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F. Couvidat and
K. Sartelet

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

F. Couvidat^{1,*} and K. Sartelet¹

¹CEREA, Joint Laboratory École des Ponts ParisTech/EDF R&D, Université Paris-Est, 77455 Marne-la-Vallée, France

* now at: Institut National de l'Environnement Industriel et des Risques, Verneuil-en-Halatte, France

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Correspondence to: F. Couvidat (florian.couvidat@ineris.fr)

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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 on the aqueous phase of particles, activity coefficients, phase separation).

Each surrogate can be hydrophilic (condenses only on the aqueous phase of particles), hydrophobic (condenses only on the organic phase of particles) or both (condenses on 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 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 dynamic representation of secondary organic aerosols (SOA) is used with OA divided into layers, the first layer at the center of the particle (slowly reaches equilibrium) and the final layer near the interface with the gas phase (quickly reaches equilibrium).

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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 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, they 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 3-D 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 because they can be highly viscous liquid (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 organics 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., 2012, 2013) and the Model to Predict the Multiphase Partitioning of Organics (MPMPO)

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(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 separation of organic matter into several phases due to saturation. Moreover, AEC and H^2O contrary to MPMPO, assume condensation only on 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 but does not take into account the non-ideality of the organic phase.

To represent organic aerosol formation and take into account the previous phenomenon as accurately as possible, the Secondary Organic Aerosol Processor (SOAP), destined to be implemented in 3-D air quality models is developed. 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 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 compounds 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^2O and AEC has been developed. It uses a molecular surrogate approach and distinguishes two types of surrogate SOA species: hydrophilic species (which condense only into an aqueous phase except

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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 on all phases as in MPMPO) depending on user specification. The process already present in H²O (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.

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 H²O. Similarly to H²O, the model uses a method of Newton-Raphson to efficiently compute the partitioning of each compounds 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 particle size distribution is divided into sections (inside a section/bin, all particles have the same diameters). Inside a bin, compounds condense on the aqueous phase or/and the organic matter. Furthermore, each bin can be separated into several phases and several layers.

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

2.2 Organic aerosol formation at equilibrium

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:

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

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

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

- 10 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).

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

- 15 with T the temperature (in K), M_{ow} the mean molar mass of the organic phase (in g mol^{-1}) and the saturation vapour pressure P_i^0 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 is generally determined experimentally at a temperature T_{ref} . The partitioning coefficient is extrapolated from T_{ref} to T
- 20 by using the enthalpy of vaporization ΔH_i (in J mol^{-1}) according to the Clausius–Clapeyron

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equation.

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

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

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

with RH the relative humidity, M_{water} the molar mass of water (in g mol^{-1}) and $\gamma_{\text{water,org}}$ 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 formation of inorganic aerosol, which must be computed previously with an inorganic aerosol model like ISORROPIA (Nenes et al., 1998) to provide input for the model such as pH, concentrations of inorganic ions, ionic strength and the liquid water content of aerosols.

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

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

with $\gamma_{i,\text{aq}}$ the activity coefficient of i in the aqueous phase and $X_{i,\text{aq}}$ 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 $M \text{ atm}^{-1}$).

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

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

5 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) of the aqueous phase (in $\mu\text{g m}^{-3}$) and $K_{aq,i}$ the aqueous-phase partitioning coefficient (in $\text{m}^3 \mu\text{g}^{-1}$) which is computed with Eq. (9).

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

10 with ρ_{water} the density of the aqueous phase (in kg m^{-3}), M_{aq} the molar mass of the aqueous phase (in g mol^{-1}) which can be slightly different from the molar mass of water due to the presence of other compounds and ζ_i the activity coefficient by reference to infinite dilution. ζ_i is computed with Eq. (10).

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

15 where $\gamma_{i,\text{aq}}^{\infty}$ is the activity coefficient at infinite dilution in water, which is computed with UNIFAC. However, UNIFAC only compute 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).

$$20 \gamma_{i,\text{aq}} = \gamma_{\text{LR}} \gamma_{\text{MR}} \gamma_{\text{SR}}, \quad (11)$$

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γ_{LR} , γ_{MR} and γ_{SR} are respectively the activity coefficients at long, medium and short range interactions. γ_{SR} is computed with UNIFAC whereas γ_{LR} and γ_{MR} are computed with the AIOMFAC method and parameters (Zuend et al., 2008, 2011; Zuend and Seinfeld, 2012) and model the influence of inorganic ions on the partitioning of organic compounds.

Similarly to the case of condensation onto an organic phase (Eq. 4) The partitioning coefficient is extrapolated from T_{ref} to T by using the enthalpy of vaporization ΔH_i (in J mol^{-1}) with Eq. (12).

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

Moreover, some compounds are acids that can dissociate in the aqueous phase. 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 amount of water 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.

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 compounds if it is hydrophilic

(condense on the aqueous of particles) or hydrophobic (condense on the organic phase of particles) or hydrophilic and hydrophobic (condense on both phases). If there are no compound which is both hydrophilic and hydrophobic, the condensation on the organic phase can be solved separately from the condensation on the aqueous phase.

5 The system is then uncoupled. On the opposite, if there is at least one compound which is hydrophilic and hydrophobic, the condensation on the organic phase and the condensation on the aqueous phase must be solved simultaneously. The system is then coupled and consumes more CPU time.

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

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

which gives when combined to Eq. (2):

$$A_{\text{p},i} = A_{\text{tot},i} \frac{K_{\text{p},i} M_0}{1 + K_{\text{p},i} M_0}. \quad (15)$$

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):

$$\text{error} = M_0 - \sum_i A_{\text{tot},i} \frac{K_{\text{p},i} M_0}{1 + K_{\text{p},i} M_0}. \quad (16)$$

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

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

20 which gives if combined to Eq. (8):

$$A_{\text{aq},i} = A_{\text{tot},i} \frac{K_{\text{aq},i} \text{AQ}}{1 + K_{\text{aq},i} \text{AQ}}. \quad (18)$$

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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).

$$\text{error} = \text{AQ} - \text{inorganics} - \sum_i A_{\text{tot},i} \frac{K_{\text{aq},i} \text{AQ}}{1 + K_{\text{aq},i} \text{AQ}} \quad (19)$$

For a coupled system, the total concentration of i in all phases $A_{\text{tot},i}$ is:

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

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

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

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

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

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

$$\text{error}_{\text{aq}} = \text{AQ} - \text{inorganics} - \sum_i A_{\text{tot},i} \frac{K_{\text{aq},i} \text{AQ}}{1 + K_{\text{aq},i} \text{AQ} + K_{\text{p},i} M_o}. \quad (24)$$

2.2.4 Saturation and separation of phases

To determine whether separating the organic phase into several organic phases makes the system more stable, the Gibbs energy G is computed using different system configurations (different number of phases).

