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Spatial and temporal variation of sources contributing to quasi-ultrafine particulate matter $PM_{0.36}$ in Augsburg, Germany

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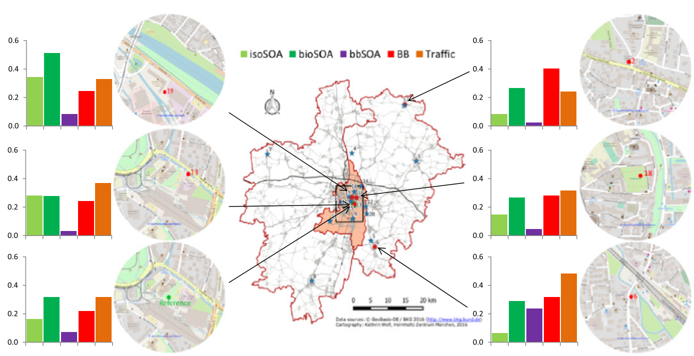
HIGHLIGHTS

- Weekly unattended long term and multi-sites parallel sampling of daily $PM_{0.36}$
- Primary and secondary sources of OC separated by PMF analysis based on chemical markers
- Temporal correlation and spatial variability of source contributions to quasi-UFP revealed
- The results are indicative for exposure assessment in health effect study
- Partial differentiation of source-specific regional and local influence

GRAPHICAL ABSTRACT



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ABSTRACT

Objective: to study the sources contributing to quasi-ultrafine particle (UFP) organic carbon and the spatial temporal variability of the sources.
Method: 24 h quasi-UFP (particulate matter <0.36 μm in this study) was sampled at a reference site continuously and at one of 5 other sites (T1, T2, T3, T4 and B1) in parallel in Augsburg, Germany from April 11th, 2014 to February 22nd, 2015, attempting to conduct 2-week campaigns at each site in 3 different seasons. Positive matrix factorization (PMF) was applied to measured organic tracers for source apportionment analyses. Pearson correlation coefficient *r* and coefficient of divergence (COD) were calculated to investigate spatial temporal variation of source contributions. Result.
5 sources were identified comprising biomass burning (BB), traffic emissions (Traffic), biogenic secondary organic aerosol (bioSOA), isoprene originated secondary organic aerosol (isoSOA) and biomass burning related secondary organic aerosol (bbSOA). In general, good temporal correlation and uniform distribution within the study area are found for bioSOA and bbSOA, probably resulting from regional formation/transport. Lower temporal correlation and spatial heterogeneity of isoSOA were found at the city background site with local influence from green space and less traffic impact. BB demonstrated very good temporal correlation, but higher contributions at sites influenced by local residential heating emissions were observed. Traffic showed the least seasonality and lower correlation over time among the sources. However, it demonstrated low spatial heterogeneity of

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absolute contribution, and only a few days of elevated contribution was found at T3 when wind came directly from the street nearby.
Conclusion: temporal correlation and spatial variability of sources contributing to the organic fraction of quasi-UFP vary among sites and source types and show source-specific characteristics. Therefore, caution should be taken when using one monitor site measurement to assess human exposure in health effect studies of quasi-UFP.

1. Background

For epidemiological studies on health effect of ambient air pollution, exposure assessment needs to consider temporal and/or spatial variation of pollutants. In short term studies investigating the temporal variation, usually observation from one monitoring site is used to represent the exposure of population in the whole study area, assuming high temporal correlation of the pollutant. In long term studies investigating the spatial variability, very often observations from several sites are considered and even modeling such as land use regression model are applied to predict the spatial variability (Wolf et al., 2017). Although substantial variation was found among different study areas located in Europe, studies have generally shown regional homogeneity and relatively low spatial variability of PM mass concentration (e.g. $PM_{2.5}$ and PM_{10}, which refer to PMs with aerodynamic diameters <2.5 and 10 μm, respectively) in comparison with other pollution metrics such as NO_x and particle numbers dominated by smaller particles (Bressi et al., 2013; Eeftens et al., 2015; Eeftens et al., 2012). Particularly, there is less difference between traffic and urban background sites. The temporal spatial variability of different metric is therefore variable. The temporal spatial variability is mainly due to the difference in source contribution. Moreover, the temporal spatial change of individual source contribution varies from source to source. Therefore, it is worth to investigate temporal spatial variability of source contribution at different sites and their influential factors.

