A Large Underestimate of Formic Acid from Tropical Fires: Constraints from Space-Borne Measurements

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ABSTRACT: Formic acid (HCOOH) is one of the most abundant carboxylic acids and a dominant source of atmospheric acidity. Recent work indicates a major gap in the HCOOH budget, with atmospheric concentrations much larger than expected from known sources. Here, we employ recent space-based observations from the Tropospheric Emission Spectrometer with the GEOS-Chem atmospheric model to better quantify the HCOOH source from biomass burning, and assess whether fire emissions can help close the large budget gap for this species. The space-based data reveal a severe model HCOOH underestimate most prominent over tropical burning regions, suggesting a major missing source of organic acids from fires. We develop an approach for inferring the fractional fire contribution to ambient HCOOH and find, based on measurements over Africa, that pyrogenic HCOOH:CO enhancement ratios are much higher than expected from direct emissions alone, revealing substantial secondary organic acid production in fire plumes. Current models strongly underestimate (by 10 ± 5 times) the total primary and secondary HCOOH source from African fires. If a 10-fold bias were to extend to fires in other regions, biomass burning could produce 14 Tg/a of HCOOH in the tropics or 16 Tg/a worldwide. However, even such an increase would only represent 15−20% of the total required HCOOH source, implying the existence of other larger missing sources.

1. INTRODUCTION

Formic acid (HCOOH) is one of the most important organic acids in the atmosphere. It is a significant contributor to precipitation acidity in unpolluted areas, and a central component of the volatile organic compound (VOC) oxidation cascade.1−5 Recent work has revealed a major gap in our present understanding of the atmospheric HCOOH budget, with observed concentrations much larger than can be reconciled with current estimates of its sources.5−8 In this study, we apply new space-based observations from the Tropospheric Emission Spectrometer (TES) satellite sensor to better quantify the source of atmospheric HCOOH from tropical biomass burning, and assess the degree to which this source can help close the large budget gap for this species.

Atmospheric HCOOH in continental regions is thought to derive predominantly from the oxidation of VOCs, particularly unsaturated species, by ozone and OH.5,9,10 Other potential secondary sources include acetaldehyde tautomerization3,4 and reaction of methyl peroxy radicals (CH3O2) with OH.12,13 The terrestrial biosphere is by far the largest source of VOCs to the global atmosphere,14,15 and the distribution of atmospheric HCOOH is consistent with a substantial biogenic (secondary or primary) source.5,9 However, elevated concentrations are also observed in polluted air,16,17 in fire plumes,18−20 and in marine regions where elevated concentrations and deposition fluxes imply a large source for marine-derived HCOOH precursors.21,22

Known direct sources of atmospheric HCOOH include emissions from biomass and biofuel burning, fossil fuels, terrestrial vegetation, and soil.1,7,18,20,23−25 Of these, direct emissions from open fires are currently estimated at 0.05% to 0.6% those of CO (molar basis), on average, depending on the type of vegetation being burned.7 However, several studies have demonstrated that, along with direct fire emissions, substantial secondary production of HCOOH occurs within smoke plumes as the coemitted organic gases get oxidized (e.g., refs 18, 19, 20, 26, and 27). While the magnitude of this downwind production is clearly variable,28 it seems likely from these studies that the secondary source of HCOOH from fires is significantly greater than the amount directly emitted. Quantifying this source has proven challenging, however, as in situ measurements generally provide only a limited space-time snapshot of the fire plume evolution.
Satellite measurements can provide unique constraints on this problem by providing an integrated picture of the total HCOOH produced by a given fire through time. In this paper, we use recent aircraft observations to evaluate new HCOOH retrievals from TES, and employ the satellite data to derive new insights into the contribution of tropical fires to the global HCOOH budget. Of the available space-based HCOOH measurements, the TES data provide the best sensitivity in the lower troposphere, which is a major advantage for examining surface sources. Based on a regression method for inferring the pyrogenic fraction of the measured HCOOH abundance, we show here that the integrated HCOOH:CO enhancement ratio (including direct emissions + secondary production) is ∼10 times higher than expected from current understanding of biomass burning emissions and chemical aging. We then apply the GEOS-Chem chemical transport model (CTM) to assess the potential implications of this underestimate for the tropical and global atmospheric HCOOH budget.

