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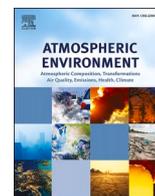
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Role of ecosystem-atmosphere exchanges of semi-volatile organic compounds in organic aerosol formation

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HIGHLIGHTS

- A module for air/soil/vegetation exchanges of SVOC have been implemented into CHIMERE.
- Strong deposition of primary SVOC from biomass burning in winter was simulated with the exchange module contrary to the Wesely approach.
- However, similar concentrations of secondary organic aerosols were simulated in summer with the Wesely approach and the exchange module.
- Re-emissions (inversion of the exchange flux toward emissions) of SVOC accumulated in ecosystems are theoretically possible.

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ABSTRACT

Deposition of the gas fraction of Semi-Volatile Organic Compounds (SVOC) may be an important removal pathway and may strongly influence concentrations of organic aerosols due to the gas-particle partitioning of SVOC. All the studies on this process are based on the classic Wesely resistance approach that uses Henry's law constants to calculate a deposition rate scaled on the deposition rate of SO₂. However, even highly hydrophobic SVOC could be efficiently removed by the vegetation and soils as shown by numerous studies on Persistent Organic Pollutant (POP) modeling. Moreover, the re-volatilization of deposited SVOC is possible and could influence organic aerosol concentrations.

An atmosphere-soil-vegetation module was developed and implemented in the 3D air quality model CHIMERE 2017 β to represent the accumulation of compounds in the different compartments of the biosphere and the exchanges between them. The soil compartment was represented with a multi-layer approach (the layers corresponding to different in-soil depths) to simulate the multiphase diffusion of compounds inside the soil. Exchanges of SVOC between the air, soil and vegetation compartments were simulated using bi-directional approaches based on R_g (the gas-phase partitioning in the soil compartment) and K_{va} the vegetation-air partitioning coefficient. Parameters were estimated based on the physical properties of the compounds and their molecular structure.

Simulations performed over Europe show that air-vegetation-soil exchanges may be a more efficient removal pathway than dry deposition of particles for SVOC with a gas-phase fraction above 10%. Considering air-vegetation-soil exchanges in the simulations lead to a decrease of organic aerosol concentrations by 15% and primary SVOC (considered as hydrophobic compounds) may be efficiently removed by those pathways (contrary to what is calculated with the Wesely approach). This decrease of concentrations is mainly due to air-vegetation exchanges. During summer, the use of the Wesely approach may lead to a slight overestimation of deposition fluxes (leading to an underestimation of concentration by 1%).

Re-volatilization may limit the amount of deposited SVOC. Depending on assumptions, simulations showed that re-emissions (inversion of exchanges toward the emissions) in summer of SVOC accumulated during winter is theoretically possible and may be a minor source of organic aerosol.

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1. Introduction

While the air-ecosystem nexus is often studied for meteorology and climate applications, food and security, or to better assess the CO₂ sequestration power of the biosphere (Lefèvre et al., 2007; Boone et al., 2017; Silva and Lambers, 2020), effect of interactions between the atmosphere and biosphere compartments on air pollutants remains an important issue (He et al., 2021). However, recently, Barwise and Kumar (2012) made a practical review for appropriate plant species selection to designing vegetation barriers for urban air pollution abatement, referring to an exhaustive list of works on the effect of vegetation on urban air pollution.

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) and comes from the partitioning of Semi-Volatile Organic Compounds (SVOC) between the gas and aerosol phases. Using the resistance approach of Wesely (1989), several studies suggested that a large part of SVOC are highly soluble in water (effective Henry's law constant higher than 10⁵ M atm⁻¹) making the gas-phase fraction of SVOC sensitive to dry and wet deposition (Bessagnet et al., 2010; Knote et al., 2015). Due to the gas-particle partitioning of SVOC, this removal pathway could have a strong impact on Secondary Organic Aerosol (SOA) concentrations. Bessagnet et al. (2010) estimated that omitting the dry deposition of gas-phase SVOC could lead to the overestimation of organic aerosols by 50% over Europe. Over the continental United States, Knote et al. (2015) estimated that this process leads to a decrease of 40% and 52% for anthropogenic and biogenic SOA, respectively. Due to the importance of dry deposition of gas-phase SVOC on organic aerosol concentrations, works on this process are crucial to improve the representation of organic aerosols in air quality models.

While a large part of organic aerosols is highly soluble in water, some primary compounds are also very hydrophobic (like long-chain alkanes, aromatics and polycyclic aromatic hydrocarbons). However, the Wesely approach does not consider the specificity of SVOC and only use the Henry's law constants as a way to scale the deposition rate to the SO₂ deposition rate. Moreover, as the Wesely approach is based on the Henry's law constant, with this approach, simulated deposition of highly hydrophobic SVOC is insignificant while for most SOA compounds, deposition is an efficient removal process. Furthermore, Wu et al. (2012) measured a high deposition velocity for peroxyacetyl nitrate (a compound with a low solubility), whereas the two models tested based on the Wesely approach failed to reproduce this velocity.

However, another approach is used in the modeling of atmospheric concentrations of persistent organic pollutants (POPs) where the exchanges between the atmosphere, soil and vegetation compartments are considered (Lammel et al., 2018; Quéguiner et al., 2010; Loizeau et al., 2014; Hansen et al., 2004; Gusev et al., 2005). Whereas these compounds are highly hydrophobic, their deposition on vegetation and soil surfaces is accounted for. Moreover, studies on POP exchange processes have shown that these exchanges can reach an equilibrium and can even lead to re-volatilization of accumulated organic compounds from the soil (Lammel et al., 2018) and vegetation (Barber et al., 2003, 2004) compartments. To our knowledge, no studies focused on the role of air-vegetation-soil bi-directional exchanges of SVOC on organic aerosol concentrations while Niinemets et al. (2014) emphasized the need to consider these exchanges for organic compounds.

While the modeling of POPs concentrations and the Wesely approaches both aim at considering the exchanges of SVOC between the air and the different types of surfaces, they entirely differ on the way to apprehend the processes at work (bi-directional fluxes of POPs vs. uni-directional fluxes for all SVOC). This study aims at reconciling both approaches by implementing an explicit air-vegetation-soil exchange module in the air quality model CHIMERE and to study the effect of these exchanges on organic aerosol concentrations. Air-vegetation-soil exchanges will be referred as air-ecosystem exchanges hereafter. The

term ecosystem also refers to aquatic ecosystems but only the exchanges with terrestrial ecosystems are considered in this study. Deposition to aquatic ecosystems is however considered in the CHIMERE model as a non-reversible flux. In this study, vegetation and soil are considered as two separated compartments. It should be noted that in some studies terrestrial ecosystem are viewed as a single compartment (for example, Sutton et al. (1998) in the case of ammonia exchanges).

2. Method

A module inspired from Jacobs and van Pul (1996) to treat the exchanges of SVOC as well as a few polycyclic aromatic hydrocarbons (naphthalene, phenanthrene and pyrene) between the soil or vegetation and atmosphere was implemented in the CHIMERE 2017β (Couvidat et al., 2018) by using some parameters such as the constant octanol-water K_{ow} or the Henry's law constants, estimated with Secondary Organic Aerosol Processor (SOAP) model (Couvidat and Sartelet, 2015). The module takes into account the transport of organic compounds inside the soil, the degradation inside the soil and vegetation compartments and assumes that there is no transfer between soil and vegetation. However, some compounds are probably taken by roots and some compounds are probably transferred from vegetation to soil due to loss of leaves, these processes are not considered. The module also accounts for deposition of both gas and particles onto the soil or intercepted by vegetation. In the case of interception, compounds are accumulated at the surface of the leaves until they are washed-out by rain.

2.1. Model overview of CHIMERE 2017β

In CHIMERE 2017β, organic aerosol is simulated with the Hydrophilic/Hydrophobic Organic (H²O) mechanism (Couvidat et al., 2012). This mechanism considers the formation of SVOC from biogenic (isoprene, monoterpenes, sesquiterpenes) and anthropogenic precursors (like toluene, xylenes) under high-NO_x and low-NO_x conditions. It uses the molecular surrogate approach in which surrogate compounds are associated with molecular structures to estimate several properties and parameters. This mechanism distinguishes two kind of surrogate compounds: hydrophilic compounds (assumed to condense on the aqueous phase of particles) and hydrophobic compounds (assumed to condense on the organic phase of particles). The properties and precursors of the different surrogate compounds are summarized in Table 1.

H²O uses the following naming nomenclature for SOA. The species names begin by "Bi" for biogenic compounds and by "An" for anthropogenic compounds. The suffix of the name corresponds to the species type. "A2D" and "A1D" mean that the species are hydrophilic and are respectively a diacid and a monoacid. "A0D" means that the species is hydrophilic and non-dissociative. "NIT" and "NIT3" mean that the compound is an hydrophobic nitrate or trinitrate. "BiP", "BmP" and "CiP" mean that the compounds are hydrophobic and are more or less volatile (IP and mP for low and medium saturation vapor pressure, respectively). AnBiP, AnBmP and AnCiP represent SOA formed by the oxidation of aromatic species. BiA0D, BiA1D, BiA2D and BiNIT represent SOA formed by oxidation of monoterpenes, BiBiP and BiBmP by oxidation of sesquiterpenes. Finally, BiMGA, BiNGA are acids formed by oxidation of isoprene under high-NO_x conditions; BiMT, BiPER and BiDER are formed under low-NO_x conditions and BiNIT3 by oxidation of isoprene by the nitrate radical NO₃ (refer to Couvidat and Seigneur (2011) for details).