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

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

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 it is kept. Iteratively, to determine the number of organic phases, one phase is added until the Gibbs energy increases.

2.3 Dynamic gas uptake by organic particles

2.3.1 Diffusion of organic compounds in spherical organic particles

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

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

with $C(r, t)$ the molar concentration of radius r at time t , D_{org} the organic-phase diffusivity and R_{org} the organic-phase reaction rate. 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):

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

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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 :

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

with τ_{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 concentration at equilibrium = $K_p M_o A_g$. In this equation 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 $\mu\text{g m}^{-3}$) 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 τ_{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 α_{layer} such as:

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

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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 , α_1 , α_2 , α_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 ($N_{\text{layer}} = 3$), 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 $A_{p,i}^{\text{layer,bin}}$ in a bin due to condensation limited by the diffusion of organic compounds in the organic phase is described by the Eq. (34), which describes the evolution of the concentration $A_{p,i}^{\text{bin,layer}}$ compared to an equilibrium concentration (Pankow model) $A_{\text{eq}}^{\text{bin,layer}} = A_{g,i} K_{p,i}^{\text{bin,layer}} M_o^{\text{bin,layer}}$.

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

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

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

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

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 an inorganic aqueous phase and a solid phase. The morphology can affect the time for an organic phase to reach

equilibrium. For example, for a same particle diameter, a particle entirely organic will need more time to reach equilibrium than a particle constituted by a solid kernel in the center surrounded by an organic phase (because the organic compounds do not penetrate the particle all the way to the center). We propose here to take into account more complex morphologies by using a morphology factor $f_{\text{morph}}^{\text{layer}}$, which modifies the characteristic time of a layer $\tau_{\text{dif}}^{\text{layer}}$ expressed in Eq. (32) such as:

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

Eq. (34) then becomes:

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

with $k_{\text{diffusion}}$ defined as in Eq. (36).

The morphology factors can be determined numerically. We determined here morphology factors in the case of a spherical particle with a solid kernel at the center of the particle by solving the differential equation for diffusion (Eq. 26) and by fitting the morphology factors to minimize the differences between Eqs. (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). The variations of the morphology factors with the volume fraction f_s are shown in Fig. 2. The morphology factors can be represented by polynomial expressions such as:

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

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. The same methodology could be applied to other morphologies (like non-spherical particles).

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 equation (Seinfeld and Pandis, 1998):

$$5 \quad \frac{dm_i}{dt} = \frac{2\pi D_p D_{\text{air}} M_i}{RT} f(Kn, \alpha) (P_i - P_{\text{eq},i}) \quad (40)$$

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 $P_{\text{eq},i}$ the pressure at equilibrium, which is different from the saturation vapour pressure due to the Kelvin effect.

$$10 \quad \frac{P_{\text{eq},i}}{P_i^0} = \exp\left(\frac{2\sigma M_{\text{ow}}}{RT \rho_{\text{organic}} R_p}\right) \quad (41)$$

with σ the surface tension, ρ_{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^{-1} 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^{-3} is used.

The size distribution of particles is discretized into sections. In each section/bin, the concentrations $A_{p,i}^{\text{bin}}$ 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:

$$20 \quad A_{p,i}^{\text{bin}} = N^{\text{bin}} m_i^{\text{bin}} 10^6 \quad (42)$$

with N^{bin} the number of particles in section “bin” per cubic meter.

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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 $\text{JK}^{-1} \text{mol}^{-1}$, T in K, M_i in g mol^{-1} .

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

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

with M_o^{bin} the mass of the organic matter in the bin, $K_{p,i}^{\text{bin}}$ the organic-phase partitioning coefficient of the bin taking into account the Kelvin effect by using $P_{\text{eq},i}$ in Eq. (3) instead of the saturation vapour pressure.

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

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

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

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

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

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

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

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

5 If the partitioning coefficients $K_{p,i}^{\text{bin,layer}}$ are constants over the layers which is the case when the formation of organic aerosols is limited only by absorption (diffusion in this case does not influence concentrations), then:

$$K_{p,i}^{\text{bin,layer}} = K_{p,i}^{\text{bin}} \quad (49)$$

and:

$$\begin{aligned} A_{g,i} K_{p,i}^{\text{bin}} M_{\text{o}}^{\text{bin}} - A_{p,i}^{\text{bin}} &= A_{g,i} K_{p,i}^{\text{bin}} \sum_{\text{layer}}^{N_{\text{layer}}} M_{\text{o}}^{\text{bin,layer}} - \sum_{\text{layer}}^{N_{\text{layer}}} A_{p,i}^{\text{bin,layer}} \\ &= \sum_{\text{layer}}^{N_{\text{layer}}} (A_{g,i} K_{p,i}^{\text{bin,layer}} M_{\text{o}}^{\text{bin,layer}} - A_{p,i}^{\text{bin,layer}}) \end{aligned} \quad (50)$$

By combining Eqs. (50) and 47:

$$\sum_{\text{layer}}^{N_{\text{layer}}} \frac{dA_{p,i}^{\text{bin,layer}}}{dt} = \frac{k_{\text{absorption}}}{K_{p,i}^{\text{bin}} M_{\text{o}}^{\text{bin}}} \sum_{\text{layer}}^{N_{\text{layer}}} (A_{g,i} K_{p,i}^{\text{bin,layer}} M_{\text{o}}^{\text{bin,layer}} - A_{p,i}^{\text{bin,layer}}). \quad (51)$$

Hence, by using Eq. (35):

$$\frac{dA_{p,i}^{\text{bin,layer}}}{dt} = \frac{k_{\text{absorption}} V_{\text{layer}}}{K_{p,i}^{\text{bin,layer}} M_{\text{o}}^{\text{bin,layer}}} (A_{g,i} K_{p,i}^{\text{bin,layer}} M_{\text{o}}^{\text{bin,layer}} - A_{p,i}^{\text{bin,layer}}). \quad (52)$$

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. 52) 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).

