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# **The Secondary Organic Aerosol Processor (SOAP v1.0) model: a unified model with different ranges of complexity based on the molecular surrogate approach**

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## Abstract

The Secondary Organic Aerosol Processor (SOAP v1.0) model is presented. This model is designed to be modular with different user options depending on the computing time and the complexity required by the user. This model is based on the molecular surrogate approach, in which each surrogate compound is associated with a molecular structure to estimate some properties and parameters (hygroscopicity, absorption into the aqueous phase of particles, activity coefficients and phase separation).

Each surrogate can be hydrophilic (condenses only into the aqueous phase of particles), hydrophobic (condenses only into the organic phase of particles) or both (condenses into both the aqueous and the organic phases of particles). Activity coefficients are computed with the UNIFAC thermodynamic model for short-range interactions and with the AIOMFAC parameterization for medium and long-range interactions between electrolytes and organic compounds. Phase separation is determined by Gibbs energy minimization.

The user can choose between an equilibrium representation and a dynamic representation of the organic aerosol. In the equilibrium representation, compounds in the particle phase are assumed to be at equilibrium with the gas phase. However, recent studies show that the organic aerosol (OA) is not at equilibrium with the gas phase because the organic phase could be semi-solid (very viscous liquid phase). The condensation or evaporation of organic compounds could then be limited by the diffusion in the organic phase due to the high viscosity. A simplified dynamic representation of secondary organic aerosols (SOA) is used with OA divided into layers, the first layer being at the center of the particle (slowly reaches equilibrium) and the final layer being near the interface with the gas phase (quickly reaches equilibrium).

According to preliminary results, the non-ideality of the aerosol (including interactions with inorganic ions and separation of the organic phase into several phases) should be taken into account in models as it may affect SOA formation. Moreover, some compound should not be assumed only hydrophilic or only hydrophobic as they can condense on both the organic and the aqueous phases.

# 1 Introduction

Fine particles are regulated because of their impact on human health. Furthermore, they degrade atmospheric visibility and influence climate change. It is therefore necessary to develop models able to predict particle formation, which can be used to predict their impact on health and environment and evaluate emission mitigation policies. Particulate organic matter (OM) represents a large fraction of the total fine particulate mass, typically between 20 and 60% (Kanakidou et al., 2005; Yu et al., 2007; Zhang et al., 2007). Therefore, efforts have to be made to represent OM as accurately as possible in models. Three-dimensional air quality models, which estimate particles concentrations, need to have a simplified representation of organic species. Because of the large number of organic species involved originating from diverse anthropogenic and biogenic sources, species need to be lumped according to their properties (for example by lumping species with similar saturation vapor pressures). In the surrogate based methodology, molecular structures are attached to surrogate compounds representing a large number of SOA species to estimate several properties (e.g., condensation into an aqueous phase, oligomerization, hygroscopicity, non-ideality).

In 3D air quality models, several assumptions are made on the thermodynamics of OA such as equilibrium between the gas phase and the particle phase, ideality, no phase separation. However, these assumptions could strongly impact organic aerosol formation. For example, some experimental recent studies emphasize the need to take into account dynamical aspects of the formation of OA rather than assuming thermodynamic equilibrium with the gas phase because OA can be highly viscous (Virtanen et al., 2010; Cappa and Wilson, 2011; Pfrang et al., 2011; Shiraiwa et al., 2011; Vaden et al., 2011; Shiraiwa and Seinfeld, 2012; Abramson et al., 2013).

Some OA models already represent the formation and the condensation of organic compounds using the surrogate approach: the AER/EPRI/Caltech (AEC) model (Pun et al., 2002, 2006), the Hydrophilic/Hydrophobic Organic model ( $H^2O$ ) (Couvidat et al., 2012a,b) and the Model to Predict the Multiphase Partitioning of Organics (MPMPO) (Griffin et al., 2003). However, none of these models takes into account the dynamics of the condensation of organic compounds, the influence of interactions between organic and inorganic compounds on activity

coefficients and the phase separation of particulate organic matter into several organic phases whereas the interplay of these phenomena should be taken into account in models (Shiraiwa et al., 2013). Moreover, AEC and H<sup>2</sup>O contrary to MPMPO, that each compound may condense into only one phase (the organic or the aqueous phase). Computation of activity coefficients and phase separation at equilibrium has been extensively developed in the thermodynamic model AIOMFAC (Zuend et al., 2008, 2010, 2011; Zuend and Seinfeld, 2012). Shiraiwa et al. (2012) developed a multi-layer model KM-GAP which treats explicitly the condensation and particle diffusion of organic compounds as well as heat transfer and particle-phase reactions.

To represent organic aerosol formation and take into account non-ideality, phase separation and the viscous state of OA, the Secondary Organic Aerosol Processor (SOAP), destined to be implemented in 3D air quality models is developed and presented here. This model is designed to be modular with different user options depending on the computing time and the complexity required by the user. The user can choose between an equilibrium representation and a dynamic representation of organic aerosols, between ideality and non-ideality (with or without phase separation and interactions with inorganic ions) and on which phases each surrogate compound can condense (the organic phases, the aqueous phase or all phases). This paper presents the development of SOAP and the results of several test cases.

## 2 Model development

### 2.1 Overview

SOAP is based on the methodology used in the models H<sup>2</sup>O and AEC. It uses a molecular surrogate approach and distinguishes two types of surrogate SOA species: hydrophilic species (which condense only into an aqueous phase except at low humidity) and hydrophobic species (which condense only into an organic phase due to their low affinity with water). However, in SOAP, each species can also be both hydrophilic and hydrophobic (condense into all phases as in MPMPO) depending on user specification.

The processes already present in H<sup>2</sup>O (condensation into an aqueous phase, oligomerization,

hygroscopicity, non-ideality) are implemented in SOAP as well as some new processes such as phase separation and interactions of organic compounds with inorganic compounds via activity coefficients. A molecular structure is assigned by the user to each surrogate compound. A default structure is provided for each surrogate, as in H<sub>2</sub>O. This structure is used to compute the non-ideality of aerosols via activity coefficients. If the user specifies that a compound is both hydrophilic and hydrophobic, the repartition between phases is done according to the value of activity coefficients. However, the user can decide that a compound is only hydrophilic or only hydrophobic, if for example, the absorption of the compound in one of the two phases is negligible (for example alkane or lowly oxidised compounds are probably not absorbed by the aqueous phase of particles). Moreover, if there is no compound that is both hydrophilic and hydrophobic, the condensation into the organic phase can be solved separately from the condensation into the aqueous phase. The system is then uncoupled. On the opposite, if there is at least one compound which is hydrophilic and hydrophobic, the condensation into the organic phase and the condensation into the aqueous phase must be solved simultaneously. The system is then coupled and consumes more CPU time. The user may prefer an uncoupled system for 3D application due to higher time efficiency.

Another difference is the possibility in SOAP to use two different approaches to model gas/particle interactions: the equilibrium approach and the dynamic approach. In the equilibrium approach, aerosols are assumed to be at thermodynamic equilibrium with the gas phase as in H<sub>2</sub>O. Similarly to H<sub>2</sub>O, the model uses a method of Newton-Raphson to efficiently compute the partitioning of each compound between the gas and particle phases. In the dynamic approach, the dynamic of the condensation and particle diffusion of organic compounds is treated with a multi-layer representation of OA (the organic mass is divided into several layers having different characteristic times to reach equilibrium). The dynamic approach developed in this study is a simplified approach to take into account particle-phase diffusion with a low number of layers, and a computation time as low as possible to be used in 3D air quality models. It does not describe particle-phase diffusion as thoroughly as in KM-GAP (Shiraiwa et al., 2012).

The particle size distribution is divided into sections (inside a section/bin, all particles are assumed to have the same diameters). Inside a bin, compounds condense into the aqueous phase

or/and the organic phases. Furthermore, each bin can be separated into several phases and several layers.

The code can be downloaded at <http://cerea.enpc.fr/en/modeles.html>

## 2.2 Organic aerosol formation at equilibrium

- 5 The fundamental equations used in SOAP to represent the partitioning between gas and particles under the equilibrium assumption are now described.

### 2.2.1 Equilibrium between the gas phase and an organic phase

The equilibrium between the gas phase and an organic phase is described by Raoult's law:

$$P_i = \gamma_{i,org} X_{i,org} P_i^0 \quad (1)$$

with  $P_i$  the partial pressure of the compound  $i$ ,  $\gamma_{i,org}$  the activity coefficient of  $i$  in the organic phase,  $X_{i,org}$  the molar fraction of  $i$  in the organic phase and  $P_i^0$  the saturation vapor pressure of  $i$ . Pankow (1994) rewrote Eq. (1) into Eq. (2) to compute the absorption of organic compounds by an organic phase:

$$\frac{A_{p,i}}{A_{g,i}} = K_{p,i} M_o \quad (2)$$

with  $A_{p,i}$  the concentration of  $i$  in the organic phase (in  $\mu\text{g m}^{-3}$ ),  $A_{g,i}$  the concentration of  $i$  in the gas phase (in  $\mu\text{g m}^{-3}$ ),  $M_o$  the concentration of the organic phase (in  $\mu\text{g m}^{-3}$ ) and  $K_{p,i}$  the organic-phase partitioning coefficient (in  $\text{m}^3 \mu\text{g}^{-1}$ ) which is computed using Eq. (3) (Pankow, 1994).

$$K_{p,i} = \frac{760 \times 8.202 \times 10^{-5} \times T}{M_{ow} \gamma_{i,org} P_i^0 \times 10^6} \quad (3)$$

with  $T$  the temperature (in K),  $M_{ow}$  the mean molar mass of the organic phase (in g/mol) and  $P_i^0$  the saturation vapor pressure (in torr). In SOAP, activity coefficients are computed with the thermodynamic model UNIFAC (UNIversal Functional group Activity Coefficient Fredenslund

et al. (1975)). Moreover,  $P_i^0$  or partitioning constants  $K_{p,i}$  are the same as those used in  $H^2O$  (they are generally determined by fitting to experimental results obtained in environmental chambers at a temperature  $T_{ref}$ ). The partitioning coefficient is extrapolated from  $T_{ref}$  to  $T$  by using the enthalpy of vaporization  $\Delta H_i$  (in J/mol) according to the Clausius-Clapeyron equation.

$$\frac{K_{p,i}(T)}{T} = \frac{K_{p,i}(T_{ref})}{T_{ref}} \exp\left(\frac{\Delta H_i}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (4)$$

The absorption of water by the organic phase is computed with Eq. (5) derived from Eq. (1) applied for water.

$$A_{p,water} = \frac{M_{water} M_o RH}{\gamma_{water,org} M_{ow}} \quad (5)$$

with  $RH$  the relative humidity,  $M_{water}$  the molar mass of water (in g/mol) and  $\gamma_{water,org}$  the activity coefficient of water in the organic phase.

## 2.2.2 Equilibrium between the gas phase and an aqueous phase

SOAP does not currently take into account the formation of inorganic aerosols. An inorganic aerosol model like ISORROPIA (Nenes et al., 1998) must be called separately and prior to the call of SOAP to provide inputs to SOAP: pH, concentrations of inorganic ions, ionic strength and the liquid water content of aerosols.

The equilibrium between the gas and the aqueous phases can be described by Raoult's law (Eq. 6) but also by Henry's law (Eq. 7) if infinite dilution is assumed:

$$P_i = \gamma_{i,aq} X_{i,aq} P_i^0 \quad (6)$$

with  $\gamma_{i,aq}$  the activity coefficient of  $i$  in the aqueous phase and  $X_{i,aq}$  the molar fraction of  $i$  in the aqueous phase.

$$C_i = H_i P_i \quad (7)$$

with  $C_i$  the concentration (in M) of species  $i$  in the aqueous phase,  $P_i$  in atmosphere and  $H_i$  the Henry's law constant (in M/atm).