2. HCOOH MEASUREMENTS

2.1. Space-Based Observations of HCOOH. Space-based HCOOH retrievals have been reported from (i) the Atmospheric Chemistry Experiment—Fourier Transform Spectrometer (ACE-FTS), a limb-viewing solar occultation instrument; (ii) the Infrared Atmospheric Sounding Interferometer (IASI), a nadir-viewing FTS; and (iii) TES, also a nadir-viewing FTS. Of these, the high spectral resolution (0.06 cm⁻¹) nadir view, and strong thermal contrast (due to an early afternoon overpass) afforded by TES combine to yield the best sensitivity to lower atmospheric HCOOH. This is a major advantage for examining surface sources. However, it comes at the price of relatively low spatial density: the TES nadir footprint is 5 × 8 km² separated by ~25 km along-track in step and stare mode (used for the aircraft comparisons discussed in this paper) and by ~200 km in global survey mode.

Details of the TES HCOOH retrieval methodology are provided by Cady-Pereira et al. Briefly, the retrieval employs optimal estimation to minimize the difference between the observed upwelling infrared radiances (ν-vibrational band at 1105 cm⁻¹) and a forward radiative transfer model. Two a priori profiles are used, for “enhanced” and “clean” cases, with selection between the two based on the brightness temperature difference between the HCOOH absorption peak and a nearby window region.

HCOOH is relatively weakly absorbing in the infrared spectrum, and so the TES retrievals generally return at most one piece of information. We therefore collapse each retrieved profile to a single mixing ratio weighted to the vertical region of maximum sensitivity (a so-called representative volume mixing ratio, RVMR). Figures 1 and S1 show examples of HCOOH measurement from TES, including the rows of the averaging kernel (AK, illustrating the vertical sensitivity of the retrieval), the a priori profile, the retrieved profile, and the RVMR, for cases with enhanced and low levels of HCOOH, respectively. The vertical sensitivity varies with atmospheric conditions including temperature, thermal contrast, and the abundance of HCOOH itself; the TES HCOOH retrieval is typically most sensitive between approximately 500 and 900 hPa, as seen in Figure 1. The AK trace gives the degrees of freedom for signal (DOFS), representing the statistical significance (i.e., information content) of the retrieval, and in the case of HCOOH is most commonly between 0 and 1.

2.2. Aircraft Observations. We use measurements from two North American aircraft campaigns to evaluate the TES HCOOH retrievals. The first, Megacity Initiative: Local and Global Research Observations (MILAGRO), sampled air over Mexico and downwind over the Gulf of Mexico during March 2006. The Intercontinental Chemical Transport Experiment (INTEX-B) took place during April–May 2006 and focused mainly on sampling pollution inflow to western North America. In both cases we make use of HCOOH measurements by Crounse et al. aboard the NSF/NCAR C130 aircraft, which have an estimated uncertainty of 30% + 150 ppt. The HCOOH measurements were performed by chemical ionization mass spectroscopy based on negative ion cluster reactions of CF₃O⁺, the C130 was based out of Mexico City and Seattle during the two campaigns, and sampled from the surface to 7.5 km altitude. All measurements are reported as 0.5 s averages and in units of ppt. Flight tracks for MILAGRO and INTEX-B are as shown in Figure 2.

3. HCOOH SIMULATION

We use the GEOS-Chem CTM as an intercomparison platform to (i) evaluate the new HCOOH measurements from TES against aircraft data, and (ii) interpret the TES observations in terms of new top-down constraints on the amount of HCOOH emitted and produced from tropical fires. GEOS-Chem is a 3D Eulerian model driven by assimilated meteorological data from the NASA Goddard Earth Observing system (GEOS-5.2.0). The GEOS-5 fields have 0.5° × 0.666° horizontal resolution and 72 vertical levels. We degrade these here to 2° × 2.5° × 47 levels, and use a 15 min transport time step.

