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**SOA formation yields in atmosphere**

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## **1. INTRODUCTION**

## 2. THEORY

### 2.1 Diffusion in binary mixtures

Diffusion illustrates mass convection in medium from greater concentration to lower concentration. Fick's law states diffusion flux

$$J = -D_{AB} \frac{dn}{dx}, \quad (2.1)$$

where  $D_{AB}$  is binary diffusion coefficient and  $n$  molecule number concentration.

Diffusion coefficient for binary gasmixtures can be calculated from Reid et al. (1987)

$$D_{AB} = 0.001 \cdot T^{1.75} \frac{\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{p(V_A^{1/3} + V_B^{1/3})^2}, \quad (2.2)$$

where unit of diffusion coefficient is  $\text{cm}^2/\text{s}$ , temperature  $T$  is Kelvin, molar masses  $M$  are  $\text{g/mol}$  and pressure  $p$  is bar. Diffusion volumes  $V$  can be calculated from values for atomic diffusion volumes which are for carbon C 15.9, for hydrogen 2.31, for oxygen 6.11, for nitrogen 4.54, for heterocyclic ring -18.3 and for air 19.7.

Diffusion related vapor mean free path according to Pirjola and Kulmala (1998)

$$\lambda = \frac{3D_{AB}}{\bar{c}_A}, \quad (2.3)$$

where  $\bar{c}_A$  is velocity of gas molecules

$$\bar{c}_A = \sqrt{\frac{8RT}{\pi M_A}}, \quad (2.4)$$

where  $R$  is ideal gas constant  $8.31446 \text{ J/Kmol}$ .

For example  $\text{C}_{10}\text{H}_{16}\text{O}_{10}$  molecule ( $M_A \approx 300$ ) with one heterocyclic ring, diffusion volume  $V_A \approx 250$ . Diffusion coefficient of this molecule in air in temperature 290 K and pressure 1 atm is  $0.0489 \text{ cm}^2/\text{s}$ . Related mean free path  $\lambda$  is 102.65 nm.

## 2.2 Condensation sink

Condensation sink represents rate how rapidly condensable vapor molecules condenses on existing aerosol in units 1/s. It can be calculated from

$$CS = 2\pi D \int_0^\infty d_p \beta(d_p) n(d_p) dd_p = 2\pi D \sum_i \beta d_{pi} N_i, \quad (2.5)$$

where  $d_{pi}$  is the diameter of a particle in size class  $i$ ,  $N_i$  is corresponding particle number concentration (Dal Maso et al., 2002) and  $D$  is diffusion coefficient of condensing vapor. Transition regime correction factor  $\beta_m$  according to Fuchs and Sutugin (1971) is

$$\beta_m = \frac{1 + Kn}{1 + \left( \frac{4}{3\alpha_m} + 0.337 \right) Kn + \frac{4}{3\alpha_m} Kn^2} \quad (2.6)$$

where  $\alpha_m$  is the sticking coefficient which represents probability of molecule to stick in to the particle. Dimensionless Knudsen number is

$$Kn = \frac{2\lambda}{d_p}, \quad (2.7)$$

where  $\lambda$  is the effective mean free path of the condensing vapor molecules in the gas. Knudsen number is the ratio of two length scales. Mean free path  $\lambda$  characterizes the gas with respect to the transport of mass and particle diameter  $d_p$  characterizes the droplet.

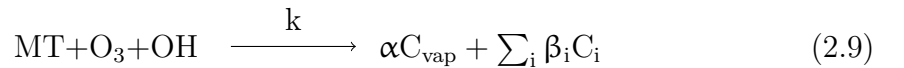
One can semiempirically represent condensation sink as a function of aerosol mass as follows

$$CS = 2 \cdot 10^{-4} \cdot N^{0.37} M^{0.63}, \quad (2.8)$$

where  $N$  is particle number and  $M$  particle mass.

## 2.3 Proposed chemical reaction of monoterpene, SLLV source

Monoterpene reaction with ozone and hydroxyl produces SLLV product with molecular yield of  $\alpha$  and other products with mass yields of  $\beta_i$

