Measured ammonia emissions from tropical and subtropical pastures: A comparison with 2006 IPCC, 2019 Refinement to the 2006 IPCC, and EMEP/EEA (European Monitoring and Evaluation Programme and European Environmental Agency) inventory estimates

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ABSTRACT

Agriculture is the largest source of ammonia (NH₃) emissions. As NH₃ is an indirect greenhouse gas, NH₃ measurements are crucial to improving greenhouse gas emission inventory estimates. Moreover, NH₃ emissions have wider implications for environmental and human health. Only a few studies have measured NH₃ emissions from pastures in the tropics and subtropics and none has compared emissions to inventory estimates. The objectives of this study were to (1) measure NH₃ emissions from dairy pastures in tropical and subtropical regions; (2) calculate NH₃ emissions factors (EF) for each campaign; and (3) compare measured EF with those based on the 2006 Intergovernmental Panel on Climate Change (IPCC) Tier 1, 2019 Refinement to the 2006 IPCC Tier 1, and the European Monitoring and Evaluation Programme/European Environmental Agency (EMEP/EEA) Tier 2 inventory estimates. Pasture NH₃ emissions were measured on 3 dairy farms in Costa Rica. On each dairy, NH₃ emissions were measured twice during the wet season and once during the dry season using a micrometeorological integrated horizontal-flux mass-balance method. Emissions were measured from excreta (dung and urine) deposited by grazing cattle and the subsequent application of organic (slurry) or synthetic fertilizer (ammonium nitrate or urea). Measured EF for all campaigns [from grazing cattle excreta and any subsequent slurry or fertilizer application; 4.9 ± 0.9% of applied nitrogen (mean ±

SE)] were similar to those of the EMEP/EEA Tier 2 approach (6.1 ± 0.9%; mean ± SE) and 4 times lower than 2006 IPCC and 2019 Refinement to 2006 IPCC Tier 1 default estimates (17.7 ± 1.4 and 18.2 ± 0.9%, respectively; mean ± SE). Measured EF for excreta deposited on pasture and excreta both deposited on pasture and slurry application [3.9 ± 2.1 and 4.2 ± 2.1% (mean ± 95% CI), respectively] were 5 times lower than default EF assumed by 2006 IPCC and 2019 Refinement to 2006 IPCC methodology (both 20 and 21%, respectively), whereas EMEP/EEA estimates were similar [6.0 and 4.6 ± 0.3% (mean ± 95% CI), respectively]. This suggests an overestimation of EF from excreta deposited on pasture and slurry applications in tropical and subtropical regions by IPCC methodologies. Furthermore, rainfall, which is not included as a parameter in the current EMEP/EEA Tier 2 methodology, appeared to reduce NH₃ emissions, suggesting that accounting for this in the inventory methodologies could improve inventory estimates.

Key words: NH₃ emission, dairy, pasture, tropical

INTRODUCTION

Ammonia (NH₃) emissions are an environmental concern, both globally and locally. Globally, NH₃ emissions are an indirect source of nitrous oxide (N₂O) emissions, which contribute to global warming (IPCC, 2006b). Locally, NH₃ emissions cause eutrophication, soil acidification, loss of biodiversity, and, in combination with other atmospheric pollutants, the formation of fine particulate matter, which has damaging effects on human health (Giannadaki et al., 2018). In addition, NH₃ emissions are an economic concern because the loss of

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agronomic nitrogen increases the amount of commercial fertilizer needed to optimize crop and pasture yields (UNECE, 2015).

Agriculture is the largest source of NH_3 emissions worldwide, with emissions from livestock manure being a major contributor (Behera et al., 2013). In Central and South America, direct soil emissions and emissions from excreta deposited on pastures were estimated to have contributed 6% of global anthropogenic NH_3 emissions in 2012 (EDGAR; <http://edgar.jrc.ec.europa.eu/>).

Due to the growing demand for livestock products, global meat and dairy production is predicted to increase by 15 and 22%, respectively, by 2027, compared with the 2015–2017 period (OECD-FAO, 2018). In Latin America and the Caribbean (LAC), this production might increase at an even higher rate. In recent years the livestock sector in LAC had an annual growth rate of 3.5%, which was 67% greater than the global annual growth rate (2.1%; OECD-FAO, 2018).

