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Formation of secondary organic aerosols from the ozonolysis of dihydrofurans

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Water vapour concentration for experiments with dried air samples.

A series of experiments was conducted to estimate the water concentration under "dry conditions". We have used a degassed sample of solid sulfur trioxide (>99%, stabilized, Aldrich) contained in a glass flask to obtain different SO_3 concentrations in the reactor (as it was done in previous studies (Jayne, 1997). Freshly dried synthetic air from a liquid nitrogen trap was mixed with SO_3 in the teflon reactor and the mixture was continuously monitored by the CPC for 40 minutes. Fig. S1 shows the results for experiments with SO_3 concentration in the range 1 to 12ppb. No particles could be observed for experiments with low initial SO_3 concentrations. On the other hand, NPF (new particle formation) was observed for the experiments with SO_3 in the range 6 to 12 ppb. Under these experimental conditions, nucleation is attributed to the formation of H_2SO_4 from the reaction of SO_3 and the residual H_2O.

The overall gas-phase reaction $H_2O + SO_3 \rightarrow H_2SO_4$ exhibits a second-order dependence on water vapor concentration, the first-order rate coefficient for the SO_3 loss being $k= 3.90x10^{-41}exp(6830.6/T)[H_2O]^2$ (Jayne, 1997)

Taking into account that the approximate H_2SO_4 gas phase concentration able to nucleate is around $5x10^6$molecule cm^{-3} (Metzger, 2010), the concentration of water in the reactor may be obtained by simulating the SO_3 and H_2SO_4 profiles for different guessed H_2O profiles. Thus for example, since no NPF was observed for the experiment with 2ppb of SO_3, the expected water concentration must be below 15ppb. On the other hand from the experiment with 6ppb of SO_3, a 20 ppb water concentration is required to reproduce the observed nucleation time. From all the experiments carried out, we estimate that the residual water concentration in the reactor is 20±10ppb. To check for permeation through the reactor wall, some experiments have been also carried out with dry air after 1 hour in the reactor. The results were similar to those carried out with freshly dried air.