The simulation of HCOOH in GEOS-Chem is discussed in detail by Millet et al. Photochemical oxidation of precursor VOCs provides the largest model source of atmospheric HCOOH; this totals 53 Tg/a and includes alkene ozonolysis, photooxidation of isoprene, monoterpenes and alkenes, and photoinduced tautomerization of acetaldehyde (with subsequent oxidation of vinyl alcohol yielding HCOOH).

Biogenic emissions of HCOOH and its precursors are estimated with the Model of Emissions of Gases and Aerosols
from Nature (MEGANv2.1)\textsuperscript{15,40} implemented in GEOS-Chem as described by Hu et al.\textsuperscript{31} Other direct emissions of HCOOH from fossil fuels, domestic biofuel use, soils and agriculture are computed in the model as described previously.\textsuperscript{43,44} Open fire emissions of HCOOH are derived from the Global Fire Emissions Database (GFEDv3; ref 42), with emission factors (molec/kg dry matter) of 7.86 \times 10^{21} (agricultural waste), 1.03 \times 10^{22} (tropical deforestation), 7.07 \times 10^{21} (extra-tropical forests), 7.07 \times 10^{21} (peatland fires), 2.75 \times 10^{21} (savanna fires), and 1.03 \times 10^{22} (woodland fires).\textsuperscript{23,42}

Removal of atmospheric HCOOH occurs via wet and dry deposition, photochemical oxidation by OH, and dust uptake. Wet deposition in GEOS-Chem includes scavenging in convective updrafts, washout, and rainout as described by Amos et al.,\textsuperscript{45} while dry deposition is computed based on a standard resistance-in-series parametrization.\textsuperscript{44,45} Photochemical degradation of HCOOH by OH proceeds at k = 4.5 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} based on the current IUPAC recommendation.\textsuperscript{46} Irreversible uptake of HCOOH on dust is estimated following Paulot et al.

Unless otherwise noted, when comparing the TES HCOOH retrievals with the simulated amounts from GEOS-Chem we sample the model at the time and location of the satellite overpass, and apply the TES observation operator to generate a model profile as it would be observed by TES:

\[ \hat{x} = x_a + A(x - x_a) \]  

(1)

This procedure applies the TES vertical sensitivity and a priori assumptions to the model output, thus ensuring an internally consistent comparison between the two. Here, \(x_a\) is the TES a priori profile, \(x\) is the native model profile interpolated to the TES vertical grid, \(A\) is the TES averaging kernel matrix, and \(\hat{x}\) is the model HCOOH profile as seen by TES. We subsequently collapse \(\hat{x}\) to a single RVMR by applying the same weighting function used for the TES data.

4. RESULTS AND ANALYSIS

4.1. Evaluation of TES HCOOH Measurements using Aircraft Data. As there are few TES observations that coincide precisely in time and space with the aircraft measurements employed here, we use the GEOS-Chem CTM as a transfer standard for comparing the two. The degree of consistency between the TES:model and aircraft:model correlations then provides an indirect evaluation of the TES data against the airborne measurements. An underlying assumption in the approach is that any model bias in the HCOOH simulation would manifest itself in a consistent way versus both the space-based and airborne data sets.

For the TES-model comparisons, we select TES retrievals having DOFS > 0.1 that coincide spatially (within 2° × 2.5°) and temporally (within 1 h) with a MILAGRO or INTEX-B flight track and average them over the GEOS-Chem horizontal grid. A given TES observation is included only when there are two or more successful retrievals per model grid cell and 1 h averaging period, in order to avoid undue influence from statistical outliers. We then convert the simulated HCOOH profile to a single RVMR value for comparison with TES. For the aircraft-model comparisons, we sample the model along the flight track and at the time of measurement, and average the data to the model grid. We restrict the comparisons to flight data between 500 and 900 hPa, corresponding to the vertical range where the TES HCOOH retrieval is most sensitive.

