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Estimating the contribution of photochemical particle formation to ultrafine particle number averages in an urban atmosphere

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HIGHLIGHTS

- A new method to determine source type contributions of ultrafine particles
- Identifying photochemical particle formation events
- Quantifying their contribution to annual average levels of ultrafine particles
- Discriminating particles from photochemical particle formation and traffic
- Photochemical particle formation events play a major role in the summer season
- The simplistic source apportionment helps exposure assessment

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ABSTRACT

Ultrafine particles (UFPs, diameter < 100 nm) have gained major attention in the environmental health discussion due to a number of suspected health effects. Observations of UFPs in urban air reveal the presence of several, time-dependent particle sources. In order to attribute measured UFP number concentrations to different source type contributions, we analyzed observations collected at a triplet of observation sites (roadside, urban background, rural) in the city of Leipzig, Germany. Photochemical new particle formation (NPF) events can be the overwhelming source of UFP particles on particular days, and were identified on the basis of characteristic patterns in the particle number size distribution data. A subsequent segmentation of the diurnal cycles of UFP concentration yielded a quantitative contribution of NPF events to daily, monthly, and annual mean values. At roadside, we obtained source contributions to the annual mean UFP number concentration (diameter range 5–100 nm) for photochemical NPF events (7%), local traffic (52%), diffuse urban sources (20%), and regional background (21%). The relative contribution of NPF events rises when moving away from roadside to the urban background and rural sites (14 and 30%, respectively). Their contribution also increases when considering only fresh UFPs (5–20 nm) (21% at the urban background site), and conversely decreases when considering UFPs at bigger sizes (20–100 nm) (8%). A seasonal analysis showed that NPF events have their greatest importance on UFP number concentration in the months May–August, accounting for roughly half of the fresh UFPs (5–20 nm) at the urban background location. The simplistic source apportionment presented here might serve to better characterize exposure to ambient UFPs in future epidemiological studies.

1. Introduction

Ultrafine particles (UFPs, Diameter < 100 nm) in urban air have gained attention due to a number of suspected health effects. Although contributing only little to particulate mass concentration, UFPs have considerable relevance for total particle number and surface. A main rationale for the health relevance of UFPs has been their small size, thus implying significant deposition in the deep lung and possible penetration through body tissue (HEI, 2013).

Since the late 1990s, a number of epidemiological studies indicated that human morbidity and mortality are affected by ambient UFP concentrations (e.g., Peters et al., 1997; Franck et al., 2011). At the time, this research was triggered by technical innovation, notably the ability to measure particle number size distributions and UFP number concentrations continuously. Nevertheless, the overall body of evidence for health effects of UFPs is still very limited in comparison to the many studies available for PM_{10} and $PM_{2.5}$ (Rückerl et al., 2011; HEI, 2013). UFPs are unlikely to become legally regulated in the very near future (WHO, 2013). According to these authoritative assessments, new epidemiological studies are desirable, which

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provide sound estimates of UFP exposure, and also include a source apportionment of UFPs.

The particular health-relevance of UFPs derives from the fact that combustion processes are a main source of UFPs in urban areas (Kumar et al., 2014). In cities around the world, much of ambient UFP exposure results from road traffic (Morawska et al., 2008).

High-temperature combustion in vehicular engines generates soot particles mainly bigger than 30 nm (Kittelson, 1998; Harris and Maricq, 2001), but also considerably smaller particles (Dp < 30 nm) when unburnt vapors nucleate in the cooling exhaust gas downstream (Giechaskiel et al., 2005). Diesel soot particles contain a solid core of elemental carbon coated with hydrocarbons of varying volatility. Exhaust gas nucleation particles, in contrast, are typically made of hydrocarbons and sulfate forming by nucleation during dilution and cooling of the exhaust. Although not consisting of a solid core, the latter may also contain carbon fragments and metallic ash. Various studies have reported on the chemical composition of particulate material emitted by diesel or gasoline engines (e.g., Graham, 2005; Maricq, 2007), although only few provided a specific chemical composition of ultrafine particles (e.g., Grose et al., 2006; Tobias et al., 2001; Sakurai et al., 2003). The tightening of emission standards during the past years has led to the development of engines that emit considerably less particle mass, while on the other hand, the emitted number of ultrafine particles may be even higher for some new engine techniques (Ntziachristos et al., 2004).

Many studies have attempted to characterize the temporal and spatial variability of ultrafine particles in urban areas (e.g., Costabile et al., 2009; Birmili et al., 2013). Evidently, the spatial variability of UFP concentrations depends on the spatial proximity to sources (Zhu et al., 2002) but also the dispersion conditions governed by topography, current wind speed and direction, and temperature inversions (Birmili et al., 2009a; Zwack et al., 2011).

