Response to referee 1:
Author’s response in Blue

This is a nicely written paper that contributes new data to help improve understanding of urban sources and levels of PAHs and their derivatives, including day vs night variability.

Thank you for reviewing our paper. Your comments and suggestions were very helpful and we believe the paper has been improved.

What is still missing from the paper in my opinion, is an expression of the study’s significance. i.e. what is novel about this study and how/where do the results make an impact on advancing the field of science. I would expect this for a paper in ACP.

To the best of our knowledge, this study is the first to provide data on the organic chemical composition of $PM_{2.5}$ over short time sampling periods (3h) in the city of Beijing. In addition, the statistical relationship between NPAHs and HONO raises the importance of studying the chemical relationship between them, which may impact the HONO budget in the atmosphere and improve related models. Other correlations (CO, NO, SO_2) were also important in identifying source emissions.

Author’s changes in manuscript, (the following text has been added at the end of the introduction):

This paper explores the feasibility of higher frequency sampling in Beijing, to support the identification of emissions sources from diagnostic ratios and correlations with atmospheric gas pollutants. These measurements also raise the potential importance of the chemical relationship between NPAHs and HONO which may impact the HONO budget in the atmosphere and, if included, improve related models. This study comes after three years of declaring the anti-pollution action plan and strategy taken by the municipal government of Beijing and published in September 2013 (Ministry of Ecology and Environment The People's Republic of China, Beijing toughens pollution rules for cleaner air, 2013), trying to increase the number of days with good air quality index by prohibiting coal combustion, promoting clean energy vehicles and public transport and helping industrial transformation and upgrading to new technologies.

Line 76-86: Why only target PM and not gas-phase? Some explanation is warranted here I think. Also, when comparing results to other studies is this always based on PM and not total?

One of the main objectives of this project (APHH) was to investigate in depth the chemical composition of $PM_{2.5}$ (organics, minerals and ions) and identify emission sources at receptor site. The gas phase measurements of PAHs and derivatives were not a part of this project and the lack of this data can underestimate the exposure risk assessment.

Results were compared to those in the particulate phase in wintertime only. A new study has been added to the comparison (Feng et al., 2019) and text (L.191) modified as follows.

Author’s changes in manuscript:

Our average value was comparable to the reported value in a recent study (Feng et al., 2019) at the campus of Peking University health science centre, a short distance from our sampling site (~1 mile), where the authors reported a total PAHs average concentration in winter Beijing (2014 - 2015) of 88.6 ± 75 ng m^{-3}.

Line 83: Do the longer nighttime samples compared to daytime samples introduce a source of bias in the results? For instance, related to particle capture efficiency which changes as the filter becomes more loaded. Another question is heterogeneous reactions on the filter during the 15hrs the samples are being collected and exposed to a high volume of atmospheric oxidants. If these reactions are occurring they will impact the 15h samples to a greater extent. This issue has been considered in the literature and I think the authors should at least raise this concern.

Data from long sampling times may be biased by sampling artefacts in which an increase in uncertainty on each of the most reactive PAHs compounds may occur due to reactions with gas phase oxidants. Previous studies (Schauer et al., 2003, Goriaux et al., 2006) suggested an underestimation of PAHs concentrations by up to 100% and 200% (under high ozone levels) due to ozone deposition on filters and subsequent chemical decomposition of PAHs. However, at medium ozone levels (30-50 ppb), Schauer et al., 2003, underestimated PAHs values by 30%.

In addition, Tsapakis and Stephanou 2003, have studied under different atmospheric environment (ozone concentration and time sampling) the effect of ozone denuder on gas phase PAHs and particle-bound PAHs. According to this study, ozone affects mostly the gas phase measurement of PAHs (up to 50%) but regarding the particle phase, weaker effect with no apparent difference was suggested at low ozone concentration.

To the best of our knowledge, comparison studies using two different samplers were mostly conducted in Europe where concentrations of PAHs are much lower than in Beijing which may increase the uncertainty. In this study, particles filters were stored at -20ºC directly after collection and during transit. The ozone concentrations at night varied between 2 and 21ppb (mean 6.4 ppb, n=16).

Moreover, heterogeneous oxidation processes could occur either in the atmosphere or during the sampling of aerosols and major focus in previous laboratory studies (Ringuet et al., 2012a, Jariyasopit et al., 2014; Zimmermann et al., 2013) was given to the formation of OPAHs and NPAHs. The mechanisms and levels of formation of these derivatives are still far from being fully understood, especially that the reaction of PAHs with oxidants (OH radicals, ozone) is highly influenced by surface coverage and PAHs loading (up to 2 orders of magnitude) (Keyte, I.J., 2013 and references therein) i.e. particles were shown to exhibit a potential inhibiting factor on the reactivity of PAHs due to slow diffusion of oxidants and inaccessibility of PAHs in the bulk particle. Previous studies reported that the formation of NPAHs during high-volume sampling is not significant and calculated to be < 3% (Arey et al., 1988) and < 0.1 % (Dimashki et al., 2000). Therefore, considering the above and our sampling conditions, our estimation of sampling artefacts range between 10 and 20%.

References:

Goriaux, M. et al., Environ. Sci. Technol., 40, 6398–6404, 2006.
Schauer, C. et al., Environ. Sci. Technol. 37, 2861-2868, 2003.
Tsapakis and Stephanou, Atmospheric Environment, 37, 4935–4944, 2003.

Arey, J. et al., Env. Sci. Tech, 22, 457-462, 1988
Dimashki, M. et al., Atmospheric Environment 34, 2459-2469, 2000.
Keyte, I.J., Chem. Soc. Rev., 42, 9333-9391, 2013.
Zimmermann, K., et al., Environ. Sci. Technol., 47, 8434−8442, 2013.
Ringuet, J., et al., Atmospheric. Environment., 61, 15–22, 2012.
Jariyasopit, N., et al., Environ. Sci. Technol., 48, 412–419, 2014.

Author’s changes in manuscript, (A new text has been added to paragraph ‘‘Data analysis and error evaluation’’ (L.161)):
Another source of error can be attributed to sampling artefacts and this has been discussed in previous studies (Schauer, C. et al., 2003, Goriaux, M. et al., 2006, Tsapakis and Stephanou, 2003). The absence of an ozone denuder to trap the gas phase oxidants may lead to an underestimation of the true values of PAHs due to chemical decomposition. Therefore, data from long sampling times and under high ozone ambient concentrations may be biased by sampling artefacts by more than 100 % (Schauer et al., 2003, Goriaux et al., 2006). However, at low ozone levels, negative artefacts were considered not significant (Tsapakis and Stephanou 2003), whilst, at medium ozone levels (30-50 ppb) PAHs values were underestimated by 30 % (Schauer et al., 2003). In addition, heterogeneous reactions during particle sampling may occur only on the monolayer surface coverage with limited diffusion of oxidants to the bulk particles (Keyte et al., 2013 and references therein). Previous studies reported that the formation of NPAHs during high-volume sampling is not significant and calculated to be < 3 % (Arey et al., 1988) and < 0.1 % (Dimashki et al., 2000).
Considering the role of ozone (always below 30 ppb in this study, with a mean value: 10.4 ± 8.8 ppb), in addition to sampling time and temperature, the estimation of the negative sampling artefacts on our data range between 10 and 20 %, with the highest error estimation attributable to longest sampling time (15h).

Line 203-205 and elsewhere: please use consistent number of significant figures when reporting concentrations. In this section it ranges from 2 to 4. I think that either 2 or 3 significant figures is appropriate given method uncertainties.
Concentrations corrected in the manuscript and tables.

Line 369+: I think the spatial variability within Beijing may be even more important than seasonal variability. The authors believe their results are representative of "Beijing" and present them as e.g. "...concentrations for Beijing". However, I wonder if that is appropriate without first investigating the representativeness of their sampling site for the entire metropolis of Beijing. There is also the potential for a dominant impact due to a local source (or sources) that may impact or bias results at a given site. The authors should be careful to address this possibility and not overstate the representativeness of their results (or other results from single sites in other studies), when making comparisons e.g. Beijing vs Athens.

We agree that spatial variability is also important in megacities but most studies focused their discussion on seasonal variability probably because of the lack on data from other districts.

Author’s changes in manuscript: (L.193)
The urban location in this study (Fig. S1) was surrounded by busy roads, residential buildings, an underground railway, restaurants and further afield thermal power stations. PAHs concentrations are anticipated to decline closer to the mountains in the North and West of Beijing due to air mass trajectory, aging and distance from emission sources. Results from this study can be considered representative (within the margin of error) of the urban area in Beijing including districts such as Chaoyang, Haidian, Fengtai, Xicheng, Dongcheng, Shijingshan covering an approximate population of 12 million. Future studies in less populated districts and different areas of the metropolitan of Beijing would be helpful for comparison of population exposures.

Response to referee 2:
Author’s response in Blue

The authors present a rich data set examining the concentrations of PAH’s in atmospheric particulate matter in Beijing. PAHs are known to increase the toxicity of aerosols and this work advances our understanding of their dynamics in the atmosphere. The analytical methodology applied in this work is impressive and carefully reported. Where this manuscript needs improvement is the discussion and presentation of the data. I recommend the authors work to increase the clarity of the results, and their interpretations, to ensure their work is as impactful as possible.
Thank you for your comments, corrections and recommendations. Your careful review and thorough reading helped us to better present the data and we believe the paper has been improved.

General Comments:
Comment 1: The authors have a very data rich paper, but often don’t report a measure of variability (e.g., standard deviation). This is particularly potent given the title of the manuscript. In the text and in the tables a measure of variability should be included, and discussed, when reporting any data. Specifically, standard deviations should be included in table 2.
The variations of concentrations for each compound were presented in Table 2 as minimum and maximum and standard deviations were presented in Figure 1, which now replaced by box and whiskers plots according to your recommendation below (L.662). The text has been corrected and values of SD for individual compounds and the average total concentration have been added in Table 2, abstract, results and conclusions. In the discussion we have been limited to comparison with Benzo[a]pyrene and total average of PAHs and derivatives. Variations for individual PAHs not frequently reported. We believe the variability of each compound reported in this paper might be helpful for future comparison.

Comment 2: The authors present this work as a higher resolution examination of PAH dynamics because they use relatively high resolution (3h) samples. Despite this, there is almost no discussion of temporal dynamics other than day vs. night or 3h vs. 9h vs. 15 h. I would like to see the authors look into the temporal dynamics on given days and investigate drivers of PAH variability beyond correlation.

This paper explores for the first time the feasibility of higher frequency sampling in Beijing. Whilst we successfully show that this time resolution can be achieved, the relatively short-term data for Beijing has led us to use 24 h averages for comparison and discussion purposes with other work. Temporal dynamics (diurnal, daily, seasonal) of PAHs are influenced by a number of factors such as emission sources, $PM_{2.5}$ concentrations, mixing height level, photolytic effect and gas-particle partitioning. To investigate drivers of PAHs variability beyond correlation and emission sources, we refer primarily to spatial and seasonal variations within the area of sampling. To the best of our knowledge, no high resolution data available in Beijing. The data from summer campaign are under investigation, preliminary results show notably lower average value (~13 times) than the average 24 h total PAHs concentrations in this study (97 ng m^{-3}). In summer, concentrations of 2 and 3 ring PAHs were mostly below limit of quantification (in the particle phase) and the average 24 h concentration of B[a]P was 0.8 ± 2 ng m^{-3}, far lower than the average in winter (15 ± 9 ng m^{-3}). PAH partitioning is strongly temperature-dependent; summer time probably also contributes to enhanced photo-degradation of PAHs and photochemical formation of derivatives, and the absence of major sources contributors such as residential heating and combustion. We will add more discussion in our next paper, comparing the temporal dynamics between winter/summer Beijing and Summer New delhi.

It is clear that individual PAHs concentrations are related to $PM_{2.5}$ concentrations as shown in Fig. S2, with contribution from specific emission sources at mid-day. We have reported in this paper that 9-Nitroanthracene appears to accumulate at night and to undergo a photo-degradation during the daytime. We will follow the behaviour of this compound and other component on our ongoing investigation of the summer campaign.

Comment 3: Was there meteorological data available at your study site? PAH lifetime, emission and phase are likely influenced by temperature or solar flux. Additionally, analysis of wind direction trends during the specific emission periods would provide additional insight into the importance of different sources. If this data exists, including it in the analysis could increase the impact of the results

We have reported in the text that no significant correlations were seen between PAHs and meteorological parameters (Relative Humidity and Temperature). Results from correlation of PAHs and derivatives with temperature and relative humidity are shown in Table S1.