Comparison results are shown in Figure 3. For the MILAGRO case, a reduced major axis regression of airborne versus modeled HCOOH yields a moderate correlation (\(R = 0.56\)) and a slope of 3.9 ± 0.2 (uncertainty values indicate 95% confidence intervals), in-line with the large model underestimate discussed earlier. The corresponding TES:model regression has \(R = 0.55\) and slope of 3.5 ± 0.8. The TES:model regression is thus 8 ± 20% below the aircraft:model value (based on a Monte Carlo simulation of the bootstrapped regression parameters), so that the two are statistically indistinguishable. However, the TES:model correlation is inflated somewhat by the convolution of the simulated profile with the TES observation operator (see Figure S2 for an extreme example of this). When we instead compute the model RVMR directly from the native simulated HCOOH profile by applying the weighting function used for TES HCOOH, we obtain a TES:model correlation of \(R = 0.41\) and a slope (4.8 ± 1.0) that is higher but still statistically indistinguishable from the aircraft:model slope.

For the INTEX-B region, we see an even larger model underestimate relative to the aircraft data, with an aircraft:model slope of 15.7 ± 1.2 and \(R = 0.55\). Figure 3 shows that while the observed HCOOH mixing ratios are frequently between 0.5 and 1.5 ppb, the simulated amounts within the region of maximum TES sensitivity are all < 0.1 ppb. The TES:model slope is lower (3.1 ± 1.0, \(R = 0.42\)) than the aircraft:model value, but the correlation here is driven entirely by the TES observation operator (as in Figure S2). When we omit this and compute the model RVMR directly from the simulated HCOOH profile, the TES:model correlation disappears (\(R = 0.19\)) and as a result one cannot draw any firm inferences based on the value of the slope. The airborne
measurements and the TES RVMR values generally fall in a similar range of 0−2 ppb, but the model’s inability to capture the abundance and distribution of atmospheric HCOOH in the INTEX-B region prevents a more quantitative comparison.

Overall, we conclude on the basis of the MILAGRO comparisons that the TES HCOOH data appear consistent with the aircraft measurements to within approximately 30%. In a similar way, Shephard et al.47 recently evaluated TES HCOOH retrievals based on airborne measurements over the Canadian Oil Sands, and found differences between the two that averaged between 10 and 60%. However, airborne HCOOH measurements are still quite sparse, and more are needed to derive a more comprehensive measure of the uncertainty in current space-based HCOOH retrievals.

4.2. Quantifying the HCOOH Source from Tropical Fires. Figure 4 shows the global distribution of atmospheric HCOOH as measured by TES during 2009 along with the simulated amounts from GEOS-Chem sampled as described in Section 3 (Eq 1). Also plotted are the seasonal differences between TES and the simulated amounts from GEOS-Chem. The most prominent enhancements in the TES data and the largest model underestimates occur over the tropics during periods of widespread biomass burning. In particular, we see strongly elevated HCOOH over northern hemisphere (NH) Africa (December−February, DJF), SH Africa (June−August, JJA and September−November, SON), Amazonia (JJA and SON), and northern Australia (SON). While the timing of these enhancements is captured by GEOS-Chem (as model fire emissions are computed using MODIS fire count observations), the simulated magnitude is clearly too low. Here, we apply these TES-model comparisons to derive a new top-down understanding of the integrated primary and secondary HCOOH source from tropical fires.