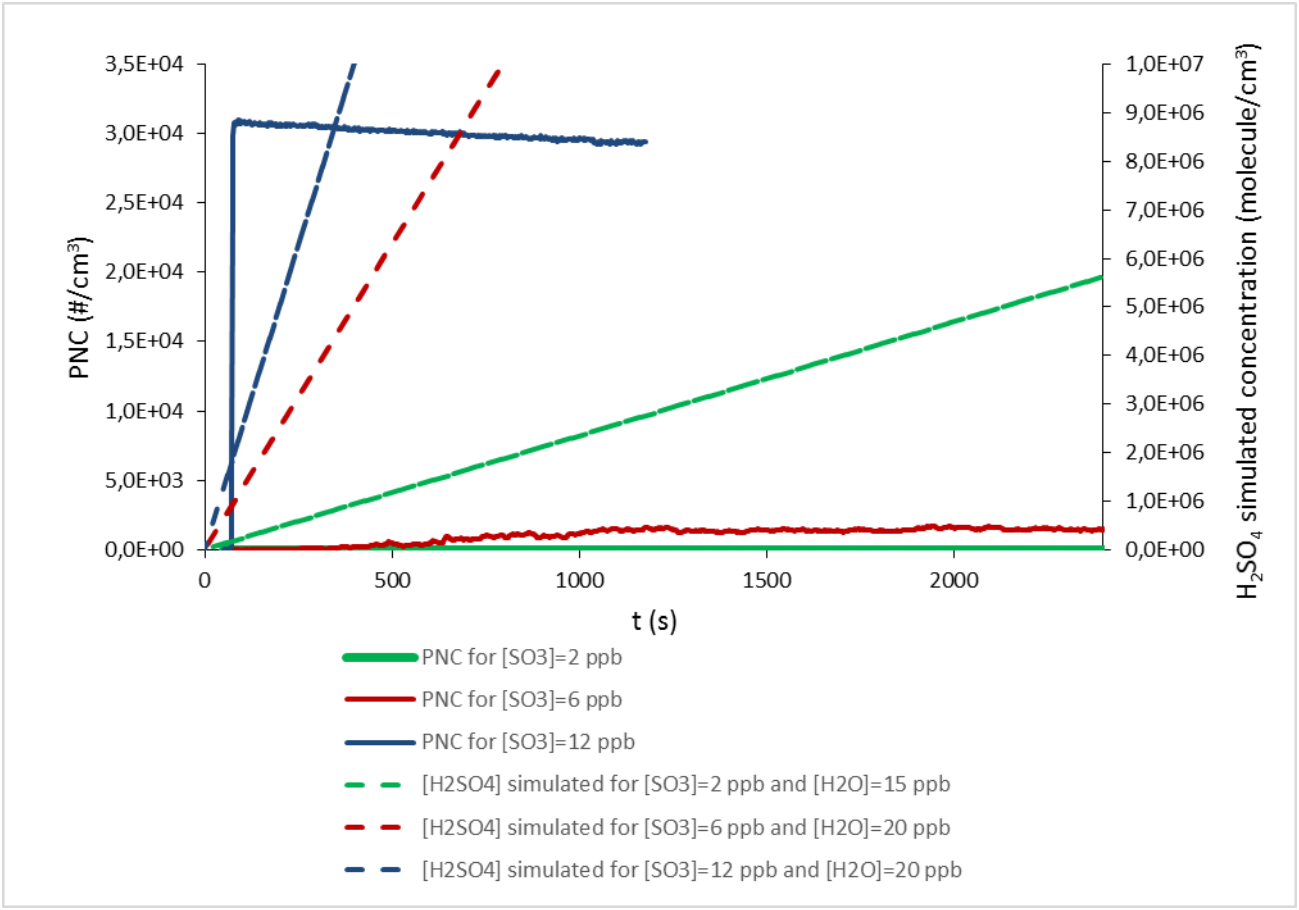

Figure S1. Particle number concentration for different the reaction of SO_3 with residual H_2O and simulated profiles of H_2SO_4 for given SO_3 and H_2O concentrations.

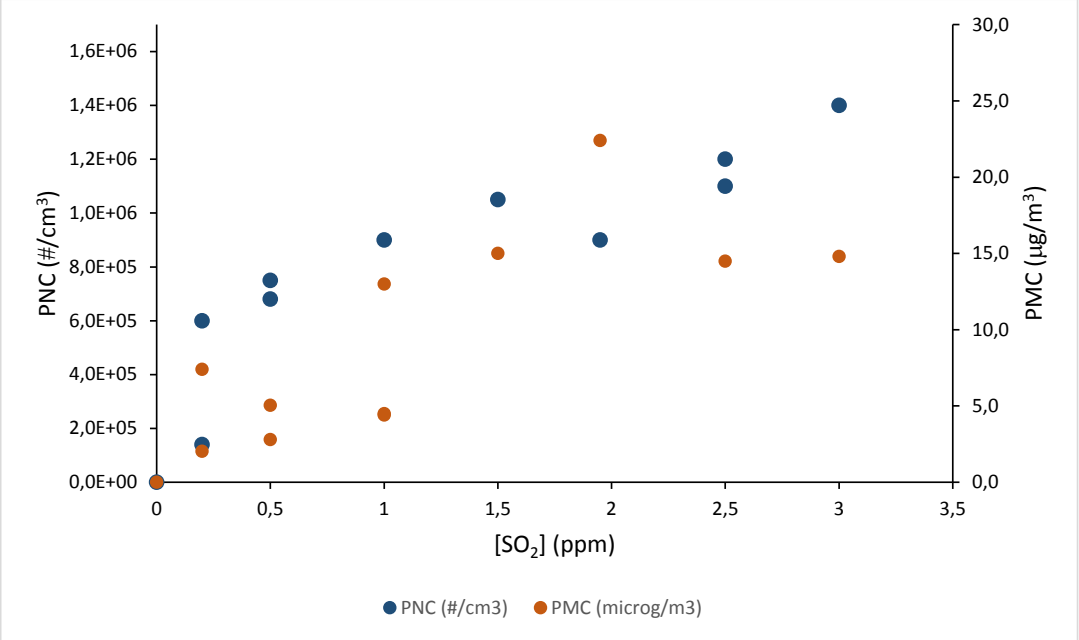

Figure S2. Maximum particle number concentration and maximum mass concentration in experiments with different SO_2 initial concentrations. For this series of experiments, the initial concentrations of 2,5-DHF and ozone were 0.5 and 1.0 ppm respectively. Relative humidity=0.

