An assessment of the concentrations of particulate polycyclic aromatic hydrocarbons (PAHs) in the aftermath of a chemical store fire incident

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Abstract: PM_{10} airborne particles and soot deposit collected after a fire incident at a chemical store were analyzed in order to determine the concentrations of polycyclic aromatic hydrocarbons(PAHs). The samples were extracted with 1:1 hexane-dichloromethane by ultrasonic agitation. The extracts were then subjected to gas chromatography-mass spectrometric(GC-MS) analysis. The total PAHs concentrations in airborne particles and soot deposit were found to be 3.27 ± 1.55 ng/m^3 and 12.81 ± 24.37 µg/g, respectively. Based on the molecular distributions of PAHs and the interpretation of their diagnostic ratios such as PHEN/(PHEN + ANTH), FLT/(FLT + PYR) and BeP/(BeP + BaP), PAHs in both airborne particles and soot deposit may be inferred to be from the same source. The difference in the value of IP/(IP + BgP) for these samples indicated that benzo[g, h, i]perylene and coronene tend to be attached to finer particles and reside in the air for longer periods. Comparison between the molecular distributions of PAHs and their diagnostic ratios observed in the current study with those reported for urban atmospheric and roadside soil particles revealed that they are of different sources.

Keywords: airborne particles; soot deposit; PAHs

Introduction

The word "combustion" is used to refer to the oxidation reaction that produces fire. The products of combustion can be divided into four categories: (a) flame; (b) heat; (c) fire gases; and (d) smoke(Hartzel, 1981; Barnett, 2001). For combustion to occur several factors need to be presented. The first requirements are fuel and oxygen. Fuel for a fire may range from trees in a forest, to furniture in a home and to gasoline in an automobile. The oxygen in the reaction usually comes from the surrounding air. The next requirement for combustion is an initiating energy source, or source of ignition. Ignition sources may be in the form of a spark, a flame, or even a very hot object. The ignition source must provide enough energy to start the chemical reaction. Finally, a chemical chain reaction (reaction that continuously fuels itself) must occur between the fuel and oxygen for combustion to take place (Barnett, 2001). The products that a fire releases, and the rate at which it releases them, depend on the fuel and on the fire's burning rate. Some fuels will produce more heat than others as they burn, and some will produce different kinds of gases. A fire that burns slowly may produce different products than one that burns quickly. The burning rate also affects the rate at which a fire releases products(Barnett, 2001).

The impact of toxic material(e.g., PAHs) from the fire to the environment is dominated by the atmospheric dispersion. Concentrations in the plume follow from the amount of material released(source strength), and the plume rise is determined by the heat release and the effect of nearby buildings. Further downwind, the atmospheric turbulence governs the concentration patterns(Rasmussen, 1998). The formation of PAHs has been reported in a variety of fire accidents. For example, private residential fires (Wobst, 1999; Ruokojärvi, 2000), chemical fires(Meharg, 1998), vehicle fires (Wichmann, 1995), incineration of medical wastes(Levendis, 2001), petroleum fires (Saeed, 1998), municipal waste landfill fires(Ruokojärvi, 1995), and forest fires(Gabos, 2001). These compounds are a large group of organic compounds with two or more benzene rings. They have a relatively low solubility in water but are highly lipophilic, result from incomplete combustion of organic (carbonaceous) material, and have been identified to have carcinogenic and mutagenic effects. Generally, they are associated with particulate matter, especially soot (Zander, 1980; Finlayson-Pitts, 1986; Larson, 1994).

The main objective of the current study is to determine the PAHs levels and distributions in (a) PM_{10} airborne particles and (b) soot deposit collected after a fire incident at a chemical store.

