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Soil, slurry and application effects on greenhouse gas emissions

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ABSTRACT

In conjunction with soil type and climate, the use of nitrogen fertilizers is a major factor affecting nitrous oxide emissions. This study compares injection of pig slurry and pig slurry digestate at 15 or 20 cm depths with trailing-hose application followed by immediate incorporation. The work was based on a laboratory microcosm experiment with undisturbed soil cylinders (0–30 cm depth) from three arable soils (Histosol, Gleysol and Plaggic Anthrosol). Soil cylinders were fertilized with pig slurry and pig slurry digestate (150 kg N/ha) and emissions of N_2O, CH_4 and CO_2 were monitored. The comparison of application techniques over a 37-day period show that soil type and application technique, had a strong ($P < 0.001$) impact on N_2O emissions. Fertilization with pig slurry showed no significantly higher N_2O emissions than pig slurry digestate. Fertilizer injection significantly increased N_2O emissions compared to fertilization with a trailing-hose with incorporation.

Keywords: organic fertilization; manure; injection technique

Loss of soil nitrogen (N) is wholly negative in its impact: (i) nitrous oxide (N_2O) contributes to global warming; (ii) a valuable plant nutrient is lost and must be replaced; (iii) nitrate leaching and run-off pollutes groundwater and water bodies and directly contributes to eutrophication of natural ecosystems; (iv) ammonia (NH_3) emissions indirectly contribute to eutrophication of natural ecosystems and to indirect emissions of N_2O when the reactive N is later released (Well and Butterbach-Bahl 2010).

Soil N_2O emissions originate mainly from microbial processes such as nitrification and denitrification (Clemens et al. 1997). These processes depend on soil moisture, temperature, texture, mineral N and organic carbon (C) content. In particular, N fertilization and tillage are important factors influencing soil N_2O fluxes (Morken and Sakshaug 1998). Nitrous oxide after carbon dioxide and methane (CH_4), is one of the main anthropogenic greenhouse gases. Due to its high global warming potential compared to CH_4 and CO_2 it is a relevant greenhouse gas, even at low concentrations (IPCC 2007).

If liquid organic fertilizers are applied to the soil surface using band spreaders or broadcast spreaders, then 20–40% of the total ammoniacal N can be lost (Nyord et al. 2008). Injection reduces NH_3 losses up to 2% of total ammoniacal N (Huijsmans et al. 2003). If liquid organic fertilizers are inserted 15–20 cm below the soil surface, denitrification is increased by the formation of anaerobic zones due to the presence of easily-decomposable inorganic N and organic C (Flessa and Beese 2000). Thus, manure injection may lower NH_3 emissions but it can increase N_2O emissions (Boeckx and Van Cleemput 2001).

Earlier studies (Velthof et al. 1997, Velthof and Mosquera 2011, Aguilera et al. 2013) examined manure application with different manure application techniques. In general with manure application organic C and NH_4^+ in soil increases and yields in high denitrification rates with N_2O losses. But clear differences between application techniques cannot be shown.

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The objective of the present study was thus to test the impact of liquid manure application techniques (trailing-hose + incorporation, injection 15 cm and injection 20 cm) on greenhouse gas emissions in a laboratory-scale, incubation experiment under controlled temperature and moisture conditions, to control for external variables, before maize sowing. Moreover, we aimed to test the impact of manure type (pig slurry (PS) and pig slurry digestate (PSD)) and soil type (Histosol, Gleysol and Plaggic Anthrosol).

MATERIAL AND METHODS

Soil characterization and soil sampling. In this experiment, three different arable soils (Gleysol, Plaggic Anthrosol and Histosol) from northwest Germany (52°48'N, 08°01'E) were used (Table 1).