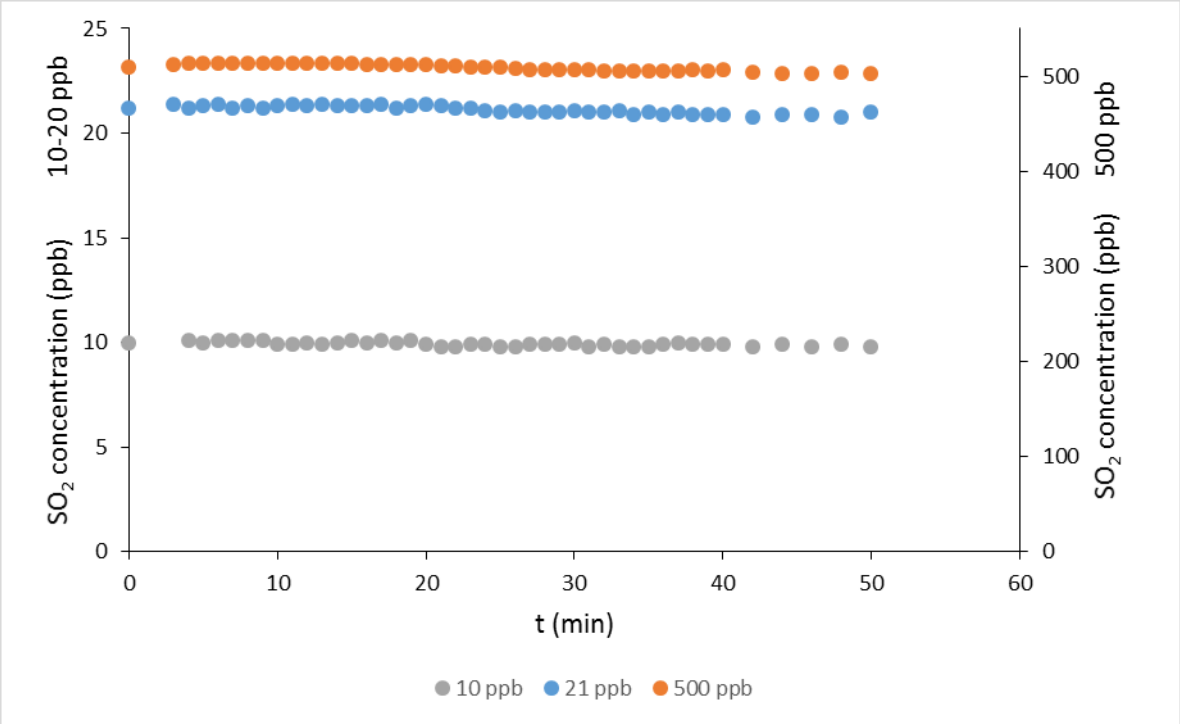

Figure S3. SO_2 profiles during ozonolysis reactions of 2,5-DHF and ozone (0.5 and 1.0 initial concentrations, respectively) starting from different SO_2concentrations. Similar results were obtained for 2,3-DHF.

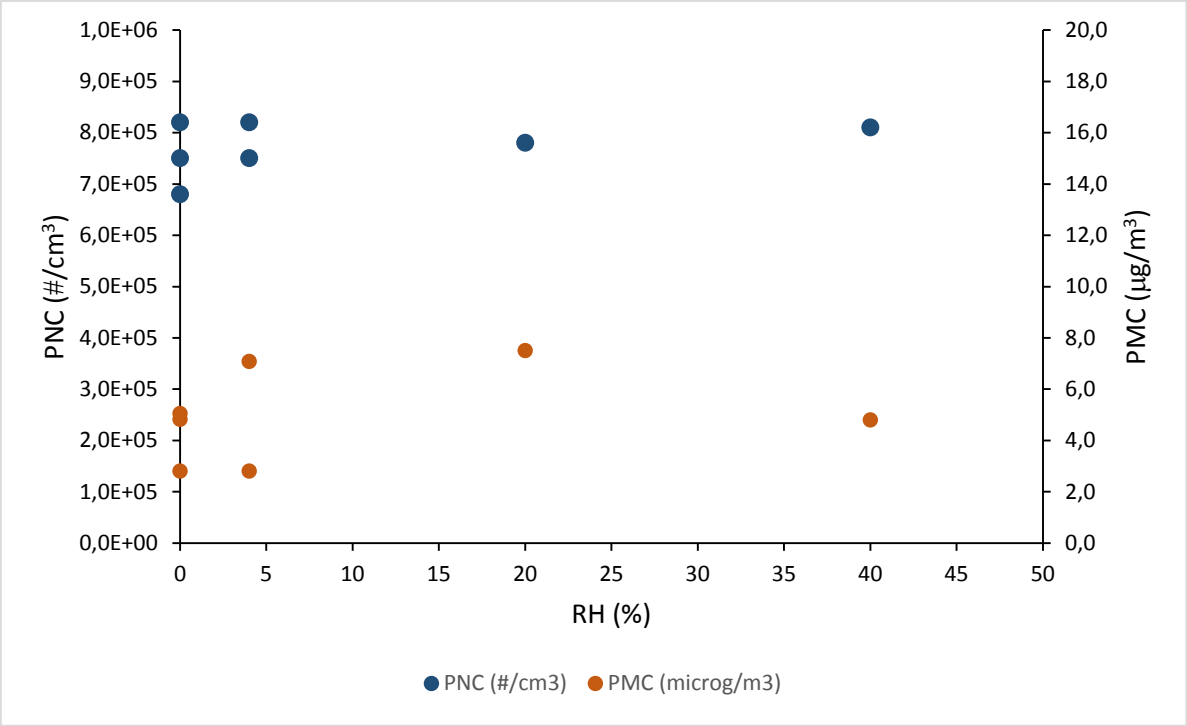

Figure S4. Maximum particle number concentration and maximum mass concentration in experiments carried out under different RH. For this series of experiments, the initial concentrations of 2,5-DHF, ozone and SO_2 were 0.5, 1.0 and 0.5 ppm respectively.