As Henry's law is often used to express the partitioning between the gas and the aqueous phases, a modified Henry's law is used to extrapolate infinite dilution conditions to all conditions using an aqueous-phase partitioning coefficient  $K_{aq,i}$ :

$$\frac{A_{aq,i}}{A_{g,i}} = K_{aq,i}AQ \quad (8)$$

with  $A_{aq,i}$  the concentration of  $i$  in the organic phase (in  $\mu\text{g m}^{-3}$ ),  $A_{g,i}$  the concentration of  $i$  in the gas phase (in  $\mu\text{g m}^{-3}$ ),  $AQ$  the total concentration (organics + inorganics including water) of the aqueous phase (in  $\mu\text{g m}^{-3}$ ) and  $K_{aq,i}$  the aqueous-phase partitioning coefficient (in  $\text{m}^3/\mu\text{g}$ ) which is computed with Eq. (9):

$$K_{aq,i} = \frac{H_iRT}{\rho_{water}\zeta_i \times 1.013 \times 10^{11}} \times \frac{18}{M_{aq}} \quad (9)$$

with  $\rho_{water}$  the density of the aqueous phase (in  $\text{kg m}^{-3}$ ),  $M_{aq}$  the molar mass of the aqueous phase (in  $\text{g/mol}$ ) which can be slightly different from the molar mass of water due to the presence of other compounds and  $\zeta_i$  the activity coefficient by reference to infinite dilution.  $\zeta_i$  is computed with Eq. (10):

$$\zeta_i = \frac{\gamma_{i,aq}}{\gamma_{i,aq}^\infty} \quad (10)$$

where  $\gamma_{i,aq}^\infty$  is the activity coefficient at infinite dilution in water, which is computed with UNI-FAC. However, the original UNIFAC (Fredenslund et al., 1975) only computes the activity coefficients due to short-range interactions and does not take into account medium and long range interactions due to the presence of electrolytes in the aqueous phase. In the aqueous phase, activity coefficients are computed from Eq. (11) (Zuend et al., 2008):

$$\gamma_{i,aq} = \gamma_{LR}\gamma_{MR}\gamma_{SR} \quad (11)$$

$\gamma_{LR}$ ,  $\gamma_{MR}$  and  $\gamma_{SR}$  are respectively the activity coefficients at long, medium and short range interactions.  $\gamma_{SR}$  is computed with UNIFAC whereas  $\gamma_{LR}$  and  $\gamma_{MR}$  are computed with the

AIOMFAC method. The last two parameters model the influence of inorganic ions on the partitioning of organic compounds (Zuend et al., 2008, 2011; Zuend and Seinfeld, 2012). Similarly to the case of condensation into an organic phase (Eq. (4)), the partitioning coefficient is extrapolated from  $T_{ref}$  to  $T$  by using the enthalpy of vaporization  $\Delta H_i$  (in J/mol) as described in Eq. (12):

$$\frac{K_{aq,i}(T)}{T} = \frac{K_{aq,i}(T_{ref})}{T_{ref}} \exp\left(\frac{\Delta H_i}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (12)$$

However, some compounds are acids that can dissociate in the aqueous phase. Therefore, partitioning coefficients are modified to take into account acidic dissociation as done by Pun et al. (2006).

The absorption of water by the aqueous phase is computed with Eq. (13) derived from Eq. (1):

$$A_{aq,water} = \frac{M_{water}AQ \times RH}{\gamma_{water,aq}M_{aq}} \quad (13)$$

with  $\gamma_{water,aq}$  the activity coefficient of water in the aqueous phase. As the amount of water absorbed by inorganics is already given by the inorganic model used for the inputs of SOAP (for example ISORROPIA), we assumed that the total amount of water (from inorganics and organics) computed by SOAP should at least be equal to the amount of water given by the inorganic model. Therefore, if the amount of water computed by SOAP is lower than the amount computed by the inorganic model, it is replaced by the amount computed by the inorganic model. This problem arises because inorganics are not computed within SOAP (in that case, there would be no numerical issue) and water concentrations can be lower in SOAP than in the inorganic model ISORROPIA for several reasons. First, there can be numerical differences between SOAP and ISORROPIA because different parameterisations are used in SOAP and ISORROPIA to compute water. Second, the amount of water absorbed by the aerosol can be different from the sum of the water amount absorbed by inorganics and the water amount absorbed by organics. Choi and Chan (2002) found that organic species can either reduce or enhance the water absorption of inorganic compounds. Depending on the conditions, the amount of water computed by SOAP could be higher without organics than with.

### 2.2.3 Equilibrium between the gas phase and several particulate phases

SOAP can compute the partitioning of compounds between the gas phase and several particulate phases. The user can specify for each compound if it is hydrophilic (condense into the aqueous phase of particles) or hydrophobic (condense into the organic phase of particles) or both hydrophilic and hydrophobic (condense on both phases).

For an uncoupled system (compounds cannot be both hydrophobic and hydrophilic), for hydrophobic compounds, the total concentration of  $i$  in all phases  $A_{tot,i}$  is:

$$A_{tot,i} = A_{p,i} + A_{g,i} \quad (14)$$

which gives when combined to Eq. (2):

$$A_{p,i} = A_{tot,i} \frac{K_{p,i} M_o}{1 + K_{p,i} M_o} \quad (15)$$

A method of Newton-Raphson is then used to solve Eq. (15) and to minimize the error (an accuracy threshold is provided by the user):

$$error = M_o - \sum_i A_{tot,i} \frac{K_{p,i} M_o}{1 + K_{p,i} M_o} \quad (16)$$

For an uncoupled system, for hydrophilic compounds, the total concentration of  $i$  in all phases  $A_{tot,i}$  is:

$$A_{tot,i} = A_{aq,i} + A_{g,i} \quad (17)$$

which gives if combined to Eq. (8):

$$A_{aq,i} = A_{tot,i} \frac{K_{aq,i} A Q}{1 + K_{aq,i} A Q} \quad (18)$$

A method of Newton-Raphson is then used to solve Eq. (18) and to minimize the error (an accuracy threshold is provided by the user):

$$error = A Q - A Q_{inorg} - \sum_i A_{tot,i} \frac{K_{aq,i} A Q}{1 + K_{aq,i} A Q} \quad (19)$$

with  $AQ_{inorg}$  the concentration of inorganic compounds in the aqueous phase. For a coupled system, the total concentration of  $i$  in all phases  $A_{tot,i}$  is:

$$A_{tot,i} = A_{p,i} + A_{aq,i} + A_{g,i} \quad (20)$$

which gives if combined to Eq. (2) and (8):

$$A_{p,i} = A_{tot,i} \frac{K_{p,i}M_o}{1 + K_{aq,i}AQ + K_{p,i}M_o} \quad (21)$$

$$A_{aq,i} = A_{tot,i} \frac{K_{aq,i}AQ}{1 + K_{aq,i}AQ + K_{p,i}M_o} \quad (22)$$

Similarly, a method of Newton-Raphson is used to solve simultaneously Eq. (21) and (22) and to minimize the errors ( $error_p$  and  $error_{aq}$ ).

$$error_p = M_o - \sum_i A_{tot,i} \frac{K_{p,i}M_o}{1 + K_{aq,i}AQ + K_{p,i}M_o} \quad (23)$$

$$error_{aq} = AQ - AQ_{inorg} - \sum_i A_{tot,i} \frac{K_{aq,i}AQ}{1 + K_{aq,i}AQ + K_{p,i}M_o} \quad (24)$$

## 2.2.4 Saturation and separation of organic phases

If compounds having a low affinity with each other coexist inside a single organic phase, the organic phase may become saturated by some compounds and may become unstable. In that case, the separation of the organic phase into several organic phases may occur. To determine whether separating the organic phase into several organic phases makes the system more stable, the Gibbs energy  $G$  is computed as in Erdakos and Pankow (2004); Zuend et al. (2010); Zuend and Seinfeld (2012) using different system configurations (different number of phases):

$$G = \sum_i \sum_{\phi} n_i^{\phi} \mu_i^{\phi} \quad (25)$$

with  $\phi$  an index of the various phases (gaseous and liquid),  $n_i^\phi$  the number of moles of species  $i$  in phase  $\phi$  and  $\mu_i^\phi$  the chemical potential of  $i$  in phase  $\phi$ .

The most stable configuration of the system has the lowest Gibbs energy. Therefore, if by adding one organic phase the Gibbs energy decreases, then the system is more stable and phase separation takes place. If the Gibbs energy does not decrease, the previous solution (before adding one organic phase) is more stable and is kept. The number of organic phases is determined iteratively: one phase is added until the Gibbs energy increases.

### 2.3 Dynamic gas uptake by organic particles

The dynamic approach, which is presented hereafter, is a simplified approach to take into account particle-phase diffusion with a low number of layers, and a computation time as low as possible to be used in 3D air quality models. The main assumptions are described here.

The first assumption is that the organic-phase diffusion coefficient is constant over the entire particle. It does not depend on the distance to the center of the particle. Although this assumption may not be valid, it is reasonable because, currently, to our knowledge, there is no parameterization to evaluate the order of magnitude of organic-phase diffusion coefficients.

The second assumption is that the concentrations in one layer can be described independently from the concentrations in the other layers. This hypothesis means that in the model there is no exchange of compounds between layers and that the compounds condense directly from the gas phase to the layer or that they evaporate directly from the layer to the gas phase by taking into account an equilibration time specific of the layer. Compounds condense into a layer or evaporate from a layer as if the other layers had the same affinity with compounds. Effects of entrapment of compounds inside central layers by the layers closer to the interface with the gas phase (compounds inside the central layers having a low affinity with the compounds of the layers at the interface will not be able to evaporate whereas compounds having a high affinity with the central layer but having a low affinity with the layers at the interface will not be able to condense into the central layer) are not taken into account. The model should give however a good estimation of the capacity of the organic aerosol to absorb compounds (by taking into

account the time for each layer to reach equilibrium due to diffusion in the particle).

The third assumption is that the organic phases and the aqueous phase evolve separately, i.e., there is no kinetic of transfer of compounds between the organic phases and the aqueous phase, due to the complexity of representing properly those transfers, which should strongly depend on the morphology of particles. If a compound tends to go from the aqueous phase to the organic phase, it has first to go from the aqueous phase to the gas phase and then from the gas phase to the organic phase. For example, in case of evaporation of the aqueous phase (that can be due to a strong change of the relative humidity), this assumption can create some evaporation/recondensation issue (compounds evaporate and recondense after some time into the organic phase according to condensation/evaporation fluxes) whereas a part of organic compounds should go directly from the aqueous phase to the organic phase. It could also be possible that if an aqueous phase and an organic phase coexist into the same particle that organic compounds do not condense directly from the gas phase into the organic phase (because the kinetic is too slow) but condense first into the aqueous phase and then go from the aqueous phase to the organic phase (if it is quicker for a compound to condense into the organic phase by this pathway). However, it can also be argued that if there is an aqueous phase (the relative humidity is too high), the organic phase may not be significantly viscous.

