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# The ALFAM2 database on ammonia emission from field-applied manure: Description and illustrative analysis

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## ABSTRACT

Ammonia ($NH_3$) emission from animal manure contributes to air pollution and ecosystem degradation, and the loss of reactive nitrogen (N) from agricultural systems. Estimates of $NH_3$ emission are necessary for national inventories and nutrient management, and $NH_3$ emission from field-applied manure has been measured in many studies over the past few decades. In this work, we facilitate the use of these data by collecting and organizing them in the ALFAM2 database. In this paper we describe the development of the database and summarise its contents, quantify effects of application methods and other variables on emission using a data subset, and discuss challenges for data analysis and model development. The database contains measurements of emission, manure and soil properties, weather, application technique, and other variables for 1895 plots from 22 research institutes in 12 countries. Data on five manure types (cattle, pig, mink, poultry, mixed, as well as sludge and "other") applied to three types of crops (grass, small grains, maize, as well as stubble and bare soil) are included. Application methods represented in the database include broadcast, trailing hose, trailing shoe (narrow band application), and open slot injection. Cattle manure application to grassland was the most common combination, and analysis of this subset (with dry matter (DM) limited to < 15%) was carried out using mixed- and fixed-effects models in order to quantify effects of management and environment on ammonia emission, and to highlight challenges for use of the database. Measured emission in this subset ranged from < 1% to 130% of

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applied ammonia after 48 h. Results showed clear, albeit variable, reductions in $NH_3$ emission due to trailing hose, trailing shoe, and open slot injection of slurry compared to broadcast application. There was evidence of positive effects of air temperature and wind speed on $NH_3$ emission, and limited evidence of effects of slurry DM. However, random-effects coefficients for differences among research institutes were among the largest model coefficients, and showed a deviation from the mean response by more than 100% in some cases. The source of these institute differences could not be determined with certainty, but there is some evidence that they are related to differences in soils, or differences in application or measurement methods. The ALFAM2 database should be useful for development and evaluation of both emission factors and emission models, but users need to recognize the limitations caused by confounding variables, imbalance in the dataset, and dependence among observations from the same institute. Variation among measurements and in reported variables highlights the importance of international agreement on how $NH_3$ emission should be measured, along with necessary types of supporting data and standard protocols for their measurement. Both are needed in order to produce more accurate and useful ammonia emission measurements. Expansion of the ALFAM2 database will continue, and readers are invited to contact the corresponding author for information on data submission. The latest version of the database is available at http://www.alfam.dk.

## 1. Introduction

Ammonia ($NH_3$) emission from animal manure and synthetic fertilizers constitutes a large loss of reactive nitrogen (N) from agricultural systems (Bouwman et al., 2011). For agriculture, N loss from manure represents a cost, since it must be replaced with synthetic or additional organic fertilizer (Sutton et al., 2011). For society, $NH_3$ in the atmosphere is implicated in particulate formation and associated health impacts, and contributes to ecosystem degradation when it is deposited on land or water (Bobbink et al., 2010; Sutton et al., 2011; Erisman et al., 2013). Indirectly, $NH_3$ emission also contributes to $N_2O$ emission by increasing the rate of nitrogen cycling in natural ecosystems that receive deposited $NH_3$ (Davidson, 2009).

Globally there is consensus that agriculture, and in particular livestock manure, is the largest source of $NH_3$ and ammonium ($NH_4^+$) in the atmosphere (Beusen et al., 2008). The main sources are manure (urine and faeces) in animal houses, stored manure, and manure applied to fields. In many countries, emission from manure handled as slurry is the single largest source of $NH_3$ to the atmosphere, and emission from field-applied slurry is a major part of this (Hutchings et al., 2001; Rotz et al., 2014). Accurate estimates of $NH_3$ emission are important for national inventories, field- and farm-scale N budgets, and to evaluate the effect of emission reduction practices as part of improved nutrient management. Therefore, a large number of experiments on $NH_3$ emission from livestock manure applied to fields have been carried out in the past few decades (see reviews by Webb et al., (2010) and Sintermann et al., (2012)), and several models for estimating $NH_3$ emission have been developed (e.g., Søgaard et al., 2002; Rotz et al., 2014; Langevin et al., 2015). Standardisation of experimental results and collection in a database can increase the utility and accessibility of experimental data, which can then be used for multiple purposes, including development or evaluation of both emission factors and models. The ALFAM project on $NH_3$ emission from field-applied manure demonstrated this: the resulting database and the related ALFAM model (Søgaard et al., 2002) have been widely used (215 citations as of 17 August 2017 according to Google Scholar). But many emission measurement experiments have been carried out since the publication of the ALFAM database, and measurement techniques have been refined (Sintermann et al., 2012). Preservation of these emission measurements, which have been used to determine emission factors, along with supporting data in an accessible (numeric) form, is essential. Given the current interest in $NH_3$ emission from both regulatory and research perspectives, expansion and improvement of the ALFAM database is needed.

The primary objective of this article is to present the ALFAM2 database, which consists of data from the original ALFAM database and new data. The ALFAM2 database contains about twice as many observations as ALFAM, and provides more information by adding new variables related to emission. In this article, we: 1) describe and summarise the new ALFAM2 database; 2) use statistical models to attempt to quantify effects of application methods and other factors on emission, 3) discuss challenges for data analysis and model development based on the database, and 4) recommend ways to standardize and improve the quality of ammonia emission measurements.

## 2. Methods

### 2.1. The ALFAM2 database

#### 2.1.1. Data collection

The database described in this work is a combination of the original ALFAM database (Søgaard et al., 2002) and newer data. New data were entered into a spreadsheet template by each research group that collected them, or transferred to the template from other files provided by the group. Research groups in Europe, Canada, and the US known to us to have made $NH_3$ emission measurements were invited to submit data. (New contributions are also welcome, and readers are invited to contact the corresponding author for information on data submission.) The following types of variables were included: identification (project, publication, experiment, field, plot code, treatment), location (latitude, longitude, topography, field name), soil (texture, moisture, pH, temperature, tillage), weather (air temperature, wind speed, precipitation, relative humidity, solar radiation), manure (source, bedding, dry matter, total ammoniacal nitrogen (TAN), pH, treatments), application (time, method, rate, incorporation), crop (type, height, coverage), and emission (interval time, measurement method, plot size, background $NH_3$ (g) concentration upwind of the emitting surface, average emission rate). Two types of data were collected: plot-level (concerning a single physical plot from which emission was measured) and measurement interval-level (concerning a single time interval with one estimate of $NH_3$ emission rate, for a single physical plot). Plot-level data included plot identification, location, soil, manure, application, and crop data. Measurement interval-level data also included weather and emission for each interval, which varied in length among experiments and within individual plots. Weather data included average air temperature, wind speed, and precipitation for each interval. Emission data were reported as average $NH_3$ flux (typical unit, kg $ha^{-1}$ $h^{-1}$) for each measurement interval. Application methods and emission measurement methods (McGinn and Janzen, 1998) were selected from a list of possibilities or defined by the submitter.

#### 2.1.2. Data processing, calculations, and database organization

All data processing and analysis was done using R version 3.3.1 (R Core Team 2017). The general steps were:

1 Data from the original ALFAM study were read from a spreadsheet file, and column names and factor levels were added.
2 Minor changes were made to ALFAM data (described directly

below).

3 Data from each individual ALFAM2 research institute were read from one or more spreadsheet files, standardised (measurement units, spelling of categorical variable levels, date and time format), and merged with the original ALFAM data.
4 Cumulative emission and other new variables were calculated.
5 Plot-level data were taken from the first observation for each plot (e.g., slurry type) or else calculated (e.g., weather averages and cumulative emission).
6 Data were saved in two files: plot-level and interval-level.

Only minor changes were made to the original ALFAM data. A note was added to all observations from a single institute explaining that measurements are now thought to be biased (see Section 3.3). For three institutes the broad measurement method category "micro-meteorological" was replaced with more specific levels based on knowledge of the authors (integrated horizontal flux (IHF) for institutes 105 and 106, and ZINST for institute 107). Date format was corrected for several plots, and corrections were made to about 30 interval start times for institutes 104, 105, and 107. Finally, the wind speed measurement height for institute 105 was corrected from 0.25 cm to 25 cm.

Two files were produced in order to meet expected needs of users. To find values of cumulative emission after a specific time (e.g., 48 h) or the entire measurement event duration, the smaller plot-level file (File S1) will be more convenient. Each observation contains data on a single plot. In a small number of cases, emission was measured from a single plot simultaneously by more than one method, and therefore multiple observations exist for some plots in the plot-level file. Each observation contains a unique plot/measurement method code ("pmid" variable in the files, for **p**lot-**m**easurement method **id**entification code), as well as a plot id ("pid" variable in the files). For data on emission rates over time, the interval-level file (File S2) is required. In this file, multiple observations are included for each plot. Two related text files describe the variables and headers (Files S3 and S4). The latest version of all four files are also available from http://www.alfam.dk

Interval duration (h) (the time over which a single average emission rate was measured) was entered directly in the ALFAM2 spreadsheet template, or else calculated from interval start and end dates and times (if available). Cumulative time since application (to the end of a measurement interval) was calculated as the difference between the date and time at the end of an interval and slurry application date and time, or, if slurry application date and time was not given, as the sum of previous and the current interval durations (use of this approach assumes that application occurred at the start of the first interval for each plot). Interval emission (kg ha$^{-1}$ as N) was taken as the product of reported average emission rate (kg ha$^{-1}$ h$^{-1}$) and the interval duration. Cumulative emission (kg ha$^{-1}$) at the end of each interval was the sum of these values from the current and all previous measurement intervals. A missing emission rate for a single interval resulted in missing cumulative emission for that and all following intervals.

In order to facilitate comparison of plot-level cumulative emission among plots, values of cumulative emission were also estimated for a set of standardised durations (1, 4, 6, 12, 24, 48, 72, and 96 h after application) by linear interpolation of cumulative emission. This approach assumes that $NH_3$ flux in each interval was constant and equal to the average value, which could be inaccurate for long intervals. No estimate was made in cases where the first measurement interval ended after the standardised duration, to prevent likely underestimation of emission (e.g., 1 h emission was not estimated if the first measurement interval ended at 2 h). Emission estimates were not made beyond reported times, i.e., extrapolation was not done. The number of emission measurement intervals and the minimum and maximum duration were determined for each plot and included in the plot-level file.

