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Investigation of secondary formation of formic acid: urban environment vs. oil and gas producing region

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Table S1. Comparisons of measured and modeled formic acid in previous studies.

Studies	Location and time	Model	Notes
1	Atlantic Ocean (1996.10-11)	MOGUNTIA	Model results are 8 times lower than observations.
2	Amazonia, Congo, Virginia	MOGUNTIA	Model underestimates HCOOH both in free troposphere and boundary layer.
3	Marine air, and those in Poisson et al.	MATCH-MPIC	Measurements are underestimated by a factor of 2 or more, except in Amazon.
4	Kitt Peak, US	MATCH-MPIC	Measured concentrations are substantially higher than the model-calculated values.
5	Various sites	IMPACT	Model underestimates HCOOH compared to observations at most sites.
6	Various sites (MILAGRO, INTEX-B)	GEOS-Chem	Sources of formic acid may be up to 50% greater than the estimates and the study reports evidence of a long-lived missing secondary source of formic acid.
7	North Sea (2010.3)	Trajectory model with MCM V3.2 & CRI	Model underestimates HCOOH concentrations by up to a factor of 2. The missing sources are considered to be both primary emissions of HCOOH of anthropogenic origin and a lack of precursor emissions, e.g. isoprene.
8	Satellite measurements (IASI/MetOp)	IMAGESv2	The globally source of formic acid (100-120 Tg) is 2-3 times more than that estimated from known sources. And, 90% of HCOOH produced is biogenic in origin, mainly from tropical and boreal forests.
9	Flight measurements around UK (2010.9)	Trajectory model with MCM v3.2 & CRI	Model underpredicts formic acid emissions by a factor of 2-3 (up to 4). Agreement is improved by including direct emissions. The underprediction of HCOOH sources can be accounted by increasing concentrations of propene (2-12 ppb).
10	London, UK (2012.1)	STOCHEM-CRI 3D	Observations indicate a direct anthropogenic emission of HCOOH from vehicle emissions. Global models indicate that these emissions are dominated in the northern hemisphere where global model underestimates HCOOH most significantly.
11	Satellite measurements (TES)	GEOS-Chem	HCOOH measured by TES 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 during summer and over biomass burning regions.

1. (Baboukas et al., 2000); 2. (Poisson et al., 2000); 3. (von Kuhlmann et al., 2003); 4. (Rinsland et al., 2004)*; 5. (Ito et al., 2007)*; 6. (Paulot et al., 2011); 7. (Le Breton et al., 2012)*; 8. (Stavrakou et al., 2012); 9. (Le Breton et al., 2014); 10. (Bannan et al., 2014)*; 11. (Cady-Pereira et al., 2014);

Table S2. Modifications to excited biradicals from ozonolysis of alkenes and other unsaturated compounds.

Excited biradicals	Precursors[a]	Branching ratios to form biradicals (CH_2OO)	
		MCM v3.2	Modified MCM
CH2OOA	C2H4, HMACR	0.37	0.54
CH2OOB[b]	C3H6, STYRENE, BUT1ENE, PENT1ENE, MBO, ACR	0.24	0.45
CH2OOC	MEPROPENE, ME2BUT1ENE	0.18	0.42
CH2OOD	C4H6	0.24	0.24
CH2OOE	C5H8	0.22	0.54
CH2OOF	BPINENE	0.37	0.37
CH2OOG	MACR	0.37	0.37
CH2OOJ[c]	MVK	N/A	0.50

a. Chemical names in MCM v3.2;

b. CH_2OOB is also formed from MVK, but the yield of formic acid from MVK is different from C_3H_6, thus a new excited biradical is added (CH_2OOJ).

c. CH2OOJ is added to MCM v3.2 in this study to represent yield of MVK individually.

