Supplement of

Bacteria in clouds biodegrade atmospheric formic and acetic acids

Leslie Nuñez López, Pierre Amato, and Barbara Ervens

Correspondence to: Barbara Ervens barbara.ervens@uca.fr

Table S1. Irreversible processes in the aqueous phase. The kinetic data are the same as used in the model study by Khaled et al. (2021). The biodegradation rate constants are calculated based on the lab data by Vaïtilingom et al. (2011).

Chemical reactions					
	Reactants		Products	k [M^{-1} s^{-1}]	E_a/R [K]
R1	$SO_2 + O_3$	→	$S(VI) + O_2$	$2.4\cdot10^4$	
R2	$HSO_3^- + O_3$	→	$S(VI) + O_2$	$3.7\cdot10^5$	5530
R3	$SO_3^{2-} + O_3$	→	$S(VI) + O_2$	$1.5\cdot10^9$	5280
R4	$H_2O_2 + HSO_3^- + H^+$	→	$S(VI) + H_2O$	$7.2\cdot10^7$ M^{-2} s^{-1}	4000
R5	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	$8.3\cdot10^5$	2720
R6	$O_2^- + HO_2$	→	$H_2O_2 + O_2$	$9.7\cdot10^7$	1060
R7	$OH + CH_2(OH)_2$	→	$HO_2 + HCOOH$	$1\cdot10^9$	1000
R8	$OH + CH_3OOH$	→	$CH_3O_2 + H_2O$	$2.4\cdot10^7$	1680
R9	$OH + CH_3OOH$	→	$HO_2 + HCOOH$	$61\cdot10^6$	1680
R10	$O_3 + O_2^-$ (+ H^+)	→	$OH + 2\ O_2$	$1.5\cdot10^9$	2200
R11	OH + CHOCHO	→	HO_2 + CHOCOOH	$1.1\cdot10^9$	1516
R12	OH + CHOCOOH	→	$HO_2 + H_2C_2O_4$	$3.6\cdot10^8$	1000
R13	$OH + CHOCOO^-$	→	$HO_2 + H_2C_2O_4$	$2.9\cdot10^9$	4300
R14	$OH + C_2O_4^{2-}$	→	$O_2^- + 2\ CO_2 + OH^-$	$1.6\cdot10^8$	4300
R15	$OH + HC_2O_4^-$	→	$HO_2 + 2\ CO_2 + OH^-$	$1.9\cdot10^8$	2800
R16	$OH + H_2C_2O_4$	→	$HO_2 + 2\ CO_2 + H_2O$	$1.4\cdot10^6$	
R17	$OH + CH_3C(O)COO^-$	→	$HO_2 + CO_2 + CH_3COO^-$	$7.2\cdot10^8$	
R18	$OH + CH_3C(O)COOH$	→	$HO_2 + H_2O + CH_3COOH$	$1.2\cdot10^8$	
R19	$OH + CH_3CHO$	→	$HO_2 + CO_2 + CH_3COOH$	$3.6\cdot10^9$	
R20	$OH + CH_3C(O)CHO$	→	HO_2 + CHC(O)COOH	$1.1\cdot10^9$	1516
R21	$OH + HCOO^-$	→	$HO_2 + CO_2 + H_2O$	$3.2\cdot10^9$	1000
R22	OH + HCOOH	→	$HO_2 + CO_2 + H_2O$	$1.3\cdot10^8$	1000
R23	$CH_3O_2 + CH_3O_2$	→	$CH_2O + CH_3OH + HO_2$	$1.7\cdot10^8$	2200
R24	$H_2O_2 + OH$	→	$HO_2 + H_2O$	$3\cdot10^7$	1680
R25	OH + WSOC	→	WSOC + HO_2	$3.8\cdot10^8$	
R26	$OH + CH_2OHCHO$	→	$CH_2OHCOOH + HO_2$	$1.2\cdot10^9$	
R27	$OH + CH_2OHCOOH$	→	CHOCOOH + HO_2	$5.4\cdot10^8$	
R28	$OH + CH_2OHCOO^-$	→	CHOCOOH + HO_2	$1.2\cdot10^9$	
R29	$OH + CH_3COOH$	→	0.85 CHOCOOH + 0.15 HCHO + HO_2	$1.5\cdot10^7$	1330
R30	$OH + CH_3COO^-$	→	0.85 CHOCOOH + 0.15 HCHO + HO_2	$1\cdot10^8$	1800
R31	$CH_3(O)O_2 + O_2^-$	→	CH_3COOH	$1\cdot10^9$	
R32	$CH_3(O)O_2 + CH_3(O)O_2$	→	$2\ CH_3O_2$	$1.5\cdot10^8$	
Biodegradation				k_{bact} [L $cell^{-1}$ s^{-1}]	
R33	$HCOOH/HCOO^-$ + Bacteria	→	Products	$1.5\cdot10^{-13}$	
R34	CH_3COOH/CH_3COO^- + Bacteria	→	Products	$8.7\cdot10^{-14}$	

