

### **Comment on manuscript on acp-2020-576**

Overall, this manuscript is short on bright spots and largely repeats known conclusions. The current level does not meet the publication standards of Atmospheric Chemistry and Physics.

I am not sure that using the same sampling and analysis methods to carry out TSP size-grading sampling in northern and southern China can be an advantage of this study. Because the results presented by the authors are comparable to those of other studies, this equivalence, to some extent, may indicate that the measurements are comparable despite the differences in sampling and analysis methods.

Reply: Thank you for your comment. Public concerns on polycyclic aromatic hydrocarbons (PAHs) are mainly due to their carcinogenic potential. As the largest developing country in the world, China is the largest PAHs emitter and has high cancer risks caused by PAHs exposure. PAHs in different size particles have different health impacts. Thus, it is essential to understand size distribution of PAHs levels and sources and discover their difference in health risks among typical regions of China (e.g. north vs. south, urban vs. remote). These results are helpful to provide a basis for PAHs pollution control and health effects reduction in different regions of China. Unfortunately, most previous studies on atmospheric PAHs are undertaken at several sites within a local or regional scale in China. Due to the inconsistency in sampling methods, frequency and duration in these local and regional campaigns, it is difficult to draw a national picture of PAHs pollution in the air of China. To the best of our knowledge, our national observation is one of the first studies to acquire comprehensive information concerning spatiotemporal characteristics, source apportionment and health risks of size-segregated PAHs over a large national scale.

Based on our observation, we find that PAHs and BaP<sub>eq</sub> are dominated in PM<sub>1.1</sub> at all sites,

indicating that high carcinogenicity of PAHs is accompanied with ultrafine particles. Nationwide increases in both PAH levels and inhalation cancer risks occur in winter, probably due to the unfavorable meteorological conditions and enhanced emissions of coal combustion and biomass burning. Moreover, in the revised manuscript, we add more discussion focusing on PAHs and BaP<sub>eq</sub> sources in different size particles and among urban, sub-urban and remote sites. We find that coal combustion is the major source of BaP<sub>eq</sub> in all size particles at most monitoring sites. We believe that these findings provide insights into PAHs pollution and its potential effect on public health in China. Thus, this information is helpful to provide a basis for PAHs pollution control and health effects reduction in different regions of China.

The correlation analysis between PAH concentration and meteorological parameters in this manuscript might be reconsidered. The meteorological parameters, T, SR, and BHL, were low in winter and high in summer, while the concentration of PAHs changed in the opposite way. This difference constitutes an inverse correlation between these meteorological parameters and the concentration of PAHs. Therefore, the authors' emphasis on the worsened PAH pollution in winter caused by adverse meteorological conditions is lack of argument. It is suggested to analyze the correlation between PAH concentration and meteorological parameters in northern and southern China in each season, and it is better to normalize the concentration at different sites. On the other hand, it is well known that the effect of meteorological conditions on pollutants is nonlinear. If feasible, it is desirable to use a nonlinear model to evaluate and even quantify the effect of meteorological conditions on the concentration of PAHs.

Reply: Thank you for your suggestion. Theoretically, adverse meteorological conditions (low

temperature, solar radiation and boundary layer height, etc.) indeed lead to the increase of particulate PAHs. PAHs are semi-volatile compounds (SVOCs) and can partition between the gas and particle phases. The gas-particle (G/P) partitioning behavior of atmospheric PAHs can be described as equations (1) and (2) (Pankow, 1994).