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

with $A_{p,i}^{\text{bin}}$ of a compound i in the organic phase in the a specified bin (in $\mu\text{g m}^{-3}$) k computed by Eq. (54).

$$k^{-1} = \frac{1}{f_{\text{morph}}^{\text{layer}} k_{\text{diffusion}}} + \frac{K_{p,i}^{\text{bin,layer}} M_o^{\text{bin,layer}}}{k_{\text{absorption}} V_{\text{layer}}} \quad (54)$$

2.3.5 Characteristic time to reach equilibrium

The system of differential Eq. (53) to solve is stiff, as in the same layer/bin, some species will reach equilibrium much quicker than others (Capaldo et al., 2000). To solve it efficiently, it is necessary to solve seperatly cases at equilibrium from other cases, which will be solved dynamically. To determine the characteristic time to reach equilibrium, Eq. (53) is rewritten using the total concentrations and defining $f_i^{\text{bin,layer}} = A_{p,i}^{\text{bin,layer}} / A_{p,i}^{\text{bin}}$ (if $A_{p,i}^{\text{bin,layer}}$ different from zero):

$$\frac{dA_{p,i}^{\text{bin,layer}}}{dt} = k \left(A_{\text{tot},i} K_{p,i}^{\text{bin,layer}} M_o^{\text{bin,layer}} - A_{p,i}^{\text{bin,layer}} \left(1 + \frac{K_{p,i}^{\text{bin,layer}} M_o^{\text{bin,layer}}}{f_i^{\text{bin,layer}}} \right) \right) \quad (55)$$

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This differential equation is solved by assuming $f_i^{\text{bin,layer}}$ and $K_{p,i}^{\text{bin,layer}} M_o^{\text{bin,layer}}$ constant:

$$A_{p,i}^{\text{bin,layer}}(t) = A_{\text{eq}} + \left(A_{p,i}^{\text{bin,layer}}(t=0) - A_{\text{eq}} \right) \cdot \exp\left(-\frac{t}{\tau_{\text{eq}}}\right) \quad (56)$$

with A_{eq} the concentration at equilibrium and τ_{eq} the characteristic time to reach equilibrium.

$$A_{\text{eq}} = \frac{A_{\text{tot},i} K_{p,i}^{\text{bin,layer}} M_o^{\text{bin,layer}}}{1 + \frac{K_{p,i}^{\text{bin,layer}} M_o^{\text{bin,layer}}}{f_i^{\text{bin,layer}}}} \quad (57)$$

$$\tau_{\text{eq}}^{-1} = \left(1 + \frac{K_{p,i}^{\text{bin,layer}} M_o^{\text{bin,layer}}}{f_i^{\text{bin,layer}}} \right) k. \quad (58)$$

τ_{eq} can be used to estimate the time necessary to reach equilibrium and therefore to identified cases which should be assumed at equilibrium when solving the system of Eq. (53).

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 modelled, 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 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 Eqs. (38) and (52) by taking into account the phase of the components:

$$\frac{dA_{p,i}^{\text{bin,layer,phase}}}{dt} = k \left(A_{g,i} K_{p,i}^{\text{bin,layer,phase}} M_o^{\text{bin,layer,phase}} - A_{p,i}^{\text{bin,layer,phase}} \right) \quad (59)$$

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with $M_o^{\text{bin,layer,phase}}$ the total organic concentrations in the specified organic phase in a specified bin and layer (in $\mu\text{g m}^{-3}$), $A_{p,i}^{\text{bin,layer,phase}}$ and $K_{p,i}^{\text{bin,layer,phase}}$ the concentration and partitioning coefficient of the compound i and k are computed by Eq. (60).

$$k^{-1} = \frac{1}{f_{\text{morph}}^{\text{layer}} k_{\text{diffusion}}} + \frac{K_{p,i}^{\text{bin,layer,layer}} M_o^{\text{bin,layer,layer}}}{k_{\text{absorption}} V_{\text{layer}}} \quad (60)$$

At each time step, thermodynamic evolution is first computed. The number of phases and the separations of compounds between phases are then computed for each layer and each bin assuming equilibrium between phases. To compute the concentrations with several 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 phase₁ and phase₂:

$$Y_i^{\text{bin,layer,phase1}} X_i^{\text{bin,layer,phase1}} = Y_i^{\text{bin,layer,phase2}} X_i^{\text{bin,layer,phase2}} \quad (61)$$

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:

$$\frac{A_{p,i}^{\text{bin,layer,phase1}}}{A_{p,i}^{\text{bin,layer,phase2}}} = \frac{A_{p,i}^{\text{bin,layer,phase1}}}{A_g} \times \frac{A_g}{A_{p,i}^{\text{bin,layer,phase2}}} = \frac{K_{p,i}^{\text{bin,layer,phase1}} M_o^{\text{bin,layer,phase1}}}{K_{p,i}^{\text{bin,layer,phase2}} M_o^{\text{bin,layer,phase2}}} \quad (62)$$

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

$$\left(\exp\left(-\frac{2\sigma M_{\text{surf}}^{\text{bin}}}{RT\rho_{\text{organic}}R_p}\right) \right)^{\text{phase1}} = \left(\exp\left(-\frac{2\sigma M_{\text{surf}}^{\text{bin}}}{RT\rho_{\text{organic}}R_p}\right) \right)^{\text{phase2}} \quad (63)$$

$M_{\text{surf}}^{\text{bin}}$, ρ_{organic} and σ must be the same in the two phases.