1 Experimental

1.1 Site description

The fire incident that took place on 28th July 2000 had destroyed the entire chemical store, which was located at the "basement" floor of the building. Hundreds of chemicals, both organic and inorganic, meant for teaching and research purposes were stored there. These chemicals were kept in glass or plastic bottles as received from the supplier. Due to the intense heat from the fire, many glass bottles were broken resulting in most of the chemicals had to be disposed. The building consists of four other levels. One airborne particulate sample was collected at each floor starting from 31st October to 7th November 2000. The PM_{10} concentrations are in the range of 30.93 to 55.72 $\mu g/m^3$. Soot deposit were collected on the 3rd and 4th October 2000 from the "basement" (FSP1), first level (FSP2), lecturer's rooms(FSP3) and research laboratories(FSP4) on the second, third, and fourth levels respectively. Another sample was taken from the adjacent wings to the third and fourth levels (FSP5).

1.2 Sampling and sample preparation

Airborne particulate samples were acquired using a PM_{10}

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high-volume air sampler (Ecotech, Australia) fitted with annealed (400℃ for 6 h) glass fiber filters (20.3 cm × 25.4 cm, Whatman EPM 2000, England), and operated at a flow rate of ~1.12 m^3/min. Sampling was carried out over a 24 h period. Before weighing, all fresh and exposed filters were conditioned for 24 h in a dry-box where the temperature was maintained at 25℃ with the relative humidity at 45%. Exposed filters were then cut into two halves. One-half was cut into small pieces and stored in a 250 ml glass jar to which ~5 ml of dichloromethane was added to inhibit microbial activity, and kept refrigerated until the day of analysis. Soot deposit was collected using a small brush. The particles (sieved ⩽53 μm) were stored in a 14 ml vial and kept in this manner until the day of analysis.

1.3 Extraction

1.3.1 Extraction of airborne particles

Half-filters were extracted three times using ultrasonic agitation for a fifteen-minute period each with 60 ml of 1∶1 hexane-dichloromethane. The extractions were carried out within the filter storage jar. The extracts were then filtered using a filtration unit containing an annealed glass fiber filter for the removal of insoluble particles. The filtrate was first concentrated on a rotary evaporator and then using a stream of dry nitrogen gas to a volume of approximately 500 μl. The volume was then adjusted to 500 μl exactly by addition of 1∶1 hexane-dichloromethane.

1.3.2 Extraction of soot deposit

Soot deposit samples(0.24—0.70 g) were extracted by ultrasonic agitation. One 30 min extraction was carried out in 10 ml vial with 5 ml of 1∶1 hexane-dichloromethane. The extracts were then filtered using Pasteur pipette fitted with annealed glass fiber filters and precleaned glass wool at the narrow end in order to remove fine particles. The filtrate was then collected in 10 ml vial, and the solvent was evaporated to almost dryness by using a stream of dry nitrogen gas. The volume was then adjusted to 100—1000 μl exactly by addition of 1∶1 hexane-dichloromethane.

1.4 Instrumental analysis

The analyses were carried out on a Hewlett-Packard Model 6890 gas chromatograph-mass spectrometer fitted with a fused silica capillary column coated with 5% diphenyldimethylpolysiloxane (HP-5MS, 30 m long, 0.25 mm i.d., 0.25 μm film thickness). The instrument was operated at full-scan mode with an initial flow of 1.2 ml/min; nominal initial pressure: 10.4 psi; average velocity: 40 cm/s; injection mode: splitless (1 min); temperature of injector: 290℃. The GC-MS operating conditions were as follows: isothermal at 60℃ for 2 min, temperature program 60—280℃ at 6℃/min, held isothermal at 280℃ for 20 min and using helium as the carrier gas. Data for qualitative analysis were acquired in the electron impact (EI) mode (70 eV), scanning from 50—550 mass units at 1.50 s/scan.

1.5 Identification and quantification

The identification of PAHs was based on the GC-MS data(i.e. m/z M^+ fragmentograms, retention times compared to that of external standards, and/or mass spectra). Quantification was performed from the GC profiles using the external standard method. Average response factors were calculated for each compound. All quantifications were based on the compounds area derived from the ion fragmentogram.

