

Basic biogenic aerosol precursors: Agricultural source attribution of volatile amines revised

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[1] Despite recent evidence on an important role of volatile amines in the nucleation of particulate matter, very scarce information is available on their atmospheric abundance and source distribution. Previous measurements in animal housings had identified livestock husbandry as the main amine source, with trimethylamine (TMA) being the key component. This has led to the assumption that the agricultural sources for amines are similar as for ammonia, emitted throughout the cascade of animal excretion, storage and application in the field. In this study, we present the first micrometeorological flux measurements as well as dynamic enclosure experiments showing that the amine source strength from stored slurry is negligible, implying significant consequences for the global amine emission inventory. In the case of cattle, amine production is attributed to the animal's rumination activity and exhalation is suggested to be an important emission pathway, similar to the greenhouse gas methane. Fodder like hay and silage also emits volatile amines, potentially assigning these alkaloid compounds a key function in enhancing particle formation in remote areas. **Citation:** Kuhn, U., J. Sintermann, C. Spirig, M. Jocher, C. Ammann, and A. Neftel (2011), Basic biogenic aerosol precursors: Agricultural source attribution of volatile amines revised, *Geophys. Res. Lett.*, 38, L16811, doi:10.1029/2011GL047958.

1. Introduction

[2] The formation of new particles through nucleation of gases is observed ubiquitously in the earth's atmosphere and is an important contributor to the global aerosol number budget [Spracklen *et al.*, 2008; Hallquist *et al.*, 2009]. It is linked to the production of cloud condensation nuclei (CCN), which affect global climate by its direct and indirect net negative radiative forcing. In classical nucleation theories [e.g., Seinfeld and Pandis, 1998], basic (alkaline) compounds are assumed to significantly enhance nucleation by readily combining with acidic components like sulfuric, nitric or organic acids. Volatile amines (methylamine, dimethylamine, trimethylamine, among others) are odorous nitrogen-bearing organic compounds that represent the major residual of alkaloid constituents in the earth's atmo-

sphere beside ammonia (NH₃). Already in a pioneer study with a smog chamber in the late seventies, the light back-scattering by particles was found to increase after addition of volatile amines [Pitts *et al.*, 1978]. But only recently, the importance of amines in nucleation has become evident [Angelino *et al.*, 2001; Mäkelä *et al.*, 2001; Kurtén *et al.*, 2008, Smith *et al.*, 2010; Bzdek *et al.*, 2010; Berndt *et al.*, 2010]. Based on thermodynamic studies, volatile amines are considered to be more important for nucleation than NH₃, even when the gas-phase amine concentrations are only a thousandth of NH₃ [Kurtén *et al.*, 2008; see also Loukonen *et al.*, 2010]. Likewise, very recent experimental data gave evidence that small atmospheric salt particle clusters (<3 nm) are most likely ammonium salts rather than ammonium salts, and amines rather than ammonia may be components of nucleation, even in cases where ammonium salts are formed initially [Bzdek *et al.*, 2010].

[3] The attention paid by the aerosol scientific community towards volatile amines strongly contrasts with the very scarce information available on their sources and atmospheric abundance. Primarily based on similarities between enhanced amine and NH₃ concentration observed within livestock buildings, it was assumed that the main agricultural sources of amines and their global distribution are similar to that of NH₃ [Schade and Crutzen, 1995]. Agriculture constitutes the most important global source of NH₃, primarily by way of emissions from cattle manure [Steinfeld *et al.*, 2006]. Accordingly, cattle husbandry was accounted for the major share of agricultural amine emissions (86.4% of all animal categories) [Schade and Crutzen, 1995], and was also presumed to dominate the global budget of volatile amines, among other sources like marine seawater, biomass burning, sewage treatment, waste incineration, and industrial activities [Ge *et al.*, 2011]. An average proportionality factor of 0.7% for amine emissions relative to NH₃ occurring throughout the whole chain of emissions from animal husbandry has been applied to existing NH₃ emission inventories to calculate a first (and only) global estimate of agricultural amine emissions, inferring a total of 0.15 ± 0.06 Tg N per year [Schade and Crutzen, 1995] (see also Ngwabie *et al.* [2008] for a German inventory). Trimethylamine (TMA) was attributed to be the key compound with a contribution of 74% (or 0.11 Tg N a^{-1}) of all amines [Schade and Crutzen, 1995]. However, there have been first indications [Sun *et al.*, 2008] that the assumption of similar source mechanisms for amines and NH₃ from animal husbandry and thus a constant emission ratio between them might not be valid. Within the present study, we carried out specific measurements to identify the effective contribution of various potential source processes for amines. Our mea-

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surements mainly focused on TMA as a surrogate for all other amines.