Table S3. Chemical mechanism added to MCM v3.2 for vinyl alcohol chemistry, HCHO+HO$_2$ reaction and CH$_3$O$_2$+OH reaction

Reactions	Rate constants[a], cm^3 molecule^{-1} s^{-1}
Vinyl alcohol oxidation mechanisms proposed by Archibald et al. (2007)	
VINOH + OH = VINOHOHO2 + HO2	6.00D-12
VINOHOHO2 + NO = NO2 + HCHO + HO2 + HCOOH	8.46D-12
VINOHOHO2 + NO3 = NO2 +HCHO + HO2 + HCOOH	2.50D-12
VINOHOHO2 + HO2 = VINOHOHOOH	1.35D-11
VINOHOHOOH = HCHO + HCOOH + HO2 + OH	J(41)[b]
VINOHOHOOH + OH = VINOHOHO2	2.13D-11
Vinyl alcohol oxidation mechanisms proposed by So et al. (2014)	
VINOH + OH = HCOOH + OH + HCHO	3.80D-11
VINOH + OH = HOCH2CHO + HO2	2.40D-11
VINOH + OH = VINOHOHO2	5.20D-12
VINOHOHO2 + NO = HCOOH + HCHO + NO2	1.00D-11
Photo-tautomerization of vinyl alcohol (Andrews et al., 2012)	
CH3CHO = VINOH	J(13)*1.5[c]
Tautomerization of vinyl alcohol by acids (da Silva, 2010)	
CH3CHO = VINOH	1.17D-19*TEMP^1.2 *EXP(-279.8/TEMP)*[Acids][d]
VINOH = CH3CHO	4.67D-26*TEMP^3.3 *EXP(2269/TEMP)*[Acids]
Reaction of HCHO+HO$_2$ (Jenkin et al., 2007;Atkinson et al., 2006)	
HCHO + HO2 = HOCH2O2	9.7D-15*EXP(625/TEMP)
HOCH2O2 = HO2 + HCHO	2.4D+12*EXP(-7000/TEMP)
HOCH2O2 + HO2 = HOCH2O2H	5.6D-15*EXP(2300/TEMP)*0.5
HOCH2O2 + HO2 = HCOOH	5.6D-15*EXP(2300/TEMP)*0.3
HOCH2O2 + HO2 = OH + HOCH2O	5.6D-15*EXP(2300/TEMP)*0.2
HOCH2O2 + NO = NO2 + HOCH2O	5.6D-12
HOCH2O2 + HOCH2O2 = HCOOH + HOCH2OH	5.7D-14*EXP(750/TEMP)
HOCH2O2 + HOCH2O2 = HOCH2O + HOCH2O	5.5D-12
HOCH2O2H + OH = HOCH2O2	3.1D-11*0.12
HOCH2O2H + OH = HCOOH + OH	3.1D-11*0.88
HOCH2O = HCOOH + HO2	5D+14
HOCH2OH + OH = HCOOH + HO2	1.1D-11
Reaction of CH$_3$O$_2$+OH (Bossolasco et al., 2014)	
CH3O2 + OH = CH2OOA	2.8D-10

a. The unit is for second order reactions. The units for first order reactions are s^{-1}.
b. J(41) is the photolysis frequency of methyl hydroperoxide (CH$_3$OOH) in MCM v3.2 (http://mcm.leeds.ac.uk/MCM/parameters/photolysis.htt).
c. J(13) is the photolysis frequency of acetaldehyde (CH$_3$CHO) in MCM v3.2.
d. [Acids] is the total concentrations of organic acids (formic acid, acetic acid, propionic acid and pyruvic acid) measured in the two campaigns.

Table S4. Yields of formic acid from OH oxidation of aromatics in literature

Species	**Notes/Yields**	**References**
Benzene	13±5%	(Berndt et al., 1999)
Benzene	detected, 12±2%[b]	(Berndt and Böge, 2001)
Benzene/phenol/catechol	detected	(Borrás and Tortajada-Genaro, 2012)
Toluene	detected	(Chien et al., 1998)
Benzene/toluene	detected	(Bandow et al., 1985)
Xylenes	detected	(Bandow and Washida, 1985b)
TMB[a]	detected	(Bandow and Washida, 1985a)
1,3,5-TMB	detected	(Fisseha et al., 2004)
1,3,5-TMB	6.1%	(Baltensperger et al., 2005)
1,3,5-TMB	11%	(Wyche et al., 2009)
1,3,5-TMB	detected (up to 2%)	(Müller et al., 2012)
1,3,5-TMB	detected	(Praplan et al., 2014)

a: TMB indicates trimethylbenzene.

b: The experiments used both OH radical and ozone as the oxidants.

