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Satellite evidence for a large source of formic acid from boreal and tropical forests

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18 Formic acid (HCOOH) has been identified as a major contribu-
19 tor to acidic rain in remote environments^[1, 2] but its atmospheric
20 cycle is far from being understood. Along with direct emissions
21 by human activities, vegetation fires, and green plants, its major
22 and most uncertain source is photochemical, and predominantly
23 biogenic^[3, 4]. Severe underpredictions of observed formic acid con-
24 centrations by large scale models in earlier studies^[5, 6, 7] pointed to
25 the existence of missing sources. Here we use spaceborne formic
26 acid column measurements^[8] as input to an advanced source in-
27 version algorithm coupled with a global atmospheric model to ob-
28 tain an improved formic acid global budget. We deduce an annual
29 formic acid source of 100-120 Tg, i.e. 2-3 times higher than esti-
30 mated from known sources, with a biogenic contribution of about
31 90%, mostly from tropical and boreal forests. Model comparisons
32 with independent formic acid observations strengthen our conclu-
33 sions and provide indirect validation for the satellite measurements.
34 The implications of the larger formic acid source on precipitation
35 acidity are substantial, especially over boreal forests in summer-
36 time, where the extra biogenic source results in a pH decrease of
37 0.25-0.5.

38 Known sources of formic acid in the atmosphere include fossil fuel and
39 biofuel combustion^[9], biomass burning^[10], plants^[11], dry savanna soils^[12],
40 formicine ants^[13], cloud processing^[2], abiological formation on rock surfaces^[14],

41 and photochemical oxidation of volatile organic precursors^[15]. Among these
42 sources, the contributions of savanna soils, ants, rocks, and in-cloud forma-
43 tion are very uncertain, but most probably minor.

44 Based on current inventories, primary formic acid emissions amount to
45 ca. 10 Tg annually on the global scale (Table 1). The largest contribu-
46 tion to the global formic acid budget is due to the photo-oxidation of non-
47 methane hydrocarbons, representing more than 80% of the secondary source
48 (Table 1). In the base version of the IMAGESv2 global chemistry-transport
49 model^[16, 17] used in this work to simulate the formic acid budget, the annual
50 production from biogenic precursors is estimated at ca. 20 Tg, about twice
51 lower than in a recent modelling study^[7]. The major part of this secondary
52 flux is due to isoprene oxidation by OH (8.9 Tg) and by ozone (3.9 Tg),
53 followed by monoterpene oxidation (3 Tg). The contribution of isoprene and
54 monoterpenes is, however, particularly uncertain due to the scarcity of labo-
55 ratory experiments of HCOOH formation under atmospheric conditions. For
56 example, the estimated impact of isoprene is largely dependent on the un-
57 certain fate of key intermediates produced at high yields according to recent
58 studies, like dihydroxy epoxides from HO₂-reactions of the isoprene peroxy
59 radicals^[18] and hydroperoxy-enones from peroxy isomerisations^[19]. Formic
60 acid is removed from the atmosphere through oxidation by OH, accounting
61 for 27% of the global sink, and dry and wet deposition (cf. Supplementary
62 Section 3), resulting in a global lifetime of 3-4 days.

63 Global models substantially underpredict the observed HCOOH abun-

64 dances from available ground-based and aircraft measurements^[5, 6, 7], point-
65 ing to the existence of missing sources. Their quantitative estimation is, how-
66 ever, very difficult due to the scarcity and limited representativity of these
67 measurements. Recently acquired vertical profiles from two satellite sensors
68 (ACE-FTS and MIPAS)^[20, 21] are of limited usefulness for probing the emis-
69 sions, as they sample only the upper troposphere and lower stratosphere.

70 The new generation IASI/MetOp satellite sensor, launched in 2006, mea-
71 sures in the thermal infrared and has two major advantages compared to its
72 predecessors: high spatial resolution and twice daily global coverage^[22, 23].
73 Recently global day-time measurements of formic acid have been obtained
74 and are discussed in detail in Ref.[8]. By limiting the retrieval to clear sky
75 scenes with a large thermal contrast ($>5\text{K}$), the theoretical error on the to-
76 tal column does not exceed 60%, but leads to fewer high-latitude data and
77 to exclusion of oceanic observations. Figure 1 and Supplementary Figures
78 S1, S2 illustrate the IASI-retrieved HCOOH monthly column abundances
79 in 2009. The enhanced values observed above the mid and high-latitudes
80 of the Northern Hemisphere during the growing season testify to the exis-
81 tence of a strong source, most likely of biogenic origin, since the biomass
82 burning emission patterns do not generally coincide with enhanced columns
83 (Supplementary Figure S3). Elevated values are also observed in the tropics,
84 above densely vegetated areas. Comparison of the IASI columns with the
85 IMAGESv2 model predictions (Fig. 1) corroborate earlier studies reporting
86 large model underestimations^[5, 6, 7].

87 To help interpret this discrepancy, we test the impact of two possible ad-
88 ditional sources: (a) the heterogenous oxidation of organic aerosols by OH^[7],
89 assumed to form one HCOOH molecule per OH lost, and (b) the generation
90 of 0.5 HCOOH in the photolysis of hydroperoxy-enones from isoprene^[19].
91 These hypotheses acknowledge the poor characterisation of organic aerosol
92 aging and the large uncertainty associated with the isoprene oxidation mech-
93 anism. The global modelled annual organic aerosol source (~ 100 Tg) ac-
94 counts for direct emissions and secondary organic aerosol formation (Sup-
95 plementary Section 4) and results in an extra global annual HCOOH flux
96 of 27 Tg, whereas a larger source (ca. 40 Tg) is issued by the hypothesised
97 HCOOH production through the hydroperoxy-enones (Supplementary Sec-
98 tion 2). Although both scenarios lead to significant enhancements in the
99 HCOOH columns allowing for some improvement in the model predictions,
100 especially in tropical regions like Indonesia and Amazonia, they prove inad-
101 equate to reconcile the model with the high observed columns in mid and
102 high-latitude areas (Fig. 1, Supplementary Figure S4), underscoring the need
103 for an even larger HCOOH source.

104 To properly quantify the formic acid source required to reproduce the
105 space-based constraints we use the adjoint source inversion method to infer
106 “top-down” emissions at the resolution of the global model^[24] (cf. Methods).
107 Two optimisation experiments are designed and performed, both constrained
108 by monthly IASI columns. Along with the vegetation fire source, we opti-
109 mise either a direct HCOOH emission from vegetation (Opt1), or, a secondary

110 HCOOH source from the OH-oxidation of an as-yet-unidentified biogenic pre-
111 cursor, with a global lifetime taken equal to about one day (Opt2, Table 1).
112 These simple settings are meant to represent situations in which the missing
113 HCOOH source is due to direct emission or photochemical formation on very
114 short time frames, or through a collection of compounds leading to HCOOH
115 formation after a number of unspecified intermediate steps.

116 Both optimisations predict the existence of a substantial biogenic source
117 of HCOOH estimated at about 90-110 Tg annually, i.e. 3.5 times larger than
118 in the a priori budget, as illustrated in Table 1. This brings the contribu-
119 tion of biogenic sources to 90% of the global HCOOH budget, the remainder
120 being due to fires and human activities. The optimisation improves signifi-
121 cantly the agreement between the model and IASI columns in terms of both
122 column amplitude and seasonality, also at high northern latitudes where the
123 differences were more pronounced, as shown by comparisons in Fig. 1, Supple-
124 mentary Figures S1-S2 and Table S1. The extra emission over boreal forests
125 is presumably largely due to oxidation of biogenic volatile compounds from
126 coniferous trees, for which HCOOH formation pathways remain so far unex-
127 plored. A large contribution of primary biogenic HCOOH emissions cannot
128 be excluded, but appears less likely, since high emissions of HCOOH from
129 plants are not corroborated by reported flux measurements^[25, 26].

130 The extra secondary HCOOH source inferred from the Opt2 inversion is
131 estimated at 65 Tg annually, of which tropical ecosystems (30 S-30 N) and
132 extratropical latitudes (30-90 N) contribute 40 Tg and 24 Tg annually, re-

133 spectively. The strong contribution of boreal forests seen in its geographical
134 distribution (Fig. 3) clearly suggests that oxidation of terpenoids emitted by
135 these forests generates substantial amounts of HCOOH. The seasonal varia-
136 tion of the extra source displays a summertime maximum at high latitudes,
137 which is however less pronounced than in isoprene and terpene emission in-
138 ventories used in global models (Supplementary Figure S5). Interestingly,
139 relatively high emissions are derived also during spring at these latitudes,
140 possibly reflecting higher base emission rates in spring (compared to summer
141 and autumn), as found in recent field studies of monoterpene emissions^[27]. In
142 the tropics the HCOOH precursor emission is largest at the end of the dry sea-
143 son, but is weakly correlated with the vegetation fire source, which is however
144 of low magnitude. Note that, should the entire missing source of HCOOH
145 be attributed to monoterpenes only, a total molar yield of 200% HCOOH
146 in the oxidation of monoterpenes would be required; however, the contribu-
147 tion of terpenoid compounds other than isoprene and monoterpenes might be
148 substantial, since field measurements over boreal forests have suggested the
149 existence of large emissions of undetected short-lived organic compounds^[28].

150 Both the magnitude and distribution of the source inferred from IASI
151 are found to be only weakly sensitive to model uncertainties as shown by
152 the results of sensitivity studies detailed in Supplementary Section 8. In
153 particular, we investigated the influence of uncertainties in the wet and dry
154 deposition parameterisations, the chemical scheme, and the assumed errors
155 on the spaceborne data. In most cases, the deduced annual global biogenic

156 source is found to differ by less than 10% from the reference case, confirming
157 the robustness of the inferred estimates.

158 In an attempt to evaluate the IASI-derived source, we have conducted ex-
159 tensive comparisons of the model with independent HCOOH measurements
160 (Supplementary Section 5). Comparisons with infrared column measure-
161 ments (FTIR) at Wollongong and Reunion Island show substantial improve-
162 ments after optimisation, as seen from the average bias reduction by a factor
163 of 3 or more at both locations (Fig. 2). At ground level, the a priori model
164 underprediction of HCOOH concentration measurements in air and precip-
165 itation by large factors gives way to an a posteriori mean underestimation
166 by a factor of about two or less in all regions (Supplementary Figure S6-S7).
167 More precisely, the average gas-phase (liquid) concentration is increased from
168 0.29 ppbv ($1.32 \mu\text{mol/L}$) in the a priori simulation to 0.78-1.17 ppbv (4.0 -
169 $4.2 \mu\text{mol/L}$) in the optimisation runs, to be compared to the observed 1.33
170 ppbv ($6.7 \mu\text{mol/L}$). Consistent with these results, the optimisation brings
171 also the model significantly closer to airborne concentration measurements
172 above North America and the Pacific (Supplementary Figure S8). Over-
173 all, these comparisons lend confidence to the IASI dataset, and therefore to
174 the strong biogenic source inferred from the optimisation. The comparisons,
175 however, also point to a limited ability of the model to capture the observed
176 variability and vertical profile. Although this is largely due to the limited
177 representativity of local measurements, it might also reflect the existence of
178 important shortcomings in the representation of the formic acid sources and

179 sinks.

180 We quantify the global impact of the IASI-constrained HCOOH source
181 on precipitation acidity using the calculated wet deposition fluxes of nitrate,
182 sulphate, ammonium, formate and acetate ions (Supplementary Section 7).
183 The inferred decrease in pH due to the additional HCOOH source is es-
184 timated at 0.25-0.5 over boreal forests in summertime, and 0.15-0.4 above
185 tropical vegetated areas throughout the year (Supplementary Figure S9).
186 Our model simulations predict that formic acid alone accounts for as much
187 as 60-80% of the rainwater acidity over Amazonia, in accordance with in
188 situ measurements^[29], but also over boreal forests during summertime. Its
189 contribution is also substantial at mid-latitudes, in particular over much of
190 the US, where it reaches 30-50% during the summer (Supplementary Fig-
191 ure S10). Given the remaining underestimation of a posteriori modelled
192 HCOOH concentrations against independent measurements (Supplementary
193 Table S5), the large calculated impacts on precipitation acidity are probably
194 conservative estimates. They underscore the importance of HCOOH in acid
195 deposition in different environments, although its consequences for ecosys-
196 tems are likely limited due to the assimilation of simple carboxylic acids by
197 the biota^[30].

198 In this letter we have revisited the formic acid global distribution and
199 budget, using source inversion constrained by space observations. We found
200 a biogenic source of formic acid of the order of 100 Tg annually, much larger
201 than the current state-of-the-art estimates. A large fraction of this source

202 originates in boreal and tropical forests, and although it remains mostly
203 unidentified, it is likely to be of secondary origin. These findings suggest that
204 formic acid is a high-yield product in the oxidation of organic compounds
205 emitted abundantly by plant ecosystems, such as monoterpenes and other
206 terpenoids, and underscore the need for further research on the emissions
207 and chemistry of biogenic precursors.

208 **Methods**

209 **Modelling**

210 The simulations are performed with the IMAGESv2 global chemistry
211 transport model for the year 2009, after a four-month spin-up time. The
212 model resolution is $4^\circ \times 5^\circ$ with 40 vertical levels. The accompanying Sup-
213 plementary material includes : details on HCOOH sources and sinks used in
214 the base model (Sections 1-3), a description of the organic aerosol module
215 (Section 4), a description of ground-based and aircraft measurements used
216 for validation purposes and comparisons with the model predictions (Section
217 5), discussion on the uncertainties of the IASI columns (Section 6), on the
218 impact of formic acid sources on precipitation acidity (Section 7), and on
219 the conducted sensitivity inversions (Section 8). Results are illustrated in
220 Supplementary Figures S1-S12 and Tables S1-S7.

