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EFFECT OF DIGESTATE, LIQUID AND SOLID MANURE APPLICATION ON CHEMICAL PROPERTIES OF SOIL*

Agnieszka Wysocka-Czubaszek

ORCID: 0000-0002-1334-3809
Department of Agri-Food Engineering and Environmental Management
Białystok University of Technology in Białystok, Poland

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Abstract

The growing number of biogas plants results in increasing digestate volume used as fertilizer on arable land. This study compared the influence of digestate addition on soil chemical properties with traditional organic fertilizers such as liquid and solid cattle manure and with mineral fertilizer. The digestate supplied soil with a significant amount of NH_4-N, whose nitrification was slower comparing to soils treated with mineral fertilizer and liquid cattle manure. Digestate also slightly increased concentration of water-soluble phosphorus in soil and added high amounts of plant-available potassium and dissolved organic carbon. Therefore, the application of digestate should follow the same rules as traditional liquid fertilizers; however, its agronomic use should be based not only on N, but also on P and K content.

Introduction

Nitrogen (N) fertilizers consumption in the European Union is high and rises, with the levels per hectare of agricultural area increasing from 67.4 kg ha^{-1} in 2006 to 74.4 kg ha^{-1} in 2015. On the same time-scale, application rate of phosphorus (P) fertilizers decreased from 7.5 kg ha^{-1} in 2006 to 6.3 kg in 2015 (*Agri-environmental*... 2017). In Poland, N fertilizers consumption also increased and in 2017 was equal to 78.7 kg ha^{-1} and a similar trend was observed for P fertilizers, i.e. reduction to 9.1 kg ha^{-1} in 2015 followed by a rise to 10.2 kg ha^{-1} in 2017 (SO 2018). Poland is the

Address: Agnieszka Wysocka-Czubaszek, Białystok University of Technology, ul. Wiejska 45A, 15-351 Białystok, Poland, e-mail: a.wysocka@pb.edu.pl
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fifth country in the EU-28 in terms of P fertilizers application rate and 14 in the case of N fertilizers consumption per 1 ha (*Agri-environmental*... 2017). Although N and P fertilizers enhance crop production, their losses from agricultural system contribute to environmental contamination (VELTHOF et al. 2009). The most important among these are ground and surface water contamination leading to worsening of drinking water quality and eutrophication. Application of N fertilizers also results in high N_2O emissions and therefore contributes to global climate change (IPCC 2013). Prices of N fertilizers are rather unstable, because ammonia, urea and ammonium nitrate are produced from natural gas, the price of which is linked to oil prices. The prices of P fertilizers produced from phosphate rock which is a non-renewable resource mined outside the EU are also high as a result of high production and transportation costs (*Agri-environmental*... 2017). Therefore, the increasing application of organic fertilizers may decrease the use of mineral fertilizers and benefit both economy and environment. The new promising organic fertilizer is a post-fermentation sludge (digestate), which is a by-product of an anaerobic digestion (AD) from biogas plants. The digestate is characterized by high ammonium-N (NH_4-N) content (RIGBY and SMITH 2013), the total amount of phosphorus and potassium at a level similar to that of the substrate used for biogas production (INSAM et al. 2015) and high organic matter content (TAMBONE et al. 2010). The AD of P organic compounds results in partial mineralization of organic-P, which is rapidly associated with particulate-bound solids. The water-soluble phosphorus fraction (P_w) is also reduced substantially after AD process (GÜNGÖR and KARTHIKEYAN 2008). The addition of digestate to soil has no serious ecotoxicological effect on plants and soil biota (PIVATO et al. 2016), but rather enhances microbial activity (ODLARE et al. 2008). Fertilization with digestate improves overall carbon balance in soil (IOCOLI et al. 2019) as a consequence of low CO_2 emissions and results in higher macroelements content in harvested plants (KOSZEL and LORENCOWICZ 2015).

Between 2009 and 2016 the number of biogas plants in Europe has grown from 6,227 to 17,662 installations (*EBA*... 2018). This growth resulted in increase of digestate volume used as fertilizer in European agriculture. However, the variability of digestate composition and unknown stability may generate problems during its storage and may cause unfavourable impacts on soil (ALBURQUERQUE et al. 2012, INSAM et al. 2015). Although digestate is perceived as a valuable fertilizer (SZYMAŃSKA et al. 2018), there is a growing concern about its potential negative environmental impact, especially in case of nitrogen, which may be leached or volatilized. Therefore N dynamics in soil after its fertilization with digestate has been subjected to numerous research, both incubation experiments (GRIGATTI et al. 2011, GÓMEZ-BRANDÓN et al. 2016, CAVALLI et al. 2017) and field studies (CAVALLI et al. 2016, SIGURNJAK et al. 2017). The N dynamics in soil fertilized with digestate is quite well recognized and depends mainly on digestate and soil properties, as well as on the rate and time of application (RIGBY and SMITH 2013, MARTIN et al. 2015, TAMBONE and ADANI 2017). High amount of ammonium-N added to soil triggers several processes in the soil, such as nitrification, immobilisation and emission. Rapid oxidation of NH_4-N added with digestate to soil is observed in first two weeks after soil fertilization, with nitrification conversion of total nitrogen (TN) added in a range of 41–84%, depending on the digestate (ALBURQUERQUE et al. 2012, DE LA FUENTE et al. 2013).