Figures

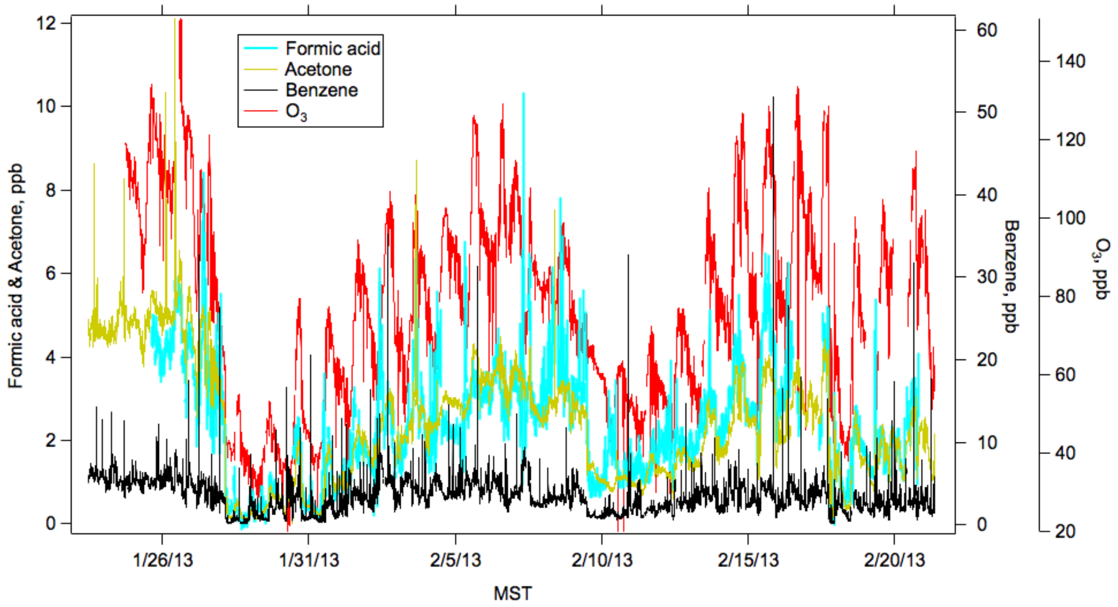

Figure S1. Time series of formic acid, acetone, benzene and ozone in UBWOS 2013. The 1-minute averaged data are shown here.