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

$$K_{p,i}^{\text{bin,layer,phase}} = \frac{760 \times 8.202 \times 10^{-5} \times T}{M_{\text{ow}}^{\text{bin,layer,phase}} V_{i,\text{org}}^{\text{bin,layer,phase}} P_i^0 \times 10^6} \exp\left(-\frac{2\sigma M_{\text{surf}}^{\text{bin}}}{RT\rho_{\text{organic}} R_p}\right) \quad (64)$$

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

$$M_{\text{surf}}^{\text{bin}} = \frac{\sum_i \sum_{\text{phase}} A_{p,i}^{\text{bin,surface,phase}}}{\sum_i \sum_{\text{phase}} \frac{A_{p,i}^{\text{bin,surface,phase}}}{M_i}} \quad (65)$$

For the characteristic time, it is assumed to be the same between each organic phase to prevent a compound from being absorbed dynamically into a phase whereas it is at equilibrium on another phase. The characteristic time is then computed according to the following equation derived from Eqs. (58) and (60).

$$\tau_{\text{eq}}^{\text{bin,layer,phase}} = \frac{1}{f_{\text{morph}}^{\text{layer}} k_{\text{diffusion}} + \frac{\sum_{\text{phase}} K_{p,i}^{\text{bin,layer,layer}} M_o^{\text{bin,layer,layer}}}{k_{\text{absorption}} V_{\text{layer}}}} \cdot \frac{1 + \frac{\sum_{\text{phase}} K_{p,i}^{\text{bin,layer,phase}} M_o^{\text{bin,layer,phase}}}{f_i^{\text{bin,layer}}}}{1} \quad (66)$$

2.3.7 Absorption into the aqueous phase

For concentrations in the organic phases, the dynamic evolution follows Eq. (59) but the dynamic evolution of concentrations in the aqueous phase follows Eq. (67) because

condensation/evaporation is assumed to not be limited by diffusion in the aqueous phase and a multi-layer representation is then not useful.

$$\frac{dA_{aq,i}^{bin}}{dt} = k_{\text{absorption}} \left(A_{g,i} - \frac{A_{aq,i}^{bin}}{K_{aq,i}^{bin} AQ^{bin}} \right). \quad (67)$$

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

5 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. Equations (67) and (59) are still valid but $k_{\text{absorption}}$ in Eqs. (67) and (60) must be corrected to take into account there is a chance that a compound trying to condense onto a phase encounters the wrong phase, i.e. a
10 phase on which it may not condense.

The chance for a compound to encounter $f_{\text{surf}_{aq}}$ an aqueous phase is computed with Eq. (68):

$$f_{\text{surf}_{aq}} = \frac{S_{aq}}{S_{\text{tot}}} \quad (68)$$

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

15 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:

$$f_{\text{surf}_{aq}} = \frac{V_{aq}}{V_{aq} + V_{org}} = \frac{\frac{AQ^{bin}}{\rho_{\text{aqueous}}}}{\frac{AQ^{bin}}{\rho_{\text{aqueous}}} + \sum_{\text{layer}} N_{\text{layer}} \sum_{\text{phase}} N_{\text{phase}} \frac{M_o^{bin, \text{layer}, \text{phase}}}{\rho_{\text{organic}}}}. \quad (69)$$

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

$$k_{\text{absorption}} = f_{\text{surf}_{\text{aq}}} \times 2\pi D_p D_{\text{air}} N^{\text{bin}} f(Kn, \alpha). \quad (70)$$

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

$$k_{\text{absorption}} = (1.0 - f_{\text{surf}_{\text{aq}}}) \times 2\pi D_p D_{\text{air}} N^{\text{bin}} f(Kn, \alpha). \quad (71)$$

2.3.9 Thermodynamic equilibrium

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

Concentrations of organic compounds in the organic phase are computed according to Eq. (72).

$$A_{p,i}^{\text{bin,layer,phase}} = \text{conc}_{i,\text{eq}} \frac{K_{p,i}^{\text{bin,layer,phase}} M_o^{\text{bin,layer,phase}}}{1 + \text{ratio}_{i,\text{eq}}} \quad (72)$$

with $\text{conc}_{i,\text{eq}}$ the total concentration of compound i at equilibrium (sum of the gas phase concentrations and of organic phase concentrations in layers and bins at equilibrium) computed with Eq. (73) and $\text{ratio}_{i,\text{eq}}$ the ratio of the concentration of compound i at equilibrium in the particle phase to the concentration in the gas phase computed with Eq. (74) (similar to Eq. (15) for several bins, layers and phases).

$$\text{conc}_{i,\text{eq}} = A_{\text{tot},i} - \sum_{\text{bin}} \sum_{\text{layer}} \sum_{\text{phase}} (1 - \lambda^{\text{bin,layer,phase}}) A_{p,i}^{\text{bin,layer,phase}} \quad (73)$$

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$$\text{ratio}_{i,\text{eq}} = \frac{\sum_{\text{bin}} \sum_{\text{layer}} \sum_{\text{phase}} \lambda^{\text{bin,layer,phase}} A_{p,i}^{\text{bin,layer,phase}}}{A_g} = \sum_{\text{bin}} \sum_{\text{layer}} \sum_{\text{phase}} \lambda^{\text{bin,layer,phase}} K_{p,i}^{\text{bin,layer,phase}} M_o^{\text{bin,layer,phase}} \quad (74)$$

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

$$\lambda^{\text{bin,layer,phase}} = \begin{cases} 1 & \text{if } \tau_{\text{eq}}^{\text{bin,layer,phase}} < t_{\text{equilibrium}} \text{ (case at equilibrium)} \\ 0 & \text{if } \tau_{\text{eq}}^{\text{bin,layer,phase}} \geq t_{\text{equilibrium}} \text{ (dynamic case)} \end{cases} \quad (75)$$

The system is solved iteratively, as now detailed. The composition of the particles are first estimated using Eqs. (72) to (75). If the concentrations computed from this estimation are different from the one 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 $t_{\text{equilibrium}}$ (for example 100 s). For these compounds, assuming equilibrium will give errors because these compounds will condense almost entirely on the bin with the higher organic mass instead of condensing on each bins according to the kinetics of condensation. To prevent this problem, low-volatility case (with $K_{p,i}^{\text{bin,layer,phase}} > 10$) are assumed dynamic.

2.3.10 Methodology used to compute the evolution of concentrations

The method used to solve the evolution of concentrations is shown in Fig. 3. First, an equilibrium computation is done for initial concentrations and for cases at equilibrium.

