

Introduction

The rapid economic development during the last three decades in China has led to a severe decrease in air quality, especially in densely populated regions such as Beijing, Shanghai, and the Pearl River Delta (Chan and Yao, 2008). Although during last years a number of measures for air pollution control have been implemented especially in the capital Beijing, air pollution is still regarded to be one of the top environmental concerns in China during the next decade. To better characterize the processes leading to the frequently observed high concentrations of air pollutants on a regional scale, the international field campaign “Campaigns of Air Quality Research in Beijing 2006” (CAREBEIJING2006) was conducted in summer 2006. Organized by the Peking University, project partners from Japan, Korea, Hong Kong, Germany, and China studied the various aspects of gaseous and particulate air pollution in a megacity environment. In this contribution, we present chemical data of size-resolved particles, obtained by a 5-stage Berner impactor during 3 weeks at both an urban and a suburban site in the area of Beijing, China.

Sampling and Analysis

Samples were taken in August and September 2006 (Table 1) at two sites in parallel (Figure 1): An urban site was located on the campus of the Peking University (PKU) in the north-west area of Beijing, which is surrounded by busy streets, commercial companies and stores, and residential apartments. The inlet was on the roof of a five-story building at approx. 20 m above ground. A second site was located near the suburb Yufa, approx. 50 km south of PKU, on top of the building of Huangpu University (about 20 m above ground). The close vicinity there is dominated by mainly farmland and the residential area of the Yufa suburb. Particle sampling was carried out using five-stage Berner cascade impactors (Hauke, Austria) with cut points of 0.05, 0.14, 0.42, 1.2, 3.5, and 10 μm aerodynamic particle diameter ($D_{p, \text{aer}}$). The sampling time of the impactors was about 4-5 hours.

The samples were analyzed for inorganic ions (Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , K^+ , Ca^{2+} , Na^+ , Mg^{2+}) by ion chromatography and capillary electrophoresis, carbon sum parameters (OC, EC, WSOC), and a variety of organic compounds such as dicarboxylic acids (by capillary electrophoresis), C_{20} to C_{34} n-alkanes, and 18 different PAHs (both by gas chromatography - mass spectrometry) and nitrooxy-organosulfates with molecular weight 295 (by liquid chromatography – mass spectrometry). Details on the applied analytical methods can be found elsewhere (van Pinxteren et al., 2009). Information on the boundary layer height (BLH) was derived from lidar measurements which took place approx. 10 km east of the PKU site (Takegawa et al., 2009). The origins of the sampled air masses were estimated by calculating 96-hours-backward trajectories using the HYSPLIT model (Draxler and Rolph, 2003).

Table 1: Sampling times during CAREBEIJING at PKU and Yufa.

Date	PKU Time (local)	Yufa Time (local)	Air mass origin
17/08/2006	07:00 - 17:00	07:00 - 17:00	south
22/08/2006	03:30 - 08:30	03:30 - 08:30	north
22/08/2006	09:40 - 14:00	09:00 - 14:00	north
22/08/2006	14:30 - 19:00	14:30 - 19:00	north
22/08/2006	21:00 - 02:00	21:00 - 02:00	north
24/08/2006	04:00 - 09:00	04:00 - 09:00	south
24/08/2006	09:30 - 14:00	09:30 - 14:00	south
24/08/2006	14:30 - 19:00	14:30 - 19:00	south
24/08/2006	21:00 - 02:00	21:00 - 02:00	south
25/08/2006	09:30 - 14:00	09:30 - 14:00	south
25/08/2006	14:30 - 19:00	14:30 - 19:00	south
29/08/2006	09:30 - 14:00	09:30 - 14:00	east
29/08/2006	14:30 - 19:00	14:30 - 19:00	east
30/08/2006	04:00 - 09:00	04:00 - 09:00	east
30/08/2006	14:30 - 19:00	14:30 - 19:00	east
31/08/2006	04:00 - 09:00	04:00 - 09:00	east
31/08/2006	10:00 - 14:15	09:30 - 14:00	east
31/08/2006	14:30 - 19:00	14:30 - 19:00	east
01/09/2006	09:45 - 14:15	09:30 - 14:00	east
01/09/2006	14:30 - 19:00	14:30 - 19:00	east

