Measurement report: Emission factors of NH₃ and NHₓ for wildfires and agricultural fires in the United States

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Abstract. During the 2019 Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ) study, the NASA DC-8 carried out *in situ* chemical measurements in smoke plumes emitted from wildfires and agricultural fires in the contiguous US. The DC-8 payload included a modified proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) for the fast measurement of gaseous ammonia (NH₃) and a high-resolution time-of-flight aerosol mass spectrometer (AMS) for the fast measurement of submicron particulate ammonium (NH₄⁺). We herein report data collected in smoke plumes emitted from six wildfires in the Western US, two prescribed grassland fires in the Central US, one prescribed forest fire in the Southern US, and 66 small agricultural fires in the Southeastern US. Smoke plumes contained double to triple digit ppb levels of NH₃. In the wildfire plumes, a significant fraction of NH₃ had already been converted to NH₄⁺ at the time of sampling (≥2 h after emission). Substantial amounts of NH₄⁺ were also detected in freshly emitted smoke from corn and rice field fires. We herein present a comprehensive set of emission factors of NH₃ and NHₓ, with NHₓ = NH₃ + NH₄⁺. Average NH₃ and NHₓ emission factors for wildfires in the Western US were 1.86 ± 0.75 g kg⁻¹ of fuel burned and 2.47 ± 0.80 g kg⁻¹, respectively. Average NH₃ and NHₓ emission factors for agricultural fires in the Southeastern US were 0.89 ± 0.58 g kg⁻¹ and 1.74 ± 0.92 g kg⁻¹, respectively. Our data show no clear inverse correlation between modified combustion efficiency (MCE) and NH₃ emissions. The observed NH₃ emissions were significantly higher than measured in previous laboratory experiments in the FIREX FireLab 2016 study.

1 Introduction

Ammonia (NH_3) is an important trace gas in the Earth's atmosphere that is mostly emitted from agriculture, traffic, the oceans and biomass burning. In the presence of acids, NH_3 rapidly partitions to aerosol particles, which in turn impact air quality and climate (Seinfeld and Pandis, 2016). In much of the atmosphere, NH_3 exhibits a major influence on particle acidity (pH), which is a major controlling parameter for many important aerosol physical and chemical processes (*e.g.*, Pye et al., 2020; Nault et al., 2021). NH_3 is also the largest contributor to deposition of nitrogen from the atmosphere to soil and vegetation, causing surface water eutrophication, soil acidification, and ultimately biodiversity loss (*e.g.*, Bobbink and Higgs, 2014).

Fires emit NH_3 predominantly during smoldering combustion, which occurs at low temperatures (*e.g.*, Lobert et al., 1990; Yokelson et al., 1996, 1997; Goode et al., 1999; McMeeking et al., 2009; Burling et al., 2010; Roberts et al., 2020). NH_3 is typically the third most abundant nitrogen compound (after N_2 and NO) and the most abundant reduced nitrogen compound emitted from fires (Lobert et al., 1990; Roberts et al., 2020; Lindaas et al., 2021).

An important parameter for investigating the atmospheric impact of NH_3 is the emission factor, EF_{NH_3}, which is the mass of NH_3 (in g) that is emitted per mass of fuel burned (in kg). Several literature reviews (Andreae and Merlet, 2001; Akagi et al, 2011; Andreae, 2019; Prichard et al., 2020) report EF_{NH_3} values for different types of fire fuels. A closer look at the literature reveals that emissions from fuels that are typical of the United States (US) have mostly been studied in the laboratory (*e.g.,* Yokelson et al., 1996; McMeeking et al., 2009; Burling et al., 2010; Stockwell et al., 2015; Selimovic et al., 2018; Roberts et al., 2020). Previous work has shown that laboratory fires may not realistically simulate fires occurring in the real world due to different burning conditions and the lack of heterogeneity in fuels (*e.g.*, Yokelson et al., 2013; Hodshire et al., 2019). Only very few studies have reported EF_{NH_3} derived from measurements carried out in the field (*e.g.*, Lindaas et al., 2021).

The limited availability of field data is mostly because NH_3 is difficult to measure. NH_3 is a "sticky" molecule that easily adsorbs onto inlet and instrumental surfaces. This makes fast airborne measurements of NH_3 particularly challenging. Müller et al. (2014; see Supplement) have shown that proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) can be used for airborne NH_3 measurements, although with some limitations tied to a relatively slow time response and a poor detection limit due to a large intrinsic background. The conventional University of Innsbruck PTR-ToF-MS instrument has measured NH_3 with such constraints in previous airborne studies (Sun et al., 2015; Kelly et al., 2018; Guo et al., 2021; Da Pan et al., 2021).

The Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ) study was a joint NOAA/NASA effort to investigate the atmospheric impact of wildfires and agricultural fires in the contiguous US (Warneke et al., 2022). In summer 2019, the NASA DC-8 Airborne Science Laboratory performed *in situ* measurements in smoke plumes emitted from wildfires in the Western US and agricultural fires in the Southeastern US. The aircraft payload included a modified PTR-ToF-MS instrument that was optimized for the fast measurement of NH_3. It also included an aerosol mass spectrometer (AMS) for fast

measurement of submicron particulate ammonium (NH_4^+). This allowed us to measure and report a set of emission factors of NH_3 and NH_x, with $NH_x = NH_3 + NH_4^+$, for different types of fires.

2 Methods

70 **2.1 FIREX-AQ**

The FIREX-AQ experiment has been described in detail by Warneke et al. (2022). During the 2019 field campaign, NH_3 and NH_4^+ were measured aboard the NASA DC-8 in smoke plumes emitted from six wildfires in the Western US (Shady, Williams Flats, Castle, Ridge Top, Mica/Lick Creek, Horsefly), two prescribed grassland fires in the Central US (Hickory Ridge State Wildlife Management Area, Tallgrass Prairie National Preserve), and one prescribed forest fire in the Southern US (Black
75 Water River State Forest) (Fig. 1).

