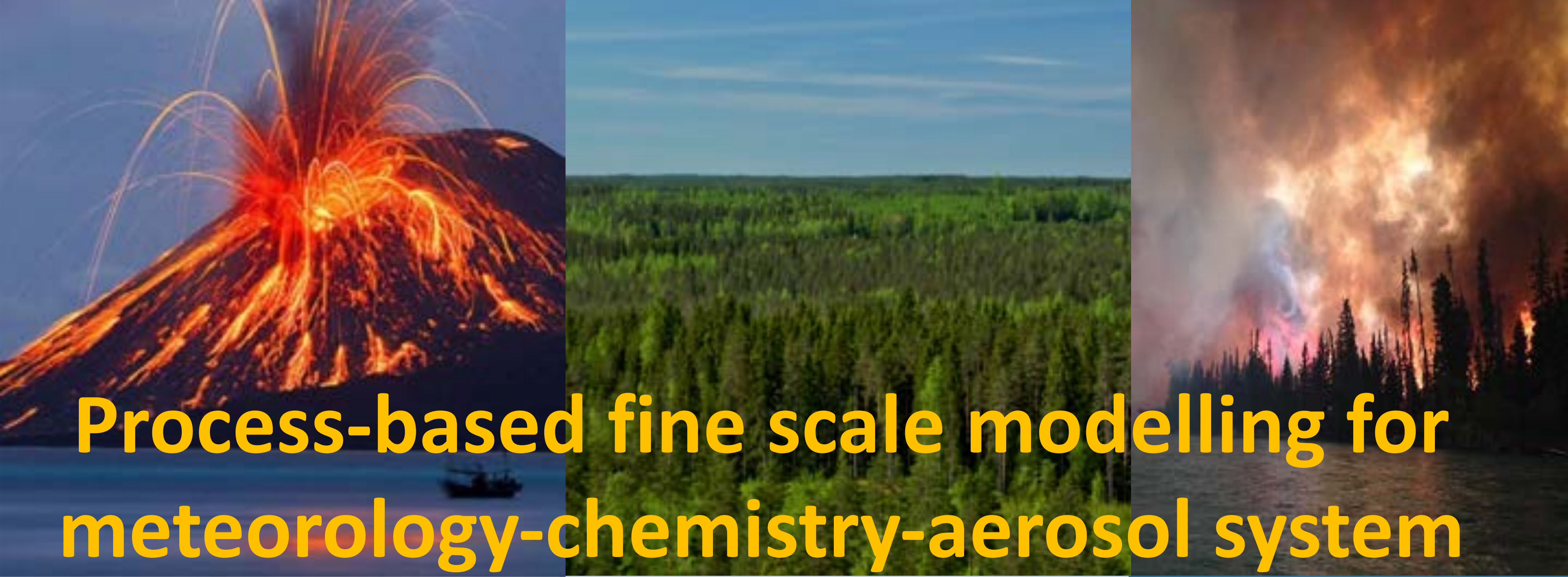
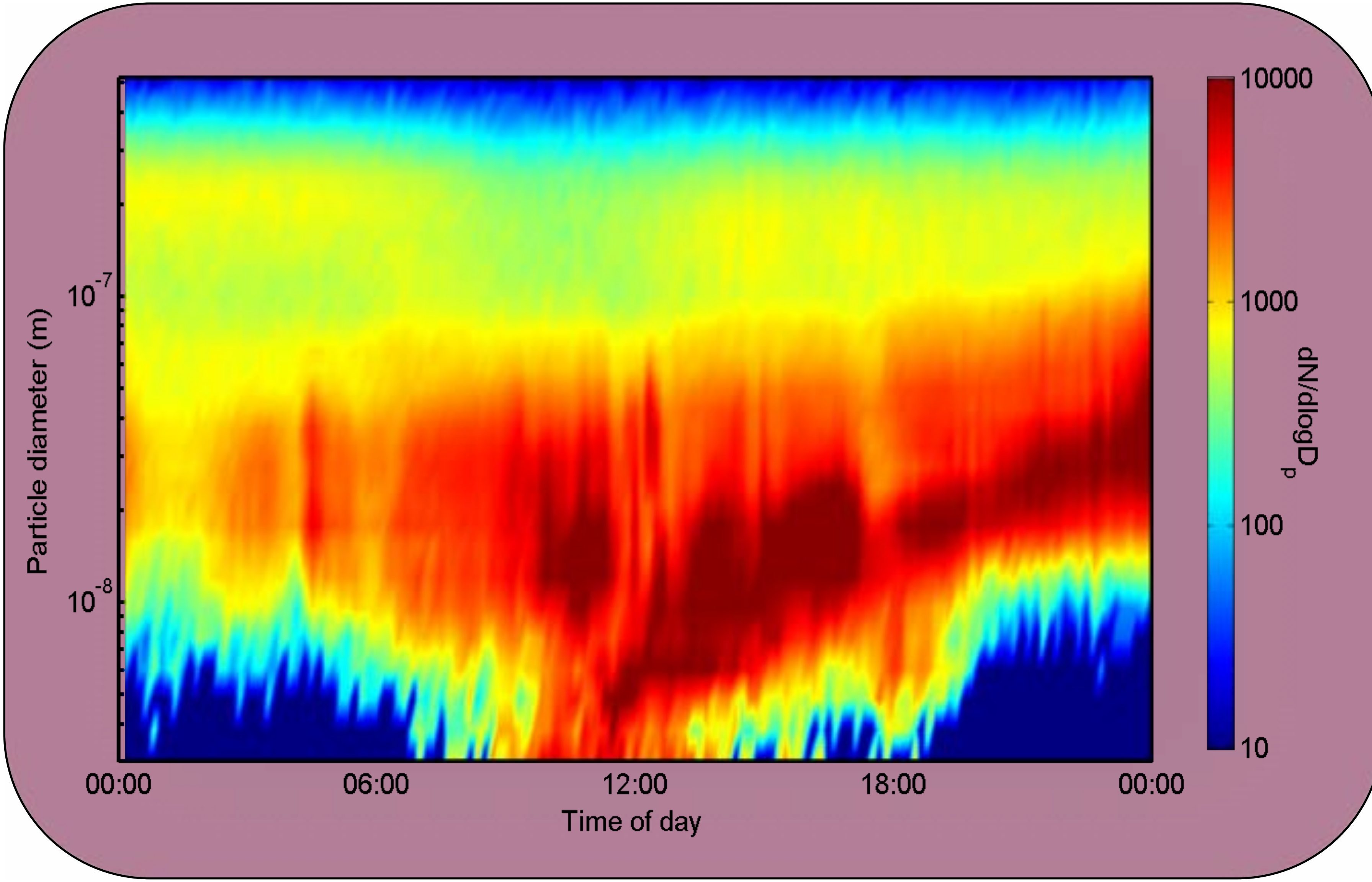