Applied TAN (kg ha$^{-1}$) was calculated as the product of volumetric (m$^3$ ha$^{-1}$) or gravimetric (t ha$^{-1}$) manure application rate and the TAN concentration (g kg$^{-1}$), and was used to normalise emission. Manure density was assumed to be 1000 kg m$^{-3}$ when volumetric application rate was reported. Plot-level measurement interval duration-weighted weather averages (temperature, solar radiation, and wind speed) were calculated for a set of standardised times (6, 12, 24, and 48 h), as well as for the complete duration of each emission event by Eq. (1). Rainfall totals were also calculated for these times, and additionally, an average rate (mm h$^{-1}$) was calculated.

$$\bar{y} = \sum_{i=1}^{k} y_i d_i \Big/ \sum_{i=1}^{k} d_i \quad (1)$$

In Eq. (1), $\bar{y}$ = weighted average value, $y_i$ = reported variable value for a single interval $i$, and $d_i$ = duration of measurement interval $i$ (h). Summation was over only those measurement intervals where cumulative time was less than or equal to the standardised times used. Where data were missing in early intervals, weather averages for times that include these intervals are also missing.

### 2.2. Data analysis

#### 2.2.1. Data selection

All submitted observations were retained in the database, and the summary presented below is based on all the data in the database. But the analysis (development of statistical models) presented here was carried out on a subset of the plot-level dataset. Data for cattle slurry applied to grassland were used for analysis, because it was the largest most-balanced subset (819 observations in total, 485–568 used in the models). Observations with less common types of manure (see Section 3.1) were excluded. The complete database also included solid manures with high DM (up to 37% for cattle manure), but those with values above 15% were excluded from the analysis, since the focus was on slurry. Six observations did not include a DM measurement and were also excluded. Lastly, three application methods with few observations (band spreading on slots (institute 203 only), closed slot, and pressurised injection (institute 102 only)) were excluded. And a single observation from institute 207 was excluded due to improper operation of the injection machinery (pid = 1486). No emission measurement methods were excluded from the analysis.

#### 2.2.2. Statistical models

Factors affecting emission (including research institute) were explored to identify and quantify important effects, and highlight some challenges for data analysis and use of the database. Two types of models were used: linear mixed-effects models applied to complete data subsets (Section 2.2.1), and linear fixed-effects models applied separately to results from individual experiments. For both, $\log_{10}$-transformed 48 h cumulative emission (absolute or normalised by TAN application rate to give a relative value) was the response variable. Selection of 48 h was arbitrary. A shorter time would increase the size of the data subset, but emission values would be farther from "total" emission. For this subset, 48 h emission was generally close to final emission (median value: 94%) while 24 h emission was substantially lower (median value: 86%). For only those trials that continued at least 72 h relative 48 h emission was slightly lower (median of 93%). A total of 74 observations were excluded because trial duration did not extend to 48 h. To use 72 h instead, an additional 127 observations would have to have been excluded. Because the pattern of relative emission over time may vary with application method and other predictor variables, the value selected for duration will likely affect parameter estimates. A single model was fit using 24 h emission to provide a comparison.

The $\log_{10}$ transformation of response variables was used for multiplicative effects of predictors on emission (Steel, 1997). For example, we assumed that trailing hose application always has the same effect when expressed as a fraction of emission resulting from broadcast application. Or, a 1% increase in slurry dry matter would always have the same fractional effect on emission. While probably not completely accurate, these responses are more reasonable than those for no transformation (additive effects of predictors and constant absolute effects on emission). With the transformation, the response variable (cumulative emission) can never be below zero, but there is no upper bound on emission, which could then be greater than applied TAN. However, for this relatively large and varied dataset, only a small number of predicted values exceeded applied TAN. (Interpretation of coefficients when the response or predictor variables are $\log_{10}$-transformed is discussed in Supplemental file S6).

Mixed-effects models were used to quantify effects of slurry characteristics, environment, management, and unexplained effects associated with institutes. This approach is appropriate for hierarchical (in these data observations from the same institute are not independent) and unbalanced data (Pinheiro and Bates, 2000; Raudenbush and Bryk, 2002). Fixed-effect predictors included application technique (categorical, or a factor), slurry TAN concentration ($g\,kg^{-1}$ as N, omitted from two models), slurry dry matter (% of total mass), slurry pH (omitted from one model), application rate ($t\,ha^{-1}$ or $m^3\,ha^{-1}$, which were used interchangeably), air temperature (°C), wind speed ($m\ s^{-1}$ at 2.0 m height), and crop height (cm). Predictor values for air temperature and wind speed were 24 h weighted averages (Eq. 1), or, if these were unavailable (49 observations for wind and 83 for air temperature), 48 h weighted averages were used instead. Each of these variables has a theory-based mechanistic relationship to $NH_3$ emission and effects have been observed in individual experiments (e.g., Huijsmans et al., 2001; Misselbrook et al., 2005; Thorman et al., 2008). Most database variables could affect $NH_3$ emission, but other possible predictors were missing from a large number of observations, and so were not considered. However, the variable set selected above is arbitrary, and other sets with fewer or more observations may be reasonable (and would produce different model results).

Slurry TAN concentration and application rate were $\log_{10}$-transformed to allow for the possibility of a direct relationship between their values and emission rate. When necessary, wind speed was adjusted to a reference height of 2.0 m based on Eq. (2.55) in Guyot (1998) (Eq. (2)).

$$v_r = v_m \ln(h_r/z_0)/\ln(h_m/z_0) \tag{2}$$

In Eq. (2), $v$ = wind speed ($m\ s^{-1}$), $h$ = height of measurement (m), $z_0$ = roughness parameter (m), and subscripts $r$ and $m$ indicate reference and measurement. The roughness parameter was estimated as

**Table 1**
Summary of data contributed to the ALFAM2 database by institute. All counts by manure type, application method, crop, and measurement method are number of unique plots. See Table S1 for full names of institutes and contact information.

| Code | Institute | Country | Experiments[a] | Plots | Intervals | Manure types[b] | Application methods[c] | Crops[d] | Measurement methods[e] | Duration (h)[f] |
|---|---|---|---|---|---|---|---|---|---|---|
| 101 | ADAS | UK | 8 | 79 | 553 | 79 p | 79 bc | 79 stub | 79 wt | 89, 93, 94 |
| 102 | AUN | NO | 2 | 9 | 36 | 9 c | 3 bc, 3 pi, 3 th | 6 grss, 3 soil | 9 mm | 165, 168, 171 |
| 103 | CRPA | IT | 10 | 75 | 928 | 75 p | 52 bc, 5 os, 18 th | 42 grss, 14 soil, 19 stub | 15 chamb, 60 wt | 24, 68, 96 |
| 104 | DIAS | DK | 18 | 46 | 352 | 8 c, 38 p | 23 bc, 2 cs, 21 th | 27 othr, 19 soil | 30 mm, 16 wt | 138, 159, 212 |
| 105 | IGER[g] | UK | 40 | 263 | 1879 | 242 c, 21 p | 245 bc, 6 os, 3 th, 9 ts | 261 grss, 2 othr | 33 ihf, 230 wt | 24, 124, 258 |
| 106 | IMAG | NL | 44 | 119 | 1062 | 102 c, 17 p | 47 bc, 6 cs, 34 os, 3 th, 29 ts | 119 grss | 119 ihf | 54, 92, 97 |
| 107 | IUL/FAT | CH | 29 | 121 | 1070 | 2 b, 113 c, 5 p, 1 s | 117 bc, 2 os, 2 th | 111 grss, 10 stub | 55 zinst, 66 wt | 27, 53, 102 |
| 108 | JTI | SE | 10 | 88 | 88 | 26 c, 41 m, 21 p | 17 bc, 3 cs, 26 os, 34 th, 8 ts | 65 grss, 23 soil | 88 chamb | 18, 72, 145 |
| 201 | AAFC | CA | 10 | 109 | 2597 | 109 p | 109 bc | 58 grss, 51 soil | 109 wt | 117, 235, 458 |
| 202 | ADAS-RR | UK | 3 | 109 | 747 | 91 c, 18 p | 63 th, 46 ts | 18 cer, 61 grss, 15 othr, 15 stub | 109 ihf | 140, 189, 1422 |
| 203 | ARDC | CA | 10 | 120 | 1576 | 120 c | 60 bc, 60 ths | 24 grss, 96 soil | 24 ihf, 96 wt | 328, 333, 338 |
| 204 | AT | DK | 7 | 24 | 173 | 14 c, 10 p | 7 bc, 7 os, 10 th | 9 grss, 8 othr, 3 soil, 4 stub | 3 chamb, 21 zinst | 105, 192, 338 |
| 205 | AU | DK | 6 | 87 | 551 | 20 c, 67 p | 16 cs, 10 os, 61 th | 64 cer, 20 grss, 3 stub | 18 wt, 69 zinst | 94, 139, 168 |
| 206 | CAU-LU | DE | 16 | 197 | 2147 | 69 c, 81 o, 47 p | 197 th | 52 cer, 84 grss, 61 mz | 9 bls, 188 cps | 26, 52, 141 |
| 207 | INH–HAFL | CH | 16 | 47 | 880 | 42 c, 1 o, 4 p | 27 bc, 3 os, 12 th, 5 ts | 47 grss | 47 bls | 24, 49, 121 |
| 208 | INRA | FR | 7 | 23 | 11228 | 13 c, 6 n, 4 p | 8 bc, 8 th, 1 ts | 1 cer, 19 soil, 1 stub | 21 agm, 2 fides | 52, 390, 508 |
| 209 | MU | IT | 6 | 8 | 2327 | 8 c | 7 bc, 1 os | 3 grss, 1 soil, 4 stub | 6 bls, 2 ec | 98, 158, 291 |
| 210 | NMI-WUR | NL | 7 | 16 | 159 | 16 c | 16 bc | 16 grss | 8 ihf, 8 wt | 94, 282, 911 |
| 211 | SDU | DK | 4 | 138 | 858 | 48 c, 16 m, 32 m, 26 n, 16 p | 4 cs, 106 th | 118 cer, 20 stub | 8 chamb, 130 cps | 1, 65, 78 |
| 212 | TEAGASC | IE | 6 | 68 | 450 | 50 c, 18 p | 20 bc, 18 th, 30 ts | 18 cer, 50 grss | 18 chamb, 50 ihf | 24, 160, 170 |
| 213 | USDA | US | 2 | 2 | 38 | 2 c | 2 bc | 2 stub | 2 ihf | 150, 171, 192 |
| 214 | WUR | NL | 50 | 147 | 1208 | 90 c, 57 p | 88 bc, 4 cs, 51 os, 4 ts | 89 grss, 29 soil, 29 stub | 147 ihf | 8, 86, 100 |

Notes: Institute codes start with 1 for data from the original ALFAM database, and 2 for new data.