2 Results and discussion

2.1 PAHs in airborne particles

Only 15 PAHs were quantified in this study. Those PAHs were(according to their elution orders) phenanthrene (PHEN, m/z 178), anthracene (ANTH, m/z 178), fluoranthene(FLT, m/z 202), pyrene (PYR, m/z 202), benz[a]anthracene(BaA, m/z 228), chrysene(CHR, m/z 228), benzofluoranthene(BF, m/z 252), benzo[e]pyrene (BeP, m/z 252), benzo[a]pyrene (BaP, m/z 252), perylene (PER, m/z 252), indeno[1,2,3-c,d]pyrene (IP, m/z 276), dibenz[a,h]anthracene (dBahA, m/z 278), benzo[g,h,i]perylene (BgP, m/z 276), anthanthrene (ANTN, m/z 276), and coronene (COR, m/z 300).

The total PAH concentration was found to be 3.27 ± 1.55 ng/m^3 with individual PAH concentrations ranging from 0.003—2.078 ng/m^3 (Table 1). The total PAH concentration is lower than those measured in urban locations in Kuala Lumpur, Malaysia(6.24 ± 4.58 ng/m^3, Table 1; Omar, 2002). The difference in concentrations of PAHs in the two samples reflects the different nature of those samples. As a comparison, the total PAHs concentration of uncontrolled landfill fire is reported to be 810 ng/m^3 (Ruokojärvi, 1995). The total concentration of PAHs in the combustion gases(particles and vapor) during simulated house fires range between 6.4 to 470 mg/m^3 (Ruokojärvi, 2000). The lower concentrations found in this study may also be due to the fact that the particles were collected three months after the incident. It is unavoidable since in this case it was impractical to collect the samples earlier.

Table 1 PAHs in airborne particles

Sample PAHs, ng/m^3	Fire							KL[*]	
	Base-ment	First	Second	Third	Fourth	Average	SD (n=5)	Ave-rage	SD (n=24)
PHEN	0.016	0.013	0.013	0.014	0.012	0.014	0.001	0.17	0.11
ANTH	0.004	0.003	0.002	0.002	0.002	0.003	0.001	0.09	0.05
FLT	0.021	0.025	0.028	0.017	0.017	0.022	0.005	0.12	0.08
PYR	0.027	0.030	0.039	0.023	0.021	0.028	0.007	0.33	0.21
BaA	0.020	0.014	0.020	0.015	0.007	0.015	0.005	0.16	0.12
CHR	0.084	0.066	0.092	0.063	0.047	0.070	0.018	0.19	0.13
BF	0.061	0.027	0.027	0.032	0.020	0.033	0.016	0.59	0.45
BeP	0.095	0.045	0.041	0.056	0.028	0.053	0.026	0.57	0.23
BaP	0.087	0.031	0.032	0.058	0.018	0.045	0.028	0.47	0.36
PER	0.103	0.032	0.035	0.065	0.032	0.053	0.031	0.18	0.14
IP	0.145	0.068	0.051	0.088	0.041	0.078	0.041	0.69	0.57
dBahA	0.038	0.012	0.008	0.012	0.006	0.015	0.013	0.05	0.05
BgP	1.220	0.559	0.428	0.876	0.339	0.684	0.362	1.35	0.95
ANTN	0.133	0.071	0.083	0.114	0.000	0.080	0.051	0.17	0.19
COR	3.340	1.687	1.472	2.890	1.001	2.078	0.991	1.11	0.94
Total	5.391	2.683	2.371	4.325	1.588	3.272	1.549	6.24	4.58
	Ratios								
PHEN/(PHEN + ANTH)	0.81	0.80	0.87	0.86	0.88	0.85	0.04	0.64	0.09
FLT/(FLT + PYR)	0.44	0.46	0.42	0.42	0.44	0.44	0.01	0.28	0.03
BeP/(BeP + BaP)	0.52	0.59	0.56	0.49	0.61	0.56	0.05	0.57	0.04
IP/(IP + BgP)	0.11	0.11	0.11	0.09	0.11	0.10	0.01	0.33	0.08

