PERGAMON

AE International – Asia, Central and South America and North America

Atmospheric Environment 37 (2003) 2259–2267

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Concentrations and source characterization of polycyclic aromatic hydrocarbons in pine needles from Korea, Mexico, and United States

Hyun-Min Hwang[1], Terry L. Wade*, Jose L. Sericano

Geochemical and Environmental Research Group, College of Geosciences, Texas A & M University,
833 Graham Road, College Station, TX 77845, USA

Received 11 July 2002; accepted 30 January 2003

Abstract

Pine needle samples were collected from Korea, Mexico, and the United States (total 9 sites) to compare the concentrations and sources of polycyclic aromatic hydrocarbons (PAHs). Total PAH concentrations ranged from 31 to 563 ng g^{-1} (wet wt.) and showed clear differences between rural (clean) and urban/industrialized (contaminated) sites. The lowest and highest concentrations were found in samples from a rural site in Korea and northern part of Mexico City, respectively. The PAH distribution patterns and the ratio of the sum of combustion specific PAHs ($\sum$COMB) to total PAHs ($\sum$PAHs) in samples from Korea and United States were similar, implying similar sources. At these sites, three-ring PAHs accounted for 63–73% of the total PAHs and phenanthrene was the predominant compound. Samples from Mexico City, however, had different PAH patterns and much higher $\sum$COMB/$\sum$PAHs ratios (0.70 and 0.73). Four-ring PAHs were dominant ($\sim$50%) and pyrene was the most abundant compound. Phenanthrene to anthracene and fluoranthene to pyrene ratios may provide an additional indication of different sources. The ratios of methylphenanthrene to phenanthrene suggest that the contribution of diesel-operated vehicles to the signature of PAHs is more significant in samples from Mexico City than other sites. Enriched high molecular weight PAHs and the ratios of some selected compounds found in Mexico City samples may be the results of more extensive combustion activities and a higher proportion of non-catalyst-equipped vehicles. This study confirms the usefulness of pine needles for source characterization as well as atmospheric organic contaminants monitoring on large spatial scales (e.g., national or global).

Keywords: Pine needles; PAHs; Sources; $\sum$COMB; Vehicle emission

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in our environment and arise mainly from incomplete combustion of fossil fuels, organic materials, and wood (pyrogenic). PAHs are also found in petroleum (petrogenic) (NRC, 1983). The mechanism of PAH formation is complex, but PAHs are apparently formed through pyrolysis and pyrosynthesis (Baird, 1995; Mastral and Callen, 2000). On heating, organic compounds are partially cracked to smaller and unstable fragments (pyrolysis). These fragments are highly reactive free radicals with a very short lifetime and are converted to more stable PAHs through pyrosynthesis. While pyrogenic PAHs produced by incomplete combustion at high temperature have 2–6 rings and less alkylated substitution, petrogenic PAHs, which are

---

*Corresponding author. Tel.: +1-409-862-2323; fax: +1-409-690-0059.

E-mail address: terry@gerg.tamu.edu (T.L. Wade).

[1] Current address: Department of Civil and Environental Engineering, University of California, Davis, One Shields Ave., Davis, CA 95616, USA.

1352-2310/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S1352-2310(03)00090-6

produced at relatively low temperature, have preferentially 2–3 rings and a predominance of alkylated PAHs (NRC, 1983; Masclet et al., 1987). Emissions from incomplete combustion can be categorized as mobile (e.g., gasoline and diesel engine exhausts) and stationary (e.g., coal-fired power plant, residential heating) sources. PAH emission from stationary sources has been decreasing since the 1950s due to change in fuel usage from coal to petroleum and enhanced emission control (Latimer and Quinn, 1996; US EPA, 2000). Mobile sources, however, are increasing especially in urban areas. The increasing vehicle traffic associated with population growth in metropolitan areas can be responsible for increasing PAH concentrations and consequent degradation of air, soil and watershed quality (Van Metre et al., 2000). PAHs are a major health concerns in most urban areas due to their high concentrations, and carcinogenic and mutagenic properties (IARC, 1983).

The epicuticular waxy layer in pine needles accumulates organic contaminants from surrounding air. Therefore, pine needles have been used as passive samplers to assess ambient atmospheric concentrations of persistent organic contaminants, such as PAHs, PCBs, organochlorine pesticides, and polychlorinated dibenzo-*p*-dioxins on regional/global scales (Safe et al., 1992; Strachan et al., 1994; Tremolada et al., 1996). Pine needles can be easily collected and are less expensive than operating air sampling stations. Gaseous diffusion from the air to the waxy layer in plant leaves has been shown to be a major uptake process for these lipophilic organic contaminants (McLachlan et al., 1995) and hence the concentrations of target compounds measured in pine needles represent the integrated concentrations of those chemicals in surrounding air over time. The concentration of persistent organic compounds in pine needles is a function of atmospheric concentration and physicochemical properties (e.g., hydrophobicity, vapor pressure) of the compound as well as ambient temperature (Bacci et al., 1990; Simonich and Hites, 1994; Kömp and McLachlan, 1997).