Effect of ozone and 2,5-DHF initial concentrations.

Several experiments were also carried out to find the effect of concentrations of ozone and 2,5-DHF on the production of SOA. Keeping fixed concentrations of SO_2 and 2,5-DHF, the increase of ozone led to increase of the particles number concentration and mass concentration, as it is shown in figure S5.

Likewise, keeping constant the SO_2 and ozone initial concentrations, an increase of 2,5-DHF lead to the increase of both PNC and PMC, figure S6. Both ozone and 2,5-DHF dependences suggest that their primary reaction is closely coupled to the production of particles. The acceleration of the reaction of ozone with 2,5-DHF enhances the formation of particles. In this sense, the SOA yield, defined as the ratio between the total mass concentration and the total concentration of reacted 2,5-DHF, for any experiment was linear for most of the reaction time, Figure S7.

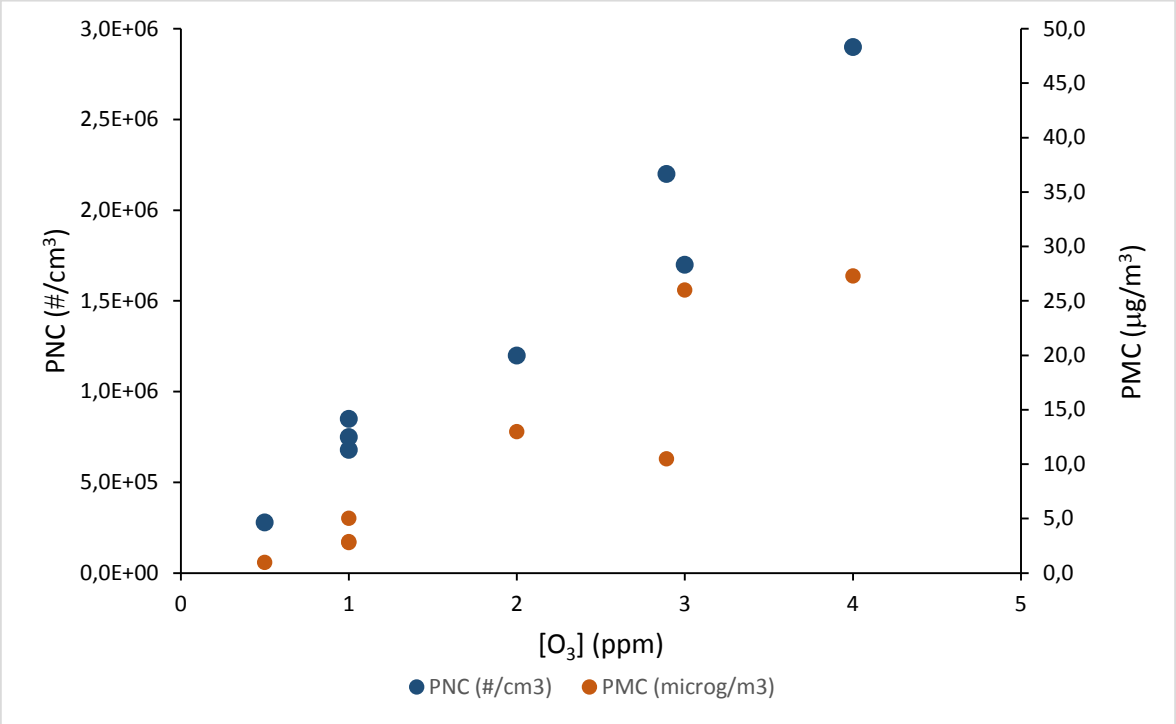

Figure S5. Maximum particle number concentration and maximum mass concentration in experiments carried out under different ozone concentrations. For this series of experiments, the initial concentrations of 2,5-DHF and SO_2 were 0.5 ppm and RH = 0.