To constrain the biomass burning contribution to atmospheric HCOOH, we exploit the simultaneous measurements of HCOOH and CO from TES to derive pyrogenic HCOOH:CO enhancement ratios (ERs) for major tropical fire regions. CO is valuable in this context as a long-lived fire tracer: use of the HCOOH:CO correlation allows us to quantify the pyrogenic HCOOH source relative to other chemical compounds, independent of model errors related to the fires themselves (amount of biomass consumed, injection height, etc.).48,49 The TES CO retrieval is described elsewhere30,47−52 and has an estimated retrieval uncertainty of 10−20%. Past work has

Figure 3. Cross-comparison of space-based (TES) and airborne (MILAGRO; INTEX-B) HCOOH measurements using GEOS-Chem as an intercomparison platform. Aircraft data corresponds to 900−500 hPa to match the region of maximum TES sensitivity. TES data are colored according to their degrees of freedom for signal (DOFS > 0.1 are shown). Each red line shows a reduced major axis fit to the data with parameters given inset. For the middle row the TES observation operator has been applied to the corresponding model values; for the bottom row the native model values are shown. The dashed black lines depict the 1:1 relationship. Note the differing y-scales for the left and right columns.
generally found good agreement (within 5−10%) between TES CO and independent aircraft observations.50

We examine here the four tropical areas shown in Figure 5, each of which exhibits a large seasonal HCOOH amplitude that is coherent with the regional fire cycle (Figure 4). For each area, we compute HCOOH and CO RVMR values as described above, employing all retrievals having DOFS > 0.1 that fall within the fire season. In the case of CO we apply the HCOOH vertical weighting function, so the resulting CO and HCOOH RVMR values reflect consistent vertical sampling.

To isolate the pyrogenic HCOOH:CO signal for a given location and season, we decompose the HCOOH RVMR (HCOOH\textsuperscript{TOT}) into two components—a contribution from biomass burning (HCOOH\textsuperscript{F}, including both primary emissions and secondary production from coemitted VOCs), plus a contribution from all other sources (HCOOH\textsuperscript{O}):

\[
\text{HCOOH}^{\text{TOT}} = \text{HCOOH}^{\text{F}} + \text{HCOOH}^{\text{O}}
\]

Similarly,

\[
\text{CO}^{\text{TOT}} = \text{CO}^{\text{F}} + \text{CO}^{\text{O}}
\]

Combining, and expressing as a differential, we obtain

\[
\frac{\Delta \text{HCOOH}^{\text{TOT}}}{\Delta \text{CO}^{\text{TOT}}} = f_{\text{CO}}(F) \left[ \frac{\Delta \text{HCOOH}^{\text{F}}}{\Delta \text{CO}^{\text{F}}} \right] + f_{\text{CO}}(O) \left[ \frac{\Delta \text{HCOOH}^{\text{O}}}{\Delta \text{CO}^{\text{O}}} \right]
\]

Where \(f_{\text{CO}}(F) = \frac{\Delta \text{CO}^{\text{F}}}{\Delta \text{CO}^{\text{TOT}}}\) and \(f_{\text{CO}}(O) = \frac{\Delta \text{CO}^{\text{O}}}{\Delta \text{CO}^{\text{TOT}}}\) are the CO enhancements from fire and other sources. The left-hand-side of eq 4 represents the major axis regression slope of HCOOH
Values computed in the same way as was done in the MODIS test of the pyrogenic HCOOH:CO emission ratio in the CO budget over southern and northern Africa, respectively, to 6.7 ± 6.7 (mol %) over southern Africa that are within 30°–40° of the simulated model values derived from the sensitivity run. The approach works less well over Amazonia and north Australia. There, the HCOOH:CO correlation is low, likely reflecting weaker fire emissions than is the case over Africa (Figure S4). This low correlation degrades our ability to resolve the pyrogenic contribution to HCOOH:CO and leads to large errors in the inferred ERs (Table 1). In the case of Amazonia, the regression-based HCOOH:CO ER derived from the model output is negative (though indistinguishable from zero, or the simulated model value, at the 2σ level).

