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Impact of the oasis effect on wind tunnel measurements of ammonia volatilization from urea

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Keywords: NH₃, wind tunnel, oasis effect, urea.

List of abbreviations:

A	Area (m^2)
AAFC	Agriculture and Agri-Food Canada
B_{SAT}	Ratio of B_{TOT} and CEC
B_{TOT}	Total base content of a sample ($\text{meq } 100 \text{ g}^{-1}$)
CEC	Cation exchange capacity ($\text{meq } 100 \text{ g}^{-1}$)
ΔC	Air $\text{NH}_3\text{-N}$ concentration difference between the entrances of the two halves of the tunnel ($\text{mg NH}_3\text{-N L}^{-1}$)
F	NH_3 flux rate ($\text{mg NH}_3\text{-N h}^{-1} \text{ m}^{-2}$)
ΔF	NH_3 Flux difference between the two halves of the tunnel ($\text{mg NH}_3\text{-N h}^{-1} \text{ m}^{-2}$)
IHF	Integrated horizontal flux
NH_3	Ammonia
pH_{water}	pH of sample in 1:1 mixture with water
pH_{SMP}	pH of sample in 1:1:2 mixture of sample, water and buffer
r	Radius (m)
RH	Relative humidity (%)
SAS	Statistical Analysis Software
TA	Titrateable acidity ($\text{Mol OH}^- \text{ kg}^{-1}$)
TAN	Total ammoniacal nitrogen
v	The flow rate of air through the wind tunnel (L h^{-1})

ABSTRACT

The validity of emission factors derived from small-scale measurements of ammonia (NH_3) volatilization has been questioned in the literature because gaseous NH_3 concentration gradients differ at the edge of the measurement plot and may result in higher emissions than at field-scale. We studied this 'oasis effect' using two very long (22-m) wind tunnels constructed indoors over soil plots fertilized with surface-applied urea (20 g N m^{-2}). We hypothesized that NH_3 flux would be highest at the start of the tunnel and decrease with distance. Air NH_3 concentration was measured every 2 m along each tunnel for two weeks after urea application; NH_3 flux did not decrease along the length of the tunnels. Of the 60 measurement periods when there was significant NH_3 volatilization, only two had a significant non-linear relationship ($P \leq 0.05$) between NH_3 concentration and distance. For the other periods, the NH_3 concentration increased linearly with distance ($P \leq 0.05$). The background NH_3 concentration difference between halves of the tunnels was not significantly related to NH_3 flux difference ($P > 0.1$). Our results indicate that wind tunnel measurements of NH_3 volatilization fertilized using urea are not impacted by a measurable oasis effect.

INTRODUCTION

As air passes over surfaces that have different thermal, moisture or physical properties, a new boundary layer regime develops from the leading edge. The transition between the regimes is not immediate and the adjustment of the air to the new surface is called the leading-edge effect (Oke 1987), or the oasis effect. In the case of a dry to moist

transition, the rate of evaporation increases due to sensible heat advection and the steeper water vapour concentration gradient above the moist surface (the classic example being an oasis of water in a desert). The initially high evaporation rate begins to lessen away from the leading edge because the water vapour concentration in the air increases and weakens the vertical gradient. Eventually, the horizontal and vertical vapour fluxes stabilize, and an equilibrium over the new surface is established (Oke 1987).

In the case of NH_3 volatilization experiments, there is often no change in surface properties between the emitting and non-emitting soil surfaces, so the boundary layer remains unchanged. As air flows from an NH_3 -free surface and passes over an NH_3 -emitting surface, however, the vertical NH_3 concentration gradient in the boundary layer is greater near the edge than at the center of fertilized areas, suggesting a greater NH_3 volatilization rate at the edge of the field compared to further into the field (i.e. the oasis effect). It has been suggested that small-plot NH_3 volatilization measurements from manured soils are overestimates of field-scale emissions because of the oasis effect (Génermont et al. 1997; Génermont et al. 1998; Sommer et al. 2003; Loubet et al. 2010; Sintermann et al. 2012). In these studies, the oasis effect has been quantified using resistance and advection models for situations where animal slurry was applied to land. A resistance framework can be used to model vertical transfer through the laminar and atmospheric boundary layers (Monteith and Unsworth, 1990) and has been adapted for use with NH_3 by Sommer and Oleson (2000). Unlike a one-dimensional resistance model, an advection model incorporates height and distance from the edge of the field (e.g. Loubet et al., 2001). Using such models, Sommer et al. (2003) estimated that the oasis

effect should cause the NH_3 flux to decrease by more than half at a distance of 20 m compared to the edge of the field.

