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Supplement of

Modelling studies of HOMs and their contributions to new particle formation and growth: comparison of boreal forest in Finland and a polluted environment in China

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Supplement

Section 1

Table S1 A summary of the measurements at SMEAR II and SORPES.

| Measurement parameter | SMEAR II | | SORPES | |
|---------------------------------------|-------------------------------|---------------------------|-------------------------------|---------------------------|
| | Instrument | Period used in this study | Instrument | Period used in this study |
| Aerosol size distribution (3-1000 nm) | DMPS | 2013.1-2013.12 | - | - |
| Aerosol size distribution (6-800 nm) | - | - | DMPS | 2014.1-2014.12 |
| O ₃ | Thermo Fishser Scientific 49i | 2013.1-2013.12 | Thermo Fishser Scientific 49i | 2014.1-2014.12 |
| SO ₂ | Thermo Fishser Scientific 43i | 2013.1-2013.12 | Thermo Fishser Scientific 43i | 2014.1-2014.12 |
| NO/NO ₂ | Thermo Fishser Scientific 42i | 2013.1-2013.12 | Thermo Fishser Scientific 42i | 2014.1-2014.12 |
| Global radiation | Meteological sensor | 2013.1-2013.12 | Meteological sensor | 2014.1-2014.12 |
| Temperature | Meteological sensor | 2013.1-2013.12 | Meteological sensor | 2014.1-2014.12 |
| Relative humidity | Meteological sensor | 2013.1-2013.12 | Meteological sensor | 2014.1-2014.12 |
| VOCs | PTR-MS | 2013.1-2013.12 | GC-MS | 2014.9-2014.10 |
| H ₂ SO ₄ , HOM | CI-APi-TOF | 2013.4-2013.6 | - | - |

Section 2: The descriptions of MALTE model

The MALTE (model to predict new aerosol formation in the lower troposphere) model can be used as one- or zero-dimensional model to simulate new particle formation in the lower troposphere (Boy et al., 2006). This study uses the zero-dimensional version of the MALTE model, i.e. MALTE-BOX, to investigate the differences of HOM and its role in the formation and growth of new particles at SMEAR II station and SORPES station. The configuration of MALTE-BOX model is shown in Fig S1.

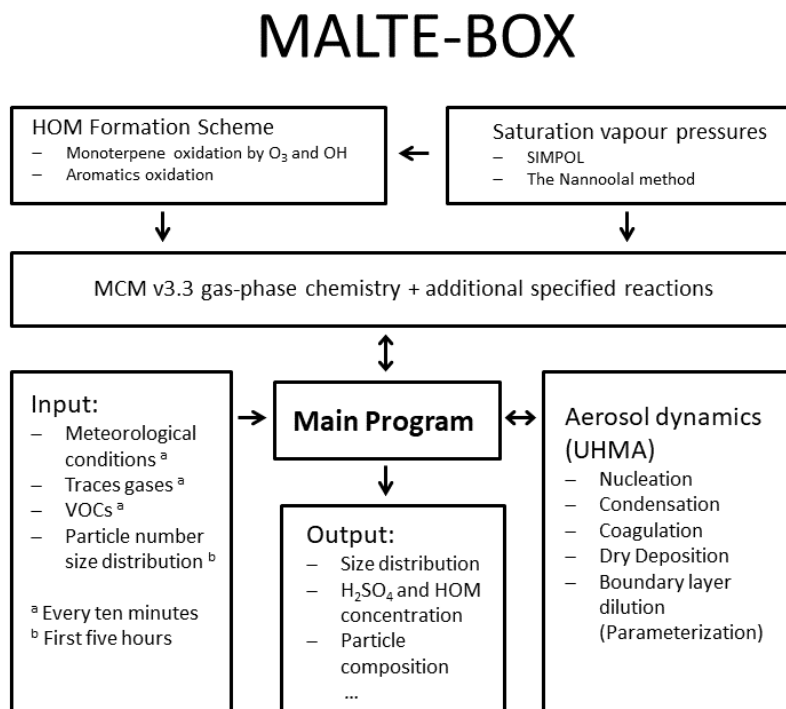


Figure S1. Schematic diagram of the MALTE-BOX model.

