Temperature effects on multiphase reactions of organic molecular markers: A modeling study
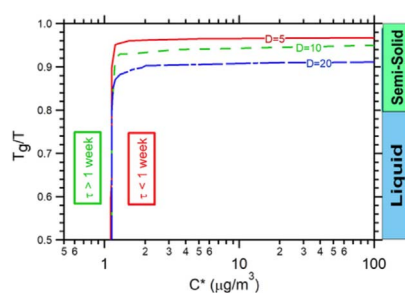
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GRAPHICAL ABSTRACT

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Various molecular markers are used in source apportionment studies. In early studies, molecular markers were assumed to be inert. However, recent studies suggest that molecular markers can decay rapidly through multiphase reactions, which makes interpretation of marker measurements challenging. This study presents a simplified model to account for the effects of temperature and relative humidity on the lifetime of molecular markers through a shift in gas-particle partitioning as well as a change in viscosity of the condensed phase. As a model case, this study examines the stability of levoglucosan, a key marker species of biomass burning, over a wide temperature range relevant to summertime and wintertime. Despite the importance of wood combustion for space heating in winter, the lifetime of levoglucosan in wintertime is not well understood. The model predicts that in low-temperature conditions, levoglucosan predominantly remains in the particle phase, and therefore its loss due to gas-phase oxidation reactions is significantly reduced. Furthermore, the movement of the levoglucosan from the bulk of the particle to the particle surface is reduced due to low diffusivity in the semi-solid state. The simplified model developed in this study reasonably reproduces upper and lower bounds of the lifetime of levoglucosan investigated in previous studies. The model results show that the levoglucosan depletion after seven days reduces significantly from ~98% at 25 °C to < 1% at 0 °C under dry conditions. The depletion of levoglucosan increases at higher relative humidities. However, at temperatures below 0 °C, levoglucosan appears to be a useful marker (lifetime > 1 week) even at 60% relative humidity irrespective of the assumed fragility parameter D that controls estimated diffusivity. The model shows that lifetime of an organic molecular marker strongly depends on assumed D especially when a semi-volatile marker is in semi-solid organic aerosol.

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1. Introduction

Biomass burning is one of the major primary sources of natural and anthropogenic pollutants (Gorin et al., 2006; Krecl et al., 2008; Pandis et al., 2016; Saarikoski et al., 2008; Saffari et al., 2013; von Schneidemesser et al., 2015). While western nations use biomass (including wood) for space heating and recreational purposes, several Asian, African and South American countries use it as a major energy resource. In the United States and Europe, domestic wood combustion is an important source of space heating and a significant source of particulate matter in winter (Caseiro et al., 2009; Crilley et al., 2015; Fine et al., 2002; Krecl et al., 2008; Szidat et al., 2006; Wang et al., 2011a, 2011b). Even though wood burning has been classified as a carbon neutral energy source, burning wood releases hazardous organic chemicals and particles, thereby increasing the aerosol burden on the atmosphere (Bari et al., 2011, 2009; Kim et al., 2013; Kocbach Bolling et al., 2009; Naeher et al., 2007; Shen et al., 2011).

In winter, the higher probability of temperature inversions and weak sunlight to break the inversion reduces the dilution of pollutants (Seinfeld and Pandis, 2006), and hence, wood smoke presents a significant risk to human health (World Health Organization, 2015).

The first step to framing control policies for wood smoke emissions is to correctly assess the contribution of wood smoke to air pollution. Therefore, a reliable quantitative marker is required to accurately quantify the contribution of wood smoke to ambient air pollution. Although non-mineral potassium (K) has been widely used as a marker species of biomass burning, the presence of other major sources (e.g., cooking) and the wide variability among wood types limit the utility of K as a marker species of wood smoke (Schauer et al., 2001). In contrast, organic markers tend to be more source-specific, but not inert. Levoglucosan, a chemical generated by pyrolysis of cellulose and hemicellulose during the biomass burning process, has been widely considered a useful molecular marker of biomass burning smoke over the last few decades (Elias et al., 2001; Fraser and Lakshmanan, 2000; Schauer and Cass, 2000; Simoneit et al., 2000, 2004, 1999, Simoneit and Elias, 2001, 2000). However, recent work (Hennigan et al., 2010) has questioned the assumed inertness of levoglucosan. They studied summertime chemistry experimentally and reported a short lifetime, or e-folding time, of levoglucosan on the order of 1–2 days. A theoretical study (May et al., 2012) also discussed the lifetime of levoglucosan and reported similar lifetimes. These studies also concluded that levoglucosan is semi-volatile, and hence its gas-phase oxidation in addition to the condensed phase oxidation can lead to its short lifetime. The apparent short lifetime of levoglucosan implies that air pollution source apportionment studies using levoglucosan as one of the markers may underestimate the contributions from biomass burning since aged smoke may be depleted in levoglucosan. Hence, the applicability of levoglucosan may be questionable at least under temperature conditions relevant to summer prescribed/wildfires. However, in winter, wood smoke emissions from residential stoves are significant contributors to air pollution. Additionally, lifetime of biomass burning markers at low temperatures may have significant implications for geochemical studies using biomass burning markers in ice cores to estimate wildfire several hundred years ago (Kawamura et al., 2012). At colder temperatures, gas-particle partitioning and condensed phase reactions are likely to significantly differ from those in summer.

