



Trimethylamine emissions in animal husbandry

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Abstract. Degradation of plant material by animals is an important transformation pathway in the nitrogen (N) cycle. During the involved processes, volatile reduced alkaline nitrogen compounds, mainly ammonia (NH₃) and aliphatic amines such as trimethylamine (TMA), are formed. Today, animal husbandry is estimated to constitute a main source of aliphatic amines in the atmosphere with TMA being the main emitted compound. Here, we show how the interaction between faeces and urine in animal production systems provides the primary source for agricultural TMA emissions. Excreted urine contains large quantities of urea and TMA-N-oxide, which are transformed into NH₃ and TMA, respectively, via enzymatic processes provided by microbes present in faeces. TMA emissions from areas polluted with urine–faeces mixtures are on average of the order of 10 to 50 nmol m⁻² s⁻¹. Released amines promote secondary aerosol particle formation in the agricultural emission plume. The atmospheric lifetime of TMA, which was estimated to be of the order of 30 to 1000 s, is determined by the condensation onto aerosol particles.

1 Introduction

Atmospheric reduced nitrogen species, such as amines or ammonia (NH₃), are crucial for secondary aerosol particle formation as they constitute the alkaline counterparts to acidic vapours, such as sulfuric and nitric acid (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006). Recent publications have suggested that aliphatic amines exhibit a po-

tential for aerosol particle formation orders of magnitude higher than that of NH₃ (Murphy et al., 2007; Kurten et al., 2008; Barsanti et al., 2009; Loukonen et al., 2010; Almeida et al., 2013). The influence of anthropogenically induced secondary particle formation has a potentially high impact on earth's radiative forcing (Lohmann and Feichter, 2005; IPCC, 2013) and human health (Pope et al., 2002). There is a large knowledge gap for linking amine sources, their distribution, and secondary particle formation (Andreae, 2013; Kulmala et al., 2013). Additionally, measurements of ambient amine concentrations are scarce. However, among the volatile aliphatic amine species, trimethylamine (TMA) release from agriculture constitutes the most dominant source and, consequently, TMA has been found to be the dominant gas-phase aliphatic amine (compared to methylamine (MMA) and dimethylamine (DMA), for example) at agricultural sites with a molar ratio TMA : NH₃ between 0.3 and 1 % at animal housing and feedlots (Hutchinson et al., 1982; Schade and Crutzen, 1995; Kuhn et al., 2011) (see also Kuwata et al., 1983; Grönberg et al., 1992; Kallinger and Niessner, 1999; Rappert and Müller, 2005; Schade and Ngwabie, 2005; Filipy et al., 2006; Ngwabie et al., 2008; Blanes-Vidal et al., 2009; Feilberg et al., 2010; Ge et al., 2011; Trabue et al., 2011; Dawson et al., 2014). Based on this narrow range, Schade and Crutzen (1995) provided an estimate of the global aliphatic amine emissions by scaling with the more detailed assessed NH₃ emissions. Subsequently, it has been shown that the TMA–NH₃ analogy is not generally transferable to all agricultural emission stages, as stored cattle slurry is considerably TMA-depleted. The

global agricultural amine supply has been refined accordingly (Kuhn et al., 2011). Since cattle rumen content contains a very high proportion of volatile TMA, Kuhn et al. (2011) discussed the hypothesis that ruminants may exhale high concentrations of TMA by rumination. However, no measurements under real conditions have so far supported this hypothesis. The relevance of amine emissions to aerosol particle formation (Almeida et al., 2013) motivates this study to gain more information on the formation mechanism and emission of agricultural TMA. The focus lies on TMA emission pathways in dairy systems, investigated by ambient trace gas concentration as well as laboratory dynamic chamber measurements. We further discuss the fate of the identified agricultural TMA emissions and their role in secondary aerosol particle formation.

2 Material and methods

2.1 Concentration measurements at the dairy cattle barn

Measurements were carried out in summer 2011 at a dairy cattle barn at the Federal Research Station in Posieux, Switzerland (7.10653° E, 46.7692° N; 640 m a.s.l.). The herd consisted of 60 dairy cows (average live weight 680 kg, average annual milk production of 8500 kg per cow) milked twice a day: early in the morning and in the afternoon. Before and after milking, the cattle spent approximately 3 to 5 h in the barn complex in a farmyard (surrounded on three sides by the barn). During most of this time they had access to feeding stations providing them a concentrated ration of a cereal mix, offered in individual amounts based on standardised current milk production and maintenance requirements. They also had access to feed bunks to consume a limited daily amount of maize silage. The remainder of the day the herd was on pasture. The yard's concrete ground was cleaned with automatic scrapers, usually within 1 h after the cattle had left. Based on high-temperature chemical ionisation mass spectrometry (HT-CIMS), proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS), and cavity ring-down spectroscopy (CRD) (see Sect. 2.3), diurnal patterns of ambient trace gas concentrations in the outdoor yard were measured at 3 m height over 3.5 days. In addition, short-period trials were pursued measuring close (within 10 cm) to the mouth of ruminating cattle. Measured target trace gas species were NH₃, TMA, acetone, and CH₄.

2.2 Emission measurements with dynamic chambers

In order to quantify TMA and NH₃ emissions in a controlled environment, a dynamic chamber (Pape et al., 2009) was placed over different excretion substrates (see below) inside a climate-controlled (20 °C, relative humidity of 60 %) well-ventilated room. Given steady state and no trace gas destruction or creation, such as chemical conversion inside the

chamber, the substrate chamber flux F_{cham} is derived by

$$F_{\text{cham}} = \frac{Q}{A} \cdot \rho_d (c_{\text{cham}} - c_{\text{amb}}), \quad (1)$$

where Q is the purging air flow rate, A denotes the area of investigated surface inside the chamber, ρ_d is the density of dry air, and c_{cham} and c_{amb} represent the trace gas mixing ratios inside and outside of the dynamic chamber, respectively (Pape et al., 2009).