$$K_{p,OM} = \frac{RT}{10^6 \overline{MW}_{OM} \zeta_{OM} P_L^o} \quad (1)$$

$$P_L^o = P_L^{o,*} \exp\left[\frac{\Delta H_{vap}^*}{R} \left(\frac{1}{298.15} - \frac{1}{T}\right)\right] \quad (2)$$

where  $K_{p,OM}$  represents the absorptive G/P partitioning coefficient of individual PAH,  $R$  ( $\text{m}^3 \text{ Pa} / (\text{K/mol})$ ) is the ideal gas constant,  $T$  (K) is the ambient temperature.  $\overline{MW}_{OM}$  (g/mol) is the mean molecular weight of organic matter (OM) and is assumed to be 200 g/mol (Xie et al., 2014),  $\zeta_{OM}$  is the scale activity coefficient of each compound in the absorbing phase and is usually assumed to be unity.  $P_L^{o,*}$  is the vapor pressure of each PAH at 298.15K and  $\Delta H_{vap}^*$  is vaporization enthalpy of the liquid at 298.15K. Thus, for a specific PAH in a single OM phase at a fixed relative humidity, the G/P partitioning should be driven by ambient temperature only. As Figure 1 showed, the decrease of ambient temperature can cause the increase of  $K_{p,OM}$ . This means that the decrease of ambient temperature would result in the increase of individual PAH in the particulate phase assuming a constant total concentration in the air.

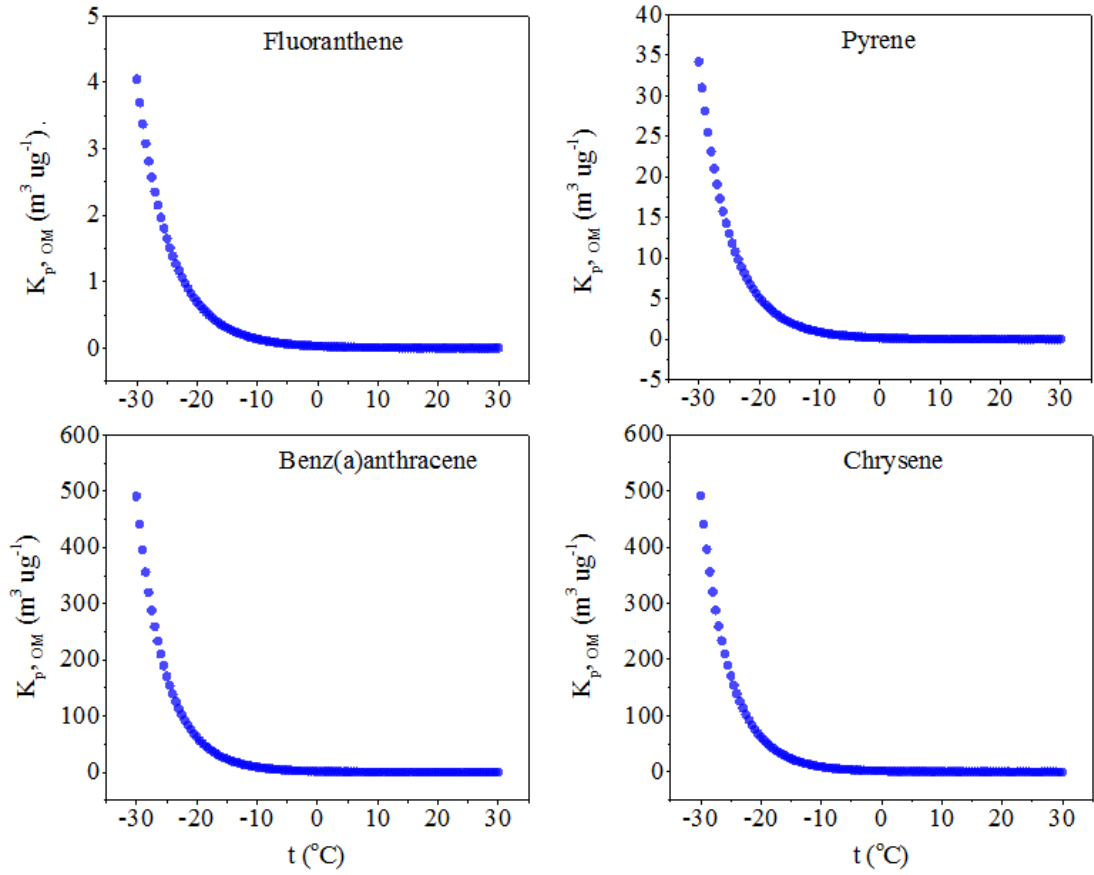


Figure 1 The  $K_{p,OM}$  ( $\text{m}^3 \text{ug}^{-1}$ ) under different temperature.

