Polycyclic aromatic hydrocarbons in urban air:
Concentration levels, patterns and source analysis in Yokohama, Japan and Nairobi, Kenya
都市大気中の多環芳香族炭化水素：
横浜とケニア、ナイロビにおける濃度レベル、組成、および、発生源の解析

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ABSTRACT

This thesis describes research done on particle bound polycyclic aromatic hydrocarbons (PAHs) in two different cities, Yokohama, Japan and Nairobi, Kenya.   The main aim of the research was to provide information on levels, profiles and sources of selected PAHs in different areas in both cities.   Atmospheric particle air samples in Yokohama, were collected near specific industries, for example motor vehicle assembly, steel, cement and chemical manufacturing plants, power generation, gas processing plant, and municipal waste incineration, where there is little information on PAH profiles.   Other areas sampled included traffic area, Yokohama National University and residential area.   In Nairobi, the samples were collected in three different areas; traffic, industrial and residential.   The samples were stored under freezing conditions until extraction.   Extraction was done using Soxtherm machine, cleaned and analyzed by gas chromatography mass spectrometry (GC-MS).

In Nairobi, Kenya, principal component analysis showed four significant principal components accounting for 82% of the variance.   The first principal component (35%) was associated with fuel burning. The second principal component (27%) was associated with traffic emissions (diesel and gasoline).   The other two principal components, which accounted for 12% and 8%, could not be interpreted with certainty.   In Yokohama, principal component analysis with varimax rotation for a five-factor solution explained 70% of the variance.   Factor 1 explaining 28% of the variance was interpreted as traffic emissions.   Factor 2 explaining 20% was associated to industrial activities (power, steel, cement and gas processing plants).   Factor 3 and 4 each explaining 10% of the variance were combined and interpreted as municipal waste incineration and domestic fuel burning in residential areas. Factor 5 accounting for 9% could not be interpreted with certainty.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants formed during the incomplete combustion of organic matter (Mackay and Hickie, 2000).   Profiles obtained from environmental monitoring might differ from actual source data due to such factors as mixing of PAHs from different sources, degradation during transport, weather conditions, and type of fuel used in a particular source (Simcik et al., 1997).   Therefore, site-specific PAH signatures help relate the compositional profiles from suspected sources to local and regional atmospheric conditions.   In this study Preceding PCA, individual PAH concentrations were transformed to individual PAH percentages, divided by the total PAH concentrations measured in each sample and multiplied by 100 (Kim et al., 2004).

2. Materials and Methods

Atmospheric particle samples were collected on quartz filters (QR100, Advantec, Japan; cut to 3.2-cm diameter and preheated to 450∘C for 4 hours), using a mini-pump (Sibata, Tokyo, Japan) at 5 L•min^{-1}.   The PAH analysis was adapted from previously published methods (Pleil et al., 2004; USEPA, 1996).   Briefly, the filter samples were spiked with 100 µL of 1.25 µg/mL of deuterated PAH mixture containing naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysened12, perylene-d12, and benzo[ghi]perylene-d12 prior to extraction (EPA 8270 surrogate mix, Sigma-Aldrich, USA).   Automated Soxhlet equipment (Soxtherm, Gerhardt, Germany) was used in extracting the PAHs from the filter samples.   Two µL of the extracted sample in the vial was injected into a GC/MS (Agilent HP6890 series GC and HP5973 series MS) equipped with a DB-5 capillary column (60 m × 0.25 mm i.d.; 2.5 µm film thickness, J&W Scientific, Folsom, CA) and detected by selected ion monitoring (SIM) mode.

3. Results and Discussions

Statistical analysis was performed using statistical software (StatSoft Inc, Tulsa, USA).   The data was analyzed for sources by isomer ratios, Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF).

Briefly, PAH levels in Yokohama were dominated by the 3- and 4-ring PAHs (phenanthrene and pyrene) the geomean levels ranged 28.2 - 82.3 ng•m^{-3} and 8.5 - 29.5 ng•m^{-3}, respectively.   In Nairobi the 6-ring benzo[ghi]perylene and 4-ring pyrene were more dominant and their geomean levels were 6.2 - 18.7 ng•m^{-3} and 11.3 -

16.1 ng•m^{-3}, respectively. Geomean levels of carcinogenic benzo[a]pyrene ranged 1.3 - 1.8 ng•m^{-3} in Yokohama and 5.1 - 7.1 ng•m^{-3} in Nairobi. Isomer ratio analysis in both cities was able to differentiate traffic from non-traffic sources.

The cancer risk associated with total particle bound PAHs was calculated from the value of unit risk of 9×10^{-5} per ng•m^{-3} provided by the WHO, Europe. In Nairobi, this risk was found to be 1.3×10^{-3} in residential, 1.2×10^{-3} in traffic, and 9.0×10^{-3} in industrial areas, respectively. The risk associated with total PAHs in Yokohama was 2.7×10^{-4} in Yokohama National University area and approximately 4.0×10^{-4} in industrial, municipal waste incineration, and residential areas.

In Nairobi, principal component analysis showed four significant principal components accounting for 82% of the variance. The first principal component (35%) was associated with industrial oil combustion. The second principal component (27%) was associated with traffic emissions (diesel and gasoline). The other two principal components, which accounted for 12% and 8%, could not be interpreted with certainty. Further study is needed for interpreting all the sources of PAH in Nairobi, which will require more data points.

In Yokohama, principal component analysis with varimax rotation for a five-factor solution explained 70% of the variance. Factor 1 explaining 28% of the variance was interpreted as traffic emissions. Factor 2 explaining 20% was associated to industrial activities (power, steel, cement and gas processing plants). Factor 3 and 4 each explaining 10% of the variance were combined and interpreted as municipal waste incineration and domestic fuel burning in residential areas. Factor 5 accounting for 9% could not be interpreted with certainty but due to a high loading of anthracene, this factor could be linked to industrial sources.

Cluster analysis results for Yokohama data was used together with wind direction data in the interpretation of the PAH sources. At hierarchical distance of 60, five clusters were obtained and four were used in this data analysis. Assuming that Yokohama National University area is the receptor area influenced by PAH from different sources, several samples showed some influence from industrial, municipal waste incineration and traffic areas. Samples collected in the first municipal waste incineration area north and south of the plant showed changes in the profiles when the wind was directly blowing from the plant to the sampling point. The only PAH that could be explained with certainty was retene because its contribution was directly affected by the wind direction.

Positive Matrix Factorization (PMF) algorithm was used for source analysis of Yokohama PAH data. The results showed that a stable solution was obtained for a seven-factor solution. The seven PAH source profiles obtained were interpreted as follows, factor 1 (steel manufacturing, 26%), factor 2 (motor vehicle, 25%), factor 3 (municipal waste incineration, 11%), factor 4 (gasoline, 11%), factor 5 (other sources, 10%), factor 6 (oil burning, 9.4%) and factor 7 (residential fuel burning, 7.6%). The source contribution factors results were regressed against the total PAHs data and a good fit with a regression coefficient of 0.99 was obtained suggesting that the PMF modeled data predicted the measured concentration well. The results from the PMF analysis complimented factor analysis data because sources like steel manufacturing, oil burning, and gasoline could be interpreted.

4. Conclusions

In Yokohama source analysis showed that traffic emissions, industrial sources are major sources of PAHs, whereas municipal waste incineration and residential areas were minor sources. In Nairobi overall source analysis from isomer ratios and PCA indicated that fuel burning and traffic emissions were the major sources of PAH levels in the three sampled areas in Nairobi and other sources were not outstanding or could not be explained because of PAH source mixing.

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