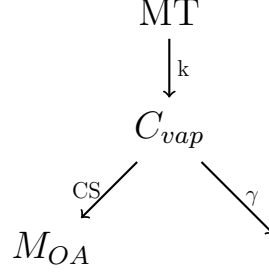


Source of SLLV vapor is then

$$Q_{\text{vap}} = \alpha k P, \quad (2.10)$$

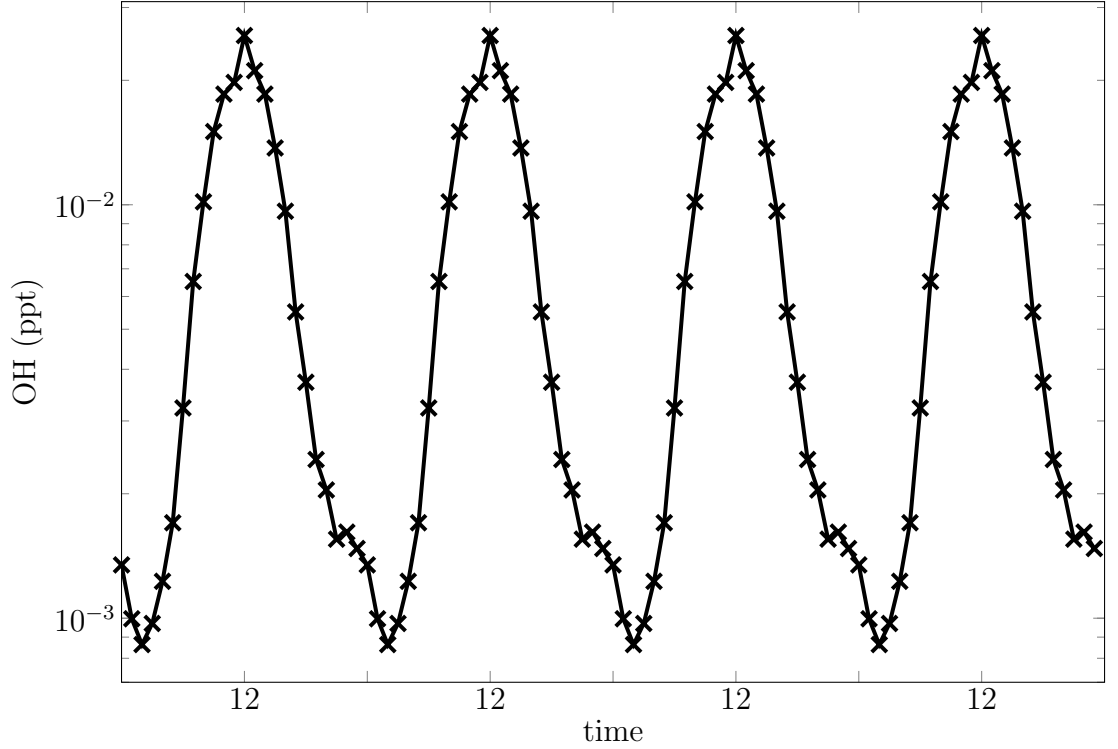
where  $P$  is precursor (monoterpene) concentration and overall reaction rate  $k = k_{O_3}[O_3] + k_{OH}[OH]$  is reaction rate of ozone times ozone concentration plus reaction rate of hydroxyl times hydroxyl concentration.

Proposed SLLV product sinks



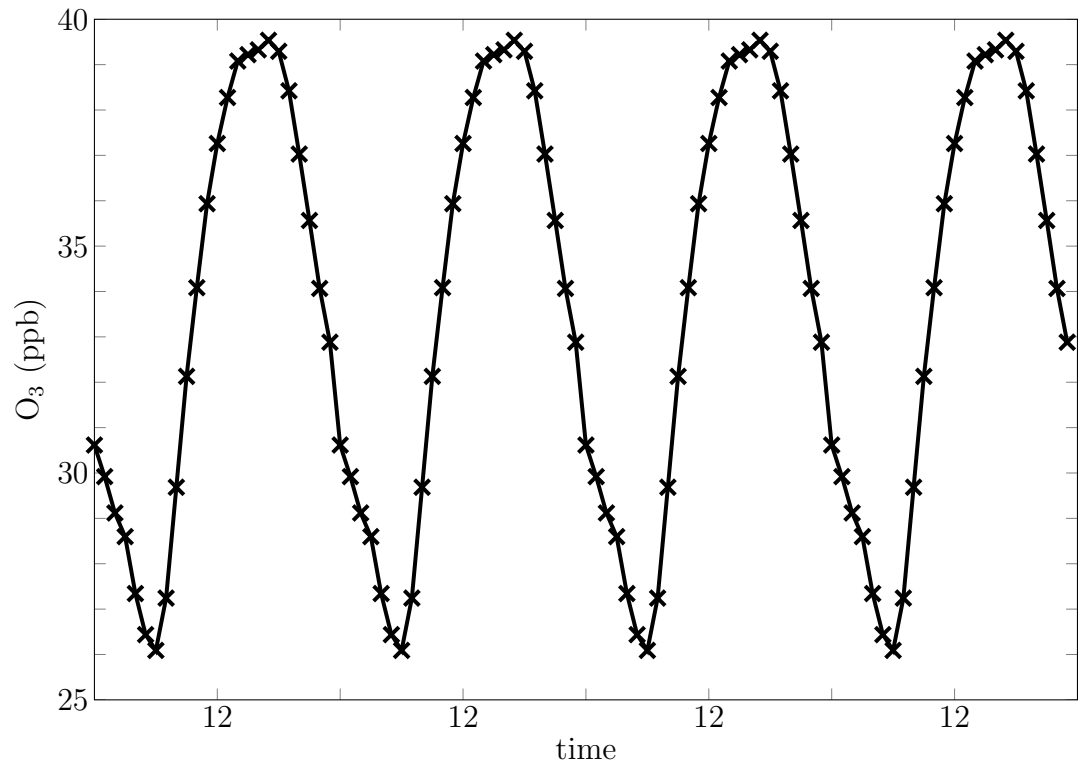
**Figure 2.1:** Proposed routes for monoterpene precursor MT reaction (rate  $k$ ) SLLV product  $C_{vap}$ . To aerosol  $M_{OA}$  with rate CS or to walls or other losses with rate  $\gamma$