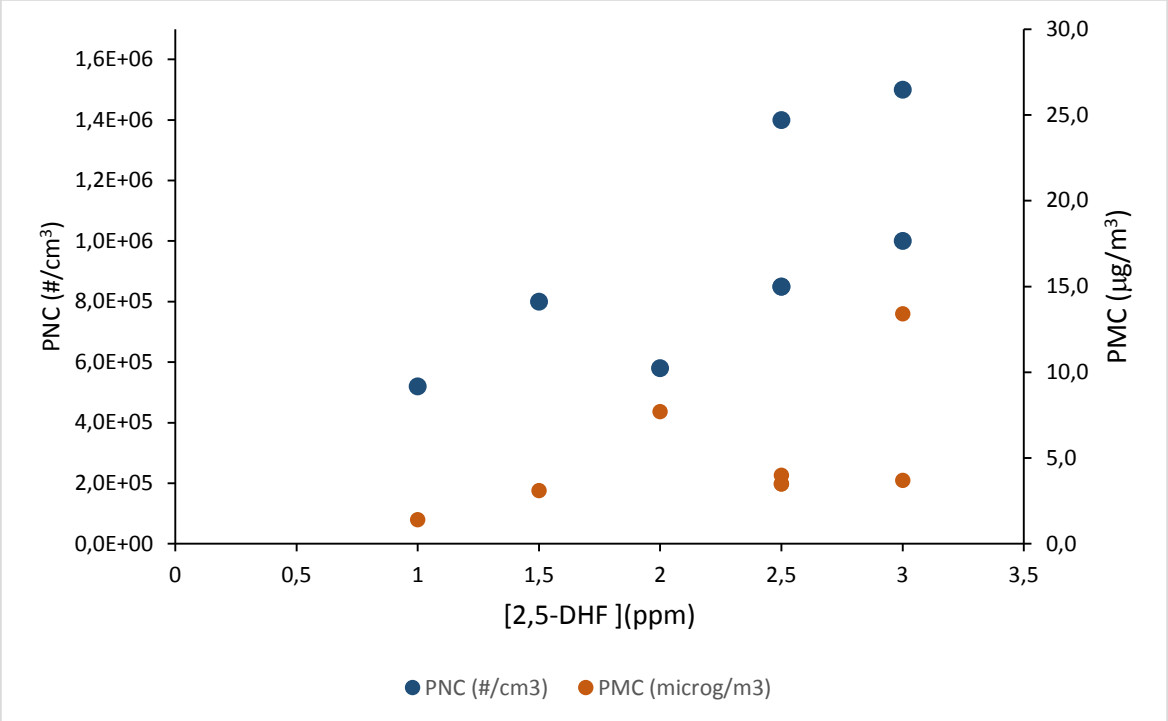

Figure S6. Maximum particle number concentration and maximum mass concentration in experiments carried out under different 2,5-DHF concentrations. For this series of experiments, the initial concentrations of ozone and SO_2 were 0.5 ppm. RH = 0.

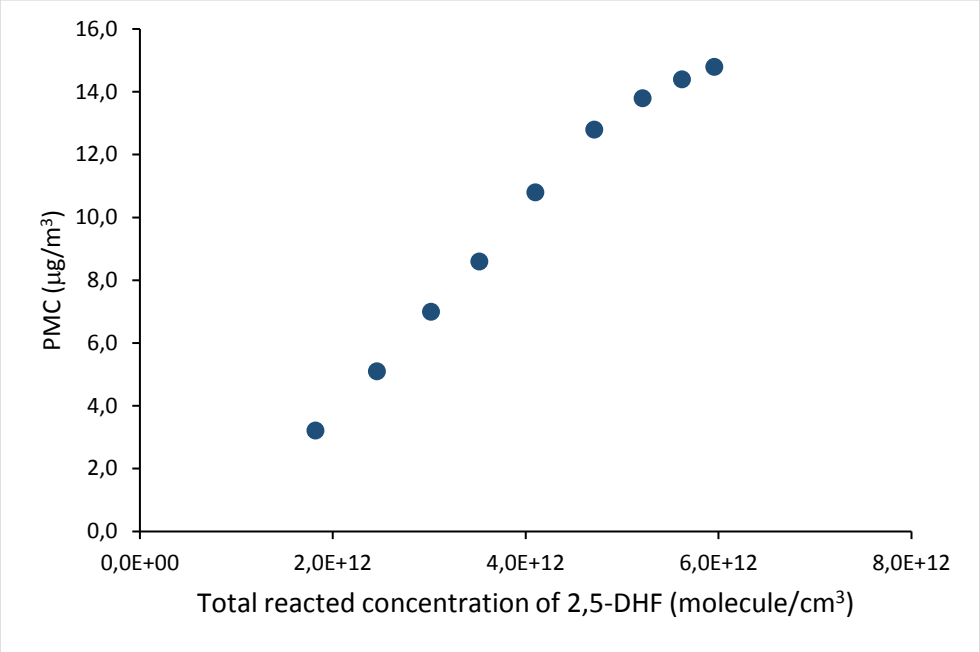

Figure S7. Particle mass concentration formed during a typical experiment against the total concentration of reacted 2,5-DHF.

