DOCTORAL THESIS

Pollution characteristics of polyaromatic organic contaminants in $PM_{2.5}$ from typical regions of China

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ABSTRACT

Air pollution has become a serious environmental issue around the world. Among the multiple pollutants like NO_x and O_3, the atmospheric particulate matter with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) has been the most serious problem lately. The daily life and health of general public are greatly affected by $PM_{2.5}$. For instance, the extended exposure to $PM_{2.5}$ was reported to have association with increased prevalence of heart and lung diseases.

China has suffered from serious $PM_{2.5}$ pollution for many years. The vast territory, abundant anthropogenic activities and various geographical features make the formation mechanisms and possible health effects of $PM_{2.5}$ become diverse and complicated. Because of that, regional study is necessary to control $PM_{2.5}$ pollution and reduce the associated health risks. Taiyuan and Guangzhou are two typical megacities with strong regional characteristics in North and South China, both of which are subjected to $PM_{2.5}$ pollution for long time. Through the analysis of $PM_{2.5}$ samples collected from Taiyuan and Guangzhou, it will benefit the investigations of sources and toxicities of $PM_{2.5}$ in Northern and Southern regions in China.

Due to the complexity, research on components of $PM_{2.5}$ is important. Polyaromatic organic contaminants are an important $PM_{2.5}$ composition because of their relatively high concentration and obvious toxicity. In this study, polycyclic aromatic hydrocarbons (PAHs), nitro-PAHs (NPAHs), hydroxy-PAHs (OHPAHs) in $PM_{2.5}$ samples from Taiyuan and Guangzhou were determined. A novel atmospheric pressure gas chromatography-tandem mass spectrometry

(APGC-MS/MS) method with higher sensitivity was developed. 19 PAHs, 18 NPAHs and 12 OHPAHs in $PM_{2.5}$ were analyzed with the method detection limits of 0.021 (PAHs), 0.001 (NPAHs) and 0.005 (OHPAHs) pg m^{-3}, respectively. The developed APGC-MS/MS method provided acceptable recoveries (70 – 120%) and precision (RSD < 15%).

$PM_{2.5}$ samples collected from Taiyuan and Guangzhou from May. 2017 to April. 2018 were analyzed for 19 PAHs, 18 NPAHs and 12 OHPAHs. The pollution characteristics, including contamination levels, sources and possible influences on human health, were investigated and compared between the two sampling sites. Compared to Guangzhou, Taiyuan had higher contamination levels for most of the determined PAHs, NPAHs and OHPAHs in $PM_{2.5}$. Except for NPAHs, whose major source was the OH· radical-initiated secondary formation, the predominant pollution sources of PAHs and OHPAHs in $PM_{2.5}$ were different in these two cities. The mixed primary source of coal combustion and traffic emission was predominant for both PAHs and OHPAHs in $PM_{2.5}$ from Taiyuan. But in Guangzhou, single primary traffic emission was major source. Higher carcinogenic health risks of $PM_{2.5}$ were found in Taiyuan for adults, children and infants compared to Guangzhou based on the determined concentrations of PAHs and NPAHs. Obvious temporal and spatial variations among Taiyuan and Guangzhou were seen, which indicated that the pollution status of PAHs, NPAHs and OHPAHs in $PM_{2.5}$ in Taiyuan was serious. The pollution levels of $PM_{2.5}$-bound PAHs and NPAHs in Guangzhou also became higher in recent years.

Besides PAHs and their derivatives, 14 emerging polycyclic aromatic sulfur heterocycles (PASHs) were detected in $PM_{2.5}$ collected from Taiyuan and

Guangzhou. They were assessed by accurate quantification, investigation of contamination levels and pollution sources, and the preliminary studies of pollutant-induced toxic effects. A novel APGC-MS/MS method was developed for the determination of the PASHs in $PM_{2.5}$ with superior sensitivity of 0.052 – 1.673 pg m^{-3}. Higher contamination levels in atmosphere were found in Taiyuan at ng m^{-3}. Coal combustion/secondary formation and traffic emission/secondary formation were found as pollution sources of the PASHs in $PM_{2.5}$ from Taiyuan and Guangzhou, respectively. Dithiothreitol (DTT) and cell viability assays were performed for the preliminary assessment of PASH-induced reactive oxygen species (ROS) production and cell toxicity based on the exposure dosage for human. The results indicated that PASHs in $PM_{2.5}$ collected from Taiyuan could lead to oxidative stress and human bronchial epithelial cells' death. The toxicity results suggest that more efforts are necessary to control the local primary sources and secondary formation of PASHs in $PM_{2.5}$.

In summary, a novel analytical method using APGC-MS/MS was developed and successfully applied for determination of different polyaromatic organic contaminants in $PM_{2.5}$. 19 PAHs, 18 NPAHs, 12 OHPAHs and 14 PASHs in $PM_{2.5}$ collected from Taiyuan and Guangzhou, the typical regions in North and South China, were determined. The pollution characteristics, including contamination levels, sources, health risks and temporal/spatial distributions were investigated and compared. Significantly different pollution characteristics of PAHs, NPAHs and OHPAHs in $PM_{2.5}$ showed a close connection between pollution features with local economic structures. For the 14 emerging PASHs, their pollution status, sources and implication for human health in these two sites were studied.

Compared to Guangzhou, Taiyuan had relatively higher exposure levels and health risks of PASHs in $PM_{2.5}$ for local people. The study of pollution characteristics of the polyaromatic organic contaminants in $PM_{2.5}$ from representative areas could provide a useful guidance for $PM_{2.5}$ pollution control and general public health protection in China.

Table of Contents