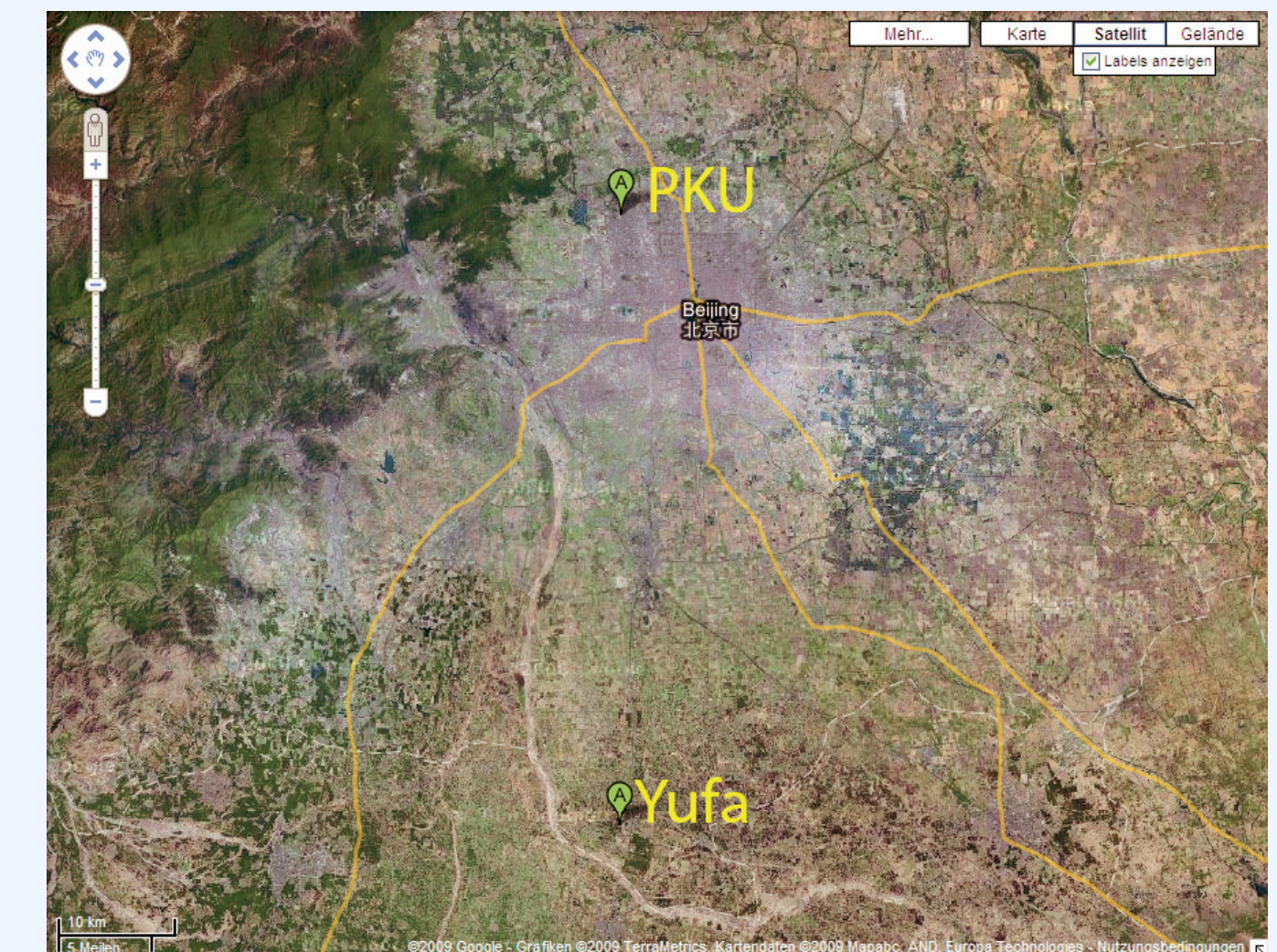


Figure 1: Sampling locations during CAREBEIJING: urban PKU and suburban Yufa.

