Identifying fire plumes in the Arctic with tropospheric FTIR measurements and transport models

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We would like to thank the referees for these comments. We have responded to the comments and modified the paper accordingly as described below.

Responses to Referee #1

The authors present a study of biomass burning products such as CO, HCN, C2H6, C2H2, HCOOH, and H2CO. The study is based on ground-based FTIR measurements performed at Eureka and Thule. Time series of the species listed above are presented and compared with model calculations. Periods of increased amounts of biomass burning products are detected. These fire events are studied using trajectory and a chemical transport model. Finally, emission ratios of the above mentioned species were derived. The subject is fully appropriate for publication in ACP. I recommend publication after minor revisions.

Specific comments:

- Is there any trajectory passing both sites, Eureka and Thule, or another NDACC site?
This would allow you to study differences in composition along the trajectory.

We have identified five plumes possibly reaching both Eureka and Thule stations, but have not addressed the chemical degradation along the trajectory in this paper. We agree that studying the differences in the plume composition along the trajectory is an important topic. This study will be addressed in ongoing work (e.g., AGU poster: E. Lutsch, C. Viatte, K. Strong, Y. Kasai, J.W. Hannigan, E. Nussbaumer (2014), Abstract A53B-3226 presented at 2014 Fall Meeting, AGU, San Francisco, Calif., Dec. 15-19).

- For a better coverage of the Arctic it would be beneficial to include all the Arctic FTIR sites. This would also better reflect the title which mentions 'in the Arctic'.

Inclusion of all Arctic NDACC sites was beyond the scope of this work but is being considered in a follow-on study (e.g., AGU poster of Lutsch et al., 2014 included Poker Flat, Alaska). Analysis of new tropospheric species (C_2H_2, CH_3OH, H_2CO, and $HCOOH$) and reanalysis of the Eureka and Thule datasets using the new SFIT4 retrieval code, was the central focus of this paper.

- p.26371: 'our measurements suggest slightly higher emissions of C_2H_2 in biomass burning plumes' (& Fig. 10): However, the differences are within the error bars.

We have deleted this sentence.

Technical comments:
- In the printer friendly version, 'ff' is printed in Italian; at least my printer does so.

This is not evident to the authors so we were unable to correct it.

- In Figs. 4d, 5 -8, fonts are too small

We enlarged the fonts of these Figures.

Responses to Referee #3

The paper of Viatte et al., addresses an important topic, since the authors want to quantify emission factors of biomass burning in the Arctic by ground based column observations. They use multiannual timeseries of observations of several tracers including CO, HCN, HCHO, C_2H_2, C_2H_6, HCOOH and CH_3OH in Thule and Eureka to identify plumes. From the enhancement ratio of the tracers they estimate emission factors. They do this by using a combination of Lagrangian tools (HYSPLIT, STILT), and satellite observations to estimate the source region and transport time. The trace gas observations are compared to the results of the MOZART-4 model, which according to the authors shows a good agreement between the observations. Exception is Ethane during winter, when the model is far too low. The authors conclude that the model generally underestimate the emissions compared to the observations.

The paper is well written and clearly addresses an aspect of high interest, which is in the scope of ACP. My main points are a clarification of the statistics to derive the emission factors based on the enhancement ratios. Second the plume travel and source fire determination need to be clarified, which is important for the short-lived species. In particular the altitude of the plume location from the column measurements is not motivated at all. This however strongly determines the initialization of the Lagrangian tools and therefore source region and travel time. Therefore the initialization altitude of the Lagrangian analysis needs to be addressed, since it determines strongly the source region (fire type!) as well as travel time. I therefore recommend the paper for publication after the following points are addressed

Major: For the enhancement ratios the slopes between species have to be calculated. Which algorithm is used and how is the error in both species accounted for in the regression? The differences from the respective fit algorithm can be substantial particularly when neglecting the fact, that both quantities carry errors and the number of pairs per fit is small (six pairs is the minimum according to the statement on p.26367, l.24). See Cantrell, ACP, 2008

We have clarified the statistics to derive emission ratios and revised the whole manuscript using an improved statistical approach to derive enhancement ratios. We used the York algorithm, which is a linear least-square fitting accounting for uncertainties in both the x and y variables (York, D., Evensen, N. M., Lopez Martinez, M., and De Basabe Delgado, J.: Unified equations for the slope, intercept, and standard errors of the best straight line, Am J. Phys., 72(3), 367–375, 2004).

This improved approach for the linear regression fitting changes the estimation of emission ratios and factors by small fractions which are within measurement uncertainty, except for HCOOH at Eureka. New and old estimations of emission ratios and emission factors, using bivariate and standard least-squares methods, respectively, are summarized in Table A (below). Relative differences between emission factors derived from the standard linear regression algorithm and the bivariate one are 2.9% and 4.8% for HCN, -0.9% and 3.0% for C_2H_6, 5.3% and -6.7% for C_2H_2, 73.5% and 16.7% for HCOOH at Eureka and Thule, respectively, and 9.6% for CH_3OH at Eureka. These changes do not exceed the measurement uncertainty, except for HCOOH at Eureka, which is now more consistent with Thule data. These changes do not affect the main conclusion and discussions of the paper, thus we have updated all figures, tables and number in the text accordingly using the bivariate approach.