## 2.4 Hydroxyl radical concentration diurnal variation in atmosphere



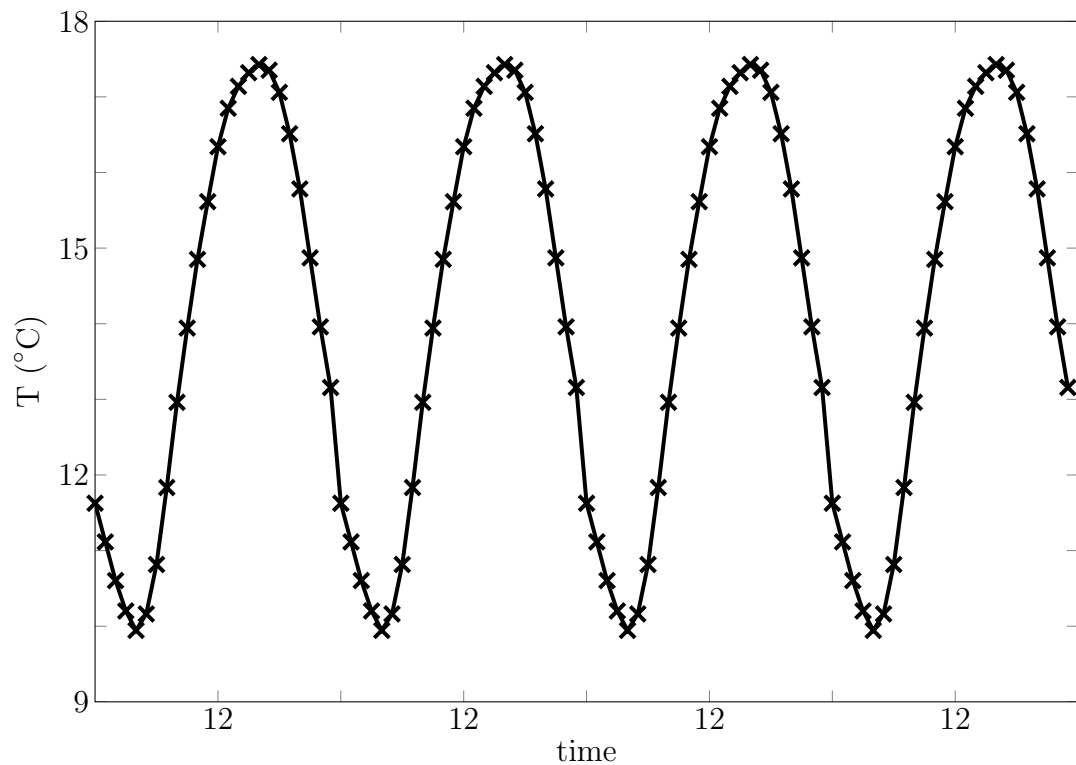
**Figure 2.2:** Diurnal variation of hydroxyl radical median concentration measured in spring and summer 2007 in Hyytiälä on new particle formation event days. Hourly data-points (crosses) are from Petäjä et al. 2009 and solid line is used in modelling. Time is from midnight to midnight and noons are marked.

## 2.5 Ozone concentration diurnal variation in atmosphere



**Figure 2.3:** Diurnal variation of mean ozone concentration measured summertime in 1997-2003 in Hyytiälä on new particle formation event days. Hourly datapoints (crosses) are from Lyubovtseva et al. 2005 and solid line is used in modelling.

## 2.6 Diurnal variation of atmospheric temperature



**Figure 2.4:** Diurnal variation of mean temperature measured summertime in 1997-2003 in Hyytiälä on new particle formation event days. Hourly datapoints (crosses) are from Lyubovtseva et al. 2005 and solid line is used in modelling.

This temperature variation is used in monoterpene emission modelling.

