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Mitigation of ammonia emissions: A short-term study to compare field strategies in semi-arid Mediterranean irrigated systems

Short title (<12 words): A short-term study to compare field strategies for ammonia emission mitigation

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Core ideas

- NH_3 emissions from slurry splash-plate (SP) spreading can be <4% of the NH_4^+ applied
- Trail hoses (TH) reduce NH_3 emissions from slurries vs. SP at cereal tillering
- At sowing, low slurry dry matter bridges the gap on NH_3 emissions between TH and SP

Abbreviations: AL, ammonia losses; DM, dry matter; PS, pig slurry; S-, sowing; SP, splash-plate; SWC: soil water content; T-, tillering; TH, trail hose; WFC, water content at field capacity; WFPS: water-filled pore space.

Abstract

Abatement of ammonia (NH_3) emissions is crucial in calcareous soils under semiarid Mediterranean climates. The aim of the study was to compare NH_3 emissions using different slurry application methods. An experiment was carried out on a clay loam soil to evaluate NH_3 emissions before sowing (S-) and at winter cereal tillering (T-). Pig slurry was applied using two methods, one which applied slurry by splashing it over a plate (SP) and the other applied slurry in strips using trail hoses (TH). Emissions were measured using semi-static chambers at variable intervals for 12-13 d (315.5 h for S- and 287 h for T-). Maximum NH_3 flux emissions were always observed during the earliest period of measurements after slurry spreading (3.5-5 h). Before sowing, regardless of the method, accumulated NH_3 losses (during 315.5 h) ranged between 2-3 kg NH_3-N ha^{-1} because of the low dry matter (DM) of the slurry content (<2%) which enhanced infiltration. Losses represented about 2-3% of the total N applied. At cereal tillering, average accumulated losses of NH_3 (during 287 h) were 1.7 kg N ha^{-1} using TH (1.1% of total N applied), and were as high as 5.4 kg N ha^{-1} (3.2% of total N applied) using SP. Because N top-dressing is recommended as a measure to increase its efficiency, TH is recommended vs. SP. Thus, this short-term study concludes that TH may reduce NH_3 emissions in semi-arid environments. Further study of these strategies is recommended under different climate and soil conditions.

Keywords: agricultural gas emissions, nitrogen, pig slurry, splash-plate, trail hose.

Introduction

Livestock slurry used as fertilizer is a source of ammonia (NH_3) emissions that contribute between 30% and 50% of total emissions in European countries (Reidy et al., 2008). It is crucial to reduce these emissions because of their highly negative effects on the environment and on health and because N losses through NH_3emissions reduce the value of animal slurries as fertilizer.

Ammonia volatilization rates depend on the concentration of ammonium nitrogen in the soil solution and the resistance of NH_3 to movement from the soil matrix (Sommer et al., 2004).

In Spain, the splash-plate (SP) method is the most popular system of slurry application. Slurry applications using trailing hoses (TH) are presumed to reduce NH_3 emissions in comparison with SP, but the cost of the machinery doubles and maintenance of grinders is costly. While TH applies the slurry in strips over the ground, the SP method forces the slurry to splash over an inclined plate to uniformly spread the slurry over the soil/crop surface. Thus, the TH method reduces the area of the NH_3 source at the soil surface. Slurry injection within the soil is rarely used in semiarid areas because it is very expensive, difficult to apply (i.e. because the soils are dry), and the advantages in preventing N emissions are limited (Yagüe and Bosch-Serra, 2013).

Accurate techniques in order to measure NH_3 emissions are available, such as those based on micrometeorological methods (Misselbrook et al., 2005) and the ^{15}N balance method (Lara-Cabezas et al., 1999), but they rarely affordable. However, semi-static chambers are affordable (Grant et al., 1996), allowing the monitoring of different treatments in the same crop season as they can be adapted to small flux-footprint areas. In general, the accuracy is suitable for operational field applications (Shigaki and Dell, 2015) and they are used to compare NH_3 losses from different treatments, although it was found that they underestimated NH_3 emissions compared with the integrated horizontal flux method or with the inverse dispersion method (Yang et al., 2017).

A wide range of ammonia emissions, ranging from 0 to 100% of the ammonium N applied has been reported (Hafner et al., 2017). Differences were attributed to local weather (i.e. temperature and air humidity, wind speed) and soil conditions (i.e. texture, soil humidity) which partly explain them. Ammonia volatilization also depends on slurry composition (Bosch-Serra et al., 2014), the distribution of its particle sizes (Sommer et al., 2006) and field management practices (Webb et al., 2010). According to Huijsmans et al. (2001), ammonia volatilization also tends to decrease as the canopy height increases.