In this study, we investigated atmospheric PAH concentration found in lipid layer of pine needles from three countries (total 9 sites). Sampling sites were chosen to compare different kinds and degrees of human activities. The purpose of this research was to examine differences between rural and urban/industrial areas and to assess sources of PAHs.

2. Methods

2.1. Study sites and sample collection

Pine needle samples were collected from three countries (9 sites). Site information and sampling time are given in Table 1. The youngest pine needles at the end of branches (1–2 years) were collected from the ground, wrapped in combusted aluminum foil, and placed in zip-lock bag. Samples were stored frozen (−20°C) until chemical analysis was performed.

2.2. Sample analysis

The PAH analysis method was slightly modified from Lauenstein and Cantillo (1998). About 10 g of wet pine needle samples were extracted for 4 h with dichloromethane in open-top glass column. Deuterated surrogate standards (naphthalene-d_8, acenanaphthene-d_{10}, phenanthrene-d_{10}, crysene-d_{12}, and perylene-d_{10}) were

Table 1
Sampling sites

	Location	Study area	Species	Collection time	Possible major PAH sources
Site 1	Yeoju, Korea	Rural	*P. densiflora*	May, 1998	Diffusion from high concentration area
Site 2	Cheju Island, Korea	Rural	*P. thunbergii*	May, 1999	Diffusion from high concentration area
Site 3	Seoul, Korea	Urban/residential	*P. densiflora*	May, 1998	Vehicle emission
Site 4	Mexico City, Mexico	Urban/residential	*P. maximartinezii*	April, 1999	Vehicle emission
Site 5	Mexico City, Mexico	Urban/industral	*P. maximartinezii*	April, 1999	Vehicle and industrial emissions
Site 6	Conroe, TX, USA	Rural	*P. taeda*	June, 1998	Diffusion from high concentration area
Site 7	College Station, TX, USA	Semiurban/ residential	*P. taeda*	June, 1998	Vehicle emission
Site 8	College Station, TX, USA	Semiurban/ residential	*P. taeda*	June, 1998	Vehicle emission
Site 9	Houston, TX, USA	Urban/residential	*P. taeda*	May, 1999	Vehicle emission

added before extraction for quantification. Extracts were cleaned by silica/alumina column chromatography and further purified by gel-permeation HPLC. In order to determine recovery rate, deuterated internal standards (fluorene-d_{10} and benzo[a]pyrene-d_{12}) were added after final concentration to 1 ml. PAHs were separated and analyzed with a HP 6890 gas chromatography equipped with a $30\,\mathrm{m} \times 0.25\,\mathrm{mm}$ DB-5MS fused silica capillary column with 0.25 μm film thickness and a HP 5973 mass selective detector (MSD). The MSD was operated in the electron impact ionization (EI) mode and in the selected ion monitoring (SIM) mode (70 eV). Quantification was performed using the molecular ion (mass-to-charge ratio). Peaks were confirmed based on retention time and secondary ions. The oven temperature was programmed to start initially at 60°C, increased to 150°C at $15^\circ\mathrm{C\,min^{-1}}$, increased to 220°C at $5^\circ\mathrm{C\,min^{-1}}$, increased to 300°C at $10^\circ\mathrm{C\,min^{-1}}$, and held for 10 min.

3. Results and discussion

The concentrations (in $\mathrm{ng\,g^{-1}}$ of wet sample) of polycyclic aromatic hydrocarbons in pine needles are given in Table 2. Total PAH concentrations ($\sum$PAHs) vary from 31 to $563\,\mathrm{ng\,g^{-1}}$. Clear differences between urban/industrial and rural areas can be recognized by $\sum$PAHs. Total PAH burdens in samples from site 5 ($563\,\mathrm{ng\,g^{-1}}$) and site 3 ($192\,\mathrm{ng\,g^{-1}}$) were 18 and 6 times, respectively, higher than in sample from site 1 ($31\,\mathrm{ng\,g^{-1}}$), which can be characterized as a background site.

Total PAH concentrations from other studies are summarized in Table 3 to compare with this study. Because the concentrations of this study are on a wet weight basis, the concentrations obtained by this study were divided by 0.5 (50%) in order to compare with other studies. According to other studies, uncertainty caused by relating concentrations determined on either wet or dry weight basis is not significant. Strachan et al. (1994) found fairly constant moisture contents (44–51%) in 1–5 years old pine needles (Scotch pine, *Pinus sylvestris*) collected along a transect running from western Germany to northern Sweden. Lang et al. (2000) reported similar moisture contents (51–55%) in pine needles (white pine) collected from both urban and mountain sites from April to December. Hwang et al. (2002) also found constant moisture contents (50–55%) in pine needles from Houston, TX, USA. In spite of the differences in total number of PAHs measured and in analytical procedures, relatively lower concentrations

Table 2
Concentrations of individual PAH compound ($\mathrm{ng\,g^{-1}}$ wet wt.) and selected PAH ratios