The partitioning of SVOC is computed with the SOAP model. This model computes the partitioning of organic compounds between the gas and particle phases according to the complexity required by the user. It uses the molecular structures of the surrogate compounds to estimate several properties and parameters (hygroscopicity, absorption into the aqueous phase of particles, activity coefficients and phase partitioning). In this study, the equilibrium approach is used and activity coefficients

Table 1
Properties of the surrogate SOA species.

Surrogate	Precursors	Type	H ^a	p ^{0b}	ΔH _{vap} ^c	Comments
BiMT	isoprene	hydrophilic	0.805	1.45 × 10 ⁻⁶	38.4	–
BiPER		hydrophilic	0.111	2.61 × 10 ⁻⁶	38.4	–
BiDER		hydrophilic	2.80	4.10 × 10 ⁻⁷	38.4	–
BiMGA		hydrophilic	1.13 × 10 ⁻²	1.4 × 10 ⁻⁵	43.2	pK _a = 4.0
BiNGA		hydrophobic	–	1.4 × 10 ⁻⁵	43.2	K _{p,eff} = K _p (1+K _{oligo}) ^d
BiNIT3		hydrophobic	–	1.45 × 10 ⁻⁶	38.4	–
BiA0D	monoterpenes	hydrophilic	4.82 × 10 ⁻⁵	2.70 × 10 ⁻⁴	50	Oligomerization according to Couvidat et al. (2012)
BiA1D		hydrophilic	2.73 × 10 ⁻³	2.17 × 10 ⁻⁷	50	pK _a = 3.2
BiA2D		hydrophilic	6.52 × 10 ⁻³	1.43 × 10 ⁻⁷	50	pK _{a1} = 3.4, pK _{a2} = 5.1
BiNIT		hydrophobic	–	2.5 × 10 ⁻⁶	109	–
BiBIP	sesquiterpenes	hydrophobic	–	6.0 × 10 ⁻¹⁰	175	–
BiBmP		hydrophobic	–	3.0 × 10 ⁻⁷	175	–
AnBIP	aromatics	hydrophobic	–	6.8 × 10 ⁻⁸	50	–
AnBmP		hydrophobic	–	8.4 × 10 ⁻⁶	50	–
AnClP		hydrophobic	–	non volatile	–	–

^a Henry's law constant [(μg μg⁻¹ water)/(μg m⁻³)].

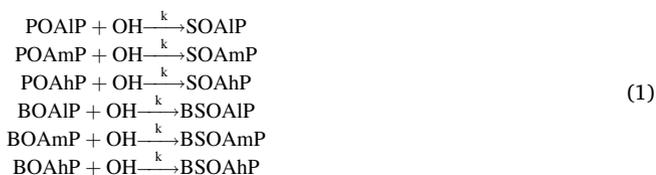
^b Saturation r pressure [torr].

^c Enthalpy of vaporization [kJ.mol⁻¹].

^d K_{oligo} (equal to 64.2) is used to take into account the formation of oligomers (Couvidat et al., 2012). K_{p,eff} is the effective partitioning constant and K_p is the partitioning constant calculated as in Pankow (1994).

are computed with the UNIFAC (UNiversal Functional group Activity Coefficient; Fredenslund et al. (1975)) thermodynamic model for short-range interactions.

Following Couvidat et al. (2012), primary organic aerosols are assumed to be semi-volatile compounds: the model assumed that the compounds exist in both the gas and particle phases, the gas-particle partitioning being calculated as a function of their thermodynamic properties. In this study, primary organic aerosols from biomass burning (BOA) and primary organic aerosols from other sources (POA) are split into different compounds. POA are split as described by Couvidat et al. (2012), three compounds: POAIP (K_p = 1.1 m³ μg⁻¹), POAmP (K_p = 0.0116 m³ μg⁻¹) and POAhP (K_p = 0.00031 m³ μg⁻¹) having respectively a low, medium and high volatility to follow the dilution curve of POA in Robinson et al. (2007). Similarly, BOA are split into three compounds: BOAIP (K_p = 18.3 m³ μg⁻¹), BOAmP (K_p = 0.04 m³ μg⁻¹) and BOAhP (K_p = 0.00023 m³ μg⁻¹) having respectively a low, medium and high volatility to follow the dilution curve of BOA in May et al. (2013). The aging of these compounds is also taken into account with a reaction with OH which leads to less volatile compounds (SOAIP, SOAmP and SOAhP, BSOAIP, BOAmP, BSOAhP) via the following reactions:



with k the kinetic rate constant equal to 2 × 10⁻¹¹ molecules⁻¹ cm³ s⁻¹. The aging step is assumed to lead to a decrease of volatility by a factor 100.

For these compounds, no molecular structure is attached due to the lack of information. Couvidat et al. (2012) used a default structure (assumed to be representative primary compounds) for the computation of the gas-particle partitioning.

In Couvidat et al. (2018), dry deposition of gases is represented via the resistance analogy of Wesely (1989). For gases, v_d is calculated with:

$$v_d = \frac{1}{R_a + R_b + R_c} \quad (2)$$

with R_a the aerodynamic resistance associated with turbulent transport in the atmosphere, R_b the quasi-laminar layer resistance and R_c the

surface resistance. The algorithm is described in Menut et al. (2013). The surface resistance depends on the nature of the surface and is generally broken down into three categories: water, ground and vegetation. For the deposition of gases to water and vegetation, the parameterizations depend on the Henry's law constants of the compound.

2.2. Modeling scheme of bi-directional exchanges between compartments

In this study, a module for bi-directional exchanges between the air, vegetation and soil compartments is developed according to parameterizations available in the literature. The developed scheme is illustrated by Fig. 1. The aerodynamic, quasi-laminar layer and the in-canopy aerodynamic resistances are computed as in Menut et al. (2013).

2.2.1. Soil-atmosphere exchanges

In our study, to treat soil-atmosphere exchanges, processes of absorption and desorption of organic vapors by soil as well as the diffusion of organic compounds inside the soil are considered through a discretization of the soil into 13 layers. Diffusion inside the first layer (at the surface) was assumed to be negligible and the thickness of the first layer is computed as a function of the chemical properties of the compound in order to correspond to a characteristic time of diffusion equal to 1 s. The thickness of the following layer was chosen to fit with a diffusion time scale coherent with the CHIMERE time step (equal to 10 min), while the thickness of deeper layers was increased to cover a total thickness above 20 cm, such as:

$$H_{l+1} = f_l H_l \quad (3)$$

with l the index for the soil layer, H_l the thickness of the layer and f_l a factor set to 1.75638.

The input flux of atmospheric organic compounds to the first layer is computed with:

$$\frac{\partial C_T}{\partial t} = \frac{F_{as} + F_{trans} + F_{p,dep} + F_{wet,gases} - F_{deg}}{H_1} \quad (4)$$

with C_T the concentration of the organic compound in the soil, F_{as} the net flux of organic vapors at the interface, F_{trans} the vertical transport flux of organic compounds, F_{deg} the degradation flux due to the soil chemistry and F_{p,dep} the deposition flux of particles (dry and wet, without the intercepted fraction by vegetation) and F_{wet,gases} the wet deposition flux for gaseous compounds.

