

学位論文要旨

Interaction between water-saturated Kosa particles and polycyclic aromatic hydrocarbons

飽湿状態における黄砂と多環芳香族炭化水素との相互
作用に関する研究

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Abstract

Kosa (Asian dust) particles are potential carriers of polycyclic aromatic hydrocarbons (PAHs) in the atmosphere. The heterogeneous interaction between them may lead to worsened air quality and enhanced cytotoxicity and carcinogenicity of ambient particulates in downwind areas, and this topic requires in-depth exploration. In this study, Kosa samples were collected from four Asian dust sources, and their physical properties and chemical compositions were determined, showing great regional differences. The physical and chemical interactions of different Kosa particles with naphthalene (Nap; model PAH) were observed in aqueous systems. The results showed that Kosa particles from the Loess Plateau had weak adsorption to Nap, which was fitted by the Langmuir isotherm. There was no obvious adsorption to Nap found for the other three Kosa samples. This difference seemed to depend mainly on the specific surface area and/or the total pore volume. In addition, the Nap in the aqueous solution did not undergo chemical reactions under dark conditions and longwave ultraviolet (UV) radiation but degraded under shortwave UV radiation, and 2-formylcinnamaldehyde and 1,4-naphthoquinone were the first-generated products. The degradation of Nap in the aqueous solution was probably initiated by photoionization, and the reaction rate constant (between $1.44 \times 10^{-4} \text{ min}^{-1}$ and $8.55 \times 10^{-4} \text{ min}^{-1}$) was much lower than that of Nap with hydroxyl radicals. Instead of inducing or promoting the chemical change in Nap, the Kosa particles slowed photodegradation due to the extinction of radiation. Therefore, it is inferred that Kosa particles have no substantial effect on the transportation and transformation of PAHs in the atmosphere.

Introduction

Kosa (Asian dust) is a large contributor to atmospheric aerosols and has attracted worldwide attention for posing a large challenge to global climate, visibility, and human health. East Asia is one of the world's largest dust sources. Moreover, East Asian countries, especially China, are macroconsumers of fossil and biomass fuels, where both parent and substituted polycyclic aromatic hydrocarbons (PAHs) remain at high levels in the atmosphere. During the prevalence of Kosa, a simultaneous increase in Kosa particles and particulate PAHs has been sometimes observed in downwind areas, and a rapid production of PAH derivatives has been observed in the later Kosa episode. Due to the presence of transition metal ions and oxides, as well as the heterogeneous interactions with some gaseous molecules, Kosa particles are believed to act as carriers and reaction vessels for PAHs during long-range transportation and downward diffusion. The heterogeneous interaction between Kosa and PAHs may lead to worsened air quality and enhanced cytotoxicity and carcinogenicity of ambient particulates in downwind areas, therefore, this topic requires in-depth exploration.

The purpose of this laboratory study was to clarify the primitive function of Kosa particles on PAHs, which may drive the atmospheric behavior of PAHs, the generation of secondary aerosols and their health effects. Naphthalene (Nap) was chosen as the model PAH because of its high water

solubility and vapor pressure, simple structure, and atmospheric abundance. In the present study, the heterogeneous interactions between Nap and different Kosa particles were investigated in aqueous systems, considering the complex mineralogy, hygroscopicity of Kosa and its collision with PAH molecules.

Methods

The Kosa samples used in this study were collected from different Asian deserts, including the Gobi Desert, Taklimakan Desert, Horqin Sandy Land and Loess Plateau. Locations of the sampling sites are shown in **Fig. 1**. The particle size, specific surface area, and porosity of the Kosa samples were measured. Moreover, fifteen metallic elements and nine water-soluble inorganic ions of each Kosa sample were detected.



Fig. 1. Locations of the geographic origin of Kosa samples. Sample Kosa 1 was collected from the Gobi Desert (105.4°E, 38.5°N, Inner Mongolia, China), Kosa 2 was from the Taklimakan Desert (84.3°E, 40.2°N, Xinjiang, China), Kosa 3 was from the Horqin Sandy Land (122.3°E, 43.0°N, Inner Mongolia, China) and Kosa 4 was from the Loess Plateau (108.9°E, 34.5°N, Shaanxi, China).

