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Research Paper

Model for calculating ammonia emission from stored animal liquid manure

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ABSTRACT

Ammonia (NH_3) emissions from agriculture have increased by 90% from 1970 to 2005, and agriculture is now the largest source of NH_3 to the atmosphere. Calculated national NH_3 emissions from agriculture using static emission factors do not reflect regional conditions. We propose, parameterize and test a simple model to calculate emission rates which incorporates effects of temperature, pH, total ammoniacal nitrogen (TAN) concentration, exposed storage area, and storage cover. This is the first time that several known algorithms were combined in this semi-dynamic user-friendly model concept and that model parameters (uploaded on the internet) were estimated from a unique database comprising 44 studies. The calculator is designed to be used correctly even if there exists only little knowledge about manure chemistry or micrometeorology, and can calculate emissions with a low demand for input data Calculations using the new model are as accurate as the standard method. The proposed approach has two advantages compared to the standard alternative: it does not require an estimate of TAN flow through the store, and calculated values reflect management (e.g., storage area or covers), TAN concentration, pH and temperature based on well-established principles. The simple and process-related approach has the potential to deliver more accurate estimates after a more precise parameterization from dedicated studies where the focus is on emission measurements, slurry composition characterization, air and slurry temperature and turbulence. To facilitate this approach, data need to be collected over relatively short time intervals (less than twice per day) to ensure that they cover cardinal diurnal conditions at the same time and right place. A spreadsheet implementation of the model is publicly available from https://github.com/sashahafner/AMOSTO.

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Abbreviation

A	Liquid manure store area (m^2)
$C_{NH_3,s}$	NH_3 concentration in the air immediately adjacent to the liquid surface (g NH_3-N m^{-3})
$C_{NH_3,a}$	ambient atmospheric NH_3 concentration (g NH_3-N m^{-3}),
C_{TAN}	Concentration of TAN (g NH_3-N m^{-3})
EF_{TAN}	emission factor (No unit)
$F_{Can,NH3}$	ammonia emission calculated with an empirical Canadian model (g NH_3 m^{-2} h^{-1})
F_{NH_3}	flux of NH_3 in g NH_3-N m^{-2} s^{-1}
$F_{NH_3,uc}$	flux of NH_3 from an uncovered store (*uc*) (g NH_3-N m^{-2} s^{-1})
H_{NH_3}	Henry's law constant (no units)
K_{H,NH_3}	Henry's constant (mol L^{-1} atm^{-1}, Table 1)
$K(u)$	the transfer coefficient (m s^{-1})
MTC_{NH3}	mass transfer coefficient calculated using the resistance approach and $C_{NH_3,s}$ as state variable (m s^{-1})
$MTC_{NH3,uc}$	mass transfer coefficient of uncovered store using $C_{NH_3,s}$ as state variable (m s^{-1})
MTC_{TAN}	mass transfer coefficient in algorithms using TAN as a state variable (m s^{-1})
T	temperature (°C or in K)
TAN	Total Ammoniacal Nitrogen concentration (NH_3+NH_4^+, g[N] L^{-1})
χ_{NH_3}	annual NH_3 emission (g [NH_3-N] y^{-1})
R	gas constant (0.08205746 L atm K^{-1} mol^{-1})
R_a	aerodynamic resistance representing the resistance of the turbulent air layer (s m^{-1})
R_b	laminar resistance (s m^{-1})
R_c	resistance to transport within the surface layer of the source (s m^{-1})
R_{uc}	resistance to transport from the surface of a non-covered liquid to the air (s m^{-1})
Rco	resistance to transport in a cover (s m^{-1})
u	Wind speed (m s^{-1})
uc	uncovered liquid manure
Q	total volume of liquid manure flowing through the storage during one year (m^3 y^{-1})
$F_{NH_3,uc}$	flux of NH_3 from an uncovered store (uc) (g [NH_3-N] m^{-2} s^{-1})

1. Introduction

Ammonia (NH_3) emissions from agriculture have increased by 90% between 1970 and 2005, and agriculture is now the largest source of NH_3 to the atmosphere (Sailesh et al., 2013; Sutton, Erisman, Dentener, Moller, 2008). The NH_3 emitted is a threat to human health, because it reacts with acidic compounds in the atmosphere (Walker et al. 2006), subsequently forming fine particles (PM2.5) that cause lung diseases (Wang et al., 2017). Ammonia deposited onto land or waters may exceed the critical nitrogen (N) loads of the ecosystems, causing eutrophication and altering natural ecosystems (Cox et al., 2014; Erisman et al. 2015; Hertel et al., 2013; Pardo et al., 2015; Sutton et al., 2011). Emissions from manure stores can represent significant losses of nitrogen (N) from the farm system at a cost to the farmer (Leytem et al., 2011, 2013; Liu et al., 2014).

Given the needs of both inventory compilers and farmers alike, there is a requirement for models that can be used to calculate valid estimates of national or farm scale NH_3 emissions. To do this, model calculations should reflect climate, manure management, and storage conditions. Calculation of NH_3 emissions at the farm scale and in national or regional inventories are generally calculated using emission factors (EF) for uncovered and untreated liquid manure (Hutchings et al., 2001; IPCC, 2019; Sommer et al., 2019), and reductions in emission due to management is calculated by adjusting this EF by a reduction factor related to the treatment (Nielsen et al., 2020, p. 559). Emission factors are calculated using average emissions over time in studies carried out under a variety of weather conditions, different management of stores and variation in composition of slurry, as seen in the annexes to Sommer et al. (2019). Annual NH_3 emission (χ_{NH_3}, g NH_3–N y^{-1}) is calculated as follows

$$\chi_{NH_3} = EF_{TAN}*C_{TAN}*Q \quad (1)$$

Where EF_{TAN} is an emission factor (dimensionless), Q (m^3 y^{-1}) is the total volume of liquid manure flowing through the storage in one year, and C_{TAN} the average concentration of total ammoniacal nitrogen (TAN = NH_3+NH_4^+, g N m^{-3}).

In practice, the EF_{TAN} are not related to variations in climate and manure composition. To account for some of the variation, animal categories are included, and the averages are based on season weighted emission data and expert assumptions. The estimated EFs for liquid manure stores are very imprecise as shown in a recent study, where coefficient of variation (CV) of the average EF calculated by Sommer et al. (2019) was above 50%. This relatively large CV was due to data being collected from studies measuring emission from liquid manure contained in different categories of stores, imprecise data about composition of liquid manure and problems in transforming the data to an annual emission while also attempting to account for seasonal variations in emissions. Instead of EF, more complex validated models could help farmers and consultants to identify management practices that reduce emissions. Public service officers/technicians need a model to develop transparent and trusted regulatory policies and to calculate annual national NH_3 emissions inventories that reflect more realistic farm emissions, including the influence of climate and management. The model must be simple and must not demand more activity or management data than in the present model. However, with time the users may be able to provide more information, which with the model concept presented here can be included in the calculations.