In semi-arid Mediterranean areas, slurry application at the winter cereal tillering stage (February-March) is advisable as it reduces the cost of mineral fertilizers and prevents slurry accumulation in pits throughout the year. Thus, in these agricultural systems, the control of ammonia emissions is a response to an environmental threat but it must also be matched with maximum slurry reuse as fertilizer throughout the cropping season. The objective of the study described here was to compare NH_3 emissions using TH *vs.* SP methods when pig slurry was applied before sowing (over bare soil) and when the crop (winter cereal) was at the tillering stage.

Materials and Methods

The site

The experiment was carried out over a winter barley crop (*Hordeum vulgare* L.) in Spain (41º 47’ 41”N, 0º 43’ 42”E; 267 m a.s.l.) during the 2015-2016 cropping season. Soil classification was Xeric Torriorthent (Soil Survey Staff, 2014). The topsoil sub-layer (0.2 m depth) had a clay loam texture. The soil water content (SWC), in disturbed samples, at -33 kPa (water content at field capacity, WFC) and at -1500 kPa (permanent wilting point, PWP) was 24% and 14% over soil weight (w/w), respectively. The soil was saturated when the water-filled pore space (WFPS) equalled 44% (w/w, water/soil). The electrical conductivity was 0.19 dS m^{-1} (soil:water, 1:5) and cation exchange capacity was 12.4 $cmol^{+}$ kg^{-1}, the organic matter content was 27.9 g kg^{-1}, the pH was 8.2 (soil:water, 1:2.5) and the carbonate content was 327 g kg^{-1}.

The climate is semi-arid Mediterranean. Irrigation is required to reach high yields, which for winter barley were close to 8 Mg ha^{-1}.

Experimental set up

There were two treatments: pig slurry applied with a SP and pig slurry applied with a TH. They were applied at two crop stages but in different plots (a total of 12 plots were set up). Treatments were arranged in a randomized block design with three replications. One control plot was added in each block (no N fertilizer applied).

Treatments were applied before sowing (S-) over bare soil (December 1, 2015), and at cereal tillering (T-), when the crop canopy covered the soil surface (March 14, 2016), using standard equipment. Barley was sown on December 15, 2015. Each treated plot was 9 m (width, SE direction) x 25 m (length oriented along the prevailing wind direction, NW). It was located in the middle of an area of 18 m (SE) x 57 m (NW). Adjacent plots with same dimensions acted as control. Slurries came from the same farm and they were sampled from each tank before field application and refrigerated for further analysis. The dry matter (DM) content was obtained by a gravimetric method at 105°C, the organic and the ammonium N were determined according to methods 4500-NH_3B-C from APHA (2012).

Before the slurry application at sowing, the stubble of the previous crop (*Zea mays*, L.) was buried by superficial tillage. The rate of slurry applied at S- was 42 Mg ha^{-1} (2.15 kg total-N Mg^{-1}; 1.64 kg NH_4^+-N Mg^{-1}) using the splash-plate (S-SP), and 37 Mg ha^{-1}

(2.23 kg total-N Mg^{-1}; 1.65 kg NH_4^+-N Mg^{-1}) using trail hoses (S-TH). At cereal tillering (T-), 41 Mg ha^{-1} (4.10 kg total-N Mg^{-1}; 3.0 kg NH_4^+-N Mg^{-1}) was applied using splash-plate (T-SP), and 38 Mg ha^{-1} (4.10 kg total-N Mg^{-1}; 2.60 kg NH_4^+-N Mg^{-1}) using trail hoses (T-TH).

For the SP method, the plate was adjusted to uniformly spread the slurry and to avoid dispersive fluxes out of the experimental plot. For the TH method, tubes (4.5 cm diameter) separated 26 cm apart deployed the slurry over the ground. In December the slurry was buried (~0.20 m) using a combined disc-harrow plus a roller 27.5 h after application. In March, slurry was not buried because vegetation was established.

The temperature and relative humidity of the air were recorded on a half-hourly basis at 2-m above the soil surface using a data logger Testo 175H1 (Testo SE & Co. KGaA, Lenzkick, Germany) in the middle of the field. Rainfall and wind speed measurements were available nearby (~ 8 km; Fig. 1).