221 **Method for source inversion**

222 The source inversion is realised through minimisation of the cost function

223 J , which measures the misfit between the model and the observations. By
 224 using the adjoint model method, the derivatives of the cost function J are
 225 computed with respect to a number of control variables \mathbf{f} (emission param-
 226 ters)

$$J(\mathbf{f}) = \frac{1}{2}[(H(\mathbf{f}) - \mathbf{y})^T \mathbf{E}^{-1}(H(\mathbf{f}) - \mathbf{y}) + \mathbf{f}^T \mathbf{B}^{-1} \mathbf{f}], \quad (1)$$

227 where $H(\mathbf{f})$ is the model operator acting on the control variables, \mathbf{y} is the
 228 observation vector, \mathbf{E} , \mathbf{B} are the covariance matrices of the errors on the
 229 observations and the emission parameters \mathbf{f} , respectively, and T is the trans-
 230 pose. The method makes use of a priori distributions for biogenic and pyro-
 231 genic emissions, obtained from available inventories (Supplementary Section
 232 1). The adjoint method enables handling of problems with large numbers
 233 of control variables, e.g. emission inversions at the model resolution. The
 234 cost function is minimised through an iterative descent algorithm which uses
 235 the forward and the adjoint model of IMAGESv2. About 50 iterations are
 236 usually needed to reach the minimum and derive the “top-down” emission es-
 237 timates. The norm of the gradient of the cost function is reduced by a factor
 238 ≥ 1000 after optimisation. In both optimisations, the pyrogenic and biogenic
 239 emission source strengths are updated (ca. 12,000 emission parameters). The
 240 errors on the emission parameters, i.e. the square roots of the diagonal el-
 241 ements of \mathbf{B} , are assumed to be a factor of two for biogenic emissions, and
 242 a factor of 2.5 for biomass burning, whereas spatiotemporal correlations are
 243 introduced through the off-diagonal elements^[24]. The matrix \mathbf{E} is assumed

244 diagonal. The errors on IASI columns are taken as the quadratic sum of a
245 30% relative error and a 4×10^{15} molec.cm⁻² absolute error. This estimate
246 does not account for a possible bias in the IASI measured columns. The
247 latter could not be quantified due to the lack of correlative measurements.
248 At Wollongong, however, we find IASI columns to be biased 30% low as
249 compared to FTIR ground-based measurements in 2008-2009, with a high
250 degree of correlation (0.84, Supplementary Section 6). Note also that the
251 model inversions do not account for the heterogeneous vertical sensitivity of
252 IASI. The application of a vertical smoothing to the model columns could
253 potentially decrease the global HCOOH source by ca. 10%.

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338 **Additional information**

339 Correspondence and requests for materials should be addressed to T. S.

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356 **Author contributions**

357 T.S. and J.-F.M. obtained the results, drafted the manuscript and pre-
358 pared the figures. J.P. developed the isoprene degradation mechanism used
359 to estimate the photochemical source of formic acid in the model. A.R.,

360 L.C., P.-F.C., D.H. and C.C. carried out the first retrievals of formic acid
361 observations from space. C.C. contributed also actively in the development
362 of the IASI sensor. C.V. and M.D.M. retrieved the FTIR data at Reunion
363 Island. N.D., D.G., N.J. and C.P.-W. retrieved the FTIR observations at
364 Wollongong.

365 **Competing Financial Interests Statement**

366 The authors declare no competing financial interests as defined by the Na-
367 ture Publishing Group or other interests that might be perceived to influence
368 the results and discussion reported in this paper.

Figure legends

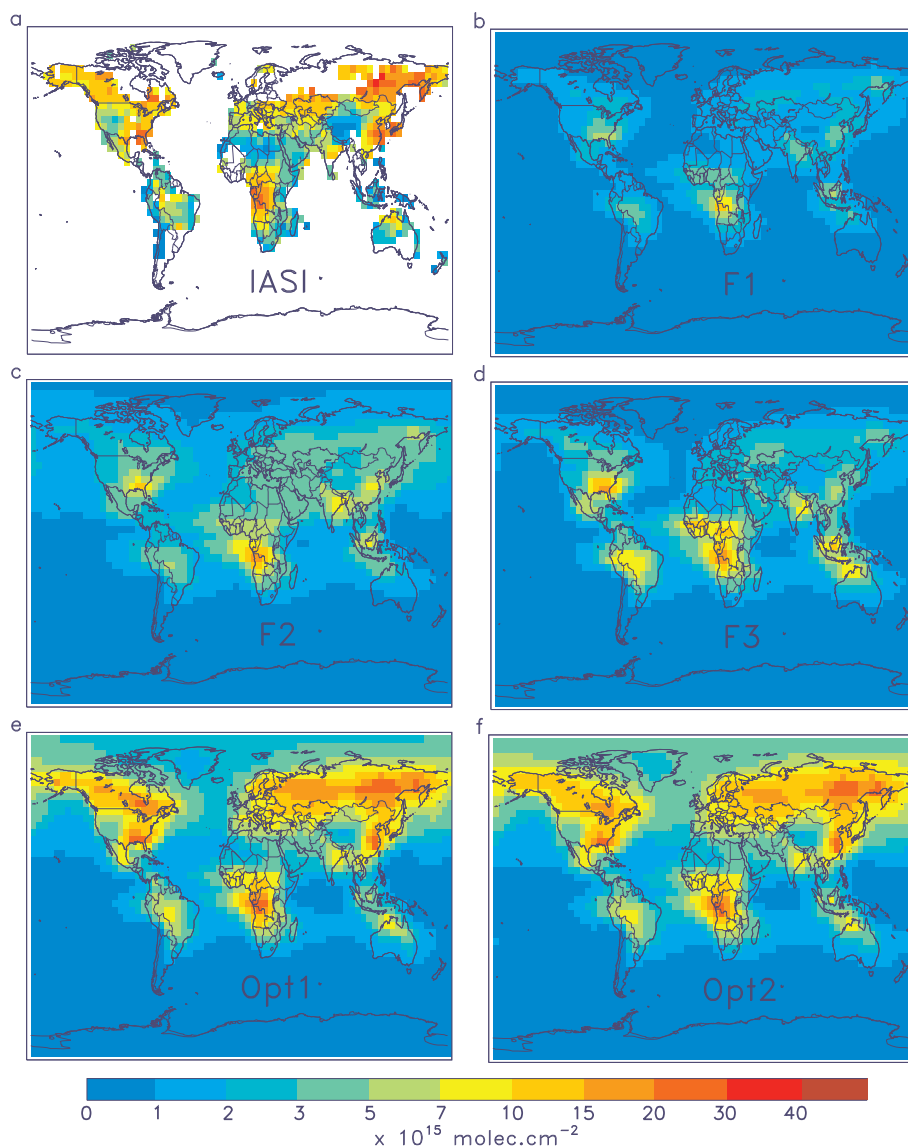


Figure 1: **Monthly averaged HCOOH columns in June 2009 (expressed in $10^{15} \text{ molec.cm}^{-2}$).** **a**, Observed by IASI. **b**, Simulated by the standard model (F1, Table 1). **c**, Simulated assuming that HCOOH is produced in the heterogeneous oxidation of organic aerosols by OH (F2). **d**, Simulated accounting for a production of HCOOH in the photolysis of hydroperoxy-enones from isoprene (F3). **e-f**, Inferred from source inversion assuming either a primary (Opt1) or a secondary (Opt2) biogenic HCOOH source (Table 1).

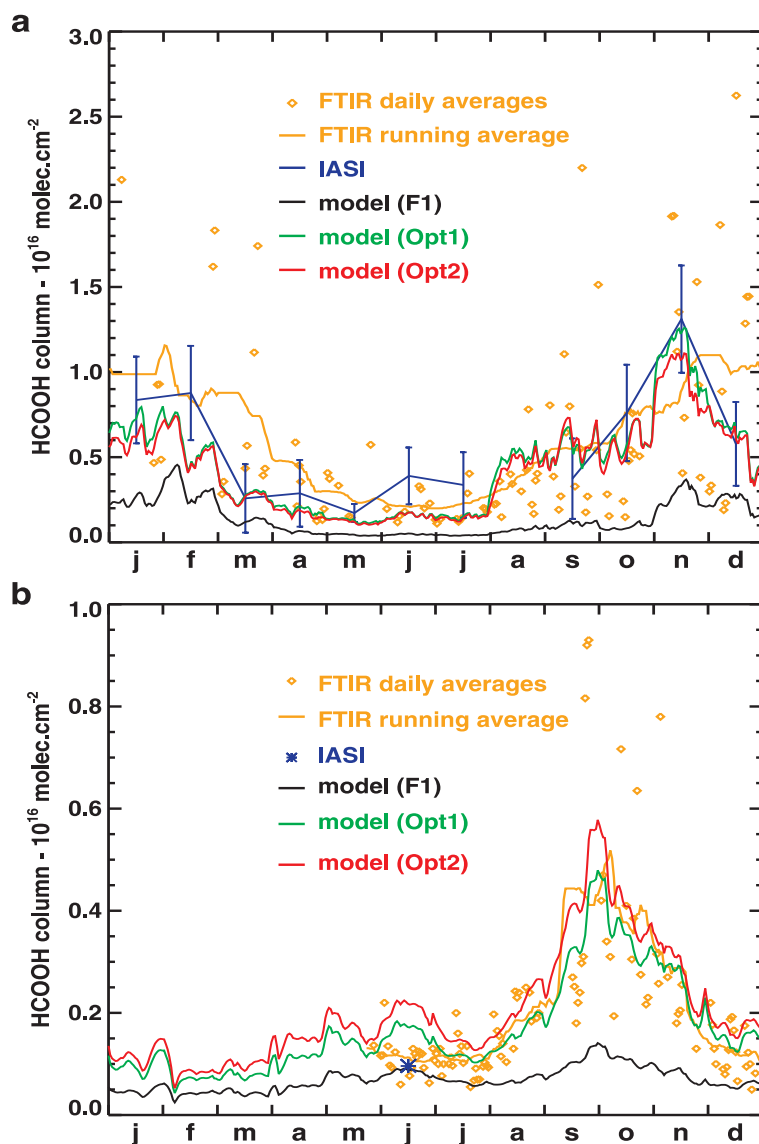


Figure 2: Comparisons between FTIR, IASI and modelled HCOOH columns in 2009. **a**, Daily and 30-day running FTIR column averages at Wollongong (34.41 S, 150.88 E) (orange) and model results from the standard simulation F1 (black) and the two inversions Opt1 (green) and Opt2 (red). Average IASI columns within a radius of 4 degrees around the site and their standard deviations are shown in blue. **b**, Same for Reunion Island (21 S, 55 E). Except for June, IASI columns are not available at this site due to the thermal contrast requirement for their retrieval.

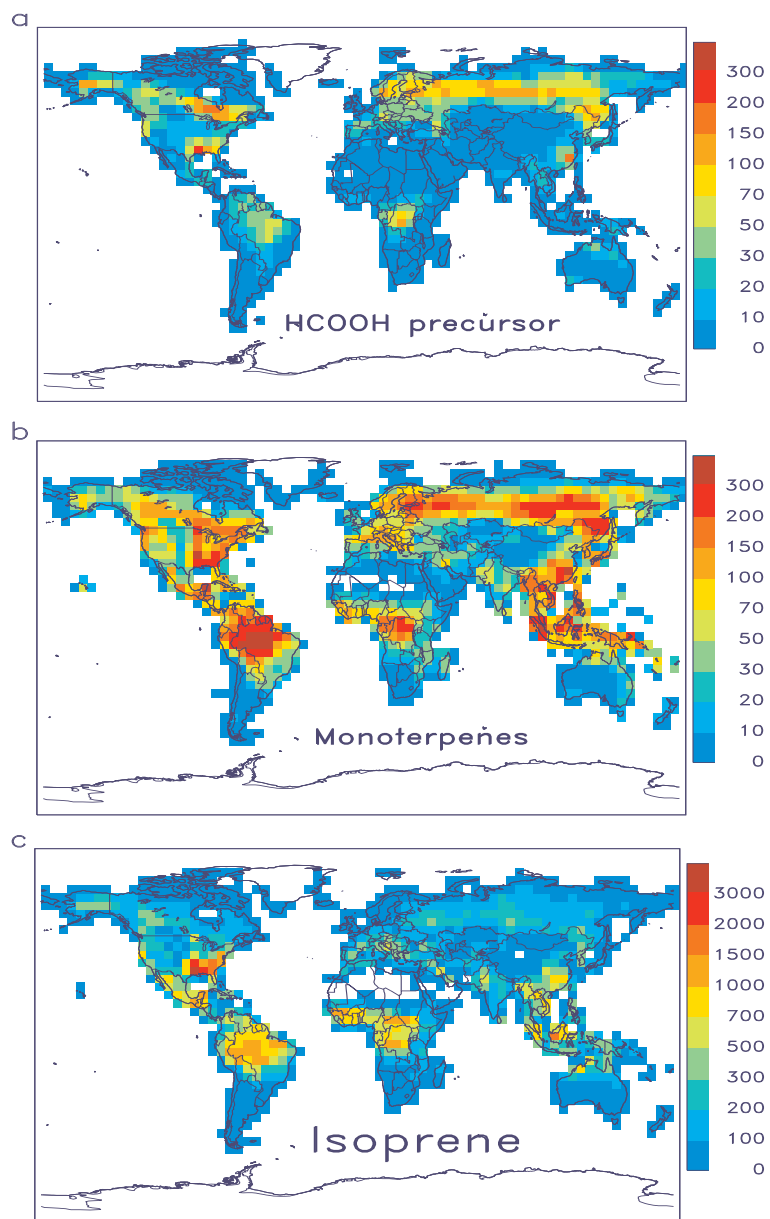


Figure 3: **Global distribution of biogenic emissions in $\mu\text{g C m}^{-2} \text{s}^{-1}$ in July 2009.** **a**, HCOOH precursor as deduced from the Opt2 inversion (Table 1). **b-c**, Monoterpene and isoprene emissions from MEGAN inventory, cf. Supplementary Section 1.