The overall aim of this study was to develop a model for NH_3 emissions from stored liquid manure that reflects environmental conditions and manure management, which can be used in practice as an alternative to fixed EFs. Based on an analysis of published data, our specific objectives were to:

- Describe a novel compilation of algorithms forming a simple and process-oriented concept for calculating NH_3 emissions from untreated and uncovered stored liquid manure that includes effect of manure composition, climate, and mitigation measures
- Show that - even with little knowledge about manure chemistry or micrometeorology -, the new concept implemented in a calculator estimates emissions with a low demand for input data and is as accurate as the standard emission factors.
- Demonstrate accuracy of results obtained by this approach on compiled emissions data and in an example involving standard management of stored slurry

2. Data collection

Data were collected from articles published in peer reviewed journals and proceeding articles presented at international conferences. The articles were identified by searching in the Web of Science Core Collection using the following string of search words: ammonia and (emission or evaporation) and (liquid manure or slurry) and (lagoon or tank) and (livestock or animal). Data from studies of NH_3 emission from uncovered and untreated pilot or farm scale liquid manure stores were selected for the development of the concept of a process-based emission model with little demand for input data so that it that can be used in inventories. The store categories defined by Kupper et al. (2020) were used, i.e. farm scale are stores used in practice, pilot scale are experimental vessels ≥ 0.5 m^3 situated outdoor and laboratory scale are vessels ≤ 0.5 m^3. Lagoons are earthen basins, which often have a large surface area, while tanks are containers made by concrete or steel which are partly buried in the soil and often have a smaller surface area than lagoons.

Exclusion criteria for data were (I) data completely unrelated to the need for parameterization of the model; (II) data from general knowledge papers; and (III) data from experiments that did not follow the method standards given for scientific research. Data was extracted to the database from articles presenting studies that clearly meet the inclusion criteria, one author transferred data from the article and a second author checked the data. If disagreements between the two authors occurred a third author would check the data transferred. If data were missing from records, then the authors of the articles or the author's research groups (see Acknowledgements) were contacted and asked to provide these data.

For the analysis of efficiency of NH_3 emission mitigation techniques, data were collected from laboratory, pilot and farm scale studies where emission from untreated and uncovered stored liquid manure had been related to emission from liquid manure stored with covers or liquid manure mixed with an additive.

Emission of NH_3 from liquid manure stores was typically reported as average emission rate over some period of time. These values were extracted from papers together with the following supporting data (where available): season, animal type, country, store type and scale (lab, pilot, and farm), liquid manure composition (total ammoniacal nitrogen concentration ($TAN = NH_3 + NH_4^+$), total nitrogen (TN) concentrations, dry matter (DM), pH), weather (air temperature, wind speed), liquid manure temperature, and emission measurement method. The emission rate from uncovered and covered liquid manure was converted to g NH_3–N m^{-2} s^{-1}. Abatement technology effects were typically reported as emission reduction relative to a control condition and most studies reported emissions from an uncovered control and covered liquid manure. Extracted supporting data included: type of technology, layer thickness (if relevant), store category i.e. farm, pilot scale and laboratory scale as defined above, TAN and pH concentration, temperature and emission measurement method.

3. The model

3.1. Concepts

Volatilisation of NH_3 from stored liquid manure is largely affected by TAN concentration, pH, equilibrium processes and weather conditions i.e. wind and temperature (Baldé et al., 2018; Grant et al. 2016; Harper et al., 2000, 2004; Leytem et al., 2018; Sommer, 1997). For tanks, wind turbulence is important but the effect on emission may be influenced by the tank walls (Grant & Boehm, 2018). The release of NH_3 is related to variables influencing emission processes at the surface of the liquid manure. Therefore, focus should be on surface liquid manure composition when identifying the variables that have the greatest influence on emission rate.

Empirical models assume emission is linearly related to temperature and wind speed (Baldé et al., 2018; Leytem et al., 2018), or temperature, wind speed, TAN and pH (Harper et al., 2004; Leytem et al., 2018), an example is the following model (Baldé et al., 2018).

$$F_{NH3,Tu} = 0.99 + 0.057*T + 0.18*u \quad R^2 = 0.94 \tag{2}$$

$F_{NH3,Tu}$ is the NH_3 emission (g NH_3 m^{-2} h^{-1}) from a store containing liquid manure with no crust covering the surface, T is surface temperature (°C) and u wind speed (m s^{-1}). These models often do not account for the exponential nature of release of $NH_3(g)$ in relation to temperature and wind speed, and pH and TAN concentrations are not included. The models can be used to calculate emissions from lagoons where liquid manure composition and weather conditions are within the data boundaries of measured emissions used to develop the models (Leytem et al., 2018).

De Visscher et al. (2002) showed that a mechanistic and an empirical model performed equally well explaining 70% of the variation in data measurements of emission from lagoons. Deviations between data calculated using the mechanistic model and measured data were distributed more evenly than when using the empirical model. The R^2 of the linear relation between emission calculated with empirical models using wind and temperature data and measured emission varied between 0.61 and 0.94 in the studies of Grant et al., (2013a) and (Baldé et al., 2018), and R^2 was in the range 0.58–0.94 with calculations using empirical models that include temperature and liquid manure composition (Harper et al., 2004; Grant et al., 2016; Leytem et al., 2018; Sommer, 1997). A cover of crust reduced the effect of climatic conditions on emission (Baldé et al., 2018; Sommer, 1997) and gave the lowest R^2 when developing empirical models for liquid manure lagoons using air temperature and wind as predicting variables (Baldé al. 2018).

One should keep in mind that an empirical model relating NH_3 emission to wind and air temperature developed for one store may give erroneous results when used for other stores, because composition (TAN, pH), surface layers and geometry may vary between stores and emission will likely be correlated with these variables. Air temperature is often used when modelling the emissions, but emission rate is more strongly correlated with surface temperature (McGinn et al. 2008; Baldé et al., 2018). Solar radiation significantly affects emission (Flesch et al. 2009; Sommer, 1997), and may be used to calculate surface temperature.

Most process-based models include slurry composition, temperature, wind speed and turbulence in the calculations as follows (Sherlock and Goh, 1985; Olesen & Sommer, 1993).

$$F_{NH_3,unc} = K(u)^*\left(C_{NH_3,s} - C_{NH_3,a}\right) \tag{3}$$

Where $F_{NH_3,unc}$ (g NH_3–N m^{-2} s^{-1}) is the flux of NH_3 from an uncovered store (*unc*) while *K(u)* is the mass transfer coefficient (m s^{-1}), $C_{NH_3,s}$ (g NH_3–N m^{-3}) is the NH_3 concentration in the air immediately adjacent to the surface at liquid if no cover or at cover, and $C_{NH_3,a}$ is the ambient atmospheric NH_3 concentration, which in most models is assumed to be negligible and is therefore omitted from Eq. (3). $C_{NH_3,s}$ concentration is exponentially related to temperature and pH and linearly related to C_{TAN} (C_{TAN} = $[NH_3]$+$[NH_4{}^+]$) and is included in most models calculated using air temperature (Rotz et al., 2014). Apart from wind speed (u), the mass transfer coefficient $K(u)$ depends on surface roughness, temperature and surface coverings, and may be calculated using the resistance concept (Olesen & Sommer, 1993; Rotz et al., 2014):

$$K(u) = \frac{1}{R_a + R_b + R_c}. \tag{4}$$

where R_a (s m^{-1}) is the aerodynamic resistance representing the resistance of the turbulent air layer between a height where the atmosphere is not affected by emissions and the aerodynamic roughness length of the surface, R_b is a laminar resistance between the surface layer and the turbulent layer, which is dominated by molecular diffusion, and an interfacial resistance (R_c) representing the resistance to transport within the surface layer of the source of $C_{NH_3,s}$.