In the atmosphere, PAHs removal by OH can be described as:

$$\frac{dC_{PAH}}{dt} = -k * [OH] * C_{PAH} \quad (3)$$

where  $k$  is the rate constant for the reaction of a PAH with OH radical,  $C_{PAH}$  is the concentration of individual PAH in the air. Solar radiation (SR) directly affects photochemistry in the air. As Figure 2 showed, solar radiation values during our campaign positively correlated with the concentrations of hydroxyl radical [OH] which were estimated based on the empirical equation (4) (Ehhalt and Rohrer, 2000). Thus, the decrease of SR can indeed lower [OH] and accumulate PAHs in the air, resulting in the increase of PAHs concentrations.

$$[OH] = a(JO^1D)^\alpha (JNO_2)^\beta \frac{bNO_2+1}{cNO_2^2+dNO_2+1} \quad (4)$$

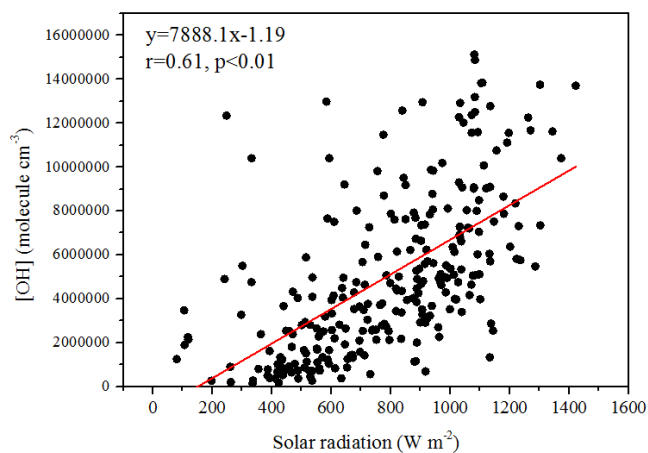


Figure 2 Correlation between OH concentration and solar radiation.

For the influence of boundary layer, low height of boundary layer can inhibit the vertical diffusion of PAHs, which leads to PAHs accumulation and increased concentrations.

We agree with the reviewer that the effect of meteorological conditions on pollutants is nonlinear. It is better to use a nonlinear model to evaluate the effect, which is out of the scope of the current study. At least above discussion illustrates theoretical inverse relationships between these meteorological parameters (temperature, solar radiation and boundary layer height) and the concentration of particulate-bound PAHs.

As suggested by the reviewer, we try to analyze the correlations between PAH concentrations and meteorological parameters in each season. Unfortunately there is only six samples in each season at a site. Instead, we divide the one-year data into warm and cold seasons based on the ambient temperature. As Figure 3 showed, at most sites in the northern and southern China, PAHs negatively correlated with temperature (T), boundary layer height (BLH) and solar radiation (SR) in both cold ( $T < 10^{\circ}\text{C}$ ) and warm ( $T > 10^{\circ}\text{C}$ ) seasons. Thus, coupled with above theoretical discussion, we believe our correlation analysis does reflect the effect of meteorological parameter on PAH concentrations.

