Semi continuous sampling of atmospheric ultrafine and accumulation mode particles for chemical speciation using a rotating drum impactor in series with sequential filter sampler

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# Abstract

Unattended automatically continuous 1 week sampling of size segregated daily ambient particulate matter (PM) was achieved using rotating drum impactor (RDI) in series with a sequential filter sampler. Midpoint collection aerodynamic diameter of the 3rd (last) RDI stage using quartz fiber filters (QFF) as substrate was tested to be 0.36 µm. Comparability of two such sampler sets was verified by parallel sampling to meet the requirement of an epidemiological study on the association of finest PM and health based on a long term multiple sites ambient PM sampling and monitoring campaign. *In situ* derivatization thermal desorption Gas Chromatograpy Time Of Flight Mass Spectrometry (IDTD-GC-TOFMS) method was applied to 12 days of parallel size segregated daily ambient samples from Augsburg, Germany using this sampling concept. PAHs, levoglucosan and polar markers (dicarboxylic acids, cis-pinonic acid, etc.) were quantified from the filter (< 0.36 µm). PAHs and levoglucosan from both filter and RDI strip samples (0.36 - 1 - 2.4 - 10 µm). Meteorological data as well as particulate number concentration (PNC) were obtained. The findings are that wind speed was generally negatively correlated with measured compounds, especially with compounds in PM < 0.36 µm; PAHs and levoglucosan in PM < 0.36 µm were correlated mainly with number concentration of PM > 50 nm instead of PM < 50 nm; enrichment of PAHs can be either in the lower accumulation mode PM (< 0.36 µm) or higher accumulation mode PM (> 0.36 µm); secondary origin acids in PM < 0.36 µm show totally different variation pattern from PAHs and were positively associated with ambient temperature.

**Highlights**

Method for automatically unattended long term (1 week) daily sampling of size segregated ambient samples for chemical speciation using RDI in series with filter sampler.

Thermal desorption derivatization method applied for fast size segregated daily sample analysis.

PAHs and secondary polar markers quantified simultaneously in the finest PM < 0.36 µm.

Association of size segregated chemical composition in sub fine PM fraction with other meteorological parameters as well as PNC investigated.

**Keywords**

Size segregated particulate matter; PAH; polar markers; rotating drum impactor; chemical speciation

# Introduction

Ambient PM sampling techniques in many cases collect particulate matter (PM) smaller than 10 μm (PM10), 2.5 μm (PM2.5) or sometimes 1 µm (PM1) on filter substrates. Due to the rising concern of adverse health effect of PM within accumulation mode (< 500 nm) and ultrafine (<100 nm) size range ([Kelly and Fussell, 2012](#_ENREF_14)), further differentiation of PM in the size range below 2.5 μm is necessary. For this purpose, cascade impactors which have a long history for particulate matter sampling are frequently used ([Marple, 2004](#_ENREF_17); [Marple and Willeke, 1976](#_ENREF_18)). To study the link between ultrafine particle composition and adverse health effects, the separate sampling of the accumulation mode and ultrafine PM is desired as it predominantly holds the freshly emitted particle fraction from anthropogenic combustion sources ([Gu et al., 2011](#_ENREF_12)). Thus, separating the accumulation mode and ultrafine PM may offer a better data base for correlation of PM properties with health outcomes.

The Rotating Drum Impactor (RDI) is a special category of slit cascade impactors originally designed by Lundgren ([Lundgren, 1967](#_ENREF_16)) for time- and size-resolved sampling of PM. In contrast to the conventional flat impaction plate, a rotating drum is used as the substrate holder. It automatically rotates a specific step after a certain time interval set by the user and collects samples on a new substrate position. Using a series of such drum impaction stages, an RDI can provide size- and time-resolved PM samples simultaneously. Usually, impactors are designed to separate ambient PM into very small size fractions, such as Microorifice Uniform Deposit Impactor (MOUDI) or Electrical Low Pressure Impactor (ELPI). However, elaborate fractionation may result in prolonged sampling times with all its negative effects on the chemical conditions of the individual samples or in a reduced quantity of sample mass which may be close to or even below the detection limit of the chemical analysis method ([Sanderson et al., 2014](#_ENREF_30)). Additionally, the samples on the lower stages are often exposed to low pressure to achieve the high impaction velocity. This, however, alters the sample conditions, especially with respect to disintegration and potential evaporation of semi-volatile components ([Kavouras and Koutrakis, 2001](#_ENREF_13)). Thus, the reduced PM size resolution capability of a 3-stage RDI together with a tolerable pressure drop at the last stage may be a benefit for ambient PM sampling with subsequent chemical component analysis. Additionally, for practical purposes during field campaigns and long term ambient PM sampling, wider nozzles and repetitive position changes on the substrate reduce the risk of blocking the nozzle and enhance sampling stability and data comparability.