The cylindrical chamber with walls of PFA (Perfluoroalkoxy alkane) film had an enclosed headspace volume of 41 L and was continuously flushed at 60 L min⁻¹ of ambient air. It was setup on a base into which a circular plastic sample container ($A = 0.049 \text{ m}^2$) was placed. c_{amb} and c_{cham} were measured for NH₃ and TMA by CRD, HT-CIMS, and impinger sampling combined with ion chromatography (IC) analysis.

On 9 February 2012, urine and faeces were collected upon excretion at the cattle barn in Posieux. Stored slurry from the slurry pit was also collected. The samples were sealed airtight, cooled, and brought to the laboratory within 6 h. The substrates were subdivided and recombined to a 2 : 1 urine–faeces mixture immediately before the first measurement. For this, 1 L subsamples were prepared in the sample containers. Both sets, the subsamples and remaining fractions, were stored in separate climate rooms under similar conditions throughout the entire experiment period of about 160 h. For measurements, each subsample was put inside the dynamic chamber for 30 to 60 min. After some minutes it was stirred for 1 min. Average fluxes were calculated subsequently to stirring considering chamber equilibration time (with respect to NH₃ and TMA wall adsorption and desorption effects), which was determined to be less than 5 min. pH values were monitored (pH-3310, WTW, Germany). The pH rod was cleaned using demineralised water following each measurement. To estimate maximum emission potentials of the volatile pools of NH₃ and TMA, each substrate was additionally investigated at the beginning, during, and at the end of the whole measurement period by adding NaOH solution to 1 L aliquots from the parallel samples immediately before measurement until substrate pH exceeded 12. This way, dissolved TMA and NH₃ are supposed to be driven into the gas phase. Between all treatments the chamber lid was opened for a minimum of 10 min to let the chamber volume and surfaces equilibrate with the ambient concentration.

2.3 Concentration determination

2.3.1 At the dairy cattle barn

Concentrations of trace gas species were recorded online, with a combination of PTR-TOF-MS for volatile organic compounds (VOCs; including TMA) (Ionicon Analytik GmbH, Austria; Jordan et al., 2009; Graus et al., 2010), HT-CIMS (based on PTR-MS, Ionicon Analytik GmbH,

Austria) for NH_3 and TMA (Sintermann et al., 2011), and a CRD analyser for CH_4 (Los Gatos Research, CA, USA). Flexible inlet lines were used in order to sample at different locations. PTR-TOF-MS and HT-CIMS subsampled from a common 24 m 1/2 in. OD PFA inlet line flushed at about 80 L min^{-1} . The inlet line was heated above 150°C in order to achieve response times for NH_3 and TMA of the order of seconds (Sintermann et al., 2011). The CRD sampled through a parallel 1/4 in. OD PFA tube. For distinct TMA and NH_3 calibration events with PTR-TOF-MS and HT-CIMS, impingers (64712-U, Supelco, USA) sampled air in $15 \text{ mL H}_2\text{SO}_4$ (0.1 mol L^{-1}) solution with an airflow rate of 0.6 nL min^{-1} . The solution was analysed offline by IC as described by Kuhn et al. (2011). Applying two impingers in series resulted in TMA and NH_3 breakthrough of less than 2 %, even at high concentration levels of approximately 800 ppb NH_3 and 10 ppb TMA. The HT-CIMS instrument was operated with $E/N \approx 121 \text{ Td}$ at 180°C . With this setup, TMA is detected primarily at m/z 58 with an E/N -dependent fraction also occurring at m/z 59 (10–35 %), whereas acetone peaks at m/z 59 with a minor fraction at m/z 58 (15 %). This potential for cross-interference has been included as a range of possible values in the HT-CIMS concentration calculation for TMA. PTR-TOF-MS and HT-CIMS were calibrated for TMA and NH_3 , respectively, by impingers sampling ambient air in parallel ($n = 8$ for NH_3 , $n = 6$ for TMA). The HT-CIMS zero offset was determined by zero air measurements, with air provided by an LN Industries (Geneva, Switzerland) permeation device. The PTR-TOF-MS calibration setup for selected VOCs (as in Taipale et al., 2008) and concentration calculation procedures are described in more detail in the Supplement.

2.3.2 Dynamic chamber measurements

The climate room $\text{NH}_{3\text{amb}}$ concentration was continuously monitored using a CRD instrument (Picarro Inc., CA, USA) with a 15 cm long 1/4 in. OD PFA inlet, sampling with 0.5 nL min^{-1} close to the dynamic chamber inflow. Additionally, $\text{NH}_{3\text{amb}}$ and TMA_{amb} concentrations were periodically determined with impingers (as outlined in Sect. 2.3.1). These data revealed that TMA did not accumulate in the climate room, and hence TMA_{amb} was set constant; this also corresponded to HT-CIMS observations before and after the dynamic chamber measurements. The chamber headspace concentrations, TMA_{cham} and $\text{NH}_{3\text{cham}}$, were continuously monitored at the centre of the volume by means of HT-CIMS (operated similarly as during the cattle barn concentration measurements) equipped with a 65 cm long 1/4 in. OD PFA inlet line, heated to 150°C and flushed at 0.9 nL min^{-1} . In addition, the impinger system described in Sect. 2.3.1 was operated in parallel to the HT-CIMS inside the dynamic chamber for some occasions. The CRD and HT-CIMS were calibrated for NH_3 using gas from a standard bottle (50 ppm NH_3) down-mixed by a mass flow controller with zero con-