Volumetric soil water content was determined by a sample ring (100 cm^3, dry matter calculation by drying for 48 h by 105°C). Soil pH was measured in suspension of soil and 0.01 mol/L $CaCl_2$ in a ratio of 1:5, measurement was done with a pH-meter. The organic C was determined by elementary analysis. Therefore a soil sample was treated with HCl and heated to 900°C, the released CO_2 was measured by an infrared detector (DIN ISO 10694:1995-03-01, 1995). Total N was analysed by heat treatment (900°C) of a soil sample, whereas organic N is volatilized (DIN ISO 13878:1998-11, 1998). Soils were analysed for their soil mineral N concentrations before starting the experiment and after a period of 37 days. To analyze soil mineral N concentrations (NH_4^+ and NO_3^-), a soil core was pressed out of its Plexiglas™ tube and homogenized on day 37 after the fertilization event. A soil sample of 100 g, was then extracted using 0.0125 mol/L $CaCl_2$ applied using a 4:1 volume ratio. For measurements a segmented flow analysis system (SFAS) (SKALAR, Breda, the Neatherlands) was used.

For the last two years the used soils had been fertilized annually with 30 m^3/ha pig slurry (150 kg N/ha), and maize had been grown in monoculture. Before soil cultivation and fertilization in spring, 28 undisturbed, cylindrical, soil monoliths (40 cm high, 14.4 cm diameter) were taken from each of the three locations.

Microcosm experiment. The experimental treatments simulating three application techniques (trailing-hose + incorporation in 5 cm, injection depth 15 cm and injection depth 20 cm). The second (crossed) experimental factor was treatment with different organic fertilizers (PS and PSD). The treatments were tested in three soils (Histosol, Gleysol and Plaggic Anthrosol). For every treatment four replications were incubated in a randomized design.

We simulated a below-root injector called Premaister (Kotte Landtechnik, Rieste, Germany) developed for fertilizing maize with liquid organic fertilizers before sowing. This injection technique was compared to a trailing-hose with cultivator incorporation. For control unfertilized and untreated soil columns were used.

Before incubation, the basal 10 cm of subsoil was removed from the sample with a piston, to give each soil cylinder the same headspace (1.6 L). Soil cylinders were then installed in a microcosm system (Hantschel et al. 1994). Each soil cylinder was placed on a suction plate comprising a 0.45 µm polyamide filter membrane. To adjust the soil samples to defined moisture levels, they were first saturated with 100 mol/L 0.02 m $CaCl_2$ solution (to simulate rain water). After saturation, samples were drained by establishing a pressure of –100 hPa at the suction plate to lower soil water content

Table 1. Soil characteristics, carbon and nitrogen concentration, nitrate and ammonium N concentrations, bulk density and soil water content of the three soils

	Gleysol	Plaggic Anthrosol	Histosol
Sand (% DM)	73.40	83.30	83.30
Silt (% DM)	13.00	8.30	8.90
Clay (% DM)	13.60	6.00	4.90
C_{org} (%)	1.70	2.40	12.14
N_{total} (%)	0.20	0.20	0.85
C/N	8.50	12.00	14.23
NO_3^--N (mg/100 g DM)	5.95	5.00	4.35
NH_4^+-N (mg/100 g DM)	0.18	0.43	2.60
pH	5.1	5.8	4.3
Bulk density (g/cm^3)	1.28	1.27	0.74
H_2O vol. (%)	28.11	21.82	49.23
WFPS (target)	55.00	42.00	67.00

DM – dry matter; WFPS – water filled pore space

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to field capacity. After three days, all columns of any particular soil had very similar water contents (Vol. %). The experiment was carried out at 12°C, because this is the average soil temperature in the region when slurry is usually applied. After 10 days of pre-incubation in the microcosm system, fertilizer applications were commenced.

The soil monoliths used for the injection treatments were carefully pressed out of their Plexiglas™ tubes and the top 15 or 20 cm portions were removed. A furrow of defined volume (63 cm^3) and shape (a prism, 4.9 cm wide, 2.6 cm deep and 10 cm long) was formed in the unsifted, compacted bottom soil with a custom V tool. For variant comparison and to show soil effects, 50 mL (equivalent to 150 kg N/ha) of PS or PSD was applied to the furrow of each soil column with a syringe (Table 2).

The topsoil sample (c. 3 L) was sieved (5 mm sieve) before being replaced in the tube from which it was removed, to simulate the mixing of soil during PS and PSD application. For the trailing-hose treatment with immediate incorporation (TH + I 5 cm), only 5 cm of top soil were removed from the monolith. This was sifted and mixed with 50 mL PS or PSD.