The intercepted fractions by vegetation f_{dry} and f_{wet} (for dry and wet deposition respectively) are computed according to Pröhl (2009) as a

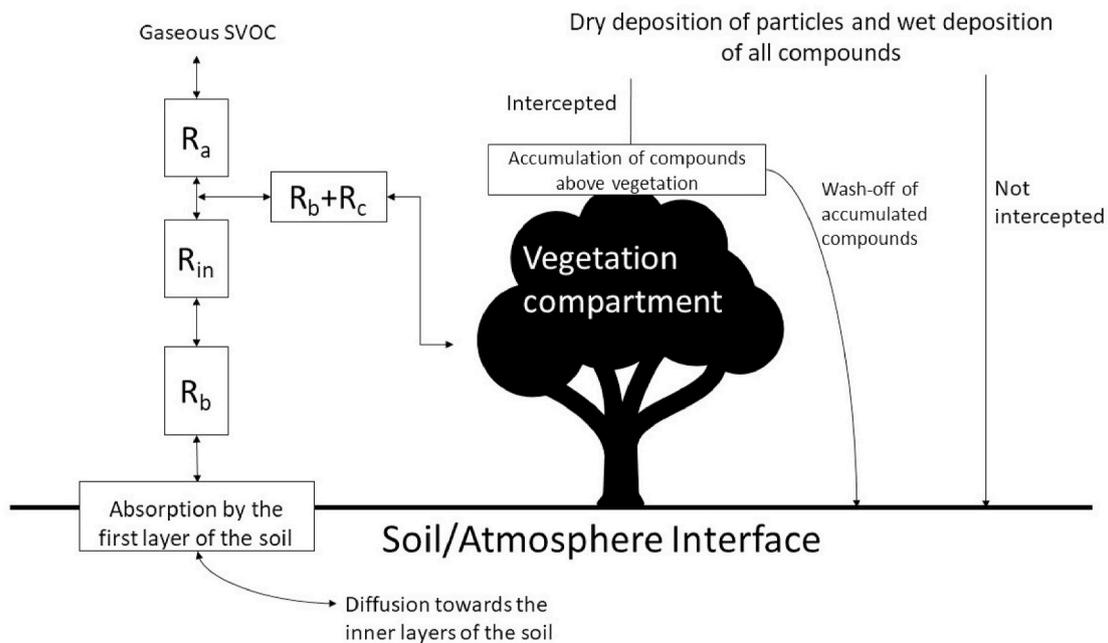


Fig. 1. Bi-directional exchange scheme between the air, vegetation and soil compartment used in this study. R_a is the aerodynamical resistance, R_b is the quasi laminar layer resistance, R_c is the canopy resistance and R_{in} is the in-canopy aerodynamical resistance.

function of the Leaf Area Index (LAI):

$$\begin{aligned} f_{dry} &= 1 - \exp(-0.316LAI) \\ f_{wet} &= 0.1375LAI^{0.819} \end{aligned} \quad (5)$$

The washing-off of compounds accumulated onto vegetation was taken into account with the following kinetic rate based on van den Berg et al. (2016):

$$k_{wash} = 0.05P \quad (6)$$

with P the precipitation in mm s^{-1} . Washed-off particles are transferred to the first layer of the soil.

The properties of soil (bulk density of the soil ρ_s , organic carbon content f_{oc} , porosity Φ and soil pH) is taken from the Harmonized World Soil Database (HWSD) (Nachtergaele et al., 2012).

The net flux of organic vapors at the soil-atmosphere interface F_{as} is defined as:

$$F_{as} = \frac{C_{a,s} - C_g}{R_b} \quad (7)$$

with $C_{a,s}$ the air concentration above the quasi-laminar layer, C_T the total concentration of the organic compound in the soil compartment, and C_g the concentration of the compound in the gas-phase of the soil (in ng m^{-3} of air).

The flux of chemical degradation is assumed to be a first order kinetic:

$$F_{deg} = k_{deg,soil} C_T \quad (8)$$

with $k_{deg,soil}$ the degradation kinetic parameter of organic compounds in soils. $k_{deg,soil}$ is calculated with:

$$k_{deg,soil} = f_a k_a + f_l k_l + f_s k_s \quad (9)$$

with f_a , f_l and f_s the fraction of the compound in the gaseous, aqueous and solid phase respectively. k_a , k_l and k_s are the kinetic parameter of degradation in the gaseous, aqueous and solid phase. Based on Guoin et al. (2000), these parameters are evaluated to be between 1.6×10^{-5} and $1.6 \times 10^{-6} \text{ s}^{-1}$ for k_a , between 1.6×10^{-6} and $1.6 \times 10^{-7} \text{ s}^{-1}$ for k_l and between 5.0×10^{-7} and $1.6 \times 10^{-8} \text{ s}^{-1}$ for k_s .

2.2.2. Soil multiphase partitioning

To treat soil-atmosphere exchanges, the absorption and desorption of organic vapors by soil as well as the diffusion in the soil is taken into account depending on the multiphase partitioning. The methodology of Jacobs and van Pul (1996) is used to express the total concentration of the organic compound in the soil compartment C_T (in ng m^{-3}) as a function of C_s (in ng kg^{-1} of solid matter), C_g (in ng m^{-3} of gas), C_{aq} (in ng m^{-3} of water) and C_{doc} (in ng m^{-3} of water) the concentrations in the solid phase, in the gaseous phase, in the aqueous phase and in the dissolved organic matter, respectively.

$$C_T = \rho_s C_s + \alpha_w (C_{aq} + C_{doc}) + \alpha_a C_g \quad (10)$$

with ρ_s the bulk density of the soil (in kg m^{-3}), α_w the volumetric water content of the soil and α_a the volumetric air content of the soil.

With Eq. (10), the fraction f_a , f_l and f_s are calculated with the following equations:

$$\begin{aligned} f_a &= \frac{\alpha_a C_g}{C_T} \\ f_s &= \frac{\alpha_w (C_{aq} + C_{doc})}{C_T} \\ f_s &= \frac{\rho_s C_s}{C_T} \end{aligned} \quad (11)$$

Following Jacobs and van Pul (1996), C_g , C_l and C_s are computed using partitioning coefficients:

$$C_T = R_l C_l = R_s C_s = R_g C_g \quad (12)$$

where $C_l = C_{aq} + C_{doc} = C_{aq}(1 + c_{doc} K_{doc})$ the soil solute concentration (in ng m^{-3}), c_{doc} the concentration of dissolved organic carbon in soil solute (in kg m^{-3}), K_{doc} the dissolved organic carbon/water partitioning coefficient (in $\text{m}^3 \text{ kg}^{-1}$), R_l the soil solute partitioning coefficient, R_g the gaseous phase partitioning coefficient and R_s the soil partitioning coefficient.

As in Gusev et al. (2005), c_{doc} is chosen equal to 0.5% to the total organic carbon content f_{oc} :

$$c_{doc} = 0.005 f_{oc} \rho_s \quad (13)$$

The partitioning coefficients are computed with the following equations:

$$\begin{aligned} R_l &= \alpha_w + \frac{\rho_s f_{oc} K_{oc} + \alpha_a K_{aw}}{1 + c_{doc} K_{doc}} \\ R_s &= R_l \frac{1 + c_{doc} K_{doc}}{f_{oc} K_{oc}} \\ R_g &= R_l \frac{1 + c_{doc} K_{doc}}{K_{aw}} \end{aligned} \quad (14)$$

with K_{oc} the organic carbon/water partitioning coefficient (in $\text{m}^3 \text{kg}^{-1}$) and K_{aw} the air water partitioning coefficient (dimensionless).

K_{aw} is computed with the following equation:

$$K_{aw} = \frac{101.3}{HRT_s} \quad (15)$$

with H the Henry's law constant (in M atm^{-1}), R the universal gas constant, T_s the soil temperature (in K), 101.3 is a conversion factor.

K_{oc} (in $\text{m}^3 \text{kg}^{-1}$) is computed according to Karickhoff (1981):

$$K_{oc} = \frac{K_{oc}^{adim}}{\rho_{s,ref}} = 0.000411 \frac{K_{ow}}{\rho_{s,ref}} \quad (16)$$

with K_{oc}^{adim} the dimensionless K_{oc} and $\rho_{s,ref}$ a reference density (chosen equal to 1300 kg m^{-3}). K_{doc} is computed according to Poerschmann et al., 2001:

$$K_{doc} = 0.001 \times 10^{0.98 \log(K_{ow}) - 0.39} \quad (17)$$

2.2.3. Vertical transport in soil

The vertical flux of organic compounds F_{trans} takes into account both the diffusion of organic compounds inside the soil and the convective flux due to water transport. It is computed as:

$$F_{trans} = \frac{\partial}{\partial z} \left(D_e \frac{\partial C}{\partial z} - V_e C_T \right) \quad (18)$$

with D_e the effective diffusion coefficient and V_e the effective velocity.

$$D_e = \frac{\xi_g D_a}{R_g} + \frac{\xi_l D_l}{R_l} + D_d \quad (19)$$

where D_a , D_l and D_d are the diffusion coefficients in the air and water, D_d is the bioturbation coefficient (equal to $6 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ according to McLachlan et al. (2002)), ξ_g and ξ_l are the gas and liquid tortuosities. The diffusion coefficient were set to $0.06 \text{ cm}^2 \text{ s}^{-1}$ for the diffusion in air and $6 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ for diffusion in water for all SVOC (which corresponds to the order of magnitude of the diffusion coefficients for POPs). ξ_g and ξ_l are computed as:

$$\xi_g = \frac{\alpha_a^{10/3}}{\Phi^2} \quad (20)$$

$$\xi_l = \frac{\alpha_l^{10/3}}{\Phi^2} \quad (21)$$

With the porosity Φ and assuming that the convective water flux is equal to the precipitation rate, the effective velocity V_e is calculated with:

$$V_e = \frac{P}{R_l} \quad (22)$$

with P the precipitation rate (in m s^{-1}).

2.3. Vegetation-atmosphere exchanges

The net flux of absorption $F_{gas,veg}$ of organic vapors by vegetation is given by:

$$F_{gas,veg} = \frac{1}{R_b + R_c} \left(C_{a,v} - \frac{C_v}{K_{va}} \right) \quad (23)$$

with $C_{a,v}$ the concentration above the quasi-laminar resistance, C_v the concentration inside the vegetation, R_c is the canopy resistance and K_{va} the vegetation-air partitioning coefficient (or bioaccumulation factor).