Batch adsorption experiments were performed in a thermostatic shaker water bath at 20°C to evaluate the adsorption capacity of each Kosa sample to Nap. The batch adsorption experiment under acid conditions was conducted to simulate the acidified Kosa caused by the uptake of acidic gases. Three common acids in the atmosphere, sulfuric acid (H₂SO₄), nitrate acid (HNO₃), and hydrochloric acid (HCl), were used as acid additives. The Nap in the solution was detected by a high-performance liquid chromatographer (HPLC) coupled with an UV detector.

The reactivity experiments were performed in a chamber under various conditions: the light/dark conditions included dark, longwave (365 nm) and shortwave (254 nm) UV irradiation; the solvent conditions included acid (pH = 4.5) and acid-free aqueous solutions, methanol solution and

water-free conditions; and there were conditions with and without Kosa particles. Each experiment consisted of a set of samples under the same conditions, and a sample was removed for extraction and analysis at a predetermined time (0-6 h). The Nap and products in each sample were detected by the HPLC system. Two products detected in the experiment were separated from the samples during the HPLC analysis and were analyzed qualitatively by gas chromatography-mass spectrometry (GC-MS).

Results and discussion

(1) Both the physical and chemical properties of the Kosa samples varied with geographic origin. The Kosa sample from the Loess Plateau had the finest particle size and the largest specific surface area and total pore volume, while the particle and pore size were uniform among the other three Kosa samples. The four Kosa samples were characterized by a high content of crustal elements and a low level of transition metal elements, whereas the mass fraction of each element varied largely. In addition, these four Kosa samples had different compositions on water-soluble inorganic ions, but the main components all were deliquescent salts.

(2) The results showed that Kosa particles from the Loess Plateau had weak adsorption to Nap, which was fitted by the Langmuir isotherm (**Fig. 2**). There was no obvious adsorption to Nap found for the other three Kosa samples. This difference seemed to depend mainly on the specific surface area and/or the total pore volume. However, the adsorption capacity of zeolites, a microporous mineral, was substantially higher than that of the Kosa samples investigated. In addition, acid conditions inhibited the adsorption of Kosa particles to Nap. Thus, Kosa particles exhibit a weak or negligible adsorption effect on Nap and have little superiority in adsorbing more hydrophobic PAHs.

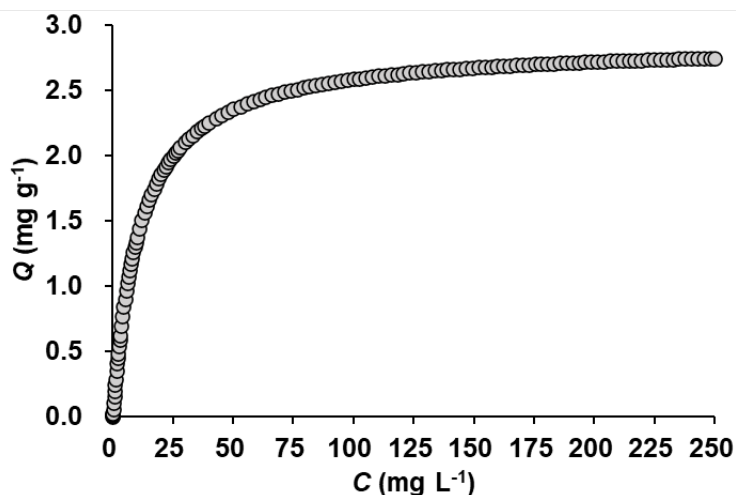


Fig. 2. The adsorption of Nap on 10 mg of the Kosa sample fitted by the Langmuir adsorption isotherm. C is the concentration of Nap aqueous solution, mg L^{-1} ; Q is the adsorption amount of Nap per unit quality of the Kosa sample, mg g^{-1} .

