

HCOOH
measurements from
space

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HCOOH measurements from space: TES retrieval algorithm and observed global distribution

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5 other terminal alkenes (e.g., Neeb et al., 1997; Lee et al., 2006; Paulot et al., 2011), alkynes (Hatakeyama et al., 1986; Bohn et al., 1996), and acetaldehyde (Andrews et al., 2012; Clubb et al., 2012). Primary sources of HCOOH include biomass and bio-fuel burning (e.g., Goode et al., 2000), biogenic emissions from plants and soils (e.g., Kesselmeier et al., 1998; Kuhn et al., 2002; Jardine et al., 2011; Sanhueza et Andreae., 1991), agriculture (e.g., Ngwabie et al., 2008), and urban emissions (e.g., Kawamura et al., 1985; Talbot et al., 1988).

10 HCOOH is removed from the atmosphere mainly through wet and dry deposition. Photochemical loss is relatively slow ($\tau \sim 25$ days), so that any HCOOH formed or vented outside of the boundary layer can be transported for long distances in the free troposphere (Paulot et al., 2011). Irreversible uptake on dust can be significant under some conditions, but appears to be minor on a global scale (Hatch et al., 2007; Paulot et al., 2011). The overall atmospheric lifetime for HCOOH is estimated at 3–4 days (Stavrakou et al., 2012).

15 The above HCOOH sources are poorly quantified, and recent work has revealed major inconsistencies between model predictions and observed HCOOH concentrations. Paulot et al. (2011) found that HCOOH levels predicted by the GEOS-Chem chemical transport model (CTM) exhibited a persistent low bias relative to available ground-based and airborne observations. The comparisons implied a large missing secondary source of HCOOH; proposed candidates to explain the model-measurement discrep-
20 ancies included missing biogenic or biomass burning precursors, as well as organic aerosol oxidation. Stavrakou et al. (2012) also found evidence of a large model underestimate of atmospheric HCOOH on the basis of satellite measurements from the Infrared Atmospheric Sounding Interferometer (IASI), and attributed the discrepancy to
25 a missing primary or secondary source from terrestrial vegetation.

The first space-borne observations of atmospheric HCOOH were based on observations of biomass burning events from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) (Rinsland et al., 2006, 2007). The ACE-FTS makes solar occultation measurements using limb-viewing geometry, and the

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resulting data are restricted to the upper troposphere and lower stratosphere. Another limb instrument, the MIPAS-ENVISAT emission spectrometer, was used to examine the regional and seasonal variability of HCOOH at 10 km, and revealed very strong seasonal cycles over southern Africa and Indonesia-Australia (Grutter et al., 2010). The IASI FTS instrument retrieves HCOOH in nadir viewing mode (Coheur et al., 2009), providing measurements of tropospheric HCOOH from upwelling thermal infrared radiances. Razavi et al. (2011) applied a simple and computationally efficient retrieval strategy (based on brightness temperature differences between a clear window and an HCOOH absorption feature) to invert the IASI observations into total column concentrations and provide a global picture of the distribution of atmospheric HCOOH, albeit with large uncertainties. The present paper will describe the retrieval of HCOOH from global, high spectral resolution nadir Tropospheric Emission Spectrometer (TES) measurements, an FTS on NASA's Aura platform (Beer et al., 2001).

TES's high spectral resolution (0.06 cm^{-1}), spatial resolution ($5\text{ km} \times 8\text{ km}$), good signal-to-noise ratio (SNR) in the 1B2 band ($920\text{--}1150\text{ cm}^{-1}$; Shephard et al., 2008), and radiometric stability (Connor et al., 2011) provide the capacity to measure atmospheric concentrations of several weakly absorbing species: ammonia (Shephard et al., 2011; Zhu et al., 2013; Pinder et al., 2011), methanol (Cady-Pereira, 2012; Wells et al., 2012, 2013) and HCOOH, as is described in this paper. The high spectral resolution allows the use of spectral microwindows in the retrieval that both increase computational efficiency and reduce the impact of interfering species. Furthermore, Aura is in a sun-synchronous orbit with daytime and nighttime overpasses at 13:30 and 01:30 (mean local solar time). Since TES is a nadir-viewing thermal infrared instrument, the high thermal contrast between the surface and lower troposphere around the time of the early afternoon overpass translates to enhanced sensitivity to boundary layer HCOOH.

Together, the above characteristics have the potential to make TES more sensitive to surface HCOOH variations than other available infrared satellite sensors. Combining these sensor capabilities with a rigorous global retrieval provides the opportunity to obtain global information on lower tropospheric HCOOH with greater accuracy than has

2005), which has been well validated (e.g., Shephard et al., 2009; Mlawer et al., 2012; Alvarado et al., 2013).

2.2 TES HCOOH microwindows

5 The TES HCOOH retrieval uses the ν_6 -vibrational band at 1105 cm^{-1} . Figure 1 shows simulated radiance signals for relevant atmospheric species in this relatively clean spectral window region. The background and enhanced concentrations used to calculate these spectral sensitivities are given in Table 1. Note that line intensities for this region from HITRAN 2008 (Rothman et al., 2009), which are based on Vander Auwera et al. (2007), are up to two times greater than the HITRAN 2004 values (Rothman et al., 2005). This large change implies that earlier HCOOH measurements derived using HITRAN 2004 are too large by a similar amount.

10 Microwindows for the TES HCOOH retrieval are presented in Table 2. While the HCOOH spectral feature in this region includes two side lobes, between 1192 and 1196 cm^{-1} and between 1112 and 1120 cm^{-1} , we find that using the information in these lobes often leads to unstable retrievals when the HCOOH spectral signal is weak. The signal in these features tends to rise above the noise level only for large concentrations of HCOOH.

2.3 Building a priori profiles and constraints

15 Simulated HCOOH mixing ratios from the GEOS-Chem CTM are shown in Fig. 2 for January and July 2004. Concentrations are elevated over the continents and in the summer hemisphere, reflecting the predominantly terrestrial and photochemical nature of the HCOOH sources in the model. The highest HCOOH levels are predicted over and downwind of regions with strong biogenic and pyrogenic emissions, such as the tropics and the southeastern United States. Only rarely do the simulated surface concentrations exceed 2 ppbv.

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Alvarado et al. (2011) used GEOS-Chem output to build an initial pair of a priori profiles for retrieving HCOOH from TES (Fig. 3): a clean profile, defined as the average of all profiles that did not exceed 0.2 ppbv below 500 hPa, and an enhanced profile, defined as the average of the remaining cases. The initial constraint matrices were derived from the model variability across all profiles classified as “clean” or “enhanced”. These a priori values were then used for TES HCOOH retrievals during the NASA ARCTAS (Jacob et al., 2010) campaign over a boreal fire. These few retrievals successfully reduced the residuals in the HCOOH spectral window and returned reasonable results, but when the same a priori information was used in a set of retrievals carried out over southeast Australia during the Black Saturday fires of 2009, the retrieval was frequently not able to find a solution. An example of this is shown in Fig. 4b and c. Further analysis of the retrieval showed that even the enhanced a priori profile led to very weak Jacobians, which when combined with a weaker HCOOH signal (1 K for the Australia cases vs. 2 K for the ARCTAS case), did not allow the retrieval to reduce the residuals.