K_{va} is calculated according to McLachlan and Horstmann (1998):

$$K_{va} = mK_{OA}^n \quad (24)$$

with K_{OA} the octanol-air partitioning coefficient. m and n parameters are depending on the type of vegetation equal respectively to 22.91 and 0.445 for grass; 38 and 0.69 for evergreen forests; 14 and 0.76 for deciduous forests.

Following Gusev et al. (2005), the evolution of concentration inside vegetation is computed with:

$$\frac{dC_v}{dt} = \frac{a_v}{LAI} F_{gas,veg} - k_{deg,veg} C_v \quad (25)$$

with a_v the specific surface area of vegetation in $\text{m}^2 \text{m}^{-3}$ (assumed to be equal to $8000 \text{ m}^2 \text{m}^{-3}$) and LAI the leaf area index and $k_{deg,veg}$ the kinetic parameter of degradation inside the vegetation. R_a and R_b the aerodynamic and the boundary layer resistances are computed as in Menut et al. (2013). R_c is computed as a function of the type of vegetation and the molecule properties with the equation Eq. (26) and Eq. (29). For grass, following McLachlan et al. (1995), R_c is calculated with the octanol-air partitioning coefficient K_{OA} and a transfer coefficient k_v (in m s^{-1}) such as:

$$R_c = \frac{1}{k_v K_{OA}} \quad (26)$$

with:

$$\log(k_v) = -5.29 \log(V_m) + 1.43 \quad (27)$$

with V_m the molar volume of the compound (in $\text{cm}^3 \text{mol}^{-1}$).

Similarly, for evergreen forest, R_c is calculated according to Horstmann and McLachlan (1998):

$$\log(k_v) = -5.61 \log(V_m) + 2.94 \quad (28)$$

For deciduous forest, R_c is calculated according to Riederer (1990) as:

$$\frac{1}{R_c} = \frac{1}{R_{cut}} + \frac{1}{R_{sto}} \quad (29)$$

with R_{cut} the cuticular resistance and R_{sto} the stomatal resistance.

The stomatal resistance is calculated with:

$$R_{sto} = R_{H_2O} \sqrt{\frac{M}{M_{H_2O}}} \quad (30)$$

with R_{H_2O} the resistance for water vapors (equal to 2000 s m^{-1}), M the molar mass of the compound and M_{H_2O} the molar mass of water in g mol^{-1} .

Following Pekar et al. (1999), The cuticular resistance is calculated with:

$$R_{cut} = \frac{K_{aw}}{P_c} \quad (31)$$

with P_c the permeance coefficients across cuticular membranes, which can be calculated according to Kerier and Schönherr (1988):

$$P_c = \frac{238}{V_m} \log K_{cw} - 12.48 \quad (32)$$

with V_m the molar volume (in $\text{cm}^3 \text{mol}^{-1}$) and K_{cw} the cuticle-water

partitioning coefficient computed with:

$$\log(K_{cw}) = 0.97 \log(K_{ow}) + 0.057 \quad (33)$$

In this study, V_m was calculated with a density of 1.3 kg m^{-3} representative of SOA (Ng et al., 2007).

2.4. Estimation of soil and vegetation properties

For SVOC, K_{ow} is calculated with the SOAP model by computing the partitioning of the surrogate compounds between water and octanol with the UNIFAC model. For hydrophobic SVOC species, Henry's law constants were calculated as in Couvidat and Seigneur (2011); Couvidat et al. (2018), by using the sub-cooled saturation vapor pressure P^0 and the activity coefficient of compound i at infinite dilution inside water computed with UNIFAC γ_i^∞ such as:

$$H_i = \lim_{C_i \rightarrow 0} \left(\frac{C_i}{P_i} \right) = \frac{\rho_{\text{water}}}{M_{\text{water}} \times \gamma_i^\infty \times P_i^0} \quad (34)$$

with ρ_{water} the density of water and M_{water} the molar mass of water.

For primary SVOC POAIP, POAmP and POAhP, the molecular structures of the linear alkanes with volatilities close to those of the surrogate compounds were used (C_{20} for POAhP C_{24} for POAmP and C_{29} for POAIP). For their oxidation products (SOAIP, SOAmP and SOAhP), their properties were calculated by replacing two alkane groups by two ketone groups in the molecular structure of the precursor, to estimate properties for a slightly oxidized molecule.

For primary SVOC from biomass burning, according to Schauer et al. (2001), SVOC can be composed of some hydrophobic compounds (like alkanes, aromatics or PAH) and some hydrophilic compounds (like levoglucosan, guaiacol and *v* syringol). For simplification purposes, SVOC from biomass burning are assumed to be hydrophobic and the properties of POAIP, POAmP and POAhP were used for BOAIP, BOAmP and BOAhP.

The main properties of SVOC are shown in Table 2. To evaluate the impact of air-soil exchanges, characteristic times for re-emissions from vegetation τ_{veg} , for re-emissions from soil τ_{soil} and for the degradation

inside the soils τ_{deg} are evaluated. A value of 10 s cm^{-1} was used for R_a and LAI was set to 1 to evaluate the order of magnitude of the parameters.

τ_{deg} is calculated with:

$$\tau_{deg} = \frac{1}{k_{deg,soil}} \quad (35)$$

The range of estimated τ_{deg} was evaluated using the range of $k_{deg,soil}$ evaluated in section 2.2.1.

The characteristic time τ_{soil} is calculated with:

$$\tau_{soil} = R_a R_g L_s \quad (36)$$

with L_s a characteristic length for absorption of organic compounds in soils. L_s is calculated such as the characteristic time for diffusion inside a layer of depth L_s is equal to the lifetime of the compound τ_{deg} giving:

$$L_s = \sqrt{\frac{D_e}{k_{deg,soil}}} \quad (37)$$

τ_{veg} is evaluated with:

$$\tau_{veg} = \frac{R_a K_{va} LAI}{\alpha_v} \quad (38)$$

According to the estimations of τ_{deg} , SVOC should have a lifetime in soils between a few weeks (for compounds with higher kinetics of degradation) to more than a year (for those with lower kinetics of degradation). The lower lifetimes are obtained for the hydrophilic compounds (which are present almost entirely in the aqueous phase of soils) due to the higher kinetics of degradation in the aqueous phase.

Most compounds have a very high characteristic time of evaporation from soils (more than a few years) and re-emissions for these compounds can probably be neglected. However, for several compounds (BiAOD, POAhP, BOAhP, POAmP and BOAmP), τ_{soil} is low during summer (due to their higher volatilities and lower hydrophilicities) and re-emissions could be significant, especially for compound POAhP and BOAhP. Moreover, the lifetime of evaporation is much higher in winter, indicating that in

Table 2

Evaluated ecosystem properties of the surrogate SOA species. Values assuming hydrophilic SVOC are shown for biomass burning organic aerosol. The range of possible value for the degradation in soils is shown for τ_{deg} .

Surrogate	T = 298 K					T = 278 K		
	H (mol L ⁻¹ atm ⁻¹)	log(K _{ow})	τ_{veg} (days)	τ_{evap} (days)	τ_{deg} (days)	H (mol L ⁻¹ atm ⁻¹)	τ_{veg} (days)	τ_{evap} (days)
AnBlP	2.5×10^8	2.94	330	77000	23–655	9.3×10^8	770	2.6×10^5
AnBmP	1.2×10^9	3.29	1700	8.0×10^5	23–690	9.9×10^9	4200	3.1×10^6
AnClP	2.0×10^{10}	7.04	4.5×10^6	6.7×10^{10}	23–720	1.7×10^{10}	4.7×10^6	7.2×10^{10}
BiAOD	1.1×10^5	3.22	2.6	64.	23–682	4.0×10^5	7	266
BiA1D	1.5×10^9	2.60	680	2.4×10^5	22–600	6.0×10^9	1700	9.1×10^5
BiA2D	8.0×10^9	2.71	2500	1.6×10^6	22–620	3.9×10^{10}	6200	5.9×10^6
BiBlP	2.3×10^8	5.28	13000	4.0×10^7	23–720	2.0×10^{10}	5.0×10^5	2.7×10^9
BiBmP	4.4×10^5	5.30	178	28000	23–720	4.2×10^7	6700	5.4×10^6
BiDER	2.3×10^{11}	−0.31	214	2.0×10^6	7.5–76	7.4×10^{11}	400	5.9×10^6
BiMGA	6.3×10^9	0.19	39	59000	8.0–80	2.7×10^{10}	80	2.3×10^5
BiMT	6.6×10^{10}	−0.31	90	5.7×10^5	7.5–76	2.1×10^{11}	170	1.7×10^6
BiNGA	4.9×10^8	1.24	36	9500	13–170	1.9×10^9	73	32000
BiNIT	1.9×10^6	4.02	64	6410	23–710	3.4×10^7	560	1.5×10^5
BiNIT3	4.2×10^7	2.12	26	2850	20–450	1.1×10^8	52	7300
BiPER	4.2×10^9	0.61	57	46000	9–99	1.3×10^{10}	113	1.3×10^5
POAhP	3.6×10^{-3}	9.2	0.23	1.84	23–720	3.1×10^{-2}	2.3	51
POAIP	1.4×10^{-3}	12.6	28	1930	23–720	8.6×10^{-3}	330	68000
POAmP	2.3×10^{-3}	10.7	1.9	40.	23–720	1.1×10^{-2}	15	779
SOAhP	280.	7.35	29	1980	23–722	1300	160	24000
SOAIP	117.	10.8	3660	2.2×10^6	23–722	860.	41000	7.3×10^7
SOAmP	218.	8.9	272	1.5×10^4	23–722	1210	2000	9.4×10^5
BOAhP	3.6×10^{-3}	9.2	0.23	1.84	23–720	3.1×10^{-2}	2.3	51
BOAIP	1.4×10^{-3}	12.6	28	1930	23–720	8.6×10^{-3}	330	68000
BOAmP	2.3×10^{-3}	10.7	1.9	40.	23–720	1.1×10^{-2}	15	779
BSOAhP	280.	7.35	29	1980	23–722	1300	160	24000
BSOAI	117.	10.8	3660	2.2×10^6	23–722	860.	41000	7.3×10^7
BSOAmP	218.	8.9	272	1.5×10^4	23–722	1210	2000	9.4×10^5