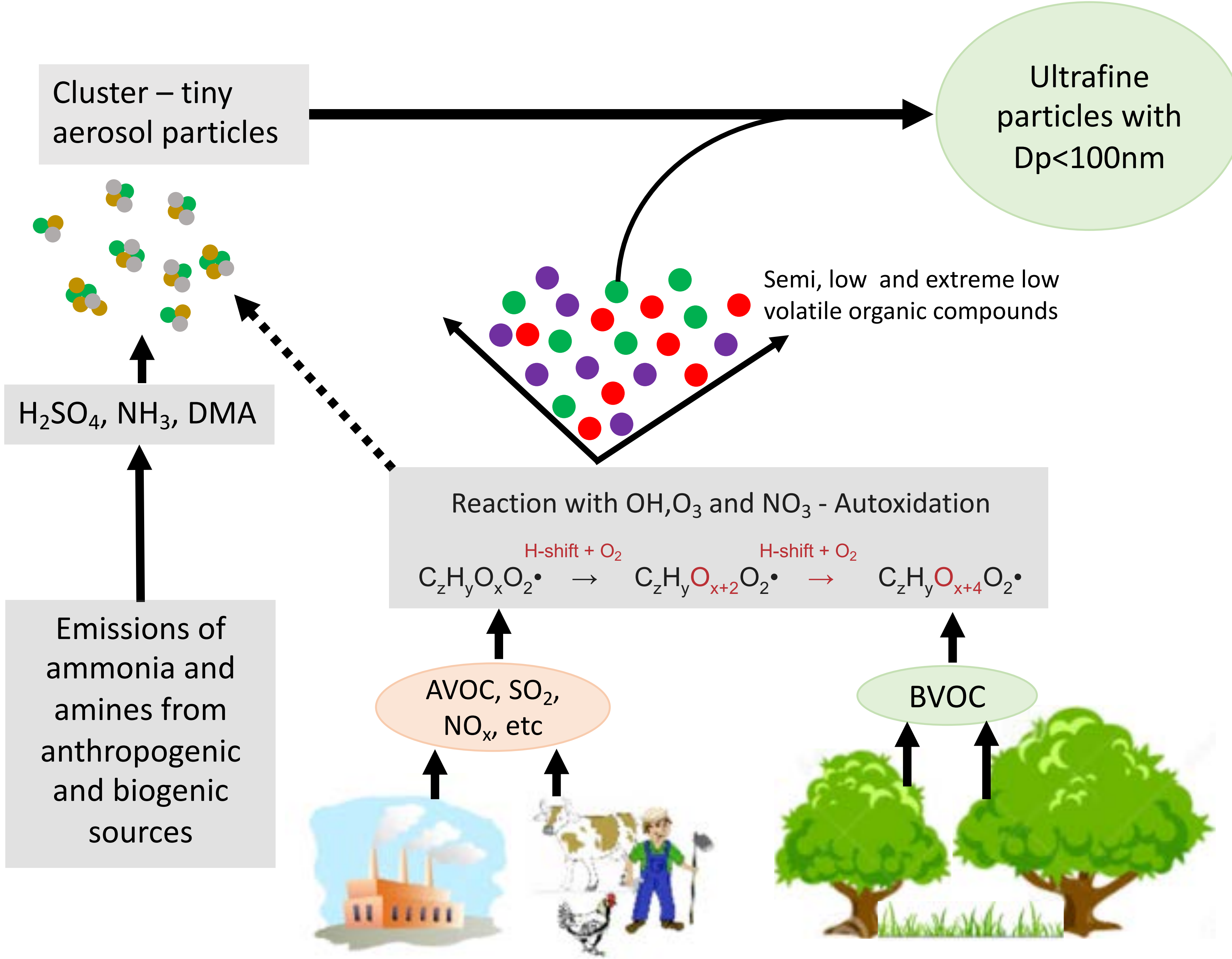
Process-based fine scale modelling for meteorology-chemistry-aerosol system



