TNA User Report

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Project title	Phase State of Particles Formed in Seeded Oxidation of Mixed SOA Precursors
Name of the accessed chamber	Manchester Aerosol Chamber (MAC)
Number of users in the project	2
Project objectives (max 100 words)	A particularly novel area of interest driving the current study is the systematic understanding of how the phase state (and any associated diffusive limitation behaviour) will be influenced with increasing complexity of mixed precursors. The scientific objectives of the current project will be to characterise the fraction of particles that exhibit behaviour indicative of existing in the solid phase as a function of relative humidity, produced in the oxidation of mixtures of parent VOCs under a range of conditions.
Description of work (max 100 words):	A series of experiments were planned to investigate the formation of SOA in iso-reactivity mixtures aiming to produce particles including oxidation products of a variety of precursors. Three parent VOCs have been chosen and the experiments investigated single component, binary and ternary mixtures under photo-oxidation conditions. A three-arm impactor combined with a CPC, which was described in detail in Liu et al. (2017) will be deployed from PKU group. The suite of supporting online instrumentation from NCAS-UMan will include DPMS, HTDMA, CCN counter, thermodenuder, AMS, semi-continuous GC-MS and iodide-CIMS as well as filter collections for offline molecular analyses.

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[1] Physics; Chemistry, Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

[2] UNI= University and Other Higher Education Organisation;
RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);
SME= Small and Medium Enterprise;
PRV= Other Industrial and/or Profit Private Organisation;
OTH= Other type of organization.

[3] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher EXP= Engineer; ACA= Academic; TEC= Technician.

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Gordon McFiggans

Chamber name and location: Manchester Aerosol Chamber, Simon Building G.03

Campaign name and period: Secondary organic aerosol formation on seeded particles from mixed volatile organic compounds, 4th March – 10th May, 2019

Text:

Introduction and motivation

Following the pioneering work of *Virtanen et al.* [2010], there has been considerable recent effort to resolve the influences of particle phase state from a number of perspectives mainly relating to retardation of diffusion or mobile components, including water. This includes potential impacts on chemical and physical processes, such as gas-particle partitioning of semi-volatile organic species [*Renbaum-Wolff et al.*, 2013; *Shiraiwa and Seinfeld*, 2012; *Shiraiwa et al.*, 2011; *Vaden et al.*, 2011; *Zaveri et al.*, 2014], heterogeneous reactions or liquid phase reactions [*Koop et al.*, 2011; *Kuwata and Martin*, 2012; *Shiraiwa et al.*, 2011; *Zhang et al.*, 2018]. These processes affect the ice nucleation abilities and cloud condensation nuclei activation of aerosol particles [*Frey et al.*, 2018; *Ignatius et al.*, 2016; *Murray*, 2008; *Murray et al.*, 2010; *Pöschl*, 2011; *Reid et al.*, 2018; *Shiraiwa et al.*, 2017; *Slade et al.*, 2017].

Field studies have aimed to characterize phase state of aerosol particles based on the analysis of particle bounce factors [*Dahneke*, 1971; *Stein et al.*, 1994]. In a real atmosphere, the phase state of aerosol particles varied significantly under various environments. For example, background atmospheric particles (mainly SOA) over isoprene-dominated Amazon rainforest were preliminary in liquid with high ambient RH and temperature [*Bateman et al.*, 2015], and nonliquid PM increased as the measurement site was influenced by anthropogenic airmass from urban pollution and biomass burning [*Bateman et al.*, 2017]. However, in the monoterpene-dominated boreal forest of northern Finland, atmospheric particles (mainly SOA) showed amorphous, solid-like phase state [*Virtanen et al.*, 2010]. The enhanced fraction of particulate sulfate can lead to loss of particle bounce and atmospheric particles with high fraction of sulfate showed a liquid-like phase state under moderate and high ambient RH (e.g. urban area [*Liu et al.*, 2017], subtropical coastal megacity [*Liu et al.*, 2019], south-eastern US rural site [*Pajunoja et al.*, 2016], North-eastern near forest area [*Slade et al.*, 2019]). When the terpene-dominant SOA increased at nighttime [*Slade et al.*, 2019] or ambient RH dropped under 60% [*Liu et al.*, 2017], the nonliquid PM increased. To isolate the factors impacting the phase state, studies have been conducted in the laboratory elucidating a RH-dependent [*Saukko et al.*, 2012] and mass loading of formed secondary organic aerosol (SOA) dependent [*Jain et al.*, 2018] phase state behaviour of SOA from individual biogenic and anthropogenic volatile organic compound (VOC) oxidation. In addition, the phase transition of SOA on seeded ammonium sulfate particles varied with VOC precursors [*Saukko et al.*, 2015]. All these findings gave us a particularly novel area of interest driving the current study is the systematic understanding of how the phase state (and any associated dissuasive limitation behaviour) will be influenced with increasing complexity of mixed precursors.