By default, the RDI can be equipped with a single backup filter to collect the finest particles while it automatically moves the drums and continues sampling without stopping or interrupting the sample flow. In our application, the backup filter after the last drum was removed and the RDI was connected to a sequential filter sampler in series to achieve an automatic change of the backup filter. Thereby, the drums and backup filters can be synchronized to start sampling and switch to new samples simultaneously.

It has been observed in other studies that the particle collection characteristics of impactors are altered when a thick porous material is used as a substrate instead of a dense film or foil. Normally the porous substrate will shift the cutoff diameter towards smaller diameters and also reduce the sharpness of the cutoff curve ([Demokritou et al., 2004](#_ENREF_10); [Kavouras and Koutrakis, 2001](#_ENREF_13); [Lee et al., 2005](#_ENREF_15); [Rao and Whitby, 1978](#_ENREF_23); [Saarikoski et al., 2008](#_ENREF_27); [Sillanpaa et al., 2004](#_ENREF_31)). However, sometimes the usage of porous substrates such as quartz fiber filter (QFF) or Polyurethane Foam (PUF) is preferable to mitigate problems like over-load, particle bounce off and re-entrainment ([Demokritou et al., 2004](#_ENREF_10); [Lee et al., 2005](#_ENREF_15); [Rao and Whitby, 1978](#_ENREF_23)). For the intended 24 h ambient PM sampling, especially the overload was a major concern. Additionally, from the analytical point of view, an identically prepared substrate like QFF for both impactor and filter samples is preferable and it also avoids the usage of adhesive coatings, which interfere with chemical analysis ([Wang et al., 2014](#_ENREF_35)).

To meet the requirements of future epidemiological studies, data from at least two different sites (reference and roaming) in parallel are required. Therefore, first objective of the present study was to prove that sampling with two sets of such combinations of commercially available RDIs and sequential samplers deliver comparable results in terms of chemical composition of collected size segregated samples.

Organic chemical compound analysis of size segregated ambient PM is challenging. First, size fractioned sampling generates an elevated number of samples, thereby requiring an analytical method of high throughput to deal with the analytical workload. Second, the total PM mass is divided into several fractions thereby reducing the compound amounts in each fraction and challenge for analytical sensitivity in the case of trace chemical marker compound analysis. Prolonging sampling time to several days or combing several samples were common ways in order to analyze the size distribution of organic compounds such as PAHs ([Di Filippo et al., 2010](#_ENREF_11); [Park et al., 2007](#_ENREF_20); [Rogula-Kozlowska, 2014](#_ENREF_26); [Saarnio et al., 2008](#_ENREF_28); [Sahu et al., 2008](#_ENREF_29)). Solvent extraction based methods are widely used to analyze size fractionated PM target compounds. Direct sample analysis can be a good solution to overcome these two difficulties. Firstly, it saves sample preparation time and secondly more sample portions can be introduced for a single analysis. Therefore, another objective of this study is to apply the IDTD-GC-TOF-MS ([Orasche et al., 2011](#_ENREF_19)) method used for routine chemical marker analysis of ambient particle samples by our group to size segregated samples. Additionally for this objective, analysis of a couple of polar compounds mostly associated with the secondary organic aerosol was integrated in this method.

# Methods

## Collection characteristics of the RDIs

The three stage RDIs used in our study were manufactured by the Swiss Federal Laboratories for Materials Science and Technology (Empa, Dübendorf, Switzerland) and have been used in previous studies for time and size segregated PM sampling and analysis ([Bukowiecki et al., 2007](#_ENREF_5); [Bukowiecki et al., 2005](#_ENREF_6); [Richard et al., 2010](#_ENREF_24); [Richard et al., 2011](#_ENREF_25)). The nominal midpoint cutoff diameters at three stages are given to be 2.5 μm, 1 μm and 0.1 μm, respectively. Bukowiecki verified the deposition uniformity by this impactor. They also tested the 50 percent aerodynamic cutoff diameters to be 2.4 µm and 1.0 µm for the 1st and 2nd stages, respectively ([Bukowiecki et al., 2009](#_ENREF_7)). In the following text, these two values are used as the midpoint cutoff diameters of stage 1 and 2, respectively.