Recent studies have drawn attention to the health effects of smaller particles, especially ultrafine particulate matter (UFP), which often refers to PM < 100 nm, whereas quasi-UFP refers to PM up to several hundred nanometers (e.g. 150 nm, 250 nm, 400 nm, etc.) (Birmili et al., 2014; Oberdorster, 2001; Rueckerl et al., 2011; Terzano et al., 2010). Saffari et al. (2014a) reported the association between smaller PM size fractions and higher activity of intrinsic reactive oxygen species (ROS) generated by rat alveolar macrophage cells exposed to ambient PM in vitro. An epidemiological study in Augsburg, Germany revealed association between short term ultrafine particle exposure (indicated as particle number concentrations) and recurrent of human cardiovascular events (Wolf et al., 2015). However, the exposure estimation of smaller particles is much less developed than the exposure estimation of $PM_{2.5}$ and PM_{10}. Little is known regarding their chemical properties and sources, which are both intrinsically related to their health effect. Moreover, chemical composition and sources are also closely related. Regarding the toxicological effects of chemical components in quasi-UFP, one study found that organic carbon (OC), water soluble organic carbon (WSOC) and concentration of water soluble transition metals of $PM_{0.25}$ were associated with ROS activity generated through in vitro test of rat alveolar macrophage cells, and another study reported association between Dithiothreitol (DTT) activity and chemical species such as PAHs, hopanes, etc. (Saffari et al., 2013; Saffari et al., 2014b). $PM_{0.4}$ caused ROS and DNA damage in cultured human cells were found to be induced by winter PM fractions and its DNA damage in winter correlates with the presence of organic compounds (Longhin et al., 2013). However, these studies were still under the condition of in vitro tests and therefore introduce great uncertainties when extrapolating to humans. Besides, it is difficult to draw consistent conclusions from existing studies as each one having its particular design regarding both exposure and response assessments. Further studies need to address these issues.

Differences in source contributions have impact on PM mass, number counts and chemical composition, and therefore may have influence on health effect. Using molecular marker based chemical mass balance (MM-CMB) model to differentiate the sources that contribute to OC of $PM_{0.25}$ at different sites, Saffari et al. (2015) found that difference in source strength was the main reason for oxidative potential differences at different sites. Their result shows that mobile emissions and secondary organic aerosol (SOA) explained 58% of the spatial and temporal variability of oxidative potential of $PM_{0.25}$ at 3 locations. Spatial variation of UFP/quasi-UFP was rarely studied except for number concentration. Studies on their spatiotemporal variability shall provide hints on exposure evaluation, physicochemical property characterization and atmospheric transformation. A study of 10 distinct areas in the megacity of Los Angeles, USA found that $PM_{0.25}$ mass was relatively spatially homogeneous, and only uneven distribution of its elemental carbon (EC), nitrate and several toxic metals over shorter spatial scales was demonstrated (Daher et al., 2013). Applying CMB model to chemical speciation data of $PM_{0.25}$ and $PM_{2.5}$ in Los Angeles–Long Beach harbor, Yao et al. (2004) found that spatial variation of sources contributing to OC and ultrafine mass was not very pronounced except for certain sites.

To have a better understanding of the spatial variation of quasi-UFP (in this study: $PM_{0.36}$) with regard to its source contributions to OC, this study separated sources of primary organic aerosol (POA) and secondary organic aerosol (SOA) using positive matrix factorization (PMF) based on organic species and carbonaceous components. PMF is a receptor model which resolves the sources of atmospheric aerosols based on the observations of markers or other parameters at receptor site, and unlike CMB model, it does not necessarily require prior knowledge on the emission profiles (Sowlat et al., 2016; Viana et al., 2008). It was also used in spatiotemporal studies of PM_{10} sources in the Augsburg region (Gu et al., 2013a; Qadir et al., 2014).

2. Methods

2.1. Sampling

PM sampling was carried out in Augsburg, Germany from April 11th, 2014 to February 22nd, 2015 with some short breaks of a few days mostly in between as shown in Table 1. 24 h PM samples were continuously taken at the ambient aerosol monitoring station on the campus of the University of Applied Sciences Augsburg, Germany (reference site, FHS), and in parallel on one of 5 other sites (master sites), 4 of which are located in the urban area of Augsburg (T1-T3 and B1) and one (T4) in a small town about 35 km away from the reference site (refer to Fig. 1 for the distributions of sampling sites in Augsburg area and supplementary Fig. 3–7 for local surrounding structures of reference site and each master site). Details of the reference sampling site and surroundings have been described in previous publications (Pitz et al., 2008a; Pitz et al., 2008b). Parallel sampling at each master site was conducted with a second sampler of identical setup. Three 2-week sampling campaigns were carried out at the master sites to include 3 seasons at each site, resulting in 6 weeks of sampling at each of the master sites (Table 1). However, at T4, only one sampling campaign was successfully completed in autumn, and the winter period is missing at T1.

Samples were collected using sampling sets consisting of a 3-stage rotating drum impactor (RDI) mounted on top of a Partisol filter sampler (Partisol™ 2025i Sequential Air Sampler, Thermo Scientific, USA).