The replaced soil was compacted in a defined manner using a piston (600 g, 14.4 cm diameter, fall height 20 cm). Preliminary tests had shown that the soil thus compacted had a density similar to that in the field (bulk density 1.2 g/cm^3) after injection using a commercial, below-root slurry injector.

Immediately after fertilizer application, the heads of the soil cylinders were closed with a gastight cover having an air inlet/outlet. The headspace was later flushed with a fresh air flow of 20 mL/min. Sampling of the exhaust air for N_2O, CH_4 and CO_2 analyzes was done with glass vials (20 mL) for 37 days (Well et al. 2006). Sampling was done daily at the same time.

Table 2. Fertilizer characteristics, total nitrogen, NH_4^+-N and pH of fertilizer

	Pig slurry digestate	Pig slurry
Dry matter (%)	6.11	8.85
N_{total} (% FM)	0.51	0.5
NH_4^+-N (% FM)	0.25	0.21
N_{total} per soil tube (mg)	255	250
NH_4^+ per soil tube (mg)	125	125
pH	7.5	7.2

FM – fresh matter

N_2O, CH_4 and CO_2 measurement. Gases were analyzed with a gas chromatograph (GC 2014, Shimadzu, Duisburg, Germany) modified as described previously (Loftfield et al. 1997). For parallel N_2O, CH_4 and CO_2 measurement the system is equipped with an electron capture detector (ECD) and a flame ionization detector (FID). Samples with N_2O concentration > 3000 ppb were additionally measured with a different gas chromatograph (GC 7890A, Agilent, Santa Clara, USA) with an ECD and a headspace auto-sampler (GC-PAL, CTC, Zwingen, Switzerland). For quality control, a sequence of ten control samples with ambient concentrations was measured at least weekly. Samples were measured only if the coefficient of variation of the peak areas was smaller than 3% (usually it was < 2%) during these tests. Emission fluxes (F) of N_2O, CO_2 and CH_4 were calculated from the measured differences between the concentrations of these gases in the microcosm's inflowing (C_{in}) and outflowing (C_{out}) air streams as:

$$F = (C_{out} - C_{in}) \times Q/A$$

This difference was multiplied by the air flow rate (Q) which was divided by the surface area (A) of the microcosm. Fluxes (N_2O, CO_2 and CH_4) were monitored and cumulative values calculated over the full 37 days duration of the experiment.

Statistical analyses were conducted with the *R*-statistic software (R Core Team 2014) and, comprised analysis of variance (ANOVA) and a Tukey's test. Typically for N_2O fluxes, treatments with higher fluxes exhibited an increased standard deviation between replicates. Thus a log10-transformation of cumulative fluxes was applied prior to statistical analysis.

RESULTS AND DISCUSSION

Nitrous oxide. In 37-day time run N_2O emissions from the Histosol were highest in comparison to the Gleysol and the Plaggic Anthrosol. In all treatments double peaks in N_2O emissions can be seen (Figure 1).

Calculation of cumulative fluxes (daily means over 37 days) showed the lowest ($P < 0.001$) N_2O fluxes in the Plaggic Anthrosol, while the highest ($P < 0.001$) were in the Histosol (Table 3). In the