3.2. *Proposed model*

In the studies reviewed here, NH_3 emission is related to the surface area of the source, and not to the volume of liquid manure as assumed in Eq. (1). Therefore, we hypothesise that with models developed based on these data some of the variability in calculated emission rate can be eliminated by calculating emission per surface area using TAN concentration (C_{TAN}, g m^{-3}) as input variable as follows:

$$F_{NH_3} = \varepsilon\tau_{TAN}{}^*C_{TAN} \tag{5}$$

Where F_{NH_3} is the flux of NH_3 in g NH_3–N m^{-2} s^{-1} and $\varepsilon\tau_{TAN}$ (m s^{-1}) is a transfer coefficient which may be related to wind speed, surface roughness, temperature and surface coverings. This equation may be used if liquid manure pH is not known. The store's area (A, m^2) must be known and by multiplying F_{NH_3} with A the emission from the store is calculated. An advantage of this model is that there is no need to estimate the rate of liquid manure flowing through the store (Q in Eq. (1)) and that flux depends on TAN concentration.

It is $C_{NH_3,s}$in equilibrium with [NH_3 (aq)], dissolved in the liquid manure that is transferred from the surface of the liquid to the atmosphere. Therefore, a better concept would be to use a mass transfer coefficient related to $C_{NH_3,s}$ (g NH_3–N m^{-3}) in equilibrium with the [NH_3(aq)] (g NH_3–N m^{-3}). For that, Eq. (5) can be replaced with:

$$F_{NH_3,unc} = \varepsilon\tau_{NH3,unc}{}^*C_{NH_3,s} \tag{6}$$

Where $F_{NH_3,unc}$ (g NH_3–N m^{-2} s^{-1}) is the flux of NH_3 from an uncovered store while $\varepsilon\tau_{NH3,unc}$ is the mass transfer coefficient (m s^{-1}) having the same format as $\varepsilon\tau_{TAN}$ in Eq. (5) but a different value, because $C_{NH_3,s}$ is used instead of [TAN]. $\varepsilon\tau_{NH3,unc}$is affected by mass transfer through air and is mainly dependent on wind speed, surface roughness and temperature. Bulk characteristics are used in calculations with the present model, therefore, effects of the difference between bulk temperature, TAN and pH and these properties at the surface will affect this parameter. The processes in the liquid that affect emission is the equilibrium of $C_{NH_3,s}$ with [NH_3(aq)], which is controlled by Henry's law constant (H_{NH_3}). The [NH_3(aq)] concentration is a function of C_{TAN} and hydrogen ion concentration [H^+] and the equilibrium constant (K_N, Table 1).

The value of $\varepsilon\tau_{NH3,unc}$can be calculated using mechanistic micrometeorological models (Olesen & Sommer, 1993) or empirical equations (Baldé et al., 2018; De Visscher et al., 2002; Harper et al., 2000, 2004; Montes et al., 2009; Grant et al., 2013a, 2016; Waldrip et al., 2014; Zahn et al., 2001). The mentioned models have a large demand for input variables and knowledge about the surrounding of the store.

Alternatively, $\varepsilon\tau_{NH3,unc}$can be calculated from emission measurements, slurry composition etc. In this study, data from 23 studies of NH_3 emission have been used to calculate a default $\varepsilon\tau_{NH3,unc}$ for liquid manure stored in concrete stores or lagoons. The calculations do not include the effect of wind, due to a lack of data. The $C_{NH_3,s}$ can be calculated as follows:

$$C_{NH_3,s} = \frac{1}{H_{NH_3}}\frac{C_{TAN}}{1 + \frac{[H^+]}{K_N}} \tag{7}$$

C_{TAN} and $[H^+]$ are bulk concentrations in this model, K_N is the NH_3–NH_4^+ equilibrium constant (dimensionless), and Henry's

Table 1 – Equilibrium constants of volatile components dissolved in liquid manure and manure (Beutier & Renon, 1978). Temperature (T) is in K.

Reaction	K_{H,NH_3} (mol L^{-1} atm^{-1}) and K_N (no dimensions)	K_{H,NH_3} and p K_N at 25 °C
$NH_3(g) \rightleftharpoons NH_3(aq)$	$\ln(K_{H,NH_3}) = -(160.559 - 8621.06/T - 25.6767{*}\ln(T) + 0.035388\,T)$	60.381
$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$	$\ln(K_N) = -177.95292 - 1843.22/T + 31.4335{*}\ln(T) - 0.0544943T$	9.24

law solubility constant H_{NH3} is dimensionless (aqueous:gas, e.g., mol m^{-3} in solution/mol m^{-3} in gas phase) and calculated as follows:

$$H_{NH_3} = K_{H,NH_3} * R * T \tag{8}$$

Where K_{H,NH_3} is the Henry's law volatility constant (mol L^{-1} atm^{-1}, Table 1), R is the gas constant (0.08205746 L atm K^{-1} mol^{-1}) and T the temperature (K).

The effect of surface cover can be estimated as follows:

$$\varepsilon\tau_{NH3} = \frac{1}{R_{unc} + R_c} \tag{9}$$

Where R_{unc} (s m^{-1}) is the resistance to transport from the surface of a non-covered liquid to the air and R_c (s m^{-1}) is the resistance to transport in a cover. The transfer coefficient ($\varepsilon\tau_{NH3}$) can be calculated if TAN, pH and the temperature of the system are known by combining Eqs. (6) and (7).

$$\varepsilon\tau_{NH3} = F_{NH3} \Bigg/ \left(\frac{1}{H_{NH3}} \frac{[C]_{TAN}}{1 + \frac{[H^+]}{K}} \right) \tag{10}$$

The temperature dependent equilibrium constants are given in Table 1.

The flux from the stored liquid without cover ($F_{NH_3,unc}$) is calculated using Eq. (6) and measured TAN, pH, temperature and the default $\varepsilon\tau_{NH_3,unc}$ for uncovered liquid manure. It follows that the resistance to transport from an uncovered liquid manure (R_{unc}) is calculated as follows

$$R_{unc} = \frac{C_{NH_3,s}}{F_{NH_3,unc}} \tag{11}$$

Measured reduction in emission for a range of mitigation technologies can be used to calculate the resistance to transport (R_c) induced by the cover. Most studies present the reduction efficiency as a percentage or fraction of emission from uncovered stored liquid manure. The flux from a covered liquid manure store is calculated as follows:

$$F_{NH_3,c} = F_{NH_3,unc} * x \tag{12}$$

where x is the emission from covered liquid manure as a fraction of the emission from uncovered liquid manure. In the new suggested approach, the resistance to transport through the cover (R_c) can be calculated with Eq. (13).

$$R_c = \frac{C_{NH_3,s}}{F_{NH_3,c}} - R_{unc} \tag{13}$$

With a few exceptions (Baldé et al., 2018) the articles reviewed in this study do not present the concentration of TAN or pH in the surface layers. Therefore, default values for TAN and pH based on representative samples are used here with the aim to show that this simple concept can be used in practise for calculating NH_3 emission from stored liquid manure. The model was implemented in a spreadsheet that is publicly available from https://github.com/sashahafner/AMOSTO.

4. Emission data

Data were extracted from 43 articles published in peer reviewed journals and reports providing more information about the data given in the articles (Table 2). The present data were collected from 18 farm scale studies, where emission from 13 liquid manure stores was measured with micrometeorological methods, one with wind tunnels and four with dynamic chambers covering a small fraction of the surface. Data from studies where emission was measured with a mass balance method were excluded because they are used to estimate the emission over long time intervals and may include losses by oxidized N forms or N_2 resulting in an overestimation of NH_3 losses.

