

Source Identification of Polycyclic Aromatic Hydrocarbons (PAHs) In Agriculture and Forestry Area using Ambient Air and Soil

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Introduction

Sources of PAHs are very various and ubiquitous in the environment. The important sources of PAHs are imperfect combustion processes such as family heating that use fossil fuel of oil, use of coal and various industrial facilities such as power plant, forest fire, incinerator, cooking etc.¹⁻⁴

Organic chemicals such as PAHs in flue gas from incinerator have important atmospheric process and are removed from the atmosphere by dry and wet deposition process to soil.⁵ And, PAHs of gas and particle phases through the deposition process and scavenging can be accumulated to soil in environmental.^{3,6-7}

This study was carried out to investigate the PAHs level in flue gas, ambient air and soil, and to assess the PAHs profile pattern from these Medias. Furthermore, flue gas from incinerator, ambient air and soil were collected from agriculture and forestry areas in order to conduct source identification by using Statistical analysis, such as Dendrogram and cross-plot analysis.

Materials and Methods

Sample collection

The samples used in this study were ambient air, soil and emission flue gas. Ambient air was sampled twice in summer and winter, and 28 soil samples were collected to investigate sixteen priority PAHs including the 6 carcinogenic PAHs in agriculture and forestry area in 2007. Figure 1 shows the locations that all samples were collected. Two emission gas samples from incinerator which were considered as the only point source in the study areas were also sampled to compare with other matrices.

Extraction

Ambient air and soil samples were extracted by the Soxhlet extraction. Emission gas sample was extracted using the Soxhlet extraction and Liquid-Liquid extraction. Before the extraction, spiking was held using ¹³C₁₂-labeled-PAH Congener as internal standards. The extract samples were concentrated by the Rotary Vacuum Evaporator. The concentrated extract samples were placed in the dry thermo bath where the conversion of solvent occurred. By adding N₂, n-hexane and dichloromethane was removed and only Hexane with PAHs remained.

Clean Up

130 ° C 16 hours activated silica gel column was used. N-Hexane with dissolved PAHs was passed through the silica gel column. Afterward, the 100mL solution with 10% dichloromethane and 90% hexane was eluted from the silica gel column. The eluted materials were concentrated to approximately 200uL.^{7,9}

GC-MS Chromatography of PAHs

Instrumental analysis of PAHs was held by using High Resolution Gas Chromatography and Mass Spectrometry (SHIMADZU QP2010, SHIMADZU). The Capillary column used was a HP-5 MS (30m x 0.25mm x 0.25um).