The addition of digestate do not influence the total phosphorus (TP) content in soil, however, increases the water-soluble phosphorus (P_w) content (HUPFAUF et al. 2016) and extractable P concentration (BACHMANN et al. 2011). The increase in extractable P is slower in soils amended with digestate than in soil fertilized with mineral fertilizer due to differences in the composition of organic and mineral amendments. Digestate as other organic fertilizers contains a variety of inorganic and organic P compounds, which are mineralized at different rates. Inorganic P fertilizers may contain P only in form of orthophosphates which are immediately available for soil chemical reactions and therefore increase the extractable P content in soil immediately after application (MÓRTOLA et al. 2019).

The aim of the study was the comparative analysis of chemical properties in soil treated with organic fertilizers, digestate and mineral fertilizer.

Materials and Methods

Soil and fertilizers characteristics

The incubation experiment was conducted on five treatments: unfertilized soil (S_1, S_2), soil fertilized with digestate (D), soil fertilized with liquid cattle manure (LCM), soil fertilized with solid cattle manure (SCM) and soil fertilized with commercial mineral fertilizer containing N and P (MF). The soil selected for an incubation experiment was a loamy sand consisted of 83% sand (2–0.05 mm), 16% silt (0.05–0.002 mm) and 1% clay (< 0.002 mm) and was classified as light soil according to agronomic categories (SOIL SCIENCE SOCIETY OF POLAND 2008). The soil was sampled from arable field at the organic farm near Karczmisko village located 19 km north of Białystok (53°17’N, 23°11’ E, 147 m a.s.l.). The soil was collected from the plough horizon (0–20 cm) twice: in April 2016 (S_1) and in November 2017 (S_2). Soil collected in April 2016 was used for incubation experiment conducted on soil treated with D which was a part of first set of incubation experiment. Soil sampled in November 2017 was used for experiment conducted on soil amended with MF, LCM and SCM, which was performed in the second set. The soil was air-dried and sieved through 2 mm mesh prior to incubation and then re-moistened and pre-incubated for a week at 25°C. The main soil properties were as follows: pH in 1 M KCl 4.75±0.12, total organic carbon (TOC) 15.46±1.08 g kg^{-1}, total nitrogen (TN) 0.90±0.02 g kg^{-1}, total phosphorus (TP) 0.860±0.06 g kg^{-1}, total potassium (TK) 1.01±0.04 g kg^{-1}, exchangeable acidity (EA) 3.45±0.52 $cmol_{(+)}$ kg^{-1}, total exchangeable cations (TEB) 4.09±0.30 $cmol_{(+)}$ kg^{-1}, cation exchange capacity (CEC) 7.54±0.34 $cmol_{(+)}$ kg^{-1} and base saturation (BS) 45.63±5.15%. Digestate was obtained from commercial mesophilic biogas plant, where maize silage (80%), chicken droppings (10%) and potato pulp (10%) were co-digested. The liquid cattle manure and solid cattle manure were collected from a dairy farm. The liquid cattle manure containing a mixture of water, urine and soluble fecal components was sampled from the channel below the litter-bedded floor. The solid manure consisting of feces and straw was collected from the manure heap outside the building. Chemical properties of the organic material are shown in Table 1. A commercially available fertilizer contained 18% of the nitrogen in form of ammonium and 46% of phosphorus in form of monoamonium and diammonium phosphate (37% of P was soluble in water).

Table 1

Characteristics of organic fertilizers

Parameter	Digestate (D)	Liquid cattle manure (LCM)	Solid cattle manure (SCM)
pH	7.58±0.03*a*	7.99±0.04*b*	8.03±0.06*b*
Total solids (TS) [%]	5.87±0.05*a*	1.16±0.01*b*	16.73±0.21*c*
Volatile solids (VS) [%]	77.53±0.36*a*	71.78±1.08*b*	83.17±0.52*b*
Total Kjeldahl nitrogen (TKN) [g kg^{-1}]	71.02±2.28*a*	67.64±0.38*a*	24.87±2.71*b*
Total organic carbon (TOC) [g kg^{-1}]	395.17±41.92*a*	406.64±9.74*a*	396.46±18.94*a*
Total phosphorus (TP) [g kg^{-1}]	12.54±0.55*a*	10.21±0.38*b*	5.03±0.24*c*
Total potassium (TK) [g kg^{-1}]	58.21±1.01*a*	80.53±0.57*b*	21.28±1.34*c*
C/N ratio	6	6	16

Values are given on a dry weight basis. Values in the same row with the same letters are not statistically different according to Tukey's test ($p < 0.05$)

Incubation

After a week of pre-incubation, in every experimental microcosm, soil (equal to 100 g dry weight) was mixed with organic or mineral fertilizer in amount equal to 170 kg N ha^{-1}, which is the N application rate permissible per year in case of organic fertilizers (Act of 10 July 2007... Journal of Laws of 2018 item 1259). The exact amount of organic material and mineral fertilizer was calculated assuming the plough depth of 0.2 m. The bulk density of soil was 1.51 g cm^{-3}. The unfertilized soil (S_1, S_2) was treated as a control. Each treatment and control was run in triplicate for each day of sampling. The aerobic incubation was carried out in darkness, at the temperature of 25±1°C, and constant soil moisture at 60% of water-holding capacity (WHC). Soils were kept in 100 ml plastic vessels covered with Parafilm, the breathable material, which ensured the gas exchange and stable moisture at the same time (De La Fuente et al. 2010). The moisture was checked every 3–4 days by weighing samples and WHC was adjusted by adding distilled water drop by drop. For analyses of inorganic N (NO_3-N, NH_4-N), water-extractable phosphorus (P_w) and pH, soils were sampled at day 0, 2, 7, 14, 21, 28, 42 and 56. The analysis of dissolved organic carbon (DOC) was performed on samples taken at day 0, while the measurements of TN, TP, TK, TOC content as well as concentration of plant-available potassium (K_{dl}) were performed just after soil fertilization (day 0) and at the end of incubation (day 56).

