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Simon, Valérie  and Moreau, Lucile  and Romdhana, Mohamed Hédi  and Sablayrolles, Caroline  and Vignoles-Montrejaud, Mireille  and Lecomte, Didier *Emissions of Polycyclic Aromatic Hydrocarbon Particulates from combustion of different fuels*. (2012) *Fresenius Environmental Bulletin*, 21 (4a). 946-955. ISSN 1610-2304

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EMISSIONS OF POLYCYCLIC AROMATIC HYDROCARBON PARTICULATES FROM COMBUSTION OF DIFFERENT FUELS

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ABSTRACT

The use of biomass as fuel for combustion allows partial replacement of fossil fuels and the reduction of fossil carbon dioxide emissions. Nevertheless, combustion of biomass waste may generate toxic pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs) whose production is related to the combustion temperature, oxygen consumption and origin of the biomass fuel.

In the present study, experimental protocols for biomass combustion and analytical quantification of PAHs were carried out. Six types of fuel were burned in a tubular reactor: two bio-solids dried differently (air drying and fry drying), oil-shale, used cooking oil (for recycling) and two types of woody biomass (oak and beech). The combustion tests were performed at 850°C with fixed bed samples weighing about 1 g. The identification and quantification of PAHs in the particulate phase were performed by ultrasonic extraction followed by high-resolution gas chromatography coupled to low-resolution mass spectrometry. The 16 main EPA-classified PAHs have been identified. The results show that emissions of fry-dried sludge are approximately 5000 $\mu\text{g g}^{-1}$, thus 10 times greater than those of wood and 10 times lower than those of used cooking oils. Toxicity of the particulate phase was essentially due to benzo(a)pyrene and benzo(b)fluoranthene.

KEYWORDS: PAHs, emissions, Fry-dried sludge, Air-dried sludge, Woody biomass, Oil shale

1. INTRODUCTION

Biomass combustion is a very important processing operation as it gives a large volume reduction and recovery of energy, and should thus be considered for destruction of toxic biomass such as wastewater treatment plant by-products. However combustion, while once regarded as an effective solution, is now facing environmental problems due to stricter air pollution standards, especially particulate and gaseous emissions.

According to the European Council Directive 96/62/EC, European Union Member States must establish limit values for incineration emissions. Moreover, Directive 2000/76/EC requires limitation of the effects of waste incineration and co-incineration on the environment, in particular emissions to air, soil, surface water and groundwater with the resulting risks to human health.

Ash, carbon dioxide and water are the major combustion effluents. Other compounds such as sulfur oxides (SO_x), nitrogen oxides (NO_x), heavy metals, chlorinated hydrocarbons (dioxins and furans), volatile organic compounds and polycyclic aromatic hydrocarbons (PAHs) are produced in smaller quantities but are more dangerous in terms of environmental impact and human health [1-5]. Polycyclic aromatic hydrocarbons (PAHs) consist of two or more fused benzene rings, and most of them are semi-volatile and highly carcinogenic and mutagenic [6-11]. The atmospheric PAHs are gas phase partitioned and adsorbed to particulate matter according to their vapour pressure and atmospheric conditions [12]. Low molecular weight PAHs tend to be more concentrated in the gaseous phase, while those with higher molecular weights are often associated with particulates, and the PAHs recognized as carcinogenic are also mostly found with particulate matter. The formation of organic hydrocarbons during incineration is affected by many operating parameters such as type of fuel [13-16], but also combustion temperature, waste composition, flow rate and composition of feed gas [5, 17-20]. Certain studies have shown that PAH emissions are at a maximum between 800°C and 1000°C for wood [21] and for acrylic waste [22], whereas a drop in emissions between 500 and 800°C has been observed during the incineration of wastewater treatment plant sludges [23]. An increase in the concentration of oxygen in the feed gas results, in the case of wastewater treatment plant sludges, in an increase in PAH emissions at temperatures between 500°C and 800°C [23]. For coal combustion, an excess of at least 10% oxygen decreases particulate PAH emissions to almost zero, whereas emission of particles increases with 5 to 40% excess oxygen [15]. The flow of air through the combustion oven is also important. Incineration with a low airflow for temperatures between 700-800°C and with a higher flow for temperatures between 900-1000°C

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favours a decrease in PAH emissions [19, 24]. The combustion mode also has an impact. In fluidized bed combustion, bed material mixes well with air, and its combustion flame is different from that of a fixed bed. For low temperature fixed bed combustion, PAHs are formed through pyrolysis, however, at high temperatures, PAHs are formed from precursors [25].