It may be expected that SOA formed from the oxidation products of mixtures of parent hydrocarbons (biogenic or anthropogenic) will exhibit properties imparted from the individual components. For example, the carbon number and degree of oxygenation of the molecules in the mixed SOA particles will influence their mobility in the condensed phase and those of other condensing components including water.

Scientific objectives

The scientific objectives of the current project will be to characterise the fraction particles that exhibit behaviour indicative of existing in the solid phase as a function of relative humidity, produced in the oxidation of mixtures of parent VOCs under a range of conditions. The system will be chosen to include those that have been found to interact in the production of heavily oxygenated molecules (HOM) forming SOA in recent studies (isoprene and α-pinene photo-oxidation, [*McFiggans et al.*, 2019]) and also those that produce nitrogen-containing organic species (e.g. aromatic photo-oxidation in the presence of NO_x).

Reason for choosing the simulation chamber / calibration facility

The Manchester Aerosol Chamber (MAC) has been used to investigate the chemical and physical properties of SOA formed from a range of precursors [*Alfarra et al.*, 2012; *Frey et al.*, 2018] as well as real emissions [*Wyche et al.*, 2014]. With well-controlled experiment conditions and well-developed cleaning and operation procedures, MAC is therefore suitable for the investigation of systems with ranging complexity when associated with appropriate instrumentation.

Method and experimental set-up

The aerosol particles for the experiments were produced in MAC. The system is run as a batch reactor with an 18 m^3 (3m (H) * 3m (L)*2m (W)) FEP Teflon bag supported by three aluminium frames, in which the upper and the lower frame can move freely with the expansion or collapsing as sampling air is introduced or extracted of the chamber. The Teflon bag is enclosed in a housing with temperature and relative humidity controlled by the air conditioner. Two 6kW Xenc lamps and a series of halogen lamps (16 #/row*7) are mounted inside of the enclosure housing. The combination of halogens and Xenon arc lamps is chosen to be a good representative to mimic solar spectrum in the wavelength of 290-800 nm [*Alfarra et al.*, 2012]. The calculated photolysis rate of O^1D (jO^1D) in MAC was $3.6 * 10^{-5}$ s^{-1} (290-340 nm) [*Alfarra et al.*, 2012].

Some important inputs including seed particles, VOC precursors, NO_x, water vapor were injected into chamber before lights on. The ammonium sulfate (AS)/ammonium bisulfate (ABS) seed particles for

SOA condensation were nebulized and injected into the drum to mix before being flushed into chamber. VOC precursors (α-pinene, isoprene, o-cresol) can be injected into a heated glass bulb and transferred into the chamber with the flow of high purity nitrogen (ECD grade, 99.997%). Here, to investigate the formation of SOA in iso-reactivity VOC mixtures, the experiments will investigate single component, binary and ternary mixtures under low-NOx oxidation conditions (VOC/NO_x=8). NO_x (as NO_2 in this study) was introduced through a cylinder with the flow of high purity nitrogen (ECD grade, 99.997%). Therefore, experiments in MAC can be in well-controlled conditions including precursors species, concentrations, and initial RH, T. A series of state-of-art instruments for gas phase and particles phase measurements are equipped to monitor humidity, temperature, chemical composition in the gas and particle phase, number size distribution, particle hygroscopicity and CCN activity, phase state, volatility of the aerosol particles inside of chamber.

