Supercritical Fluid Extraction and Chromatographic Analysis of Polynuclear Aromatic Hydrocarbons in Iligan City and Cagayan de Oro City Street Dusts: A Method Development and Application Study

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Abstract

The development and application of optimized analytical procedures for the determination of selected polynuclear aromatic hydrocarbons (PAHs) namely naphthalene, phenanthrene, fluoranthene, pyrene, and benzo[a]pyrene in street dusts is described. Samples were extracted by supercritical fluid extraction (SFE), followed by concentration of the extract using Kuderna-Danish concentrator. Cleanup was done by passing the extract through silica gel column and eluting with 1:1 hexane/dichloromethane solvent mixture. Analysis was performed by HPLC with fluorescence detection. The developed SFE method achieved an overall accuracy of 99.86% with an overall precision of 9.48% RSD. The developed SFE-HPLC method was used to analyze street dusts samples collected from Iligan City and Cagayan de Oro City representing concrete/heavily-trafficked, asphalt/heavily-trafficked, and asphalt/lightly-trafficked streets. PAHs concentration ranged from 0.005 to 12.04 microgram per gram (□g/g) with phenanthrene and fluoranthene concentrations found to be above the maximum permissible level for the protection of human health. Compared to asphalt, traffic has greater contribution to phenanthrene, fluoranthene, and pyrene concentrations.

Keywords: supercritical, SFE, street dusts, chromatographic,
polynuclear aromatic, PAH

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Introduction

Polynuclear aromatic hydrocarbons (PAHs) have long been recognized as hazardous environmental chemicals. Studies have shown that several of these compounds are carcinogenic and/or mutagenic, thus, posing a health threat to humans (Chuang *et al.*, 1995; Jones *et al.*, 1989; Wagrowski, 1997). Mainly formed during the combustion of coal and petroleum, PAHs are widely distributed in soils and sediments throughout the world. On urban street surfaces, PAHs of various origins (*e.g.*, weathered materials of street surfaces, automobile exhaust, lubricating oils, gasoline, diesel fuel, tire particles, and atmospherically deposited materials) are present as street dusts. The street dust material is washed from roads during heavy rain storms and transported to rivers, wastewater treatment plants, and estuaries. Although street dusts are considered to be one of the important sources of PAHs in the aquatic environment and could also be a significant contributor of PAH in house dusts, the data available on PAHs in street dusts are limited (Takada *et al.*, 1990 and Chuang *et al.*, 1995).

Supercritical fluid extraction (SFE) has gained increased attention as a replacement for conventional liquid solvent extractions like sonication or Soxhlet extraction. As a sample preparation technique, SFE offers the advantage of reduced solvent usage as well as some potential for separating analytes and interferences during extraction while giving results comparable, if not better, to those of conventional liquid extraction methods (Song and Ashley, 1999; Guo *et al.*, 1999).

The present report describes the development and use of supercritical fluid extraction and high performance liquid chromatography as sample preparation and analyte detection techniques, respectively, in the determination of the presence, abundance, and profile of five selected PAHs of prime concern in terms of environmental significance. The relative importance between heavy traffic and asphalt as contributing factors/source materials for PAHs in street dusts was likewise evaluated..

Experimental

Supercritical Fluid Extraction of Samples. All supercritical fluid extractions of samples were done using an ISCO SFX 2130 System (ISCO, Inc., Lincoln, Nebraska), with carbon dioxide as the supercritical fluid. A schematic diagram of the SFE system is shown in **Figure 1.**

Optimization of HPLC Parameters and PAHs Linear Calibration Curves. Identification and quantitation of the PAHs were effected by reference to responses of known standards, using Shimadzu LC-10AS HPLC with fluorescence detector and Wakosil-II-5C18~AR (reversed phase) column. A response test was done on each of the PAH test solution. Upon knowing the response profile of all analytes, the optimum conditions (mobile phase composition, flow rate, injection volume as well as detector wavelength) for all target PAHs in the HPLC system were then determined. Then calibration curve for each PAH analyte was prepared by running a series of HPLC analysis using different concentrations of standard solutions of the analytes.

