## Detection of Polycyclic Aromatic Compounds at Jungfraujoch High-Alpine Research Station using Two-Step Laser Mass Spectrometry

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# DETECTION OF POLYCYCLIC AROMATIC COMPOUNDS AT JUNGFRAUJOCH HIGH-ALPINE RESEARCH STATION USING TWO-STEP LASER MASS SPECTROMETRY

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Jungfraujoch (JFJ) is considered to be a location for background free troposphere measurements. Aerosol particles collected at JFJ are analyzed to characterize adsorbed polycyclic aromatic compounds (PACs). Aerosol samples were collected from March 21 to 25, 2000 and from August 1 to 9, 2000. Samples were then analyzed by two-step laser mass spectrometry (L2MS). The mass spectra show higher relative concentrations of PACs present on samples collected during the August sampling period versus the March sampling period. L2MS data from March indicates good correlation with black carbon aerosol data measured in parallel. This suggests that long range transport of aerosol from combustion is responsible for the majority of PACs observed. Data from August unexpectedly showed markers indicative of environmental tobacco smoke (ETS). The contribution to total aerosol may be small, but the relative signal of ETS markers correlates well with the number of visitors coming daily to JFJ, pointing to a local source of ETS.

*Keywords:* Polycyclic aromatic compounds; Laser mass spectrometry; Aerosol

## INTRODUCTION

Jungfraujoch (JFJ) is a high-alpine research station 3580 m above sea level in the Swiss Alps (46.55°N latitude, 7.98°E longitude) and is considered to be a location for background free troposphere measurements in Europe, for certain time periods [1,2]. Concentrations of gas phase compounds such as CO, $C_2H_6$, $O_3$, and HCN have been recorded continuously since the early 1980s [3–6] and have provided databases for assessing chemical changes in the atmosphere of central Europe. More recently, JFJ has become part of the joint Global Atmosphere Watch (GAW) as a baseline station, which also includes Zugspitze (2962 m in Germany) and Sonnblick (3106 in Austria) high-alpine stations [2].

More recently, research has been conducted at JFJ high alpine research station in order to characterize aerosol [1,2,7]. Measurements include particle concentration [7], size

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distributions [7–10], transport [11], trace metal, other inorganic components [7–9,12], and elemental carbon concentration [1,2,7–9,13]. In addition, recent studies on the occurrence of oxidants such as $O_3$, $NO_x$, and $HO_2$ were conducted to determine diurnal variations and whether these variations are due to photochemistry or transport [5,14–17].

To date the only investigation at JFJ of specific organic compound classes in the aerosol phase have been conducted by Krivacsy *et al.* who analyzed polyconjugated acids and neutral compounds of varying water solubility [18]. No measurement of aerosol bound polycyclic aromatic hydrocarbons (PAHs) and polycyclic aromatic compounds (PACs) has been performed at this site to determine which PAH and PAC compounds may be present, how much is present, and what possible sources can be attributed to the presence of these compounds. This is important, as PAHs and PACs are two classes of compounds that are indicative of human activity as a result of combustion of organic material. These compounds are found in many cases associated with carbonaceous soot particles generated during combustion, and PAHs/PACs with three or more aromatic rings are almost exclusively aerosol bound.

L2MS has been shown to have a very high selectivity and sensitivity to aromatic compounds in general [19–21] and is therefore ideally suited for the characterization of PAHs and PACs found on the aerosol collected at JFJ. Detection limits for individual aerosol bound PAHs have recently been determined in our laboratory. Depending on the compound, they are in the range of $50\ldots300$ pg/filter [22]. Using the air volume sampled in this study, this translates to $5\ldots30$ pg/m$^3$ air.

The goal of the present study was to assess the contribution of anthropogenic sources to the aerosol at JFJ to determine if these sources are having an impact at a baseline measurement location. Using L2MS, we have identified several PAHs as well as other aromatic compounds (PAC) on aerosol sampled from JFJ. An absolute quantitation was not attempted, but the relative ion signal of both PAH and PAC compounds are compared to Aethalometer data, which measures particulate black carbon. This comparison allows for some insight into a particular aerosol class in which the PAH compounds are most likely associated at JFJ.

