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Measurement of gas-phase OH Radical Oxidation and Film Thickness of Organic Films at the Air-Water Interface using Material Extracted from Urban, Remote and Wood Smoke Aerosol - Supplementary Infromation†

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The presence of an organic film on a cloud droplet or aqueous aerosol particle has the potential to alter the chemical, optical and physical properties of the droplet of the particle. In the study presented, water insoluble organic materials extracted from urban, remote (Antarctica) and wood burning atmospheric aerosol were found to have stable compressible films at the air-water interface that were typically ∼6–18 Å thick. These films are reactive towards gas-phase OH radicals and decay exponentially, with bimolecular rate constants for reaction with gas-phase OH radicals of typically 0.08–1.5 $\times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}. These bimolecular rate constants equate to initial OH radical uptake coefficients estimated to be ∼0.6–1 except woodsmoke (∼0.05). The film thickness and the neutron scattering length density of the extracted atmosphere aerosol material (from urban, remote and wood burning) were measured by neutron reflection as they were exposed to OH radicals. For the first time neutron reflection has been demonstrated as an excellent technique for studying the thin films formed at air-water interfaces from materials extracted from atmospheric aerosol samples. Additionally the kinetics of gas-phase OH radicals with a proxy compound, the lipid 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) was studied displaying significantly different behaviour demonstrating it is not a good proxy for atmospheric materials that may form films at the air-water interface. The atmospheric lifetimes, with respect to OH radical oxidation, of the insoluble organic materials extracted from atmospheric aerosol at the air-water interface were ∼40–700 minutes. Relative to a possible physical atmospheric lifetime of 4 days, the oxidation of these films is important and needs inclusion in atmospheric models. The optical properties of these films were previously reported [Shepherd *et al., Atmospheric Chemistry and Physics*, 2018, 18, 5235-5252] and there is a significant change in top of the atmosphere albedo for these thin films on core-shell atmospheric aerosol using the film thickness data and confirmation of stable film formation at the air-water interface presented here.

1 Supplementary Information

1.1 KM-SUB modelling and Markov Chain Monte Carlo (MCMC) procedure - supporting info

The kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB) is a kinetic model framework based on

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the Pöschl-Rudich-Ammann (PRA) framework[1,2]. Here, we employed KM-SUB to describe the kinetic decays of real organic films observed by neutron reflectivity measurements. Owing to the lack of chemical information, the reaction scheme was kept simple and is presented in Eq. 5 of the main text. Product evaporation and dissolution were not considered in this model. Again, there is no information regarding the chemical nature of the products, so the constraint of model parameters associated with adsorption, desorption and dissolution was not possible. The inclusion of a residue in the model returned better fits to the data (see fits in Fig. S1).

If there is an uncertainty in the experimental datapoints, there must also be an uncertainty in the model input parameters. The aim of the MCMC algorithm is to sample the probability distribution for a given model-data system. Estimates for the probability distribution of the (varying) model parameters are also possible. Details of the MCMC algorithm, why and how to use it are presented in great detail by Hogg and Foreman-Mackey[3]. As a general summary:

- A bound is set for each varying parameter.
- An ensemble of parameter sets is initialised within these bounds.
- The algorithm is iterated by accepting or rejecting a proposal parameter set based on the likelihood (goodness-of-fit) at the previous step.
- This chain of values walks around the parameter space and eventually equilibrates around the region of maximum likelihood.

In this study, the emcee Python package is used to carry out MCMC sampling[4]. An ensemble of chains (walkers) is initialised and the algorithm iterated until each walker equilibrates around the region of maximum likelihood. An estimate for the probability distribution for the model-data fit as well as for the varying model parameter (k_{surf}) is then obtained. A plot of the central 50 % of model outputs from this procedure is presented in Fig. S1 For each MCMC procedure, 120 walkers were used and iterated 200 times. A burn-in time (i.e. the number of steps before the walkers equilibrated) was between 50 -150, depending on the model-data system. In total, for each MCMC run, the model was run $120 \times 200 = 24000$ times. All model parameters, except for the varied surface reaction coefficient (k_{surf}), were held to values used in a previous modelling study of OH radicals reacting with levoglucosan and abietic acid (biomass burning markers)[5]. These values are summarised in Table 1 As the desorption lifetimes of the OH radical (τd,OH) and k_{surf} are highly correlated[5], τd,OH was held at 1×10^{-7} s.

Figure 1 shows the result of the global optimisation and MCMC sampling procedure for each of the kinetic decays fitted to in this study. The interquartile range of MCMC model outputs shows good agreement with the experimental data, giving us confidence in the model fit. The model fits better with the data when considering a residue at the end of the reaction (e.g. Fig. 1(b)).

Notes and references

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3 D. W. Hogg and D. Foreman-Mackey, *The Astrophysical Journal Supplement Series*, 2018, **236**, 11.

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Table 1 Constrained model parameters used in the KM-SUB model.

model parameter	Description (unit)	Value
δ_{film}	The molecular diameter of the organic film (nm)	(see Table 1 of the main text)
δ_{OH}	The molecular diameter of the OH radical (nm)	0.3
$T_{\mathrm{d,OH}}$	The surface desorption lifetime of OH (s)	1×10^{-7}
ω_{OH}	The mean thermal velocity of the OH radical (cm s^{-1})	6.1×10^{4}
T	Temperature (K)	298
$\alpha_{\mathrm{s,0,OH}}$	The surface accommodation coefficient for the OH radical on a free substrate	1

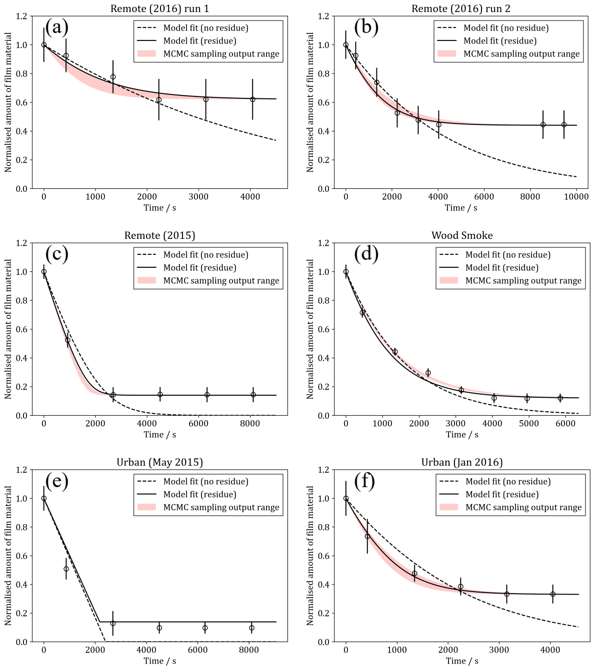

Fig. 1 Model fits from global optimisation of the KM-SUB model to each dataset (with and without a residue) for (a) Remote sample (2015); (b) Wood smoke; (c) Urban sample (January 2016) and Urban sample (May 2015). The interquartile range of MCMC outputs is also plotted for each model-data system.