PAHs Recovery Study from Silica Gel Cleanup Step: 1:1 versus 2:1 n-hexane/dichloromethane. Quantitative amount of a standard solution of PAH analyte mixture (five-component) in cyclohexane was passed through or loaded onto a silica gel column and eluted sequentially with both n-hexane and 2:1 n-hexane:dichloromethane solvent systems. The target n-hexane/dichloromethane fraction was collected, solvent-exchanged with acetonitrile then concentrated through N2 purging before analysis by HPLC. The above procedure was repeated, this time using 1:1 instead of the 2:1 ratio of n-hexane/dichloromethane. Eluates from unloaded columns were also analyzed.

fluoranthene, pyrene and benzo[a]pyrene, respectively. Linear regression analyses of all standard calibration curves (see **Figures 2** and **3**) gave values for the square of the correlation coefficients (r2) in the range 0.987-0.999, indicating excellent correla

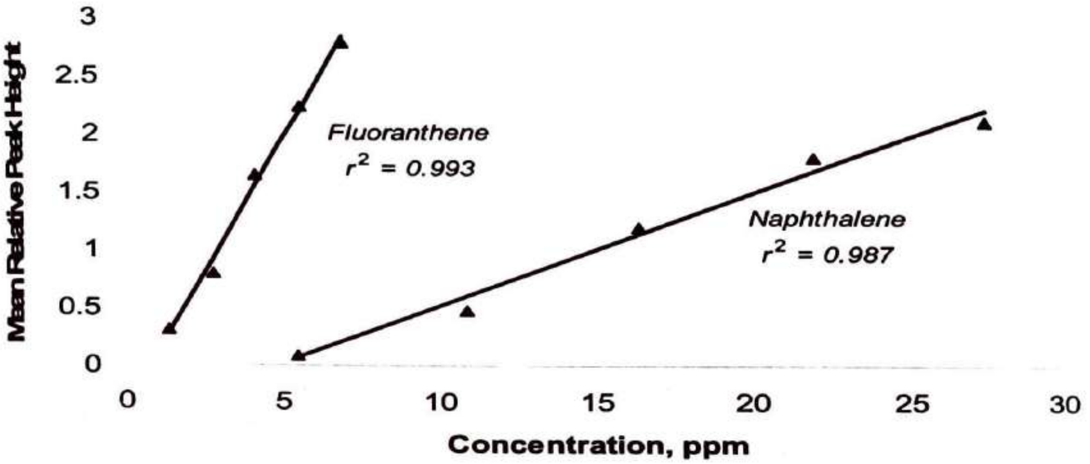

Figure 2. The standard calibration curves for naphthalene and fluoranthene based from internal standard technique.

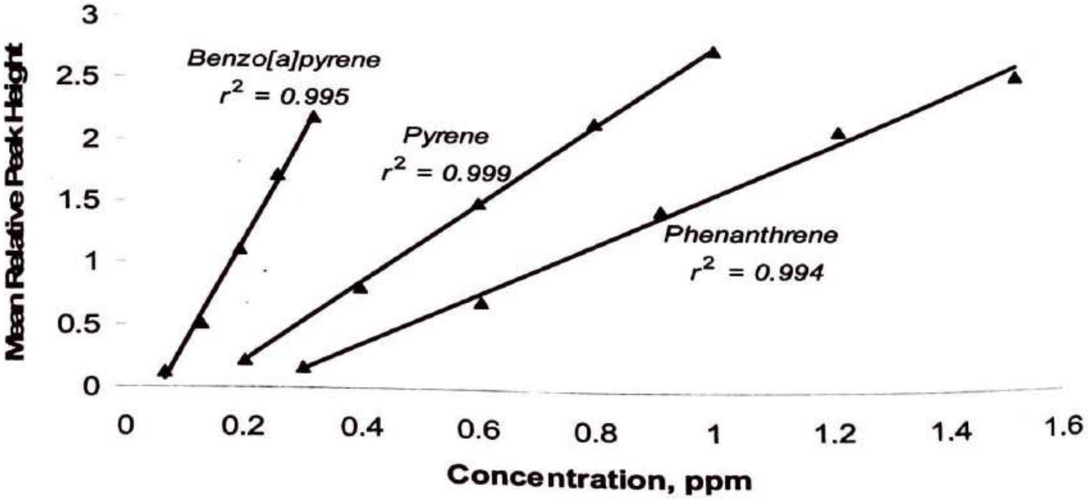

Figure 3. The standard calibration curves for phenanthrene, pyrene, and benzo[a]pyrene based from internal standard technique.