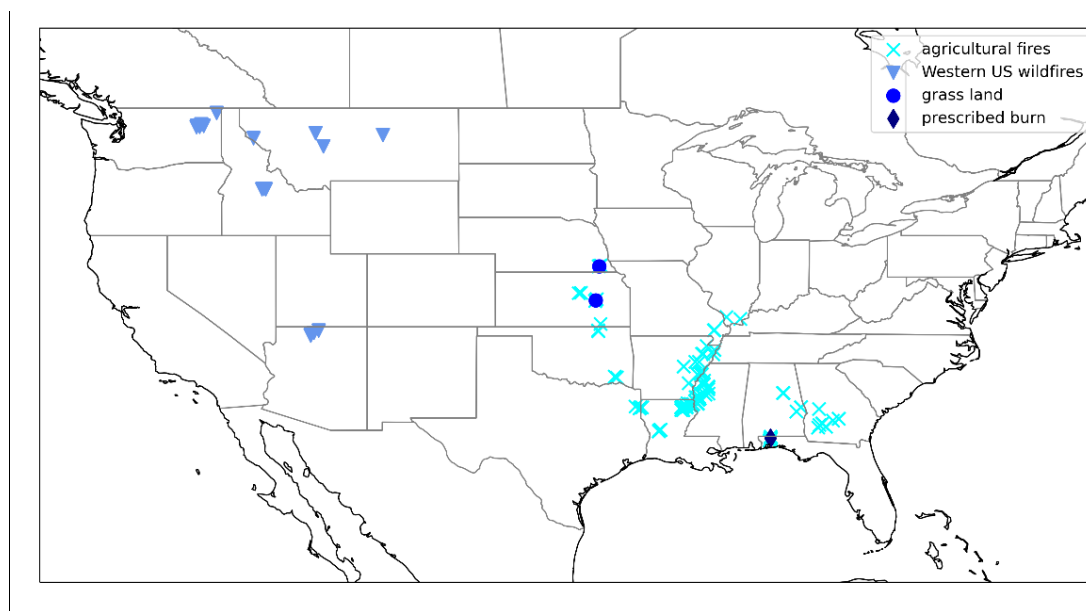



Figure 1: Location of the fires that were sampled by the NASA DC-8 during the FIREX-AQ 2019 campaign and for which NH_3 and NH_4^+ data were obtained.

Several downwind transects were typically flown in the smoke plumes emitted from the wildfires. In addition, the NASA DC-
80 8 sampled smoke plumes from a large number of agricultural fires in the Southeastern US. These small plumes were typically sampled twice in perpendicular direction. We successfully measured NH_3 and NH_4^+ in plumes emitted from 66 agricultural fires.

Vegetation and fuel type information is summarized in Tab. S1. Information about fuel types was obtained from the 30 m Fuel Characteristic Classification System (FCCS; Ottmar et al., 2007), the 30 m Cropland Data Layer classification 2019 dataset,
85 and ground intelligence.

2.2 Instrumentation

A modified PTR-ToF-MS instrument was used for fast-response measurements of NH_3 aboard the NASA DC-8 during FIREX-AQ. The conventional airborne PTR-ToF-MS analyzer has been described in detail by Müller et al. (2014). Only the modifications pertinent to the fast measurement of NH_3 are thus described here.

For reducing the instrumental NH_3 background, 12-25 standard cubic centimeters per minute (sccm; "standard" herein means referenced to a temperature of 273.15 K and a pressure of 101325 Pa) of ultra-pure helium (6.0; Praxair Inc., Danbury, CT, US) were introduced into the source drift region between the drift tube and the ion source. This reduced the backflow of nitrogen into the plasma region and suppressed NH_3 formation in the plasma (Müller et al., 2020, and references therein).

For improving the instrumental time response to NH_3, all stainless-steel parts in the drift tube were surface-passivated with a functionalized hydrogenated amorphous silicon coating (Piel et al., 2021), and the drift tube was heated to 120 °C. Surface passivation and heating significantly reduces the adsorption of NH_3 to instrumental surfaces, lowering the instrumental response time to ~2 seconds (see Figure 4 of Piel et al., 2021).

A series of inlet configurations were tested during the initial phase of the FIREX-AQ campaign. The fastest response to NH_3 was achieved when air was sampled at a flow rate of ~60 standard liters per minute (slpm) through a heated Teflon PFA tube (length: ~2 m, inner diameter: 3.96 mm, wall temperature: 60 °C). Evaporation of ammonium nitrate particles in the main sampling line was not investigated, but is believed to be small due to the short sample residence time (<25 ms). For inertially separating particles from the analyte air, a small flow was subsampled from the main inlet line in rearward direction and directed into the drift tube through a Teflon PFA tube (length: ~10 cm, outer diameter: 3.175 mm, temperature: 120 °C). The subsampling flow was set to ~250 sccm via a pinch valve applied on the PFA tube. An NH_3 time response of a few seconds was ultimately achieved (see Results section).

We performed three types of calibrations in the field: i) periodic in-flight calibrations using a dynamically diluted calibration standard in a pressurized cylinder (10 ppm NH_3 in N_2; Praxair Distribution Inc., Lancaster, CA, U.S.A.), ii) a ground-based calibration using a dynamically diluted calibration standard in a pressurized cylinder (2.7 ppm NH_3 in N_2; provided by NOAA's Chemical Sciences Laboratory), iii) a ground-based calibration using an NH_3 permeation source (provided by NOAA's Chemical Sciences Laboratory). While results from the cylinder-based calibrations were in good agreement, the permeation tube based calibration yielded an instrumental response factor that was a factor of two higher. For resolving this inconsistency, we carried out an extensive post-mission NH_3 calibration in the laboratory. For that purpose, an artificial atmosphere (NH_3 in air) was generated in a 250 L environmental ("smog") chamber equipped with a Fourier Transform Infrared (FT-IR) spectrometer (Bruker IFS 66v/S). The concentrations of NH_3 (accuracy: ±5 %) were determined from the FT-IR spectra (120 m path length, 0.125 cm^{-1} spectral resolution) in a global non-linear least squares spectral fitting procedure (Griffith, 1996) employing the absolute cross sections of NH_3 (Gordon et al., 2017). The instrumental response factor derived from the post-mission calibration agreed to within ±15 % with the response factors obtained during the in-flight calibrations. We concluded that the permeation rate determined in pre-campaign laboratory measurements had changed in the field. The estimated accuracy

of the reported NH$_3$ mixing ratios is ±15 %. We note that this accuracy estimate is not valid when NH$_3$ mixing ratios abruptly changed and inlet/instrument surfaces were not equilibrated.