2. Method

[4] Potential sources of amine and NH_3 volatilization from animal husbandry were investigated by (i) cattle housing indoor air concentration measurements, (ii) dynamic enclosure studies of various substrates in the laboratory and (iii) the first micrometeorological flux measurements after slurry application in the field using the Aerodynamic Gradient Method (AGM) [Monteith and Unsworth, 1990]. Slurry is a composite of dung, urine, straw and water. In order to characterize its emission potentials, both (i) aliquot samples of slurry stored at the farm's underground pit collected prior to its application in the field and (ii) fresh rumen juice samples derived from fistulated cows, were distilled by addition of NaOH, subsequent steam-heating, and transfer of the vapor phase to a gas collection main of H_2SO_4 (0.5 M).

[5] The AGM method was complemented by an Eddy Covariance (EC) flux technique applied by means of a high temperature Chemical Ionization Mass Spectrometer (PTRMS technique with electron transfer applying O_2^+ as primary reaction agent), specifically customized for fast and simultaneous NH_3 and TMA analysis [Sintermann *et al.*, 2011]. Applying standard PTRMS drift tube temperatures of 60°C , TMA was detected predominantly at m/z 58 (i.e., after abstraction of one H atom), with some contribution of m/z 59 and m/z 60, consistent with earlier measurements by means of Selected Ion Flow Tube (SIFT) technique by Španěl and Smith [1998]. With the instrumental characteristics applied here (inlet lines temperature 150°C , drift tube at 180°C) the contribution of m/z 59 and m/z 60 ceased. NH_3 was fully assigned to m/z 17.

[6] For the AGM method and the laboratory experiments we used classical glass impinger liquid accumulation sampling systems to collect amines and NH_3 in air, with subsequent offline Ion Chromatography (IC) analysis to ensure compound identification and quantification. Accumulation of compounds was utilized by bubbling sample air through 20 ml of 0.01 molar H_2SO_4 by means of constant flow pumps (GilAir -5, Sensidyne Florida, USA) with a flow of 1 L min^{-1} for 1–10 hours. The sampling efficiency of the investigated alkaloid species was $>98\%$, based on test measurements applying two sequential impingers. The precision was $\pm 3\%$, based on simultaneously collection of air samples in the field. For IC analysis we used a Dionex Model DX 500 IC/HPLC System (Sunnyvale, CA, USA) with an Automated Sampler (AS5), Gradient Pump (GP50), a $970 \mu\text{l}$ PEEK injection loop, an Ionpac CS10 (4 mm) main analytical column with an Ionpac CG10 (4 mm) guard column for the compound separation, and a Conductivity Detector (ED40) with Cation Self-Regenerating Suppressor (CSRS 300). High purity Methanesulfonic Acid was used as eluent with a flow rate of 1 mL min^{-1} . Calibration was achieved either by serial dilution of a commercial NH_4^+ standard solution, or by dissolving respective A.C.S. reagent grade hydrochlorides of Methylamine, Ethylamine, Dimethylamine, and Trimethylamine (all chemicals from Sigma-Aldrich, St. Louis, USA). The analytical accuracy for NH_3 and TMA estimated from the calibration curve ($0.01 - 4.0 \text{ mg L}^{-1}$, $R^2 > 0.99$) was better than 5% for both com-

pounds. The detection limit in the aqueous phase (chromatographic peak three times the standard deviation of the background noise in the base line of the chromatogram) was better than $0.4 \mu\text{g L}^{-1}$, the respective minimum detectable concentration in air using a two hour sampling period (120 liters of volume) was 15 ppt for TMA and 85 ppt for NH_3 .