These results pointed to the need for a more enhanced a priori profile, corresponding to scenarios with much higher HCOOH concentrations than predicted by the CTM. This is consistent with the findings of Paulot et al. (2011), who found that atmospheric HCOOH tends to be underestimated by GEOS-Chem, at times by a factor of four or more. Aircraft measurements during the Intercontinental Transport Experiment-Phase B (INTEX-B) and Megacity Initiative: Local and Global Research Observations, (MILAGRO) campaigns also confirm the general tendency of GEOS-Chem to underestimate HCOOH (Fig. 5). Therefore, we concluded that the current state of understanding for HCOOH, as implemented in GEOS-Chem, does not provide an adequate representation of the distribution and variability of atmospheric HCOOH for deriving an appropriate a priori for the TES retrieval. We instead constructed an enhanced a priori profile based on the IASI a priori (Razavi et al., 2011) and an analysis of HCOOH measurements from the MILAGRO campaign, and a clean a priori based on the MILAGRO data alone (Fig. 6). As we discuss in Sect. 3.3, clean profiles are in general below the TES detectability level. The diagonals of the covariance matrices used for constructing

the constraint matrices were set to allow approximately 20 % variability for the clean cases and 50 % variability for the enhanced cases. Constraining the clean cases more tightly greatly reduces the chance of false positives, i.e., artificial detection of elevated HCOOH when there is little information from the observations. These constraints will be refined as needed when more global information becomes available. The refined retrieval with the enhanced prior reduces the residuals to an acceptable level, as can be seen in the bottom panel of Fig. 4.

2.4 A priori selection

For the TES CH₃OH algorithm (Cady-Pereira et al., 2012), the a priori type is selected according to location and month from a database derived from GEOS-Chem output over the entire Earth for a year. We found that this approach was not feasible for HCOOH, given the mismatch between the GEOS-Chem output and measured atmospheric concentrations. Instead we created an a priori selection algorithm based on the brightness temperature (BT) difference between the peak of the HCOOH signal and a nearby “window” region. This is similar to the approach followed for the TES NH₃ retrieval (Shephard et al., 2011), and is the basis of the IASI HCOOH and CH₃OH retrieval algorithms (Razavi et al., 2011). However, unlike with IASI, in this case we are only using the BT difference to select an a priori profile for use in the subsequent full optimal estimation retrieval.

Figure 7 shows a simulated TES spectrum in the region where HCOOH is active along with the HCOOH signal, defined as the difference between forward model runs with and without HCOOH. The HCOOH peak and window signals are calculated over 1105.04–1105.16 cm⁻¹ (region A) and 1108.88–1109.06 cm⁻¹ (region B) respectively. The BT difference between the peak and window regions only provides an estimate of the true HCOOH signal, which can be represented by the peak outlined in red from 1104.50 to 1105.64 cm⁻¹. The estimated and true signals are correlated, but the relationship is not exact; different atmospheric conditions (e.g., water vapor amounts, surface conditions) lead to different ratios between the two parameters. In Fig. 8 we

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show a scatter plot of the SNR (the true HCOOH signal divided by the expected noise) and the estimated signal from the BT difference, obtained from 561 different FM runs (see details in Sect. 3.2). There is a clear linear relationship between the two, with a correlation coefficient of 0.94. However, the degree of scatter illustrates that even in a simulation environment with no spectral noise and no retrieval errors in other species, the BT difference approach provides, at best, a first guess, which is its function in the TES HCOOH algorithm.

To select the a priori profile to use in a particular TES HCOOH retrieval, the BT difference is first calculated at the spectral points listed above, and then transformed by the linear relationship shown in Fig. 8 to provide an estimate of the SNR. If the absolute value of the SNR is greater than 2, then the enhanced a priori is used in the retrieval, otherwise the clean a priori is selected. In our discussion of the Black Saturday fire observations (Sect. 2.3), we noted that unless the a priori was significantly enhanced the retrieval did not move towards a solution due to weak measurement sensitivity (small Jacobian values). While in many retrieval implementations the initial guess profile and the a priori are identical, this is not compulsory, and we find that in order to avoid null space issues (from weak Jacobians) in the TES HCOOH retrieval it is necessary to set the initial guess profile to the enhanced a priori in all cases.

3 TES HCOOH product

3.1 TES HCOOH retrieval characteristics

While the HCOOH spectral signature can be clearly seen in the residuals for the Australian Black Saturday retrieval shown in Fig. 4, HCOOH is only weakly absorbing, and thus the retrieval can only provide a limited amount of information. The averaging kernel in the sample retrieval in Fig. 9 has 0.92 degrees of freedom for signal (DOFS) and is most sensitive between 800 and 700 hPa. This averaging kernel shape is typical of the TES HCOOH retrievals, where the peak in vertical sensitivity ranges from 900 to

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600 hPa depending on the atmospheric state (e.g., thermal contrast, concentration of HCOOH, temperature profile). However, the DOFS are usually lower than in this example: for 7700 successful TES retrievals performed over land during July 2009, 54 % had DOFS > 0.1, and of those 54 % had DOFS > 0.5 and 24 % had DOFS > 0.8.

Since there are often one or fewer pieces of information in an individual measurement, the shape of the retrieved profile is strongly determined by the a priori profile. Retrieving column (or partial column) scale factors rather than vertically resolved full profiles is a common strategy adopted where there is limited vertical information provided by the measurement. However, this implicitly assumes a profile shape and that the measurement is equally sensitive over all of the retrieved column. Performing the HCOOH retrieval on a number of vertical profile levels has the advantage of capturing the region of maximum vertical sensitivity for each case, which varies from profile to profile depending on the atmospheric state.

In order to compare TES HCOOH with models or in situ observations, we apply the Representative Volume Mixing Ratio (RVMR) (Payne et al., 2009; Shephard et al., 2011) method to map the retrieved profile VMRs to a subset of values that are more representative of the information content provided by TES; in the case of HCOOH this is typically one value. In other words, we aggregate the information provided by the satellite into a single metric that is minimally affected by the retrieval a priori:

$$RVMR = \exp\left(\sum_i w_i x_i\right) \quad (1)$$

where for each level i , w is the weighting function (in log space) derived from the TES sensitivity as represented by the averaging kernel, and x is the log of the retrieved mixing ratio. An example HCOOH RVMR is shown for the Black Saturday fires in Fig. 9 with the representative vertical range of the RVMR also indicated.

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3.2 Results from simulated retrievals

We carried out a series of simulated retrievals to test the performance of the TES HCOOH measurement in a situation where the “true” HCOOH profile is known. Simulated TES spectra were calculated from 561 TES Level 2 profiles with prescribed (“truth”) HCOOH profiles. These simulated HCOOH profiles were generated by applying a scale factor to either the clean or the enhanced a priori profile; the scale factor was calculated as the product of a value ranging from 10 at the surface to 1 above 300 mbar, and a random variable ranging between 0.5 and 1.0. The simulated radiances were computed for each profile by adding random noise that is typical of the actual TES instrument noise in this spectral region (0.2–0.3 K). These simulated radiances were then provided as inputs to the retrieval algorithm. The a priori profile was selected according to the algorithm described in Sect. 2.4, and the initial guess was set to the enhanced a priori.

From the 561 spectra, we obtained 334 retrieved profiles with DOFS greater than 0.1, and the TES observational operator (defined in the Appendix) was then applied to the prescribed “true” HCOOH profiles. Retrievals with DOFS < 0.1 were excluded from the following analysis, since after applying the TES operator the “true” and retrieved profiles in those cases would both be very similar to the a priori profile, which would bias the statistics.