## EXPERIMENTAL

All aerosol samples were collected and analyzed by L2MS as previously described by Haefliger *et al.* [20,21] and by Morrical and Zenobi [19]; only a brief description of relevant sampling procedures is given here. Aerosol was sampled from a total aerosol inlet that ran from outside to an indoor sampling port onto quartz fiber filters in an observation tower at 3580 m asl. The temperature of the sampling was maintained at room temperature and independent of the outside temperature. Samples were collected from March 21 to 25 and again from August 1 to 9, 2000, both times using a 24-h collection period per sample starting from approximately 15:00 CET each day. A collection period of 24 h with a flow rate of 7.5 L/min was deemed to be necessary in order to obtain an adequate sample as determined by a one-day experiment on March 18 to determine the overall aerosol filter loading. The total air volume sampled was 10.8 m$^3$ and this volume of air proved to be just adequate for proper analysis, especially for the March sampling campaign.

Following the collection of each sample, the filter was kept frozen at approximately $0°C$ for the remainder of the field campaign. Samples were stored frozen and wrapped

in aluminum foil to minimize the loss of any semi-volatile compounds present on the collected aerosol and to prevent photo-oxidation from occurring. Sample filters were frozen in liquid $N_2$ just before introducing them into the vacuum system of the mass spectrometer, the only sample preparation step carried out prior to analysis by L2MS. Although the sample will slowly warm up, freezing the sample filter in liquid $N_2$ keeps it sufficiently cold during the time of the analysis to prevent the loss of semi-volatile compounds in the vacuum.

A relative measure of the total PAH ion abundance from a given sampling period was obtained by summing the integral of 11 peaks in the mass spectra from both March and August. Peaks at $m/z$ 178, 192, 206, 220, and 234 represent phenanthrene and alkylated phenanthrenes. Other peaks at $m/z$ 202, 228, 252, 276, 300, and 302 are also included in the total PAH abundance. These ions were chosen primarily because they are known to correspond to PAHs common in most combustion sources and they are present in the majority of the analyses conducted on the JFJ samples.

Complementary black carbon (BC) data in $ng/m^3$ measured by an aethalometer (AE-30, Magee Scientific) was obtained alongside in March as part of the Cloud and Aerosol Characterization Experiment (CLACE) 2000. The aethalometer measures the absorption of aerosol collected on a filter using a number of wavelengths of light ranging from the visible to infrared. For this study, the channels at 590, 615, 660, 880, and 950 nm were employed. It has been determined that almost all of the absorption by aerosol in the visible light range is associated with carbonaceous aerosol, with the exception of a small absorption by haemitite ($Fe_2O_3$) [2]. This has been shown to be a very low contribution and is present at JFJ only during Saharan dust storm events [9]. The absorption coefficients of $\sigma_{ap} = 14.09$, 13.53, 12.65, 9.44, and $8.79 \, m^2/g^{-1}$ were used to calculate the BC concentration in $ng/m^3$ for each of the five channels used in the aethalometer. There was evidence of a dust event on March 23. As a result, the values from an additional channel at a short wavelength (450 nm) were omitted from the BC measurement as any interference from Sahara dust would show as an increased absorption, and therefore higher BC value, at this wavelength. The other five channels agreed to within 6% for all days used in this study. The BC data was taken in 1-h time intervals and is represented here as a 24-h median value of 1-h samples that match the aerosol-sampling period. Aethalometer data was also obtained for the sampling period in August using a single channel aethalometer (AE-10, Magee Scientific).

In addition to aerosol data, the daily number of visitors to JFJ was obtained from the railway station that services the site. The number of visitors was obtained because some of the data during the August sampling period suggests a possible local contribution to PAC detected.

## RESULTS AND DISCUSSION

The two sampling periods covered in this study, March 21–25 and August 1–9, represent dramatically different conditions at the JFJ. Typically, the overall particle counts at the site (routinely measured using a Scanning Mobility Particle Sizer or SMPS) were much higher in the summer months than during the spring sampling. This is well known from previous studies [10,11]. Due to the dramatically lower particle counts encountered in the March campaign, no PAHs were detected on the filter sample

collected on March 21–22. Also, no sample was available for March 22–23 due to experimental difficulties.