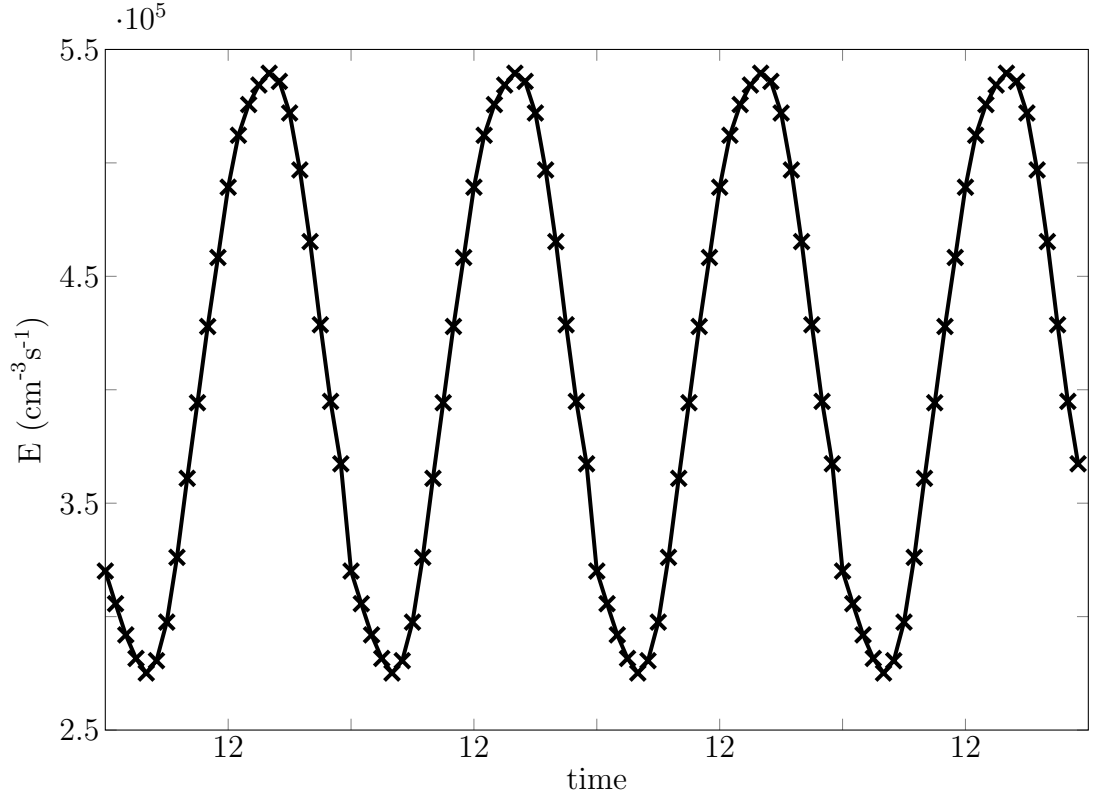


## 2.7 Diurnal variation of monoterpene emissions

The temperature dependence of the monoterpene emission is described by Guenther et al. (1993)

$$E = E_{30} \exp[\beta(T - 30^\circ\text{C})], \quad (2.11)$$

where  $E$  is the emission,  $E_{30}$  is the normalized emission potential and  $\beta$  is the temperature dependence coefficient. Commonly used value for  $\beta$  is  $0.09^\circ\text{C}^{-1}$  and emission potential value  $1.37 \text{ mg/m}^2\text{h}$  (Rinne et al., 2007) was used to obtain diurnal variation of monoterpene emissions presented in figure 2.5. Emission unit milligrams per squaremetre of land per hour was trasformed to concentration per second ( $\text{cm}^{-3}\text{s}^{-1}$ ) considering atmospheric box  $1000\text{m} \times 1\text{m} \times 1\text{m} = 1000\text{m}^3$  with height 1km.



**Figure 2.5:** Diurnal variation of monoterpene emissions using G93 model. Hourly data-points (crosses) are calculated from G93 and solid line is used in modelling.

### 3. METHODS

Particle size distribution varies in time through different processes as nucleation, condensation, coagulation, sedimentation and dilution. These changes can be modelled with general dynamic equation (GDE) (Seinfeld and Pandis, 1998)

$$\begin{aligned} \frac{\partial n(v, t)}{\partial t} = & \frac{1}{2} \int_0^v K(v-q, q) n(v-q, t) dq - n(v, t) \int_0^\infty K(q, v) n(q, t) dq \\ & - \frac{\partial}{\partial v} [I(v) n(v, t)] + J_0 \delta(v - v_0) + S(v) - R(v), \end{aligned} \quad (3.1)$$

where  $I$  is particle volume changing rate,  $J_0$  is nucleation rate,  $K$  is coagulation coefficient,  $n$  is size distribution function,  $R$  particle loss rate,  $S$  particle sources emission rate,  $t$  is time,  $v$  and  $q = v + dv$  are particle volumes and  $\delta(v - v_0)$  is Dirac's delta function which is one whenever  $v = v_0$  and otherwise zero. Two first term of equation represents coagulation, third term condensation, fourth nucleation, fifth other particle sources and the last other particle sinks like deposition.

#### 3.1 Used sectional aerosol model

In sectional model particle size distribution is divided in desired amount of size sections which are characterized with two parametres: particle size and concentration. Particle population is considered monodispersive in each section. In this study moving center model was used where section borders are fixed but particle sizes can vary inside sections (Korhonen, 2004). Model takes into account particle coagulation, dilution and nucleation, vapor condensation in to the particles, vapor dilution and loss to walls (or other places).

Coagulation is modelled with parts of discrete general dynamic equation (Seinfeld and Pandis, 1998)

$$\frac{dN_k}{dt} = \frac{1}{2} \sum_{j=g^*}^{k-g^*} K_{j,k-j} N_j N_{k-j} - N_k \sum_{j=g^*}^{\infty} K_{k,j} N_j, \quad (3.2)$$

where first term represents increase of particles in section  $k$  and second term reduction of particles through coagulation.

Condensation growth of particles is modelled by growing section size using growth

rate (Seinfeld and Pandis, 1998)

$$\frac{dd_p}{dt} = \frac{2M_{vap}I}{\pi\rho d_p^2 N_A}, \quad (3.3)$$

where  $M_{vap}$  is condensing vapor molecular mass,  $\rho$  particle density,  $N_A$  Avogadro's number and  $I$  flux of molecules to the particle phase. It is obtained from

$$I = 2\pi d_p D C_{vap} \beta_m, \quad (3.4)$$

where  $D$  is diffusion coefficient,  $C_{vap}$  concentration of condensing vapor and  $\beta_m$  obtained from equation 2.6.