Chemical analyses

Particle-size distribution was analyzed according to Bouyoucos method modyfied by Casagrande and Prószyński (*Gleby i utwory...* PN-R-04032:1998), bulk density was determined in undisturbed soil samples in a steel cylinder with a volume of 100 cm^3, pH in 1M KCl (soil to potassium chloride ratio of 1:2.5) was measured with HQ40D meter (Hach, USA). The EA was determined by Kappen method, exchangeable bases were extracted with 1 M ammonium acetate (Ostrowska et al. 1991), magnesium and calcium were measured by flame AAS (Avanta PM, GBC Scientific Equipment Pty Ltd, Australia), Na and K were determined using flame photometer (BWB Technology, UK). The results were used to calculate TEB, CEC and BS. Total solids (TS) and volatile solids (VS) in organic fertilizers were measured according to standard methods (*Standard methods...* 1999). The soil moisture was determined on 10 g of a sample by drying in 105±2°C until constant weight. Soil inorganic-N (exchangeable and soluble) was extracted with a solution of 1% K_2SO_4 (soil to solution ratio 1:10) for 24 h (*Analiza chemiczno-rolnicza...* PN-R-04028:1997).

The NO_3^--N and NH_4^+-N content in filtrates was determined by UV-1800 spectrophotometer (Shimadzu, Japan). The P_w was extracted with distilled water (soil to water ratio 1:10) by rotary-shaking for 1 h at 10 reciprocations per minute (SHARPLEY et al. 2006) and it was measured in filtrates with UV-1800 spectrophotometer (Shimadzu, Japan). The K_{dl} content, after extraction with calcium lactate solution, was analyzed using flame photometer (BWB Technology, USA). Organic carbon (TOC) in soil and organic amendments was determined in TOC-L analyzer with SSM-5000A Solid Sample Combustion Unit (Shimadzu, Japan). Total Kjeldahl nitrogen (TKN) was determined by the Kjeldahl method in Vapodest 50 s analyzer (Gerhardt, Germany). After nitric acid/hydrogen peroxide microwave digestion in ETHOS One (Milestone s.r.l., Italy) the content of P was determined with ammonium metavanadate method using UV-1800 spectrophotometer (Shimadzu, Japan) and the K content was measured using flame photometry (BWB Technology, USA). The analyses were run in triplicate.

Calculations and statistical analysis

The quantitative recovery of inorganic N from fertilizers at day 0 was calculated by subtracting inorganic N (as a sum of NO_3-N and NH_4-N content) in control soil from those measured in treated soils. The recovery was also expressed as percentage of TN added to the soil. The quantitative availability of inorganic N at the end of incubation was calculated in similar way i.e. the content of inorganic N in control soil at day 56 was subtracted from inorganic N content of treated soil at day 56. The availability was also expressed as percentage of TN added to the soils with fertilizers. The two-way Anova was used to test the statistical effects of fertilizer, time and their interactions on the following variables: NO_3-N, NH_4^+-N, P_w content and pH. The non-parametric one-way Anova (Welch test) was used on following variables: K_{dl}, TN, TOC, TP, TK, TOC and DOC at the level of accepted statistical significance of $p < 0.05$. The homogeneity of variance and normality were checked prior to ANOVA using Levene and Shapiro-Wilk tests, respectively. All the statistical analyses of data were performed using STATISTICA 12 software (StatSoft, Poland).

Results

Characteristics of organic fertilizers

All three amendments differed in almost all parameters, except the TOC content (Table 1). The highest TS and VS values characterized SCM (16.73±0.21 % and 83.17±0.52 %TS, respectively) and the lowest values were found in LCM (1.16±0.01 % and 71.78±1.08 %TS, respectively). The pH of both manures was similar and amounted to 7.99±0.03 for LCM and 8.03±0.06 for SCM (Table 1). Digestate (D) characterized with pH equal to 7.58±0.03. TKN content was the lowest in SCM (24.87±2.71 g N kg^{-1}), while both D and LCM were characterized with much higher amount of N. TP content in studied organic fertilizers followed the sequence: D > LCM > SCM, while TK content was the highest in LCM (80.53±0.57 g K kg^{-1}) and the lowest in SCM (21.28±1.34 g K kg^{-1}).