4.1. *Ammonia emissions from uncovered liquid manure*

The average emissions from stored liquid manure ranged from 2.7 to 13.2 g NH_3–N m^{-2} s^{-1} (Table 3), which is in line with the data collected by Kupper et al. (2020). The highest emission rate was from stores containing anaerobic digested liquid manure, which have a relative high TAN concentration and a high pH. The emission from cattle liquid manure stored in lagoons was the lowest, which may be due to a low TAN concentration which has counteracted a high pH. The emission from dairy cow liquid manure in tanks was higher than the emission rate from cattle liquid manure in lagoons probably due to a higher TAN concentration, which offset a lower pH. High emissions from pig liquid manure stored in tanks may be related to a high TAN concentration. High emissions from pig liquid manure stored in lagoons with low TAN may be due to high temperatures. It is interesting that liquid temperature is higher than air temperature for all categories. There are more emissions data than TAN, pH and air temperature data. This imbalance between measurements of emission and measured liquid manure characteristics and temperature restricted the size of the dataset used for model development.

Table 2 – Overview of store categories and techniques used in studies with information about NH_3 emission from the stored liquid manure. Definitions of scale of store category are from Kupper et al. (2020).

Scale of study	Micro meteorological method	Wind tunnel	Dynamic chamber	Static chamber/closed chamber	TAN or N mass balance	All methods
Farm (Used in practice)	13	1	4			18
Pilot (>0.5 m^3)	2	13			1	16
Laboratory (<0.5 m^3)			6	2	1	9
All scales	15	14	10	2	2	43

Table 3 – Measured emission rates for uncovered liquid manure stored in concrete tanks and lagoons, in brackets is given standard deviation (SD) and number of data (n). For individual values and sources, see supplementary material.

Source	Storage type	Emission rate	DM	Total N	TAN conc.	pH	Temperature (air)	Temperature (liquid)
		10^{-5} g NH_3–N m^{-2} s^{-1}	%	g N L^{-1}	g L^{-1}		°C	°C
Pig	Tanks	6.0 (6.4, 26)	7.3 (9.1, 23)	4.3 (1.0, 21)	2.9 (1.1, 25)	7.6 (0.3, 25)	11.7 (7.0, 26)	13.3 (7.4, 13.0)
Pig	Lagoon	6.7 (6.5, 45)	1.0 (0.6, 18)	0.94 (0.8, 38)	0.7 (0.6, 46)	7.9 (0.4, 46)	18.1 (8.7, 28)	20.0 (6.6, 24)
Anaerobic digested	Tanks	13.2 (11.7, 6)	5.25 (3.0, 6)	4.4 (2.3, 6)	2.7 (0.5, 6)	8.0 (0.2, 6)	7.2 (7.1, 6)	14.5 (5.0, 3)
Cattle	Tanks	2.7 (2.4, 35)	5.28 (3.1, 23)	3.2 (1.1, 22)	1.5 (0.7, 32)	7.4 (0.4, 32)	10.5 (7.9, 31)	14.9 (6.4, 16)
Cattle	Lagoon	3.9 (2.9, 19)	ND[a]	0.38 (0.21, 6)	0.3 (0.3, 7)	8.03 (0.23, 6)	13.7 (6.4, 17)	16.8 (6.4, 17)
All	All	9.9 (20.6, 144)	4.2 (5.8, 83)	2.5 (2.0, 95)	1.6 (1.3, 127)	7.8 (0.5, 128)	12.5 (8.1, 121)	16.7 (6.8, 63)

[a] No data.

Table 4 – NH_3 emissions from stored liquid manure with mitigation technologies (covered or treated) in % of emissions from stored liquid manure without mitigation (uncovered, untreated) and resistance to transport through cover (*Rc*). SD is standard deviation and n is the number of data records. For individual values and sources see supplementary material.

Cover or treatment	Emission from covered and treated liquid manure in pct. of control			Resistance to transport – Cover, s m^{-1}		
	Average	SD	N	Average	SD	N
Straw	33	23	23	1373	970	13
Surface crust – natural	45	22	11	388	353	6
Clay pebbles	41	34	13	2134	1429	7
Floating PVC (non porous)	16	9	15	1522	1518	11
Biocover (porous sheet)	66	36	6	241	224	2
Corrugated sheets	46	22	4	112	61	2
Lid	6	5	5	4444	3974	4
Tent	17	10	4	891	686	4
Oil	14	13	8	1435	628	3
Peat	24	27	6	12,778	12,910	5
Wood chips	53	45	4	Nc[a]		
Acid	29	23	9	Nc[a]		

[a] Not calculated.

4.2. *Reduction efficiency of mitigation technologies*

Reduction measures include (i) increased resistance to transport using a cover on the surface of the stored liquid manure and are related to porosity, cover thickness and cation exchange, or (ii) reduction of liquid ammonia [NH_3(aq)] due to a reduction of pH. When including the effect of these technologies in the calculations the length of the emission period should be included when assessing reduction efficiencies. The effect of a surface crust will increase with length of storage period, because it may take 20–30 d for a surface crust to form (Misselbrook et al., 2005). In contrast, the effect of adding acid once may decrease, because the pH of the liquid manure will increase with time following acid addition (Petersen et al. 2012).

Ammonia emissions can be reduced by a surface crust layer on stored manure (Table 4), which reduces convection of air immediately over the free liquid manure surface and convection in the top liquid manure layers (Santonja et al., 2017). The efficacy of surface crust layers as a mitigation method is questioned (Kupper et al., 2020), because crusts do not develop on all liquid manure type and may sink in periods of cold weather. At DM below ca. 2.2% a crust did not always develop on cattle liquid manure (0.62 m storage height) and at higher DM a 0.1 m layer developed in a study by Misselbrook et al. (2005). If crust developed on liquid manure with a low DM (2.2% DM), then crust formation took 50 days and at 4–5.9% DM ca. 30 days (Misselbrook et al., 2005). The density of a crust is greater than 1 kg L^{-1}, therefore crusts will only float to the surface if bubbles produced anaerobically adhere to it. Gas production and crust formation is limited at low DM or temperature. Shallow stores may contain less DM material per height to volume ratio, thereby limiting DM formation and gas production via microbial activity (Smith et al., 2007). Fibre content also affects crust formation (Misselbrook et al., 2005) which explains why pigs fed a non-fibrous diet can lead to stored pig liquid manure having minimal crusting (Smith et al., 2007). Furthermore, crust with a wet surface appears to influence the degree of reduction in NH_3 emissions. For example, a wet surface crust covering a liquid manure lagoon did not reduce NH_3 emissions (Grant & Boehm, 2018) or was less effective in reducing emissions from a pilot liquid manure store than a dry crust (Misselbrook et al., 2005).

Chopped straw covers reduced NH_3 emission significantly (Table 4), but the mitigation effect can be diminished by wind, which blows the straw layer to the leeward side of a store (Sommer, 1997), and at low temperatures or DM content, which can lead to the straw layer sinking due to low gas formation (Botermans et al., 2010). The reduced emissions due to covering with straw or other organic material may, in addition to creating a diffusion barrier, be a result of absorption of NH_4^+ to negatively charged surfaces (Kemppainen, 1987). Manure solids with a high cation exchange capacity have a higher absorption potential than straw (Misselbrook & Powell, 2005).