The soil water content within the 0 to 0.1 m depth was determined gravimetrically before each fertilizer application, at the end of measurements, and after the rainy period at tillage.

Quantification of volatilized NH_3 and statistical analysis

Accumulated ammonia losses were determined using semi-open static chambers adapted from Nômmik (1973) and Alves et al. (2011) designs. The chambers consisted of a polished cylinder (19.5 cm diameter and 19.5 cm height) made of low density polyethylene terephthalate, 0.5 cm thick and of light greyish blue colour. Therefore, it was assumed that the cylinder surface minimized conductive and radiative heat transfer for winter and early spring periods. Three chambers were placed per plot, just after slurry application. The latter were placed as follows. One chamber was placed in the middle of the plot and the other two were aligned, each at a distance of 1.5 m from the center along the mean streamwise direction (NW) and at 0.5 m across. These two chambers were not located in the middle of the plot because measurements made by foam I must account for the spatial variability of the soil and sources. The latter was specially required when slurries were applied using TH. Therefore, the minimum fetches were 11 m and 4 m along the mean streamwise direction and crosswind, respectively. Thus, a total of nine chambers were set up per treatment. Chamber distribution was the same for plots acting as controls. Chambers were settled 2.5 cm deep in the soil. Two discs of polyurethane plastic foam (0.021±0.001SD g cm^{-3}), previously soaked with a fixed volume (80 mL) of an acid solution containing oxalic acid in acetone (3% w/v) and dried in a ventilated hood, were deployed inside the chamber. Their diameter was 19.5 cm and their thickness 2.0 cm. At the top (17 cm above the ground), a foam (foam II) was fixed using a mesh of plastic tissue to carefully place it 5.5 cm up from the foam deployed below (foam I). The latter was deployed 7.5 cm above the ground using crossed steel wires and, therefore, it was above the canopy level (5 cm tall) at tillering stage. Thus, while foam I acted as a sink of NH_3 transferred by molecular diffusion from the soil, foam II acted as a sink of NH_3 emitted by the surrounding sources. Minimum lateral contamination was expected because the plot was oriented along the prevailing wind direction and minimum distance between the edges of two adjacent plots was 9 m. The center of the plot along the mean streamwise closely met the rule 1 m (height):100 m (distance along the fetch) valid at neutral conditions (0.17:12.5=0.014). Foam II was deployed so close to the ground that the stability parameter can, in practice, be considered zero.

At tillering, during a rain period lasting from 5 h up to 167 h after slurry application, chambers were protected with plastic bags (volume 250 L). During this period, data obtained from Foam II were removed from the study. The replaced foams were kept in zip lock freezer bags to transport them to the laboratory. Each foam disc was soaked four times by a hand double cylinder wringer with 100 mL distilled water each time. The extract collected was diluted with water up to 500 mL. Next, NaOH (40% w/v) was added for pH adjustment and ammonia was quantified using a selective electrode (Crison, micropH 2002). A total of 810 foams were analysed, 378 before sowing and 432 at tillering. Ammonia concentration was calculated by subtracting the threshold level determined from foams of the control.

Before sowing, ammonia concentration was calculated at 3.5, 27.5, 51.5, 75.5, 147.5, 219.5 and 315.5 h after slurry application. At tillering (close to the stem elongation stage), the chambers operated up to 287 h after slurry application to obtain stable amounts of accumulated NH_3. At the beginning, for a period of three days after slurry application, the sampling frequency was daily. Afterwards, samples were taken every two-three days. The cumulative NH_3 volatilization was calculated by integrating the emissions measured in each period. Total ammonia-nitrogen losses were related to the total N (Nt) and ammonium N (NH_4^+-N) applied with PS, to express the NH_3 losses (AL) as a relative percentage (AL_Nt and AL_NH_4^+-N, respectively). The reduction efficiency (abatement in NH_3 emissions) of TH *vs.* SP was calculated.

The package SAS V8.2 (SAS Institute, 1999-2001) was used to perform an analysis of variance to compare values of total and relative NH_3-N emissions for each slurry application method. Analyses were done before sowing and at the cereal tillering stage. Separation of means was done by applying the Duncan multiple range test (α=0.05).

