Form 2

Dissertation Abstract

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Dissertation title	Characteristic study on the chemical compositions in urban suspended fine particles during allergenic pollen scattering period （花粉飛散期における都市部大気浮遊微粒子中の有害化学物質の特性に関する研究）		

Abstract

※ *The abstract should be in keeping with the structure of the dissertation (objective, statement of problem, investigation, conclusion) and should convey the substance of the dissertation*

This thesis is main about “Characteristic study on the chemical compositions in urban suspended fine particles during allergenic pollen scattering period” and included in 5 chapters to expound. The keywords focused on chemical compositions in fine particles of Shanghai and Saitama during the spring pollen scattering period.

Thence, the 1st chapter is to the general background and introduction. With the rapid development of urbanization and industrialization all over the world, atmospheric contaminants increased sharply in recent decades. Ambient air in industrial and urban environments is constantly receiving fresh emissions of ultrafine particles from the anthropogenic sources, such as vehicle emissions and atmospheric photochemical reactions. According to the 2014 World Health Organization report, air pollution lead to the deaths of around 7 million people in worldwide in 2012. It has reported that the air pollution could cause several diseases, allergies and even deaths to humans. The dominant compositions could be divided into three groups, aerosol components, inorganic and organic components, respectively. Depends on the size distribution of ambient particles, there are usually 3 species of particles, $PM_{2.5}$, $PM_{2.5\text{-}10}$ and PM_{10}. As one Chinese student in Saitama University, I am very interested in the current state of the atmosphere in China and Japan. Particularly, I lived in Shanghai during my master's degree and now lives in Tokyo Area in Japan. Both Shanghai and Tokyo are known around the world for their developed economy, modern technology and huge resident population. Currently, they also encountered some environmental pollution problems since recent decades. Thence, Shanghai in China and Saitama in Japan were selected as the main research objects in my doctoral thesis. Specifically, atmospheric particles were collected in Shanghai and Saitama during the spring period, 2017. One of the highlights was that the high-volume sampler could collect more particles with 5 different sizes ($PM_{1.1}$, $PM_{1.1\text{-}2.0}$, $PM_{2.0\text{-}3.3}$, $PM_{3.3\text{-}7.0}$, and >7.0 μm). $PM_{2.0}$ were divided into $PM_{1.1}$, $PM_{1.1\text{-}2.0.}$ In these particle samples, pollen allergens are measured as main bio-aerosol component, water-soluble ions and elements are as the inorganic part to measure while polycyclic aromatic hydrocarbons (PAHs) which reported as one carcinogen were considered as the organic contents to analyze the distribution and the probable sources in 5 different size particles. The primary task is to ensure the allergic pollen scattering period in Shanghai and Saitama, then to investigate the characteristics of allergenic particles, water-soluble ions, elements and PAHs in ambient particles during the pollen scattering period in Shanghai and Saitama. Especially for the health assessment from trace elements and PAHs. Furthermore, the interaction and the relationship among species components is one interesting aspect to explore. At last, to summary the similarities and differences of the ambient particles in Shanghai and Saitama during

the sampling periods.

The 2nd chapter is primary to measure the distribution and characteristics of pollen allergens in atmospheric particles of Shanghai and Saitama, 2017. In Shanghai, *Platanus acerifolia* which are planted in large quantities on the roadside of Shanghai are investigated to the main source of allergenic pollens with main allergens *Pla a1, Pla a 2 and Pla a 3*. Here, *Pla a 3* was measured as the typical of main pollen allergens in the atmosphere of Shanghai. To explore the distribution of *Pla a 3* in the atmosphere, a specific IgE antibody for *Pla a 3* was prepared from r*Pla a 3*-sensitized rats. ELISA method was selected to measure the allergenicity of both r*Pla a 3* and *Pla a 3* in pollen of *Platanus*. The results demonstrated that the pollen scattering period were concentrated in mid-March to mid- April in Shanghai, especially the peak of most natural *Pla a 3* occurred in the middle of April in Shanghai. The total protein in ambient particles of Shanghai were main distributed in $PM_{1.1}$ while the *Pla a 3* were main located in the coarse particles (>7.0 μm) during the *Platanus* pollen season. In Saitama, from the beginning of March, the primary allergenic pollen are from *Japanese cypress* instead of *Cryptomeria japonica* with allergic proteins which named as *Chao 1, Chao 2 and Chao 3*. The highest point in Saitama University named 10F sampling site and roadside of route 463 defined as Roadside sampling site were elected to measure the allergenic particles. The surface plasmon resonance (SPR) results indicated that the total allergens in 10F were obviously higher than that in Roadside which indicated that the 30m height point was higher levels of allergens. The main pollen scattering period was also in middle of March to middle of April and could be last to May. Considering of the size distribution of ambient particles, pollen allergens were trend to be distributed in $PM_{1.1}$ not only in 10F but Roadside sampling sites while the allergic particles could be found in each size particles. Briefly, it was no doubt that not only Saitama but Shanghai were affected by the obvious pollen allergens in the Mid - March to Mid – April. *Pla a 3* is first time to measure the main distributed in the content of pollen and could be released by the high humidity condition. In the atmosphere, *Pla a 3* were trend to locate in the coarse particles (>7.0 μm) while Chao 1 were main in $PM_{1.1}$. The higher sampling site was trend to with higher allergic concentrations.

