Organic speciation of ambient quasi-ultrafine particulate matter (PM$_{0.36}$) in Augsburg, Germany: Seasonal variability and source apportionment

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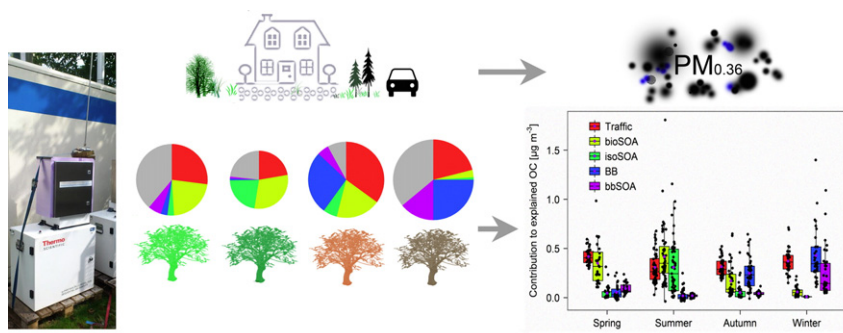[d] Environmental Science Center (WZU), University of Augsburg, Augsburg, Germany
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HIGHLIGHTS

- Unattended long term sampling of particulate matter below 360 nm
- Chemical speciation of primary and secondary organic source markers
- Successful application of positive matrix factor analysis for source apportionment
- 5 primary and secondary sources separated to explain majority of OC variability
- Secondary organic aerosols (SOAs) originated from different biogenic and anthropogenic sources separated

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

To investigate the organic composition and their sources of very fine atmospheric particulate matter (PM), size-segregated PM was sampled using rotating drum impactor (RDI) in series with a sequential filter sampler in Augsburg, Germany, from April 2014 to February 2015. Organic speciation analysis and organic carbon/elemental carbon (OC/EC) analysis was performed for the smallest size fraction PM$_{0.36}$ (PM < 360 nm). Different OC fractions were determined by thermal optical EC/OC analyzer, and OC2, OC3 and OC4 refer to OC fractions that were derived at 280, 480 and 580 °C, respectively. Positive matrix factorization (PMF) analysis was applied for source apportionment study. PMF resolved 5 sources including biogenic dominated secondary organic aerosol (bioSOA), isoprene dominated SOA (isoSOA), traffic, biomass burning (BB) and biomass burning originated SOA (bbSOA). On annual average, PMF results indicate the largest contribution of biogenic originated SOA (bioSOA plus isoSOA) to OC, followed by traffic and then BB related sources (BB plus bbSOA). Traffic was found to be associated with the smallest particles; whereas bioSOA and BB are associated with larger particles. Secondary organic marker compounds from biogenic precursors, OC2, OC3 and bioSOA, isoSOA source factors show summer maximum. Polycyclic aromatic hydrocarbons (PAHs), biomass burning markers, OC4 and BB, bbSOA source factors show winter maximum. Hopanes and the traffic source factor show little seasonal variation. Summer peaks of OC3 and OC2 are well modeled by PMF and are attributed mainly to biogenic SOA. OC4 was

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generally poorly modeled due to lack of characteristic low volatile markers. Summer maxima of biogenic SOA related compounds and source factors are positively correlated with temperature, global radiation, O_3 concentration and mixing layer height (MLH). Winter maxima of BB related compounds and source factors are negatively correlated with temperature and MLH; whereas positively correlated with NO_2 level.

1. Introduction

Airborne particulate matter (PM) has often been associated with a range of adverse health effects. Previous studies mostly focused on PM_{10}, which are respirable particles, and $PM_{2.5}$, which are particles capable of penetrating into gas exchange region of lung (alveoli). Recent toxicological and epidemiological studies have drawn the attention to adverse health effects of even smaller particles, such as ultrafine particles (UFP, generally referring to particles <100 nm), especially among the susceptible population Oberdorster (2001). Several characteristics of smaller particles may lead to notable detriment to human health. Despite their substantial or even dominating contribution to particle number counts as well as large surface area, due to minor contribution to mass they are not controlled by mass based legislations. Because of size dependent deposition of inhaled particles in the respiratory system, UFP could penetrate deeper and tend to deposit in the alveolus region and furthermore UFP seem to be more resistant to phagocytosis of alveolar macrophages (Oberdorster, 2001; Renwick et al., 2001; Moller et al., 2002). One major concern is the possibility of UFP translocating to secondary target organs such as the liver, kidney and central nervous system etc. (Oberdörster et al., 2004; Elder et al., 2006; Kreyling et al., 2009).