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9
Acenaphthylene	1.67	5.90	6.14	3.84	8.33	1.23	1.10	2.33	1.43
Acenaphthene	0.59	1.01	1.39	0.75	1.68	0.65	1.84	1.40	5.07
Fluorene	3.16	8.54	9.62	2.87	15.8	15.3	4.78	19.4	28.9
Phenanthrene	11.0	15.2	91.5	10.3	84.8	25.7	42.1	43.3	49.2
Methylphenanthrene	3.86	4.81	22.3	7.85	41.7	8.96	14.5	14.2	11.3
Anthracene	0.41	0.98	4.81	0.26	2.39	0.89	2.46	1.62	3.21
Dibenzothiophene	1.09	1.20	5.50	1.54	12.6	2.72	3.20	4.23	2.54
Fluoranthene	2.55	5.02	20.0	12.0	66.9	8.92	8.78	14.9	20.1
Pyrene	1.65	3.51	13.7	19.3	118	3.09	3.50	5.64	11.3
Benz(a)anthracene	0.39	0.54	1.37	2.56	11.6	1.73	3.28	2.76	0.97
Chrysene	1.10	4.36	7.58	18.3	49.8	7.16	11.8	10.7	4.53
Benzo(b)fluoranthene	0.79	2.25	2.90	7.66	40.0	2.52	4.12	4.05	2.61
Benzo(k)fluoranthene	0.37	0.71	0.75	2.30	7.24	0.58	1.41	1.30	0.67
Benzo(e)pyrene	0.51	1.01	1.45	3.57	24.9	0.89	1.91	1.59	1.25
Benzo(a)pyrene	0.55	0.73	0.69	1.47	9.15	0.83	1.15	1.08	1.22
Indeno(1,2,3-c,d)pyrene	0.65	0.90	1.21	3.45	28.2	0.98	2.52	1.63	1.04
Benzo(g,h,i)perylene	0.64	1.04	1.32	3.87	39.7	0.94	2.82	1.67	1.12
Total PAHs	31	58	192	102	563	83	111	132	146
Total COMB	9	20	51	75	396	28	41	45	45
Ratios									
Ph/An	27	16	19	40	35	29	17	27	15
Fl/Py	1.55	1.43	1.46	0.62	0.57	2.89	2.51	2.64	1.79
COMB/PAHs	0.30	0.35	0.27	0.73	0.70	0.33	0.37	0.34	0.31
MPh/Ph	0.35	0.32	0.24	0.76	0.49	0.35	0.34	0.33	0.23

Table 3
Concentrations of PAHs in pine needles

Concentrations ($\mathrm{ng\,g^{-1}}$ dry wt.)	Study area	No. of PAHs	Site	Reference
22–140	Forest	11	Lake Gardsjon, Sweden	Brorström-Lunden and Löfgren (1998)
62	Rural	17	Korea	This study
64–141	Forest	10	Spring Valley, ID, USA	Lang et al. (2000)
166	Rural	17	Lake Conroe, TX, USA	This study
19–3090	Rural	17	UK	Tremolada et al. (1996)
243	Semiurban	17	College Station, TX, USA	This study
384	Urban	17	Seoul, Korea	This study
204	Suburban (Residential)	17	Mexico City, Mexico	This study
498–859	Semiurban (downtown)	10	Moscow, Idaho, USA	Lang et al. (2000)
600–1600	Semiurban (downtown)	10	Bloomington, IN, USA	Simonich and Hites (1994)
1126	Urban/industrial	17	Mexico City, Mexico	This study
202–2226	Urban/suburban	23	Houston, TX, USA	Hwang et al. (2002)
1000–6100	Urban/industrial	25	Sweden	Kylin (1993)
8325	Industrial	16	Sokolov, Czech	Holoubek et al. (2000)

($<200\,\mathrm{ng\,g^{-1}}$ dry wt), in general, were found in rural/remote areas. However, Tremolada et al. (1996) reported a wide range of concentrations (19–3090 $\mathrm{ng\,g^{-1}}$ dry wt) in samples from rural/remote areas in the UK. This was due to unusually high concentrations of phenanthrene (50–80% of the total PAHs) compared to other PAH compounds. In urban/industrial areas, total PAH concentrations varied between 400 and 8325 $\mathrm{ng\,g^{-1}}$ (dry wt).

Gaseous diffusion from the air to the waxy layer in plant leaves has been shown to be a major uptake process for lipophilic organic contaminants (McLachlan et al., 1995) and therefore air–vegetation partitioning can be estimated by octanol–air partition coefficients. Some studies (Morosini et al., 1993; McLachlan et al., 1995; Tremolada et al., 1996) have calculated the atmospheric concentrations of semivolatile organic compounds using octanol–air partition coefficients (K_{oa}). Tremolada et al. (1996) calculated air concentrations of PAHs using the air to pine needle bioconcentration factors, which were calculated from K_{oa}, and then compared with measured air concentrations. They found that only fluorene and phenanthrene air concentrations can be well predicted reasonably using K_{oa}, while compounds having $\log K_{\mathrm{oa}}$ values higher than 8 had lower measured concentrations up to 100 times than estimated air concentrations possibly due to much longer time to reach equilibrium and/or additional major bioconcentration pathways like particle deposition (McLachlan et al., 1995). So in this study, atmospheric concentrations of only 3-ring PAHs ($\log K_{\mathrm{oa}} < 8$) were calculated (Table 4). Average temperatures during sample collection dates were around 18°C (sites 1–5) and 25°C (sites 6–9) (NCDC, 2002). The estimated phenanthrene concentrations in pine needles from sites 3 (Seoul) and 9 (Houston) are similar to the measured annual average vapor phase concentrations (Park et al., 2001, 2002).

