AGRICULTURAL AND FOOD SCIENCE

Agricultural and Food Science (2023) 32: 128–138

https://doi.org/10.23986/afsci.130086

Greenhouse gas and reactive N-gas emissions from a horse paddock – relationship to physicochemical properties of soil

Marja Maljanen[1], Emilia Marttila[1,2] and Hem Raj Bhattarai[3]

[1]Department of Environmental and Biological Sciences, University of Eastern Finland, P.O. Box 1627, 70211 Kuopio, Finland

[2]Centre for Economic Development, Transport and the Environment, Environmental Protection Unit, Alvar Aallon katu 8, 60100 Seinäjoki, Finland

[3]Natural Resources Institute Finland, Production Systems, Grasslands and Sustainable Farming Unit, Halolantie 31 A, 71750 Maaninka, Finland

e-mail: marja.maljanen@uef.fi

The horse industry today in Europe is an increasing leisure or sporting activity. Due to considerable input of nutrients via dung and urine, horse paddocks can be significant sources of greenhouse gases (GHG) and reactive nitrogen (N)-gases. However, horse paddocks have not been studied intensively in contrast to e.g., dairy cow pastures. Here we report GHG emissions from one selected horse paddock in Eastern Finland. During the first year, GHG emissions from the site and surrounding grassland area were measured with closed static chamber method. In the following year soil samples were taken from the sites to study GHG emission and reactive N-gas (nitrous acid and nitric oxide) emissions in the laboratory. The paddock area emitted significant amounts of N-gases and methane compared with surrounding areas during wet season. N-gas emissions also increased with increasing soil mineral N concentration. We conclude that horse paddocks can be significant but local sources of greenhouse gases and wet soil conditions should be avoided to mitigate the emissions.

Key words: equine, manure, greenhouse gas, soil, emission, nitrogen

Introduction

The horse industry has an important role in the national economy and agriculture in many European countries, not only as horse race activity and betting, however also as a leisure activity (Liljenstolpe 2009). Horse farms are located more often in urban or suburban areas, where horse dung is a waste and disposal of it can be costly especially in urban areas (Havukainen et al. 2020). On the other hand, horse dung can also be utilized as fertilizer or as bioenergy (Havukainen et al. 2020). Although, horse dung is often removed from the paddock as part of the regular management practice, horse paddocks are never totally manure free. Horse manure is rich in organic carbon (C), organic nitrogen (N), and also phosphorus (P) and it can pose considerable risk to the environment due to ground and surface water contamination via nutrient leaching and runoff (Airaksinen et al. 2007, Parvage et al. 2013, Maltais-Landry et al. 2018). On the other hand, horse manure can make the paddock as a source of C and N containing greenhouse gases that have direct influence on climate warming and atmospheric chemistry (Baldocchi et al. 2012, Maljanen et al. 2016). The high amount of decomposing organic matter in the dung can serve as a substrate for soil microbial processes producing carbon containing greenhouse gases (GHG) such as carbon dioxide (CO_2) and methane (CH_4) from paddocks, especially when conditions are suitable, e.g., in anaerobic wet conditions (Conrad 1996). Horses themselves can also produce methane through their digestive process, through the fermentation of fibrous feed. However, as the amount of methane produced by horses as non-ruminants is relatively small compared with ruminants, such as cattle (Kienzle and Zeyner 2010, Elghandour et al. 2019), we can assume that there are also less CH_4 emissions from horse excreta.

The manure decomposition process can be also a source of mineral N which subsequently can fuel soil microbial N-cycling processes (including nitrification and denitrification) and thus can promote the production/emission of associated N gases, particularly another greenhouse gas nitrous oxide (N_2O), other atmospherically relevant N gases such as nitric oxide (NO) and nitrous acid (HONO) (Su et al. 2011, Maljanen et al. 2016, Bhattarai et al. 2018), and also ammonia (NH_3) (Weir et al. 2017). Regarding atmospheric chemistry, HONO is an important source of hydroxyl radical (OH) in the atmosphere, and it can oxidize, for example CH_4 contributing towards lowering its atmospheric burden. Hydroxyl radicals also participates in cloud formation and thus have cooling effect (Claeys 2004, Petters et al. 2006). In the atmosphere NO gas regulates ozone cycle and nitrate radical formation and participates in acid rain formation (Atkinson 2000).

Received 19 May 2023 / Accepted 23 August 2023
The Scientific Agricultural Society of Finland

Studies assessing the emissions of these C and N containing gases from horse paddocks are lacking, thus limiting our knowledge regarding the effect of these areas on the atmosphere. There is substantial evidence that dairy pastures with animal excreta are a source of greenhouse gases, and their emission rates vary according to the manure quantity and availability (Rotz 2017). However, the emission dynamics of C and N containing gases from horse paddock can be very different from dairy pastures. Firstly, since horses are not ruminants and the quantity and properties of manure differ from that of dairy cows (Airaksinen 2006, Maltais-Landry et al. 2018). Secondly, the input of manure into the paddocks is constant throughout the year in contrast to dairy cows, which are in the northern parts of Europe spending time outside mainly during the short grazing season. These aspects make horse paddock as different kind of source regarding C and N containing gases compared with dairy cow paddocks. However, the effect of horse manure on the paddock's soil physicochemical properties and their temporal and spatial dynamics in relation with the emissions of C and N containing gases have not been studied.

In Finland 73 400 horses produce approximately 18 t of manure per year (Havukainen et al. 2020) and a portion of the manure is often left outside in the paddocks at least for some periods. Furthermore, horses in Finland are kept outside in the paddocks (or grazing on pasture during summer) throughout the year exposing paddock soil continuously to excreta. In this study we aim to assess the emission rates and dynamics of all three greenhouse gases, CO_2, CH_4 and N_2O, and atmospherically important HONO and NO gases from one horse paddock in Finland, where horses were kept daily year-round. Here, we measured *in-situ* N_2O and CH_4 emissions and ecosystem respiration (CO_2) and the relationship between gas fluxes and soil properties in the studied site. Additionally, we studied the production potential of HONO and NO gases by measuring their emissions rates and soil physical and chemical properties in laboratory conditions using soils sampled from the same horse paddock and surrounding areas. We hypothesized that horse paddock soils can be significant sources of all three greenhouse gases and HONO and NO gases as result of high and continuous organic matter and N-input via excreta.

Materials and methods

Study site and management of the paddock

The study site located in Kuopio, Eastern Finland (62°57'19" N, 27°46'32" E) on a farm housing about 40 horses. The paddock area was 2500 m^2 and the soil type was silt/clay (Fig. 1) and it was established about 30 years prior to the study on grass sward and there were no underground drainage. Throughout years 2018 and 2019 a total of four horses were spending about 8–10 hours daily in the paddock. The vegetation inside the paddock was efficiently grazed by horses and they were fed also with dry horse hay daily (3 kg per horse, N content about 2%). In addition, the rest of the daily dry hay dose (7 kg per horse) and additional fodders were given inside the barn.