Submicrometer (50% cutoff size for a vacuum aerodynamic diameter ~1 µm (about 850 nm geometric diameter for most fire plumes based on in-field calibrations) NH$_4^+$ was measured by an Aerodyne high-resolution time-of-flight AMS instrument (DeCarlo et al., 2006; Canagaratna et al., 2007), with a time resolution of up to 10 Hz time. The accuracy (2σ) of the NH$_4^+$ data is estimated to be ±34 % (Bahreini et al., 2009), while the detection limit was typically much smaller (25 ppt at 1 Hz in clean air, ~200 ppt in fire plumes). The inlet flow was optimized to allow for near real time sampling (0.3 s residence time) and to minimize particle volatilization in the inlet. We note that, based on the current state of knowledge, the AMS NH$_4^+$ data collected in fresh smoke plumes suffer from a minor ($\leq 20\%$) positive interference from reduced organic nitrogen compounds, which are known to be abundant constituents of biomass burning particles (*e.g.*, Mace et al., 2003). A general correction is still under development based on positive matrix factorization (PMF) analysis.

Carbon monoxide (CO) and methane (CH$_4$) were measured by the Differential Absorption Carbon Monoxide Measurement (DACOM) instrument (Sachse et al., 1991), which is based on mid-infrared wavelength modulation spectroscopy. The uncertainty in the CO data is 2.1 ± 0.2 ppb; the uncertainty for CH$_4$ is about 1 %. Carbon dioxide (CO$_2$) was measured by a LICOR model 7000 analyzer (Vay et al., 2009), which is based on nondispersive infrared absorption spectroscopy. For CO$_2$ < 500 ppm, the accuracy is 0.25 ppm and the precision is 0.1 ppm, while for higher mixing ratios the total uncertainty is about 2 %.

2.3 Emission factor, modified combustion efficiency

We used the carbon mass balance method for calculating EF_{NH_3} (Yokelson et al., 1996; 1999). The underlying assumption is that the carbon in the fire fuel is predominantly emitted as CO$_2$, CO and CH$_4$. EF_{NH_3} (in g kg^{-1}) is thus described by the simplified equation (1):

$$EF_{NH_3} = \frac{\Delta NH_3}{\Delta CO_2 + \Delta CH_4 + \Delta CO} \times \frac{17}{12} \times F_c \times 1000 \quad (1)$$

Δ is the above background mixing ratio in the plume of the respective trace gas, 17 is the molar mass of NH$_3$ (in g mol^{-1}), and 12 is the molar mass of carbon (in g mol^{-1}). F_c is the fraction of carbon in the fuel, which is typically in the 0.45-to-0.55 range (Akagi e al., 2011). We assumed F_c to be 0.50 and note here that the resulting 10% uncertainty in EF_{NH_3} is small compared to the natural variability of EF_{NH_3}. A problem in the calculation of EF_{NH_3} arises from the fact that NH$_3$ is a "sticky" compound. When the aircraft first penetrates a smoke plume, NH$_3$ molecules typically adsorb onto inlet and instrumental surfaces, thereby delaying the signal response of the analyzer. When the airplane exits the plume, the desorbing NH$_3$ molecules cause a signal tailing (Fig. 2a). For calculating Δ, we thus applied the method described in the Supplement of Müller et al. (2016) and calculated cumulative volume mixing ratios including the immediate period (10 s) before the plume was encountered

(background) and the period after the plume encounter (seconds to minutes) when the NH_3 signal tailed off (Fig. 2b). The signal tailing was particularly pronounced during the initial phase of the campaign (before 24 August 2019) when the inlet configuration had not yet been optimized. During the later phase of the campaign, only a few seconds of tailing were observed. NH_x is the sum of NH_3 and NH_4^+; EF_{NH_x} was calculated as the sum of EF_{NH_3} and $EF_{NH_4^+}$. The modified combustion efficiency (MCE) was calculated as $\Delta CO_2/(\Delta CO_2+\Delta CO)$.

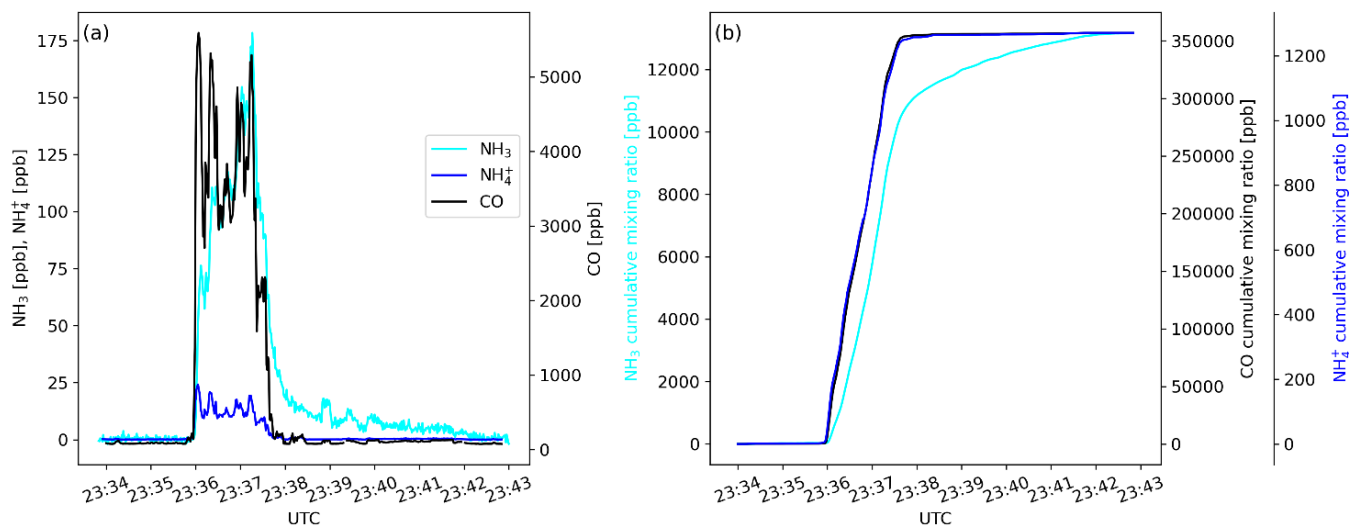



Figure 2: Time traces of (a) mixing ratios of NH_3, NH_4^+, and CO and of (b) cumulative mixing ratios of NH_3, NH_4^+, and CO as measured during a transect of the Williams Flats fire plume on 7 August 2019.