The TES HCOOH:CO ERs shown in Table 1 range from 2.6 ± 0.3 mol % (i.e., ppb/ppb expressed as %) and 2.8 ± 0.4 mol % over southern and northern Africa, respectively, to 6.7 ± 2.1 mol % and 4.5 ± 5.1 mol % over Amazonia and northern Australia. These values are insensitive to the choice of distance threshold used for determining the background ratio ΔHCOOH/(ΔCO) (with relative differences < 4% for Africa, < 2% for Australia, and < 17% for Amazonia when varying the distance threshold from 1 to 3 model grid squares). We also carried out a sensitivity analysis to test how uncertainty in the fCO (F) and fCO (O) weighting factors could bias the pyrogenic ΔHCOOH/(ΔCO) ERs inferred from the TES data. Perturbing fCO (O) by ±50% changes the TES ERs by < 4% for NH and SH Africa, by ~30% for North Australia, and by >100% for Amazonia. The results are thus consistent with the findings from the model test above, and indicate that the HCOOH:CO regression approach provides robust pyrogenic ERs over the African fire regions, has higher uncertainty over North Australia, and is unreliable over Amazonia. As shown in Figure S4, the modeled seasonal cycle of fire emissions over NH and SH Africa is distinct from that of biogenic emissions, whereas the two cycles are more aliased over Australia and Amazonia. The distinct pyrogenic/biogenic seasonal cycles, combined with larger overall fire emissions, allow more robust separation of the HCOOH fire signal over Africa than is the case over the other regions. Furthermore, we also see in Table 1 that the pyrogenic

### Table 1. ΔHCOOH/ΔCO Enhancement Ratios over Tropical Fire Regions in 2009

<table>
<thead>
<tr>
<th>study region</th>
<th>fire months</th>
<th>R²</th>
<th>ΔHCOOH&lt;sub&gt;TES&lt;/sub&gt;/ΔCO&lt;sub&gt;TES&lt;/sub&gt; (mol %)</th>
<th>ΔHCOOH&lt;sub&gt;GC&lt;/sub&gt;/ΔCO&lt;sub&gt;GC&lt;/sub&gt; (mol %)</th>
<th>simulated ΔHCOOH/ΔCO&lt;sub&gt;GC&lt;/sub&gt; (mol %)</th>
<th>derived ΔHCOOH/ΔCO&lt;sub&gt;GC&lt;/sub&gt; (mol %)</th>
<th>mean primary EF (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH Africa</td>
<td>NDJFM</td>
<td>0.51</td>
<td>2.7 ± 0.4</td>
<td>2.8 ± 0.4</td>
<td>0.19 ± 0.02</td>
<td>0.14 ± 0.12</td>
<td>0.26</td>
</tr>
<tr>
<td>SH Africa</td>
<td>JJASO</td>
<td>0.57</td>
<td>2.6 ± 0.3</td>
<td>2.5 ± 0.3</td>
<td>0.32 ± 0.03</td>
<td>0.20 ± 0.07</td>
<td>0.34</td>
</tr>
<tr>
<td>Amazonia</td>
<td>ASOND</td>
<td>0.26</td>
<td>5.9 ± 0.9</td>
<td>6.7 ± 2.1</td>
<td>0.13 ± 0.02</td>
<td>-0.59 ± 0.65</td>
<td>0.39</td>
</tr>
<tr>
<td>N Australia</td>
<td>SOND</td>
<td>0.28</td>
<td>5.1 ± 3.3</td>
<td>4.5 ± 5.1</td>
<td>0.25 ± 0.05</td>
<td>0.70 ± 0.74</td>
<td>0.25</td>
</tr>
</tbody>
</table>

ΔHCOOH/ΔCO correlation as observed by TES. *Ambient ΔHCOOH/ΔCO ratio as observed by TES. Uncertainty values given in the table represent 2σ. *Pyrogenic ΔHCOOH/ΔCO enhancement ratios are derived from the TES HCOOH and CO measurements based on CO weighting terms from GEOS-Chem and MODIS fire counts, as described in-text. #Simulated pyrogenic ΔHCOOH/ΔCO enhancement ratios in GEOS-Chem are derived from a sensitivity run with fire emissions perturbed globally by 10%. *Pyrogenic ΔHCOOH/ΔCO enhancement ratio estimated from the GEOS-Chem output as is done for the TES data. Mean direct pyrogenic ΔHCOOH/ΔCO emission ratio as predicted by GPEV3/GEOS-Chem.
ERS derived from TES data for NH and SH Africa differ only slightly from the corresponding total ERs \( \left( \frac{\Delta \text{HCOOH}}{\Delta \text{CO}_2} \right) \), revealing the dominance of fires in setting the HCOOH:CO relationship over these regions. Accordingly, we focus the following discussion on results obtained over NH Africa and SH Africa.