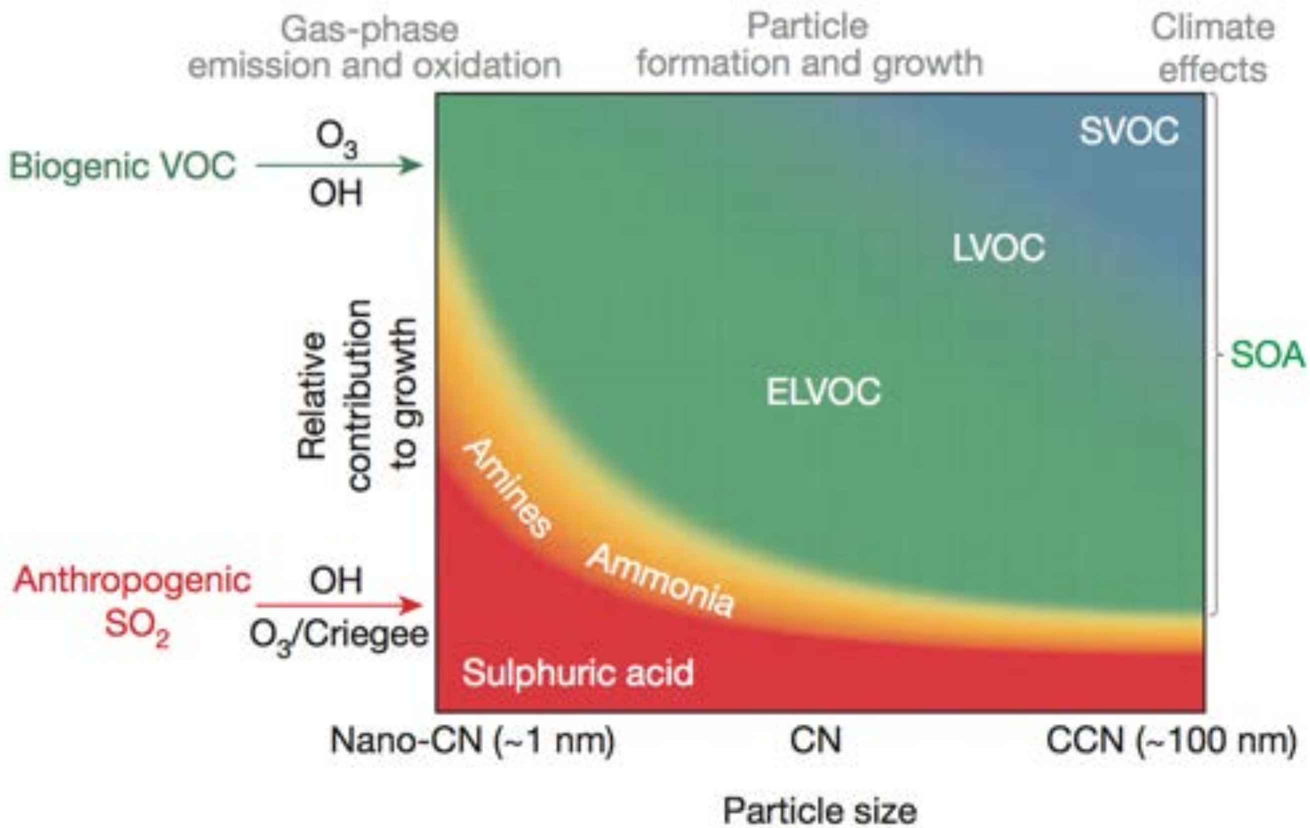


10⁻⁷
10⁻⁸
Particle diameter (m)
00:00
06:00
12:00
18:00
00:00
Time of day
10000
1000
100
10
dN/dlogD_p


Cluster – tiny aerosol particles
Ultrafine particles with Dp<100nm
Semi, low and extreme low volatile organic compounds
H_2SO_4, NH_3, DMA
Reaction with OH,O_3 and NO_3 - Autoxidation
H-shift + O_2
H-shift + O_2
$C_zH_yO_xO_2$• → $C_zH_yO_{x+2}O_2$• → $C_zH_yO_{x+4}O_2$•
Emissions of ammonia and amines from anthropogenic and biogenic sources
AVOC, SO_2, NO_x, etc
BVOC

ELVOC

(Extreme-Low Volatile Organic Compounds)



A large source of low-volatility secondary organic aerosol (Ehn et al., Nature, 2014)

Formation of highly oxidized multifunctional (HOM; O:C≥0.7) organic compounds by autoxidation of monoterpenes (MT)

$MT\ (C_{10}H_{16}) + O_3 \nrightarrow \gamma C_{10}H_{15}O_2\text{-}OO\cdot$ (γ = 9 % for α-pinene)

$C_{10}H_{15}O_2\text{-}OO\cdot \xrightarrow{\text{H-shift+}O_2} C_{10}H_{15}O_4\text{-}OO\cdot$ (1^{st} H-shift + O_2)

$C_{10}H_{15}O_4\text{-}OO\cdot \xrightarrow{\text{H-shift+}O_2} C_{10}H_{15}O_6\text{-}OO\cdot$ (2^{nd} H-shift + O_2)

$C_{10}H_{15}O_6\text{-}OO\cdot \xrightarrow{\text{H-shift+}O_2} C_{10}H_{15}O_8\text{-}OO\cdot$ (3^{rd} H-shift + O_2)