Table S2. Aqueous phase equilibria. The data are the same as used in the model study by Khaled et al. (2021).

				K_a [M]
E1	H_2O	$\rightleftharpoons$	$OH^- + H^+$	$1.0 \cdot 10^{-14}$
E2	HO_2	$\rightleftharpoons$	$O_2^- + H^+$	$1.60 \cdot 10^{-5}$
E3	CHOCOOH	$\rightleftharpoons$	$CHOCOO^- + H^+$	$6.60 \cdot 10^{-4}$
E4	HCOOH	$\rightleftharpoons$	$HCOO^- + H^+$	$1.77 \cdot 10^{-4}$
E5	$H_2C_2O_4$	$\rightleftharpoons$	$HC_2O_4^- + H^+$	$6.40 \cdot 10^{-2}$
E6	$HC_2O_4^-$	$\rightleftharpoons$	$C_2O_4^{2-} + H^+$	$5.25 \cdot 10^{-5}$
E7	HNO_3	$\rightleftharpoons$	$NO_3^- + H^+$	22
E8	$SO_2 \cdot H_2O$	$\rightleftharpoons$	$HSO_3^- + H^+$	0.013
E9	HSO_3^-	$\rightleftharpoons$	$SO_3^{2-} + H^+$	$6.60 \cdot 10^{-8}$
E10	H_2SO_4	$\rightleftharpoons$	$HSO_4^- + H^+$	1000
E11	HSO_4^-	$\rightleftharpoons$	$SO_4^{2-} + H^+$	0.102
E12	NH_3	$\rightleftharpoons$	$NH_4^+ + OH^-$	$1.76 \cdot 10^{-5}$

Table S3. Phase transfer parameters. The parameters are the same as used in the model study by Khaled et al. (2021). The Henry's law constant for acetic acid is the same as used by Brimblecombe and Clegg (1988), its α and D_g values are estimated to be same as for similar compounds.

Species	M_g [g mol^{-1}]	α	D_g [cm^2 s^{-1}]	K_H [M atm^{-1}]
O_3	48	0.05	0.148	$1.14 \cdot 10^{-2}$
H_2O_2	34	0.1	0.118	$1.02 \cdot 10^{5}$
OH	17	0.05	0.153	25
HO_2	33	0.05	0.104	$9 \cdot 10^{3}$
HCHO	30	0.02	0.164	$4.99 \cdot 10^{3}$
CH_3O_2	47	0.0038	0.135	310
CH_3OOH	48	0.0038	0.135	310
HNO_3	63	0.054	0.132	$2.1 \cdot 10^{5}$
N_2O_5	108	0.0037	0.110	1.4
SO_2	64	0.035	0.128	1.23
HCOOH	46	0.012	0.153	5530
$(CHO)_2$	58	0.023	0.115	$4.19 \cdot 10^{5}$
CH_3COCHO	72	0.1	0.115	$3.2 \cdot 10^{4}$
NH_3	17	0.1	0.1	60.7
CH_3COOH	60	0.1	0.1	5500

Table S4. Gas phase formation and loss processes of formic and acetic acids. The full gas phase mechanism is the same as used in Barth et al. (2021).