The site location in this study was an urban site in Beijing (Fig S1), surrounded by busy traffic roads, residential buildings, underground, restaurants and thermal power stations. PAHs concentrations may fluctuate when getting closer to the mountains in the North and West of Beijing due to air mass trajectory, aging or moving away from emission sources. A wind-rose plot of the entire campaign is presented in Fig S4, showing that winds arriving at the site blow from the North East for much of the time. Contribution to gas phase concentrations of SO_2 (L281-284) was attributed to a specific anthropogenic source such as the Beijing Taiyanggong thermal power station in the North East.

Comment 4: Organization. This manuscript, although data rich, is poorly organized with many acronyms, lots of in text data, and unclear conclusions. I recommend the authors make an attempt to trim the text. Specifically, many data references in the discussion could be replaced with reference to the appropriate figure or table. This will allow the readers to better understand the author's conclusions by cleaning up the text.

Acronyms were used only to shorten target compounds full name in the text and they are listed in Table 1. Acronyms in the conclusion has been replaced by the full name of each compound used to clarify the information to the reader without referring to Table 1.

References to appropriate Tables and Figures have been added to the discussion

Author’s changes in manuscript:

In the conclusions:

(L.388) Benzo[a]pyrene; (L.393) 2+3Nitrofluoranthene/1-Nitropyrene; (L.400) 9-Nitroanthracene.

In the discussion:

- (L.232) As shown in Fig. 4, other ratios can be useful
- (L.271) parameters (Relative Humidity and Temperature) as shown in Table S1
- (L.292) For NPAHs, as shown in Table S1, no significant correlation
- (L.307) As shown in Table S2, 9-Nitroanthrancene
- (L.340) BaP_{eq} for the whole sampling period was 23.6 ng m^{-3} (Table 3).
- (L.340) As shown in Table 2, 6-NCHR has not been quantified
- (L.344) in urban air of Beijing ranged from 10^{-5} to 10^{-3} > 10^{-6} (Table 3).
- (L.349) the 24 h average estimated cancer risk (Table 3) from inhalation exposure to

Comment 5: The authors could improve their argument for the specific significance of their work. The authors do a good job of detailing PAHs in aerosol but don’t discuss their site in significant detail. Please elaborate on why there is a pressing need to study PAHs in Beijing within your introduction

New text addressing this point has been added at the end of the introduction section.

Author’s changes in manuscript:

This paper explores the feasibility of higher frequency sampling in Beijing, to support the identification of emissions sources from diagnostic ratios and correlations with atmospheric gas pollutants. These measurements also raise the potential importance of the chemical relationship between NPAHs and HONO which may impact the HONO budget in the atmosphere and, if included, improve related models. This study comes after three years of declaring the anti-pollution action plan and strategy taken by the municipal government of Beijing and published in September 2013 (Ministry of Ecology and Environment The People's Republic of China, Beijing toughens pollution rules for cleaner air, 2013), trying to increase the number of days with good air quality index by prohibiting coal combustion, promoting clean energy vehicles and public transport and helping industrial transformation and upgrading to new technologies.

Comment 6: For a field study, site selection and significance is very important. Please add some discussion of how representative your site is compared to Beijing in general, what the strengths of the site are, and what are some possible weaknesses.

Most studies focused their discussion on seasonal variability probably because of the lack on data from other districts. New text has been added to the results and discussion

Author’s changes in manuscript (Section 3.1 - L. 193):
The urban location in this study (Fig. S1) was surrounded by busy roads, residential buildings, an underground railway, restaurants and further afield thermal power stations. PAHs concentrations are anticipated to decline closer to the mountains in the North and West of Beijing due to air mass trajectory, aging and distance from emission sources. Results from this study can be considered representative (within the margin of error) of the urban area in Beijing including districts such as Chaoyang, Haidian, Fengtai, Xicheng, Dongcheng, Shijingshan covering an approximate population of 12 million. Future studies in less populated districts and different areas of the metropolitan of Beijing would be helpful for comparison of population exposures.

Specific Comments

Line 20: Restructure the list of compounds. As written, it is easy to miss the period after the major PAHs and not realize a new list has started for the major OPAHs. Use the same sentence structure for each type to avoid confusing the reader.
Corrected

Line 38: comma after "organic carbon"
Corrected

Line 58: Clarify "geographic peripheral expansion"
Corrected

Author's changes in manuscript (underlined text):
a major focus has been given to Chinese cities such as Shanghai, Beijing, Guangzhou, Tianjin, and Shenzhen because of their population growth and geographic peripheral expansion in manufacturing capacity and energy industries which are located throughout each of the city's manufacturing zones.

Line 60: change "PAH on 24 PM2.5 sampling" to "PAH concentrations in 24 h averaged samples".
Corrected

Author's changes in manuscript:
The majority of previous studies have reported PAH concentrations in 24 h averaged samples during short-term and long-term measurements campaigns

Line 62: Remove "sampling and" as written it is redundant.
Removed

Line 65 – 67: Your reference to PMF here seems out of place as you do not perform PMF on your results or discuss it as a future method of analysis.
We did mention the PMF model as an example because it is widely used in parallel with diagnostic ratios.

Line 76: Can you really show a sampling campaign? Sampling scheme or setup would be more appropriate.
Corrected

Line 82: Please clarify your sampling technique here. You say the filter was changed every three hours, but in line 80 you say also performed nine hour sampling during the day.
Author's changes in manuscript: (L.82)
The daytime sampling started at 8:30 in the morning and the filter was changed every 3 h. During low particulate loading conditions, the daytime sampling started at 8:30 in the morning for a sampling duration of 9 h.

Line 83: Rephrase the nighttime sampling period time from. A clearer phrasing could be "Night-time sampling began at ~17:30 and ended at 08:30 the following day."
Author's changes in manuscript:
Night-time sampling began at ~ 17:30 and ended at 08:30 the following day.

Line 88: Was a method blank also performed? If so please explicitly state, if not, please explain how sources of contamination were investigated.

New text added to Data analysis and error evaluation (L.145)

Author's changes in manuscript:

To determine any sources of contamination during sample preparation and the analytical procedure, the solvent (acetonitrile) and field blanks (n=2) were analysed following the same procedure as for the samples (Extraction, SPE, Evaporation). Most target compounds were found to be below LOD (S/N=3) or orders of magnitude (up to 10^3- 10^4) lower than was found in the samples. A small number of compounds found in field blanks (1,8-Naphthalic anhydride, Benzo[a]fluorenone, 1-Nitronaphthalene, 9-Nitroanthracene) have a higher contribution (4-30 %) to very few filters (2 to 5 samples) collected over a 3 h time period, if this was co-incident with low particulate loading conditions. The contribution to each compound from field blanks has been corrected in the final data.

Line 91: What is the purity of these standard compounds? Could there be non-deuterated forms of them within the standard which could contaminate the samples?
Minimum purity of D2-standard compounds was 98%. Results from clean filters spiked with deuterated-compounds did not show contribution on our target compounds.

Line 102: I'm assuming these were calculated from your deuterated standard compounds. Add a statement saying so. Also, it would be useful to have an idea of the variation of the extraction efficiency as well as the range. Add the mean and standard deviation here if possible. Additionally, if samples were adjusted to account for extraction efficiency that should be stated.

We have adjusted concentrations to recovery efficiencies and it was stated in the text (L.103)

Author's changes in manuscript:

The average recovery efficiencies calculated from surrogate standards ranged from 85% to 96% (Phenanthrene-d10: 95 ± 9 %; Pyrene-d10: 101 ± 7 %; 9-Fluorenone-d8: 98 ± 13 %; 9,10-Anthraquinone-d8: 102 ± 11 %; 1-Nitronaphthalene-d7: 93 ± 8 %; 3-Nitrofluoranthene-d9: 101 ± 11 %) and the target compounds concentrations were calculated incorporating measured recovery efficiencies.

Line 138: Does the simultaneous measurement mean each filter extract was spiked with deuterated compounds, the 16 PAH standard mixture, or the standard curve?
Filters were spiked before extraction. The calibration standards (16 PAHs standard mix and deuterated mix) were measured every day during the sequence analysis of the samples in order to follow the response of the instrument and the drift of the calibration curve.

Line 148: This is a very odd way to discuss precision. Why don't you simply state the mean RSD ± σ from all sample replicates of each type? Since your intraday and interday are similar, there may not be any need to state both numbers.
As we didn't use the standard reference materials from EPA as a reference for method validation, we think it is important to show the response of the instrument for each compound in replicates samples between days in order to include the average RSD in the error estimation.

Line 154: Please restructure this. You have not yet introduced systematic error, but this reads as if you've already discussed it.
There is no particular introduction for systematic error as they are different for each type of study and measurement. In this study, we have related the systematic error to the influence of the sample matrix during the analysis sequence on the quantification step and the calibration offset (L.154-155).

Line 157: Systematic error is not uncertainty so you cannot combine it with your precision estimates. You could propagate the uncertainty associated with the systematic error to better constrain your overall uncertainty.
Corrected, "uncertainty" removed

Author's changes in manuscript (L.157):
Therefore, the overall estimated error, combining the precision and the systematic effects, is less than 20%.

Line 158: This, combined with the calculation of extraction efficiencies, is a way to constrain systematic errors. I recommend combining this section with lines 154-157 and your discussion of extraction efficiencies in 102.
This section has been modified and combined with line 145 please refer to the response to question (L.88) above.

Line 164: Add "The number of…has"
Corrected

Line 166: Rephrase for clarity. "In China, the official PM2.5 annual and 24hr average standards are 35 µg m-3 and 75 µg m-3, respectively,"
Author's changes in manuscript:
In China, the official air quality guidelines for $PM_{2.5}$ expressed as annual mean and 24 h average limit are 35 µg m^{-3} and 75 µg m^{-3}, respectively.

Line 168-169: Either this statement is incorrect, or your methods section is incorrect. In your methods section, you state that you've collected 3, 9, and 15 hour averaged samples. Please fix or clarify.
$PM_{2.5}$ concentrations were averaged to 24 h for comparison with the official guidelines, also they were averaged to the filter sampling times and presented in Fig. 6 and Fig. S3

Author's changes in manuscript (L.170):
Concurrent $PM_{2.5}$ concentrations were averaged to the filter sampling times (3 h, 9 h, 15 h) and are shown in Fig.6 and Fig. S3.

Line 169: A more appropriate way of presenting this would be the mean and standard deviation. "During sampling, the average 24h averaged PM2.5 was X ± Y…."
Author's changes in manuscript (L.170):
The average 24 h concentration was 108 ± 82 µg m^{-3} (range: 10 - 283 µg m^{-3}), exceeding the 24 h limit value on 10 of the 18 sampling days.

Line 171: Same as above, the mean and standard deviation would be very meaningful here.
Corrected

Line 174: Again, the mean and standard deviation would be very meaningful here.
Corrected

Line 171 – 178: All of this information would be presented better in a table. Consider adding the summary data in this paragraph to the top of each section in table 2.
Concentrations of each compound and the summary data (total average) are presented in Table 2, and new Fig. 1.

Line 179 - 193: Is there any reason why these specific PAHs are important or interesting besides them being found in the highest concentrations? Some discussion of the particularly interesting compounds would improve the quality of this manuscript.
These specific 16 PAHs are considered representatives for all PAHs and they are defined by the United States Environment Protection Agency (EPA) (L.105). They have known toxicity equivalence factors (Table S3) and considered carcinogenic to human health. The particularity of these compounds and their presence in the particulate phase were discussed in paragraph diagnostic ratios to identify emission sources (L.218). Other particularities were suggested to anthracene and 9-Nitroanthracene (L.306-316).

Line 193: Can you mention some specific controls the local government has put in place or cite some of the policies? If they are effective, as you are implying, perhaps they could be applied in other locales, and it would be useful for the reader to know more about them.
Author's changes in manuscript:
Introduction (L.73): This study comes after three years of declaring the anti-pollution action plan and strategy taken by the municipal government and published in September 2013

(Ministry of Ecology and Environment The People's Republic of China, Beijing toughens pollution rules for cleaner air, 2013), trying to increase the number of days with good air quality index by prohibiting coal combustion, promoting clean energy vehicles and public transport and helping industrial transformation and upgrading to new technologies.

Results and discussion section 3.1 (L.194):
Our average value (97 ng m^{-3}) was comparable to the reported value in a recent study (Feng et al., 2019) at the campus of Peking University health science centre, a short distance from our sampling site (~1 mile), where the authors reported a total PAHs average concentration in winter Beijing (2014 - 2015) of 88.6 ± 75 ng m^{-3}. The lower average concentration of total PAHs reported in this study and Feng et al., (2019) can potentially be attributed to the efforts from municipal government to improve air quality and control emissions by reducing combustion sources.