### 2.3.1 Diffusion of organic compounds in spherical organic particles

The diffusion of organic compounds at a radius  $r$  at time  $t$  inside a spherical particle is governed by the following Eq. (Seinfeld and Pandis, 1998):

$$\frac{\partial C}{\partial t} = D_{org} \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) + R_{org}(r, t) \quad (26)$$

with  $C(r, t)$  the molar concentration at radius  $r$  at time  $t$ ,  $D_{org}$  the organic-phase diffusivity and  $R_{org}$  the organic-phase reaction rate. By assuming  $D_{org}$  constant, the solution of this equation (with  $C(r, 0) = 0$  and  $C(R_p, t) = C_s$ ,  $R_p$  being the radius of the particle) without organic-phase

reaction is according to Seinfeld and Pandis (1998):

$$\frac{C(r,t)}{C_s} = 1 + \frac{R_p}{r} \sum_{n=1}^{\infty} (-1)^n \frac{2}{n\pi} \sin \frac{n\pi r}{R_p} \exp\left(-\frac{n^2\pi^2 D_{org} t}{R_p^2}\right) \quad (27)$$

By integrating Eq. (27) over the volume of a spherical particle, the following equation is found for the concentration in the particle phase  $A_p$ :

$$\frac{A_p(t)}{A_{eq}} = 1 - \sum_{n=1}^{\infty} \frac{6}{n^2\pi^2} \exp\left(-\frac{n^2 t}{\tau_{dif}}\right) \quad (28)$$

with  $\tau_{dif}$  the characteristic time for diffusion in the center of the particle:

$$\tau_{dif} = \frac{R_p^2}{\pi^2 D_{org}} \quad (29)$$

with  $A_{eq}$  the organic phase concentration at equilibrium with the gas phase ( $A_{eq} = K_p M_o A_g$ ). In Eq. (28),  $A_p$  can be interpreted as the sum of an infinity number of layers of concentration  $A_p^{layer}$ :

$$A_p = \sum_{layer=1}^{\infty} A_p^{layer} \quad (30)$$

$$A_p^{layer} = V_{layer} A_{eq} \left(1 - \exp\left(-\frac{\alpha_{layer} t}{\tau_{dif}}\right)\right) \quad (31)$$

where  $A_p^{layer}$  is the concentration (in  $\mu\text{g}/\text{m}^3$ ) in a layer of volume fraction  $V_{layer}$  determined by the fraction of the volume of the particle constituted by the layer and with a characteristic diffusion time  $\tau_{dif}^{layer}$  expressed in Eq. (32).

$$\tau_{dif}^{layer} = \tau_{dif} / \alpha_{layer} \quad (32)$$

Numerically, Eq. (28) can be approached by a finite number of layers  $N_{layer}$  and by fitting the parameters  $V_{layer}$  and  $\alpha_{layer}$  such as:

$$A_p = \sum_{layer=1}^{N_{layer}} A_p^{layer} \quad (33)$$

First, for a given concentration  $A_{eq}$ , a given  $D_{org}$ ,  $R_p$ , we estimate  $A_p(t)$  using Eq. (30). Then  $V_1, V_2, V_3, \alpha_1, \alpha_2, \alpha_3$  are fitted such as satisfying Eq. (33). The values of these parameters do not depend of the choice of  $A_{eq}$ ,  $D_{org}$  and  $R_p$ .

For example, if we choose to have 3 layers ( $N_{layer}=3$ ), then  $V_1=0.6, V_2=0.26, V_3=0.14, \alpha_1=0.9878, \alpha_2=6.2558, \alpha_3=68.8666$ , Eq. (33) gives a good approximation of Eq. (30) as shown in Fig. 1.

The evolution of concentrations  $A_{p,i}^{bin,layer}$  in a bin and a layer due to the condensation of species  $i$  limited by the diffusion of organic compounds in the organic phase is described by the Eq. (34), which describes the evolution of the concentration  $A_{p,i}^{bin,layer}$  compared to an equilibrium concentration (Pankow model:  $A_{eq}^{bin,layer} = A_{g,i} K_{p,i}^{bin,layer} M_o^{bin,layer}$ ) (with the assumption that the concentrations in one layer can be described independently from the concentrations in the other layers).

$$\frac{dA_{p,i}^{bin,layer}}{dt} = k_{diffusion} (A_{g,i} K_{p,i}^{bin,layer} M_o^{bin,layer} - A_{p,i}^{bin,layer}) \quad (34)$$

with  $M_o^{bin,layer}$  the total mass of organics in the layer computed with Eq. (35) by assuming that the density of the organic matter is constant over layers and  $k_{diffusion}$  the kinetic coefficient for diffusion (in  $s^{-1}$ ) computed with Eq. (36) as the inverse for the characteristic diffusion time in a layer.

$$M_o^{bin,layer} = V_{layer} M_o^{bin} \quad (35)$$

$$k_{diffusion} = \frac{\alpha_{layer}}{\tau_{dif}} \quad (36)$$

### 2.3.2 Diffusion of organic compounds in more complex particles

The previous equations correspond to the diffusion of organic compounds into an entirely organic spherical particle. However in the atmosphere, particles generally have more complex geometries and can also be constituted by solid and/or inorganic phases. The morphology affects the time for an organic phase to be diffused in the particle. For example, for a same particle diameter, a particle entirely organic needs more time to reach equilibrium with the gas phase than a particle constituted by a solid core in the center surrounded by an organic phase (because the organic compounds do not penetrate the particle all the way to the center, they are only diffused inside the coating). As diffusion of organic compounds is affected by the presence of solid phases, morphology factors are designed to take into account this solid phase where diffusion of organics may not occur. We assume that this solid phase is located at the core of particles based on Katrinak et al. (1993); Sachdeva and Attri (2007); Wang et al. (2014). Models, such as KM-GAP, treating explicitly the diffusion of compounds inside particles do not need those factors. As in SOAP, the volume of layer has to be constant, only the characteristic time for diffusion can be affected by the morphology. We propose here to parameterize the effects of a solid core by defining morphology factors  $f_{morph}^{layer}$ , which affect the time to reach equilibrium with the gas phase. The characteristic time for diffusion of a layer  $\tau_{dif}^{layer}$  expressed in eq. (32) becomes:

$$\tau_{dif}^{layer} = \frac{\tau_{dif}}{f_{morph}^{layer} \alpha_{layer}} \quad (37)$$

Eq. (34) then becomes:

$$\frac{dA_{p,i}^{bin,layer}}{dt} = f_{morph}^{layer} k_{diffusion} (A_{g,i} K_{p,i}^{bin,layer} M_o^{bin,layer} - A_{p,i}^{bin,layer}) \quad (38)$$

with  $k_{diffusion}$  defined as in eq. (36).

The morphology factors can be determined numerically (at least for some simple case). We determined here morphology factors in the case of a spherical particle with a solid core at the center of the particle. The differential equation for diffusion (Eq. 26) is solved and morphology

factors are fitted to minimize the differences between Eq. (26) and (38) for various volume fractions of the solid phase  $f_s$  (volume of the solid phase in the particle over the volume of the particle). This fitting procedure is described into more details in the supplementary materials. The variations of the morphology factors with the volume fraction  $f_s$  are shown in Fig. 2. The morphology factors for a solid core particle can be represented by a polynomial expression such as:

$$f_{morph}^{layer} = A_{layer} f_s^4 + B_{layer} f_s^3 + C_{layer} f_s^2 + D_{layer} f_s + 1 \quad (39)$$

The values of the polynomial parameters are shown in Table 2. Typically, the presence of a solid phase would result in a morphology factor greater than 1, reducing the characteristic diffusion time of organics in the particle. This parameterization only takes into account the simple case of a spherical solid core at the center and not the wide range of morphologies present in the atmosphere. A similar methodology or a methodology based on observations could be applied to other morphologies which could greatly affect the characteristic times for diffusion. For example, morphology factors for the effect of the presence of an aqueous phase on characteristic time for diffusion could be determined (at least as a function of the mass of the aqueous phase and the affinity of compounds with water). Currently, the model assumes there is no effect of the aqueous phase on the characteristic times.

### 2.3.3 Condensation/evaporation of organic compounds

The evolution of the mass  $m_i$  of species  $i$  in an organic particle of diameter  $D_p$  by condensation of organic compounds limited by their absorption into the organic phase is described by the following Eq. (Seinfeld and Pandis, 1998):

$$\frac{dm_i}{dt} = \frac{2\pi D_p D_{air} M_i}{RT} f(Kn, \alpha) (P_i - P_{eq,i}) \quad (40)$$

with  $T$  the temperature,  $R$  the universal gas constant (equal to  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $D_p$  the diameter of the particle,  $D_{air}$  the diffusivity of compound  $i$  in air,  $f(Kn, \alpha)$  the transition regime

formula of Fuchs and Sutugin (1971) and  $P_{eq,i}$  the pressure at equilibrium with the gas phase, which differs from Raoult's law due to the Kelvin effect.

$$\frac{P_{eq,i}}{P_i^0} = \gamma_{i,org} x_i \exp\left(\frac{2\sigma M_{ow}}{RT \rho_{organic} R_p}\right) \quad (41)$$

with  $\sigma$  the surface tension,  $\rho_{organic}$  the density of the organic phase,  $M_{ow}$  the mean molar mass of the organic phase and  $R_p$  the radius of the particle. A surface tension of 24 mN/m is chosen, which is roughly the surface tension of organic compounds according to Seinfeld and Pandis (1998) and a density of the organic phase of 1300 kg/m<sup>3</sup> is used.

The size distribution of particles is discretized into sections. In each section/bin, the concentrations  $A_{p,i}^{bin}$  of a compound  $i$  in the organic phase in the specified bin (in  $\mu\text{g m}^{-3}$ ) can be linked to  $m_i^{bin}$  the mass of  $i$  of particles in the bin (in g) via the following equation:

$$A_{p,i}^{bin} = N^{bin} m_i^{bin} 10^6 \quad (42)$$

with  $N^{bin}$  the number of particles in section "bin" (#/m<sup>3</sup>).

The partial pressure of  $i$  is linked to the concentration  $A_{g,i}$  via:

$$P_i = \frac{A_{g,i} RT}{M_i} 10^6 \quad (43)$$

with  $P_i$  in Pascals,  $R$  in  $\text{J K}^{-1} \text{mol}^{-1}$ ,  $T$  in K,  $M_i$  in g/mol.

By combining Eq. (40),(42) and (43), the condensation/evaporation of the organic species  $i$  is described by:

$$\frac{dA_{p,i}^{bin}}{dt} = k_{absorption} \left( A_{g,i} - \frac{A_{p,i}^{bin}}{K_{p,i}^{bin} M_o^{bin}} \right) \quad (44)$$

with  $M_o^{bin}$  the mass of the organic matter in the bin,  $K_{p,i}^{bin}$  the organic-phase partitioning coefficient of the bin taking into account the Kelvin effect.

$$K_{p,i}^{bin} = \frac{760 \times 8.202 \times 10^{-5} \times T}{M_{ow}^{bin} \gamma_{i,org} P_i^0 \times 10^6} \exp\left(-\frac{2\sigma M_{ow}^{bin}}{RT \rho_{organic} R_p}\right) \quad (45)$$

The kinetic rate of absorption  $k_{absorption}$  is:

$$k_{absorption} = 2\pi D_p D_{air} N^{bin} f(Kn, \alpha) \quad (46)$$

The evolution of particle phase concentrations in the different layers can be inferred by rewriting Eq. (44) into Eq. (47):

$$\frac{dA_{p,i}^{bin}}{dt} = \sum_{layer}^{N_{layer}} \frac{dA_{p,i}^{bin,layer}}{dt} = \frac{k_{absorption}}{K_{p,i}^{bin} M_o^{bin}} (A_{g,i} K_{p,i}^{bin} M_o^{bin} - A_{p,i}^{bin}) \quad (47)$$

and by defining  $K_{p,i}^{bin,layer}$  the partitioning coefficient of a compound  $i$  in a bin and a layer.

$$K_{p,i}^{bin,layer} = \frac{760 \times 8.202 \times 10^{-5} \times T}{M_{ow}^{bin,layer} \gamma_{i,org} P_i^0 \times 10^6} \exp\left(-\frac{2\sigma M_{ow}^{bin,surface}}{RT \rho_{organic} R_p}\right) \quad (48)$$

with  $M_{ow}^{bin,surface}$  the mean molar mass of the layer at the surface of the particle.