Nitrogen transformation in soil

The addition of organic and mineral fertilizers to the soil increased NH_4-N concentration at day 0 in the order: MF > LCM > D > SCM. The highest inorganic-N recovery at the first day of incubation was observed in soil fertilized with MF (100%) and LCM (82.5%). Much lower inorganic-N recovery was found for soils amended with D and SCM, equal to 59.5% and 42.3%, respectively (Table 2). The NH_4-N content was affected by fertilizer and sampling date and their interaction (Table 3). Its content decreased in all fertilized soils and both control soils throughout the course of incubation; however, the dynamics differed among the incubated soils. In soils amended with LCM and SCM, regardless the difference in initial NH_4-N concentration (51.79±2.88 and 26.72±0.08 mg N kg^{-1} for LCM and SCM, respectively), the NH_4-N content rapidly decreased in first 7 days of incubation and reached values ca. 2 mg N kg^{-1}. In soil treated with MF, the NH_4-N concentration dropped from 65.35±7.29 mg N kg^{-1} (day 0) to 14.59±0.57 mg N kg^{-1} at day 7 and to 0.63±0.04 mg N kg^{-1} at day 14. Slightly different NH_4-N dynamics was observed in soil fertilized with D, where NH_4-N content increased from 49.15±2.89 mg N kg^{-1} (day 0) to 77.03±3.81 mg N kg^{-1} at day 2 and then ammonium concentration decreased rapidly through next 12 days to 5.11±0.79 mg N kg^{-1}.

The NO_3-N content in all soils (except controls) ranged between 20.73±3.20 and 26.66±0.06 mg N kg^{-1} at day 0. In soil fertilized with SCM the NO_3-N content exceeded the NH_4-N concentration after first 12 hours and rose slowly from 20.73±3.20 mg N kg^{-1} (day 0) to 55.50±2.97 mg N kg^{-1} at the end of incubation. In soils receiving LCM and MF, changes in NO_3-N

Table 2

Summary of mineral N recoveries and availabilities

Specification	S_1	Soil + D	Soil + LCM	Soil + SCM	Soil + MF	S_2
Day 0						
pH in 1M KCl	4.57±0.02	4.78±0.01	5.97±0.03	5.91±0.04	5.78±0.02	5.73±0.01
NO_3-N [mg kg^{-1}]	22.01±0.36	22.85±1.60	18.42±1.94	20.73±3.20	26.66±0.07	21.05±1.00
NH_4-N [mg kg^{-1}]	15.38±0.88	49.15±2.89	51.79±2.88	26.72±0.08	65.35±7.29	2.40±0.54
Inorganic-N recovery [mg kg^{-1}]	–	33.73	46.75	23.99	68.56	–
Inorganic-N recovery [% of TN added]	–	59.5	82.5	42.3	100	–
Day 56						
pH in 1M KCl	4.46±0.02	4.42±0.02	5.72±0.01	5.80±0.10	5.35±0.04	5.57±0.06
NO_3-N [mg kg^{-1}]	44.99±3.45	90.62±1.93	65.25±10.53	55.50±2.97	98.69±3.27	38.22±1.34
NH_4-N [mg kg^{-1}]	0.41±0.07	0.99±0.17	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Inorganic-N availability [mg kg^{-1}]	–	41.22	27.03	17.28	60.47	–
Inorganic-N availability [% of TN added]	–	72.7	47.7	30.5	100	–

S_1 – a control for D treatment; soil + D – soil treated with digestate (D); soil + LCM – soil treated with liquid cattle manure (LCM); soil + SCM – soil treated with solid cattle manure (SCM); soil + MF – soil treated with mineral fertilizer (MF); S_2 – a control for LCM, SCM and MF treatments

Table 3

Two-way ANOVA for the chemical parameters measured throughout the incubation

Parameter	Treatment		Time		Treatment x time	
	F	*p*	F	*p*	F	*p*
NO_3-N	494.18	< 0.0001	343.86	< 0.0001	24.21	< 0.0001
NH_4-N	639.94	< 0.0001	1766.84	< 0.0001	196.32	< 0.0001
P_w	1347.25	< 0.0001	1136.46	< 0.0001	394.72	< 0.0001
pH	11591.00	< 0.0001	153.00	< 0.0001	14.00	< 0.0001

concentration were characterized with similar pattern. The NO_3-N content increased rapidly from 18.42±1.94 and 26.66±0.06 mg N kg^{-1} (for LCM and MF, respectively) at day 0 to 62.61±1.15 and 81.66±3.39 mg N kg^{-1} (for LCM and MF, respectively) at day 7 and exceeded the NH_4-N concentration at day 3. In next weeks of incubation the NO_3-N content increased very slowly to 65.25±10.53 and 98.69±3.27 NO_3-N mg N kg^{-1}, for LCM and MF, respectively. Although in soil treated with D, the dynamics of NO_3-N content had similar overall pattern, the nitrification rate was slower and the highest concentration of NO_3-N was observed after 21 days of incubation (Figure 1).