Results

During the 24h after slurry application, the mean temperature of the air was about 5 ºC higher at tillering than at sowing (Figs. 1A, D). Before sowing, fog maintained the humidity of the air around 80%, i.e. no rainy events were observed (Fig. 1B) and the field was not irrigated. At tillering, the humidity of the air was around 90% for a period starting 5 h after slurry application up to 167 h because drizzle events (a total of five events) occurred. The total rain was 18.4 mm (Fig. 1E). Calm predominated at sowing but at tillering mean wind speed ranged between 1 and 2.5 m s^{-1} (Figs. 1C, F).

Before sowing (Fig. 1B), the SWC (0-0.1 m) was at the permanent wilting point (14%, w/w) and it increased up to 17% (w/w) at the end of the experiment. At tillering, the SWC was 16% (w/w); it increased up to 23% (167 h after slurry application) and reached the initial value (16%) 360 h after application (Fig. 1E). Thus, SWC ranged between 36-52% of WFPS at saturation.

Before sowing, maximum estimated fluxes from measured NH_3 concentrations were recorded just after slurry application (0-3.5 h), regardless of which foam was measured and the application method. For foam I, the maximum estimated fluxes were 313 g NH_3-N h^{-1} ha^{-1} for SP and 200 g NH_3-N h^{-1} ha^{-1} for TH. For foam II, the estimates were 248 g NH_3-N h^{-1} ha^{-1} for SP and 151 g NH_3-N h^{-1} ha^{-1} for TH. During this period (3.5 h), AL_Nt was 40% (Foam I) regardless of the dispersal method. Before slurry burying (0-27.5 h), AL_Nt increased up to 73% and 64% using SP and TH, respectively. At the end of the experiment (315.5 h after slurry application), no differences between methods were found for AL_Nt and AL_NH_4^+-N. Regardless of which foam was measured, the reduction efficiency was 0.31. However, the total accumulated NH_3-N losses were lower than 3 and 2 kg NH_3-N ha^{-1} for SP and TH respectively (Table 1) which led to non-significant differences in NH_3 abatement between methods.

At cereal tillering, maximum estimated fluxes were also recorded immediately after slurry application (0-5 h). For foam I, maximum estimated fluxes were 422 g NH_3-N h^{-1} ha^{-1} for SP which was significantly higher than using TH (35 g NH_3-N h^{-1} ha^{-1}). Later in the experiment, significant differences between methods (Foam I) were not observed.

For Foam II, the tendency of TH to reduce emissions (62 g NH_3-N h^{-1} ha^{-1}) *vs*. SP (154 g NH_3-N h^{-1} ha^{-1}) was also initially (0-5h) observed ($p = 0.09$, Table 1).

The initial losses (period of 5h) calculated using Foam I results led to AL_Nt = 10% and AL_Nt = 39% using TH and SP, respectively (Table 1). Losses rose 65% (SP) and 38% (TH) in the initial 23 h period (Table 1). At the end of the experiment (287 h after slurry application), no differences between methods were found for AL_Nt and AL_NH_4^+-N. The reduction efficiency was 0.68 (Foam I). The total accumulated NH_3-N losses were 5.4 and 1.7 kg NH_3-N ha^{-1} for SP and TH respectively (Table 1) with no differences between methods ($p=0.089$). After the rainy period (from 167 h to 287 h), no significant difference was also found using Foam II.

Discussion

Measurements were taken under climatic conditions and SWC representative of semiarid agricultural systems. As high pressures predominated during the campaign, the control was reliable to establish the base line emission. Slurries were applied when the SWC equalled 31% and 37% (w/w) of WFPS at saturation and at S- and T-, respectively. The low soil water content enhances the infiltration of slurry liquid and hence the mass transport of NH_4^+ into the soil (Sommer and Jacobsen, 1999). Thus, slurry infiltration rates were favoured and microbial processes related to other N losses than NH_3 volatilization (e.g. denitrification) were constrained (Smith, 2017).

Before sowing, the ammonia losses from slurry applied to bare soil (Table 1) were lower than those reported for a similar area (Yagüe and Bosch-Serra, 2013). The buried residues from the previous crop (maize) increased superficial roughness which combined with low slurry DM content (<2%) favored slurry infiltration in the first 3.5h. Thus, the source area exposed to the air was reduced (Sommer et al., 2003). Quick infiltration also could strengthen ammonium sorption by soil colloids, mainly as the cation exchange capacity of soil increases (Fenn and Kissel, 1976). Ammonium sorption reduces ammonia concentration in the soil solution (Venterea et al., 2015) and, therefore, the ammonia transfer to the atmosphere is minimized. Prompt infiltration kept the maximum AL_NH_4^+-N losses below 3% and 4% for TH and SP, respectively (Foam I, Table 1). Overall, in semi-arid environments, with low soil water content and quick infiltration, the presumed potential TH advantage vs. SP could be masked.