Following the second assumption in which compounds condense into a layer or evaporate from a layer as if the other layers had the same affinity with compounds, Eq. (47) becomes:

$$\frac{dA_{p,i}^{bin,layer}}{dt} = \frac{k_{absorption}}{K_{p,i}^{bin,layer} M_o^{bin}} (A_{g,i} K_{p,i}^{bin,layer} M_o^{bin,layer} - A_{p,i}^{bin,layer}) \quad (49)$$

Hence, by using Eq. (35):

$$\frac{dA_{p,i}^{bin,layer}}{dt} = \frac{k_{absorption} V_{layer}}{K_{p,i}^{bin,layer} M_o^{bin,layer}} (A_{g,i} K_{p,i}^{bin,layer} M_o^{bin,layer} - A_{p,i}^{bin,layer}) \quad (50)$$

### 2.3.4 Condensation/evaporation and diffusion of organic compounds

The evolution due to both condensation/evaporation and diffusion is obtained by combining the evolution due to condensation/evaporation (Eq. 50) and to diffusion alone (Eq. 38) with the assumption that the characteristic of the combined effect of condensation/evaporation and diffusion is equal to the sum of characteristic times of condensation/evaporation and diffusion).

$$\frac{dA_{p,i}^{bin,layer}}{dt} = k \left( A_{g,i} K_{p,i}^{bin,layer} M_o^{bin,layer} - A_{p,i}^{bin,layer} \right) \quad (51)$$

with  $A_{p,i}^{bin}$  of a compound  $i$  in the organic phase in the a specified bin (in  $\mu\text{g m}^{-3}$ )  $k$  computed by Eq. 52.

$$k^{-1} = \frac{1}{f_{morph}^{layer} k_{diffusion}} + \frac{K_{p,i}^{bin,layer} M_o^{bin,layer}}{k_{absorption} V_{layer}} \quad (52)$$

### 2.3.5 Characteristic time to reach equilibrium with the gas phase

The system of differential equations (51) to solve is stiff, as in the same layer/bin, some species reach equilibrium with the gas phase much quicker than others (Capaldo et al., 2000). To solve it efficiently, it is necessary to solve separately cases at equilibrium from other cases, which are solved dynamically. To determine the characteristic time to reach equilibrium with the gas phase, Eq. (51) is rewritten using the total concentrations and defining  $F_i^{bin,layer} = A_{p,i}^{bin,layer} / A_{p,i}$  (if  $A_{p,i}^{bin,layer}$  is different from zero):

$$\frac{dA_{p,i}^{bin,layer}}{dt} = k \left( A_{tot,i} K_{p,i}^{bin,layer} M_o^{bin,layer} - A_{p,i}^{bin,layer} \left( 1 + \frac{K_{p,i}^{bin,layer} M_o^{bin,layer}}{F_i^{bin,layer}} \right) \right) \quad (53)$$

This differential equation is solved by assuming that  $F_i^{bin,layer}$  and  $K_{p,i}^{bin,layer} M_o^{bin,layer}$  are constant (or do not vary much over one time step):

$$A_{p,i}^{bin,layer}(t) = A_{eq} + \left( A_{p,i}^{bin,layer}(t=0) - A_{eq} \right) * \exp\left(-\frac{t}{\tau_{eq}}\right) \quad (54)$$

with  $A_{eq}$  the concentration at equilibrium with the gas phase and  $\tau_{eq}$  the characteristic time to reach equilibrium.

$$A_{eq} = \frac{A_{tot,i} K_{p,i}^{bin,layer} M_o^{bin,layer}}{1 + \frac{K_{p,i}^{bin,layer} M_o^{bin,layer}}{F_i^{bin,layer}}} \quad (55)$$

$$\tau_{eq}^{-1} = \left( 1 + \frac{K_{p,i}^{bin,layer} M_o^{bin,layer}}{F_i^{bin,layer}} \right) k. \quad (56)$$

$\tau_{eq}$  is used to estimate the time necessary to reach equilibrium with the gas phase and therefore to identify cases that should be assumed at equilibrium when solving the system of Eq. (51)

### 2.3.6 Generalisation to several organic phases

The organic matter can be separated into several organic phases. Whereas the evolution of condensation/evaporation is dynamically modeled, phase separation and the repartition of compounds between organic phases are assumed to be at equilibrium. They are assumed to occur instantaneously: if an organic phase is saturated, it is divided instantaneously into several organic phases. The dynamic evolution due to condensation/evaporation in viscous particles is described by the following equation derived from Eq. (38) and Eq. (50) by taking into account the phase of the components:

$$\frac{dA_{p,i}^{bin,layer,phase}}{dt} = k (A_{g,i} K_{p,i}^{bin,layer,phase} M_o^{bin,layer,phase} - A_{p,i}^{bin,layer,phase}) \quad (57)$$

with  $M_o^{bin,layer,phase}$  the total organic concentrations in the specified organic phase in a specified bin and layer (in  $\mu\text{g m}^{-3}$ ),  $A_{p,i}^{bin,layer,phase}$  and  $K_{p,i}^{bin,layer,phase}$  the concentration and partitioning coefficient of the compound  $i$ .  $k$  is computed by equation (58):

$$k^{-1} = \frac{1}{f_{morph}^{layer} k_{diffusion}^{layer}} + \frac{K_{p,i}^{bin,layer,layer} M_o^{bin,layer,layer}}{k_{absorption} V_{layer}} \quad (58)$$

At each time step, thermodynamic evolution is first computed. The number of organic phases and the distribution of compounds between organic phases are then computed for each layer and each bin by assuming equilibrium between phases. To compute the concentrations with several organic phases at equilibrium we first study the conditions that have to be respected. The first condition is that the activities of each compound  $i$  are equal in each phase. For example, for two phases  $phase_1$  and  $phase_2$ :

$$\gamma_i^{bin,layer,phase_1} x_i^{bin,layer,phase_1} = \gamma_i^{bin,layer,phase_2} x_i^{bin,layer,phase_2} \quad (59)$$

The second condition, which is that each phase may be at equilibrium with the gas-phase (if condensation is too quick to be solved dynamically), can be written as:

$$\frac{A_{p,i}^{bin,layer,phase_1}}{A_{p,i}^{bin,layer,phase_2}} = \frac{A_{p,i}^{bin,layer,phase_1}}{A_g} \times \frac{A_g}{A_{p,i}^{bin,layer,phase_2}} = \frac{K_{p,i}^{bin,layer,phase_1} M_o^{bin,layer,phase_1}}{K_{p,i}^{bin,layer,phase_2} M_o^{bin,layer,phase_2}} \quad (60)$$

To respect these two conditions, the Kelvin effect must be the same for each phase.

$$\left( \exp\left(-\frac{2\sigma M_{surf}^{bin}}{RT \rho_{organic} R_p}\right) \right)^{phase_1} = \left( \exp\left(-\frac{2\sigma M_{surf}^{bin}}{RT \rho_{organic} R_p}\right) \right)^{phase_2} \quad (61)$$

$M_{surf}^{bin}$ ,  $\rho_{organic}$  and  $\sigma$  must be the same in the two phases.

Therefore, if there are several organic phases, the partitioning coefficient must be computed with the following equation:

$$K_{p,i}^{bin,layer,phase} = \frac{760 \times 8.202 \times 10^{-5} \times T}{M_{ow}^{bin,layer,phase} \gamma_{i,org}^{bin,layer,phase} P_i^0 \times 10^6} \exp\left(-\frac{2\sigma M_{surf}^{bin}}{RT \rho_{organic} R_p}\right) \quad (62)$$

with  $M_{surf}^{bin}$  the mean molar mass of all organic phases at the surface of particles.

$$M_{surf}^{bin} = \frac{\sum_i \sum_{phase} A_{p,i}^{bin,surface,phase}}{\sum_i \sum_{phase} \frac{A_{p,i}^{bin,surface,phase}}{M_i}} \quad (63)$$

The characteristic times are assumed to be the same for all the organic phases to prevent a compound from being absorbed dynamically into an organic phase whereas it is at equilibrium with another organic phase. The characteristic time is then computed according to the following equation derived from Eq. (56) and Eq. (58).

$$\tau_{eq}^{bin,layer,phase} = \frac{1}{\frac{f_{morph}^{layer} k_{diffusion}}{1 + \frac{\sum_{phase} K_{p,i}^{bin,layer,phase} M_o^{bin,layer,phase}}{f_i^{bin,layer}}} + \frac{\sum_{phase} K_{p,i}^{bin,layer,layer} M_o^{bin,layer,layer}}{k_{absorption} V_{layer}}} \quad (64)$$

### 2.3.7 Absorption into the aqueous phase

For concentrations in the organic phases, the dynamic evolution follows Eq. (57) but the dynamic evolution of concentrations in the aqueous phase follows Eq. (65) because condensation/evaporation is assumed to not be limited by diffusion in the aqueous phase and a multi-layer representation is then not useful.

$$\frac{dA_{aq,i}^{bin}}{dt} = k_{absorption} \left( A_{g,i} - \frac{A_{aq,i}^{bin}}{K_{aq,i}^{bin} A_Q^{bin}} \right) \quad (65)$$

### 2.3.8 Absorption into a particle with an aqueous phase and organic phases

Under most atmospheric conditions, particles are probably not entirely organic or entirely aqueous. The surface of particles is probably covered partially by both the organic matter and partially by the aqueous phase. Eq. (65) and (57) are still valid but  $k_{absorption}$  in Eq. (65) and (58) must be corrected to take into account that there is a chance that a compound trying to condense into a phase encounters the wrong phase, i.e. a phase into which it may not condense.

The chance for a compound to encounter  $f_{surf_{aq}}$  an aqueous phase is computed with Eq. 66:

$$f_{surf_{aq}} = \frac{S_{aq}}{S_{tot}} \quad (66)$$

with  $S_{aq}$  the surface of particles that is aqueous and  $S_{tot}$  the total surface of particles.

To evaluate this parameter, we assume that the surface of the particle is only covered by the aqueous phase and the organic phases and that the ratio of the aqueous surface over the organic surface is equal to the ratio of the volume of the aqueous phase over the volume of the organic phases:

$$f_{surf_{aq}} = \frac{V_{aq}}{V_{aq} + V_{org}} = \frac{\frac{AQ^{bin}}{\rho_{aqueous}}}{\frac{AQ^{bin}}{\rho_{aqueous}} + \sum_{layer} N_{layer} \frac{\sum_{phase} N_{phase} \frac{M_o^{bin,layer,phase}}{\rho_{organic}}}} \quad (67)$$

For the condensation in the aqueous phase, by taking into account the chance for a compound to encounter the aqueous phase,  $k_{absorption}$  is:

$$k_{absorption} = f_{surf_{aq}} \times 2\pi D_p D_{air} N^{bin} f(Kn, \alpha) \quad (68)$$

For the condensation in the organic phases, by taking into account the chance for a compound to encounter the organic phases,  $k_{absorption}$  is:

$$k_{absorption} = (1.0 - f_{surf_{aq}}) \times 2\pi D_p D_{air} N^{bin} f(Kn, \alpha) \quad (69)$$

### 2.3.9 Redistribution of compounds between layers

To use the approach described in this paper, the mass of layers must stay constant and the mass of each layer must respect the condition given by Eq. (35), which specifies the mass of the layer with respect to the total mass of the particle. However, due to rapid condensation or evaporation of the layer near the interface, concentrations of organic compounds may need to be redistributed over layers to respect this condition. If compounds are not redistributed some layers may become larger (due to the differences in fluxes) and the layer near the interface may for example become larger than the layer at the center of the particle. Moreover, as the volume of the particle changes with condensation/evaporation, the concentration of a layer can be transferred to other layers. If a particle grows due to condensation into the layer at the interface, compounds that were previously in the layer are “pushed” into more internal layers and the newly condensed compounds are at the interface layer. On the opposite, if a particle shrinks due to evaporation of the layer at the interface, the missing mass of the layer will be taken from more internal layers. For a case of evaporation, the mass of the layer at the interface may be too low (due to the more rapid evolution at the interface) and the missing mass of the layer is taken from layers at the inside of the particle, i.e. concentrations are redistributed from the outside to the inside. For a case of condensation, the mass of the layer at the interface may be too high, the exceeding mass of the layer is redistributed over the layers at the inside of the particle, i.e. concentrations are redistributed from the inside to the outside. The algorithm is detailed in Table 3.