Under these ideal simulated conditions where the truth is known, profile comparisons of the retrieved vs. true profiles in Fig. 10 show that the retrievals have a very small mean bias of -0.02 ppbv, with a standard deviation of ± 0.37 ppbv at 825 hPa. These results demonstrate that the retrieval strategy performs well under ideal conditions where everything in the atmospheric state is known perfectly except HCOOH.

More insight can be gained by binning the retrieval bias and variance according to the a priori type, as show in Table 2. Our simulated data set contains 100 cases with a clean a priori and 234 with an enhanced a priori. Note that the set of profiles classified as clean have retrievals that are significantly influenced by the a priori.

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Figure 10 shows that the TES retrieval tends to adjust the amount of HCOOH in the vertical region where TES is most sensitive, between 700 and 900 hPa. Although this is an expected result for a satellite-based infrared nadir retrieval, the overall retrieved profile shape can become somewhat distorted compared with the a priori or initial guess, as the measurement is insensitive to certain parts of the vertical profile (e.g., at the surface or above 500 mb). In general, this type of behavior will occur when the sensitivity of the infrared signal varies throughout the vertical column (as is the case for HCOOH). Use of the RVMR provides a key advantage in this regard for comparing TES data with in situ measurements or with model output, as it allows the comparison to be performed where the satellite observation actually provides information.

3.3 TES HCOOH detection threshold

The minimum concentration threshold for detecting HCOOH from TES can be defined as the value where the $SNR \equiv 1$; below that point the retrieved value is principally determined by the a priori. In Fig. 11 we show the SNR, defined in Sect. 2.4, as a function of the thermal contrast (the difference between the surface temperature and the air temperature at the first retrieval level) for the set of simulated radiances discussed in the previous section. The points have been color-coded based on the maximum concentration of each “true” profile. The environmental conditions (e.g., surface properties, atmospheric temperature profile) impact the infrared signal for a given HCOOH abundance. We see that thermal contrast plays a significant role in the strength of the HCOOH signal. We find that profiles with a maximum HCOOH concentration below 0.5 ppbv are in general not detectable by TES. Profiles with a maximum HCOOH abundance between 0.5 and 4.0 ppbv can be detected if there is sufficient thermal contrast, with greater contrast necessary as the HCOOH concentration decreases. Finally, if the profile reaches 4.0 ppbv or greater, TES will be able to detect HCOOH under almost any atmospheric conditions, except for very low thermal contrast.

When using remote sensing data, one frequently needs to assess how much information is being provided by the measurement, as opposed to the a priori assumption,

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for a given retrieval. In the case of the TES HCOOH measurements, the end user generally has no information on the SNR values; however, the retrieval does provide the DOFS, which is correlated with the signal strength (Fig. 12). When the HCOOH signal is less than the noise level ($\text{SNR} < 1$) the DOFS are generally less than 0.5. This implies that the retrieved profile will be very similar to the prior, or equivalently, that the retrieval has added little to the estimate of the true state. There are a number of circumstances that can lead to retrieved HCOOH amounts with low DOFS, including: clean conditions with low concentrations of HCOOH, cold scenes with limited infrared radiance, cloudy conditions, and cases with little thermal contrast between the surface and the atmospheric layers containing HCOOH, as shown in Fig. 11.

3.4 TES HCOOH error estimates

Error estimates derive directly from optimal estimation retrievals (Rodgers, 2000; Worden et al., 2004); see Eq. (A3) in the Appendix. The retrieval errors can then be mapped into RVMR space via the same weighting matrix (\mathbf{W}) used to calculate the RVMR itself (Cady-Pereira et al., 2012):

$$\mathbf{E} = \mathbf{W}\mathbf{H}^{-1}\mathbf{W}^T \quad (2)$$

where \mathbf{E} is the error in the RVMR, and \mathbf{H} is the Hessian, computed as:

$$\mathbf{H} = \mathbf{S}_a^{-1} + \mathbf{K}^T \mathbf{S}_n^{-1} \mathbf{K} \quad (3)$$

(refer to the Appendix for definitions of \mathbf{S}_a , \mathbf{K} , and \mathbf{S}_n).

Figure 13 shows estimated errors in the HCOOH RVMR for a TES Global Survey from July 2009. The absolute error lies in general in between 0.5 and 1.0 ppbv, and increases with increasing HCOOH; while there are some large outliers in the relative error, especially when HCOOH is low, the estimated relative errors are mostly in the 10 % to 35 % range.

For the error analysis performed here we have not explicitly taken into consideration any systematic components (i.e., the last term in Eq. A3). One potential source

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of systematic error in the retrieval is uncertainty in the spectroscopic parameters; for example, line intensity errors would yield directly proportional errors in the retrieved HCOOH concentrations. HCOOH spectroscopic parameters used in these retrievals are from the HITRAN 2008 data base (Rothman et al., 2009), with estimated uncertainties in the line intensities of $\sim 7\%$ (Vander Auwera et al., 2007). Since this error is small relative to the overall estimated error for the TES HCOOH measurement it is ignored for this initial analysis, but could be important for future retrieval improvements. Another potential source of systematic error is the propagation of errors from other retrieved parameters (i.e. temperature, water vapor retrievals, surface temperature and emissivity) onto the HCOOH retrieval. We have not taken into account these systematic or cross-state errors in this initial analysis. Our assumption is that these errors are small relative to the estimated random errors, as the retrieval microwindow is narrow and the first step of the retrieval (i.e., for surface temperature and emissivity) will have reduced the background radiance residuals to (or close to) the noise level. Conclusive characterization of the full uncertainty (i.e. both systematic and random components) in the TES HCOOH measurements requires comparisons with independent data; such comparisons will be presented in a subsequent paper.

4 Results from TES Global Surveys

Figure 14 shows the global and seasonal distribution of atmospheric HCOOH as measured by TES (2009 Global Surveys) and as simulated by GEOS-Chem. Due to the lower SNR over the oceans (from the expected low HCOOH concentrations and reduced thermal contrast), we include here only retrievals over land. There is also a paucity of successful HCOOH observations over desert regions such as North Africa and the Arabian Peninsula, due to retrieval challenges arising from the strong silicate spectral feature in surface emissivity for these areas.

The GEOS-Chem HCOOH simulation is as described by Paulot et al. (2011), with recent updates (Chaliyakunnel et al., 2014). In particular, biogenic VOC emissions are

computed in the model based on MEGANv2.1 (Guenther et al., 2012), using plant functional type distributions from the Community Land Model version 4.0 (Lawrence et al., 2011). Biomass burning emissions are derived from the GFEDv3 data base (van der Werf et al., 2010). The GEOS-Chem chemical mechanism has been updated here to include explicit treatment of Criegee intermediates as well as the production of vinyl alcohol (and subsequently HCOOH; Archibald et al., 2007) from the keto-enol tautomerization of acetaldehyde (Andrews et al., 2012; Clubb et al., 2012).

For each successful TES HCOOH retrieval over land, we sample GEOS-Chem at the time and location of the measurement, and apply the TES observational operator to the model profile. This last step ensures a self-consistent comparison that accounts for the vertical sensitivity of the satellite measurement. We compute RVMR values for both TES and GEOS-Chem as described in Sect. 3.1; these are then averaged seasonally and onto the $2^\circ \times 2.5^\circ$ GEOS-Chem model grid.

We see in Fig. 14 that the broad spatial distribution of HCOOH simulated by GEOS-Chem has some similarities to that observed by TES. For example, in both cases we see elevated HCOOH concentrations in the tropics and in the Northern Hemisphere during summer. However, the model RVMRs are persistently low compared to TES, typically by a factor of two or more. The TES data thus corroborate other recent studies based on aircraft, surface FTS, and satellite measurements that have pointed to large-scale missing sources of atmospheric HCOOH (Stavrakou et al., 2012; Paulot et al., 2011).

