehydration or weight loss. The presence of sulphate in drinking-water can also result in a noticeable taste; the lowest taste threshold concentration for sulphate is approximately 250 mg/litre as the sodium salt. Sulphate may also contribute to the corrosion of distribution systems. In the light of the above considerations, no health-based guideline value for sulphate in drinking water is proposed. However, there is an increasing likelihood of complaints arising from a noticeable taste as concentrations in water increase above 500 mg/litre."

In DEFRA (2015) report chapter 1.8 Environmental impacts is mentioned: "Natural ecosystems are not usually S limited, so increasing S fertilizer applications is not considered likely to have adverse environmental impacts. However, there is an EU guideline for SO_4^{2-} in drinking water (250 mg l^{-1}) hence to avoid this limit being breached, S applications should be matched to crop requirements."

In Estonia, the limit for drinking water S-SO_4 is 250 mg l^{-l} (RTL 2001). The lysimetric test of acidified slurry found the S-SO_4 content increased to 180 mg l^{-1}, if a single portion of 45 m^3 ha^{-1} was applied.

Conclusions based on the results from 2017

The use of acidified slurry 1 x 45 m^3 ha^{-1} increased soil pH by 0.1 pH_{KCl} units, which requires 0.2–0.4 t ha^{-1} $CaCO_3$ to neutralise, depending on soil type.

In addition to leaching of Ca, acidified slurry also increased the leaching of K and Mg (to a lesser extent), while leaching of N and P decreased. The decrease in N and P leaching can also be explained by their better absorption of plants by the interaction of S.

Acidified slurry increased the phytomass and its protein content of barley and grassland. When using acidified slurry, the grass contained more P.

Slurry acidification, on one hand, reduces the loss of N-NH_3 and improves the use of N and P and on the other hand results in soil acidification and greater need for liming, as well as an increase in S-SO_4 leaching, which endangers groundwater and drinking water quality.

If, following N and limit values, according to environmental protection demands, – then, the annual amount of slurry should remain within range 30 m^3 ha^{-1}. However, to minimise S leaching, it has been suggested that only 15 m^3 ha^{-1} is safe, as confirmed by our test results. Using 15 m^3 ha^{-1} acidified slurry resulted in the least negative effects on soil properties.

The application rate of acidifying slurry is important. For example, in Denmark, 12.5 t ha^{-1} of the slurry is used, while according to specialists, some farmers in Estonia should use to 50–60 m^3 ha^{-1}. In the first case, the negative impact on the acidified slurry on soil is minimal or non-existent. In the second case, the risk of excessive S is higher and can increase the need for liming and the risk of contamination in groundwater. The need to use large amounts of manure is due to the size of the farms and the increased transport costs. Also, the storage facilities are often insufficient. Consequently, at least in Estonia, alternatives to acidification of slurry are needed. Perhaps it would be beneficial to use bacteria to reduce nitrogen losses and improve slurry properties?

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2018, Results and Discussion