The redistribution algorithm creates numerical diffusion as a small fraction of the mass of a layer is always transferred to other layers. This redistribution effect should decrease if the number of layers increases but it is necessary for 3D application to keep the number of layers low. However, the redistributed amount should be low compared to absorbed amount of organic compounds. Similarly, in 3D air quality model, concentrations and number of particle in size sections have to be redistributed between sections so that the bounds diameters of sections are kept constant, which does also create some numerical issues. In SOAP, the diameters of sections evolve according to the mass that condenses or evaporates (without changing the number

in sections) and there is no size redistribution between sections. However, a size-section redistribution algorithm should be added to the code if coagulation is added (for modeling purposes) or in 3D models (in which SOAP would be implemented) after the call of SOAP.

### 2.3.10 Thermodynamic equilibrium

For numerical stability, some compounds in some bins and layers are assumed to be at equilibrium with the gas phase because equilibrium is reached very fast (for example for very volatile compounds). To identify cases where equilibrium with the gas phase should be assumed, a criterion  $t_{equilibrium}$  is used. If the characteristic time to reach equilibrium with the gas phase is lower than  $t_{equilibrium}$ , the case is considered at equilibrium whereas if it is higher than  $t_{equilibrium}$ , the case is solved dynamically.

Concentrations of organic compounds in the organic phase are computed according to Eq. (70):

$$A_{p,i}^{bin,layer,phase} = conc_{i,eq} \frac{K_{p,i}^{bin,layer,phase} M_o^{bin,layer,phase}}{1 + ratio_{i,eq}} \quad (70)$$

with  $conc_{i,eq}$  the total concentration of compound  $i$  at equilibrium with the gas phase (sum of the gas-phase concentration and of organic-phase concentrations in layers and bins at equilibrium) computed with Eq. (71) and  $ratio_{i,eq}$  the ratio of the concentration of compound  $i$  at equilibrium with the gas phase in the particle phase to the concentration of  $i$  in the gas phase computed with Eq. (72) (similar to Eq. (15) for several bins, layers and phases).

$$conc_{i,eq} = A_{tot,i} - \sum_{bin} \sum_{layer} \sum_{phase} (1 - \lambda^{bin,layer,phase}) A_{p,i}^{bin,layer,phase} \quad (71)$$

$$ratio_{i,eq} = \frac{\sum_{bin} \sum_{layer} \sum_{phase} \lambda^{bin,layer,phase} A_{p,i}^{bin,layer,phase}}{A_g} \quad (72)$$

$$= \sum_{bin} \sum_{layer} \sum_{phase} \lambda^{bin,layer,phase} K_{p,i}^{bin,layer,phase} M_o^{bin,layer,phase}$$

With  $\lambda^{bin,layer,phase}$  defined such as:

$$\begin{aligned}\lambda^{bin,layer,phase} &= 1 && \text{if } \tau_{eq}^{bin,layer,phase} < t_{equilibrium} \text{ (case at equilibrium)} \\ &= 0 && \text{if } \tau_{eq}^{bin,layer,phase} \geq t_{equilibrium} \text{ (dynamic case)}\end{aligned}\tag{73}$$

The system is solved iteratively, as now detailed. The composition of the particles is first estimated using Eq. (70) to (73). If the concentrations computed from this estimation are different from those obtained in the previous iteration, a new estimation of concentrations is computed. The algorithm is detailed in Table 1. Step 7 and step 2 prevent the non-convergence due to high variations of concentrations by reducing the variations between two iterations.

Some numerical issues can arise from the equilibrium representation especially for low-volatility compounds with high value of  $t_{equilibrium}$  (for example 100 s). For these compounds, assuming equilibrium with the gas phase will give errors because these compounds will condense almost entirely on the bin with the higher organic mass instead of condensing on each bin according to the kinetics of condensation. To prevent this problem, low-volatility cases (with  $K_{p,i}^{bin,layer,phase} > 10$ ) are assumed dynamic.

### 2.3.11 Methodology used to compute the evolution of concentrations

The method used to solve the evolution of concentrations is shown in Fig. 3. As mentioned in the previous section, the model uses a hybrid method combining a dynamic representation where concentrations evolve as a function of time (for cases with characteristic times higher than a  $t_{equilibrium}$  value specified by the user) with an equilibrium representation (for cases with characteristic times lower than the  $t_{equilibrium}$  value). In the equilibrium representation, the distribution of organic compounds between phases and the gas/particle partitioning of cases with characteristic times lower than  $t_{equilibrium}$  are computed.

In the dynamic representation, concentrations evolving dynamically (cases with characteristic times higher than  $t_{equilibrium}$ ) are computed as a function of the time step with the second-order Rosenbrock scheme ROS2 (Verwer et al., 1999) for time integration. The time step can be rejected (the computation is redone with another time step) if the error between the second order

and the first order concentrations are too high (higher than an EPSEER parameter specified by the user). In that case, the time step decreases until the error is lower than EPSEER (until the time step is accepted). If the time step is very low, the ROS2 scheme increases the time step to obtain the optimal time step.

5 To compute concentrations, the model first initializes required properties (activity coefficients, the number of phases in each layer and the characteristic times). For the first time step, the model calls a first time the equilibrium representation. Once the equilibrium is reached, the model computes the dynamic evolution with the dynamic representation. Because concentrations changed, the gas/particle partitioning of cases at equilibrium changed, the equilibrium  
10 representation is then called again. For the next time steps, the dynamic and equilibrium representations are called once each, until the ending time of the simulation is reached.

### 3 Results

#### 3.1 Test cases

15 The behavior of the model is tested over two test cases using realistic concentrations and meteorological conditions. These two cases are extracted from the simulations of Couvidat et al. (2012a) and Couvidat et al. (2012b) over Europe and Paris area. The first test case corresponds to a summer period with high concentrations of biogenic SOA. The second test case corresponds to a summer period with high concentrations of anthropogenic compounds. These two test cases are referred hereafter as the “biogenic test case” and the “anthropogenic test case”.  
20 The surrogates are the same as in the aerosol model H<sup>2</sup>O, which was used by Couvidat et al. (2012a,b). The total concentrations (gas + particle) of each surrogate compound are given in Table 4. For both test cases, the liquid water content of aerosol, the pH, the ionic strength and the concentrations of inorganic ions are computed with the ISORROPIA model (Nenes et al., 1998) for a specified relative humidity (RH). The volume of the solid core of each size section  
25 is computed from the concentrations of solid species (like dust, black carbon, solid inorganic given by ISORROPIA) to compute morphology factors. In H<sup>2</sup>O, the species that are representa-

tive of primary and aged SVOC (POAIP, POAmP, POAhP, SOAIP, SOAmP and SOAhP) do not have a molecular structure attached. Therefore processes depending on the molecular structure (like absorption on the aqueous phase) are not estimated for those species. They are assumed to be hydrophobic and their influence on the activity coefficients of other species is taken into account by assigning to them a default molecular structure representative of primary aerosol and lowly oxidized compounds. This default structure is constituted of 40% of  $C_{23}H_{47}COOH$ , 5% of  $C_8H_{17}CH=CHC_7H_{14}COOH$ , 15% of 4-(2-propio)-syringone, 12% of  $C_{29}H_{60}$  and 28% of 2-carboxybenzoic acid based on (EPRI, 1999). In SOAP, the same default structure as in  $H_2O$  can be used if the user does not provide a molecular structure.

## 3.2 Equilibrium representation

### 3.2.1 Influence of activity coefficients on organic aerosol formation (without phase separation of the organic phase)

The effect of non-ideality on aerosol concentrations is strong and complex. To determine the impact of non-ideality, tables 5 and 6 show respectively with and without the ideality assumption the concentrations of organic aerosol for both test cases formed from the various precursors as well as the concentrations of water. The compounds are here assumed to be both hydrophilic and hydrophobic except for the species POAIP, POAmP, POAhP, SOAIP, SOAmP and SOAhP, which are simply assumed to be hydrophobic, with the default molecular structure used in Couvidat et al. (2012a).

Concentrations of compounds in the organic phase tend to decrease strongly when non-ideality is assumed (except for aromatics in the biogenic case due to non-linear effects), especially for the compounds formed from isoprene oxidation (most of them are very hydrophilic and therefore have low affinity with very hydrophobic compounds) and for some of the compounds formed from monoterpenes. Concentrations of hydrophilic compounds in the aqueous phase either increase or decrease depending on conditions. For the compounds formed from isoprene oxidation, their concentrations increase from  $0.70 \mu g m^{-3}$  for ideality to  $1.24 \mu g m^{-3}$  in the biogenic case for non-ideality with long, medium and short ranges interactions and to

1.29  $\mu\text{g m}^{-3}$  for non-ideality with only short-range interactions. It seems to indicate that in this case short-range interactions between organic compounds tend to stabilize hydrophilic organic compounds in the aqueous phase whereas medium-range and long-range interactions between organic and inorganic compounds tend to destabilize hydrophilic organic compounds. These results are consistent with the result of previous study (Couvidat et al., 2012a) where assuming ideality at infinite dilution can lead to an underestimation of the concentrations of hydrophilic species inside the aqueous phase of particles. Therefore, the concentrations of hydrophilic organic compounds in the aqueous phase probably depend strongly on other compounds and on the non ideality of aerosols.

Determining a priori if a compound is hydrophilic or hydrophobic is not straightforward. Table 7 shows that some compounds seem clearly hydrophobic (BiA2D, BiA1D, AnB1P, BiB1P, BiBmP, AnC1P, BiNGA, BiNIT3, BiNIT) or hydrophilic (BiA0D) as they partition only into one phase. However, some compounds are present in both the organic and aqueous phases. AnBmP seems to be both hydrophilic and hydrophobic and can change of phase depending on conditions. Moreover, BiA2D, BiA1D and BiMGA were assumed to be hydrophilic in  $\text{H}_2\text{O}$  whereas it seems from these test cases that they are mainly hydrophobic. The fact that these compounds were assumed hydrophilic is probably due the choice of a criterium not representative of all atmospheric conditions. BiA2D and BiA1D were assumed hydrophilic based on their octanol/water coefficient (Pun et al., 2006), which is probably not representative of atmospheric conditions. BiMGA was assumed hydrophilic based on the results of Couvidat and Seigneur (2011). According to this study, BiMGA condenses mostly on the aqueous phase if the liquid water content of aerosols is high (superior to the concentration of the organic phase), which is not the case in the two test cases. Moreover, if medium-range and long-range interactions are not taken into account, the distribution of the compounds between phases change significantly. For the biogenic test case, if medium-range and long-range interactions are not taken into account as in Couvidat and Seigneur (2011), the fraction in the organic phase decreases from 75% to 33% for particulate BiA2D, from 89% to 46% for particulate BiA1D. For the anthropogenic test case, the fraction in the organic decreases, from 99% to 76% for particulate BiA2D, from 100% to 85% for particulate BiA1D and from 59% to 46% for particulate BiMGA. It is there-

fore possible for these compounds to be present in both phases depending on conditions.

### 3.2.2 Saturation and phase separation

Species having very different properties do not mix well together and phase separation can be computed by Gibbs energy minimization (see section 2.2.4). Table 8 presents the concentrations with or without phase separation for the biogenic test case at RH=30% without an aqueous phase. In this case, without phase separation, both hydrophilic and hydrophobic compounds want to condense into the organic phase which is mainly constituted by hydrophobic compounds. Assuming phase separation in this case does not strongly influence concentrations of hydrophobic compounds, which decrease slightly. However, a second organic phase is created by phase separation which is constituted mainly by very oxidized compounds (BiPER, BiDER and BiMGA). For the anthropogenic case, at RH=30%, phase separation do not happen because the concentrations of hydrophilic compounds are too low for the organic phase to be saturated.