A related issue has emerged because, throughout Central and South America, livestock are produced in pasture-based systems, one of the main drivers of deforestation, with deforestation being a leading cause of rising greenhouse gas levels in the atmosphere (Curtis et al., 2018). To reduce the rate of deforestation and promote reforestation, it is proposed that livestock production be increased through intensification of existing pasture-based systems (Cohn et al., 2014), as has been done in Costa Rica (MAG, 2019). Intensification of pasture-based systems in the tropics, however, would result in increased fertilizer applications and stocking rates. These, in turn, would increase the amount of N deposited on pastures through excreta from grazing cattle as well as fertilizer and manure applications (Rudel et al., 2015) and thus, increase the risk of NH_3 volatilization (Børsting et al., 2003; Smits et al., 2003).

Only a few field studies in Australia (Catchpoole et al., 1983; Harper et al., 1983; Prasertsak et al., 2001; Lam et al., 2018) and none in LAC have measured NH_3 emissions from tropical and subtropical pastures using noninvasive micrometeorological techniques. Therefore, more measurements of NH_3 emissions from tropical and subtropical pastures are needed to validate inventory estimates.

Currently, inventory estimates for NH_3 emissions of excreta (urine and dung) deposited by grazing cattle, as well as for fertilizer and manure applications from pastures in LAC, are made using 2006 Intergovernmental Panel on Climate Change (IPCC) Tier 1 default emissions factors (EF; the % of applied N volatilized as $\text{NH}_3\text{-N}$; IPCC, 2006b). We are concerned, however, that these 2006 IPCC Tier 1 EF may lack accuracy and

precision. Specifically, they do not distinguish between different types of organic or synthetic fertilizers or environmental and soil factors, although it has been long established that these factors can have a large impact on NH_3 volatilization from pastures (Núñez et al., 2007). In 2016, Tier 2 EF for NH_3 emissions were developed by the European Monitoring and Evaluation Programme (EMEP) and European Environmental Agency (EEA; EMEP/EEA, 2016a,b); in 2019, a refinement to the 2006 IPCC EF was completed (IPCC, 2019). Both the EMEP/EEA Tier 2 EF and the 2019 Refinement to the 2006 IPCC Tier 1 EF account for NH_3 emissions from different types of synthetic fertilizers. In addition, the EMEP/EEA Tier 2 EF differentiate between different manure management practices (EMEP/EEA, 2016a) and include the effect of climate and soil pH (EMEP/EEA, 2016b).

Given the limitations related to such estimations, the objectives of this study were to (1) measure NH_3 emissions from dairy pastures in the tropics and subtropics; (2) calculate NH_3 EF for each measurement campaign; and (3) compare measured EF with those provided by the 2006 IPCC Tier 1, 2019 Refinement to 2016 IPCC Tier 1, and EMEP/EEA Tier 2 methodologies.

MATERIALS AND METHODS

Between January 2018 and April 2019, pasture NH_3 emissions measurements were conducted on 3 commercial dairy farms in the Cartago province of Costa Rica, the country's second largest milk producing province (INEC, 2015). On each dairy farm, NH_3 measurements took place twice during the wet season and once during the dry season. Measurements were conducted from pastures that were managed under rotational grazing. As the time between grazing and subsequent slurry or synthetic fertilizer applications (urea or ammonium nitrate) was too short to distinguish between the 2 emission sources, NH_3 emissions from animal excreta and subsequent fertilizer applications were accounted for together. A combined EF across all N sources was therefore derived for each measurement campaign. Measured EF were compared with EF estimates based on 2006 IPCC Tier 1, 2019 Refinement to the 2006 IPCC Tier 1, and EMEP/EEA Tier 2 methodologies. Details of each measurement campaign, including soil and environmental factors, are presented in Table 1.

Study Sites

One dairy was the commercial dairy farm of the Tropical Agricultural Research and Higher Education Center (CATIE), located 3 km south east of Turrialba

Table 1. Details of measurement periods, emission sources, nitrogen (N) applications, meteorological conditions, and pasture conditions during the 3 campaigns on each of the 3 dairy farms