[7] Taking advantage of our institute's livestock facilities, we were able to obtain fresh samples of enteric rumen fluid from two fistulated cows. To perform direct TMA/ NH_3 exchange measurements with the rumen fluid, it was incubated in a cylindrical dynamic glass enclosure system (9 cm in diameter, 15 cm in height) purged with air (1.5 L min^{-1}) humidified and purified by means of bubbling through 0.1 molar H_2SO_4 , followed by a bottle of pure water prior to entering the enclosure. The same system was used for the first emission measurements on samples of fresh cattle dung (enclosed 5 min after excretion) and dried grass (hay and silage), with samples being piled on the base of the enclosure to cover the complete bottom. For reasonable inter-comparison of exchange data, calculated emission rates were based on enclosure ground area.

3. Results and Discussion

3.1. Animal Housing Indoor Concentrations

[8] In our measurements, the abundance of amines, both in ambient air concentrations and emission rates was always strongly dominated by TMA (50–80%) as has been reported in earlier publications for concentrations in animal housings [Schade and Crutzen, 1995] and feedlots [Hutchinson *et al.*, 1982]. Other observed amine compounds were dimethylamine (DMA), monomethylamine (MMA), and ethylamine (EM), with MMA showing the highest relative variability. Even though not all amines co-varied at exactly the same ratios and thus may not have fully identical sources, we consider TMA as a key compound for assessing the budget and characteristics of atmospheric amines. Our observed TMA/ NH_3 concentration ratios in cattle housings were found to be in a range of about 0.3–1.0% (Table 1), confirming earlier observations of enhanced amine concentrations in indoor air [e.g., Schade and Crutzen, 1995; Ngwabie *et al.*, 2008]. While these findings led to the assumption of similar source mechanisms for amines and NH_3 from animal husbandry in earlier reports, we carried out specific measurements to identify the effective contribution of various source processes for the two trace gases.

3.2. Cattle Slurry/Dung Emission

[9] Both our results after application of slurry in the field over grass- and cropland by means of a micrometeorological flux method (Figure 1, top) as well as corresponding trace gas exchange measurements on fresh cattle dung in the laboratory by means of a dynamic enclosure system (Figure 1, bottom) showed that TMA emissions exhibited a temporal trend similar to NH_3 . Peak emissions were observed in an initial phase of a few hours, followed by an exponential decay of emission. However, the respective TMA/ NH_3 emission ratios never exceeded 0.01%, and thus were about two orders of magnitude lower than expected from the animal housing indoor air concentration measurements. Accordingly low TMA/ NH_3 concentration ratios (0.0018–0.0035%; Table 1) were also found in distillates of

Table 1. Observed Gas and Liquid Phase Concentrations, Fluxes (Aerodynamic Gradient Method, AGM) and Emission Rates (enclosure) of Cattle Amine Sources and Sites^a

	Gas Phase Concentrations		
	NH ₃ (ppb)	TMA (ppb)	TMA/NH ₃ (%)
Indoor animal housing (n = 3)	552–2601	4.21–7.64	0.29–1.02
	Fluxes After Slurry Application (AGM, Field)		
	NH ₃ (nmol m ⁻² s ⁻¹)	TMA (nmol m ⁻² s ⁻¹)	TMA/NH ₃ (%)
Stored slurry applied over grassland (n = 2)	684–3055	0.050–0.29	0.0073–0.0095
Stored slurry applied over cropland (n = 2)	531–2976	0.0–0.31	0.0–0.0105
	Emission Rates After Incubation (Enclosure, Lab)		
	NH ₃ (nmol m ⁻² s ⁻¹)	TMA (nmol m ⁻² s ⁻¹)	TMA/NH ₃ (%)
Fresh cattle dung (n = 4)	2709–4348	0.064–0.111	0.0024–0.0032
Rumen juice (n = 2; 1 young, 1 senior cow)	1681–9129	112–562	6.2–7.8
Hay (n = 2)	16–32	0.06–0.12	0.37–0.40
Silage (n = 2)	143–162	0.31–0.36	0.21–0.22
	Liquid Phase Concentrations (Distillates)		
	NH ₄ ⁺ (μmol mol ⁻¹)	TMA ⁺ (nmol mol ⁻¹)	TMA ⁺ /NH ₄ ⁺ (%)
Stored slurry, prior to grassland application (n = 6)	1599 (± 116)	54.7 (± 13.1)	0.0035 (± 0.0011)
Stored slurry, prior to cropland application (n = 3)	1128 (± 90)	17.6 (± 5.7)	0.0018 (± 0.0004)
Fresh rumen juice (1 young, 1 senior cow)	197–226	3756–6163	1.7–3.1

