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| 論　文　名 | 「Research on Factors Affecting Concentrations of Polycyclic Aromatic Hydrocarbons in Polluted and Clean Areas（汚染地域及び清浄地域における多環芳香族炭化水素濃度に影響を与える因子の研究）」 |
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# 論文要旨

Atmospheric pollution is a very serious problem in the world, especially in developing countries such as Vietnam. Organic pollutants have been a concern because they are persistent, can transform into more toxic pollutants and travel to other areas from the pollution sources. Polycyclic aromatic hydrocarbons (PAHs) are one of the most well-known atmospheric organic pollutants. PAHs are formed from the incomplete combustion of organic materials including biomass, gasoline, diesel, and coal. In Antarctica, diesel engines are used for research, travel and life; therefore, it is possible that very clean environment in Antarctica is polluted easily by PAHs. There are 12 priority PAHs in the Environmental Protection Agency of Unites States, which are carcinogenic and mutagenic to human health. In this thesis, the effects of

sources and weather conditions on the PAHs concentrations in Vietnam (polluted area) and Antarctica (clean area) were researched.

In Vietnam, the public has been aware of the air pollution; however, details of pollutants, concentrations, and health effects are not well-informed. Moreover, the scientific data based on the chemical characteristics of air pollution is deficient and poor-managed in Vietnam. The reasons are due to the lack of sampling equipment and the high-cost of analytical processes. Even in Ho Chi Minh City (HCMC), the center of economy of Vietnam, the pollution has not been well-investigated. Therefore, in this thesis, an attempt to find alternative sampling methods and analysis methods was performed for acquiring more information of the air pollution in HCMC.

$PM_{2.5}$ is defined as particulate matter (PM) in the atmosphere which have the aerodynamic diameter equal or smaller than 2.5 µm. $PM_{2.5}$ becomes a concern for human health because of not only its ability to penetrate the respiratory system but also toxic compounds attached on its surface. There are many sampling methods to collect $PM_{2.5}$ in the atmosphere. High-volume-air-sampler is the most popular one, but it is heavy and big. In the search of more flexible and mobile method, the low-volume-air-sampler was used to collect $PM_{2.5}$ in our previous study. However, both methods have low resolution (8-hour to 3-days) and semi-continuous or discontinuous. To have better resolution and continual sample source, the monitoring tape from air monitoring station was considered.

This study had an access to the monitoring tapes from the HCMC air monitoring station. $PM_{2.5}$ of the old monitoring tapes from HCMC were used for analyzing PAHs. Interestingly, the PAHs concentrations can be obtained from the monitoring tape, despite the inevitable loss of PAHs during sampling and storing. The resolution of the sample is 24-hour; thus, daily variation as well as seasonal trend of PAHs can be observed. Moreover, a unique event happened during sampling period, Vietnamese New Year holidays, gave a special effect to the air quality. The data gained from the monitoring tape opens more opportunities

to learn further information of chemical composition in particles.

The span of sampling period is one year; thus, around 200 samples were available. With a large quantity of samples, the conventional analysis process for PAHs was not suitable. Gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC) are common methods for analyzing PAHs. The analysis time of GC/MS or HPLC for one sample is comparable, and ranges from 45 to 90 minutes. However, the extraction and clean up processes take up many times and solvents as well as human labor. The extraction time can take from 60 minutes to one day per one sample, depended on the extraction methods. The clean-up process, which is necessary when the air is highly polluted, takes a period of time depended on how contaminated the sample is. Thus, there is a need for a simpler extraction method to shorten the analysis of PAHs. The thermal desorption is used for extracting volatile organic compounds (VOCs) from PM samples, and recently used for semi-VOCs and PAHs. Therefore, the thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) was employed with the advantage of simplicity and quickness.

In Chapter 1, the general knowledge about $PM_{2.5}$ and PAHs including sources, abundance, characteristics and effects on environment and human is introduced. The introduction of the air pollution in HCMC, the necessity of continuous samples and quick analysis method are presented. Two common analysis methods of PAHs, which are HPLC and GC/MS, are explained and compared. For the extraction process used for HPLC, liquid-liquid extraction was used. For the GC/MS method, the thermal desorption method was used for extraction. The comparison of both analysis methods and extraction methods was investigated. The TD-GC/MS method and the optimization for analyzing PAHs are briefly described in the chapter. In addition, the factors affecting the PAHs concentrations including the burning of incense stick for religious in Vietnam, and the activities of research, expedition and life in Antarctica are examined. In both places, the weather conditions showed a strong impact on the air quality.

Chapter 2 introduced the application of TD-GC/MS for analyzing PAHs from the monitoring tape. The study evaluated the possibility of using the tape from air monitoring station for PAHs data. Seasonal variation of $PM_{2.5}$-bound PAHs in HCMC, Vietnam, was investigated by using TD-GC/MS for analyzing filters from an air monitoring station. The optimization of TD-GC/MS parameters showed good results with linearity for most of the measured PAHs, method limit of detection (0.016 – 0.352 ng), and desorption efficiency (95.9 – 100 %). The analysis of PAHs was performed 4 years after the sample collection. To evaluate loss of PAHs in 4 years, the loss under different temperatures and time was examined. The PAHs in real samples were less prone to evaporation than the standard spiked samples at both 25 °C and 100 °C. The concentrations of $PM_{2.5}$ and PAHs were lower in the rainy season and higher in the dry season. The toxic equivalent quantity (TEQ) was higher in the dry season than in the rainy season. Meteorological parameters had a powerful effect on both $PM_{2.5}$ and PAH concentrations, as well as TEQ values, especially wind speed, wind direction, and rainfall. The primary emission source was the exhaustion of gasoline vehicles in both seasons, with a mixture of biomass combustion and industrial sources in the dry season.