Lines 203-213: Is there a specific reason by people report these specific ratios? Do they mean anything other than the relative amount of each type? As written, they seem like a random descriptor that isn't adding much meaning to your observations.
The use of these ratios shows the possible contribution of PAHs to OPAH and NPAH, the observed levels simplify the comparison with other studies. In other words, even if the concentration of total PAH is much higher in China than Europe, using these specific ratios facilitate the comparison, and highlight the chemical transformation under similar conditions such as winter.

207: Wouldn't the average of the ratio within all the samples be more meaningful. Or maybe a total ratio of total measured PAH:NPAH?
Previous studies have reported the total 24 h average for each series of compound. The use of the average 24 h is more meaningful here and represents the mean concentration of all samples and these ratios represent the total average concentration of each series of compound. The symbol "∑" added to the text.

214: Does daily mean 24 h averaged? As written the discussion of BaP seems out of place. Are there specific air quality standards for the other compounds studied? If so, please discuss them as well.
It means 24 h and it was compared with the 24 h average limit value for China. This paragraph was moved up to the beginning of this section (L.170). "24 h" added to the text.
According to WHO, BaP is a suitable marker of particle-bound PAH and typically represents a substantial proportion of the total carcinogenic potential of the parent PAH.

Author's changes in manuscript:
The daily (24 h) concentration of Benzo[a]pyrene ranged from 4.46 to 29.8 ng m^{-3} (average 15 ± 8.9 ng m^{-3})

225: As written, it's unclear which ratio is being explained after the semicolon.
Author's changes in manuscript: (L.225)
values of FLT/(FLT + PYR) less than 0.4 and IcdP/(IcdP + BghiP) less than 0.2, are mostly related to incomplete combustion.

254: I believe you are trying to say you used an isomeric standard to estimate the sensitivity to a compound where a standard is not available. Please add some citation explaining why this is okay with this class of compounds and a statement explaining why you expect the sensitivities to be similar within your analytical setup. Also, if you have measured any other isomer pairs, it might strengthen your case if you show the reader that they have similar sensitivities.
This approach was based on previous studies cited in L.256-258. Any recommended article from the referee would be very helpful. It is not necessarily that isomers show the same sensitivities and the best way to check that is to analyse the isomer pairs. Using a Q-TOF-MS as in our study helped bring the sensitivity of isomer to the same level by taking into account transition and qualifier ions. PAH isomers used in this study showed relatively same sensitivities.

Author's changes in manuscript: (L.255)
PAH isomer pairs (Table 1) in standard mixtures showed similar sensitivities for each concentration used, therefore, we assume an equal sensitivity for 2-NFLT and 3-NFLT during analysis.

266 – 316: Correlation can be problematic especially when dealing with interlinked species and non-random sampling. Due to your long averaging times for your filters, and (I'm assuming) relatively quick gas phase measurements it may be difficult to make any concrete conclusions.
It is true that the use of correlation between the gas phase measurements of atmospheric oxidants and the chemical composition of the particle phase does not prove a chemical link but it can support a chemical reaction pathway such as the positive strong correlation between ANT and 9-NANT in particle phase. This suggestion supports the heterogeneous formation pathway of 9-NANT (in parallel, ANT gas phase to 9-NANT particle), which mean 9-NANT is closely related to ANT and not to direct emissions.

278: High CO correlation is not necessarily an indicator of regional sources as you would expect correlations to be high near the sources as well.
Yes, but we cannot exclude regional emissions due to the long lifetime of CO.

272-273: Please explain what values/units you used in your correlation analysis. Right now it is unclear if you used the average concentration over the sampling period, the integrated concentration, or something else (i.e., the median).
Fig. 5 shows an example of the unit values and type of data used for correlation. The concentrations (ng m^{-3}) used are the total for each class of compounds (PAHs, OPAHs, NPAHs) in each sample (3h, 9h, 15h). Concentrations of the gas phase species were in ppt/ppb levels and have been time-averaged to the filter sampling times. There is no need to show units to test the correlation of significance between two variables.

306-311: Could this be reversed? Could HONO levels be essential to forming secondary 9-Nitroanthracene?
The loss rate of HONO on dust aerosols was shown to be negligible (k' = 4×10^{-9}, El zein et al., 2013) and not important in comparison with its photolysis rate in daytime ∼1.3×10^{-3} s^{-1} or deposition at night-time. Therefore, the adsorption of HONO on aerosols and its contribution to products formation either during the day or the night-time can be considered as negligible.
Reference: El Zein, A.; Romanias, M.; Bedjanian, Y.: Kinetics and Products of Heterogeneous Reaction of HONO with Fe_2O_3 and Arizona Test Dust. Environ. Sci. Technol. 2013, 47, 6325−6331

312: "1/3, 1/9" if you are going to use this symbology to refer to the sampling types, be consistent throughout the paper.
Removed from the manuscript.

340: Again, some description of the variation of the data is needed.
Corrected

662: This data would be better presented in box and whisker plots.
Figure 1 modified to box and whisker plots

672: Figure 2 boarders on illegible. This may have occurred during formatting, but this figure needs to be fixed before publication.
Figure 2 modified and re-arranged

707: Wouldn't box and whisker plots again be better here as well?
We think this figure is the best way to show this information to the reader, with no need for box plots

734: The bars on the plot are very difficult to see. One way to make this clearer could be to make the width of the bars proportional to the sampling time.
Figure 6 modified

Variability of polycyclic aromatic hydrocarbons and their oxidative derivatives in wintertime Beijing, China.

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Abstract. Ambient particulate matter (PM) can contain a mix of different toxic species derived from a wide variety of sources. This study quantifies the diurnal variation and nocturnal abundance of 16 Polycyclic Aromatic Hydrocarbons (PAHs), 10 Oxygenated PAHs (OPAHs) and 9 Nitrated PAHs (NPAHs) in ambient PM in central Beijing during winter. Target compounds were identified and quantified using Gas Chromatography – time of flight mass spectrometry (GC-Q-TOF-MS). The total concentration of PAHs varied between 18 and 297 ng m^{-3} over 3 h daytime filter samples and from 23 to 165 ng m^{-3} in 15 h night-time samples. The total concentrations of PAHs over 24 h varied between 37 and 180 ng m^{-3} (mean: 97 ± 43 ng m^{-3}). The total daytime concentrations during high particulate loading conditions for PAHs, OPAHs and NPAHs were 224, 54, and 2.3 ng m^{-3}, respectively. The most abundant PAHs were fluoranthene (33 ng m^{-3}), chrysene (27 ng m^{-3}), pyrene (27 ng m^{-3}), benzo[a]pyrene (27 ng m^{-3}), benzo[b]fluoranthene (25 ng m^{-3}), benzo[a]anthracene (20 ng m^{-3}) and phenanthrene (18 ng m^{-3}). The most abundant OPAHs were 9,10-Anthraquinone (18 ng m^{-3}), 1,8 Naphthalic anhydride (14 ng m^{-3}) and 9-Fluorenone (12 ng m^{-3}) and the three most abundant NPAHs were 9-Nitroanthracene (0.84 ng m^{-3}), 3-Nitrofluoranthene (0.78 ng m^{-3}) and 3-Nitrodibenzofuran (0.45 ng m^{-3}). ∑PAHs and ∑OPAHs showed a strong positive correlation with the gas phase abundance of NO, CO, SO_2, and HONO indicating that PAHs and OPAHs can be associated with both local and regional emissions. Diagnostic ratios suggested emissions from traffic road and coal combustion were the predominant sources for PAHs in Beijing, and also revealed the main source of NPAHs to be secondary photochemical formation rather than primary emissions. $PM_{2.5}$ and NPAHs showed a strong correlation with gas phase HONO. 9-Nitroanthracene appeared to undergo a photo-degradation during the daytime and showed a strong positive correlation with ambient HONO (R=0.90, P<0.001). The lifetime excess lung cancer risk for those species that have available toxicological data (16 PAHs, 1 OPAH and 6 NPAHs) was calculated to be in the range 10^{-5} to 10^{-3} (risk per million people range from 26 to 2053).

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1 Introduction

Outdoor air pollution contains a complex set of toxicological hazards and has become the largest detrimental environmental effect on human health (WHO/IARC., 2016). Exposure to outdoor high particulate loading of $PM_{2.5}$ (aerodynamic diameter less than 2.5 μm) is linked to harmful health effects, particularly affecting urban populations (Raaschou et al., 2013; Hamra et al., 2014). The major sources of $PM_{2.5}$ in urban areas are incomplete combustion or gas-to-particle conversion, and they contain a varied mix of chemicals including inorganic ions, organic carbon and elemental carbon (Bond et al., 2004; Saikawa et al., 2009). Polycyclic Aromatic Hydrocarbons (PAHs) and their oxidative derivatives (Nitrated PAHs and Oxygenated PAHs) are one class of species with high toxic potency (Zhang et al., 2009; Jia et al., 2011; Wang et al., 2011a). PAHs released in the atmosphere come from both natural and anthropogenic sources; anthropogenic emissions include incomplete combustion of fossil fuels, agricultural burning, industrial and agricultural activities and are considered predominant (Ravindra et al., 2008; Zhang et al., 2009; Poulain et al., 2011; Kim et al, 2013; Abbas et al., 2018); natural contributions such as volcanic eruptions and forest fires are reported to be a less significant contributor to total emissions (Xu et al., 2006; Abbas et al, 2018).

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Vapour phase PAHs can undergo gas phase reactions with oxidants in the atmosphere (including hydroxyl, ozone and nitrate radicals) leading to the generation of a range of nitrated-PAHs and oxygenated-PAHs (Atkinson et al., 1990; Atkinson and Arey., 1994; Sasaki, 1997). Atmospheric reaction with chlorine atoms in the presence of oxygen has also been suggested as a new formation pathway of OPAHs (Riva et al., 2015). OPAHs and NPAHs are often more toxic than the parent PAHs, showing a direct-acting mutagenicity on human cells (Durant et al., 1996; Hannigan et al., 1998; Purohit and Basu, 2000; Wang et al., 2011a; Benbrahim et al., 2012). Beside their formation in the gas phase, OPAHs and NPAHs can also be produced by heterogeneous reactions (Ringuet et al., 2012a, Jariyasopit et al., 2014; Zimmermann et al., 2013; Wenyuan et al., 2014; Keyte et al., 2013). Many of these derivatives can also be linked to primary emissions from motor vehicles and combustion processes (Rogge et al., 1993, Albinet et al., 2007a; Jakober et al., 2007; Shen et al., 2012; Nalin et al., 2016).

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Many studies in different countries have focused on studying toxic organic pollutants in $PM_{2.5}$ because they fall within the respirable size range for humans (Sharma et al., 2007; Ringuet et al., 2012b, Farren et al., 2015). In the last decade, a major focus has been given to Chinese cities such as Shanghai, Beijing, Guangzhou, Tianjin, and Shenzhen because of their population growth and geographic peripheral expansion in manufacturing capacity and energy industries which are located throughout each of the city's manufacturing zones. This has made China the world leader in energy consumption, but also the world's highest emitter of $PM_{2.5}$ and PAHs (Lin et al., 2018; Zhang et al., 2009; Xu et al., 2006). The majority of previous studies have reported PAH concentrations in 24 h averaged samples during short-term and long-term measurements campaigns (Tomaz et al., 2016; Alves et al., 2017; Niu et al., 2017; Benjamin et al., 2014; Wang et al., 2011a). However, a long averaging period creates some limitations such as sampling artefacts, notably where changing atmospheric photolysis conditions (air humidity, temperature, wind direction, ozone or other oxidant concentrations) may have a significant influence on PAHs concentrations and oxidation rates (Albinet et al., 2007b; Albinet et al., 2009, Goriaux et al., 2006, Tsapakis and Stephanou., 2003; Tsapakis and Stephanou., 2007, Ringuet et al., 2012b). More intensive and higher frequency measurements in field campaigns have been suggested as a means to improve the positive matrix factorization model performance (Tian et al., 2017, Srivastava et al., 2018). A few studies have used twice daily (12 h) sampling (Albinet et al., 2008; Zhang et al., 2018; Farren et al., 2015; Ringuet et al., 2012b), obtaining limited information on variability in concentrations during the daytime and night-time (Tsapakis and Stephanou., 2007). Shorter time periods for sampling (3 h and 4 h) are still very limited (Reisen and Arey., 2004; Srivastava et al., 2018). Considering the above, this paper determines the

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temporal diurnal and nocturnal variation of the $PM_{2.5}$-bound concentrations of PAHs, OPAHs and NPAHs from the air of Beijing in China, it shows the role of photochemistry in the formation of OPAHs and NPAHs and associate the fate and evolution of PAHs, OPAHs and NPAHs with the gas phase concentrations of other pollutants (O_3, CO, NO, NO_2, SO_2, HONO), the cancer risk associated with inhalation of $PM_{2.5}$ was calculated. This paper explores the feasibility of higher frequency sampling in Beijing, to support the identification of emissions sources from diagnostic ratios and correlations with atmospheric gas pollutants. These measurements also raise the potential importance of the chemical relationship between NPAHs and HONO which may impact the HONO budget in the atmosphere and, if included, improve related models. This study comes after three years of declaring the anti-pollution action plan and strategy taken by the municipal government of Beijing and published in September 2013 (Ministry of Ecology and Environment The People's Republic of China, Beijing toughens pollution rules for cleaner air, 2013), trying to increase the number of days with good air quality index by prohibiting coal combustion, promoting clean energy vehicles and public transport and helping industrial transformation and upgrading to new technologies.