In the revised manuscript, we add more discussion about the effect of meteorological parameter on PAH concentrations in [Line 297-305](#) and [Line 318-323](#). And Figure 3 was added in supporting information file and the revised manuscript as Figure S10. The detail theoretical discussion information had been added to the supporting information as Text S1 ([The line numbers here refers to the ‘tracking changes’ file](#))

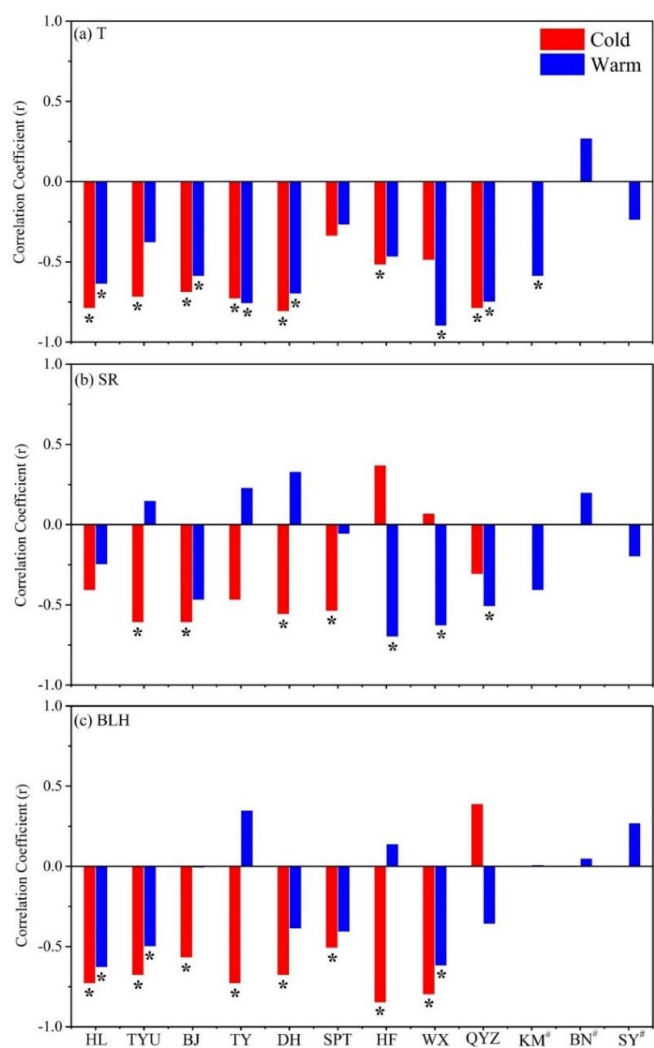


Figure 3 Correlation coefficient (r) of PAHs with T (a), SR (b) and BHL (c) at 12 sites in cold and warm season.

\*:  $p < 0.05$

#: the ambient temperature in KM, BN and SY are all exceed ten degree, there are no cold season in these three sampling sites.

In addition, the source analysis of PAHs does not seem to be in-depth. It is expected to link the source contribution to the health risks of a specific PAH. This relation will improve the understanding of the impact of changes in emission sources on the composition and health risks of PAHs, which will be more conducive to the development of effective local control measures.

Reply: Thank you for your suggestion. BaP carcinogenic equivalent concentration ( $BaP_{eq}$ ) is widely used to evaluate the health risks of PAHs. In the revised manuscript, we add more discussion focusing on source apportionment of  $BaP_{eq}$  as well as  $\sum_{24}PAHs$  in different size particles and urban, sub-urban and remote sites. To the best of our knowledge, this is one of the first studies to acquire comprehensive information concerning observation-based source apportionment of size-segregated PAHs and  $BaP_{eq}$  over a large national scale.