Other notes: Data from most ALFAM2 institutes have been presented in publications (publication codes used in database are included in square brackets after each citation, if available): 106 (NMI): Huijsmans et al., (2001), 201 (AAFC): Chantigny et al., (2004) (3), Chantigny et al., (2007) (2), Chantigny et al., (2009) (1); 203 (ARDC): Bittman et al. (2005) (2), Bhandral et al., (2009) (1); 204 (AT): Misselbrook and Hansen (2001) (3), Hansen et al., (2003) (2), Hansen et al., (2004) (4), Hansen and Birkmose (2005) (1); 205 (AU): Thomsen et al., (2010) (1), Nyord et al., (2012) (2), Nyord et al., (2013) (4); 206 (CAU-LU): Gericke et al., (2012) (2), Ni et al., (2012) (1), Ni et al., (2013) (3), Koester et al., (2014) (4); 207 (INH–HAFL): Häni et al., (2016) (1); 208 (INRA): Génermont et al.(1998) (5), Loubet et al., (2010) (2), Loubet et al. (2011a,2011b) (3), Cohan et al. (2012) (1), Personne et al., (2015) (4); 209 (MU): Carozzi et al., (2012) (3), Carozzi et al. (2013a) (2), Carozzi et al. (2013b) (1), Ferrara et al., (2016) (4); 210 (NMI): Bussink et al. (1994) (1); 212 (TEAGASC): Dowling et al., (2008) (1), Meade et al., (2011) (2), Bourdin et al., (2014) (3); 213 (USDA): Thompson and Meisinger (2004) (1); 214 (WUR): Huijsmans et al., (2003) (1), Huijsmans and Schils (2009) (2).

[a] Projects, experiments, plots, and intervals columns all have counts.

[b] Slurry types: c = cattle, p = pig, m = mink, b = poultry, s = sludge, o = other.

[c] Application methods: bc = broadcast, th = trailing hose/band spreading, ths = trailing hose application on slots, ts = trailing shoe, os = open slot, pi = pressurised injection.

[d] Crops: soil = bare soil, grss = grass, stub = stubble, cer = small grain, mz = maize, othr = other.

[e] Measurement methods: agm = aerodynamic gradient, bls = backwards Lagrangian model, chamb = chamber, cps = calibrated passive sampler, ec = eddy covariance, fides = FIDES, ihf = integrated horizontal flux, mm = micrometeorological, wt = wind tunnel, zinst = ZINST.

[f] Total measurement duration minimum, mean, and maximum.

[g] IGER is now called Rothamsted Research, which contributed new data as part of institute combination 202 (ADAS-RR).

**Table 2**
Number of unique plots in the ALFAM2 database for each combination of manure source, application method, and crop.

| Source | App. method | Crop | | | | | |
|---|---|---|---|---|---|---|---|
| | | Grass | Bare soil | Cereal | Maize | Stubble | Other |
| Cattle | Broadcast | 475 | 60 | 0 | 0 | 20 | 1 |
| Cattle | Trailing shoe | 125 | 0 | 1 | 0 | 0 | 1 |
| Cattle | Trailing hose | 93 | 7 | 57 | 25 | 21 | 11 |
| Cattle | Open slot | 110 | 1 | 0 | 0 | 0 | 0 |
| Cattle | Closed slot | 4 | 2 | 0 | 0 | 4 | 0 |
| Cattle | Tr. hose. on slots | 12 | 48 | 0 | 0 | 0 | 0 |
| Pig | Broadcast | 128 | 100 | 0 | 0 | 116 | 9 |
| Pig | Trailing shoe | 5 | 0 | 0 | 0 | 0 | 0 |
| Pig | Trailing hose | 20 | 22 | 104 | 16 | 11 | 30 |
| Pig | Open slot | 3 | 6 | 6 | 0 | 5 | 0 |
| Pig | Closed slot | 2 | 5 | 14 | 0 | 4 | 0 |

Note: Uncommon sources (chemical concentrate, mink, mixed slurry, poultry, sludge, and other) and pressurised injection are omitted here.

1/10th of the crop height when height was available, otherwise, it was set to 0.01 m (Foken, 2008).

Models included interactions between application method and all other predictors individually (first-order interactions only). All numeric predictors (quantitative) were centred by subtracting the overall mean value from each individual reported value so main effects of application methods could be evaluated under mean conditions. These mean conditions were: slurry TAN concentration (as N): 2.07 g kg$^{-1}$, slurry application rate: 41.4 t ha$^{-1}$, slurry dry matter concentration: 5.55%, slurry pH: 7.46, air temperature: 13.2 °C, wind speed: 2.72 m s$^{-1}$, and crop height: 9.24 cm. Broadcast application was taken as the reference application method.

Two random-effect predictors were included in the mixed-effects models: institute, and a factor for emission measurement method/soil type combination nested within institute (along with an implied residual error term). These effects are expected to include effects of variables not measured and any biases in application and measurement methods, as discussed in more detail in Section 3.3. It is reasonable to expect dependencies among all observations from within a single institute, but also among observations made using the same measurement technique (in cases where more than one technique was used by a single institute) and at the same location. The emission measurement method/soil type factor was included to account for the latter dependencies. Because data are observational and there is very little crossed structure within the database, it would be difficult or impossible to separate effects of measurement method and soil type, and we did not try to do so. Mixed-effects models were fit using the lme() function in the nlme package by maximising the restricted log-likelihood (Pinheiro et al., 2016). A few models were compared using Akaike's "An Information Criterion" (AIC) (Sakamoto et al., 1986) using the AIC() function in the stats package (R Core Team, 2017), and in this case, the maximum likelihood method was used for parameter estimation.

We focused on three models. Model 1 used absolute cumulative 48 h emission (kg ha$^{-1}$ as N) as the response variable and all the predictors listed above (13 institutes, 485 observations). Model 2 did not include TAN concentration (to avoid likely spurious responses to TAN and other predictors apparent in model 1) and instead used relative cumulative 48 h emission (fraction of applied TAN) as the response variable (same data subset as model 1). Model 3 was similar to model 2 but did not include slurry pH, in order to use a larger data subset (14 institutes, 568 observations). All observations with acidified slurry were excluded for model 3. The sensitivity of model coefficients to data from individual institutes was assessed by evaluating the effect of individually removing data from each of the 13 institutes used for model 2 on coefficients.

Experiment-based models were used to estimate application method effects from individual data subsets for each experiment. This simple approach provides a method for estimating effects of application techniques free of most assumptions about effects of other variables, and has been applied before (Huijsmans and Schils, 2009). The response variable was $\log_{10}$-transformed 48 h cumulative emission and application method was the only predictor. Grouping of observations into experiments was done by data submitters. Broadcast application was used as the reference method, and experiments were included in the analysis if broadcast and either trailing hose, trailing shoe, or open slot injection application was used. Data subsets were smaller than for the models described above: 5 institutes, 11 experiments, and 24 plots for trailing hose; 4 institutes, 24 experiments, and 85 plots for trailing shoe; and 4 institutes, 25 experiments, and 61 plots for open slot injection. The lm() function in the stats package (R Core Team, 2017) was used for parameter estimation, but for most experiments, replication was absent (there was only one plot for each application technique), and estimates were simply observed values for individual plots. Hypothesis tests were not possible in these cases, and are not reported in any cases.

## 3. Results and discussion

### 3.1. Database summary

The complete database contained 30907 measurement-interval level observations and 1899 plot-level observations from 1895 plots. In total, 22 institutes from 12 countries contributed data (Table 1). Data were strongly unbalanced: cattle manure applied to grassland was best represented in the database (Table 2). Most results were for application of cattle and pig manure (1083 plots for cattle and 606 for pig), and other types of manure (mink, poultry, mixed, and "other") and other fertilizers (chemical concentrate and sludge) were much less common. Most data, 1664 plots, were from Europe, with the remainder from the US and Canada.

#### 3.1.1. Variable summary

Manure characteristics, application rates, and emission rates all showed large variation within the database, both among and within slurry type (Figs. 1 and 2 show results for cattle and pig manure only). This variation is characteristic of animal production in industrialized countries, and reflects differences in diet and manure management. Dry matter concentration was usually below 5% for pig slurry, and below 10% for cattle, although many observations had higher values. Slurry pH was between 7 and 8 for most observations. A small number of plots from three institutes received acidified slurry (24 plots from institute 205, 9 from institute 210, and 49 from institute 211). Broadcast was the most common application method (927 plots). Trailing hose was used on more than half as many plots (559), while all other methods—trailing shoe, open- and closed-slot injection, band spreading on slots, and pressurised injection—were used on fewer than 150 plots each. Pressurised injection and band spreading on slots was each done by only a single institute. Micrometeorological measurement of emission was the most common approach on a plot basis (763 plots, including 492 integrated horizontal flux (IHF), 145 ZINST, 62 backwards Lagrangian stochastic model-based (bLS), 21 aerodynamic gradient, and 39 from the original ALFAM database simply identified as "micromet", which included ZINST, IHF, and the perimeter profile method (Schjoerring et al., 1992)), followed by 682 wind tunnel plots. Measurements from calibrated passive samplers (Gericke et al., 2011) (318 plots) were less common than wind tunnel measurements, followed by even fewer chamber measurements (132 plots). Details on measurement methods and other variables can be found in the publications listed in Table 1.

