

Interactive comment on “Exceptional emissions of NH₃ and HCOOH in the 2010 Russian wildfires” by Y. R’Honiet

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Received and published: 22 January 2013

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We commend the authors on an excellent, interesting paper. After consulting with the authors we agreed that a comment clarifying an issue regarding our (and some others') past measurements of formic acid (HCOOH) in smoke plumes might be helpful and of general interest.

Formic acid has long been known as a difficult molecule to study because of a very strong tendency to form hydrogen bonded dimers (e.g. Bonner and Hofstadter, 1938).

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As a consequence, the HITRAN formic acid line strengths for the ν_6 band near $9 \mu\text{m}$ (1105 cm^{-1}) were a factor of 1.9 too low until the 2008 edition (Perrin and Vander Auwera, 2007; Rothman et al., 2009; Vander Auwera et al., 2007). Remarkably, the old commercial reference spectrum we had for formic acid had line strengths for this band that were also too small by a similar factor of 2.28 (within 20%). In our older work, we averaged the retrievals from the pre-2008 HITRAN with the retrievals based on the old reference spectrum causing our HCOOH mixing ratios to be a factor 2.1 ± 0.2 too high. This scaling factor can be used to correct our HCOOH data that was collected and analyzed up to 2007 and published up to early 2010. The factor can also be used to correct previously published intercomparisons. For example, Christian et al., (2004) reported that a PTR-MS observed HCOOH mixing ratios that were 42% of our open-path FTIR mixing ratios and this was attributed incorrectly to sample line losses when in fact the PTR-MS values were about 88% of the “true” values.

The reference spectrum for HCOOH in the PNNL IR data base (Sharpe et al., 2004) to which we now have access agrees with the 2008 HITRAN parameters within 15%. In addition, our HCOOH mixing ratios using both of the newer reference data agree well with mixing ratios obtained with a new chemical ionization mass spectrometer (CIMS) designed for measurement of organic acids (Veres et al., 2010). We therefore have high confidence in the new values.

To recognize and correct the error in our earlier work, in Akagi et al. (2011) we revised all the HCOOH emission factors from our old papers downwards by 2.1 to reflect the reference data change and we incidentally also significantly revised our old glycolaldehyde emission factors upwards to reflect a newer, better reference spectrum for this molecule (Johnson et al. 2010). Specifically, work up to and including Christian et al., (2010) was corrected and work starting with Burling et al., (2010) already used the new reference data and did not need correction. We do not have any easy way to correct all the old $\Delta\text{HCOOH}/\Delta\text{CO}$ values we reported in plumes in previous papers so they all remain a factor of 2.1 too high. Specifically, in the papers the authors cited by Goode

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et al., (2000) and Yokelson et al., (2007), the $\Delta\text{HCOOH}/\Delta\text{CO}$ ratios for the plumes in Alaska and Brazil, should be divided by 2.1. However, the factor by which these ratios change with aging is still valid: namely a factor of 2-2.5 in \sim 2.5 hours in Alaska and a factor of 5.5 in less than one day in Brazil. In Yokelson et al., (2009) an increase in the $\Delta\text{HCOOH}/\Delta\text{CO}$ ratio in an aging smoke plume by a factor of 2.5 in about one hour was observed by the Caltech CIMS, which is an independent measurement technique. In addition, in recent work (Akagi et al., 2012) we observed $\Delta\text{HCOOH}/\Delta\text{CO}$ increase by a factor of 7.34 as a smoke plume aged 4.5 hours. In the case of Akagi et al. (2012) the data is all based on the new HCOOH cross-sections so no correction is needed. Our comment is made mainly to clarify the status of our older work and we all agree that a brief mention of the corrected values strongly supports the IASI results in the author's paper. The fact that the IASI data can document continued and widespread increases in $\Delta\text{HCOOH}/\Delta\text{CO}$ beyond the initial fast rises we have measured in individual plumes in aircraft is very exciting.

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