	Reactants		Products	k [cm^3 s^{-1}]	E_a/R [K]
Rg1	Isoprene + O_3	$\rightarrow$	0.2 CH_3COOH + 0.1 OH + 0.27 HO_2 + 0.06 HO_2 + 0.6 HCHO + CH_3COOH + 0.4 MACR + 0.3 MVK + 0.07 C_3H_6 + 0.2 $CH_3(O)O_2$	$9.6\cdot10^{-18}$	
Rg2	$CH_3(O)O_2$ + HO_2	$\rightarrow$	0.1 O_3 + 0.7 $CH_3C(O)OOH$ + 0.3 CH_3COOH	$1.8\cdot10^{-11}$	360
Rg3	HCOOH + OH	$\rightarrow$	CO_2 + H_2O + HO_2	$1.5\cdot 10^{-12}$	
Rg4	CH_3COOH + OH	$\rightarrow$	0.7 OH + 0.7 CH_3CHO + 0.3 $C_2H_5O_2$	$1\cdot10^{-11}$	200

Table S5. Initial mixing ratios of gas phase species [ppb] and concentrations of aqueous phase species [μg m_{air}^{-3}]; all other species are not initialized

Gas phase species	Mixing ratio [ppb]
O_3	60
H_2O_2	1
HCHO	0.1
HCOOH	0.5
CH_3COOH	0.2
HNO_3	1
SO_2	2
NH_3	1
NO	3
NO_2	0.1
CO	150
Isoprene	1
Toluene	2
Ethylene	0.5
CH_4	1850 (const.)
Aqueous phase species	**Concentration**
WSOC	20 μM
Bacteria cells	0.1 cm_{air}^{-3}

Table S6. Rates for all processes shown in Figure 6, at the end of 1-hour simulation time and for D_d = 20 μm. The upper part of the table lists the rates in units of 10^{-16} $\mathrm{mol\,g_{air}^{-1}\,s^{-1}}$. These numbers allow the comparison of rates related scaled by the aqueous phase volumes. The bottom part of the table reports the same rates (only aqueous phase) in units of 10^{-9} $\mathrm{mol\,L_{aq}^{-1}\,s^{-1}}$. These units allow comparing the two droplet classes. If the chemical composition were identical in both classes, the rates should be identical, too. Any deviation is caused by the biodegradation in drop class 2.

Acid	pH	PT_1	S_{aq1}	L_{aq1}	PT_2	S_{aq2}	L_{aq2}	L_{Bact}	S_g	L_g
		10^{-16} mol g_{air}^{-1} s^{-1}								
Formic acid	3	-2.5	2.9	-0.45	0.87	0.003	$-4\cdot10^{-4}$	-0.87	0	-0.77
	4.6	3.7	5.3	14	2.0	0.006	-0.011	-2.0	0	-0.22
	5.6	1.2	11	27	0.49	0.013	-0.008	-0.5	0	-0.015
Acetic acid	3	-3.0	3.1	-0.004	0.15	0.003	$-3.5\cdot10^{-6}$	-0.15	0.38	-6.4
	4.6	-8.2	8.9	-0.05	0.31	0.009	$-5\cdot10^{-5}$	-0.32	0.85	-5.4
	5.6	-10	16	-0.74	0.98	0.02	$-7\cdot10^{-4}$	-1.0	1.1	-3.4
		10^{-9}mol L_{aq}^{-1} s^{-1}								
Formic acid	3	-0.61	0.72	-0.11	210	0.72	-0.11	-210		
	4.6	0.91	1.3	-3.5	500	1.4	-2.8	-500		
	5.6	0.3	2.8	-6.6	120	3.1	-2.0	-120		
Acetic acid	3	-0.74	0.76	$-8.7\cdot10^{-4}$	37	0.76	$-8.5\cdot10^{-4}$	-38		
	4.6	-2.0	2.2	-0.012	77	2.2	-0.012	-79		
	5.6	-2.5	4.0	-0.18	240	4.6	-0.17	-250		

