Physicochemical Properties and Origin of PM1 Measured at a Rural Background Site

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PHYSICOCHEMICAL PROPERTIES AND ORIGIN OF PM_1 MEASURED AT A RURAL BACKGROUND SITE

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INTRODUCTION

Measurements at rural background sites representative of wider areas are important to study the influence of regional and long-range transport as well as the long-term trends in PM characteristics (Putaud et al., 2010; Schwarz et al., 2016; Poulain et al., 2020). The National Atmospheric Observatory Košetice (NAOK), officially classified as a central European rural background site, participates in the European Monitoring and Evaluation Programme (EMEP), Aerosol, Clouds, and Trace Gases Research Infrastructure Network (ACTRIS), and Global Atmosphere Watch (GAW) network. Several studies were conducted at the NAOK site however, detailed work focused on the seasonal variability in PM chemical composition data with high temporal and spatial resolutions is still lacking. Therefore, the focus of this study was to characterise individual episodes of high mass and number concentrations based on highly-time resolved measurement and linked to different air mass types, thereby offering insights into the physicochemical properties and sources of aerosol particles arriving at a rural background site.

MEASUREMENT AND METHODS

Two intensive campaigns (July 2019 and January – February 2020) were conducted. Size-resolved PM chemical composition, as well as particle number size distribution in the size range 10 – 800 nm were measured every 5-min by a compact time of flight aerosol mass spectrometer (C-ToF-AMS, Aerodyne) and a Mobility Particle Size Spectrometer (MPSS, IFT TROPOS, Leipzig, with CPC 3772, TSI). 1-min PM_1 equivalent black carbon (eBC) concentrations were determined by aethalometer (AE33, Magee Scientific) simultaneously with 4-h PM2.5 organic and elemental carbon concentrations (Sunset Laboratory Inc.). Besides, PM_1 were collected for 12 h by a sequential sampler (LVS-3, Sven Leckel Ingenieurbüro) for subsequent chemical analyses (water-soluble ions and monosaccharide anhydrides). Finally, 1-h $PM_{2.5}$ mass concentrations (Environnement SA,

MP101M) and meteorological parameters were also recorded.

The standard data processing procedure of AMS was carried out by running the Squirrel v1.62 programme in Igor Pro data analysis software (WaveMetrics, Inc.).

The statistical data treatment was performed using R version 3.6.1 with the ggplot2 (Wickham, 2016) and Openair (Carslaw and Ropkins, 2012) packages.

To determine the collection efficiency (CE; Drewnick et al., 2005) in the AMS, PM_1 filter sampling with subsequent ion chromatography (IC) analysis was conducted in parallel with the AMS measurements.

The effective density (ρ_{eff}) and material density (ρ_m) was estimated along with the dynamic shape factor (χ) inferred from the two densities.

96 h backwards trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Rolph et al., 2017) with a 500 m a.g.l. (above ground level) starting position and Global Data Assimilation System (GDAS) Archive Information at a resolution of 1° x 1° as input data. The calculations were initialized every 6 h for the cluster analysis. For the episodes of high mass concentrations, the trajectory ensemble option with calculation initialized every hour and a total duration of 72 h was utilized. The trajectories were further clustered using Hysplit4 software based on the total spatial variance. From HYSPLIT, the planetary boundary layer height data were extracted. For the planetary boundary layer height calculations, the 0.25° x 0.25° Global Forecast System (GFS) dataset was used as input data to obtain a 3 h temporal resolution.

RESULTS AND CONCLUSIONS

The average PM_1 concentration (sum of NR-PM_1 and eBC) was 8.6 ± 3.7 $\mu g \cdot m^{-3}$ and 10.1 ± 8.0 $\mu g \cdot m^{-3}$ for summer and winter, respectively. NR-PM_1 was mainly composed of organics during both campaigns, followed by either SO_4^{2-} (summer) or NO_3^- (winter). The size distribution of NR-PM_1 species was dominated by the accumulation mode in both seasons, with larger particles for all species in winter as a result of aerosol ageing. Organics showed the smallest modal diameter from all NR-PM_1 chemical species, which suggests its condensation on pre-existing particles (Tab. 1).