Lack of significant differences between the methods was consistent regardless of the foam. Foam I and foam II were two independent methods for estimating the source strength. Flux measurement in foam II may be better conceived as a rough estimation of the surface eddy flux within the flux foot-print area superimposed to far-field eddy fluxes that were estimated using foam II in the control plots.

The results obtained support the European Directive (European Union, 2016) which emphasizes the need to bury slurries within 4 h after spreading because maximum fluxes were observed within such periods.

At cereal tillering and during the first day after slurry application, emissions observed with Foam I (Table 1) after using SP were consistently higher than after using TH because of the larger slurry exposure (ground and leaves). For this case, the slurry DM content (3.3%; T-SP) led to at least some of the slurry remaining on the leaves, within the canopy. Hoses deposited the slurry directly onto the ground, favouring infiltration. Besides, the boundary layer would be larger due to the presence of the plants, so the wind speed at the soil surface would be reduced compared to the wind speed at the canopy height. Therefore, ensuring that the slurry reaches the soil (as in the TH method) would reduce the amount of wind that the slurry is exposed to, which would be expected to also reduce the NH_3 volatilization losses. Although the canopy could act as sink of ammonia (Rochette et al., 2008), in this study it did not play a role because the plants were in the dark.

Measurements obtained using Foam II during the initial period (0-5 h) led to non-significant differences between methods (Table 1). Fluxes measured using foam I and foam II can be presumed to be close when the strength of the source is planar, uniform and unlimited which allows us neglect divergence in a planar turbulent flow. The latter conditions are rarely met in the field. At tillering, sources were vertically distributed using the SP method, and not uniformly distributed at the surface using the TH method, which favoured divergence at levels close to the ground (regardless of the method). Moreover, during the 5 h prior to the rain event, the turbulence must be expected to be highly tridimensional and intermittent, masking measurements using foam II in an unpredictable way. Moreover, during this period, methods of measurement are expected to be unreliable including the eddy covariance method (Foken, 2012). Therefore, it may be assumed that measurements made using foam I were more reliable.

Rainfall washed slurry from the leaves and favoured infiltration. However, after the rainy period no effect on emissions was observed because the maximum losses had taken place during the first day after application.

Conclusions

At cereal sowing, no significant advantages of TH *vs*. SP on NH_3 emissions abatement were found when slurries with a low DM content were applied over a bare soil. When soils are usually below 40% of WFPS at saturation, quick slurry infiltration is enhanced which may explain the absence of differences between the two methods. Nevertheless, as 40% of total N losses were observed during the first 3.5 h after spreading (0.7 and 1.1 kg NH_3-N ha^{-1} for TH and SP, respectively), slurry burying as soon as possible after application is recommended.

At cereal tillering, TH improved initial NH_3 emission abatement vs. SP because the source was displaced above the ground by SP application. The final emission difference between methods was 3.7 kg NH_3-N ha^{-1} and maximum losses using TH were 1.7 kg NH_3-N ha^{-1}. Despite the level of significance which was 0.089, TH might be recommended vs. SP because the difference mainly corresponds to the initial period.

Because N top-dressing is recommended, it is concluded that TH improves the ammonia abatement vs. SP. This short-term study supports some of the recommended NH_3 abatement practices in the European Union.

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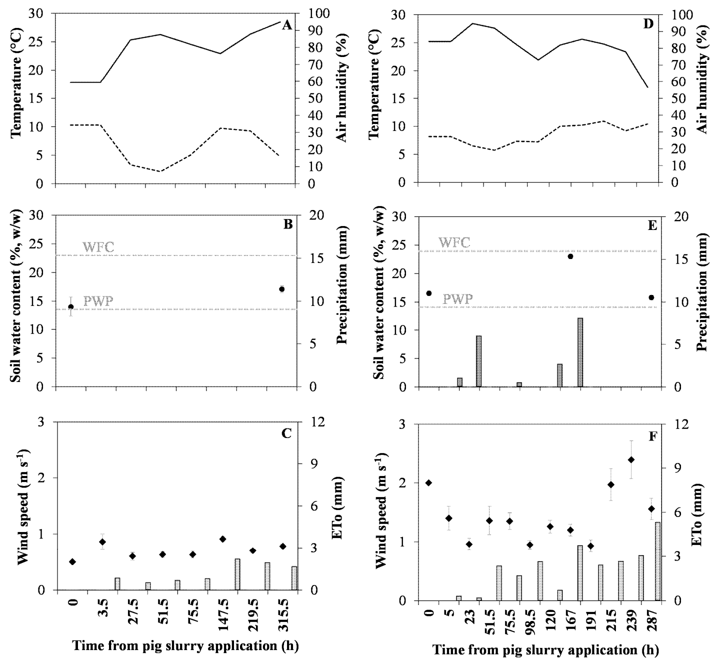