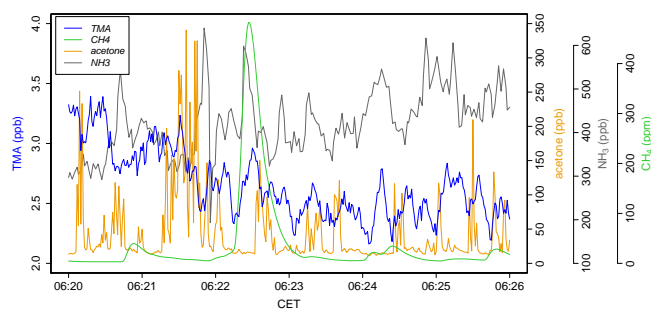


Figure 1. High-resolution time series of acetone, NH_3 , and TMA (8 s moving average) during measurements in front of the mouth of a ruminating cow at the outdoor yard on 28 July 2011; the average TMA : NH_3 ratio for this period was 0.65 %.

centration bottled synthetic air. This zero air stream was guided through two large (0.25 L) impingers with H_2SO_4 solution (0.01 mol L^{-1}) and demineralised water, setup in a temperature-regulated water bath in order to ensure gas relative humidity of 60 % at 20°C – the same as in the climate room. For NH_3 calibration, the NH_3 gas was mixed into this air stream. The air stream was supplied to the CRD and HT-CIMS over a T-piece with an overflow. Overflow impinger sampling with IC analysis was applied to check the calibration gas concentration. These calibrations were performed over at least 2.5 h to ensure sufficient equilibration time with involved surfaces. TMA calibration factors for HT-CIMS were obtained by comparison with impinger samples that had been collected during parallel operation of HT-CIMS and impingers inside the dynamic chamber. Applying two impingers in series resulted in less than 3 % breakthrough even at mixing ratios of approximately 3 ppm NH_3 and 80 ppb TMA.

3 Results

3.1 Concentration measurements

3.1.1 Exhaling cow

To test the hypothesis that ruminating animals exhaling TMA-enriched breath is the main TMA source, air was sampled close to the mouth of a ruminating cow. Figure 1 shows such a test with high time-resolution. Peaks in the acetone concentration time course mark the collection of air enriched by the animal's respiration (Elliott-Martin et al., 1997; Turner et al., 2012). CH_4 is related to eructation and respiration. NH_3 and TMA concentrations in the surrounding air were highly variable. They did not significantly correlate with the observed peaks in acetone and CH_4 . The mean TMA concentration was 2.7 ppb with a maximum of 4.5 ppb while the average TMA : NH_3 ratio during the displayed period was 0.65 % (see Sect. 3.1.2).

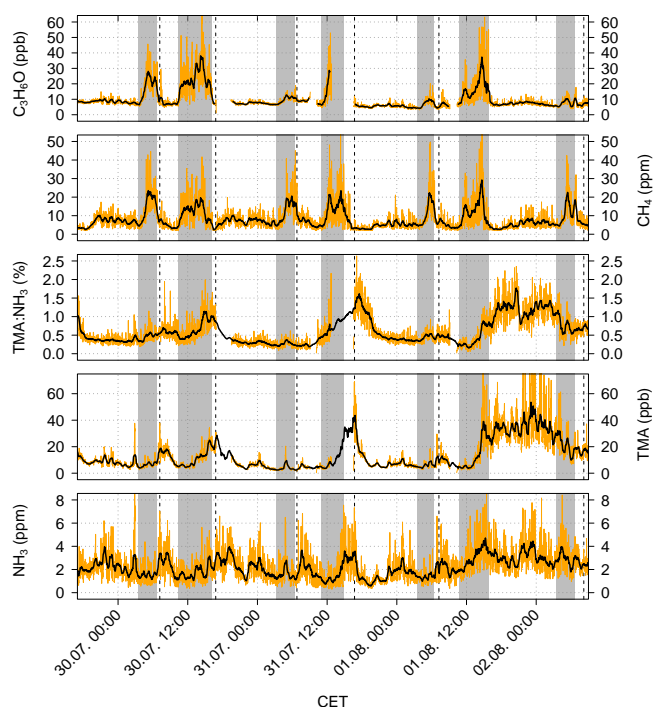


Figure 2. One-minute (orange) and 30 min (black) moving average trace gas concentrations measured in the outdoor yard; the presence of the animals is indicated with grey bars; ground scraping is represented by vertical dashed lines.

3.1.2 Diurnal variations at the outdoor barn area

Over a period of 3.5 days, trace gas concentrations were monitored in the farmyard (Fig. 2). The animals were usually away on pasture, but were gathered twice a day in the yard in the early morning and around noon (grey bars in Fig. 2). Typical concentration levels without the direct influence of animals were approximately 8 ppb acetone, 3 to 7 ppm CH_4 , 2 ppm NH_3 , 6 ppb TMA, corresponding to 0.3 % TMA : NH_3 . The animals' presence immediately correlated with strongly elevated acetone and CH_4 concentrations (Figs. 2 and 3). In contrast, NH_3 and TMA concentrations, as well as the ratio, began to increase subsequent to the cows' arrival, with a delay of around 2 h. However, their maximum average levels of approximately 4 ppm NH_3 , 50 ppb TMA, and 1.5 % TMA : NH_3 were reached when the cattle were gone and persisted as long as the barn's concrete floor was polluted with an excrement layer. The highest 1 min TMA values were approximately 120 ppb and TMA : NH_3 peaked at 2.6 %. The activation of the ground scraper and water cleaning of the ground (dashed line in Fig. 2) preceded declines in TMA and TMA : NH_3 levels. Typically, the concentration peaks were more pronounced in the afternoon than in the morning. An interesting feature from Fig. 2 is the plateau of the TMA and NH_3 concentrations as well as their ratio observed on the afternoon of 1 August onwards.