PAH Recovery from Silica Gel Cleanup: 1:1 versus 2:1 n-hexane/dichloromethane . Other compounds that are coextracted from the sample may be present and thus interfere in the detection of PAHs analytes. Thus elimination of these interferences is necessary. But before any developed cleanup technique can be utilized, it should demonstrate that the recovery of each compound of interest is no less than 85% (U.S. EPA, 1982).

Before using silica gel cleanup technique, the extract solvent must be exchanged with cyclohexane. **Figure 4** shows the graphical comparison of PAH recoveries for the silica gel cleanup method. Except for naphthalene, the mean % recovery for all analytes using the two ratios (1:1 and 1:2) of hexane/dichloromethane solvent systems as eluents were all above 85. However since the % recovery for all target PAHs using 1:1 n-hexane/dichloromethane was in the range 90% - 96%, this was then chosen as the eluting solvent in subsequent analysis.

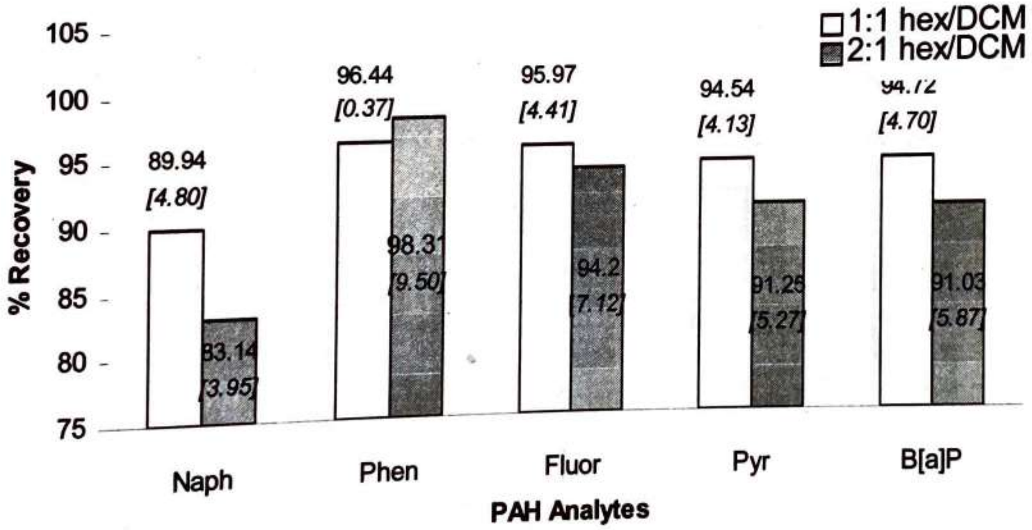

Figure 4. Graphical comparison of PAH recoveries for the silica gel cleanup method using 1:1 vs 2:1 (v/v) n-hexane/DCM ratio.

Extraction Efficiency: SFE versus Soxhlet. In the absence of standard reference material (SRM), the recovery of spiked analytes from a sample is a routine procedure in developing and validating the extraction methods used. This study however did adsorption and equilibration processes, after fortification or spiking of analytes onto the sample, to simulate a native or real-world sample (Reighard and Olesik, 1996). Before extraction, the spiked samples were aged for a period of at least a month to allow spiked analytes to migrate to remote or stronger binding sites in the sample matrix. This is in contrast to the process of analyte spiking and subsequent extraction a few minutes to a few hours later. In such case, the extraction of the spiked analytes varies significantly from the extraction of native analytes (Burford *et al.*, 1993).

The results from the developed SFE method were compared with those from the accepted and known-to-be-accurate Soxhlet extraction method. **Figure 5** shows the graphical comparison of SFE and Soxhlet recoveries. The overall accuracy expressed as % recovery obtained using SFE was 99.86% while that of Soxhlet was 107.81%. Both SFE and Soxhlet methods gave comparable mean % recoveries for all analytes except for fluoranthene. However, because of its high %RSD, the fluoranthene data from Soxhlet method was considered less reliable. *t*-test showed that the mean % recoveries for all analytes are the same for the two methods. Thus, the developed SFE method, which offers the advantage of speed and reduced solvent usage, was considered acceptable for its intended purpose.