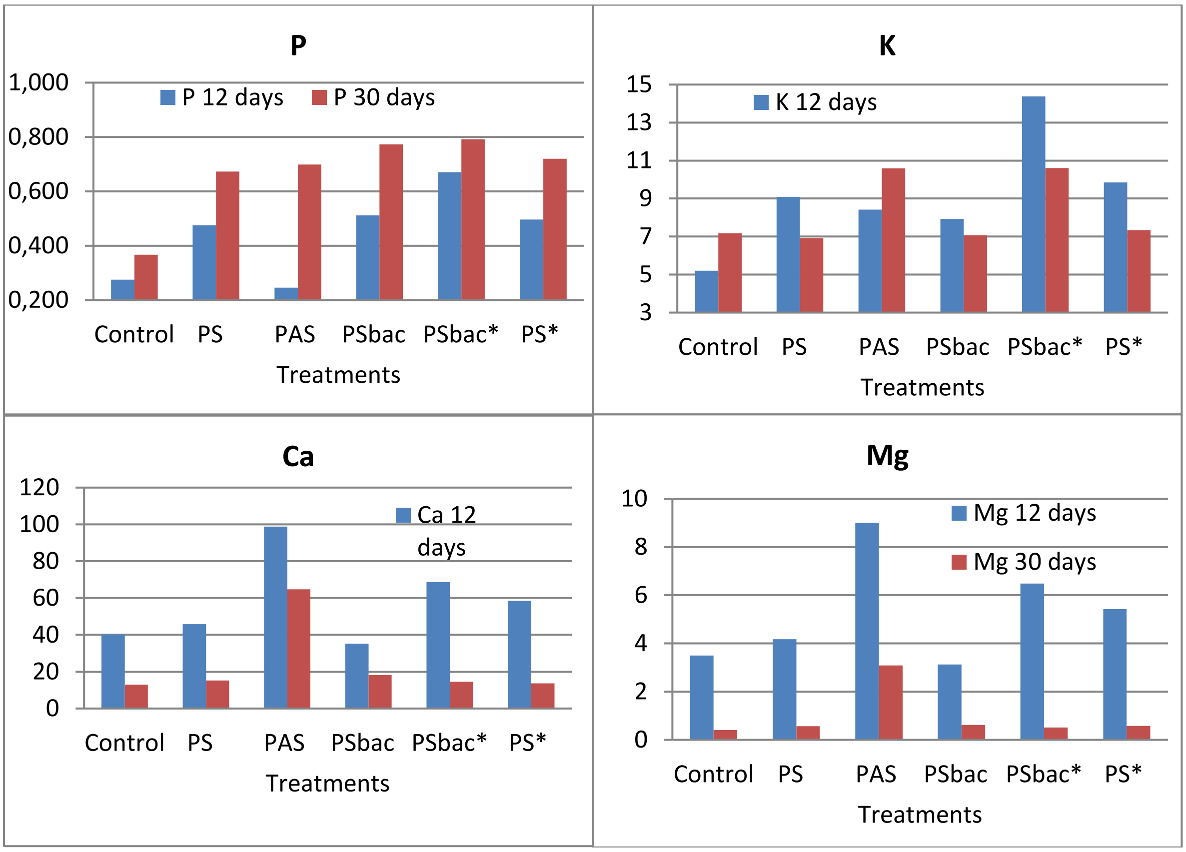
The effect of acidified slurry on the leaching of plant nutrients from the soil and on the soil

Our 2018 findings research largely agreed with previous year's results. The dynamics of soil nutrient leakage is shown in Figure 4. Leaching of most of the measured elements (Ca, Mg, SO_4 and N) was more intense during the first 12 days, except P, which was higher in the later filtrate. The use of slurry increased the leaching of the elements. Acidification of the slurry increased Ca and Mg leaching even further, while leaching of N_{tot} and NO_3-N leaching was the lowest.

In the treatments with slurry enriched bacteria preparation leached from soil less Ca and Mg compared to the treatments with acidified slurry. The leaching of the elements also depended on whether the slurry was spread on the surface of the soil, or if injected into the soil. The N compounds that leached in the first days, this is the first 12 days, of the experiment, leached more when slurry was injected into the soil.

Data from soil analyses (Table 8) revealed that, among the soil K and S content decreased most. Acidification of the slurry further reduced the soil's K content. The main reasons for the loss of K leaching and consumption by plants. Soil acidity increased by pH 0.1 unit if 45 m^3 acidified slurry was used. The soil was also acidified if slurry was injected into the soil (degradation of the organic matter). Also following 2 consecutive years where the soil was fertilised with 45 m^3 ha^{-1} acidified slurry, (the soil acidity increased, the soil pH decreased from 5.0 to 4.9 in the first year, and to 4.8 in the second year). Poor leaching and incomplete use of S by plants accumulated S in soils, and the sulphate content increased from 4 to 30–74 mg SO_4 kg^{-1}, respectively. The use of 45 m^3 ha^{-1} of acidified slurry increased the S content in soil ca 10 times, up to 159 kg of S (S% in the slurry was 0.310 and 0.032, respectively, Table 2). In that way, the soil SO_4 content has increased by only 2.6-fold. Thus, in addition to oilseed rape, the maize has a high S consumption, and thus the 45 m^3 ha^{-1} of the acidified slurry can be accepted. The need for soil liming is increasing, but there is no risk of water pollution.