The PAH distribution patterns (3–6 ring PAHs) are shown in Fig. 1. Three- and four-ring PAHs are dominant at all sites and account for 74–96% of the total PAHs. The obvious difference in PAH distribution patterns between Mexico City and other sites clearly indicate different sources of PAHs. Four-ring PAHs are found as the most abundant compounds in the two Mexico City samples and three-ring PAHs at other sites. Pyrene (4-ring PAH) is the predominant compound in Mexico City samples. Phenanthrene (3-ring PAH) predominance and similar PAH distribution patterns found in non-Mexico City sites indicate similar combustion activity in those areas. Bae et al. (2002) reported that PAHs from gasoline-operated vehicles were more prominent than diesel-operated vehicles in Seoul. Enrichment of 4-ring PAHs, especially fluoranthene and pyrene, in samples from Mexico City (sites 4 and 5) indicate more diesel fuel consumption than other study sites. Actually, diesel consumption accounts for 26% of the total fuel use for transportation in Mexico City (Rafael-Morales and Gortar, 2002). Sjögren et al. (1996) showed that emission rates of the sum of fluoranthene and pyrene were up to 15 times higher than those of phenanthrene in heavy-duty engines using 10 different diesel fuels. Marr et al. (1999) reported higher concentrations of fluoranthene and pyrene in emissions from heavy-duty diesel vehicles by a factor of 6–7 compared to light-duty vehicles. Fraser et al. (1998b), however,

Table 4
Physico-chemical properties of 3-ring PAHs and their atmospheric concentrations estimated from the PAH concentrations in pine needles

	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene
Log K_{ow}[a]	4.07	4.03	4.47	4.50	4.46
H[b] (at 18°C)	7.46	10.9	5.96	2.65	3.50
Log K_{oa}[c] (at 18°C)	6.58	6.38	7.08	7.46	7.30
H[b] (at 25°C)	12.7	18.5	9.81	4.29	5.64
Log K_{oa}[c] (at 25°C)	6.36	6.16	6.87	7.26	7.10
Concentration[d]					
Site 1	1.64	0.74	1.73	3.83	0.17
Site 2	5.81	1.27	4.67	5.28	0.41
Site 3	6.05	1.74	5.26	31.8	2.02
Site 4	3.78	0.94	1.57	3.57	0.11
Site 5	8.20	2.11	8.62	29.5	1.01
Site 6	1.57	1.06	10.7	11.3	0.47
Site 7	1.41	2.99	3.33	18.5	1.31
Site 8	2.98	2.28	13.5	19.1	0.86
Site 9	1.83	8.25	20.2	21.7	1.70

[a] Octanol/water partition coefficient (Mackay et al., 1992).

[b] Henry's law constant (Pa m^3 mol^{-1}) (Bamford et al., 1999).

[c] Octanol/air partition coefficient (calculated using the equation given by Kömp and McLachlan (1997)).

[d] Estimated atmospheric concentrations (ng m^{-3}) (calculated using the equations given by Bacci et al. (1990) and Paterson et al. (1991)).

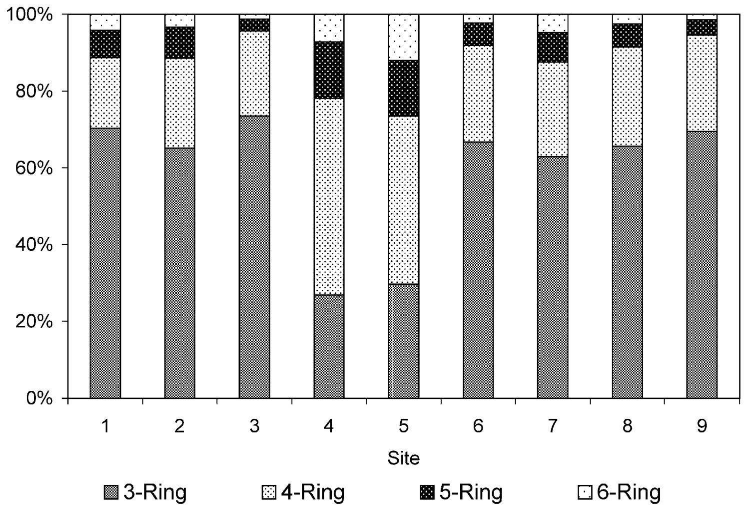

Fig. 1. PAH (3–6 rings) distribution patterns.

found that emission rate of phenanthrene was 3 times higher than the sum of fluoranthene and pyrene in roadway tunnel emission, which is dominated by catalyst-equipped automobile.

