Emission of intermediate, semi and low volatile organic compounds from traffic and their impact on secondary organic aerosol concentrations over Greater Paris

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ABSTRACT

Exhaust particle emissions are mostly made of black carbon and/or organic compounds, with some of these organic compounds existing in both the gas and particle phases. Although emissions of volatile organic compounds (VOC) are usually measured at the exhaust, emissions in the gas phase of lower volatility compounds (POA_{vapor}) are not. However, these gas-phase emissions may be oxidised after emission and enhance the formation of secondary organic aerosols (SOA). They are shown here to contribute to most of the SOA formation in Central Paris. POA_{vapor} emissions are usually estimated from primary organic aerosol emissions in the particle phase (POA). However, they could also be estimated from VOC emissions for both gasoline and diesel vehicles using previously published measurements from chamber measurements. Estimating POA_{vapor} from VOC emissions and ageing exhaust emissions with a simple model included in the Polyphemus air-quality platform compare well to measurements of SOA formation performed in chamber experiments. Over Greater Paris, POA_{vapor} emissions estimated using POA and VOC emissions are compared using the HEAVEN bottom-up traffic emissions model. The impact on the simulated atmospheric concentrations is then assessed using the Polyphemus/Polair3D chemistry-transport model. Estimating POA_{vapor} emissions from VOC emissions rather than POA emissions lead to lower emissions along motorway axes (between -50% and -70%) and larger emissions in urban areas (up to between $+120\%$ and $+140\%$ in Central Paris). The impact on total organic aerosol concentrations (gas plus particle) is lower than the impact on emissions: between -8% and 25% along motorway axes and in urban areas respectively. Particle-phase organic concentrations are lower when POA_{vapor} emissions are estimated from VOC than POA emissions, even in Central Paris where the total organic aerosol concentration is higher, because of different assumptions on the emission volatility distribution, stressing the importance of characterizing not only the emission strength, but also the emission volatility distribution.

1. Introduction

Particles, especially fine particles, lead to adverse effects on human health (e.g. Pope et al., 1995), and to visibility reduction. They also affect the manner in which radiation passes through the atmosphere and represent an uncertain component of climate change. Particles are made of different compounds: dust, inorganic aerosol, organic aerosol (OA), black carbon (BC), metals, etc. Organic compounds have a large range of molecular weights and functionalities, which determine their volatility (their capacity to partition between the gas and particle phases), and other properties (e.g. their water solubility, which affects their capacity to partition to the particle phase depending on the environment). Volatile organic compounds (VOC) are usually defined as compounds that only exist in the gas phase (roughly $\leq C_{12}$, see Gentner

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et al. (2017)). Organic aerosol may exist in both the gas (OA$_{vapor}$) and particle (OA) phases (Robinson et al., 2007). The total of the gas and particle phases of organic aerosol is referred to as OA$_{total}$, following the naming convention of Murphy et al. (2014). OA$_{total}$ is made of different compounds, which are usually classified depending on their volatility: intermediate volatility organic compounds (IVOC), semi volatility organic compounds (SVOC) and low volatility organic compounds (LVOC). A glossary summarizing the notation used is provided in Appendix A.

Atmospheric concentrations. In the atmosphere, high concentrations of OA are observed in winter in some urban areas (Petit et al., 2015; Cheng et al., 2016). In summer, OA concentrations may mostly originate from the oxidation of biogenic VOC emitted from the vegetation (Sartelet et al., 2012; Chrit et al., 2017). However, in winter in urban areas, OA concentrations may mostly originate from the oxidation of anthropogenic VOC and gas-phase organic aerosol of volatility lower than VOC (OA$_{vapor}$). These VOC and OA$_{vapor}$ may have different origins, such as wood-burning and traffic-related activities (Baudic et al., 2016; Denier van der Gon et al., 2015; Beekmann et al., 2015). Air-quality models, which simulate the fate of organic compounds in the atmosphere, tend to under-estimate OA concentrations in urban areas (Couvidat et al., 2013; Hayes et al., 2015). This under-estimation could be partly due to the gas-phase primary organic aerosol emissions (POA$_{vapor}$), which are currently missing from most emission inventories (Robinson et al., 2007; Couvidat et al., 2012; Denier van der Gon et al., 2015).

Organic precursors from traffic. For a long time, it was assumed that vehicular-derived particles were predominantly a direct tailpipe emission, but recent studies indicate that a larger fraction is secondary (Platt et al., 2013; Gordon et al., 2014a, b), i.e. it is formed through atmospheric physico-chemical processes of precursors, which form secondary organic aerosols (SOA, Zhang et al., 2007; Jimenez et al., 2009). Organic compounds emitted from gasoline and diesel vehicles are found in both the gas and particle phases (Schauer et al., 1999, 2002). Exhaust (primary emitted) particles were considerably reduced by the introduction of particle filters in diesel vehicles (DPF) (Platt et al., 2013; Gordon et al., 2014b; Kim et al., 2016). Platt et al. (2013) and Gordon et al. (2014a, b) measured directly the ageing of the exhaust emissions in reaction chambers from tested vehicles incorporating a range of engines and exhaust aftertreatment technologies, including DPF and diesel oxidation catalysts. They found that the SOA fraction, formed from the oxidation of VOC and POA$_{vapor}$, largely dominates the primary organic aerosol (POA) fraction (e.g. Gentner et al., 2017). Amongst VOC, the main known precursors are aromatics (Odum et al., 1997; Dawson et al., 2016), such as the so-called BTEX (benzene, toluene, ethylbenzene, and xylene). Although gasoline fuel contains a larger percentage of aromatics than diesel fuel (Louis et al., 2016), Martinet et al. (2017) measured similar BTEX emissions from recent gasoline and diesel vehicles. However, Euro 1 and Euro 2 gasoline vehicles emit 10 times more BTEX than recent vehicles. Gas and particle phase primary organic aerosol (POA$_{total}$) are made of different chemical species, such as high molecular weight alkanes (> C$_{12}$), high molecular weight aromatics and cyclic compounds, which are likely to be the major contributors to SOA (Schauer et al., 1999, 2002; May et al., 2014; Zhao et al., 2015, 2016).

