Long range transport of PAHs with aeolian dusts from eastern Asian continent to Japan : adsorption and stability of PAHs on mineral surfaces

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学位の種類	博士（理学）
学位記番号	博甲第824号
学位授与の日付	平成18年3月22日
学位授与の要件	課程博士（学位規則第4条第1項）
学位授与の題目	Long Range Transport of PAHs with Aeolian Dusts from Eastern Asian Continent to Japan -Adsorption and Stability of PAHs on Mineral Surfaces- （東アジア大陸から日本への黄砂に伴う PAHs の長距離運搬　－鉱物表面における PAHs の吸着とその安定性－）
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Abstract

Long range transport of Polycyclic aromatic hydrocarbons (PAHs) with Asian dust was investigated by collecting Aerosol particles through a year from April 2003 at Kanazawa, Japan. PAHs content in Asian dust particles were highly variable in different Asian dust events. Developed kinetic model showed that sorption rate of less volatile PAHs than BaP on Asian dust particles are too low to be accumulated. The origin of those PAHs in Asian dust particles would be originally PAH-polluted soil particles around industrialized area (e.g. loess regions around industrialized area). Back trajectory analyses also showed Asian dust with high less volatile PAHs content would have derived from loess area while Asian dust with undetectable amount of PAHs would have had source region in Mongolia and northern China. The stability of Pyr (a model PAHs) on different component of Asian dust particles was investigated under controlled temperature and relative humidity (RH) condition with/without light irradiation. Sianol and aluminol catalyze PAHs decomposition in the dark with enhanced catalytic effect by rinse in RH and light irradiation. Clay minerals protect Pyr against rise in RH and light irradiation to last several days. Most realistic carrier of PAHs is clay minerals. Geologic materials contribute atmospheric circulation of PAHs over long distance than previously thought.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that contain more than two fused benzene ring. They are originated by incomplete combustion of fossil fuel and release atmosphere in both gas and aerosol phase depending on their volatility. Since some of PAHs are carcinogenic and mutagenic, their behavior in the environments has attracted much concern. Long range transport have been reported by many researchers in various locations. On the other hand, those from eastern Asian continent over Sea of Japan have not well investigated even growing emissions are expected there by rapid industrial development in China and Russia. Asian dust particles have known to accumulate anthropogenic sulfate and nitrate in the atmosphere. PAHs may be adsorbed as in the case of sulfate and nitrate but such topics has not revealed yet. To understand the role of Asian dusts for atmospheric transport of PAHs over long distance, the conditions for Asian dust to carry substantial amount of PAHs shold be figured out. The stability of PAHs on different components of Asian dust particles should also be clarified to understand the fate of PAHs associated with dust particles during transportation. This study focused on long range transport of PAHs with Asian dust particles over long distance.

Materials and method

To observe the long range transport of PAHs, aerosol particles were collected through a year from April 2003, at Kanazawa, Japan. Asian dust particles were collected in three sampling intervals: Dust period 1 (May 11 to 19), Dust period 2 (May 28 to April 9) and Dust period 3 (April 9 to 25). Asian dust particles dominated in coarse particle size range (2.1-11 μ m). PAHs in coarse and fine particles (<1.1 μ m) were analyzed separately. The stability of Pyrene (Pyr) on the model component of Asian dust particles (quartz, α-alumina, kaolinite, montmorillonite, humic acid and humic acid sorbed quartz) were investigated under controlled temperature and relative humidity (RH) condition with/without light irradiation. The experimental period was set for 3 days.