Table 2: Mean concentrations during CAREBEIJING at PKU and Yufa.

	PKU, Beijing average (min-max)	Yufa, Beijing average (min-max)
Mass and Inorganic ions ($\mu\text{g m}^{-3}$)		
PM mass	133 (27-324)	112 (20-288)
Chloride	0.9 (0.3-3.9)	1.1 (0.5-1)
Nitrate	16 (1.5-48)	9.5 (0.5-35)
Sulfate	25 (2.3-76.9)	20 (1.5-52)
Sodium	0.4 (0.1-1.7)	0.3 (0.0-9)
Ammonium	9.6 (0.5-28)	7.9 (0.8-21)
Potassium	1.9 (0.4-5.6)	1.7 (0.2-6.2)
Magnesium	0.2 (0.1-0.5)	0.2 (0.1-0.4)
Calcium	2.3 (0.9-4.2)	1.2 (0.4-3.1)
Carbon sum parameters ($\mu\text{g m}^{-3}$)		
OC	9.9 (2.7-22)	9.5 (3.5-26)
EC	9 (1.4-23.1)	8.5 (1.9-21)
TC	18.9 (4.1-44.7)	18 (6.3-44)
WSOC	5.7 (0.2-12)	3.8 (0.1-8.7)
Dicarboxylic acids (ng m^{-3})		
Oxalate	307 (50-782)	280 (49-691)
Malonate	66.2 (11.3-147.6)	54 (3.6-117)
Succinate	44 (8.4-142)	32 (17-55)
Glutarate	48 (17-108)	22 (6.9-62)
Tartrate	9.4 (3.8-24)	9.2 (3.8-19)
Malate	26 (2.6-64)	20 (2.3-54)
Tartrate	8.7 (3.1-22)	7.8 (4.1-13)
Alkanes and PAHs (ng m^{-3})		
Sum alkanes	53 (6.2-152)	65 (0.2-225)
Sum PAHs	12 (0.9-39)	14 (0.4-3)

Urban vs. suburban

In Table 2 the PM_{10} concentrations (sum of impactor stages) of PM mass, inorganic ions, carbon sum parameters, dicarboxylic acids, sum of determined alkanes and the sum of PAHs are presented. The mean concentrations during CAREBEIJING usually lie well in the range of previously reported concentration for the highly polluted Beijing area. Regarding the differences between urban PKU and suburban Yufa, Table 2 shows that for total mass and most of the compounds the deviations between the mean concentrations were within 20%. Calculating t-tests for the different compounds revealed that only for Ca^{2+} and Mg^{2+} the difference between their mean concentrations at PKU and Yufa was statistically significant at the 95 % confidence level ($\alpha = 0.05$). These ions are main components of crustal material and the significant difference between their concentrations might be a result of a higher dust resuspension due to the heavy traffic around the PKU site. Construction dust from the many construction areas in Beijing might be another reason.

Diurnal profiles

In Figure 2 rough diurnal profiles are shown which were obtained during an intensive measurement period with relatively stable meteorological conditions and slowly moving air masses from areas south of Beijing. To account for the dilution effect of BLH dynamics we normalized the measured concentrations to a fixed BLH of 1000 m. For the night sample with an additional nocturnal inversion layer at a very low altitude, we used the upper layer for data correction. A strong diurnal variation of particle sulfate concentration with increasing values from morning to afternoon was observed, which could be attributed to regional production. Similar observations were made for oxalic acid. Generally, water soluble organic carbon concentrations were enhanced by a factor of 2 in fine particles during the studied period of intense photochemistry. Also some primary ions accumulate during the two-day intensive period due to the relatively stagnant weather conditions and continuous emissions over the metropolitan area. Possible sources include coal combustion, waste incineration, domestic and field biomass burning, construction dust and crustal matter. Elemental carbon, alkanes, and PAHs showed clear nighttime concentration maxima obviously due to enhanced emissions and a relatively low mixing volume during night. For the newly studied compound group of nitrooxy-organosulfates only qualitative data could be obtained due to the lack of authentic standards. Highest peak areas in the chromatograms were found for the night sample, indicating an influence of night-time chemistry and/or anthropogenic activities on the concentrations of such compounds.