Notes: [*] Omar *et al*. (2002)

The molecular distributions of PAHs for the five studied airborne particulate samples resemble each other closely with BgP and COR being the most abundant compounds(Fig. 1a,

based on the average of all samples). BgP and COR are also reported to be the most abundant PAHs in atmospheric particles (Gordon, 1973; Grosjean, 1993). These distributions are however different from those observed for Kuala Lumpur urban atmospheric samples(Fig. 1b) (Omar, 2002). The major difference is that the concentration of COR is higher than the concentration of BgP. CHR is also quite prominent in the studied samples.
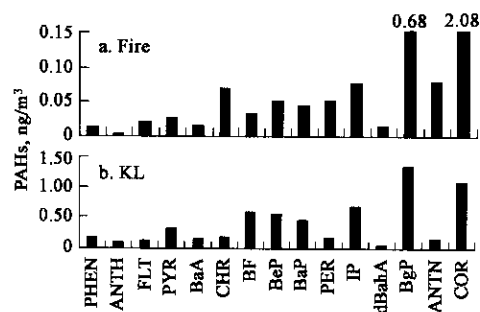

Fig.1　Distributions of PAHs in airborne particles

The diagnostic ratios for smoke samples are as follows (Table 1; mean $\pm$ SD; $n = 5$): (a) PHEN/(PHEN + ANTH) = 0.85 ± 0.04; (b) FLT/(FLT + PYR) = 0.44 ± 0.01; (c) BeP/(BeP + BaP) = 0.56 ± 0.05; and (d) IP/(IP + BgP) = 0.10 ± 0.01. Except for BeP/(BeP + BaP) ratio, which has the same value as that measured for Kuala Lumpur samples, the other diagnostic ratios differed. In addition, weak correlation (R^2 = 0.4841, n = 15) between both samples is observed (Fig. 2). These results implied that PAHs are of different origins. The similarity in BeP/(BeP + BaP) with values of 0.56 and 0.57 may indicate that both type of samples were fresh and/or no photochemical oxidation had occurred(Nielsen, 1988). This is based on the fact that BaP and is more reactive than BeP in the environment (Nielsen, 1988) and both isomers are released in a ratio of 1:1 from most combustion sources (Spitzer, 1993).
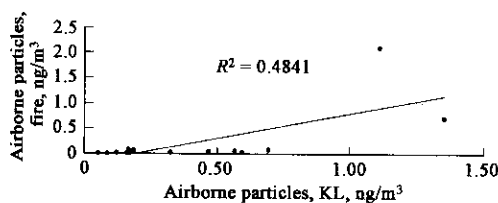

Fig.2　Correlations of PAHs in airborne particles

The highest PAHs concentration was observed for the "basement" where the chemical store was located, while the lowest concentration was at the fourth level, which is the last floor of the building. The higher concentration observed for the third level compared to the other two lower floors may be because the sample was collected from a badly ventilated room.

2.2　PAHs in soot deposit

The main PAHs identified were the same as those found in air-smoke samples. The total PAH concentration was found to be 12.81 ± 24.37 $\mu g/g$ with individual PAH concentrations ranging from 0.09—1.63 $\mu g/g$(Table 2). The concentrations of PAHs in soot deposit are much higher than those measured for urban roadside soil particles (Table 2) (Omar, 2002).