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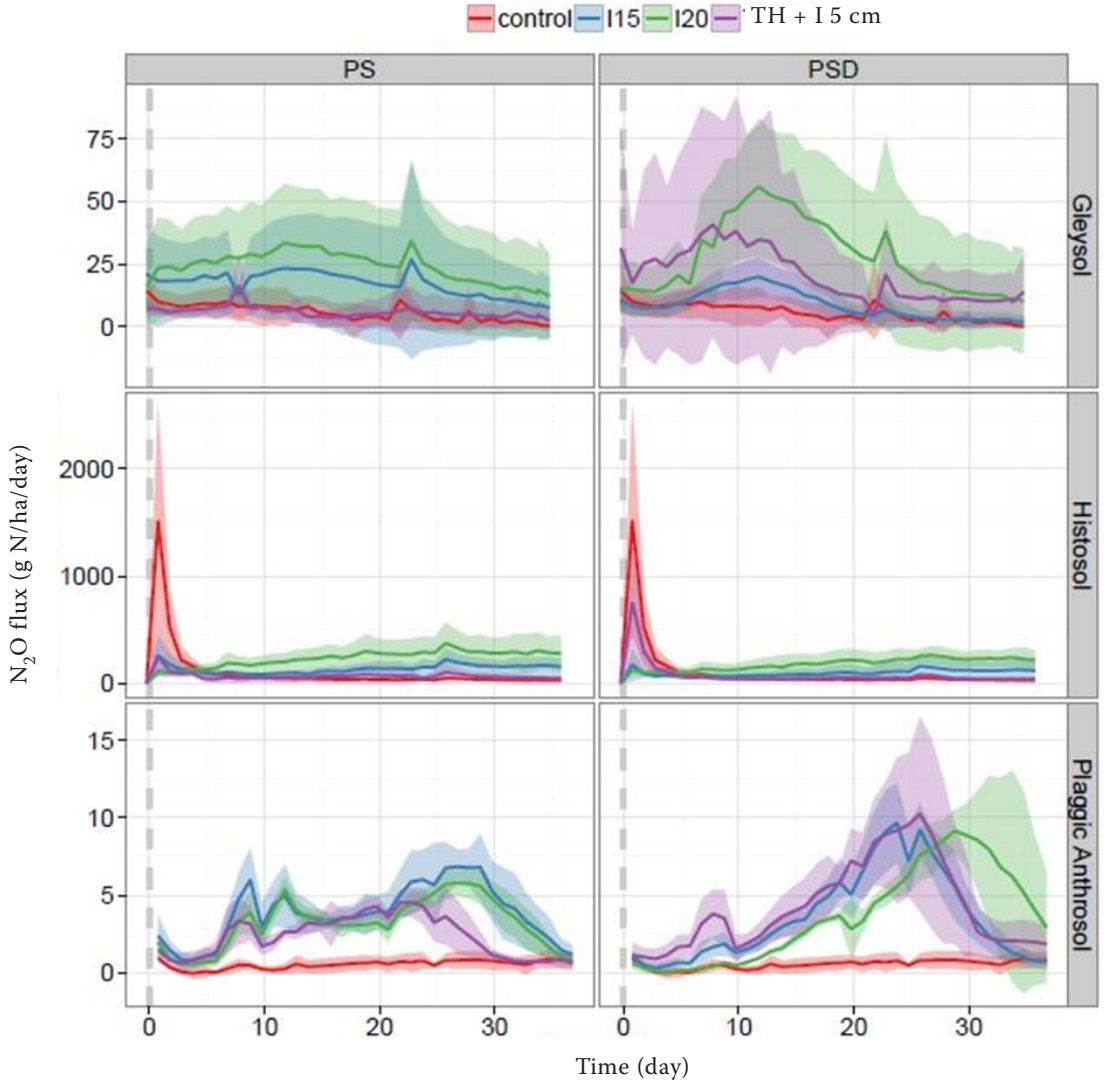

Figure 1. Nitrous oxide fluxes from three soils (Gleysol, Plaggic Anthrosol and Histosol) over a period of 37 days with injection (I15 – injection 15 cm; I20 – injection 20 cm) and trailing-hose incorporations (TH + I 5 cm – trailing-hose + incorporation in 5 cm) of pig slurry (PS) and pig slurry digestate (PSD) (n = 4). Means (bold lines) and standard deviations (colored areas)

Histosol the treatment combination I20 PS showed significantly higher fluxes than the control and the treatment combination TH + I 5 cm PSD.

A double peak in N_2O was reported before (Köster et al. 2011), where the first peak could be explained with denitrification based on ^{15}N tracing studies. It can be speculated that the first peak can be explained by bacterial denitrification, because CO_2 fluxes were still high in the first days after manure application (Figure 2).

Soil type significantly ($P < 0.001$) influenced N_2O emission. Elevated N_2O fluxes are known to result from the combined effect of labile organic C and NH_4^+ from the manure and elevated mineral N when soil moisture is high (Velthof and Mosquera 2011, Aguilera et al. 2013). PS applications tended to show higher N_2O emissions than PSD fertilization but the differences were not significant. These results are comparable to Velthof and Mosquera (2011) who compare the effect of pig slurry and cattle slurry. It can be shown that the application technique and the soil significantly influence N_2O emissions (Table 4).