Table 1: Description of the simulations and inversions performed in this study, and global HCOOH budget calculated with IMAGESv2 and comparison with previous work. Notes : (a) includes biofuel burning and cattle emissions, (b) includes a soil source of 1.8 Tg yr^{-1} , (c) of which 19.3 Tg yr^{-1} is due to known sources and 64.7 Tg yr^{-1} to unidentified precursors, (d) A priori budget, but an estimated extra source of 2 Tmol yr^{-1} is invoked to reconcile the model with HCOOH observations, (e) includes a dust sink of 1.38 Tg yr^{-1} .

F1	standard simulation					
F2	including a production of HCOOH in the heterogeneous oxidation of organic aerosols (OA) by OH					
F3	including a production of HCOOH in the photolysis of hydroperoxy-enones from isoprene					
Inversion - Opt1	derive a primary HCOOH biogenic source using IASI					
Inversion - Opt2	derive a secondary HCOOH biogenic source using IASI					
<i>Sources (Tg/yr)</i>	F1	F2	F3	Opt1	Opt2	Paulot et al. 2011
Anthropogenic	4	4	4	4	4	2.28^a
Pyrogenic	2.9	2.9	2.9	4	4	1.5
Biogenic primary	5.6	5.6	5.6	88	5.6	4.37^b
Photochemical						
Biogenic	19.3	19.3	58.3	19.3	84^c	42.2
Anthrop./pyrog.	4.2	4.2	4.2	4.6	4.6	6.35
OA+OH	0	27	0	0	0	(15)
Total	36	63	75	120	102	56.7^d
<i>Sinks (Tg/yr)</i>						
OH oxidation	9.6	19	20	27	28.4	10.6
Dry deposition	12.7	19.9	26.8	49.5	33.6	26.0^e
Wet deposition	13.7	24.1	28.2	43.4	40	20.1
Lifetime (days)	4	4.5	3.8	3.5	4.3	3.2

1 Supplementary Information for

2 **Satellite Evidence for a Large Source of Formic**
3 **Acid From Boreal and Tropical Forests**

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32 1 Emissions of Formic Acid in the IMAGESv2 33 global CTM

34 The IMAGESv2 global chemistry-transport model is run at $4^\circ \times 5^\circ$ resolution
35 and is resolved at 40 vertical levels from the surface up to the lower strato-
36 sphere. The model meteorology is provided by ERA-Interim analyses of the
37 ECMWF data center. The model has been extensively described in previous
38 work [S1, S2, S3, S4], except for the model updates detailed in this Supplement.
39 The model simulations are performed for year 2009, after a four-month spin-up
40 time starting on September 1, 2008.

41 Global fossil fuel and biofuel NMVOC emissions are obtained from the
42 RETRO^[S5] database for the year 2000, which is overwritten by the 2009 REAS^[S6]
43 inventory over Asia. The global annual anthropogenic source of formic acid (in-
44 cluding biofuel use) amounts to 2.2 Tg yr^{-1} , when the contribution of HCOOH
45 to the carboxylic acids emissions in these inventories is assumed to be 25%.
46 Formic acid emissions from cattle are estimated at 1.8 Tg yr^{-1} ^[S7]. The emis-
47 sions of the main biogenic precursors of formic acid, isoprene and the monoter-
48 penes, are both obtained from inventories based on the MEGAN model^[S8]. The
49 global annual sources of isoprene and monoterpenes in 2009 amount to 424 Tg
50 and 97 Tg, respectively.

51 Vegetation fire emissions are obtained from the latest version of the Global
52 Fire Emission Database^[S9], by applying updated (in 2007) emission factors^[S10].
53 For HCOOH, the emission factors are 1.13, 2.43 and 0.63 g HCOOH/kg of dry
54 matter for tropical, extratropical, and savanna burning, respectively, and the
55 global biomass burning flux is estimated at 2.9 Tg for the year 2009. Monthly
56 HCOOH biomass burning emissions between May and August 2009 are shown
57 in Fig. S3. Monthly emissions of HCOOH from leaves are the average of the
58 fluxes estimated between 1983 and 1995 by the ORCHIDEE global dynamic
59 vegetation model^[S11], and amount at 5.6 Tg yr^{-1} .

60 2 Photochemical Sources of Formic Acid

61 This section deals with the photochemical HCOOH formation in the standard
62 (F1, Table 1) version of IMAGESv2.

63 2.1 Isoprene oxidation by OH

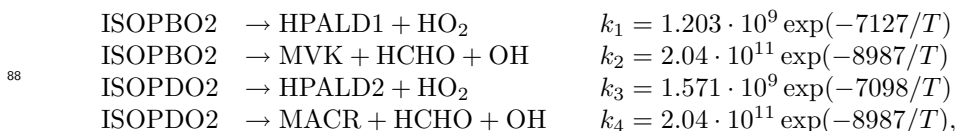
64 The OH-initiated isoprene oxidation mechanism in IMAGESv2 is based on
65 the new theoretically-based LIM0 mechanism^[S12, S13], which has been imple-
66 mented in IMAGESv2 and evaluated against aircraft observations^[S4]. This
67 scheme puts forward that isomerisation reactions of specific isomer/conformer
68 peroxy radicals from isoprene lead to the formation of HOx radicals and photo-
69 labile hydroperoxy-enones, most likely hydroperoxy methylbutenals (HPALDs)
70 at rates faster than those of traditional reactions of the isoprene peroxy radicals

71 with NO and HO₂ in most remote atmospheric regimes, offering thereby a likely
 72 explanation for the high abundances of HOx radicals observed in isoprene-rich
 73 areas^[S14, S15]. Unfortunately, the rates of key isomerisation reactions in LIM0
 74 remain uncertain, in particular the 1,6-H shift of the δ -hydroxy peroxy radi-
 75 cals leading to the formation of the HPALDs. Based on the results of isoprene
 76 oxidation experiments conducted at low NOx levels^[S16], the theoretical best
 77 estimate for these rates appeared to be likely overestimated by a factor of 2 or
 78 3^[S13, S17]. However, even such a rate reduction has only limited consequences
 79 on the yields of the primary products, due to the strongly non-linear dependence
 80 of the yields on the 1,6-H shift rates^[S13, S4].

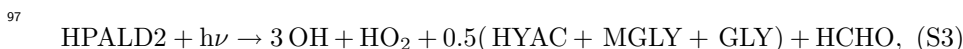
81 In IMAGESv2 the reaction of isoprene with OH is written as



82 where ISOPBO2, ISOPDO2 are the peroxy formed through OH addition to
 83 the terminal carbons, and ISOPEO2 represent the peroxy formed through addi-
 84 tion to the inner carbons. The δ -hydroxy peroxy radicals are not explicitly
 85 included, since their traditional reaction products have negligible yields accord-
 86 ing to LIM0 in most atmospheric conditions. The isomerisation of the isoprene
 87 hydroxyperoxy is accounted through the reactions :

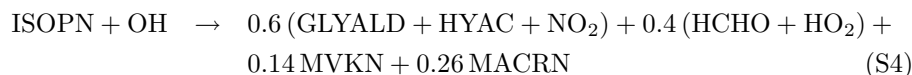


89 where T is the temperature (in K) and MVK, MACR denote methylvinylketone
 90 and methacrolein, respectively. The adopted rates k_1 - k_4 (in s⁻¹) account for a
 91 factor of 2 reduction of the theoretical best estimates for the 1,6-H shift rates of
 92 the δ -hydroxy peroxy radicals^[S4]. Photolysis is believed to be the main sink re-
 93 action of the HPALDs accounting for about two thirds of the global sink^[S4], and
 94 leading to the regeneration of one or several OH radicals. However, the further
 95 oxidation of the photolysis products remains to be elucidated. In the current
 96 version of the mechanism^[S4], the photolysis of the HPALDs is represented as



98 where GLY, MGLY, HYAC, and GLYALD are abbreviations for glyoxal, methyl-
 99 glyoxal, hydroxyacetone and glycolaldehyde, respectively. The possibility that
 100 HPALD oxidation leads to additional HCOOH formation is explored in the F3
 101 simulation (Table 1).

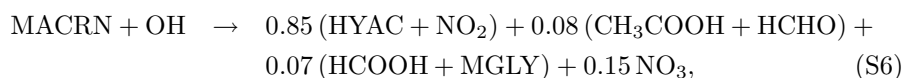
102 A yield of 6% of isoprene nitrates (ISOPN) is assumed in the reaction of
 103 isoprene peroxy radicals with NO. Their oxidation by OH leads to HCOOH
 104 formation^[S18], as summarised below :



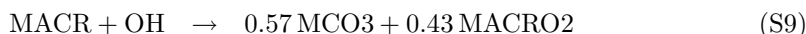
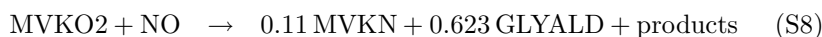
105



106



107 where MVKN and MACRN are nitrates produced in the oxidation of MVK and
108 MACR by OH :



109 The oxidation by OH of isoprene hydroxy-hydroperoxides issued by the reac-
110 tion of isoprene peroxy radicals with HO₂ leads to the formation of epoxides^[S16]
111 (IEPOX) :



112 Their further oxidation by OH is assumed^[S16] to lead to (among others) HCOOH
113 and GLYALD :

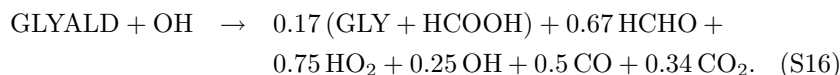


114



115 Note however that HCOOH is not produced from IEPOX according to the
116 protocol rules of the Master Chemical Mechanism^[S17].

117 According to a laboratory study of the Orléans group^[S19], the oxidation of
118 GLYALD is also a source of HCOOH :



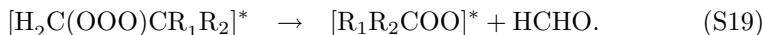
119 Glycolaldehyde is mainly produced from the oxidation of MVK, ISOPN, IEPOX
 120 and the HPALDs (see above). It is also a major product in the oxidation
 121 of ethylene by OH^[S20]. Another laboratory study by the Orléans group^[S21]
 122 proposed that HCOOH is formed in the OH-oxidation of hydroxyacetone, a
 123 major secondary product in the oxidation of isoprene; however, the proposed
 124 formation mechanism appears rather unusual. More recent experiments^[S22]
 125 give evidence that this production does not occur at atmospheric conditions,
 126 and hence is not accounted in this study.

127 2.2 Ozonolysis of alkenes

128 The ozonolysis of alkenes proceeds via the addition of O₃ to the C=C bond to
 129 form a primary ozonide which rapidly decomposes to one or two sets of Criegee
 130 intermediate (CI) plus a carbonyl^[S23, S24]. In the case of terminal alkenes
 131 (H₂C=R₁R₂), ozonolysis forms the smallest CI, [H₂COO]* :



132



133 Due to the high exothermicity of the overall reaction (S17-S19), both products
 134 are chemically activated and only a fraction of the energy-rich CIs becomes
 135 collisionally stabilised, while the rest undergoes various “prompt” unimolecular
 136 reactions. This stabilised fraction is close to 0.37 (average of 5 experimental
 137 studies)^[S25] for [H₂COO]* originating from C₂H₄ + O₃. Larger values are
 138 expected in the case of higher alkenes, for which a larger fraction of the energy
 139 will be partitioned to the larger fragment R₁C(O)R₂. Nevertheless, we adopt
 140 here the value of 0.37 for the cases of C₃H₆, MACR and MVK.

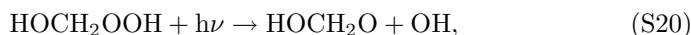
141 In tropospheric conditions, reaction of the stabilised Criegee intermediates
 142 (SCIs) with H₂O is generally by far the dominant sink of the SCIs. Laboratory
 143 experiments^[S24, S26, S27, S28, S29] of alkene ozonolysis indicate that the reac-
 144 tion of H₂COO with H₂O forms formic acid and hydroxymethyl hydroperoxide
 145 (HMHP). It has been shown^[S24, S28], that the formation of formic acid in the
 146 laboratory was partly or entirely due to the decomposition of HMHP to HCOOH
 147 + H₂O. The precise extent to which this formation occurred by heterogeneous
 148 reactions on the reactor walls is uncertain. A theoretical investigation^[S30] con-
 149 firmed that the reaction of H₂COO with H₂O leads to the formation of HMHP.
 150 The predominant pathway in atmospheric conditions was found to be the reac-
 151 tion with the H₂O dimer: the rate constants for the reaction of H₂COO with
 152 the H₂O monomer and the water dimer were calculated to be 8.2 · 10⁻¹⁸ and
 153 1.46 · 10⁻¹² molec.⁻¹cm³s⁻¹, respectively.