Dilution of particle concentration is modelled with equation

$$\frac{dN_k}{dt} = -\gamma_{dil} N_k, \quad (3.5)$$

where  $\gamma_{dil}$  is dilution coefficient in units 1/s. It is inverse value of aerosol lifetime  $\tau$ .

Used condensing vapor concentration gradient

$$\frac{dC_{vap}}{dt} = Q - CS \cdot C_{vap} - \gamma C_{vap} - \gamma_{dil} C_{vap}, \quad (3.6)$$

takes into account vapor source rate  $Q$ , vapor loss rate to particles  $CS$  and to walls  $\gamma$  and vapor dilution rate  $\gamma_{dil}$ .

See connection with  $CS$  and  $I$

$$CS = \sum_i I_i N_i. \quad (3.7)$$

This is connection between particle growth and vapor loss to particles. These differential equations 3.2, 3.3, 3.5 and 3.6 are solved numerically using Runge-Kutta-method (Dormand and Prince, 1980) and time evolution of number distribution function  $dN/dd_p$  is gained among other results.

### 3.2 Used monoterpene reaction model

Monoterpene precursor concentration  $P$  was modelled using differential equation

$$\frac{dP}{dt} = E - k_{OH}[OH] \cdot P - k_{O_3}[O_3] \cdot P. \quad (3.8)$$

This monoterpene concentration varies through chemical reaction 2.9 and biogenic emissions  $E$ .

### 3.3 How models was used

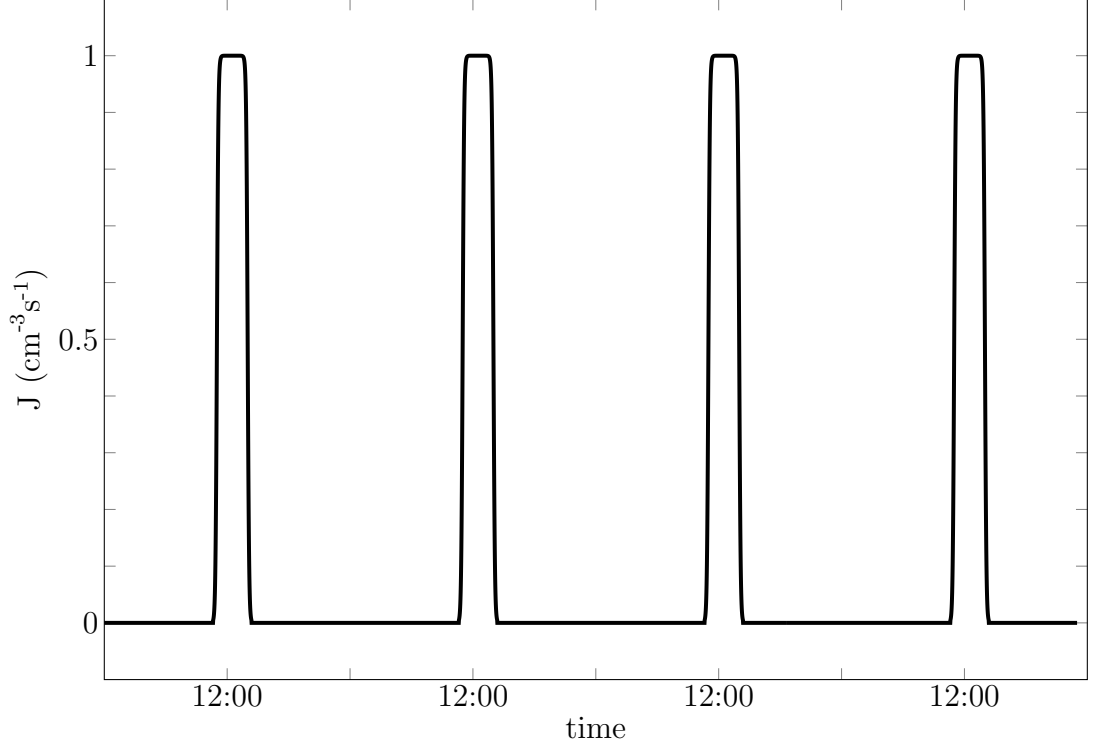
In this study diurnal atmospheric SOA formation was modelled with 60 size sections between sizes 1 nm and 1  $\mu\text{m}$ . Used constants and variables are presented in table 3.1.

**Table 3.1:** Used values in modelling.

Constant	Symbol	Unit	Value
Stoichiometric yield of SLLV	$\alpha$	-	0.08
Sticking coefficient	$\alpha_m$	-	1
Dilution coefficient	$\gamma_{dil}$	1/s	$5 \cdot 10^{-6}$
SLLV wall loss coefficient	$\gamma$	1/s	$5 \cdot 10^{-5}$
SLLV vapor mean free path	$\lambda$	nm	102.65
Particle density	$\rho$	g/cm <sup>3</sup>	1.4
Geometric mean deviation GMD	$\sigma$	-	1.6
Diffusion coefficient of SLLV	$D_{AB}$	cm <sup>2</sup> /s	0.0489
Reaction rate of ozone	$k_{O_3}$	cm <sup>3</sup> s <sup>-1</sup>	$9 \cdot 10^{-17}$
Reaction rate of hydroxyl	$k_{OH}$	cm <sup>3</sup> s <sup>-1</sup>	$5 \cdot 10^{-11}$
Molar mass of SLLV	$M_{vap}$	g/mol	300
Molar mass of monoterpene	$M_{MT}$	g/mol	137
Pressure	$p$	atm	1
Temperature	$T$	K	290
Time vector	$t$	hours	0 - 95
Count median diameter CMD	$\mu$	nm	80
Background number concentration	$N$	1/cm <sup>3</sup>	500

Nucleation was modelled with nucleation rate  $J$  of 3 nm particles presented in figure 3.1. Nucleation starting at 11:00 and ending at 14:00.