Data description

Size-resolved aerosol rebound fraction can be measured by three-arm particle rebound impactor apparatus with RH adjustment system. The schematic diagram of the three-arm impactor is shown in Fig 3-3, detailed description of instrumentation information can be found in *Liu et al.* [2017]. Here, a brief description is given. Generally, there are three single-stage impactors operated in parallel in the system combined with one CPC. The first impactor is not equipped with a plate (step 1 in Fig 3-3), that means particles can go through the first impactor directly, representing whole particle population (N1). The second impactor is equipped with a non-coated plate (step 2 in Fig 3-3), which provides a solid surface and allows particles rebounding from impactors. The particle population measured after the second impactor represents the sum of particles that don't strike the impactor and that strike but rebound from the impactor. The third impactor is equipped with a grease-coated plate (step 3 in Fig 3-3). The coated grease is quite sticky and all particles striking on the plate will be stuck. Therefore, the number population after grease-coated plate stands for particles that don't strike the impactor. Finally, the rebound fraction *BF* is defined in equation [1].

$$BF = \frac{N_2 - N_3}{N_1 - N_3} \qquad [1]$$

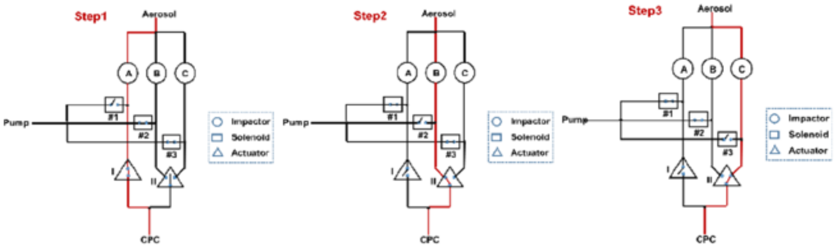

Fig 3-3 Schematic of the three-arm impactor, source from *Liu et al.* [2017]

Preliminary results and conclusions

Figure 2 shows the BF of SOA on seeded particles oxidized from different concentrations of α-pinene. The tendency of rebound behavior has no change with different VOC concentrations, in which the rebound becomes weaker at first and then comeback stronger. But the concentration of VOC precursor influences the rate of rebound behavior change. Higher VOC concentration expedites the BF going back to unit in the early stage.

Figure 3~5 shows the BF of SOA on AS/ABS seeded particles oxidized from single VOC precursors (α-pinene, isoprene, o-cresol). The BF results vary significantly with different VOC system. For α-pinene system, massive SOA was formed with the mass ratio of organic/inorganic (O/I) up to units digit, and the BF tendency is decreasing and then going up (Figure 3). For cresol system, the SOA formation is lower with O/I less than one unit, showing a similar BF trend as α-pinene. However, the rate of SOA formation is slower, and the change of rebound behavior is more distinct (Figure 4). For isoprene system, the SOA formation is quite low with O/I is only 0.13 after 6-hour photo-oxidation, and the BF goes down and hardly recovers (Figure 5).

The BF tendency of binary systems are presented in Figure 6~8. For the mixture of isoprene and α-pinene system, the BF behavior change seems to be dominated by α-pinene (Figure 6). For the mixture of cresol and α-pinene system, the BF behavior change shows the same as the mixture of isoprene and α-pinene, besides, the rate of change is faster than cresol alone (Figure 7). For the mixture of cresol and isoprene system, the BF change of AS seeds behavior seems like cresol system, going down and then returning slowly; but for ABS seeds, the BF becomes lower and could not return any more, which may be due to the different chemical behavior on neutral and acidic seed particles (Figure 8).

The phase state of seed particles can influence the SOA generation, and therefore reflects on the rebound behavior. As is shown in Figure 9, there is almost no SOA generating (O/I≈0.008) in the case of dry AS seeds for isoprene system, and the BF keeps in unit as initial. However, the situation is quite different for isoprene and α-pinene binary system on AS seed. The BF of both the dry and deliquesced AS seeds system behave similar to α-pinene system, and the O/I is up to 10 of dry seeds system (Figure 10), which is several times higher than that in the case of deliquesced seeds system, the higher percentage of ammonium is also observed at the same time. We infer that the chemical behavior of the two system is different, which result in the abnormal consequence.