Data from 180 plume transects were included in our analysis of the wildfire emissions. We only used data from plume transects in which CO mixing ratios exceeded 300 ppb for more than 20 seconds and from plumes in which MCE values were stable (standard deviation of MCE < 0.05). Data from seven plume transects were excluded due to missing NH_3, NH_4^+ or CH_4 data. Our EF analysis was not based on a single plume transect in closest proximity to the wildfire, as we observed in several plumes that $\Delta NH_3/\Delta CO$ increased during a few initial downwind transects (Fig. 3).

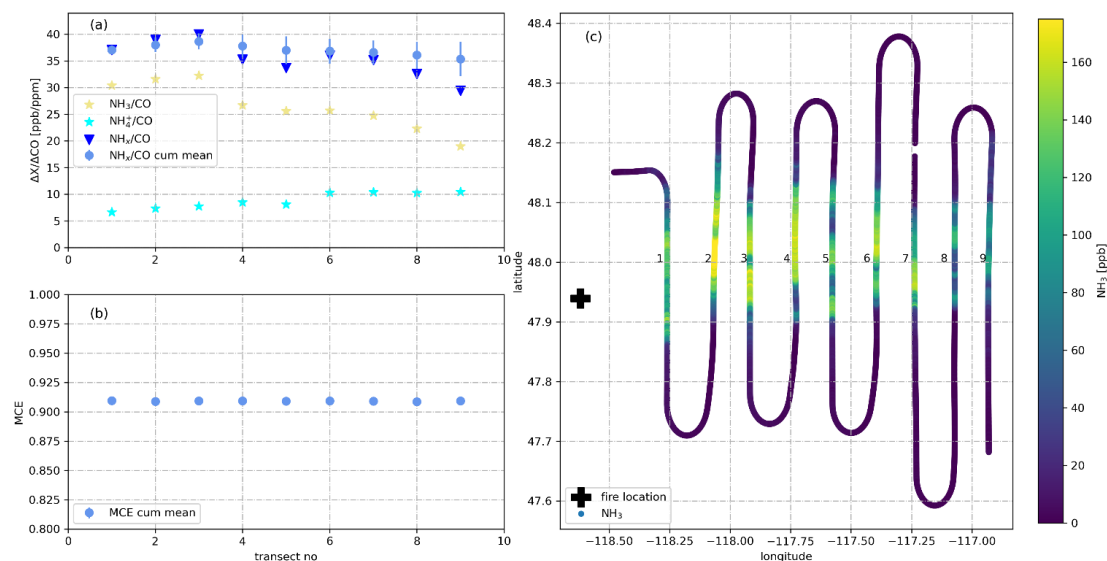



Figure 3: (a) NH_3/CO, NH_4^+/CO, NH_x/CO and cumulative mean NH_x/CO as measured during nine downwind transects of the plume emitted from the Williams Flats Fire on 7 August 2019. NH_3/CO increases during the first three transects which were thus used for determining EF_{NH_3} and EF_{NH_x}. **(b)** Mean MCE as measured for the same nine downwind transects. MCE remains stable at ~0.91 indicating stable burning conditions. **(c)** Lat/lon plot showing the location of the fire (black cross) and the flight track color-coded in the NH_3 mixing ratio.

The reason for this increase (typically <15 %) is unclear. We included all plume transects in our analysis, up to where $\Delta NH_3/\Delta CO$ reached its maximum and derived an average EF_{NH_3} and EF_{NH_x} ($\pm$ standard deviation, SD). All SDs reported herein only reflect the measured variability and do not include measurement uncertainties in the underlying variables (NH_3, NH_4^+, CO_2, CO, CH_4). Data from 164 plume transects were included in our analysis of the agricultural fire emissions. Data from 12 plume transects were excluded due to missing NH_3 or NH_4^+ data.

3 Results and Discussion

3.1 Airborne measurements of NH_3 in smoke plumes

Fig. 4a shows the mixing ratio of NH_3 as measured by the PTR-ToF-MS instrument on 7 August 2019 aboard the NASA DC-8. The aircraft flew nine downwind transects at an altitude of 5160 m above sea level (ASL) for sampling the plume emitted from the Williams Flats Fire in Washington State. The NH_3 signal increased with CO when the plane entered the plume, exhibited a similar time trend as CO within the plume and decreased to background levels outside the plume, although with some tailing (few minutes). NH_3 maxima ranged from 110 to 200 ppb, which were typical maximum NH_3 levels measured in fire plumes throughout the 2019 FIREX-AQ field campaign. Also shown in Fig. 4a is the time trace of NH_4^+ as measured by the AMS instrument, with maximum mixing ratios ranging from 42 to 65 ppb. The observation of significant amounts of NH_4^+

indicates that NH_4^+ was primary emitted (as for example observed by Lewis et al., 2009) and/or gaseous NH_3 had been partly converted to particulate NH_4^+ by the time of sampling (≥ 2 h after emission). A rapid conversion can be caused by the fast reaction of NH_3 with primary emitted acids such as hydrochloric acid (HCl), nitric acid (HNO_3) and organic acids, or occur more slowly downwind via the reaction of NH_3 with secondary formed acids. As stated in section 2.2, the NH_4^+ measurement suffered from a minor ($\leq 20\%$) positive interference from reduced organic nitrogen compounds.