Results and Discussions

Based on different seasonal trend of PAHs in coarse and fine particles, Asian dust in Dust period 3 was found to contain significant amount of PAHs (especially less voatile PAHs).To reveal specific conditions for the Asian dust particles to carry substantial amount of PAHs, kinetic model based on collision theory of gases was developed. The model can access sorbed and desorbed amount of PAHs on the dust particles in the atmosphere as a function of reaction time. The model showed that sorption rates of volatile PAHs such as Phenanthrene (Phe) and Pyr on the Asian dust particles in urban atmosphere are high enough to be equilibrated with the dust particles. However, the fractions of volatile PAHs in Asian dust particles derived from atmospheric reaction would be usually minor due to low possibility to encounter polluted atmosphere in

PAHs, rapid desorption rates from the dust particles and low organic material fractions in the dust particles. The kinetic model also revealed that sorption rates of less volatile PAHs than Bnzo[a]pyrene (BaP) would be extremely low to be accumulated on the dust particles during transportation. The adsorption kinetic consideration suggested that PAHs associated with Asian dust particles are not likely derived from atmospheric reactions especially for less volatile PAHs. They would be derived originally PAH-polluted soil particles from some industrial areas (e.g. loess regions around industrialized area). Back trajectory analyses reveled that Asian dust in Dust period 3 would have originated around Loess plateau while other "unpolluted" Asian dust would have come from different source regions such as Mongolia and northern China.

Pyr was chosen as model PAHs. Quartz showed a strong catalytic effect for the decomposition of Pyr even these were coated with sorbed humic acid. Pyr sorbed on montmorillonite remained stable in the dark during the experimental period (3 day). Moisture in the experimental cell also decreased the stability of Pyr especially on α-alumina. Light irradiation decreased the stabilities of Pyr on quartz and montmorillonite while the decomposition rate on montmorillonite was slower than on quartz in the dark. Photochemical degradation of Pyr on humic acid was not observed.

Conclusions

From the above observation and experimental results, the actual situation of Asian dust to be a carrier of considerable amount of PAHs over long distance is outlined as follows. The Asian dust to carry large amount of PAHs would be originated around industrialized area in loess region in China where soil particles are already contaminated from ambient industrial area. During transportation, PAHs on Asian dust particles encounter direct irradiation of sunlight and high RH conditions (e.g. over Sea of Japan). At those conditions, PAHs sorbed on quartz and feldspar (with aluminol and sianol) would further decompose by photochemical and moisture effects to decrease the stability of PAHs. On the other hand, considerable amount of PAHs on clay minerals would persist against those effects. Therefore, PAHs (especially less volatile PAHs than BaP) in Asian dust particles transported over Sea of Japan would be dominantly associated with clay minerals. The role of geologic materials for atmospheric circulation of PAHs over long distance is significant than previously thought.

学位論文審査結果の要旨

提出学位論文について各審査委員が個別審査を行うとともに、平成18年2月10日開催の口頭発表を踏まえて、同日開催の論文審査委員会にて検討し、以下の通り判定した。

本論文は、東アジアにおける深刻な環境問題と認識されてきた化石燃料の不完全燃焼由来の多環芳香族炭化水素（PAH）の長距離輸送とそれに関わる黄砂や黄砂構成鉱物の役割を解明するための基礎研究であり、その要点は次の通りである。

中国大陸からの黄砂によるPAH越境移動の有無を確かめるため、黄砂現象が観測される時期を含む1年間のエアロゾル採集を毎週実施し、バイモーダルに分布するエアロゾルの粒径分布データを基に、大小2つの粒径別にPAHを測定した。各粒径におけるPAH含有量の変動パターン、吸着の速度論的解析、空気塊軌跡解析等から、黄土高原付近でPAHに汚染された土壌が黄砂となって運搬されている可能性を初めて示した。また、運搬過程で劇的に変化する様々な温度や湿度条件下での鉱物表面とPAHの相互作用を理解するため、温度・相対湿度制御下での気相－固相反応実験装置を新たに開発した。その結果、石英などの酸化物鉱物では、暗所であっても数日で吸着PAHのほとんどが分解すること、モンモリロナイトなどの粘土鉱物では比較的安定にPAHを保持して運搬媒体となり得ることを明らかにした。

以上のように、本研究は黄砂によるPAHの長距離輸送とその過程における黄砂構成鉱物との相互作用の理解に大きく貢献するものであり、本論文は博士（理学）の学位に十分値すると判断される。