Of the variety aspects that need to be characterized for atmospheric ultrafine PM, the organic composition of UFP and their sources are of special interest. Using source apportionment models, impact of a variety of source contributions to ambient PM could be reconstructed. Positive matrix factorization (PMF) is a widely used multivariate receptor model (Paatero and Tapper, 1994) that does not necessarily need a prior knowledge of source profiles, which makes it powerful in general source apportionment studies. Viana et al. (2008) reviewed the source apportionment studies in Europe using different models from 1987 to 2007 and found 4 main sources types which are from vehicular emission, crustal, sea-salt, and a mixed industrial/fuel-oil combustion and a secondary inorganic aerosol. It is worth mention that the sources that could be resolved depend on the input variables. Their source specificity, either as single compound or as pattern, is crucial in source identification. For source apportionment of atmospheric PM based on quantified concentrations, commonly used input variables are the elements (metals) concentrations, concentrations of inorganic ions as well as organic marker compounds. Some source apportionment studies also used particulate number concentrations in different size classes to resolve source contributions mainly to ambient PM (Gu et al., 2011; Vu et al., 2015). As the particles become smaller, carbonaceous fraction could contribute even more to the PM mass and be the dominating contributor to ultrafine PM mass. (Kleeman et al., 2008; Kam et al., 2012). The carbonaceous component impacts on physical and chemical properties and is strongly associated with adverse health effects of PM. Individual compounds or compound groups could be responsible for different health risks, such as mutagenic or carcinogenic potential of some PAHs (Lin et al., 2008). Source apportionment of the redox activity of quasi-ultrafine particles ($PM_{0.49}$) performed in Greece found vehicular traffic and residential wood burning as the major contributors to the measured redox activity of $PM_{0.49}$ at urban traffic site and at the urban background site, respectively (Argyropoulos et al., 2016). Specific organic markers and marker fingerprints are valuable source indicators (Viana et al., 2008; Lin et al., 2010; Noziere et al., 2015) and have widely been used by PMF as input variables to apportion the sources of $PM_{2.5}$ and PM_{10} (Wagener et al., 2012; Wang et al., 2012). Primary sources

could be traced by organic molecular markers known from emission profiles. For instance levoglucosan is commonly used as biomass combustion marker because it comes from cellulose degradation during biomass burning (Simoneit, 2002; Lin et al., 2010) and hopanes are used as a markers of traffic emissions because engines that use lubricating oil emit hopanes (Lin et al., 2010). Compounds formed from atmospheric reactions of volatile biogenic or anthropogenic precursors can be used to assess the contribution of secondary organic aerosols (SOA) to ambient PM. Due to its complexity, SOA is difficult to be characterized and not as well studied in source apportionment studies as primary organic aerosols (Kroll and Seinfeld, 2008; Noziere et al., 2015). Typically secondary organic compounds are derived from oxidation of precursors in the gas phase and gas to particulate partitioning of oxidized semivolatile products thereafter. Therefore, SOA compounds are usually highly oxidized, polar and contribute to water soluble organic carbon (WSOC) of PM. SOA markers from the most important biogenic emissions, isoprene and pinene (α and β-pinene), have been identified and used in $PM_{2.5}$ and PM_{10} aerosol source apportionment studies (Ding et al., 2008; Zhang et al., 2010; Peng et al., 2013).

Only a few source apportionment studies on UFP based on chemical composition have been reported yet. Kim et al. (2016) analyzed the sources of size segregated PM (including ultrafine PM) in Cleveland using PMF based on inorganic ions, elements and OC/EC, and identified 4 sources for ultrafine PM at urban sites, comprising steel production/ road dust, coal combustion/motor vehicles, oil combustion and secondary nitrate aerosols, and 5 sources at rural sites, including steel production/coal, motor vehicles, road dust, soil and secondary nitrate aerosols. Using gases, OC/EC and element concentrations as input data, Kuwayama et al. (2013) performed PMF analysis for $PM_{0.1}$ and could detect traffic related and wood combustion sources. Despite the frequent application of organic markers as input data in source apportionment studies on $PM_{2.5}$ and PM_{10} samples, its application to UFP and quasi-ultrafine particles is extremely rare. Applying chemical mass balance (CMB) based method, Shirmohammadi et al. (2016) and Argyropoulos et al. (2016) reported sources apportionment study of $PM_{0.18}$ and $PM_{0.49}$ using chemical composition including organic markers such as PAHs and levoglucosan, respectively. Based on source factors achieved from a PMF based study on $PM_{2.5}$, Shirmohammadi et al. (2016) were able to resolve one factor for total secondary organic carbon. One study in Leipzig, Germany applied PMF to organic markers (PAHs, hopanes, levoglucosan etc.), elements and ions for size-segregated PM and resolved sources of traffic, coal combustion, biomass combustion, photochemistry, cooking for $PM_{0.14}$ and the sources mentioned plus secondary inorganic aerosol for accumulation mode PM in size-range 0.14–0.42 μm and 0.42–1.2 μm and it compared source contributions in summer and winter (van Pinxteren et al., 2016).

Major aim of our study is to investigate the seasonality of the chemical composition and source contributions of the carbonaceous fraction of quasi-ultrafine ambient PM. Daily $PM_{0.36}$ samples were collected from April 2014 to February 2015 at an urban background station in Augsburg, Germany. Detailed chemical characterization of organic molecular markers for various sources was carried out applying in-situ derivatization direct thermal desorption gas chromatograph mass spectrometry (IDTD-GC-TOF-MS, Li et al., 2016). PMF was applied to identify and asses contributions of primary (traffic, biomass combustion) and secondary (from biomass combustion, isoprene, terpenes) sources to carbonaceous aerosols. Size-segregated particulate number concentrations and OC sub-fractions were included as auxiliary PMF parameters.