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Supplementary Material

Ozone uptake and formation of reactive oxygen intermediates on glassy, semi-solid and liquid organic matter

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A. Limiting cases and the kinetic cube

The cases of limiting behaviour are distinguished by three classification parameters:[1] The surface to total loss rate ratio (STLR, decision step 1) assesses the reaction location, the saturation ratio (SR, decision step 2) assesses the supply of reactive gas, and the mixing parameter (MP, decision step 3) assesses the homogeneity of the system.

The classification scheme demands different parameters depending on the outcome of the respective preceding decision step (see Fig. 4 in Berkemeier *et al.*[1]). Most classification parameters require the output of a depth-resolved kinetic model and are given in Eqs. (S1) – (S6), where $[\mathrm{X}]_\mathrm{s}$, $[\mathrm{Y}]_\mathrm{ss}$, $[\mathrm{X}]_{\mathrm{b}k}$ and $[\mathrm{Y}]_{\mathrm{b}k}$ are the concentration of reactants X and Y in the sorption layer (s), quasi-static surface layer (ss) and *k*-th bulk layer (b*k*), respectively.

The STLR is the sole parameter of the first decision step. It compares the rate of ozone loss at the surface to the sum of all losses in the bulk layers, but neglects loss of X by self-reaction.

$$\mathrm{STLR} = \frac{k_{\mathrm{SLR1}}[\mathrm{X}]_\mathrm{s}[\mathrm{Y}]_\mathrm{ss}}{k_{\mathrm{SLR1}}[\mathrm{X}]_\mathrm{s}[\mathrm{Y}]_\mathrm{ss} + \sum_{i=1}^{n} k_\mathrm{BR}[\mathrm{X}]_{\mathrm{b}i}[\mathrm{Y}]_{\mathrm{b}i}} \qquad \text{(S1)}$$

In case of a high contribution of surface reaction (SLR1), the surface saturation ratio (SSR) is used to determine whether the system is close to the (non-reactive) Langmuir adsorption equilibrium or supply of reactive gas by gas diffusion or surface accommodation is limiting the reaction. SSR relates the surface coverage $\theta_{\mathrm{s,X}}$ to its saturation concentration in absence of chemical reaction $\theta_{\mathrm{s,X,sat}}$.

$$\mathrm{SSR} = \frac{\theta_{\mathrm{s,X}}}{\theta_{\mathrm{s,X,sat}}} = \frac{4[\mathrm{X}]_\mathrm{s}}{\omega_{\mathrm{O3}}\alpha_{\mathrm{s,0}}\tau_{\mathrm{D,O3}}[\mathrm{X}]_\mathrm{g}} + \sigma_\mathrm{X}[\mathrm{X}]_\mathrm{s} \qquad \text{(S2)}$$

In case of a high contribution of bulk reaction (BR), the bulk saturation ratio (BSR) determines whether the near-surface bulk (layer b1) is saturated according to Henry's law.

$$\mathrm{BSR} = \frac{[\mathrm{Y}]_{\mathrm{b1}}}{H_{\mathrm{cp,O3}}[\mathrm{X}]_\mathrm{g}} \qquad \text{(S3)}$$

If saturation of surface or bulk is not achieved, the gas-phase diffusion correction parameter C_g can discriminate between limitation of gas supply by gas diffusion or surface accommodation.

$$C_{\mathrm{g}} = \frac{[\mathrm{X}]_{\mathrm{gs}}}{[\mathrm{X}]_{\mathrm{g}}} \tag{S4}$$

A surface reaction that is not hindered by supply of reactive gas might be limited by diffusion of bulk constituent Y to the surface, which is assessed by the surface mixing parameter, $\mathrm{SMP}_{\mathrm{Y}.}$

$$\mathrm{SMP}_{\mathrm{Y}} = \frac{[\mathrm{Y}]_{\mathrm{b}1}}{\max([\mathrm{Y}]_{\mathrm{b}k})} \tag{S5}$$

A bulk reaction on the other hand can be limited by diffusion of reactive trace gas X, bulk constituent Y, or both. This is assessed by comparing reacto-diffusive lengths l_{rd} to the system size (e.g. particle radius r_{p}). The reacto-diffusive length is calculated analogously to previous works[2], but using effective bulk concentrations $[\mathrm{Y}]_{\mathrm{b,eff}}$ and $[\mathrm{X}]_{\mathrm{b,eff}}$ that account for spatial inhomogeneity of both reaction partners. These effective concentrations can be regarded as average concentrations in the region of overlap of the counter-diffusing species X and Y.