Tab. 1: Mode diameter of mass distributions of species measured by AMS (D_p corresponds to the vacuum aerodynamic diameter (D_{va})) for the summer and winter campaigns.

	Org	SO_4^{2-}	NO_3^-	NH_4^+
Summer D_{va} (nm)	334	377	401	497
Winter D_{va} (nm)	413	501	547	517

Since the winter aerosols were less oxidized than the summer ones (comparing m/z 44 and 43), the importance of local sources in the cold season was to be considered. Although aged continental air masses from the south-east (SE) were rare in summer (7 %), they were related to the highest concentrations of PM_1, eBC, and all NR-PM_1 species, especially SO_4^{2-} and NH_4^+. In winter, slow continental air masses from the south-west (SW) (44 %) were linked to inversion conditions over central Europe and were associated with the highest concentrations among all NR-PM_1 species as well as PM_1 and eBC (Fig. 1). The average PM_1 material density (ρ_m) corresponded to higher inorganic contents in both seasons (summer: ~1.30 $g.cm^{-3}$ and winter: ~1.40 $g.cm^{-3}$). The dynamic shape factors (χ)

decreased slightly with particle mobility diameter (D_m) in both seasons.

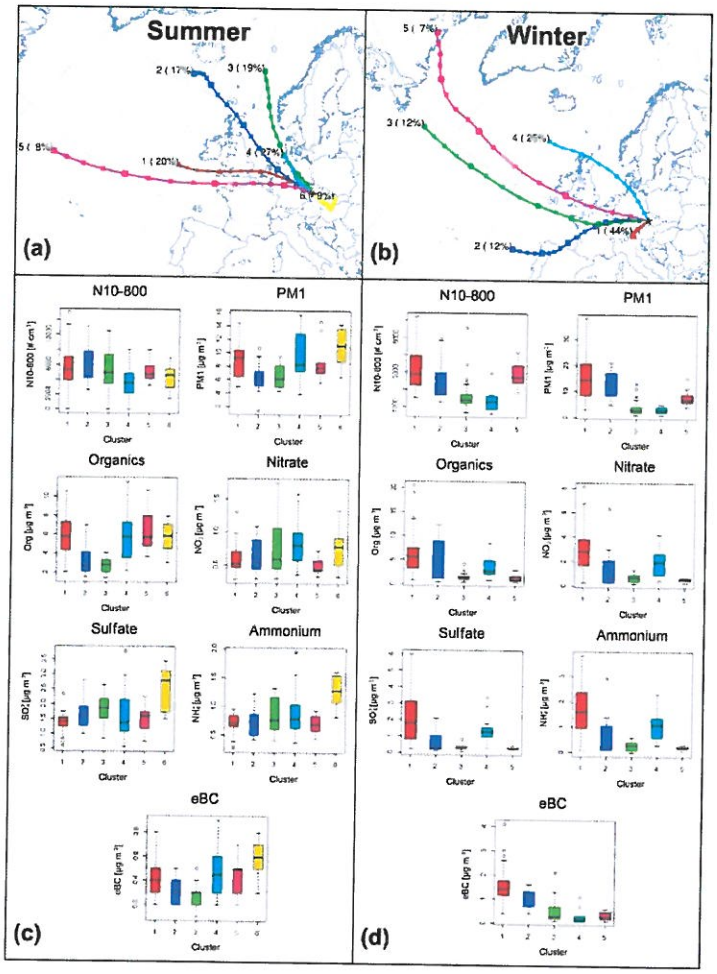

Fig. 1: Geographical locations of the means of the clusters observed in summer (a) and winter (b) along with boxplots of the PM_1, N10–800, organic, nitrate, sulfate, ammonium, and eBC concentrations in individual clusters measured during the summer (c) and winter (d) campaigns. The boxes are color coded as the clusters, the black horizontal line is the median, the boxes border the 25th and 75th percentiles, and the whiskers represent 1.5 x IQR.

By examining individual episodes of high mass and number concentrations, we show that the seasonal differences in the physicochemical properties of aerosol particles were caused by the diversity of sources and were related to the different air masses and meteorological conditions during summer and winter season. We also confirmed the relation between particle size and age reflected both in its oxidation state and shape factor. The results of these specific properties (density, shape, and oxidation state of particles) have general validity and thus transcend the regional character of this study.

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