Fig. 4b shows the mixing ratios of NH_3, NH_4^+ and CO as observed when the NASA DC-8 crossed a plume emitted from a small cornfield fire in the Mississippi River Valley on 26 August 2019 at an altitude of 325 m ASL. All data are shown at the frequency they were recorded (5 Hz), which resulted in an increased noise for NH_3. The tailing was however reduced to a few seconds with the improved PTR-ToF-MS inlet. We show the 5-Hz data for demonstrating that we succeeded in measuring such small fire plumes from a jet aircraft. For further analysis, we used the 1 second integrated data. Notably, the AMS instrument detected significant amounts of NH_4^+ in this very fresh plume, indicating that either direct emission from the fire or a rapid conversion of NH_3 to NH_4^+ had occurred. The latter could be caused by the fast reaction of NH_3 with HCl, which is emitted in significant amounts from agricultural fires (Liu et al., 2017). Another plausible explanation is the resuspension of recently applied ammonium nitrate fertilizer.

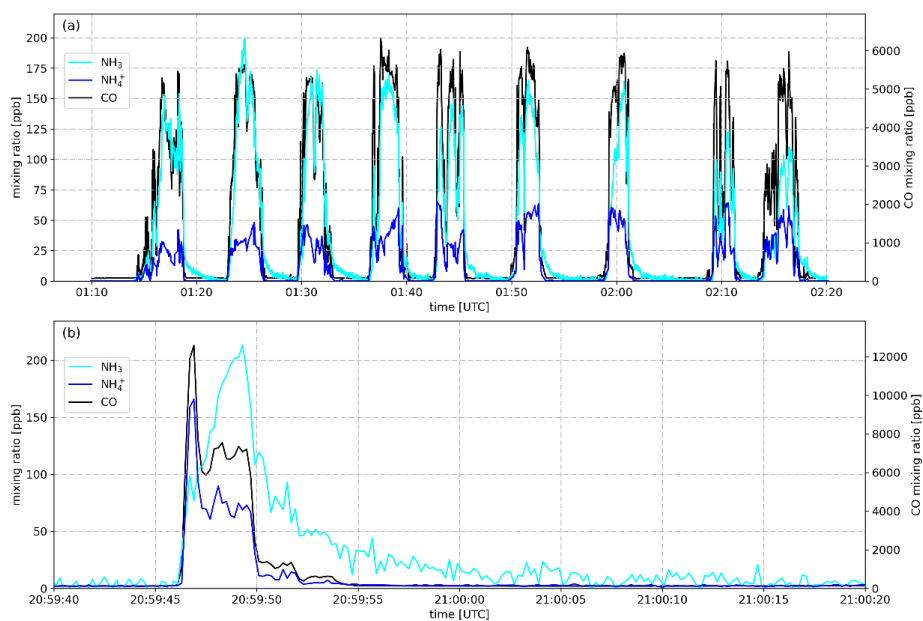



Figure 4: Mixing ratios of NH_3, NH_4^+, and CO as measured when the NASA DC-8 transected (a) the plume emitted from the Williams Flats Fire on 7 August, 2019 in downwind direction and (b) the plume emitted from a small corn field fire in the Mississippi River Valley on 26 August, 2019.

Due to the fact that NH_4^+ was already present in very fresh smoke (due to direct emission or rapid conversion), we will herein also report EF_{NH_x}, as suggested in previous work by Hegg et al. (1990). In Fig. 5a, we plot EF_{NH_x} against EF_{NH_3} for the six Western US wildfires investigated during the 2019 FIREX-AQ field campaign. The two EFs are highly correlated ($R^2 = 0.96$),

205   with the slope of the linear regression curve being close to unity (1.07 ± 0.05). This regression analysis suggests that NH_4^+ added ~0.5 g kg^{-1} (offset of the regression line: 0.47 ± 0.11) to EF_{NH_x} throughout the campaign. The offset may be interpreted as the typical direct NH_4^+ emission factor (or fast conversion of NH_3).

In the case of the agricultural burns, the NASA DC-8 sampled the plumes in very close proximity to the fires. EF_{NH_x} and EF_{NH_3} had again a regression slope of ~1. The offset was mainly caused by elevated NH_4^+ emissions and low NH_3 emissions

210   from some of the cornfield fires (Fig. 5b).

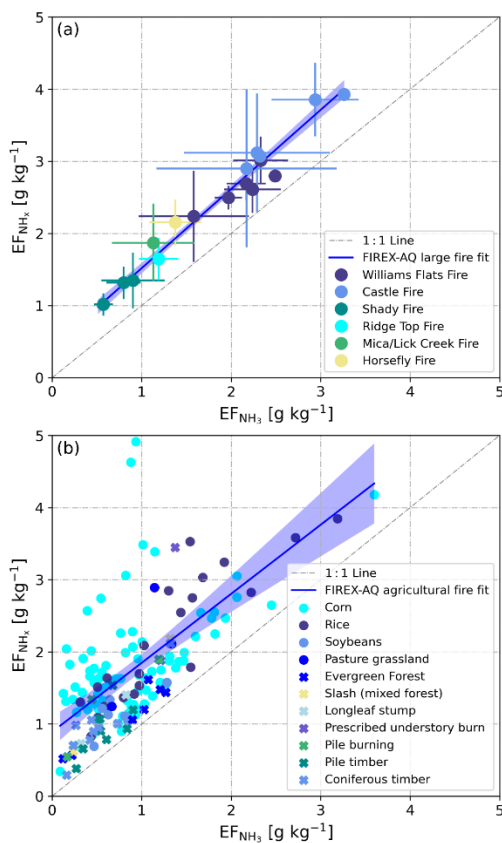



Figure 5: EF_{NH_x} *vs.* EF_{NH_3} **as derived from** *in situ* **measurements in the plumes of (a) six wildfires and (b) 66 small agricultural fires. In the upper figure, SD bars represent the observed natural variability (measurement uncertainties in NH$_3$ and NH$_x$ not included). In the lower figure, circles represent field-dominated fuels and crosses represent timber-**

215   **dominated fuels (see section 3.3). The blue lines represent linear regression curves of the average values for wildfires (a) and of all agricultural data in (b). Shaded areas are 95% confidence bands.**

3.2 NH₃ and NHₓ emissions from wildfires in the Western US

In situ measurements of NH_3 and NH_4^+ were made in smoke plumes emitted from six wildfires in the Western US. Tab. 1 provides a detailed overview of EF_{NH_3} and EF_{NH_x} derived from these measurements. Plumes from the Shady, Williams Flats and Castle Fires were sampled multiple times and we list the data from each of the sampling patterns as well as the average value. EF_{NH_3} and EF_{NH_x} were lowest for the Shady Fire. The low emissions may be caused by the difference in fuels, which in the case of the Shady Fire was modified or managed xeric understory (see Tab. S1).