154 Assuming that HMHP is the only product in the reaction of H₂COO with
 155 H₂O, HMHP yields in the ozonolysis of C₂H₄ (0.37), C₃H₆ (0.16), MVK (0.32)
 156 and MACR (0.22) are adopted, based on the [H₂COO]* stabilisation fraction

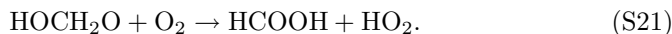
157 observed for $\text{C}_2\text{H}_4 + \text{O}_3$ (0.37) and on the IUPAC recommendation^[S25] for
 158 the $[\text{H}_2\text{COO}]^*$ branching ratio in the alkene + ozone reaction. For isoprene, we
 159 adopt the average HMHP yield from two studies (0.23)^[S24, S31]. The case of
 160 monoterpenes is discussed in the subsection 2.3.

161 HMHP has been commonly observed at levels comparable to those of methyl
 162 hydroperoxide in the boundary layer over isoprene-rich areas^[S32, S33, S34, S35],
 163 supporting the view that isoprene and other biogenic alkenes are an impor-
 164 tant source of HMHP. These observations also show that fast decomposition
 165 of HMHP is unlikely at atmospheric conditions. We therefore neglect HMHP
 166 decomposition in the model. Should some decomposition (to $\text{HCOOH} + \text{H}_2\text{O}$)
 167 occur, our assumption would not lead to a large underestimation of HCOOH
 168 formation, because the atmospheric degradation of HMHP leads primarily to
 169 HCOOH anyway, as detailed below.

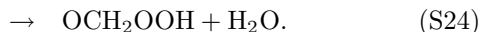
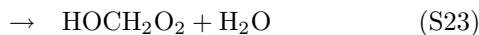
170 HMHP photolysis proceeds by cleavage of the peroxidic bond^[S25]:



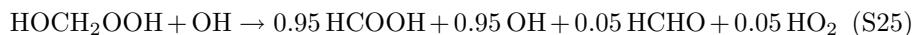
171 which is immediately followed by



172 The HMHP absorption cross sections are slightly lower than those of methyl
 173 hydroperoxide^[S36], which makes photolysis a very minor sink. Reaction with
 174 OH proceeds by H-abstraction from the carbon, from the hydroperoxide or from
 175 the hydroxy group^[S37]:



176 In lower tropospheric conditions, HOCH_2O_2 decomposes thermally to HCHO
 177 and HO_2 ^[S38, S39]. The radicals formed in Reactions (S22) and (S24) decom-
 178 pose rapidly to $\text{HCOOH} + \text{OH}$ ^[S40] and $\text{HC(O)OOH} + \text{H}$, respectively^[S37].
 179 The first channel (Reaction S22) is by far dominant^[S37], as confirmed by the
 180 experimental HCOOH yield^[S36] of 95% in the reaction of HMHP with OH. As
 181 the stronger hydroxy O–H bond should keep the third channel negligible, we
 182 write Reactions (S22)-(S24) as



183 with an adopted reaction rate of $3 \cdot 10^{-11} \text{ molec.}^{-1} \text{ cm}^3 \text{ s}^{-1}$.

184 HMHP also undergoes dry and wet deposition. Dry deposition is calculated
 185 using the deposition velocity calculated for H_2O_2 . The parameterisation of
 186 wet deposition accounts for the high Henry’s law’s constant of HMHP^[S41],
 187 $1.24 \cdot 10^{-8} \exp(9700/T) \text{ M atm}^{-1}$.

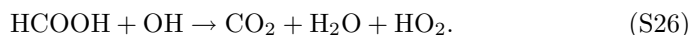
188 An additional loss process for HMHP is provided by its dissolution in liq-
189 uid cloud droplets followed by (water-assisted) decomposition to HCHO +
190 H₂O₂[S41, S42]. Whereas the decomposition lifetime is less than an hour at
191 neutral pH conditions, it is relatively slow at typical pH values found in clouds
192 (4-5), with a lifetime ranging between several hours and several days[S42]. It is
193 therefore neglected in the model.

194 2.3 Oxidation of monoterpenes

195 HMHP can also be produced in the ozonolysis of exo-cyclic (or epi-cyclic)
196 monoterpenes (e.g. β -pinene and sabinene[S25], but not α -pinene). For such
197 large alkenes, decomposition of the primary ozonide to HCHO and a large
198 Criegee intermediate (reaction S19) is largely dominant (> 80%)[S43]. In this
199 case, even though the energy channelled to [H₂COO]* in the minor ozonolysis
200 route (reaction S18) is at most a few kcal/mol, such that all will be stabilized,
201 the yield of HMHP remains small, of the order of 20% or less. This formation is
202 neglected in the model. Instead, a direct HCOOH formation is assumed, with a
203 yield of 10% in the reactions of monoterpenes with O₃ and OH, to account for
204 the possible but very uncertain formation of HCOOH, mostly from secondary
205 chemistry, in the still largely unexplored chemical mechanism of monoterpenes.
206 First-generation molar yields of formic acid were found to range between 2
207 and 11% in laboratory studies of monoterpene oxidation by OH[S44, S45] and
208 O₃[S46]. Evidence for higher yields due to the further degradation of the primary
209 products is provided by the OH-initiated monoterpene oxidation experiments
210 of Larsen *et al.*[S47]. Yields ranging between 28% (for α -pinene) and 54% (for
211 limonene) were obtained after 20 minutes of intense photooxidation. Since the
212 total yield of identified small organic compounds (HCOOH, HCHO, CO, CO₂
213 and acetone) represented between 28% and 46% of the reacted terpene on a car-
214 bon basis in these experiments, the further oxidation of the remaining products
215 (i.e. 54-72% of the carbon flux) might bring the overall molar yield of HCOOH
216 in these laboratory conditions to much larger values, possibly of the order of
217 100%. Caution is required, however, since an unrealistic radiation source (Hg
218 lamp peaking at 254 nm) was used in these experiments, which probably caused
219 a strong photolysis of aldehydic compounds. Still, these results clearly suggest
220 that HCOOH is a likely end-product in a large number of terpene degradation
221 pathways.

222 3 Sinks of Formic Acid

223 The only gas-phase sink of formic acid is reaction with OH, represented in the
224 model as



225 Its rate expression, $k=2.27 \cdot 10^{-14} \cdot \exp(786/T) + 9.85 \cdot 10^{-13} \cdot \exp(-1036/T)$ im-
226 plies higher rate values in the cold upper troposphere, compared to boundary

227 layer conditions^[S7]. The use of a temperature-independent rate^[S25] will be
 228 tested in a sensitivity inversion, as described in Section 8.

229 The dry deposition velocity over land is parameterised as a function of the
 230 leaf area index (LAI) obtained from MODIS^[S48]. It increases linearly from 0
 231 to 1.2 cm s^{-1} for an LAI of $6 \text{ m}^2 \text{ m}^{-2}$. Wet scavenging is calculated based on
 232 ECMWF precipitation, cloud fraction and convective updraft fields^[S49]. The
 233 effective Henry’s law constant (in M atm^{-1}) is calculated with^[S50, S51]

$$K_{H,\text{eff}} = [2.5 \cdot 10^{-5} \cdot \exp(5700/T)] \cdot (1 + 1.8 \cdot 10^{-3}/[\text{H}^+]) \quad (\text{S27})$$

234 and assuming a pH of 4.5.

235 Finally, the effect of reversible uptake by ice clouds is also considered. Par-
 236 titioning to ice particles is calculated with

$$[X_s]/[X_g] = S_{\text{ice}} \cdot K_{\text{linC}} \quad (\text{S28})$$

237 with $[X_s]$ and $[X_g]$ the ice surface and gas phase concentrations, respectively (in
 238 molec.cm^{-3}), S_{ice} the surface area density of ice ($\text{cm}^2 \text{ cm}^{-3}$) and K_{linC} (in cm)
 239 the partitioning coefficient in the linear regime of the adsorption isotherm^[S52]

$$K_{\text{linC}} = 4 \cdot 10^{-12} \cdot \exp(7000/T), \quad (\text{S29})$$

240 where it has been taken into account that the fractional surface coverage ($\theta =$
 241 $K_{\text{linC}} \cdot [X_g]/N_{\text{max}}$) is much less than unity in atmospheric conditions. The ice
 242 surface area density is parameterised based on the ice water content (IWC, in
 243 g m^{-3}) assuming a scaling ratio of 10 between the cross-sectional area and the
 244 surface area density^[S53, S54]:

$$S_{\text{ice}} = 10^{-3} \cdot \text{IWC}^{0.9} \quad (\text{S30})$$

245 The effect of cirrus gravitational settling on the vertical distribution of HCOOH
 246 is estimated using Eq. (S28) and the parameterisation of the ECMWF IFS model
 247 for the ice settling velocity^[S49]. This effect, however, is found to be very small.

248 4 Organic Aerosol Modeling in IMAGESv2

249 This section presents the organic aerosol module in the model. The heteroge-
 250 neous oxidation of organic aerosols by OH is assumed to generate HCOOH in
 251 the F2 run (Table 1). Three sources of organic aerosol (OA) are considered :

- 252 • Direct emission of Primary Organic Aerosol (POA) due to anthropogenic
 253 sources^[S55] (13.5 TgC/year or 23.6 Tg/year) and biomass burning^[S9]
 254 (12.2 TgC/year or 21.3 Tg/year). POA has hydrophilic and hydrophobic
 255 components. Conversion of hydrophobic to hydrophilic POA due to aging
 256 is represented by an e-folding time of 1 day^[S56].

- 257 • Reversible Secondary Organic Aerosol (SOA) formation due to the parti-
258 tioning of semi-volatile organic compounds. We adopt the approach of the
259 two-product model^[S57, S58] for estimating this production of SOA from
260 isoprene, terpenes and aromatics. The product yields and partitioning pa-
261 rameters of the condensable compounds from aromatics^[S57], isoprene^[S59]
262 and sesquiterpenes^[S58] are based on laboratory data. For monoterpenes,
263 we adopt a ten-product model^[S60], with parameters derived from sim-
264 ulations using a detailed α -pinene oxidation and SOA formation model
265 (BOREAM)^[S61, S62]. The model accounts for a dependence of the yields
266 on the NO_x regime and on the nature of the primary oxidant (O₃, OH or
267 NO₃). The partitioning coefficients (not only for α -pinene SOA, also for
268 other condensable compounds) are corrected to account for water uptake,
269 based on BOREAM model simulations^[S60].
- 270 • Irreversible SOA formation due to the production of essentially non-volatile
271 compounds (e.g. oligomers and polymers). In IMAGESv2, the formation
272 of SOA from glyoxal and methylglyoxal is included as an irreversible
273 process^[S63, S49]. It is assumed to be very fast in liquid clouds. On aque-
274 ous aerosols, a constant reactive uptake coefficient ($2.9 \cdot 10^{-3}$) is assumed.

275 The model accounts for wet and dry deposition of aerosols and aerosol pre-
276 cursors. The wet removal scheme^[S49] is based on ECMWF cloud and precip-
277 itation data. The semi-volatile gaseous SOA precursors are assumed to be as
278 water-soluble as glyoxal, given the high solubility of typical multi-functional
279 SOA components.

280 The global SOA source calculated by IMAGESv2, ca. 100 Tg/year, com-
281 pares well with the recent estimate of 140 ± 90 Tg/year derived from aerosol
282 mass spectrometer (AMS) measurements^[S64]. Note however that our modelled
283 SOA is overwhelmingly (> 90%) biogenic, whereas AMS measurements suggest
284 a large (100 Tg/year) anthropogenically-controlled contribution. Comparisons
285 with surface OC concentrations measurements of the IMPROVE (Interagency
286 Monitoring of Protected Visual Environments)^[S65] and EMEP (European Mon-
287 itoring and Evaluation Programme)^[S66] network suggests that our modelled
288 SOA source is overestimated by almost a factor of two over the Eastern US
289 during summertime and that it is largely underestimated over Europe.

290 5 Ground-based and Aircraft Measurements

291 To evaluate the model performance, we use Fourier Transform Infrared (FTIR)
292 column measurements of HCOOH at Wollongong in southeast Australia (34.41
293 S, 150.88 E), and Reunion Island in the southern Indian Ocean (21 S, 55 E)^[S7].
294 The retrievals adopted the improved spectroscopic parameters for the HCOOH
295 ν_6 absorption band near 1105.4 cm^{-1} (HITRAN 2008)^[S67, S68].

296 Further, we use a compilation of in situ concentration measurements in sur-
297 face air and in precipitation water (Tables S2, S3 and S4). The observed concen-
298 trations are compared with the modelled concentrations in 2009, interpolated at
299 the measurement locations and averaged over the same months (Figs. S6, S7).
300 The significant dispersion before and after optimisation most likely reflects the
301 large spatiotemporal variability of HCOOH and the limited representativity of
302 local measurements from many different years in comparison with model val-
303 ues for 2009 at $4^\circ \times 5^\circ$ resolution. When considering all measurements, the
304 correlation coefficient is equal to 0.5 for surface air concentrations and 0.3 for
305 precipitation water concentrations in the a priori simulations. After optimisa-
306 tion, the correlation coefficient for both air and water concentrations is equal to
307 ca. 0.45.

