Abstract

Atmospheric aerosol is a ubiquitous component of the Earth atmosphere. By mass, aerosol natural sources override anthropogenic ones, the latter constituting less than 5% to the total aerosol loading (Jaenicke, 2008). Nevertheless, in urban environment the contribution can increase to 80-90%. Since anthropogenic sources are mostly associated with high temperature processes, urban aerosol number size distribution is usually dominated by ultrafine particles - UFPs (d<100 nm). The UFPs have the highest surface/mass ratios among aerosol particles and bond the highest pollutant loading as per particle mass. Additionally, the UFPs exhibit the highest deposition efficiency in deep region of the human respiratory tract. Therefore, this study focuses to urban aerosol particle spatial-temporal, physical and chemical characterization and source apportionment with special emphasis to the UFPs.

The first study in residential district of Ostrava-Radvanice and Bartovice, an air pollution *hot spot* in Europe, identified industry being dominant sources of UFPs. High particle number concentrations (NC) were measured at the *hot spot*, with peaks up to 1.4×10^5 particles cm^{-3} during plume events, i.e. downwind an industrial facility. The plume-originating UFPs were mostly composed of 19−44 nm nanoparticles heavily enriched up to 4.5% of mass with carcinogenic polycyclic aromatic hydrocarbons (PAHs). The industry nanoparticles have short residence time and quickly attach to accumulation mode particles, which explains their enrichment with PAH's, the most serious threat at the at the hot-spot. Also, such finding helps to assess better industrial UFPs impact to human health, since particles of 20−40 nm in diameter exhibit twice the deposition efficiency in pulmonary alveoli than other UFPs (Venkatamaran et al., 1999). The methodology of source impact measurements focusing on particle NC and size distribution (SD) presented in this manuscript combines highly time-and-space airborne and ground-level measurements. This integrated measurement strategy can be applied to identify specific industrial sources in other hot-spots worldwide.

The aerosol NC and the SD can vary at different heights of the planetary boundary layer (PBL). In-situ vertical profile measurements in the PBL, especially up to 300 m height above ground level, are rare. Airship measurements are capable of providing high time-and-space resolution of aerosol vertical distribution directly in the lower troposphere. Airborne measurements in manuscript 2 revealed two temperature inversion layers, at heights 70m and 120m. In the early morning, coarse particles were accumulated below the lower inversion layer with mass

concentrations up to 50 µgm^{-3}, reflecting coarse aerosol sources on the ground, while the UFPs were found enriched, up to 2.5x10^{4} particles cm^{-3}, in the PBL at heights between 90-120m. This indicate a fanning plume from distant source with high emission height and UFPs increase was not registered at the ground. At noon, a sharp increase in number concentrations of UFPs up to 3.7x10^{4} particles cm^{-3} was registered at heights of 380-400m. Since the PBL stratification ceased and gradual turbulent mixing evolved, sudden increase of ultrafine particles concentration 1.5-2x10^{4} particles cm^{-3} was also registered at the ground. By this way we were able to discriminate sources of UFPs at the hot-spot.

In the same European air pollution *hot spot* presented in the manuscript 1, a more comprehensive study on particles sources was performed, spanning the whole size range, from 14 nm – 10 µm (manuscript 3). The methodology employed in this study, applying Positive Matrix Factorization (PMF) to the particle SD spectra, allowed the identification of sources contributing principally to particle NC and, in particular, to the UFPs. Two factors were resolved in the ultrafine size range: industrial UFPs (28%, number mode diameter - NMD 45 nm), industrial/fresh road traffic nanoparticles (26%, NMD 26 nm). Three factors were resolved in the accumulation size range: urban background (24%, NMD 93 nm), coal burning (14%, volume mode diameter - VMD 0.5 µm), regional pollution (3%, VMD 0.8 µm) and one factor in the coarse size range: industrial coarse particles/road dust (2%, VMD 5 µm). The organic markers homohopanes correlate with coal combustion and the levoglucosan correlates with urban background. The PMF analysis on mass chemical composition ($PM_{0.09-1.15}$) revealed four factors: secondary inorganic aerosol/coal combustion/biomass burning (SIA/CC/BB, 52%), road dust (18%), sinter/steel production (16%), and iron production (16%). The factors in the ultrafine size range have a positive correlation with sinter/steel production and iron production factors. PAHs measured in 24-hour PM_1 were associated with coal combustion factor, with (r^2 = 0.68), with R-homopane (r^2=0.88) and levoglucosan (r^2 = 0.67). Nevertheless, 24 hours PAHs measurement is not adequate for the source apportionment and higher time resolution is needed to apportion the sources without ambiguity.

The physical and chemical properties of the aerosol SD are variable in space and time according to the meteorological conditions and the sources. The manuscript 4 investigates the size distribution properties with focus on the intermodal fraction. Fine, coarse and intermodal (1-2.5 µm) fractions mass concentration and chemical composition were measured in four Czech locations (industrial-residential hot spot; suburban-residential;

Prague urban and suburban). It was found that the highest mass concentration of all fractions with Fe as the predominant element was measured at the hot spot. Additionally, in case of dry atmospheric condition, the $PM_{1-2.5}$ correspond to the PM coarse fraction; on the other hand, with higher relative humidity, the fine fraction grows into the intermodal fraction, and the $PM_{2.5}$ can be a more representative indicator for the fine fraction.