$C_{10}H_{15}O_8\text{-}OO\cdot \xrightarrow{\text{H-shift+}O_2} C_{10}H_{15}O_{10}\text{-}OO\cdot$ (4^{th} H-shift + O_2)

Reactions terminating the autoxidation, leading to formation of stable HOMs:

$C_{10}H_{15}O_x\text{-}OO\cdot + HO_2 \rightarrow C_{10}H_{15}O_x\text{-}OH$

$C_{10}H_{15}O_x\text{-}OO\cdot + RO_2 \nrightarrow \alpha\cdot C_{10}H_{15}O_x\text{-}OH + \beta\cdot C_{10}H_{14}O_x{=}O + \gamma\cdot C_{10}H_{15}O_x\text{-}O\cdot + (1\text{-}\alpha\text{-}\beta\text{-}\gamma)\cdot C_{20}H_{30}O_{x+4}$

$C_{10}H_{15}O_x\text{-}OO\cdot + NO \rightarrow \alpha\cdot C_{10}H_{15}O_x\text{-}ONO_2 + \beta\cdot C_{10}H_{14}O_x{=}O + \gamma\cdot C_{10}H_{15}O_xO\cdot + (1\text{-}\alpha)\cdot NO_2$

$C_{10}H_{15}O_xOO\cdot \rightarrow C_{10}H_{15}O_xOH$

We have developed a HOM mechanism that comprise 1773 reactions and 208 new compounds.

The mechanism has been coupled to the Master Chemical Mechanism v 3.3

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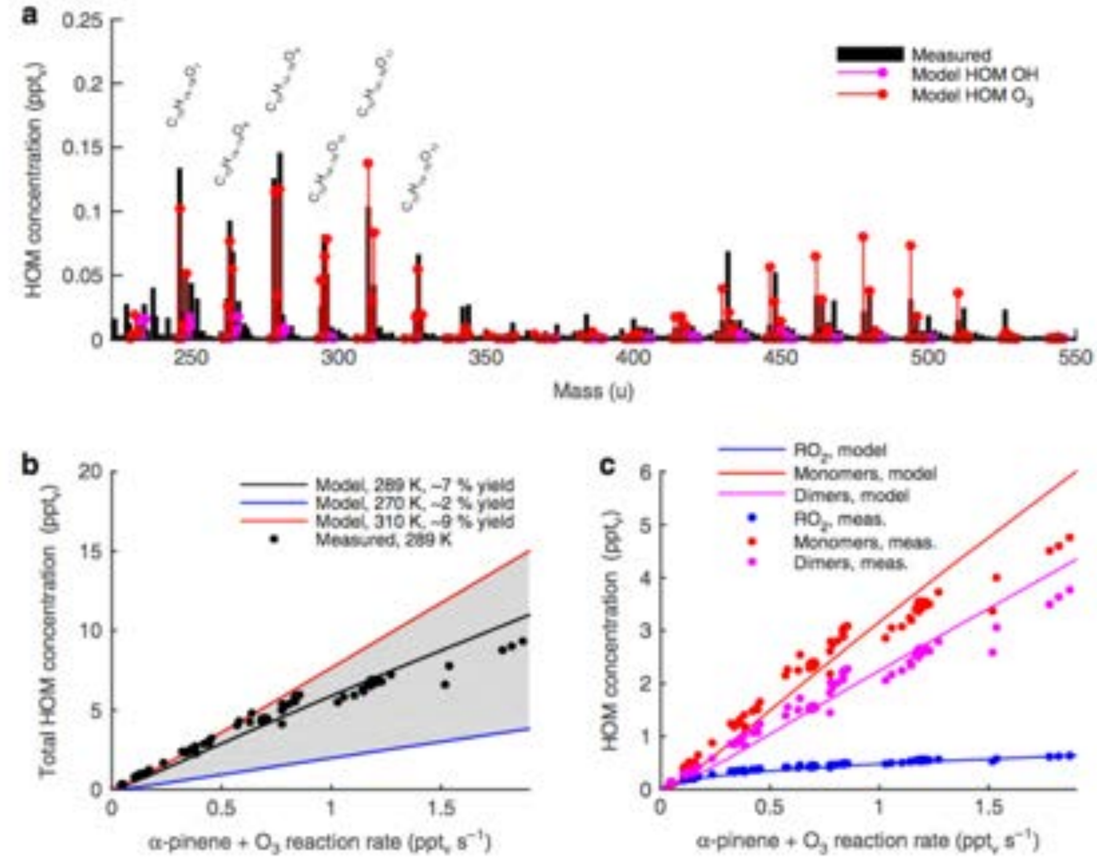
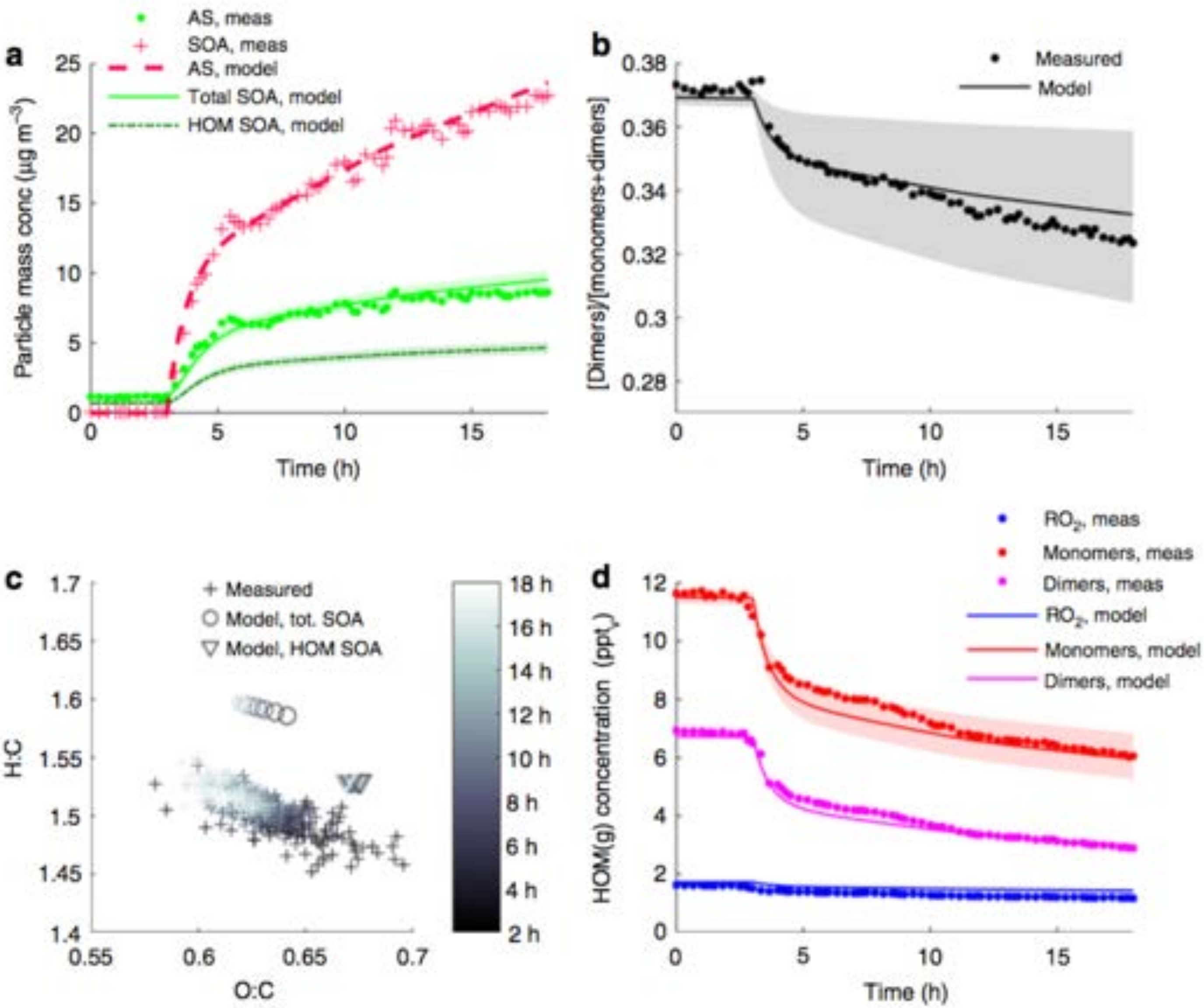
The role of highly oxygenated organic molecules in the Boreal aerosol-cloud-climate system