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2 Experimental Steps

2.1 Sampling site and method

The sampling setup shown in Fig. S1 was located at the Institute of Atmospheric Physics, Chinese Academy of Sciences in Beijing (39°58'28" N, 116°22'15" E) as part of the Air Pollution and Human Health (APHH) research programme. $PM_{2.5}$ filter samples were collected on the roof of a 2-storey building about 8m above ground level using a High-Volume Air Sampler (Ecotech HiVol 3000, Victoria, Australia) operating at 1.33 m^3 min^{-1}. Daytime particles were collected every three-hours during high PM concentration levels, nine-hours at low PM levels and over 15 h at night-time during 18 continuous days (22 November 2016 to 9 December 2016). Fifty-seven samples in total were collected. The daytime sampling started at 8:30 in the morning and the filter was changed every 3 h. During low particulate loading conditions, the daytime sampling started at 8:30 in the morning for a sampling duration of 9 h. Night-time sampling began at ~17:30 and ended at 08:30 the following day. Prior to sampling, the quartz filters (20.3 × 25.4 cm) (supplied by Whatman (Maidstone, U.K.)) were baked at 550 °C for 5 h in order to eliminate any organic matter. After sampling, filters were wrapped in aluminium foil, sealed in polyethylene bags and stored at -20 °C until extraction and analysis.

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2.2 Extraction method and clean up

All collected samples were extracted using an Accelerated Solvent Extractor automated system (Dionex, ASE 350). Prior to extraction, 1/16th (surface area equivalent to 25.7 cm^2) of each filter was cut using a hole puncher (Ø=27 mm) and for each batch of 6 samples, one sample was spiked with a mixture of two deuterated-PAHs (Phenanthrene-D10; Pyrene-D10), two deuterated-OPAHs (9-Fluorenone-D8; 9,10-Anthraquinone-D8), and two deuterated-NPAHs (1-Nitronaphthalene-D7; 3-Nitrofluoranthene-D9), as surrogate standards for PAHs, OPAHs and NPAHs, respectively, with concentration on filters corresponding to 400 ng (40 µl, 10 ng $µl^{-1}$ in

Acetonitrile). All punched samples were cut to small pieces and packed into 5 mL stainless steel extraction cells. Extractions were carried out in acetonitrile as follows: Oven at 120°C, pressure at 1500 psi, rinse volume 60% and 60 s purge time for three consecutive 5 min cycles. Extracts (V=20ml) were evaporated to approximately 6 mL under a gentle stream of nitrogen before the clean-up step. All samples and blanks were purified on a SPE silica normal phase cartridge (1g/6ml; Sigma Aldrich) to reduce the impacts of interfering compounds in the matrix and to help maintain a clean GC injection inlet liner. After the clean-up step, the solution of each sample was evaporated to 1 mL under a gentle stream of nitrogen at room temperature (20°C) and transferred to 1.5 mL autosampler amber vial. Each concentrated sample was stored at 4°C until analysis. The average recovery efficiencies calculated from surrogate standards ranged from 85% to 96% (Phenanthrene-d10: 95 ± 9 %; Pyrene-d10: 101 ± 7 %; 9-Fluorenone-d8: 98 ± 13 %; 9,10-Anthraquinone-d8: 102 ± 11 %; 1-Nitronaphthalene-d7: 93 ± 8 %; 3-Nitrofluoranthene-d9: 101 ± 11 %) and the target compounds concentrations were calculated incorporating measured recovery efficiencies.

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2.3 Chemical standards

The chemical compounds that have attracted the most attention in previous studies are the 16 priority PAHs and their derivatives, defined by the United States Environment Protection Agency (EPA). The choice of the organic compounds investigated in this study is based on those associated with the particle phase and commercially available standards. All compounds are listed in Table 1 and were purchased from Sigma Aldrich, Alfa Aesar and Santa Cruz Biotechnology in the UK and had a minimum purity of 98%. In parallel to individual standards, a mixed solution of the 16 EPA PAHs (CRM47940, Supelco, Sigma Aldrich) of 10 µg ml^{-1} in acetonitrile was also used. Standard solutions for calibrations were prepared in acetonitrile (HPLC grade, 99.9% purity, Sigma Aldrich). Deuterated compounds were supplied by C/D/N isotopes and distributed by QMX Laboratories Ltd (Essex, UK).

2.4 GC/MS Analysis

Target compounds were quantified using a GC - accurate mass Quadrupole Time-of-Flight GC/MS system (GC Agilent 7890B coupled to an Agilent 7200 Q-TOF-MS). Parent PAHs were separated in a 35 min analysis time using a capillary HP-5MS Ultra Inert GC column (Agilent; 5%-Phenyl substituted methylpolysiloxane; length: 30 m, diameter: 0.25 mm, film thickness: 0.25 µm). Inlet injections of 1 µL were performed in pulsed splitless mode at 320 °C using an automated liquid injection with the GERSTEL MultiPurpose Sampler (MPS). Helium was used as a carrier gas at 1.4 mL min^{-1}. The GC oven temperature was programmed to 65 °C for 4 min as a starting point and then increased to 185 °C at a heating rate of 40 °C min^{-1} and held for 0.5 min, followed by a heating rate of 10 °C min^{-1} to 240 °C and then ramped at 5 °C min^{-1} until 320 °C and held isothermally for further 6 min to ensure all analytes eluted from the column. The MS was operated in Electron Ionisation (EI) mode at 70 eV with an emission current of 35 µA. Calibration solutions were injected 3 times in the same sequence for samples and covered the range from 1pg µL^{-1} to 1000 pg µL^{-1}.

The method development for OPAHs and NPAHs was based on previous studies (Albinet et al., 2006; Albinet et al., 2014; Bezabeh et al., 2003; Kawanaka et al., 2007) using Negative Chemical Ionisation (NCI) performed at 155 eV and 48 µA, with methane (CH$_4$, research grade 5.5, Air Liquide) as reagent gas. Target compounds

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were eluted using the RXi-5ms (Restek GC column) with similar phase and characteristics to HP-5ms. Analysis was performed in 29.2 min and the GC settings were as follows: 1 µL of each sample was injected in pulsed splitless mode at 310 °C, Helium flow was set to 1.2 mL min^{-1}, the initial oven temperature of 70 °C was held for 4 min, followed by a heating rate of 60 °C min^{-1} until 190 °C and then raised to 270 °C at rate of 25 °C min^{-1} and ended with 5 °C min^{-1} until 320 °C, held for 10 min. A 10-point calibration curve within the range 0.5 pg µL^{-1} to 1000 pg µL^{-1}, was obtained with the correlation coefficients from the linear regression from 0.980 to 0.999.

2.5 Data analysis and error evaluation

Data acquisition were recorded and processed using the Agilent Qualitative and Quantitative analysis software. Target compounds were isolated using Extracted-Ion Chromatograms (EIC) and identified by the combination of retention time and mass spectral match against the calibration standards measured simultaneously within the samples. The limit of detection (LOD) was defined as the valid lowest measurable peak response to peak noise near the elution time of the target peak (S/N = 3) in a mix of standards solutions. As the chemical noise increases during the analysis of real samples the Limit of Quantification (LOQ) was defined S/N=10. These recommendations are in accordance with previous analytical studies (Nyiri et al., 2016; Ramírez et al., 2015). LOD values were evaluated from standards solutions and ranged between 1 pg and 20 pg for PAHs, 0.01 pg and 0.2 pg (except 1-naphthaldehyde 0.5 pg) for OPAHs and 0.02 pg to 0.25 pg for NPAHs.

To determine any sources of contamination during sample preparation and the analytical procedure, the solvent (acetonitrile) and field blanks (n=2) were analysed following the same procedure as for the samples (Extraction, SPE, Evaporation). Most target compounds were found to be below LOD (S/N=3) or orders of magnitude (up to 10^3 - 10^4) lower than was found in the samples. A small number of compounds found in field blanks (1,8-Naphthalic anhydride, Benzo[a]fluorenone, 1-Nitronaphthalene, 9-Nitroanthracene) have a higher contribution (4-30 %) to very few filters (2 to 5 samples) collected over a 3 h time period, if this was co-incident with low particulate loading conditions. The contribution to each compound from field blanks has been corrected in the final data.

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We evaluated the precision of the method by calculating the relative standard deviations (%RSD) from replicate analysis as shown in Table 1. For PAHs, the precision of sample replicates (n=10) during inter-day and intra-day varied from 1.8% to 8.9% (mean 5.2%) and 1.2% to 8.7% (mean 3.4%), respectively. The %RSD average for deuterium labelled compounds was about 3.6%. For OPAHs and NPAHs, two different concentrations of standards were analysed (50 pg; n=6 and 400 pg; n=6); inter-day precision of 10 OPAHs gives an average %RSD of 6.8% (range: 5.4 - 8.9%) and intra-day precision of 5.6% (3.2 - 7.8%). Similar to OPAHs, repeatability and reproducibility between days for NPAHs varied from 3.9% to 8.4% (mean 5.5%) and 3.2% to 9.7% (mean 5.2%), respectively. Hence, the estimated random error quantified by the standard deviation of the measurements did not exceed 7% on average. The systematic error may be due to the influence of the sample matrix during the analysis sequence on the quantification step and the calibration offset. It was estimated to be a maximum 10% from the measured recovery of the deuterium species (Garrido-Frenich et al., 2006). Therefore, the overall estimated error, combining the precision and the systematic effects, is less than 20%.

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Another source of error can be attributed to sampling artefacts and this has been discussed in previous studies (Schauer, C. et al., 2003, Goriaux, M. et al., 2006, Tsapakis and Stephanou, 2003). The absence of an ozone denuder to trap the gas phase oxidants may lead to an underestimation of the true values of PAHs due to chemical decomposition. Therefore, data from long sampling times and under high ozone ambient concentrations may be biased by sampling artefacts by more than 100 % (Schauer et al., 2003, Goriaux et al., 2006). However, at low ozone levels, negative artefacts were considered not significant (Tsapakis and Stephanou 2003), whilst, at medium ozone levels (30-50 ppb) PAHs values were underestimated by 30 % (Schauer et al., 2003). In addition, heterogeneous reactions during particle sampling may occur only on the monolayer surface coverage with limited diffusion of oxidants to the bulk particles (Keyte et al., 2013 and references therein). Previous studies reported that the formation of NPAHs during high-volume sampling is not significant and calculated to be < 3 % (Arey et al., 1988) and < 0.1 % (Dimashki et al., 2000).

Considering the role of ozone (always below 30 ppb in this study, with a mean value: 10.4 ± 8.8 ppb), in addition to sampling time and temperature, the estimation of the negative sampling artefacts on our data range between 10 and 20 %, with the highest error estimation attributable to longest sampling time (15h).

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3 Results and discussion

3.1 Temporal variations of PAHs, OPAHs and NPAHs in $PM_{2.5}$

The volume of literature on $PM_{2.5}$ has rapidly increased over the last two decades and various disciplines have contributed to improve understanding about source emissions, chemical composition, and impact on people's behaviour and health. In China, the official air quality guidelines for $PM_{2.5}$ expressed as annual mean and 24 h average are 35 µg m^{-3} and 75 µg m^{-3}, respectively (WHO 2016; Ministry of Ecology and Environment The People's Republic of China, 2012). During the sampling period of this study (Nov - Dec 2016), $PM_{2.5}$ was measured every hour and ranged from 3.8 to 438 µg m^{-3}, with an average concentration of 103 µg m^{-3}. The average 24 h $PM_{2.5}$ concentration was 108 ± 82 µg m^{-3} (range: 10 - 283 µg m^{-3}), exceeding the 24 h limit value on 10 of the 18 sampling days. Concurrent $PM_{2.5}$ concentrations were averaged to the filter sampling times (3 h, 9 h, 15 h) and are shown in Fig.6 and Fig. S3. The daily (24 h) concentration of Benzo[a]pyrene ranged from 4.46 to 29.8 ng m^{-3} (average 15 ± 8.9 ng m^{-3}), exceeding the 24 h average limit value of 2.5 ng m^{-3} for China (Ministry of Ecology and Environment The People's Republic of China, 2012) on all of the 18 days of sampling period.