The soil treatments with bacteria-enriched slurry contained more nutrients, and the pH of the soil was 0.1 units higher than in treatments with acidified slurry.



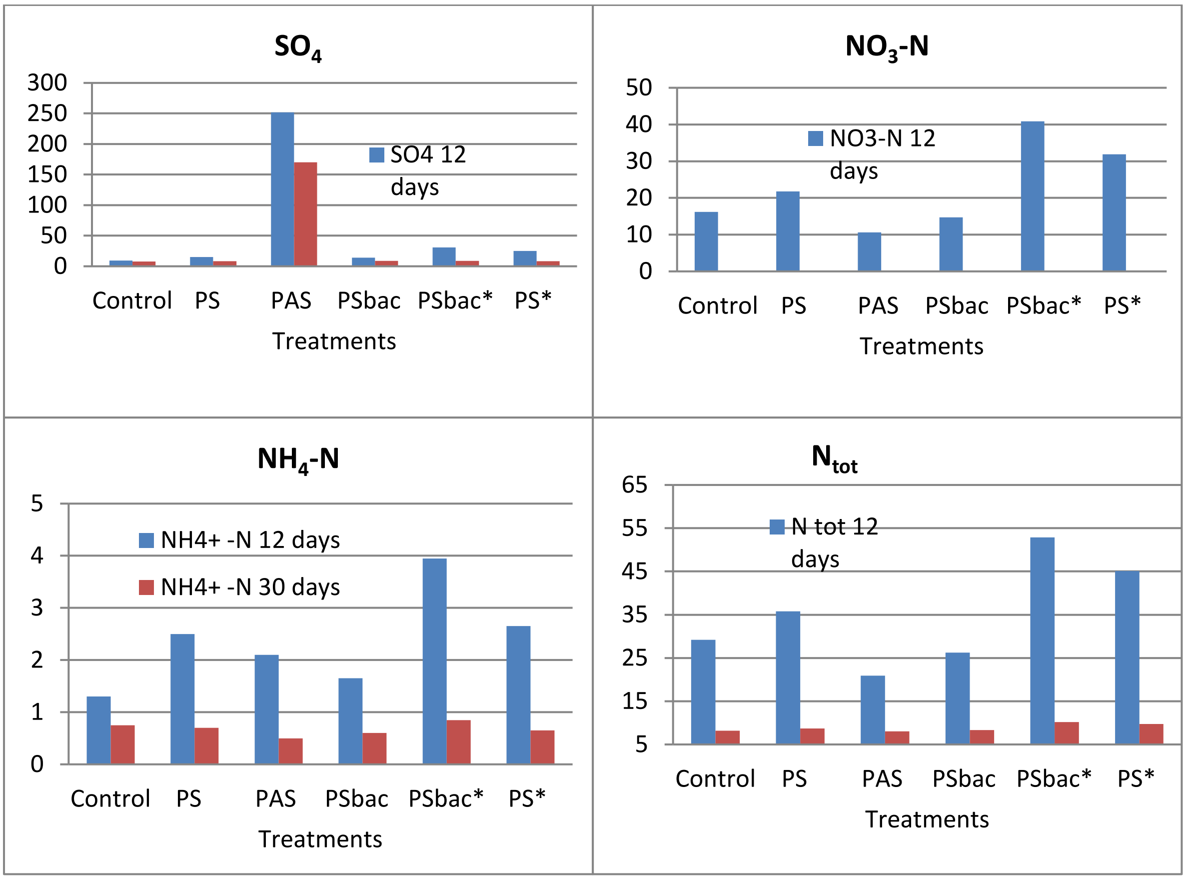


Figure 4. Leaching effect of pig slurry (45 m^3 ha^{-1}) treated and applied in different ways. The content of elements in the soil under maize plants. * - The slurry was injected into the soil at a depth of 15 cm.