Focusing on PM in the accumulation mode and ultrafine size range, i. e. the PM on the backup filter behind the third stage, the cutoff behavior of the 3rd stage is critical for the comparability and future data interpretation in our studies. Additionally, the collection characteristics with QFF as substrate should be verified. Therefore the size dependent collection efficiencies of both RDIs used in the study were tested using indoor particles.

In an experimental setup (Fig. 1a), indoor aerosol was pumped through the RDI at the nominal flow rate of 16.7 l min-1. A differential mobility analyzer (DMA, model 3081, TSI Inc., Shoreview, USA) and condensation particle counter (CPC, model 3025A, TSI Inc., Shoreview, USA) were connected to the outlet of the RDI to determine the PM size distribution. DMA and CPC were calibrated with latex standard spheres (Distrilab, Leusden, The Netherlands) prior to measurement. Size distribution with the impactor was determined with ungreased aluminum foils or QFF covered drum installed, reference distributions with empty drum housings, i. e. with the drums removed. The collection efficiency (CDp) was calculated for each size channel of the DMA using equation (1).

(1)：.

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Fig. 1. a, experimental set up to test the collection efficiency of the RDIs’ last impaction stage; b, collection efficiency curves of both RDIs’ last impaction stage using QFF as impaction substrate.

## Parallel field sampling

Field sampling was performed in parallel, to test comparability of sampling as well as analysis methods. The field sampling setup is shown in Fig. 2a. Each RDI was adapted as a pre-impactor to the subsequent filter sampler (Partisol™ 2025i Sequential Air Sampler, Thermo Scientific, USA). The RDI was mounted vertically on top of the filter sampler. The airflow after the third stage of the RDI was directed straight down to the filter without any bending. Sampling flow rate was controlled by the filter sampler to be 16.7 l min-1 which is also the nominal flow rate of the RDI. Both combination sets were placed side by side for multiple 24-hour sampling periods at the ambient aerosol monitoring station in the campus of the University of Applied Sciences Augsburg (Augsburg, Germany). Detailed description of the sampling site and surroundings can be found in previous publications ([Pitz et al., 2008a](#_ENREF_21); [Pitz et al., 2008b](#_ENREF_22)).

Each drum of the RDIs was tightly covered with QFF strips being identical to the filter with respect to matrix composition and structure. Both drum strips and backup QFF filters (T293, Munktell, Grycksbo, Sweden) were baked at 500 ℃ overnight before usage. Filters and drum samples were collected from the samplers once a week. Samples were taken between 25th March and 10th April, 2014 (supplement Table S1). In total, 12 days of valid parallel sample pairs were available for chemical analysis (Table S1).

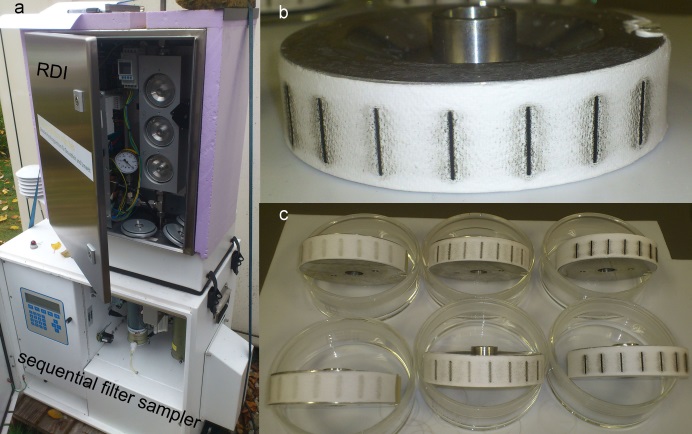


Fig. 2. a, one of the two sets of samplers were operated in parallel during the sampling period at the reference site in University of Applied Sciences Augsburg; b, stage 3 loaded with 7 daily ambient PM samples; c, all 3 stages of both RDIs loaded with samples.