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Fig. 1 shows the measured concentrations of PAHs in the 3 h daytime samples ranging from 18 to 297 ng m^{-3} (average 87.3 ± 58 ng m^{-3}) and from 23 to 165 ng m^{-3} (average 107 ± 51 ng m^{-3}) in the 15 h night-time samples. The 24 h total concentrations (combined results from daytime and night-time samples) of the 16 PAHs varied between 37 and 180 ng m^{-3} (average 97 ± 43 ng m^{-3}). PAHs derivatives showed the following trends: total OPAHs concentrations varied from 3.3 to 55 ng.m^{-3} (average: 26 ± 16 ng m^{-3}) in daytime and from 8.9 to 95 ng m^{-3} (average: 41.6 ± 26 ng m^{-3}) at night-time; OPAHs were approximately 25 and 14 times higher than average NPAHs in the daytime (average: 1.03 ± 0.74 ng m^{-3}, range: 0.13-2.3) and night-time (average: 3.06 ± 1.8 ng m^{-3}, range: 0.57-6.43), respectively.

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PHE (See Table 1 for abbreviations), FLT, PYR, BaA, CHR, BbF and BaP were the largest contributors to the total PAH concentration. 9-FLON, 9,10-ANQ and 1,8-NANY were the three major O-PAHs species. The most abundant NPAHs were 3-NDBF, 9-NANT and 3-NFLT. The temporal profile and contributions of each compound to the total concentration are shown in Fig. 2 and detailed in Table 2. The highest concentrations recorded in this study were in the day of 29 Nov 2016; concentrations of all target compounds in the particulate phase are displayed in Fig. S2. Some nitro-compounds (5-NAC, 1-NPYR, 6-NCHR, 6-NBaP) were below LOQ in a few samples while one oxy-compound (1,8-Naphthalic anhydride) was outside the dynamic range and limit of linearity of the calibration curve for samples with high mass loading (Table 2). Similar dominant compounds were found in different urban cities (Xi'an, Jinan, Beijing) of China (Bandowe et al. 2014, Zhang et al. 2018, Wang et al., 2011c). The average 24 h total PAH concentrations (97 ng m^{-3}) in this study was higher than the average value reported for Guangzhou city in the south of China (average 45.5 ng m^{-3}, from Liu et al., 2015), however, it was lower than average values reported for Xi'an city in winter (range 14-701 ng m^{-3}; average 206 ng m^{-3} from Wang et al., 2006) and in the suburb of Beijing in winter (average 277 ng m^{-3}, from Feng et al., 2005). Our average value (97 ng m^{-3}) was comparable to the reported values in a recent study (Feng et al., 2019) at the campus of Peking University health science centre, a short distance from our sampling site (~1 mile), where the authors reported a total PAHs average concentration in winter Beijing (2014 - 2015) of 88.6 ± 75 ng m^{-3}. The lower average concentration of total PAHs reported in this study and Feng et al., (2019) can potentially be attributed to the efforts from municipal government to improve air quality and control emissions by reducing combustion sources in the intervening years. The urban location in this study (Fig. S1) was surrounded by busy roads, residential buildings, an underground railway, restaurants and further afield thermal power stations. PAHs concentrations are anticipated to decline closer to the mountains in the North and West of Beijing due to air mass trajectory, aging and distance from emission sources. Results from this study can be considered representative (within the margin of error) of the urban area in Beijing including districts such as Chaoyang, Haidian, Fengtai, Xicheng, Dongcheng, Shijingshan covering an approximate population of 12 million. Future studies in less populated districts and different areas of the metropolitan of Beijing would be helpful for comparison of population exposures.

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Concentrations of PAHs in PM$_{10}$ (range: 3.2 - 222.7 ng m^{-3}) in Beijing were found in previous studies to be lower than in PM$_{2.5}$ (Wang et al., 2011c). The concentration of PAHs in this study were much lower than reported in certain other megacities, for example, Delhi, India in winter season 2003 (range: 948-1345 ng m^{-3}; mean: 1157 ± 113 ng m^{-3} from Sharma et al., 2007) and Mexico City, Mexico in October 2002 (range: 60-910 ng m^{-3}; mean: 310 ng m^{-3} from Marr et al., 2004). Average concentrations for total PAH in the first 3 h filter of the day (8:30-11:30 am; Monday to Friday; mean: 112 ng m^{-3}) were 1.5 times higher than the rest of the day, and 1.6 times higher than the same first 3 h on a Sunday. A potential reason of the elevated concentrations in the morning hours is due to the rush hour traffic during working days, coupled to a period of shallow boundary layer.

The mean total concentrations in Table 2 for the 3 h integration samples of OPAHs and NPAHs were 28.7 ± 21 ng m^{-3} (range: 1.8 - 87.9 ng m^{-3}) and 1.17 ± 1 ng m^{-3} (range: 0.15 - 3.92 ng m^{-3}). Average night-time was 41.6 ng m^{-3} (OPAHs) and 3.06 ng m^{-3} (NPAHs), concentrations which were 2.6 and 35 times lower than the average total PAH in the night samples. The ratios of mean concentrations of PAH divided by concentration of OPAH

Commented [A29]: SD, Response to Referee 2 comment 1 and NPAH for the 3 h samples were 3 and 74. Ratios of combined daytime and night-time samples (24 h) were on average 2.9 (range 1.9 - 4.6) for ∑PAHs/∑OPAHs and 47.4 (range 25 - 79) for ∑PAHs/∑NPAHs. Lower ratios were reported from a winter study in Xi'an – China, where ∑PAHs/∑OPAHs ranged from 1.75 to 1.86 and ∑PAHs/∑NPAHs ranged from 34 to 55.2. On the other hand, similar trends to our study were recorded for ∑PAHs/∑OPAHs in Europe such as Athens in Greece in winter (ratio 28.9/6.9 = 4.2) (Andreou and Rapsomanikis., 2009) and Augsburg in Germany in winter (ratio 11/3.2 = 3.4) (Pietrogrande et al., 2011). Further monitoring studies are needed to confirm trends of NPAHs in China.

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3.2 Diagnostic ratios to identify emission sources

The concentration ratios between different PAHs are widely used to assess and identify pollution emission sources (Tobiszewski and Namieśnik., 2012 and references therein). The ratios of FLT/(FLT + PYR) and IcdP/(IcdP + BghiP) isomer pairs are commonly used to distinguish between emission sources such as coal/biomass burning or the incomplete combustion of petroleum. Values of FLT/(FLT + PYR) and IcdP/(IcdP + BghiP) higher than 0.5 indicate dominance of a coal/biomass burning source. Values of FLT/(FLT + PYR) between 0.4 and 0.5 and IcdP/(IcdP + BghiP) between 0.2 and 0.5 suggest a higher influence from fossil fuel combustion. Values of FLT/(FLT + PYR) less than 0.4 and IcdP/(IcdP + BghiP) less than 0.2, are mostly related to incomplete combustion (petrogenic origin) (Yunker et al., 2002; Pio et al., 2001). The measured ratios in this study are shown in Fig. 3 and ranged from 0.53 to 0.67 (mean 0.56) during the day (3 h and 9 h samples), while at night (15 h samples) varied between 0.51 and 0.54 (mean 0.52) indicating primary emissions from coal and biomass burning. Lower values were observed for IcdP/(IcdP + BghiP); daytime ratios were between 0.39 and 0.5 (3 h and 9 h samples) indicated the dominance of petroleum combustion. At night, the ratio in most samples was slightly higher than 0.5, with some values below, suggesting mixed sources with likely higher contributions coming from residential heating using coal and wood at night.

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As shown in Fig. 4, other ratios can be useful to confirm the contribution from local traffic and to discriminate vehicle emissions such as BaP/BghiP, FLU/FLU+PYR and BaP/BaP+CHR (Tobiszewski and Namieśnik., 2012 and references therein). The BaP/BghiP ratios were significantly higher than 0.6 indicating a major influence from road traffic, while FLU/FLU+PYR ratios suggested a predominant petrol contribution (ratio < 0.5) instead of diesel engines (ratio > 0.5). Results shown in Fig. 4 identify traffic emissions and in particular petrol engines as the major emitter of PAHs. In PM$_{2.5}$, the 5- and 6-rings PAHs species (BaP, IcdP, BghiP) were previously attributed to petrol engines, while lower molecular weight with 3-rings (ACY, AC, FLU, PHE, ANT) and 4-rings (FLT, PYR, BaA, CHR) were closely related to diesel vehicle emissions (Chiang et al., 2012; Wu et al., 2014 and references therein). Previous studies in Beijing and Guangzhou in China suggested similar contributions from coal and petroleum combustion, focusing on vehicular traffic (petrol and diesel) as potential sources for PAHs (Gao and Ji., 2018; Liu et al., 2015; Wu et al., 2014, Niu et al., 2017).

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NPAHs can be used to track the photochemistry of PAHs with OH and NO$_3$ radicals, both of which can generate secondary photochemical products of NPAHs and OPAHs from primary PAH emissions (Zhang et al., 2018; Ringuet et al., 2012b; Wang et al., 2011a). 1-NPYR originates mainly from primary emissions and in particular from diesel vehicles (Keyte et al., 2016, Schulte et al., 2015), whilst 2-NFLT has been reported to be absent in

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direct combustion emissions, instead produced from the gas-phase reactions of FLT with OH radicals in presence of NOx during the day or NO_3 radicals at night. 2-NPYR comes solely from the reaction of PYR with OH radicals (Ramdahl et al., 1986; Arey et al., 1986; Atkinson et al., 1987; Ciccioli et al., 1996). Accordingly, the ratio 2-NFLT/1-NPYR has been widely used as diagnostic, with a value greater than 5 indicating a major contribution from photochemical processes, whilst a ratio value less than 5 means an important contribution from direct emissions (Albinet et al., 2008; Wang et al., 2011a; Ringuet et al., 2012b; Bandowe et al., 2014; Tomaz et al., 2017; Zhang et al., 2018).

In this study, the 2-NFLT was not quantified because the standard compound was not commercially available, subsequently, we have used 3-NFLT isomer as a substitution of 2-NFLT. PAH isomer pairs (Table 1) in standard mixtures showed similar sensitivities for each concentration used, therefore, we assume an equal sensitivity for 2-NFLT and 3-NFLT during analysis. A previous study reported that the concentration of 3-NFLT compared to 2-NFLT is relatively very low in ambient air (Bamford et al., 2003); in addition, the separation of both isomers (2- and 3-NFLT) using the most common GC-MS column for PAHs separation, HP-5ms and DB-5ms, was not possible (Zhang et al., 2018; Bandowe et al., 2014; Ringuet et al., 2012b; Albinet et al., 2008). Hence, we assume that the sum of 2- and 3-NFLT is closely representative of the original ratio 2-NFLT/1-NPYR. Therefore, we adopted the ratio 2+3NFLT/1-NPYR, which varied between 4 and 19 during the daytime (mean: 12) and from 3.6 to 30.4 in the night-time (mean: 8.8) (Fig. S3). Most daytime values exceeded significantly the benchmark ratio of 5, while at night-time the average value was lower. These results indicate the predominance of OH-radicals-initiated reactions controlling the formation of 2-NFLT in presence of NO_2 and sunlight.

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3.3 Correlation with gaseous pollutants

O_3, CO, NO, NO_2, SO_2 and HONO were also measured at the same site location as the $PM_{2.5}$ sampling. Inlets were installed outside lab containers at approximately 3-4 m above ground (Fig. S1). Online measurements of the gas phase species have been time-averaged to the filter sampling times. No correlations of significance were seen between PAHs and meteorological parameters (Relative Humidity and Temperature) as shown in Table S1.

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∑PAHs and ∑OPAHs had a similar strong positive correlation (R= 0.82 to 0.98) in the 9 h and 15 h samples with CO, NO, NO_2, SO_2 and HONO (Table S1). NO is known as an effective tracer for local traffic emissions, it and behaves as a short-lived intermediate (Bange 2008, Janhäll et al., 2004). CO is mainly produced from incomplete combustion and has a relatively long atmospheric lifetime (3 months on average) and undergoes long-range transport (Peng et al., 2007 and references therein). The high correlations with primary pollutants such as NO and CO during the daytime and night-time indicate that PAHs and OPAHs are primarily emitted from local sources may also be associated with regional scale emissions. Significant correlations were observed with SO_2, a pollutant mostly emitted from power plants outside the city (Lee et al., 2011). This strong relationship with SO_2 could be explained by the contribution of anthropogenic sources such as the Beijing Taiyanggong thermal power station (39°58′42″N 116°26′19″E), and is consistent with the domain air masses arriving at the sites from the North East for much of the time (Fig. S4).

