NH$_3$ Emissions From Treated Buffalo Manure Application In Mediterranean Climate And Comparison To ALFAM Model

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Abstract

Ammonia volatilization is widely recognized as one of the major environmental European problems, due to the increase in livestock farming activities. As a consequence, accurate ammonia assessment is needed in order to control ammonia emissions and to update national emission inventories. Besides some uncertainties still related to the measurement methods, another important issue is the necessity of investigating a different kind of fertilizers. In the last few years, considerable attention has been paid to many manure treatments prior to field application.

This study aims to assess ammonia emissions from the field application of separated buffalo manure digestate in the Mediterranean climate, in order to improve the emission inventory for this animal species, reared mostly in South Italy. Two measuring methods were used: wind tunnel (WT) and Integrated Horizontal flux (IHF). Moreover, ammonia emission measured were compared to those obtained running the statistical regression model ALFAM. This model based on Michaelis-Menten type equation is often used to predict cumulative ammonia loss and since it is based on a significant dataset is useful to discuss the effectiveness of the emission measured.

The total ammonia losses measured in 7 days were 26.39 and 49.24 kg N ha^{-1}, for WT and IHF, respectively. Although the predicted total emissions were 40.99 and 36.56 kg N ha^{-1}, for IHF and WT, respectively, it is possible to observe the good accordance of the ALFAM model with the temporal pattern of both methods.

Keywords: Statistical model, open field monitoring, anaerobic digestion, manure application, wind tunnel, Integrated Horizontal flux

1. Introduction

Manure treatments have been gaining importance in recent years. In particular, they have been utilized on dairy farms in order to improve the manure management, thanks to economic incentives, increasing the number of animals bred and development of new technologies (Evans et al., 2018). As a consequence, some studies started to investigate the influence of the manure treatment (slurry separation, anaerobic digestion, slurry aeration and straw cover) on greenhouse and NH$_3$ emission after field application (Amon et al., 2006), in order to limit those emissions according to next National Emission Ceilings EU Directive adoption.

Therefore, accurate ammonia assessment is needed in order to control ammonia emissions and to update national emission inventories, but it is necessary to overcome some uncertainties still related to the measurement methods. This study aims to assess ammonia emissions from the field application of separated buffalo manure digestate in the Mediterranean climate, in order to improve the emission inventory for this animal species, reared mostly in South Italy (Infascelli et al., 2010; Pindozzi et al. 2013). Ammonia volatilization measurements were provided using two methods simultaneously: wind tunnel (WT) and Integrated Horizontal flux (IHF). Additionally, ammonia emissions measured were compared to those obtained running the statistical regression model ALFAM (Søgaard, et al. 2002). This is often used to compare ammonia losses estimated with those obtained with experimental trials, in order to discuss the effectiveness of the results (Minoli et al., 2015).

2. Materials and Methods

On July 2017 a field trial was carried out in Acerra (40°57'57.5"N, 14°25'34.9"E), on agricultural soil, in order to measure the ammonia emission, that occurs after the fertilizer application. Climate is Mediterranean according to Emberger's index, while soil is sandy loam texture according to the USDA Textural Classification System. The main chemical soil characteristics are summarized in Table 1.

Table 2.1. Main soil characteristics

pH	Organic C (%)	TKN (%)	OM (%)	CEC (mS cm^{-1})	NO$_3$-N (ppm)	NH$_4$-N (ppm)	P$_2$O$_5$ (ppm)	K$_2$O (ppm)
7.55	1.61	0.19	2.77	0.23	34.21	2.92	127.13	1950.52

A regional weather station 200 m far from the plot monitored the micrometeorological data during the test.

Separated buffalo manure digestate was applied on bare soil using splash plate spreader for the IHF circular plot and by hand on the WT covered surface. The experimental set-up is reported in Table 2.