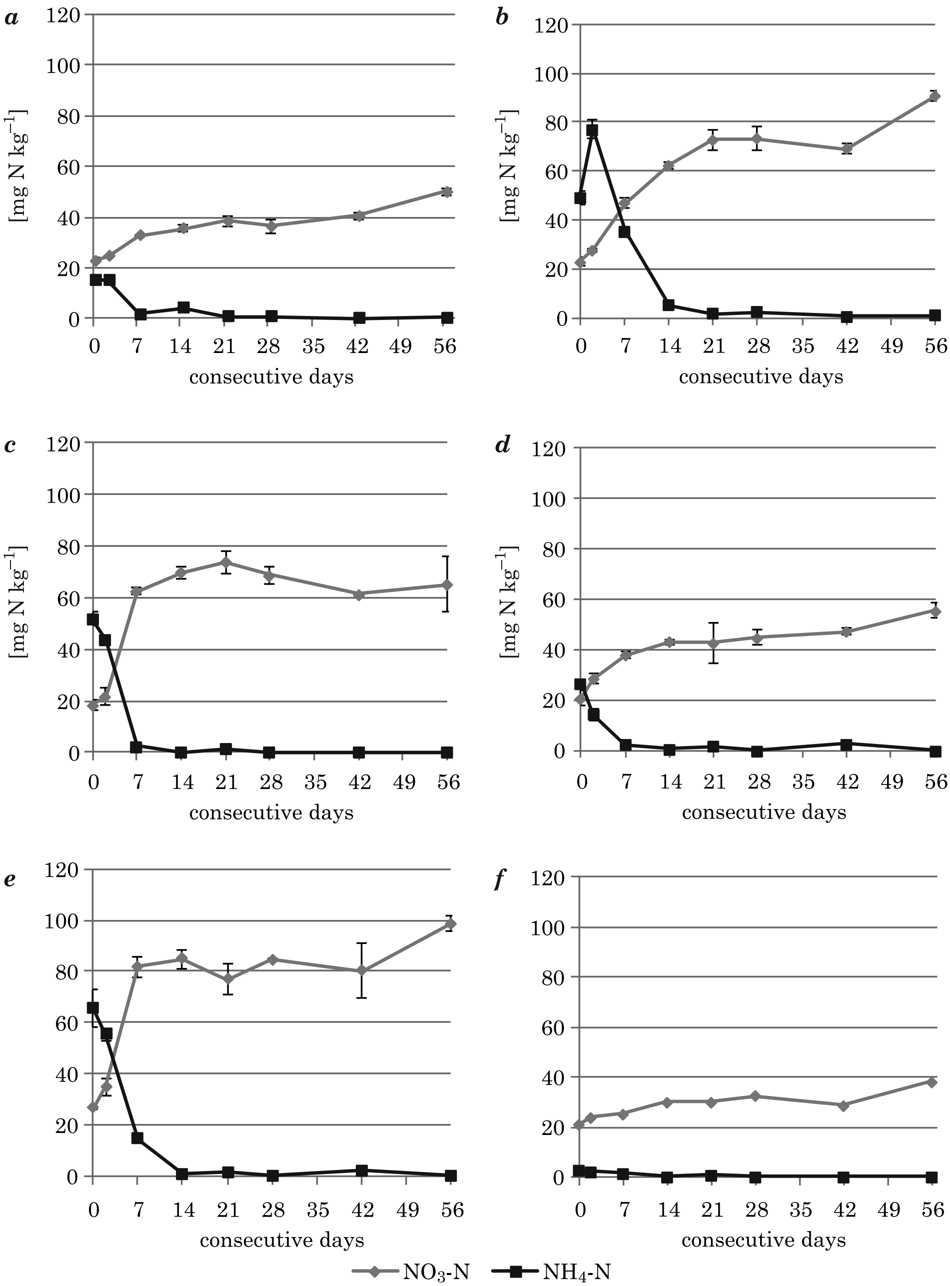

Fig. 1. Inorganic N (NO_3-N and NH_4-N) dynamics (mean value ± standard deviation; where absent, bars fall within symbols) in studied soils: *a* – control (S_1); *b* – soil + digestate (D); *c* – soil + liquid cattle slurry (LCM); *d* – soil + soild cattle manure (SCM); *e* – soil + mineral fertylizer (MF); *f* – control (S_2). Soil S_1 is a control for D treatment, soil S_2 is a control for LCM, SCM and MF treatments

Influence of fertilization on soil properties

The soil pH was affected by fertilizer and sampling date and their interaction (Table 3). At day 0 the addition of organic fertilizers increased the pH in order (pH units): LCM (+0.24) > D (+0.22) > SCM (+0.18). The rise of soil pH resulted from high pH of all organic fertilizers (Table 1). The addition of MF did not affect the soil pH. The highest decrease in pH in two first weeks of incubation was observed for both D and MF treatments, 0.33 and 0.34 pH units, respectively while LCM addition caused a drop of 0.18 pH units. The daily rate of pH decrease in first two weeks was 0.243 pH units day^{-1} for MF, 0.236 pH units day^{-1} for D and 0.0131 pH units day^{-1} for LCM. In the period from 14 to 56 day the pH values were stable (Figure 2). In the SCM treatment, the decrease rate was slower in first 14 days (0.0017 pH units day^{-1}) and was faster thereafter (0.0021 pH units day^{-1}). Throughout 56 days of incubation the pH decreased in following order (pH units): MF (0.42) > D (0.36) > LCM (0.25) > SCM (0.11).

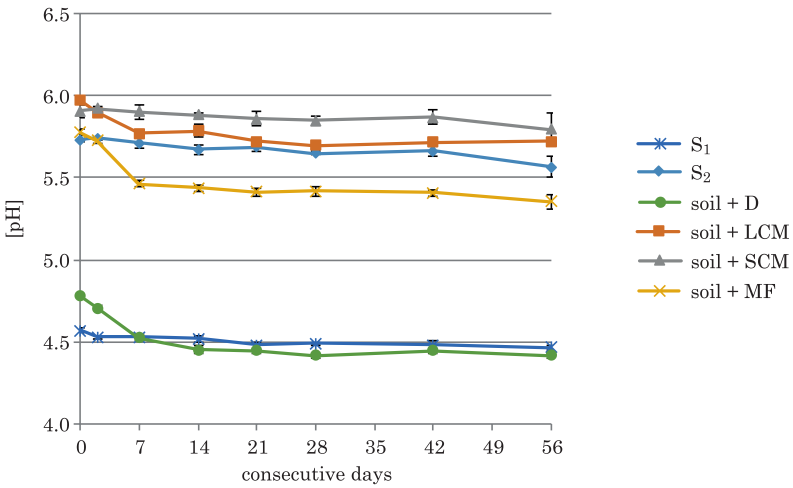

Fig. 2. Soil pH in 1 M KCl dynamics (mean value ± standard deviation; where absent, bars fall within symbols). Treatment codes: S_1 – a control for D treatment; soil + D – soil treated with digestate (D); soil + LCM – soil treated with liquid cattle manure (LCM); soil + SCM – soil treated with solid cattle manure (SCM); soil + MF – soil treated with mineral fertilizer (MF); S_2 – a control for LCM, SCM and MF treatments