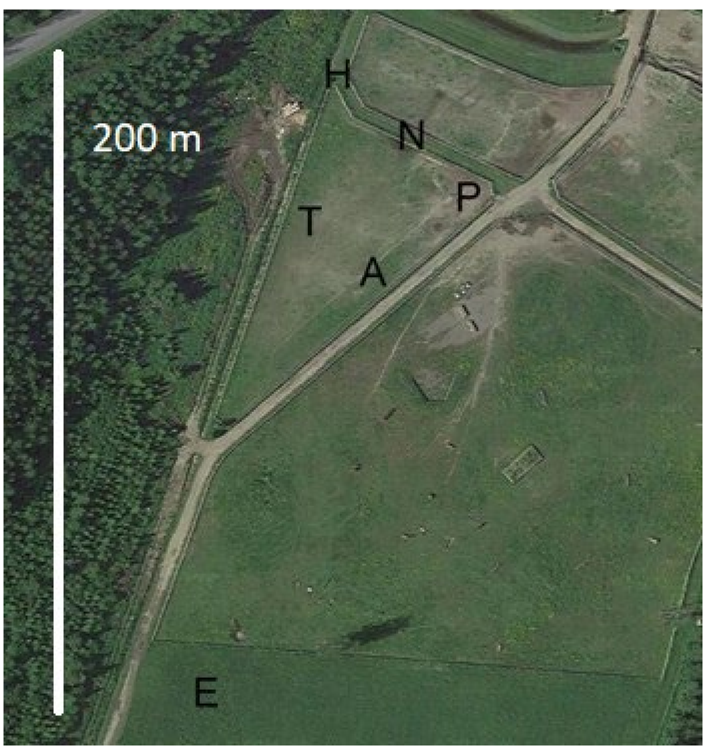

Fig. 1. An aerial photo (Google Maps 2023) of the study site and sampling points. The sampling points P, A, T, H and N were either inside or at proximity of the horse paddock. Sampling points, P, A and T were inside the paddock, P = close to the paddock's gate, the most affected zone, A = feeding area and T = randomly occupied area. Sampling points H and N were at paddock's proximity, and were ungrazed and unfertilized grassland, Hay field (E) used in the laboratory experiments located about 100 meters south from the paddock.

Our visual assessment on grazed areas of the grass sward identified that *Phleum pratense*, *Festuca pratensis* and *Trifolium repens* were the vegetation species preferred by horses on the paddock. Whereas, species, such as *Matricaria discoidea*, *Ranunculus acris* and *Gnaphalium uliginosum* were rejected ones. Outside the paddock, on the grassland area (Fig. 1), the most dominant plant species were *Hieracium vulgate*, *Prunella vulgaris*, *Ranunculus acris* and *Taraxacum officinale*. As part of management practice, horse dung was removed from the paddock area with a tractor in the spring after snow melted in May but not during the study period between June and October. Grass was cut in June and July outside the paddock and there was no grazing on that grassland area. In 2019 an adjacent hay field (mixture of *Phleum pratense* and *Festuca pratensis*) on same soil type was also included in laboratory experiments.

Field measurements

We conducted field measurements ten times during a period from June to October in 2018 to estimate the emission rates of N_2O and CH_4 emissions and ecosystem respiration (CO_2) with a closed static chamber method. There were five gas and soil sampling points; three inside the paddock (P, A and T) and two outside of the paddock (H and N) of which point N was on a slope receiving some surface runoff from the paddock (Fig. 1). The sampling points inside the paddock were selected as heavily occupied by the horses (P close to the gate and A feeding area) and less occupied area (T) (Fig. 1). Gas flux measurements were made manually, using three replicates on each sampling point. To avoid the direct effect of dung on the gas fluxes, chambers for gas flux measurements were installed on soil surfaces with no visible dung piles. Round metal chambers (ø 30 cm, h 26 cm) were twisted in the soil and gas samples (25 ml) were collected through a sampling line using a gas tight 50 ml syringe from the headspace of the chamber at 5, 15, 25, and 35 min after chamber enclosure. Gas samples were then injected into pre-evacuated vials (Labco Exetainer®) and concentrations of CH_4, CO_2 and N_2O were analyzed with a gas chromatograph (Agilent 6890N, Agilent Technologies, Germany) in the laboratory. There was an additional 1 m long open tube (inner Ø 2 mm) installed on the top of the chamber to stabilize the pressure when samples were drawn from the chamber. Gas flux rates were calculated from the linear increase or decrease of the gas concentrations in samples. All gas flux results were accepted if CO_2 concentrations in the chamber headspace were increasing linearly ($R^2 > 0.8$). Zero or close to zero CH_4 and N_2O flux rates were not omitted. Additionally, soil samples were collected during gas sampling days for analysis of some soil physicochemical properties. Three samples (sampling depth 10 cm, corer diameter 5 cm) taken from each sampling point were pooled and sieved for the analysis. Soil pH, electrical conductivity (EC), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and dissolved organic carbon (DOC) concentration, and gravimetric moisture (GM) were measured in all samples. Additionally, soil bulk density (BD) and organic matter content (OM) were measured once in October 2018 using five replicate volumetric samples (height 5 cm, diameter 5 cm) from the topsoil of each location. Nitrate and nitrite concentrations were measured with Ion Chromatograph (Dionex ICS-2100, Thermo Scientific) and DOC with TOC analyzer (TOC-L, Shimadzu) from Soil: Milliq H_2O (1:2.5 V: V) extractions. Ammonium concentration was measured using colorimetric method (Fawcett and Scott 1960) from soil:1M KCl extractions (1:2.5 V: V). For gravimetric moisture determination soil was dried at 105 °C for 24h and organic matter was determined as loss in ignition at 550 °C for 2h.

Laboratory measurements

To study the production potential of N_2O, NO and HONO, in 2019 we conducted flux measurements in laboratory conditions using soil samples from the same P and N sampling points and additionally from adjacent hay field (E) with similar soil type, located about 100 meters form the paddock. This additional sampling point on the same soil type was included because it is not affected by the horse manure and only mineral N fertilizers were applied there. Therefore, point E serves as a background control for point P and N. Due to logistical reasons, *in-situ* measurements of HONO and NO emissions rates were not possible in our study. Soil samples were collected five times from the study sites between 15 May and 31 July 2019. Soil was sampled from the depth of 0–10 cm and was homogenized, sieved (mesh size 4 mm) and packed into PVC soil cores with height 15 cm and inner diameter 19 cm (Bhattarai et al. 2019). The soil cores were kept at room temperature (20 °C) in the laboratory and the GHG fluxes were measured using closed static chamber technique using a PVC chamber (H = 22 cm, inner Ø 20 cm), which was placed gas tight on the top of the soil cores during gas sampling. Gas collection for CH_4, CO_2 and N_2O analysis and flux calculation were done similarly as in field sampling. HONO and NO measurements were made simultaneously using a dynamic chamber method and a Teflon® chamber fitted on the PCV cylinder. HONO concentration in the headspace of the chamber was measured with a Long Path Absorption Photometer instrument LOPAP® (Quma Elektronik GmbH, Germany) and NO concentration with Thermo 42i NOx analyzer (Thermo Fisher Scientific, USA). The detailed description of the methods can be found in Bhattarai et al. (2018). All gas fluxes were measured once from each sample and the soil extraction with H_2O and KCl for the analysis were done in the following day after gas flux measurements. All analysis of soil physiochemical properties (pH, EC, NO_3^-, NO_2^-, NH_4^+, GM) were done similarly as with the samples collected in 2018.