Oil layers may reduce NH_3 emission but tend to absorb to the dry matter floating on the surface and loose efficiency with time, if the layer is thin (3 mm), but is efficient at higher thicknesses (Hörnig, Türk, & Wanka, 1999). The efficiency may be reduced due to crack formation (Sommer et al., 1993).

Covering liquid manure with PVC sheets, or the like, is efficient in reducing NH_3 emissions. Through porous biocovers and geotextile covers the gas produced in the liquid manure diffuses through the cover and prevents these from being lifted from the surface and being blown away. In the Danish standards, there must be openings to avoid generating an oxygen to CH_4 ratio between 5 and 15, as gas mixtures in these ratios can be explosive. The emission caused by these openings is not known but negligible emissions of NH_3 were measured from 2000 m^3 liquid manure stored in a self-buoyant impermeable plastic bag (polyester with double polyvinyl chloride layer) mounted with 6 chimneys through which gas produced was released (Viguria, Sanz-Cobeã, López, Arriaga, & Merino, 2015).

Acidification of liquid manure reduces NH_3 emission due to reduction in $[NH_3(aq)]$. The acid may be added to the liquid manure in the animal building or at the start of a storage period outside, where the target pH is typically 6.0 (Petersen et al. 2016; Petersen et al. 2014; Sommer et al., 2017). The pH may increase with time from below 6 immediately after acidification, with one study showing an increase to the level of untreated liquid manure after 84 days (Owusu-Twum et al., 2017), probably due microbial consumption of VFAs (Petersen et al., 2012) or the decomposition of organic compounds (Eriksen et al., 2008). This increase in pH may cause NH_3 emissions to increase with time after acidification (Dai & Blanes-Vidal, 2013; Petersen et al., 2012; Sommer et al., 2017). In a study with pig liquid manure, pH increased very little (ca. 0.2 units) and NH_3 emissions from acidified liquid manure was low throughout the study (Petersen et al., 2014). Smaller increases in pH with time following addition of a “slow release” acidifying agent like alum ($(Al_2(SO_4)_3)$ may increase efficacy of the acidification (Regueiro et al., 2016).

Laboratory experiments using small containers for storage and for short time periods (weeks) tend to give very high efficiencies of treatment (Portejoie et al., 2003). At pilot and full scale, the measured treatment efficiency is affected by the management of the control treatment, for example, if a treatment with crust formation is compared to a stirred control treatment, the calculated reduction efficiency tends to be larger (Sommer et al., 1993) compared to when reduction is calculated using emission from crust compared to control liquid manure store without crust and not being stirred (Misselbrook et al., 2005). Further, a treatment may be more efficient during periods with high NH_3 emission potential compared to times with low emission potential, e.g. reduction efficiencies are lower in cold than in warm seasons (Loyon et al., 2007; Xue et al., 1999). During winter, emission from liquid manure covered with a straw layer was 40% of that from uncovered and during summer it was 13% of the emission measured from uncovered liquid manure (Petersen et al., 2013).

4.3. Parameter estimation and model test

The data compiled were used to estimate the resistance to transport parameter and to test model accuracy. Not all compiled studies included sufficient data for calculation of emission factors or mass transfer coefficients, which requires TAN concentration, pH and temperature. Here, in 7 studies TAN was not measured, similar to Kupper et al. (2020), who found that only 84% of NH_3 studies presented TAN values. In 7 studies, pH was not measured. Often, information about TAN concentration and pH is given only for the start or the start and end of a measurement period. Measurement of air temperature was carried out in all full-scale studies where micrometeorological methods were used. Most studies included measurement of bulk liquid manure temperature, and a few reported incident solar radiation. Small dynamic chamber creates an environment that deviates much from the open environment, therefore, these data were not used when calculating the mass transfer coefficient ($\varepsilon\tau$) and resistance to transport from uncovered liquid manure stores (R_{unc}). It has been shown that measurements using a wind tunnel do not deviate significantly from micrometeorological measurements (Sommer & Misselbrook, 2016). Therefore, windtunnel and micrometeorological measurements were included in the calculations of R_{unc}.

4.4. Calculating resistance to transport

The estimated mass transfer coefficients ($\varepsilon\tau$) for uncovered liquid manure should be similar for all slurry categories, if data used for estimating the parameters was liquid surface layer characteristic and temperature. This was not the case in this study, there was a larger variation of estimated F_{NH_3} between the six categories using Eq. (5) than between the more similar transfer coefficient $\varepsilon\tau_{NH3}$ calculated using Eq. (10) (Fig. 1). So, the approach given by Eq. (10) can be considered superior as it complies closer with the theoretical requirement of $\varepsilon\tau$ s not being strongly affected by slurry type.

Still there is a large variation in the mean $\varepsilon\tau_{NH3}$ calculated using equation (10) and this is partly due to the fact that wind speed and turbulence are not included in the calculation of $\varepsilon\tau_{NH3}$. Furthermore, the data collected from the studies were not specifically obtained for carrying out the calculations, specifically, emission data, slurry characteristics and temperature were not measured or recorded at corresponding intervals.

One reason for differences between animal liquid manure categories could be that the chemistry (Sommer & Husted, 1995) and transport of components (Hafner et al. 2017) varies between these, and this may affect the relative difference between surface and bulk pH, TAN and temperature. Transport of TAN and total inorganic carbon buffer components to the surface may be affected by slurry viscosity that differs between digestate, cattle and pig slurry and so will the effect of having large lagoons without walls and storage tanks with walls that affect wind and turbulence. The effect of this variation in characteristic of the three liquid manure categories and two storage types was reduced by defining liquid manure (and solution) and storage category for these when calculating a Runc (Fig. 2).

The R_c calculated using the extracted data differed much between liquid manure category (data not shown). In theory, the R_c for a cover should not vary between these, but much of this is due to the variation in estimated R_{unc} for each category (Fig. 2 and Table 5). Instead of estimating the resistance to transport with eq (13), we introduce the following standard method to calculate effect of covers on emissions:

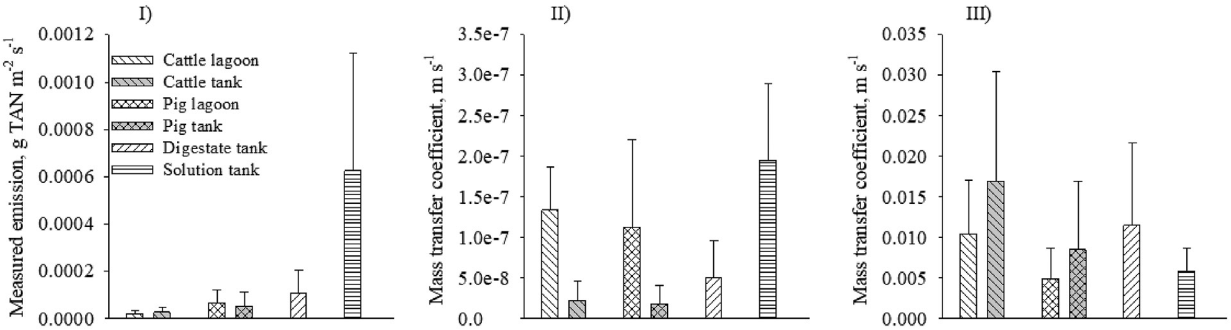

Fig. 1 – Measured emission (F_{NH_3}) and Mass Transfer Coefficient ($\varepsilon\tau$) for transport of NH_3 from uncovered stored liquid manure. The coefficient is the average emissions or calculated with Eq.'s 5–10 as follows: I: Measured emission, II) $\varepsilon\tau$ derived from measured emission divided by TAN concentration ($\varepsilon\tau_{TAN}$; eq (5)) and III) $\varepsilon\tau$ derived from measured emission divided by C_{NH3} i.e. air concentration of NH_3 in equilibrium with liquid NH_3 concentration calculated using bulk slurry concentration data ($\varepsilon\tau_{NH3,unc}$, Eq. (10)). Error bars: standard deviation.