Figure 1 shows two mass spectra from March 23 to 24 and August 7 to 8 respectively. These were the days in which the highest PAH and PAC ion signals were measured with the L2MS for the respective sampling campaigns. From Fig. 1a it can be seen that the March 23–24 aerosol contains PAH including acenapthylene ($m/z = 152$), fluorene
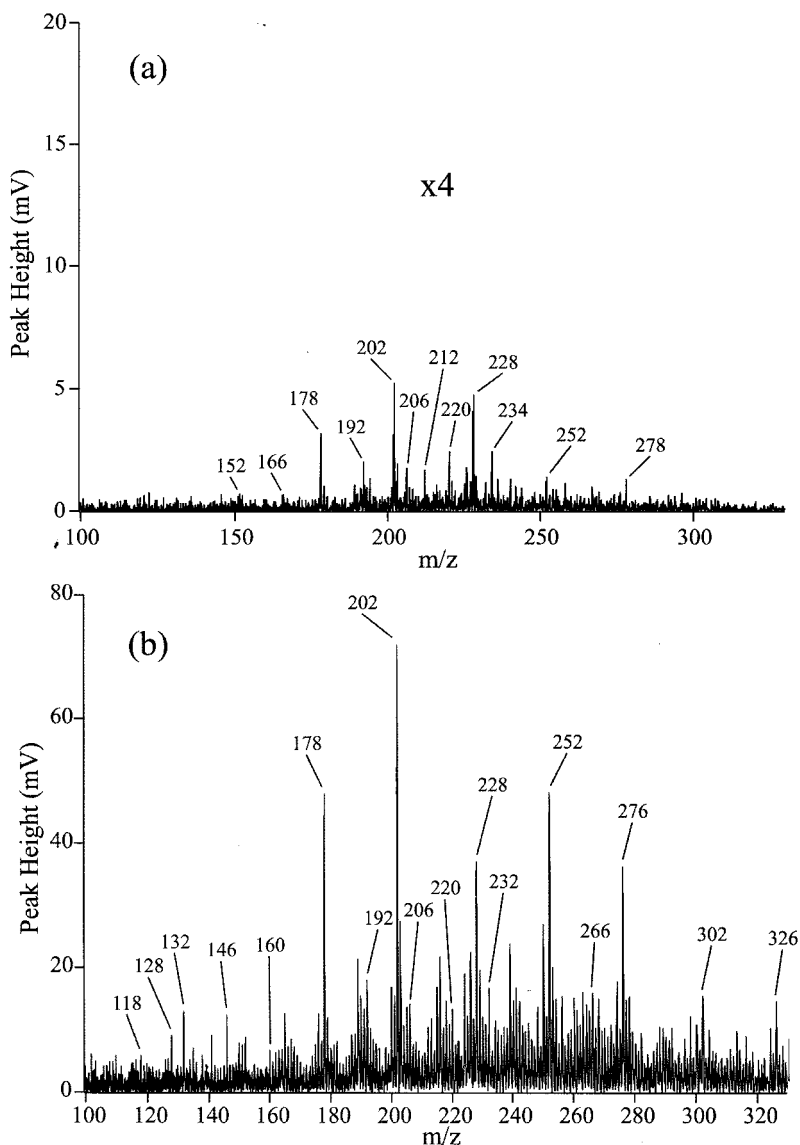


FIGURE 1   L2MS data taken at Jungfraujoch from 24-h samples collected on (a) March 23–24, 2000 and (b) August 7–8, 2000. The mass spectrum from March 23 to 24 consists primarily of PAHs and alkylated PAHs. The mass spectrum from August 7 to 8 contains many more ions including potential Environmental Tobacco Smoke markers at $m/z$ 118, 132, 146 and 160. Note that the $y$ axis in (a) is enlarged by a factor of 4 compared with (b).

($m/z = 166$), phenanthrene ($m/z = 178$), alkyl phenanthrenes ($m/z = 192, 206, 220$ and 234), pyrene and fluoranthene ($m/z = 202$), chrysene and cogeners ($m/z = 228$), benzo[a]pyrene and cogeners ($m/z = 252$) and benzo[b]chrysene and cogeners ($m/z = 278$). These PAHs are typically observed from various sources of combustion, such as diesel, gasoline, or heating oil and are not specific to any particular source [20,21]. As a result, it is not possible to determine a specific source of the aerosol containing these PAH. The fairly high relative abundance of acenapthylene and fluorene is noteworthy, as these compounds are not typically found in the particle phase. The average outdoor temperature at JFJ was approximately $-10°C$ in March which probably contributes to their presence on the aerosol, although some losses may occur because the filter itself was at room temperature during sampling (approximately $25°C$).