Weather varied widely within the database (Fig. 3). Air temperature (24 h weighted averages) ranged from below 0 °C to 29 °C, although extreme values were rare. The most common wind speeds (24 h weighted average of measured values) were between 1 and 3 m s$^{-1}$, but maximum values were above 15 m s$^{-1}$. Rainfall quantity was not

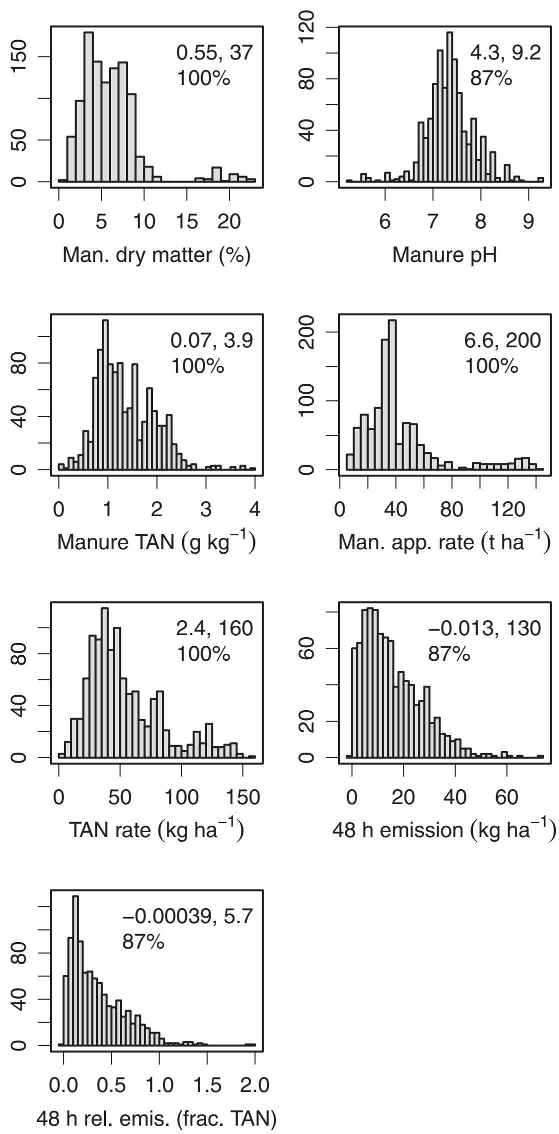


**Fig. 1.** Histograms of select manure and application variables for all observations with cattle manure application. Y axis shows frequency (count) of plots. Numeric values in upper right show range of values and percentage of plot-level observations with data. Values more than 4 standard deviations from the mean are omitted from the plot (but included in the reported range).

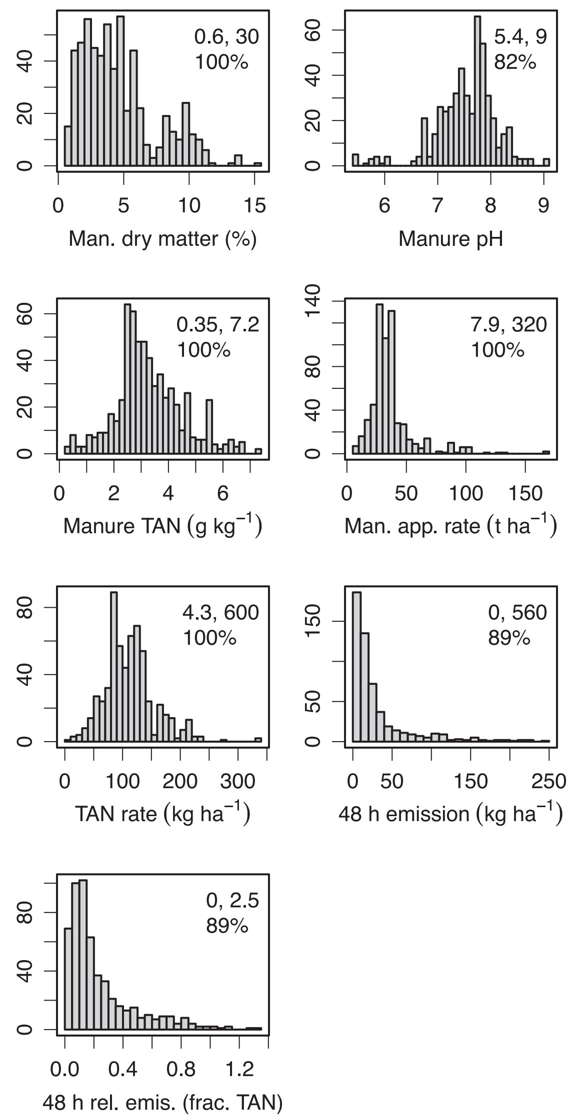


**Fig. 2.** Histograms of select manure and application variables for all observations with pig manure application. Other details are as in Fig. 1.

recorded for about one-third of all plots (626 of 1895). Nearly half of the remainder (634 of 1269) had zero rain. Interval-level data showed that a majority of intervals (23222 of 30907) had zero rain, possibly reflecting an intentional bias (i.e., avoiding starting an experiment when rain is expected). Soil bulk density and pH varied widely among plots (Fig. 3).

#### 3.1.2. *Emission summary*

The duration of emission measurements varied from about 1 h to more than 59 d, and exceeded 48 h for most plots (1733 of 1895) (Table 1). Emission rates from individual plots generally showed a characteristic (but highly variable) trajectory over time (Fig. 4). The initial rate was highest, and was followed by a roughly first-order decline over the first half day. After this, the rate continued to decline but much more slowly. While some plots showed a monotonic decline in emission rate over time, many showed temporary increases (often in the second and subsequent day), presumably due to diurnal changes in weather. However, in nearly all cases, the highest emission rates were measured soon after application. Even for the longest trials (emission measurements carried out for > 96 h) about half of total emission had generally occurred after 12 h (median of 49%) and had occurred after 48 h in almost all cases (5th percentile of 49%) (Table 3). Cumulative 48 h emission varied among and within institutes from < 0 (small net deposition of $NH_3$, observed for two plots) to nearly 7-fold applied TAN, although only in 64 of 1895 cases did emission exceed TAN application (Fig. 5).

### 3.2. *Factors that affect ammonia emission (model results for cattle slurry applied to grassland)*

#### 3.2.1. *Mixed-effects models*

Results from models 1 and 2 (see Section 2.2 for a description of the models) showed that both trailing hose and open slot injection reduced emission compared to broadcast application, by about 50% for trailing hose and 70% for open slot injection (Tables 4 and 5). The trailing shoe reduction was smaller than that for trailing hose (about 30%), while the opposite is expected, since trailing shoe avoids application of slurry to foliage. Confounding, imbalance, and differences in application technique among institutes may have played a role in the magnitude of this result. The sensitivity analysis showed that a single institute (212) depressed the trailing shoe effect. Without data from 212, the reduction

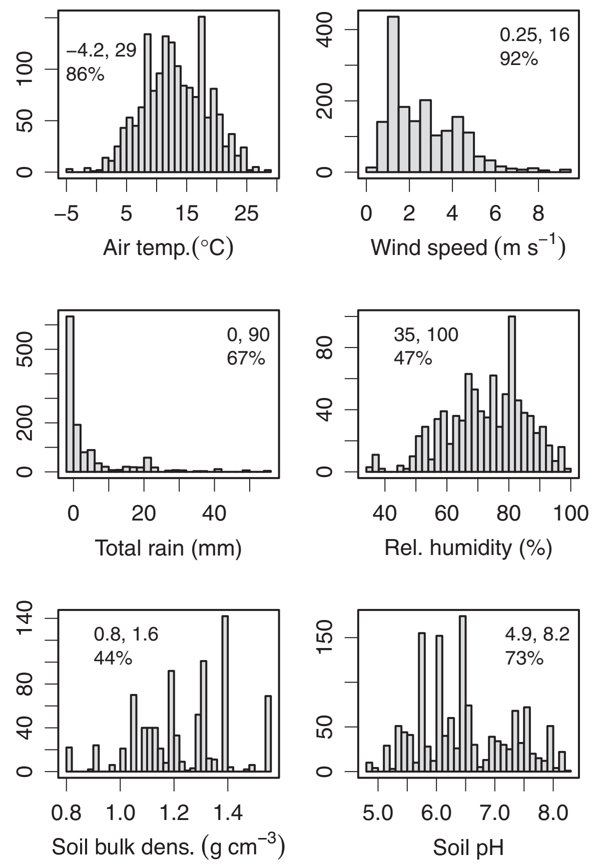


**Fig. 3.** Histograms of select weather and soil variables for all plot-level observations.

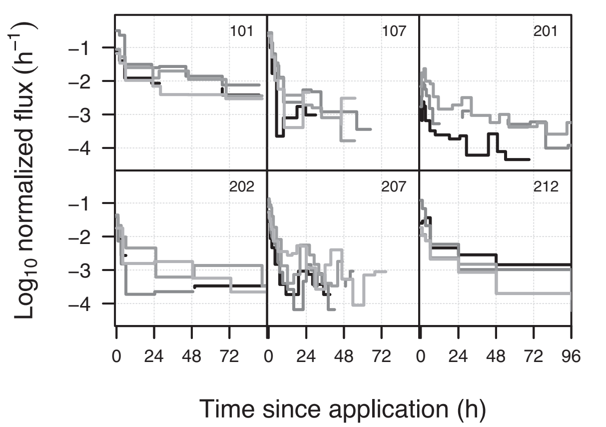


**Fig. 4.** Relative ammonia emission rates shown for three plots from a sample of six institutes. Average rates are shown as horizontal lines over the measurement interval. The y axis shows $\log_{10}$ of normalised flux (emission rate divided by applied TAN). Negative emission rates are not shown.

due to the use trailing shoe application increased to 64% (Table S10). Nearly one-third of the trailing shoe observations were from this institute. Apparent effects of other application methods were less sensitive to omission of data from individual institutes (Table S10). The reduction in emission due to trailing hose found here was larger than the average of 35% reported in a recent review (Webb et al., 2010), although the range in this review was large (0%-75%). The trailing shoe reduction reported in this review was 65%, which is much larger than the overall value determined here, but close to the 64% found with the omission of data from institute 212. Differences are probably simply a matter of data selection, and reflect uncertainty in effects of application methods.

Emission appeared to increase with slurry pH for broadcast and open slot injection only (Tables 4 and 5). But, the effect was highly dependent on which data were included in model fitting. The response found for trailing hose data was dependent on data from acidified slurry from institutes 205 and 210; omitting these data (but retaining the remainder of the observations for these institutes) resulted in a negative (but not significant) pH coefficient (i.e., reduced emission with increasing pH values) for trailing hose (coefficient $= -0.12$, $P = 0.16$). The magnitude, and, in some cases, sign (the direction of an effect) of pH coefficients was sensitive to exclusion of data from individual institutes (Table S10). The pH coefficient for open slot injection was less sensitive than other methods to data inclusion, but data from institutes 106 and 214 reduced the overall effect. The majority of open slot injection observations were from these two institutes (69 of 81 for models 1 and 2). We have to conclude that the magnitude of the effect of pH on emission cannot be estimated from these results.

Slurry pH is known to have a large effect on ammonia emission (Bussink et al., 1994) but no consistent effect was observed here. One possible explanation is that measurement error in pH is large compared to variability among observations. The majority of pH values were between 7 and 8 for both cattle and pig (Figs. 1 and 2). We have observed differences as large as 0.5 units (larger in some cases) between pH measured in the field and later in the laboratory on samples stored in sealed bottles under refrigeration (S. Hafner and T. Nyord, personal observation; Huijsmans et al., 2015). Even larger changes could possibly occur over time if $CO_2$ is allowed to escape (Bussink et al., 1994; Huijsmans et al., 2015).