$$\mathrm{BMP}_{\mathrm{XY}} = \frac{1}{2}\left(\frac{l_{\mathrm{rd,X}}}{l_{\mathrm{rd,X}} + \frac{r_{\mathrm{p}}}{\exp(1)}} + \frac{l_{\mathrm{rd,Y}}}{l_{\mathrm{rd,Y}} + \frac{r_{\mathrm{p}}}{\exp(1)}}\right) \tag{S6a}$$

with

$$l_{\mathrm{rd,X}} = \sqrt{\frac{D_{\mathrm{b,X}}}{k_{\mathrm{BR}}[\mathrm{Y}]_{\mathrm{b,eff}}}} \tag{S6b}$$

and

$$[\mathrm{Y}]_{\mathrm{b,eff}} = \sum_{j=1}^{n} \frac{k_{\mathrm{BR}}[\mathrm{X}]_{\mathrm{b}j}[\mathrm{Y}]_{\mathrm{b}j}}{\sum_{i=1}^{n} k_{\mathrm{BR}}[\mathrm{X}]_{\mathrm{b}i}[\mathrm{Y}]_{\mathrm{b}i}}[\mathrm{Y}]_{\mathrm{b}j} \tag{S6c}$$

If systems fall between limiting cases, multiple reaction channels contribute, each having their own limiting parameters. The higher level parameters SR and MP (decision steps 2 and 3) are then calculated by weighting with the preceding parameters. Every reaction channel thus contributes to the overall classification parameter.

$$\mathrm{SR} = \mathrm{STLR} \cdot \mathrm{SSR} + (1 - \mathrm{STLR}) \cdot \mathrm{BSR} \tag{S7}$$

$$\begin{aligned} \mathrm{MP} = \mathrm{STLR}\left(\mathrm{SSR} \cdot \mathrm{SMP}_{\mathrm{Y}} + (1 - \mathrm{SSR}) \cdot C_{\mathrm{g}}\right) + (1 - \mathrm{STLR}) \\ \cdot \left(\mathrm{BSR} \cdot \mathrm{BMP}_{\mathrm{XY}} + (1 - \mathrm{BSR}) \cdot C_{\mathrm{g}}\right) \end{aligned} \tag{S8}$$

B. Normalized sensitivity coefficients and parameter uniqueness

For every input parameter λ_i, a normalized sensitivity coefficient $S(\lambda_\mathrm{i})$ can be calculated using Morris' elementary effects method[3] and the definition in Eq. S9.

$$S(\lambda_i) = \frac{\lambda_i}{Q_\mathrm{mod}} \frac{dQ_\mathrm{mod}}{d\lambda_i} = \frac{d \log Q_\mathrm{mod}}{d \log \lambda_i} \tag{S9}$$

If, for all times and all conditions, a linear combination of $S(\lambda_i)$'s can be found to express another $S(\lambda_i)$, these parameters are not orthogonal.

$$\sum \nu_i \, S(\lambda_i) = 0 \tag{S10}$$

The orthogonality described above can be seen readily in Figure S3: Summing up the sensitivity coefficients of k_BR, $k_\mathrm{bs,O3}$ and $D_\mathrm{b,O3}$ yields the sensitivity coefficient of $H_\mathrm{cp,O3}$.

$$S(k_\mathrm{BR}) + S(k_\mathrm{bs,O3}) + S(D_\mathrm{b,O3}) = S(H_\mathrm{cp,O3}) \tag{S11}$$

Hence, once normalised sensitivity coefficients $S(\lambda_i)$ are calculated for all input parameters λ_i this method is computationally much more efficient than evaluating the model for all possible combinations of input parameters. We tried all possible combinations of up to 5 parameters λ_i with a discrete set of 16 possible coefficients ν_i: -3, -2, -3/2, -1, -2/3, -1/2, -1/3, -1/4, 1/4, 1/3, 1/2, 2/3, 1, 3/2, 2, 3, and up to 7 parameters λ_i with a smaller set: -2, -1, -1/2, 1/2, 1, 2. Besides the already mentioned, the only other set of linear dependent sensitivities found using this technique was $S(\alpha_\mathrm{s,0})$ and $S(\tau_\mathrm{d,O3})$. This dependence was already known as $\alpha_\mathrm{s,0}$ was held fixed during the optimization. Note that while this method can detect local dependencies between input parameters, it is not possible to exclude the existence of other, not directly connected minima in the search space such as the alternative high $D_\mathrm{b,O3}$ solution described in Sect. 3.3.