Figure 1b, showing L2MS data from a sample collected on August 7–8, contains many more ions than the spectrum form the March campaign, as well as a strikingly different distribution of compounds. Particularly interesting are the ions at $m/z = 118, 132, 146$ and $160$. These have been previously identified by Morrical and Zenobi [19] as possible marker ions for environmental tobacco smoke (ETS). These signals may be small but they were reproducibly observed in all the mass spectra, collected during the August campaign, with the exception of a couple days with very low particle concentrations that yielded very low intensity spectra. The many other ions present in Fig. 1b may also in fact be due to ETS as the mass spectrum closely resembles those obtained for ETS.

Since these are the first measurements made at JFJ to analyze PAHs and PACs on aerosol, it was important to try and determine which size fraction of the aerosol these compounds are associated with. Since our sampling method collected all aerosol $< 10 \mu m$, it cannot be determined which fraction of the aerosol collected contains PAH. The PAH data obtained with L2MS was thus compared with BC data to see if there is a correlation between BC measures and the PAH found on the filters.

Figure 2 shows a comparison of total PAH ion abundance to BC for the period of March 21–25, 2000. Figure 2 is a plot of the integrated total ion signal of PAH obtained in the mass spectra on March 21–22, 23–24 and 24–25 versus BC in $ng/m^3$. From this plot it can be seen that there is a correlation between the PAH signal and the BC concentration, suggesting at least during these sampling periods, that PAH are associated with carbonaceous aerosol. When the BC concentration is at its lowest (March 21–22) there is no detectable PAH ion signal.

The two sources for the presence of PAHs at JFJ are long range transport and/or local sources. Everything at JFJ is powered by electricity, however, the smokers among the visitors (sometimes more than 5000 daily), could be another possible source for these compounds. Occasional flybys from helicopters and airplanes may also contribute to local interference in these measurements. Based on the mass spectral signature it seems likely that the PAHs observed in the March data are due to long range transport. The relatively small number of significant peaks in the spectrum (noise level is about $0.5 mV$) makes it likely to be fossil fuel combustion and not due to biomass combustion, which typically produces a much more complicated mass spectrum [19,21]. However, because of the low ion abundance from the March analysis it is possible that other less abundant ions were present but simply not in concentrations sufficient for detection by L2MS.
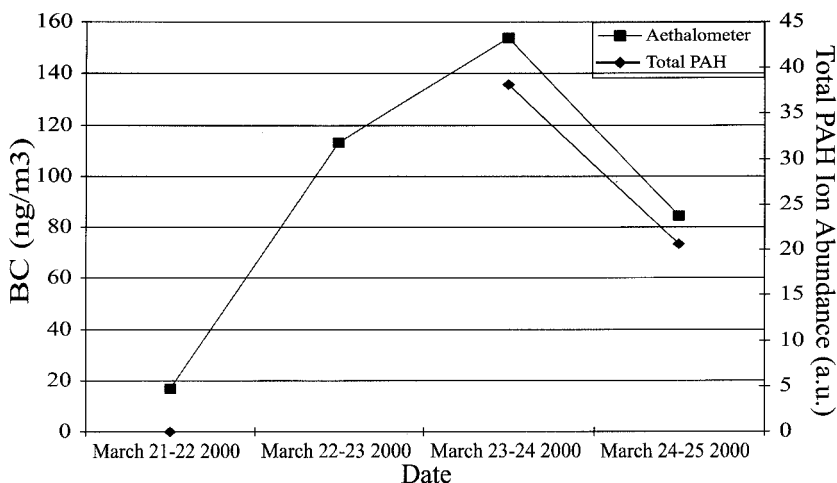
FIGURE 2   Plot of total PAH ion signal and black carbon (BC) measurements from an aethalometer. A good agreement exists between the relative increase and/or decrease in PAH ion signal from the mass spectrum and the mass concentration of BC.

It was suspected from the ions at $m/z = 118, 132, 146$ and $160$ appearing in the August data that there was a local interference from visitors smoking on JFJ. Smoking is not allowed in the indoor section of the observation tower but there is an outdoor platform where tourists can smoke. The aerosol sampling inlets are located approximately 10 m above this outdoor observation platform. This sampling location may be close enough to sample ETS being generated on the platform below.