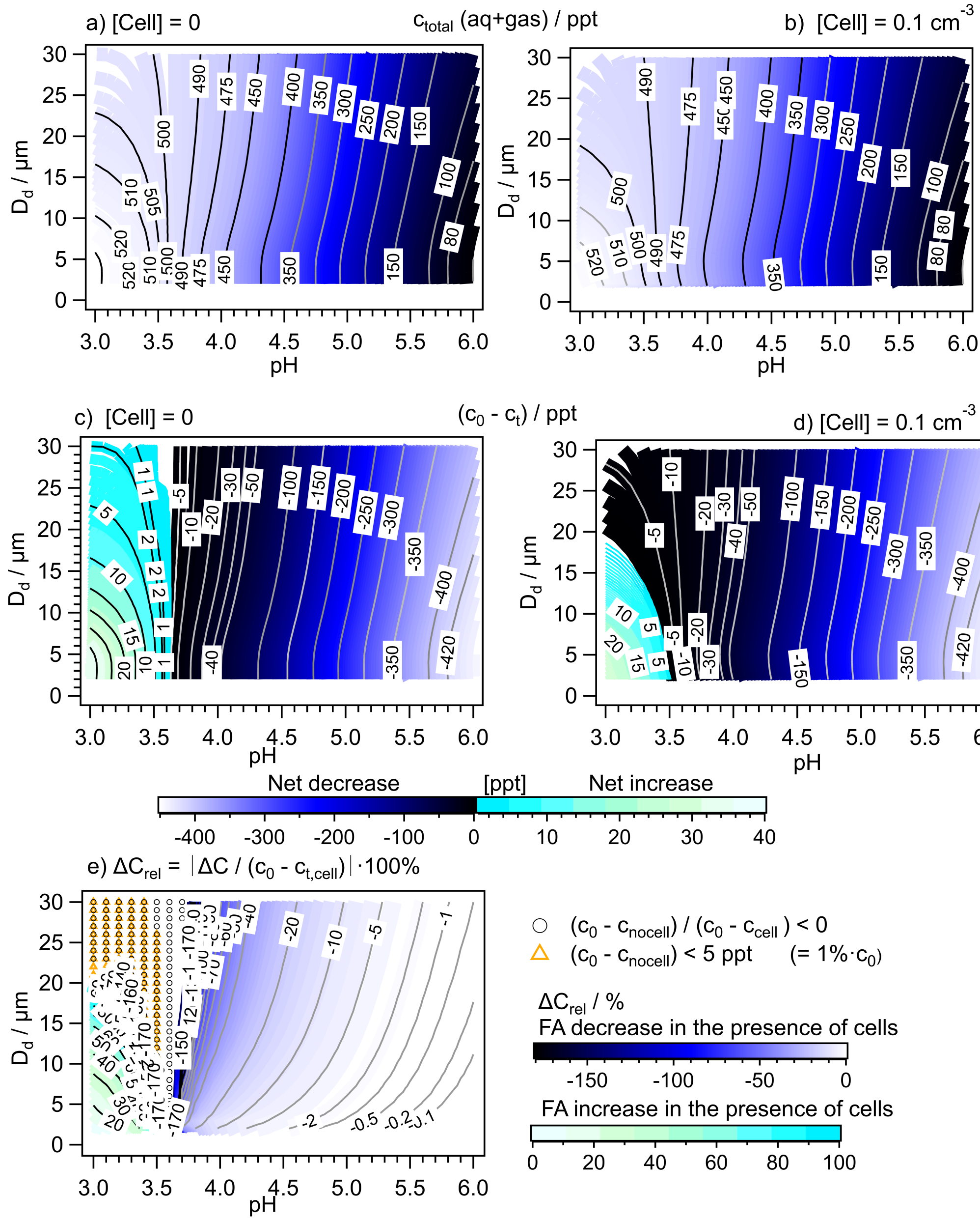

Figure S1. Results from 900 1-hour simulations (30 pH values, 30 drop diameters, Total formic acid concentrations (gas + aqueous) and absolute concentration difference $((c_0 - c_t)$ in the absence of bacteria (a, c) and in the presence of bacteria (b, d). e) Relative difference in concentration due to bacteria according to Equation 6. The threshold of $c_0 - c_{t,nocell}$ in panel e) is chosen to avoid displaying very high values by dividing by an irrelevant small concentration difference