^aFor fluxes and exchange rates the impinger data within the first 6 hours of observation are given (n is the number of samples/measurements).

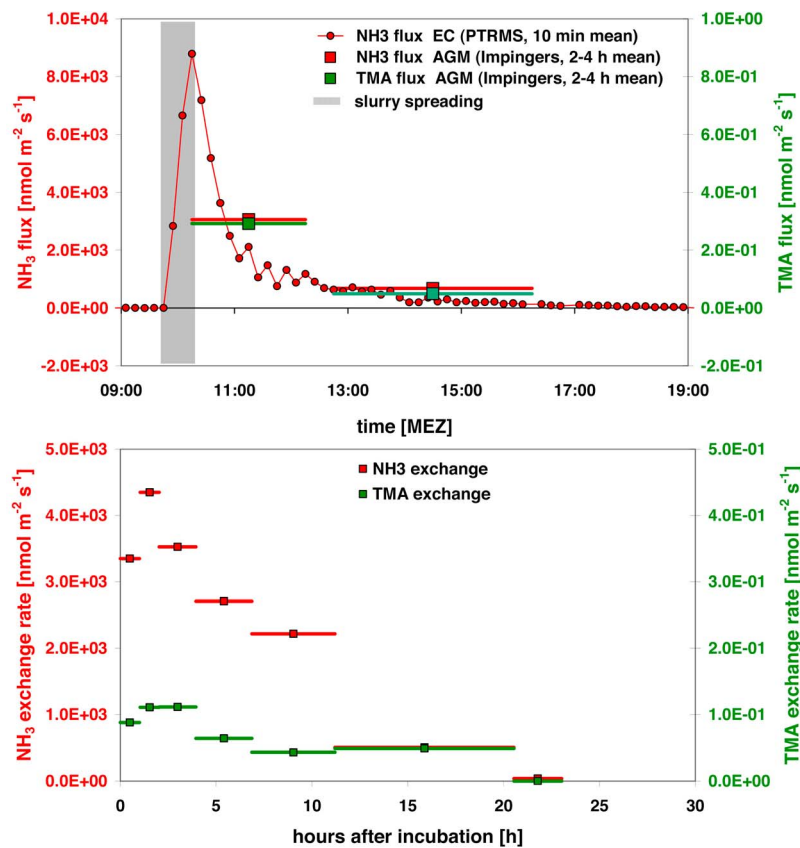


Figure 1. (top) Fluxes of NH₃ (red) and TMA (green) before/after application of stored slurry (gray bar) over a grassland site on 06 August 2009 in Oensingen, Switzerland. Squares are results from an Aerodynamic Gradient Method (AGM), with horizontal lines indicating impinger accumulation periods. Circles are results from an Eddy Covariance System (EC) by means of a customized PTRMS [Sintermann *et al.*, 2011]. (bottom) NH₃ and TMA emission rates of fresh cattle dung measured by means of dynamic enclosure studies.