some extent part of these compounds can be stored inside soils in winter and be re-emitted during summer. For the volatilization flux from vegetation, the characteristic times is lower, and more compounds could be re-emitted.

3. Results

SVOC concentrations refer hereafter to the concentrations of the semi-volatile organic compounds present in all the different phases. SVOC are present in the different compartments according to the fluxes of exchange between the different compartments. BOA concentrations correspond to the sum of the particle concentrations of BOAIP, BOAmP and BOAhP as well as their aging product (BSOAlP, BSOAmP, BSOAhP). POA concentrations correspond to the sum of the particle concentrations of POAIP, POAmP and POAhP as well as their aging product (SOAIP, SOAmP, SOAhP).

3.1. Simulation setup

The model was run over Europe with a resolution of 0.5° for the year 2013 with a spin-up of 1 year (corresponding to the order of magnitude of the lifetime of compounds inside soils) to initialize the concentrations in the different compartments. The raw meteorology (including the volumetric soil water content) was obtained from the European Centre for Medium-Range Weather Forecast (ECMWF) model.

Anthropogenic emissions of gases and particles were taken from the EMEP inventory (Vestreng, 2003) for year 2013. However, Denier van der Gon et al. (2015) has shown that residential wood burning (RWB) emissions of PM_{2.5} are underestimated by a factor 2–3 over Europe by the EMEP inventory. Underestimation factors from Denier van der Gon et al. (2015) are applied to correct the inventory.

The time profile of RWB emissions is an important issue, the method of Adelman and Baek (2012) to temporalize emissions as a function of the daily minimum temperature T_{min} was applied to compute daily temporal factors (DTF). Based on information from the French National Inventory (data available on <http://emissions-air.developpement-durable.gouv.fr/>), 0.5% of the PM_{2.5} emissions from the residential activity sector are due to other residential activities than RWB (for example emissions due to the production of hot water). The temporalization of emissions is done with the following equation:

$$DTF_i = 0.995 \frac{42.12 - 0.79T_{min,i}}{\sum_{j=1}^{N_{days}} 42.12 - 0.79T_{min,j}} + \frac{0.005}{N_{days}} \quad (39)$$

with i the day index, $T_{min,j}$ the minimum daily temperature in F and N_{days} the number of days in the year.

The evolution during the year of the emissions of primary SVOC compounds is shown in Fig. 2.

Several simulations were carried out to analyze the effect of air-ecosystem exchanges processes:

- Ref: the deposition is considered as in Bessagnet et al. (2010); Couvidat et al. (2018) with a classic non-reversible pathway based on Wesely (1989).
- NoExc: Exchanges between air and ecosystems are not considered.
- SoilVeg: exchanges with soil and vegetation are considered. The higher values of the kinetics of degradation are used. SVOC from biomass burning are assumed hydrophobic.
- Fast: Like the “SoilVeg” simulation except that the degradation in ecosystems is assumed to be instantaneous. This simulation therefore does not account for the impact of the re-volatilization of organic compounds on concentrations.

The decrease of OM averaged concentrations (compared to the “NoExc”) simulation for the different simulations are summarized in Table 4.

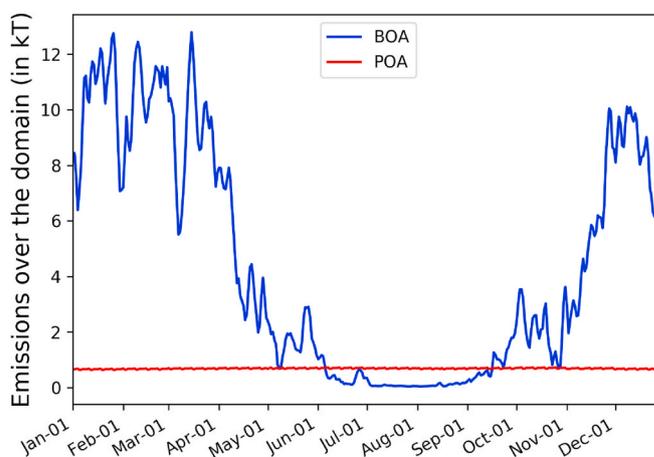


Fig. 2. Evolution of emissions in kilotons (kT) of primary anthropogenic SVOC for biomass burning (BOA, in blue) and other sources (POA, in red) during the year 2013. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Averaged deposition velocities in the gas ($V_{d, gas}$) and particle ($V_{d, part}$) phases and total deposition velocity ($V_{d, tot}$, weighting of $V_{d, gas}$ and $V_{d, part}$ as a function of the gas-phase fraction) and contribution of the gas-phase dry deposition to the total dry deposition of the compounds.

SVOC	Gas-phase fraction (in %)	$V_{d, gas}$ (cm/s)	$V_{d, part}$ (cm/s)	$V_{d, tot}$ (cm/s)	Contribution of gas-phase dry deposition (in %)
BOAIP	0.41	5.82	0.114	0.137	17.4
BOAmP	30.3	1.65	0.101	0.571	87.7
BOAhP	97.1	1.05	0.074	1.018	99.8
BSOAlP	0.26	2.51	0.164	0.170	3.84
BSOAmP	5.21	1.68	0.166	0.245	35.7
BSOAhP	65.2	1.61	0.129	1.10	95.9
AnBlP	57.2	2.15	0.169	1.30	94.5
AnBmP	94.7	2.18	0.178	2.08	99.5
BiA0D	1.97	1.22	0.172	0.193	12.5
BiA1D	70.8	2.02	0.144	1.474	97.1
BiA2D	52.2	2.08	0.174	1.168	92.9
BiBlP	1.37	1.32	0.164	0.180	10.0
BiBmP	56.1	1.48	0.160	0.903	92.2
BiDER	12.1	2.07	0.191	0.419	59.9
BiMGA	98.2	2.08	0.151	2.045	99.9
BiMT	24.5	2.07	0.191	0.650	77.8
BiNGA	90.7	1.98	0.152	1.81	99.2
BiNIT	87.4	1.37	0.118	1.21	98.8
BiNIT3	96.2	1.49	0.130	1.44	99.7
BiPER	28.0	2.12	0.199	0.737	80.5
POAIP	15.8	1.38	0.121	0.319	68.1
POAmP	77.6	1.30	0.097	1.029	97.9
POAhP	98.9	0.86	0.078	0.856	99.9
SOAIP	1.45	1.48	0.172	0.191	11.2
SOAmP	38.6	1.52	0.178	0.695	84.3
SOAhP	87.1	1.54	0.145	1.36	98.6

3.2. Gas-phase and particle-phase dry deposition velocities

Each surrogate compound is present both in the gas and particle phases and are deposited via two competitive dry deposition pathways: the gas-phase dry deposition and the particle-phase dry deposition. The dry deposition of particles is computed as a function of the size distribution using the Wesely approach. To simulate the size distribution, particles are separated into 10 size bins covering a diameter range from 0.01 μm to 10 μm . In order to determine the importance of the gas-phase dry deposition compared to particle dry deposition, the average gas-phase fraction of each surrogate compound and their deposition velocities are shown in Table 3. This table shows the averaged gas-phase

Table 4

Simulated average decrease over the domain of OM concentrations for the different processes for each quarter of year 2013. JFM: From January to March, AMJ: from April to May, JAS: from July to September, OND: from October to December.