Then at each time step, the dynamic evolution is first computed for dynamic cases and after that the equilibrium partitioning for equilibrium cases is then computed. The dynamic evolution is solved with the second-order Rosenbrock scheme ROS2 (Verwer et al., 1999) for the time integration.

The mass of each layer must respect the condition given by Eq. (35), which specifies the mass of the layer with respect total mass. 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. 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.

3 Results

3.1 Test cases

The behaviour of the model is tested over two test cases using realistic concentrations and meteorological conditions. This two cases are extracted from the simulations of Couvidat et al. (2012) and Couvidat et al. (2013) 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 but with high concentrations of anthropogenic compounds. These two test cases are referred hereafter as the “biogenic test case” and the “anthropogenic test case”. The surrogate are the same as in the aerosol model H^2O , which was used by Couvidat et al. (2012, 2013). The total concentrations (gas + particle) of each surrogate compounds are given in Table 3. For both test cases, the liquid water content of aerosol, the pH, the ionic strength and

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the concentrations of inorganic ions are computed with the ISORROPIA model (Nenes et al., 1998) for a specified relative humidity (RH). As in H²O, some species do not have a molecular structure attached (AnCIP, POAIP, POAmP, POAhP, SOAIP, SOAmP and SOAhP) and therefore process depending on the molecular structure (like absorption on the aqueous phase) are not estimated. However, their influence on the activity coefficients of other compounds is taken into account by using a default molecular structure as in H²O.

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 4 and 5 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, because they do not have a molecular structure attached as in Couvidat et al. (2012).

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 μg m⁻³ for ideality to 0.82 μg m⁻³ in the biogenic case for non-ideality and with long, medium and short ranges interactions and to 1.20 μg m⁻³ for non-ideality

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and without long and medium ranges interactions but with short-range interactions. It seems to indicate that in these cases 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. Therefore, the concentrations of hydrophilic organic compounds in the aqueous phase probably depend strongly on the concentrations of inorganic compounds.

Determining a priori if a compound is hydrophilic or hydrophobic is not straightforward. Table 6 shows that some compounds seem clearly hydrophobic (BiA2D, BiA1D, AnBIP, BiBIP, BiBmP, AnCIP, BiNGA, BiNIT3, BiNIT) or hydrophilic (BiA0D) as they partition only on 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 H²O 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 90 % to 33 % for particulate BiA2D, from 96 % to 46 % for particulate BiA1D and from 93 % to 81 % for particulate BiMGA. For the anthropogenic test case, the fraction in the organic decrease from 99 % to 76 % for particulate BiA2D, from 100 % to 85 % for particulate BiA1D and from 62 % to 46 %

for particulate BiMGA. It is therefore 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 Sect. 2.2.4). Table 7 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 on 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 does 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 on 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

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is tested for various humidities and diffusion coefficients for the biogenic and anthropogenic cases. Figures 4 and 5 show the concentrations in the organic phase for the biogenic and anthropogenic cases respectively whereas Figs. 6 and 7 show concentrations in the aqueous phase for the biogenic and anthropogenic cases respectively. The influence of the $t_{\text{equilibrium}}$ parameter is also tested in these figures. For all compounds, accommodation coefficient is taken equal to 0.5 and gas-phase diffusion coefficient is taken equal to $0.1 \text{ cm}^2 \text{ s}^{-1}$ so that condensation is mainly limited by diffusion in the organic phase. These two parameters are used for Eqs. (70) and (71).

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 $10^{-20} \text{ m}^2 \text{ s}^{-1}$, the organic aerosol reaches equilibrium within a few hours. For diffusion coefficient lower than $10^{-20} \text{ m}^2 \text{ s}^{-1}$, the formation of organic aerosol is strongly limited by diffusion. At higher humidity with an aqueous phase, for the same diffusivity, 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 the particle). Therefore, for constant diffusion coefficients, as particles get bigger, characteristic times to reach equilibrium get higher at high humidity. However, diffusion coefficients are probably much higher at high humidity than at lower humidity because the organic phase would be less viscous (less oligomerization due to esterification for example and water is less viscous). It may then be possible that at high humidity, the organic aerosol reaches the equilibrium sooner than at low humidity. Experiments or methods to estimate diffusion coefficients as a function of composition are needed to assert this point.

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

for 3-D applications, the dynamic approach is very time consuming and it is therefore interesting to use higher $t_{\text{equilibrium}}$ parameter.

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 diffusion of organic compounds. Simulations with SOAP with comparison to measurements will have to be done, to validate the model and to test the influence of each process and parameters on organic aerosol formation.

To improve the representation of aerosols, several processes should be added to the model. 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 are taken into account. However, organic compounds can also impact the formation of inorganic compounds due to those interactions. This process will be fully taken into account by adding inorganic aerosol formation. 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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While the system has not converged (or has not reached a maximum number of iterations):

1. $n = 1$
2. $\text{factor} = 1/n$
3. Compute the new estimation of the concentrations $A_{p,i,\text{new}}^{\text{bin,layer,phase}}$ according to Eq. (72).
4. $\text{Errors} = (A_{p,i,\text{new}}^{\text{bin,layer,phase}} - A_{p,i}^{\text{bin,layer,phase}}) / A_{p,i}^{\text{bin,layer,phase}}$
5. $A_{p,i}^{\text{bin,layer,phase}} = \text{factor} \times A_{p,i,\text{new}}^{\text{bin,layer,phase}} + (1 - \text{factor}) \times A_{p,i}^{\text{bin,layer,phase}}$
6. Compute $M_o^{\text{bin,layer,phase}}$
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

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

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

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**Table 3.** Conditions of the test cases and type of each compounds.

Compounds	Concentration ($\mu\text{g m}^{-3}$)	Concentration ($\mu\text{g m}^{-3}$)	Assumed type in H_2O
	Biogenic test case at $T = 295\text{ K}$	Anthropogenic test case at $T = 293\text{ K}$	
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_2SO_4	1.70	1.44	
HNO_3	1.83	5.07	
NH_3	1.07	1.77	

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	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

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F. Couvidat and
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	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	0.51	1.04	0.14	0.54
sesquiterpenes	0.19	0.0	0.08	0.0
isoprene	0.27	0.82	0.02	0.13
aromatics	0.10	0.11	0.07	0.01
primary SVOC	0.08	0	0.68	0.0
oxidised primary SVOC	1.06	0	2.18	0.0
Water	0.08	0.80	0.06	2.66

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**Table 7.** Concentrations (in $\mu\text{g m}^{-3}$) with or without phase separation for the biogenic test case at RH = 30 %.