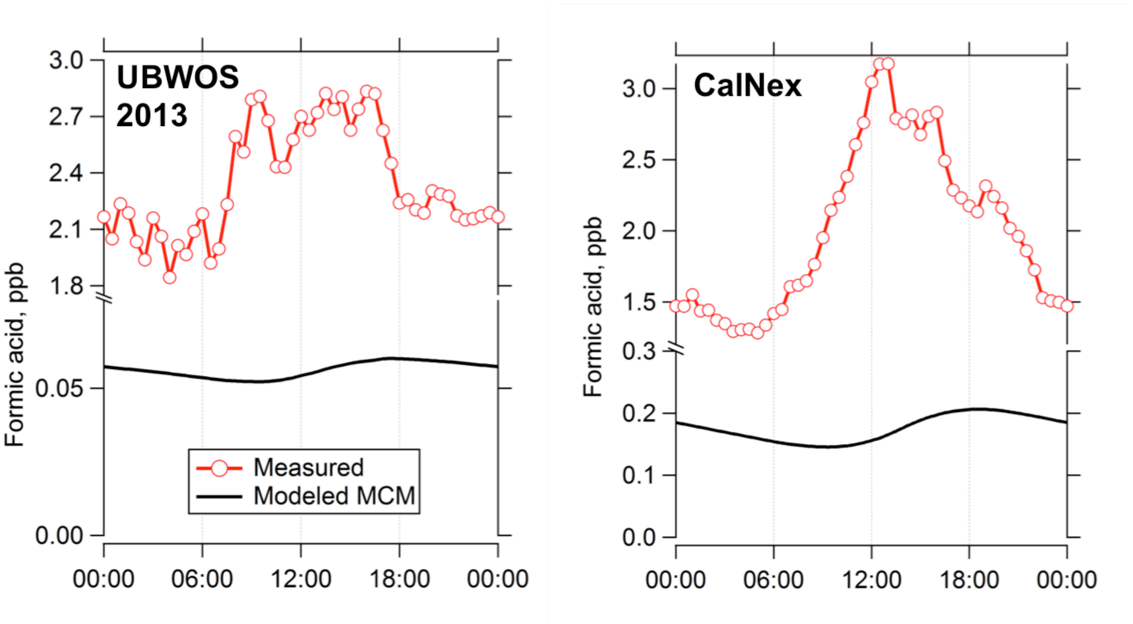

Figure S2. Comparisons of formic acid concentrations between measurements and simulations of the base case from the box model.

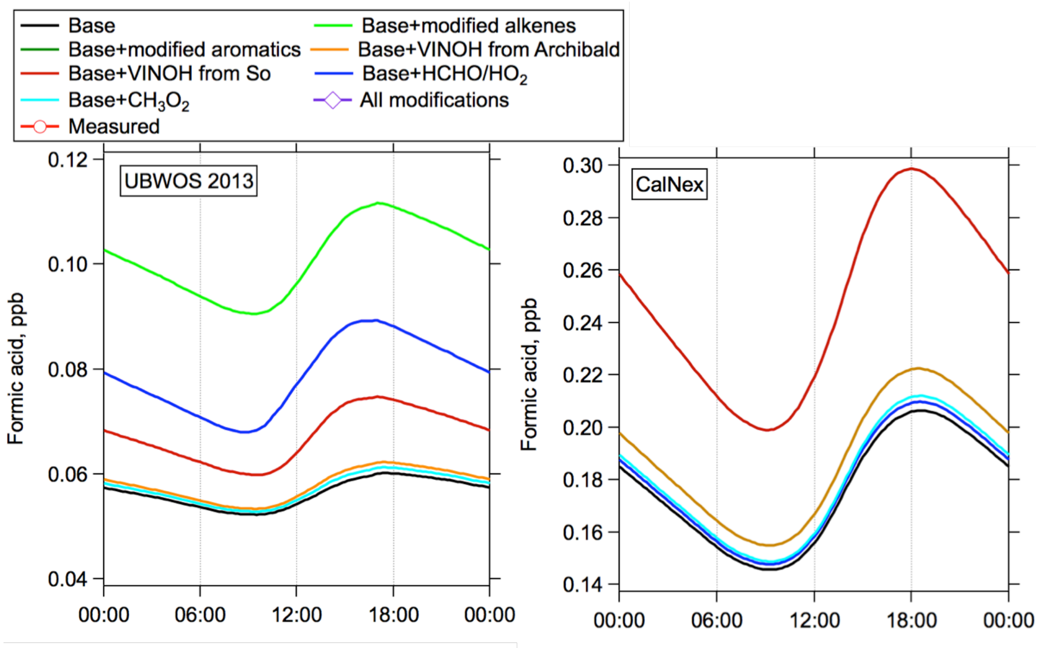

Fig. S3. Comparison of measured and modeled diurnal profiles of formic acid for UBWOS 2013 (left) and CalNex (right). Same as Fig. 4, but only the lower ranges of y-axis are shown. Some of the traces are not visible in the ranges of y-axis of the two plots. For the whole range of the plots, refer to Fig. 4 in the main text.