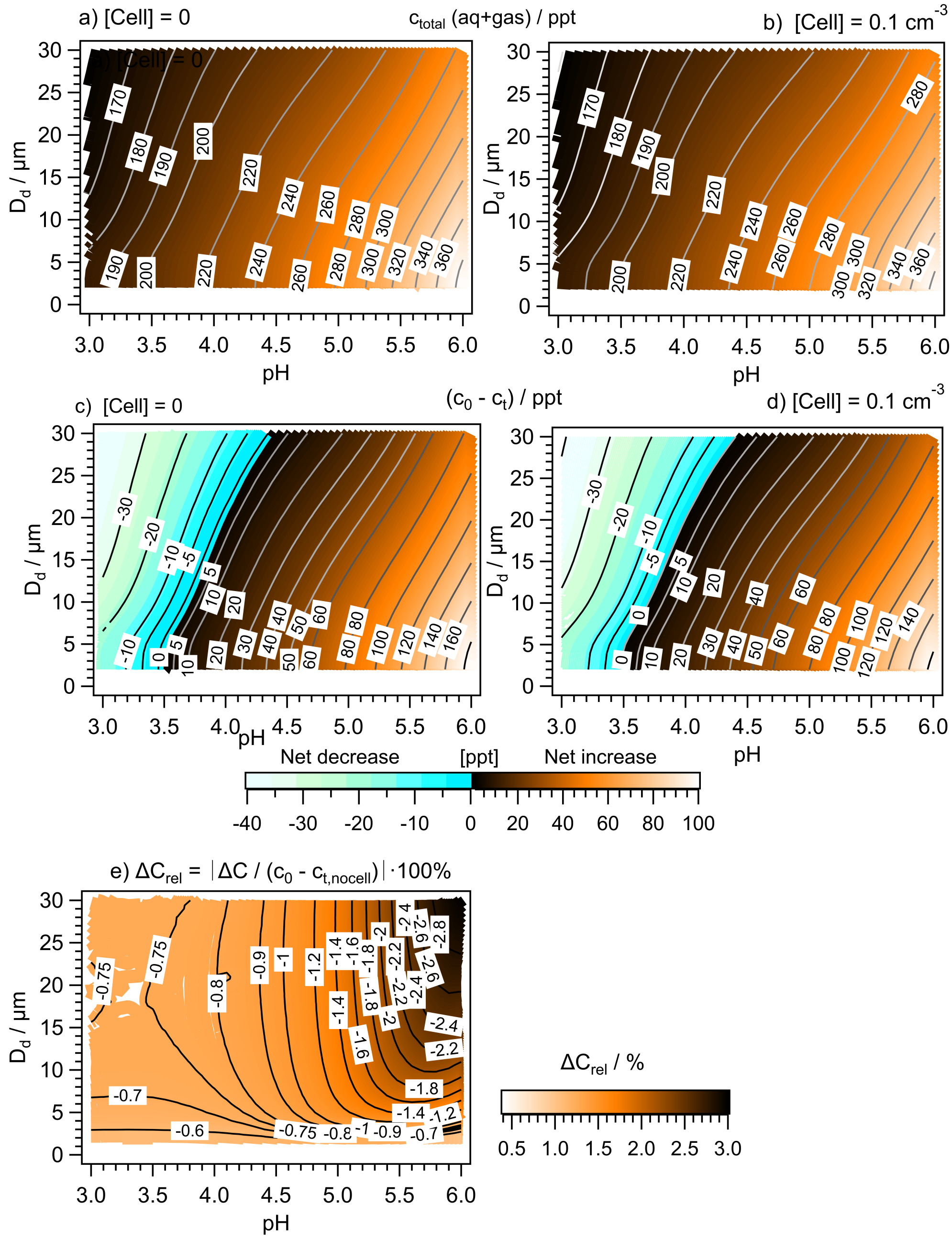

Figure S2. Results from 900 1-hour simulations (30 pH values, 30 drop diameters, Total acetic acid concentrations (gas + aqueous) and absolute concentration difference ($(c_0 - c_t)$ in the absence of bacteria (a, c) and in the presence of bacteria (b, d). e) Relative difference in concentration due to bacteria according to Euqation 6

References

Barth, M. C., Ervens, B., Herrmann, H., Tilgner, A., McNeill, V. F., Tsui, W. G., Deguillaume, L., Chaumerliac, N., Carlton, A. G., and Lance, S.: Box Model Intercomparison of Cloud Chemistry, Journal of Geophysical Research Atmospheres, 126, e2021JD035 486, https://doi.org/10.1029/2021JD035486, 2021.

Brimblecombe, P. and Clegg, S. L.: The Solubility and Behaviour of Acid Gases in the Marine Aerosol, J. Atmos. Chem., 7, 1–18, 1988.

Khaled, A., Zhang, M., Amato, P., Delort, A.-M., and Ervens, B.: Biodegradation by bacteria in clouds: an underestimated sink for some organics in the atmospheric multiphase system, Atmospheric Chemistry and Physics, 21, 3123–3141, https://doi.org/10.5194/acp-21-3123-2021, 2021.

Vaïtilingom, M., Charbouillot, T., Deguillaume, L., Maisonobe, R., Parazols, M., Amato, P., Sancelme, M., and Delort, A.-M.: Atmospheric chemistry of carboxylic acids: microbial implication versus photochemistry, Atmospheric Chemistry and Physics, 11, 8721–8733, https://doi.org/10.5194/acp-11-8721-2011, 2011.