The molecular distributions of PAHs for the soot deposit samples are shown in Fig. 3a. Based on the average of the

five studied samples, FLT, PYR, and BgP are the most abundant compounds. These compounds have also been found to be dominant in deposited soot samples from simulated house fires (Ruokojärvi, 2000). Furthermore, these distributions are different from those observed for Kuala Lumpur urban roadside soil particles, which showed the highest PAH level at only lower molecular weight compounds (Fig. 3b) (Omar, 2002). Also no correlation was found between the two types of samples(R^2 = 0.2259, n = 15) (Fig. 4). It should be pointed out that the different nature of the studied particles (i.e., soot and soil particles) as well as the different particle size (soot particles $\leqslant$ 53 μm versus roadside soil particles $\leqslant$ 600 μm) might have influenced the distribution of PAHs.

Table 2　PAHs in soot deposit

Sample	Fire							KL*	
PAHs, $\mu g/g$	FSP1	FSP2	FSP3	FSP4	FSP5	Average	SD ($n = 5$)	Average	SD ($n = 24$)
PHEN	1.489	0.215	0.023	0.097	0.018	0.368	0.632	0.043	0.024
ANTH	0.371	0.035	0.008	0.018	0.009	0.088	0.159	0.005	0.004
FLT	5.853	0.433	0.048	0.226	0.020	1.316	2.542	0.028	0.013
PYR	7.186	0.600	0.059	0.302	0.021	1.634	3.113	0.039	0.016
BaA	3.956	0.293	0.038	0.171	0.014	0.895	1.715	0.005	0.005
CHR	5.241	0.603	0.077	0.272	0.026	1.244	2.246	0.02	0.007
BF	5.432	0.500	0.080	0.273	0.026	1.262	2.338	0.008	0.007
BeP	3.869	0.319	0.055	0.191	0.018	0.890	1.669	0.013	0.007
BaP	4.340	0.160	0.032	0.199	0.016	0.949	1.897	0.006	0.005
PER	1.422	0.067	0.017	0.078	0.009	0.319	0.617	0.004	0.004
IP	4.018	0.272	0.053	0.197	0.023	0.912	1.739	0.006	0.004
DBahA	0.614	0.024	0.007	0.023	0.005	0.135	0.268	0.001	0.001
BgP	6.225	0.366	0.080	0.297	0.035	1.401	2.700	0.02	0.016
ANTN	1.180	0.032	0.009	0.042	0.010	0.255	0.518	0.002	0.006
COR	5.105	0.298	0.058	0.214	0.030	1.141	2.219	0.02	0.023
Total	56.300	4.217	0.643	2.600	0.278	12.808	24.371	0.220	0.142
Ratios									
PHEN/(PHEN + ANTH)	0.80	0.86	0.75	0.84	0.66	0.78	0.08	0.90	0.03
FLT/(FLT + PYR)	0.45	0.42	0.45	0.43	0.49	0.45	0.03	0.42	0.05
BeP/(BeP + BaP)	0.47	0.67	0.63	0.49	0.53	0.56	0.09	0.72	0.08
IP/(IP + BgP)	0.39	0.43	0.40	0.40	0.39	0.40	0.01	0.25	0.1

Note: * Omar et al., 2002

The diagnostic ratios for soot deposit samples are as follows(Table 2; mean $\pm$ SD; $n = 5$): (a) PHEN/(PHEN + ANTH) = 0.78 ± 0.08; (b)FLT/(FLT + PYR) = 0.45 $\pm$ 0.03; (c) BeP/(BeP + BaP) = 0.56 ± 0.09; and (d) IP/(IP + BgP) = 0.40 ± 0.01. The first, second, and third ratios are closed to those measured for airborne particles (Table 1) reflecting the similarity in origin. However, the ratio IP/(IP + BgP) is higher for the soot samples as compared to the air particles (0.1) which in turn indicates that BgP and COR tend to be attached to finer particles and reside in the air for longer periods.

The highest PAHs concentration is observed for "FSP1" where the chemical store was located, while the lowest concentration is for " FSP5 ", which was collected from adjacent wings to the last two floors.