Item	Tropical lowland dairy ¹				Tropical/subtropical highland dairy 1 ¹				Tropical/subtropical highland dairy 2			
	January 2018	February 2018	April 2018	June 2018	October 2018	March 2019	August 2018	November 2018	February 2019			
Emission measurement	Jan 19–Feb 6	Feb 19–Mar 16	Apr 2–Apr 26	Jun 26–Jul 16	Oct 17–Oct 31	Mar 1–Mar 18	Aug 14–Aug 24	Nov 6–Nov 30	Feb 6–Feb 15			
Emission source	Excreta and ammonium nitrate									Excreta and urea		
Excreta, kg of N/ha	41.5	36.6	48.6	62.3	51.3	37.9	32.5	26.1	27.3			
AN, ² kg of N/ha	29.0	29.0	29.0	0	0	0	0	0	0			
Urea, kg of N/ha	0	0	0	0	0	64.2	0	8.6	0			
Slurry, kg of N/ha	0	0	0	22.1 ³	13.0 ⁴	0	0	0	0			
Season	Wet	Wet	Dry	Wet	Wet	Dry	Wet	Wet	Dry			
Temperature, °C	20.6 ± 2.8	20.9 ± 3.1	21.7 ± 2.9	16.6 ± 1.9	16.4 ± 1.9	15.4 ± 2.3	17.1 ± 1.9	17.1 ± 2.0	16.3 ± 2.8			
Rain, mm	81	63	39	234	56	22	30	78	0			
Wind frequency, % of time with wind >0 m/s	60	75	53	100	99	100	98	99	100			
Wind velocity when wind >0, m/s	1.1 ± 0.7	1.2 ± 0.8	1.4 ± 0.8	3.3 ± 1.3	2.9 ± 1.5	4.3 ± 1.4	3.6 ± 1.5	3.3 ± 1.4	4.5 ± 1.7			
Pasture composition	44 ± 10% <i>Cynodon dactylon</i> (Estrella), 51 ± 6% <i>Brachiaria arrecta</i> (Tanner), and 5 ± 5% other									0 ± 9% <i>Cynodon dactylon</i> (Estrella), 15 ± 9% <i>Sacateburro</i> , 8 ± 11% <i>Pennisetum clandestinum</i> (Kikuyu), and 6 ± 9% other		
Soil type	Loam (40.6 ± 0.3% sand, 34.9 ± 1.5% silt, and 24.6 ± 1.2% clay) ⁵									Loam (49.9 ± 5.2% sand, 35.9 ± 3.7% silt, and 14.1 ± 1.8% clay)		
Soil pH	5.7	— ⁵	5.8	5.8	5.8	5.9	5.7	5.6	5.6			
Soil N, %	0.31	—	0.38	0.81	0.81	0.67	0.74	0.68	0.76			
Soil carbon, %	3.0	—	4.1	8.1	8.2	7.6	9.7	8.5	9.7			
Soil OM, ⁶ %	5.2	—	7.0	14.0	14.2	13.03	16.7	14.6	16.7			
Soil bulk density, g/cm ³	—	1.03 ± 0.13	—	0.72 ± 0.10	0.66 ± 0.11	0.73 ± 0.08	—	0.67 ± 0.05	0.67 ± 0.02			

¹Meteorological data were lost and replaced by data from National Meteorological Institute during the following dates: 1500 h on Jan 18, 2018, to 1330 h on Jan 30, 2018; 1500 h on Mar 14, 2019, to 0750 h on Mar 15, 2019; 0850 to 1520 h on Jul 6, 2018; 1510 h on Oct 16, 2018, to 1720 h on Oct 17, 2018; 1025 to 1125 h on Oct 30, 2018; 0200 to 1700 h on Mar 7, 2019; and 1900 h on Mar 7, 2019, to 0950 h on Mar 15, 2019.

²AN = ammonium nitrate.

³Slurry contained 0.07% total N.

⁴Slurry contained 0.048 ± 0.002% total N, 0.95 ± 0.17% DM, and ammonium-N 0.025 ± 0.002% (mean ± SD).

⁵Indicates that no measurements were conducted.

⁶Soil OM was calculated by multiplying % soil carbon by 1.724.

in a tropical rainforest climate (Af on the Köppen-Geiger climate classification) at 638 m above sea level (hereafter, the tropical lowland dairy). The other 2 dairies were located 11 km east of the city of Cartago in a summer tropical monsoon climate and dry winter subtropical highland climate (Am and Cwb on the Köppen-Geiger climate classification, respectively) at 1,714 and 1,603 m above sea level (hereafter, tropical/subtropical highland dairies 1 and 2, respectively). On all dairy farms, lactating cows were grazed under a rotational regimen and supplemented with additional feed (forage and nonforage feeds) in the livestock housing twice a day, before milking. On the tropical lowland dairy and the tropical/subtropical highland dairy 1 cows returned to grazing after p.m. milking during each measurement campaign. On tropical/subtropical highland dairy 2, cows only returned to grazing after p.m. milking when pasture availability was high during the wet season measurement campaigns and stayed indoors overnight during the dry season campaign.