Compound	Without saturation	With saturation		
	A_p	1st phase	2nd 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 A1. Notations.

A_{eq}	the concentration in the organic phase at equilibrium
$A_{\text{g},i}$	the concentration of i in the gas phase (in $\mu\text{g m}^{-3}$)
$A_{\text{p},i}$	the concentration of i in the organic phase (in $\mu\text{g m}^{-3}$)
$A_{\text{p},i}^{\text{bin}}$	the concentration of i in the organic phase (in $\mu\text{g m}^{-3}$) in a diameter bin
$A_{\text{p},i}^{\text{bin,layer}}$	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
$A_{\text{aq},i}$	the concentration of i in the aqueous phase (in $\mu\text{g m}^{-3}$)
$A_{\text{aq},i}^{\text{bin}}$	the concentration of i in the aqueous phase in a diameter bin (in $\mu\text{g m}^{-3}$)
$A_{\text{tot},i}$	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 $\text{m}^2 \text{s}^{-1}$)
D_{org}	diffusivity of the compound in the organic phase (in $\text{m}^2 \text{s}^{-1}$)
$f_{\text{p},i}^{\text{bin,layer}}$	fraction of $A_{\text{p},i}$ in a diameter bin and in a layer of the particle
$f_{\text{morph}}^{\text{layer}}$	morphology factor
$f_{\text{surf,aq}}$	the chance for a compound to encounter an aqueous phase at the surface of the particle
$f(K, n, \alpha)$	transition regime formula
G	Gibbs energy
H_j	Henry's law constant (in M atm^{-1})
$K_{\text{aq},i}$	the aqueous-phase partitioning coefficient
$K_{\text{aq},i}^{\text{bin}}$	the aqueous-phase partitioning coefficient of a diameter bin
$K_{\text{p},i}$	the organic-phase partitioning coefficient
$K_{\text{p},i}^{\text{bin,layer}}$	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
$k_{\text{absorption}}$	kinetic rate parameter of the absorption equation
$k_{\text{diffusion}}$	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^{-1})
M_i	mean molar mass of i (in g mol^{-1})
m_i	mass of i in a particle
m_i^{bin}	mass of i in a particle of the bin

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Table A1. Continued.

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 $\mu\text{g m}^{-3}$)
$M_o^{\text{bin,layer}}$	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^{-1})
M_{water}	molar mass of water
n_i^ϕ	number of moles of compound i in the phase ϕ
N_i^{bin}	number of particles in a diameter bin (in m^{-3})
P_i^0	the saturation vapour pressure of i
P_i	partial pressure of i
$P_{\text{eq},i}$	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 measured
V_{layer}	volume fraction of the layer
V_{aq}	volume of the aqueous phase
V_{org}	volume of the organic phase
$X_{i,\text{aq}}$	molar fraction of i in the aqueous phase
$X_{i,\text{org}}$	molar fraction of i in the organic phase
α	accomodation coefficient
α_{layer}	ratio of the characteristic time for diffusion of the layer to the characteristic time for diffusion of the center of the particle
$\gamma_{i,\text{aq}}$	activity coefficient of i in the aqueous phase
$\gamma_{i,\text{aq}}^\infty$	activity coefficient of i at infinite dilution in water
$\gamma_{i,\text{org}}$	activity coefficient of i in the organic phase
$\gamma_{\text{water,aq}}$	activity coefficient of water in the aqueous phase
$\gamma_{\text{water,org}}$	activity coefficient of water in the organic phase
ΔH_i	enthalpy of vaporization of i (in J mol^{-1})
μ_i^ϕ	chemical potential of i
ξ_i	activity coefficient of i in the aqueous phase by reference to infinite dilution
τ_{dif}	characteristic for diffusion
τ_{eq}	characteristic time to reach equilibrium

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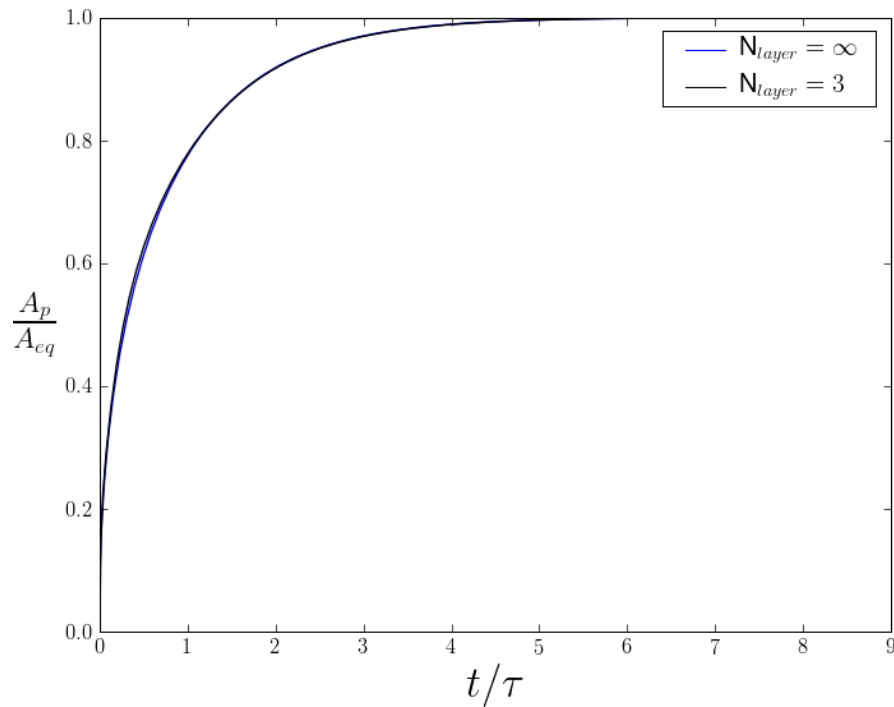


Fig. 1. Evolution of the ratio $A_p(t)/A_{eq}$ as a function of the ratio t/τ_{dif} .