Samples from two Mexico City sites exhibit significantly higher fraction of high molecular weight PAHs (4- to 6-ring PAHs; 70% and 73%) compared to other sites (32±4%). While a large proportion of high molecular weight parent PAHs is typical characteristic of a combustion origin (pyrogenic), the enrichment of low molecular weight PAHs (parent and alkylated) is common in fresh fuels (petrogenic) (Masclet et al., 1987; Budzenski et al., 1997). Typical combustion origin PAHs can be represented by the sum of major combustion specific compounds ($\sum$COMB) which are fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)-pyrene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene (Prahl and Carpenter, 1983). The ratio of $\sum$COMB to $\sum$PAHs ($\sum$COMB/$\sum$PAHs) was higher in samples from Mexico City by a factor of 1.9–2.7, indicating that there are more extensive combustion activities in Mexico City than other sites. Less efficient emission control system in the Mexican vehicle fleet may also account for this high $\sum$COMB/$\sum$PAHs ratios in the two Mexico City samples. Approximately 60% of the vehicles in Mexico City were not equipped with a catalytic converter until the late 1990s (Faiz et al., 1996; Schifter et al., 2000). According to Rogge et al. (1993), non-catalyst vehicles emit 27 times more PAHs, especially high molecular weight PAHs, than catalyst-equipped vehicles.

The concentrations of selected marker compounds (e.g., retene, coronene and 4,5-dimethyl phenanthrene) and PAH ratios (e.g., Ph/An, Fl/Py, and MPh/Ph) have been developed and used for the source identification of PAHs (Gschwend and Hites, 1981; Ramdahl, 1983; Yunker et al., 2002). Due to overlap of characteristic PAH patterns from each source and selective decay of more labile compounds, single ratio may not be enough to determine sources. Thus, instead of using single ratio, coupling of two or more indicators is helpful to compare different sources. Plotting phenanthrene to anthracene (Ph/An) ratio against fluoranthene to pyrene (Fl/Py) ratio can be a valuable way to investigate sources. A Ph/An ratio of less than 10 and Fl/Py ratio of greater than 1 have been used to indicate pyrogenic origins of PAHs (Baumard et al., 1998). However, unlike sediment samples in which PAH distribution patterns are well preserved, air samples, especially vapor phase, which are exposed to sunlight and reactive gases (e.g., NO_x, and SO_x), may show different ratios compared to the sources due to selective decay of more labile compounds. According to many laboratory and field studies, for example, anthracene always degrades faster than phenanthrene in vapor and particle phases (Behymer and Hites, 1988; Masclet et al., 1986). Thus, in aged air or pine needle samples far from point sources, much higher Ph/An ratios have been found compared to sediment or freshly emitted exhaust samples. Fraser et al. (1998b) and Schauer et al. (1999) reported for Ph/An ratio around 7 in the vapor phase in roadway tunnel exhaust and tailpipe emissions. Lang et al. (2000) found higher Ph/An ratios (10–23) in pine needles from a mountain site than in samples from a downtown site (4–11). These findings indicate preferential decay of anthracene compared to phenanthrene as vehicle emission is the primary source of PAHs for both sites. Using time series samples, Simcik et al. (1999) and Fraser et al. (1998a) showed progressive relative depletion of anthracene compared to phenanthrene by photochemical reactions.

Ph/An ratios obtained from this study were plotted against Fl/Py ratios (Fig 2). Kylin (1993) and Brorström-Lunden and Löfgren (1998) obtained similar Ph/An ratios in pine needle samples from various regions to those of this study. High Ph/An ratios (25–850) were reported by Tremolada et al. (1996) in pine needle samples from rural/remote areas in the UK. The results obtained in this and other studies demonstrate that relative decay rates of PAHs should be considered when assessing possible sources in air and vegetation samples. For example, high Ph/An ratios of 27 (sites 8 and 1) and 29 (site 6) from this study may indicate strong PAH input from petrogenic sources. However, other ratios (e.g., Fl/Py and MPh/Ph) suggest that these high Ph/An ratios are not likely due to dominant contribution of petrogenic sources but likely due to faster decay of photolabile anthracene than relatively stable phenanthrene in pine needles.

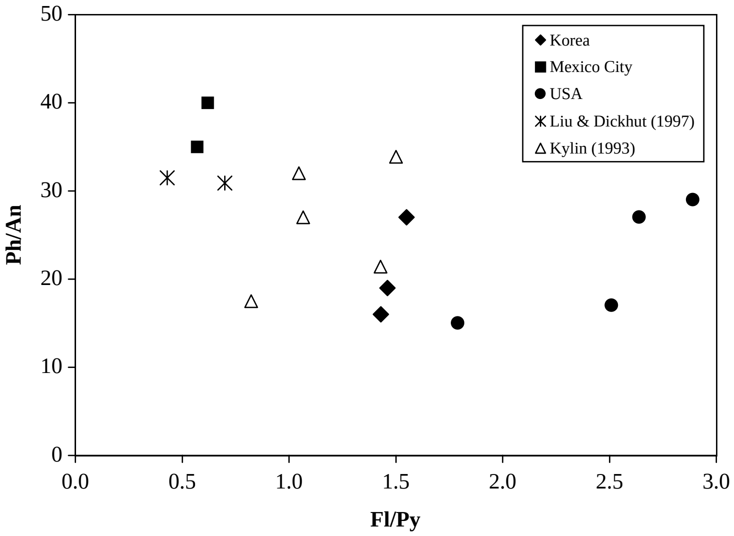

Fig. 2. Plot of phenanthrene to anthracene (Ph/An) ratios against fluoranthene to pyrene (Fl/Py) ratios.