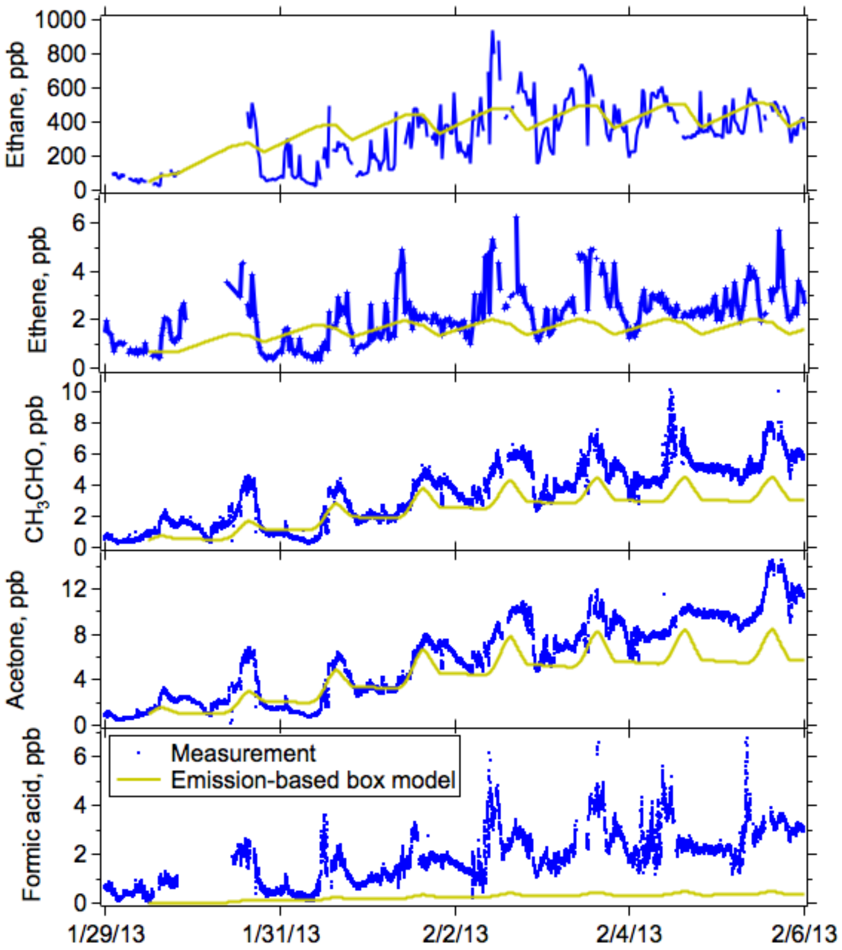

Fig. S4. Comparisons of measurements and modeled results from the emission-based box model for ethane, ethene, acetaldehyde, acetone and formic acid in Jan. 29 - Feb. 6, 2013 during UBWOS 2013.