POA$_{total}$ emissions. Air-quality models, such as the one of the air-quality modelling platform Polyphemus used here, use emission inventories as input data to compute the concentrations of pollutants. Although VOC emissions are provided by emission inventories, POA$_{vapor}$ emissions are not. Because of their semi-volatile properties, measurements of POA$_{total}$ in the exhaust are difficult. For example, POA$_{total}$ may condense on or evaporate from filters depending on the dilution and atmospheric conditions, e.g., temperature, leading to uncertainties in measuring organic particles. Furthermore, the gas/particle emission ratio (POA$_{vapor}$/POA) depends on the time elapsed between emissions and measurements. Kim et al. (2016) estimated that

depending on vehicles and road-driving cycles, thermodynamic equilibrium between gas and particles may take up to 8 min to be reached. A time elapsed between emission and measurement shorter than this characteristic time to reach equilibrium can lead to lower concentrations in the particle phase than those that would be estimated assuming thermodynamic equilibrium, because the equilibrium between gas and particles has not yet been reached. Therefore, measurements of OA performed using online (e.g. aerosol mass spectrometers) and off-line (e.g. filters) measurement techniques may lead to different gas/particle ratio POA$_{vapor}$/POA. Because of the difficulties to estimate POA$_{total}$ emissions, they have been estimated using different methods, such as measurements performed for linear alkanes (Kim et al., 2016). Kim et al. (2016) estimated that the gas/particle ratio of alkane emissions for passenger cars in France is about 1.5. By assuming that the gas/particle ratio of emissions is the same as the ratio of alkane emissions, Zhu et al. (2016) used this 1.5 ratio to compute winter air-quality over Greater Paris, and found relatively good agreement with measurement for January 2009. Other publications used the same POA$_{vapor}$/POA ratio of 1.5 to estimate POA$_{total}$ (Bergström et al., 2012; Koo et al., 2014).

Because measurements of POA depend on temperature, Jathar et al. (2014b) and Zhao et al. (2015, 2016) recommend to estimate emissions of POA$_{vapor}$ using a IVOC/NMHC ratio, with NMHC being non-methane hydrocarbons. Following the measurements of May et al. (2013a, b) and Gordon et al. (2014a, b), and by performing a gas-phase carbon-balance analysis, Jathar et al. (2014b) determines the average contribution of unspeciated organic compounds (assumed to be mainly IVOCs) to non-methane organic gas (NMOG). Zhao et al. (2015, 2016) quantified IVOC emissions for a fleet of gasoline and diesel vehicles through gas chromatography/mass spectrometry analysis of adsorbent samples collected from a constant volume sampler. Zhao et al. (2016) found a IVOC/NMHC ratio similar to Jathar et al. (2014b) for gasoline vehicles (a ratio IVOC/NMHC of about 17% against a ratio IVOC/NMOG of 25% in Jathar et al. (2014b)), but lower for diesel vehicles (a ratio IVOC/NMHC of about 60% against a ratio IVOC/NMHC of 20% in Jathar et al. (2014b)). Note that the difference between NMOG and NMHC, which is of the order of 10% (Gierczak et al., 2017), may not explain the differences between the two approaches for diesel vehicles, for which a large fraction of IVOC may not be accounted for in NMHC measurements (Zhao et al., 2016).

Jathar et al. (2014a) and Zhao et al. (2015, 2016) modelled in 0D the ageing of exhaust emissions by taking into account the molecular structure of IVOC. Jathar et al. (2014a) showed that SOA formation may be sufficiently well reproduced in air-quality model by modelling the ageing of IVOC precursors as a fuction of the precursor volatility, without differences in the molecular structure.

IVOC emissions have often been included in air-quality models, proportionally to POA emissions, resulting in better model to measurements comparisons in terms of both SOA magnitude and diurnal variability (e.g. Dzepina et al., 2009; Hodzic et al., 2010; Couvidat et al., 2013; Hayes et al., 2015; Woody et al., 2016; Murphy et al., 2017). Jathar et al. (2017) used the ratio estimated by Jathar et al. (2014b) in the air-quality model CMAQ to estimate IVOC emissions by reapportioning the existing NMOG emissions between VOC and IVOC. They found that over southern California, IVOC forms as much SOA as VOC, in agreement with chamber experiments performed using emissions of gasoline vehicles (Gordon et al., 2014b; Zhao et al., 2016). The contribution of IVOC to air quality may be even more important in Europe, where diesel vehicles are more common than in North America (Dunmore et al., 2015). Ots et al. (2016) presented a first estimation of diesel IVOC emissions for European cities. They estimated IVOC emissions to be about 2.3 times the amount of VOC emissions from diesel and gasoline vehicles. Their estimation is higher than those of Gordon et al. (2014a) and Zhao et al. (2015). Their IVOC emissions were estimated from the measured ratio of diesel IVOC + VOC concentrations to gasoline-VOC concentrations measured in Central London during the