	JFM	AMJ	JAS	OND
Effect of atmosphere/ecosystem exchanges (“SoilVeg” compared to “NoExc”)	17%	17%	15%	17%
Effect of dry deposition of gas-phase SVOC according to the Wesely resistance scheme (“Ref” compared to “NoExc”)	2.1%	16%	16%	4.9%
Effect of atmosphere/ecosystem exchanges with instantaneous degradation of SVOC in ecosystems (“Fast” compared to “NoExc”)	32%	23%	20%	0.29%

deposition velocities in the gas ($V_{d,gas}$) and particle ($V_{d,part}$, accounting for the particle size distribution) phases. The total dry deposition velocity ($V_{d,tot}$) is defined as the apparent deposition velocity of the surrogate compound in both phases. It is the weighting of $V_{d,gas}$ and $V_{d,part}$ as a function of the gas-phase fraction.

All the studied surrogate SVOC compounds have a high averaged gas-phase deposition velocity above 1 cm/s whereas $V_{d,part}$ is between 0.1 and 0.2 cm/s. Due to these differences in the deposition velocities, condensation of SVOC onto particles will protect them from dry deposition. Moreover, the gas-phase exchanges were found to be the dominant removal pathway for all compound with a gas-phase fraction above 10%. Altogether, air/ecosystem exchanges could contribute to 30% and 50% of the total removal by dry deposition of SOA and primary organic aerosols (sum of BOA and POA), respectively.

3.3. Effect of air-ecosystem exchanges on organic aerosol concentrations

Fig. 3 shows the evolution of mean OM concentrations over Europe for year 2013 with and without air-ecosystem exchanges. According to the model, air-ecosystem exchanges (“SoilVeg” simulation) can lead to a decrease of OM concentrations (compared to the “NoExc” simulation) around 15% on average over Europe through all the year. With the “Ref” simulation, a low decrease of OM concentrations is simulated (about a few percent) in winter but a decrease around 16% is simulated during summer (slightly stronger than the decrease obtained with the “SoilVeg” simulation).

The significant decrease of OM concentrations during winter estimated with the “SoilVeg” simulations (and not simulated with the “Ref” simulation) is due to the fact that the deposition of primary SVOC from biomass burning is only taken into account in the “SoilVeg” simulation. Indeed, in the “Ref” simulation, deposition is calculated as a function of the Henry’s law constant. Negligible deposition is estimated for hydrophobic SVOC compounds with this parameterization. On the other hand, the “SoilVeg” simulation considers the absorption of hydrophobic SVOC by the organic matter of soils and by vegetation that therefore leads to significant deposition.

This deposition is however limited by the degradation of those compounds in soils and vegetation and their volatilization. With a slow degradation, the volatilization of SVOC from soils may lead to high concentrations above the quasi-laminar layer that will limit the magnitude of the deposition flux. On the opposite, assuming an instantaneous degradation of SVOC will lead to an increase of deposition fluxes and therefore lower concentrations. The estimated decrease of concentrations with the “Fast” simulation compared to the “NoExc” simulation is around 30%. Revolatilization therefore prevents the loss of around 15% of OM (half the loss obtained with the “Fast” simulation) in winter.

In summer, because the secondary compounds are more oxidized, similar concentrations are simulated with the “SoilVeg” and “Ref” simulations. In the two parameterizations, deposition for most compounds will appear as non-reversible (because of the high Henry’s law constant

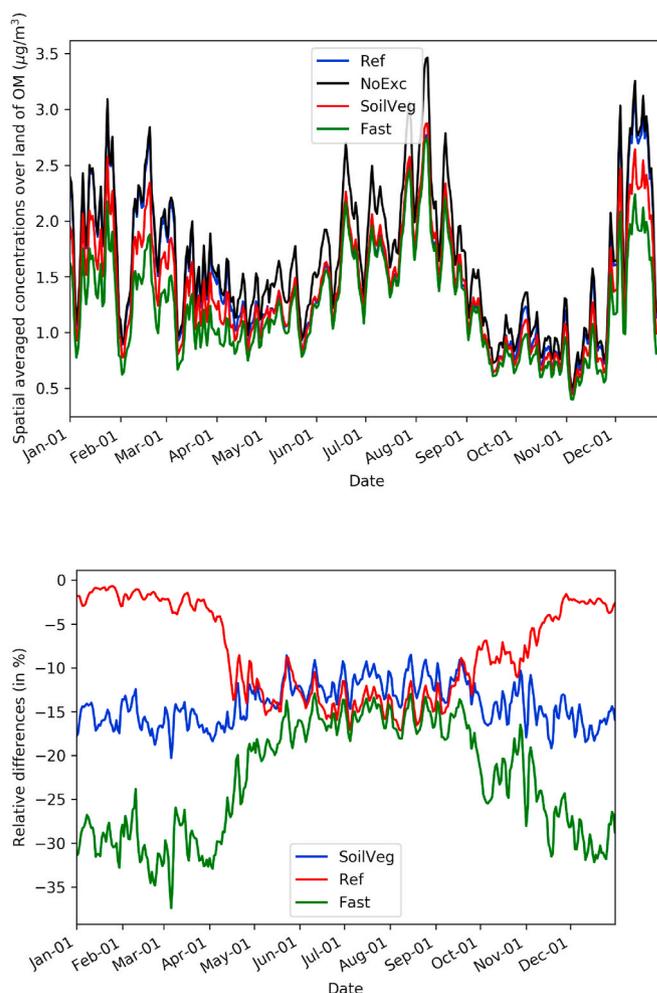


Fig. 3. Temporal evolution of spatial averaged concentrations over land of OM (in $\mu\text{g m}^{-3}$) (top) and effects of the different processes on those concentrations (bottom).

of the compounds). While it could be possible that the parameterization of Bessagnet et al. (2010) underestimates primary SVOC deposition in winter, this parameterization could be reliable for SOA simulation as it gives concentrations similar to those simulated with the exchange module developed in this study. The “SoilVeg” simulation can however be higher than the “Ref” simulation (by a few percent) in summer while the “Fast” simulation is always lower than the “Ref” simulation. This feature indicates that volatilization of SVOC from soils has a slight impact on SOA formation.

Fig. 4 shows maps of concentrations for the “NoExc” and the “SoilVeg” simulations, as well as the relative differences of the “SoilVeg” simulation with the “Ref”, “NoExc” and “Fast” simulations for the months of January and July. This figure shows that the decrease or increase of concentrations are quite homogeneous spatially. In January and July, over most of Europe, the relative differences between the “SoilVeg” and the “NoExc” simulations are above -30% for most areas. However, in Northern and Eastern Europe, differences below -30% (and reaching -80%) are simulated in winter but these areas correspond generally to area with low concentrations of organic aerosols (less than $2 \mu\text{g m}^{-3}$). The differences between the “SoilVeg” and the “Fast” simulation show that not taking into account volatilization can lead to an underestimation between 5% and 30% in winter and below 5% in summer for most of Europe.

The influence of air-ecosystem exchanges on SOA concentrations varies according to the compound volatility with stronger impact for the most volatile compounds. For the “SoilVeg” simulation, the average