Statistical methods

The correlations between measured gas flux rates and soil variables were tested with non-parametric Spearman rank correlation since the gas flux data was not normally distributed according to Shapiro Wilks test and the differences between groups were tested with Kruskall- Wallis test (IBM ® SPSS ® Statistics, version 27.0.1.0, IBM Corp.).

Results

Field measurements

The growing season in 2018 was very dry and warm, the mean temperature was 20.8 °C in the nearby weather station in July 2018. Maximum soil (depth 5 cm) temperature during the sampling days was measured in July (25 °C) and the lowest in October (0.5 °C). Gravimetric soil moisture content was low during the study period being the lowest in the end of July (less than 10% in the paddock soils, Table 1). The soil pH (H_2O) was an average 5.8 in all sampling points, but slightly higher in P and A sampling points. Mineral N concentrations varied temporally and between sampling points (Table 1). Nitrate concentration inside the paddock (P) peaked in late June being 83 ug NO_3^--N g^{-1}. The highest NO_2^- and NH_4^+ concentrations were measured also inside the paddock from T sampling point in early June (Table 1). Soil organic matter content inside the paddock was higher (7.10, 7.29 and 7.90%) than outside (6.92 and 6.01%) at P, A, T, H and N location, respectively. Soil bulk density was slightly higher inside the paddock being 1.38, 1.25, 1.35, 1.23 and 1.24 g cm^{-3} at P, A, T, H and N locations, respectively.

Table 1. Measured soil properties of samples taken during gas flux measurements in situ from each sampling point. The values represent the mean of three replicates.

Point	Day	pH	EC	GM	DOC	NO_3^-	NO_2^-	NH_4^+
P	1 June 2018	5.95	191	18.5	35.2	36.1	2.86	16.4
	13 June 2018	6.03	74	22.8	34.8	8.47	0.73	13.8
	27June 2018	5.28	336	21.8	51.5	83.8	1.57	19.4
	11 July 2018	5.83	60	14.8	34.9	3.17	0.28	1.26
	20 July 2018	5.85	98	18.2	39.3	2.75	0.25	3.07
	31 July 2018	6.00	300	6.63	125	2.43	2.11	53.5
	7 August 2018	5.95	63	19.6	28.0	1.94	0.47	1.62
	22 August 2018	5.90	158	10.4	32.6	6.09	0.15	10.9
	10 September 2018	5.66	63	16.8	21.9	6.77	0.04	739.0
	4 October 2018	6.04	35	29.0	21.7	5.35	0.42	829.0
A	13 June 2018	5.72	67	20.1	25.4	7.47	0.30	9.68
	27 June 2018	5.03	282	21.9	29.1	61.8	0.61	31.6
	11 July 2018	5.44	46	20.0	38.0	2.84	0.30	1.00
	20 July 2018	5.21	187	11.5	30.5	0.57	1.48	5.38
	31 July 2018	5.44	94	7.49	32.3	0.55	0.02	2.54
	7 August 2018	5.71	71	21.0	42.4	1.62	0.15	1.37
	22 August 2018	5.65	70	8.95	23.1	0.93	0.49	1.46
	10 September 2018	5.39	130	18.2	23.3	17.5	0.43	134.0
	4 October 2018	5.89	22	33.5	23.5	2.01	0.80	9.65
T	1 June 2018	5.65	40	23.0	37.4	3.00	0.03	9.00
	13 June 2018	6.56	548	19.0	232	32.0	4.70	101.0
	27 June 2018	5.66	39	19.7	43.0	1.96	0.03	6.31
	11 July 2018	5.46	39	19.4	29.2	3.77	0.08	2.93
	20 July 2018	5.45	68	10.9	59.4	0.67	<0.01	6.05
	31 July 2018	5.52	70	9.08	38.0	0.66	<0.01	4.95

	7 August 2018	5.65	52	18.7	24.2	0.76	0.10	2.67
	22 August 2018	5.54	52	12.1	25.7	0.94	0.47	3.66
	10 September 2018	5.62	40	18.2	24.8	2.70	0.09	16.7
	4 October 2018	5.85	18	33.6	13.0	3.84	0.35	7.94
H	13 June 2018	5.90	34	15.0	26.8	0.63	0.10	3.55
	27 June 2018	5.88	32	18.2	39.5	<0.01	0.02	1.63
	11 July 2018	5.88	29	25.1	35.4	0.15	0.21	1.44
	20 July 2018	5.73	43	9.34	42.0	0.32	0.02	1.56
	31 July 2018	5.62	54	14.3	30.0	0.33	<0.01	3.47
	7 August 2018	5.76	42	24.3	24.4	0.26	0.23	1.33
	22 August 2018	5.64	53	14.2	36.1	0.25	0.22	2.04
	10 September 2018	5.74	42	20.0	25.1	1.37	0.22	13.4
	4 October2018	6.08	11	34.5	21.9	0.52	0.94	11.2
N	1 June 2018	5.86	25	14.5	29.5	0.22	0.01	3.94
	13 June 2018	5.95	17	17.3	9.49	0.21	0.06	2.28
	27 June 2018	5.90	25	22.2	34.6	0.08	<0.01	0.97
	11 July 2018	5.75	24	19.0	29.4	0.09	<0.01	0.69
	20 July 2018	5.58	37	14.5	31.8	<0.01	<0.01	1.11
	31 July 2018	5.68	62	11.7	41.6	<0.01	<0.01	1.01
	7 August 2018	5.65	37	20.1	25.6	0.12	<0.01	0.43
	22 August 2018	5.69	37	15.5	26.6	0.07	0.09	0.95
	10 September 2018	5.93	22	20.7	21.9	0.05	0.05	5.43
	4 October 2018	6.00	12	34.8	13.9	0.85	0.32	8.21

GM = gravimetric moisture (%); pH = pH (H_2O), EC = electrical conductivity (µS cm^{-1}); DOC = dissolved organic carbon in soil (µg C g^{-1}); NO_3- = soil nitrate concentration (µg N g^{-1}); NO_2- = soil nitrite concentration (µg N g^{-1}); NH_4+ = soil ammonium concentration (µg N g^{-1})

Nitrous oxide emissions varied between sampling points and sampling times (Fig. 2) and they did not correlate with air or soil temperature or soil moisture, but emissions increased with increasing NO_3^- and NO_2^- concentration (Table 2). The highest measured emissions (up to 1980 µg N_2O-N $m^{-2}h^{-1}$) were detected inside the paddock in early June (Fig. 2). Unfortunately, gas analysis on June 27 failed and no gas data is available from that day. Cumulative N_2O production calculated by multiplying the mean emission between each two sampling times with the number of days between these dates during the study period of 125 days were 9.1, 3.8 and 0.21 kg N_2O-N ha^{-1} (sampling points P, A, and T inside the paddock) and 0.81 and 0.08 kg N_2O-N ha^{-1} (sampling points H and N outside the paddock).