## 2.3 Meteorological data monitoring

The meteorological parameters including air temperature, relative humidity, wind speed and wind direction were measured by the Bavarian Environmental Agency (Bayerisches Landesamt für Umwelt, LfU). The LfU site is located 4 km south to the city center.

## 2.4 Particle number concentration measurement

Particle size distribution (PSD) from 5 nm to 10 µm was determined by a combination of a customized twin differential mobility particle sizer (TDMPS) and an aerodynamic particle sizer (APS) ([Pitz et al., 2008a](#_ENREF_21)). The size segregated PNC was calculated for the size ranges of 5 - 50 nm, 50 - 360 nm, 360 - 1000 nm, 1.0 - 2.5 µm and 2.5 - 10 µm, respectively.

## 2.5 Organic species measurement

Chemical components of PM collected on drum strips as well as the filters were analyzed by IDTD-GC-TOF-MS method ([Orasche et al., 2011](#_ENREF_19)). A brief description of the method can be found in the supplement.

The method was proven to be able to quantify polycyclic aromatic hydrocarbons (PAH), oxygenated PAHs, alkylated PAHs, some acids generated by wood combustion and polyols such as abietic acid and levoglucosan ([Orasche et al., 2011](#_ENREF_19" \o "Orasche, 2011 #70)). For the present study some polar compounds were evaluated additionally and integrated into the compounds’ calibration procedure, including dicarboxylic acids, cis-pinonic acid, 3-hydroxyglutaric acid, 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA), 2-methylerytheritol, 4-nitrophenol and 4-nitrocatechol. Authentic 3-MBTCA was used for identification only. Quantification of 3-MBTCA was based on the calibration curve of 3-hydroxyglutaric acid, which has a similar structure.

# Results and discussion

## 3.1 Comparison of both samplers

**3.1.1 Collection characteristics of the RDIs’ last stages**

Collection efficiency curves of stage 3 for both RDIs are shown in Fig. 2b. Aerosol density ρp =1.4 g.cm-3 was used to calculate the aerodynamic diameter ([Birmili et al., 2010](#_ENREF_4)) from the electrical mobility diameter measured by SMPS. The means and the standard deviations (10 repetitions from RDI #2, 5 repetitions from RDI #1) are shown in Fig. 1b. The graphs show that both RDIs have very similar collection patterns.

To calculate the *CDp,50%* value, each repetition of measured collection curve was fitted with a sigmoid function curve. *T* test was applied to 10 values from RDI #1 and 5 values from RDI #2. The *t* value is 0.408 and *p* value is 0.69; no significant difference could be demonstrated between the midpoint collection diameters of both RDIs at a significance level of 0.05. Besides, from the graph we could not find any systematical shift between the two collection curves either. In the main PM collection size range from 0.2 µm to 0.6 µm, there was no one direction separation between the two collection curves. To mention that, there was a time delay between the measurements of the two aerosol distributions used to calculate the collection curve, which makes the calculation sensitive to the indoor PM distribution change. The average 50% aerodynamic collection diameter (*CDp, 50%*) for stage 3 was found to be about 0.36 µm. This is much larger than the nominal cutoff diameter of 0.1 µm. Calculated Stoke’s number is 0.366. The summary of the 4 size fractions sampled then would be < 0.36 µm, 0.36 - 1 µm, 1 - 2.4 µm and 2.4 - 10 µm.

**3.1.2 Influence on the collection efficiency when using QFF substrate**

It can also be observed from Fig. 1b that at around 600 nm, the collection efficiency reaches its maximum with an average percentage of 80 percent. It has been repeatedly reported in other studies that porous material facilitates the collection efficiency by shifting the midpoint cutoff value towards lower diameter as well as mitigating the bouncing off and re-entrainment artifact ([Demokritou et al., 2004](#_ENREF_10); [Lee et al., 2005](#_ENREF_15); [Saarikoski et al., 2008](#_ENREF_27); [Sillanpaa et al., 2004](#_ENREF_31)). From our test using aluminum foil as a substrate, a shift to larger diameters in the collection curve as well as lower maximum collection efficiency were observed (see supplement Fig. S1). This reveals the low collection capacity of the ungreased aluminum substrate as well as high sampling artifact, at least during the sampling start period without a substantial loading of ambient particles on the substrate. As mentioned, greasing of the aluminum foils was problematic for our study because of the interference with organic compound speciation. Fig. 1b also shows that, for the PM < 200 nm, around 10 percent of the particles were additionally collected. The excess collection characteristic of QFF substrate is probably due to other effects instead of impaction, for instance, the penetration of aerosols into the fiber layer at high velocity ([Kavouras and Koutrakis, 2001](#_ENREF_13); [Rao and Whitby, 1978](#_ENREF_23)) or the diffusion losses to the surface of the filter material. During the further traveling process of the PM, some particles may be trapped by filtration mechanisms such as interception or diffusion ([Sillanpaa et al., 2004](#_ENREF_31)). As is also shown in the view of the sampled strips in Fig. 2b, specifically, there was residue PM spreads out on both sides of the central impacted strips. This “shadow” may cause slight underrepresentation of the < 0.36 µm PM collected on the filter.