Fertilization with organic materials did not influence TOC in soil, which varied within the range 13.27±0.46 – 15.06±0.96 g C kg^{-1} at day 0 and was at the same level at the end of incubation experiment. However, the addition of all organic fertilizers, except of SCM, increased the DOC concentration at day 0 comparing to control (Figure 3).

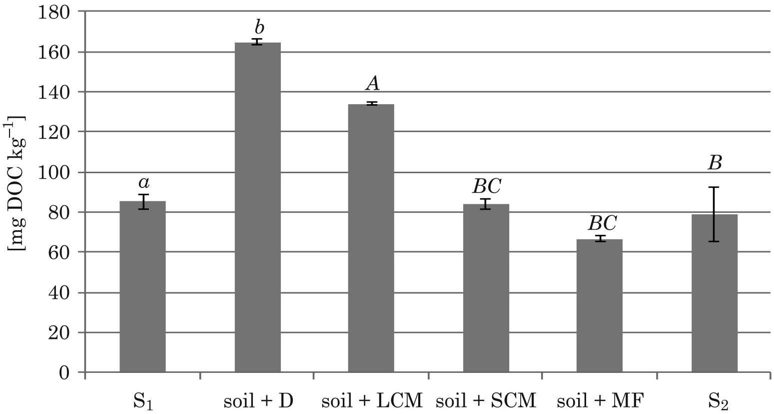

Fig. 3. Dissolved organic carbon (DOC) content (mean value ± standard deviation) at day 0. Treatment codes: S_1 – a control for D treatment; soil + D – soil treated with digestate (D); soil + LCM – soil treated with liquid cattle manure (LCM); soil + SCM – soil treated with solid cattle manure (SCM); soil + MF – soil treated with mineral fertilizer (MF); S_2 – a control for LCM, SCM and MF treatments Bars with the same letter are not significantly different according to the Tukey test (p < 0.05). Lower case letters indicate significant differences between S_1 and D treatment, upper case letters indicate significant differences among S_2 and LCM, SCM and MF treatments

The application of fertilizers slightly increased the water soluble phosphorus (P_w) content by ca. 4 mg P kg^{-1}, in case of D, LCM and SCM, while fertilization with MF supplied soil with high amount of P_w, increasing its content to 42.25±1.06 mg P kg^{-1}. In all soils fertilized with organic fertilizers the rapid decrease in P_w content was observed in the first week of incubation to the level similar to the P_w concentration in controls (Figure 4).

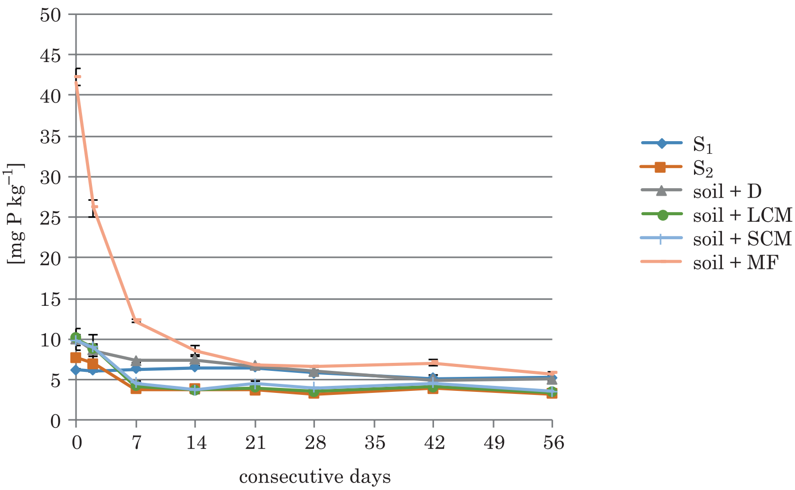

Fig. 4. Concentration of water-soluble phosphorus (Pw) in relation to time (mean value ± standard deviation; where absent, bars fall within symbols). Treatment codes: S_1 – a control for D treatment; soil + D – soil treated with digestate (D); soil + LCM – soil treated with liquid cattle manure (LCM); soil + SCM – soil treated with solid cattle manure (SCM); soil + MF – soil treated with mineral fertilizer (MF); S_2 – a control for LCM, SCM and MF treatments

Only in soil fertilized with MF, the P_w content was slightly higher than in control until day 56. The incorporation of organic and mineral fertilizers in soil increased the TP content comparing to S_1 and S_2, although this increase was not statistically significant. The TP content at day 0 was the highest in soil fertilized with MF (0.522±0.028 g P kg^{-1}) and the lowest in soil amended with D (0.410±0.048 g P kg^{-1}).