It can be presumed that in the Histosol easily degradable organic C, inorganic N and small gas diffusivity due to high moisture increase microbial respiration by creating anoxic hot spots in the injection slit (Flessa and Beese 2000, Velthof

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Table 3. Mean daily cumulative nitrous oxide, carbon dioxide and methane fluxes from three soils (Gleysol, Plaggic Anthrosol and Histosol) over a running time of 37 days with injected (I15 – injection 15 cm; I20 – injection 20 cm) and trailing-hose incorporated (TH + I 5 cm – trailing-hose + incorporation in 5 cm) pig slurry (PS) and pig slurry digestate (PSD) (n = 4). Means and standard deviations (SD)

Soil	Treatment	Fertilizer	N_2O (g N/ha/day)	SD	α < 0.05	CO_2 (kg C/ha/day)	SD	α < 0.05	CH_4 (kg C/ha/day)	SD	α < 0.05
Gleysol	control	untreated	6	3	bc	20	6	a	–1	0	b
	TH + I	PS	6	4	bc	20	9	a	–1	0	ab
	I15	PS	17	19	be	19	5	a	–1	1	b
	I20	PS	24	21	cef	16	5	a	–1	1	b
	TH + I	PSD	20	0	be	24	10	a	–1	0	b
	I15	PSD	9	4	bcd	14	1	a	–1	0	ab
	I20	PSD	29	22	def	16	3	a	–1	1	ab
Plaggic Anthrosol	control	untreated	1	0	a	14	2	a	–2	0	ab
	TH + I	PS	2	0	b	15	1	a	–2	1	ab
	I15	PS	4	1	bc	16	3	a	–1	0	ab
	I20	PS	3	0	bc	15	3	a	–1	1	ab
	TH + I	PSD	4	2	bc	16	2	a	–2	1	a
	I15	PSD	4	1	bc	16	2	a	0	0	ab
	I20	PSD	4	1	bc	14	1	a	0	1	a
Histosol	control	untreated	87	30	efg	20	4	a	1	0	c
	TH + I	PS	68	42	eh	25	5	a	1	0	c
	I15	PS	135	40	gh	21	2	a	1	0	c
	I20	PS	238	112	h	21	1	a	1	1	c
	TH + I	PSD	70	24	efg	25	5	a	1	1	c
	I15	PSD	96	57	fh	23	4	a	1	1	c
	I20	PSD	179	69	gh	20	5	a	2	2	c

and Mosquera 2011, Aguilera et al. 2013). In the two other soils N_2O fluxes are not affected by the application method because the general N_2O emission level is low (Velthof et al. 1997).

Carbon dioxide fluxes. During the first 24 h to 48 h after fertilizer application there was an increase in CO_2 emission. In the soil columns with PS and PSD injection and TH + I 5 cm, CO_2 emissions were not significantly ($P > 0.05$) higher than in the undisturbed controls (Figure 2, Table 3).

Fatty acids included in slurries are metabolized in the first days after the slurry application. The addition of easily available labile carbon from slurry and digestate led to a priming effect with an increased CO_2 exhibition (Velthof and Mosquera 2011). High CO_2 fluxes in the first days after manure application identify bacterial mineralization and denitrification of soil organic N (Köster et al. 2011). CO_2 fluxes from the Histosol tended to be higher because the conditions (organic C and H_2O) for mineralization and denitrification are very good in this soil.

Methane fluxes. Emissions of CH_4 increased during the 48 h period following fertilizer application. CH_4 fluxes remain above the levels of the control treatment after fertilizer application. But over the complete trial duration there are no differences in cumulative CH_4 emissions (Table 3).

Methane emissions in this study can be compared to those of Chadwick and Pain (1997), they noted that slurry itself is responsible for higher CH_4 losses after application, because of the easy available organic C fractions that react with soil organic matter.