## 3.2 Organic species analysis results

**3.2.1 Quantified organic species**

Organic composition including PAHs and levoglucosan were investigated from the filters as well as the three RDI stages. For coarse particles (2.4 - 10 µm) only the comparatively volatile pyrene, fluoranthene and levoglucosan were detected, the other PAHs with higher molecular weight were below limit of quantification (LOQ) (see measured compounds and their LOQ values in supplement Table S2). Therefore, this fraction was not included in the following discussion. Polar markers except levoglucosan were only quantified in the smallest fraction samples (< 0.36 µm) as derivatization for these markers from the RDI samples was not reproducible. 2-methylerytheritol, a tracer of isoprene photooxidation ([Claeys et al., 2004](#_ENREF_8)), was not included in the discussion because it was not detected for most of the samples.

**3.2.2 Comparability of samples from both samplers sets**

A paired *t* test of daily value from both sampling sets was applied to statistically evaluate the comparability on each individual compound level. The result is shown in supplement Tables S3 and S4. No evidence of significant differences could be found for nearly all the measured compounds in all size fractions (α=0.05). The only exception is that fluoranthene and pyrene concentrations in the size fraction < 0.36 µm from sampler #1 are significantly lower than from sampler #2. Of all the quantified PAHs, these two have the highest volatility, what might have led to a loss during sample transport, storage or preparation.

Fig. 3 shows that measured pairs of samples coincide with the 1:1 line very well with limited random variation in both directions. Polar markers are found at higher concentration than PAHs; while levoglucosan originating mainly from wood combustion, shows the highest concentration. Besides, polar compounds somehow diverge more from the 1:1 line, which most probably results from a lower analytical reproducibility of the derivatization. With regard to these compounds, full derivatization of multiple functional groups was necessary to have good quantification results. Additionally, when comparing the actual concentration as well as concentration variation of the samples, the mean difference of the two sets of samples is very low. The comparable results discussed above give a strong indication that there is no systematic different behavior between the two samplers. This warranted our plan to investigate spatial variability of accumulation mode PM by collecting parallel samples at two sites in a long term sampling campaign.

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Fig. 3 Scatter plot of measured compound concentrations from sampler set #1 to sampler set #2 with 1:1 line shown on the plot as well.

## 3.3 Chemical compounds concentration time series

**3.3.1 PAHs and levoglucosan time series and their** **internal correlations**

Time series of PAHs and levoglucosan concentrations from different size fractions are shown in Fig. 4a. In this short sampling period, the concentrations vary a lot (see supplement Table S5 for the concentration means and ranges); especially for the submicron PM. Correlation analysis results (all discussed correlation heatmap see supplement Fig. S2 and S3) shows that PAHs and levoglucosan measured within each size range samples were strongly correlated with each other. There was a strong correlation between high molecular weight (HMW) PAHs (> 4 ring) within each size range (0.8 < r <1). The correlation between low molecular weight (LMW) PAHs fluoranthene and pyrene with other HMW PAHs was good but not so strong (0.7 < r < 0.9). In addition, PAHs in 0.36 -1 µm and 1 - 2.5 µm PM were also strongly and positively correlated (0.7 < r < 1). However, correlations between PAHs in PM < 0.36 µm and the other two coarser size ranges (> 0.36 µm) were generally weaker (majority of r in 0.5 - 0.8). Similar variation trends of PAHs and levoglucosan for each size range can been seen from Fig. 4a. From above, despite of the common combustion forming mechanism for PAHs, there is still distinction in size segregated submicron PAHs as well as different MW PAHs. In the following two sections 3.3.2 and 3.3.4, we will describe the association of this variation pattern with other parameters we measured. However, from this limited sample period we cannot explain how exactly this is linked to the source contribution or aerosol evolution in the atmosphere.

