TEMPORAL TRENDS OF ATMOSPHERIC PAHS: IMPLICATIONS FOR THE INFLUENCE OF THE CLEAN AIR ACTION

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Introduction

Air pollution has been a major environmental problem in China in the past decade. For example, in January 2013, persistent heavy haze pollution occurred in most parts of northern and central China (Tao et al. 2014). To address heavy air pollution, China promulgated the toughest-ever Air Pollution Prevention and Control Action Plan (Clean Air Action) in 2013. After the Clean Air Action was implemented, the emissions and concentrations of primary air pollutants ($PM_{2.5}$, PM_{10}, SO_2, NO_2, CO, and O_3) exhibited markedly decreasing trends in China (except for O_3).

Polycyclic aromatic hydrocarbons (PAHs), as ubiquitous pollutants in the atmosphere, are formed by incomplete combustion of fuels containing carbon[1]. Similar to the influence on primary air pollutants, the Clean Air Action could also have direct and/or indirect influences on the temporal trend of atmospheric PAHs[2, 3]. However, the related studies are limited in China due to the complicated issues with PAH studies in the atmosphere. The sampling, treatment and analysis of PAHs in the atmosphere are complicated[4, 5], especially for long-term study programs over many years.

Following the national policy in China, Harbin also implemented the Clean Air Action Plan from 2014 to 2019. Therefore, in this study, to study the influence of the Clean Air Action on the temporal trend of atmospheric PAHs, a case study of the long-term measurement of atmospheric PAHs in Harbin in northeastern China from June 2014 to May 2019 was conducted.

Materials and methods

Sampling and analytical procedure of PAHs

The air samples were collected at an urban site (latitude: 45°45′28″ N; longitude: 126°40′49″ E) in Harbin, the capital city of Heilongjiang Province in northeastern China. Normally, almost weekly air samples were collected by a high-volume air sampler from June 2014 to May 2019. In total, 194 pairs of gas phase and particle phase samples (total suspended particles) were collected in the long-term monitoring program. Gas phase and particle phase samples were collected on polyurethane foam (PUF) plugs and glass fiber filters (GFFs), respectively. After sampling, GFFs and PUFs were spiked with surrogates and then extracted and purified by the Soxhlet extraction method and active silica gel column, respectively. In total, 15 priority PAHs were analyzed by an Agilent 6890N GC coupled with an Agilent 5973 mass spectrometer detector: acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), BaA, benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), indeno[l,2,3-cd]pyrene (IcdP), and benzo[g,h,i]perylene (BghiP).

Quality assurance/quality control (QA/QC)

For each batch of real samples, one lab blank was added to check the background interference during the experiment. The results indicated that only trace levels of low molecular weight PAHs could be detected in laboratory blanks. The average recoveries of the three surrogates (Flu-D10, Pyr-D10, and Perylene-D12) were 80%, 87%, and 69% for PUF samples and 75%, 92%, and 80% for GFF samples, respectively. The final reported concentrations were surrogate corrected but not blank corrected. The instrument and method detection limits ranged from 0.10 ng/mL to 0.73 ng/mL and from 0.0180 ng/m^3 to 0.0774 ng/m^3, respectively.

Data sources of primary air pollutants and meteorological factors

The daily average concentrations of the six primary air pollutants, $PM_{2.5}$, PM_{10}, SO_2, NO_2, CO, and O_3, were adopted from the China National Environmental Monitoring Center Network. The meteorological factors, including temperature (TEM, °C), wind speed (WIN, m/s), relative humidity (RHU, %), and precipitation (PRE, mm), were obtained from the NCEP/NCAR Reanalysis dataset (National Center for Environmental Prediction/National Center for Atmospheric Research Reanalysis 1, 2014).

Data analysis method

For the analysis of the temporal trend, a simple harmonic regression method was applied to assess the long-term trends and half-lives of PAH concentrations in the atmosphere[6, 7]. To study the influence of meteorological factors on the temporal trend of PAHs in the atmosphere in Harbin, a stepwise multiple linear regression (MLR) model is applied[8, 9].