On the tropical lowland dairy, measurements were conducted on pastures with 88 ± 4 lactating dual-purpose cattle (mean $\pm$ SD). During the measurement campaigns (January 2018, February 2018, and April 2018), cows grazed on 0.52 ha of pasture [one half of the pasture after p.m. milking (0.26 ha) and the other half after a.m. milking (0.26 ha)] for 16.4 ± 1.0 h (mean $\pm$ SD); average milk production was 22.6 ± 1.6 kg/cow per day (mean $\pm$ SD), and average DMI was 19.7 ± 0.7 kg/cow per day [10.4 ± 0.6 kg of forage and nonforage feed DM/cow per day (concentrate feeds and cut forages) and 4.4 ± 2.9 kg of pasture/cow per day (mean $\pm$ SD)]. On the tropical/subtropical highland dairy 1, measurements were conducted on 94 ± 7 lactating Holstein cows (mean $\pm$ SD). During the measurement campaigns (June 2018, October 2018, and March 2019), cows were grazed on 0.17 ± 0.02 ha (mean $\pm$ SD) for 9.2 ± 0.3 h, average milk production was 31.6 ± 1.0 kg/cow per day (mean $\pm$ SD), and average DMI was 24.2 ± 0.2 kg/cow per day [19.8 ± 2.7 kg of forage and nonforage feed DM/cow per day and 4.4 ± 2.9 kg of pasture/cow per day (mean $\pm$ SD)]. On tropical/subtropical highland dairy 2, measurements were conducted on pastures with 127 ± 11 lactating Brown Swiss cows (mean $\pm$ SD) during all 3 measurement campaigns (August 2018, November 2018, and February 2019). In addition, measurements were conducted on 23 dry cows that grazed the same pasture 2 d after the lactating cows during the August 2018 measurement campaign. During the 3 measurement campaigns, lactating cows were grazed on 0.44 ± 0.02 ha of pasture for 8.0 ± 0.3 h (mean $\pm$ SD). Average milk production was 21.3 ± 1.0 kg/cow per day (mean $\pm$ SD), and average DMI

was 21.2 ± 0.7 kg/cow per day [13.8 ± 1.6 kg of forage and nonforage feed DM/cow per day and 7.4 ± 1.2 kg of pasture/cow per day (mean $\pm$ SD)].

Measurements of Ammonia Emissions

Pasture NH_3 measurements consisted of baseline measurements before grazing (1–4 d) and emission measurements during and after grazing, including emission measurements from any subsequent postgrazing application of slurry or synthetic fertilizer (9–29 d). Ammonia emissions were measured using the micrometeorological integrated horizontal-flux method (Denmead et al., 1977) and passive flux samplers (PFS; Leuning et al., 1985). For each measurement campaign, 5 PFS coated in a 3% solution of oxalic acid in methanol were deployed on a downwind vertical mast (4 m) at approximate heights of 4.0, 3.0, 2.0, 1.0, and 0.5 m (exact heights recorded on each occasion) in the pasture from which emission measurements were to be made. At the same time, 3 PFS were deployed on an upwind mast in an untreated neighboring pasture at approximate heights of 4.0, 2.0, and 0.5 m to measure the background flux. Closed PFS were deployed on the upwind mast at heights of 1.0 and 3.0 m and used as blanks. The PFS were deployed for periods between 8 and 96 h, depending on expected NH_3 emissions. Following exposure, the PFS were eluted with 40 mL of deionized water and the extracts were stored at $<4^\circ\text{C}$ until analyzed for ammonium (Misselbrook et al., 2005b).

During each measurement campaign, temperature, rainfall, and wind direction and velocity were recorded every 5 min by a Davis Instruments Vantage Pro II meteorological station (Hayward, CA) within 50 m of the treated pasture. When meteorological data were lost, they were replaced by hourly data from a weather station of the National Meteorological Institute (IMN, San José, Costa Rica) within 5 km of each pasture (Table 1).