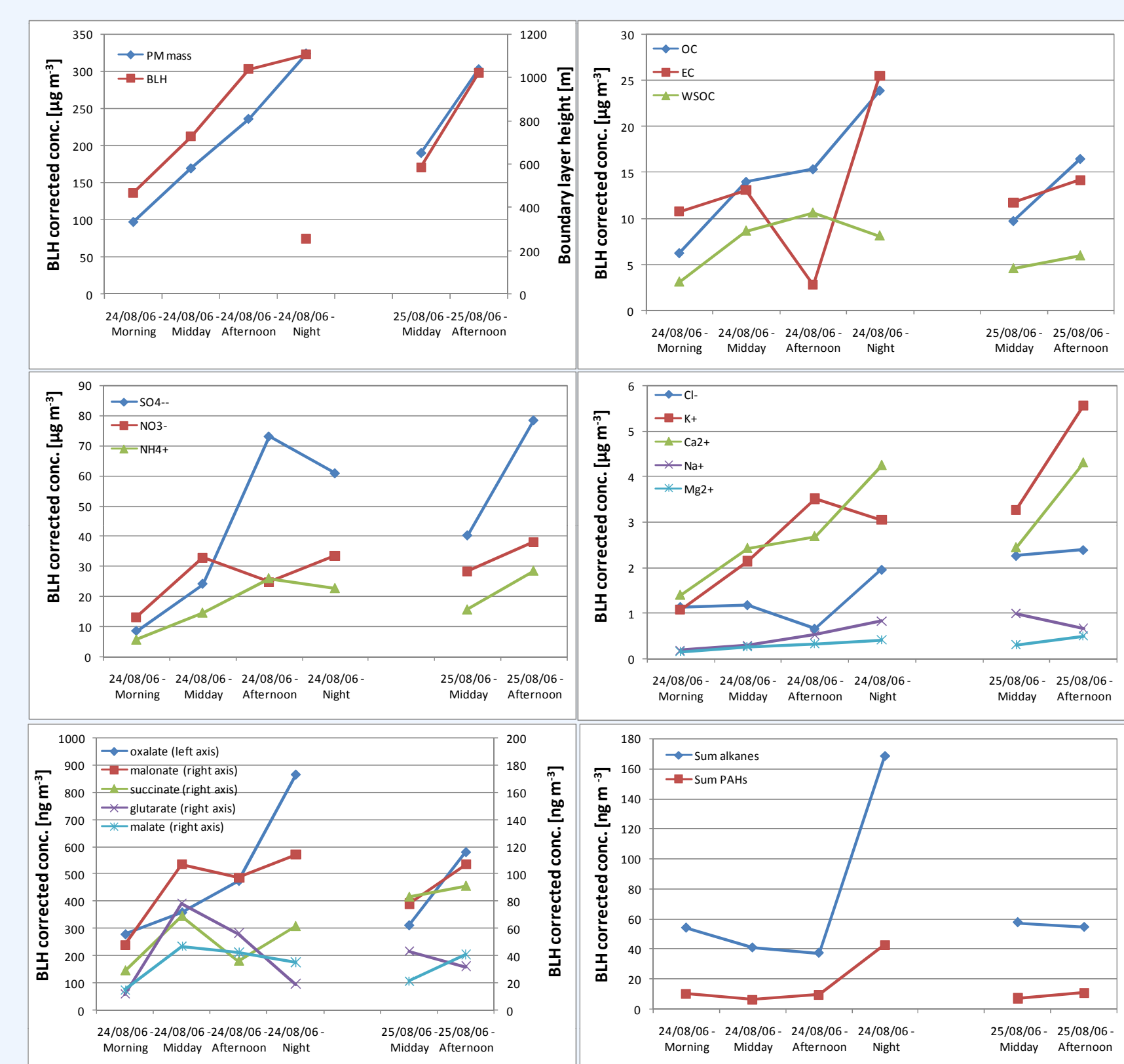


Figure 2: Diurnal profiles of BLH corrected PM_{10} concentrations of different particle constituents during intensive period 24 - 25 August 2006.