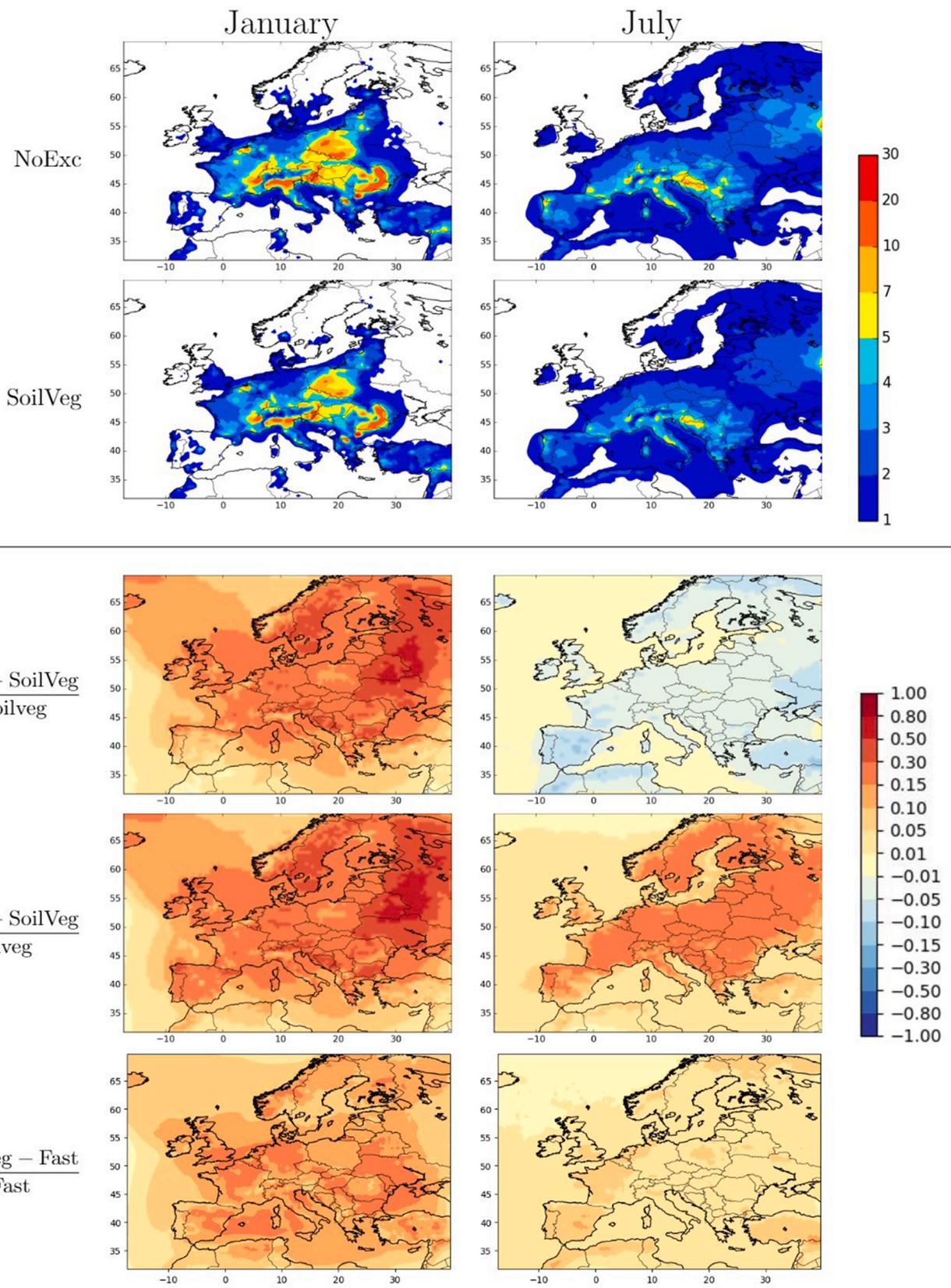


Fig. 4. Temporal evolution of spatial averaged concentrations over land of OM (in $\mu\text{g m}^{-3}$) (top) and effects of the different processes on those concentrations (bottom).

decrease of concentrations (compared to the NoExc simulation) is stronger for the aromatic SOA concentrations (21%) and lower for the SOA concentrations from isoprene (9%). The decrease is around 11% for monoterpenes and sesquiterpenes SOA. The decrease of concentrations simulated in the “Fast” and “Ref” simulations are similar (respectively, 21% and 22% for isoprene SOA, 31% and 32% for aromatic SOA, 15% and 14% for sesquiterpene SOA, 13% for monoterpene SOA).

3.4. Effect of air-ecosystem exchanges on BOA concentrations in winter and summer

The strong decrease of winter BOA concentrations simulated with the “SoilVeg” simulation (by comparison to the NoExc simulation) is due to the strong decrease of OM from wood burning SVOC (decrease around 17%) while it represents around 90% of OM. Most of the decrease is due to the decrease of concentrations of compound BOAmP (representing BOA compounds with medium volatilities) and its oxidation product BSOAmP (representing together 43% of BOA concentrations in January in the NoExc simulation) and of compound BOAhP (representing BOA compounds with high volatilities) and its oxidation products BSOAhP (and 19% of BOA concentrations in January in the NoExc simulation). The mean decreases are around 16% for BOAmP and BSOAmP and 54% for BOAhP and BSOAhP.

Volatilization of biomass burning SVOC from the soil and vegetation compartment has a strong impact on deposition as the decrease of BOA concentrations (by comparison to the NoExc simulation) is much more important with the “Fast” simulation (decrease around 32%). The decreases reach 37% for BOAmP and BSOAmP and 84% for BOAhP and BSOAhP.

Absorption by vegetation is the main removal process of SVOC as only 3.7% of biomass burning SVOC are absorbed by the soil in the “SoilVeg” simulation. In the “Fast” simulation, deposition into vegetation becomes even more important as the mass of biomass burning SVOC absorbed by vegetation over Europe is increased by a factor 1.9. On the contrary, the mass of biomass burning SVOC absorbed by the soil is decreased by 67%. The decrease of the amount of biomass burning SVOC absorbed by soils while the amount absorbed by vegetation increases is due to the competition between deposition on these two types of surface (the increase of the amount deposited onto one of the surface types will limit the amount deposited onto the other).

The low amount of biomass burning SVOC absorbed into soils is due to the in-canopy aerodynamic resistance that strongly limits the deposition flux. Without taking this resistance into account (assumed negligible), the amount of biomass burning SVOC deposited onto soils would increase significantly (by a factor of 94 compared to the “Fast” simulation and by a factor 31 compared to the “SoilVeg” simulation) and would be higher by 28% than the amount deposited onto vegetation.

The amount of gaseous biomass burning SVOC deposited depends on the lifetime of organic compounds in soils and vegetation. While the “SoilVeg” simulation uses the shortest estimated lifetime values (12 days for primary compounds), the “Slow” simulation uses the highest values (140 days for primary compounds). With the “Slow” simulation a decrease of around 13.6% of BOA concentrations compared to the “NoExc” simulation is simulated (slightly less important than the decrease of 17% simulated with “SoilVeg”). Strong differences are however simulated between the “Fast” and the “SoilVeg” simulation during summer as illustrated in Fig. 5. For the “SoilVeg” and the “NoExc” simulation, domain-averaged BOA concentrations are low during summer (around $0.006 \mu\text{g m}^{-3}$ and $0.008 \mu\text{g m}^{-3}$). However, in the “Slow” simulation, concentrations are higher by a factor 10 (concentrations around $0.06 \mu\text{g m}^{-3}$). While the concentrations are still low, this feature indicates that re-emissions of deposited compounds are theoretically possible. The high lifetimes in the “Slow” simulation and the use of bi-directional parameterization allowing a potential re-emission (around half of the mass absorbed by soil and vegetation was re-emitted this way), allow biomass burning SVOC to still be present in the atmosphere during summer.

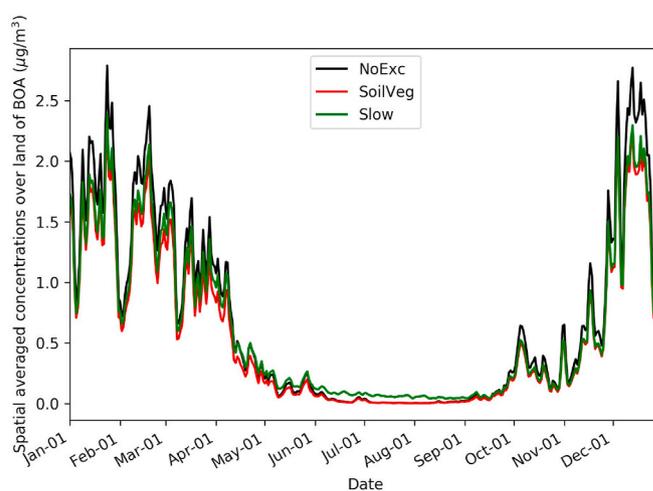


Fig. 5. Temporal evolution of spatial averaged concentrations over land of BOA (in $\mu\text{g m}^{-3}$) for different simulations.

3.5. Sensibility of results to the K_{va} and R_c parameters

As deposition onto vegetation is the main removal process in our simulations, a sensitivity analysis on the main parameters of the vegetation/atmosphere exchanges was carried out. The sensitivity to two parameters was analyzed: the bioaccumulation factor K_{va} and the canopy resistance R_c . Four additional simulations were done:

- increasing by a factor 10 K_{va}
- decreasing by a factor 10 K_{va}
- increasing by a factor 10 R_c
- decreasing by a factor 10 R_c

The simulated decreases of OM concentrations (compared to the “NoExc” simulation) for the “SoilVeg” simulation and the different sensitivity simulations are shown in Fig. 6. The decrease estimated with the R_c sensitivity simulations only differ by $\pm 0.7\%$ (during winter, simulated decreases of 16.3 and 17.1% for R_c multiplied and divided by 10 against 17.0% in the “SoilVeg” simulation), indicating that the vegetation-atmosphere exchange is not limited by the canopy resistance and that the model is not sensitive to the exact value of R_c .

However, the K_{va} sensitivity simulations lead to a change of the decrease of $\pm 5\%$ during winter (simulated decreases of 22 and 12% for

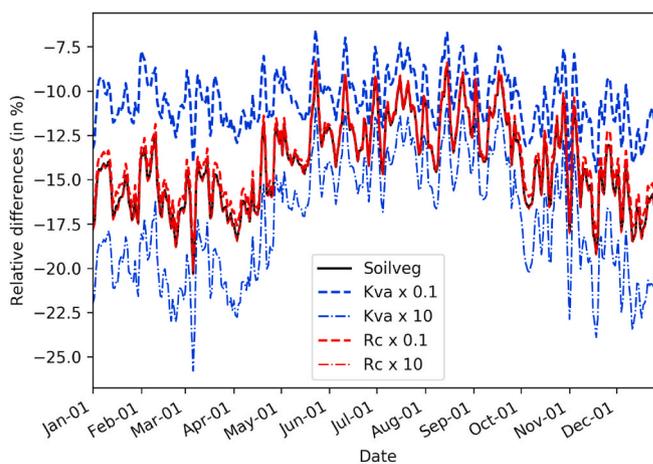


Fig. 6. Temporal evolution of spatial averaged OM concentration decrease over land (in %) due to soil-ecosystem exchanges for the “SoilVeg” simulation and the different sensitivity simulations.