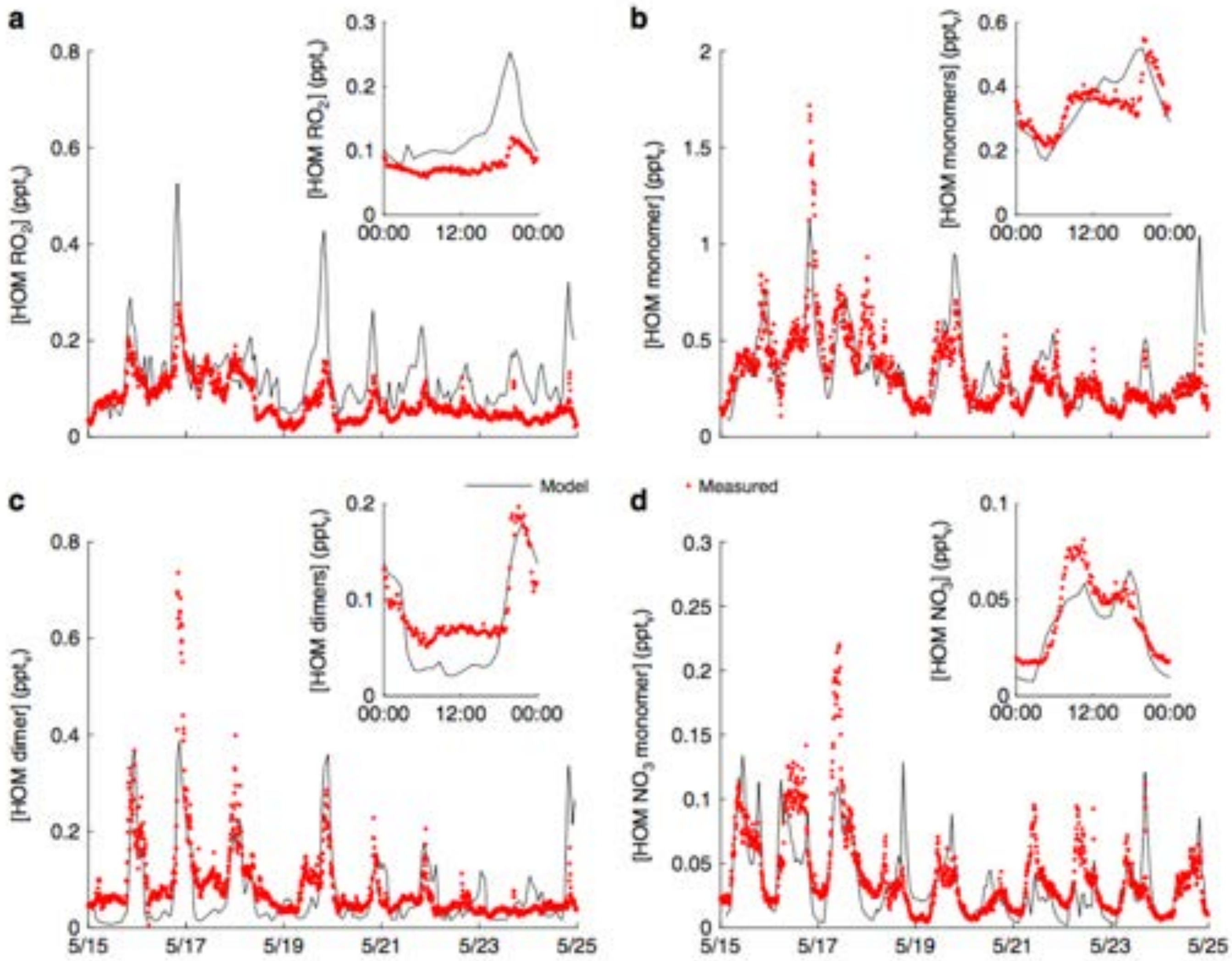
Pontus Roldin[1*], Mikael Ehn[2], Theo Kurtén[3], Tinja Olenius[4], Matti P. Rissanen[2], Nina Sarnela[2], Jonas Elm[5], Pekka Rantala[2], Liqing Hao[6], Noora Hyttinen[7], Liine Heikkinen[2], Douglas R. Worsnop[2,8], Lukas Pichelstorfer[2,9], Carlton Xavier[2], Petri Clusius[2], Emilie Öström[1], Tuukka Petäjä[2], Markku Kulmala[2], Hanna Vehkamäki[2], Annele Virtanen[6], Ilona Riipinen[4] & Michael Boy[2]