Table 2.2: Experimental set-up

Method	Duration	Application			Manure properties		
		Technique	Rate (kg tot N ha^{-1})	Area (m^2)	TAN (mg l^{-1})	DM (%)	TKN (mg l^{-1})
IHF WT	7 days	Splash plate spreader Manual	176	1256 0.32	737	6.657	2214

2.1. Ammonia losses assessment

Ammonia emission measurements were carried out using a micrometeorological method and a chamber method: Integrated Horizontal Flux method (IHF) by Wood et al. (2000) and Wind tunnel (Scotto di Perta et al., 2016).

Specifically, in the case of Integrated Horizontal Flux method (IHF) by Wood et al. (2000), glass tubes (Schjoerring et al., 1992), previously treated with a solution of oxalic acid and acetone, were employed. These samplers were positioned in a pair at 4 and 3 heights of rotating masts, to catch the main wind direction, placed in the centre of fertilized plot and 80 m far at the background, respectively. The main principle of the method is to calculate the vertical NH$_3$ flux from the emitting area, equating to horizontal flux measuring ammonia concentration in the air at different heights above the surface.

Wind tunnel (Scotto di Perta et al., 2016), consisting of a chamber placed on a rectangular fertilized surface, that allows to simulate the wind action on the surface, by means of a fan. WT is equipped of two sampling points at the inlet and at the outlet sections. Acid traps were used to trap NH$_3$ volatilized. They were furnished with sulphuric acid solution, flow meter and suction pump. Acid solutions were replaced every 2 hours for the first two days and every three to four hours for the remaining two days. The concentration of NH$_3$ trapped both in oxalic and sulphuric solutions were measured spectrometrically using the FIAstar 5000 system (FOSS, Denmark) in the laboratory.

2.2. The ALFAM model

Measured ammonia emissions were compared to the predicted emissions by the ALFAM model (Søgaard, et al. 2002). The model is the result of a statistical analysis of NH$_3$ emissions data, measured in seven European countries (Denmark, Italy, the Netherlands, Norway, Sweden, Switzerland and UK) over the years. At the base of the model there is the kinetic of Michaelis-Menten-type:

$$N(t)= N_{max} \frac{t}{t+K_m} \qquad (1)$$

Where N(t) is the cumulative NH$_3$ volatilization over time (t); N$_{max}$ is the total NH$_3$ loss when time approaches infinity and K$_m$ is time interval when N(t) reaches 0.5N$_{max}$.

The cumulative NH$_3$ emission is estimated according to a set of parameters affecting NH$_3$ volatilization, reported in Table 3.

Table 3. Input of ALFAM model

Method	Soil moisture	Temperature (°C)	Wind speed (m s^{-1})	DM (%)	TKN (g kg^{-1})	Application Rate (t ha^{-1})
IHF WT	dry	26.13	1.23 0.3	6.657	0.737	79.62

2.3. Statistics

Ammonia emission rate were evaluated for each method and compared. Linear regression was performed to assess the relationship between the NH$_3$ measured and predict fluxes measured with IHF and WT, respectively. Moreover, RMSE (Fox, 1981), EF (Nash and Sutcliffe, 1970), CRM (Loague and Green, 1991) were also calculated to further investigate the accuracy of linear regression. Specifically, EF contributes to know the efficiency of the model: negative values prove that the mean value of observations is a better predictor than the model; positive values instead show that there is a good agreement between the model and the observed data. The agreement is total if EF is equal to 1. Lastly, CRM indicates the inclination of a method to overestimate (if <0) or underestimate (if >0) the NH$_3$ fluxes.

3. Results and Discussion

Cumulative ammonia emission curves obtained after 7 days of measurements are shown in Figure 1a. The total ammonia losses were 26.39 and 49.24 kg N ha^{-1}, for WT and IHF method, respectively. The highest ammonia emission rates occurred in the first hours after fertilization and decreased substantially after 24 h. This was due to manure hydrolysis process occurring before application (Ferrara, 2010), usually on the floors of animal house within 24 h of deposition (Sommer et al., 2013) and for this reason the ammonia emission process proved to be faster.