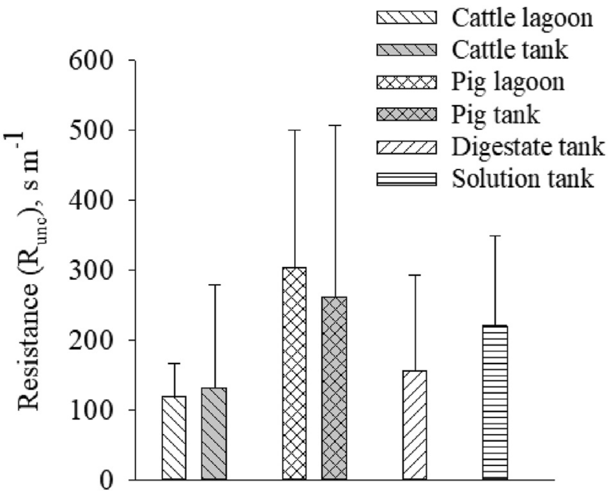

Fig. 2 – Resistance to transport (R_{unc}) calculated as the inverse of $\varepsilon\tau_{NH3,unc}$ (Fig. 1). Error bars; standard deviation.

$$x = \frac{R_{unc}}{R_c + R_{unc}} \tag{14}$$

where x denotes the reduction of emission due to the cover or other mitigation measures (Table 4) derived from measurements at pilot or full-scale liquid manure stores. In this analysis, data extracted from 29 studies of NH_3 emission (S1, supplementary data) were used to calculate a transfer coefficient for covered animal liquid manure stored in concrete stores or lagoons. Due to a lack of data, the calculation does not include the effect of wind speed.

4.5. *Accuracy of the model calculation*

Emission rates calculated by the model have some correlation to measured rates (Fig. 3). However, precision is low, as shown by the scatter in the plots and low r^2 once 4 extreme points have been removed. Additionally, there is evidence that the model may underestimate high emission (shown by the regression line slopes below unity). This can be explained by only very few available high emission measurements in the parameterization, and additional evaluation under high emission conditions would be valuable. Causes of the discrepancies include the neglect of actual wind speed, causing inaccurate transfer coefficients, and the neglect of the gradients of concentrations and temperature in the slurry liquid (using a single bulk measurement where a near-surface value would be more accurate).

Table 5 – Resistance to transfer of NH_3 from the surface of uncovered slurry, calculated using atmospheric mass balance and wind tunnel measuring methods and excluding data that are more than 100% higher than the average resistance for the category. SD is standard deviation and n is the number of data records.

		R_{unc}. (s m^{-1})		
		Average	SD	n
Lagoon	Cattle	118	47	6
Tank	Cattle	131	146	24
Lagoon	Pig	303	197	34
Tank	Pig	262	244	16
Tank	Digestate	156	136	36
Tank	Solution	219	129	8
All		200	182	126

The transport coefficient is inversely proportional to the sum of the resistances involved (Eq. (4)). The aerodynamic resistance R_a is inversely proportional to friction velocity $u*$ (Monteith & Unsworth, 1990, p. 291; Foken et al., 2008). The laminar resistance R_b varies less with $u*$ typically with an exponent of near −0.7, reported e.g. as $u*^{-0.67}$ by Thom (1972) and $u*^{-0.76}$ by Monteith and Unsworth (1990, p. 291). With friction velocity proportional to wind speed (exactly in neutral stratification, approximately in stable and unstable stratification), the transport coefficient for an uncovered slurry store is in good approximation proportional to wind speed. So is, consequently, the emission rate, as observed over lagoons (Leytem et al., 2018).

In our modelling approach, we have neglected this wind speed dependence. In theory, nearby weather station data could be used, and for stores located in flat, open terrain

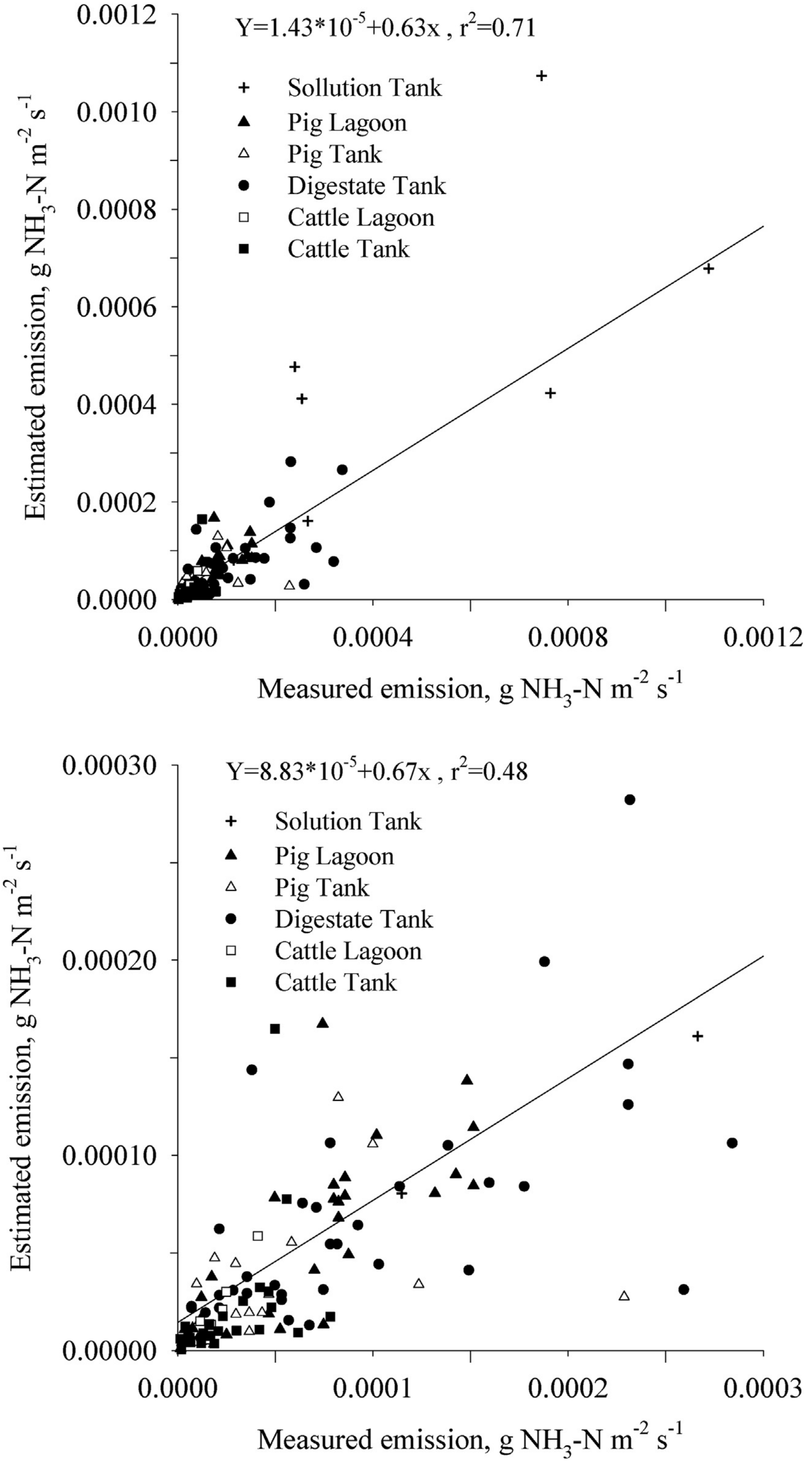

Fig. 3 – Calculated NH_3 emission using equation (6) versus measured NH_3 emission from uncovered liquid manure stores. Left: all data; right: presenting data less than 0.00035 g NH_3–N m^{-2} s^{-1}, using all data except for four higher than 0.00035 g NH_3–N m^{-2} s^{-1} stores.