Different pollution regimes

Based on a back trajectory analysis the samples were grouped into three categories with air mass origin north, east, and south of Beijing. The results of this classification are listed in Table 1 for each sample. In Figure 3 the size-resolved concentrations of PM mass and particle constituents as well as their PM_{10} concentrations, averaged over the three categories are shown. Generally, during northern and eastern air mass origin the concentration levels are comparable for most of the compounds both between the two air mass categories and between the two sampling sites. Clear differences, however, can be seen when comparing the concentration ratios for South/North and South/East for different compounds. EC as a primary pollutant shows PM_{10} concentrations that are enhanced by a factor of 2-3 during southern air origin. In contrast, the secondary compounds sulfate, nitrate, and ammonium exhibit South/North ratios for PM_{10} of 11, 6, and 15, respectively, at PKU. While the concentration increase can be noted within all particle size ranges except the ultrafine fraction ($D_{p, \text{aer}} = 0.05$ - $0.14 \mu\text{m}$), the highest South/North ratios are usually found on impactor stage 3 ($D_{p, \text{aer}} = 0.42$ - $1.2 \mu\text{m}$) with values of 21, 12, and 35 for sulfate, nitrate, an ammonium, respectively. For sulfate and nitrate the ratios are clearly smaller on the remaining impactor stages (2, 4, and 5), while for ammonium they were similarly high for the coarse particle fraction (stages 4 and 5). Additionally, concentrations at the urban PKU site tend to be higher. South samples showed lowest wind speeds and shortest back trajectories during CAREBEIJING. These findings indicate that during periods of stagnant or nearly stagnant air masses and highly active photochemistry the urban emissions of both primary compounds and precursors for secondary compounds lead to an additional pollutant loading on top of the already elevated regional level. During periods of cleaner air masses with higher wind speeds (North and East category) hardly any differences in the concentration levels of the different compounds can be observed between the two sampling sites.