In preliminary conclusion, at the beginning of the photochemistry, the rebound ability of SOA becomes weaker due to the sticky SOA layer on the surface of particles. As the reaction goes on, if the SOA formation is sufficient, the particle tends to be internal mixed with lower hygroscopicity and liquid water content, which lead to the particles act as more solid-like and 'tighter'. In addition, the phase state of seed particles can influence SOA formation, and solid seed particles may not constrain SOA formation.

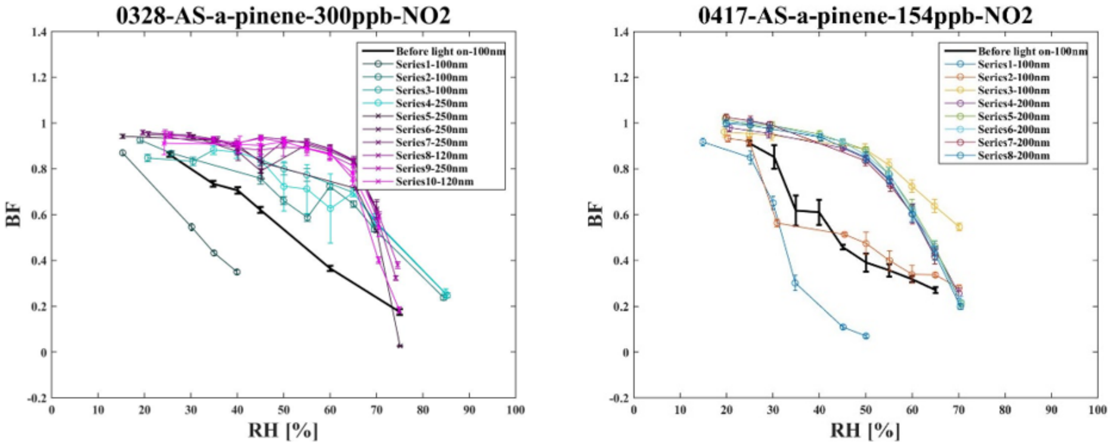

Figure 2. The comparison of BF in α-pinene system with different VOC concentration.

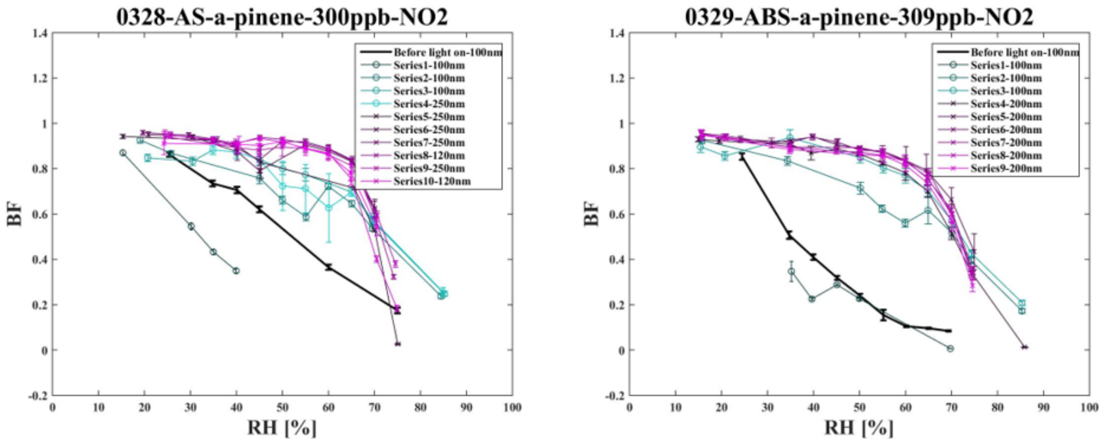

Figure 3. The BF of α-pinene system.