Ph/An ratios from two Mexico City samples (35 and 40) are higher than those in samples from other sites (21 ± 6). The differences of Fl/Py ratios are apparent in samples from each country (Fig. 2), indicating different sources although different atmospheric decay could also be a contributing factor. Different ratios are likely due to the differences in fuel consumption pattern, fuel composition and exhaustion system of vehicle. Site 5 is near a highway, which runs through an industrial area, and thus PAH sources are likely a combination of industrial and vehicular fuel combustions and unburned fuels. Ph/An and Fl/Py ratios found in pine needles from sites 4 and 5 indicate more petrogenic sources than other sites and match to those (31 and 0.5, Fig. 2) for vapor samples collected from metropolitan industrialized area adjacent to southern Chesapeake Bay, USA (Liu and Dickhut, 1997). Because of the differences in physico-chemical properties (e.g., volatility), PAH ratios are generally restricted to PAHs having the same and/or similar molecular weight, volatility, hydrophobicity, etc. Therefore, the comparison of PAH ratios in different sample matrix like vapor phase in the air and pine needles may not cause significant differences.

As an additional indicator of PAH sources, the ratio of the sum of methylphenanthrene isomers to phenanthrene (MPh/Ph) has been applied. Pyrolytic PAHs are characterized by a high abundance of parent compounds but petrogenic PAHs are dominated by alkylated compounds. Therefore, the typical values of MPh/Ph for petrogenic origin range 2–6, while MPh/Ph is generally less than 1 for pyrogenic origin (Garrigues et al., 1995; Budzenski et al., 1997). In case of vehicle emission, PAHs may come from both pyrosynthesis (pyrogenic) and unburned fuel (petrogenic), which survived combustion. Because combustion temperature of diesel engines are lower than gasoline engines and diesel fuel contains relatively higher concentrations of alkylated PAHs compared to gasoline (Nielsen, 1996), more fuel may survive combustion in diesel engine and higher MPh/Ph ratios are likely in diesel emission. The ratios of MPh/Ph in particles emitted from diesel engine were reported from 1.73 to 8.17 and lower ratios (0.7) for gasoline emission (Takada et al., 1990; Schauer et al., 1999). In Baltimore Harbor tunnel study, Benner et al. (1989) found that the MPh/Ph ratios of 1.1 and 1.6 in vapor phase and particulate phase samples that had significant diesel sources. Schauer et al. (1999) also reported MPh/Ph ratios higher than 1.0 in vapor phase (1.2) and in particulate phase (2.2) in diesel truck exhaust. In recent roadway tunnel study by Fraser et al. (1998b), the MPh/Ph ratio was found as 0.3 in vapor phase. It's likely due to the predominance of the catalyst-equipped automobile and catalyst-equipped light-duty vehicles (e.g., vans) in the traffic.

The MPh/Ph ratios obtained in this study range from 0.23 to 0.76 (Table 2). The lower MPh/Ph ratios (0.23 ± 0.76) in samples from Korea and the United States represent strong PAH input from gasoline combustion and/or less unburned fuels. The higher MPh/Ph ratios (0.49 and 0.76) in the two Mexico City samples indicate that the contribution of diesel operated vehicles to PAHs is more significant in Mexico City than for the other sites. The MPh/Ph ratios can be used to estimate the proportion of some stable PAH compounds (e.g., B[e]P) from diesel exhaust (Nielsen, 1996). Since fuels have been reformulated and vehicle exhaustion techniques have advanced, fuel compositions and exhaustion system of each study mentioned above are not the same, and hence, instead of values used by Nielsen (1996), different MPh/Ph ratios (1.21 for diesel, 0.23 for gasoline) were used in calculation. The estimated contribution of diesel emission to B[e]P is 26 and 54% for Mexico City and less than 11% for the other sites. This estimation also indicates that the contribution of diesel-operated vehicles to the signature of PAHs in samples from Mexico City is higher than the other study sites.

4. Conclusion

Different PAH distribution in pine needles between urban/industrial and rural areas are observed. The obvious differences in PAH distribution patterns between Mexico City and other sites clearly indicate different PAH sources. A large proportion of high molecular weight PAHs in Mexico City samples is characteristic of combustion sources and was confirmed by high ratio of $\sum$COMB to $\sum$PAHs. Compound ratios indicated the mixture of pyrogenic and petrogenic sources of PAHs in all samples. Plot of Ph/An ratio against Fl/Py ratio showed differences in fuel consumption pattern, fuel compositions, and exhaustion system of vehicles. The results obtained in this and other studies demonstrate that relatively different decay rates of PAHs complicate assessing possible sources in air and vegetation samples. $\sum$MPh/Ph ratios indicated the predominance of gasoline sources of PAHs in samples from Korea and the United States and PAHs from diesel are higher in Mexico City compared to the other sites. This study confirms that pine needles are useful tool to assess regional or global atmospheric contamination from PAHs and provide indication of sources of those compounds.

Acknowledgements

We would like to thank Dr Javier Alcala-Herrera for collecting the samples from Mexico City.

References

Bacci, E., Calamari, D., Gaggi, C., Vighi, M., 1990. Bioconcentration of organic chemical vapors in plant tissues: experimental measurements and correlation. Environmental Science and Technology 24, 885–889.