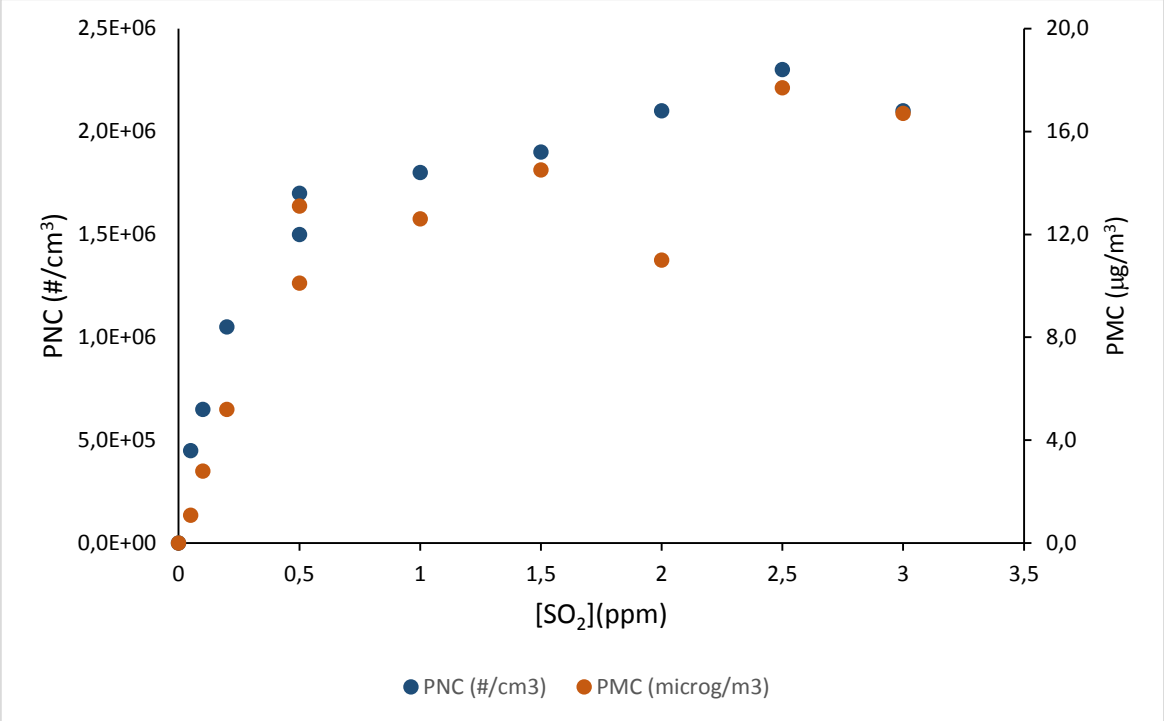

Figure S8. Maximum particle number concentration and maximum mass concentration in experiments with different SO_2 initial concentrations. For this series of experiments, the initial concentrations of 2,3-DHF and ozone were 0.5 and 1.0 ppm respectively. Relative humidity=0.

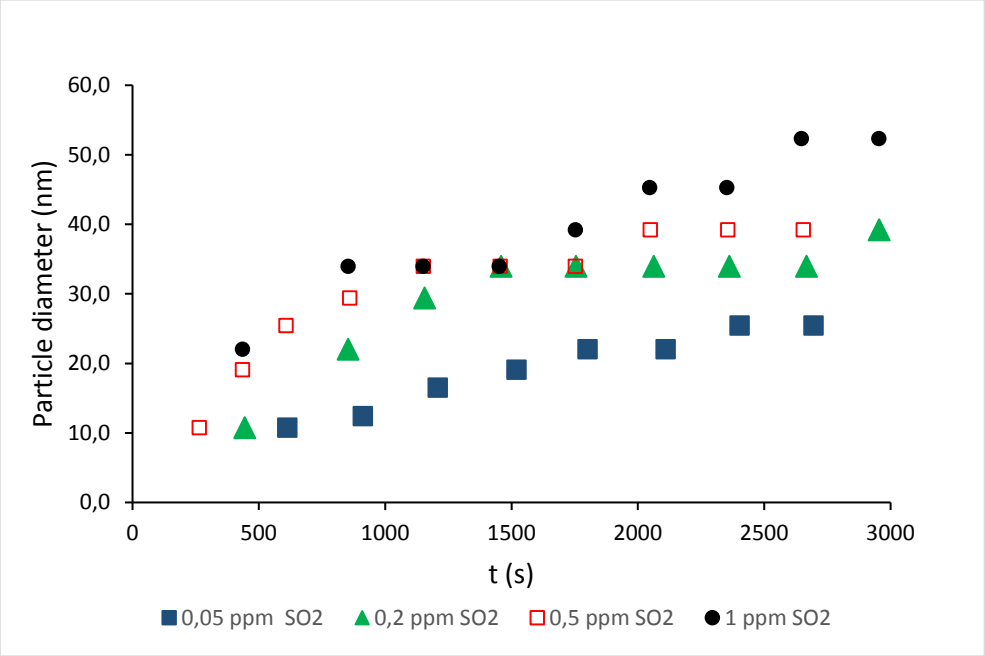

Figure S9. Average particles' diameters growth for some experiments with 0.5 ppm of 2,3-DHF and 1 ppm of ozone initial concentrations under dry conditions and variable SO_2.