Black carbon measurements were made in August and a comparison of total ion signal and BC is shown in Fig. 3. Unlike the data obtained in March, there is not a very good correlation between BC and total PAH ion-signal in August. Figure 3b shows a comparison of BC to the ions identified as ETS markers. It can be seen that there is a somewhat better correlation between the ETS markers and BC, although ETS is not composed primarily of BC [23]. Therefore, a local interference from tourists smoking would not necessarily show up in the BC measurements.

After making this observation, we decided that it was necessary to obtain data from the railway as to the number of people traveling up to JFJ each day. Figure 4 shows a comparison of the total PAH ion signal and ETS markers to the number of visitors that come up to JFJ daily. The total PAH ion signal (Fig. 4a) does not match well with the number of tourists and therefore, suggests that there is a significant contribution from other sources for the PAH observed. However, when comparing the number of tourists to the ion signal from the ETS markers a good correlation ($R^2 = 0.79$) is observed. The plot of this data is shown in Fig. 4b. There is a clear trend that the number of people present at JFJ follows with the overall ion signal of the ETS markers and allows for the possible identification of one source of local interference at the JFJ site. It also demonstrates the ability of using marker compounds for the identification of certain combustion sources in an outdoor environment.

This study was not designed to quantify the contribution of ETS to the total aerosol, and therefore the significance of ETS at JFJ is presently unclear. The excellent sensitivity of the L2MS allows for the detection of very small quantities of such compounds even in relatively clean environments. Thus, even minute amounts (pg/filter range) of
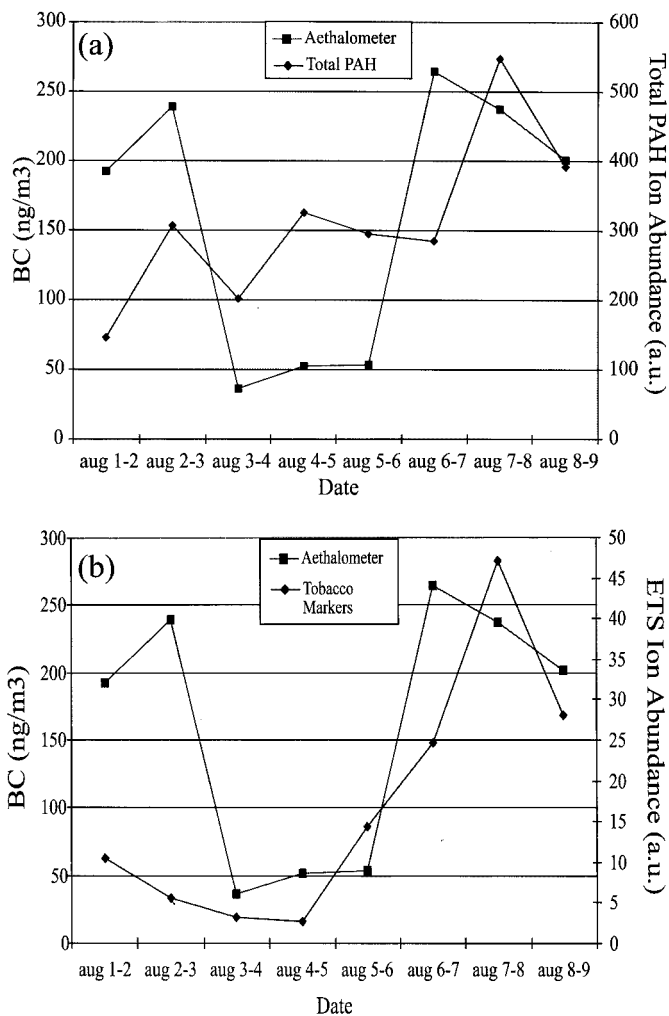
FIGURE 3  Comparison of BC mass concentration with (a) Total PAH ion signal and (b) Tobacco marker ion signal for the sampling period of August 1–9, 2000. Relatively poor correlation exists between total PAH ion signal and BC suggesting that PAH observed in August is not exclusively associated with BC as PAH observed in March. Tobacco marker ion signal shows somewhat better correlation but is clearly not strongly associated with BC.