Tab S1 Kinetic input parameters for KM-SUB.

Parameter	**Unit**	**Description**
$\boldsymbol{k}_{\mathbf{BR}}$	cm^3 s^{-1}	bulk reaction rate coefficient
$\boldsymbol{k}_{\mathbf{SLR1}}$	cm^2 s^{-1}	surface layer reaction rate coefficient
$\boldsymbol{k}_{\mathbf{SLR2}}$	cm^2 s^{-1}	surface layer reaction rate coefficient, self-reaction
$\boldsymbol{k}_{\mathbf{bs,O3}}$	cm s^{-1}	bulk to surface transfer rate coefficient, O_3
$\boldsymbol{k}_{\mathbf{ssb,Y}}$	s^{-1}	surface to bulk transfer rate coeff., shikimic acid
$\boldsymbol{D}_{\mathbf{b,O3}}$	cm^2 s^{-1}	bulk diffusion coefficient, O_3 in shikimic acid
$\boldsymbol{D}_{\mathbf{b,Y}}$	cm^2 s^{-1}	self-diffusion coefficient, shikimic acid
$\boldsymbol{H}_{\mathbf{cp,O3}}$	mol cm^{-3} atm^{-1}	Henry's law solubility coeff., O_3 in aq. organics
$\boldsymbol{K}_{\mathbf{bs}}$	cm	surface equilibrium constant, shikimic acid
$\boldsymbol{\tau}_{\mathbf{d,O3}}$	s	desorption lifetime, O_3
$\boldsymbol{\alpha}_{\mathbf{s,0}}$		surface accommodation coefficient, O_3
$\boldsymbol{D}_{\mathbf{g,O3}}$	cm^2 s^{-1}	gas phase diffusivity, O_3
$\boldsymbol{\sigma}_{\mathbf{O3}}$	cm^2	adsorption cross-section, O_3

Tab S2 Kinetic input parameters for KM-SUB. Parameters marked with an asterisk (*) were not changed during global optimization. In the last row, r_i indicates the residue arising from all data sets at the respective RH using $f_i = 1/12$. For 24 % and 92 % RH, the residues are given from top to bottom in order of ascending $[O_3]_g$.

Parameter	**Unit**	**0 % RH**	**24 % RH**	**45 % RH**	**69 % RH**	**83 % RH**	**92 % RH**
Kinetic parameters							
$k_{BR,1}$	$cm^3\ s^{-1}$	4.39×10^{-18}					
$k_{SLR,1}$	$cm^2\ s^{-1}$	8.52×10^{-16}					
$k_{SLR,2}$	$cm^2\ s^{-1}$	4.31×10^{-17}					
$k_{bs,O3}$	$cm\ s^{-1}$	0.60	0.65	0.69	0.83	1.60	23.2
$k_{ssb,Y}$	s^{-1}	9.6×10^{-5}	3.2×10^{-4}	8.3×10^{-4}	8.4×10^{-4}	4.2×10^{-4}	7.0×10^{-8}
$D_{b,O3}$	$cm^2\ s^{-1}$	6.2×10^{-12}	5.3×10^{-12}	6.1×10^{-12}	1.9×10^{-9}	8.0×10^{-8}	9.1×10^{-7}
$D_{b,Y}$	$cm^2\ s^{-1}$	1.0×10^{-21}	8.4×10^{-19}	5.3×10^{-18}	5.1×10^{-17}	2.1×10^{-16}	2.1×10^{-7}
$H_{cp,O3}$	$mol\ cm^{-3}\ atm^{-1}$	1.8×10^{-4}	1.6×10^{-4}	1.4×10^{-4}	1.0×10^{-4}	5.5×10^{-5}	4.0×10^{-5}
K_{bs}	cm	2.0×10^{-9}	2.3×10^{-9}	3.4×10^{-9}	4.1×10^{-9}	3.8×10^{-9}	9.3×10^{-9}
$\tau_{d,O3}$	s	5.32×10^{-4}					
$\alpha_{s,0}{}^{*}$		0.5					
$D_{g,O3}{}^{*}$	$cm^2\ s^{-1}$	0.14					
Geometric and thermodynamic parameters							
σ_{O3}	cm^2	2.42×10^{-14}					
$\sigma_{Y}{}^{*}$	cm^2	3.34×10^{-15}					
$[Y]_{b,0}{}^{*}$	cm^{-3}	5.27×10^{21}	4.87×10^{21}	4.50×10^{21}	3.84×10^{21}	3.02×10^{21}	2.04×10^{21}
$\delta_{layer}{}^{*}$	cm	3.0×10^{-8}	3.0×10^{-8}	6.0×10^{-8}	1.0×10^{-7}	2.0×10^{-7}	7.5×10^{-7}
Residuals							
r_i		0.00312	0.00342 0.00323 0.00236 0.00226	0.00159	0.00052	0.00036	0.00093 0.00104 0.00066 0.00086