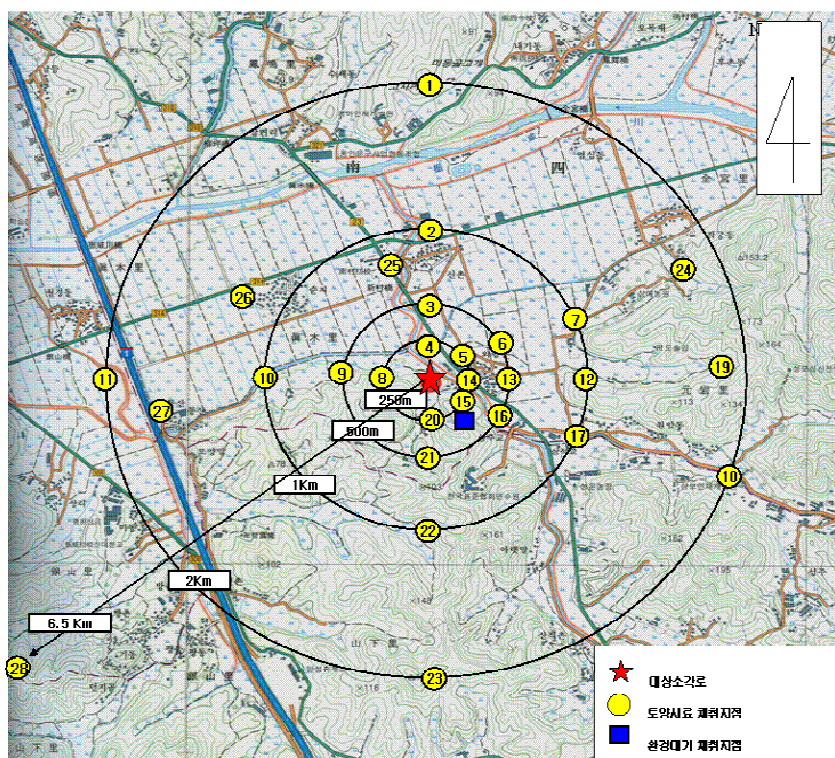


Fig. 1. Sampling location.

Result and Discussion

Concentration levels of PAHs in flue gas, ambient air and soil samples

Fig. 2 shows the concentration level and profiles of sixteen priority PAHs in flue gases, ambient air and soil samples. Sixteen priority PAHs concentration in flue gases were varied by the season: 547.55 $\mu\text{g}/\text{m}^3$ in winter and 182.99 $\mu\text{g}/\text{m}^3$ in summer. The concentrations of carcinogenic PAHs from the flue gas were 120.48 $\mu\text{g}/\text{m}^3$ in winter and 0.02 $\mu\text{g}/\text{m}^3$ in summer. Concentration level of ambient air samples in winter and summer were 140.99 ng/m^3 in winter and 35.94 ng/m^3 in summer. Also, the concentration levels of carcinogenic PAHs from ambient air were 22.5 ng/m^3 and 7.67 ng/m^3 in each season. Concentration level of soil samples ranged from 68.99 ng/g

d.w. to 6730.95 ng/g d.w. and average concentration was 632.19 ng/g d.w..

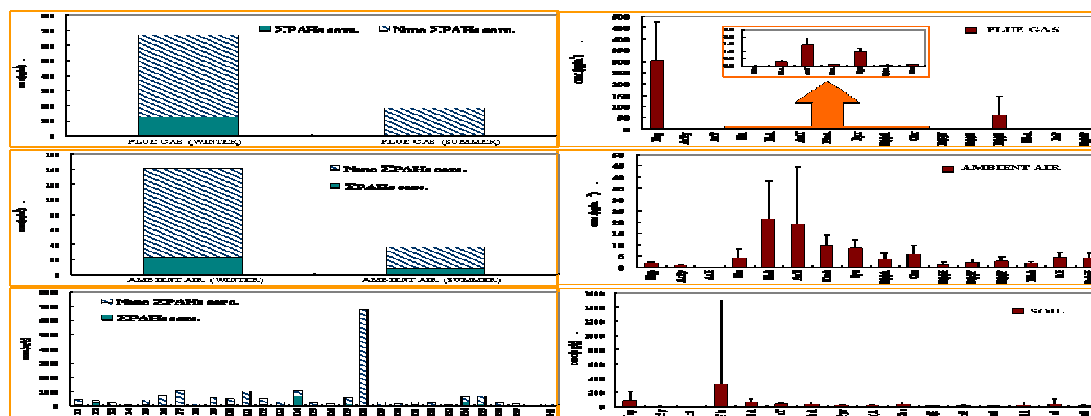


Fig. 2. Concentration and profiles of 16 PAHs in flue gas, ambient air and soil samples.

Characteristics of PAHs for rings

Analysis for ring groups was carried out to characterize specific character of samples. Ratio of 2 rings group including Naphthalene largely dominated in concentration in flue gas samples. On the other hand, ambient air for ratio of sixteen PAHs by ring groups exhibited as 3 Ring > 4 Ring > 5 Ring > 6 Ring > 2 Ring groups in the order. Moreover, soil sample showed similar order with ambient air like 3 Ring > 4 Ring > 2 Ring > 5 Ring > 6 Ring groups (Fig. 3).