ETS produce substantial L2MS signals. Future studies should aim at a quantification of such background interference from the beginning.

The substantially greater relative ion signal of samples collected in August as compared to March may reflect the greater overall organic contribution to the aerosol present at JFJ in the summer versus winter conditions, even though the total aerosol mass concentrations recorded during these periods are similar ($\sim 4\,\mu g/m^3$). However, on average the BC concentration is greater in August than in March by a factor of almost two. Since the mass spectra obtained from the March samples are close to the detection limits of the L2MS instrument, it is possible that many of the same compounds are present in March that were observed in August but were merely
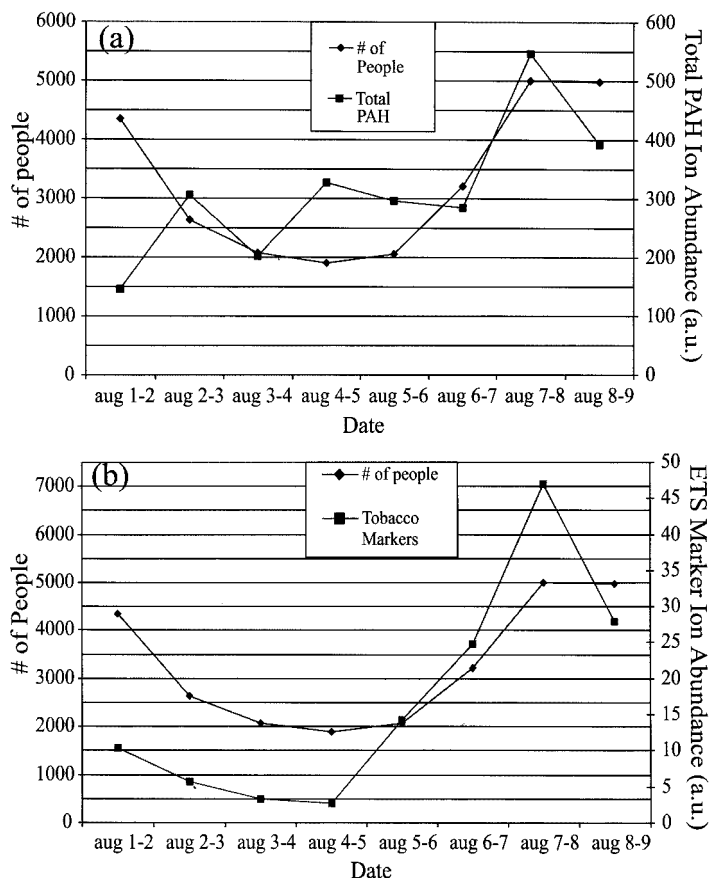
FIGURE 4   Comparison of (a) Total PAH ion signal with the number of people visiting the Jungfraujoch daily and (b) Tobacco marker ion signal with the number of people visiting the Jungfraujoch. The total PAH ion signal does not correlate well with the number of daily visitors, however, the tobacco marker ion signal follows the same general trend as the number of visitors.

below the instrumental detection limits. The good correlation with BC data in March suggests that most of the PAH detected are due to transport from remote sources and not due to local interference as the number of visitors was at least three times lower in March than in August. In addition, colder temperatures tend to limit the number of people going outside.

Local interference poses a potential problem for organic analysis of aerosol and gas phase at the site as often 24-h (or longer) sampling periods must be employed in order to obtain an adequate sample for analysis. It was not known quantitatively what the contribution of local sources such as tourists, helicopters, and airplanes was to the carbonaceous aerosol, but it was observed that if helicopters and airplanes pass, a brief spike in the aerosol concentration occurs (as observed in BC concentration and/or total particle counts). It has been determined by Nyeki et al. that the only time JFJ can be considered to be in the free troposphere is between 0300 and 0900 [2]. The remaining times are considered to be particle boundary layer conditions [2]. However, because sampling for organic analysis requires a longer time period than the time period suggested by Nyeki et al., there is the chance of interference

when making organic compound measurements on aerosols from either local sources or from the rise of the particle boundary layer up to JFJ. It is therefore important to be able to identify and eliminate these sources of interference so that a true background measure of organic compounds on aerosol, such as PAH, can be obtained.

## *Acknowledgements*

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