Measurements of NH_3 emissions taken at small ($< 10 \text{ m}^2$), medium (circles of radius $20 \text{ m} < r < 50 \text{ m}$) and field scales ($> 5000 \text{ m}^2$) were compared by Sintermann et al. (2012). A significant difference between emission factors from the three measurement scales was found ($P \leq 0.001$), and it was hypothesized that the difference could have been caused by the difference in NH_3 flux measurement and calculation techniques between measurement scales. The oasis effect was a suggested explanation for the greater emission factors from small and medium scale measurements most often obtained using wind tunnels and the integrated horizontal flux (IHF) methods, respectively (Sintermann et al. 2012). However, Sintermann et al. (2012) also found a greater overestimation of NH_3 emission factors for medium-scale (IHF) than for small-scale (wind tunnel) experiments, whereas models predict the oasis effect is more important at smaller scale (Loubet et al. 2010).

Sommer et al. (2015) determined that wind tunnel measurements of NH_3 volatilization varied from IHF measurements when the wind speed in the tunnel was set to 1 m s^{-1} , but that the two were similar when wind speed was adjusted to ambient wind speeds at a height of 0.25 – 0.3 m. Their results imply that instead of the scale of measurement, the fixed wind speed used in wind tunnels may be responsible for the measurement discrepancy between the two techniques because the wind tunnel would fail to account for the effect of variation in ambient wind speed on NH_3 emissions. Mannheim et al. (1995) compared field measurements of NH_3 emissions from wind tunnels (2 m^2) and the IHF method (2500 m^2) after manure application. They determined that the

measured NH_3 emission was the same for both methods with a wind speed between $0.6 - 2.3 \text{ m s}^{-1}$, but that IHF measurements were not dependable for wind speeds below 0.3 m s^{-1} . At low speeds, it is difficult to accurately calculate the development of the boundary layer; key to capturing the entire flux profile needed for the IHF method. Mannheim et al. (1995) concluded that the accuracy of wind tunnel measurements exceeds that of the IHF method because wind tunnels can produce accurate NH_3 emission measurements at low wind speeds. Miola et al. (2015) determined that short term NH_3 emission measurements ($< 6 \text{ h}$) by static chambers were underestimated compared with wind tunnel measurements when using typical wind speeds and attributed this to the difference in wind speed between the two techniques. Ryden and Lockyer (1985) reported that when wind velocity in the tunnel was close to ambient, ammonia emission rates were not significantly different from those obtained by mass balance. Hudson and Ayoko (2008) concluded that wind tunnels are more likely than chambers to represent natural processes when determining emission rates. Parker et al. (2013) also determined that NH_3 flux is highly dependent on air flow rate and is correlated with vapour flux; they suggested applying a correction factor to flux data from flux chambers and wind tunnels to more closely simulate field conditions under all but the driest of surface conditions.

Other factors potentially contributing to the suggested overestimation of NH_3 by wind tunnel flux measurements are the assumptions that turbulent flow is negligible in the wind tunnel, and that the tunnel does not change the friction velocity or roughness length of the surface (Loubet et al. 1999a,b). Loubet et al. (1999b) showed that the boundary layer formed at the inlet of their tunnel had stabilized 1 m into the tunnel, and therefore the effects of turbulence and changing friction velocity could be removed by including an

extra one meter section of tunnel over unfertilized soil to the 2-m tunnel that measured NH_3 emissions. However, not all wind tunnel experiments use an extra section of tunnel, and therefore the adjusting air flow profile could induce variability into the NH_3 emission factors reported in previous studies.

Saha et al. (2011) assessed the impact of wind tunnel size on ammonia emission estimation using a computational fluid dynamics model. NH_3 flux was lower in higher-ceiling wind tunnels at a fixed wind speed, because it allowed a thicker boundary layer, and thus a greater resistance to emission of NH_3 . The higher ceiling allowed more of the air to be flushed through an area of the tunnel with lower NH_3 concentration, thereby moving less NH_3 to the end of the tunnel. This is similar to the findings of Smith and Watts (1994) who compared two wind tunnels of different size and determined that the larger tunnel gave consistently lower emission rates.

Previous studies have therefore found that the wind tunnel technique for measuring NH_3 emissions is susceptible to biased NH_3 volatilization estimates because of an oasis effect (Sommer et al. 2003; Sintermann et al. 2012), changes in wind speed (Mannheim et al. 1995; Miola et al. 2015; Sommer et al. 2015), and boundary layer characteristics (Saha et al. 2011). However, no experimental research has been conducted to test directly the impact of the oasis effect on wind tunnel NH_3 flux measurements. The objective of this study was thus to determine if wind tunnel NH_3 volatilization measurements are affected by the oasis effect.

MATERIALS AND METHODS

The experiment was conducted in May 2013 in a warehouse on the AAFC Chapais farm in Lévis, Quebec, Canada. The experiment was performed indoors to avoid large fluctuations in temperature and humidity and any associated impact on the emissions of NH_3 . One window at each end of the warehouse remained open to allow air to circulate and help keep temperatures from rising too high during the day. The front doors of the building were opened and closed a few times every day as personnel entered and exited.