Previous work (May et al., 2012) developed a model to account for oxidation of semi-volatile markers in the gas-phase and on the particle surface assuming particles are well-mixed. The model showed that temperature can have a significant effect on the lifetime of marker species primarily through the shift in gas-particle partitioning. On the other hand, an increasing number of studies suggest that viscosity of organic aerosol increases as a result of decrease in temperature, and therefore the particle interior cannot be assumed as well-mixed (Rothfuss and Petters, 2017; Shiraiwa et al., 2017). For instance, Arangio et al. (2015) investigated evolution of biomass burning markers, levoglucosan and abietic acid, using Kinetic Multi-layer model of Gas-Particle interactions (KM-GAP) that treats explicitly all steps of mass transfer and chemical reactions of organic compounds partitioning between gas, particle surface, and particle bulk phase. Their model suggests that temperature and relative humidity have significant influences on the lifetime of molecular markers by changing the viscosity and diffusivity of materials in aerosol particles. However, Arangio et al. (2015) did not include gas-phase oxidation of marker species, and hence, the lifetime predicted in their study is considered an upper limit.

This study builds upon previous studies that suggest gas-particle partitioning and condensed phase diffusivity may control the lifetime of biomass burning marker species. We hypothesize that under high-temperature conditions, the well-mixed assumption used in May et al. (2012) is appropriate, and under low-temperature conditions, diffusivity within particles may control the lifetime of marker species as in Arangio et al. (2015). We aim at bridging the gap by developing a simple model based on coupled ordinary and partial differential equations that can account for gas-particle partitioning as well as phase state of the particle. The model reasonably reproduces upper and lower bounds of the lifetime of levoglucosan suggested in previous studies. In addition, the model shows the transition of the lifetime of levoglucosan between low and high-temperature conditions. Even though this study focuses on levoglucosan, in principle, the same approach is applicable to a variety of organic molecular markers.

2. Model development

A system of differential equations is proposed to quantify the concentration of the levoglucosan in the particle and gas phase. The model is then non-dimensionalized and solved numerically. Fig. 1 illustrates the different processes taking place in the system. The assumptions and initial conditions used in framing the problem are as follows. The particle and gas phase levoglucosan are in equilibrium and uniform across respective phases at time $t = 0$. The overall loss of the levoglucosan is driven by the gas-phase reaction, particle phase reaction (on the particle surface) between levoglucosan and OH radical, and the equilibrium between the particle and the gas-phase levoglucosan.

Additionally, as the temperature declines, a larger amount of the levoglucosan partitions to the particle phase at equilibrium. For example, more than 99% of the total levoglucosan is estimated to partition to the particle phase at 0 °C, while only 75% at 25 °C. Equation (1) shows the gas-particle partitioning of a marker:

$$\xi_i = \left(1 + \frac{C_i^*(T)}{C_{OA}}\right)^{-1}, \tag{1}$$

where ξ_i is the fraction of the marker that stays in the particle at equilibrium, C_{OA} is the mass concentration of organic aerosol (OA), C_i^* is the saturation concentration of species i in a mixture. C_i^* is related to the saturation concentration C_i^o of a pure species i via the activity coefficient (ζ): $C_i^* = \zeta C_i^o$ (Donahue et al., 2011). Donahue et al. (2011) modeled ζ based on the similarity between solute (marker species) and solvent (OA) in terms of O/C ratio. Assuming levoglucosan (O/C = 0.83) is mixed in fresh biomass burning OA with O/C ≈ 0.25, ζ is estimated to be approximately 3 (Donahue et al., 2011). For aged OA with a higher O/C, ζ is expected to be closer to 1. This work assumes $\zeta = 1$ for simplicity since saturation concentration (C_i^o) is typically a much greater source of uncertainty with it typically being 1-2 orders of magnitude (Barley and McFiggans, 2010). The saturation concentration C^* at any temperature can be estimated using the Clausius-Clapeyron equation based on the heat of vaporization and C^* value at a reference temperature (May et al., 2012).

As the time passes, the gas phase concentration depletes and drives the mass transfer of the levoglucosan from the particle surface governed by gas-particle equilibrium. The loss of the levoglucosan concentration on the particle surface leads to the diffusion of the levoglucosan from