Results and discussion

Using the harmonic regression method, the temporal trends were observed for the 6 primary air pollutants ($PM_{2.5}$, PM_{10}, SO_2, NO_2, CO, and O_3) in the atmosphere in Harbin from June 2014 to May 2019. For the five years, the average concentrations for the six primary air pollutants were 60.4 μg/m^3, 88.5 μg/m^3, 39.4 μg/m^3, 49.8 μg/m^3, 1.03 mg/m^3, and 48.8 μg/m^3. Obvious long-term temporal trends and seasonal variations were observed for $PM_{2.5}$, PM_{10}, SO_2, NO_2, and CO with half-lives of 3.42 ± 0.164, 6.66 ± 0.520, 5.56 ± 0.344, 4.06 ± 0.133 and 11.3 ± 1.33 years, respectively. Among the six pollutants, O_3 is the only one with an increasing trend over the five years of the study. A similar increasing trend with O_3 was also observed in other cities in China[10]. Compared with the other five pollutants, a reversed temporal trend and seasonal variation were found for O_3, with a doubling time of 4.41 ± 0.293 years and higher concentration in summer seasons than in other seasons.

Table 1. Statistical summary of atmospheric Σ_{15}PAHs (ng/m^3) in Harbin for the five years from June 2014 to May 2019

1	GM[a]	GSD[b]	Mean	SD[c]	Median	Range (min - max)[d]	Range (25th% - 75th%)[e]
2014/6-2015/5	120	2.63	207	266	98.7	34.0 - 1080	57.4 - 176
2015/6-2016/5	103	2.91	193	252	67.2	23.0 - 1090	47.2 - 264
2016/6-2017/5	81.9	2.86	152	236	45.1	17.6 - 1300	37.1 - 190
2017/6-2018/5	79.7	3.32	174	244	49.0	12.0 - 895	32.3 - 184
2018/6-2019/5	58.7	2.65	97.6	125	36.7	13.1 - 673	27.7 - 145
All	87.8	2.94	169	235	63.2	12.0 - 1300	37.7 - 174

[a]Geometric mean; [b]Geometric standard deviation; [c]Standard deviation; [d]The minimum value to the maximum value; [e]The 25th percentile value to the 75th percentile value.

The concentrations of Σ_{15}PAHs in the total phase (gas phase plus particle phase) in the atmosphere in Harbin from June 2014 to May 2019 are summarized in Table 1. For the total phase, the concentrations of Σ_{15}PAHs ranged from 12.0 to 1300 ng/m^3, with a geometric mean concentration (± geometric standard deviation) of 87.8 ± 2.94 ng/m^3 over the five years of the study. The annual geometric mean concentrations of Σ_{15}PAHs were 120, 103, 81.9, 79.7, and 58.7 ng/m^3 for the five years. It is interesting to note that a dramatic decreasing trend was observed for the concentration of Σ_{15}PAHs. However, the concentrations of PAHs in Harbin were still higher than those in other long-term atmospheric monitoring programs worldwide[11-13]. Therefore, the higher atmospheric concentrations and related health risks to humans in Harbin need to attract more attention in the future.

The temporal trends of Σ_{15}PAHs in different phases in the atmosphere in Harbin from June 2014 to May 2019, fitted by the harmonic regression method, are shown in Fig. 1. It is interesting to note that obvious decreasing trends were observed for the atmospheric PAHs in Harbin over the five years of the study. The half-lives for the total phase, gas phase, and particle phase PAHs were 3.23 ± 0.370, 2.94 ± 0.295, and 4.27 ± 0.666 years. These half-lives are shorter than those obtained in other long-term monitoring programs. For example, in the U.K. TMOP network, the half-life was 5.9 years for Σ_{15}PAHs from 1991 to 2005[14]. Efforts to reduce pollution sources were verified to be the primary reason for the decrease in PAH concentrations[14]. The shorter half-lives and higher concentrations of PAHs observed in the present study indicated a faster decreasing rate of PAH concentrations in Harbin. The results confirmed the effectiveness of actions implemented in Harbin on reducing pollution sources of PAHs.