Table 1: EF_{NH_3} and EF_{NH_x} derived from *in situ* measurements in the plumes of 6 wildfires in the Western US.

Name	State	Date (dy.mo.yr)	EF_{NH_3} (g kg⁻¹) mean	SD	EF_{NH_x} (g kg⁻¹) mean	SD	MCE mean	SD
Shady 1ˢᵗ pattern	ID	25.07.2019	0.57	0.11	1.02	0.15	0.906	0.003
Shady 2ⁿᵈ pattern	ID	25.07.2019	0.80	0.19	1.32	0.23	0.892	0.007
Shady 3ʳᵈ pattern	ID	25.07.2019	0.90	0.35	1.35	0.39	0.887	0.029
Shady mean			**0.76**	**0.22**	**1.23**	**0.26**	**0.895**	**0.013**
Williams Flats 1ˢᵗ pattern	WA	03.08.2019	1.58	0.62	2.24	0.63	0.908	0.003
Williams Flats 2ⁿᵈ pattern	WA	03.08.2019	2.24	0.32	2.61	0.33	0.907	0.005
Williams Flats	WA	06.08.2019	2.33	0.31	3.01	0.33	0.894	0.004
Williams Flats 1ˢᵗ pattern	WA	07.08.2019	2.49	0.07	2.80	0.09	0.905	0.004
Williams Flats 2ⁿᵈ pattern	WA	07.08.2019	1.97	0.15	2.50	0.16	0.909	0.001
Williams Flats 3ʳᵈ pattern	WA	07.08.2019	2.17	--	2.69	--	0.901	0.001
Williams Flat mean			**2.13**	**0.28**	**2.64**	**0.29**	**0.904**	**0.003**
Castle 1ˢᵗ pattern	AZ	12.08.2019	2.29	0.81	3.12	0.82	0.884	0.003
Castle 2ⁿᵈ pattern	AZ	12.08.2019	2.94	0.49	3.85	0.51	0.890	0.002
Castle longitudinal transect	AZ	12.08.2019	2.32	--	3.07	--	0.864	--
Castle 1ˢᵗ pattern	AZ	13.08.2019	2.17	1.01	2.90	1.09	0.895	0.007
Castle 2ⁿᵈ pattern	AZ	13.08.2019	3.26	--	3.93	--	0.892	--
Castle mean			**2.60**	**0.77**	**3.37**	**0.81**	**0.885**	**0.004**
Ridge Top	MT	02.08.2019	1.19	0.22	1.65	0.29	0.940	0.011
Mica/Lick Creek	ID	02.08.2019	1.13	0.46	1.87	0.54	0.913	0.021
Horsefly	MT	06.08.2019	1.38	0.29	2.15	0.32	0.859	0.010

Average EF_{NH_3} and EF_{NH_x} values for the six wildfires in the Western US were 1.86 ± 0.75 g kg⁻¹ and 2.47 ± 0.80 g kg⁻¹, respectively. We compare our results to those obtained in two recent studies. Lindaas et al. (2021) investigated NH_3 emissions from wildfires in the Western US during the 2018 WE-CAN campaign. We calculated an average EF_{NH_3} of 1.48 ± 0.91 g kg⁻

[1] for the WE-CAN data. This is slightly lower than the average EF_{NH_3} reported herein, but within the combined uncertainties of the two methods: ±12% for the quantum-cascade tunable infrared laser direct absorption spectrometer (QC-TILDAS) used
230 during WE-CAN, and ±15% for the PTR-ToF-MS analyzer used during FIREX-AQ. Selimovic et al. (2018) investigated emissions from fires fueled by a wide range of US vegetation types in the FIREX FireLab 2016 laboratory study. We only used the data for FIREX-AQ relevant fuels (see Tab. S1) and obtained a significantly lower average EF_{NH_3} of 0.67 ± 0.38 g kg^{-1} for the FIREX FireLab data. This finding seems to confirm that laboratory fires do not realistically simulate wildfires (*e.g.*, Yokelson et al., 2013, Hodshire et al., 2019) and thereby underestimate real-world emissions of NH$_3$.