K_{va} multiplied and divided by 10 against 17% in the ‘‘SoilVeg’’ simulation) and of $\pm 2\%$ during summer. While for most organic compounds, concentrations were found to have a low sensitivity to the K_{va} parameter (change of the decrease of $\pm 2\text{--}3\%$ through all the year for non-RWB organic compounds), for BOA, a change of the decrease of $\pm 6\%$ was obtained due to the high sensitivity for BOAhP and BSOAhP compounds ($\pm 14\%$) and for BOAmP and BSOAmP compounds ($\pm 6\%$).

4. Conclusions

An air-soil-vegetation exchange module was implemented in the air quality model CHIMERE and simulations were performed over Europe for year 2013 to analyze the influence of the processes on organic aerosols. A decrease of organic aerosol concentrations around 15% through all the year was obtained when implementing this new processes. This module indicates that the approach of Wesely (1989) used by some air quality models may lead to an underestimation of organic aerosol concentrations in summer by not considering the effect of re-volatilization. This approach probably also leads to an overestimation of concentrations during winter by not considering the deposition of primary SVOC (assumed hydrophobic in this study). Exchanges between the atmosphere and vegetation were found to be most efficient removal process as the air-soil exchanges (and the subsequent diffusion of organic compounds in the soil) contributed to only 6% of the loss of compound. In summer, re-volatilization of SVOC accumulated during winter was found to be a minor but possible source of SVOC in the atmosphere as long as the lifetime of these compounds in the soil and vegetation compartments is high enough.

The conclusions of this study have to be balanced because of the assumptions made and limitations. First, primary SVOC were considered all to be highly hydrophobic and were represented by several linear alkane compounds to calculate their properties. While a large part of primary SVOC should indeed be highly hydrophobic (like long-chain alkanes, aromatics and polycyclic aromatic hydrocarbon), a fraction of the primary SVOC should be polar and hydrophilic, especially for SVOC from wood burning emissions (Schauer et al., 2001). Second, due to lack of information on the calculation of some parameters, parameterizations determined for POPs (that are generally very hydrophobic) had to be used for the calculations of the canopy resistance R_c and the vegetation

air partitioning coefficient (or bioaccumulation factor) K_{va} . A sensitivity analysis showed that results were not sensitive to R_c . However, BOA compounds are sensitive to the K_{va} parameter. An uncertainty of a factor 10 on the K_{va} parameter can lead to an additional decrease of organic aerosols due to air-ecosystems exchanges of $\pm 7\%$.

However, the results of this study show that parameterization of Wesely (1989) may not be appropriate for SVOC deposition and emphasize the need to better characterize the air-soil-vegetation nexus especially the air-vegetation exchanges. One major issue is the absence of appropriate measurements to investigate deeper this process. Evaluation of the gas-phase dry deposition is scarce and are often focused on ozone or SO_2 (Finkelstein et al., 2000) or some VOC compounds (Wu et al., 2012). However, SOA gather compounds with various properties that are often difficult to estimate and that strongly differ from other compounds. Specific experiments would be needed to investigate the importance of air/ecosystem exchanges, especially for compounds from biomass burning. Furthermore, in the current state of air quality models, using an air-soil-vegetation approach may lead to a decrease of model performance. Indeed, models tend to underestimate OM and OC (Organic Carbon) concentrations. Couvidat et al. (2018) reported strong underestimations of OC concentrations (reaching a mean fraction bias of 87%). Mircea et al. (2019) found similar underestimations for other air quality models evaluated in the EURODELTA exercise over Europe (underestimation around 80%). By increasing deposition, it is likely that the underestimation will increase by using this kind of approach.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Notations

α_a	the volumetric air content of the soil $\text{m}^3 \text{m}^{-3}$
α_w	the volumetric water content of the soil $\text{m}^3 \text{m}^{-3}$
γ_1^∞	the activity coefficient of the compound at infinite dilution inside water dimensionless
ρ_s	bulk density of the soil kg/m^3
$\rho_{s,ref}$	a reference bulk soil density kg/m^3
τ_{deg}	characteristic time for degradation inside soils s
τ_{soil}	characteristic time for re-emissions from soil s
τ_{veg}	characteristic time for re-emissions from vegetation s
ξ_g	the gas tortuosity dimensionless
ξ_l	the liquid tortuosity dimensionless
Φ	soil porosity m^3/m^3
c_{doc}	the concentration of dissolved organic carbon in soil solute $\text{kg} \text{m}^{-3}$
f_a	the fraction of the compound in the gaseous phase of the soil compartment dimensionless
f_{dry}	intercepted fraction of the dry deposition flux of particles dimensionless
f_{oc}	soil organic carbon content dimensionless
f_l	the fraction of the compound in the aqueous phase of the soil compartment dimensionless
f_s	the fraction of the compound in the solid phase of the soil compartment dimensionless
f_{wet}	intercepted fraction of the wet deposition flux dimensionless
k_a	the kinetic of degradation in the gaseous phase of the soil compartment s^{-1}
$k_{deg,soil}$	the degradation kinetic parameter of organic compounds in soils s^{-1}
$k_{deg,veg}$	the kinetic parameter of degradation inside vegetation s^{-1}
k_l	the kinetic of degradation in the liquid phase of the soil compartment s^{-1}

k_s	the kinetic of degradation in the solid phase of the soil compartment s^{-1}
k_{wash}	washing-off (of compound accumulated onto vegetation by interception) kinetic parameter s^{-1}
v_d	the deposition velocity m/s
C_{aq}	the concentration in the aqueous phase of soils $ng\ m^{-3}$
C_{doc}	the concentration in the dissolved organic matter inside soils $ng\ m^{-3}$
C_g	the concentration in the gaseous phase of soils $ng\ m^{-3}$
C_s	the concentration in the solid phase of soils $ng\ m^{-3}$
C_T	the concentration of the organic compound in the soil $ng\ m^{-3}$
C_V	the concentration inside the vegetation compartment $ng\ m^{-3}$
D_a	diffusion coefficient of the compound in the air m^2s^{-1}
D_d	bioturbation coefficient m^2s^{-1}
D_e	the effective diffusion coefficient in the soil m^2s^{-1}
D_l	diffusion coefficient of the compound in water m^2s^{-1}
F_{as}	the net flux of organic vapors at the interface $ng\ m^{-2}\ s^{-1}$
F_{deg}	the degradation flux due to the soil chemistry $ng\ m^{-3}\ s^{-1}$
$F_{p,dep}$	the deposition flux of particles (dry and wet, without the intercepted fraction by vegetation) $ng\ m^{-2}\ s^{-1}$
F_{trans}	the flux of vertical transport of organic compounds $ng\ m^{-2}\ s^{-1}$
$F_{wet,gases}$	the wet deposition flux for gaseous compounds $ng\ m^{-2}\ s^{-1}$
H	Henry's law constant mol/L/atm
H_l	the thickness of the layer m
K_{aw}	the air water partitioning coefficient dimensionless
K_{cw}	the cuticle-water partitioning coefficient dimensionless
K_{doc}	the dissolved organic carbon/water partitioning coefficient $m^3\ kg^{-1}$
K_{OA}	the octonal-air partitioning coefficient dimensionless
K_{oc}	the organic carbon/water partitioning coefficient $m^3\ kg^{-1}$
K_{oc}^{dim}	the dimensionless K_{oc} dimensionless
K_{ow}	the octonal water partitioning coefficient dimensionless
K_{va}	the vegetation-air partitioning coefficient (or bioaccumulation factor) a dimensionless
L_s	characteristic length for absorption of organic compounds in soils m
LAI	leaf area index $m^2\ m^{-2}$
M	molar mass $g\ mol^{-1}$
M_{water}	molar mass of water $g\ mol^{-1}$
P	precipitation rate $m\ s^{-1}$
P^0	the sub-cooled saturation vapor pressure of the compound torr
P_c	the permeance coefficient across cuticular membranes $m\ s^{-1}$
R	the universal gas constant $J\ mol^{-1}\ K^{-1}$
R_a	the aerodynamic resistance associated with turbulent transport in the atmosphere $s\ m^{-1}$
R_b	the quasi-laminar layer resistance $s\ m^{-1}$
R_c	the surface resistance $s\ m^{-1}$
R_{cut}	the cuticular resistance $s\ m^{-1}$
R_g	the gaseous phase partitioning coefficient dimensionless
R_l	the soil solute partitioning coefficient dimensionless
R_s	the soil partitioning coefficient dimensionless
R_{sto}	the stomatal resistance $s\ m^{-1}$
T_s	the soil temperature K
$V_{d,gas}$	gas-phase dry deposition velocity $cm\ s^{-1}$
$V_{d,part}$	particle-phase dry deposition velocity $cm\ s^{-1}$
$V_{d,total}$	total (dry+particle) dry deposition velocity $cm\ s^{-1}$
V_e	the effective velocity in the soil $m\ s^{-1}$
V_m	the molar volume of the compound $cm^3\ mol^{-1}$

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