The net horizontal flux of pasture $\text{NH}_3\text{-N}$ emissions was calculated in 2 steps according to Leuning et al. (1985). First, the mean horizontal flux, $\overline{uc}$ (kg of $\text{N}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) at each height for each sampling period was calculated as follows:

$$\overline{uc} = \frac{M}{At},$$

where M is the mass of $\text{NH}_3\text{-N}$ collected (mg) in the sampler during the sampling period, t (s), and A is the effective cross-sectional area of the sampler (m^2) as determined in wind tunnel calibrations. Second, the net

horizontal flux of $\text{NH}_3\text{-N}$ from the treated area (F , μg of $\text{N}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) was obtained by subtracting the integrated horizontal flux of the upwind mast (uw) from that of the downwind mast (dw):

$$F = \frac{1}{x} \left[\int_0^z (\overline{uc})_{\text{dw}} dz - \int_0^z (\overline{uc})_{\text{uw}} dz \right],$$

where x represents the mean fetch length, based on the geometry of the pasture, and z (m) the height of the uppermost sampler.

Experimental pastures were chosen to ensure flat uniform surfaces with few nearby trees to avoid wind disturbance. For periods when windspeed was 0 m/s, a fetch length of 0 m was assigned. The cumulative emission over the entire measurement campaign (from grazing cattle excreta and any subsequent slurry or fertilizer application) was derived by summing the net flux determined for each sampling period. Emission fluxes over time for each campaign are reported in Supplemental Figures S1 to S9 (<https://doi.org/10.3168/jds.2019-17825>).

Estimation of Ammonia Emissions

Ammonia emissions were estimated using 2006 IPCC Tier 1 (IPCC, 2006b), 2019 Refinement to 2006 IPCC Tier 1 (IPCC, 2019), and EMEP/EEA Tier 2 methodology (EMEP/EEA, 2016a,b). For this, it was necessary to estimate the amount of N deposited by grazing animals and applied in the form of slurry or fertilizer on the pasture. Estimates of N deposited on the pasture were based on estimated daily N excretion per cow, number of grazing cows, and the time spent grazing per day. Fertilizer and slurry N applications rates were estimated based on the amount of slurry or synthetic fertilizer applied and its N content.

Daily N deposited per cow was calculated as the difference between N intake and N output in milk. Nitrogen intake was estimated based on a calculation of the feed DMI needed to meet the energy requirements of the dairy cows following 2006 IPCC methodology (IPCC, 2006a) and the N content of the feed consumed. Net energy requirements for maintenance, activity, lactation, and pregnancy used farm-specific data on cow live weight (measured using a scale for the tropical lowland dairy and a body tape for the tropical/subtropical highland dairies), the 0.17 coefficient for activity, milk yield and composition (recorded on farm), and assumed that 80% of lactating animals in the herd were pregnant (IPCC, 2006a). We assumed no net change in live

weight by the cows, and hence no net energy requirement for gain or loss. The DM, gross energy, and N intake from feed provided in the livestock housing was calculated based on the amount of feed consumed. The amount of total feed consumed was estimated assuming a diet energy digestibility (% digestible energy) of 65% for feeds supplemented in the animal housing and for the pasture (based on 55–75% of digestible energy for good pastures, good preserved forages, and grain-supplemented forage-based diets) and a diet energy density of 18.45 MJ/kg of DM (IPCC, 2006a).

Composition of feed provided in the livestock housing and grazed pasture were determined from samples taken for each measurement campaign. At a.m. and p.m. milkings during the first pasture measurement, feed samples were taken, and the amount of feed provided was recorded. Quadrat (50 × 50 cm) samples were taken from the measured pasture before the cows entered for grazing, and pasture species composition was determined by visual assessment. Feed and pasture samples were stored at -20°C until oven-dried at 55°C to a constant weight. Dried samples were ground to pass through the 2-mm screen of a Wiley mill (Arthur H. Thomas Co., Philadelphia, PA) and analyzed for total N.