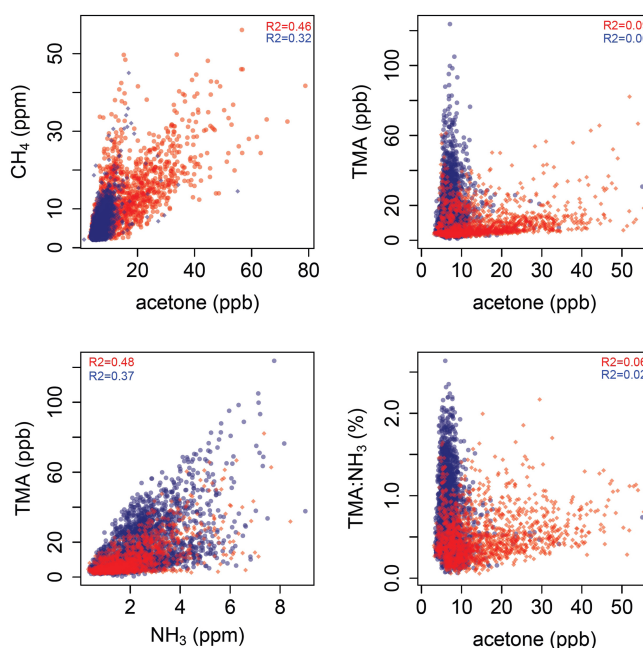


Figure 3. Mixing ratio correlation plots (1 min averages) for the period 29 July 17:00 to 2 August 9:00 (also shown in Fig. 2) of (a) CH_4 vs. acetone, (b) TMA vs. acetone, (c) TMA vs. NH_3 , (d) TMA : NH_3 vs. acetone; red circles are the measurements during presence of cows, blue diamonds are in absence of cows.

Under usual operation, the yard's ground is cleaned a short time after the cows leave the barn. This cleaning procedure did not take place that one afternoon and the excrement mixture remained on the ground until the next morning. During that entire episode, the elevated TMA concentration levels remained. Simultaneously measured wind speeds (at 1.5 m a.g.l.) in the farmyard were always below 1 m s^{-1} coming from variable directions. Ambient air temperature was lowest in the early morning at 13 to 15 °C, and peaked during daytime at 23 to 26 °C. We therefore assume that the observed air concentrations are not mainly caused by variations of atmospheric transport capacity, but that the measured concentrations primarily scale with emission rates.

Figure 3 summarises the findings of Fig. 2 with scatterplots subdivided into values reflecting periods with and without cattle. Figure 3 shows that high levels of acetone and CH_4 correlate and are linked to direct emissions from the animals, whereas the occurrence of high NH_3 and especially TMA concentrations is decoupled from direct animal emissions.

3.2 Emission measurements

Figure 4 summarises the dynamic chamber emission measurements for NH_3 and TMA. NH_3 emissions were dominated by volatilisation from the urine–faeces mixture. After about 45 h, emissions began to decrease again. Direct faecal and urinary emissions played a minor role. pH values tended

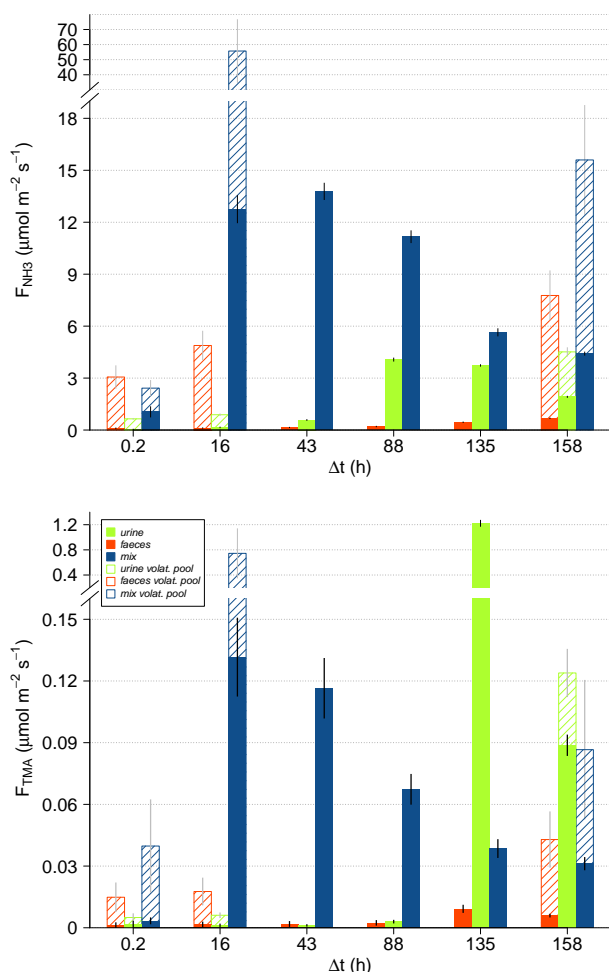


Figure 4. Dynamic chamber NH₃ and TMA emission rates from samples of urine, faeces, and their mixture, as well as emission rates from parallel samples with pH raised > 12 (“volatile emission pool”).

to increase with increasing emissions. Specifically, faeces pH remained below 7 with a slight increase towards the end of the measurement period, mixture pH increased from 7.7 to 8.5 and declined down to 8.1 after 160 h, and urine pH rose from 8.5 to 9.5. Potential NH₃ emissions were in general much larger than actual emissions, whereby the mixture exhibited the by far largest emission potential. NH₃ emissions from stored slurry (0.3 μmol m⁻² s⁻¹) were lower than from the substrates because the composition of stored slurry reflects a long-term equilibrium.