10 1. The chemistry mechanisms

The gas-phase chemistry mechanisms consist of the Master Chemical Mechanism (MCM) version 3.3.1, the additional specified reactions related to the new particle formation (NPF) and HOM formation mechanisms. The MCM is a near-explicit chemical mechanism to describe the detailed gas-phase chemical processes involved in the tropospheric degradation of a series of primary emitted volatile organic compounds (VOCs) (Jenkin et al., 2003;Saunders et al., 2003). The inorganic chemistry, i.e. the thermal gas-phase reactions, gas-particle reactions and photolysis reactions are included in the MCM as well. The users can select the primary VOCs based on their own specific studies in the MCM website (http://mcm.leeds.ac.uk/MCMv3.3.1/) and extract the chemical mechanisms. The additional specified

reactions related to the NPF, e.g. the reactions of carene and the oxidation of SO₂ by the stabilized Cregee Intermediate (sCI) radicals with increased reaction rates according to Mauldin III et al. (2012), are added in the chemistry mechanisms.

In current version of MALTE-BOX model, the HOM formation mechanisms are included in the chemistry mechanisms. The mechanism of HOM formation from monoterpene oxidation is based on Ehn et al. (2014). It explicitly describes the processes of the peroxy radicals (RO₂) formed from ozone and OH oxidation of monoterpenes and the sequential steps of intramolecular H-shift and O₂ additions (Ehn et al., 2014; Crouse et al., 2013; Öström et al., 2017). Two monoterpenes, i.e. α -pinene and limonene, which contain endocyclic double bonds are assumed to form HOM initiated by the reactions with ozone. 10% of the first-generation α -pinene + O₃ oxidized products and 30% of the first-generation limonene + O₃ oxidized products were assumed to undergo H-shift and O₂ additions in this study. The molar yields of α -pinene, β -pinene, limonene and carene oxidized by OH to undergo autoxidation were estimated to be 1%, 1.4%, 2.5% and 1%, respectively. The mechanism of HOM formation from aromatics is based on Molteni et al. (2016) (Molteni et al., 2016). A molar yield of 3% for the OH oxidation of the aromatics species was assumed to be HOM. The aromatics species include benzene, toluene, ethyl benzene, o-/m-/p-xylene, 1,3,5-/1,2,3-/1,2,4-trimethylbenzene in this study.

The gas-phase chemistry mechanisms, including the inorganic and selected organic reactions from MCM, the additional specified reactions and HOM formation mechanisms are inverted into the Fortran codes and solved by using the Kinetic Pre-Processor (KPP). The KPP is an open-source software tool that assists the computer simulation of chemical kinetic systems (Damian et al., 2002). In general, 3568 variable species and 10714 reactions are in the chemistry mechanisms of MALTE-BOX in this study.

2. The aerosol dynamics module

The aerosol dynamics are solved by the size segregated aerosol model, UHMA (University of Helsinki Multicomponent Aerosol model) (Korhonen et al., 2004). The aerosol dynamics module includes the processes of nucleation, condensation, coagulation, dry deposition and dilution caused by planetary boundary layer evolution.

Several mechanisms, which are based on the empirical parameterizations of field measurements, can be used to simulate the nucleation of critical clusters in current version of MALTE-BOX. The equation of the nucleation parameterizations can be represented as:

$$J=k*[H_2SO_4]^p[HOM_{nuc}]^q$$

It is used for sulfuric acid activation nucleation when p=1 and q=0 (Kulmala et al., 2006) and the kinetic nucleation of two sulfuric acid molecules when p=2 and q=0 (McMurry and Friedlander, 1979). This study used the kinetic nucleation of sulfuric acid and one HOM_{nuc} molecule (p=1 and q=1). The HOM_{nuc}

is formed with a molar yield of 10^{-5} for each monoterpene reacted with OH (Roldin et al., 2015). Riccobono et al. (2014) proposed the nucleation parameterization as $p=2$ and $q=1$ based on the experiments in the CLOUD chamber. It represents the HOM_{nuc} activation nucleation when $p=0$ and $q=1$ (Ehn et al., 2014) and the kinetic nucleation of two HOM_{nuc} when $p=0$ and $q=2$. The activation or kinetic coefficient (k -value) can be set for each case to achieve the highest correlation compared to the measured newly formed particles. The variations of the k -values can reflect the variability of other unaccounted compounds involved in the particle or cluster formation and initial growth (Kuang et al., 2008).