Bae, S., Yi, S., Kim, Y., 2002. Temporal and spatial variations of the particle size distribution of PAHs and their dry deposition fluxes in Korea. Atmospheric Environment 36, 5491–5500.

Baird, C., 1995. Environmental Chemistry. Freeman, New York, pp. 275–276.

Bamford, H.A., Poster, D.L., Baker, J.E., 1999. Temperature dependence of Henry's Law constants of thirteen polycyclic aromatic hydrocarbons between 4°C and 31°C. Environmental Toxicology and Chemistry 18, 1905–1912.

Baumard, P., Budzinski, H., Garrigue, P., 1998. Polycyclic aromatic hydrocarbons in sediments and mussels of the western Mediterranean Sea. Environmental Toxicology and Chemistry 17, 765–776.

Behymer, T.D., Hites, R.A, 1988. Photolysis of polycyclic aromatic hydrocarbons adsorbed on fly ash. Environmental Science and Technology 22, 1311–1319.

Benner Jr., B.A., Gordon, G.E., Wise, S.A., 1989. Mobile sources of atmospheric polycyclic aromatic hydrocarbons: a roadway tunnel study. Environmental Science and Technology 23, 1269–1278.

Brorström-Lunden, E., Löfgren, C., 1998. Atmospheric fluxes of persistent semivolatile organic pollutants to a forest ecological system at the Swedish west coast and accumulation in spruce needles. Environmental Pollution 102, 139–149.

Budzenski, H., Jones, I., Bellocq, J., Pierad, C., Garrigues, P., 1997. Evaluation of sediment contaminantion by polycyclic aromatic hydrocarbons in the Gironde estuary. Marine Chemistry 58, 85–97.

Faiz, A., Weaver, C.S., Walsh, M., 1996. Air Pollution from Motor Vehicles. Standards and Technologies for Controlling Emissions. World Bank, Washington, DC.

Fraser, M.P., Cass, G.R., Simoneit, B.R., Rasmussen, R.A., 1998a. Air quality model evaluation data for organics. 5. C_6–C_{22} nonpolar and semipolar aromatic compounds. Environmental Science and Technology 32, 1760–1770.

Fraser, M.P., Cass, G.R., Simoneit, B.R., 1998b. Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. Environmental Science and Technology 32, 2051–2060.

Garrigues, P., Budzinski, H., Mantiz, M.P., Wise, S.A., 1995. Pyrolytic and petrogenic inputs in recent sediments: a definitive signature through phenanthrene and chrysene compound distribution. Polycyclic Aromatic Compounds 7, 275–284.

Gschwend, P.M., Hites, R.A., 1981. Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. Geochimica et Cosmochimica Acta 45, 2358–2367.

Holoubek, I., Korinek, P., Seda, Z., Schneiderova, E., Holoubkova, I., Pacl, A., Triska, J., Cudlin, P., Caslavsky, J., 2000. The use of mosses and pine needles to detect persistent organic pollutants at local and regional scales. Environmental Pollution 109, 283–292.

Hwang, H-M., Wade, T.L., Sericano, J.L., 2002. Concentrations, aerial distribution, and sources of PAHs in pine needles from Houston, TX. Proceedings of the 23rd Annual SETAC Meeting, Salt Lake City, UT.

IARC (International Agency for Research on Cancer), 1983. IARC monographs on the evaluation of the carcinogenic risk of chemicals to human. Polynuclear aromatic compounds, Part I, Chemical, environmental, and experimental data. World Health Organization, Geneva, Switzerland.

Kömp, P., McLachlan, M.S., 1997. Octanol/air partitioning of polychlorinated biphenyls. Environmental Toxicology and Chemistry 16, 2433–2437.

Kylin, H., 1993. Airborn lipophilic pollutants in pine needles. Ph.D. Dissertation, University of Stockholms, Stockholms, Sweden.

Lang, Q., Hunt, F., Wai, C.M., 2000. Supercritical fluid extraction of polycyclic aromatic hydrocarbons from white pine (*Pinus strobes*) needles and its implications. Journal of Environmental Monitoring 2, 639–644.

Latimer, J.S., Quinn, J.G., 1996. Historical trends and current inputs of hydrophobic organic compounds in an urban estuary: the sedimentary record. Environmental Science and Technology 30, 623–633.

Lauenstein, G.G., Cantillo, A.Y., 1998. Sampling and analytical methods of the National Status and Trends Program Mussel Watch Project: 1993–1996 update, NOAA Technical Memorandum NOS ORCA 130. National Oceanic and Atmospheric Administration, Silver Spring, MD, USA.

Liu, K., Dickhut, R.M., 1997. Surface microlayer enrichment of polycyclic aromatic hydrocarbons in southern Chesapeake Bay. Environmental Science and Technology 31, 2777–2781.

Mackay, D., Shiu, W.Y., Ma, K.C., 1992. Illustrated Handbook of Physical and Chemical Properties and Environmental Fate of Organic Chemicals. Lewis Publisher, Boca Raton, FL, USA.

Marr, L.C., Kirchstetter, T.W., Harley, R.A., Miguel, A.H., Hering, S.V., Hammond, S.K., 1999. Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. Environmental Science and Technology 33, 3091–3099.