308 Aircraft campaign measurements of HCOOH from three expeditions are also
309 used for comparisons (Fig. S8) :

- 310 1. The PEM-Tropics A (Pacific Exploratory Mission-Tropics A) mission con-
311 ducted in August-October 1996 as part of NASA's Global Tropospheric
312 Experiment (GTE) with focus on the remote tropical regions of the Pa-
313 cific ocean. The data, compiled onto a 5×5 degrees grid with a vertical
314 resolution of 1 km^[S69], can be accessed through the data composites web
315 page (http://acd.ucar.edu/~emmons/DATACOMP/camp_table.htm).
- 316 2. The SONEX (Subsonic assessment, Ozone and Nitrogen oxide EXperi-
317 ment) airborne field campaign conducted between October and November
318 1997 aboard a DC-8 NASA aircraft in the vicinity of the North Atlantic
319 flight corridor^[S70].
- 320 3. The National Aeronautical Space Administration (NASA) Intercontinen-
321 tal Chemical Transport Experiment, Phase B (INTEX-B) aircraft mission
322 conducted in spring 2006 (1 March to 15 May) over the region of Mex-
323 ico in March (first phase) and over the Pacific in April and May (second
324 phase)^[S71].

325 A comparison between the observed and the modelled HCOOH concentra-
326 tions averaged over large regions before and after optimisation is provided in
327 Table S5.

328 6 Uncertainties on IASI HCOOH columns

329 The error of 60% on the IASI HCOOH columns is a theoretical error based only
330 on forward simulations for an individual measurement. Other sources of error
331 include propagating errors from level 2 data (e.g. total water column, thermal
332 contrast) and possible bias errors, such as uncertainty in the assumed profile
333 of formic acid or on the spectroscopy. The total error can only be rigorously
334 quantified with an extensive validation of the IASI columns but unfortunately

335 there are currently few correlative measurements of the formic acid total columns
336 for such an analysis.

337 An explicit comparison with FTIR ground-based measurements at Wollon-
338 gong and Reunion Island site (Figure 2 of the letter and Fig. S11) shows a high
339 degree of correlation ($R^2 = 0.84$). Data from other FTIR sites, like Thule and
340 Bremen have been obtained from Figs. 3 and 4 of Ref. [S7]. However, at these
341 sites spatially co-located IASI measurements are not available for comparison,
342 unless a very large $8^\circ \times 8^\circ$ area is considered around each station, making the
343 comparison of very little value for validation. From these restricted comparisons
344 there is thus no indication for a significant IASI overall bias.

345 The error adopted in the inversions consists in an absolute error of 4×10^{15}
346 molec.cm⁻² and a 30% relative error. This was chosen in order to avoid overly
347 optimistic error bars for the low concentrations. We acknowledge the crudeness
348 of this error estimate, and therefore, sensitivity inversions using either doubled
349 or halved errors were performed. These tests are presented and discussed in
350 Section 8.

351 7 Impact on Precipitation Acidity

352 The pH of precipitation is estimated in the model based on the wet deposition
353 fluxes of $\text{HNO}_3/\text{NO}_3^-$, SO_4^{2-} , $\text{NH}_3/\text{NH}_4^+$, $\text{CO}_2/\text{HCO}_3^-$ and the carboxylic
354 acids HCOOH and CH_3COOH , accounting for their respective dissociation con-
355 stants, $1.8 \cdot 10^{-4}$ and $1.8 \cdot 10^{-5}$ mol/L^[S51]. Dust aerosols, and therefore, alkaline
356 components such as Ca^{2+} , Na^+ and K^+ , are neglected in the model, leading to
357 a likely underestimation of precipitation pH.

358 8 Sensitivity Inversions

359 This section explores the impact of possible errors in key model parameters on
360 the inversion results. In each sensitivity inversion (Table S6), a parameter or
361 input dataset of the Opt2 standard optimisation is varied, and new emissions are
362 obtained. The resulting global emissions and sinks are summarised in Table S7.

363 Acknowledging the broad IASI column error estimate used in the reference
364 optimisations (see “Methods” section), additional inversions were performed
365 using either doubled (Opt2-Errx2) or halved (Opt2-Err:2) IASI errors. Chang-
366 ing these errors affects the balance between the first term of the cost function
367 (cf. Eq. (1), “Methods” section) representing the model-data bias and the
368 second term which measures how far the optimised emissions are from the a
369 priori. Halving the errors results in an almost negligible increase (6% globally).
370 Doubling the IASI column errors leads to a decrease (13%) in the optimised
371 emissions, as the optimisation is more constrained by the a priori. The latitu-
372 dinal distribution of the emissions (Fig. S12) remains unaffected, except in the
373 summertime Southern hemisphere in the 20° - 35° S band, where the optimisa-
374 tion results appear less robust. However, the comparison with ground-based

375 FTIR data at Wollongong (Fig. 2) indicates that IASI errors are not likely to
376 be larger than our reference estimates.

377 Dry deposition accounts for about one third of the global HCOOH sink in
378 IMAGESv2, based on a simple parameterisation. The contribution of dry de-
379 position could be higher, however, as reactive uptake by vegetation has been
380 recently shown to enhance the deposition of many oxygenated VOCs^[S72]. We
381 therefore conducted a source inversion with HCOOH deposition velocities over
382 land increased by 50% (Opt2-Dry). In spite of this strong increase, the inferred
383 global HCOOH emission is increased by only 6% (Table S7), because dry de-
384 position over land represents only a relatively small fraction of the global sink,
385 and because the stronger surface sink reduces the vertical tropospheric gradient
386 and therefore the surface HCOOH concentrations.

387 Uncertainties related to wet scavenging (about 38% of the global HCOOH
388 sink in IMAGESv2) include uncertainties in the meteorological fields and in the
389 gas/liquid partitioning ratio for HCOOH, calculated from the effective Henry’s
390 law constant for HCOOH, itself dependent on pH. Using an alternative dataset
391 for convective and stratiform precipitation (the NCAR/NCEP Reanalysis^[S73])
392 (<http://www.esrl.noaa.gov/psd/>) in inversion Opt2-NCEP results in a longer
393 HCOOH lifetime with respect to wet deposition (10.5 vs. 12.2 days), primarily
394 because stratiform precipitation in NCEP is much less widespread at tropical
395 latitudes, compared to ERA-Interim fields. This change has however only very
396 little impact on the optimised HCOOH emissions, cf. Table S7.

397 Including an on-line dynamical calculation of cloud pH in the model leads to
398 a negligibly (3%) longer HCOOH lifetime, compared to the reference model cal-
399 culations assuming pH=4.5. However, the pH might be underestimated, given
400 that alkaline components from e.g. dust are neglected. The results of opti-
401 misation Opt2-pH5, assuming pH=5, indicate a low sensitivity of the overall
402 HCOOH sink to the cloud pH: the global lifetime is decreased by about 5%,
403 and the global HCOOH source needed to match the IASI column measurements
404 is increased by about 4 Tg yr⁻¹.

405 The rate used in the model for HCOOH+OH, and obtained from a theoret-
406 ical study^[S74], implies a negative temperature dependence in the atmospheric
407 range, leading to higher rates in the upper troposphere. However, laboratory
408 measurements conducted at and above 297 K (IUPAC recommendation^[S25])
409 indicate a negligible temperature dependence. The sensitivity inversion Opt2-
410 kOH conducted with the IUPAC recommendation ($4.5 \cdot 10^{-13}$ molec.⁻¹cm³ s⁻¹,
411 independent of temperature) leads to a 7% increase of the global HCOOH life-
412 time, in spite of the higher value of the rate in the lower troposphere. The
413 global biogenic source of HCOOH is decreased by almost 4 Tg yr⁻¹ (i.e. by 4%)
414 compared to the reference optimisation.

415 The isoprene chemical mechanism used in the model includes peroxy radical
416 isomerisations leading to compounds (hydroperoxy-enones) for which the sub-
417 sequent chemistry remains largely unexplored; furthermore, the isomerisation
418 rates are themselves uncertain. In optimisation Opt2-Isom, these isomerisa-
419 tions are simply ignored. This mechanistic change increases the production

420 of HCOOH due to isoprene oxidation by 5.7 Tg yr^{-1} , mostly due to enhanced
421 HCOOH formation through (1) the epoxide channel of the isoprene peroxys, and
422 (2) HMHP formation due to isoprene ozonolysis. The contribution of ozonolysis
423 to the isoprene sink is increased from 8% to 14.5% when the 1,6 H-shifts are
424 suppressed, due to lower OH abundances over forested areas. The global pro-
425 duction of isoprene epoxides is increased from 40 to 106 Tg annually. Isoprene
426 ozonolysis and the epoxide oxidation by OH are both significant pathways to
427 HCOOH formation in our mechanism. An additional effect of the mechanistic
428 change is the increased overall lifetime of HCOOH, from 4.3 to 4.6 days, also
429 due to the lower OH levels calculated when the isomerisation reactions of the
430 isoprene peroxys are ignored. Note that the higher OH levels calculated with the
431 LIM0 mechanism are supported by comparisons with observations over Ama-
432 zonia and over the US^[S4]. As a consequence of the higher formation rate and
433 overall lifetime of HCOOH in this sensitivity inversion, the annual global source
434 needed to match the IASI measurements is slightly decreased from 102 to 98
435 Tg.

436 The optimisation results for the biogenic HCOOH source are also dependent
437 on assumptions for the pyrogenic source, also retrieved in the optimisations.
438 E.g. increasing the pyrogenic a priori emissions, or increasing the fraction of
439 biomass burning emissions released at high altitudes, where HCOOH is longer-
440 lived, could in principle increase the contribution of fires to the total column,
441 thereby reducing the need for large biogenic emissions. The optimisation Opt2-
442 Inj uses a fire injection profile^[S75] with substantially higher fractions injected
443 in the middle (30%) and upper (30%) troposphere, compared to the profile^[S76]
444 used in IMAGESv2. The results (Table S7) show that the vertical distribution
445 of pyrogenic emissions has only a negligible influence on the derived budget and
446 lifetime. The optimised global emissions due to vegetation fires is decreased
447 (from 4.0 to 3.5 Tg yr^{-1}) when adopting the alternative injection height profile,
448 as a consequence of the longer lifetime of formic acid at higher altitudes. This
449 confirms the minor role played by vegetation fires in determining the HCOOH
450 column distribution.

451 In conclusion, the optimisation results appear to be robust, since the an-
452 nual global biogenic source is found to range between 77 and 96 Tg, when the
453 additional HCOOH production is assumed to be secondary. The lowest emis-
454 sions (77 Tg yr^{-1}) are obtained when assuming unrealistically large errors on
455 the IASI column data. Still, it must be acknowledged that the real uncertainty
456 might be larger, since the above sensitivity experiments cannot possibly cover
457 the full range of possible uncertainties.

9 Tables

Table S1: Mean percentage biases (model-observations) and correlation coefficients calculated for the standard model simulation F1 and the Opt2 inversion constrained by IASI data. Results from the Opt1 inversion are very similar to those from Opt2 and are not shown here. N is the number of observational elements used in the inversion, i.e. monthly averaged IASI HCOOH columns at the resolution of the model.

<i>Region</i>	<i>N</i>	<i>Mean bias</i>				<i>Correlation coefficient</i>	
		F1	Opt2	F1	Opt2		
N.America 30-70 N, 60-170 W	475	-80.8	-11.0	0.43	0.72		
Tropical America 30 S-20 N, 30-80 W	489	-72.3	-12.5	0.84	0.91		
Africa 40 S-30 N, 20 W-45 E	814	-71.7	-10.8	0.75	0.93		
Asia 10 S-55 N, 60-160 E	856	-73.2	-14.2	0.34	0.80		
Oceania 40 S-10 N, 110-170 E	402	-72.9	-14.1	0.44	0.84		
Boreal (55-88 N)	419	-85.8	-13.4	0.33	0.71		
Tropics (25 S-25 N)	1869	-70.5	-12.2	0.70	0.91		
Globe	3768	-75.4	-13.6	0.59	0.87		

Table S2: In situ measurements of HCOOH mixing ratio expressed in pptv.

<i>Location</i>	<i>Coordinates</i>	<i>Period</i>	<i>HCOOH</i>	<i>Ref.</i>
<i>North America</i>				
Mt. Lemmon, Tucson	32.4N 249.2E	Feb	130	[S77]
Socorro, New Mexico	36N 254E	Jun-Aug	700	[S78]
Langmuir, New Mexico	33.9N 253E	Jun-Aug	600	id.
id.	id.	Jun-Aug	1050	id.
Pagosa Springs, Colorado	37.2N 253E	Jun	1310	[S77]
Wolf Creek, Colorado	37.5N 253.3E	Jun	1190	id.
NW Dakota	45.5-49N			
	256-260E	Jun	2640	id.
id.	id.	Jul	1810	id.
id.	id.	May	110	id.
Oregon, Cape Meares	45.5N 236E	Sep	180	id.
id.	id.	Oct	60	id.
Pennsylvania	41N 283E	Jul-Aug	2500	[S79]
Charlottesville, Virginia	38N 281.7E	Jun	1820	[S80]
Shenandoah park, Virginia	38N 281.7E	Sep	5400	[S81]
Virginia	37N 283.7E	Mar-Sep	1890	[S82]
Virginia	id.	Oct-Feb	695	id.
<i>South America</i>				
Venezuelan savannah	8N 297E	Apr	450	[S83]
Venezuelan savannah	8.5N 298E	Sep	450	[S84]
N. Venezuela	10.5N 293E	Mar	1700	[S85]
id.	id.	Jun	710	id.
id.	id.	Oct	960	id.
id.	id.	Dec	610	id.
La Selva, Costa Rica	10.4N 276.1E	Apr-May	905	[S86]
Central Amazonia	4S 300E	Jul-Aug	1590	[S87]
Rondonia, Brazil	10S 298E	May	1600	[S88]
id.	id.	Sep-Nov	10500	id.
Ducke Reserve-Manaus	3S 300E	Jul-Aug	1880	[S80]
id.	id.	Apr-May	510	[S89]
<i>Other regions</i>				
Schoeneben, Austria	48.7N 13.9E	Mar-Apr	1066	[S90]
id.	id.	Sep	620	id.
N.Congo rainforest	2N 18E	Feb	500	[S91]
Mayombe, SW Congo	4.5N 12.5E	Jul-Aug	260	[S92]
Dayalbagh, India	28.5N 77.2E	Jan-Dec	1700	[S93]
id.	id.	May-Oct	1300	id.
id.	id.	Nov-Apr	1800	id.
Gopalpura, India	27N 78E	Jul-Sep	1700	[S94]

Table S3: In situ measurements of HCOOH concentration in precipitation ($\mu\text{mol/L}$, volume-weighted averages) in North and South America.