The form of fertilizer N and amount applied (if appropriate) to the pasture were recorded for each farm. Slurry was applied at the tropical/subtropical highland dairy 1 using a cannon slurry spreader at low pressure during both wet season measurement campaigns 1 d after the cows grazed the pasture (August 2018 and October 2018). Slurry consisted of dung and urine excreted during feed supplementation and milking and wash water from the livestock housing and milking parlor. Slurry was sampled during the first campaign after the slurry tank had been thoroughly mixed by pumping and during the second campaign by positioning 5 buckets in random locations on the field during slurry application. The sampled slurry was stored at 4°C until analyzed for total N and DM. In addition, the sampled slurry from the October 2018 campaign was analyzed for total ammonium N (TAN) and pH. The volume of slurry application and slurry N content was then used to estimate the slurry N application rate. As cattle spent only about 6 h/d in livestock housing (mainly during milking), and water was used to clean the parlors, the total N, TAN, and DM contents of the slurry were very diluted ($<0.05\%$, $<0.03\%$, and $<1.0\%$, respectively; Table 1). Indeed, slurry composition was similar to that of dirty water (AHDB, 2017).

Ammonia emission predictions were made based on 2006 IPCC Tier 1, 2019 Refinement to 2006 IPCC Tier 1, and EMEP/EEA Tier 2 methodology and the

estimated amounts and forms of N deposited on each pasture during each measurement campaign. The 2006 IPCC Tier 1 default EF estimates that 10% (uncertainty range 3 to 30%) of N from applied synthetic fertilizer and 20% (uncertainty range 5.0 to 50%) of N from all organic fertilizer (including slurry applications and animal excreta deposited on a pasture) are volatilized as $\text{NH}_3\text{-N}$. In contrast, the 2019 Refinement to 2006 IPCC Tier 1 default accounts for differences between fertilizer types, and estimates that 15 (uncertainty range 3.0 to 43%) and 5% (uncertainty range 0 to 20%) of N from urea and ammonium-nitrate, respectively, are volatilized as $\text{NH}_3\text{-N}$. For organic fertilizer (slurry) and animal excreta deposited on pasture by grazing cattle, the default EF is 21% (uncertainty range 0 to 31%). The EMEP/EEA Tier 2 methodology estimates that under warm climate conditions with normal soil pH ($\text{pH} \leq 7$) 19.8 and 2.0% of N from urea and ammonium nitrate, respectively, are volatilized as $\text{NH}_3\text{-N}$. The Tier 2 EF for grazing cattle and slurry application are 10 and 55%, respectively, of TAN excreted or applied, with TAN assumed to be 60% of the total N content, which equals an EF of 6 and 33% for applied excreta and slurry, respectively.

Soil Sampling

Soil samples to 20 cm depth were taken during each measurement campaign on each dairy farm, except for the tropical lowland dairy during the second campaign (February 2018), and analyzed for pH, N, and C. Soil bulk density was determined using the cylinder method (Blake and Hartge, 1986), with samples taken at 5 locations for each pasture to 20 cm depth.

Laboratory Analysis

Soil pH was analyzed by extraction of water in a ratio of 1:2.5 (Díaz and Hunter, 1978). Slurry pH was measured directly using a pH meter (Orion Research with glass electrode; Orion Research Inc., Cambridge, MA). Soil minerals were determined by modified Olson solution at pH 8.5 in a ratio of soil and water of 2.5:25. Analytical DM content was determined by drying samples at 105°C for 3 h (Shreve et al., 2006). Slurry DM was determined by oven drying at 105°C for 24 h. Nitrogen content of dietary supplements, pasture, soil, and slurry was determined using a ThermoFinnigan analyzer (Flash EA 1112 Elemental Analyzer Operation Manual, ThermoFinnigan Italia, Milan, Italy). The ammonium-N content was determined using the Kjeldahl method without digestion (AOAC, 1980). Ammonium concentration of the water extracts from

the PFS was analyzed by colorimetric method according to Baethgen and Alley (1989).

Statistical Analysis

The statistical analysis of measured and estimated EF was carried out using R (version 3.5.1; <https://www.R-project.org/>) with the nlme package and the following mixed-effects model:

$$Y_{ij} = \mu + m_i + d_j + e_{ij},$$

where Y_{ij} is the dependent variable (EF); μ is the overall mean; m_i is the fixed effect of method (measurement, IPCC, or EMEP); d_j is the random residual effect of dairy farm ($j = 1$ to 3); and e_{ij} is the random residual, assumed to be normally and independently distributed.