Masclet, P., Mouvier, G., Nikolaou, K., 1986. Relative decay index and sources of polycyclic aromatic hydrocarbons. Atmospheric Environment 20, 439–446.

Masclet, P., Bresson, M.A., Mouvier, G., 1987. Polycyclic aromatic hydrocarbons emitted by power stations, and influence of combustion conditions. Fuel 66, 556–562.

Mastral, A.M., Callen, M.S., 2000. A review on polycyclic aromatic hydrocarbon (PAH) emission from energy generation. Environmental Science and Technology 34, 3051–3057.

McLachlan, M.S., Welsch-Pausch, K., Tolls, J., 1995. Field validation of a model of the uptake of gaseous SOC in *Lolium multiflorum*(rye grass). Environmental Science and Technology 29, 1998–2004.

Morosini, M., Schreitmüller, J., Reuter, U., Ballschmiter, K., 1993. Correlation between C6/C14 chlorinated-hydrocarbons levels in the vegetation and in the boundary layer of the troposphere. Environmental Science and Technology 27, 1517–1523.

NCDC (National Climate Data Center), 2002. 1971–2000 Normals: monthly station normals of temperature, precipitation, and degree days, and precipitation probabilities and quintiles, TD-9641-C. National Oceanic and Atmospheric Administration, Asheville, NC, USA.

Nielsen, T., 1996. Traffic contribution of polycyclic aromatic hydrocarbons in the center of a large city. Atmospheric Environment 30, 3481–3490.

NRC (National Research Council), 1983. Polycyclic Aromatic Hydrocarbons: Evaluation of Sources and Effects. National Academy Press, Washington, DC, USA.

Park, J., Wade, T.L., Sweet, S., 2001. Atmospheric distributions of aromatic hydrocarbons (PAHs) and depositions to Galveston Bay, TX. Atmospheric Environment 35, 3241–3249.

Park, S.S., Kim, Y.J., Kang, C.H., 2002. Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. Atmospheric Environment 36, 2917–2924.

Paterson, S., Mackay, D., Bacci, E., Calamari, D., 1991. Correlation of the equilibrium and kinetics of leaf–air exchange of hydrophobic organic chemicals. Environmental Science and Technology 25, 866–871.

Prahl, F.G., Carpenter, R., 1983. Polycyclic aromatic hydrocarbon (PAH)-phase associations in Washington coastal sediment. Geochimica et Cosmochimica Acta 47, 1013–1023.

Rafael-Morales, M., Gortar, J.C., 2002. Reduced consumption and environment pollution in Mexico by optimal technical driving of heavy motor vehicles. Energy 27, 1131–1137.

Ramdahl, T., 1983. Retene—a molecular marker of wood combustion in ambient air. Nature 306, 580–582.

Rogge, W.F., Hidlemann, L.M., Mazurek, M.A., Glen, R.C., Simoneit, B.R.T., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environmental Science and Technology 27, 636–651.

Safe, S., Brown, K.W., Donnelly, K.C., Anderson, C.S., Markiewicz, K.V., McLachlan, M.S., Reischl, A., Hutzinger, O., 1992. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans associated with wood-preserving chemical sites: biomonitoring with pine needles. Environmental Science and Technology 26, 394–396.

Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R., 1999. Measurement of emissions from air pollution sources. 2. C1–C30 organic compounds from medium duty diesel trucks. Environmental Science and Technology 33, 1578–1587.

Schifter, I., Diaz, L., Lopez-Salinas, E., Ramos, F., Avalos, S., Lopez-Vidal, G., Castillo, M., 2000. Estimation of motor vehicle toxic emissions in the metropolitan area of Mexico City. Environmental Science and Technology 34, 3606–3610.

Simcik, M.F., Eisenreich, S.J., Lioy, P.J., 1999. Source appointment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. Atmospheric Environment 33, 5071–5079.

Simonich, S.L., Hites, R.A., 1994. Vegetation–atmospheric partitioning of polycyclic aromatic hydrocarbons. Environmental Science and Technology 28, 939–943.

Sjögren, M., Li, H., Rannug, U., Westerholm, R., 1996. Multivariate analysis of exhaust emission from heavy-duty diesel fuels. Environmental Science and Technology 30, 28–49.

Strachan, W.M.J., Eriksson, G., Kylin, H., Jensen, S., 1994. Organochlorine compounds in pine needles: methods and trends. Environmental Toxicology and Chemistry 13, 443–451.

Takada, H., Onda, T., Ogura, N., 1990. Determination of polycyclic aromatic hydrocarbons in urban street dusts and their source materials by capillary gas chromatography. Environmental Science and Technology 24, 1179–1186.

Tremolada, P., Burnett, V., Calamari, D., Jones, K.C., 1996. Spatial distribution of PAHs in the UK atmosphere using pine needles. Environmental Science and Technology 30, 3570–3577.

US EPA (US Environmental Protection Agency), 2000. National air pollution emission trends, 1900–1998. EPA-454-R-00-002. Washington, DC.

Van Metre, P.C., Mahler, B.J., Furlong, E.T., 2000. Urban sprawl leaves its PAH signature. Environmental Science and Technology 34, 4064–4070.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 33, 489–515.