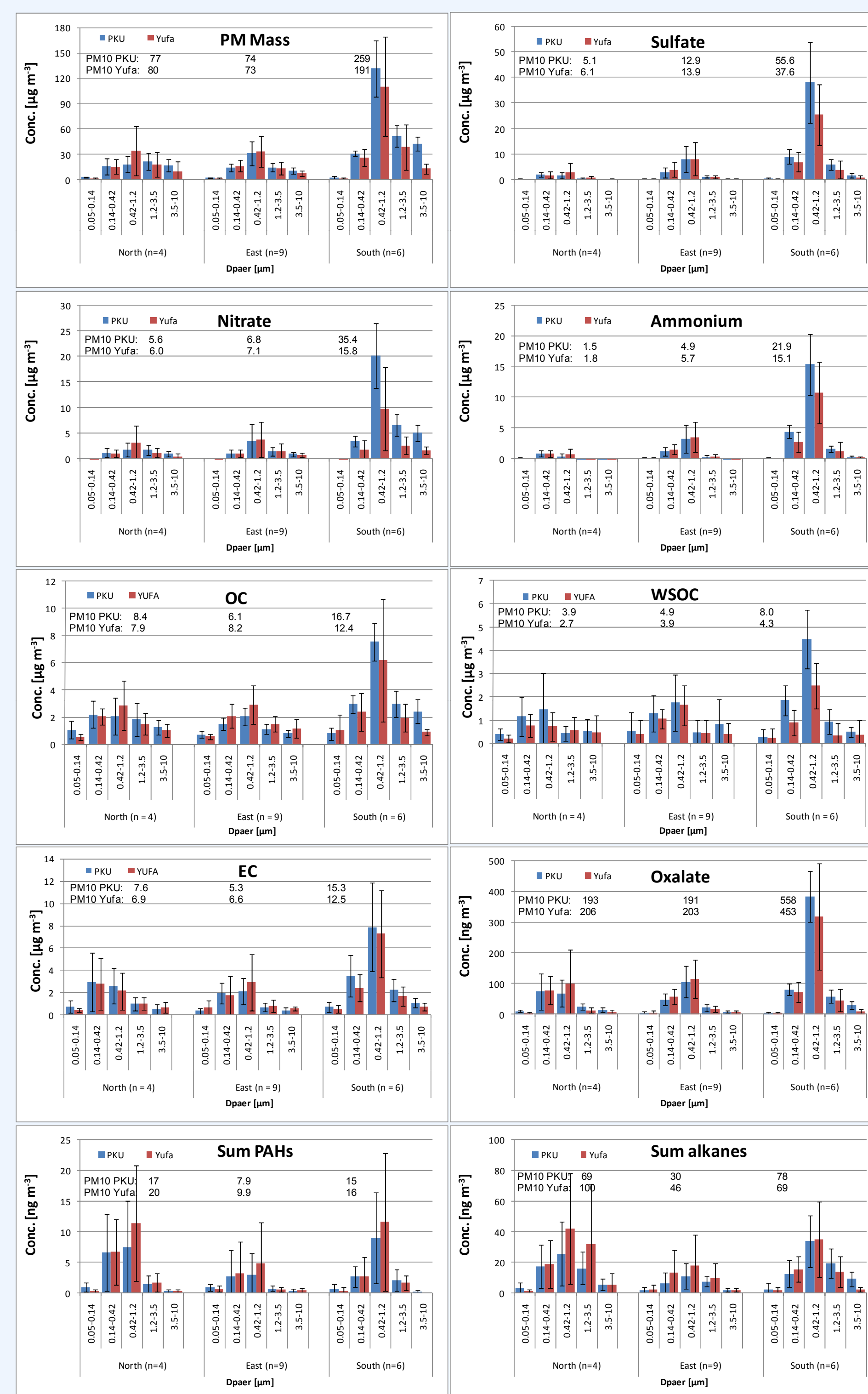


Figure 3: PM_{10} and size-resolved concentrations of particle constituents within different air mass origin categories. Error bars indicate \pm one standard deviation.

Characterization of a nucleation event

An intense nucleation event was observed at the Yufa site starting at 09:00 on 29 August 2006 and lasting into the afternoon of the following day. During this longer event three five-stage Berner impactor runs coincided with the particle formation and growth event as it is depicted in Figure 4. Figure 4a shows the particle Stokes diameter as a function of time with color-coded number concentrations in particles cm^{-3} . These data are converted to particle volumes in $\mu\text{m}^3 \text{cm}^{-3}$ as depicted in Figure 4b. In this plot the periods and size ranges where Berner impactor samples were taken and analyzed are shown as red rectangles for the Berner impactor stages 1 to 3. Finally, Figure 4c shows the main results of the Berner impactor offline chemical analysis as an overview. The main results of the offline chemical analysis could be summarized as follows:

29 August 2006, 09:30 - 14:00

- Steep increase in number concentration, leading to very high particle number concentrations up to about 50 nm in Stokes diameter
- hence only a fraction of the stage 1 mass directly influenced by the freshly formed particles
- one third of the ‘fresh particles’ mass can be attributed to ammonium sulfate (NH_4)₂SO₄ with nearly exact the stoichiometric ratio of the ammonium to the sulfate mass (found ratio 2.5, calculated 2.7)
- EC fraction of about 15 % or $0.4 \mu\text{g m}^{-3}$ to the Berner stage 1 mass. \rightarrow significant mass contributions in the sampled fresh particles originate from primary carbonaceous material.
- OC fraction of about 30 % or $0.8 \mu\text{g m}^{-3}$ to stage 1 mass \rightarrow Secondary organic aerosol (SOA) could be an important mass contribution, too

29 August 2006, 14:30 - 19:00

- higher volume concentrations and, correspondingly, more mass
- mass increase is mainly caused by ammonium sulfate (found ratio 2.6, calculated 2.7)

30 August 2006, 04:00 - 09:00

- main particle volume now found on impactor stages 2 and 3
- similar chemical composition on these stages.
- besides the main compounds now particle nitrate is observed
- large fraction of the particle stage 3 mass not explained \rightarrow possibly mineral dust mode extending into the Berner stage 3 particles