<i>Location</i>	<i>Coordinates</i>	<i>Period</i>	HCOOH	<i>Ref.</i>
<i>North America</i>				
Virginia	38.1N 281.2E	Apr-Sep	13.6	[S95]
Hampton, Virginia	38N 281.7E	Mar-Sep	6.8	[S82]
id.	id.	Oct-Feb	1.6	id.
Tennessee	35.5N 276.7E	Jan-Feb	1.0	[S96]
Tallahassee	30.5N 275.8E	Jun-Aug	18.2	[S80]
North Carolina	34.2N 282.1E	Jan-Dec	9.9	[S97]
North Carolina, 1987-89	id.	Apr-Sep	8.2	id.
North Carolina, 1987-89	id.	Oct-Mar	3.5	id.
North Carolina, 1996-98	id.	Apr-Sep	17.6	id.
North Carolina, 1996-98	id.	Oct-Mar	3.0	id.
Los Angeles, California	34.1N 241.6E	Jan-Dec	12.4	[S98]
<i>South America</i>				
Calabozo, Venezuela	8.9N 298.4E	Jan-Dec	6.5	[S99]
Parupa, Venezuela	5.7N 298.4E	Jan-Dec	6.3	[S100]
Luepa, Venezuela	5.9N 298.6E	Jan-Dec	4.2	id.
Kavanayen, Venezuela	5.6N 298.2E	Jan-Dec	2.1	id.
Yuruani, Venezuela	5N 298.8E	Jan-Dec	2.4	id.
Ayantepuy, Venezuela	5.9N 298E	Apr	4.2	[S101]
Canaima, Venezuela	6.3N 297.1	Apr	2.9	id.
J.del Tigre, Venezuela	8.7N 296.7E	Jan-Dec	8.2	[S84]
Central Amazonia	2.6S 300E	Jul-Aug	17.9	[S87]
Central Amazonia	2.6-3.1S 300E	Apr-May	3.2	[S102]
Balbina, Centr. Amazonia	1.9S 300.5E	Jan-Dec	0.5	[S103]
French Guyana	5N 306.9E	Jan-Dec	5.5	[S104]
Lake Calado, Brazil	3.2S 299.5E	Jan-Dec	2.9	[S105]
Acegua, Uruguay	32.1S 306E	Jan-Dec	7.6	[S106]
Melo, Uruguay	32.4S 306E	Jan-Dec	7.1	id.
Treinta y Tres, Uruguay	32.4S 306E	Jan-Dec	2.2	id.
Torres del Paine, Chile	51.1S 288E	Jan-Dec	5.5	[S107]

Table S4: As Table S3, for Africa, Europe and Asia-Australia.

<i>Location</i>	<i>Coordinates</i>	<i>Period</i>	HCOOH	<i>Ref.</i>
<i>Africa</i>				
Banizoumbou, Niger	13.5N 2.7E	Jun-Oct	4.7	[S108]
Amersfort, S. Africa	27.1S 30E	Jan-Dec	7.5	[S109]
L. Trichardt, S. Africa	23S 30E	Jan-Dec	12.9	id.
Lamto, Ivory Coast	6N 35E	Jan-Dec	11.1	[S104]
Zoetele, Cameroon	3.2N 12E	Jan-Dec	8.7	[S110]
Mayombe, Congo	4.5S 12.5E	Jun-Sep	10.0	[S92]
id.	id.	Jun-Oct	10.6	[S111]
id.	id.	Nov-May	6.3	id.
<i>Europe</i>				
Basque Coun., Spain	43N 357.4E	Mar-Sep	8.1	[S112]
id.	id.	Oct-Feb	3.8	id.
Faroe Isl., Denmark	62.1N 353E	summer	2.0	[S113]
Anholt Isl., Denmark	56.7N 11.5E	summer	15.0	id.
Galicia, Spain	42.5-43.2N			
	351.5-352.5E	Mar-Sep	12.7	[S114]
id.	id.	Oct-Feb	2.8	id.
Patras, Greece	38.2N 21.7E	Jan-Dec	3.8	[S115]
<i>Asia-Australia</i>				
Amsterdam Isl., Indian Oc.	37.8S 77.5E	Jan-Dec	3.2	[S116]
Dorrigo, SE Australia	30.3S 152.7E	Jan-Apr	4.6	[S117]
Bar.Tops, SE Australia	31.9S 151.6E	Jan-Apr	6.8	id.
Katherine, Australia	14.5S 132.3E	Sep-Apr	10.5	[S118]
Darwin Airport, Australia	12.5S 130.8E	Nov-Apr	4.9	[S119]
West Guizhou, China	26.3N 105.9E	Jun-Oct	4.6	[S120]
Lijiang, China	26.9N 100.2E	Jan-Dec	3.1	[S121]
Gopalpura, India	27N 78E	Jul-Sep	5.4	[S94]
Rampur, India, monsoon	27.2N 78.1E	Jul-Sep	5.1	[S122]

Table S5: Average HCOOH concentrations over large regions measured (a) at surface sites (Table S2) ; (b) in precipitation water (Table S3 and S4) ; (c) during aircraft campaigns (SONEX, INTEX-B and PEM-Tropics-A (PEM-TA)), and (d) average HCOOH columns measured by FTIR. The data are compared with model results in simulations F1-F3 and in inversion experiments assuming either a biogenic source of primary (Opt1) or secondary (Opt2) origin (see Table 1).

	Obs.	F1	F2	F3	Opt1	Opt2
<i>(a) Mixing ratio in surface air (pptv)</i>						
North America	1150	220	340	400	840	680
South America	1820	290	350	820	1410	740
Other regions	1120	510	770	740	1790	1170
<i>(b) Concentration in precipitation water ($\mu\text{mol/L}$)</i>						
North America	8.7	1.3	1.9	2.3	4.7	4.5
Europe	6.9	0.7	1.2	0.9	3.2	3.0
South America	5.2	1.0	1.4	2.8	3.6	2.9
Africa	9.0	2.8	4.8	5.4	10.1	8.4
Asia-Australia	5.4	1.4	2.3	3.5	3.1	3.0
<i>(c) Aircraft campaign mixing ratio (pptv)</i>						
North America (SONEX)	94	31	49	39	110	130
Western US (INTEX-B)	490	66	100	88	360	230
Mexico (INTEX-B)	1550	180	300	320	580	440
North Pacific (INTEX-B)	140	28	58	32	94	120
N. Trop. Pacific (PEM-TA)	40	11	31	18	20	25
S. Trop. Pacific (PEM-TA)	89	19	44	36	46	57
<i>(d) Vertical columns ($10^{14} \text{ molec.cm}^{-2}$)</i>						
Reunion Isl., Indian Ocean	20	7.8	18	14	20	24
Wollongong, Australia	59	12.5	20	36	47.5	45

Table S6: Description of the performed sensitivity inversions.

<i>Description</i>	Abbreviation
Standard inversion with secondary HCOOH source	Opt2
Errors on IASI HCOOH columns doubled	Opt2-Errx2
Errors on IASI HCOOH columns halved	Opt2-Err:2
HCOOH deposition velocity increased by 50%	Opt2-Dry
Use precipitation fields from NCEP	Opt2-NCEP
Cloud water pH assumed equal to 5	Opt2-pH5
Use IUPAC recommendation for HCOOH+OH reaction rate	Opt2-kOH
Use alternative fire injection heights ^[S75]	Opt2-Inj
Suppress isomerisation of peroxy radicals from isoprene	Opt2-Isom

Table S7: Annual estimates of sources, sinks and global lifetime of HCOOH inferred by sensitivity inversions. Units are in Tg per year. The biogenic emission estimates represent the sum of the primary biogenic source and of the IASI-derived secondary biogenic source of HCOOH.

<i>Abbreviation</i>	Global emission	Biogenic emission	Dry dep.	Wet dep.	OH oxidation	Lifetime (days)
Opt2	102.4	90.0	33.6	40.0	28.4	4.30
Opt2-Errx2	89.3	76.7	29.2	35.5	24.6	4.26
Opt2-Err:2	108.0	95.0	35.5	42.5	30.0	4.28
Opt2-Dry	108.4	96.3	40.0	40.0	28.4	4.05
Opt2-NCEP	101.5	89.0	33.8	37.4	30.3	4.55
Opt2-pH5	106.4	94.2	33.1	45.2	28.1	4.08
Opt2-kOH	98.8	86.4	31.8	39.3	27.7	4.62
Opt2-Inj	102.2	90.3	32.5	39.7	29.5	4.32
Opt2-Isom	97.8	84.8	31.1	39.8	26.9	4.57

⁴⁵⁹ **10 Figures**

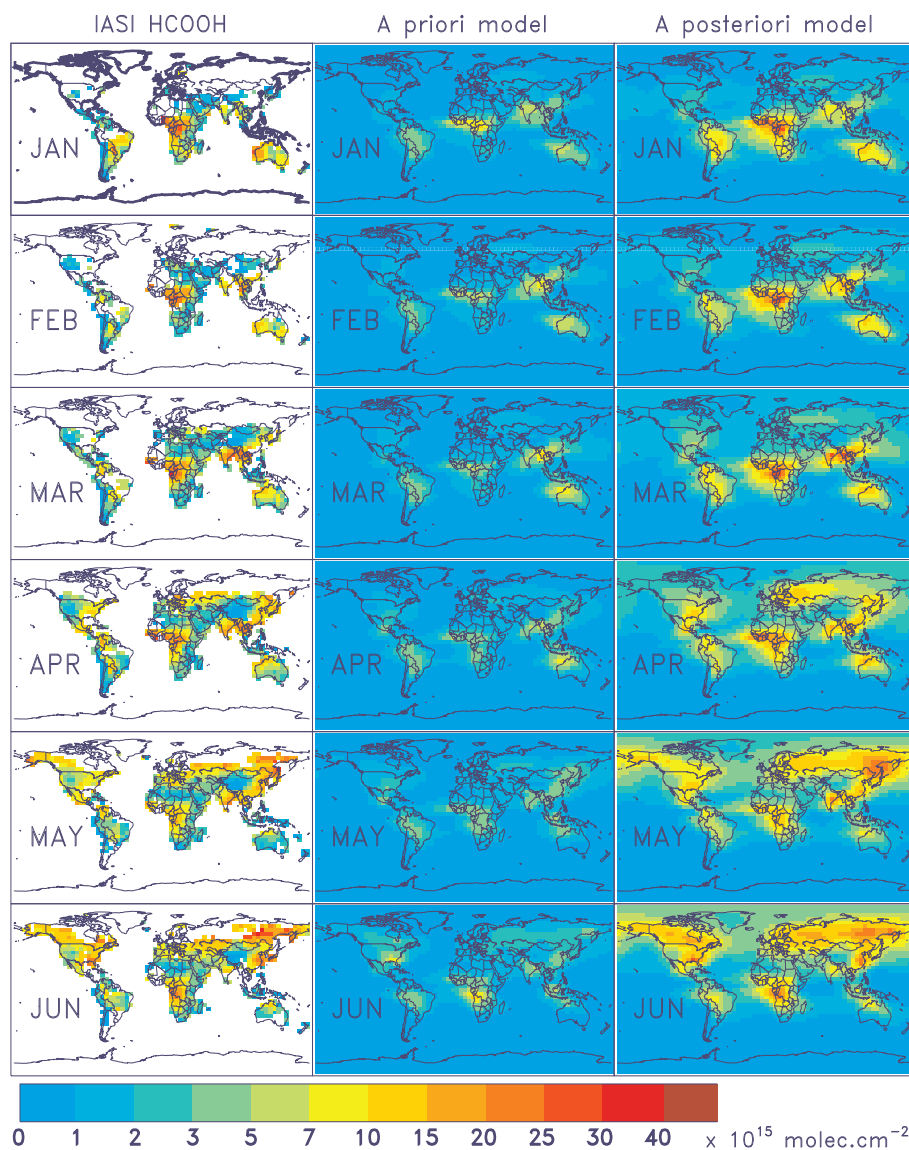


Figure S1: **Monthly averaged observed and modelled HCOOH columns between January and June 2009.** IASI columns (left column) are compared with a priori model columns (F1, middle) and optimised Opt2 HCOOH columns (right) inferred when a secondary HCOOH source of biogenic origin is assumed. Units are 10^{15} molec.cm⁻². Results from the Opt1 inversion are very similar to those from Opt2 and are not shown.