All sampling points were small net CH_4 sinks (uptake of atmospheric CH_4) and no net CH_4 emissions were measured during the study period (Fig. 2). Methane uptake decreased when soil moisture increased while there was also similar correlation with soil pH, NO_3^- and NO_2^- concentration (Table 2). On the other hand, methane uptake was increased when soil (both TS3 and TS5) and air temperature and DOC concentrations increased (Table 2). The roughly calculated cumulative CH_4 fluxes during the study period were –0.8, –1.2, –1.5, –1.1, and –1.1 kg CH_4 ha^{-1} for the sampling points P, A, T, H, and N, respectively.

Soil CO_2 flux (respiration) followed well with air and soil temperature (Fig. 2) and increased with increasing DOC concentrations (Table 2). Respiration rate had negative correlation with NH_4^+ and NO_3^- concentrations in soil (Table 2). The highest respiration rates were measured outside the paddock from grassland (H and N points), whereas inside the paddock with low vegetation coverage respiration rates were on average lower (Fig. 2). The measured respiration rate in dark has wide daily and seasonal variation. We did not measure here net CO_2 exchange, which also includes photosynthesis of plants, therefore, we cannot estimate the warming effect of CO_2. If we calculate the emissions of the N_2O and CH_4 using GWP approach (IPCC AR5, Myhre et al. 2013) then the total effect is roughly 3750, 1560, 43.4, 306 and 2.51 kg CO_2 eq ha^{-1} during 125 days for P, A, T, H and N sampling points, respectively.

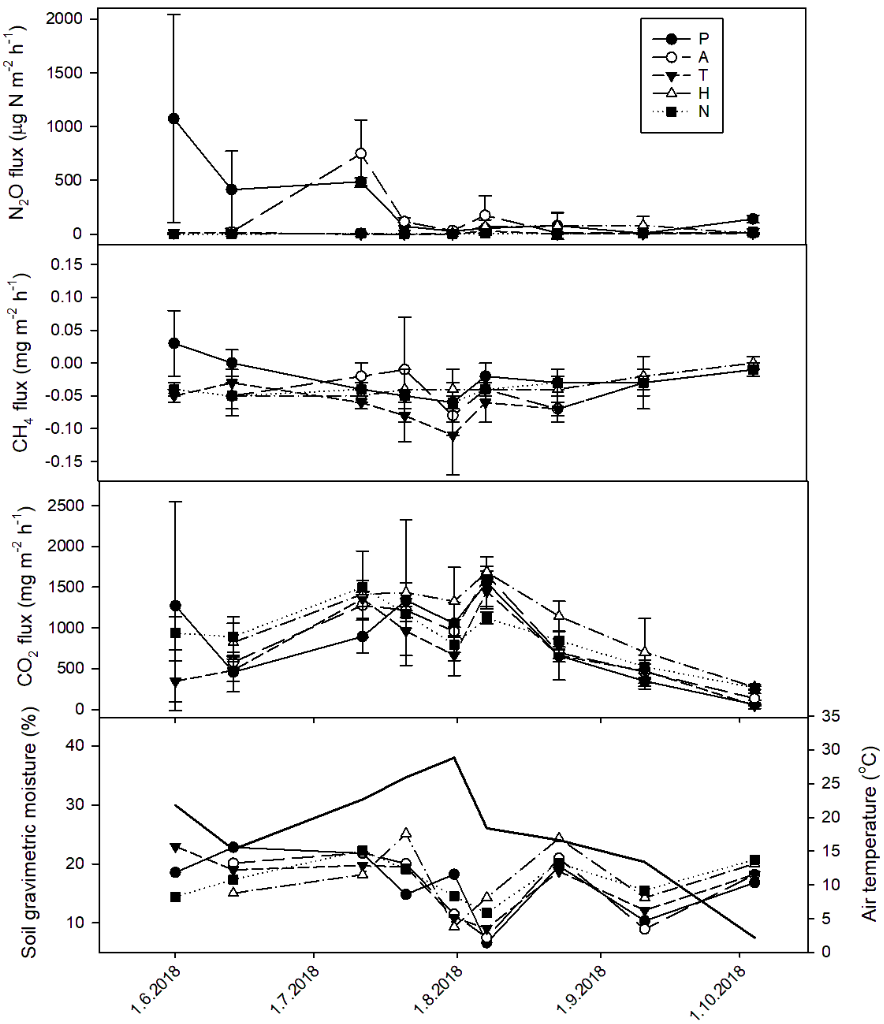

Fig. 2. Nitrous oxide (N_2O) and methane (CH_4) fluxes and ecosystem respiration (CO_2) (average ± SD, n=3) from the horse paddock soil measured *in situ* on the top. Gravimetric soil moisture (different dotted lines) and air temperature (solid thick line) during the sampling days on the bottom. P = near the gate (the most occupied), A = feeding area, T = randomly occupied, H = grassland outside the paddock (not grazed, under a slope), N = grassland outside the paddock (not grazed)

Table 2. Correlation between soil variables, air temperature, and gas emission rates from field measurements in 2018 (Spearman correlation coefficients, * = $p < 0.05$; ** $p < 0.001$)

	CH4	CO2	N2O	GM	pH	EC	DOC	NO_3^-	NO_{2-}	NH_4^+
CO2	-0.326*									
N2O	0.428**	0.100								
GM	0.550**	-0.236	0.191							
pH	0.443**	-0.250	0.171	0.336*						
EC	-0.165	0.190	0.476**	-0.425**	-0.329*					
DOC	-0.348*	0.427**	0.128	-0.359*	0.165*	0.509**				
NO_{3-}	0.330*	-0.373*	0.497**	0.230	-0.047	0.530**	0.015			
NO_2^-	0.500**	-0.289	0.490**	0.284	0.235	0.342*	-0.143			
NH_4^+	0.244	-0.564**	0.140	0.045	0.052	0.404**	-0.052	0.694**		
T_{air}	-0.607**	0.632**	-0.189	-0.548**	-0.395**	0.263	0.665**	-0.341*	-0.440**	
TS3	-0.620**	0.706**	-0.111	-0.449**	-0.468**	0.333*	0.636**	-0.361*	-0.418**	-0.366*
TS5	-0.632**	0.702**	-0.110	-0.485**	-0.474**	0.321*	0.622**	-0.375**	-0.434**	-0.318*