without obstacles nearby this could improve accuracy. Using Eq. (4) and parameterisations of the resistances, such as those given by the authors cited in the previous paragraph, would be the way to do this. However, wind speed is highly variable in time, so using it to model emissions would require doing this explicitly on a time-resolved basis and then integrating over time. Further, the relationship between wind speed and u^* above the slurry store depends on local roughness, which is determined by the structure of the upwind area (vegetation, buildings) and may change with season and vary with wind direction. Flow obstacles such as nearby trees, hedges, buildings, as well as the slurry store's walls, can reduce wind speed and $u*$ by shelter effects, or increase them by channelling or by turbulent wake effects. It is not possible to provide simple and accurate parameterisations that can capture the enormous variability of potential configurations of buildings and other structures surrounding a slurry store. As a simple step with some promise, one could distinguish classes of stores by whether they are located in open terrain, largely exposed to unmodified horizontal wind, or in a built-up or sheltered area, and determine default transfer coefficients for the "open" and "sheltered" classes separately. Conceptually, one could develop a factor describing emission reduction by sheltering in the same way as the factor describing reduction by covering.

In our approach, we have determined a default transfer coefficient as a mean from 23 studies, in which no wind speed data were available. Studies in which emission measurements are made continuously over longer time periods are likely to capture a realistic distribution of wind speed patterns and should therefore provide a good estimate of a mean transfer coefficient. In contrast, studies in which emission rates are obtained from short-term sampling are more likely to be undertaken during the day than during the night, which makes it likely that wind speeds tend to be higher than the median. Therefore, such short-term sampling is more likely to be biased to higher emissions than to lower emissions.

The model calculation could be improved if we could calculate the concentrations of components in the surface layers of the slurry. This is not an easy task, because the models must then include an assessment of pH in the surface layer (few mm), which deviates from pH of the bulk of stored liquid manure (Hafner et al., 2013; Hafner et al., 2017). In stored liquid containing NH_4^+ and HCO_3^- where convection is avoided, the pH may increase by more than one unit from 15 mm below the surface to the surface, and if convection takes place it increases by 0.2–0.4 units (Hafner et al., 2017). This is due to release of pH buffer components from the surface of liquid manure which affect pH and is known to create gradients of increased pH with depth (Hafner et al., 2017; Sokolov et al., 2019).

Temperature of the surface layer differs from bulk liquid temperature due to solar heating, evaporation of water, and heat transfer between air and liquid. Therefore, use of surface temperature should improve model performance, but measurements are rarely available for parameter estimation and application. Including the effect of rain might also improve model calculations, because rain can reduce NH_3 emissions due to dilution of TAN in the surface liquid phase (Petersen et al., 2013; Sommer, 1997).

The parameterisation of the model could be much better if studies were carried out with a focus on developing models for calculating transfer coefficients. A minimum requirement for reported variables includes bulk TAN, pH and DM, temperature, wind speed and air temperature. If the store is covered then information about the cover composition or type should be recorded, and to provide information about the length of time the liquid manure was covered. Temperature of the surface or bulk liquid manure may be assessed using simple heat transfer models (Vilms Pedersen, Martí-Herrero, Singh, Sommer, Hafner, 2020).

4.6. *Applications of the model in scenarios calculations*

The concept of the new method to quantify NH_3 emission from stored liquid manure is not accurate, which is partly due to lack of studies providing data to parameterise it. Still, it is as accurate as the present EF that account for variation in TAN concentration, liquid manure categories and amount of liquid manure stored (Fig. 1). It will give more accurate estimates of emission from a specific liquid manure store than using the EF, because it accounts for slurry characteristic, temperature over the year and surface area. The following provides some scenarios presenting the advantages of using this model.

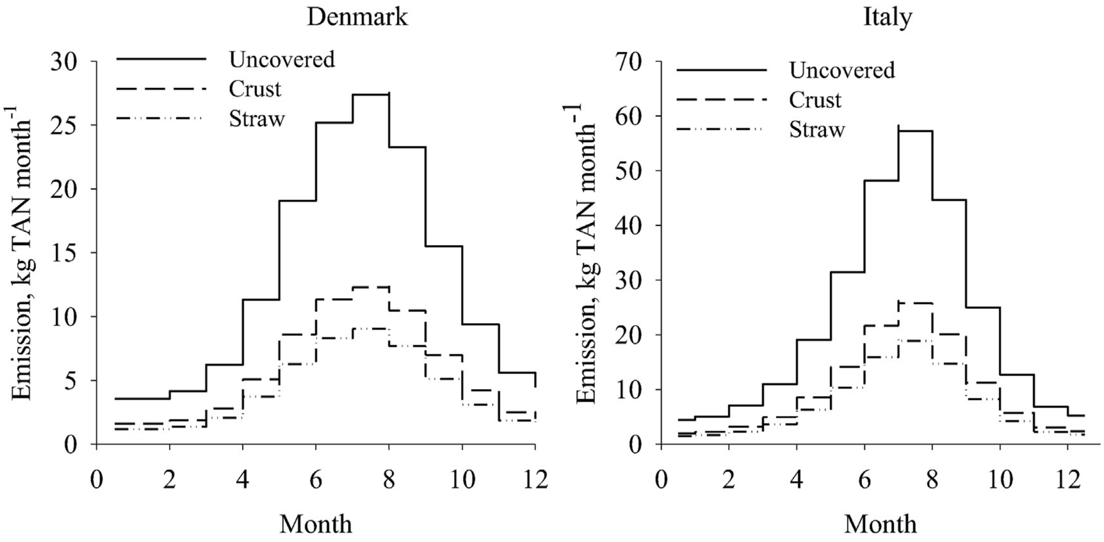

Fig. 4 – Ammonia emission from a Danish and an Italian liquid manure store using average monthly air temperature data from Sommer et al. (2009). Danish pig slurry characteristic is TAN 3.3 g N L^{-1} and pH 7.3 (Hansen et al., 2008) and the Italian is TAN 1.9 g N L^{-1} and pH 7.6 (Kupper et al., 2020).