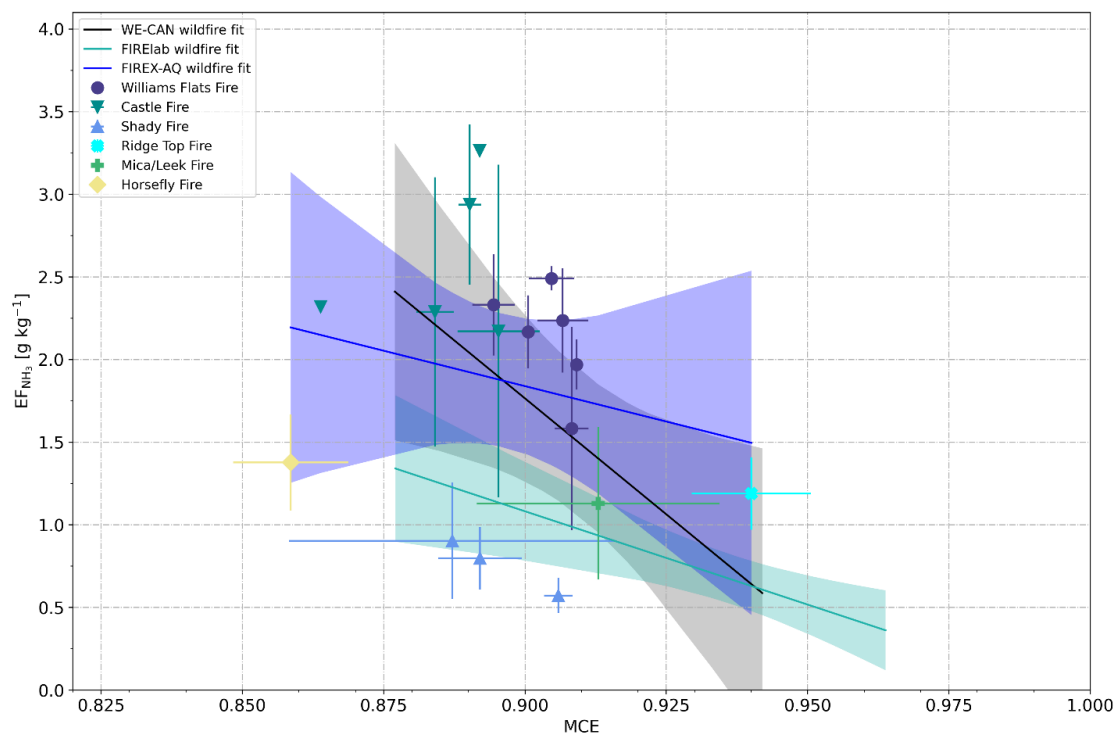
235 In Fig. 6, we plot the measured EF_{NH_3} values (6 wildfires, multiple sampling of 3 fires) as a function of MCE along with trends from the WE-CAN and FIREX FireLab studies. In the case of the FIREX-AQ data (regression line and confidence band in blue), EF_{NH_3} and MCE correlated poorly, with Pearson's coefficient of determination (R^2) being only 0.04. As opposed to the WE-CAN study (regression line and confidence band in black) and the FIREX FireLab experiments (regression line and confidence band in green), we did not find a clear inversion correlation between MCE and NH$_3$ emissions.

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Figure 6: Scatter plot of EF_{NH_3} (as measured for six Western US wildfires during FIREX-AQ and obtained from two literature sources) *vs*. MCE.

3.3 NH₃ and NHₓ emissions from agricultural fires in the Southeastern US

In situ measurements of NH_3 and NH_4^+ were made in smoke plumes emitted from 66 small agricultural fires in the Southeastern US. EF_{NH_3} values varied widely, covering a range from 0.09 to 3.60 g kg^{-1}. The following average values and standard deviations were derived: EF_{NH_3} = 0.89 ± 0.58 g kg^{-1}, EF_{NH_x} = 1.74 ± 0.92 g kg^{-1}, MCE = 0.92 ± 0.04.

We grouped the agricultural fuels into field-dominated and timber-dominated fuels. The field-dominated fuels include corn, rice, soybeans, and grassland pasture. The timber-dominated fuels include evergreen forest, coniferous timber, prescribed understory fire, pile burning, slash burning, pile timber slash mixture burns, and pile burning of longleaf pine tree stumps. Tab. 2 lists EF_{NH_3}, EF_{NH_x} and MCE for the two main categories and 11 subcategories.

Table 2: EF_{NH_3}, EF_{NH_x} and MCE as measured during FIREX-AQ for small agricultural fires in the Southeastern US burning on different types of fuel.

		EF_{NH_3} (g kg^{-1})		EF_{NH_x} (g kg^{-1})		MCE	
Fuel type	66	mean	SD	mean	SD	mean	SD
Corn	33	0.90	0.58	1.85	0.78	0.937	0.023
Rice	11	1.21	0.74	2.13	0.93	0.897	0.057
Soybean	4	0.75	0.27	1.16	0.27	0.925	0.024
Grassland Pasture	2	1.05	0.34	2.08	0.82	0.824	0.109
Field-dominated average	**50**	**0.95**	**0.60**	**1.92**	**0.92**	**0.926**	**0.042**
Evergreen Forest	1	0.83	0.47	1.13	0.44	0.914	0.027
Pile burning (mixed)	4	0.51	0.47	1.12	0.62	0.920	0.042
Slash burn (mixed forest)	2	0.78	0.76	1.40	1.10	0.918	0.063
Prescribed understory burn	1	1.39	0.19	2.67	1.11	0.864	0.022
Pile timber slash	5	0.58	0.21	0.95	0.33	0.858	0.060
Pile longleaf pine tree stump	1	0.57	0.35	1.07	0.48	0.877	0.004
Timber slash coniferous	2	0.51	0.35	0.98	0.49	0.912	0.019
Timber-dominated average	**16**	**0.67**	**0.42**	**1.19**	**0.68**	**0.896**	**0.045**

The data listed in Tab. 2 indicate that field-dominated fuels emit more NH_3 and NH_x than timber-dominated fuels. Agricultural areas are usually nitrogen-fertilized, which may cause increased NH_3 emissions. EF_{NH_x} is roughly a factor of two higher than EF_{NH_3}, which indicates higher primary NH_4^+ emissions and/or a very rapid NH_3 to NH_4^+ conversion in these fresh plumes.

Fig. 7 shows EF_{NH_3} as a function of MCE for different fuels (as measured in individual fires), the averages derived for field-dominated fuels and timber-dominated fuels and the results from four previous studies (McMeeking et al., 2009; Stockwell et al., 2015; Müller et al., 2016; Selimovic et al., 2018). Also in this case, EF_{NH_3} and MCE correlated poorly with R^2 being 0.05.