Highly oxygenated organic molecule (HOM) formation from α-pinene. Modelled and measured HOM(g) concentrations during a JPAC α-pinene ozonolysis experiment



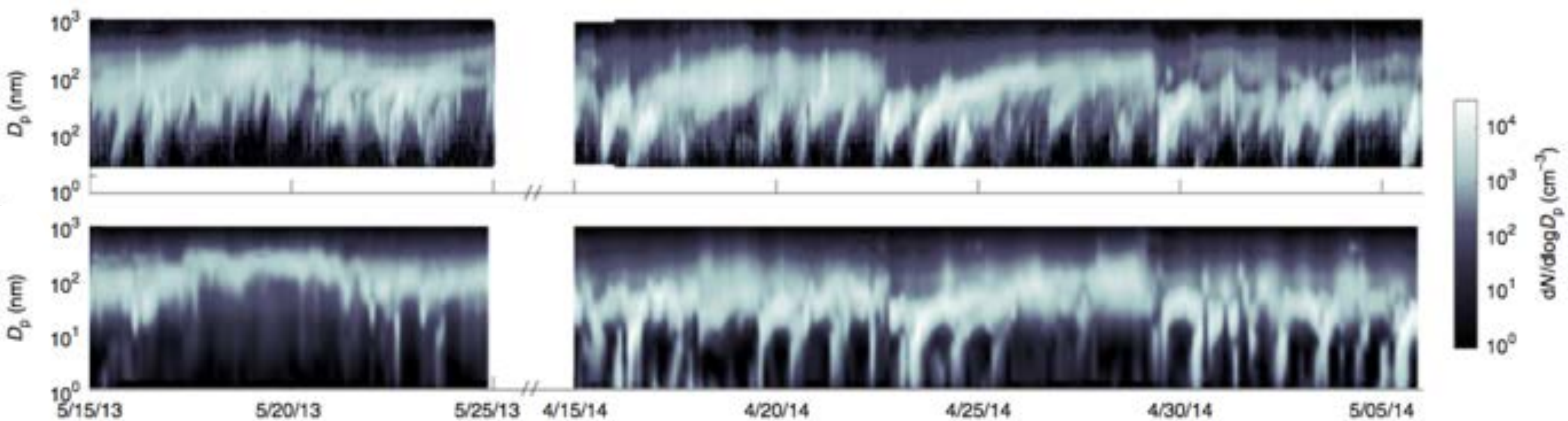


Highly oxygenated organic molecule (HOM) gas-particle partitioning. Model and measurement results from an α-pinene ozonolysis experiment with ammonium sulfate (AS) seed particles.



Highly oxygenated organic molecules (HOM) in the boreal forest. Modelled and measured HOM gas-phase concentrations at the Station for Measuring Ecosystem-Atmosphere Relations II (SMEAR II) between 15 and 24 May 2013.