In order to make further reductions in PAH polluted emissions the council directive 2004/107/EC sets target values for concentrations of benzo(a)pyrene (1 ng m^{-3}) used as a tracer for the PAH carcinogenic risk. Generally, PAHs are produced during incomplete burning or pyrolysis at high temperatures [17, 26].

Some chemical reactions may result in the formation of PAHs, such as cyclization reactions of alkyl groups and the polymerization reactions following a condensation reaction [26]. Because of their ubiquity in the environment, PAHs are found in various materials such as fossil fuels, and also in industrial biomass such as sludge from wastewater treatment plants [16, 27].

To obtain reliable data on the composition and concentrations of PAHs in particulate matter, versatile analytical methods are necessary for efficient sample processing and for subsequent chemical analyses. Traditional methods of sample preparation for the determination of particulate-bound PAHs include Soxhlet extraction, sonication, microwave-assisted extraction (MAE) or pressurized liquid extraction (PLE) [28-33]. For the analysis step, GC-MS and HPLC-fluorescence detection has been found to be the best for the determination of PAHs in environmental samples [29, 33, 34].

Various studies have sought to develop combustion experiments in order to analyze PAH emissions for different fuels, such as forest and agricultural biomass [14], wood [21], coal [15, 19, 26], urban solid waste [20, 35], sewage sludge [36], oily sludge [37], plastic waste especially polyethylene [37] and acrylic polymer [22, 24].

Emissions data for PAHs is necessary to inventory fuel burn, in order to create life cycle assessment of the combustion process. However, there is still very little information regarding the PAH emissions for dry-biomass

combustion. This is the context of the present study, to measure the PAH concentrations in combustion of air-dried (ADS) and fry-dried sludge (FDS) obtained from a pulp and paper manufacturing unit, particularly focussing on the comparison of these emissions with various other biomass burned under the same conditions.

2. MATERIALS AND METHODS

2.1. Chemicals and standards

A standard mix containing naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLR), phenanthrene (PHE), anthracene (ANT), fluoranthene (FTN), pyrene (PYR), benzo(a)anthracene (B(a)A), chrysene (CHRY), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), dibenzo(a,h)anthracene (D(ah)A), benzo(g,h,i)perylene (B(ghi)P) and indeno(1,2,3-cd)pyrene (IND) at $100 \mu\text{g mL}^{-1}$ of methanol:dichloromethane (1:1, v:v) was used for calibration (M-610 Accustandard, New Haven, CT, USA).

Deuterated PAHs were used as extraction standards (anthracene d-10 and benzo(a)pyrene d-12 at $300 \mu\text{g mL}^{-1}$ of acetonitrile) and as an internal standard (fluoranthene d-10 at $300 \mu\text{g mL}^{-1}$ of acetonitrile) (Supelco, France). Anthracene d-10 was chosen as a reference for the light PAH fraction (NAP to PYR) and benzo(a)pyrene d-12 for the heavy PAH fraction (B(a)A to B(ghi)P).

All solvents are for residue analysis (>99.8% GC; Fluka).

2.2. Fuel sampling

The fuel samples used are shown in Table 1. The dried biomass, consisting of sewage sludge produced from paper pulp manufacturing, was dried in two different ways: conventional air-drying and a fry-drying process. The air-dried sludge is obtained by drying the sample 24 h at 105°C in a forced air oven. The fry-dried sludge is prepared by immersing the sample in an electric fryer with used cooking oil [38]. The oil temperature was set at 110°C . Residence time of the sewage sludge in the fryer was 10 min. After treatment, the sludge was stored at -18°C .