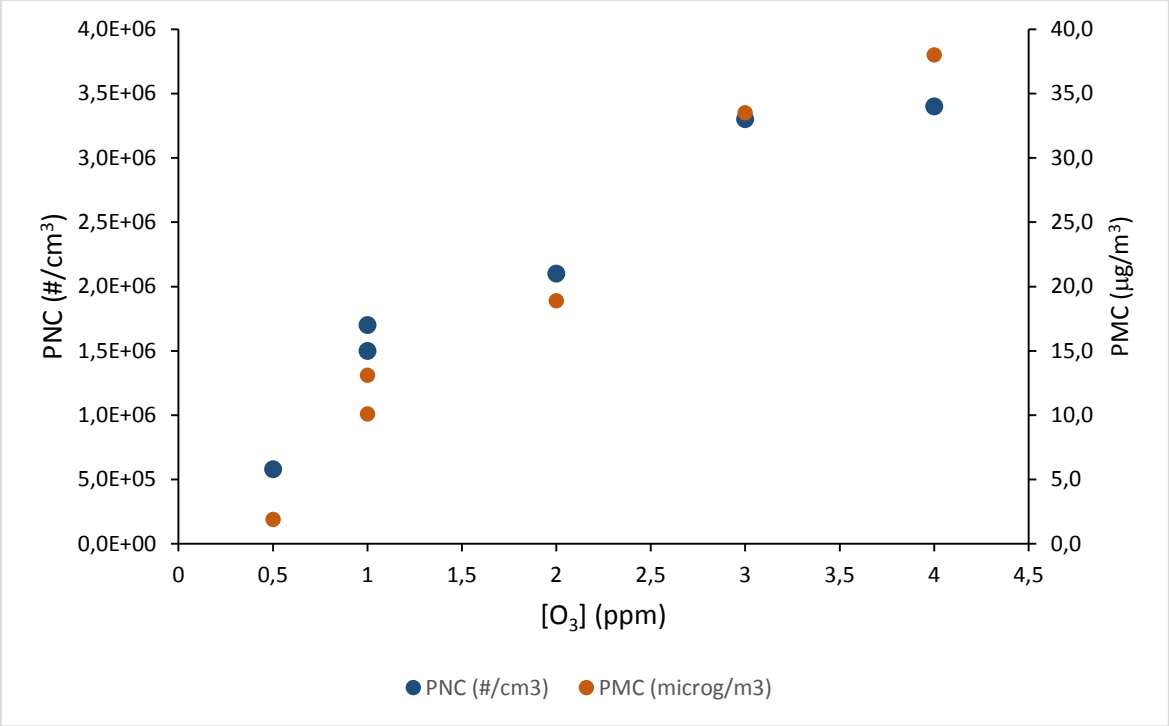

Figure S10. Maximum particle number concentration and maximum particle mass concentration in experiments carried out under different ozone concentrations and dry conditions. For this series of experiments, the initial concentrations of 2,3-DHF and and SO_2 were 0.5ppm.

Table ST1. Effect of water vapour on the SOA production for the ozonolysis of 2,3-DHF. Initial concentrations of reactants and SOA data. PNC, PMC and diameter reported values are the maximum data registered for each magnitude during the experiment.

2,3-DHF (ppm)	O_3 (ppm)	SO_2 (ppm)	HR (%)	PNC (#/cm^3)	PMC (μg/m^3)	Diameter (nm)
0.5	1	0	20	3.9	0	0
0.5	1	0	50	38	0	0
0.5	1	0	5	6.7	0	0
0.5	1	0	50	13	0	0
0.5	1	0.5	0	$1.70x10^6$	10.1	40
0.5	1	0.5	0	$1.50x10^6$	13.1	50
0.5	1	0.5	15	$1.25x10^6$	9.1	50
0.5	1	0.5	15	$1.20x10^6$	8.4	40
0.5	1	0.5	29.2	$8.50x10^5$	4.8	35
0.5	1	0.5	31.3	$6,00x10^5$	4.0	35
0.5	1	0.5	50	$6,50x10^5$	3.1	35
0.5	1	0.5	50.8	$6,50x10^5$	3	35