Due to the 2nd chapter confirmed that pollen scattering periods was concentrated from mid-March to mid-April. The 3rd chapter is about the characteristics of inorganic components in ambient particles in Shanghai and Saitama. The main components of $PM_{2.5}$ were secondary particles, organic and elemental carbon, and crustal materials. Here, 8 species water-soluble ions and 23 species elements were selected as the main inorganic contents to analyze the characteristics. Water-soluble ions were measured by IC system and elements were measured by ICP-MS system. And this was the first time to measure water-soluble ions and elements in 5 stage size-segregated fractions in Shanghai and Saitama during the spring pollen scattering periods. Firstly, the ambient particles in Shanghai were determined at the levels of 106 $\mu g/m^3$ (April 6 - 7) to 217 $\mu g/m^3$ (March 31-April 1) with great contributions from $PM_{1.1}$ and coarse particles (>7.0 μm). The ambient particles in Saitama were in the range of 74.5 $\mu g/m^3$ (March 23- 27) to 107 $\mu g/m^3$ (April 4-7) which nearly half contents of those in Shanghai. Water-soluble ions, as the important components of ambient particles, could directly affect the aerosol acidity, moisture and absorption ability. The average ionic concentrations in ambient particles were 33.6 $\mu g/m^3$ in Shanghai and 5.51 $\mu g/m^3$ in Saitama and the ionic contents which indicated that water-soluble ions were important contents in ambient particles, especially in $PM_{1.1}$. Especially, NH_4^+, SO_4^{2-} and NO_3^- as the secondary particles were almost accumulated in

$PM_{1.1}$ instead of $PM_{1.1\text{-}2.0}$. Ca^{2+}, Na^{+} and Mg^{2+} which nearly all form the crustal sources were relatively located in the coarse particles. Na^{+}/Cl^{-} molar ratios results showed that Cl^{-} contents were higher than Na^{+} in $PM_{1.1}$ and $PM_{1.1\text{-}2.0}$ of Shanghai which indicated that excessive Cl^{-} ions may come from coal combustion rather than sea salt sources. Ion balances were determined the acid-base balances for all ambient particulates. In $PM_{1.1}$, the ion balance values in Shanghai and Saitama were always nearly to 1.00 which indicated that these 8 species ions were the main contents in $PM_{1.1}$. The ion balance in coarse particles of Saitama were over1.00 and almost over 1.00 in Shanghai which might be explained by the assembled of the crustal original ions. NH_4^{+}, SO_4^{2-} and NO_3^{-} were mainly in $PM_{1.1}$ and existed as secondary particles of NH_4NO_3, NH_4HSO_4 and $(NH_4)_2SO_4$. High ionic ratios of NO_3^{-}/SO_4^{2-} and NO_2/SO_2 were indicated the strong contribution of vehicle emissions were not only in $PM_{1.1}$ of Shanghai and Saitama. In addition, ionic contents in atmosphere not only facilitate pollen breakage but also could be affect the distribution of pollen allergen in ambient particles. The size range of *Platanus* pollen suspended particles mainly was distributed from $PM_{1.1}$ while *Pla a 3* also located in $PM_{1.1}$ but could be affected form ionic contents in the coarse particles. These results suggest that Ca^{2+}, NH_4^{+}, and SO_4^{2-} promote pollen rupture to release fine particles, but the function of these ions was significantly affected by the pH conditions.