Tab S3 Fit parameters for diffusivity parameterization in Vignes-type equation (7) and correction factor α, Eq. (8). Diffusion coefficients are given in $cm^2\ s^{-1}$; factors C and D are dimensionless. Values for $D^{w}_{b,O3}$ were taken from Smith and Kay[4]. $D^{w}_{b,Y}$ has been estimated based upon work from Delgado[5] on similar organic compounds.

	C	D	D^{org}	D^{w}
$D_{b,H2O}$ (Steimer *et al.*[6])	0.279	-7.22×10^{-3}	1.71×10^{-12}	1.9×10^{-5}
$D_{b,O3}$ (this study)	-3.336	-1.287	2.90×10^{-12}	1.9×10^{-5}
$D_{b,Y}$ (this study)	-1.218	-2.065	1.17×10^{-20}	1×10^{-5}

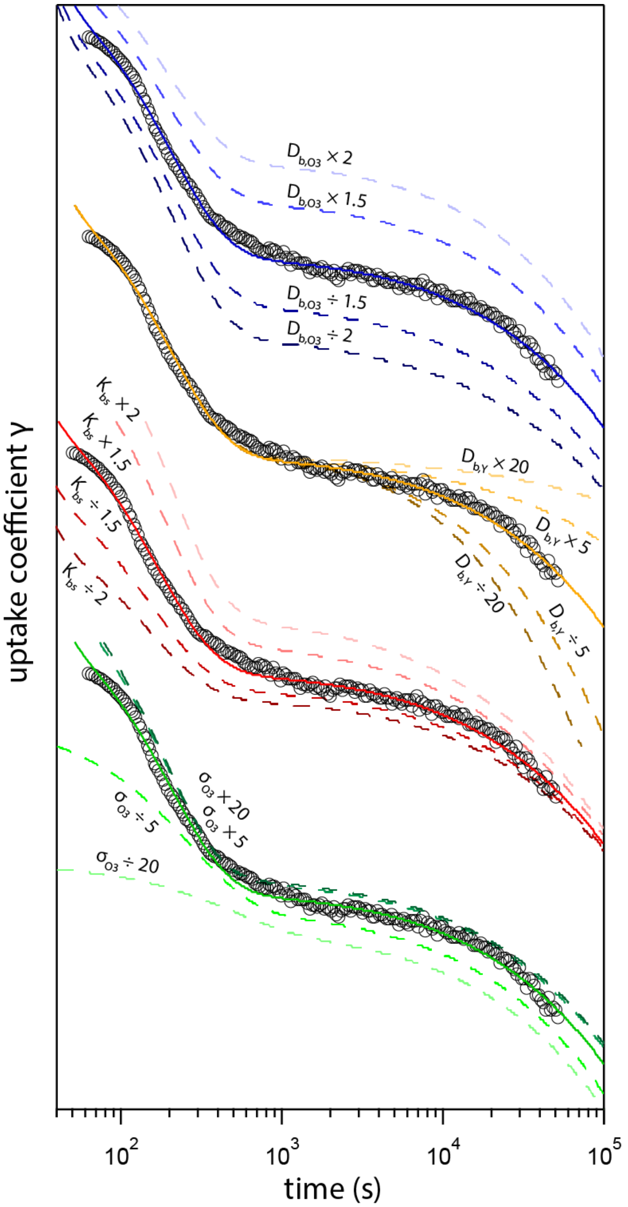

Fig S1 Dependence of uptake coefficient γ on small variations of the parameters $D_{b,O3}$ (blue), $D_{b,Y}$ (orange), K_{bs} (red) and σ_{O3} (green) and comparison to the experimental data at 68 % RH. The best fit (solid lines) is altered considerably if parameters are varied (dashed lines). For very sensitive parameters ($D_{b,O3}$, K_{bs}) already small changes alter the result significantly over the entire time range, whereas other parameters have rather small impact at specific reaction times ($D_{b,Y}$, σ_{O3}). Note that the y-axis is not continuous throughout the figure.