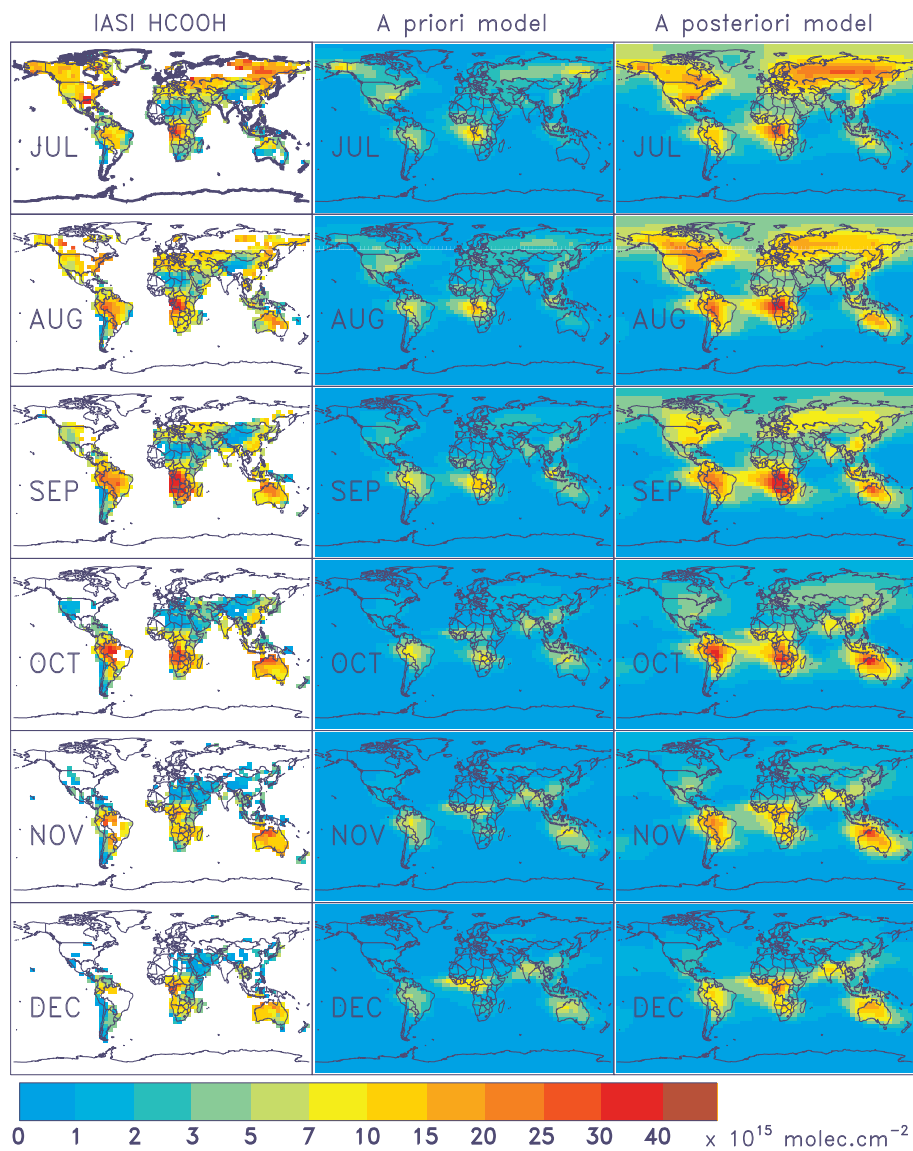


Figure S2: Same as Fig. S1, for July–December 2009.

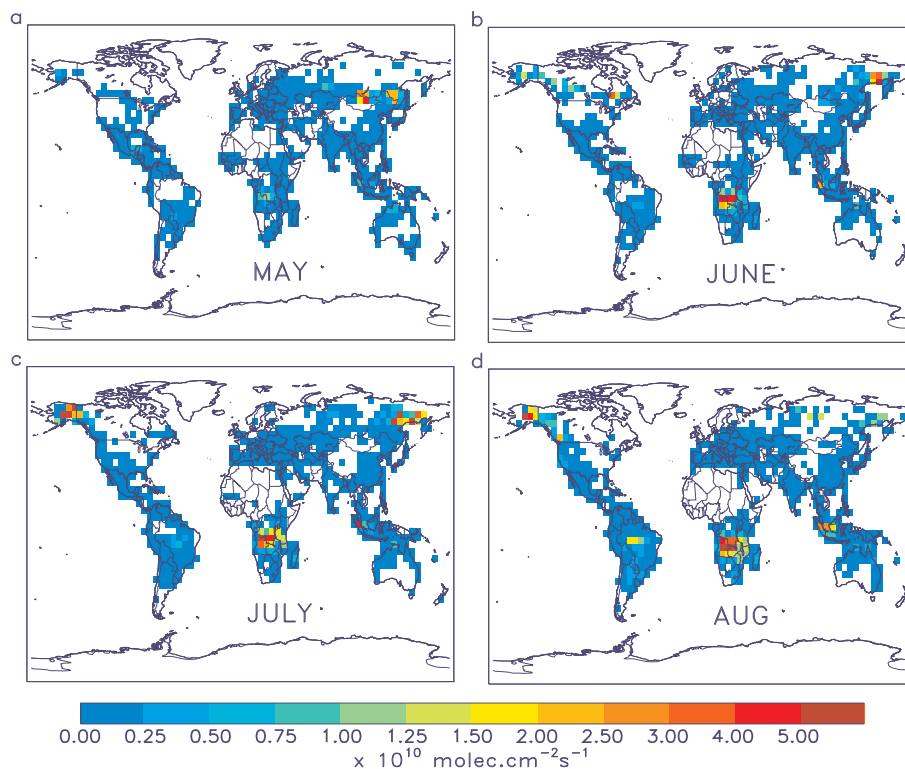


Figure S3: Monthly averaged emissions of HCOOH by biomass burning ($10^{10} \text{ molec.cm}^{-2} \text{ s}^{-1}$) from the GFEDv3 inventory^[S9]. a, May. b, June. c, July. d, August. The fire locations on this figure generally do not coincide with enhanced HCOOH columns observed by IASI (see Fig. S1-S2), except to some extent in June in boreal regions.

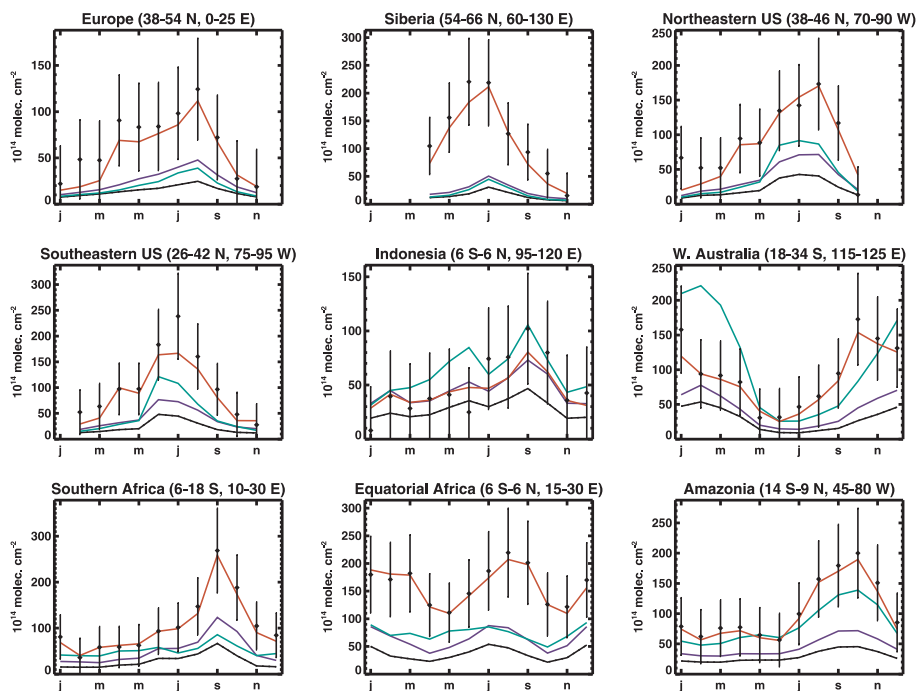


Figure S4: **Seasonal evolution over selected regions of monthly mean observed and modelled HCOOH columns.** IASI HCOOH columns (black diamonds) are compared with modelled columns of the F1 (black), F2 (purple), F3 (green), and Opt2 (red) simulations of Table 1. The error bars represent the assumed errors on IASI columns adopted in the source inversions. Results from Opt1 simulation are very close to Opt2 and are therefore not shown.

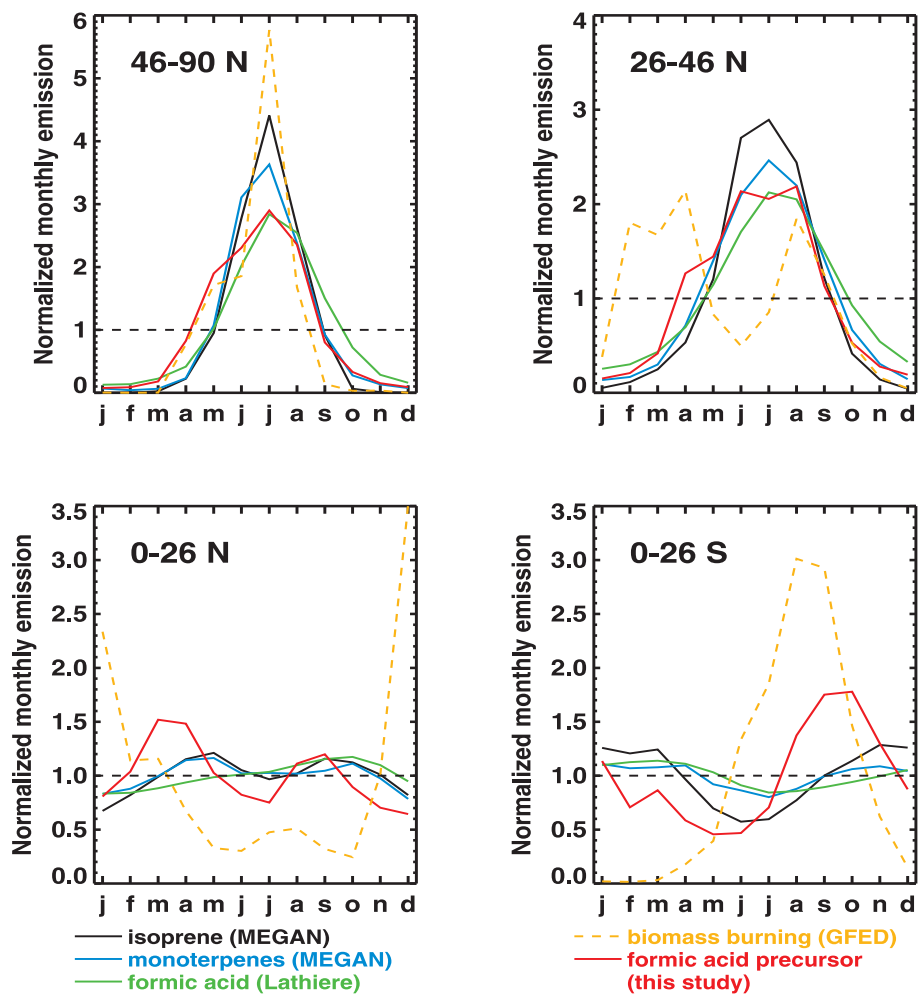


Figure S5: Monthly emissions (normalised by their annual average) for four latitude bands. Curves correspond to isoprene (in black), monoterpenes (blue), primary biogenic HCOOH (green), biomass burning HCOOH (orange), and the biogenic HCOOH precursor optimised in inversion Opt2 (red).

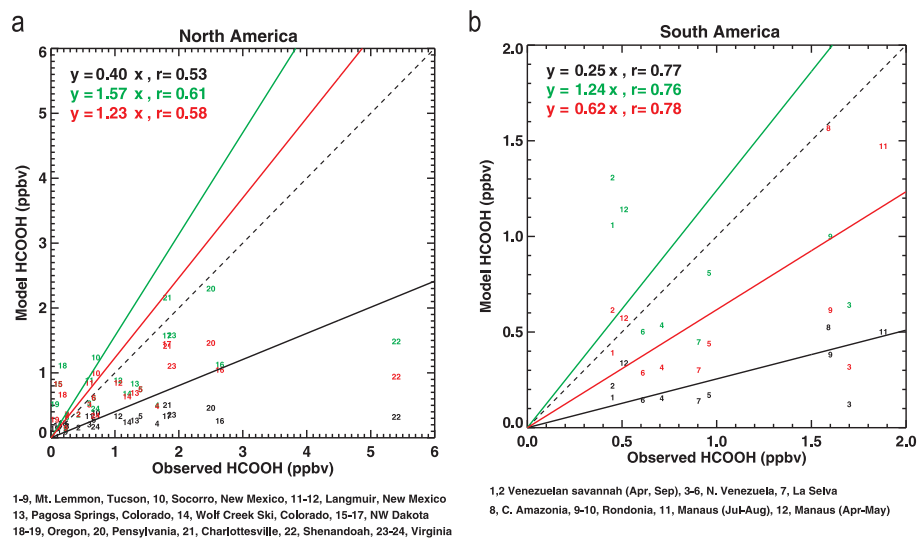


Figure S6: Ground-based HCOOH mixing ratios at North and South American sites (Table S1) against model values. Model concentrations are obtained at the same locations using the standard model (in black), and after optimisation assuming either a primary (in green) or a secondary (in red) biogenic source of HCOOH. The slopes of the regression lines indicated in the upper left corner are calculated as the arithmetic mean ratios of modelled to observed values. The correlation coefficient r for each region is given inset.