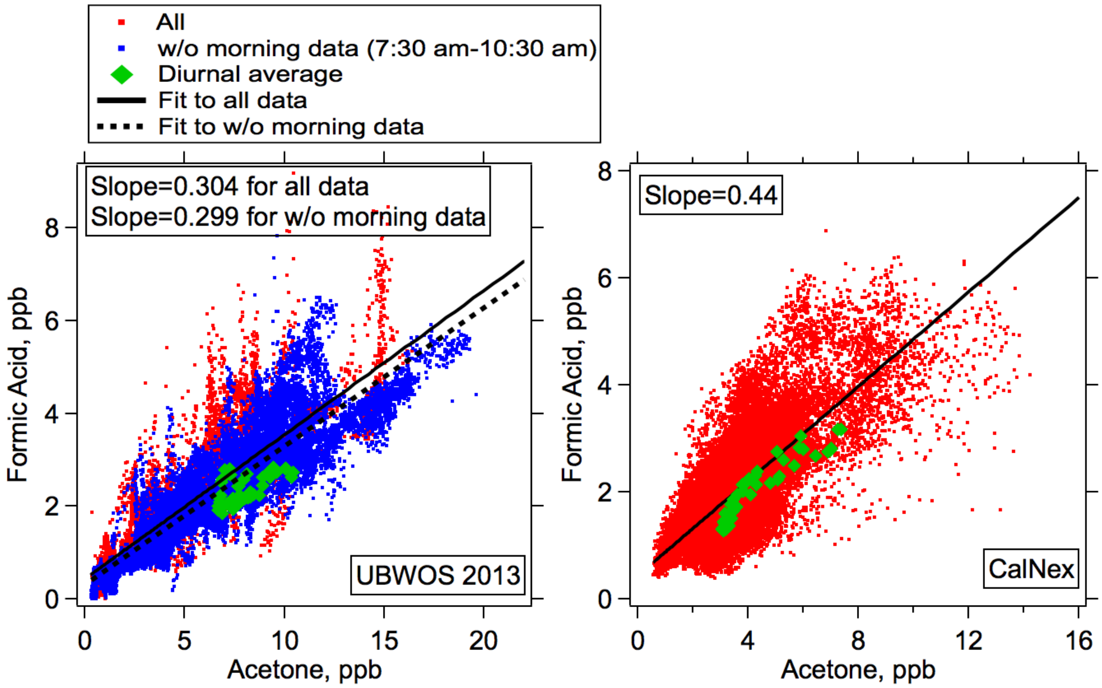

Figure S5. Scatter plots of formic acid versus acetone during UBWOS 2013 (left) and CalNex (right). Green dots are 30-min diurnal-averaged data (also shown in Fig. 6). The subset excluding morning data points (7:30 am-12:00 pm) in UBWOS 2013 is also shown.

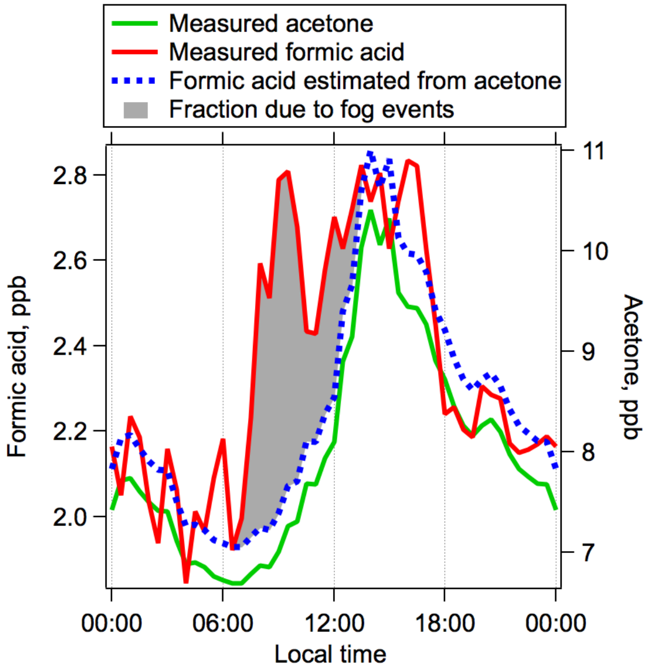

Fig. S6. Estimation of contribution from morning fog events to formic acid concentrations using measured diurnal profile of acetone in UBWOS 2013.

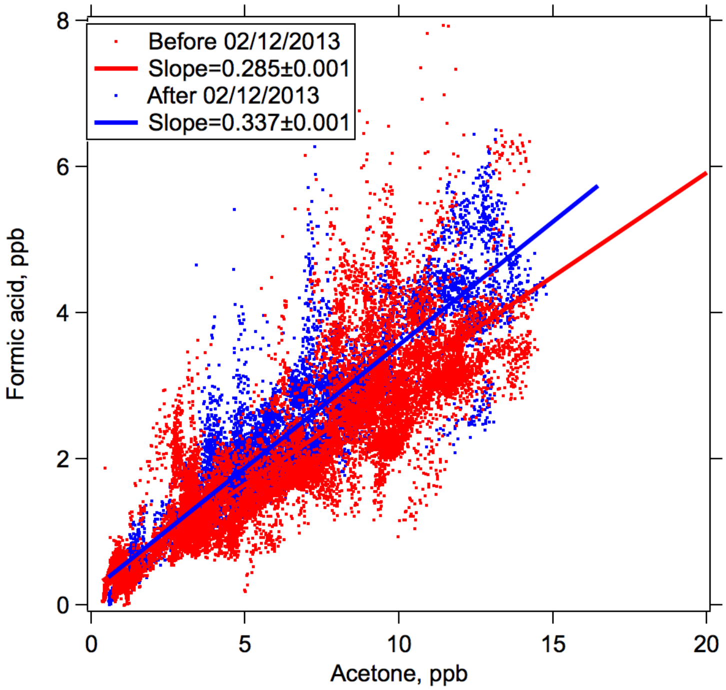

Figure S7. Scatter plots of formic acid versus acetone in UBWOS 2013. The data points are divided into two groups: before Feb. 12 and after Feb. 12, 2013. Red and blue lines are the fitted results from respective data points.

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