Some of the most pronounced model-measurement discrepancies seen in Fig. 14 occur seasonally over biomass burning regions (e.g., Amazonia, Africa, North Australia). The model concentrations are also somewhat elevated during those times, but nonetheless exhibit a dramatic low bias compared to TES. This suggests a significant missing source of HCOOH from fires, either through direct emission or secondary production from co-emitted precursors.

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5 Conclusions

Advances in infrared satellite observations are providing new global information on atmospheric species with relatively weak spectral signals, and have potential to yield valuable insights on processes driving tropospheric chemistry and air quality. In this paper, we presented the TES HCOOH retrieval, including the overall strategy, algorithm specifics, and error characterization.

Simulated retrievals show that because of its relatively weak spectral signature, measurements of HCOOH from TES in general have at most 1.0 DOFS, and usually less. The TES HCOOH retrieval is most sensitive in the mid-to-lower troposphere (850–600 hPa), with a vertical resolution of ~ 2 km. The minimum detection limit for TES HCOOH is a peak profile value of ~ 0.5 ppbv under conditions with strong thermal contrast (~ 10 K), with the detection limit increasing as thermal contrast decreases. The ensemble of simulated HCOOH retrievals also show that under ideal conditions, and in the absence of systematic errors in the spectroscopic parameters or in other retrieved quantities, the TES HCOOH retrievals are unbiased with a standard deviation of ± 0.3 ppbv. This indicates that the initial HCOOH retrieval strategy for TES performs quite well. Applying the retrieval algorithm to real TES global observations from 2009 and comparing them with the GEOS-Chem CTM, we find that TES is broadly consistent with the model results in terms of capturing the global spatial distribution of tropospheric HCOOH. However, TES HCOOH is universally higher than predicted by GEOS-Chem, and this is in agreement with recent work pointing to a large missing source of atmospheric HCOOH. The model bias is especially pronounced over biomass burning regions, suggesting that fires are one key source of atmospheric HCOOH.

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Appendix A

Brief review of the optimal estimation approach

The TES retrieval strategy uses an optimal estimation approach that minimizes the difference between the spectral radiances measured by TES and a nonlinear radiative transfer forward model. Since the retrieval is non-linear, an a priori constraint is used for estimating the true state (Bowman et al., 2006). If the estimated (retrieved) state is close to the actual state, then the estimated state can be expressed in terms of the actual state through the linear retrieval (Rodgers, 2000):

$$\hat{\mathbf{x}} = \mathbf{x}_a + \mathbf{A}(\mathbf{x} - \mathbf{x}_a) + \mathbf{G}\mathbf{n} + \mathbf{G}\mathbf{K}_b(\mathbf{b} - \mathbf{b}_a) \quad (\text{A1})$$

where $\hat{\mathbf{x}}$, \mathbf{x}_a , and \mathbf{x} are the retrieved, a priori, and the “true” state vectors respectively. The gain matrix, \mathbf{G} , maps from spectral radiance space into retrieval parameter space, and the vector \mathbf{n} represents the noise on the measured spectral radiances. The vector \mathbf{b} represents the true state for other parameters that are not measured in the HCOOH retrieval itself, but that may nonetheless impact the HCOOH retrievals results (e.g., concentrations of interfering gases, calibration, etc.). The vector \mathbf{b}_a contains the corresponding a priori values, and $\mathbf{K} = \partial\mathbf{L}/\partial\mathbf{b}$ is a Jacobian describing the dependence of the forward model radiances \mathbf{L} on the parameters in vector \mathbf{b} .

The averaging kernel, \mathbf{A} , describes the sensitivity of the retrieval to the true state:

$$\mathbf{A} = \frac{\partial\hat{\mathbf{x}}}{\partial\mathbf{x}} = \left(\mathbf{K}^T\mathbf{S}_n^{-1}\mathbf{K} + \mathbf{S}_a^{-1}\right)^{-1}\mathbf{K}^T\mathbf{S}_n^{-1}\mathbf{K} = \mathbf{G}\mathbf{K} \quad (\text{A2})$$

where \mathbf{S}_n is the instrument noise covariance matrix, and \mathbf{S}_a is the a priori constraint matrix for the retrieval. The Jacobian, \mathbf{K} , is the sensitivity of the forward model radiances to the state vector of the parameters being retrieved (i.e. HCOOH), $\mathbf{K} = \partial\mathbf{L}/\partial\mathbf{x}$. The rows of \mathbf{A} are functions (often Gaussian in shape for nadir infrared observations) with a finite

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width corresponding to the vertical resolution of the retrieved parameter. The sum of each row of \mathbf{A} provides a measure of the fraction of retrieval information that comes from the measurement rather than the a priori (Rodgers, 2000) at the corresponding altitude, provided that the retrieval is close to linear. The trace of the averaging kernel matrix gives the number of degrees of freedom for signal (DOFS) from the retrieval.

The total error covariance matrix \mathbf{S}_x for a given retrieved x parameter is given by

$$\mathbf{S}_x = (\mathbf{A}_{xx} - \mathbf{I})\mathbf{S}_a(\mathbf{A}_{xx} - \mathbf{I})^T + \mathbf{G}\mathbf{S}_n\mathbf{G}^T + \mathbf{G}\mathbf{K}_b\mathbf{S}_b(\mathbf{G}\mathbf{K}_b)^T \quad (\text{A3})$$

where \mathbf{S}_b is the expected covariance of the non-retrieved parameters. The total error for a retrieved profile is expressed as the sum of: (i) the smoothing errors (first term on the right-hand-side), i.e. the uncertainty due to unresolved fine structure in the profile; (ii) the measurement errors (second term) originating from random noise in the spectrum; and (iii) the systematic errors (last term) due to uncertainties in the non-retrieved forward model parameters, some of which are constant and some of which change from retrieval-to-retrieval (Worden et al., 2004).

When comparing modeled profiles to retrieved profiles it is necessary to calculate the profile the instrument would retrieve if it were measuring the atmosphere as represented in the model, rather than the true atmosphere. This is done by applying the TES operator, i.e. calculating the first two terms in Eq. (A1) with x as the model profile.

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**Table 1.** Background and enhanced concentrations used in Fig. 1.

Molecule	Background (molec cm ⁻²)	Enhanced (molec cm ⁻²)
H ₂ O	5.42×10^{22}	5.96×10^{22}
CO ₂	8.09×10^{21}	8.49×10^{21}
O ₃	7.35×10^{18}	8.08×10^{21}
NH ₃	1.05×10^{14}	4.91×10^{16}
HCOOH	2.16×10^{14}	2.63×10^{16}

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Table 2. Microwindows for TES HCOOH retrievals*.

Index	TES Filter	$\bar{\nu}_1$ (cm ⁻¹)	$\bar{\nu}_2$ (cm ⁻¹)	Purpose
1	1B2	1095.20	1095.32	Surface
2	1B2	1104.50	1105.64	HCOOH
3	1B2	1108.80	1109.06	Surface

* ν_1 and ν_2 represent the left and right edges of the microwindows.

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Table 3. Simulated retrieval results at 825 hPa.