The incorporation of fertilizers to the soil had also impact on potassium forms, however only organic fertilizers supplied the soil with K_{dl} and increased significantly ($p < 0.05$) its content (Figure 5). The amounts of K_{dl}

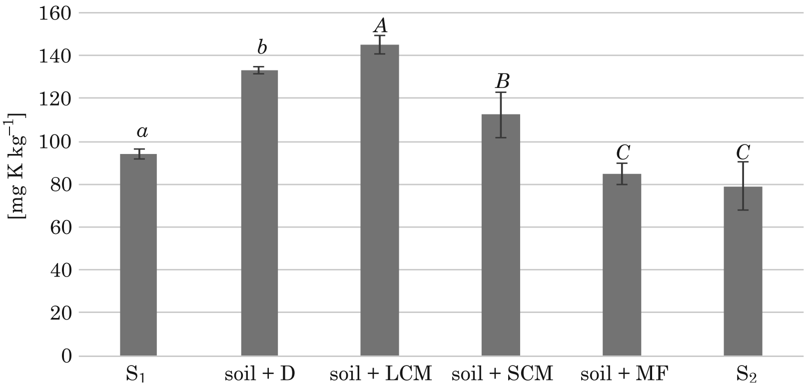

Fig. 5. Plant available K (Kdl) content (mean value ± standard deviation) at day 0. Treatment codes: S_1 – a control for D treatment; soil + D – soil treated with digestate (D); soil + LCM – soil treated with liquid cattle manure (LCM); soil + SCM – soil treated with solid cattle manure (SCM); soil + MF – soil treated with mineral fertilizer (MF); S_2 – a control for LCM, SCM and MF treatments Bars with the same letter are not significantly different according to the Tukey test ($p < 0.05$). Lower case letters indicate significant differences between S_1 and D treatment, upper case letters indicate significant differences among S_2 and CS, CM and MF treatments

at the end of incubation were similar to those from the day 0 and still they were significantly higher ($p < 0.05$) comparing to control, except for MF treatment. However, the fertilization did not increase the TK content in soil which was in the range of 1.35±0.03 to 1.69±0.06 g K kg^{-1} at the end of incubation. In both days the lowest TK content was observed for soil amended with SCM and the highest for soil fertilized with D.

Discussion

The nutrient composition differed in all 3 organic materials, with highest total Kjeldahl nitrogen (TKN) and total phosphorus (TP) content in digestate (D) and the lowest in solid cattle manure (SCM). The total solids (TS) decreased in order: SCM > D >LCM, while the highest volatile solids (VS) were found in SCM. Only total organic carbon (TOC) content was similar in all studied organic fertilizers. The chemical composition, TS and VS of D was typical for digestate produced in commercial biogas plants fed with maize silage alone or with some co-substrate constituting less than 10% of feedstock (WESTPHAL et al. 2016, NABEL et al. 2017, PROVENZANO et al. 2018). The SCM chemical properties were in a good agreement with typical ranges for this type of organic fertilizer (GRABOWSKI 2009), with rather low TS value resulting from very wet weather conditions preceding the SCM sampling from uncovered manure storage heap, which was very moist even in deeper parts. The chemical composition of LCM was characterized with much lower TS and content of nutrients than found in literature (GRABOWSKI 2009). This low level of nutrients may be a result of sampling LCM from the channel below the floor instead of storage tank. It must be emphasized that TS, VS and nutrient composition variability within every type of studied organic materials is very high (RISBERG et al. 2017) and depends on the fodder type and rate, on housing type, animal age and waste management in case of animal solid and liquid manure (HJORTH et al. 2010) while digestate characteristics depends on feedstock composition (TAMBONE et al. 2010) and quality of anaerobic digestion (AD) process.

The addition of easily-available N in the form of NH_4^+ and soluble organic C influenced the microbial activity in soil and triggered N transformation. In liquid cattle manure (LCM) nitrogen is in NH_4^+ form in 90% (GRZEŚKOWIAK 2013) and in used in this study MF nitrogen is only in NH_4^+ form therefore these two fertilizers supplied soils with the highest amounts of NH_4-N. This form of N is readily available for plants but it may be also fixed in the interlayer of clay minerals (CAVALLI et al. 2017). Lower amount of NH_4-N supplied with SCM and D resulted from higher content of N organic compounds, up to 60% in manure and 15-40% in digestate (RISBERG et al. 2017). However, high DOC content in D influenced microbial activity and in consequence the mineralization of easily-decomposable organic N compounds (ZHAO et al. 2007) resulting in the increase of NH_4-N content in soil in two days after fertilization. The important decrease of NH_4-N content occurred in all soils, except soil fertilized with D, in the first week of incubation. In soil fertilized with D, this drop in NH_4-N content from highest level to amount close to 0 took place in two weeks. In soil treated with MF the most rapid decrease of NH_4-N content was observed in first week of incubation and slower drop took place in following 7 days. This pattern of NH_4-N dynamics has been previously reported for incubation experiments (GRIGATTI et al. 2011, ALBURQUERQUE et al. 2012, DE LA FUENTE et al. 2013). The significant decrease of NH_4-N content in all fertilized soils with a concomitant rise of NO_3-N occurred through the nitrification of applied NH_4-N to the soil (GRIGATTI et al. 2011, ALBURQUERQUE et al. 2012, DE LA FUENTE et al. 2013). The nitrification was greatly stimulated by organic and mineral fertilizers inputs; however, its dynamics differed among the treatments. The most rapid nitrification was observed for soils treated with LCM and MF due to high initial NH_4-N inputs. Slower nitrification occurred in soil fertilized with SCM due to high amount of N in organic compounds. The D treatment also resulted in slower nitrification, what is contradictory to other studies on N dynamics in soils fertilized with digestates. In most incubation experiments, rapid nitrification took place in 1 or 2 weeks of incubation (GRIGATTI et al. 2011, ALBURQUERQUE et al. 2012, DE LA FUENTE et al. 2013). This slower nitrification may be the result of initial increase in NH_4-N in soil after fertilization.