	Linear least square fitting method	Eureka		Thule	
		mean ER ± SD	mean EF ± SD	mean ER ± SD	mean EF ± SD
HCN	standard	0.00343 ± 0.00115	0.35 ± 0.14	0.00407 ± 0.00236	0.42 ± 0.17
	bivariate	**0.00334 ± 0.00094**	**0.36 ± 0.17**	**0.00429 ± 0.00245**	**0.44 ± 0.25**
C_2H_6	standard	0.00957 ± 0.00244	1.10 ± 0.45	0.01177 ± 0.00437	1.35 ± 0.52
	bivariate	**0.00956 ± 0.00319**	**1.09 ± 0.74**	**0.01211 ± 0.00476**	**1.39 ± 0.68**
C_2H_2	standard	0.00384 ± 0.00143	0.38 ± 0.17	0.00307 ± 0.00083	0.30 ± 0.14
	bivariate	**0.00405 ± 0.00174**	**0.40 ± 0.25**	**0.00280 ± 0.00084**	**0.28 ± 0.18**
CH_3OH	standard	0.02566 ± 0.01114	3.14 ± 1.28		
	bivariate	**0.02813 ± 0.01252**	**3.44 ± 1.68**		
HCOOH	standard	0.00882 ± 0.00287	1.55 ± 0.73	0.01537 ± 0.00771	2.70 ± 1.11
	bivariate	**0.01531 ± 0.00403**	**2.69 ± 1.14**	**0.01790 ± 0.00937**	**3.15 ± 1.46**

Table A: Means and one-sigma standard deviations of equivalent emission ratios and emission factors (using EFco for the extratropical forest) calculated from FTIR measurements performed at Eureka and Thule for HCN, C_2H_6, C_2H_2, CH_3OH, and HCOOH. Bold numbers are obtained using bivariate least-squares method accounting for errors in both x and y variables to derive enhancement ratios, and the other numbers are the previous results using a standard least-squares method.

The total uncertainty for the regression slopes is calculated by quadrature addition of the fit uncertainties and the measurement uncertainties. Thus, errors on the regression slopes are larger than when estimated with the previous algorithm since they account for uncertainties in both the x and y variations. They are 33.6%, 54.0%, 49.5%, 32.2% and 22.8% for HCN, C_2H_6, C_2H_2, CH_3OH, and HCOOH, at Eureka respectively. Previously, they were estimated to be 12.2%, 13.3%, 14.4%, 13.3%, and 9.9% for HCN, C_2H_6, C_2H_2, CH_3OH, and HCOOH, at Eureka respectively. For Thule, errors on the slopes of the enhancement ratios are 43.5%, 33.1%, 52.5%, and 16.3% for HCN, C_2H_6, C_2H_2, and HCOOH, respectively. Previously, they were 19.0%, 8.5%, 16.0%, and 12.1%, for HCN, C_2H_6, C_2H_2, and HCOOH, at Thule.

The stated uncertainty on emission factors is the quadrature propagation of the errors on the regression slopes, the uncertainty on the emission ratio of CO from the inventory (35%), and the measurement uncertainty. They are estimated to be 49.2%, 67.3%, 61.8%, 48.7%, and 42.3% for HCN, C_2H_6, C_2H_2, CH_3OH, and HCOOH, at Eureka respectively and 57.5%, 48.7%, 63.8%, and 46.5% for HCN, C_2H_6, C_2H_2, and HCOOH, at Thule respectively.

Finally, the mean emission factors derived from the two FTIR measurements (using bivariate least-squares method to derive enhancement ratios) are 0.40 ± 0.21 g kg^{-1} for HCN, 1.24 ± 0.71 g kg^{-1} for C_2H_6, 0.34 ± 0.21 g kg^{-1} for C_2H_2, and 2.92 ± 1.30 g kg^{-1} for HCOOH. The emission factors of CH_3OH estimated at Eureka is 3.44 ± 1.68 g kg^{-1}. Previously, the mean emission factors were 0.39 ± 0.15 g kg^{-1} for HCN, 1.23 ± 0.49 g kg^{-1} for C_2H_6, 0.34 ± 0.16 g kg^{-1} for C_2H_2, 2.13 ± 0.92 g kg^{-1} for HCOOH, and 3.14 ± 1.28 g kg^{-1} for CH_3OH.

We appreciate the reviewers comments in this regard and the improvement in the completeness in the analysis.

To estimate the potential fire source region from a column measurement you need to initialize the Lagrangian tools in the whole column. How does this affect the estimates of travel time and source region? The air in the boundary layer can have a totally different origin than just above the inversion or in the troposphere. How is the altitude for the HYSPLIT or STILT initialization determined? It is only stated that STILT footprints are generated (p.26360), but not mentioned, how this is achieved (i.e. initialized).

We have added details about STILT initialization in Section 3.1.