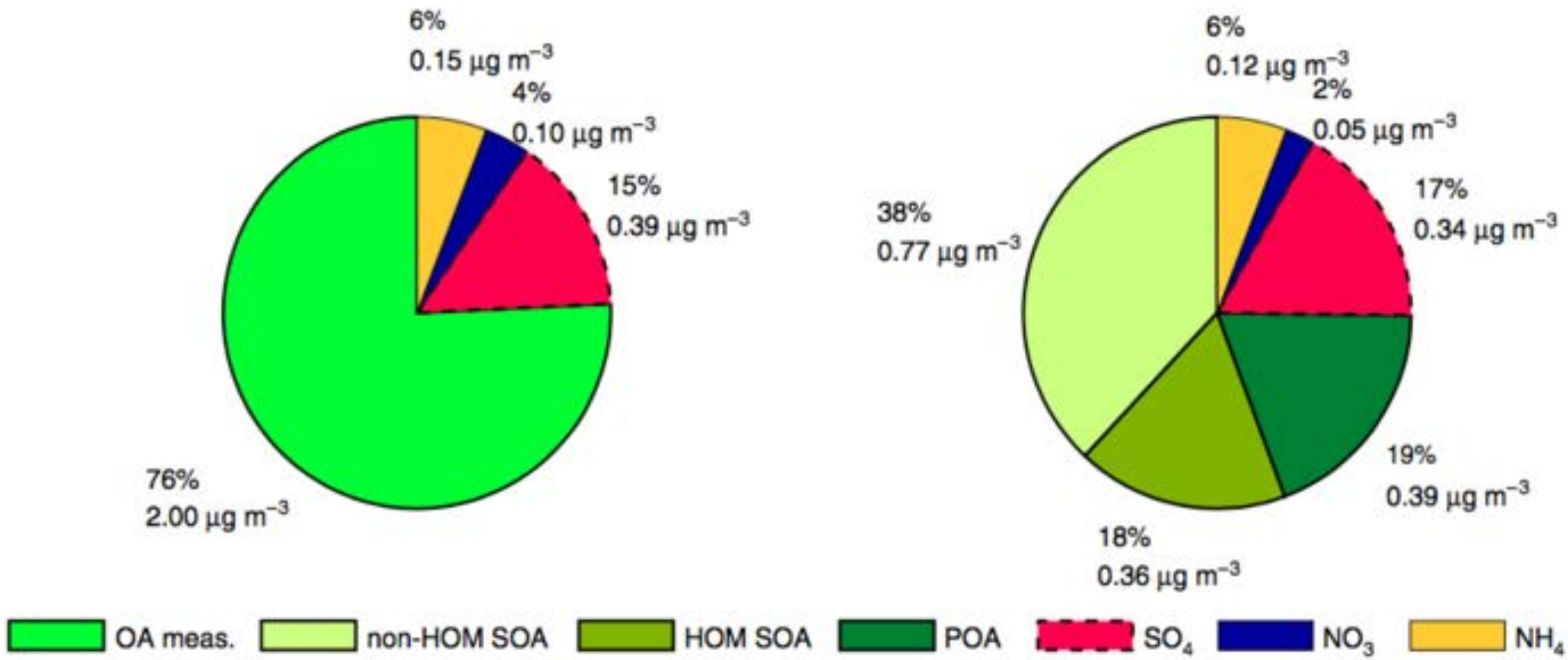
Measured and modelled particle number concentrations at the SMEAR II (Hyytiälä, Finland)



Upper plot: measurements
Lower plot: model

Roldin et al., Nature communication, 2019

Average non-refractory submicron particle chemical composition



Left plot: measurements
Right plot: model

Roldin et al., Nature communication, 2019

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The role of highly oxygenated organic molecules in the Boreal aerosol-cloud-climate system