Conversion of ppb to 1/cm<sup>3</sup> is done multipling with  $p/kT = 2.5331 \cdot 10^{19}$  air molecules/cm<sup>3</sup>.



**Figure 3.1:** 3 nm sized particle nucleation rate used in modelling

### 3.4 Analysing tools for results, how to get $\alpha$ and $\gamma$ ?

Aerosol mass yield

$$Y = \frac{\Delta M}{\Delta P}, \quad (3.9)$$

where  $\Delta M$  is formed aerosol mass and  $\Delta P$  is used precursor mass. Formed aerosol mass can be calculated

$$\Delta M = M_{tot} - M_0 + M_{dil}, \quad (3.10)$$

where  $M_{tot}$  is aerosol total mass,  $M_0$  initial aerosol mass and  $M_{dil}$  diluted aerosol mass. From particle number distribution  $dN/dd_p$ , total aerosol number  $N_{tot}$ , volume  $V_{tot}$  and mass  $M_{tot}$  is integrated considering spherical particles with density  $\rho = 1.4$  g/cm<sup>3</sup>. Diluted aerosol number  $N_{dil}$  is calculated by model from differential equation 3.5. From  $N_{dil}$  diluted mass  $M_{dil}$  can be calculated and formed aerosol mass got.

Used precursor  $\Delta P$  is calculated from

$$\Delta P = \int_0^{t_{end}} kP dt, \quad (3.11)$$

where  $t_{end}$  is elapsed time,  $k$  is formation rate and  $P$  is precursor concentration presented in equation 2.10.

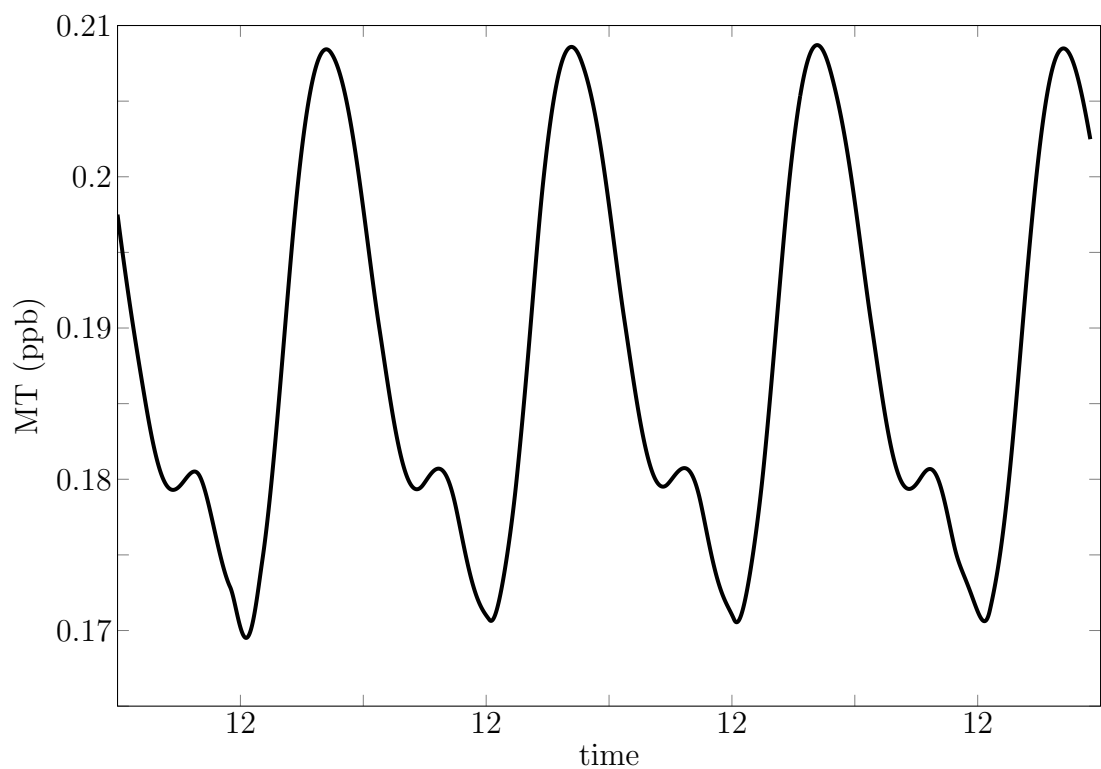
Condensation sink was calculated from equation 2.5 using particle number distri-

bution  $dN/dd_p$  and values of table 3.1.