STILT was driven by meteorological fields from the Global Data Assimilation System (GDAS, https://ready.arl.noaa.gov/gdas1.php). GDAS is output 3-hourly, on a global 1-degree latitude/longitude grid with 23 pressure surfaces ranging from 1000 to 20 hPa. Trajectories were initialized at 0, 6, 12, and 18 UTC on the following above-ground-height levels (in meters): 2, 5, 10, 25, 50, 100, 250, 500, 1000, 1500, 2500, 3500, 4500, 5500, 6500, 7500, 8500, 9500, 10500, 11500, 12500, 13500, and 14500. Each trajectory used 500 particles. Footprints from the different levels were combined as a weighted mean to create a single footprint that is

representative of a column measurement. Weights were derived as the product of the pressure at the receptor multiplied by the instrument kernel density (which was linearly interpolated to the receptor height). The trajectories were run 30 days back in time.

The FTIR makes effectively continuous measurements, both in time and in the space along the column. The chosen discretization in time accounts for any diurnal cycles and most of the variability in winds (as supplied by the GDAS wind fields). The chosen discretization along the column, when combined with the weighting, accounts for differences in the origin of air along the column. The discretization is finer near the ground in order to pick up sharp gradients at the top of the boundary layer. Errors in the wind fields and the boundary layer heights are large in the scope of the problem (Gerbig et al., 2008), and errors brought on by the discretization are not our greatest concern. Additionally, there can be differences in dispersion between trajectory ensembles, and even bifurcations within an individual trajectory ensemble. A sufficient number of particles must therefore be used to capture the variability in the origin of air within a trajectory ensemble. Using 500 particles in each initialization is very conservative, especially for a qualitative analysis. Zhao et al. (2009) and Gerbig et al. (2003), for example, used 100 particle trajectories in inversion frameworks with piece-by-piece error characterization. They found a random "particle number error" of 5% and 13%, respectively – much smaller than other errors in the estimation, especially transport error.

Therefore, the initialization choices may lead to a loss of information through discretization and the approximation of an air parcel with a finite number of particles, but this loss of information is small when other errors are considered.

Fig.4 and related discussion (p.26360, l.24 ff.): What is the benefit of the HYSPLIT trajectories in addition to the STILT dispersion model, which also relies on a Lagrangian backward calculation?

HYSPLIT backtrajectories can be easily run online (http://ready.arl.noaa.gov/HYSPLIT.php), whereas the STILT dispersion model requires more tools and experience. In this study, HYSPLIT was used to determine ("by hand") the source regions and the travel durations of the plume, while waiting for STILT outputs. In addition, since the STILT dispersion model and HYSPLIT trajectories have their own uncertainties, they provide independent tools for determining the fire source regions and travel duration of plumes reaching the Arctic region. Consistent results from these multiple datasets provides confidence in the attribution of trace gas enhancements to specific fire events.

It is stated that an ensemble of trajectories is calculated: How large is the ensemble and how is it initialized? A cluster in different altitudes? An ensemble of only three trajectories would be not very satisfying.

For each biomass burning event detected at a specific time, we ran ten HYSPLIT backtrajectories for different altitudes ranging from 3 to 12 km, and modified the end time of these backtrajectories within two hours of the observed enhancements. We looked at the consistency between the different results. We only showed three trajectories for clarity in the figure, and ran STILT to provide more confidence in the results.

To estimate the effect of the correction from travel time it would be helpful to include the enhancements before and after the correction applied in a Table to estimate the importance of travel time

We have changed Tables 5 and 6 to include enhancement ratios before and after correction from travel time (called "ER" in those Tables).

Furthermore: How is the travel altitude considered for the chemical correction of the plume (or the vertical column)? The chemical degradation strongly depends on the altitude, which therefore needs to be known

For the majority of our observed species, the lifetimes in the atmosphere are not well-known, especially in the high Arctic, and are still a matter of debate. For instance, sinks of HCN are not well quantified yet (Zeng et al., 2012), large uncertainties remain with regard to the magnitude of the sources and sinks of C_2H_2 (Parker at al., 2011) and CH_3OH (Millet et al., 2008). For HCOOH, Paulot et al. (2011) confirmed missing local sources in its Arctic budget. In addition, secondary H_2CO formation in biomass burning plumes has been proposed (Paton-Walsh et al., 2010). Overall, the transport and the degradation mechanisms of non-methane hydrocarbons (NMHCs) are poorly understood (Stavrakou et al., 2009). This motivated our initiative to monitor tropospheric species in the Arctic. Therefore, we chose to use the means of atmospheric lifetimes found in the literature (Table 3, last column) for the chemical correction of the enhancement ratios inside plumes.

Minor: Does the FINN biomass burning data set contain daily variability? On which observations is it based on?

FINN is based on MODIS thermal anomalies and is available daily (https://www2.acd.ucar.edu/modeling/finn-fire-inventory-ncar). Therefore, MOZART-4 simulations do use daily fire emissions. We have added a sentence in Section 2.2.

We have included details about this tracer-tracer method, as well as its advantages and limitations in Section 3.3.1.

We have added a column to Table 3 in order to include atmospheric lifetimes of the target species.

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