In contrast, most of the 3 h day samples showed only moderate correlations (R=0.38 to 0.74) except for HONO where significant correlations (R=0.87 to 0.94) were observed with ∑PAHs, ∑OPAHs and ∑NPAHs (Fig. 5;

Table S1). Furthermore, HONO was significantly correlated with $PM_{2.5}$ during the daytime (Fig. 5) and some significant chemical link between HONO emissions and ambient particles ($PM_{2.5}$) is implied. A similar conclusion was drawn from recent study in Beijing (Zhang et al., 2019) which suggested a potential chemical relationship between HONO and haze particles ($PM_{2.5}$) and proposed a high contribution from vehicle emissions to the night-time HONO.

For NPAHs, as shown in Table S1, no significant correlation was found in 3 h and 15 h time sampling resolution, except with HONO, where a significant difference between day and night were observed. Surprisingly, the 9 h time resolution showed a strong correlation with CO, NO, NO_2 and SO_2, potentially suggesting a direct emission of NPAHs. More likely these correlations arise because of a formation delay of NPAHs that is smoothed out by the longer daytime sampling period. In a previous study, Zimmermann et al., (2013) reported the formation of NPAHs from the heterogeneous interaction of ambient particle bound-PAHs with atmospheric oxidant. In line with the observed high values for the ratio 2+3NFLT/1-NPYR (section 3.2) and the trace levels of NPAHs concentrations in the atmosphere; the secondary formation of NPAHs by gas phase reactions followed by adsorption on particles and in parallel the heterogeneous formation on the surface of particles is supported rather than primary emissions.

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HONO plays a key role in tropospheric photochemistry, however its sources and their relative contributions to ambient HONO are still unclear, especially in the daytime. To help understand the mechanism of HONO formation in the atmosphere, each NPAHs compound has been correlated with HONO concentrations. The available data in Table S2 shows diurnal and nocturnal differences for individual correlation of NPAHs with HONO with the exception for 1-NPYR, which originates mainly from primary emissions and shows a strong correlation during the day and night. 9-Nitroanthracene had distinctive behaviour, accumulating during the night and appearing to undergo a photo-degradation during the daytime (Fig. 6). As shown in Table S2, 9-Nitroanthracene showed a strong positive correlation with HONO ($R=0.90$, $P<0.001$) in the daytime while no significant relationship was found at night-time ($R=0.15$, $P>0.05$). This suggests 9-nitroanthracene as a possible source of HONO during the daytime via the OH radical-initiated reaction leading to OH (ortho) addition and followed by intramolecular hydrogen transfer from the phenolic hydroxyl group to the nitro group.

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There was a significant positive correlation between ANT and 9-NANT ($R= 0.90$, 3 h; $R=0.94$, 9 h; $R=0.90$, 15 h; $P\leq0.001$), which may be an indication that 9-NANT is closely related to ANT. In this respect, additional simulation chamber measurements of the gas phase reaction of ANT with NO_3 radicals and for 9-Nitroanthracene with OH radicals in presence of light and under different atmospheric parameters are required for more precise assessment.

3.4 Exposure assessment

The toxicity equivalency factor (TEF) represents an estimate of the relative toxicity of a chemical compared to a reference chemical. For PAHs, Benzo[a]pyrene was chosen as the reference chemical because it is known as the most carcinogenic PAH (OEHHA., 1994, 2002) and is commonly used (Albinet et al., 2008; Tomaz et al., 2016; Alves et al., 2017; Bandowe et al., 2014; Ramírez et al., 2011) as an indicator of carcinogenicity of total PAHs.

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The toxicity of the total PAHs expressed as BaP equivalents (BaP_{eq}) is calculated from the TEFs of each target compound (Table S3) multiplied by its corresponding concentration Eq. (1):

$$\sum [BaP]_{eq} = \sum_{i}^{n=1} (C_i \; x \; TEF_i) \qquad (1)$$

where C_i correspond to the concentration of individual target compound (PAHs, OPAHs and NPAHs) in ng m^{-3}.

A widely applied procedure from the Office of Environmental Health Hazards Assessment (OEHHA) of the California Environmental Protection Agency (CalEPA) and also the World Health Organisation (WHO) was used here to evaluate and calculate the potential of contracting cancer from inhalation and exposure to $PM_{2.5}$-bound PAHs; commonly known as the lifetime excess cancer risk (ECR) Eq. (2).

$$ECR = \sum [BaP]_{eq} \times UR_{BaP} \qquad (2)$$

where two values are mostly used for $UR_{[BaP]}$ ($1.1x10^{-6}$ (ng $m^{-3})^{-1}$ (OEHHA., 2002, 2005) and $8.7x10^{-5}$ (ng $m^{-3})^{-1}$ (WHO., 2000)); Eq. (2) describes the inhalation unit risk associated with high probability of contracting cancer when exposed continuously to 1 ng m^{-3} of BaP_{eq} concentration over a lifetime of 70 years.

As shown in Table 3, the BaP_{eq} concentration includes the sum of 16 PAHs, 1 OPAH and 6 NPAHs, with the cancer risk evaluated using different sampling times according to CalEPA and WHO guidelines. The risk values may be underestimated due to lack of toxicity data for OPAHs and because our assessment excludes the gas phase contributions i.e. are only based on the health risk evaluation of the particulate phase. The average 24 h BaP_{eq} for the whole sampling period was 23.6 ± 12.4 ng m^{-3} (Table 3). As shown in Table 2, 6-NCHR has not been quantified in all samples, its contribution to the total BaP_{eq} is relatively high (mean: 8%, range: 1 - 24%) in comparison with the three major contributor from the PAH group: BaP (mean: 47.5%, range: 24 - 64%), DahA (mean: 17.8%, range: 10 - 32%) and BbF (mean: 10.1%, range: 7 - 21%). In this study, the ECR attributable to all polycyclic aromatic compounds (PACs) in urban air of Beijing ranged from 10^{-5} to 10^{-3} > 10^{-6} (Table 3) suggesting an elevated potential cancer risk for adults (Chen and Liao., 2006; Bai et al., 2009).

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It is worth noting that inhalation exposure is not the only risk related to PAHs and cancer in humans. Other sources of exposure include dermal contact and ingestion of the re-suspended dusts in matrices such as road dusts and soils all of which increase the risk value for urban residents (Wang, et al., 2011b; Wei et al., 2015). In this study, the 24 h average estimated cancer risk (Table 3) from inhalation exposure to ambient $PM_{2.5}$ based on CalEPA and WHO guidelines were 2.6 x 10^{-5} and 2.05 x 10^{-3}, respectively. Using the highest calculated ECR (2.05 x 10^{-3}) gives an estimate of 2027 additional cancer cases per million people exposed (29 cases/year) in comparison to the estimate based on CalEPA of 26 persons (0.37 cases/year).

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ECR trends were reported in previous studies from Beijing and other populated area (Bandowe et al., 2014; Alves et al., 2017; Ramírez et al., 2011; Jia et al., 2011, Liu et al., 2015, Song et al., 2018, Feng et al., 2019). In this study we considered the combination of all samples (n=54) to estimate the average 24 h cancer risk

($\sum[BaP]_{eq}$=23.6 ± 12 ng m^{-3}; range 8 – 44 ng m^{-3}) and compare it with previous studies. An average value of 17 ng m^{-3} (range 2-64 ng m^{-3}) was reported for Xi'an for the whole year between July 2008 and August 2009 (Bandowe et al., 2014). After considering the same winter period (November and December) as in our study, the average values reported for Xi'an city (31-33 ng m^{-3}) were higher than our results. In contrast, our average value was comparable to those reported in a recent study in Beijing, ranging from 21 to 38 ng m^{-3} in cold months (Feng et al., 2019), whilst in the previous study of Chen et al. 2017, they reported an average of 31.4 ng m^{-3} for outdoor air in Beijing in winter. Lower and more varied values have been also reported in Beijing in winter. Liu et al. (2007) reported an average BaP_{eq} concentration of 13.0 ng m^{-3} and 27.3 ng m^{-3} at two sampling sites on Peking University campus and 82.1 ng m^{-3} for samples collected from busy road street. It is clear that direct comparison with Beijing air from other studies is limited due to the variable number of compounds considered in each study and the differences in sampling sites and sampling periods. Other areas of uncertainty include TEF reference values and the range of BaP UR which were extrapolated from animal bioassays with limited evidence regarding the carcinogenicity to humans.

Seasonal variability is also crucial in estimating BaP_{eq} concentrations; it has been shown that BaP_{eq} values in cold months are always higher than warm months due to the increase in coal combustion, central and residential heating, lower photochemical transformation and lower volatilisation of gases favouring particle formation in winter. Previous observations in Beijing recorded $\sum[BaP_{eq}]$ of 11.1 ng m^{-3} in autumn (Jia et al., 2011) and 11.0 ng m^{-3} in warm months (April to June) (Feng et al., 2019). In comparison with Guangzhou city (south of China), BaP_{eq} was 9.24 ng m^{-3} in winter and reported to be 1.6 and 6.2 times greater than autumn and summer, respectively (Liu et al., 2015). Our results were considerably higher than those estimated for western European cities during the winter, such as Grenoble: 1.4 ng m^{-3} (Tomaz et al., 2016), Oporto: 3.56 ng m^{-3}, Florence: 1.39 ng m^{-3} and Athens: 0.43 ng m^{-3} (Alves et al., 2017). ECR values estimated for each city were 31 (Grenoble), 6.6 (Oporto), 17 (Florence) and 54 (Athens) times lower than our ECR estimation. Lower ECR levels in western European cities were attributed to cleaner energy sources, less densely populated cities, waste exporting and recycling and more effective environmental regulations.

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4 Conclusions

Temporal variations and chemical composition of $PM_{2.5}$ were measured in Beijing-China from 22 November 2016 to 9 December 2016, focusing in particular on the diurnal and nocturnal chemical formation of PAHs, OPAHs and NPAHs. The 24 h average concentration of $PM_{2.5}$ was 108 µg m^{-3} ranging from 10 to 283 µg m^{-3}, exceeding the 24 h limit value for China on 10 out of 18 sampling days. The 24 h concentrations of $\sum PAH_{16}$ varied between 37 and 180 ng m^{-3} (average 97 ± 43 ng m^{-3}), while $\sum OPAH_{10}$ ranged from 13 to 70 ng m^{-3} (average 35.6 ± 19 ng m^{-3}) and $\sum NPAH_9$ from 0.87 to 4.4 ng m^{-3} (average 2.29 ± 1.2 ng m^{-3}). Daytime concentrations during pollution episodes for PAHs, OPAHs and NPAHs were 224, 54, and 2.3 ng m^{-3}, respectively. The daily concentration of Benzo[a]pyrene exceeded the 24 h average limit value of 2.5 ng m^{-3} for China on all sampling days in this study, indicating elevated risk of disease among inhabitants.

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Diagnostic ratios of different species were used to distinguish between possible emission sources of PAHs. Coal combustion and road traffic emissions (petrol engines) were found overall to be the two dominant sources. In addition, high ratios of 2+3Nitrofluoranthene/1-Nitropyrene indicated significant secondary formation of NPAHs, especially in daytime via the OH radical-initiated reaction pathway.

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PAHs and OPAHs concentrations were correlated with CO, NO, NO_2, SO_2 and HONO, indicating that both are associated with local and regional primary emissions and in particular to traffic sources. Correlations seen previously between $PM_{2.5}$ and HONO suggested a possible links and a potential source of HONO that would affect the budget of HONO and OH radicals. The strong positive correlation between individual NPAHs and HONO during daytime was also suggestive of a potential link between these two classes of chemicals in air. One of the dominant NPAHs, the 9-Nitroanthracene had distinctive behaviour, accumulating at night and photodegrading in daytime.

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The lifetime excess cancer risk attributable to the summation of polycyclic aromatic compounds measured here and associated with $PM_{2.5}$ inhalations in Beijing was in the range of 10^{-3} according to WHO guidelines, confirming that there is statistically elevated risk of contracting cancer from this class of pollutants in this location.

Author contributions: AE led the analysis and prepared the manuscript with contributions from all authors. ACL and JFH contributed to the analysis, interpretation and writing of the paper. RED provided the data on the gas phase measurements and collected the filter samples in the field. MWW supported laboratory chemical analysis on the GC-Q/ToF-MS. All authors contributed to the corrections of the paper.

Competing interests. The authors declare that they have no competing interests.