23 species elements in ambient particulates of Shanghai were determined in the range 3.54 μg/m^3 (April 8-9) to 14.1 μg/m^3 (March 25-26) while the contents were 1.10 μg/m^3 to 3.45 μg/m^3 in Saitama. The great proportion of elements were main located in coarse particles (>7.0μm) with the great contributions from crustal elements while the trace elements were trend to distribute in $PM_{1.1}$. Crustal enrichment factors (EFcs) method is commonly to evaluate the strength of the crustal, non-crustal sources and more characteristics. The values of EFcs in $PM_{1.1}$ of Shanghai and Saitama were indicated that nearly all trace elements in $PM_{1.1}$ were mainly originated from anthropogenic sources. Kinds of Elemental ratios in $PM_{1.1}$ were represented the air pollutants were caused from different sources, such as coal and oil combustion, diesel and gasoline vehicles. Backward trajectories of air masses also showed that the long-range transportation of polluted air masses is also an important factor to air pollutions.

Atmospheric PAHs are environmental pollutants which represented a risk not only to humans but to all living organisms. PAHs were selected as the typical organic contents to measure in Chapter 4. 16 species PAHs in ambient particles with 5 different sizes of Shanghai and Saitama were measured by GC-MS system. The PAHs in ambient particles of Shanghai were in a widely range of 1.71 to 12.0 ng/m^3 and 0.87-1.16 ng/m^3 in Saitama. Both in Shanghai and Saitama, about 50% proportion of PAHs were distributed in $PM_{1.1}$ with the great contribution from the HMW PAHs groups. And the PAHs in Saitama was more stable than those in Shanghai. Diagnostic ratio method is to identify the PAHs sources involves comparing ratios of pairs of frequently found emissions. In $PM_{2.0}$, the species ratios results showed that the main sources in Saitama might be from vehicles traffic emissions while those in Shanghai might be from the coal combustion and vehicle traffic emissions. Depends on the contents of trace element, PAHs in $PM_{1.1}$, $PM_{2.0}$ of Shanghai and Saitama, some health- risk assessment models were selected to evaluate the health effects of them as shown in Chapter 5. Carcinogenic and noncarcinogenic health risk effected by trace elemental species in PM2.0 were calculated by the methods conferenced from the USEPA human health risk assessment model. Toxic equivalency factors (TEFs) for individual PAHs were used to estimate human health cancer risk associated with inhalatory exposure to PAHs. The trace elements in $PM_{1.1}$ were more

harmful than those in $PM_{1.1\text{-}2.0}$. Only in some sampling case in Shanghai have some health effects.

The TEFs of total PAHs in Shanghai were 0.424 and about 5 times higher than that in Saitama. The toxicity is main from the HMW groups and BaP is the most toxic PAH. Pollen allergens could be also affected by species ionic contents to improve the release and increase the allergenity which could increase the risk of sensitization.

In summary, the main pollen allergens, water-soluble ions, elements, and PAHs in atmospheric particles of Shanghai and Saitama were as the main research objects to be measured. Both in Shanghai and Saitama, the period form middle - March to middle-April was the main spring pollen scattering period. It was the first time to show the *Pla a 3* were distributed in the content of pollen. Ca^{2+} could promote the adsorption of *Pla a 3* on the particles surface. *Pla a 3* were main located in coarse particles of Shanghai while Cha o 1 were main in $PM_{1.1}$ of Saitama. The allergenic contents in Saitama were higher than that in Shanghai and the allergenic particles were main located in $PM_{1.1}$ of Saitama. However, the water-soluble ions, elements and PAHs in ambient particles of Shanghai were about 5 times higher than those in Saitama. Compared to $PM_{2.5}$, water soluble ions, and PAHs were main located in $PM_{1.1}$ with the main anthropogenic sources such as, vehicle emission was the most important sources of Saitama while coal combustion and traffic emissions was the main pollutant sources in Shanghai. Trace elements in $PM_{2.0}$ of Shanghai indicated some health risk to public especially these from $PM_{1.1}$. The health risks of PAHs were mainly caused from the HMW group. High levels of ambient particulates were transported by the air masses from northwestern of China, companying with local heavy traffic and local industries. Another pollutant source --- ship emissions cannot be ignored.

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