Finally, to assess the impact of the TES a priori assumptions on our findings, we repeated the analysis using a more stringent DOF cutoff of 0.5 (along with the default cutoff of 0.1). Results are shown in Table S2 and show that the resulting TES ERs over Africa differ by less than 20% from the base-case.

5. DISCUSSION

While the biomass burning HCOOH:CO ERs derived from TES over Africa range from 2.6 to 2.8 mol %, the corresponding ERs predicted by the model are an order of magnitude lower, at 0.19 to 0.32 mol %. The model ERs are also very similar to the primary HCOOH:CO emission ratios from these fires (0.26 to 0.34 mol %; Table 1).\(^{23,42}\) We therefore see that standard representations of biomass burning emissions and chemistry, as is implemented in GEOS-Chem, predict very limited near-ground HCOOH production from co-emitted VOCs. The TES data directly contradict this picture. Since direct biomass burning emission ratios for HCOOH are observationally constrained by numerous laboratory and field studies,\(^{5,20,62}\) the much higher ERs observed by TES argue for substantial and rapid secondary HCOOH production from fire emissions, a phenomenon that is clearly not captured by the model.

Evidence for significant secondary production of HCOOH in fire plumes has been reported in some previous studies. For example, Goode et al.\(^{20}\) and Yokelson et al.\(^{28}\) found on the basis of airborne measurements that HCOOH:CO ERs from fires in Alaska and the Yucatan peninsula increased by about a factor of 2 over 1–3 h of aging. Measurements downwind of fires in California and Amazonia showed evidence of an even greater increase, with HCOOH:CO ERs in aged plumes 6–8 times higher than the estimated initial values.\(^{9,26}\) On the other hand, observations of savanna fire plumes in Africa showed no clear evidence of strong photochemical HCOOH production.\(^{28}\) A challenge with field observations such as these lies in establishing the representativeness of measured ERs for the wider region, and also in quantifying the “ultimate” yield of HCOOH and related secondary species.

Pyrogenic HCOOH:CO ERs have also been inferred from previous space-based and ground-based remote sensing observations. Gonzálaz Abad et al.\(^{31}\) report an HCOOH:CO emission ratio for South American fires of 0.51 ± 0.15 mol % based on ACE-FTS occultation measurements in the upper troposphere. Vigoroux et al.\(^{63}\) deduce a similar value of 0.46 mol % in biomass burning outflow downwind of Southern Africa based on surface FTS measurements with peak sensitivity around ~5 km altitude. In both of these cases, however, the short HCOOH lifetime due to wet and dry deposition means that much of the emitted and initially produced HCOOH is likely to have been lost en route to the free and upper troposphere. Alvarado et al.\(^{43}\) applied a prototype version of the TES HCOOH retrieval to infer a HCOOH:CO ER of 0.31 ± 0.21 mol % in fresh Canadian, i.e., boreal fire plumes, whereas R’Honi et al.\(^{32}\) report ERs 3–10 times higher at 1.0–3.2 mol % based on IASI observations of the 2010 Russian wildfires, and on that basis infer a major secondary HCOOH source from the fires. While the TES FTS measurements provide stronger sensitivity to the lower troposphere than do IASI or ACE, and thus to a more direct constraint on biomass burning emissions of HCOOH and related species, the measured enhancements nonetheless reflect a convolution of (i) direct emission, (ii) photochemical production, (iii) depositional and chemical losses, and (iv) contributions from nonfire sources. Quantitative interpretation thus requires a framework that accounts for each process, as accomplished here using the GEOS-Chem model and the analysis strategy outlined above.

