Evaluating the Composition and Photochemistry of Boreal Biomass Burning Smoke Plumes Using TES

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Abstract — We use the Tropospheric Emission Spectrometer (TES) to determine the concentrations of the trace gases CO, O_3, NH_3, and formic acid (HCOOH) within boreal biomass burning plumes. We focus on 22 plumes observed by TES between June 15 and July 15, 2008 as part of the summer Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS-B) campaign. Only four of these plumes show evidence of enhanced ozone, and even in these cases the enhanced ozone may be due to intrusions of stratospheric air. We use TES retrievals of NH_3 and HCOOH within the smoke plumes to calculate their enhancement ratios relative to CO. Our preliminary analysis suggests TES can observe PAN within boreal biomass burning plumes, but further work is needed to test the robustness of this result. We find that TES is unlikely to be able to detect HCN within most smoke plumes.

Keywords: Ammonia; ARCTAS; Biomass burning; Formic Acid; Infrared; Ozone; PAN; TES

1. INTRODUCTION

Biomass burning is a major source of trace gases and particles and is an important part of the interannual variability of atmospheric composition. Recent work has used nadir-viewing satellite observations to study the emissions from biomass burning and their subsequent chemistry (Coheur et al., 2009; Verma et al., 2009; Alvarado et al., 2010; Kopacz et al., 2010).

Here we use the Tropospheric Emission Spectrometer (TES) aboard the NASA Aura satellite to determine the concentrations of the trace gases CO, O_3, NH_3, and formic acid (HCOOH) within boreal biomass burning plumes. TES made multiple special observations during the summer of 2008 over eastern Siberia, the North Pacific, and North America as part of the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS-B) campaign (Jacob et al., 2010). Boreal biomass burning plumes can influence the formation of ozone in the Arctic and midlatitudes through emissions of NO_x (e.g., Val Martin et al., 2006). Biomass burning is a significant source of NH_3 (Hegg et al., 1988), which can combine with acidic gases like H_2SO_4 and HNO_3 to form secondary aerosol. Biomass burning is also one of the major primary sources of formic acid, and some studies suggest that secondary production of formic acid takes place within the aging smoke plume (Yokelson et al., 2009).

We also use the TES special observations during ARCTAS-B, in combination with a line-by-line radiative transfer model (LBLRTM), to explore the potential of TES to detect peroxyacetyl nitrate (PAN) and HCN within boreal smoke plumes. HCN is a gas-phase tracer of biomass burning and is used to separate biomass burning CO from other sources (Holzinger et al., 1999). The primary NO_x emissions from biomass burning are rapidly converted to PAN within biomass burning plumes (Alvarado et al., 2010). This PAN can be transported over large distances and can alter ozone formation far downwind from the source (Leung et al., 2007).

Section 2 describes the methods we used to identify biomass burning plumes using TES, retrieve NH_3 and HCOOH within the smoke plumes, and calculate the spectral residuals in regions of strong absorption by PAN and HCN. Section 3 presents the results of this study and Section 4 summarizes our preliminary conclusions and our plans for future work.

2. METHODS

2.1. Identification of biomass burning plumes

Biomass burning plumes were identified following the procedure outlined in Alvarado et al. (2010). We defined a plume in TES special observations between June 15 and July 15, 2008 as areas where the retrieved CO profile exceeded 150 ppb at 510 hPa. The criteria of 150 ppb ensured that the retrievals are significantly different from the a priori values (~110 ppb). While this procedure detects thick plumes that are transported between continents (e.g., Zhang et al., 2008), it does not detect plumes near the surface (where the sensitivity is low) or very thin or dilute plumes.