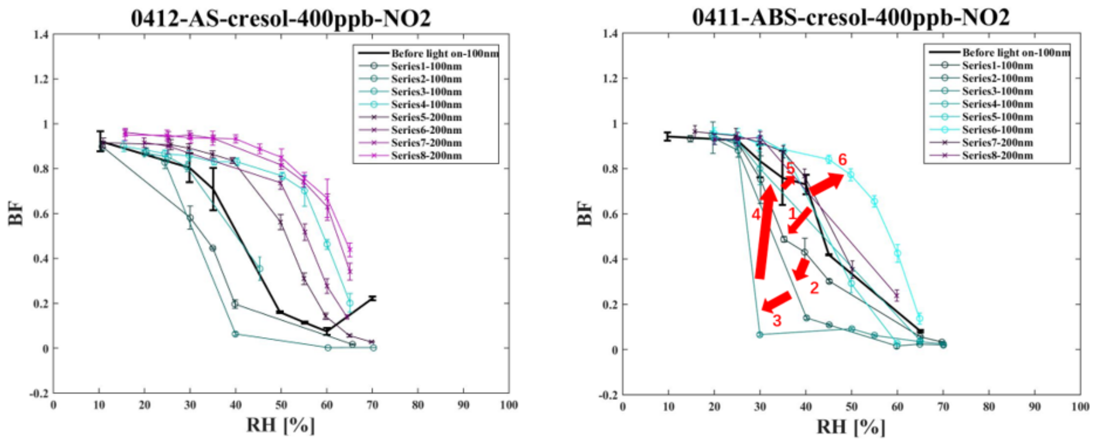

Figure 4. The BF of cresol system.

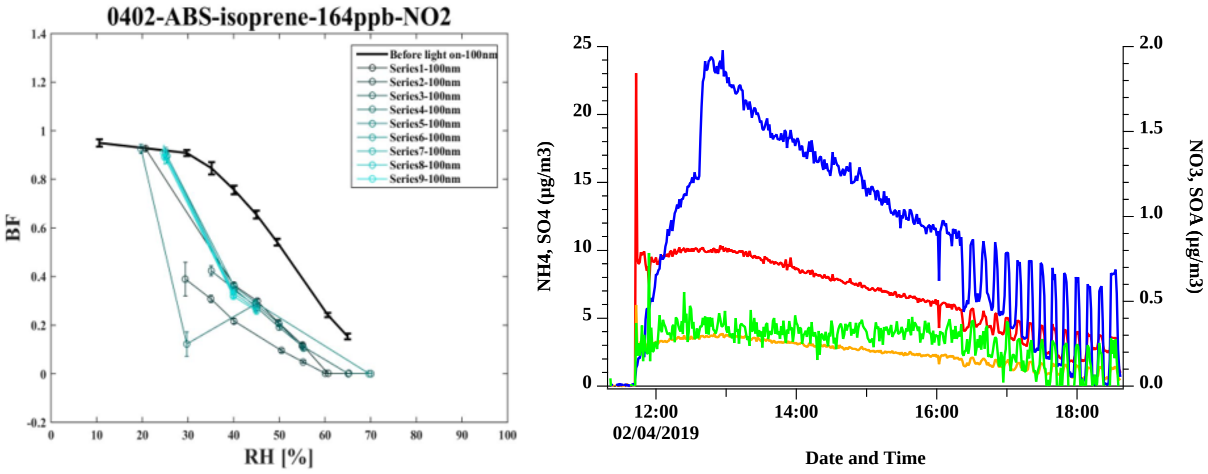

Figure 5. The BF and mass concentration of isoprene system on ABS seed.