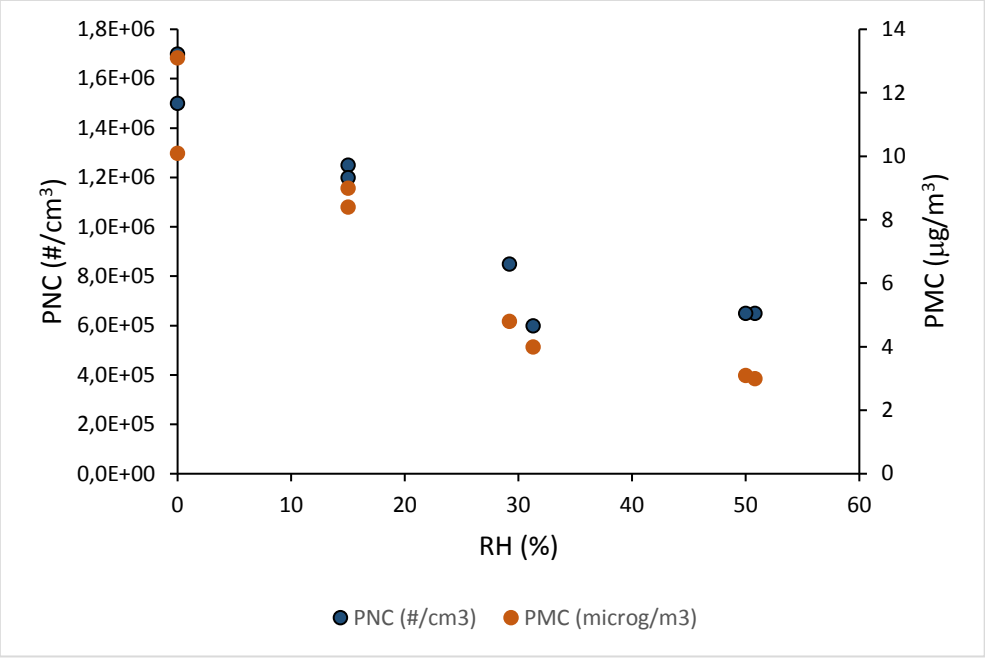

Figure S11. Effect of water vapour. Maximum particle number concentration and maximum particle mass concentration in experiments carried out under different RH. For this series of experiments, the initial concentrations of 2,3-DHF, ozone and SO_2 were 0.5, 1.0 and 0.5ppm, respectively.

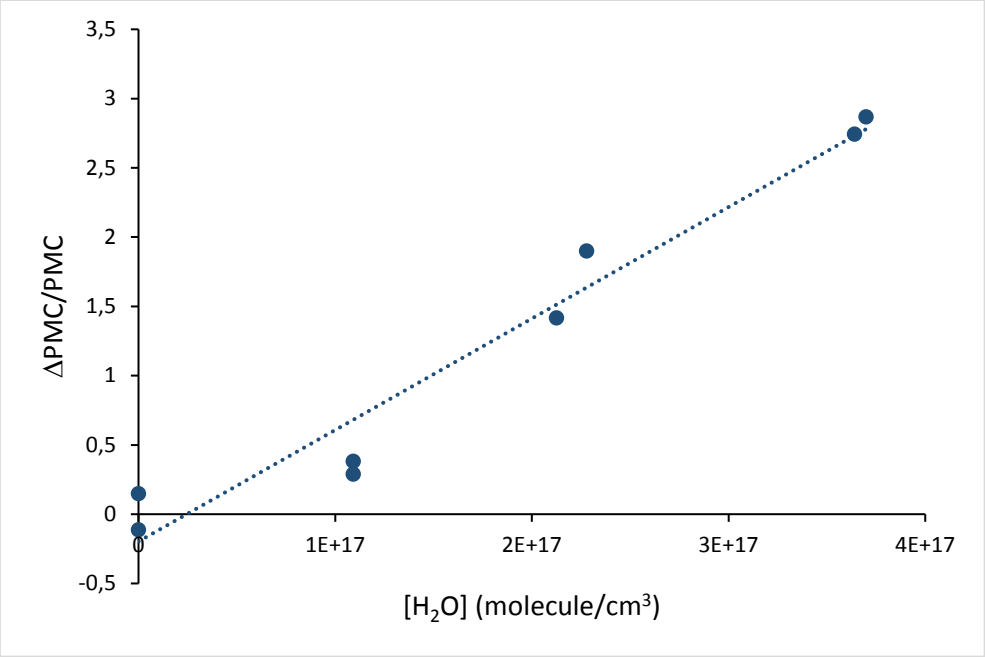

Figure S12. Decrease of the particle mass concentration with respect to the reference (dry) conditions over the actual PMC value for different water concentration. The SO_2 concentration for this series of experiments was $1{,}2\times^{13}$molecule cm^{-3}.

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