(3) The Nap in the aqueous solution did not undergo chemical reactions under dark conditions and longwave UV radiation but degraded under shortwave UV radiation, and 2-formylcinnamaldehyde (2-FCA) and 1,4-naphthoquinone (1,4-NQ) were the first-generated products. The scheme of the conversion of Nap to 2-FCA and 1,4-NQ in the aqueous phase under shortwave UV radiation was presented in **Fig. 3**. The degradation of Nap in the aqueous solution was probably initiated by photoionization, and the reaction rate constant (between $1.44 \times 10^{-4} \text{ min}^{-1}$ and $8.55 \times 10^{-4} \text{ min}^{-1}$) was much lower than that of Nap with hydroxyl radicals. Interestingly, instead of inducing or promoting the chemical change in Nap, the Kosa particles slowed photodegradation due to the extinction of radiation. In addition, acid conditions may not significantly promote the photodegradation of Nap in the saturated water layer on the surface of the Kosa particles. Therefore, the Kosa particles played a less important role in promoting the photodegradation of Nap than UV intensity and water content, which was independent of the difference in Kosa properties.

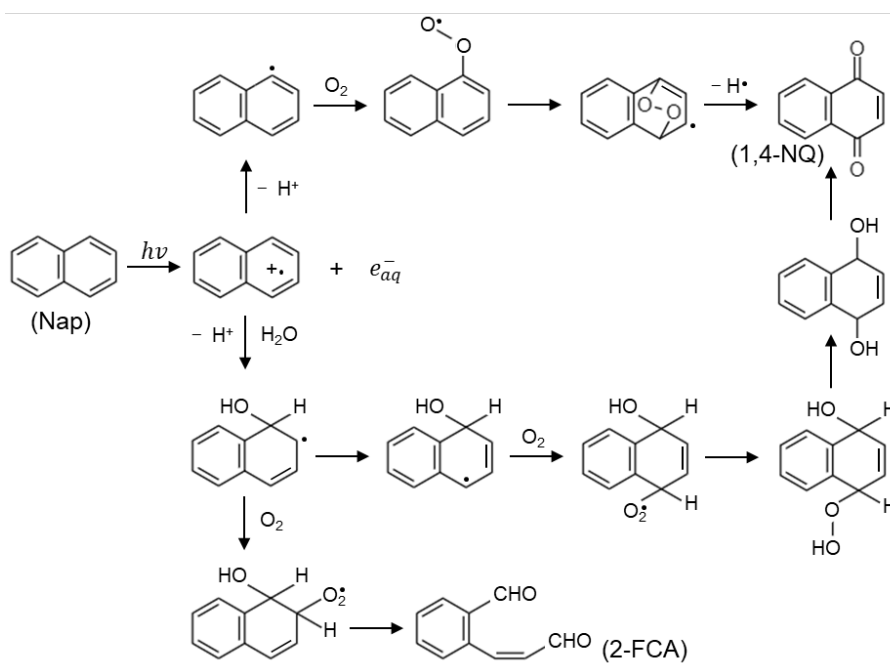


Fig. 3. Proposed photodegradation scheme of Nap in aqueous solution under shortwave UV radiation.

Conclusion

This laboratory study simulated the heterogeneous interaction of Nap with Kosa particles of different geographic origins. The results of this study revealed that Kosa particles had little promotion on the adsorption and photodegradation of Nap, which suggests that Kosa originated from the Asian continent has no substantial interaction with PAHs in the atmosphere.

審査結果の要旨

東アジアモーンsoonの影響によって、古くから大陸で発生した黄砂や硫黄酸化物、窒素酸化物などの大気汚染物質は、初冬から春先にかけて日本に越境輸送されている。一方、本学輪島大気測定局において長期観測した結果、発がん性/変異原性を有する多環芳香族炭化水素 (PAH) も同時期に便乗することが明らかにされ、日本の公衆衛生に与える相乗的な被害が危惧されながらも、輸送中における黄砂と PAH との相互作用による大気汚染物質の変質機構は十分に解明されていない。本研究では、4 つ典型的な砂漠地域でバックグラウンド黄砂を採集して、それらの物性を調べたうえ、模擬大気環境の下、モデル PAH のナフタレン (Nap) を用い、弱酸性又は弱アルカリ性の条件下、紫外線照射有無に分けて黄砂と Nap との相互作用を調べた。その結果、黄砂は Nap に対して弱い物理吸着を示すものの、Nap の光分解に寄与しないことを初めて明らかにした。また大気中 Nap の変質反応は、ラジカル反応が優位であることが示唆された。本研究は、東アジア地域における大気汚染物質の越境輸送中における変質機構の解明に斬新な知見を提供しており、審査委員会は、創薬科学専攻の学位審査基準に照らし、博士 (学術) の学位に相応しいと認め、合格とする。