Two soil plots (25 m long, 0.45 m wide) were created within the warehouse. Each soil plot was 5-cm deep and contained plant residue to ensure sufficient urease to facilitate rapid urea hydrolysis. Soils were a silty loam (plot 1; 22% clay, 58% silt) and a clay (plot 2; 44% clay, 33% silt) obtained from the 0-10 cm layer in nearby agricultural fields (Table 1). They were analysed for pH determined in a 1:1 soil:water mixture (pH_{water}) and in a 1:1:2 soil:water:buffer mixture (pH_{SMP}), total base content (B_{TOT}), cation exchange capacity (CEC), base saturation (B_{SAT}) and titratable acidity (TA) to pH 8. Analyses were conducted following standard methods (Hendershot et al. 2007; Kroetsch and Wang 2007; Izaurralde et al. 1987; Schoemaker et al. 1961). Soil water content of both plots was kept near field capacity during the experiment.

Two wind tunnels (length: 29 m, height: 0.5 m, width: 0.45 m) (Fig. 1) were built and deployed on top of the soil plots. The first 4 m of each tunnel was a humidification section without soil, where water was misted into the air prior to entering the tunnel to maintain consistent air humidity and soil moisture. Loubet et al. (1999a) tested the development of the wind speed and turbulence profile in 2 m long wind tunnels and determined that beyond 1.5 m from the entrance, the flow had fully developed. We kept

the next 3 m as an area of unfertilized soil to ensure that the airflow had stabilized when it reached the fertilized plot so that the impact of a change in flow regime was not confounded with the oasis effect. The air then passed over a 22-m long section fertilized with surface-broadcast urea (20 g N m^{-2}) before exiting at the outlet of the tunnel. Fans were attached to each tunnel entrance and exit to achieve consistent wind velocity along the length of the tunnel. Wind speed within the tunnels was measured once daily using a hot-wire anemometer (Hot Wire Thermo-Anemometer, Extech, NH, U.S.) at 2 m, 6 m, 12 m, 16 m, and 22 m along the fertilized sections of the tunnels, at heights of 10 cm, 20 cm, 30 cm and 40 cm. The average wind speed was $1.03 \pm 0.04 \text{ m s}^{-1}$ in tunnel 1, and $0.99 \pm 0.05 \text{ m s}^{-1}$ in tunnel 2. Wind speed decreased slightly (0.05 m s^{-1}) at the exhaust end of the tunnel 2, whereas wind speed in tunnel 1 remained consistent along its length. Both tunnels exhibited the shape of vertical wind speed profiles predicted by boundary layer theory on turbulent flow through a pipe (Munson et al., 1990). The maximum wind speed was measured 20 cm above the soil, away from the friction of the surface and of the tunnel ceiling. Loubet et al. (1999b) obtained a similar wind speed profile using a tunnel that was 50 cm from the surface to the ceiling, and their maximum wind speeds were measured between 5 and 11 cm heights with increasing flow rate. Temperature and relative humidity (RH) were monitored throughout the experiment inside the tunnel, at the entrances (immediately following the humidification section), and exits at a height of 25 cm using temperature and humidity probes connected to data loggers (CR-10, Campbell Scientific, Edmonton).

Experiments on the two tunnels were staggered to balance the substantial workload. The experiment on tunnel 1 ran from May 5 to 20, 2013, and tunnel 2 from May 12 to 25,

2013, each period starting at the time of urea application. Measurements were taken three times per day at 9:00, 14:00 and 19:00 during the first 10 and 11 days from tunnel 1 and 2, respectively. Measurements were then taken twice per day at 9:00 and 19:00 until the end of the experiment.

Two sampling techniques were employed to measure NH_3 concentration in the air inside the 22-m section of the tunnel where urea was applied. The first technique was an aluminum manifold with five small perforations (heights above soil: 2, 12, 22, 32, 42 cm) from which a composite air sample was obtained. Twelve manifolds were used, with one placed every 2 m along the tunnel (Fig. 1). The second method was a multi-tube approach with four individual tubes sampling air at heights of 10, 20, 30 and 40 cm every 4 m along the tunnel (six in total). The manifold measurements of NH_3 concentration were on average 7% greater than the multi-tube measurements ($P \leq 0.01$), and the variability in the normalized manifold NH_3 flux data was more pronounced than in the multi-tube data. Because of the greater variability and consistently higher concentrations of the manifold data, only the individual height measurements were included in the analysis (see Appendix). Air was drawn by vacuum pumps (Model 2107V, Gardner Denver Thomas, Munich, Germany) at a target rate of 3 L min^{-1} . The exact flow rates (L min^{-1}) of sampled air were measured using gas meters (Model GALLUS 2000, Actaris Metering Systems, SA, Australia) and NH_3 was captured by bubbling through fritted glass dispersion tubes (length, 150 mm; porosity, 145-175 μm , Ace glass Inc., Vinland, USA) into acid traps (100 mL) containing $0.005 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$. The sampling setup was the same used in previous NH_3 volatilization experiments by Rochette et al. (2009a; 2009b; 2013) Prior to the experiment, the sampler tubes were all tested in situ by blocking the tube, verifying