Figure 4 show source apportionment of  $\sum_{24}PAHs$  in different regions (a), sampling sites (b) and size particles (c). In the northern China, coal combustion was the major source of atmospheric PAHs ( $73.6 \text{ ng m}^{-3}$ , 84.2% of  $\sum_{24}PAHs$ ), followed by biomass burning ( $11.8 \text{ ng m}^{-3}$  and 13.5%) and vehicle exhaust ( $2.0 \text{ ng m}^{-3}$  and 2.3%). In the southern China, coal combustion ( $9.6 \text{ ng m}^{-3}$  and 54.8%) and biomass burning ( $6.8 \text{ ng m}^{-3}$  and 39.0%) were the major contributors, followed by vehicle exhaust ( $1.1 \text{ ng m}^{-3}$  and 6.2%) (Figure 4a). At urban and sub-urban sites, coal combustion was the largest source of  $\sum_{24}PAHs$  ( $70.4 \text{ ng m}^{-3}$ , 85.1% and  $30.5 \text{ ng m}^{-3}$ , 63.5%), followed by biomass burning ( $10.1 \text{ ng m}^{-3}$ , 12.2% and  $16.3 \text{ ng m}^{-3}$ , 33.9%) and vehicle emission ( $2.2 \text{ ng m}^{-3}$ , 2.6% and  $1.2 \text{ ng m}^{-3}$ , 2.5%), while at remote sites the contributions of coal combustion ( $9.1 \text{ ng m}^{-3}$ , 50.6% ) and biomass burning ( $7.8 \text{ ng m}^{-3}$ , 43.7%) were comparable and vehicle emission ( $1.0 \text{ ng m}^{-3}$ , 5.7%) had minor contributions. The major sources of  $\sum_{24}PAHs$  varied among different size particles in the northern and southern China (Figure 4c).

For PM<sub>>3.3</sub>-bound PAHs, the contributions of coal combustion (50.3%) and biomass burning (48.4%) were comparable in the northern China, while biomass burning (71.0%) was the largest source in the southern China. For PM<sub>1.1-3.3</sub>-bound PAHs, coal combustion (66.7%) was the dominated source in the northern China, whereas the percentage of biomass burning (53.7%) was larger than that of coal combustion (40.4%) in the southern China. For PM<sub>1.1</sub>-bound PAHs, coal combustion was the dominated source in the northern (66.6%) and southern (59.3%) China.

Figure 4 shows source apportionment of BaP<sub>eq</sub> in different regions (d), sampling sites (e) and size particles (f). Unlike  $\sum_{24}$ PAHs, coal combustion was the predominant source of BaP<sub>eq</sub> in the northern (8.1 ng m<sup>-3</sup> and 95.7%) and the southern (1.1 ng m<sup>-3</sup> and 84.7%) China. The contributions of coal contribution at urban sites (8.3 ng m<sup>-3</sup> and 96.4%) were larger than those at sub-urban (3.3 ng m<sup>-3</sup> and 90.8%) and remote (1.0 ng m<sup>-3</sup> and 82.5%) sites. Coal combustion was the dominate source in different size particles. And its contributions to PM<sub>>3.3</sub>, PM<sub>1.1-3.3</sub> and PM<sub>1.1</sub>-bound PAHs in the northern China (87.3%, 95.6% and 96.9%) were all larger than those in the southern China (76.8%, 87.3% and 88.2%).

All these discussion has been added to the revised manuscript in **Line 381-386 and Line 409-430**. And Figure 4 was added in the revised manuscript as Figure 7. We believe these findings provide insights into the linkage between the source contributions to the health risks of atmospheric PAHs and improve the understanding of the impact of changes in emission sources on the compositions and health risks of PAHs.