However, there is another important source of particles that contributes significantly to UFP exposure in urban areas: secondary new particle formation. This gas-to-particle conversion process seems to happen almost everywhere in a continental atmosphere (Kulmala et al., 2004 and references therein). According to current research, photochemically produced sulphuric acid seems to be a necessary precursor for newly formed particles (Sipilä et al., 2010). Organic vapors might also participate in nucleation (Riccobono et al., 2014), and contribute much to the growth of nucleated particles. Relatively few studies have reported the chemical composition of these newly formed particles. Smith et al. (2005) found in the U.S. that ammonium sulfate accounted for the entire sampled mass of 6–15 nm particles after a nucleation event. They also found in Mexico that for 10–33 nm particles formed from nucleation, they contained far more organics, including nitrogen-containing organic compounds, organic acids, and hydroxy organic acids, than sulfates (Smith et al., 2008).

After nucleation, particles grow by condensation into bigger size ranges, eventually up to ~100 nm on the same day. Allan et al. (2006) showed that several hours after a nucleation event, the particles in nucleation mode were principally organic in composition. In the continental boundary layer, new particle formation events tend to happen simultaneously over areas of several 10 km, regardless whether the area is rural or urban (Vana et al., 2004; Wehner et al., 2007; Birmili et al., 2013).

This implies that in an urban area, there are several sources of UFPs, which are likely to differ in terms of chemical composition. It is currently unclear whether these different types of UFPs differ in their health effects or not. If the chemical composition is different between the ultrafine particles originating from vehicle exhaust and new particle formation, it can also be hypothesized that their health effects upon inhalation and long-term exposure are different as well. To better understand the health effects of urban ultrafine particles, it is desirable to discriminate at least the major source groups.

This paper attempts to isolate the fraction of UFP concentration in an urban area that originates from regional-scale secondary new particle formation events. Based on a one-year data set of aerosol number size distribution measured at roadside, urban background and regional background sites, two methods are applied to separae the contributions of UFPs originating from new particle formation and direct traffic-emission. The overall statistics and seasonal variations of the absolute and relative contributions of particles of different origins on the total number of ultrafine particles are analyzed and discussed in detail.

2. Experimental

2.1. Measurement sites

The data used in this study was collected at three observation sites in and around Leipzig, Germany: Leipzig-Mitte (L-Mitte, roadside), Leipzig-TROPOS (L-TROPOS, urban background), and Melpitz (regional background). The three sites are part of the German Ultrafine Aerosol Network (GUAN, Birmili et al., 2009b) and also participate in the TROPOS/Saxon State Office for Environment, Agriculture and Geology study of the effects of the introduction of the Leipzig Low Emission Zone (LEZ) on particulate air quality (Rasch et al., 2013).

The measurement site Leipzig-Mitte is located at roadside in the city center of Leipzig. The site borders the inner-city ring road, and is located in immediate vicinity to the central train station. Immediately north of the site, three main roads merge at an intersection with daily average traffic volumes around 4.4×10^4 vehicles (4.8×10^4 on workdays). Leipzig-Mitte experiences significant exposure to traffic-related pollutants, which is manifested by a traffic-related increment of 10 μg m^{-3} in PM_{10} mass concentration compared to an urban background location (Engler et al., 2012). The height of the aerosol inlet is 4.5 m.

Leipzig-TROPOS is situated on the roof of the TROPOS institute building, about 4 km distant from Leipzig-Mitte. Aerosol particles are sampled at a height of 16 m above the ground. Highly-trafficked roads touch the premises only at distances of 150 m and more. A comparison of the particle number size distribution at multiple sites in Leipzig confirmed Leipzig-TROPOS as a suitable urban background location (Costabile et al., 2009).

Melpitz is located 40 km northeast of Leipzig, and surrounded by flat and semi-natural grasslands without any obstacles in all directions. Agricultural pastures and wooded areas make up the wider regional surroundings. Besides GUAN, Melpitz contributes to WMO-GAW (Global Atmosphere Watch) as a regional background site. According to a pan-European comparison of tropospheric particle number size distributions, measurements at Melpitz can be taken representative for the rural atmospheric background in Central Europe (Asmi et al., 2011).

2.2. Instrumental

Particle number size distributions are recorded on a continuous basis using Twin Differential Mobility Particle Sizers (TDMPS). The three TDMPS instruments follow the basic set-up shown in Birmili et al. (1999), but are now upgraded with automatic sheath flow control and relative humidity (RH) control as described in Wiedensohler et al. (2012). Each instrument consists of two Differential Mobility Analysers (Vienna-type DMA), and two Condensation Particle Counters (CPC models 3772 and 3025A, TSI Inc., Shoreview, U.S.A.). Nafion membrane dryers were employed so that RH in the aerosol sample and sheath flows was always kept below 40%. The TDMPS nominally scans across a particle size range 3–800 nm. Due to enhanced measurement uncertainties below 5 nm, however, only the diameter range 5–800 nm was subsequently used. The time resolution of the measurement in Leipzig-Mitte is 10 min, while it is only 20 min for Leipzig-TROPOS and Melpitz due to the presence of an additional thermodenuder. Quality assurance of the measurements involves monthly checks of the particle sizing (PLS spheres), and an annual comparison against a reference Mobility Particle Size Spectrometer