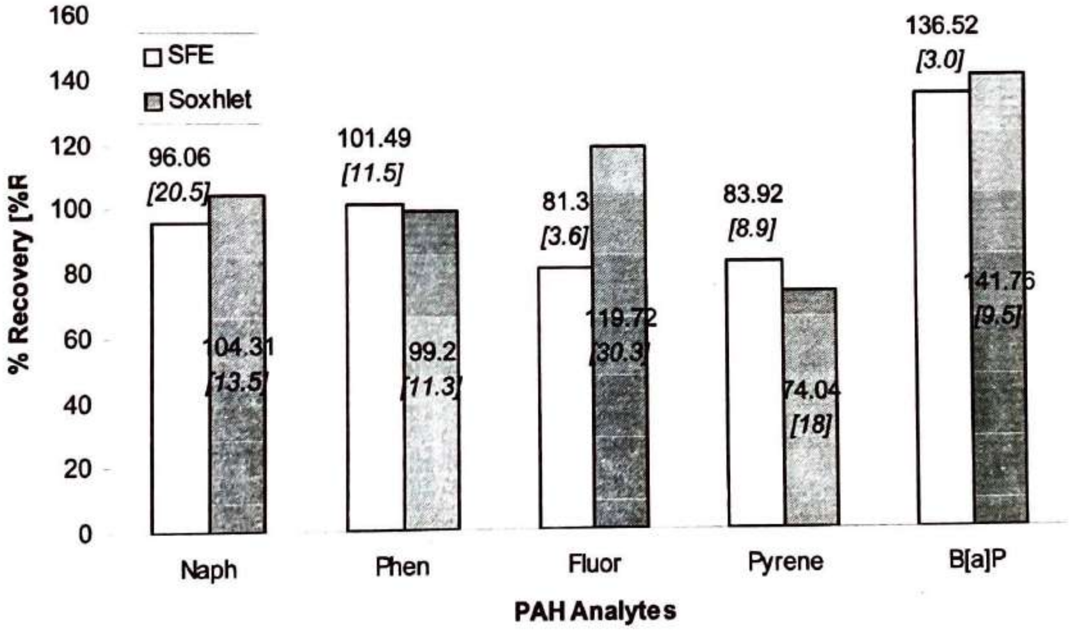

Figure 5. Graphical comparison of PAH recoveries from PAH-fortified and aged street dusts using SFE and Soxhlet extraction.

Determination of PAHs in Street Dust Samples from Iligan City and Cagayan de Oro City: Application of the Developed Method. **Figure 6** shows the results of the SFE of real street dust samples from Iligan and Cagayan de Oro Cities. Note that all target analytes were found to be present in all sampling sites. The detected concentration levels for naphthalene, phenanthrene, fluoranthene, pyrene and benzo[a]pyrene ranged from 0.090-0.239 microgram per gram (□g/g), 0.022-0.477 □g/g, 0.430-12.04 □g/g, 0.005-0.174 □g/g and 0.021-0.377 □g/g, respectively, with concentration level of fluoranthene for all 9 sites as the highest. Except for naphthalene and benzo[a]pyrene, a general concentration trend for phenanthrene, fluoranthene, and pyrene exists, and was observed to be as follows: asphalt-paved/heavily-trafficked > concrete/heavily-trafficked > asphalt-paved/lightly-trafficked. The above observation would indicate that PAH sources in heavily-trafficked sites have greater contribution to the concentration levels of the said 3 PAHs as compared to that of the asphalt contribution. Statistical analysis, however, ruled out any significant difference on the amount of PAH between concrete and asphalt-paved and between heavily-trafficked and lightly-trafficked streets.

Figure 7 shows a graphical correlation of the PAH levels in the street dust samples to U.S. EPA maximum permissible levels for the protection of human health. Note that an important finding depicted in the graph is that the phenanthrene and fluoranthene levels exceed (and are significantly different from that of) the U.S. EPA maximum permissible level.