TMA emissions behaved similarly to NH₃ emissions. Only the urine–faeces mixture showed larger emissions continuing after the first 120 h. The maximum flux during this period was 0.13 μmol m⁻² s⁻¹, and potential emissions were even higher. The following decrease down to 31.2 nmol m⁻² s⁻¹ remained far above the very small actual and potential TMA emissions from the stored slurry (0.73 and 1.3 nmol m⁻² s⁻¹ with 0.2 and 0.05 % emission ratio, re-

spectively). With the mixture, the TMA : NH₃ emission ratio was of the order of 1 % (0.3, 1.0, 0.9, 0.6, 0.7, 0.7 % for the periods in Fig. 4), consistent with the observations in Fig. 2. Faecal TMA emissions were continuously lowest, not exceeding 9.2 nmol m⁻² s⁻¹. Due to the acidic pH, no significant emissions occurred, but also the emission potential of the volatile TMA pool was low. Until around 80 h, urinary TMA emissions remained low with only minor emission potential during the first 24 h. After 130 h, however, a very large TMA emission peak, up to 1.2 μmol m⁻² s⁻¹, was observed, which decreased again towards the following measurement interval. We think this peak was induced by the contamination of the urine sample with some faecal residues on the pH electrode sometime after 88 h. During storage, corresponding bacterial action was likely to have effectively converted the concentrated TMA precursor to TMA (see discussion Sect. 4.2). Considering that ambient temperatures are usually lower than the 20 °C during our experiment (hence, more TMA will remain in the liquid phase) and assuming that in a real situation with a high stocking density there is a constant supply of excrements which mix and show an emission behaviour like the mixture in Fig. 4, we derive a typical average TMA emission rate of 10 nmol m⁻² s⁻¹ that we regard as representative for ambient situations.

4 Discussion

4.1 TMA in exhaled air

Kuhn et al. (2011) hypothesised oral TMA volatilisation from ruminating cattle as the main pathway for the generally enhanced TMA concentrations and emissions from agriculture. This might be due to TMA-enriched rumen content (pH = 6.5) being mixed with saliva of high pH (pH = 8). In our measurements close to a ruminating cow’s mouth, air influenced by the animal’s respiration was characterised by short-term concentration peaks of acetone and CH₄ (Fig. 1). Acetone, present in the blood, mainly originates from exhalation where it occurs on the ppm level (Dobbelaar et al., 1996; Elliott-Martin et al., 1997; Spinhirne et al., 2003; Turner et al., 2012). CH₄ is created in the rumen as a by-product of enteric fermentation (Russell and Wallace, 1997) and is released during eructation and exhalation (Martin et al., 2012). CH₄ release from the rumen dominates compared to release via the lung (<http://c-lockinc.com/data.php>). Elevated concentrations of CH₄ and acetone are thus directly linked to the animal’s respiration as can also be seen in Figs. 2 and 3. The high CH₄ peaks appear less frequent than those of acetone, because CH₄ is more related to eructation while acetone is rather associated with exhalation. Both time series are hence not well correlated. In order to support the hypothesis by Kuhn et al. (2011), strongly increased TMA : NH₃ values should be observed when measuring close to a ruminating cow’s mouth and when cattle stay in the barn yard.

This was not evident from our measurements (Fig. 1). In fact, TMA concentration levels and TMA : NH₃ ratios began to rise most strikingly only subsequent to the animals' presence in the yard (Fig. 2), which suggests that the main source for agricultural TMA volatilisation and high TMA : NH₃ ratios cannot be oral release from ruminating cows. The amount of volatilised TMA during rumination is insufficient to yield the observed elevated TMA concentration episodes. This may be explained by limited gas exchange between mouth and atmosphere.

4.2 Characteristics of TMA volatilisation

Periods with highest TMA concentrations and TMA : NH₃ ratios were found subsequent to the animals being in the barn yard and correlated with the existence of an excrement layer on the ground (Fig. 2). The TMA and NH₃ concentrations in the afternoon exceeded those during morning. The higher temperatures promote the volatilisation of the alkaline constituents since solubility is decreased and the hydrolysis of urea is accelerated, leading to an increase of the pH-value. When the excrement layer was removed by a scraper and cleaned with water, the emissions and hence concentrations subsided. On one occasion (1 August) cleaning was omitted until the next morning resulting in persistently high TMA levels. Our dynamic chamber emission measurements (Fig. 4) demonstrate how TMA is most rapidly and efficiently released from a mixture of urine and faeces whereas urine and faeces alone exhibited rather small emission rates. Elevating the substrate's pH to > 12 ("volatile emission pool") showed that very little TMA for volatilisation was available in urine and faeces alone. Hence, there is most likely a TMA precursor which is converted efficiently by the mixing of urine and faeces. The sudden massive TMA emission peak from urine after 135 h suggests that this precursor is contained within the urine. Several publications (see Sect. 4.3) show that TMA-N-oxide (TMAO) is excreted in urine by different mammals. We analysed urine from two Australian lactating cows for TMA and TMAO content using an established method (Johnson, 2008). Results reveal two to four times more TMAO than TMA (762–1121 μmol TMAO L⁻¹ vs. 251–386 μmol TMA L⁻¹). This fraction likely varies from animal to animal depending on diet, health, and lactation status. Humans, as another example, excrete much more TMAO than TMA with urine (TMA : TMAO < 4 %; Lee et al., 2010). TMAO was discovered at the beginning of the twentieth century in animal tissues (Suwa, 1909). It appears to have manifold physiological functions and is, for example, an important compound in marine organisms for cellular osmotic and pressure regulation (Samerotte et al., 2007) and protein stabilisation (Bennion and Daggett, 2004; Sarma and Paul, 2013). The decomposition to TMA is responsible for the smell of decaying fish (Barrett and Kwan, 1985). The ratio of TMA : TMAO in hu-