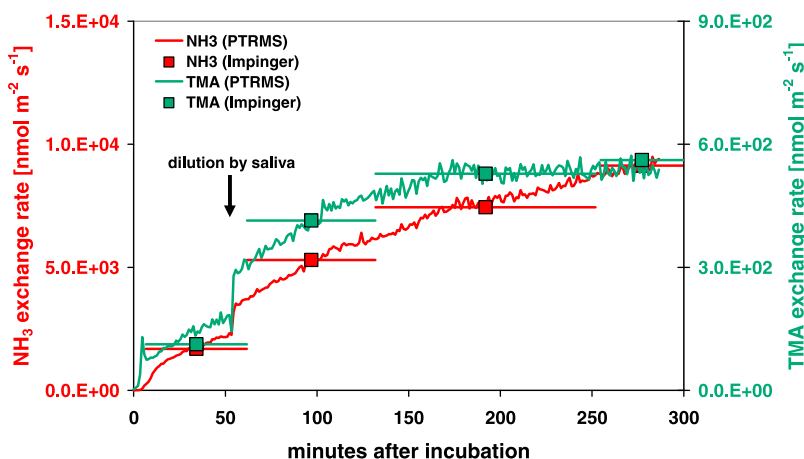


Figure 2. NH_3 and TMA emission rates of fresh cattle rumen juice measured by means of dynamic enclosure studies. Squares are results by means of impingers, with horizontal lines indicating the sample periods. Lines indicate high time resolution PTRMS data normalized to impinger concentrations. The arrow indicates 1/1 dilution of the rumen juice by artificial saliva.

samples from the farm's slurry that were taken directly prior to its application in the field, confirming the low amine emission capacity. TMA fluxes in the field were too low to be resolved with the EC flux method by means of PTRMS detection. We conclude that the emissions from dung and slurry cannot explain the observed enhanced amine concentration in the animal housing indoor air, and have to be considered not significant as global amine source. *Schade and Crutzen* [1995] supported the concept of transferring indoor TMA/ NH_3 emission ratio to outdoor grazing and slurry spreading conditions with the observations of *Hutchinson et al.* [1982] derived at a large cattle feedlot site. According to the results presented here, we conclude that the emission characteristics (source processes) in feedlots are similar to animal housings rather than to the conditions on agricultural field sites after slurry spreading.

3.3. Cattle Rumination Activity

[10] It is well known that ruminants exhale methane produced by their anaerobic enteric digestion, and this way cattle account for a significant share of the world's methane emissions to the atmosphere [*Steinfeld et al.*, 2006]. In the rumen, the largest (fore)stomach of ruminant animals (cattle, buffaloes, sheep, goats, and camels), microbial fermentation of fibrous forage produces methane, which is predominantly (98%) exhaled. Likewise, about 70% of the enteric degradation of nitrogen-bearing proteins is known to take place in the rumen, which apparently represents a biogenic source of amines. In order to test rumination as a relevant production process, we investigated the composition and the emission capacity of fresh rumen juice derived from two fistulated cows. Distillates of rumen juice revealed very high concentration ratios of dissolved TMA relative to NH_3 (about 2–3%; Table 1). Correspondingly, very high amine emission rates (6–8% relative to NH_3) from fresh rumen juice were observed by means of dynamic enclosure studies (Figure 2). The higher TMA/ NH_3 ratio in the emission rates compared to the liquid phase concentrations may be explained by the higher volatilization rate for TMA compared to NH_3 according to the difference in the Henry Constant of the two compounds. Hence, we attribute the production of amines to

enteric anaerobic microbial fermentation in the rumen, as has also been proposed for other volatile organic compounds not containing nitrogen [*Ngwabie et al.*, 2008].

[11] The rumination procedure may comprise a special role in the volatilization of basic compounds. During rumination, pre-digested forage portions are regurgitated from the rumen to the mouth. While the rumen enteric milieu is acidic (pH ~6.5), mastication in the mouth leads to alkalization of the pre-digested material by dilution with the animal's saliva (pH ~8). The increase in pH inherently amplifies the release of (formerly dissociated) basic compounds. The phenomenon of accelerated amine emissions by way of alkalization of forage material during rumination in the cattle's mouth could be simulated by adding artificial saliva (recipe by *McDougall* [1948]) to the rumen fluid during the enclosure measurements (Figure 2). After a (1/1) dilution with (TMA- and NH_3 -free) saliva, both the emissions of TMA and NH_3 increased almost twofold.