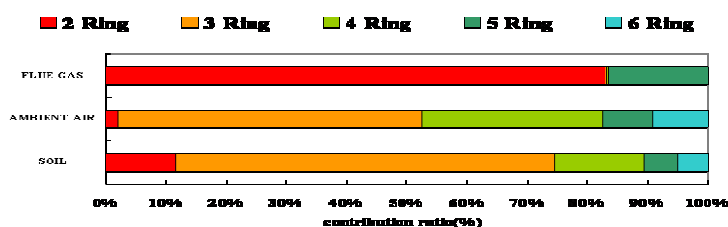


Fig. 3. Ratio of each Ring groups of 16 PAHs.

Statistical analysis

Cluster analysis was carried out for two flue gas samples, two ambient air samples and twenty-eight soil samples (Fig. 4). As a result, all ambient air and numerous soil samples were grouped into the first or second group, showing the pattern similar to the origin patterns. Otherwise, different pattern of concentration was showed in flue gas samples having the other groups. These results showed that ambient air and soils are not largely influenced by the incinerator as source in the study area.

In order to conduct source identification and discrimination of PAHs in environmental receptor media and sources, the calculation of ratios were done to specifically indicate compounds, and to distinguish and compare

the origins of pyrogenic and petrogenic from concentration of specific PAHs compounds.

Yunker et al. (2002)¹⁰ applied and proposed that for Anthracene(AnT)/Phenanthrene(PhA) vs. Fluoranthene (FluA)/ Fluoranthene+Pyrene(FluA+Pyr) of ratio to indicate compounds, and Indeno(1,2,3-c,d)pyrene(InP)/ Indeno[1,2,3-c,d]pyrene+Benzo[g,h,i]perylene(InP+BghiP) vs. Fluoranthene(FluA)/ Fluoranthene+Pyrene(FluA+Pyr) to the estimation of origins by ratio of indicate compounds to pyrogenic and petrogenic for PAHs from samples. Figure 3. shows result of cross-plot analysis for InP/(InP+BghiP) with FluA/(FluA+Pyr) and AnT/PhA, with FluA/FluA+Pyr. Most soil samples showed patterns originated from Grass/Wood/Coal combustion. The origination pattern from Grass/Wood/Coal combustion was also observed in the analysis of AnT/PhA with FluA/FluA+Pyr in soil samples and ambient air samples.

In conclusion, soil and ambient air are not influenced by incinerator, but by combustion of agricultural by-product from the agriculture and forestry area, like the areas that samples were obtained for this study. Also, it was concluded that emitted PAHs from combustion of agricultural by-product is persistent and accumulative in soil.

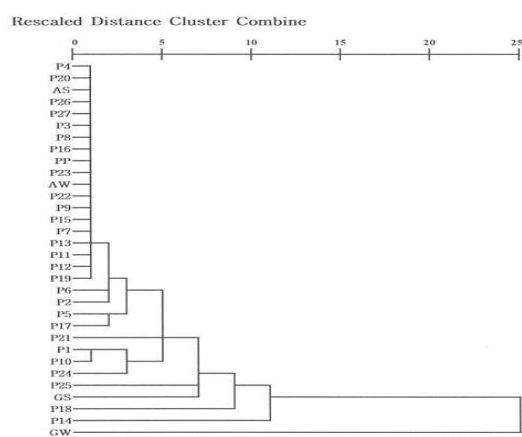


Fig. 4. Dendrogram of samples of PAHs profile
Source identification of PAHs in soil samples.

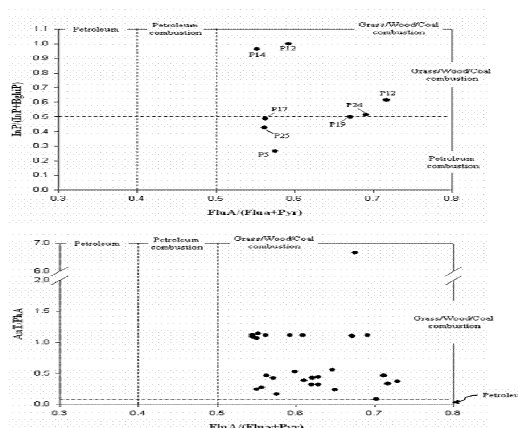


Fig. 5. cross-plot analysis (▲ : ambient air , ● : soil sample).

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