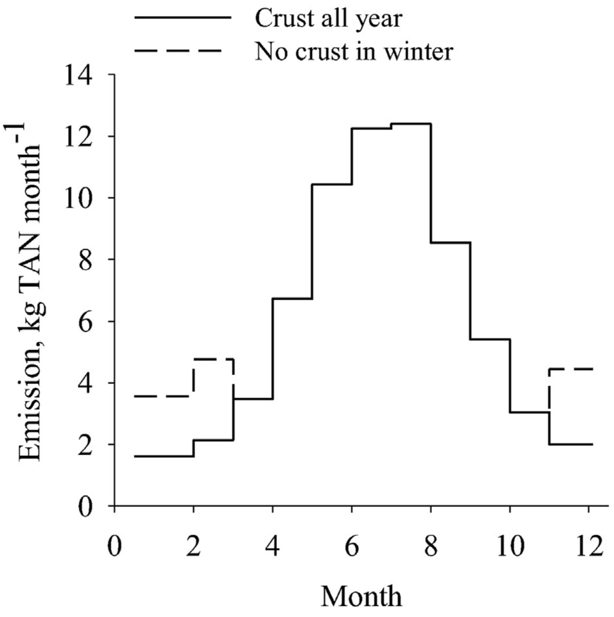

Fig. 5 – Ammonia emission from the Danish cattle liquid manure store (Using the same data as in Fig. 4) with crust covering the liquid manure all year round and sinking to the bottom during winter at temperatures below 5 °C.

Consider a small Danish and an Italian farm producing 2000 fattening pigs yearly, with each of them producing 0.5 m^3 liquid manure annually. The average monthly air temperature is similar to those used to calculate CH_4 emission from the store in the study of Sommer al (2009) and pig slurry characteristic are from Hansen et al. (2008), and Kupper et al. (2020). The surface area of the uncovered circular storage tank is 333 m^2 and slurry is emptied once per year at the start of the growing season. Consequently, the maximum depth of the slurry store is 3 m, as is assumed when reviewing the EF (Sommer et al., 2019) for the emission guidebook 2019 (European Environment Agency, 2016).

Our calculated emission for the Danish condition (Fig. 4) corresponds to 4.7% of TAN produced annually on this pig farm, which is lower than 11.4% estimated by Hansen et al. (2008), using the current methodology for calculating emissions from Danish agriculture. The emission from uncovered liquid manure in the Italian scenario corresponds to the variation in NH_3 emissions from stored liquid pig manure on pig farms in the North Italian region of Lombardi (Zilio et al., 2020). The annual emission in the Italian scenario is calculated to be 18% of the TAN produced and is due to a higher pH and air temperature ca. 4 times higher than the estimated annual emission from stored liquid pig manure in Denmark. This value is greater than the emission factor calculated using the Emission Guidebook (European Environment Agency, 2016) where the estimated EF was 12% of TAN (Sommer et al., 2019).

The model can also be used to assess the effect of mitigation practices as well as changes in efficacy of mitigation practices over time. For example, we can evaluate the reduction in emissions from use of a crust cover and the extent to which emission is affected by the crust sinking during winter due to a lack of gas bubble formation. In this scenario, it is assumed that the crust disappears when the average monthly temperature is below 5 °C (Fig. 5), which results in an increase of the annual emission by 20%. This is in line with the study of Petersen et al. (2013) who showed that NH_3 emissions were reduced by a straw cover, especially during summer storage (Petersen et al., 2013), and not much during winter due to sinking of the straw, but this had little effect on total annual emission because NH_3 emission rates are low at low temperatures.

Ammonia emission is exponentially related to temperature and pH and this makes these variables very important in the prediction of emissions (Fig. 6). Effect of temperature can be included in the calculations by using air temperature or, even better, by calculating surface liquid manure temperature

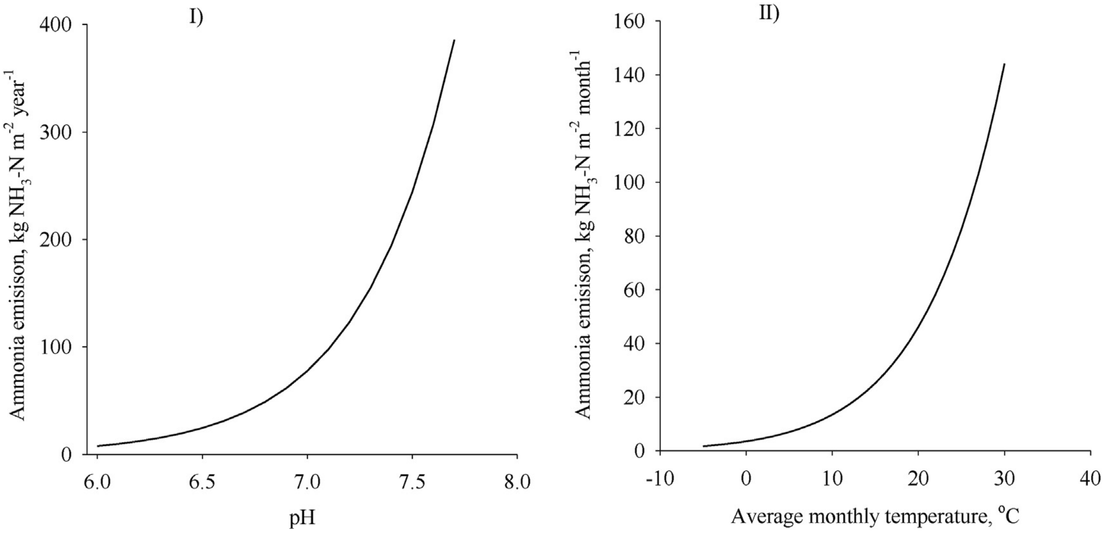

Fig. 6 – Ammonia emission from a Danish pig liquid manure tank as affected by: I) pH and II) air temperature. The data in diagram I was calculated using the monthly temperatures and pig slurry characteristics given in Fig. 4, and in diagram II slurry characteristics given in Fig. 4 was used.

if one knows the solar radiation. It is interesting that TAN is used as an important predictor in the EF calculation to estimate NH_3 emissions when pH is more important and not included in the calculations.

5. Conclusions

A concept and a simple quantitative model for calculating NH_3 emission from farm scale data that relate emission to the controlling chemical and physical processes has the potential to be useful for estimating emission from manure storages. This concept can provide calculation methods for NH_3 emission that more accurately represent site-specific liquid manure storage management, because calculations are based on formalization of processes in the liquid manure, i.e. variation in cover, temperature, pH and TAN over time and the area of stored liquid manure. Mass transfer coefficients used to calculate emissions are estimated for three liquid manure categories stored in either lagoons or tanks. The SD of the mass transfer coefficient for uncovered liquid manure ($\varepsilon\tau_{NH3,unc}$) is high, but variation in estimated $\varepsilon\tau_{NH3,unc}$ can be reduced by using data from studies including data about wind and turbulence and more frequent measurements (Day–Night or shorter intervals) of manure composition (TAN, pH) and of temperature. The model may be improved if these variables are measured at the surface liquid manure layers and in bulk samples. Solar radiation could also be a useful variable in the development of models and future “inventory calculators”.

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Sven G. Sommer: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Project administration; Resources; Visualization; Writing-original draft; Writing-review & editing.

Sasha D. Hafner: Conceptualization; Data curation; Formal analysis, Investigation; Methodology; Validation; Visualization; Resources, Writing original draft; Writing-review & editing.

Johannes Laubach: Conceptualization; Data curation; Investigation; Resources; Writing original draft; Writing-review & editing.

Tony van der Weerden: Conceptualization; Data curation; Investigation; Resources; Writing original draft; Writing-review & editing.

April B. Leytem: Conceptualization; Data curation; Investigation; Resources; Writing original draft; Writing-review & editing.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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