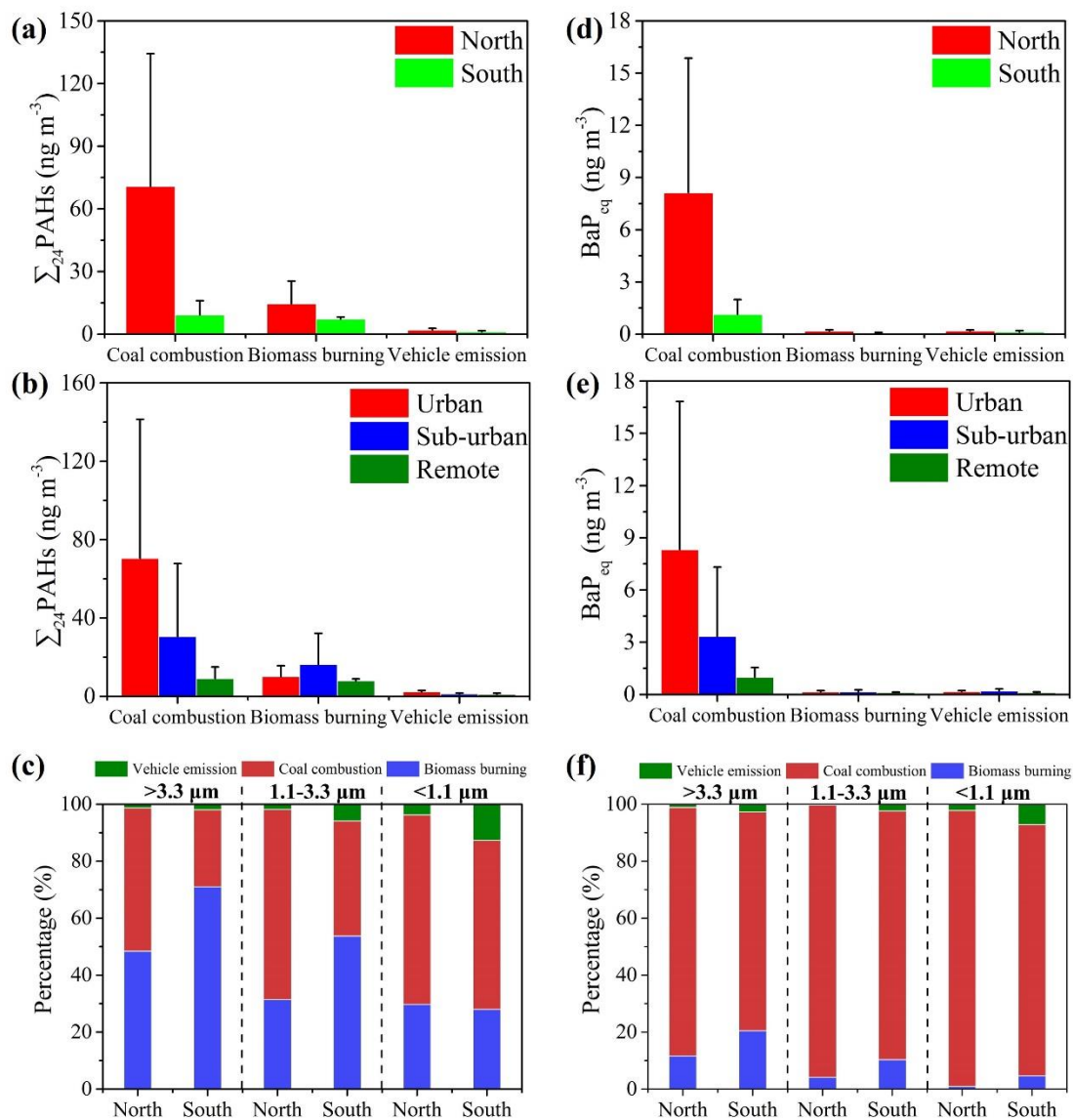


Figure 4 Source apportionment of  $\Sigma_{24}$  PAHs and BaP<sub>eq</sub> in different regions (a, c), sampling sites (b, d) and size particles (c, f).

## References

- Ehhalt, D.H., Rohrer, F., 2000. Dependence of the OH concentration on solar UV. *J. Geophys. Res.-Atmos.* 105, 3565-3571.
- Pankow, J.F., 1994. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ.* 28, 185-188.

Xie, M., Hannigan, M.P., Barsanti, K.C., 2014. Gas/particle partitioning of n-alkanes, PAHs and oxygenated PAHs in urban Denver. *Atmos. Environ.* 95, 355-362.