A-priori	Mean (ppbv)	Bias (ppbv)	SD (σ)
Clean	0.20	−0.005 (2.5 %)	±0.02 (10 %)
Enhanced	5.02	−0.06 (1.2 %)	±0.61 (12 %)

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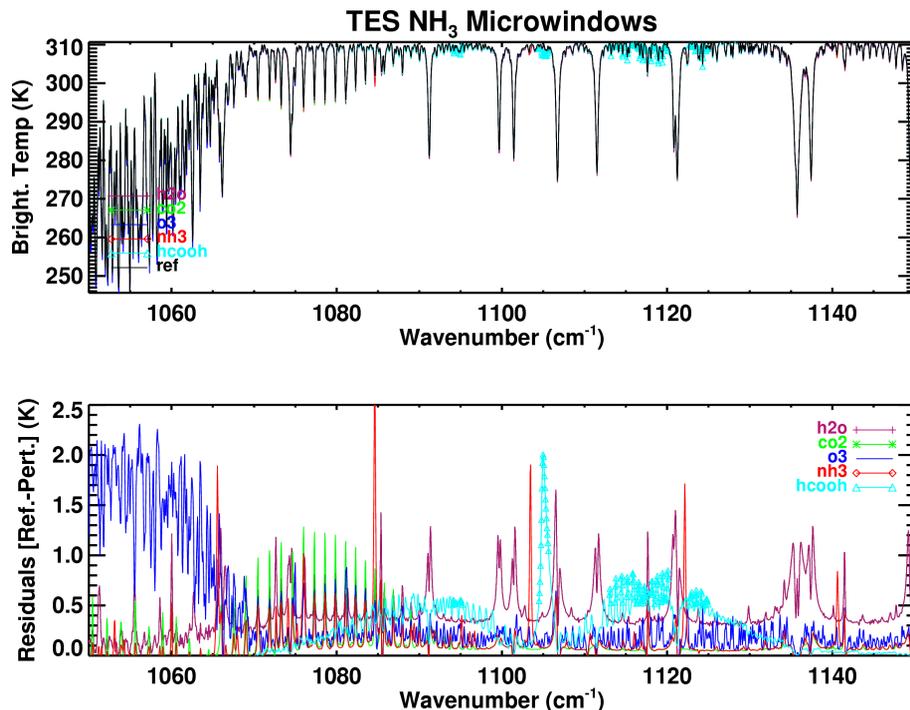
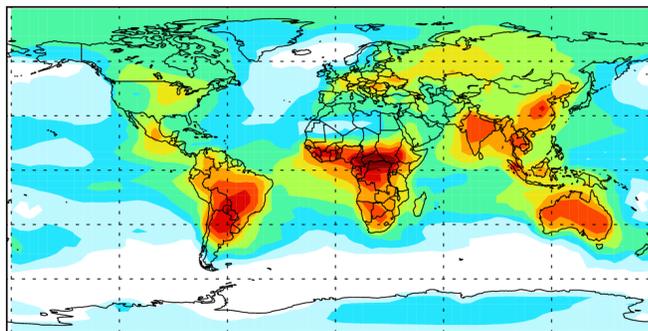


Fig. 1. TES simulated spectra and residuals. Top panel: TES simulated spectra for background amounts of H₂O, CO₂, O₃, NH₃, and HCOOH (black line), and for enhanced amounts of each molecule (colored lines). Note that in several cases the perturbed spectra are obscured by the reference spectrum. Bottom panel: residuals computed as the reference spectrum minus the perturbed spectra. In both panels the blue triangles show the microwindows used for the formic acid retrieval. See Table 1 for background and enhanced amounts.

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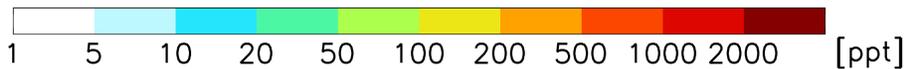
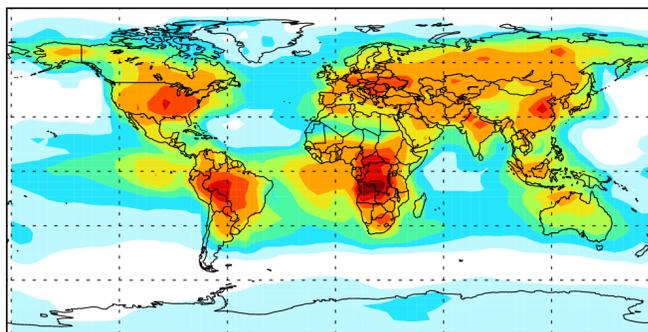


Fig. 2. HCOOH in surface air as simulated by the GEOS-Chem model for 2004.

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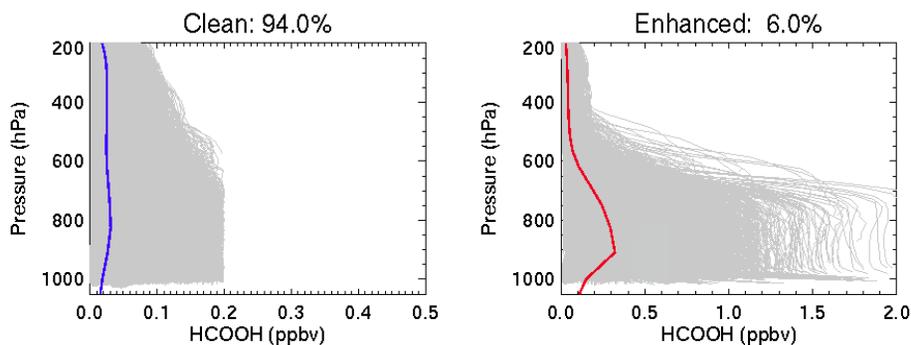


Fig. 3. HCOOH profiles simulated by GEOS-Chem over the entire globe for 2004 binned by type (in grey). The mean profiles for each category are shown in color. See text for details.

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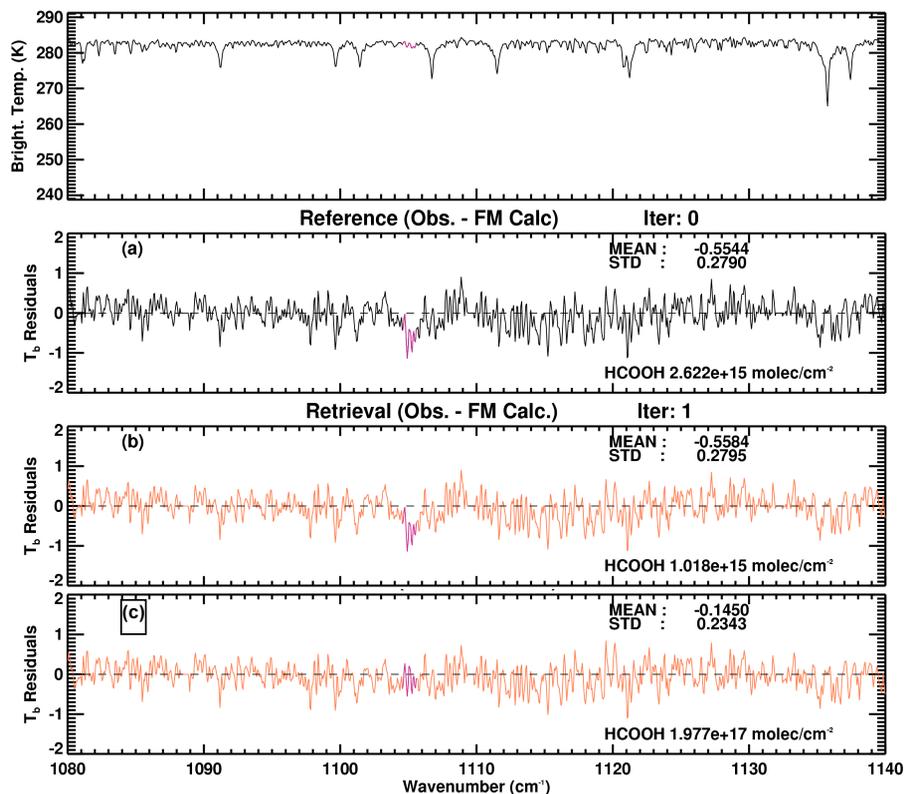


Fig. 4. TES brightness temperature and retrieval residuals from an observation taken east of Australia (24.33° S, 164.18° W) on 2 February 2009 during the Black Saturday fire event. TES BT (top panel); residual before retrieval (second panel); residual after retrieval with first a priori (third panel); residual after retrieval with final a priori (bottom panel).