2.2. TES Retrievals of NH_3, and HCOOH

We used TES retrievals of CO, O_3, NH_3, and formic acid (HCOOH) to examine the composition of boreal smoke plumes. For CO and O_3, we used the Level 2 retrievals from TES (V003, Osterman et al., 2008) as discussed in Alvarado et al. (2010). In general, the retrievals have 1 degree of freedom for signal (DOFS) below 250 hPa with the region of maximum sensitivity in the troposphere near 500 hPa. TES V003 O_3 retrievals were recently validated using ozonesonde profiles from the Arctic Intensive Ozonesonde Network Study (ARCIONS) during ARCTAS, and generally showed a positive mean bias of less than 15% (Boxe et al., 2010).

NH_3 retrievals were performed using TES Level 1B spectra (V003, Shephard et al., 2008) following the method of Shephard et al. (2011), which is being implemented in V005 of the TES Level 2 products. The retrievals generally have a region of maximum sensitivity between 700 and 900 hPa with ~1 DOFS. The minimum detection limit is 1 ppb, and the retrievals have a mean bias of +0.5 ppb (Shephard et al., 2011).

In order to use the TES retrievals of NH_3 and CO to calculate the enhancement ratio of NH_3, we first calculated a representative volume mixing ratio (RVMR) for NH_3 following the procedure of Payne et al. (2009). The CO retrieval was then transformed using the same grid and weightings applied to NH_3 to obtain a pseudo-RVMR for CO appropriate for comparison with NH_3. The molar enhancement ratio of NH_3 ($\Delta NH_3/\Delta CO$, where $\Delta NH_3 = NH_3(plume)-NH_3(background)$) was then calculated as the slope of a linear regression of the NH_3 RVMR and the CO pseudo-RVMR.

Formic acid (HCOOH) retrievals were also performed using TES Level 1B spectra (V003). The spectroscopic parameters used for HCOOH were taken from HITRAN 2008 (Rothman et al., 2009). The retrieval minimizes the residuals near the Q branch of HCOOH (~1105 cm^{-1}) between the TES Level 1B spectra and a radiative transfer calculation performed with the line-by-line radiative transfer model LBLRTM v11.7 (Clough et al., 2005). The region of maximum sensitivity for these retrievals is near 600 hPa and the retrievals have ~1 DOFS. The molar enhancement ratio of HCOOH relative to CO was then calculated following the procedure described above for NH_3.

2.3. Calculation of spectral residuals

In order to evaluate the potential of TES to detect PAN and HCN in boreal smoke plumes, we calculated the residuals between the TES Level 1B spectra (V003) and a forward run of LBLRTM v11.7 using v1.4 of the TES spectroscopic line parameters. The model is run using TES Level 2 (V004) retrievals of temperature, emissivity, reflectivity, cloud properties, H_2O, CO, O_3, and CH_4. Profiles of CO_2 and N_2O were taken from the TES Level 2 supplemental data files. Preliminary model runs using the TES retrieved cloud optical depth led to unphysical slopes in the residuals versus wavenumber between 1100 and 1200 cm^{-1}. We removed these slopes by setting cloud optical depth in this spectral region to a constant value based on the TES retrieved value at 1150 cm^{-1}.

We chose microwindows in spectral regions where forward model runs of LBLRTM showed significant changes when PAN and HCN were added. The absorption cross sections for PAN were taken from HITRAN 2008 (Rothman et al., 2009). The microwindow for HCN is in the TES 2B1 band at 712.4-712.8 cm^{-1}, corresponding to the HCN Q branch. The microwindow for PAN is in the TES 2A1 band at 1167.0-1170.0 cm^{-1}, a region of strong PAN absorption that is outside of the water line at 1165 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Ozone

The results for ozone are extensively discussed in Alvarado et al. (2010). Only 4 of the 22 biomass burning plumes observed by TES between June 15 and July 15, 2008 showed evidence of ozone increasing within the smoke plumes. Even in those cases where enhanced ozone was collocated with the smoke plumes, it was unclear that the increase was due to fire emissions. For example, Figure 1 shows the TES retrievals for CO and O_3 at 510 hPa for a set of scans near the Kamchatka peninsula on July 3, 2008. We can see that the enhanced ozone in this case is north of the plume, suggesting that it is due to a stratospheric intrusion rather than photochemical production within the smoke. Thus, when we see enhanced ozone within the plume further downwind, as in Figure 2, we cannot tell how much of the increased ozone is due to photochemical production within the smoke plume and how much is due to stratospheric air.