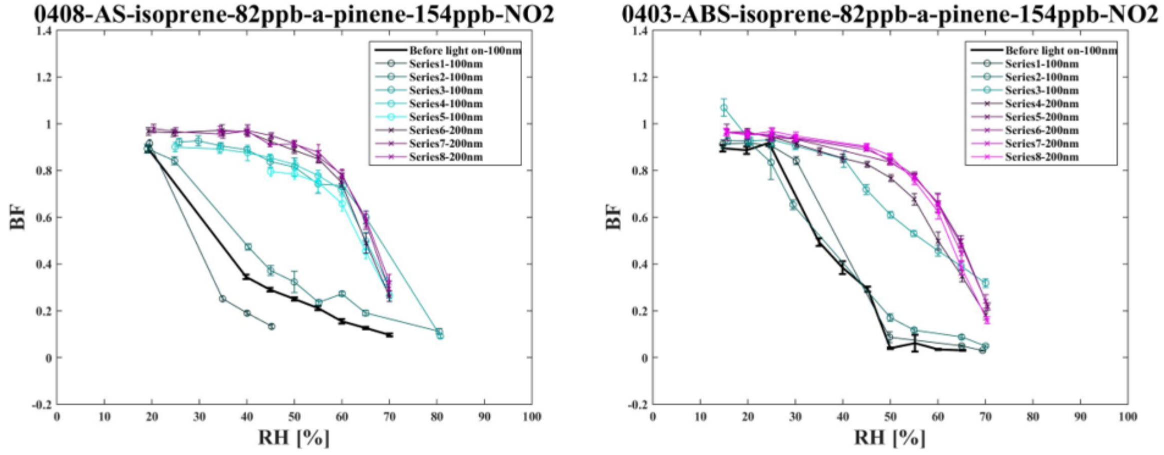

Figure 6. The BF of isoprene and α-pinene system.

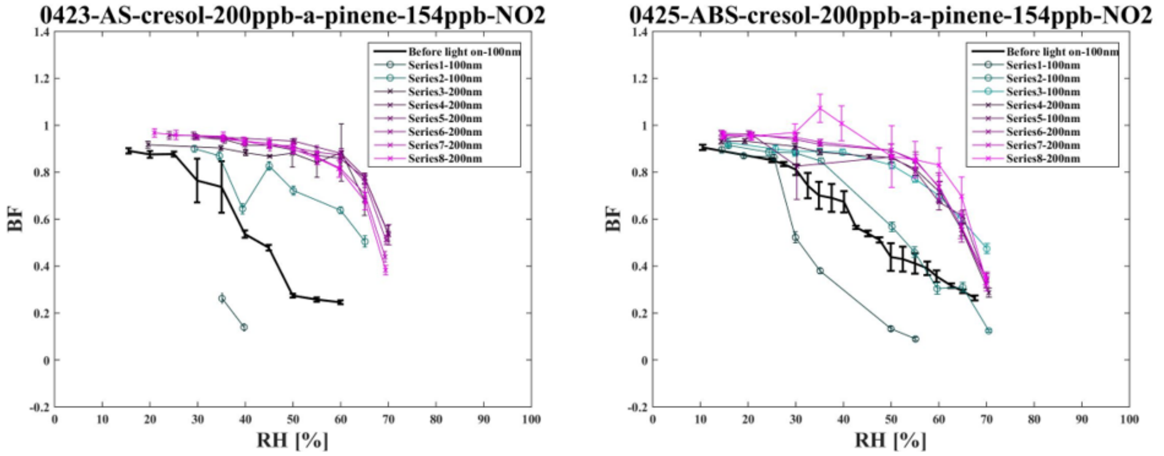

Figure 7. The BF of cresol and α-pinene system.

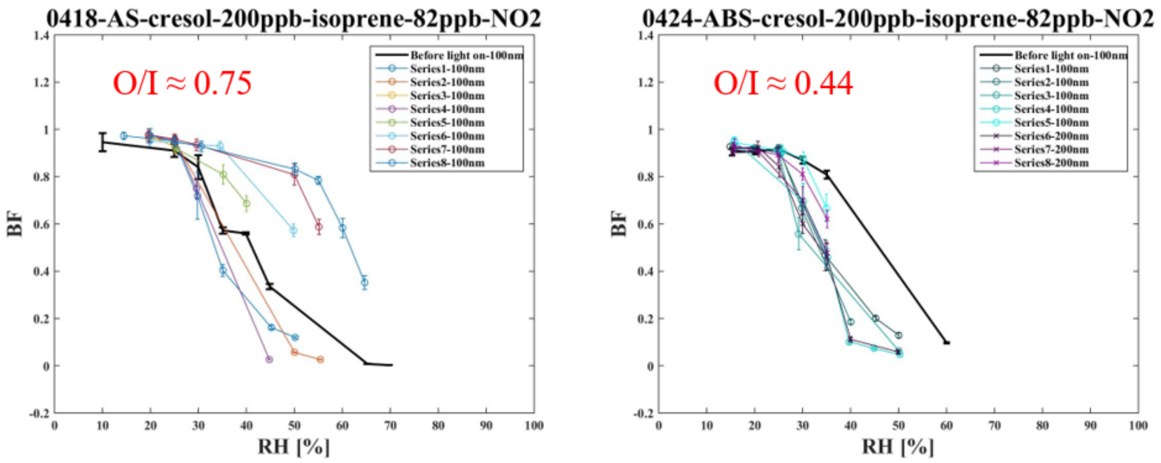

Figure 8. The BF of cresol and isoprene system.