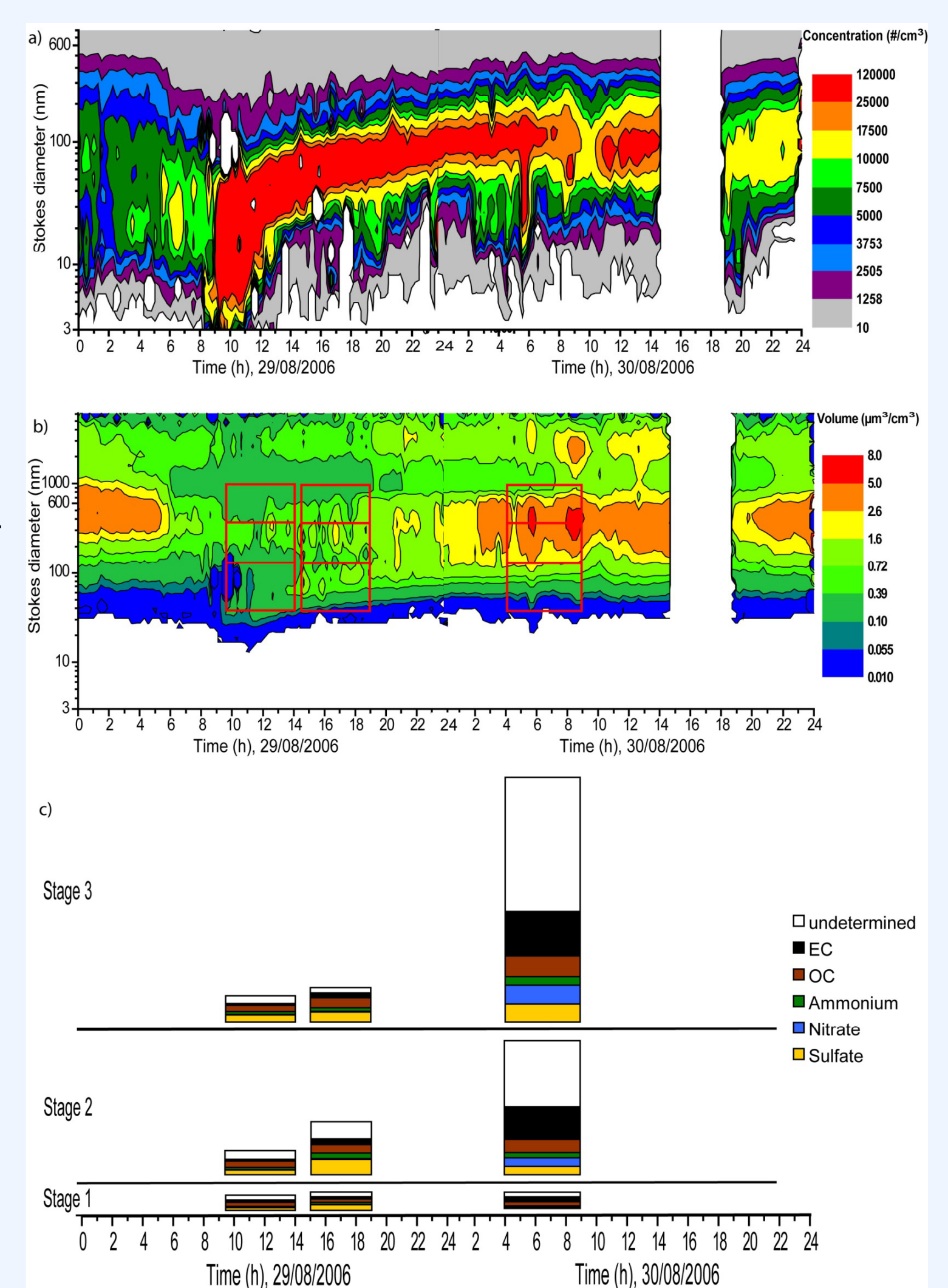


Figure 4: a) Number size distribution during nucleation event, b) Volume size distribution, c) Chemical composition of impactor stages 1 - 3 during nucleation and growth event.

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