## 4. RESULTS

### 4.1 Monoterpene concentration modelling

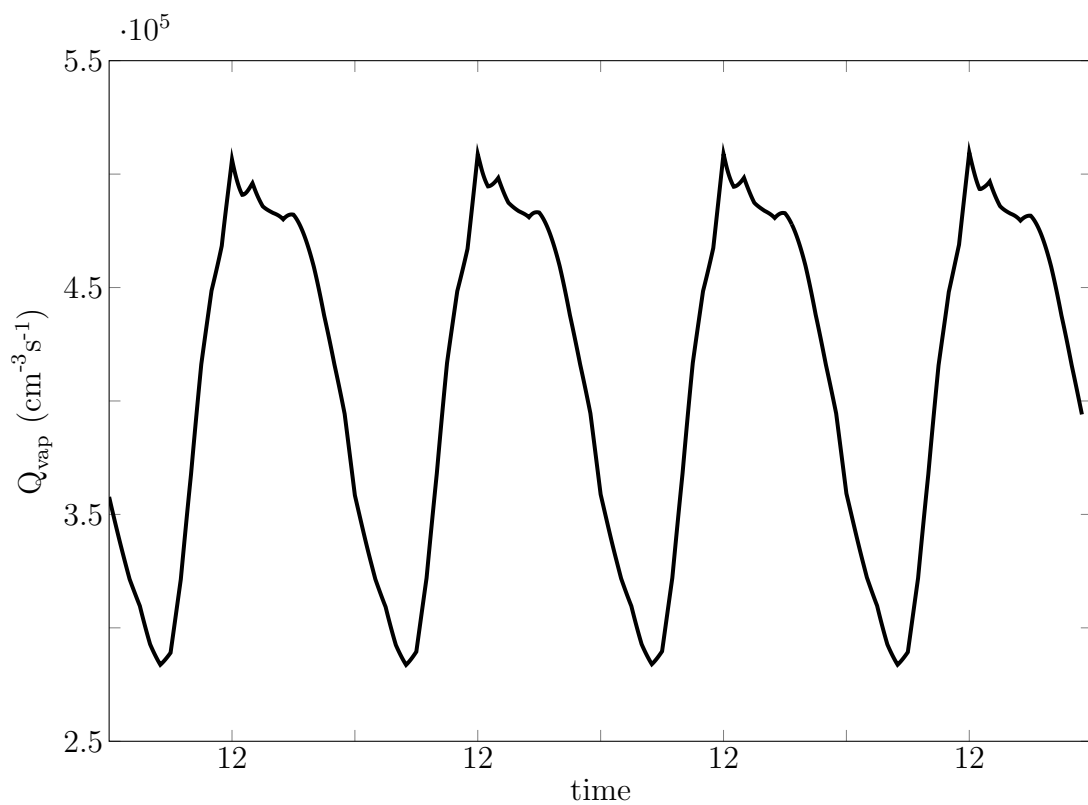
Solution of differential equation 3.8 (figure 4.1) using diurnal atmospheric values presented in chapter 2 is used to produce source  $Q_{vap}$  for condensing vapour using



**Figure 4.1:** Diurnal variation of monoterpene concentration.

equation 2.10.

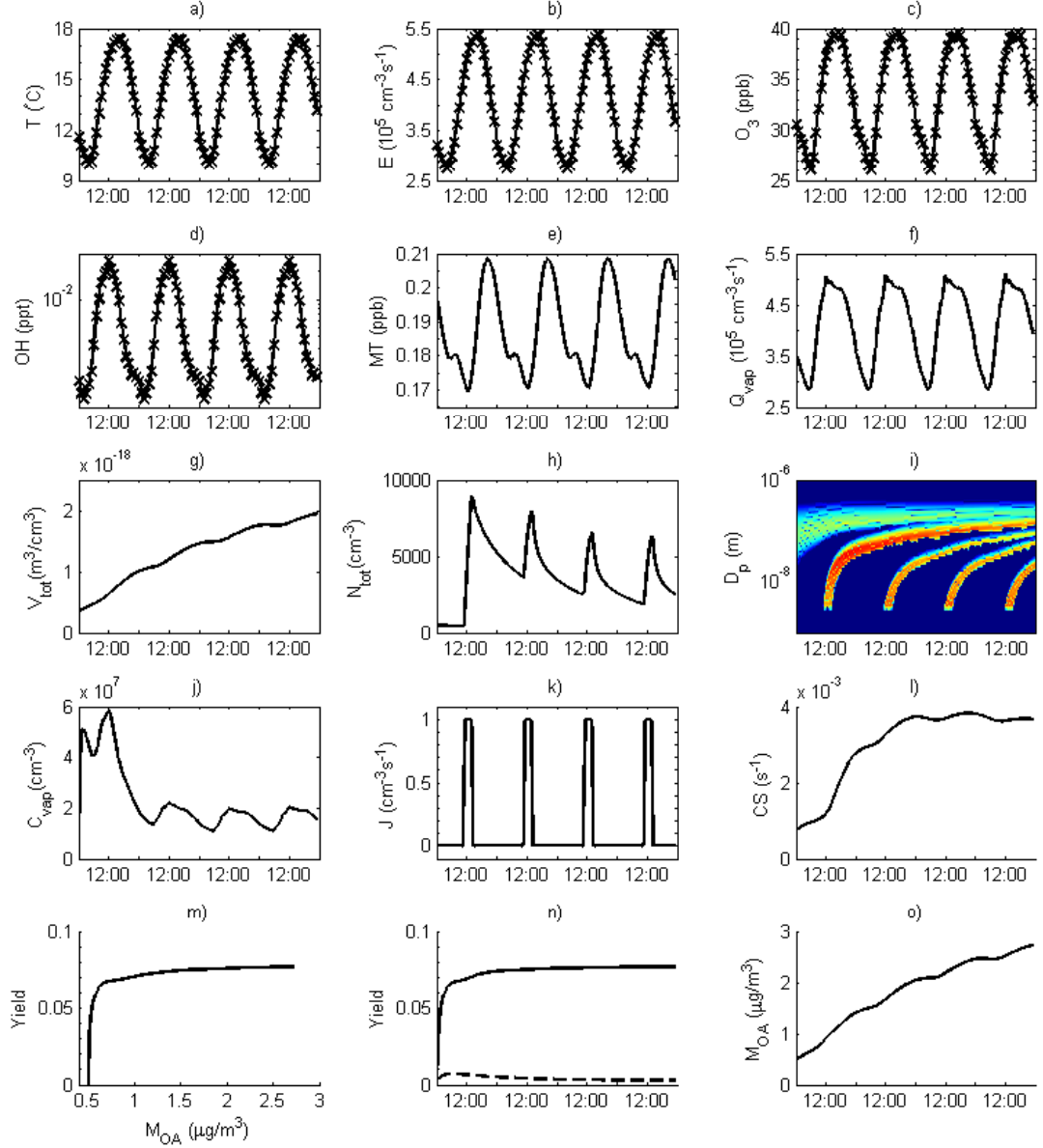
This source of condensing vapor was used in sectional model.