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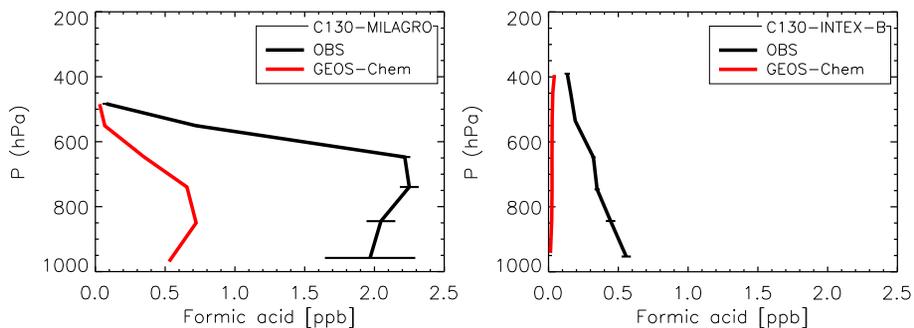


Fig. 5. Mean HCOOH profiles from GEOS-Chem and aircraft measurements during MILAGRO (left) and INTEX-B (right).

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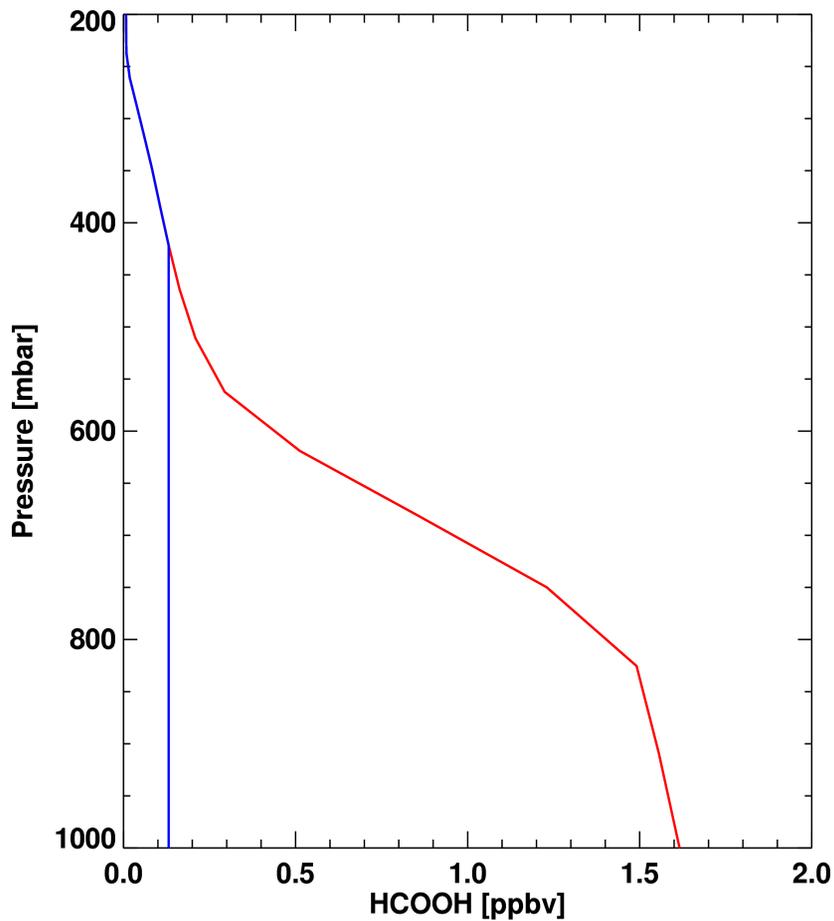


Fig. 6. Clean (blue) and enhanced (red) a priori profiles.

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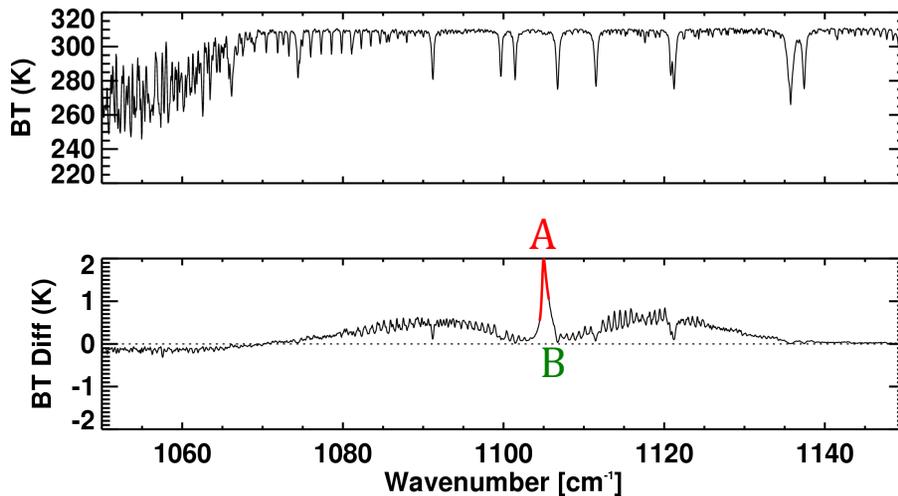


Fig. 7. Simulated TES spectrum (top panel), and HCOOH residual (bottom panel).

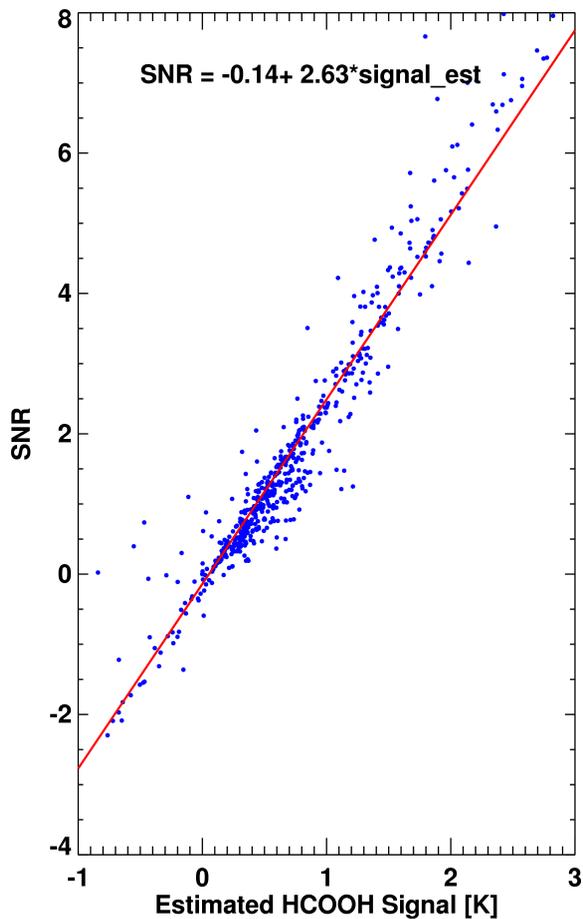


Fig. 8. HCOOH signal-to-noise ratio (SNR) vs estimated HCOOH signal (see text for definitions) with linear fit parameters.