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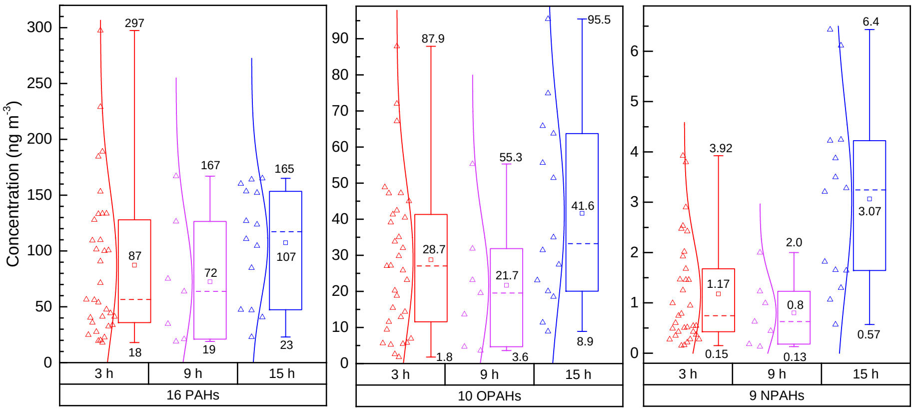

Figure 1. Concentrations of ∑PAHs, ∑OPAHs and ∑NPAHs in $PM_{2.5}$ samples during the daytime (3 h; 9 h) and night-time (15 h). Box plot represents the 25th and 75th percentiles range of the observed concentrations and the bottom and top lines indicate minimum and maximum concentrations. Square symbols represent the mean concentration, and the short dash line within the boxes represent the median. Empty Triangles correspond to the data measured over 3 h, 9 h and 15 h samples. The lines between data points and boxes reflect a normal distribution curve.

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Table 1. List of measured PAHs, OPAHs and NPAHs and their Abbreviations. Compounds are listed in order of elution.

Compound/Formula	Abbreviation	Accurate Mass (*m/z*)	%RSD	
16 PAHs		Monitored ions in EI mode	Inter-day	Intra-day
Naphthalene/$C_{10}H_8$	NAP	128.0628-127.0543-102.0464	4.6	3.2
Acenaphthylene/$C_{12}H_8$	ACY	152.0629-151.0546-126.0463	4.1	2.1
Acenaphthene/ $C_{12}H_{10}$	AC	153.0705-154.0779-152.0634	5.5	6.1

Fluorene/ $C_{13}H_{10}$	FLU	166.0782-165.0708-164.0621	4.0	2.9
Phenanthrene/$C_{14}H_{10}$	PHE	178.0789-176.0626-152.0622	4.6	3.0
Anthracene/$C_{14}H_{10}$	ANT	178.0787-176.0627-152.0620	4.7	4.2
Fluoranthene/$C_{16}H_{10}$	FLT	202.0788-200.0626-101.0388	1.8	4.5
Pyrene/$C_{16}H_{10}$	PYR	202.0788-200.0626-101.0389	3.2	1.9
Benzo[a]anthracene/$C_{18}H_{12}$	BaA	228.0927-226.0783-101.0388	6.2	1.2
Chrysene/$C_{18}H_{12}$	CHR	228.0943-226.0784-101.0387	6.0	2.6
Benzo[b]fluoranthene/$C_{20}H_{12}$	BbF	252.0941-250.0784-126.0467	4.7	2.0
Benzo[k]fluoranthene/$C_{20}H_{12}$	BkF	252.0940-250.0783-126.0468	8.9	8.7
Benzo[a]pyrene/$C_{20}H_{12}$	BaP	252.0940-250.0783-126.0466	5.2	2.3
Indeno[1,2,3-cd]pyrene/$C_{22}H_{12}$	IcdP	276.0939-274.0783-138.0467	7.2	2.6
Dibenz[a,h]anthracene/$C_{22}H_{14}$	DahA	278.1097-276.0941-139.0545	7.7	4.3
Benzo[ghi]perylene/$C_{22}H_{12}$	BghiP	276.0942-274.0783-138.0467	5.4	2.6
10 OPAHs		Monitored ions in NCI mode		
1,4-Naphtoquinone/$C_{10}H_6O_2$	1,4-NAQ	158.0420	6.3	5.1
1-Naphthaldehyde/$C_{11}H_8O$	1-NALD	156.0557	8.9	7.8
9-Fluorenone/$C_{13}H_8O$	9-FLON	180.0639	5.7	6.2
9,10-Anthraquinone/$C_{14}H_8O_2$	9,10-ANQ	208.0572	5.6	3.2
1,8-Naphthalic anhydride/ $C_{12}H_6O_3$	1,8-NANY	198.0436	6.4	5.6
Phenanthrene-9-carboxaldehyde/$C_{15}H_{10}O$	PHCA	206.0777	5.4	4.9
Benzo[a]fluorenone/ $C_{17}H_{10}O$	BaFLU	230.0791	6.4	3.2
7H-Benz[de]anthracene-7-one/ $C_{17}H_{10}O$	BANTone	230.0781	7.2	5.8
1-Pyrenecaboxaldehyde/ $C_{17}H_{10}O$	1-PYRCA	230.0786	7.5	7.2
1,2-Benzanthraquinone/ $C_{18}H_{10}O_2$	1,2-BANQ	258.0743	8.5	7.4
9 NPAHs		Monitored ions in NCI mode		
1-Nitronaphthalene/$C_{10}H_7NO_2$	1-NNAP	173.0551	4.7	4.4
3-Nitrodibenzofuran/ $C_{12}H_7NO_3$	3-NDBF	213.0475	4.4	5.1
5-Nitroacenaphthene/ $C_{12}H_9NO_2$	5-NAC	199.0682	5.6	5.3
2-Nitrofluorene/$C_{13}H_9NO_2$	2-NFLU	211.0689	5.0	5.4
9-Nitroanthracene/$C_{14}H_9NO_2$	9-NANT	223.0697	5.9	3.9
3-Nitrofluoranthene/$C_{16}H_9NO_2$	3-NFLT	247.0688	6.4	4.1
1-Nitropyrene/$C_{16}H_9NO_2$	1-NPYR	247.0691	3.9	3.2
6-Nitrochrysene/$C_{18}H_{11}NO_2$	6-NCHR	273.0847	4.7	5.4

6-Nitrobenzo[a]pyerene/ $C_{20}H_{11}NO_2$	6-NBaP	297.0845	8.4	9.7

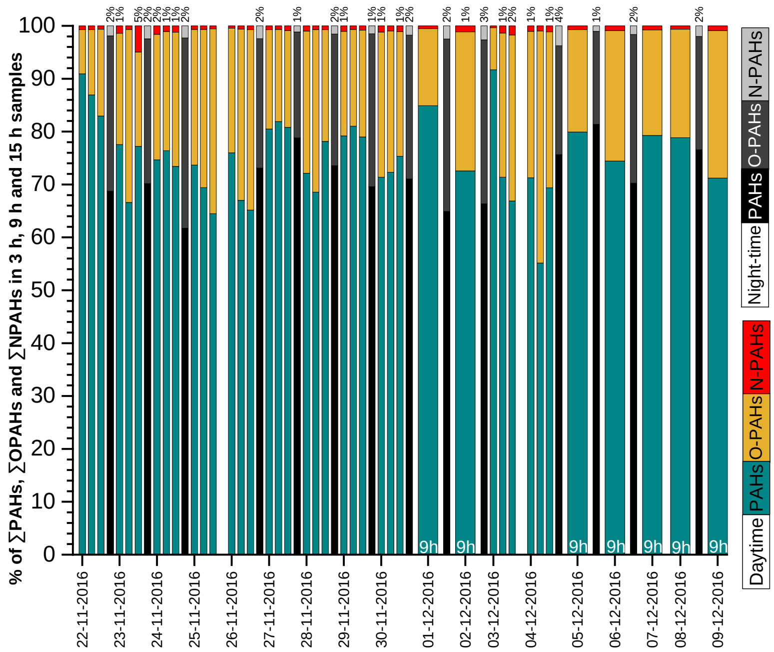

Figure 2. Time-series of ∑PAHs, ∑OPAHs and ∑NPAHs in $PM_{2.5}$ samples during the daytime (3 h and 9 h) and night-time (15h). Percentage below 1% for NPAHs are omitted for clarity. Night-time data on 25/11/2016, 03/12/2016 and 07/12/2016 are not available due to lack of samples.

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And Short Comment (SC1)

Table 2. Minimum, maximum and average atmospheric concentrations of PAHs, OPAHs and NPAHs in $PM_{2.5}$. Compounds in bold represent the highest mean contribution to the sum of all compounds.

Compound	Concentrations (ng m^{-3})		Average contribution to total (%)
	Minimum-maximum	Average	
16 PAHs	(3 h)/(9 h)/(15 h)	(3 h ± SD*)/(9 h ± SD)/(15 h ± SD)	(3 h)/(9 h)/(15 h)
NAP	(0.05-0.8)/(0.1-0.4)/(0.06-0.6)	(0.31 ± 0.2)/(0.24 ± 0.1)/(0.27 ± 0.2)	(0.48)/(0.39)/(0.25)
ACY	(0.01-1.2)/(0.1-0.8)/(0.1-1.2)	(0.31 ± 0.3)/(0.31 ± 0.2)/(0.58 ± 0.4)	(0.35)/(0.46)/(0.50)
AC	(0.03-0.13)/(0.02-0.09)/(0.01-0.2)	(0.07 ± 0.02)/(0.04 ± 0.03)/(0.07 ± 0.07)	(0.15)/(0.08)/(0.06)
FLU	(0.05-1.3)/(0.1-1.0)/(0.1-1.5)	(0.43 ± 0.3)/(0.41 ± 0.3)/(0.63 ± 0.4)	(0.53)/(0.65)/(0.56)
PHE	**(1.2-23.1)/(1.9-16.3)/(1.5-13.7)**	**(7.38 ± 5.5)/(6.30 ± 5.3)/(8.4 ± 4.0)**	**(8.83)/(9.04)/(7.84)**
ANT	(0.5-3.4)/(0.3-1.9)/(0.3-2.9)	(1.07 ± 0.7)/(0.79 ± 0.6)/(1.43 ± 0.8)	(1.48)/(1.23)/(1.32)
FLT	**(1.4-41.8)/(3.0-17.6)/(3.2-11.7)**	**(12.9 ± 10.0)/(9.10 ± 5.7)/(8.97 ± 2.7)**	**(13.9)/(13.9)/(9.67)**
PYR	**(0.7-34.6)/(2.1-15.7)/(2.9-10.7)**	**(9.85 ± 8.2)/(7.48 ± 5.0)/(8.1 ± 2.5)**	**(10.4)/(11)/(8.69)**
BaA	**(1.3-27.7)/(1.3-17.5)/(2.1-18.8)**	**(6.69 ± 6.4)/(6.52 ± 5.9)/(12 ± 5.9)**	**(7.17)/(8.23)/(11)**
CHR	**(1.4-37.5)/(2.1-20.8)/(2.7-15.9)**	**(10.5 ± 8.7)/(9.17 ± 7.17)/(11.3 ± 4.8)**	**(11.2)/(12.4)/(10.8)**
BbF	**(1.5-35.3)/(2.1-21.3)/(2.3-20.4)**	**(10.3 ± 8.5)/(8.93 ± 7.3)/(10.8 ± 5.0)**	**(11.2)/(11.8)/(10.4)**
BkF	(1.6-15.4)/(1.2-7.4)/(1.3-6.6)	(5.51 ± 3.8)/(3.94 ± 2.7)/(4.3 ± 1.5)	(6.76)/(5.80)/(4.43)
BaP	**(1.4-37.3)/(1.5-20.7)/(3.2-35.2)**	**(8.81 ± 8.6)/(8.40 ± 7.5)/(18.9 ± 12.4)**	**(9.12)/(10.3)/(16.1)**
IcdP	(1.7-16.1)/(0.9-11.6)/(1.0-18.3)	(4.79 ± 3.5)/(4.65 ± 4.3)/(9.75 ± 6.4)	(6.06)/(5.70)/(8.03)
DahA	(1.9-5.2)/(0.7-2.9)/(0.5-6.9)	(2.54 ± 0.7)/(1.46 ± 0.8)/(3.0 ± 2.1)	(4.43)/(2.46)/(2.56)
BghiP	(2.53-17.0)/(1.2-10.7)/(1.4-15.4)	(5.80 ± 3.5)/(4.70 ± 3.7)/(8.8 ± 5.1)	(7.86)/(6.47)/(7.62)
Total	(18-297)/(19-167)/(23-165)	(87.3 ± 58)/(72.5 ± 56)/(107 ± 51)	
10 OPAHs	(3 h)/(9 h)/(15 h)	(3 h ± SD)/(9 h ± SD)/(15 h ± SD)	(3 h)/(9 h)/(15 h)
1,4-NAQ	(0.02-8.1)/(0.16-3.1)/(0.1-4.2)	(2.25 ± 2.4)/(1.27 ± 1.2)/(1.66 ± 1.3)	(6.22)/(5.39)/(3.70)
1-NALD	(0.2-0.8)/(0.07-0.5)/(0.08-0.9)	(0.43 ± 0.1)/(0.20 ± 0.1)/(0.49 ± 0.3)	(2.71)/(1.19)/(1.25)
9-FLON	**(0.49-14.9)/(0.7-6.0)/(0.8-11.4)**	**(6.76 ± 4.4)/(2.56 ± 1.9)/(4.26 ± 2.8)**	**(25.8)/(14.3)/(10.2)**
9,10-ANQ	**(0.3-36.4)/(1.2-24.8)/(2.8-36)**	**(8.31 ± 8.8)/(8.65 ± 8.5)/(14.3 ± 9.9)**	**(24.3)/(35.8)/(32.7)**
1,8-NANY[a]	**(0.3-16.3)/(1.0-6.9)/(3.7-9.3)**	**(7.09 ± 5.4)/(3.69 ± 2.9)/(6.81 ± 2.8)**	**(37.9)/(33.2)/(45.6)**
PHCA	(0.1-0.9)/(0.05-0.6)/(0.06-1.9)	(0.26 ± 0.17)/(0.20 ± 0.19)/(0.71 ± 0.57)	(1.42)/(0.99)/(1.50)
BaFLU	(0.06-10.8)/(0.1-8.1)/(0.4-15.1)	(2.77 ± 3.0)/(2.72 ± 2.9)/(5.99 ± 4.8)	(7.47)/(9.73)/(12.1)
BANTone	(0.08-15.1)/(0.04-8.3)/(0.5-19.8)	(2.46 ± 3.3)/(2.63 ± 2.9)/(9.27 ± 7.3)	(6.10)/(9.05)/(19.1)
1-PYRCA	(0.007-1.8)/(0.008-1.5)/(0.05-2.4)	(0.31 ± 0.4)/(0.39 ± 0.5)/(1.0 ± 0.9)	(0.74)/(1.24)/(1.96)
1,2-BANQ	(0.02-3.6)/(0.03-2.6)/(0.2-3.9)	(0.87 ± 0.96)/(0.90 ± 0.96)/(1.99 ± 1.4)	(2.3)/(3.24)/(4.33)