that the gas counter was not recording air flow and determining that there was no air bubbling through the acid trap. At each measurement interval, the traps were sampled into polyethylene containers and frozen, then analyzed for their NH_4^+ concentration by colorimetry (Model QuickChem 8000 FIA+, Lachat Instruments Ltd, WI, U.S.). Gaseous NH_3 concentration ($\text{mg NH}_3\text{-N L}^{-1}$) was then determined by dividing the amount of $\text{NH}_4^+\text{-N}$ in the trap by the volume of air bubbled through the trap. For multi-tube samples, the mean gaseous NH_3 concentration was determined at each location by taking the average concentration of the four measurement heights. The height of maximum wind speed remained at 25 cm throughout the entire tunnel, therefore two of our measurement heights were within the surface-influenced layer and two were above it. Taking the average of the four heights gave a good approximation of the average air NH_3 concentration in the cross section of the tunnel. Using the concentration measurements nearest to the surface for our analyses may have yielded a higher average flux in the tunnel, and perhaps a more perceptible oasis effect, but would not have been representative of the wind tunnel measurement technique. In commonly employed designs, at the exit of a typical 2-m long tunnel, air passes through a flow equalizer and then through a small duct at the back of the fan where the air is sampled. This represents an average of the vertical profile of NH_3 concentration, not just the concentration in the air near the surface.

In total, across the twelve manifold samplers and six multi-line samplers in both tunnels, there were 3050 individual gas samples collected. By assessing each counter's flow rate over the period and comparing it to its average rate, gas counter readings were found to be erroneous for two samplers during two periods,. In these cases, the average flow rate of the counter for the experiment was used to determine the volume of air that

passed through the trap. All counters were re-tested after the experiment to ensure accuracy, and correction factors were applied for counters that underreported flow. An additional thirteen measurements were discarded due to issues (including the trap not being sealed or sampled air not bubbling through the trap) with the acid trap samples.

Multiple approaches were used to determine the impact of the oasis effect on NH_3 flux. The first approach calculated the NH_3 flux (F ; $\text{mg NH}_3\text{-N h}^{-1} \text{ m}^{-2}$) in the first (F_1) and second (F_2) half of each tunnel using:

$$F = \frac{v}{A} * (NH_{3,o} - NH_{3,i}) \quad (1)$$

where $\text{NH}_{3,o}$ and $\text{NH}_{3,i}$ are the average of the four measurement height gaseous NH_3 concentrations at the exit and entrance of the tunnel section ($\text{mg NH}_3\text{-N L}^{-1}$), v is the average flow rate of air in the half of the tunnel (L h^{-1}), calculated by multiplying the average wind speed in the half of the tunnel over the entire experiment by the cross sectional area of the tunnel (0.225 m^2), and A is the surface area of the plot under the tunnel (m^2) (Rochette et al. 2009a). The flux for each half of the tunnel was calculated for each measurement period, and then plotted against one another (section 2 vs. section 1). If there was an oasis effect, the flux in section 1 should be greater than that for section 2 and the slope of the best-fit line would be lower than 1.

The second approach involved calculating the flux in each 2-m section of the tunnel (F_i) for each measurement period (Eq. 1), and then determining the difference between the individual flux and the average flux across the tunnel ($\bar{F}_{\text{tunnel}}$). The presence of an

oasis effect would be marked by a decrease in the flux difference along the length of the tunnel.

The third approach used a non-linear regression of gaseous NH_3 concentration versus distance along the tunnel using:

$$[\text{NH}_3] = [\text{NH}_3]_{\max} \times (1 - e^{-kx}) \quad (2)$$

where $[\text{NH}_3]$ and $[\text{NH}_3]_{\max}$ are the gaseous concentration and maximum concentration of NH_3 in the tunnel (mg N L^{-1}), k is a regression parameter and x is the distance along the tunnel (m). The presence of an oasis effect during the measurement period would be indicated by a non-linear regression parameter. Alternatively, a linear relationship between gaseous NH_3 concentration and distance would indicate the absence of an oasis effect. Every measurement period for both tunnels was tested using this approach and regressions were considered significant when $P \leq 0.05$.