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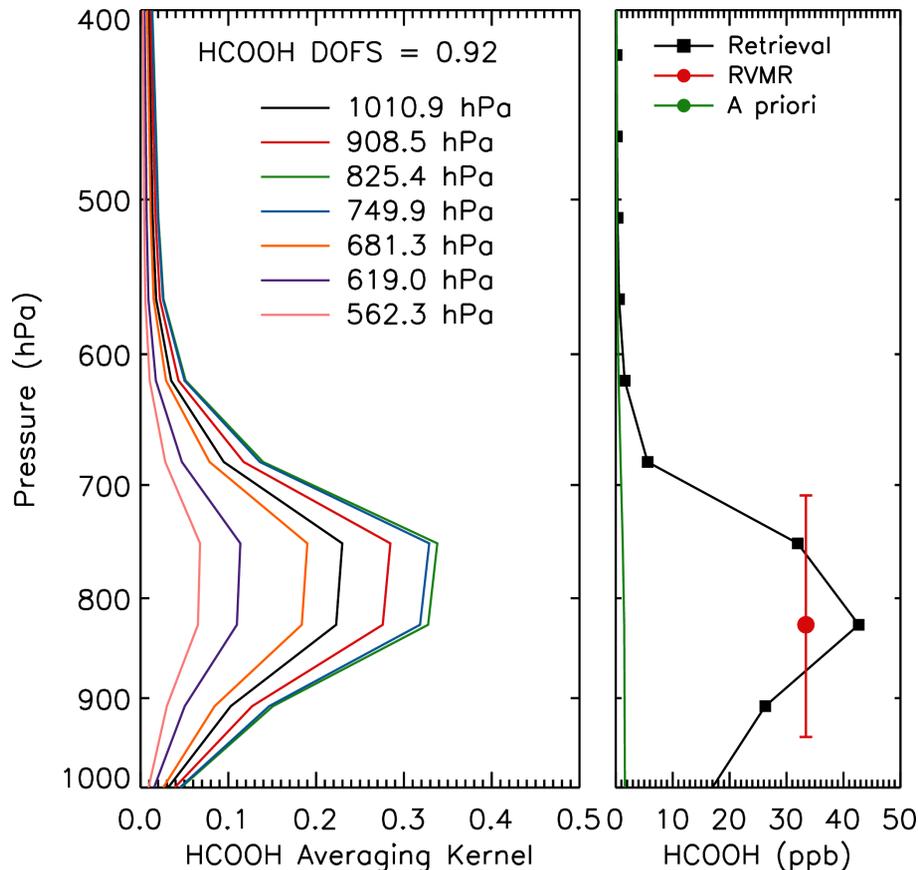


Fig. 9. Averaging kernel (left) and retrieved HCOOH profile (right) from the TES spectrum shown in Fig. 4. The red circle shows the HCOOH Representative Volume Mixing Ratio (RVMR) and the red lines show the vertical extent over which the RVMR applies. The green line is the enhanced a priori profile.

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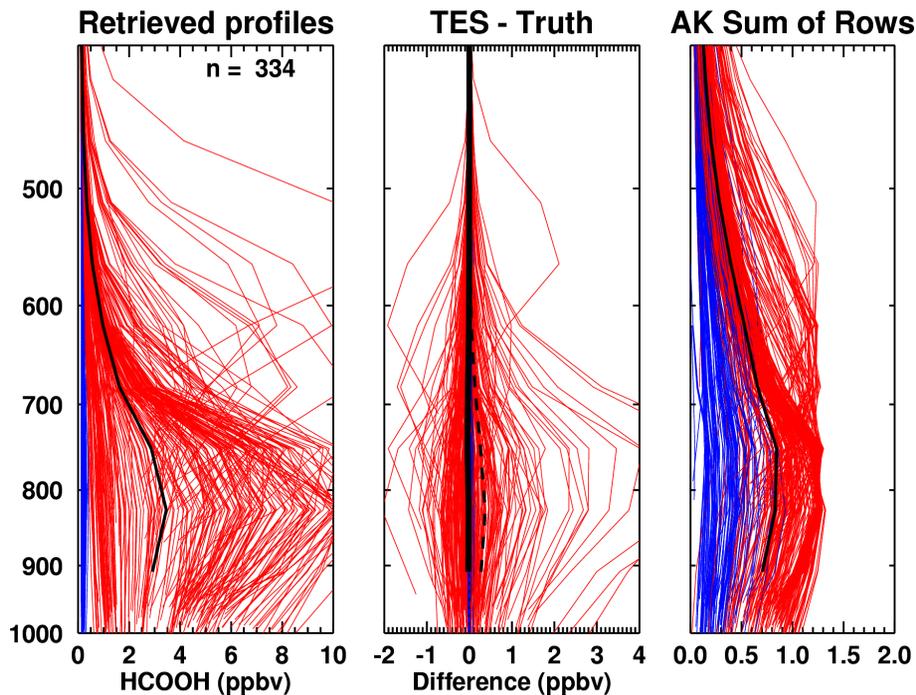


Fig. 10. Simulated HCOOH retrievals over North America in July 2008. Colored curves indicate the a priori selection (blue: clean, red: enhanced). Left panel: retrieved profiles, with the mean retrieved profile in black. Middle panel: retrieved minus true profiles. The solid line shows the mean bias, while the dashed line shows the standard deviation of the bias. Right panel: sum of the averaging kernel rows (SRAR) for each profile, with the mean in black. Means and standard deviations are not calculated for the surface level, since the height of this level ranges from above 1000 to less than 800 hPa.

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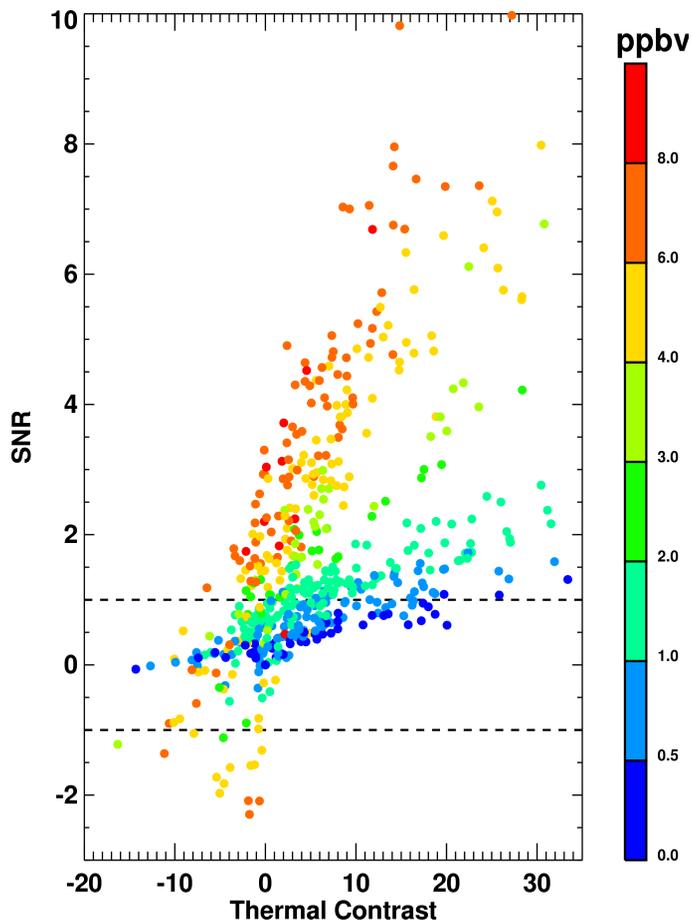



Fig. 11. Signal-to-noise ratio (SNR) vs. thermal contrast, color coded by the maximum concentration of each profile.