Another organic phase may be created if there are compounds with low oxidation state. For the biogenic case at low humidity, if the structure of nonadecane is used to represent the compounds POAIP, POAmP, POAhP, SOAIP, SOAmP and SOAhP (without a molecular structure; these compounds only condense on the less oxidized phase without impacting phase separation), a third organic phase may be created. Compounds with low oxidation state may not readily mix with slightly oxidized compounds which in turn may not readily mix with more oxidized compounds.

### 3.3 Dynamic representation

For this approach, users must choose the diffusion coefficients because there is currently, to our knowledge, no method to estimate diffusion coefficients of the organic phase as a function of the composition of organic aerosols. In the following tests, the same diffusion coefficient is used for all organic compounds. The dynamic approach is tested for various humidities and various diffusion coefficients for the biogenic and anthropogenic cases. Figures 4 and 5 show the con-

centrations in the organic phase for the biogenic and anthropogenic cases respectively whereas Figures 6 and 7 show concentrations in the aqueous phase for the biogenic and anthropogenic cases respectively. The influence of the  $t_{equilibrium}$  parameter is also tested in these figures. For all the compounds, the gas-phase diffusion coefficient is taken equal to  $0.1 \text{ cm}^2/\text{s}$  which is the order of magnitude of this parameter (Seinfeld and Pandis, 1998) and the accommodation coefficient (value between 0 and 1) is taken equal to 0.5 so that condensation is mainly limited by diffusion in the organic phase, which is the main phenomenon that we want to study here. These two parameters are used for Eq. (68) and (69).

The two test cases show similar results. At low humidity without an aqueous phase, compounds only condense on the organic matter. For these conditions, with a diffusion constant of  $10^{-20} \text{ m}^2/\text{s}$ , the organic aerosol reaches equilibrium within a few hours. For diffusion coefficient lower than  $10^{-20} \text{ m}^2/\text{s}$ , the formation of organic aerosol is strongly limited by diffusion. At higher humidity with an aqueous phase, for the same diffusion coefficient, the aerosol is much slower to reach equilibrium because the mean diameter of each bin is higher (due to the important concentration of water in particles). Therefore, for constant diffusion coefficients, as particles get larger, characteristic times to reach equilibrium get higher at high humidity. However, diffusion coefficients are probably much higher at high humidity than at low humidity because the organic phases would be less viscous (less oligomerization due to esterification for example and more water in the organic phase which would decrease viscosity) as shown by Saukko et al. (2012); Renbaum-Wolff et al. (2013). It may then be possible that at high humidity, organic aerosols reach equilibrium quicker than at low humidity. A method to estimate diffusion coefficients as a function of composition (or at least of as a function of humidity) is needed to properly represent this phenomenon.

For diffusion coefficients of  $10^{-21} \text{ m}^2/\text{s}$  or lower, using a  $t_{equilibrium}$  parameter of 100 s gives a good approximation of the results (no strong differences with a  $t_{equilibrium}$  parameter of 1 s) whereas for higher diffusion coefficients the differences with a  $t_{equilibrium}$  parameter of 1s are more important. However, these differences are generally low and become negligible after a few hours. For 0D applications where time consumption is not a limiting factor, it is recommended to use a low  $t_{equilibrium}$  parameter. However, for 3D applications, the dynamic approach is very

time consuming and it is therefore interesting to use higher  $t_{equilibrium}$  parameter.

### 3.4 Time analysis

Table 9 shows the computation time necessary to solve the biogenic case at RH=70% (relative to the time necessary to solve the case with an uncoupled and ideal system) for different configurations of the model. For the dynamic approach, the length of the computation corresponds to 600s (corresponding to a time step of a simulation with the Polyphemus air quality platform over Europe (Sartelet et al., 2007)), initial concentrations are assumed to be 80% of concentrations at equilibrium and an organic phase diffusion coefficient of  $10^{-21}$  m<sup>2</sup>/s is used. The times given here correspond to a specific case and therefore can greatly vary with initial conditions and with the chosen parameters for the numerical resolution of the system. They are provided here on an indicative basis. The dynamic approach is around 300 times slower than the equilibrium approach, making its applicability limited to short-term 3D simulations.

More reliable and complete information about the computation time cost will be provided in future studies about the implementation of the SOAP in an air quality model.

## 4 Conclusions

The Secondary Organic Aerosol Processor model is a modular model, which can compute the condensation/evaporation of organic aerosol according to two different approaches: an equilibrium approach and a dynamic approach. In the equilibrium approach, concentrations in the particle phase are assumed at equilibrium with concentrations in the gas phase. In the dynamic approach, concentrations evolve according to the kinetics of condensation and evaporation of organic compounds. The dynamic approach uses a multi-layer representation of particles to represent the particle-phase diffusion of organic compounds. Future works will focus on improving the framework of this dynamic approach to take into account varying diffusion coefficients with layers, to represent layer exchanges and transfers between the organic and the aqueous phases. Simulations with SOAP and comparisons to measurements should be performed to validate the

model and to test the influence of each process and parameter on organic aerosol formation. Comparison to a model like KM-GAP can also be useful for validation and for the development of layer exchange processes.

To improve the representation of aerosols, several processes should be added to the model.

- 5 First, interactions between organic and inorganic compounds should be fully taken into account via activity coefficients. Currently, only the influence of inorganic compounds on organic compounds is taken into account. However, organic compounds can also impact the formation of inorganic compounds due to those interactions. This process could be taken into account by adding inorganic aerosol formation to SOAP. Second, a method to estimate diffusion coefficients in the organic phase should be developed, as it is expected that composition of the organic phase greatly influences the viscosity and therefore diffusion coefficients of organic compounds. Finally, the model could be coupled to a solver for particle-phase chemistry and then represent processes such as oligomerization, which could affect the viscosity of the organic phase.

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## 5 Notations

$A_{eq}$	the concentration in the organic phase at equilibrium
$A_{g,i}$	the concentration of $i$ in the gas phase (in $\mu\text{g m}^{-3}$ )
$A_{p,i}$	the concentration of $i$ in the organic phase (in $\mu\text{g m}^{-3}$ )
$A_{p,i}^{bin}$	the concentration of $i$ in the organic phase (in $\mu\text{g m}^{-3}$ ) in a diameter bin
$A_{p,i}^{bin,layer}$	the concentration of $i$ in the organic phase (in $\mu\text{g m}^{-3}$ ) in a diameter bin and in a layer of the particle
$A_{aq,i}$	the concentration of $i$ in the aqueous phase (in $\mu\text{g m}^{-3}$ )
$A_{aq,i}^{bin}$	the concentration of $i$ in the aqueous phase in a diameter bin (in $\mu\text{g m}^{-3}$ )
$A_{tot,i}$	the concentration of $i$ in all phases (in $\mu\text{g m}^{-3}$ )

AQ	total mass of the aqueous phase including organic compounds (in $\mu\text{g m}^{-3}$ )
$AQ^{bin}$	total mass of the aqueous phase including organic compounds in a bin (in $\mu\text{g m}^{-3}$ )
C	concentration (in M)
$C_s$	concentration at the surface of the particle (in M)
$D_p$	diameter of the particle (in m)
$D_{air}$	diffusivity of the compound in air (in $\text{m}^2/\text{s}$ )
$D_{org}$	diffusivity of the compound in the organic phase (in $\text{m}^2/\text{s}$ )
$F_i^{bin,layer}$	fraction of $A_{p,i}$ in a diameter bin and in a layer of the particle
$f_{morph}^{layer}$	morphology factor
$f_{surf_{aq}}$	the chance for a compound to encounter an aqueous phase at the surface of the particle
$f(\text{Kn},\alpha)$	transition regime formula
G	Gibbs energy
$H_i$	Henry's law constant (in M/atm)
$K_{aq,i}$	the aqueous-phase partitioning coefficient
$K_{aq,i}^{bin}$	the aqueous-phase partitioning coefficient of a diameter bin
$K_{p,i}$	the organic-phase partitioning coefficient
$K_{p,i}^{bin,layer}$	the organic-phase partitioning coefficient of a diameter bin and of a layer of the particle
k	kinetic rate parameter of the absorption-diffusion equation
$k_{absorption}$	kinetic rate parameter of the absorption equation
$k_{diffusion}$	kinetic rate parameter of the diffusion equation
Kn	Knudsen number
$N_{layer}$	number of layers
$M_{aq}$	mean molar mass of the aqueous phase (in g/mol)
$M_i$	mean molar mass of i (in g/mol)
$m_i$	mass of i in a particle
$m_i^{bin}$	mass of i in a particle of the bin
$M_o$	concentration of the organic phase (in $\mu\text{g m}^{-3}$ )

$M_o^{bin}$	concentration of the organic phase in a diameter bin (in $\mu\text{g m}^{-3}$ )
$M_o^{bin,layer}$	concentration of the organic phase in a diameter bin and in a layer of the particle (in $\mu\text{g m}^{-3}$ )
$M_{ow}$	mean molar mass of the organic phase (in g/mol)
$M_{water}$	molar mass of water
$n_i^\phi$	number of moles of compound i in the phase $\phi$
$N^{bin}$	number of particles in a diameter bin (in $\text{m}^{-3}$ )
$P_i^0$	the saturation vapor pressure of i
$P_i$	partial pressure of i
$P_{eq,i}$	partial pressure of i at equilibrium (taking into account the kelvin effect)
R	the ideal gas constant
$R_p$	the rayon of the particle (in m)
$S_{aq}$	surface of particles covered by an aqueous phase
$S_{tot}$	surface of particles
RH	the relative humidity
T	the temperature
$T_{ref}$	the temperature of reference at which $P_i^0$ is determined
$V_{layer}$	volume fraction of the layer
$V_{aq}$	volume of the aqueous phase
$V_{org}$	volume of the organic phase
$X_{i,aq}$	molar fraction of i in the aqueous phase
$X_{i,org}$	molar fraction of i in the organic phase
$\alpha$	accommodation coefficient
$\alpha_{layer}$	ratio of the characteristic time for diffusion of the layer to the characteristic time for diffusion of the center of the particle
$\gamma_{i,aq}$	activity coefficient of i in the aqueous phase
$\gamma_{i,aq}^\infty$	activity coefficient of i at infinite dilution in water
$\gamma_{i,org}$	activity coefficient of i in the organic phase
$\gamma_{water,aq}$	activity coefficient of water in the aqueous phase

$\gamma_{water,org}$	activity coefficient of water in the organic phase
$\Delta H_i$	enthalpy of vaporization of i (in J/mol)
$\mu_i^\phi$	chemical potential of i
$\xi_i$	activity coefficient of i in the aqueous phase by reference to infinite dilution
$\tau_{dif}$	characteristic time for diffusion
$\tau_{eq}$	characteristic time to reach equilibrium

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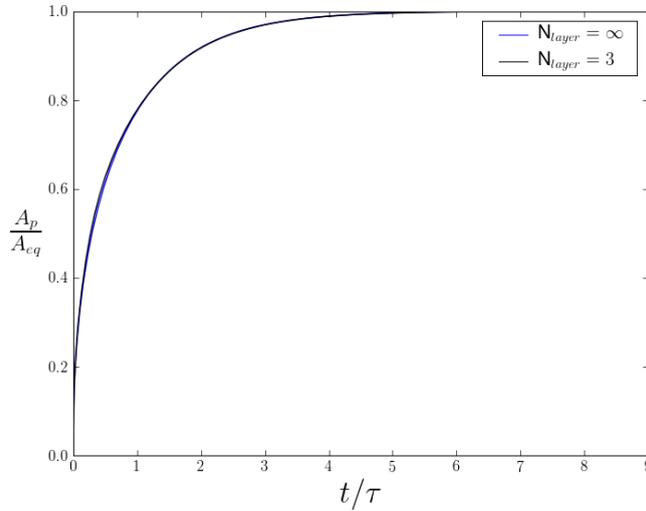
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5



**Fig. 1.** Evolution of the ratio  $A_p(t)/A_{eq}$  as a function of the ratio  $t/\tau_{dif}$ .

While the system has not converged (or has not reached a maximum number of iterations):