3.2. NH_3

For NH_3 and the other species, we focus on retrievals in a smoke plume from a Canadian fire observed by TES between 52.5-54.1° N and 90.5-91.8° W at 19:03 UTC on July 1, 2008 (TES Run #7656). This fire was chosen due to the high retrieved values for CO (> 500 ppb) and its location near a Canadian fire source. We will repeat the analysis for the other 21 detected plumes from Alvarado et al. (2010) in future work.

Figure 1. TES retrieved CO and O_3 at 510 hPa for run 7709 near the Kamchatka peninsula on July 3, 2008. The red line is the original GEOS-Chem simulation of Alvarado et al. (2010) processed with the TES observation operator.

Figure 2. Same as Figure 1, but for run 7706 in the mid-Pacific.

Figure 3 shows the NH_3 RVMR versus the CO pseudo-RVMR for four scans near the fire with cloud optical depths < 0.5. The retrievals show a strong enhancement of NH_3 that is correlated with the retrieved CO. We calculate the value of $\Delta NH_3/\Delta CO$ for this fire as 1.0%. This is within the uncertainty of the value of 3.5±3.2% recommended by the review of Akagi et al. (2010) for boreal fires and close to the range of 1.22-2.57% reported for Alaskan fires by Goode et al. (2000). Our lower value could be due to variability in the emissions of NH_3, secondary formation of ammonium sulfate and ammonium nitrate, or the vertical sensitivity of the TES retrievals. Secondary formation of ammonium nitrate in the smoke plumes is consistent with our analysis of HNO_3 and $NO_{3(p)}$ measurements made aboard the NASA DC8 during ARCTAS-B (Alvarado et al., 2010).

Figure 3. RVMR of NH_3 versus the TES retrieval for CO mapped to the same grid as the NH_3 RVMR for four scans near the Canadian fire detected at 19:03 UTC on July 1, 2008.

3.3. HCOOH

Figure 4 shows the HCOOH RVMR versus the CO pseudo-RVMR for three scans near the Canadian fire detected on July 1, 2008. Retrievals for two other scans failed due to cloud optical depth > 0.5, while a third retrieval had only 0.1 DOFS. The strong enhancement in HCOOH is correlated with the enhancements of both CO and NH_3. We calculate the value of $\Delta HCOOH/\Delta CO$ for this fire as 0.9%, larger than the value of

0.28±0.25% [illegible] the average by Akagi et al. (2010) but within the range of 0.32-1.16% reported by Radke et al. (2000). Our high values could be due to variability in the emissions, secondary production of formic acid within the plume (Yokelson et al. 2009), or the sensitivity of the TES retrievals.

Figure 6 shows the mean brightness temperature residuals (data minus model) in the PAN absorption microwindow versus TES retrieved CO mixing ratios at 510 hPa for 6 scans near the Canadian fire observed by TES on July 1, 2008 at 19:03 UTC. The two scans with CO mixing ratios below 150 ppb, and thus outside the plume based on our criteria, show residuals that are not significantly different from 0 given the noise equivalent brightness temperature difference (NEBTD) of 0.2 K in this band. Note that the NEBTD is an underestimate of the true uncertainty in the residuals, since there will also be significant contributions in this region from the uncertainties in the TES retrievals of H_2O, CH_4, O_3, clouds, and emissivity, as well as uncertainties in the climatology of N_2O.

Figure 4. RVMR of HCOOH versus the TES retrieval for CO mapped to the same grid as the HCOOH RVMR for three scans near the Canadian fire detected at 19:03 UTC on July 1, 2008.