Ammonia and nitrate. With fertilization NH_4^+ and NO_3^- contents increased, and the mineral N

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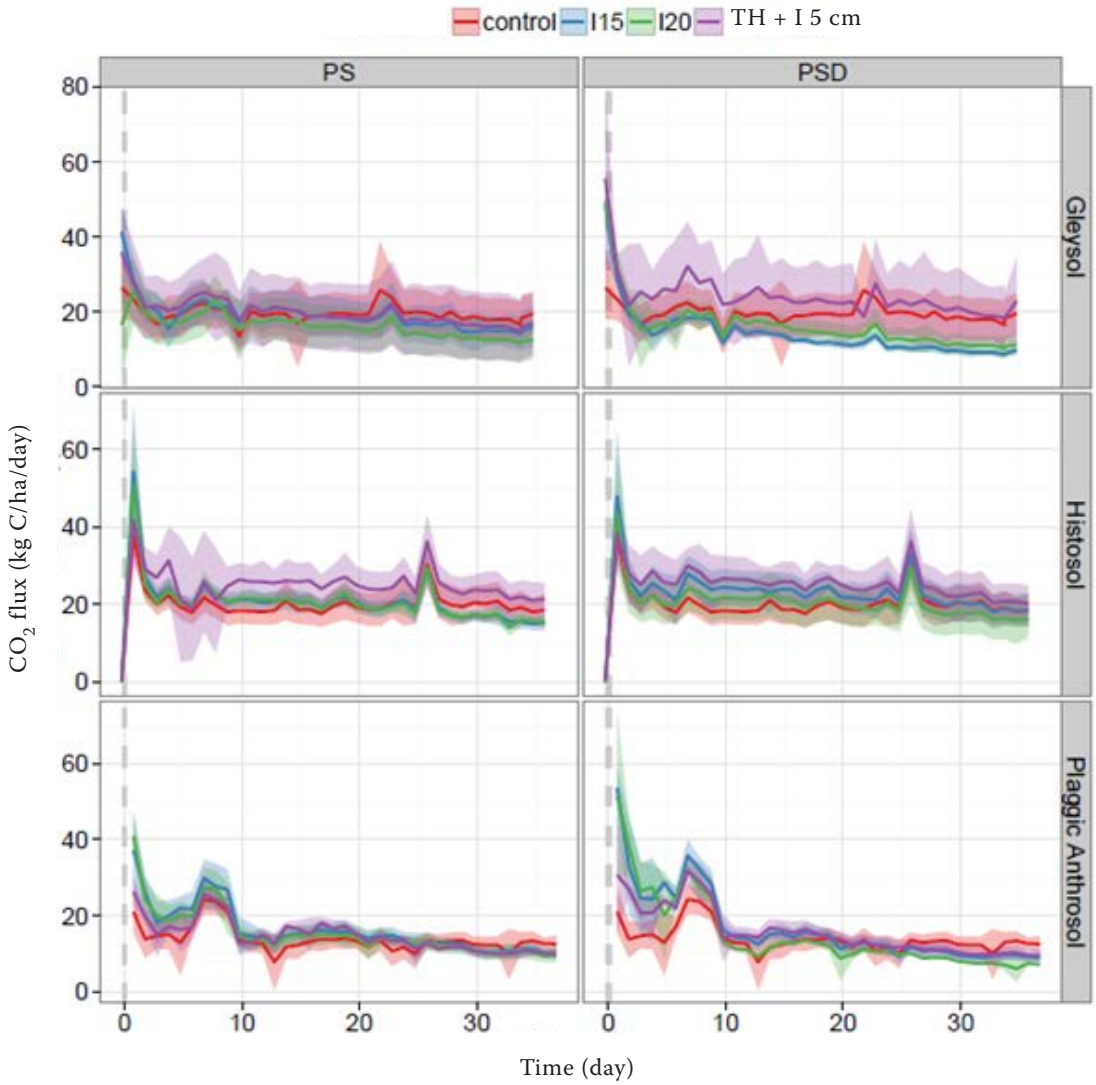

Figure 2. Carbon dioxide fluxes from three soils (Gleysol, Plaggic Anthrosol and Histosol) over a 37 days with injected (I15 – injection 15 cm; I20 – injection 20 cm) and trailing-hose incorporated (TH + I 5 cm – trailing-hose + incorporation in 5 cm) pig slurry (PS) and pig slurry digestate (PSD). Means (bold lines) and standard deviations (colored areas) (n = 4)

Table 4. Analysis of variance testing significance of experimental factors with log-transformed cumulated N_2O fluxes as the response