1.  $n = 1$

2. factor =  $1/n$

3. Compute the new estimation of the concentrations  $A_{p,i,new}^{bin,layer,phase}$  according to Eq. 70.

4. Errors =  $(A_{p,i,new}^{bin,layer,phase} - A_{p,i}^{bin,layer,phase}) / A_{p,i}^{bin,layer,phase}$  5.  $A_{p,i}^{bin,layer,phase} = \text{factor} \times$

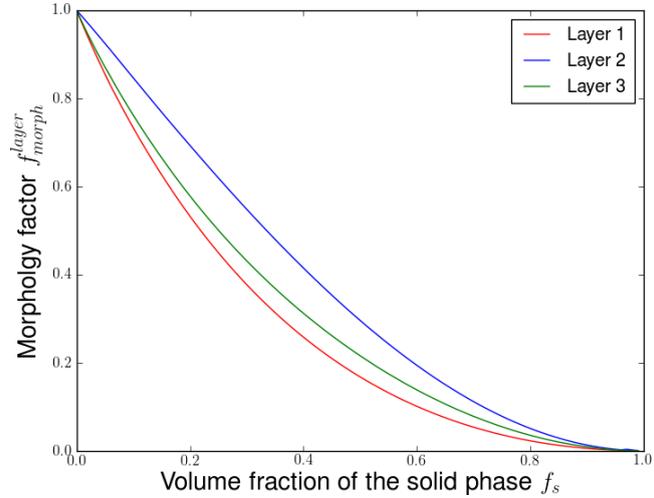
$A_{p,i,new}^{bin,layer,phase} + (1 - \text{factor}) \times A_{p,i}^{bin,layer,phase}$

6. Compute  $M_o^{bin,layer,phase}$

7. If the system can not converge (the system is in a situation where relative errors on concentrations between two steps does not change or return to old values),  $n = n + 1$

8. If the system has not converged (relative errors on concentrations between two steps are too high), return to step 2

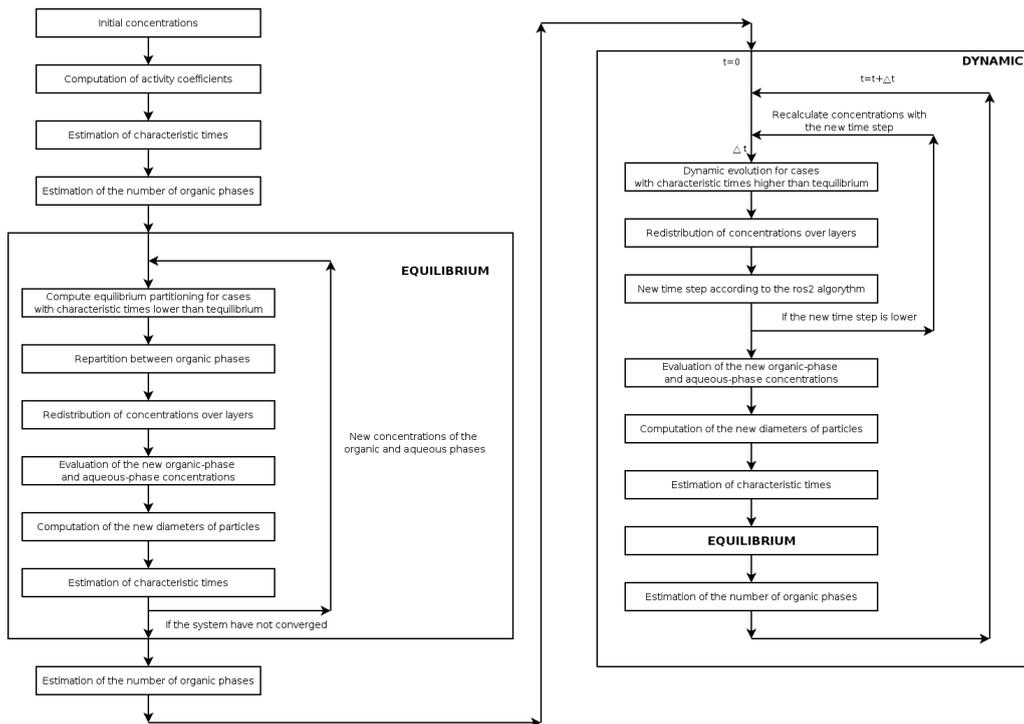
**Table 1.** Algorithm to compute the partitioning of compounds at equilibrium in the dynamic approach.



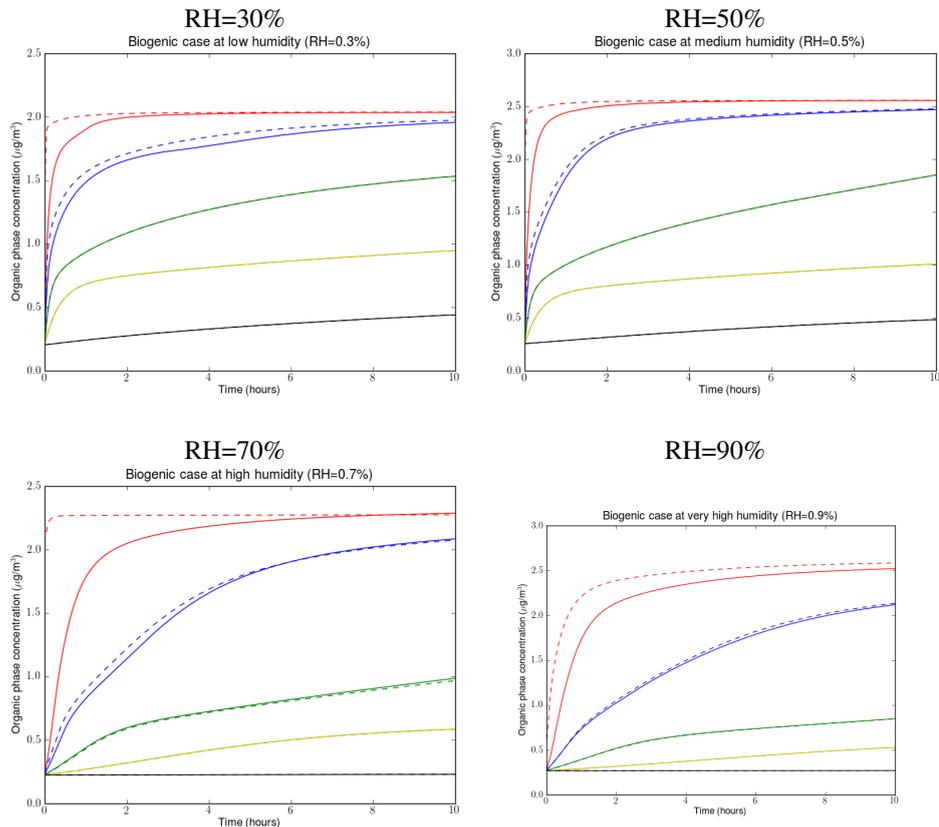
**Fig. 2.** Morphology factors as a function of the volume fraction of the solid phase.

layer	$A_{layer}$	$B_{layer}$	$C_{layer}$	$D_{layer}$
1	0.7441	-2.4296	3.6701	-2.9847
2	-0.2080	0.8614	-0.1099	-1.5436
3	0.8333	-2.2574	3.0645	-2.6404

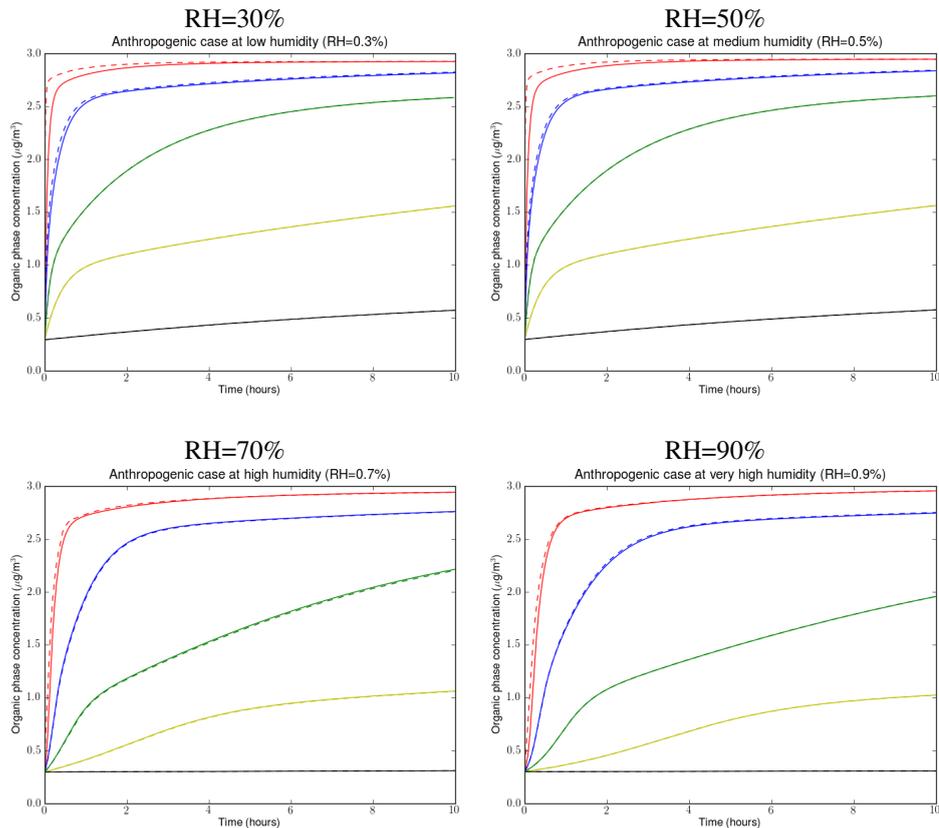
**Table 2.** Polynomial parameters for Eq. (39).



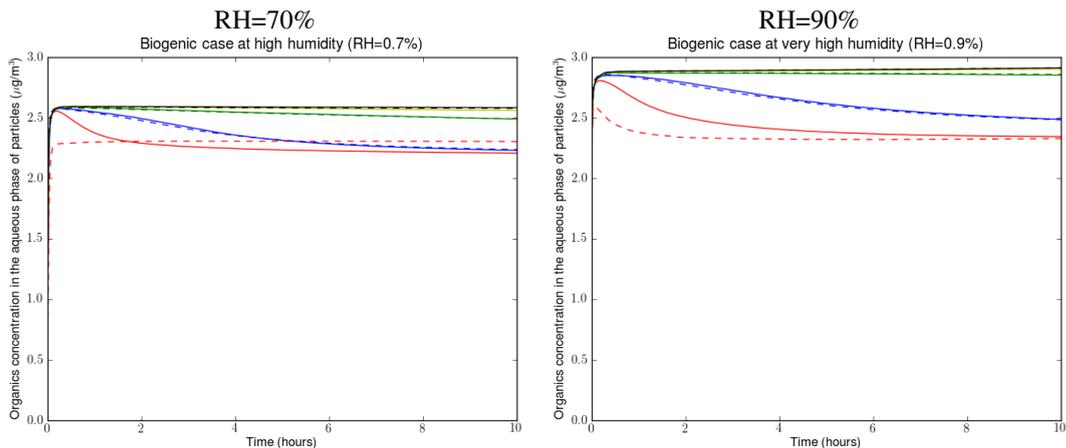
**Fig. 3.** Diagram of the method used to compute the evolution of concentrations.