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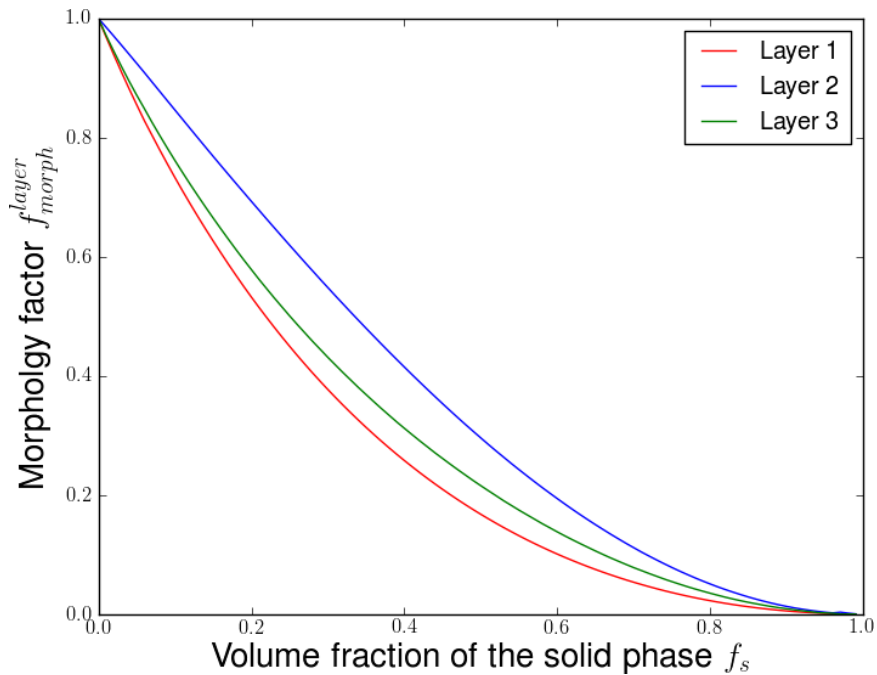


Fig. 2. Morphology factors as a function of the volume fraction of the solid phase.

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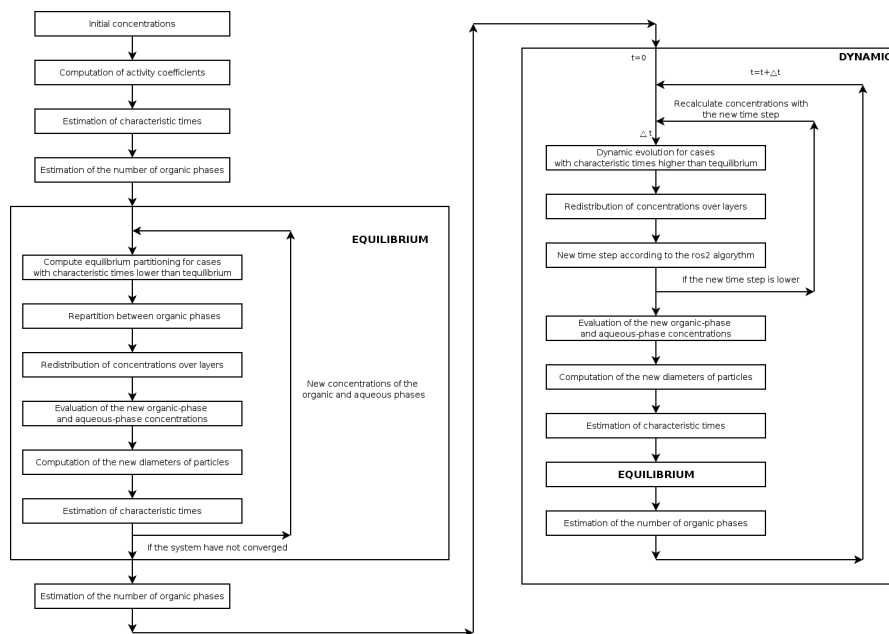


Fig. 3. Diagram of the method used to compute the evolution of concentrations.

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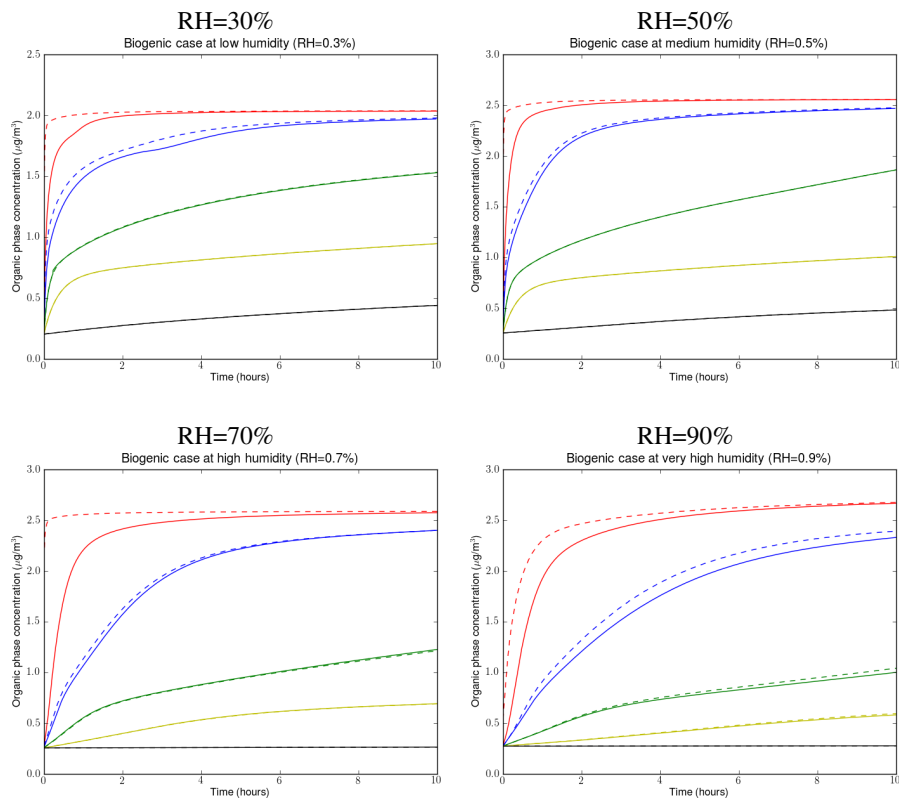