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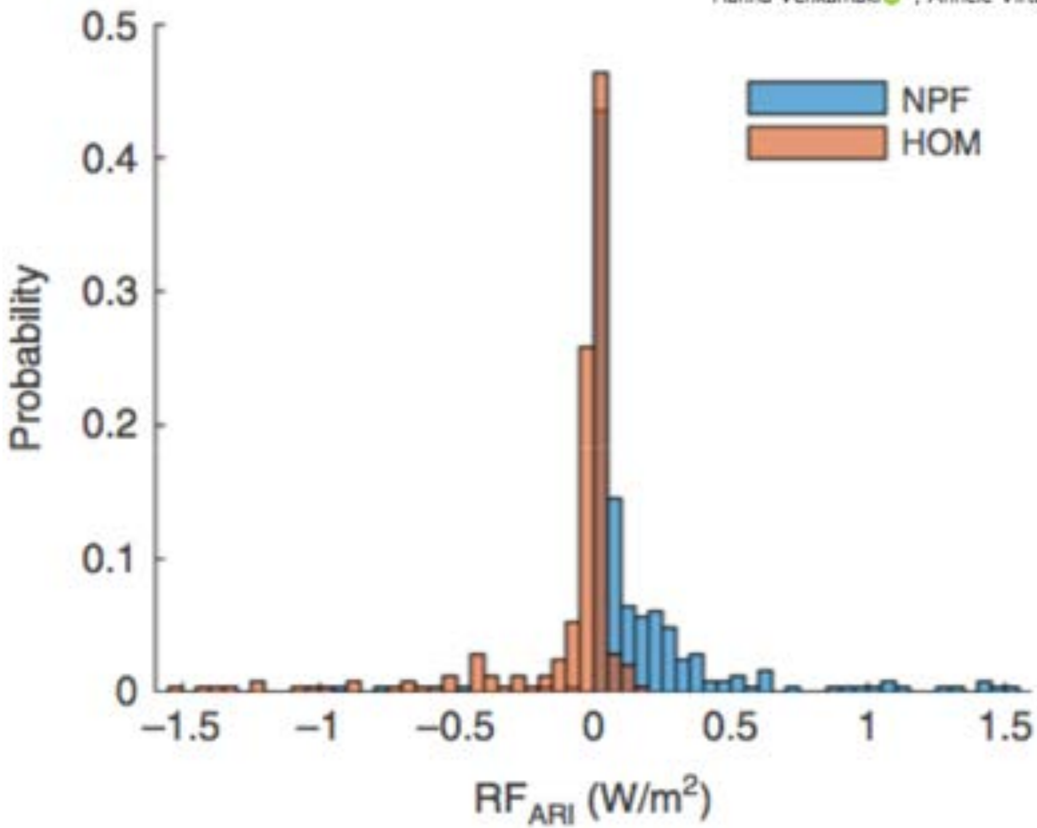
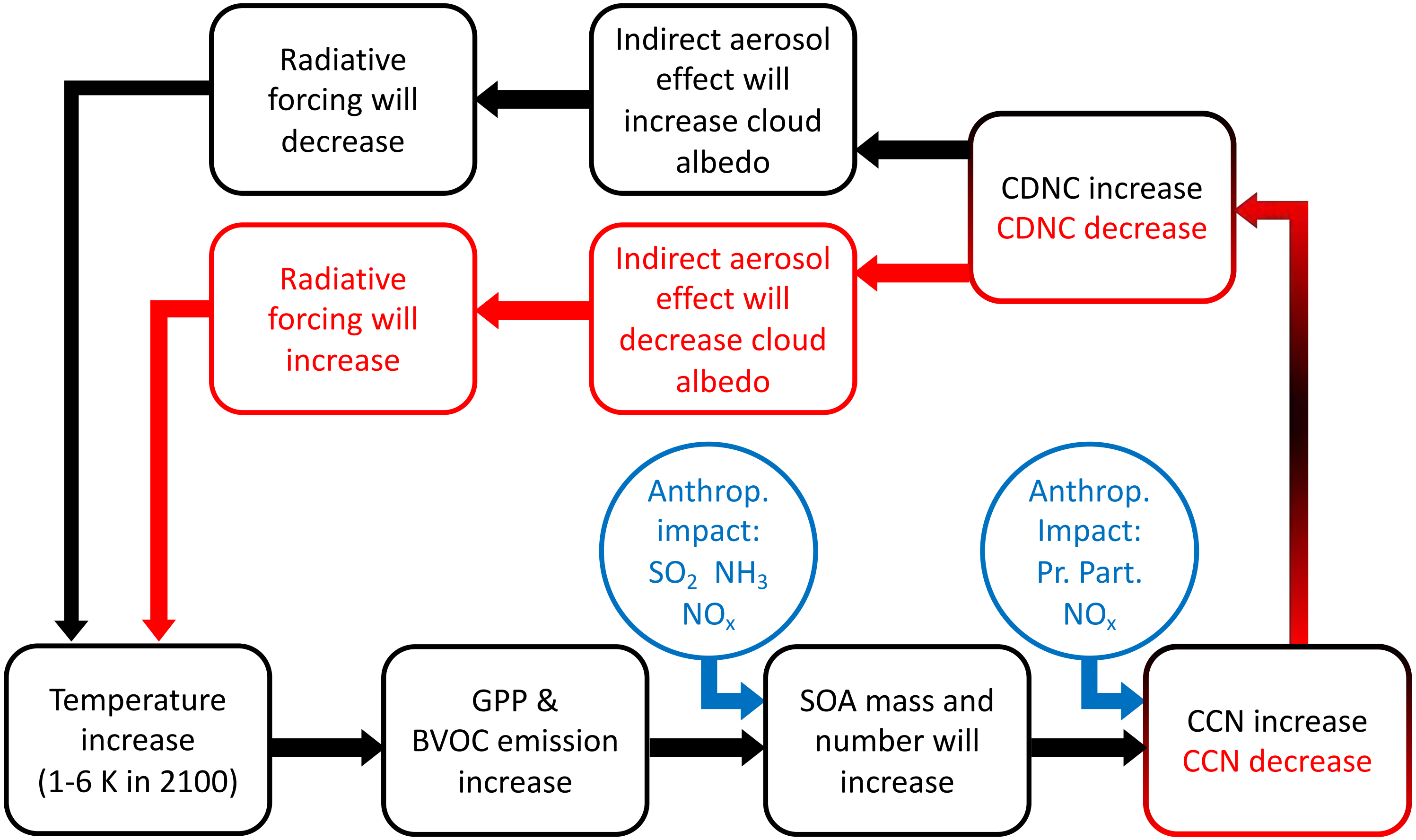


Modelled top of the atmosphere direct aerosol radiative forcing probability distributions caused by new particle formation (NPF) and HOM secondary organic aerosol (HOM SOA) formation, during clear sky conditions.



Schematic of the original Continental-Biosphere-Aerosol-Cloud-Climate feedback loop (CoBACC; Kulmala et al. 2014) denoted by black boxes and connecting lines, and the additional CoBACC loop based on the new results from Roldin et al. (2019) denoted by red boxes and connecting lines and the anthropogenic impact in blue circles (SOA = secondary organic aerosols, CCN = cloud condensation nuclei, CDNC = cloud droplet number concentration, Pr. Part. = primary particles).