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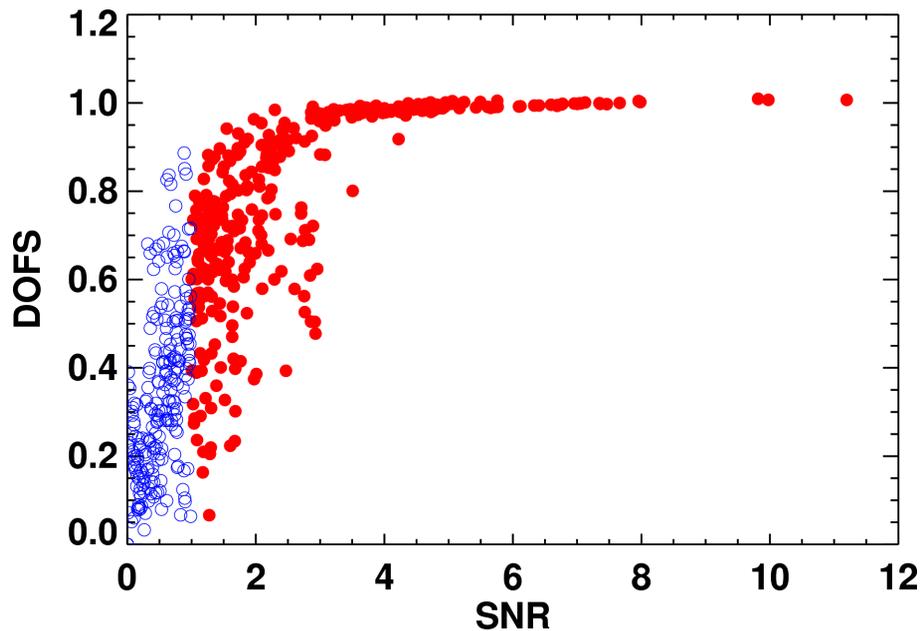
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Fig. 12. Degrees of freedom for signal (DOFS) vs. signal-to-noise ratio (SNR) for simulated retrievals.

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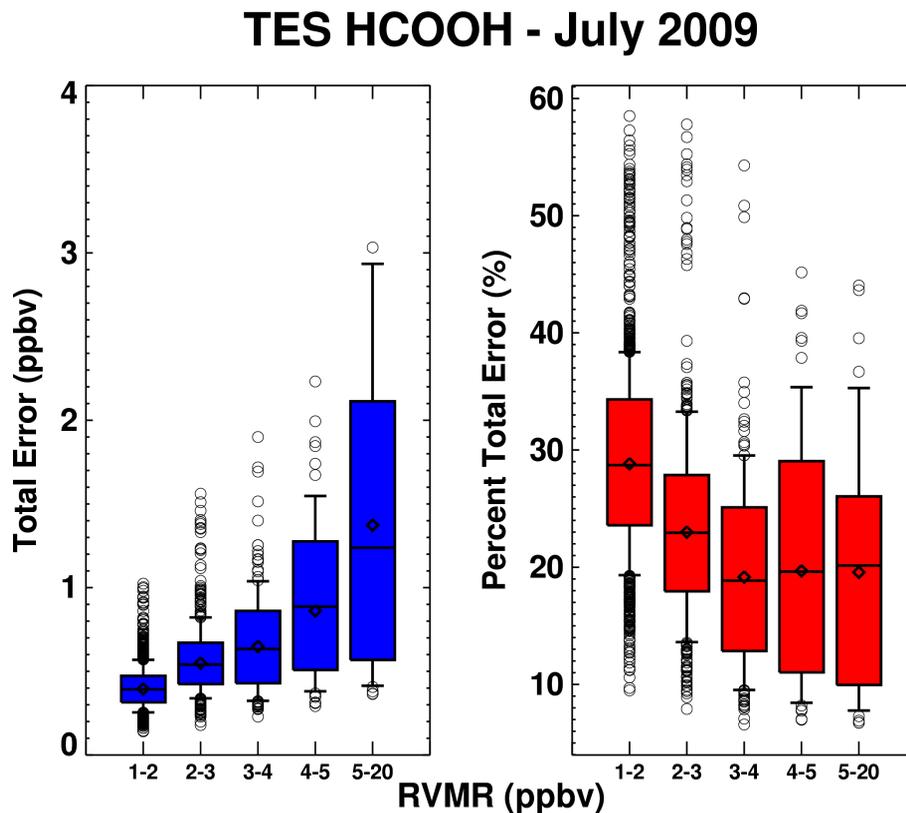


Fig. 13. HCOOH RVMR estimated errors for a TES Global Survey from July 2009, binned by RVMR value: absolute error (left panel), percent error (right panel).

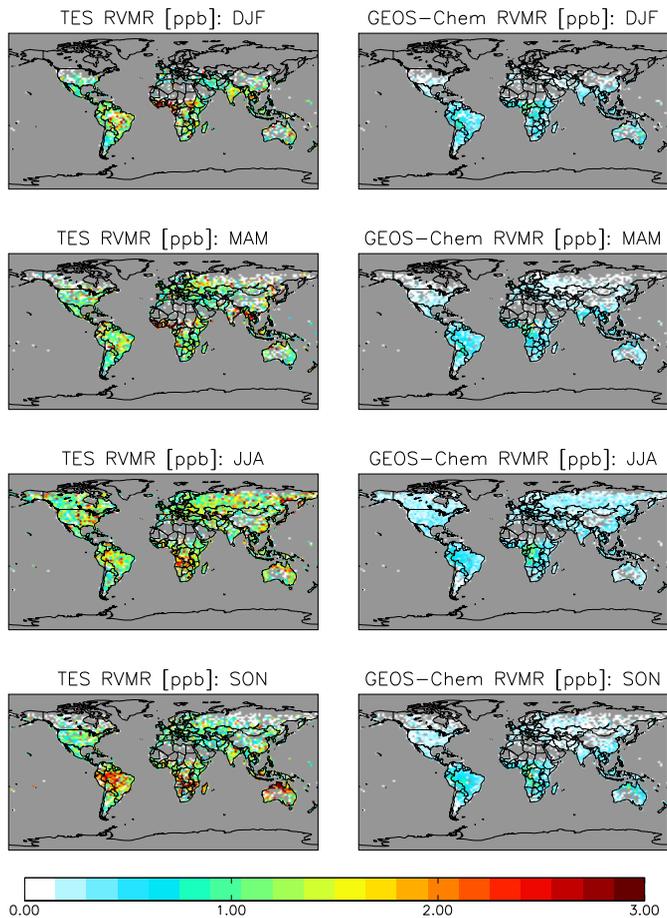


Fig. 14. HCOOH from TES 2 (left column) and GEOS-Chem with TES operator applied (right column). DJF: December, January, February; MAM: March, April, May; JJA: June, July, August; SON: September, October, November.

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