Fig. 4. Evolution of concentrations in organic phases for the biogenic case at various humidities, with initial concentrations equal to tenth the concentrations at equilibrium for $t_{\text{equilibrium}} = 1$ s (plain lines) and $t_{\text{equilibrium}} = 100$ s (dashed lines) for several organic-phase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

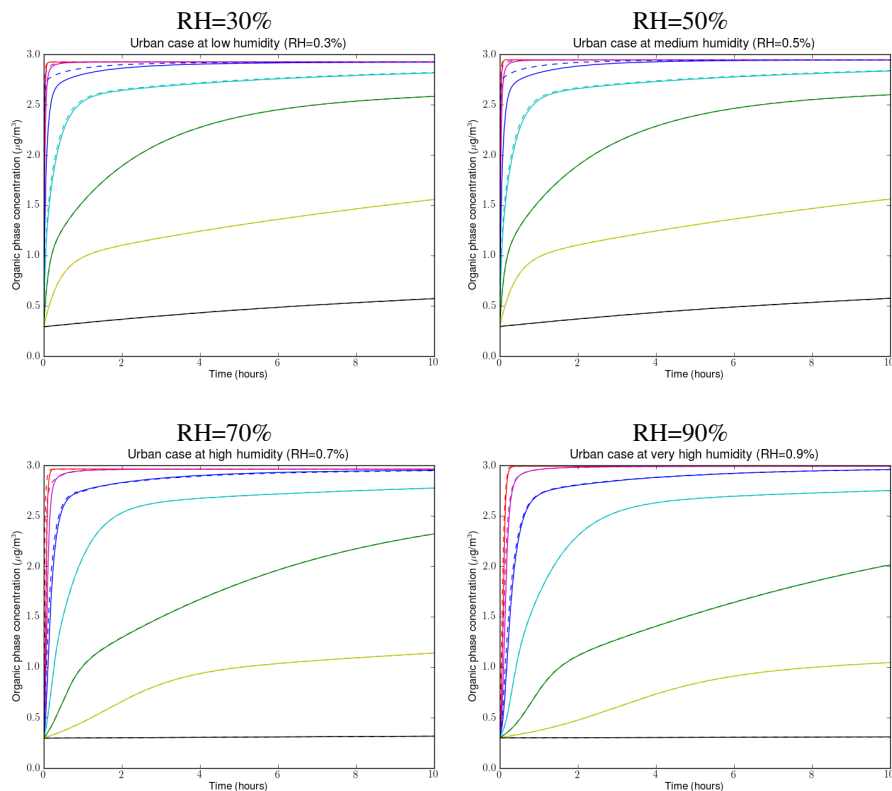


Fig. 5. Evolution of concentrations in organic phases for the anthropogenic case at various humidities, with initial concentrations equal to tenth the concentrations at equilibrium for $t_{\text{equilibrium}} = 1$ s (plain lines) and $t_{\text{equilibrium}} = 100$ s (dashed lines) for several organic-phase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

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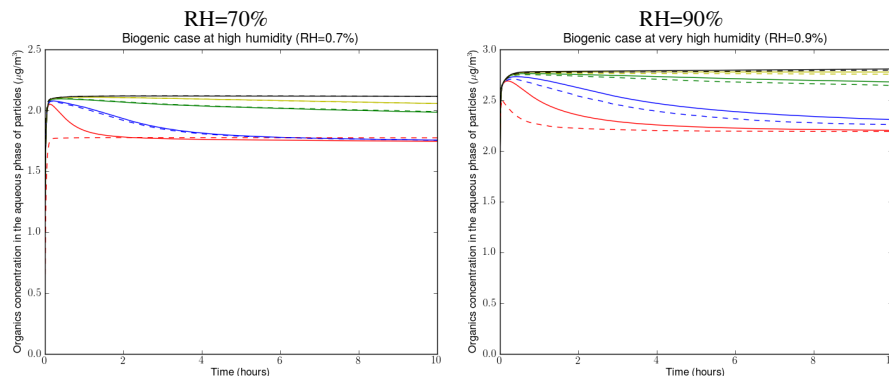
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Fig. 6. Evolution of concentrations in the aqueous phase for the biogenic case at various humidities, with initial concentrations equal to tenth the concentrations at equilibrium for $t_{\text{equilibrium}} = 1$ s (plain lines) and $t_{\text{equilibrium}}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

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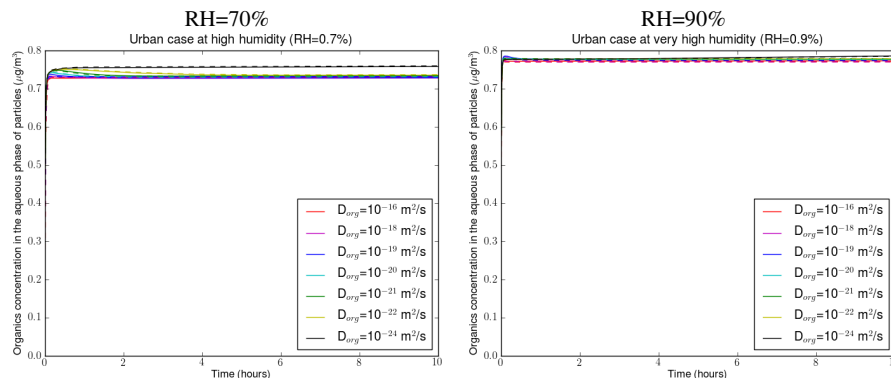
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Fig. 7. Evolution of concentrations in the aqueous phase for the anthropogenic case at various humidities, with initial concentrations equal to tenth the concentrations at equilibrium for $t_{\text{equilibrium}} = 1$ s (plain lines) and $t_{\text{equilibrium}}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

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