The fourth analysis evaluated the relationship between the average NH_3 fluxes in the first and second halves of the tunnel ($\Delta F = F_2 - F_1$) and the background NH_3 concentration difference between the inlets of the two halves ($\Delta C = C_{i,2} - C_{i,1}$). A regression of ΔF onto ΔC was used to test whether differences in NH_3 flux between the two halves of the tunnel were driven by differences in background NH_3 concentration between the inlets of each section. All regressions were done using the PROC GLM procedure in SAS (SAS 9.4, NC, U.S.).

RESULTS AND DISCUSSION

Environmental Conditions inside the Tunnels

Isolating the oasis effect required controlling other parameters that impact hydrolysis of urea and subsequent NH_3 emission rate; fluctuations in RH and temperature were minimal in both tunnels and showed no diurnal pattern. The average entrance and exit temperatures were statistically the same: 24.9 ± 1.0 °C and 24.7 ± 0.8 °C, respectively in tunnel 1; and 24.7 ± 1.2 °C and 24.8 ± 1.1 °C, respectively in tunnel 2. The average entrance and exit RH of tunnel 1 were $89.5 \pm 4.9\%$ and $92.8 \pm 4.1\%$, and those of tunnel 2 were $94.8 \pm 12.8\%$ and $92.8 \pm 9.0\%$. Maintaining a high RH was necessary to ensure consistent soil moisture along the length of the tunnel, and thus consistent urea hydrolysis. High RH may have reduced the rate at which soil TAN was emitted as NH_3 , as previous research has noted correlations between NH_3 flux and evaporative flux from simulated feedlot lagoons (e.g. Parker et al. 2013).

Although efforts were made to deliver identical humidification in both tunnels, there were a greater number of droplets being carried into tunnel 2 than tunnel 1. The RH was always near 100%, and droplets were deposited in the first 6 m of the fertilized section of the tunnel, bringing the soil moisture above field capacity and causing infiltration of urea. As a result, only measurements from 6 m to 22 m in tunnel 2 were included in the analysis. All 22 m of tunnel 1 were included in the analyses.

NH_3 Volatilization Rates

Average fluxes of NH_3 in the tunnels ($\bar{F}_{tunnel}$) increased rapidly after urea application, and reached maximum values of $32.8 \text{ mg NH}_3\text{-N m}^{-2} \text{ h}^{-1}$ after 90 h in tunnel 1

and $32.9 \text{ mg NH}_3\text{-N m}^{-2} \text{ h}^{-1}$ after 72 h in tunnel 2 (Fig. 2). Negative fluxes occurred for two days in tunnel 1 (between 264 h and 388 h; May 16 and 17), which coincided with the peak emission periods from tunnel 2 increasing the background NH_3 concentration in the warehouse (Fig. 2). In tunnels 1 and 2, the maximum air NH_3 concentration was measured at $t = 76 \text{ h}$ and 77 h respectively. During these periods, the NH_3 concentrations 22 m along the tunnel at heights of 10, 20, 30 and 40 cm were 1.1, 0.63, 0.26, and $0.23 \mu\text{g N L}^{-1}$ respectively in tunnel 1, and were 1.2, 0.64, 0.36 and $0.27 \mu\text{g N L}^{-1}$ respectively in tunnel 2. Compared to previous studies with comparable urea N application rates ($140 - 164 \text{ kg N ha}^{-1}$), our maximum NH_3 flux rates were similar to Rochette et al. 2009a ($\sim 30 \text{ mg N m}^{-2} \text{ h}^{-1}$), but lower than (Rochette et al. (2009b; 2013) which were between 100 and $120 \text{ mg N m}^{-2} \text{ h}^{-1}$. We suspect that conducting the study indoors without solar insolation led to lower soil-surface temperatures, and reduced near-surface convective mixing within the tunnels. Furthermore, the high RH of the air in the tunnel would reduce evaporative flux and reduce the NH_3 flux rate. Cumulative losses were slightly greater in tunnel 1 (19% of applied N) than in tunnel 2 (15%) likely because of lower NH_4^+ fixation in the silt than in the clay soil (O'Toole et al. 1985). Previous studies of NH_3 volatilization from broadcast urea at comparable application rates ($6 - 20 \text{ g N m}^{-2}$) had cumulative emissions ranging from 1% – 64% of applied N (Freney et al. 1983; Fenn et al. 1987; Urban et al. 1987; Bacon et al. 1989; Al-Kanani and MacKenzie 1992; Palma et al. 1998; Rochette et al. 2009a). The large range of cumulative emissions stresses the importance of soil characteristics and environmental conditions on NH_3 volatilization, and our results are within the range of emissions from comparable experiments in the literature. The small-scale plot experiments on slurry referred to by Sintermann et al. (2012) mostly had

cumulative emissions representing 15% – 30% of the total applied N, placing our cumulative emission values within the range of their study.