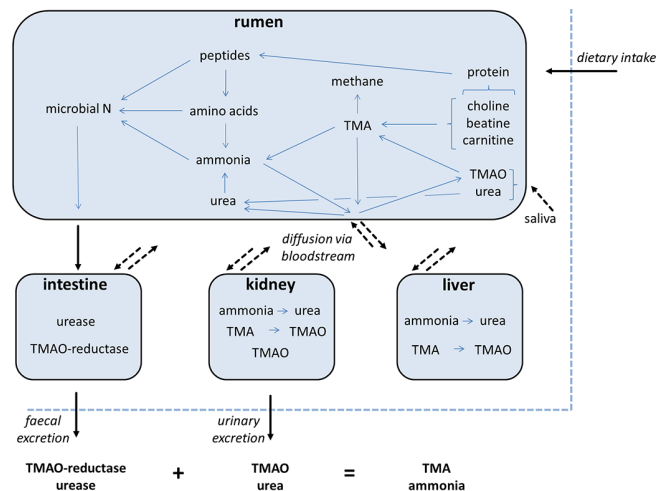


Figure 5. Main pathways of TMA and NH₃ production by the ruminant system (with the focus on TMA).

man urine is, for example, used as a diagnostic tool for a disturbed metabolism (Cashman et al., 2003; Lee et al., 2010).

TMAO converting microbes are mainly abundant in the faeces. We propose that the dynamic chamber urine sample was contaminated by bacteria from the faeces sometime after 88 h, probably through an insufficiently cleaned pH rod. The urine emission peak occurs for TMA but not for NH₃, which demonstrates that different microbial species might have been responsible for the TMA creation than those for NH₃ formation by urea hydrolysis. Alkaline conditions are required to make TMA available for volatilisation. Urea hydrolysis to NH₃ increases pH and provides the conditions for TMA release into the gas phase.

4.3 The fate of TMA in ruminants

To the best of our knowledge, a picture of ruminant TMA formation, cycling, and volatilisation, complementing the schemes given by Bain et al. (2005) and Rappert and Müller (2005), has not yet been compiled. We attempt this with Fig. 5, schematically demonstrating the fate of NH₃ and TMA in ruminants. As already indicated by Schade and Crutzen (1995), the primary source for TMA is the rapid microbial degradation of choline (Davies, 1936; Eddy, 1953; Neill et al., 1978; Zeisel et al., 1989; Bain et al., 2005; Wang et al., 2011; Craciun and Balskus, 2012) taken up with the feed (Pinotti et al., 2002). In addition, rumen microorganisms might metabolise TMA from dietary supply of carnitine, betaine, and TMAO (Davies, 1936; Mitchell et al., 1979; Zhang et al., 1999). The TMA is further used for methanogenesis. This removal process becomes saturated (Neill et al., 1978; Patterson and Hespell, 1979; Barrett and Kwan, 1985; Pinotti et al., 2002; Padmanabha et al., 2013). Rumen TMA has been found to accumulate with a molar ratio of dissolved TMA : NH₃ of 1 : 1.7 to 1 : 3.1 (Kuhn et al., 2011).

Like NH_3 , TMA diffuses through the rumen wall into plasma and blood stream (Bain et al., 2005). In the liver, the NH_3 is converted to urea as a detoxification mechanism (Meijer et al., 1990; Walt, 1993). Similarly, TMA acts detrimentally (Guest and Varma, 1992; Rappert and Müller, 2005) while liver cells are capable of enzymatically oxidising TMA to TMAO (Baker and Chaykin, 1962; Baker et al., 1963; Gut and Conney, 1993; Bennett et al., 2013). Saliva is known to contain urea, serving as additional NH_3 source in the rumen when being recycled (Wallace et al., 1997). Likewise, it seems reasonable also that TMAO, dissolved in the saliva, is being returned to the rumen, where it would be reconverted to TMA and then recycled back again to TMAO.

Several studies have found that a large TMA fraction from ingested precursor substances is excreted in form of urinary TMAO with various mammals (Davies, 1936; Norris and Benoit, 1945; Al-Waiz et al., 1987; Dacosta et al., 1990; Zhang et al., 1999). Once excreted, microorganisms reduce TMAO to TMA, subsequently convert TMA to DMA, then MMA, and finally to NH_3 under aerobic conditions (Barrett and Kwan, 1985; Kim et al., 2001; Rappert and Müller, 2005). Microorganisms are known to feed on TMAO anaerobically as well (Kim et al., 2001; Baraquet et al., 2006). This behaviour generally appears to be similar to urea hydrolysis, and both processes are responsible for the rapid occurrence of high NH_3 and TMA volatilisation rates when urine and faeces come into contact with one another (Fig. 4). The combination of both substrates is relevant since most urea- and TMAO-converting microorganisms are present in the intestine. For example, *E. coli* is found in the intestine and also occurs in excreted faeces where it can survive for weeks (Fremaux et al., 2008; Callaway et al., 2009; Hanajima et al., 2011) and can process TMAO to TMA under aerobic as well as anaerobic conditions (Gon, 2000; Baraquet et al., 2006; Ansaldi et al., 2007). Furthermore, TMA degradation occurs as stored slurry exhibits only minor TMA concentrations and emission potential (Sect 3.2; Kuhn et al., 2011). This is consistent with the observation that a variety of microorganisms are capable of efficiently degrading methylamines, including TMA, in the presence and absence of oxygen (Colby and Zatzman, 1973; Colby et al., 1979; Patterson and Hespell, 1979; Jang et al., 1999; Rappert and Müller, 2005; Ho et al., 2008; Ferguson et al., 2008; Chen et al., 2011; Yang et al., 2013).