**3.3.2 PAHs and levoglucosan’ correlation with wind speed and PNC**

Fig. 5 shows the average size segregated PNC (a) wind speed (b) and temperature (c). Correlation analysis shows that wind speed was more negatively correlated with PAHs in PM < 0.36 µm (0.6 < r <0.8) than in PM 0.36 - 1 µm (0.2 < r <0.4) (see supplement Fig. S3). This indicates that wind speed was an important metrological factor for the dispersion of the chemical species especially for the lower accumulation mode PM. The r values of size segregated PAHs and levoglucosan with size segregated PNC are shown in Table 1. (See also supplement Fig. S3). Generally, 5 - 50 nm PNC was slightly negatively correlated with all size segregated PAHs and levoglucosan. 0.36 -1 µm PNC was well positively correlated with all size segregated PAHs and levoglucosan. 0.05 - 0.36 µm PNC was more positively correlated with PAHs < 0.36 µm than that of 0.36 - 1 µm and 1 - 2.4 µm. As is shown in Fig. 5a, size fraction 5 - 50 nm shows a distinct time series pattern. For instance, PNC of sample 5 and 11 whose sampling time covered weekend shows two drops in size fraction 5 - 50 nm in contrast to two peaks of PNC in size fraction 0.05 - 0.36 µm and 0.36 -1 µm. Meanwhile, the finest PNC dominates the number concentration counts. The correlations and distinct PNC patterns could be an indication that although the finest PM smaller than 50 nm contributed considerably to the number concentration, it showed less contribution to the PAHs and levoglucosan during the sampling period. PM larger than 50 nm was the major contributor to PAH and levoglucosan found in these samples.

Table 1. r range of size segregated PAHs and levoglucosan with size segregated PNC.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Organic size range | PNC size range (µm) | | | |
| (µm) | 0.003 - 0.05 | 0.05 - 0.36 | 0.36 - 1 | 1 - 2.5 |
| < 0.36 | -0.6- 0.1 | 0.5 - 0.9 | 0.6 - 0.9 | 0.4 - 0.8 |
| 0.36 - 1 | -0.3 - -0.1 | 0.4 - 0.6 | 0.7 - 0.9 | -0.1 - 0.3 |
| 1 - 2.4 | -0.6- 0.1 | 0.2 - 0.7 | 0.6 - 0.8 | -0.2 - 0.6 |

**3.3.3 Polar marker concentrations and their correlation with wind speed, temperature and PNC**

The polar compound concentration time series is shown in Fig. 5c. These compounds provide information on the sources or oxidation status of atmospheric PM. Dicarboxylic acids are the products of photo chemical reaction in the atmosphere. Very few studies have investigated these polar tracers in the fine size range ([Agarwal et al., 2010](#_ENREF_1); [Claeys et al., 2010](#_ENREF_9)). Correlation analysis shows that 4-nitrocatechol and 4-nitrophenol were positively correlated with PAHs and levoglucosan, whereas the acids do not show such correlation. Very strong correlation (r = 0.97) was found between 3-hydroxyglutaric acid and 3-MBTCA, which is in accordance with that they are both higher generation products of -pinene oxidation ([Szmigielski et al., 2007](#_ENREF_33)). Besides, except cis-pinonic acid which shows poor correlation with other acids, the other acids were well positively correlated with each other (0.5 < r < 0.9), which might be due to the similar formation mechanism. Polar compounds in PM < 0.36 µm also show high negative correlation with wind speed like PAHs and levoglucosan. The correlation between acids and temperature was positive (0.5 < r < 0.8) and for 3-hydroxyglutaric acid, 3-MBTCA and azelaic acid, the correlation was stronger (r > 0.7). This is in accordance with their photochemical origin. Except for 4-nitrocatechol and 4-nitrophenol, which behave more like the PAHs, other polar compounds in size fraction < 0.36 µm generally had positive correlation with size segregated PNC, especially with coarse particles > 1 µm (0.6 < r < 0.9).

