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Re: Comments on the thesis of Cecilia Leoni, 'Atmospheric aerosol: Physical chemical characterization and source apportionment', submitted 2017

Both the physical and chemical properties of the inhalable size fraction of particulate matter (PM_{10}) are important for the assessment of health risks of ambient aerosols. Particularly timely are scientific studies which advance the understanding of the spatial and temporal distributions of various relevant PM size fractions (modes) in atmospheric environments strongly influenced by urban and industrial sources.

Four studies on physics and chemical composition of industrial and other anthropogenically influenced aerosol plumes are presented, building on three first-author publications i.e., two articles in the peer-reviewed scientific literature and one article published in a series of conference proceedings, as well as one co-authored manuscript (submitted). The first chapter provides a 'general introduction and motivation' with a focus on ultrafine particles, and refers to relevant, including the most recent literature. The second chapter introduces atmospheric particle measurements as far as covered in the study i.e., ground-based and airborne sampling, on-line and off-line physical analysis techniques (sizing, counting), and source apportionment modelling. The latter includes explanations of model input specific for aerosol physical parameters and related recommendations. Knowledge gaps are not clearly identified in chapters 1-2.

In the 1st manuscript, aerosol number size distributions (NSDs) and composition (with an emphasis on polycyclic aromatic hydrocarbons, PAHs) strongly influenced by an industrial source of ultrafine particles (metallurgical plant) are studied in a heavily polluted urban area (Ostrava) in winter. The measurements are both airborne (unmanned, remotely controlled airship) and from ground. The particles contain high mass mixing ratios of PAHs, ≈0.3% within the plume (sum of 8 US-EPA prioritized PAHs). Furthermore, the shrinking of ultrafine particle modes due to coagulation along transport to receptor sites within the urban PBL are quantified (for cases without new particle formation). The results illustrate the significance of mixing in the planetary boundary layer (PBL) near the source for horizontal and vertical dilution of plumes. The methodology applied is suggested to explore PAH sources in industrial urban areas.

In the 2nd manuscript, the consequences of mixing vs. stratification in the PBL above a residential area in the same urban area and during the same winter campaign on number size distributions are studied with high temporal and spatial resolution. The lower PBL is covered up to 570 m a.g.l. Observations are made which confirm the insights of similar previous studies. E.g., after dissolution of the nocturnal lowermost inversion layer at noon, number size distributions of the layer above, including nucleation events, can be tracked at the ground.

In the 3rd manuscript, a source apportionment using positive matrix factorization (PMF) is applied not only to chemical but also to physical parameters (number concentrations for a wide particle size spectrum i.e., 0.014-10 μm) of the aerosol, obtained during the same measurement campaign as studied in manuscripts 1 and 2. This is quite novel, though not done for the first time. This extension promises to better identify sources of ultrafine and fine particles, which may not contribute significantly to particulate mass (PM_{10} or $PM_{2.5}$) at te receptor site, but may be very health relevant. PMF can deconvolute source contributions from ambient concentrations and known source profiles, but has to assume that transformations along transport from emissions sources to observational site are negligible. The significance of regional sources for particulate mass, which are explored using common methods of back-trajectory statistics (potential source contribution function, PSCF, and concentration weighted trajectory, CWT), is shown for one of the identified factors (#5). The emission source studied in manuscript #1 is identified as a major source of ultrafine particles. Apart from an unambiguous particle mode (NMD = 0.045 μm), the industrial source also contributed to another ultrafine aerosol mode (NMD = 0.026 μm), which could not be separated from the another major ultrafine particle source i.e., road traffic. The health risk associated with particles emitted from coal combustion (NMD = 0.15 μm) is high, supported by a high correlation with PAH concentration. Limited by sample mass / chemical sensitivity, similar correspondencies could not be found for smaller particle modes. Higher time resolution of chemical parameters (in particular PAH) is identified as a need in order to identify sources without ambiguity and better exploit the combined analysis of aerosol chemical and physical parameters in PMF.

The 4th manuscript's subject is the size segregated mass and chemical composition of PM_{10} at each one urban and suburban sites in Ostrava and Prague, most of these in winter and one in summer. The chemical composition data are based on ion chromatography (major anions) and scanning electron microscopy in combination with energy dispersive spectroscopy (Na...Zn). The focus is the size fraction between 1 and 2.5 μm based on observations. This size fraction has attracted little attention so far, as it accounts for a minor part of PM_{10} mass, in the here presented case study for 3-8%. The main finding of this study is that the so-called fine PM ($PM_{2.5}$) in its elemental composition in fact resembles much the coarse fraction ($PM_{10-2.5}$), and more in summer than in winter, such that the additional knowledge of PM_1 is actually needed to assess the influence of pollution sources to fine PM composition.

The discussion of the results in individual articles considers the literature in a fully appropriate way, and arguments and conclusions are discernable coherent. Overall, the thesis is clearly structured and written and shows a high level of scientific understanding of the field. Its title could be more concise. A number of adequate suggestions for further research are made. It is not fully transparent up to which detail the candidate actually contributed to the methodology, its quality assurance and control, and to the article writing.

In conclusion, I consider the thesis suitable for the defence. Its quality is sufficient for obtaining a Ph.D. degree.

Mainz, 13.2.18