4.4 TMA emission measurements in the context of literature

There are aliphatic amine emissions related to poultry, sheep, horses, pigs, and cattle (Schade and Crutzen, 1995; Schade and Ngwabie, 2005). Emission flux measurements of amines are rare. Denmead et al. (1974) identified the occurrence of amine emissions by application of a micrometeorological gradient technique over an alfalfa pasture grazed by 200 sheep. They found indications of varying contributions of amine emissions to the total gaseous reduced nitrogen flux.

In a pig production facility, Feilberg et al. (2010) determined TMA emissions by monitoring barn exhaust ventilation rate and air concentrations. They found a TMA flux of 41 mg h^{-1} corresponding to 6 nmol s^{-1} per pig (however, there was also a slurry pit in the barn). Laubach et al. (2013) performed micrometeorological mass balance flux measurements of NH_3 near a cattle herd with a stocking density of 150 animals per hectare on grassland and found additional (unquantified) emission fractions of amines. Downwind of a cattle feedlot with 840 animals per hectare, Hutchinson et al. (1982) determined NH_3 and amine emissions from vertical concentration gradient measurements. The largest measured TMA emission constituted about $14.5 \text{ nmol m}^{-2} \text{ s}^{-1}$. The authors do not provide further direct information on determined TMA fluxes. Based on the given information, their TMA : NH_3 emission flux ratio was between 0.3 and 0.5 %. Assuming an average ratio of 0.4 % and using the tabulated NH_3 emission rates results in a mean (\pm standard deviation) TMA emission of $10.9 \pm 5.3 \text{ nmol m}^{-2} \text{ s}^{-1}$. This value compares well with the $10 \text{ nmol m}^{-2} \text{ s}^{-1}$ derived from our dynamic chamber experiments. It can be expected that the feedlot's high stocking density resembles conditions similar to situations in animal housing rather than, for example, for grazing cattle. Excrements cover the surface with high chances of urine and faeces interactions while there is ongoing supply. Thus, the measurements by Hutchinson et al. (1982) represent a setting comparable to our barn environment and the dynamic chamber emission trial.

With micrometeorological field measurements (eddy covariance and gradient), Kuhn et al. (2011) demonstrated that stored cattle slurry applied to grassland and cropland had only minor TMA emissions of up to $0.3 \text{ nmol m}^{-2} \text{ s}^{-1}$ with maximum TMA : NH_3 ratios of 0.1 %. Direct analysis of the slurry TMA and NH_3 content confirmed the low TMA emissions. Twigg et al. (2011) determined TMA emissions following 6-month-old cattle slurry applied to grassland by scaling eddy covariance-derived NH_3 emissions (Whitehead et al., 2008) with the observed ambient TMA : NH_3 concentration ratio (TMA determined by PTR-MS using a theoretical calibration factor). This yielded TMA emission rates of up to $3.6 \text{ nmol m}^{-2} \text{ s}^{-1}$ and a 31 h average emission rate of $0.69 \text{ nmol m}^{-2} \text{ s}^{-1}$. The concentration ratio TMA : NH_3 was on average 0.38 %, and a maximum emission rate ratio of 0.74 % was derived. These values are higher than expected from the results of this study and those of Kuhn et al. (2011). Nevertheless, we suggest that there is sufficient experimental and theoretical (Sects. 3.2 and 4.3) support for our observed low TMA emissions from stored slurry.

Currently, there are roughly 1.4×10^9 cattle on earth (FAO, 2013). Assuming that a surface between 0.5 and 5 m^2 associated with each animal constantly emits 10 to $30 \text{ nmol m}^{-2} \text{ s}^{-1}$ yields a global emission of $0.003\text{--}0.093 \text{ Tg TMA-N yr}^{-1}$. The upper estimate is a similar order of magnitude as the assessment of cattle emissions by Schade and Crutzen (1995) ($0.083\text{--}0.167 \text{ Tg TMA-N yr}^{-1}$)

refined by Kuhn et al. (2011) ($0.035\text{--}0.053\text{ Tg TMA-N yr}^{-1}$). This upscaling, based on our individual flux measurement experiments, provides a case study. Yet, it concurs well with the broad knowledge about agricultural TMA volatilisation as discussed above. Flux measurements under a wide range of environmental conditions would be required for a more detailed assessment.

4.5 Emissions of reduced N-species from agriculture and their role in secondary aerosol particle formation

Nucleation of a cluster of a few molecules is the initial step of secondary aerosol formation. Aliphatic amines and NH_3 have been identified as the neutralising components of secondary aerosol formation, which is initiated by sulfuric acid (Kulmala et al., 2013). While there is a consensus that amines are important for nucleation (Andreae, 2013; Kulmala et al., 2013), the differences between various amines regarding particle formation are not known in detail (Paasonen et al., 2012). Hence, it is assumed that aliphatic amines behave similarly and, explicitly, that TMA and DMA have similar nucleation enhancement potentials. Based on the comparison of modelling results under varying atmospherically relevant conditions to experimental results from seven different measurement sites, Paasonen et al. (2012) suggest that TMA provides the rate-limiting step for atmospheric particle formation. The presence of aliphatic amines has been shown to enhance formation rates more than thousand-fold compared to the ternary NH_3 –sulfuric-acid–water system, already at very low mixing ratios (e.g. in the case of 5 ppt of DMA compared to 250 ppt of NH_3) (Almeida et al., 2013). The quantum chemical modelling and experiments conducted by Almeida et al. (2013) resemble pristine atmospheric conditions considering DMA. The enhancing effect of TMA on secondary particle formation has been found in other modelling studies (Murphy et al., 2007; Kurten et al., 2008; Paasonen et al., 2012). Measurements of aerosol number concentration upwind, within, and downwind a cattle farm have demonstrated a threefold increase in particle concentration indicating secondary particle formation (Lammel et al., 2004).