260   The literature values match the low NH$_3$ emissions (< 1 g kg^{-1}) we observed for most agricultural fires, but the high NH$_3$ emissions from burning rice and corn residues have not been reported before.
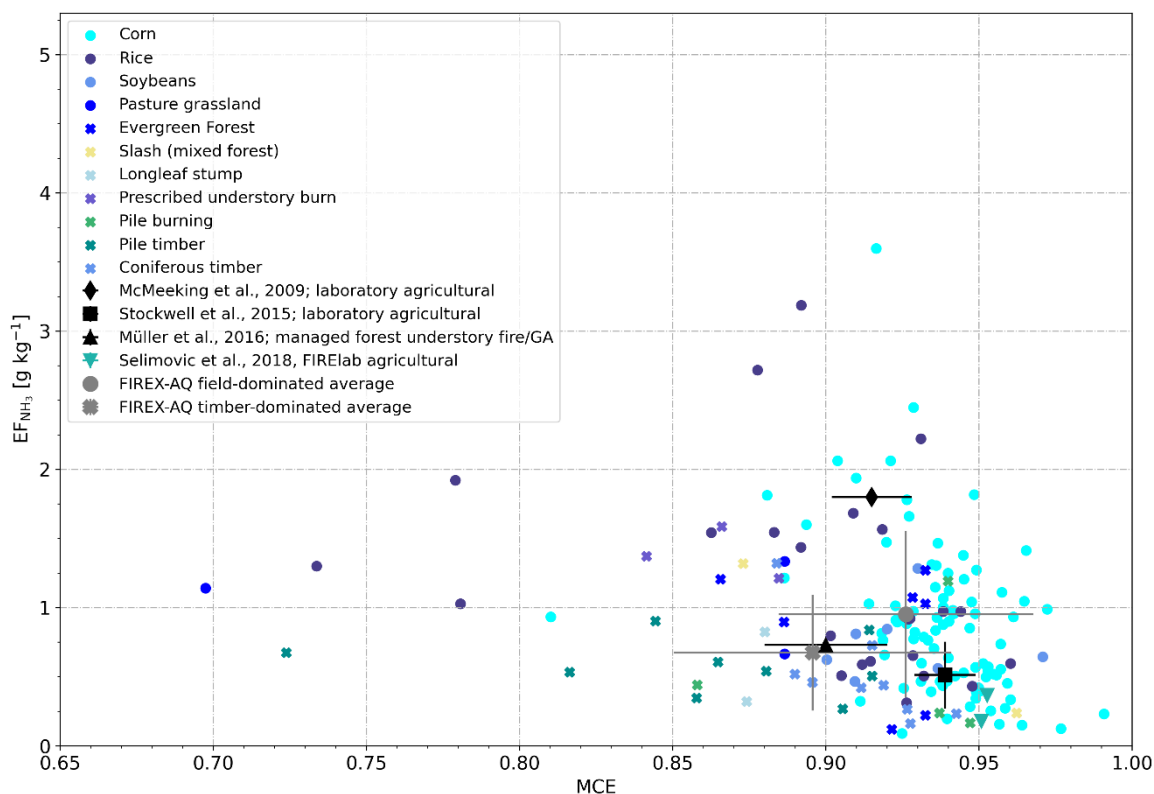
Figure 7: Scatter plot of EF_{NH_3} vs. MCE as measured for 66 agricultural fires (circles: field-dominated fuels, crosses: timber-dominated fuels) and obtained from four literature sources.

265   **3.4 NH$_3$ and NH$_x$ emissions from other fires**

We also measured NH$_3$ and NH$_4^+$ in smoke plumes emanating from two prescribed grassland fires in the Central US and one prescribed forest fire in the Southern US. These fires do not fall within the two main categories discussed in the previous two sections and are thus separately presented here. Tab. 3 lists the fire details, EF_{NH_3}, EF_{NH_x} and MCE for these three fires.

270 **Table 3: EF_{NH_3}, EF_{NH_x} and MCE as measured during FIREX-AQ for two prescribed grassland fires in the Central US and one prescribed forest fire in the Southern US.**

Fire details	EF_{NH_3} (g kg⁻¹)		EF_{NH_x} (g kg⁻¹)		MCE	
	mean	SD	mean	SD	mean	SD
Hickory Ridge State Wildlife Management Area prescribed, 29.08.2019, NE grass during the green growing season (not dry)	0.33	0.12	1.19	0.93	0.907	0.002
Tallgrass Prairie National Preserve prescribed, 29.08.2019, KS prairie tallgrass during the green growing season (not dry)	0.92	0.20	1.73	0.49	0.894	0.014
Black Water River State Forest prescribed, 30.08.2019, FL oak, mature longleaf pine, mesic and xeric shrub, grass, litter, understory	0.30	0.16	0.61	0.20	0.942	0.006

4 Conclusions

During the 2019 FIREX-AQ field campaign, we measured NH_3 and NH_4^+ aboard the NASA DC-8 in wildfire and agricultural fire plumes. We found that NH_4^+ was either directly emitted from the fire (consistent with past laboratory experiments) and/or

275 NH_3 had already partially partitioned to particulate NH_4^+ at the time of sampling. We thus also evaluated emissions of NH_x and produced a comprehensive set of EF_{NH_3} and EF_{NH_x} for wildfires in the Western US and agricultural fires in the Southeastern US. Our data show no clear inverse correlation between MCE and EF_{NH_3}. EF_{NH_3} values measured in plumes of large wildfires were similar to those observed during the 2018 WE-CAN field campaign, but significantly higher than observed in the FIREX FireLab 2016 laboratory study. We also report the first extensive set of field measurement derived EF_{NH_3} and

280 EF_{NH_x} values for different types of agricultural fires in the Southeastern US. NH_3 emissions were highest from fires of corn and rice residues. Substantial amounts of NH_4^+ were detected in freshly emitted smoke from some of the corn and rice field fires, which warrants further investigation.

Data availability

285 All the FIREX-AQ data are available at NASA's Atmospheric Science Data Center (DOI: 10.5067/SUBORBITAL/FIREXAQ2019/DATA001) (NASA, 2019).

Author contribution

LT supported the PTR-ToF-MS instrument development, performed the field measurements, performed the data analysis and interpretation, and wrote the manuscript draft. TM built and characterized the modified PTR-ToF-MS instrument and

performed field measurements. FP performed field and laboratory measurements and supported the data analysis as well as the PTR-ToF-MS instrument development. CJN supported the post-mission calibration experiments. PCJ, HG, BAN, MSK and JLJ provided the NH_4^+ data. HH, GD, JPD, JBN provided the CO_2, CO and CH_4 data. EBW, EG and AJS provided the fuel characterization information. AW conceived the modified PTR-ToF-MS instrument, supervised the measurements and data analysis, performed field measurements and finalized the manuscript. All authors commented and accepted the final version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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