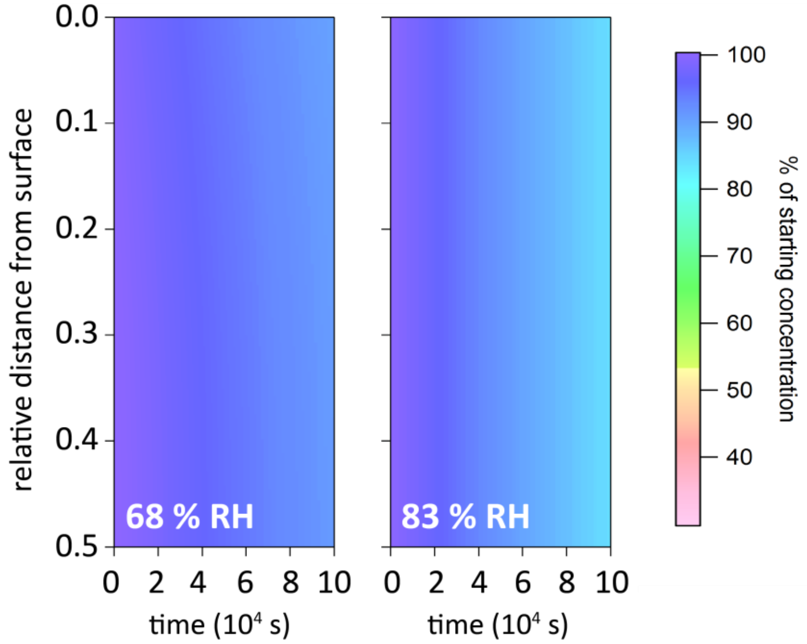

Fig S2 Depth profiles of shikimic acid concentration in a film during exposure of 178 ppb ozone as a function of time and relative humidity (RH), including the effects of reaction products on ozone diffusion. In these model runs, $D_{b,Y}$ is alleviated at 10^{-14} cm^2 s^{-1} and 10^{-10} cm^2 s^{-1} at 67 % and 83 % RH, respectively, and thus a well-mixed bulk matrix obtained.