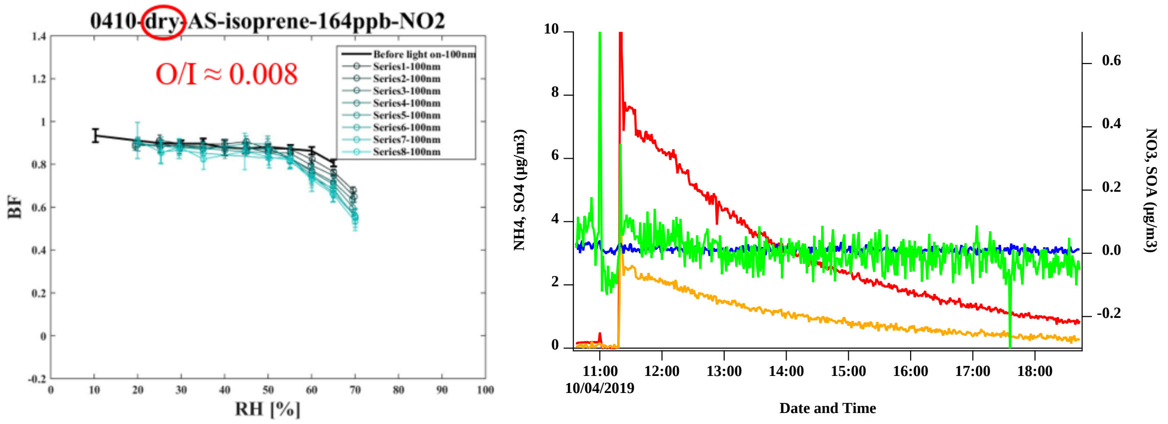

Figure 9. The BF and mass concentration of isoprene system on dry AS seed.

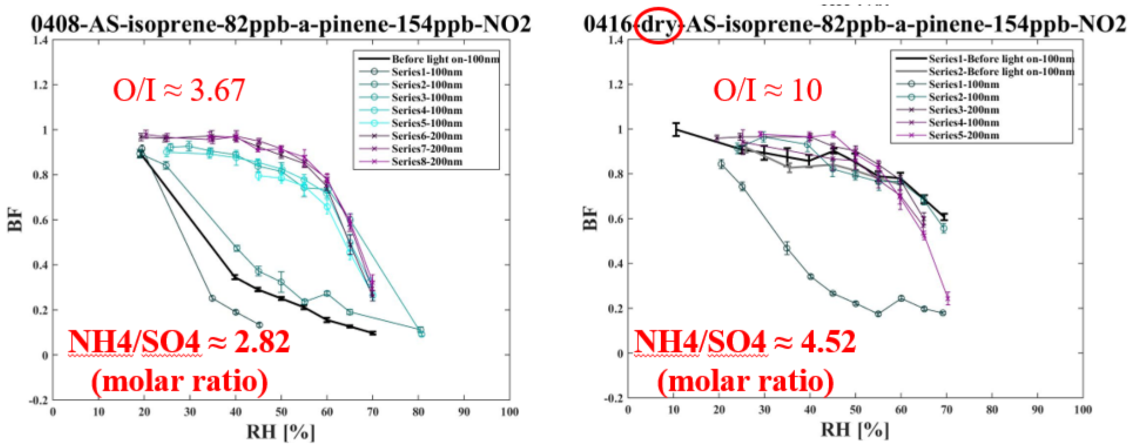

Figure 10. The BF of isoprene and α-pinene oxidation system on dry AS seed.

Outcome and future studies

Fruitful preliminary results have been collected on characterization of phase state behaviour of SOA formation on seeded particles from single and binary mixtures of biogenic (α-pinene, isoprene) and anthropogenic (o-creasol) VOCs photo-oxidation. In the future, further deep analysis combined available chemical composition, hygroscopicity, cloud condensation nuclei activity and gas-particle partitioning will be conducted. We could also try to compare with field data filtered by the same organic to inorganic ratios in environments dominated by either biogenically- or anthropogenically-derived SOA.

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