Oasis Effect

The first of our four approaches to test for the oasis effect was based on the comparison of the average NH_3 flux in the first and second half of the tunnels. There was a good agreement in both tunnels ($R^2 > 0.70$; $P \leq 0.01$) (Fig. 3). However, a wind tunnel affected by the oasis effect would have shown a consistently greater flux in the first half of the tunnel when compared to the second half. This is not supported by the symmetrical distribution of the observations above and below the 1:1 line.

The second approach was based on an analysis of the deviation from the average NH_3 flux along the tunnel (Fig. 4). There was a slight decreasing tendency in the flux data from tunnel 2, but not the large decrease in flux with increased distance from the edge predicted by Sommer et al. (2003). To investigate further, we applied the simplified advection model of Sommer et al. (2003) to determine whether it would indicate the presence of an oasis effect. The model produced significant fits for the flux data at $t = 6$ h and 24 h ($P > 0.05$). The other 83 periods in tunnel 1 and 2 did not show signs of a significant oasis effect.

The third method of analysis (non-linear regression of gaseous NH_3 concentration versus distance along the tunnel) showed that among the 60 periods with significant regression parameters ($P \leq 0.05$) (27 in tunnel 1 and 33 in tunnel 2), 48 showed a linear increase in gaseous NH_3 concentration with increasing distance (Figs. 5, 6). Only two periods between 28 and 35 h in tunnel 1 showed a significant non-linear relationship between flux and distance, and therefore a possible oasis effect (Fig. 7) ($P \leq 0.05$). The

oasis effect on NH_3 volatilization rates could depend on the relative magnitudes of the surface source strength and of the partial pressure of NH_3 in the air above the emitting surface, causing the oasis effect to only be detectable for low NH_3 fluxes. However, there was no evidence of a non-linear relationship between NH_3 concentration and distance during later periods (e.g. 178 h to 245 h) with comparable NH_3 flux that do not exhibit the oasis effect flux pattern.

During the two periods indicating a possible oasis effect, there was a relatively large increase in gaseous NH_3 concentration in the first 6 m while there was little increase further along the tunnel. We would expect the oasis effect to slightly reduce the NH_3 volatilization rate with increasing distance, not eliminate it completely, suggesting that another factor impacted the spatial distribution of NH_3 emission inside the tunnel. We hypothesize that the non-linear relationship early after deployment in tunnel 1 may have been caused by uneven soil surface water content during the first two days of operation (as adjustments were made to the rate of water input into the humidification section to obtain the desired RH) creating a wetting gradient that allowed urea to hydrolyze more quickly near the entrance as compared to further along the tunnel. This would explain why emissions were greater in the first 6 m, but nonexistent in the last 16 m of tunnel 1 during these early periods. From this third approach, we conclude that there was no evidence of an oasis effect impacting NH_3 volatilization rates measured in the wind tunnels, because there was a linear increase in gaseous NH_3 concentration with increasing distance within the tunnel during most of the measurement periods.

The fourth approach used to test for the oasis effect involved comparing the flux difference ($\Delta F = F_2 - F_1$) between the halves of the tunnel with the difference in the NH_3

concentration at the entrance of each half ($\Delta C = C_2 - C_1$). If the oasis effect were significantly impacting NH_3 volatilization, then ΔF would become more negative with increasing ΔC . For example, when the entrance NH_3 concentration for the first half of the tunnel is much lower than in the second half, we would expect a higher average flux from the first half because of a steeper vertical NH_3 concentration gradient above the emitting surface than in the second section (given that both sections have equal source strength). The results from both tunnels were combined, and then the data were divided into four groups based on their ΔC , to check whether the oasis effect was only significant within a specific range of source intensity (groups were 0-25%, 25-50%, 50-75% and 75-100% of the maximum ΔC measured). A linear regression was performed on each group of results to determine whether ΔC had a significant impact on ΔF between the two halves of the tunnel. None of the four groups indicated that ΔC was a significant regression parameter for ΔF ($P > 0.2$). ΔF should decrease with an increase in ΔC , because a greater background concentration of NH_3 should cause a reduction in NH_3 flux.

The results from all four methods of analysis revealed no measurable impact of the oasis effect on NH_3 volatilization rates in our wind tunnel experiment at any level of source intensity. These results disagree with the predictions based on the gradient-driven flux theory (Sommer et al. 2003) and the possible biases for small-scale measurements, especially those obtained using the integrated horizontal flux method discussed by Sintermann et al. (2012). Our measurements were made following urea application whereas Sommer et al. (2003) and Sintermann et al. (2012) referred to soils that had received pig slurry. The NH_3 volatilization rates are different between these amendments; slurry has its highest source intensity immediately after being applied, whereas urea takes

several hours to be hydrolyzed, thereby delaying the occurrence of peak source intensity. However, after the urea is hydrolyzed, the emissions from both N sources are affected by the same factors and if the oasis effect were to impact slurry-fertilized soils it should have a similar impact when urea is applied.