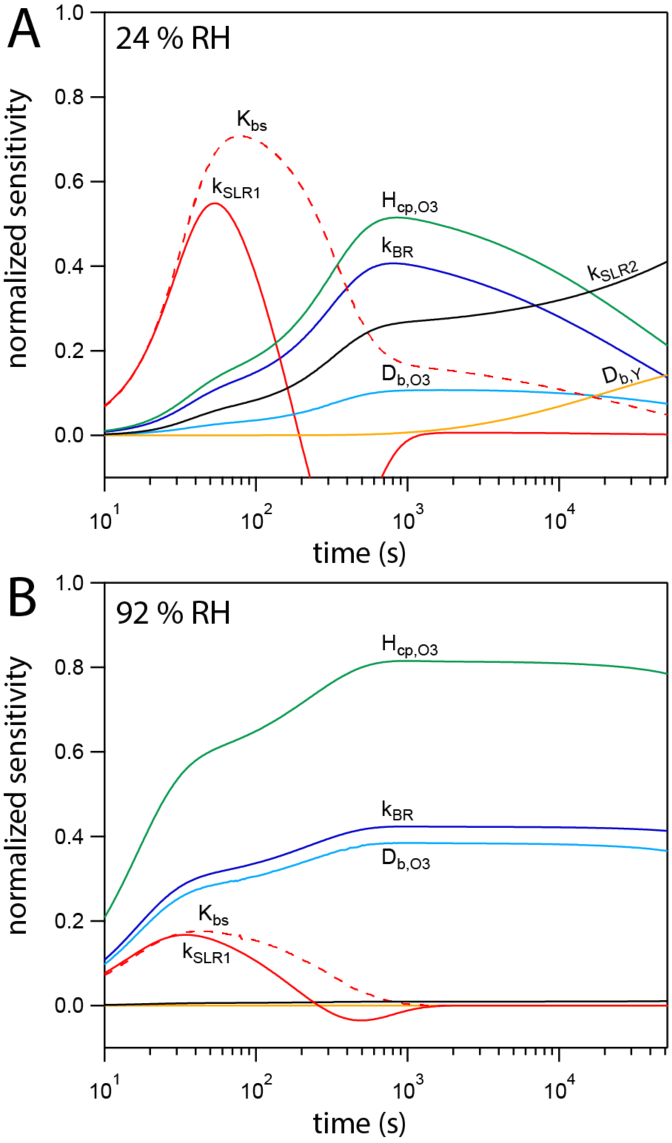

Fig S3 Sensitivity profiles of KM-SUB modelling result for the uptake coefficient γ towards the most influential input parameters for two environmental conditions: (A) 24 % RH and (B) 92 % RH.

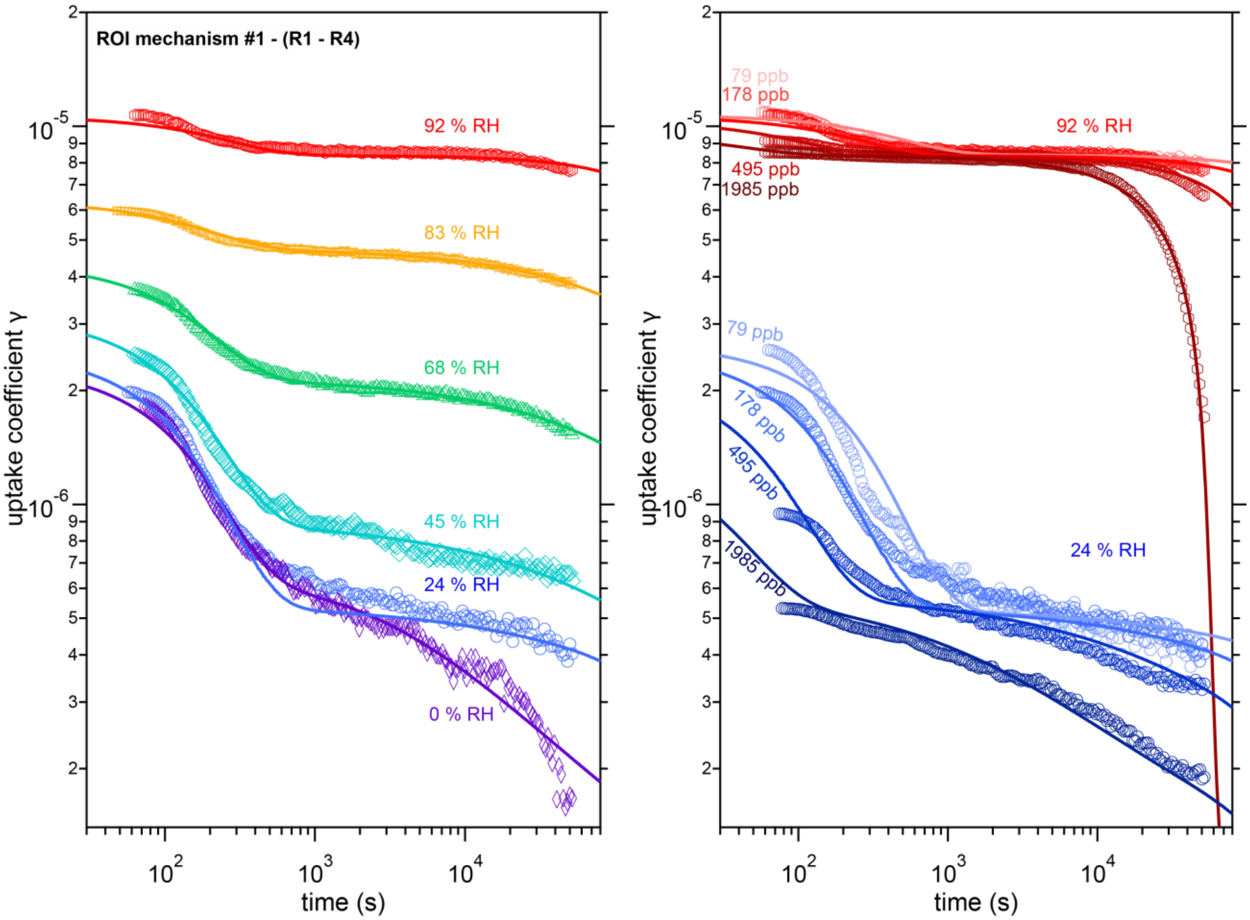

Fig S4 Observed (markers) and modelled (lines) uptake coefficients of ozone γ onto a thin film of shikimic acid as a function of exposure time using ROI mechanism #1 (R1– R4).