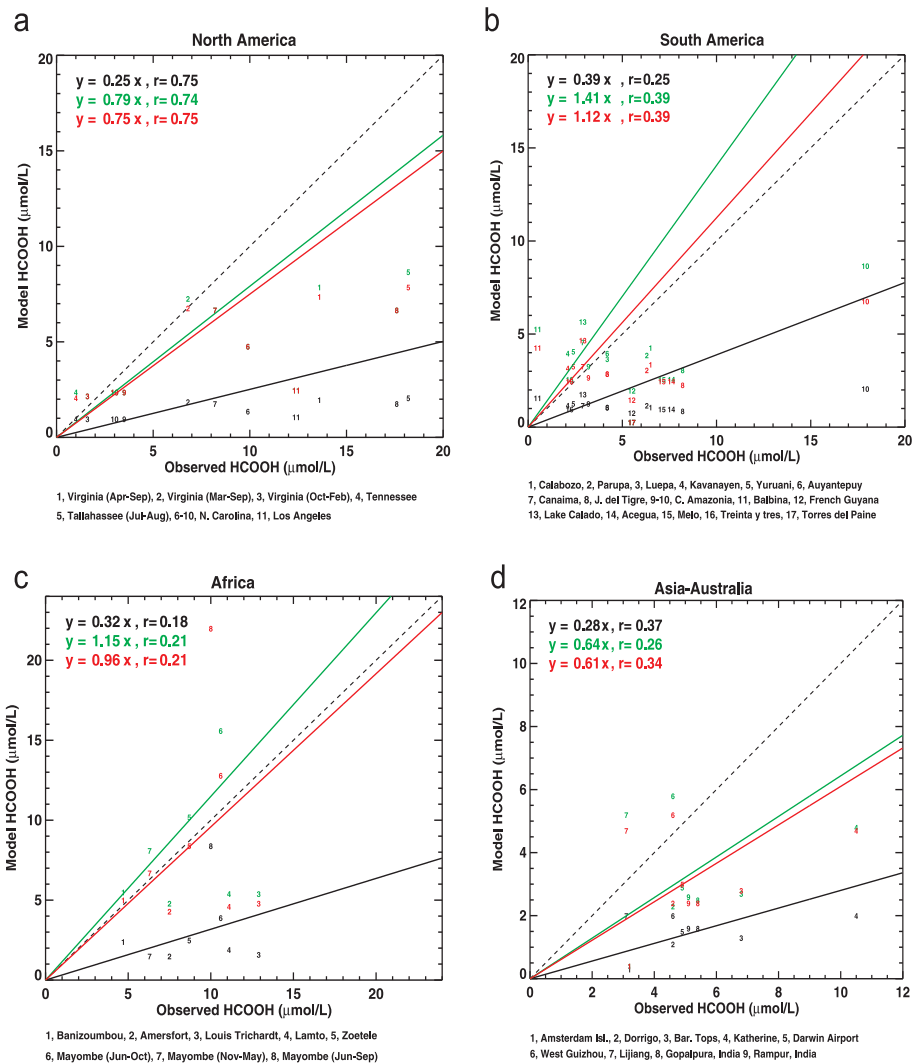


Figure S7: **Observed HCOOH concentrations in precipitation water against model values (Table S2 and S3) in different continents.** Color code is as in Fig. S6. The slopes of the regression lines indicated in the upper left corner are calculated as the arithmetic mean ratios of modelled to observed values. The correlation coefficient r for each region is given inset.

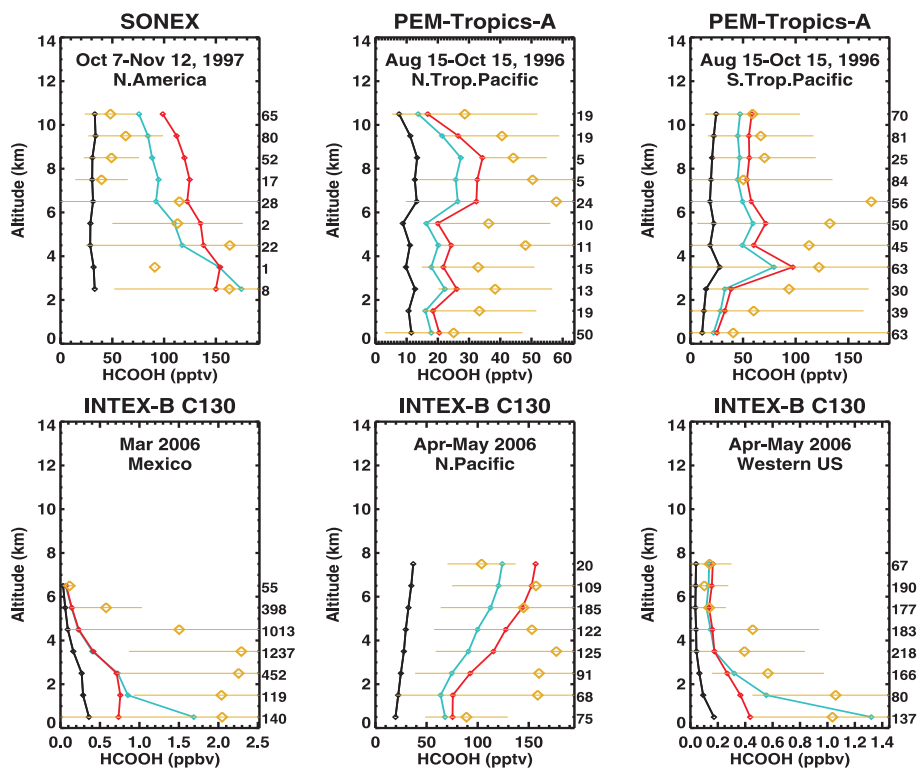


Figure S8: **Observed and modelled vertical distributions of HCOOH concentrations.** SONEX, PEM-Tropics-A and INTEX-B aircraft data over North America (25-55 N, 45-130 W), Mexico (0-25 N, 85-110 W), Western US (35-45 N, 105-125 W), North Pacific (25-55 N, 160-230 E), North Tropical Pacific (0-25 N, 180-275 W), and South Tropical Pacific (0-25 S, 180-275 W) are compared with model output in 2009 from the standard simulation F1 (black) and from Opt1 (green) and Opt2 (red). The number of observations at each altitude bin is given on the right end of each plot. Error bars are standard deviations.

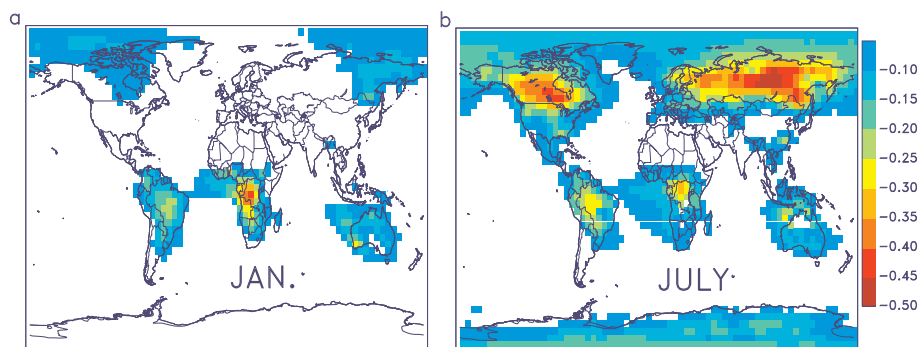


Figure S9: **Calculated change in precipitation pH due to the additional secondary biogenic source of HCOOH inferred from IASI data (Opt2).** a, In January. b, In July.

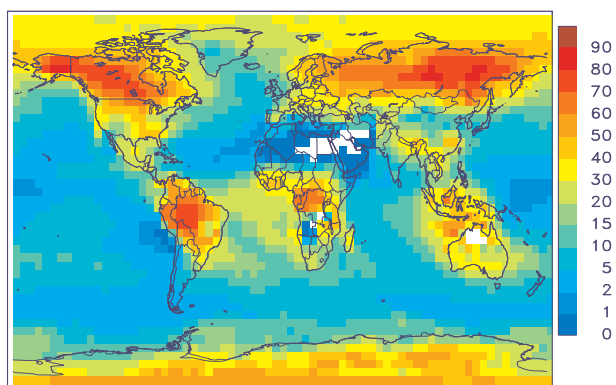


Figure S10: **Calculated contribution (%) of HCOOH to the total concentration of hydrogen cations [H⁺].** Results are from the Opt2 source inversion in July.

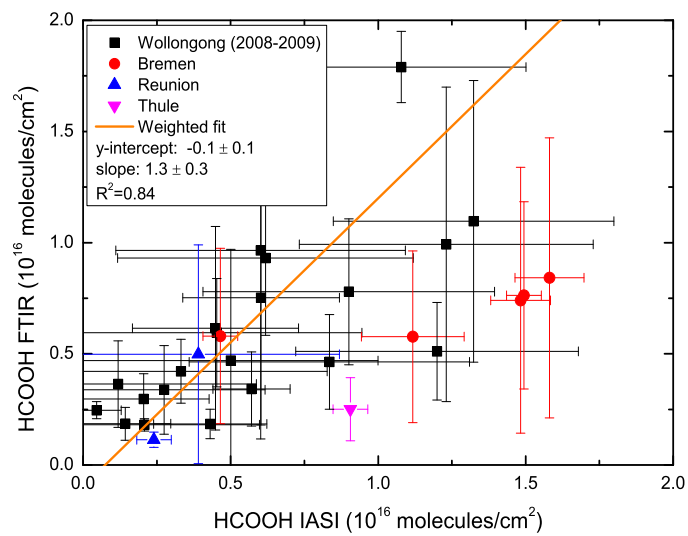


Figure S11: **Comparison between IASI columns and FTIR measurements at different sites.** FTIR data at Wollongong and Reunion Island are presented in this study, at Thule (2004-2008) and Bremen (2002-2010) are obtained from Ref. [S7]. The regression line applies to Wollongong and Reunion Island data.

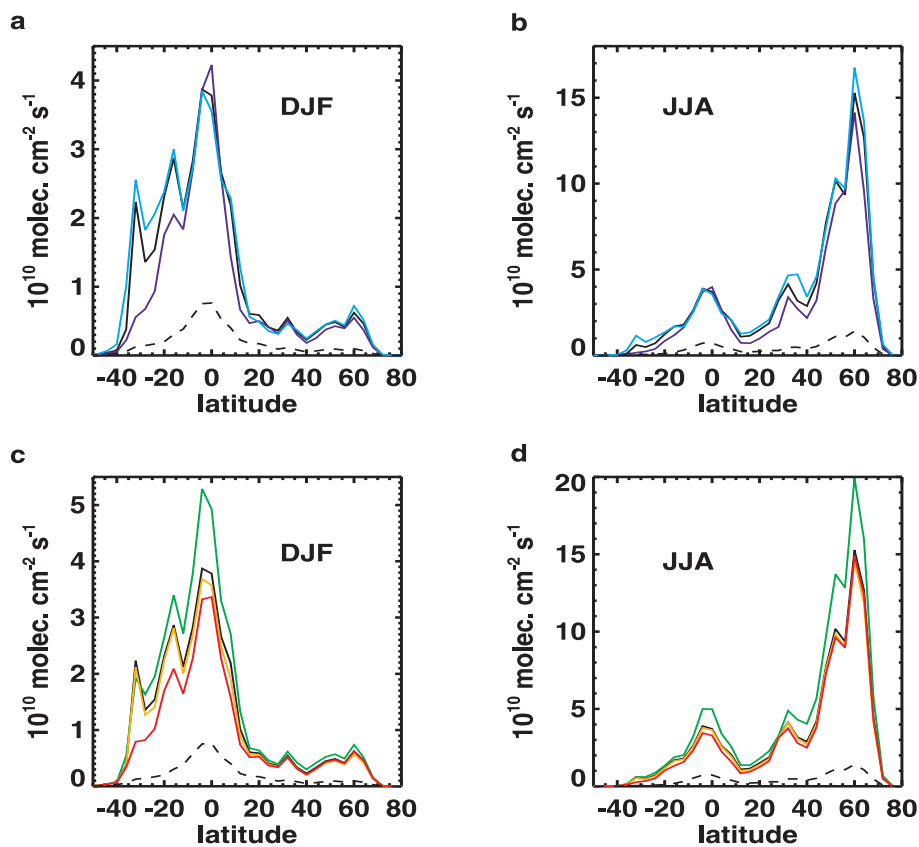


Figure S12: Latitudinal profiles of “top-down” biogenic emissions of the HCOOH precursor averaged over December-January-February (DJF) and June-July-August (JJA). **a-b**, Opt2 in black, Opt2-Err:2 in light blue, Opt2-Errx2 in dark blue. **c-d**, Opt2 in black, Opt1 in green, Opt2-kOH in orange, Opt2-Isom in red. The dashed lines represent the a priori distribution of the HCOOH precursor used in the optimisations. The other sensitivity inversions lie very close to the standard Opt2 results and are not illustrated here.

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