2.3　Comparison of PAHs distribution in airborne particles and soot deposit

Relative to low and moderate molecular weight PAHs, higher molecular weight compounds such as BgP and COR
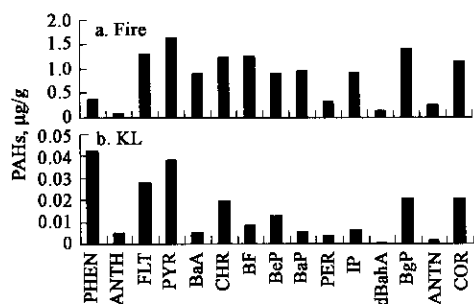
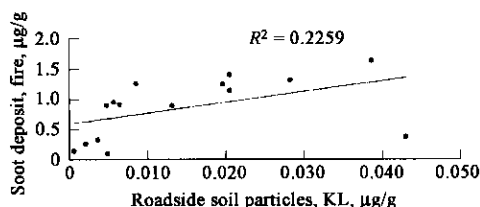Fig.3   Distributions of PAHs in soot deposits and roadside soil particles

Fig.4   Correlations of PAHs in soot deposit and roadside soil particles

were more abundant in airborne particulate samples compared to soot deposit. Lower molecular weight PAHs predominate in larger particles, which deposit faster and easier, whereas high molecular weight ones predominate in the smaller particles that deposit slowly from the atmosphere (Clarke, 1992; Venkataraman, 1994). Since the air samples were collected about three months after the fire, thus only higher molecular weight PAHs remain airborne. In addition, Aceves and Grimalt (Aceves, 1993) had also reported higher proportions of lower molecular weight PAHs in aerosols with diameter > 7.2 μm. When the particles exceed 2.0 μm in size, removal from the air by sedimentation becomes significant (Smith, 2000). Furthermore, from their measurement of PAHs associated with size-segregated aerosols, Allen *et al*. (Allen, 1996) had found that PAHs with molecular weights > 228 were associated primarily with the fine(< 2 μm) aerosol fraction and thus remain longer in the atmosphere. For airborne particulate samples, the percentage of 3—4 rings PAHs is 5.33% ± 2.20%, while for soot deposit samples the value is 42.79% ± 5.27%. The percentages of 5—7 rings PAHs are 94.67% ± 2.20% and 57.21% ± 5.27%, respectively.

3   Conclusions

The concentrations of PAHs in airborne particles and soot deposit are found to be 3.27 ± 1.55 ng/m^3 and 12.81 ± 24.37 μg/g, respectively. The molecular distributions of PAHs as well as their diagnostic ratios such as PHEN/(PHEN + ANTH), FLT/(FLT + PYR) and BeP/(BeP + BaP) implied that PAHs in both airborne particles and soot deposit originated from the same source. However, the results of this study have reinforced the arguments that higher molecular weight PAHs are attached to finer particles and thus remain longer in the air. Whereas for the soot deposit, an almost equivalent amounts of lower molecular weight and higher molecular weight PAHs are obtained.

References:

Aceves M, Grimalt J O, 1993. Seasonally dependent size distributions of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas[J]. Environmental Science and Technology, 27: 2896—2908.

Allen J O, Dookeran N M, Smith K A *et al*., 1996. Measurement of polycyclic aromatic hydrocarbons associated with size-segregated atmospheric aerosols in Massachusetts[J]. Environmental Science and Technology, 30: 1023—1031.

Barnett J R, 2001. "Fire". Microsoft® encarta® Online Encyclopedia[EB]. http://encarta.msn.com.

Clarke A G, 1992. The atmosphere[M] (Harrison, R.M. ed.). Understanding our environment: An introduction to environmental chemistry and pollution. 2nd ed. Cambridge: Royal Society of Chemistry. 5—51.

Finlayson-Pitts B J, Pitts J N Jr, 1986. Atmospheric chemistry: Fundamentals and experimental techniques[M]. New York: John Wiley and Sons. 877—895.