Regardless of uncertainty in the magnitude of the observed effect of pH, the true effect is probably large. Based on well-known principles of chemical equilibrium, an increase in pH from 7 to 8 results in a 10-fold increase in free $NH_3$, resulting in a 10-fold increase in emission rate, all else being equal. Estimates from the mixed effects models (models 1 and 2) are much lower than this expected value (a coefficient of unity) (Tables 4 and 5). Increase in surface pH due to $CO_2$ emission (which is more significant at low pH) or depletion of TAN and decrease in surface pH due to $NH_3$ emission (Sommer and Sherlock, 1996; Génermont, 1997; Chantigny et al., 2004; Hafner et al., 2012; Huijsmans et al., 2015) may moderate the pH effect in the field. Additionally, negative correlation between slurry inorganic carbon concentration and pH may exist (in cases where microbial $CO_2$ production reduces pH). If so, the effect of $CO_2$ emission on surface pH would further reduce observed pH effects on ammonia emission. The small number of published studies on acidification have shown clear reductions. For example, Huijsmans et al. (2015) measured on average a 7% reduction in emission from cattle manure applied by trailing shoe by reducing pH from ca. 7.1 to 6.8, and a reduction of 24% by reducing pH further to 6.3. These reductions were for an emission period of 80 h following the manure application; larger reductions were found during the first days after manure application. Bussink et al. (1994) measured reductions in 4 d or 10 d emission of 55%, 72%, and 85% by reducing pH from around 7.5 to 6.0, 5.0, and 4.5, respectively (some of these data are included in the ALFAM2 database). A focus on experiments where acidification was used may provide more robust estimates of the effect of pH manipulation. But these results may not apply to “natural” differences in pH (when pH was not intentionally manipulated) which may be correlated with other chemical or physical differences among slurries. Effects of slurry pH may also be complicated by interaction with soil, which could be more important for determining pH of slurry on the soil surface after the first few hours. Exclusion of observations with acidified slurry and of slurry pH as a predictor had large effects on several coefficients, with some apparent relative effects changing by a factor of 2 (compare Tables 5 and S3). While in some cases model 1 coefficients (with pH included) are probably more accurate (since differences due to pH have been accounted for), given the uncertainty in the response to slurry pH, it is not clear that this is the case in general.

Emission was positively correlated with slurry dry matter

**Table 3**
Fraction of total (final) emission reached 6, 12, 24, 48, and 72 h after manure application for plots grouped based on total trial duration, for all plots included in the database.

| Trial duration (h)[1] | Plots | Institutes | Duration (h)[2] | Percentage of total emission[2] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 6 h | 12 h | 24 h | 48 h | 72 h |
| 0–12 | 9 | 2 | 1, 8, 9 | 67, 90, 91 | | | | |
| 12–24 | 10 | 6 | 20, 24, 24 | 45, 72, 98 | 66, 90, 101 | | | |
| 24–48 | 147 | 9 | 26, 36, 48 | 15, 72, 89 | 32, 80, 94 | 71, 93, 99 | | |
| 48–72 | 417 | 10 | 49, 55, 72 | 19, 48, 88 | 28, 61, 94 | 51, 77, 98 | 81, 96, 100 | |
| 72–96 | 498 | 12 | 74, 94, 96 | 21, 53, 88 | 29, 62, 92 | 42, 76, 97 | 66, 91, 100 | 87, 98, 101 |
| 96–∞ | 818 | 19 | 97, 168, 337 | 11, 40, 80 | 18, 49, 86 | 28, 63, 94 | 49, 79, 99 | 60, 87, 100 |

Notes: 1. Trial duration bins are open to the left and closed to the right, e.g., a duration value of exactly 24 h would be in the 12–24 h bin. 2. Values are 5th, 50th (median), and 95th percentile.

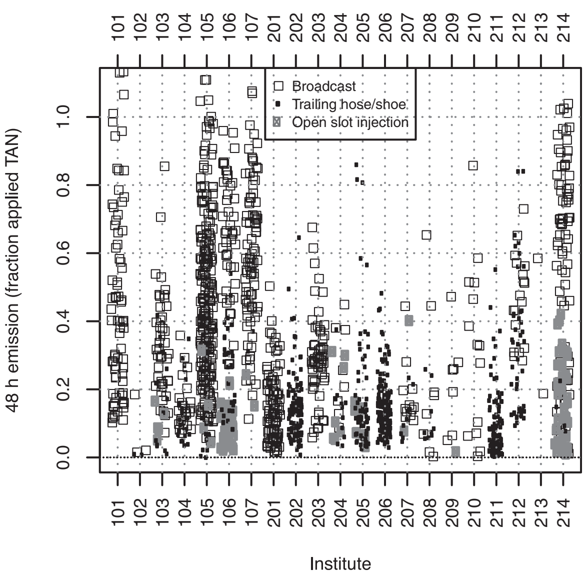


**Fig. 5.** 48 h interpolated cumulative emission from all cattle and pig slurry plots as a fraction of applied TAN, by institute. Some observations > 1.0 from the original ALFAM database are not shown.

concentration for broadcast and open slot application, but not for trailing hose or trailing shoe (Tables 4 and 5). An increase in slurry dry matter is expected to increase emission by reducing soil infiltration and increasing the fraction of slurry at the soil surface or on crop or stubble surfaces. The effect for broadcast (3% per % increase in DM) is much smaller than observed responses compiled by Sommer (2013: Table 12). The open slot injection response was larger (13–25% per % increase in DM), which may be related to inefficient injection, or insufficient infiltration, due to high dry matter. Infiltration following trailing hose application should also be affected by dry matter. Why an effect is not apparent in these data is not clear, but again confounding, imbalance, and differences in slurry application may be important. One institute, 206, had a large effect on the coefficient for trailing hose; when it was excluded, the coefficient increased above the value observed for broadcast (Table S10), although uncertainty remained high. Unusually, anaerobically digested slurry accounted for more than half the observations from institute 206 (14 of 23). Effects of anaerobic digestion on emission through increases in pH may have masked an overall effect of dry matter. Alternatively, effects of slurry dry matter on emission may simply be complex, and difficult to capture in a single model parameter. In some cases, higher dry matter could conceivably lead to a reduction in emission, for example by helping to maintain narrow application bands or increasing mass transfer resistance through crust formation. Slurry dry matter varied from 3% to 10% (or more) for each

**Table 4**
Restricted maximum likelihood estimates of fixed effect coefficients on ammonia emission from cattle slurry applied to grassland from a mixed-effects model (model 1). The response variable was $\log_{10}$ of ammonia emission (kg ha$^{-1}$ as N). The data subset used was limited to observations that included measurement of manure pH (compare to model 3, Table S3).

| Application method | Covariate | Coef. | Rel. effect | *se* | *t* | *P* | Sig. |
|---|---|---|---|---|---|---|---|
| (Intercept) | – | 1.200 | 1490.0 | 0.108 | 11.10 | 0.000 | * |
| th | – | −0.329 | −53.1 | 0.094 | −3.48 | 0.001 | * |
| ts | – | −0.156 | −30.2 | 0.096 | −1.63 | 0.104 | |
| os | – | −0.538 | −71.0 | 0.099 | −5.44 | 0.000 | * |
| bc | $\log_{10}$ TAN | 0.901 | 696.0 | 0.123 | 7.30 | 0.000 | * |
| th | $\log_{10}$ TAN | 0.323 | 110.0 | 0.408 | 0.79 | 0.430 | |
| ts | $\log_{10}$ TAN | 0.768 | 487.0 | 0.385 | 2.00 | 0.047 | * |
| os | $\log_{10}$ TAN | −0.743 | −81.9 | 0.728 | −1.02 | 0.308 | |
| bc | $\log_{10}$ app. rate | 0.787 | 512.0 | 0.166 | 4.74 | 0.000 | * |
| th | $\log_{10}$ app. rate | 0.453 | 184.0 | 0.237 | 1.91 | 0.057 | |
| ts | $\log_{10}$ app. rate | 1.530 | 3310.0 | 0.304 | 5.05 | 0.000 | * |
| os | $\log_{10}$ app. rate | 1.590 | 3780.0 | 0.201 | 7.92 | 0.000 | * |
| bc | dry matter | 0.013 | 3.0 | 0.005 | 2.40 | 0.017 | * |
| th | dry matter | −0.036 | −7.9 | 0.024 | −1.49 | 0.136 | |
| ts | dry matter | 0.009 | 2.0 | 0.022 | 0.40 | 0.690 | |
| os | dry matter | 0.097 | 25.0 | 0.030 | 3.24 | 0.001 | * |
| bc | man. pH | 0.165 | 46.1 | 0.041 | 3.99 | 0.000 | * |
| th | man. pH | 0.134 | 36.0 | 0.070 | 1.91 | 0.057 | |
| ts | man. pH | 0.157 | 43.4 | 0.100 | 1.57 | 0.117 | |
| os | man. pH | 0.362 | 130.0 | 0.113 | 3.20 | 0.001 | * |
| bc | air temp. | 0.009 | 2.0 | 0.002 | 3.72 | 0.000 | * |
| th | air temp. | 0.029 | 6.9 | 0.008 | 3.44 | 0.001 | * |
| ts | air temp. | 0.010 | 2.3 | 0.006 | 1.74 | 0.083 | |
| os | air temp. | 0.017 | 4.0 | 0.006 | 2.82 | 0.005 | * |
| bc | wind | 0.059 | 14.7 | 0.009 | 6.39 | 0.000 | * |
| th | wind | 0.068 | 16.9 | 0.042 | 1.61 | 0.107 | |
| ts | wind | 0.086 | 21.9 | 0.018 | 4.68 | 0.000 | * |
| os | wind | 0.088 | 22.6 | 0.022 | 3.97 | 0.000 | * |
| bc | crop height | 0.002 | 0.4 | 0.006 | 0.30 | 0.766 | |
| th | crop height | −0.093 | −19.2 | 0.038 | −2.42 | 0.016 | * |
| ts | crop height | −0.011 | −2.5 | 0.006 | −1.99 | 0.048 | * |
| os | crop height | −0.012 | −2.6 | 0.016 | −0.72 | 0.471 | |

Notes: Application methods (broadcast is reference method): bc = broadcast, th = trailing hose/band spreading, os = open slot, ts = trailing shoe. The "Coef." and "se" columns are the term coefficient and standard error in $\log_{10}$-transformed values. "Rel. effect" is the relative effect of an application method (% change in emission relative to broadcast reference) or covariate (% change in emission per unit change in covariate). The “Sig.” column is approximate statistical significance (* = $P$ < 0.05). Units for covariates are: TAN, g kg$^{-1}$ or g L$^{-1}$ as N; dry matter, % of wet mass; pH, pH units; application rate, t ha$^{-1}$; air temperature, °C; wind, m s$^{-1}$; crop height, cm. Data used to fit the model were from the following institutes: 102, 105, 106, 202, 203, 204, 205, 206, 207, 209, 210, 212, and 214.

application method in the subsets used in this analysis.