Figure 1. Air temperature (dashed lines) and relative humidity (solid lines), rainfall and wind speed on an hourly basis measured after slurry application before sowing (A, B, C) and at cereal tillering stage (D, E, F). The soil water content (%, w/w) is plotted taking as a reference the permanent wilting point (PWP) and the water content at field capacity (WFC). Accumulated reference evapotranspiration (ETo, Penman-Monteith equation) between measurements is included (columns). Rainfall, wind speed and Eto were recorded nearby (8 km) the experimental field. (http: //www.Ruralcat.net; Vallfogona de Balaguer).

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Table 1. Dry matter content (DM), total-N and NH_4^+-N applied with slurry, and average values of accumulated NH_3-N losses (TANL) and relative NH_3-N losses to total N applied (AL_Nt) and to NH_4^+-N applied (AL_NH_4^+-N) before sowing and at tillering, for each application method, and determined for molecular (Foam I) and turbulent (Foam II) diffusion. Standard error of the mean (n=3) is included.

Before sowing	**Traps/method of slurry application**	**TANL ($kg\ NH_3$-$N\ ha^{-1}$)**				**AL_Nt (%)**	**AL_NH_4^+-N (%)**
		0-3.5 h	**0-27.5h**	**0-51.5h**	**0-315.5 h**	**0-315.5 h**	**0-315.5 h**
Splash-plate	**Foam I**						
DM: 1.6%	Trail hoses	0.70±0.28	1.12±0.39	1.21±0.35	1.75±0.42	2.14±0.51	2.87±0.70
Total-N: 90 kg ha^{-1}	Splash-plate	1.10±0.16	1.99±0.32	2.12±0.32	2.74±0.48	3.12±0.55	3.98±0.69
NH_4^+-N: 69 kg ha^{-1}	*Significance*	0.20	0.13	0.13	0.27	0.33	0.39
Trail hoses	**Foam II**						
DM: 1.8%	Trail hoses	0.53±0.10	0.86±0.08	0.90±0.09	1.56±0.12	1.90±0.14	2.55±0.56
Total-N: 83 kg ha^{-1}	Splash-plate	0.87±0.12	1.48±0.15	1.57±0.16	2.41±0.39	2.75±0.44	3.50±0.19
NH_4^+-N: 61 kg ha^{-1}	*Significance*	0.18	0.060	0.059	0.15	0.19	0.23

Tillering	**Traps/method of slurry application**	**TANL ($kg\ NH_3$-$N\ ha^{-1}$)**				**AL_Nt (%)**		**AL_NH_4^+-N (%)**	
		0-5 h	**0-23h**	**0-287 h**	**167-287h**	**0-287 h**	**167-287h**	**0-287 h**	**167-287h**
Splash-plate	**Foam I**								
DM: 3.3%	Trail hoses	0.17±0.09	0.65±0.25	1.72±0.46	0.40±0.11	1.10±0.30	0.26±0.07	1.74±0.47	0.41±0.11
Total-N:168 kg ha^{-1}	Splash-plate	2.11±0.27	3.48±0.54	5.37±0.88	0.48±0.15	3.19±0.52	0.29±0.09	4.36±0.72	0.39±0.12
NH_4^+-N: 123 kg ha^{-1}	*Significance*	0.030	0.049	0.089	0.33	0.099	0.49	0.12	0.78
Trail hoses	**Foam II**								
DM: 4.9%	Trail hoses	0.31±0.11	ND	ND	0.26±0.08	ND	0.17±0.06	ND	0.26±0.08
Total-N:156 kg ha^{-1}	Splash-plate	0.77±0.06	ND	ND	0.26±0.07	ND	0.16±0.05	ND	0.22±0.07
NH_4^+-N: 99 kg ha^{-1}	*Significance*	0.095	ND	ND	0.97	ND	0.85	ND	0.59

ND: no data .The chambers were covered during a rainy period.