CH_4 = CH_4 emission; CO_2 = soil respiration; N_2O = N_2O emission; GM = gravimetric moisture; pH = pH (H_2O); EC = electrical conductivity; DOC = dissolved organic carbon; NO_3- = soil nitrate concentration; NO_2- = soil nitrite concentration; NH_4+ = soil ammonium concentration; Tair = air temperature during gas sampling; TS3 = soil temperature at 3 cm depth; TS5 = soil temperature at 5 cm depth

Laboratory measurements

The highest N_2O emission rates (up to 2000 µg N_2O-N m^{-2} h^{-1}) were measured from horse paddock (P) sample in the first sampling round (15 May 2019) and the lowest emissions or even small uptake from the N and E samples taken in end of July (Fig. 3). Nitrous oxide emissions from the horse paddock samples were significantly higher ($p < 0.05$), even up to two magnitudes higher, than in the other samples throughout the study period.

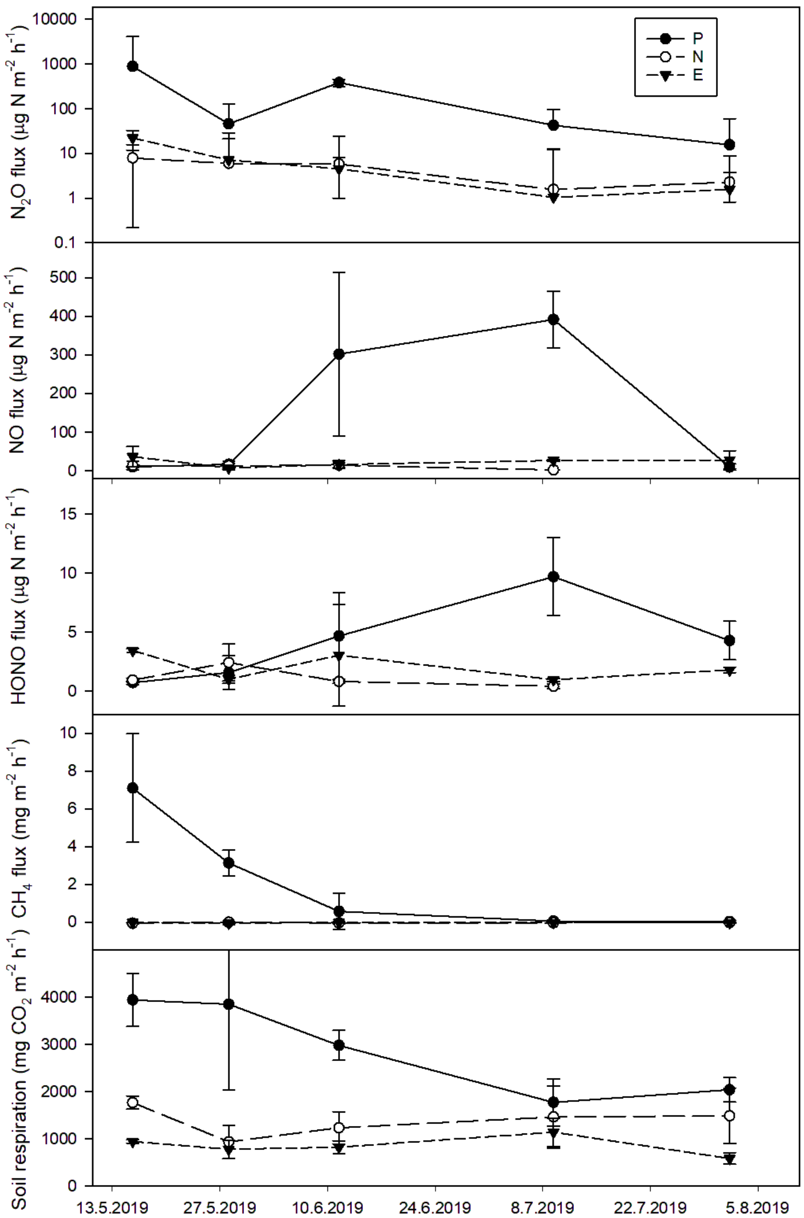

Fig. 3. Nitrous oxide (N_2O), nitric oxide (NO), nitrous acid (HONO) and methane (CH_4) emissions (average ± SD, n = 3) from the soil samples measured in the laboratory at +20 °C (sampling depth 0–10 cm). Note the logarithmic scale for N_2O emission. P = inside the paddock, near the gate (the most occupied), N = grassland outside the paddock (not grazed), and E = nearby hayfield

Emission rates from hay field (E) and grassland (N) did not differ statistically. The N_2O emission rates increased with increasing soil moisture, EC, pH, NH_4^+, NO_3^-, and NO_2^- concentrations ($p < 0.01$) (Table 3). We also observed an increasing NO_3^- concentration with decreasing NH_4^+ consumption (Table 4). The roughly estimated cumulative production from 15 May to 31 July 2019, for the period of 78 days was 7.7 kg N_2O-N ha^{-1} in horse paddock samples alone and 0.16 kg N_2O-N ha^{-1} in grassland and 0.19 kg N_2O-N ha^{-1} hayfield samples.

Table 3. Correlation between soil variables and gas emission rates from laboratory measurements 5in 2019 (Spearman correlation coefficients, * = $p < 0.05$; ** $p < 0.001$)

	CH_4	CO_2	N_2O	HONO	NO	GM	pH	EC	NO^{3-}	NO_2^-
CO2	0.512**									
N2O	0.671**	0.677**								
HONO	0.244	-0.017	0.237							
NO	0.126	0.119	0.303	0.355*						
GM	0.273	0.172	0.410**	-0.247	-0.148					
pH	0.509**	0.545**	0.469**	-0.216	-0.016	0.315*				
EC	0.591**	0.442**	0.644**	0.457**	0.403**	0.063	0.226			
NO_3^-	0.235	0.030	0.385**	0.621**	0.459**	-0.018	-0.094	0.780**		
NO_2^-	0.546**	0.594**	0.755**	0.001	0.279	-0.476**	0.504**	0.351*	0.084	
NH_4^+	0.558**	0.551**	0.790**	0.241	0.291	0.591**	0.274	0.668**	0.510**	0.651**