Absolute emission was positively correlated with the $\log_{10}$ of manure TAN concentration for broadcast and trailing shoe application (Table 4). With all else equal, mass transfer theory dictates that emission rate should increase 10-fold (1000%) per decade in TAN concentration (10-fold change in TAN). (This assumption is implicitly made when relative emission is used as a response variable, as in models 2 and 3.) Dilution of slurry with water has shown this expected effect (Frost, 1994). Except for open slot injection, none of the coefficients were clearly different from the expected value of unity. The coefficient for open slot injection was not different from zero, but was less than unity, implying that relative emission decreased as TAN concentration increased. Since emission from open slot injection is probably related to the quantity of manure remaining on or close to the surface (Hansen et al., 2003), the lack of a clear effect for injection is plausible. Exclusion of data from individual institutes had large effects for all application methods, although the sign of the effect changed only for open slot injection (Table S10). Slurry TAN concentration varied within a broad range in the database (Figs. 1 and 2), but the range was narrow for individual application methods in this data subset, particularly for trailing hose, which may have made it difficult to detect a clear

**Table 5**
Restricted maximum likelihood estimates of fixed effect coefficients for ammonia emission from cattle slurry applied to grassland from a mixed-effects model (model 2). The response variable was $\log_{10}$ of relative ammonia emission (fraction of applied ammonia). As with model 1 (Table 4), the data subset used was limited to observations that included measurement of manure pH.

| App. method | Covar. | Coef. | Rel. effect | *se* | *t* | *P* | Sig. |
|---|---|---|---|---|---|---|---|
| (Intercept) | – | −0.580 | −73.7 | 0.103 | −5.65 | 0.000 | * |
| th | – | −0.289 | −48.5 | 0.091 | −3.16 | 0.002 | * |
| ts | – | −0.134 | −26.5 | 0.083 | −1.60 | 0.110 | |
| os | – | −0.505 | −68.7 | 0.097 | −5.18 | 0.000 | * |
| bc | $\log_{10}$ app. rate | −0.229 | −40.9 | 0.163 | −1.41 | 0.161 | |
| th | $\log_{10}$ app. rate | −0.503 | −68.6 | 0.236 | −2.13 | 0.034 | * |
| ts | $\log_{10}$ app. rate | 0.563 | 266.0 | 0.292 | 1.93 | 0.054 | |
| os | $\log_{10}$ app. rate | 0.700 | 401.0 | 0.196 | 3.57 | 0.000 | * |
| bc | dry matter | 0.014 | 3.3 | 0.005 | 2.85 | 0.005 | * |
| th | dry matter | −0.041 | −9.0 | 0.022 | −1.83 | 0.068 | |
| ts | dry matter | 0.004 | 0.8 | 0.019 | 0.20 | 0.845 | |
| os | dry matter | 0.053 | 13.0 | 0.024 | 2.25 | 0.025 | * |
| bc | man. pH | 0.172 | 48.4 | 0.041 | 4.19 | 0.000 | * |
| th | man. pH | 0.090 | 23.1 | 0.069 | 1.32 | 0.188 | |
| ts | man. pH | 0.147 | 40.4 | 0.094 | 1.57 | 0.117 | |
| os | man. pH | 0.293 | 96.4 | 0.110 | 2.67 | 0.008 | * |
| bc | air temp. | 0.009 | 2.1 | 0.002 | 3.88 | 0.000 | * |
| th | air temp. | 0.026 | 6.3 | 0.008 | 3.17 | 0.002 | * |
| ts | air temp. | 0.010 | 2.2 | 0.006 | 1.72 | 0.086 | |
| os | air temp. | 0.013 | 3.0 | 0.006 | 2.22 | 0.027 | * |
| bc | wind | 0.058 | 14.4 | 0.009 | 6.29 | 0.000 | * |
| th | wind | 0.058 | 14.3 | 0.042 | 1.39 | 0.165 | |
| ts | wind | 0.083 | 21.0 | 0.017 | 4.92 | 0.000 | * |
| os | wind | 0.097 | 24.9 | 0.022 | 4.42 | 0.000 | * |
| bc | crop height | 0.002 | 0.4 | 0.006 | 0.33 | 0.745 | |
| th | crop height | −0.058 | −12.4 | 0.033 | −1.74 | 0.082 | |
| ts | crop height | −0.012 | −2.6 | 0.006 | −2.11 | 0.036 | * |
| os | crop height | −0.005 | −1.0 | 0.016 | −0.29 | 0.773 | |

Notes: see notes for Table 4.

response.

Both models 1 and 2 showed that relative emission increased with application rate (application volume) for open slot injection (coefficient > 1 for model 1, coefficient > 0 for model 2). This apparent effect for open slot injection may be due to overfilling of slots, resulting in greater slurry exposure on the soil surface. The coefficient was sensitive to inclusion of data from institute 214—when these data were omitted, it increased significantly (Table S10). More than half of the open slot injection observations were from institute 214. This sensitivity may be due to differences in injection machinery, variability in effectiveness among different locations or soil types, or bias in measurement techniques (because emission from injection is low, measurements are particularly sensitive to determination of background concentrations). There was evidence of reductions in relative emission with an increase in application rate for trailing hose application (coefficient < 1 for model 1, coefficient < 0 for model 2), but the apparent reduction for trailing hose from both models seems somewhat large: about a 30% reduction in relative emission due to a doubling in application rate ($10_{10}^{(0.453\log(2))}/2-1$ for model 1, $10_{10}^{(-0.503\log(2))}-1$ for model 2) (Tables 4 and 5). Smaller effects have been observed in experiments where application rate was varied (Thompson et al., 1990; Frost, 1994). There were no clear effects of application rate for broadcast or trailing shoe in any of the models.

Ammonia emission was positively correlated with both air temperature and wind speed for some application methods (Tables 4 and 5). The theoretical bases for these relationships are strong: equilibrium gas-phase $NH_3$ concentration increases with temperature (Hafner and Bisogni, 2009) and increased wind speeds increase gas-phase mass transfer (reduce resistance) (Olesen and Sommer, 1993), all else being equal. Based on changes in the dissociation constant and Henry's law constant, a 1.0 °C increase in temperature will increase equilibrium gas-phase $NH_3$ concentration by about 13% (based on constants in Hafner et al., 2012). Estimated model coefficients were smaller: about 2% for broadcast, 6%-7% for trailing hose, and 3%-4% per °C for open slot injection. Depletion of TAN and increases in $CO_2$ emission or crust formation under higher temperatures may moderate the effect. Of the application methods, only for open slot injection was the coefficient not sensitive to omission of data from individual institutes (Table S10). Variation in temperature was similar among the four application methods in the cattle/grass subset, and wind speed varied from 1 to 5 $m\,s^{-1}$ or more for each application method. Open slot injection data were mostly from two institutes (64 of 76 observations were from institutes 106 and 214), which may have limited the effect of confounding variables. Wind speed showed a positive effect for all methods other than trailing hose in models 1 and 2 (Tables 4 and 5). The effect was similar for the three remaining methods, but highest for open slot injection: up to a 25% increase per 1 $m\,s^{-1}$ increase in wind speed (model 2). However, all effects were sensitive to which institutes were excluded, and estimates are not robust (Table S10).

There was evidence of a reduction in emission as grass height increased. Effects were clear for trailing shoe from both models 1 and 2 (emission reduction of about 2.5% per cm of height), while a much larger effect for trailing hose (20% reduction per cm of height) was seen only in results from model 1 (Tables 4 and 5). The trailing shoe coefficient was sensitive to inclusion of data from institute 106 (Table S10). Without these data, the effect dropped (to 1.6% per cm).

Model 3, which did not include slurry pH as a predictor, and was based on a larger subset of observations, showed some significant differences from models 1 and 2 (Table S3). Most importantly, the trailing shoe reduction was even smaller (22%) and open slot injection reduction was larger (75%). A second version of model 1 fit using 24 h cumulative emission as the response variable also showed some differences in coefficients. The largest decrease in a coefficient was for $\log_{10}$ of manure TAN concentration for trailing hose, which decreased by 0.23 (42%). The pH coefficient for trailing hose showed the largest increase, which was 0.10 (26%). Coefficients for application methods differed only slightly—the largest difference was for open slot injection, which was lower by 0.06 (14%) for the 24 h response. These differences highlight both the variability in the effects observed in the data, and the difficulty in estimating effects from a complex observational dataset.

A linear response between log-transformed emission and all numeric predictors (possibly log-transformed) was assumed for all models presented in this work. For some variables the true response is known to be more complex. For example, at high dry matter content, cumulative emission has been shown to be insensitive to additional increases, presumably because infiltration is negligible (Sommer and Olesen, 1991). Similarly, a fixed increase in wind speed has a smaller effect on emission at high wind speeds than it does at low wind speeds (Olesen and Sommer, 1993). The structure of the models used is by no means perfect, but considering the high variability present in the data, it provides a reasonable and useable approach. Plots of residuals versus wind speed and other numeric predictors show no obvious trends, suggesting that the model structure is reasonable within the range of the data.