Gabos S, Ikonomou M G, Schopflocher D *et al*., 2001. Characteristics of PAHs, PCDD/Fs and PCBs in sediment following forest fires in northern Alberta[J]. Chemosphere, 43: 709—719.

Gordon G E, Bryan R J, 1973. Patterns in airborne polynuclear hydrocarbon concentration at four Los Angeles sites [J]. Environmental Science and Technology, 7: 1050—1053.

Grosjean D, 1993. Polycyclic aromatic hydrocarbons in Los Angeles air from samples collected on Teflon, glass and quartz fibres [J]. Atmospheric Environment, 17: 2565—2573.

Hartzel G E, Switzer W G, 1981. Combustion products and their effects on life safety[M]. In: Fire protection handbook(McKinnon, G. P. ed.). National Fire Protection Association. Quincy, Massachusetts. 3:19—23.

Larson R A, Weber E J, 1994. Reaction mechanisms in environmental organic chemistry[M]. Boca Raton, FL: Lewis Publishers. 28—30; 257—258.

Levendis Y A, Atal A, Carlson J B *et al*., 2001. PAH and soot emissions from burning components of medical waste: examination/surgical gloves and cotton pads[J]. Chemosphere, 42: 775—783.

Meharg A A, Wright J, Dyke H *et al*., 1998. Polycyclic aromatic hydrocarbon (PAH) dispersion and deposition to vegetation and soil following a large scale chemical fire[J]. Environmental Pollution, 99: 29—36.

Nielsen T, 1988. The decay of benzo(a)pyrene and cyclopenteno(cd)pyrene in the atmosphere[J]. Atmospheric Environment, 22: 2249—2254.

Omar N Y M J, Abas M R B, Ketuly K A *et al*., 2002. Concentrations of PAHs in atmospheric particles(PM$_{10}$) and roadside soil particles collected in Kuala Lumpur, Malaysia[J]. Atmospheric Environment, 36: 247—254.

Rasmussen B, Duijm N J, Markert F, 1998. Airborne releases from fires involving chemical waste—a multidisciplinary case study [J]. Journal of Hazardous Materials, 57: 259—275.

Ruokojärvi P, Ruuskanen J, Ettala M *et al*., 1995. Formation of polyaromatic hydrocarbons and polychlorinated organic compounds in municipal waste landfill fires[J]. Chemosphere, 31: 3899—3908.

Ruokojärvi P, Aatamila M, Ruuskanen J, 2000. Toxic chlorinated and polyaromatic hydrocarbons in simulated house fires[J]. Chemosphere, 41: 825—828.

Saeed T, Ahmad N, Al-Omair A *et al*., 1998. Comparison of the levels of PAHs present in the dust collected from different residential areas of Kuwait, 1991—1996[J]. Environmental International, 24: 197—203.

Smith K E C, Jones K C, 2000. Particles and vegetation: implications for the transfer of particle-bound organic contaminants to vegetation[J]. The Science of the Total Environment, 246: 207—236.

Spitzer T, Kuwatsuka S, 1993. Residue levels of polynuclear aromatic compounds in urban surface soil from Japan[J]. Journal of Chromatography, 643: 305—309.

Venkataraman C, Friedlander S K, 1994. Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 2. Ambient measurements and effects of atmospheric processes [J]. Environmental Science and Technology, 28: 563—572.

Wichmann H, Lorenz W, Bahadir M, 1995. Release of PCDD/F and PAH during vehicle fires in traffic tunnels[J]. Chemosphere, 31: 2755—2766.

Wobst M, Wichmann H, Bahadir M, 1999. Surface contamination with PASH, PAH and PCDD/F after a fire accidents in private residences [J]. Chemosphere, 38: 1685—1691.

Zander M, 1980. Polycyclic aromatic and heteroaromatic hydrocarbons [M]. (Hutzinger, O. ed.) The handbook of environmental chemistry (anthropogenic compounds). Vol. 3, Part A. Berlin: Springer-Verlag. 109—131.