CH_4 = CH_4 emission; CO2= soil respiration; N_2O = N_2O emission; HONO = nitrous acid emission; NO = nitric oxide emission; GM = gravimetric moisture; pH = pH (H_2O), EC = electrical conductivity; NO_3^- = soil nitrate concentration; NO_2^- = soil nitrite concentration; NH_4^+ = soil ammonium concentration

Only horse paddock samples (P) emitted CH_4 in the laboratory measurements, other samples were showing small CH_4 uptake (Fig. 3). The highest CH_4 emissions (up to 10 mg CH_4 m^{-2} h^{-1}) were measured from the very first samples taken from the horse paddock in May, when the soil was still very wet after snowmelt and thawing (Fig. 3). Thereafter CH_4 emissions decreased and in the late summer some of the samples from P sampling point were even sinks for CH_4. All N and E samples were small net sinks for atmospheric CH_4 during the study period. The roughly estimated cumulative emission from 15 May to 31 July in 2019 for the period of 78 days was 24 kg CH_4 ha^{-1} from horse paddock (P) and net uptake of –0.7 kg CH_4 ha^{-1} in grassland (N) and hayfield (E).

Table 4. Measured soil properties of samples taken for laboratory gas flux measurements from each sampling point

Point	Day	pH	EC	GM	NO_3^-	NO_2^-	NH_4^+
P	15 May 2019	6.99	125	48.7	0.87	3.97	35.5
	27 May 2019	7.36	130	32.9	0.80	2.82	9.39
	11 June 2019	6.50	160	22.8	12.4	2.32	15.9
	09 July 2019	5.84	495	11.8	55.8	1.29	3.75
	31 July 2019	6.05	299	19.0	33.6	0.01	2.88
N	15 May 2019	5.80	16	28.9	0.58	0.38	2.17
	27 May 2019	5.96	14	27.3	0.57	0.09	0.70
	11 June 2019	6.12	19	18.6	0.32	0.78	0.01
	09 July 2019	5.99	23	17.5	0.03	< 0.01	< 0.01
	31 July 2019	5.59	32	15.9	0.08	< 0.01	< 0.01
E	15 May 2019	5.75	72	31.0	21.6	0.19	13.2
	27 May 2019	5.54	66	32.4	9.02	0.09	4.95
	11 May 2019	6.13	35	29.7	2.06	0.19	0.02
	09 July 2019	5.98	54	18.9	3.40	< 0.01	1.23
	31 July 2019	5.81	64	16.6	2.95	< 0.01	< 0.01

GM = gravimetric moisture (%); pH = pH (H_2O); EC = electrical conductivity (µS cm^{-1}); NO_3^- = soil nitrate concentration (µg N g^{-1}); NO_2^- = soil nitrite concentration (µg N g^{-1}); NH_4^+= soil ammonium concentration (µg N g^{-1})

Soil respiration (CO_2 emission) was highest in horse paddock soil and decreased from May to July. The cumulative emissions of CO_2 in the field are difficult to estimate based on these measurements since the production of CO_2 is highly dependent on temperature. If we calculate the emissions of the N_2O and CH_4 only using GWP approach (IPCC AR5, Myhre et al. 2013) then the total production based on the laboratory measurements during the study period are roughly 3900, 47 and 58 kg CO_2 eq ha^{-1} for horse paddock, grassland, and hayfield, respectively.

All the studied soils were emitting also HONO and NO. The emissions of HONO varied between 0.2 to 13 µg HONO-N m^{-2} h^{-1} and NO emissions varied between 2.2 to 530 µg NO-N m^{-2} h^{-1}. In the first sampling the highest emissions of HONO and NO were measured from fertilized hay field, whereas later in the summer horse paddock soil had the highest emissions when the soil moisture was decreasing. However, there was no significant correlation between soil moisture and NO or HONO emission rates if all data was analyzed. If only horse paddock data (P) were analyzed, then HONO emissions increased when soil moisture was decreasing ($p < 0.01$). HONO and NO emission rates were correlated together ($p < 0.05$; Bhattarai et al. 2018) and they also correlated positively with soil EC and NO_3^- concentration ($p < 0.01$) but not with soil NO_2^- concentration. It can be seen clearly that NO and HONO emissions followed a similar pattern throughout the sampling time as reported by Bhattarai et al. (2018, 2019). Due to technical problems HONO and NO emissions were not measured from grassland samples at the end of July. The ratio of N_2O-N:NO-N:HONO-N emissions in paddock samples was different (60:45:1) than in grassland and hayfield samples (4:11:1) which were not receiving any manure. Thus, as expected horse manure affected paddock soil increased especially N_2O production relative to other N-gases.

Discussion

Based on the results, we can say that horse paddock soils can be significant but local sources for the studied gases. In the field measurements, we could observe that N_2O emissions increased only slightly in the autumn in sampling point N, which was located outside the paddock under a slope, close to the horse paddock fence. Horse paddocks can occasionally be very strong sources for N_2O, but also sources for CH_4 during optimal conditions, especially in the spring and early summer when soil is still wet, as we could see in the laboratory experiment. Soil compaction caused by the horses can also affect the N_2O and CH_4 production by reducing porosity of the soil and thus O_2 availability (Conrad 1996, Bilotta et al. 2007). The calculated seasonal field emission rates for N_2O from the “hot spots” (points P and A) inside the paddock were clearly higher than those measured from e.g., fertilized boreal grasslands on mineral soil measured with similar methods and climatic conditions (Virkajärvi et al. 2010, Bhattarai et al. 2018). Compared with the N-gas emissions from fresh and composted horse manure (Maljanen et al. 2016), the emissions calculated per area were even higher from the paddock, which was surprising. Weather conditions are affecting the emission rates also in the horse paddocks. In 2018 the summer was extremely dry and the GHG emissions were low whereas conditions in early summer 2019 were different and soil remained wet for longer period resulting high N_2O and CH_4 production rates in the laboratory experiments. The earlier GHG studies from cow pastures in similar climatic conditions, have been made using different approach by measuring simulated dung and urine patches and calculating the arial emission based on the coverage of these patches (Virkajärvi et al. 2010, Maljanen et al. 2012). The estimated annual emissions of CH_4 and N_2O from a cow pasture on grass swards in these studies were from –0.02 to 0.64 kg CH_4 ha^{-1} and from 3.2 to 4.1 kg N_2O-N ha^{-1}. In our study, the roughly estimated N_2O emissions from a horse paddock for 125 days were close to the annual emissions from dairy cow pastures, but CH_4 emissions were less.