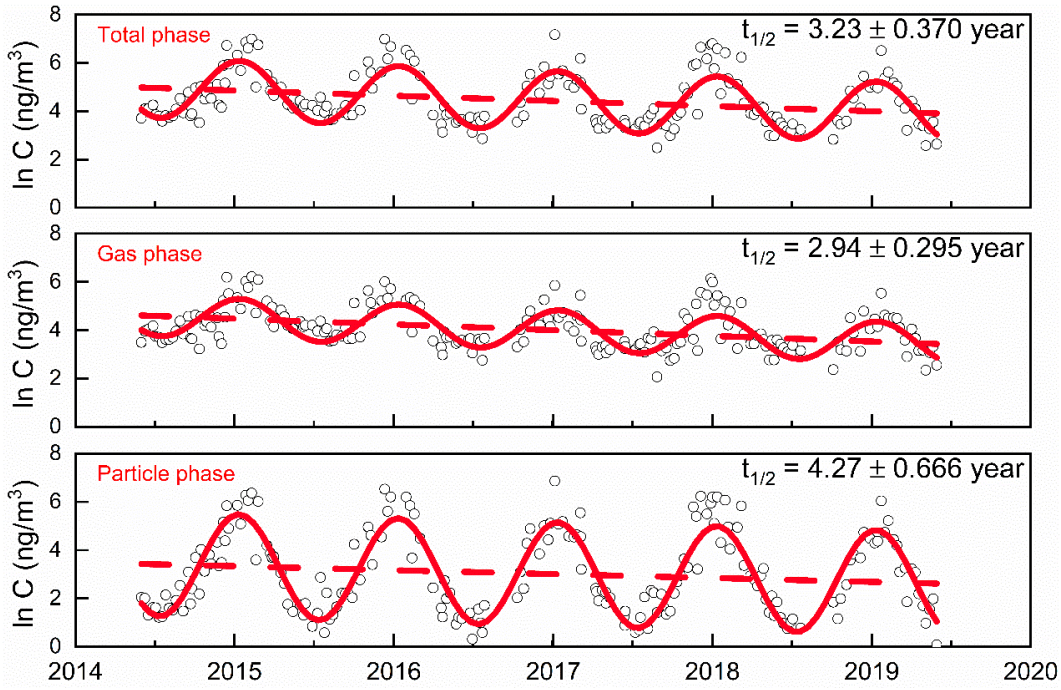

Figure 1. Temporal trends of Σ_{15}PAHs in the total phase, gas phase, and particle phase in the atmosphere in Harbin from June 2014 to May 2019

To study the influence of meteorological factors on the temporal trend of atmospheric PAHs, a simple MLR model studying the relationship between concentrations of Σ_{15}PAHs and meteorological factors was conducted. Three variables are presented in Fig. 2: monthly mean PAH anomalies in the deseasonalized but not detrended data (y_a; green), the meteorological contribution to the PAH decreasing trend calculated from the MLR meteorological model (y_m, Eq. S1-3, SI; dark blue), and the residual y_r (meteorology corrected, Eq. S1-4, SI; red). The residual was considered to be caused by anthropogenic emissions control[9]. The PAH decreasing trend from the part of the meteorology corrected (residual y_r) was -23.1 ± 9.69 ng/(m^3·y), which was 35% weaker than that in the monthly mean PAH anomaly (-35.3 ± 12.6 ng/(m^3·y)). The results indicated that only 35% of the PAH decrease can be attributable to meteorological conditions. Therefore, it can be concluded that the anthropogenic emissions control from the Clean Air Action could be another reason for the decreasing temporal trend of PAHs in the atmosphere in Harbin.

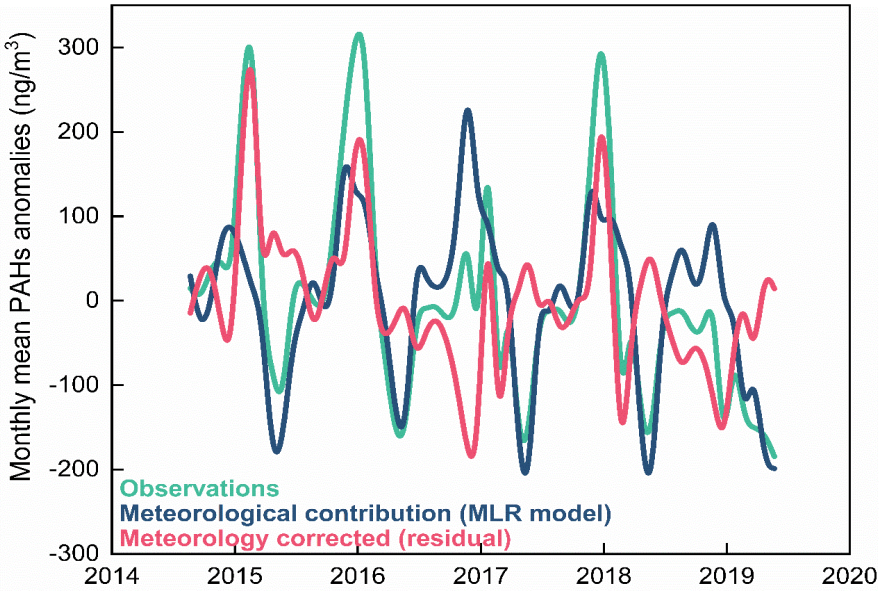

Figure 2. Time series of PAH monthly mean anomalies in the atmosphere in Harbin from June 2014 to May 2019 (green line)

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