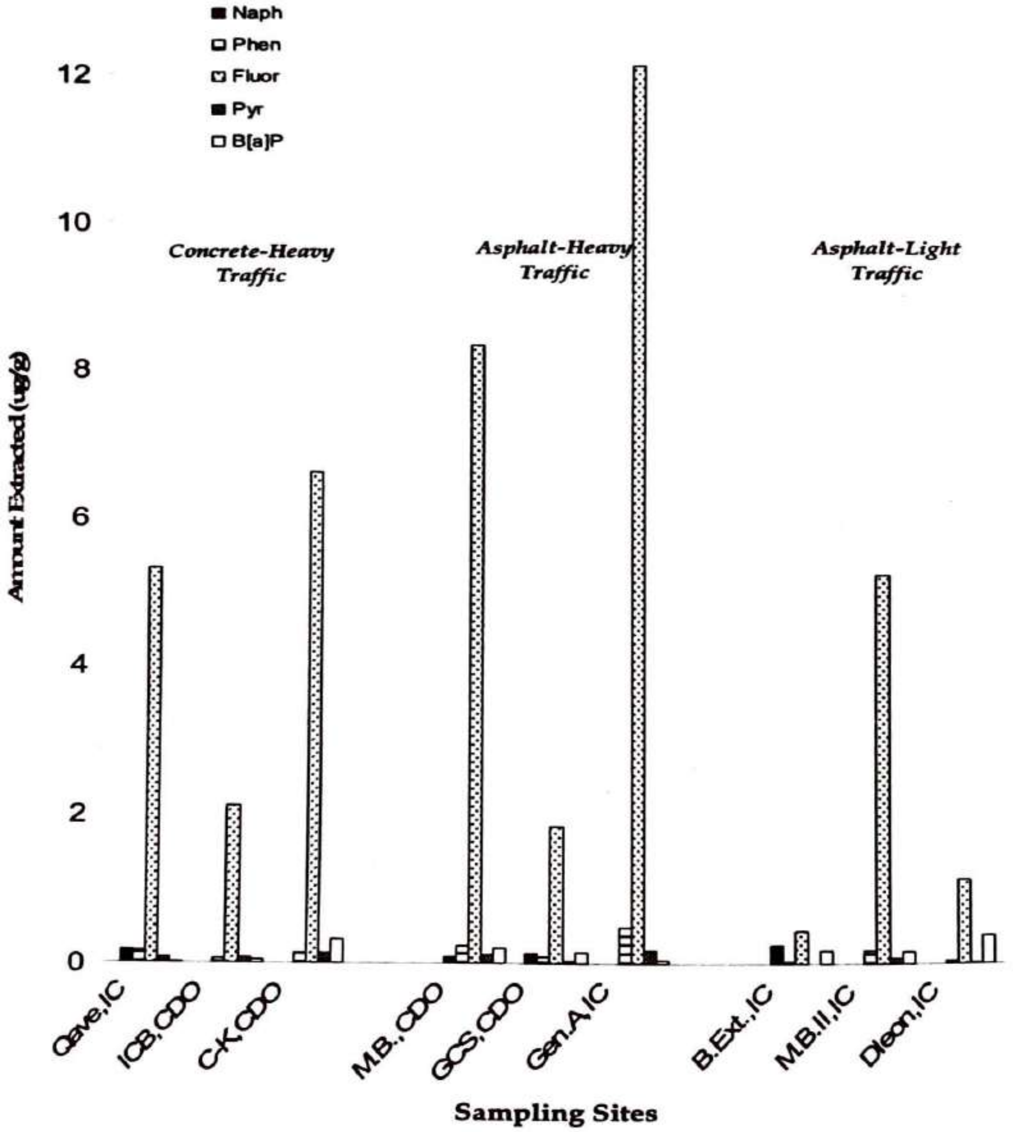

Figure 6. Graphical PAH concentration profiles in the dust samples collected from concrete/heavily-trafficked, asphalt-paved/heavily-trafficked, and asphalt-paved/lightly-trafficked streets. Quezon Ave.,IC (Qave,IC); Iligan-CDO-Butuan Superhighway, CDO (ICB,CDO); Carmen – Kauswagan Road , CDO (C-K,CDO); Marcos Bridge, CDO (MB,CDO); Gen. Capistrano St.,CDO(GC St., CDO); Gen. Aguinaldo, IC (G.A.,IC); Badelles Ext.,IC (Bext,IC); Mandulog Bridge II,IC (MBII,IC); DeLeon St.,IC (Dleon,IC).