Although the direction of effects described above was usually the same as in the original ALFAM model (Søgaard et al., 2002) and other studies (Gericke et al., 2012; Häni et al., 2016), magnitudes differed substantially. Effects in the ALFAM model reported here were calculated from the parameters given in Table 2 in Søgaard et al. (2002), which differ slightly from those used in the Excel version of the ALFAM model (http://www.alfam.dk/). Emission reductions calculated with the ALFAM model depend on time for some variables (all variables that affect $k_m$), and were evaluated at 48 h here. The ALFAM2 subset analysed here showed a larger emission reduction by trailing hose and a smaller reduction by trailing shoe (Tables 4 and 5) than in the ALFAM model, for which reductions were 42% and 34%, respectively. The open slot injection reduction, however, was nearly identical: 72% in the ALFAM model. Apparent effects of temperature found here (Tables 4

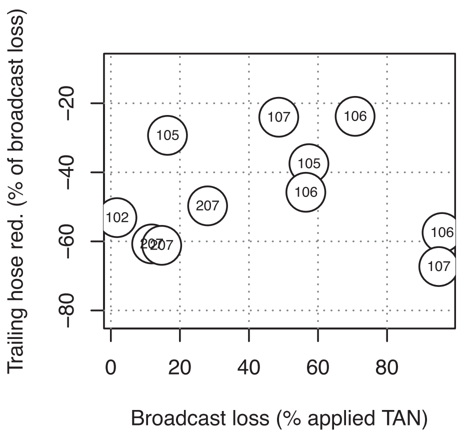


**Fig. 6.** Experiment-based comparisons of 48 h relative emission from broadcast and trailing hose application. The x-axis position shows relative emission for broadcast plots, and the relative effect of using trailing hose (change as% of broadcast emission) is shown on the y axis. Labels shows institute codes (Table 1).

and 5) were slightly larger than in the ALFAM model (2.6% per °C), while the apparent effect of wind was much larger than in the earlier model (4.7% per m $s^{-1}$ in the ALFAM model). Conversely, the overall ALFAM dry matter effect (9.0% per % dry matter) was higher than observed in the broadcast results for ALFAM2, but much smaller than the open slot injection effect (Tables 4 and 5). For broadcast application, Häni et al. (2016) observed a 20% increase per % dry matter, which is much larger than the effect found here, but a similar effect of air temperature (3.4% per °C). Gericke et al. (2012) observed a much smaller effect of temperature (1% per °C). Crop height has been shown previously to reduce emission, as reviewed by Thorman et al. (2008), who developed regression equations for the effect of both grass and winter wheat height on emission. Their grass equation shows a larger effect of height (−5% per cm). Data used in some of these studies are included in the new ALFAM2 database, and so similarity should not be taken as independent evidence of a particular magnitude of a response. Differences are not surprising, and are reflected in the sensitivity of the coefficients to both the selection of data for model fitting, and the terms that are included. Whether the differences reflect true variability in the response to weather (due, e.g., to interactions with other variables), measurement bias, site-specific variations in the way a given application method is used, specific differences in application techniques per application method, or random error is unclear.

#### 3.2.2. Application method effects by experiment

Each experiment-based model required data from a single experiment that included both broadcast and one other application method

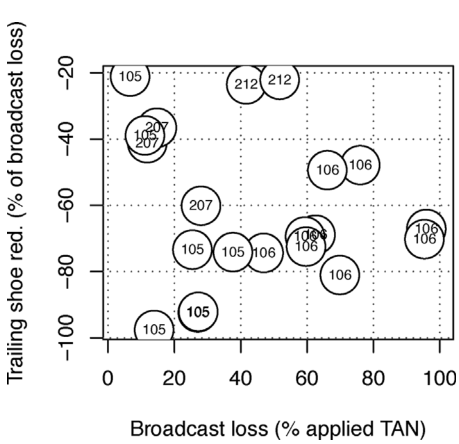


**Fig. 7.** Experiment-based comparisons of 48 h relative emission from broadcast and trailing shoe application. Details are as in Fig. 6.

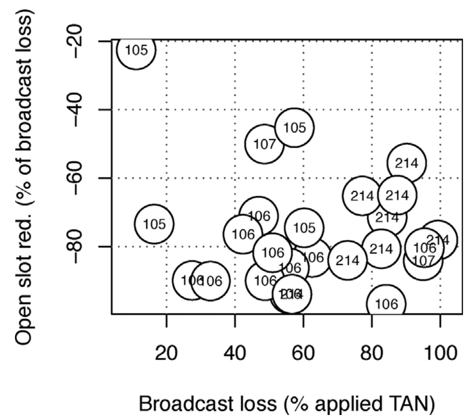


**Fig. 8.** Experiment-based comparisons of 48 h relative emission from broadcast application and open slot injection. Details are as in Fig. 6.

and results were therefore based on a smaller data subset than the mixed models were. In general, both approaches showed similar results, although results from individual experiments generally show a larger reduction for trailing shoe than trailing hose (mean values of 61% and 46%, respectively), which differs from the mixed-effects model results. The reduction ranged from 24% to 67% for trailing hose (Fig. 6), and from 21% to 97% for trailing shoe (Fig. 7). Open slot injection reduced emission by 22% to 97%, with a mean of 75% (Fig. 8). As shown by these ranges, variability in emission reductions from experiment-wise models was high. Ranges among experiments were similar to those reported in the review by Webb et al. (2010). Variability in the effect of trailing shoe compared to broadcast decreased substantially as emission increased (Fig. 7). With the possible exception of trailing shoe versus broadcast, there was no evidence that application method reductions varied with the magnitude of emission, which suggests that a multiplicative model is a reasonable approximation. Surprisingly, this result was true even for the lowest emission values (< 2% of applied TAN).

### 3.3. Differences among institutes

Mixed-effects model results showed large apparent differences in emission among institutes and among measurement method/soil type combinations (Fig. 9, Tables S4–S9). These random-effect coefficients were greater than application method coefficients in several cases (compare Fig. 6 and Tables S4 and S5 to Table 4). Estimated standard deviation of institute effects was about 0.3 for models 1 and 2, which corresponds to a factor of 2. Within-institute coefficients were generally smaller than institute coefficients (Tables S4-S9). Estimates of these coefficients were sensitive to the data subset used for model development, and their accuracy depends on the accuracy of estimates of fixed effects. But the importance of these random predictors is very clear: removing them from model 2, for example, results in a significantly poorer model, as shown by an increase in AIC from 4.3 to 136. For comparison, removing all numeric predictors (TAN concentration, application rate, dry matter, pH, air temperature, wind speed, and crop height) from model 2 results in an AIC of 126. A model with only application method and the random-effect predictors is better than one with all other fixed-effect predictors and no random-effect predictors. What has caused these differences among institutes and among measurements made by the same institute? We can identify two scenarios. In the first, emission measurements from all institutes are largely accurate, and differences are due to differences in trial conditions, possibly including variables used as predictors in the models (but with responses inaccurately captured by the models), and variables not included and possibly difficult to quantify (such as rainfall or effects of soil on infiltration). In the second scenario, biases in emission measurements, determination of accompanying variables, or slurry

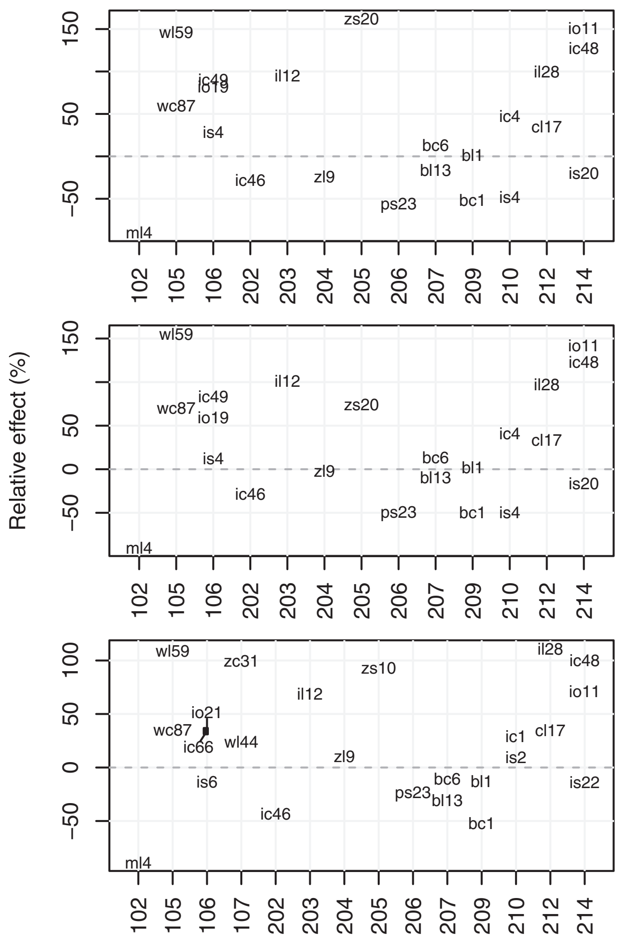


**Fig. 9.** Comparison of random effects (combined institute and measurement technique/ soil effects) among institutes for models 1 (top), 2 (middle), and 3 (bottom). The y axis position shows the magnitude of the effect on emission relative to the mean response for each individual model. Plotting symbols show measurement technique (first letter, b, bLS; c, chamber; p, calibrated passive samplers (Gericke et al., 2012); i, IHF; m, micromet.; w, wind tunnel; z, ZINST), soil type (second letter, c, clay; l, loam; o, organic; s, sand), and number of plots.

application method explain most of the apparent differences among institutes.

Can variables included in the database explain differences among institutes? Differences in emission among soil types within the same institute are large in some cases, providing evidence that soil effects could explain much of the apparent institute effects (Fig. 9). Soil hydraulic properties, pH, and the capacity for sorption of $NH_4^+$ could affect $NH_3$ emission, and earlier studies have also shown large effects of soil properties on emission (e.g., Sommer et al., 2006). There is some evidence (Fig. 9) that emission from sandy soils is consistently lower than emission from other soils within the same institute (for institutes 106, 210, and 214). But the magnitude of combined random effects does not show a consistent relationship to either soil type or measurement technique across institutes. This may be because soil interactions with slurry are not related solely to soil texture categories. However, it does leave open the possibility that differences in soil explain much of the observed differences among or within institutes. Other variables in the database may have contributed to these observed differences. For example, rain is known to affect $NH_3$ emission (Beauchamp et al., 1982), but was not included in any models here, since measurements were missing from nearly half the observations in the cattle and grass subset.