RESULTS AND DISCUSSION

Measured Ammonia Emissions

Measured NH_3 emissions were lowest for excreta and ammonium nitrate during the wet season for the tropical lowland dairy compared with the tropical/subtropical highland dairies (Table 2). Low NH_3 emissions were expected, as the Tier 2 EF for ammonium nitrate fertilizer is only 2% for warm climates and normal soil pH (EMEP/EEA, 2016b). However, the measured EF for the January 2018 campaign was close to 0%. This might have been the result of N runoff due to saturated soils caused by heavy rain before the start of the NH_3 measurements (202 mm of rain during the 3 d of baseline measurements and 15 mm of rainfall during the first 48 h of emission measurements). In addition, 6 mm of rain fell within 24 h after the application of ammonium nitrate, potentially leading to N runoff or N being moved below the soil surface, resulting in low NH_3 emissions. Similarly, during the February 2018 campaign, 15 mm of rain fell within 24 h after cows grazed the pasture and 5 mm of rain fell within 24 h of ammonium nitrate application. Rainfall has previously been shown to decrease total NH_3 emissions from applied fertilizer N and cattle slurry, with the amount and timing being of importance (Misselbrook et al., 2004, 2005b; Chambers and Dampney, 2009). Emissions were greater during the dry season (April 2018 campaign) than during the wet season campaigns (January and February 2018), as might be expected with the lower incidence of rainfall and higher temperatures.

At tropical/subtropical highland dairy 2, excreta and slurry emissions were smaller during the June 2018 campaign than during the October 2018 campaign

Table 2. Measured accumulated ammonia nitrogen ($\text{NH}_3\text{-N}$) emissions and emission factors from excreta (dung and urine) deposited by grazing cattle and organic or synthetic fertilizer (slurry or synthetic fertilizer) when applied on pastures of 3 Costa Rican dairy farms

Dairy	Measurement campaign	Emissions source	Accumulated $\text{NH}_3\text{-N}$, kg of $\text{NH}_3\text{-N}/\text{ha}$	Emission factor, % of N volatilized as $\text{NH}_3\text{-N}$
Tropical lowland dairy	January 2018	Excreta and AN	0.1	0.1
	February 2018	Excreta and AN	1.3	2.0
	April 2018	Excreta and AN	2.6	3.4
Tropical/subtropical highland dairy 1	June 2018	Excreta and slurry	2.2	2.6
	October 2018	Excreta and slurry	3.7	5.7
	March 2019	Excreta and urea	12.8	12.5
Tropical/subtropical highland dairy 2	August 2018	Excreta	1.8	5.5
	November 2018	Excreta and urea	3.4	9.7
	February 2019	Excreta	0.7	2.4

¹AN = ammonium nitrate.

(combined EF of 2.6% vs. 5.7%). The difference in NH_3 emissions cannot be explained by the higher rainfall during the June 2018 compared with the October 2018 campaign (234 vs. 56 mm) because 152 mm of the rain during June fell within the last 73 h of the measurements, nor by other factors such as temperature, as they were similar (Table 1). Measured EF for excreta and urea emissions during the dry season (March 2019 campaign) at tropical/subtropical highland dairy 1 were greater, although not markedly so, than for excreta and urea emissions from subtropical/tropical highland dairy 2 during the wet season. The combined EF, accounting for both excreta and urea fertilizer application (9.7 and 12.5% for dry and wet season, respectively) were within the range of EF reported by other authors for urea applications of subtropical pastures. Lam et al. (2018) reported an EF of 15.8% during the dry season and Harper et al. (1983) reported EF of 9, 12, 42, and 13% during spring, summer, autumn, and winter, respectively. Although for our study, we cannot derive independent EF for the excreta and urea fertilizer, EF for urea have been shown to increase with increasing application rate (Rochette et al., 2013), and this may partly explain the observed lower EF on tropical/subtropical highland dairy 2 compared with dairy 1 (9.7 vs. 12.5%) as the urea N application rate on the tropical/subtropical highland dairy 2 was lower than on the tropical/subtropical highland dairy 1 (8.6 vs. 64.2 kg of N/ha).

For excreta only, the EF on the tropical/subtropical highland dairy 2 was greater during the wet (August 2018 campaign with 30 mm of rain) than the dry season (February 2018 campaign with 0 mm of rain; 5.5 vs. 2.4%, respectively). This is contrary to what was expected because infiltration of urine into the soil is affected by the antecedent soil water content, being greater when the soil is moist than when dry (Doak, 1952). Additionally, mean temperature was only slightly lower during the February 2019 compared with

the August 2018 campaign (16.3 vs. 17.1°C). However, results are similar to emissions reported by Petersen et al. (1998), who found that NH_3 volatilization from urine ranges from 2 to 52% of urinary N and that NH_3 volatilization of dung in pastures is negligible.