Df	Sum	Sq	Mean	*F*-value	*P* (> *F*)
AT	2	17.246	0.8623	126.741	3.07e-05***
Fertilizer	1	0.0286	0.0286	0.4208	0.51929
Soil	2	251.546	125.773	184.8564	< 2.2e-16***
AT:fertilizer	2	0.2677	0.1338	19.670	0.14977
AT:soil	4	0.8348	0.2087	30.673	0.02384*
Fertilizer:soil	2	0.2347	0.1173	17.248	0.18789
AT:fertilizer:soil	4	0.0886	0.0221	0.3255	0.85966
Residuals	54	36.741	0.680		

a:*b* – interaction between *a* and *b*; AT – application technique. The control was not included in the model. *P < 0.1; ***P < 0.001

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Table 5. Mineral nitrogen (N) concentration (NH_4^+ and NO_3^-) from three soils (Gleysol, Plaggic Anthrosol and Histosol) after a running time of 37 days with injected and trailing-hose incorporated pig slurry (PS) and pig slurry digestate (PSD), mean and standard deviation (SD), statistical analysis (α < 0.05) within one soil

Soil	Treatment	Fertilizer	NH_4^+ (mg/kg)			NO_3^- (mg/kg)		
			mean	SD	α < 0.05	mean	SD	α < 0.05
Gleysol	before incubation		0.18	0.10	a	5.95	0.84	a
	control		0.13	0.09	a	20.88	2.90	b
	I15	PS	0.21	0.13	a	87.26	11.74	b
	I20	PS	0.16	0.17	a	88.39	25.02	b
	TH + I 5 cm	PS	0.18	0.09	a	70.30	23.71	b
	I15	PSD	0.23	0.20	a	102.21	16.62	b
	I20	PSD	0.25	0.24	a	93.92	6.99	b
	TH + I 5 cm	PSD	0.23	0.08	a	79.60	34.02	b
Plaggic Anthrosol	before incubation		0.43	0.17	a	5.00	0.36	a
	control		0.29	0.08	a	25.19	5.57	b
	I15	PS	0.50	0.16	a	88.91	19.33	b
	I20	PS	0.71	0.66	a	67.54	19.25	b
	TH + I 5 cm	PS	0.31	0.09	a	80.94	6.32	b
	I15	PSD	0.46	0.33	a	101.36	13.31	b
	I20	PSD	0.41	0.10	a	93.71	21.10	b
	TH + I 5 cm	PSD	0.34	0.07	a	73.54	14.82	b
Histosol	before incubation		2.60	0.95	a	4.35	1.52	a
	control		1.82	0.56	a	26.50	7.70	bcd
	I15	PS	7.70	9.83	a	102.73	28.03	b
	I20	PS	2.67	1.29	a	79.61	26.00	bc
	TH + I 5 cm	PS	11.12	10.00	a	80.67	16.21	bc
	I15	PSD	4.77	2.19	a	121.16	54.83	bc
	I20	PSD	5.73	3.67	a	155.58	87.50	bc
	TH + I 5 cm	PSD	5.02	5.80	a	100.43	15.63	bcd

contents at the end of the experiment were significantly higher than at start of the trial. Within any of the soils there were no significant differences between mineral N (N_{min}) contents (Table 5).

Most of the fertilized ammonia was converted to nitrate. This results in high denitrification because nitrate is not limited. Studies of Comfort et al. (1990) reported no significant differences in NO_3^- and NH_4^+ contents in soil after surface application compared to injection of pig slurry in a laboratory study. It can be assumed, that in a laboratory study without rainfall there is no N leaching. Only the period between manure application and maize sowing is shown in this trial. This results in higher mineral N contents in this microcosm study (> 100 mg/kg N_{min}) compared to a field trial over a complete growing season (< 10 mg/kg N_{min}) (LWK Niedersachsen 2008).

This study showed effects of application technique on N_2O, CO_2 and CH_4 emission. Differences between soils and application techniques with respect to N_2O emissions are significant ($P < 0.001$). The soil type and factors, related to it (soil moisture, aeration, respiration and soil aggregation) and the application technique are more important in determining emissions than the applied substrate. Moreover, no significant differences between pig slurry and pig slurry digestate on N_2O emissions were observed. In the future there is a need for annual field studies with different soil types and

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different locations to increase statements on the influence of different application depth and techniques on emissions after fertilizer application.

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