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Fig. 4 Measured concentrations of PAHs, levoglucosan (a) and polar markers (c) from different sample numbers (refer to supplement Table S1 for corresponding sampling date and time, lines between points only intended to guide the eye); b, calculated percentages of PAHs and levoglucosan in each size range (all 3 size fractions add up to 100 percent).

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Fig. 5 a, measured size segregated number concentrations (mean ± sd); b and c, wind speed and temperature (mean ± sd) during sampling period, respectively (lines between points only intended to guide the eye).

**3.3.4 Size distribution of PAHs and levoglucosan**

Fig. 4b shows the percentages of the PAHs and levoglucosan in different size fractions. The vast majority of the PAHs are found in the size range below 1 μm during this sampling period. There was less than 20 percent of PAHs in the PM fraction 1 - 2.5 μm. Splindler et al. also detected the highest PAHs in the fine fraction (size ranges 0.14 - 0.42 μm and 0.42 - 1.2 μm) from 169 daily samples of six years of discontinuous sampling in Melpitz, Germany ([Spindler et al., 2012](#_ENREF_32)). It can also be observed from the graph that the enrichment of less volatile HMW PAHs could be either in smallest size fraction < 0.36 μm or in the size fraction of 0.36 - 1 μm and the LMW PAHs were more enriched in the size fraction < 0.36 μm comparing to the larger molecular weight PAHs. Di Filippo et al. reported a bimodal trend of LMW PAHs at 0.1 μm and 0.4 μm and monomodal distribution of 4, 5 and 6 ring PAHs at 0.4 μm of annual average in Rome, Italy ([Di Filippo et al., 2010](#_ENREF_11)). Albinet et al. measured the size distribution of PAHs (228 a.m.u. to 300 a.m.u.) in two French alpine valleys, and their result showed that in winter averagely more PAH fraction was found in the size range 0.39 - 1.3 μm than in the size range 0.01 - 0.39 μm at the near traffic site and the rural site, and vice versa at two suburban sites; in summer at all 4 sites more PAH fraction was found in the 0.39 - 1.3 μm size range ([Albinet et al., 2008](#_ENREF_2)). Moreover, during our measurement period, a trend of elevated PAH percentages in the size fraction < 0.36 μm was observed after the 4th sample. Within this time period, this change seems to be corresponding to the temperature increase shown in Fig. 5c. The factors influencing the size distributions of organic compounds could be source contribution, compound characteristics (vapor pressure, adsorption/adsorption affinity with PM, etc.), PM characteristics, and atmospheric environmental parameters (temperature, humidity, radiation and mix layer height, etc.) which influence aerosol’s further chemical physical process/aging ([Albinet et al., 2008](#_ENREF_2); [Allen et al., 1996](#_ENREF_3); [Venkataraman and Friedlander, 1994](#_ENREF_34)). At this point, we cannot tell whether there is a dominate factor and which it is for these increased ratios in the finest size range, or whether there is a comprehensive influence behind this effect. This needs to be investigated further and we will try to address this question in the follow up sampling campaigns we conduct with these two samplers.

# 4 Summary

Modified 3-stage RDI was combined with filter sampler in series to achieve automatically size segregated atmospheric PM sampling using QFF as substrate. RDI’ 3rd stage midpoint collection diameter was tested to be 0.36 µm. IDTD-GC-TOFMS analysis method was applied to QFF samples of all size fractions for chemical species quantification. Derivatization of majority of polar compounds on the RDI drum strips was not applicable due to derivatization difficulty, so the polar markers were quantified from filter samples only; PAHs and levoglucosan were quantified from all size fractions. The comparability of two sampling sets was verified with respect to PM collection characteristics of both RDIs as well as chemical analysis result from both sampler sets.

Field campaign results indicate that wind speed was an important factor for chemical species concentration especially in the finest PM size fraction 0.36 µm. In addition, PNC < 50 nm which dominates the number counts was negatively associated with PAHs in PM < 0.36 µm; in contrast, PNC of 50 - 360 nm and 360 - 1000 nm were well positively correlated to the PAHs detected. Varied size distribution of PAHs and levoglucosan in sub size fractions of fine PM in short period was observed while reason unresolved. In finest size range (< 0.36 µm), secondary polar markers show totally different characteristics from the PAHs in accordance with their different forming mechanism. They are found to be associated with temperature which itself is known to be related to the radiation level.

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