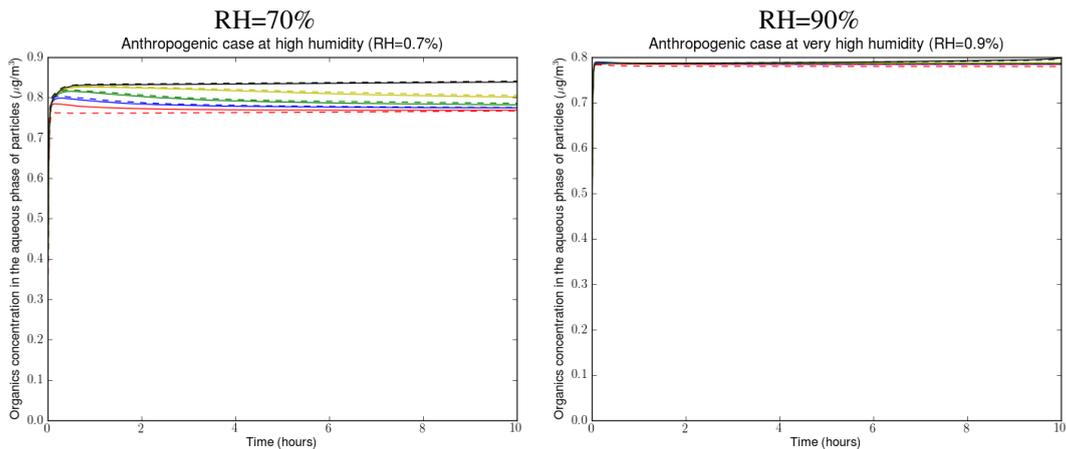
**Fig. 4.** Evolution of concentrations in organic phases for the biogenic case at various humidities, with initial concentrations equal to tenth the concentrations at equilibrium for  $t_{\text{equilibrium}}=1\text{ s}$  (plain lines) and  $t_{\text{equilibrium}}=100\text{ s}$  (dashed lines) for several organic-phase diffusivity:  $D_{\text{org}}=10^{-19}\text{ m}^2/\text{s}$  (red),  $D_{\text{org}}=10^{-20}\text{ m}^2/\text{s}$  (blue),  $D_{\text{org}}=10^{-21}\text{ m}^2/\text{s}$  (green),  $D_{\text{org}}=10^{-22}\text{ m}^2/\text{s}$  (yellow) and  $D_{\text{org}}=10^{-24}\text{ m}^2/\text{s}$  (black).



**Fig. 5.** Evolution of concentrations in organic phases for the anthropogenic case at various humidities, with initial concentrations equal to tenth the concentrations at equilibrium for  $t_{equilibrium} = 1 \text{ s}$  (plain lines) and  $t_{equilibrium} = 100 \text{ s}$  (dashed lines) for several organic-phase diffusivity:  $D_{org} = 10^{-19} \text{ m}^2/\text{s}$  (red),  $D_{org} = 10^{-20} \text{ m}^2/\text{s}$  (blue),  $D_{org} = 10^{-21} \text{ m}^2/\text{s}$  (green),  $D_{org} = 10^{-22} \text{ m}^2/\text{s}$  (yellow) and  $D_{org} = 10^{-24} \text{ m}^2/\text{s}$  (black).



**Fig. 6.** Evolution of concentrations in the aqueous phase for the biogenic case at various humidities, with initial concentrations equal to tenth the concentrations at equilibrium for  $t_{equilibrium}=1$  s (plain lines) and  $t_{equilibrium}=100$  s (dashed lines) for several organic-phase diffusivity:  $D_{org}=10^{-19}$  m<sup>2</sup>/s (red),  $D_{org}=10^{-20}$  m<sup>2</sup>/s (blue),  $D_{org}=10^{-21}$  m<sup>2</sup>/s (green),  $D_{org}=10^{-22}$  m<sup>2</sup>/s (yellow) and  $D_{org}=10^{-24}$  m<sup>2</sup>/s (black).



**Fig. 7.** Evolution of concentrations in the aqueous phase for the anthropogenic case at various humidities, with initial concentrations equal to tenth the concentrations at equilibrium for  $t_{equilibrium}=1 \text{ s}$  (plain lines) and  $t_{equilibrium}=100 \text{ s}$  (dashed lines) for several organic-phase diffusivity:  $D_{org}=10^{-19} \text{ m}^2/\text{s}$  (red),  $D_{org}=10^{-20} \text{ m}^2/\text{s}$  (blue),  $D_{org}=10^{-21} \text{ m}^2/\text{s}$  (green),  $D_{org}=10^{-22} \text{ m}^2/\text{s}$  (yellow) and  $D_{org}=10^{-24} \text{ m}^2/\text{s}$  (black).

For each bin:

If the new mass of organics  $M_o^{bin,new} = \sum_{layer} \sum_{phase} M_o^{bin,layer,phase,new}$  is higher than the mass at previous iteration or time step (before adding new compounds)  $M_o^{bin,old}$ , the redistribution is done from the interface layer to the center of the particle: from  $ilayer=N_{layer}$  to 2,  $ilayer2=ilayer-1$ .

If the new mass of organics  $M_o^{bin,new} = \sum_{layer} \sum_{phase} M_o^{bin,layer,phase,new}$  is lower than the mass at previous iteration or time step (before adding new compounds)  $M_o^{bin,old}$ , the redistribution is done from the center of the particle to the interface layer: from  $ilayer=1$  to  $N_{layer}-1$ ,  $ilayer2=ilayer+1$ :

If the mass of the layer increased:

Mass to be redistributed:

$$\Delta M = M_o^{bin,layer,new} - \alpha_{layer} * M_o^{bin,new}$$

Fraction of concentrations to redistribute:

$$f = \frac{\Delta M}{M_o^{bin,layer,new}}$$

The exceeding mass of the layer is transmitted to the next layer (ilayer 2):

$$A_p^{bin,layer2,phase} = A_p^{bin,layer2,phase} + f * A_p^{bin,layer,phase}$$

$$A_p^{bin,layer,phase} = (1-f) * A_p^{bin,layer,phase}$$

If the mass of the layer decreased:

Mass to be redistributed:

$$\Delta M = \alpha_{layer} * M_o^{bin,new} - M_o^{bin,layer,new}$$

Fraction of concentrations to redistribute from the next layer (ilayer2):

$$f = \frac{\Delta M}{M_o^{bin,layer2,new}}$$

The missing mass of the layer is taken from the next layer (ilayer 2):

$$A_p^{bin,layer,phase} = A_p^{bin,layer,phase} + f * A_p^{bin,layer2,phase}$$

$$A_p^{bin,layer2,phase} = (1-f) * A_p^{bin,layer2,phase}$$

**Table 3.** Algorithm to compute the redistribution of compounds between layers.

Compounds	Concentration ( $\mu\text{g m}^{-3}$ ) Biogenic test case at T = 295 K	Concentration ( $\mu\text{g m}^{-3}$ ) Anthropogenic test case at T = 293 K	Assumed type in H <sup>2</sup> O
BiA2D	0.07	0.02	hydrophilic
BiA1D	0.74	0.20	hydrophilic
BiA0D	1.02	0.58	hydrophilic
BiPER	1.46	0.17	hydrophilic
BiDER	0.45	0.06	hydrophilic
BiMGA	0.25	0.05	hydrophilic
AnBIP	0.03	0.05	hydrophobic
AnBmP	0.27	0.32	hydrophobic
BiBIP	0.09	0.03	hydrophobic
BiBmP	0.22	0.07	hydrophobic
AnCIP	0.07	0.03	hydrophobic
BiNGA	0.21	0.05	hydrophobic
BiNIT3	0.13	0.02	hydrophobic
BiNIT	0.44	0.13	hydrophobic
POAIP	0.10	0.71	hydrophobic
POAmP	0.02	0.69	hydrophobic
POAhP	0.03	0.91	hydrophobic
SOAIP	0.36	0.65	hydrophobic
SOAmP	0.70	1.35	hydrophobic
SOAhP	1.72	2.51	hydrophobic
H <sub>2</sub> SO <sub>4</sub>	1.70	1.44	
HNO <sub>3</sub>	1.83	5.07	
NH <sub>3</sub>	1.07	1.77	

**Table 4.** Conditions of the test cases and type of each compound.

	Biogenic test case		Anthropogenic test cases	
	$A_p$ ( $\mu\text{g m}^{-3}$ )	$A_{aq}$ ( $\mu\text{g m}^{-3}$ )	$A_p$ ( $\mu\text{g m}^{-3}$ )	$A_{aq}$ ( $\mu\text{g m}^{-3}$ )
monoterpenes	0.83	1.01	0.22	0.58
sesquiterpenes	0.28	0.0	0.10	0.0
isoprene	0.89	0.70	0.13	0.12
aromatics	0.09	0.05	0.09	0.04
primary SVOC	0.09	0	0.70	0.0
oxidised primary SVOC	1.22	0	2.28	0.0
Water	0.66	1.86	0.48	2.68

**Table 5.** Concentrations of organic aerosols formed for each precursor for both test cases at RH=70% if ideality is assumed.

	Biogenic test case		Anthropogenic test cases	
	$A_p$ ( $\mu\text{g m}^{-3}$ )	$A_{aq}$ ( $\mu\text{g m}^{-3}$ )	$A_p$ ( $\mu\text{g m}^{-3}$ )	$A_{aq}$ ( $\mu\text{g m}^{-3}$ )
monoterpenes	0.44	1.10	0.14	0.55
sesquiterpenes	0.19	0.0	0.08	0.0
isoprene	0.18	1.24	0.02	0.13
aromatics	0.09	0.16	0.07	0.01
primary SVOC	0.08	0	0.68	0.0
oxidised primary SVOC	1.04	0	2.18	0.0
Water	0.06	1.05	0.06	2.75

**Table 6.** Concentrations of organic aerosols formed for each precursor for both test cases at RH=70% if non-ideality is assumed (with short-range, medium-range and long-range interactions).

Compound	Fraction of the compound in the organic phase (in %)	
	Biogenic test case	Anthropogenic test case
BiA2D	75	99
BiA1D	89	100
BiA0D	0	0
BiPER	2	3
BiDER	2	1
BiMGA	80	59
AnBIP	75	100
AnBmP	6	50
BiBIP	99	100
BiBmP	100	100
AnCIP	100	100
BiNGA	98	99
BiNIT3	70	97
BiNIT	97	100

**Table 7.** Distributions of surrogate organic compounds between the aqueous phase and the organic phase.

Compound	Without saturation $A_p$	With saturation		
		1 <sup>st</sup> phase	2 <sup>nd</sup> phase	all phases
BiA2D	0.042	0.037	0.005	0.042
BiA1D	0.322	0.299	0.021	0.320
BiA0D	0.001	0.0	0.001	0.0
BiPER	0.031	0.026	0.030	0.056
BiDER	0.015	0.011	0.048	0.059
BiMGA	0.027	0.020	0.040	0.060
AnBIP	0.012	0.011	0.001	0.012
AnBmP	0.012	0.010	0.010	0.020
BiBIP	0.092	0.091	0.001	0.092
BiBmP	0.098	0.096	0.0	0.096
AnCIP	0.069	0.069	0.0	0.069
BiNGA	0.062	0.051	0.020	0.071
BiNIT3	0.010	0.010	0.001	0.011
BiNIT	0.043	0.041	0.001	0.042
POAIP	0.076	0.075	0.0	0.075
POAmP	0.001	0.0	0.0	0.0
POAhP	0.0	0.0	0.0	0.0
SOAIP	0.356	0.356	0.0	0.356
SOAmP	0.532	0.527	0.0	0.527
SOAhP	0.132	0.127	0.0	0.127
Water	0.020	0.018	0.012	0.030
Sum of organics	1.933	1.857	0.173	2.035

**Table 8.** Concentrations (in  $\mu\text{g m}^{-3}$ ) with or without phase separation for the biogenic test case at RH=30%.

Coupled system	Phenomena taken into account			Time for	
	Short range interactions	Long and medium range interactions	Organic phase separation	Equilibrium approach	Dynamic approach
X				1	300
	X			1.6	450
X	X			5	1700
	X	X		20	4800
X	X	X		9	2000
	X	X	X	25	4800
X	X	X	X	20	2000
	X	X	X	90	4800

**Table 9.** Time necessary to solve the biogenic case at RH=70% (relative to the time necessary to solve the case with an uncoupled system with ideality) for different configurations of the model.