Conversely, could method biases (in application method or emission measurement) explain differences among institutes? There is no obvious relationship between the sign and magnitude of institute effects and the measurements method used (Fig. 9). In fact, some of the largest differences within a single soil type are for similar measurement techniques. But a lack of consistent differences among measurement techniques does not necessary mean that biases do not exist. Instead, biases may be specific to each institute or even individual experiment. For example, wind tunnel measurements may substantially under- or overestimate emission depending on the characteristics of the wind tunnel and the difference between air flow rate through the wind tunnel and the (external) wind speed (Sommer and Misselbrook, 2016). Results from two Swiss datasets provide an example of a clear measurement bias. In experiments carried out under comparable conditions with respect to properties of the slurries applied, the experimental sites and meteorological conditions but improved measurement techniques (107: ZINST, 207: bLS), the newer data (institute 207) showed systematically lower $NH_3$ emission than the older data (institute 107) (Fig. 9). Indeed, Häni et al. (2016) describe differences between the two datasets in detail, and identified three mechanisms that have contributed a negative bias to the measurements from institute 107 (an incorrect ZINST scaling factor, inaccurate wind speed measurements, and $NH_3$ (g) transfer among plots), and a note in this ALFAM2 database warns users. But is this result common? The database provides some opportunities to compare results collected within the same country by different groups (204 and 205 from Denmark), and by the same groups at different times (106 and 214 from NL and 105 and 202 from UK). Results from the Danish institutes suggest that different groups can obtain similar results in a similar location, or not, depending on which model is used to quantify institute effects (Fig. 9). (This result highlights the limitations of models built on observational datasets.) A comparison between Dutch results (institutes 106 and 214) show that older and newer results were similar for organic soil (o in Fig. 9) and sand (s), but newer emission measurements for clay (c) are much higher for shallow injection than in older data (Fig. 9). This difference may be due to a smaller open slot injection depth in the newer experiments (Huijsmans and Schils, 2009). Results from the two UK data sets appeared somewhat different for clay soil, which is the only soil type in the later dataset (institute 202). Measurement method differed here, with higher emission for wind tunnel measurements than IHF. Together these comparisons suggest that differences in slurry application and emission measurement biases could contribute to observed institute differences. A more detailed evaluation of each of these pairs could yield additional insights.

In order to understand exactly why results differ so much among individual experiments or institutes, much more information than is included in the database is required (including complete wind and concentration profiles for IHF, and georeferenced data for all plots). If such data cannot be provided a comparison of measurement techniques (and possibly application techniques) at the same location and time may be the only way to definitively assess the contribution of measurement technique biases on results (as suggested by Sintermann et al. (2012)). A controlled release of $NH_3$, or application of chemical fertilizer could help identify the source of biases (variability in application rate accuracy for chemical fertilizer is almost certainly lower than for slurry). And measurement of crop yields (N and dry matter) and comparison to plots that received low-emission chemical fertilizer may be able to provide an independent (albeit less precise) indication of $NH_3$ emission (Huijsmans et al., 2016). In the least, these apparent differences among institutes will make it difficult to predict absolute $NH_3$ emission or evaluate emission models with confidence.

### *3.4. Implications, use, and future of the database*

The nature of the data in the ALFAM2 database should affect how it is used. It is effectively an observational dataset, and has at least three significant limitations: observations are not independent, data are not balanced, and variables are confounded. The possibility of significant systematic differences among institutes is an important finding of this study and suggests that measures should be taken during data analysis to ensure that conclusions are accurate. Fitting a naive model between one or more predictors and emission without considering correlation among observations from the same institute and effects of other variables will almost certainly result in biased coefficients and probabilities. Omitting random-effect predictors from model 2 (Table 5), for example, resulted in different coefficients for application methods, and a statistically significant negative coefficient for slurry pH for trailing hose application, among other differences (Table S11). Furthermore, data for individual variables may not be consistent among institutes or even experiments. The same levels may have different meanings, and some variables cannot be accurately described in a simple way, e.g., soil type, where names or texture may not sufficiently characterise interaction with applied slurry. Imbalance in the data means that individual institutes may have large effects on some model coefficients, whether or not the responses present in these data are representative (Table S10). Interactions between variables are almost certainly significant (e.g., soil moisture and manure dry matter), but the dataset is not close to fully crossed, and effects of these interactions may therefore inflate residuals and make hypothesis testing difficult, or, when confounding is present, contribute to bias or inaccurate effect estimates. Despite these limitations, the ALFAM2 database is clearly useful. It provides measurements of $NH_3$ emission from more than 1800 plots across a wide geographic area. These observations may be useful for developing new emission factors or evaluating existing ones. Results presented here suggest that $NH_3$ emission is affected by multiple factors associated with weather, soil, management, and slurry itself, which vary among experiments and over time. Variation in emission may reflect these effects and interactions, and not necessarily any measurement biases or methodological errors. Careful analysis of these data could yield important and useful information on factors controlling $NH_3$ emission.

Models developed from the ALFAM2 database or similar datasets may have an intrinsic limit on accuracy and precision. Changes in model coefficients as different data subsets are used (Tables 5, S3, and S10) strongly suggest that it will be difficult to assess the accuracy of any model with certainty. Although the mixed effects models described above were not developed for making emission predictions (and the inclusion of random-effect predictors limits their utility), they provide some indication of accuracy and precision. Even with random effects for each institute, soil type, and measurement method combination (which improve model fit), these mixed-effects models have large residuals (Fig. 10). Root mean square error (an estimate of the average error) is 0.21 for model 2, which represents a relative value of +62% or −38% of emission. Given the magnitude of unexplained random effects

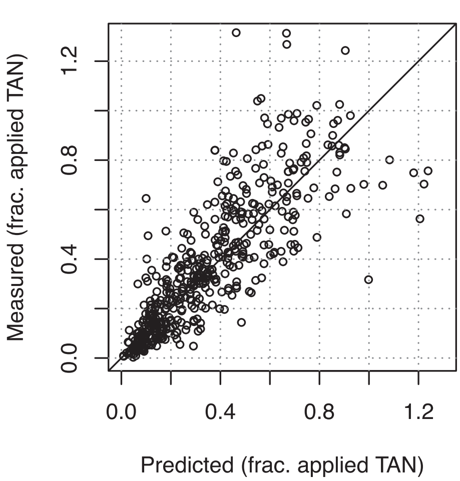


**Fig. 10.** Comparison of measured relative 48-h emission (fraction of applied TAN) and values predicted by the mixed-effects model that includes pH (model 2, Table 5). Line shows 1:1 response.

included in this model, it is unlikely that other models (empirical or mechanistic) can perform better with this dataset. While models presented in other studies may show better performance for smaller (and presumably more homogenous) data sets than the one used here (e.g., Menzi et al., 1998; Gericke et al., 2012; Langevin et al., 2015; Congreves et al., 2016; Häni et al., 2016), they are unlikely to perform better than this empirical model for the wide range of data present in the ALFAM2 database.

Expansion of the database will continue, and researchers interested in contributing data should contact the corresponding author for details on data submission. A current version of the database can be found at http://www.alfam.dk. Addition of new measurements may help clarify some questions that have been highlighted in this work, by increasing the variety of measurements and improving balance of the data. In particular, emission measurements from regions not well represented in the database would be valuable. More observations, however, should not be expected to reduce the unexplained variation observed in $NH_3$ emission.

### 3.5. Recommendations

It is clear from the discussion above that missing values for some variables in the ALFAM2 database limit its utility. When values are not available for slurry dry matter or pH, for example, it is difficult to determine if an observation is representative of a location, or why two observations differ. To ensure that future results are useful and can be compared or combined with results from other experiments, it will be important for researchers to agree on a list of required variables that should always be reported along with $NH_3$ emission. As a starting point, we recommend that, at a minimum, the following variables are always measured and reported in $NH_3$ emission experiments:

1 Soil characteristics: texture, pH, clay and organic matter content, moisture.
2 Soil management: tillage type and timing.
3 Crops: type, coverage, and height of crops or crop stubble/surface residues.
4 Slurry characteristics: type (e.g., cattle), TAN and dry matter concentrations, pH, bedding type, description of sampling and analysis, and any treatments (e.g. acidification, separation, including type).
5 Application: application method (and whether application was manual or by machine), application rate, application plot size, coverage of manure, date and time of application.
6 Emission: measurement method, measurement plot size, date and time of the start and end of each emission measurement interval, average interval emission rate.
7 Weather: air temperature, wind speed, precipitation.

The above list represents a step toward standardising $NH_3$ emission measurement experiments (and is not the first example of such an effort). Successful standardisation will require a continued collaborative effort to expand and refine this list. For some of the variables that can be difficult to describe quantitatively or for details that are less commonly documented, digital photographs could be helpful. While storage of the resulting files is not as straightforward as are the data included in the ALFAM2 database, it is possible. And for some variables, additional details may be needed. For example, since it is soil near the surface that interacts the most with applied manure, soil measurements should probably be reported from only a thin layer. Furthermore, additional measurements may be needed for producing high-quality emission measurements. For example, soil moisture alone (volumetric or gravimetric) does little to indicate how important slurry infiltration will be. Soil water potential and bulk density may be more useful, but perhaps only when combined with estimates of hydraulic conductivity. Direct infiltration measurements or even the appearance of the soil surface may be more useful. If soil conditions may have differed among plots, plot-specific measurements should be provided. Details on application can be important, including observations on coverage of the soil surface, contact with soil or crops, soil smearing, and infiltration. A description of the application machinery (if used) would also be useful, and qualitative observations on effectiveness of machinery and application may be essential. Other observations on infiltration and crust formation would be useful. Given variation in slurry analysis, a description of the sampling, replication, and analysis details for dry matter, TAN, and pH is important to document. Slurry dry matter may not sufficiently characterise the potential for infiltration, and information on bedding and viscosity may be useful (but possibly still insufficient). Useful details on emission measurement methods include anything that could vary among experiments. The location of weather measurements should be reported. In ALFAM2, weather data are reported as averages over each measurement interval. However, since variation in weather within an emission measurement interval may affect average emission, a higher resolution (e.g., 10 min averages) may be more useful for model testing and development (and should typically be available). Standardisation of measurement methods would also be valuable. Slurry pH provides a particularly important example.

Additionally, it is important for both researchers making measurements and those who use the resulting values to be clear about the purpose of the measurements. Emission estimates made in order to compare two application techniques may not represent emission under typical conditions. One concrete example of this phenomenon is the avoidance of rain during field trials, which could contribute a positive bias.

## 4. Conclusions

The ALFAM2 database is a large and diverse collection of $NH_3$ emission measurements from manure, and it should be useful for research on, and management of, $NH_3$ emission. High variability in $NH_3$ emission within the database is a product of a broad range of application, slurry, weather, and location conditions, as well as differences in measurement techniques, and other, unknown factors. Emission from cattle slurry applied to grassland shows clear effects of application methods, and effects of slurry characteristics and weather, which suggests that the data could be useful for model development or testing. Comparing $NH_3$ emission among locations will be difficult without assumptions about measurement accuracy and the source of unexplained effects. The database can be used in a myriad of ways, although users should be aware of dependencies among observations, confounding among variables, and imbalance when working with these data. These results highlight the importance of standardising $NH_3$ emission measurements and hence the need to continue research in this area. International agreement on the accuracy of emission measurement methods and standard protocols for their use, along with necessary types of supporting data and standard protocols for their measurement are all needed in order to lead to more accurate and useful $NH_3$ emission measurements.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.agrformet.2017.11.027.

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