Condensation of low volatile gas phase species is the important process in shaping the particle chemical composition and size distribution. The nucleated particle can grow to become climatically active through the condensation. Sulfuric acid and organic compounds with pure liquid saturation vapor pressure less than 0.01 Pa were chosen as condensing vapors in UHMA. The condensation is solved by using the analytical predictor of condensation scheme, which requires no iteration, conserves mass exactly, and is unconditionally stable (Jacobson, 2002). The scheme can be represented as following equation:

$$\frac{dv(q,i,t)}{dt} = k(q,i,t0) \cdot \frac{m(q)}{\rho(q)} \cdot (C(q,t) - C'(q,i,t0)),$$

where the $\frac{dv(q,i,t)}{dt}$, $k(q,i,t0)$, $m(q)$, $\rho(q)$, $C(q,t)$ and $C'(q,i,t0)$ are the volume change of component q in particle phase in section i , the mass-transfer coefficient at the time before condensation ($t0$), molecule mass of component q , density of component q , concentration of component q in gas phase and the effective saturation vapor mole concentration, respectively. The effective saturation vapor mole concentration $C'(q,i,t0)$ can be represented as: $C'(q,i,t0) = S'(q,i,t0) \cdot p(q,t0)/RT$, where $S'(q,i,t0)$ is the equilibrium saturation ratio of the condensing gas and $p(q,t0)$ is the saturate vapor pressure of gas vapors. In this study, the saturation vapor pressures of organic compounds in MCMv3.3.1 were estimated with the group contribution method by Nannoolal et al. (Nannoolal et al., 2008) using the UManSysProp online system (Topping et al., 2016). The saturation vapor pressures of HOMs were calculated by SIMPOL (Pankow and Asher, 2008) as Nannoolal et al. (2008) method produces unrealistic estimates of vapor pressures for multifunctional HOMs containing hydroperoxide or peroxy acid group (Kurtén et al., 2016). H_2SO_4 was treated as a non-volatile condensing vapor, which generally is a reasonable assumption at typical atmospheric relative humidity and NH_3 levels (Tsagkogeorgas et al., 2017).

The coagulation reflects two particles collide and stick together and is a significant sink of aerosol number but conserving the volume concentration of particle. The coagulation kernel, i.e. the coagulation rate coefficient, is the product of coalescence efficiency and collision kernel. Only the Brownian diffusion is accounted for the coagulation kernel in UHMA. The correction of non-continuum effects for small particles in the coagulation kernel is according to the Fuchs (1964). The coagulation kernel will be

calculated each time step as the change of the aerosol size distribution. The dry deposition via Brownian diffusion removes particles in small size range (e.g. below 50 nm) and via inertial impaction and gravitational settling removes large particles in the size range above a few micrometers. In UHMA, the calculation of dry deposition is based on the environmental condition of forested regions according to a semiempirical deposition model constructed by Rannik et al. (2013). The dilution of aerosols caused by planetary boundary layer evolution is considered in UHMA when using the MALTE-BOX model to simulate the ambient conditions. It is parameterized as $\frac{dN}{dt} = -\frac{dPBL}{dt} \cdot \frac{N}{PBL}$, where N is the particle number concentration in each size bin and PBL is the boundary layer height.

3. The input and output module

The measurement variables, i.e. meteorological conditions (e.g. air temperature, relative humidity, pressure and radiation), trace gases concentrations (e.g. SO₂, O₃, NO, NO₂ and CO) and VOCs (e.g. ethylene, ethane, propane, acetone, methyl vinyl ketone, n-Butane, benzene, toluene, o-/m-xylene, 1,2,3/1,2,4-trimethylbenzene, ethylbenzene, isoprene and monoterpenes), need to be input into the MALTE-BOX model every 10 min. The measured aerosol number size distribution is read into the model as initialization. In the output module, all the simulated variables can be output.

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