Chapter 3 showed the influence of cultural activities during Vietnamese New Year holidays on $PM_{2.5}$-bound PAHs. TD/GC-MS was utilized to analyze 12 PAHs in $PM_{2.5}$ samples. This is the first study about the change in air quality due to the cultural activities in Vietnam. The PAHs concentrations were depended intensely on traffic patterns, with the decrease of $PM_{2.5}$ and PAH concentrations throughout holidays. In addition, wood/coal combustion related to the firework, domestic combustion, and burning incense/candle were important sources during holidays. The value of the indeno[1,2,3-*cd*]pyrene / (indeno[1,2,3-*cd*]pyrene + benzo[*ghi*] perylene) ratio was 0.72 in VNY, which was similar to that from cooking, candle, and incense burning. The average incremental lifetime cancer risks were also evaluated. In this chapter, the cultural activities had shown their effect on PAHs concentrations, especially burning

incense stick during traditional holidays.

In Chapter 4, the chemical characteristic, burning rates and ash emission factor of $PM_{2.5}$ from Japanese and Vietnamese incense sticks were evaluated. The PAHs concentrations were positively correlated with the burning rate, and negatively related to the ash emission, especially high-molecular-weight PAHs. The Japanese incense sticks had lower concentrations of PAHs compared to the Vietnamese incense sticks. The 3- and 4-ring PAHs occupied 0 –81.53 % and 17.66 – 92.88 % of the total PAHs, respectively. The variation of ingredients is the most important factor for the PAHs concentrations. Organic compound (OC) was the dominant carbonaceous contents of the $PM_{2.5}$ from incense stick compared to elemental compound (EC). The PAHs had strong relation with EC. The char/soot ratio larger than 1, indicating most of the EC was char-EC. Inorganic components in $PM_{2.5}$ were also investigated.

Chapter 5 showed the effect of human activities, especially diesel engine, to the Antarctic environment. Instead of collecting air, the snow sampling was conducted during the research, and the PAHs concentrations in snow were measured. The sources of these PAHs were the snow mobiles and diesel electric generators used for scientific research from 29th December 2015 to 4th February 2016. Most of the measured PAH concentrations were low before the research campaign (lower than the detection limit or quantification limit), then increased due to the research activities, and finally decreased to a low level, probably because of strong blizzard winds. In addition, photolysis of the PAHs in the polluted snow samples under Antarctic conditions was investigated. However, a decrease in PAH concentration was not observed in 11 days. It was concluded that photolysis was not the main sink of the PAHs in the Antarctic snow, but the occurrence of blizzard/drifting snow decreased the PAH concentration.

Chapter 6 concludes all the information in the thesis and summaries the previous chapters.

# 審査結果の要旨

本論文は、汚染地域であるベトナムホーチミンの大気中の $PM_{2.5}$ 中の多環芳香族炭化水素類（PAHs）の季節変化の特徴と清浄地域である南極での調査活動に伴う PAHs による雪の汚染を調査した結果をまとめたものである。PAHs は発がん性が強く、健康や生態系への影響が大きい物質として近年注目されている物質である。しかし、その分析には前処理を含め煩雑な操作を必要とするため連続観測が難しい。また、南極での調査では現地へのアクセスの難しさから測定例が非常に少ない。このような状況の中、本研究では次のような新たな結果を得ている。

(１) ホーチミンのモニタリングステーションで捕集、保管されていた過去の約 1 年分の $PM_{2.5}$ 試料を利用し、熱分解／ガスクロマトグラフ／質量分析法で $PM_{2.5}$ に含まれる PAHs を測定した。その結果、過去の試料を用いてもその場での PAHs 濃度の季節変化を知ることができることを世界で初めて示した。

(２) 上記の測定期間の中でも特徴的であったベトナムの旧正月前後の PAHs を詳細に解析し、市民の大移動による交通量の変化が、PAHs の組成におおきな変化をもたらすことを明らかにした。これも従来知られていなかったことであり、非常に貴重な結果を示した。

(３)ベトナム及び日本の線香の燃焼から放出される PAHs とその中に含まれる有機炭素濃度及び元素状炭素濃度の測定を行い、それぞれの特徴を示し、健康リスク評価を行い、密閉空間での毎日の使用が危険であることを示した。

（４）南極の調査活動で使用される雪上車や発電機から放出され雪上に沈着した PAHs の測定を行い、調査によって雪中の PAHs 濃度が増加すること、ブリザードにより飛散すること、太陽光だけでは短時間では分解しないことを明らかにした。

以上の結果は、世界各地で保存されている $PM_{2.5}$ の捕集試料から過去の環境を調査することができ、特に発展途上国のような調査の遅れている地域の調査に有効であることを示したもので、大気環境分野の今後の発展に大きく寄与するものである。また、電気のないクリーンな地域での調査で PAHs による汚染がどのようにその地域に影響を与えるかを示したもので、環境調査に対する重要な指針を与えるものである。いずれも大気環境の研究領域で多大な貢献があり、申請者が自立して研究活動を行うのに必要な能力と学識を有することを示したものである。