3.4. PAN and HCN

The solid black line of Figure 5(a) shows the brightness temperature residuals (data minus model) for the scan at 53.32° N and 90.84° W (scan 96). The two lobes of PAN absorption are clearly visible on either side of the water line at ~1165 cm^{-1}. The dotted red line shows the residuals when a hypothetical PAN profile with a peak concentration of 960 ppt at 560 hPa is added to the forward model, and Figure 5(b) shows the difference between the model runs with and without PAN. Adding the PAN profile moves the mean residuals in our PAN microwindow (1167-1170 cm^{-1}) from -0.26 K to 0.03 K.

Figure 5. (a) Brightness temperature residuals (data minus model) for the TES scan at 53.32° N and 90.84° W on July 1, 2008. The solid black line does not have PAN in the forward model, while the dotted red line does include PAN. (b) Difference between the model runs with and without PAN.

Figure 6. Mean brightness temperature residuals (data minus model) between 1167 cm^{-1} and 1170 cm^{-1} versus TES retrieved CO at 510 hPa for the Canadian fire detected at 19:03 UTC on July 1, 2008. Blue circles show the values for individual scans, while the red square shows the average of the four scans in the smoke plume (CO > 150 ppb at 510 hPa). Error bars show the noise equivalent brightness temperature difference (NEBTD).

The four scans within the smoke plume in Figure 6 show negative mean residuals of between -0.26 and -0.29 K, consistent with absorption by PAN. To increase the signal to noise ratio, we averaged the residuals of the four scans within the smoke plume, which reduced the NEBTD of the average to . This gives an average residual for the four scans of -0.27±0.1 K. Thus, we find that TES can potentially detect PAN within boreal biomass burning plumes. Future work will focus on repeating this analysis for other boreal and tropical biomass burning plumes observed by TES in order to test the robustness of this result. □0.2 K4□0.1 K

In contrast, the noise in the 2B1 band (NEBTD ~0.6 K) makes it difficult to identify HCN in our calculated residuals of the TES spectra for this fire. Even when the residuals in the HCN Q branch window at 712.4-712.8 cm^{-1} are averaged for the four scans in the smoke plume we find a value of -0.3±0.3 K, which is not significantly different from zero. Given the strong retrieved mixing ratios of CO in this smoke plume and the fact that CO and HCN are emitted together by biomass burning, it appears unlikely that TES will be able to detect HCN within most boreal biomass burning plumes.

4. CONCLUSIONS

Using TES retrievals of CO and O_3 within biomass burning plumes detected during ARCTAS-B, we find little evidence for ozone enhancement in plumes. Only 4 of the 22 plumes showed evidence of enhanced ozone in the plumes, and even in those cases it was unclear if the enhancement was caused by smoke emissions. This is consistent with the previous TES study of Verma et al. (2009) who found little mean enhancement of ozone within plumes from Siberian biomass burning.

We demonstrated that NH_3 and formic acid (HCOOH) retrievals from TES can be combined with CO to calculate enhancement ratios of these species within biomass burning plumes by calculating representative volume mixing ratios for NH_3 and HCOOH and then mapping the CO retrieval to the same vertical grid. Our calculated enhancement ratios are within the range of values reported in the literature. However, more research is needed to determine the best way to compare retrievals with significantly different vertical sensitivities, such as NH_3 and CO.

We find negative residuals between the 1150 and 1175 cm^{-1} in four TES scans. The shape of these residuals is consistent with absorption by PAN. Our preliminary analysis suggests TES can observe PAN within boreal biomass burning plumes, but much further work is needed to test the robustness of this result. In contrast, due to the noise in the 2B1 band of TES, we find that it is unlikely that TES will be able to observe HCN within most biomass burning plumes.

In our future work, we plan to extend this analysis to the other biomass burning plumes detected by TES during ARCTAS-B. We will also explore other methods to detect PAN and HCN within these plumes, such as singular vector decomposition or the detection technique of Walker et al. (2010).

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