Measured and Estimated Emission Factors

The EF derived from NH_3 measurements for all campaigns (from grazing cattle excreta and any subsequent slurry or fertilizer application; mean $\pm$ SE = $4.9 \pm 0.9\%$) were similar to 2006 IPCC Tier 1 minimum estimates (mean $\pm$ SE = $3.9 \pm 0.9\%$; $P = 0.63$) and those derived using the EMEP/EEA Tier 2 approach (mean $\pm$ SE = $6.1 \pm 0.9\%$; $P = 0.98$; Figure 1). They were 4 times lower than 2006 IPCC default Tier 1 estimates (mean $\pm$ SE = $17.7 \pm 1.4\%$; $P < 0.001$) and 2019 Refinement to 2006 IPCC default Tier 1 estimates (mean $\pm$ SE = $18.2 \pm 0.9\%$; $P < 0.001$). The EF estimated by EMEP/EEA Tier 2 methodology were closest to EF derived from all measurement campaigns. This is most likely because the EMEP/EEA Tier 2 methodology approach estimates lower EF for excreta deposited by grazing cattle on pastures. Measured EF for excreta deposited by grazing cattle (mean $\pm$ 95% CI = $3.9 \pm 2.1\%$; Table 2) were 5 times lower than default EF assumed by 2006 IPCC and 2019 Refinement to 2006 IPCC methodology (20 and 21%, respectively), whereas the EF assumed by EMEP/EEA methodology (6.0%) was similar. These results, in combination with measured EF for both excreta deposited by grazing cattle and applied slurry (mean $\pm$ 95% CI = $4.2 \pm 2.1\%$; Table 2) suggest that the 2006 IPCC and the 2019 Refinement to 2006 IPCC default Tier 1 EF for cow excreta and slurry (both 20 and 21.0%, respectively) might overestimate emissions for slurry, whereas EMEP/EEA estimates are similar to those measured in this study (mean $\pm$ 95% CI = $4.6 \pm 0.3\%$). The very low slurry N and DM content ($<0.1\%$ and $<1.0\%$, respectively) are likely to explain the low

Figure 1. Measured emission factors (EF) compared with those estimated [minimum (Min), default, and maximum (Max)] by 2006 IPCC (IPCC, 2006a,b), 2019 Refinement to the 2006 IPCC (IPCC, 2019), and EMEP/EEA (2016a,b) (all $n = 9$). Emission factors are presented as least squares means of the percentage of applied nitrogen that is volatilized as ammonia nitrogen (NH₃-N). Error bars represent standard errors; least squares means not sharing common letters (a–e) are significantly different ($P < 0.05$).

NH₃ emissions from slurry (Sommer and Olesen, 1991; Misselbrook et al., 2005a). Nevertheless, both the EF for excreta and slurry should undergo further evaluation for the tropics and subtropics.

CONCLUSIONS

Our results suggest that 2006 IPCC Tier 1 and 2019 Refinement to 2006 IPCC Tier 1 methodology overestimate NH₃ emissions from excreta deposited by grazing dairy cattle on pastures in the tropics and subtropics, whereas the EMEP/EEA Tier 2 methodology does not. Further, it suggests that EF for 2006 IPCC and 2019 Refinement to 2006 IPCC methodologies overestimate EF for applications of the very dilute slurries associated with these dairy systems. To verify the findings of this study, we recommend further NH₃ measurements

from excreta and slurry in the tropics and subtropics and also recommend revision of the 2006 IPCC and 2019 Refinement to 2006 IPCC Tier 1 EF if needed. Until then, NH₃ emissions in the tropics and subtropics seem to be best predicted by EMEP/EEA Tier 2 methodology. In countries with high numbers of grazing livestock, we recommend the use of EMEP/EEA Tier 2 methodology instead of the 2006 IPCC Tier 1 or 2019 Refinement to 2006 IPCC Tier 1 methodology. Rainfall, which is not included as a parameter in the current EMEP/EEA Tier 2 methodology, appeared to influence NH₃ emissions from grazed pastures. This is of particular significance for tropical and subtropical systems due to rainfall extremes during wet and dry seasons. Accounting for this in the inventory methodologies (perhaps using a “seasonal” factor) could improve inventory estimates.

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