3.4. Grass and Silage Feed

[12] In principle, both, amines and NH_3 can ubiquitously be formed by biodegradation ("putrefaction") of reduced N-bearing organic matter [*Kataoka*, 1997], and thus animal feed represents another potential source of volatile amines. For ammonia, intact vegetation has a potentially bi-directional exchange behavior with compensation point concentrations in the low ppb range, but preferentially acts as a sink with respect to natural atmospheric concentrations [e.g., *Sutton et al.*, 2009]. In contrast, senescent leaves and decomposing plant litter are accounted as net sources for NH_3 [*Mattsson and Schjoerring*, 2003; *David et al.*, 2009; *de Ruijter et al.*, 2010]. Concerning green plant amine emissions, only references from the early 20th century are available, reporting about the incidence of volatile amines in extracts of cut plant tissues, specifically in those with high respiration activity like during bud break, flowering, or senescence [*Steiner and Löffler*, 1929; *Klein and Steiner*, 1928; *von Kamienski*, 1957]. We investigated the emission capacity of cut grass (*Lolium perenne*) with the dynamic enclosures system. While fresh samples of green grass directly after cutting did neither show significant NH_3 nor

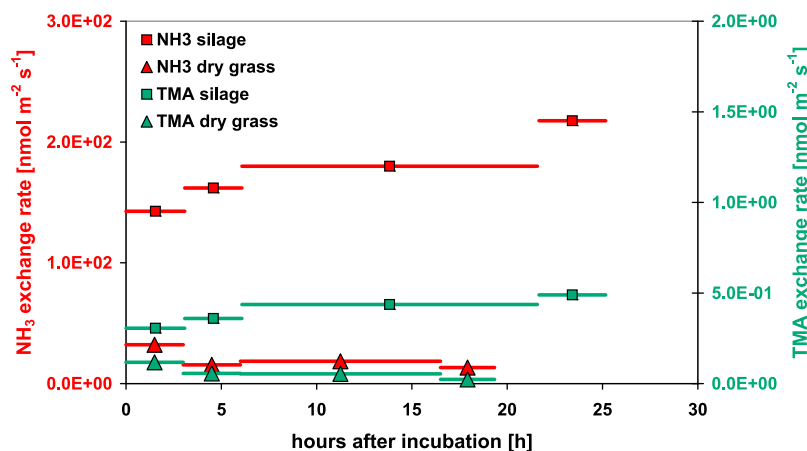


Figure 3. NH_3 and TMA emission rates of grass silage and dried grass measured by means of dynamic enclosure studies. Horizontal lines indicate impinger sample periods.

TMA emissions (data not shown), air-dried grass from the uppermost layer in a farm's hayloft and grass silage revealed significant TMA emissions scaling with NH_3 (Figure 3). Grass silage, which was enclosed and stored under anoxic humid conditions 1–2 days after cutting, showed generally stronger TMA and NH_3 emissions compared to air-dried hay. Anoxic storage conditions activate microbial fermentation similar to the conditions in a rumen, which might favor production of organic reduced N compounds. Accumulation by lack of ventilation also confers a reasonable explanation for observed higher amine emission rates, and the respective TMA/ NH_3 emission ratio for both dried grass and silage were in a similar range of 0.2–0.4%.

3.5. Relevance on Global Amine Inventory

[13] The present findings have substantial implications for the amine emission inventory. The insignificance of amine emissions from slurry applied in the field, which is accounted for about half (53%) of the global NH_3 emissions [Schade and Crutzen, 1995], would reduce the global agricultural amine emission estimate by this fraction. Residual amine sources were accounted to be the direct release from livestock buildings (32%) and from grazing ruminants (15%). Based on our findings, the latter number may be regarded as an upper limit, due to longer lasting NH_3 emission from dropped dung compared to exhalation-based field site amine emissions limited to periods when the animals are not housed (non-permanent pastures). Taking into account the above mentioned reduction in the original NH_3 -based extrapolation procedure, the updated global agricultural TMA emission ranges between 0.035 and 0.053 Tg N a^{-1} .