Table 8. The effect of pig slurry (45 m^3 ha^{-1}) treatment and application on the soil under the maize plants

Treatments	Elemental content in soil, mg kg^{-1}						
	pH_{KCl}	P	K	Ca	Mg	$N_{tot, \%}$	SO_4
Before leaching	5.1	107	117	1280	65	0.19	4.0
Control	4.9	101	48	1270	54	0.18	2.6
PS	4.9	105	42	1340	57	0.18	2.7
PAS	4.8	102	41	1220	52	0.18	6.8
PSbac	4.9	105	46	1290	58	0.18	2.7
PSbac*	4.9	105	46	1240	56	0.18	-
PS*	4.8	105	44	1250	54	0.18	-
LSD 95%	0.05	1.9	2.8	45	2.3	-	1.8

*- Slurry was injected into the soil, at a depth of 15 cm.

The effect of acidified slurry on maize yield and chemical composition

In this experiment, the soil was treated with 45 m^3 ha^{-1} of acidified liquid manure, which required 6.2 l H_2SO_4 m^3 for acidification. Thus, 159 kg of S ha^{-1} was applied to the soil. The effect of S on the yield is given in Table 9. Maize makes use of many nutrients to form a crop. The maize yield was increased by 50% by fertilisation with slurry. This yield was increased by a further 30% with acidification of the slurry. A yield equivalent of that with the acidified slurry was also obtained when the slurry with bacteria was injected into the soil. Also, the crop was richest in protein using this treatment. Under the influence of slurry, the P content of the crop increased, but the acidification of slurry reduced the P content of the crop.

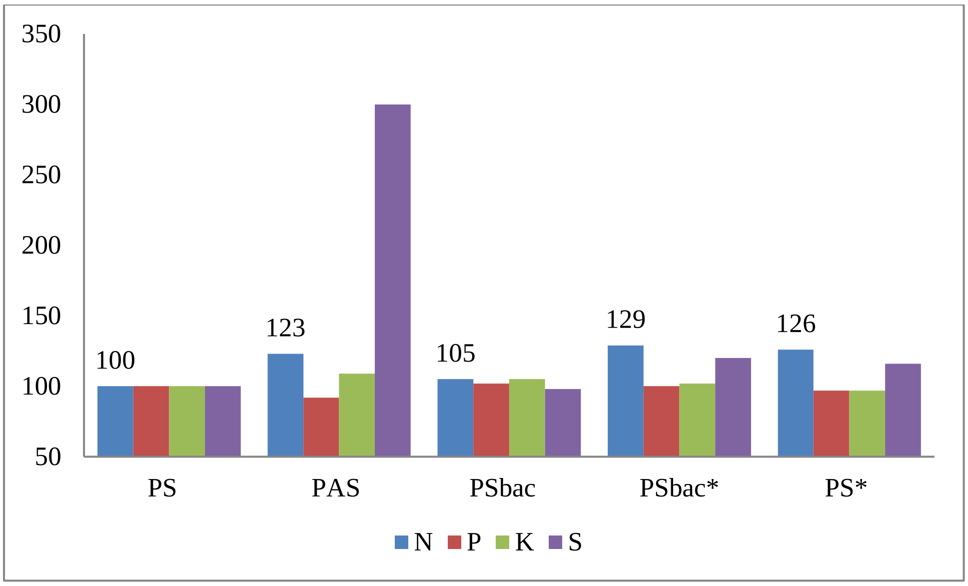
Because maize consumes a lot of S, the yield of maize decreased the S content of S-poor soil even in the case where slurry was used, and the N (protein/6.25), to S ratio of the yield was 11 to 17. If acidified manure was used, then the N:S ratio was 6.5. For example, the satisfactory S levels ranged from 0.2% to 0.4% in the dry matter and for the N:S ratio ratios, between 15:1 and 7:1 (Walker and Dawson, 2003).