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Total	(1.8-87.9)/(3.6-55.3)(8.9-95.5)	(28.7 ± 21)/(21.7 ± 18)/(41.6 ± 26)	
9 NPAHs	(3 h)/(9 h)/(15 h)	(3 h ± SD)/(9 h ± SD)/(15 h ± SD)	(3 h)/(9 h)/(15 h)
1-NNAP	(0.01-0.1)/(0.008-0.04)/(0.005-0.03)	(0.03 ± 0.02)/(0.01 ± 0.01)/(0.01 ± 0.008)	(4.38)/(3.08)/(0.57)
3-NDBF	**(0.08-1.5)/(0.02-0.06)/(0.03-2.4)**	**(0.33 ± 0.31)/(0.03 ± 0.01)/(0.89 ± 0.84)**	**(33.4)/(7.92)/(22.4)**
5-NAC[b]	(0.04-0.1)/(<LOQ)/(0.03-0.35)	(0.08 ± 0.05)/(<LOQ)/(0.18 ± 0.13)	(5.64)/(<LOQ)/(4.67)
2-NFLU	(0.03-0.3)/(0.01-0.3)/(0.01-0.5)	(0.08 ± 0.06)/(0.09 ± 0.11)/(0.26 ± 0.21)	(10.15)/(10.00)/(7.28)
9-NANT	**(0.01-1.2)/(0.06-0.1)/(0.4-2.4)**	**(0.36 ± 0.37)/(0.41 ± 0.31)/(1.18 ± 0.6)**	**(27.1)/(53.4)/(47.5)**
3-NFLT	**(0.05-1.2)/(0.02-0.5)/(0.04-1.2)**	**(0.34 ± 0.3)/(0.21 ± 0.2)/(0.54 ± 0.4)**	**(24.6)/(23.4)/(17.7)**
1-NPYR[c]	(0.01-0.1)/(0.01-0.06)/(0.008-0.2)	(0.05 ± 0.03)/(0.06 ± 0.05)/(0.02 ± 0.02)	(2.92)/(2.48)/(2.01)
6-NCHR[d]	(0.05-0.2)/(<LOQ)/(0.009-0.02)	(0.09 ± 0.06)/(<LOQ)/(0.01 ± 0.007)	(5.6)/(<LOQ)/(0.5)
6-NBaP[e]	(<LOQ)/(<LOQ)/(0.02-0.08)	(<LOQ)/(<LOQ)/(0.05 ± 0.01)	(<LOQ)/(<LOQ)/(1.26)
Total	(0.15-3.92)/(0.13-2.0)/(0.57-6.43)	(1.17 ± 1.0)/(0.80 ± 0.66)/(3.06 ± 1.8)	

[a] Quantified in 28/54 samples

[b] Quantified in 7/54 samples

[c] Quantified in 35/54 samples

[d] Quantified in 5/54 samples

[e] Quantified in 11/54 samples

* SD: Standard Deviation

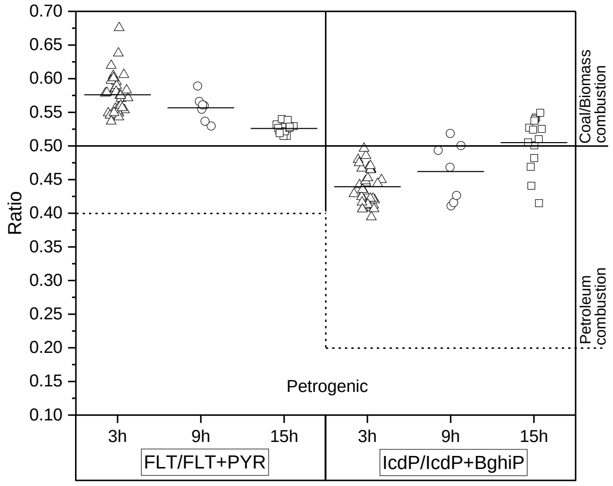

Figure 3. Column scatter of FLT/(FLT + PYR) and IcdP/(IcdP + BghiP) in the particulate phase at three different time sampling averages, open triangles and circles represent the daytime data for 3 h and 9 h samples, open squares represent the night-time data of 15 h. The dashed line separates the petroleum combustion source from petrogenic source for both ratios. The solid short line on each data set represent the mean value of ratios.

Table 3. Average concentration of $\sum BaP_{eq}$ in ng m^{-3} and cancer risk assessment for the sum of 16PAHs, 1OPAH and 6NPAHs.

Sampling hours	$\sum[BaP]_{eq}$ ng m^{-3}	$UR_{BaP} = 1.1x10^{-6}$ (CalEPA)	$UR_{BaP} = 8.7x10^{-5}$ (WHO)	Risk per million people
9 h (daytime, n=40)[a]	15.9[a]	1.75 x 10^{-5}	1.38 x 10^{-3}	17[b] – 1383[c]
15 h (night-time, n=14)	28.3	3.17 x 10^{-5}	2.46 x 10^{-3}	31[b] – 2460[c]
24 h (n=54)	**23.6**	**2.6 x 10^{-5}**	**2.05 x 10^{-3}**	**26[b] – 2053[c]**

[a] Average includes combined 3 h samples in each day (n=33) and 9 h samples (n=7)
[b] Calculated Value according to CalEPA
[c] Calculated Value according to WHO
n: number of samples

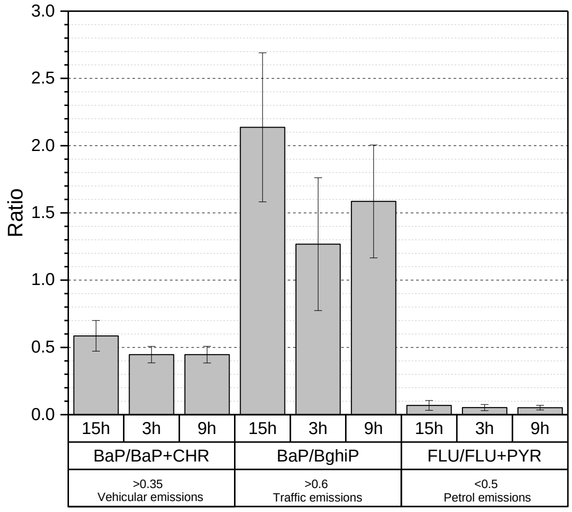

Figure 4. Column distribution of BaP/BaP+CHR, BaP/BghiP and FLU/FLU+PYR in the particulate phase for three different sampling periods. 3 h and 9 h represent samples collected during the day and 15 h for samples at night. Error bars reflect standard deviations.

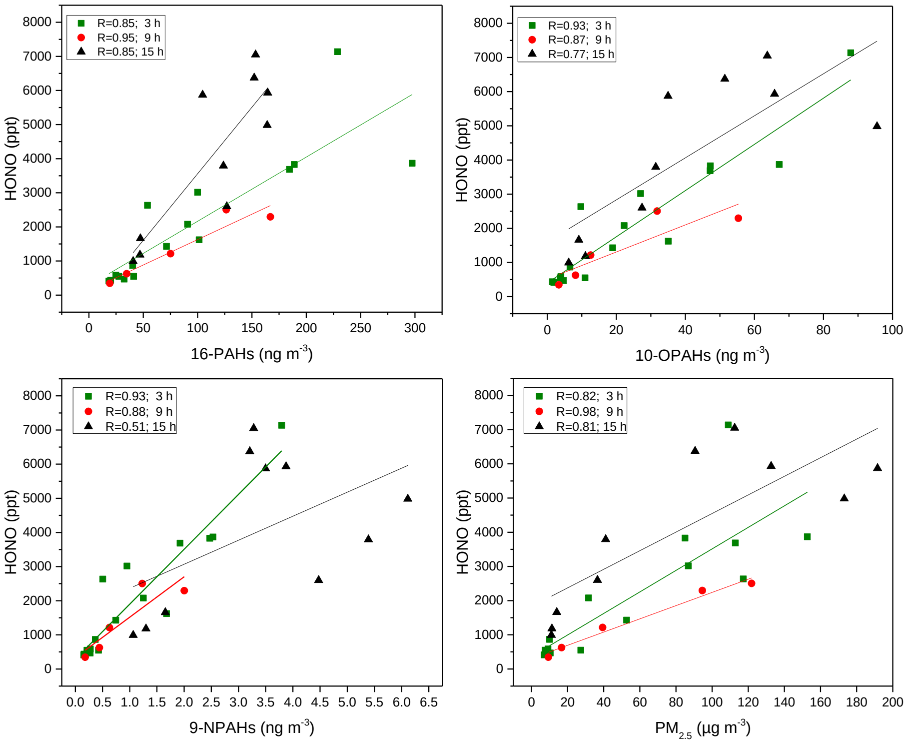

Figure 5. Correlation coefficients of ∑PAHs, ∑OPAHs, ∑NPAHs and $PM_{2.5}$ with HONO. Time sampling resolution of 3 h and 9 h refer to daytime concentrations and 15 h to nocturnal concentrations. Significance levels were between 0.001 and 0.05 except for HONO and NPAHs at night, P level > 0.05 and Pearson coefficient 0.52.

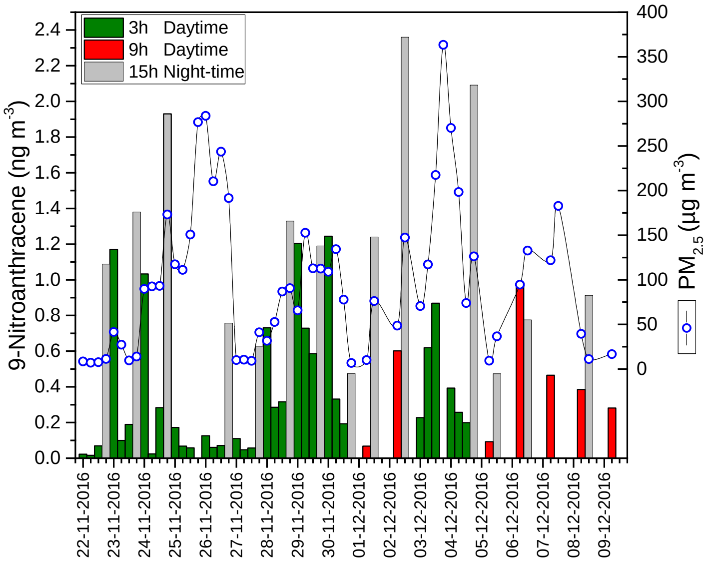

Figure 6. Temporal variation of 9-Nitroanthrance and PM$_{2.5}$ over the entire winter campaign.

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