In the laboratory experiment the maximum HONO emission rate from the horse paddock soil (about 10 ug N m^{-2} h^{-1}) was similar as from heavily N-fertilized (450 kg N ha^{-1}) grassland in corresponding climatic conditions (Bhattarai et al. 2018) but almost 10-fold lower than measured directly from horse dung (Maljanen et al. 2016). The maximum NO emission from the paddock soil was four times higher than the maximum from N-fertilized grassland (Bhattarai et al. 2018) and about the same magnitude as reported from horse dung (Maljanen et al. 2016). Compared with fresh dairy cow dung and urine patches (Maljanen et al. 2007), NO emissions from the horse paddock soil were from 10 to 50-fold higher. Emissions of NO and HONO from hay field and grassland were low and close to those measured from unfertilized plots with similar methods in the study by Bhattarai et al. (2018). The emissions of HONO and NO from the horse paddock soil (point P) could be linked to denitrification (Wu et al. 2019, Bhattarai et al. 2021) as we observed a significant positive correlation between HONO and NO emissions and NO_3^- concentrations (Table 3). Nevertheless, the HONO and NO emissions could be emitted by ammonia oxidizers also (Oswald et al. 2013, Scharko et al. 2015). Although, we did not find any significant correlation between HONO and NO emissions with NH_4^+ and NO_2^- concentrations (Table 3), it is worth noting that an increasing concentration of NO_3^- with decreasing NH_4^+ and NO_2^- concentrations (Table 4) in the paddock soil (point P) was observed. This indicates an enhanced activity of ammonia oxidizers/oxidation, which is also known to produce both HONO and NO gases (Oswald et al. 2013, Scharko et al. 2015). Therefore, based on our data it could be assumed that both microbial processes, denitrification and ammonia oxidizers/oxidation could have contributed to the HONO and NO emissions, however, further studies are required to assess and quantify the role of HONO and NO sources processes from horse paddock soil.

Our field measurements were lacking winter-time emissions due to practical reasons and therefore we cannot estimate the annual emissions. Measurements with chambers or snow gradient method (Sommerfeld et al. 1993) is difficult from frozen surface and compacted and disturbed snow cover. However, N_2O emissions can be very high in boreal climate (Kim and Tanaka 2001, Maljanen et al. 2007) and especially from soils with animal manure (Virkajärvi et al. 2010). Also, the net CO_2 exchange, including the effect of plant photosynthesis, is missing here due to practical reasons, we only measured instantaneous ecosystem respiration rates, which are known to follow soil temperatures and have clear diurnal variation. In this kind of environment, the eddy covariance method (e.g. Li et al. 2023) would be the most efficient method to catch the continuous CO_2 exchange but also CH_4 and N_2O fluxes over the very heterogeneous paddock area.

Calculation of exact seasonal/annual emission rates is very challenging also due to the heterogeneous and dynamic site. Dung and urine patches and compaction of the soil are highly affecting the gas fluxes. Because the amount of N in horse excreta depends on the protein content of the diet (Saastamoinen et al. 2021), also the amount of N in the excreta patches can vary, being higher in urine than dung. Therefore, we can assume, that there is very large temporal and spatial variation, which cannot be totally captured with laborious manual measurements with sampling intervals used here. Also, the effects of different soil types, dung management, horse density and feeding practices, weather conditions etc. should be studied further to get more precise picture of the importance of horse paddocks as GHG sources and possibilities to mitigate the emissions. Based on our results, we can state that one option to mitigate N_2O and CH_4 emissions from horse paddock soils is to avoid very wet conditions.

Acknowledgments

We thank Anna Jauhiainen allowing sampling at their farm. Ayodele Makinde, Jaana Rissanen and Ida Lähde are thanked for the help in the field and in the laboratory. The study was funded by Niemi foundation.

References

Atkinson, R. 2000. Atmospheric chemistry of VOCs and NOx. Atmospheric Environment 34: 2063–2101. https://doi.org/10.1016/S1352-2310(99)00460-4

Airaksinen, S. 2006. Bedding and Manure Management in Horse Stables. Kuopio University Publications C. Natural and Environmental Sciences 190. 91 p.

Airaksinen, S., Heiskanen, M.-L. & Heinonen-Tanski, H. 2007. Contamination of surface run-off water and soil in two horse paddocks. Bioresource Technology 98: 1762–1766. https:/doi.org/10.1016/j.biortech.2006.07.032

Baldocchi, D., Detto, M., Sonnentag, O., Verfaillie, J., Teh, Y.A., Silver, W. & Kelly, N.M. 2012. The challenges of measuring methane fluxes and concentrations over a peatland pasture. Agricultural and Forest Meteorology 153: 177–187. https://doi.org/10.1016/j.agrformet.2011.04.013

Bhattarai, H.R., Yli-Pirilä, P., Virkajärvi, P. & Maljanen, M. 2018. Emissions of atmospherically important nitrous acid (HONO) gas from northern grassland soil increases in the presence of nitrite (NO_2^-). Agriculture, Ecosystems & Environment 256: 194–199. https://doi.org/10.1016/j.agee.2018.01.017

Bhattarai, H.R., Liimatainen, M., Nykänen, H., Kivimäenpää, M., Martikainen, P.J. & Maljanen, M. 2019. Germinating wheat promotes the emission of atmospherically significant nitrous acid (HONO) gas from soils. Soil Biology and Biochemistry 136: 107518. https://doi.org/10.1016/j.soilbio.2019.06.014

Bhattarai, H.R., Wanek, W., Siljanen, H.M.P., Ronkainen, J.G., Liimatainen, M., Hu, Y., Nykänen, H., Biasi, C. & Maljanen, M. 2021. Denitrification is the major nitrous acid production pathway in boreal agricultural soils. Communications Earth & Environment 2: 54. https://doi.org/10.1038/s43247-021-00125-7

Bilotta, G.S., Brazier, R.E. & Haygarth, P.M. 2007. The Impacts of grazing animals on the quality of soils, vegetation, and surface waters in intensively managed grasslands. Advances in Agronomy 94: 237–280. https://doi.org/10.1016/S0065-2113(06)94006-1

Claeys, M. 2004. Formation of secondary organic aerosols through photooxidation of isoprene. Science 303: 1173–1176. https://doi.org/10.1126/science.1092805

Conrad, R. 1996. Soil microorganisms as controllers of atmospheric trace gases (H_2, CO, CH_4, OCS, N_2O, and NO). Microbiological Reviews 60: 609–640. https://doi.org/10.1128/mr.60.4.609-640.1996

Google Maps 2023. Photos © Airbus, CNES/Airbus, Maxmar Technologies, karttatiedot © 2023. Visited 27.7.2023

Elghandour, M.M.M.Y., Adegbeye, M.J., Barbabosa-Pilego, A., Perez, N.R., Hernandez, S.R., Zaragoza-Bastida, A. & Salem, A.Z.M. 2019. Equine contribution in methane emission and its mitigation strategies. Journal of Equine Veterinary Science 72: 56–63. https://doi.org/10.1016/j.jevs.2018.10.020

Fawcett, J.K. & Scott, J.E. 1960. A Rapid and Precise Method for the determination of urea. Journal of Clinical Pathology 13: 156–159. https://doi.org/10.1136/jcp.13.2.156