**Figure 4.2:** Diurnal variation of monoterpene concentration.

## 4.2 Atmospheric SOA formation modelling





**Figure 4.3:** Diurnal parameters during four days modelling: **a)** atmospheric temperature summertime in Hyytiälä, **b)** monoterpene emissions using G93 model, **c)** ozone concentration summertime in Hyytiälä, **d)** hydroxyl radical concentration spring and summer 2007 in Hyytiälä, **e)** modelled monoterpene concentration, **f)** modelled condensing vapor source, **g)** modelled total particle volume, **h)** modelled total particle number, **i)** modelled particle size distribution, **j)** modelled condensing vapor concentration, **k)** nucleation rate used in modelling, **l)** modelled condensation sink, **m)** molecular yield as function of aerosol mass, **n)** molecular yield as function of time (solid) and yield of vapor lost to wall (dashed) and **o)** modelled organic aerosol mass. X-axis is time starting at midnight.

## 5. MATLAB SCRIPTS AND DATA FILES

Matlab scripts and data files to get figure 4.3:

`\GitHub\AECHAMO\calculate and plot\Many_subplots_atm.m`

and `\GitHub\AECHAMO\gaskinetics_mp\MT_kinetics_night_and_day.m`

and `\GitHub\AECHAMO\Results and scripts_mp\SOA`

`formation\ATM modelling\v4\run_20130814T114856.mat`

and `\GitHub\AECHAMO\gaskinetics_mp\o3_OH_MT_T_Variable_values.m`

This documentation latex origin: `\Github\AECHAMO\documentation_mp\Atmosphere`

## **6. CONCLUSION**

## REFERENCES

- Dal Maso, M., Kulmala, M., Lehtinen, K. E. J., Mäkelä, J. M., Aalto, P., and O'Dowd, C. D. (2002). Condensation and coagulation sinks and formation of nucleation mode particles in coastal and boreal forest boundary layers. *Journal of Geophysical Research D: Atmospheres*, 107(19):1–10.
- Dormand, J. R. and Prince, P. J. (1980). A family of embedded Runge-Kutta formulae. *Journal of Computational and Applied Mathematics*, 6:19–26.
- Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R. (1993). Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses. *Journal of Geophysical Research: Atmospheres*, 98(D7):12609–12617.
- Korhonen, H. (2004). Model studies on the size distribution dynamics of atmospheric aerosols. *Doctoral thesis. University of Helsinki*.
- Lyubovtseva, Y. S., Sogacheva, L., Dal Maso, M., Bonn, B., Keronen, P., and Kulmala, M. (2005). Seasonal variations of trace gases, meteorological parameters, and formation of aerosols in boreal forests. *Boreal environment research*, 10(6):493–510.
- Petäjä, T., Mauldin III, R., Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T., and Kulmala, M. (2009). Sulfuric acid and oh concentrations in a boreal forest site. *Atmospheric Chemistry and Physics*, 9(19):7435–7448.
- Pirjola, L. and Kulmala, M. (1998). Modelling the formation of H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O particles in rural, urban and marine conditions. *Atmospheric Research*, 46(3-4):321–347.
- Reid, R., Prausnitz, J., and Poling, B. (1987). *The properties of gases and liquids*. McGraw Hill Book Co., New York.
- Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T., Hellén, H., Kajos, M., Vesala, T., and Kulmala, M. (2007). Hydrocarbon fluxes above a scots pine forest canopy: measurements and modeling. *Atmospheric Chemistry and Physics*, 7(12):3361–3372.
- Seinfeld, J. H. and Pandis, S. N. (1998). *Atmospheric Chemistry and Physics - From Air Pollution to Climate Change*. John Wiley & Sons, New York.