The plant nutrient content in the yield of fresh matter of maize depends on the use of slurry. If acidified slurry was used, then the S content was highest in the fresh maize, followed by N and K. The absorption of P by plants was probably disturbed due to high S content and, therefore, the P content in the maize plant was smallest in the treatment with

Table 9. Effect of acidified slurry (45 m^3 ha^{-1}) on maize yield and chemical composition

Treatments	Yield		Protein		P		K		Mg		S	
	DM, g	Rel.	%	Rel.	%	Rel.	%	Rel.	%	Rel.	%	Rel.
Control	20	100	4.42	100	0.168	100	1.67	100	0.153	100	0.063	100
PS	30	150	4.74	108	0.186	111	1.56	93	0.155	101	0.048	76
PAS	36	180	4.84	110	0.143	85	1.42	85	0.152	99	0.120	191
PSbac	32	160	4.64	105	0.175	104	1.53	92	0.158	103	0.044	70
PSbac*	36	180	5.09	115	0.158	94	1.33	80	0.152	99	0.048	76
PS*	34	170	5.28	120	0.160	95	1.34	80	0.165	108	0.049	78
LSD 95%	6.3	-	0.33	-	0.016	-	0.14	-	0.012	-	0.031	-

*- Slurry was injected into the soil, at a depth of 15 cm



*- Slurry was injected into the soil, at a depth of 15 cm.

Figure 5. Plant nutrient content (%) in the yield of fresh matter maize depending on the use of slurry (45 m^3).

acidified slurry. The N content in the maize plants was 20% higher than in the control for all three treatments: 23% if acidified slurry was applied on the surface of the soil, 26% if the slurry was injected into the soil, (15 cm, depth), and 29% if slurry mixed with bacteria was injected into the soil, (15 cm depth).

S-fertilizer recommendations differ across for crops and countries. In most European countries, the recommendations are for cereals, 10–20 kg S ha^{-1}; for oilseed rape, 30–40(60) kg S ha^{-1} and for grassland, 20–40 kg S ha^{-1} (Walker and Dawson, 2003). Therefore, as in the current research, it is clear that the removal of larger amounts of S by in plant is harmful to the soil, crop yield and the environment.

The soil does not bind the sulphate (neither chemically or physically), and it remains in the soil solution. Moreover, sulphate, chloride and nitrate ions are negatively absorbed in the soil. This facilitates their movement in the soil, including leaking out. Along with anions, an equivalent number of cations is always thrown out of the soil, contributing to the impoverishment of soil, primarily Ca and Mg. Also, the soil produces active acidity with the use of sulfuric acid-acidified slurry caused by hydrogen ions freely expressed in the soil solution. Although the total amount of H-ions causing active acidity in the soil solution is small, it nevertheless has a significant effect on the livelihoods of plants and microorganisms and is more harmful to plants than potential acidity (Kärblane, 1996).

Conclusions on the results for 2018

Leaching of most of the measured elements (Ca, Mg, SO_4 and N) was more intense during the first 12 days, except for P, which was higher in the later filtrate. The use of slurry increased the leaching of the elements. Acidification of the slurry increased Ca and Mg leaching even further, while the leaching of N_{tot} and NO_3-N leaching were the lowest. Soil acidity increased the pH 0.1 units if 45 m^3 ha^{-1} acidified slurry was used.

The maize yield increased by 50% because of fertilisation with slurry. Due to the acidified slurry, the yield increased by an additional 30%. Under the influence of slurry, the P content of the crop increased, but the acidification of slurry reduced the P content of the maize crop. S requires special attention since its excess endangers the quality of soil, plants and water.

Interreg Baltic Sea Region
Baltic Slurry Acidification
EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND

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Interreg
Baltic Sea Region
Baltic Slurry Acidification

EUROPEAN REGIONAL DEVELOPMENT FUND
EUROPEAN UNION

www.balticslurry.eu

Summary of the project

Baltic Slurry Acidification is an agro-environmental project financed by Interreg Baltic Sea Region under the priority area Natural resources and specific objective Clear Waters. The aim of the project is to reduce nitrogen losses from livestock production by promoting the use of slurry acidification techniques in the Baltic Sea Region and thus to mitigate eutrophication of the Baltic Sea. Baltic Slurry Acidification project was implemented in the period March 2016 - February 2019.