All organic and mineral fertilizers provided a source of plant available N, in the beginning of the experiment mainly as NH_4^+ form and after 56 days only in NO_3^- form. The MF produced the largest recovery of inorganic N equivalent to N input and this is in a good agreement with studies of RIGBY and SMITH (2013). Nitrogen availabilities at the end of incubation were decreasing in the order: D (72.7% of TN added) > LCM (47.7% of TN added) > SCM (30.5% of TN added). Similar findings were reported by CAVALLI et al. (2017).

The addition of organic fertilizers increased the pH in all soils at the beginning of experiment due to organic fertilizers alkalinity (Table 1, Figure 2). Such rise of pH in soils treated with digestate and manures was reported by CAVALLI et al. (2017). In following days, nitrification of ammonium applied with mineral fertilizer decreased soil pH rapidly in MF treatment. The nitrification of applied NH_4-N together with those mineralized from easily-decomposed organic N compounds also influenced the soil pH in all organic treatments (CAVALLI et al. 2016). Strong relation between nitrification and soil pH dynamics (CAVALLI et al. 2017) results from acidifying effect of nitrification due to proton formation (GOULDING 2016).

The total amount of organic carbon (TOC) in soil results from net balance of all carbon fluxes entering and leaving the soil over a time period. The decomposition and mineralization of organic matter depends on the microbial activity and chemical nature of organic material and leads to the release of carbon dioxide (CO_2) and other trace gases, such as methane (CH_4) and carbon monoxide (CO) form soil (RODEGHIERO et al. 2012). The variability in soil organic carbon and the level of detection, under the regime of incubation experiment, did not allow detecting the statistically significant difference between TOC content in control and treated soil.

However, the addition of soluble C in liquid organic fertilizers such as D and LCM resulted in significantly higher DOC content in fertilized soils comparing to unfertilized controls. The supply of readily metabolizable C in organic material influences the microbial activity and biomass and therefore enhances organic matter degradation and nitrification (GÓMEZ-BRANDÓN et al. 2016).

The addition of P in the form of PO_4^{3-} in MF treatment significantly enriched soil in P_w, which was significantly higher than in soils treated with organic fertilizers; however, there was also slight increase in P_w content in these soils. Higher P_w content in MF treatment is in a good agreement with BACHMANN et al. (2011), who reported P_w content slightly higher in sandy soils amended with organic fertilizers and lower in loamy soils, comparing to mineral P treatment. In pot experiment with amaranth and sorghum, the P_w content also increased after organic fertilizer application comparing to mineral fertilization with N and K only, however the P_w in amaranth soils was not clearly affected by the amendment while in sorghum soils organic fertilizers supplied higher amount of P_w than mineral NPK addition. This was due to low P_w content in the soil and rapid fixation of easily soluble P in NPK treatment (HUPFAUF et al. 2016). Soil fertilization with organic amendments, both digested and undigested, increases the P_w content in longer time period comparing to mineral control treatment (BACHMANN et al. 2014). The P_w decrease in fertilized soils was due to the enhancement of microbial activity and growth of microbial biomass (HUPFAUF et al. 2016). Microbial P in soil is affected by fertilizer type and microbial-bound P is higher in soils amended with organic material than in mineral fertilizer treatments (BACHMANN et al. 2011). The incorporation of organic and mineral fertilizers slightly increased the total phosphorus (TP) content. Its increase in soils amended with digested and undigested dairy slurry was also reported by BACHMANN et al. (2011).

The addition of mineral fertilizer (MF) to the soil did not affect the K_{dl} and total potassium (TK) content due to mineral fertilizer chemical characteristics. This fertilizer consisted only of N and P and therefore did not supply with any K. The liquid cattle manure (LCM) treatment supplied soil with the highest amount of K, due to the highest K content, while solid cattle manure (SCM) treatment added the lowest amount of K because manure had much lower K content. According to GRZEŚKOWIAK (2013), liquid cattle manure is typical N and K organic fertilizer with K_2O content equal to 7 kg m^{-3}.

Conclusions

The digestate provided a significant amount of NH_4-N to soil, however less than that supplied in mineral fertilizer or liquid cattle manure. The nitrification rate of NH_4-N was slower for soil treated with digestate comparing to soils treated with liquid cattle manure and mineral fertilizers. This may be the advantage of digestate, because slower nitrification can limit losses of N *via* leaching. Although digestate application to soil initially increased pH, the nitrification causes pH decrease with the time. Digestate provided also water-soluble P at the same level as other organic fertilizers, but supplied soil with high amount of plant-available K and dissolved organic carbon. Therefore, the application of digestate should follow the same rules as traditional liquid fertilizers; however, its agronomic use should be based on N, P and K content. It also must be emphasized that digestate, even though is a valuable fertilizer which influences soil chemical properties similarly to liquid cattle manure, may only partially replace mineral fertilizers in Poland.

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