In our experiment, urea was broadcast at the surface, and once it was hydrolyzed, total ammoniacal nitrogen (TAN: N in the form of NH_3 and NH_4^+) concentration present at the surface should have changed slowly. For a constant surface concentration of TAN, the volatilization process is dominated by atmospheric transfer and by the NH_3 concentration difference between the emitting surface and the atmosphere (Sommer et al. 2004). However, we observed a constant NH_3 flux along the length of the tunnels during most measurement periods, even though NH_3 concentration in the air increased continuously with distance. This implies that the added partial pressure of NH_3 reducing the concentration gradient between the air and the surface was insignificant when compared to the surface source strength. This not only holds true for periods with higher flux measurements ($30 \text{ mg N m}^{-2} \text{ h}^{-1}$), but also for most of those with lower flux measurements, when the NH_3 source intensity was weak ($5 \text{ mg N m}^{-2} \text{ h}^{-1}$).

The application rate used in our experiment (20 g N m^{-2}) was higher than the application rate in Sommer's model (1 g N m^{-2}); their modeled soil pH of 7 was likely lower than the pH at the urea granule microsites in our experiment (Sommer et al. 2004), and their temperature of 10°C was significantly lower than in the present study ($\sim 25^\circ\text{C}$). When ammoniacal N is dissolved in water, its proportion in the gaseous NH_3 form increases with pH, while higher temperature increases degassing into the air (Sommer et al. 2004). NH_3 emission rates from experiments on manured soils are typically greater

than those from our urea fertilized plots at similar N application rate (Génermont et al., 1997; Génermont et al., 1998; Sommer et al., 2003; Loubet et al., 2010; Sintermann et al., 2012). The maximum flux modeled by Sommer et al. (2003) was on the order of $10 \text{ mg N m}^{-2} \text{ h}^{-1}$, and is comparable to the range of flux rates observed in this experiment. Therefore, the concentration of NH_3 in the air should have been sufficient to cause a measureable oasis effect in our tunnels. We found only two periods that showed evidence of an oasis effect flux when applying the advection model from Sommer et al. (2003) to our results; these may have been caused by a transition in soil hydrolysis and TAN concentration within the tunnel. Further experimentation is required involving soil measurements and a lower RH to reproduce the model from Sommer et al. (2003), and to determine how the concentration of NH_3 in the air compares to the saturation vapour pressure of NH_3 inside the tunnel. An experiment using an application of slurry would also be a logical next step.

CONCLUSION

Our objective was to determine if wind tunnel NH_3 volatilization measurements are affected by the oasis effect. Each of the four approaches used indicated that the oasis effect did not affect NH_3 volatilization rate at any surface source intensity. Of the 60 periods with measureable NH_3 emission, only two displayed concentration profiles suggesting the presence of an oasis effect. These periods occurred during the first day following urea application and may have been caused by the adjustment of tunnel conditions, and were vastly outweighed by evidence from later periods when there was no measurable presence of an oasis effect. In light of the results obtained in this study, we

conclude that the oasis effect does not significantly affect NH_3 volatilization from wind tunnel experiments fertilized with urea and with stabilized flow entering the tunnel. The results of this study suggest that volatilization measurement biases by wind tunnels are not the result of an oasis effect, but are likely associated with other factors such wind speed and boundary-layer characteristics inside the tunnels.

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For Review Only

Figure Captions

Fig. 1: The 22-m long wind tunnel setup. The air is shown as moving from left to right along the tunnel, first passing through a 4-m long air humidification section followed by a 3-m long unfertilized soil buffer zone before passing over the 22-m long urea-fertilized soil section. Manifold samples were collected every 2 m, and individual samples at heights of 10, 20, 30 and 40 cm were collected every 4 m along the tunnel.

Fig. 2: The average NH_3 flux ($\text{mg NH}_3\text{-N m}^{-2} \text{ h}^{-1}$) in Tunnels 1 (a) and 2 (b) during the experiments.

Fig. 3: NH_3 flux ($\text{mg N m}^{-2} \text{ h}^{-1}$) regressions between the first (section 1) and second (section 2) half of Tunnels 1 and 2 during the experiment. Both slopes were significantly different from 1 ($P \leq 0.01$).

Fig. 4: The deviation between measurement points (every 4 m starting at 2 m from tunnel edge) and average tunnel flux ($\text{mg N m}^{-2} \text{ h}^{-1}$) using the manifold and the individual height data in Tunnels 1 (a) and 2 (b). The manifold data was included to demonstrate the difference in variability between the two measurement types. Only the individual height data was included in the regression analysis.