As may be seen in Figure 1a, ALFAM model curves are in good accordance with the temporal pattern of cumulative ammonia emission curves related to both methods. Nevertheless, modelled losses by ALFAM model were 40.99 and 36.56 kg N ha^{-1}, for IHF and WT, respectively.
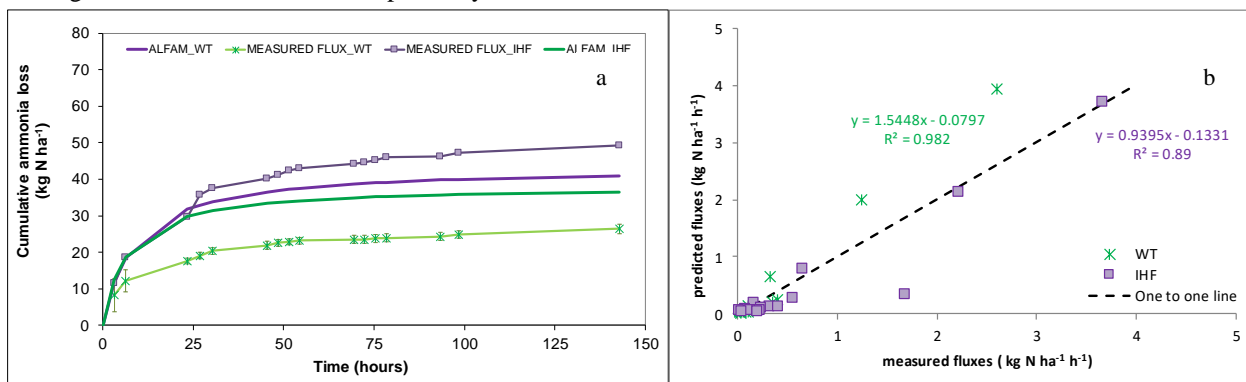

Figure 1. Comparison between NH$_3$ emissions: (a) cumulative measured and predicted cumulative NH$_3$ emissions with IHF and WT; (b) Linear regression between measured and predicted fluxes for each method

Linear regression was provided between measured and predicted fluxes for each method (Figure 1b), considered more robust than the cumulative emissions, since there is a serial correlation between the successive cumulative emission values (Sogaard et al., 2002; Misselbrook et al., 2005). As it is possible to notice the correlation between measured and predicted values are good, especially for the WT (R^2=0.982). The prediction of ALFAM fitted well the measured IHF fluxes in the first 24 h, after this time the model seems to underestimate the process, as it is also confirmed by the CRM = 0.275 (Table 4). In the same time, ALFAM model seemed to over predict the ammonia loss related to the wind tunnel (Figure 1b). similar result is provided by CRM = -0.324 (Table 4).

Table 4. Statistical indexes: coefficient of determination (R2), relative root mean square error (RRMSE), model efficiency (E), coefficient of residual mass (CRM)

	RMSE	RRMSE	EF	CRM
ALFAM_WT vs measured_WT	0.395741	109.743	0.627	-0.324
ALFAM_IHF vs measured_IHF	0.370380	54.664	0.855	0.257

These differences are probably explained with the characteristics of fertilizer used, that is a liquid fraction of digested buffalo manure. On the contrary, ALFAM model derived from the statistical analysis of measured fluxes related to cattle and pig slurry. Generally, ALFAM model proved to be a good tool for discussing the effectiveness of the results, but it may need additional testing to better simulate the emissions from treated manure.

4. Conclusions

The total ammonia losses measured in 7 days were 26.39 and 49.24 kg N ha^{-1}, for WT and IHF, respectively. Although the predicted total emissions were 40.99 and 36.56 kg N ha^{-1}, for IHF and WT, respectively, it is possible to observe the good accordance of the ALFAM model with the temporal pattern of both methods, nevertheless more studies will be needed to adapt ALFAM to treated manure.

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