As we have seen, of the regions examined here, NH Africa and SH Africa provide the clearest biomass burning fingerprint and the most reliable constraint on the amount of HCOOH produced from fire emissions. The corresponding \( \Delta \text{HCOOH}/ \Delta \text{CO} \) ERs, reflecting the overall integral of direct emissions plus chemical production during fire plume aging, are 7.9 ± 1.7 and 15.5 ± 2.5 times higher than the corresponding ratios simulated by GEOS-Chem for SH Africa and NH Africa, respectively. These ratios are reduced somewhat (to 6.7 ± 1.0 and 12.0 ± 2.4) when a more stringent DOFS > 0.5 threshold is used for data selection. The comparisons thus imply that, on average, GEOS-Chem underestimates the overall HCOOH source from these fires by approximately 10 ± 5 times.

We carried out a model sensitivity analysis to gauge how important such a source underestimate, if broadly representative, would be for the overall HCOOH budget. A 10-fold model bias throughout the tropics would imply an HCOOH source increase of 12 Tg/a. If the same bias were to extend to fires worldwide, the result would be a ~14 Tg/a increase in the global HCOOH source, which is a significant change (25%) in the overall model budget. Akagi et al.\(^{23}\) recently estimated the global nonmethane VOC source from direct fire emissions at 400 Tg/a. A pyrogenic HCOOH source of approximately 16 Tg/a (i.e., the prior GEOS-Chem estimate of 2 Tg/a plus a 14 Tg/a increase) would indicate that a substantial fraction of the reactive carbon emitted from fires goes through HCOOH during its ensuing oxidation. However, our work here is based specifically on measurements over tropical Africa. The emission rates, and ensuing secondary production, of HCOOH from fires can differ significantly depending on the biome and other environmental factors.\(^{65}\) Better understanding of this variability is needed to improve predictions of HCOOH and related compounds.

The failure of the model to capture the observed rate of HCOOH production is consistent with other work implying a larger-than-expected HCOOH source from the oxidation of atmospheric VOCs.\(^{5,7,17,65}\) It appears that HCOOH is a more important such a source underestimate, if broadly representative, would be for the overall HCOOH budget. A 10-fold model bias throughout the tropics would imply an HCOOH source increase of 12 Tg/a. If the same bias were to extend to fires worldwide, the result would be a ~14 Tg/a increase in the global HCOOH source, which is a significant change (25%) in the overall model budget. Akagi et al.\(^{23}\) recently estimated the global nonmethane VOC source from direct fire emissions at 400 Tg/a. A pyrogenic HCOOH source of approximately 16 Tg/a (i.e., the prior GEOS-Chem estimate of 2 Tg/a plus a 14 Tg/a increase) would indicate that a substantial fraction of the reactive carbon emitted from fires goes through HCOOH during its ensuing oxidation. However, our work here is based specifically on measurements over tropical Africa. The emission rates, and ensuing secondary production, of HCOOH from fires can differ significantly depending on the biome and other environmental factors.\(^{65}\) Better understanding of this variability is needed to improve predictions of HCOOH and related compounds.

While the above findings imply a large revision to present estimates of the biomass burning source of HCOOH, we see in Figures S5 and S6 that this change does not remove the large model underestimate discussed earlier. Stavrou et al.\(^{6}\) concluded based on IASI satellite data that a source of some 100–120 Tg/a was needed to explain the global HCOOH distribution, approximately twice the summed magnitude of all its known sources.\(^{5}\) While the increased HCOOH yield from fires found here helps to reduce this discrepancy, it is clear that a separate larger missing source must also exist. Given the size
of the required carbon pool, biogenically emitted compounds likely play a central role.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publication website at DOI: 10.1021/acs.est.5b06385.

Example HCOOH retrieval from TES, impact of the TES observation operator on the model HCOOH RVMR, comparisons between TES and GEOS-Chem HCOOH and CO, seasonal HCOOH emissions, TES HCOOH:CO correlations, and tables of ΔHCOOH/ΔCO enhancement ratios (PDF)

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Notes
The authors declare no competing financial interest.

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