Nucleation rates are higher with an aliphatic amine than with NH_3 ; therefore, if for example DMA was present, it would be expected to enhance the particle formation. To what extent this happens is dependent on sulfuric acid and amine concentrations. When the amine concentration exceeds that of sulfuric acid, the nucleation rates observed by Almeida et al. (2013) will occur. If the amine concentration is lower than that of sulfuric acid, it is likely that NH_3 also neutralises the remaining sulfuric acid–water clusters, and that the formation rate will be between the one determined by NH_3 (lower limit) and amine (upper limit). Typical sulfuric acid mixing ratios range between 0.005 and 5 ppt (Eisele and Tanner, 1993; Petäjä et al., 2009; Almeida et al., 2013). Unlike sulfuric acid, which is formed by oxidation of sulfur dioxide

in the atmosphere (Boy et al., 2005), amines are emitted directly from their sources (this study; Ge et al., 2011). While the sulfuric acid gets re-supplied continuously, the availability of gaseous amines for particle formation is further determined by their overall atmospheric residence time. It is influenced by dry deposition, oxidation by radicals (mainly the hydroxyl radical (OH) (TMA lifetime due to OH: 4.6 to 7.7 h; Ge et al., 2011)), and condensation onto existing particles. The lifetime due to condensation is the reciprocal of the condensation sink, which is determined by the aerosol number size distribution. The TMA lifetime due to condensation onto aerosol particles was calculated according to the condensation sink method by Kulmala et al. (2012), using the diffusion coefficient of TMA. We derive a TMA lifetime due to condensation in the range of 30 to 1000 s: 30 s for the case of a number size distribution (aerosol load) as found in the plume of a German cattle farm (Schneider et al., 2008) and several minutes in cleaner environments such as in a boreal forest in Finland (Dal Maso et al., 2007). Hence, the removal of gas-phase TMA is dominated by the condensation sink. Cattle barns and feedlots are emission hot spots for NH_3 , TMA, and also aerosol particles. The particles originate from both primary emissions as well as secondary formation. Given a lifetime of 60 s, estimated to reflect a typical condensation sink with respect to central European aerosol particle concentrations, TMA and other aliphatic amines cannot travel far in the gas phase. For example, a plume with 3 m s^{-1} wind speed would advance 1.5 km within 8.4 min, while the condensation sink would reduce the initial 10 ppb down to 1 ppt. In addition to the loss of particles, the TMA plume is diluted with cleaner air during dispersion. Assuming typical boundary layer conditions, dilution of that plume over 8.4 min would down-mix the concentration of a (conservative) gas by roughly 1 : 100 (calculated by backward-Lagrangian stochastic-based dispersion modelling in Flesch et al. (2004)). In the case of TMA, concentrations would have fallen below values typical for sulfuric acid. Consequently, gas-phase TMA can determine aerosol particle formation relatively close to the source while further away, NH_3 begins to dominate the formation.

At the Finnish boreal forest research site in Hyytiälä there is experimental evidence that particle formation events coincide with episodes of increased ambient aliphatic amine concentrations (Kieloaho et al., 2013). The prevailing ambient conditions and commonly observed low pre-existing particle concentrations at the forest site differ strongly from those of densely populated intensive agricultural regions in, for example, central Europe, surrounded by anthropogenic activities leading to higher aerosol loading.

5 Conclusions

To advance the understanding of agricultural TMA emission sources and their strength, we carried out detailed trace gas concentration measurements at a cattle barn as well as in laboratory experiments assessing TMA and NH₃ emissions from excretion substrates. TMA is not exhaled from rumination in significant amounts but is formed from excreted TMAO by microbial action. The TMAO originates from rumen TMA which is oxidised by the liver. TMAO is mainly present in urine while microbes, providing the enzymatic conversion, are primarily contained in faeces. Hence, under usual conditions, a urine–faeces mixture will yield high TMA emission rates which could explain observed elevated ambient TMA concentrations at agricultural facilities. For TMA volatilisation, a situation with alkaline pH values is required; this occurs with urine–faeces mixtures due to bacterial urea hydrolysis into NH₃. The formed TMA seems to be further microbially degraded to NH₃ resulting in comparably small TMA emissions from stored slurry. Derived average TMA emission rates from urine–faeces mixtures are of the order of 10 nmol m⁻² s⁻¹ which roughly agrees with current global agricultural TMA emissions assessed by scaling with NH₃ emission inventories.

Once emitted, gas-phase TMA participates in nucleation with a high potential efficiency for secondary particle formation but also undergoes condensation onto existing aerosol particles. Depending on the prevailing particle number size distribution, the corresponding atmospheric lifetime is estimated to range from 30 to 1000 s, with the first value being probable for agricultural areas. This confines the high particle formation potential of agricultural TMA to its source regions, with dwindling direct impact of agricultural emissions at increasing distance. Close to agricultural sources, there are relatively high NH₃ concentrations in addition to abundant amines. In the vicinity of farms, amines will be the key neutralising component in the ternary sulfuric acid–water base nucleation and can enhance the formation of new aerosol particles by a factor of 1000 compared to aerosol formation with NH₃ under otherwise equal conditions. As the air mass is transported further away from the source, the amines are depleted and NH₃ must become the primary neutralising agent. For more direct evidence of agriculturally enhanced secondary aerosol particle formation by amines, simultaneous measurements of gas-phase amines, NH₃, sulfuric acid, and particle number size distributions should be performed upwind and downwind animal farms.

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