Havukainen, J., Väisänen, S., Rantala, T., Saunila, M. & Ukko, J. 2020. Environmental impacts of manure management based on life cycle assessment approach. Journal of Cleaner Production 264: 121576. https://doi.org/10.1016/j.jclepro.2020.121576

Kienzle, E. & Zeyner, A. 2010. The development of a metabolizable energy system for horses. Journal of Animal Physiology and Animal Nutrition 94: 231–240. https:/doi.org/10.1111/j.1439-0396.2010.01015.x

Kim, Y. & Tanaka, N. 2001. Winter N_2O emission rate and its production rate in soil underlying the snowpack in a subboreal region, Japan. Journal of Geophysical Research - Atmosphere: 107. https://doi.org/10.1029/2001JD000833

Li, Y., Korhonen, P., Kykkänen, S., Maljanen, M., Virkajärvi, P. & Shurpali, N.J. 2023. Management practices during the renewal year affect the carbon balance of a boreal legume grassland. Frontiers in Sustainable Food Systems 7: 1158250. https://doi.org/10.3389/fsufs.2023.1158250

Liljenstolpe, C. 2009. Horses in Europe, EU Equus 2009. Swedish University of Agricultural Sciences (SLU). 32p.

Maljanen, M., Gondal, Z. & Bhattarai, H.R. 2016. Emissions of nitrous acid (HONO), nitric oxide (NO), and nitrous oxide (N_2O) from horse dung. Agricultural and Food Science 25: 225–229. https://doi.org/10.23986/afsci.59314

Maljanen, M., Virkajärvi, P. & Martikainen, P.J. 2012. Dairy cow excreta patches change the boreal grass swards from sink to source of methane. Agricultural and Food Science 21: 91–99. https://doi.org/10.23986/afsci.5016

Maljanen, M., Martikkala, M., Koponen, H.T., Virkajärvi, P. & Martikainen, P.J. 2007. Fluxes of nitrous oxide and nitric oxide from experimental excreta patches in boreal agricultural soil. Soil Biology and Biochemistry 39: 914–920. https://doi.org/10.1016/j.soilbio.2006.11.001

Maltais-Landry, G., Neufeld, K., Poon, D., Grant, N., Nesic, Z. & Smukler, S. 2018. Protection from wintertime rainfall reduces nutrient losses and greenhouse gas emissions during the decomposition of poultry and horse manure-based amendments. Journal of the Air & Waste Management Association 68: 377–388. https://doi.org/10.1080/10962247.2017.1409294

Myhre, G., Shindell, D., Bréon, F.-M., Collins, W., Fuglestvedt, J., Huang, J., Koch, D., Lamarque, J.-F., Lee, D., Mendoza, B.,Nakajima, T., Robock, A.,Stephens, G., Takemura, T. & Zhang, H. 2013: Anthropogenic and Natural Radiative Forcing. In: Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V. & Midgley, P.M. (eds.). Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Oswald, R., Behrendt, T., Ermel, M., Wu, D., Su, H., Cheng, Y., Breuninger, C., Moravek, A., Mougin, E., Delon, C., Loubet, B., Pommerening-Roser, A., Sorgel, M., Poschl, U., Hoffmann, T., Andreae, M.O., Meixner, F.X. & Trebs, I. 2013. HONO Emissions from Soil Bacteria as a Major Source of Atmospheric Reactive Nitrogen. Science 341: 1233–1235. https://doi.org/10.1126/science.1242266

Parvage, M.M., Ulen, B.& Kirchmann, H. 2013. A survey of phosphorous (P) and nitrogen (N) in Swedish horse paddocks. Agriculture, Ecosystems and Environment 178: 1–9. http://dx.doi.org/10.1016/j.agee.2013.06.009

Petters, M.D., Prenni, A.J., Kreidenweis, S.M., DeMott, P.J., Matsunaga, A., Lim, Y.B. & Ziemann, P.J. 2006. Chemical aging and the hydrophobic-to-hydrophilic conversion of carbonaceous aerosol. Geophysical Research Letters 33: L24806. https://doi.org/10.1029/2006GL027249

Rotz, C.A. 2017. Symposium review: Modeling greenhouse gas emissions from dairy farms. Journal of Dairy Science 101: 6675–6690. https://doi.org/10.3168/jds.2017-13272

Saastamoinen, M., Särkijärvi, S. & Suomala, H. 2021. Protein Source and Intake Effects on Diet Digestibility and N Excretion in Horses-A Risk of Environmental N Load of Horses. Animals 11: 3568. https://doi.org/10.3390/ani11123568

Sommerfeld, R.A., Mosier, A.R. & Musselman, R.C. 1993. CO_2, CH_4 and N_2O flux through a Wyoming snowpack and implications for global budgets. Nature 361: 140–142. https://doi.org/10.1038/361140a0

Su, H., Cheng, Y., Oswald, R., Behrendt, T., Trebs, I., Meixner, F.X., Andreae, M.O., Cheng, P., Zhang, Y. & Poschl, U. 2011. Soil Nitrite as a Source of Atmospheric HONO and OH Radicals. Science 333: 1616–1618. https://doi.org/10.1126/science.1207687

Scharko, N.K., Schütte, U.M.E., Berke, A.E., Banina, L., Peel, H.R., Donaldson, M.A., Hemmerich, C., White, J.R. & Raff, J.D. 2015. Combined Flux Chamber and Genomics Approach Links Nitrous Acid Emissions to Ammonia Oxidizing Bacteria and Archaea in Urban and Agricultural Soil. Environmental Science & Technology 49: 13825–13834. https://doi.org/10.1021/acs.est.5b00838

Virkajärvi, P., Maljanen, M., Saarijärvi, K., Haapala, J. & Martikainen, P.J. 2010. N_2O emissions from boreal grass and clover grass pasture soils. Agriculture, Ecosystems & Environment 137: 59–67. https://doi.org/10.1016/j.agee.2009.12.015

Weir, J., Li, H., Warren, L.K., Macon, E. & Wickens, C. 2017. Characterizing ammonia emissions from horses fed different crude protein concentrations. Journal of Animal Science 95: 3598–3608. https://doi.org/10.2527/jas.2017.1648

Wu, D., Horn, M.A., Behrendt, T., Müller, S., Li, J., Cole, J.A., Xie, B., Ju, X., Li, G., Ermel, M., Oswald, R., Fröhlich-Nowoisky, J., Hoor, P., Hu, C., Liu, M., Andreae, M.O., Pöschl, U., Cheng, Y., Su, H., Trebs, I., Weber, B. & Sörgel, M. 2019. Soil HONO emissions at high moisture content are driven by microbial nitrate reduction to nitrite: tackling the HONO puzzle. The ISME Journal 13: 1688–1699. https://doi.org/10.1038/s41396-019-0379-y