[14] The absolute numbers of TMA emission rates from vegetation observed in the present study were very low, comparable to the emissions from cattle manure. Nevertheless, vegetation may impact the global amine budget due to the vast occurrence and distribution of decaying plant organic material in managed as well as natural terrestrial ecosystems. The order of magnitude of the potential global vegetation source was estimated by a simple upscaling calculation using the mean TMA/ NH_3 emission ratio of 0.3% observed in our enclosure studies on hay and silage.

Current global NH_3 emissions from agricultural crops are estimated to about 3.6 Tg N a^{-1} [Bouwman *et al.*, 1997] or 4.0 Tg N a^{-1} [Galloway *et al.*, 2004], and the global NH_3 net source strength from natural terrestrial ecosystems is estimated to be about 4.6 Tg N a^{-1} [Galloway *et al.*, 2004]. Using the TMA/ NH_3 emission ratio as a proxy for the vegetation source would thus result in global TMA emissions in the order of 0.025 Tg N a^{-1} . This is of similar magnitude as the emissions from animal husbandry after correction for negligible emission from manure. These findings demonstrate the necessity of further exchange measurements, both in the field and under controlled environmental conditions in the laboratory.

4. Conclusions

[15] While for NH_3 the field application of slurry as agricultural fertilizer accounts for a major share of the emission source strength, we conclude that observed amine concentration enhancements in agricultural areas rather stem directly from the animals and from the animal's feed. Hence the release from animal housings and from grazing animals dominate the agricultural budget of biogenic amines, and the previous application of amine/ NH_3 proportionality factors on the total agricultural NH_3 emissions [Schade and Crutzen, 1995] seems to be questionable. If future direct measurements will confirm animal exhalation of amines as a dominant source, the amine/methane emission ratios may be a more adequate proxy for global upscaling exercises on amines from animal husbandry.

[16] Vegetation, namely plant decomposition processes, may represent an amine source of similar magnitude as animal husbandry. Both, the observed TMA/ NH_3 emission ratios of livestock farming and from vegetation were greater than 0.1% (see overview in Figure 4). Considering that amines are more important for nucleation at even lower concentrations than 0.1% of ammonia [Kurtén *et al.*, 2008], biogenic volatile amines have to be accounted the most important basic components enhancing nucleation in the atmosphere. Due to a relatively short atmospheric lifetime of only a few hours regarding reaction with the OH radical, this particularly applies to remotely situated farmland or natural

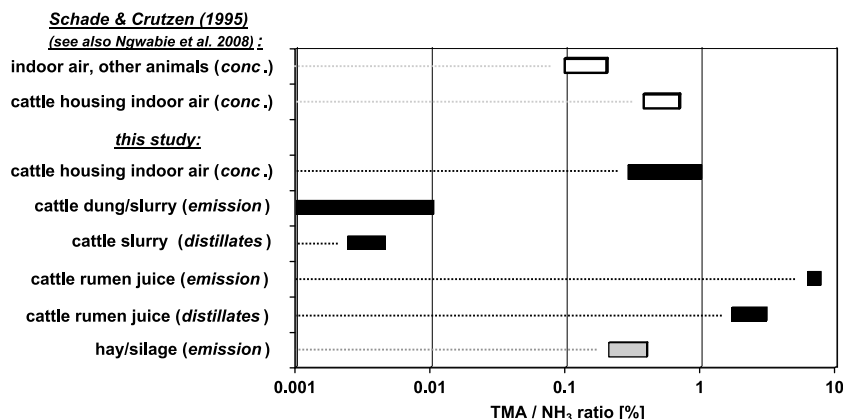


Figure 4. TMA/NH₃ ratios of animal housing air concentration and various possible amine sources in cattle husbandry (ratios either of emission rates, concentrations, or in substrate distillates).

ecosystems, missing strong sources of primary particles but being subject to ubiquitous and incessant degradation of (e.g. plant) organic matter.

[17] Other compounds found in rumen headspace samples, like, e.g., the reduced sulfur compound dimethyl sulphide (DMS) are also assumed to have an inverse “greenhouse effect” [Cai *et al.*, 2006]. To what extent the negative radiative forcing by way of enhanced particle formation via ruminant exhalations and emission by animal feed and decaying natural vegetation may counterbalance the well-known greenhouse effect of methane from cattle husbandry still has to be evaluated.

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