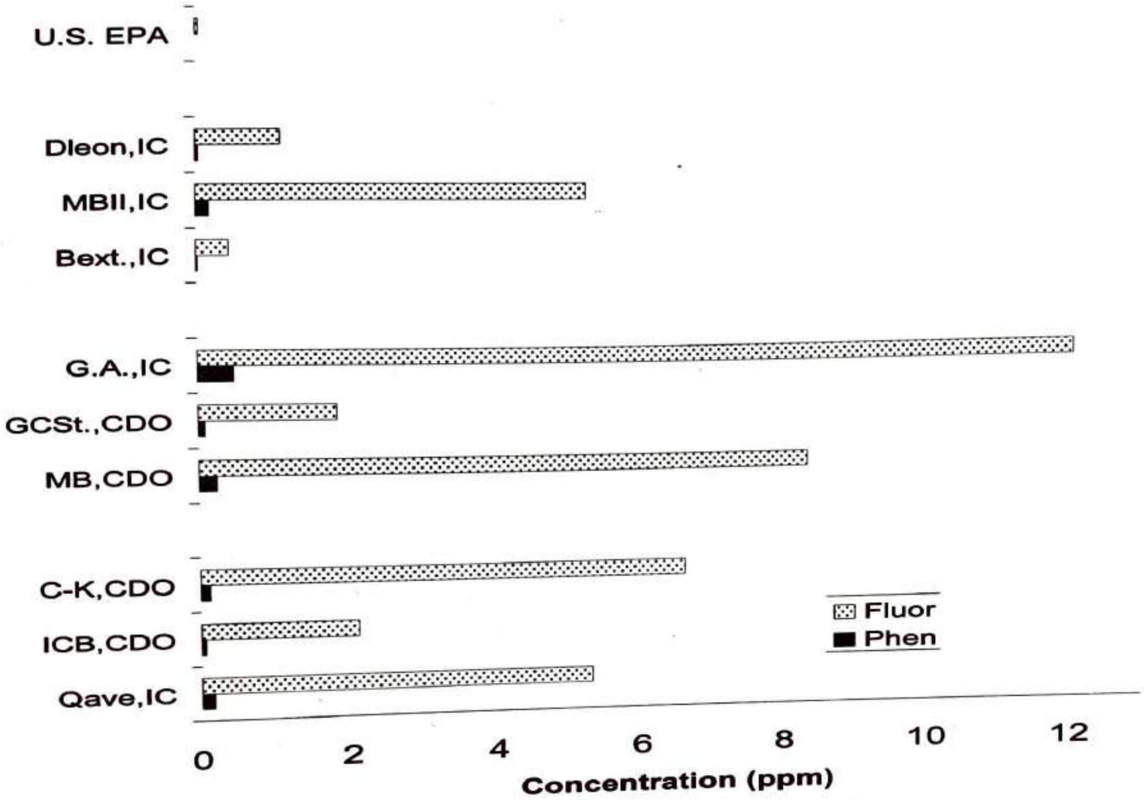

Figure 7. Graphical correlation of the PAH levels in street dust samples to U.S. EPA maximum permissible levels for the protection of human health.

Conclusion

The development, optimization, and validation of an SFE-HPLC analytical method for the isolation, detection, and quantitation of selected PAHs in street dust matrix have been presented in this study. The faster, safer and more environmentally friendly SFE extraction method was found to have performance at par with that of Soxhlet method, thus is acceptable for application purposes. Application of the developed SFE method showed the presence of phenanthrene and fluoranthene at concentration levels above the permissible levels of PAHs for the protection of human health, based on U.S. Environmental Protection Agency guidelines. Furthermore, heavy traffic was found to have greater contribution to the phenanthrene, fluoranthene, and pyrene concentration levels in street dusts as compared to the contribution attributed to the asphalt composition of a street.

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