Fig. 5: Air NH_3 concentration and distance along Tunnel 1. One measurement from each day with significant ($P \leq 0.05$) NH_3 emissions is shown (May 14 and 15 were not included because of missing data).

Fig. 6: Air NH_3 concentration and distance along Tunnel 2. One measurement from each day with significant ($P \leq 0.05$) NH_3 emissions is shown.

Fig. 7: Air NH_3 concentration and distance along Tunnel 1 for the two periods that showed distance as a significant ($P \leq 0.05$) regression parameter.

Table 1: Characteristics of the soils used in Tunnels 1 and 2. pH_{water} is the pH of the soil in a 1:1 mixture with water. pH_{SMP} is the pH determined using a mixture of 1:1:2 of soil, water and buffer. Units of elements are $\text{meq } 100 \text{ g}^{-1}$. B_{TOT} is the total base content in the soil sample ($\text{meq } 100 \text{ g}^{-1}$). Cation exchange capacity (CEC) is the total capacity of a soil to hold exchangeable cations ($\text{meq } 100 \text{ g}^{-1}$). B_{SAT} is the ratio of $\text{B}_{\text{TOT}}:\text{CEC}$ expressed as a percentage. Clay/silt/sand are expressed as a percentage. Titratable acidity (TA) is the total amount of hydrogen ions present in the soil sample attached to acids or in the form of free ions or anions ($\text{mol OH}^{-} \text{ kg}^{-1}$)

	pH_{water}	pH_{SMP}	H	Ca	Mg	K	Na	Al	B_{TOT}	CEC	B_{SAT}	Clay	Silt	Sand	TA
Tunnel 1	5.86	6.78	6.51	4.74	1.56	0.34	0.14	0.26	7.04	20.80	34.1	21.6	57.9	20.5	0.045
Tunnel 2	5.34	6.10	12.63	13.51	3.33	0.41	0.17	0.04	17.46	34.00	51.3	44.3	32.8	22.9	0.091

Fig. 1: The 22-m long wind tunnel setup. The air is shown as moving from left to right along the tunnel, first passing through a 4-m long air humidification section followed by a 3-m long unfertilized soil buffer zone before passing over the 22-m long urea-fertilized soil section. Manifold samples were collected every 2 m, and individual samples at heights of 10, 20, 30 and 40 cm were collected every 4 m along the tunnel.

215x121mm (150 x 150 DPI)

Fig. 2: The average NH_3 flux ($\text{mg NH}_3\text{-N m}^{-2} \text{h}^{-1}$) in Tunnels 1 (a) and 2 (b) during the experiments.

154x167mm (72 x 72 DPI)

Fig. 3: NH₃ flux (mg N m⁻² h⁻¹) regressions between the first (section 1) and second (section 2) half of Tunnels 1 and 2 during the experiment. Both slopes were significantly different from 1 ($P \leq 0.01$).

195x160mm (150 x 150 DPI)

Fig. 4: The deviation between measurement points (every 4 m starting at 2 m from tunnel edge) and average tunnel flux ($\text{mg N m}^{-2} \text{h}^{-1}$) using the manifold and the individual height data in Tunnels 1 (a) and 2 (b). The manifold data was included to demonstrate the difference in variability between the two measurement types. Only the individual height data was included in the regression analysis.

212x240mm (150 x 150 DPI)

Fig. 5: Air NH₃ concentration and distance along Tunnel 1. One measurement from each day with significant ($P \leq 0.05$) NH₃ emissions is shown (May 14 and 15 were not included because of missing data).

187x127mm (150 x 150 DPI)

Fig. 6: Air NH_3 concentration and distance along Tunnel 2. One measurement from each day with significant ($P \leq 0.05$) NH_3 emissions is shown.

165x227mm (150 x 150 DPI)

Fig. 7: Air NH_3 concentration and distance along Tunnel 1 for the two periods that showed distance as a significant ($P \leq 0.05$) regression parameter.

199x148mm (150 x 150 DPI)

APPENDIX

Rationale for NH₃ sampling methodology

Two methods of measuring an average of the vertical profile of NH₃ concentration were used to calculate NH₃ flux: 1) a manifold consisting of five inlets; and 2) four individual tubes (Fig. 1). Each technique was designed to sample across the height of the tunnel and in each case, an average concentration was calculated. The flux differences calculated using the manifold data were more variable than those calculated using the average of the individual height measurements (Fig. 4). This was likely because the proportion of air drawn from the individual inlets (and therefore contributing to the average) varied between manifolds. We speculate that contact between the tube and the back wall of the steel manifolds may have caused partial blockages in the 4 shorter tubes attached to the manifolds, causing air to be sampled at different rates from each of the inlets of the manifold. Whatever the reason, because of the greater variability of the manifold measurements, we opted to use only the average of individual height NH₃ concentration measurements to test the wind tunnel technique for the presence of the oasis effect.