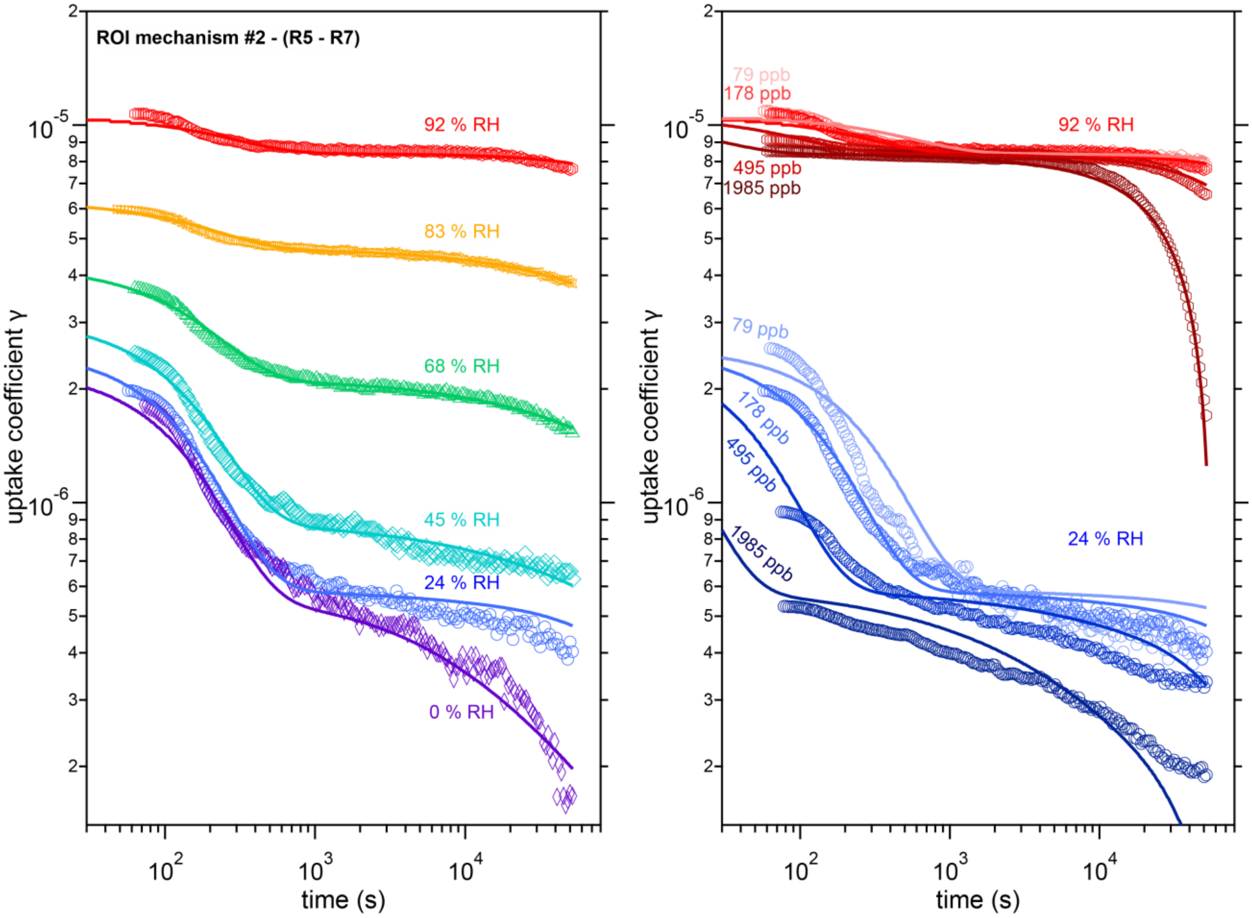

Fig S5 Observed (markers) and modelled (lines) uptake coefficients of ozone γ onto a thin film of shikimic acid as a function of exposure time using ROI mechanism #2 (R5 – R7).

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