TABLE 1 - Characterization of the fuels samples.

		Nomenclature	Sample characterization
Dried sludge	Air-drying	ADS	Sewage sludge dried at 105°C in a forced air oven for 24h
	Fry-drying	FDS	Sewage sludge fried at 110°C for 10 min
Woody biomass	Oak	OW	Sawdust composed of fine particles of oak wood ($125\text{-}200 \mu\text{m}$)
	Beech	BW	Shredded wood waste
Oil	Oil shale	OS	Mix of crushed oil shale (75%, $500\text{-}1000 \mu\text{m}$) and sand (25%)
	Used cooking oil	UCO	Used oil collected from restaurants and the food industry

TABLE 2 - C, H, O, N, S, ash, LHV, HHV analysis of fuel samples

	ADS	FDS	UCO	OS	BW	OW
N*	1.8 ± 0.5	0.7 ± 0.3	0.2 ± 0.2	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.1
C*	18.7 ± 2.9	51.4 ± 0.5	77.4 ± 0.4	15.7 ± 1.4	45.8 ± 0.2	44.6 ± 0.2
H*	1.7 ± 0.2	6.5 ± 0.6	12.3 ± 0.3	1.6 ± 0.1	5.9 ± 0.1	5.8 ± 0.2
S*	≤ 0.01	≤ 0.01	≤ 0.01	1.9 ± 0.5	≤ 0.01	≤ 0.01
O*	22.9 ± 2.6	15.9 ± 0.7	10.2 ± 0.7	19.5 ± 1.5	46.2 ± 0.2	48 ± 0.5
Ash*	54.8 ± 0.1	25.6 ± 1.5	0.6 ± 0.6	62.7 ± 0.1	1.7 ± 0.6	1.2 ± 0.4
HHV**	8.1 ± 0.1	27.0 ± 0.7	41.2 ± 0.1	7.9 ± 0.7	24.3 ± 0.1	23.6 ± 0.4
LHV**	7.7 ± 0.1	25.6 ± 0.6	37.7 ± 0.1	7.6 ± 0.6	22.9 ± 0.1	22.4 ± 0.3

*% (dry basis), ** MJ/kg (dry basis)

In order to compare the results obtained with these dried sludges, the experiments were also conducted with currently available fuels from different sources: woody biomass (oak and beech), oil shale and used cooking oil.

2.3. Chemical characterization

The fuel samples were analyzed by standard elemental and proximate analysis. The ultimate analysis gives the elemental (C, H, N, and S) compositions of the total solid matter using a self-integrated and microprocessor controlled elemental analyzer (model: NA 2100 Protein, CE Instruments). The oxygen content is calculated as the complement to 100 of the sum of carbon hydrogen, nitrogen, sulfur and ash, as in equation 1. Table 2 shows the ultimate analysis of the samples used in this study.

$$[O] = 100 - ([C] + [H] + [N] + [S] + [Ash]) \quad (1)$$

The proximate analysis is described by the ash content in a sample [Ash]. The ash content is the residue that remains after combustion at 850°C.

The Lower Heating Value of the fuel samples (LHV) is experimentally measured using the elemental analyzer. The Higher Heating Value (HHV) is calculated from the Lower Heating Values according to equation 2.

$$HHV = LHV + \frac{18}{2} [H] \Delta H_v \quad (2)$$

where ΔH_v is the latent heat of vaporization.

The results of these analyses (C, H, O, N, S, ash, LHV and HHV) are shown in Table 2 and are the average of three experiments.

2.4. Experimental combustion protocol

An experimental device was developed to enable combustion of each fuel sample and sampling of the particulate fraction in the flue gas (Figure 1). The horizontal tubular reactor was used to perform combustion. It consists of a horizontal quartz reactor of 4.5 cm diameter and 66 cm long, heated by electrical resistances placed in refractory fibers. The sample of fuel is fed in batch using a sliding tube at the input of the reactor, and fuel samples are placed in a fused ceramic crucible fixed to this sliding tube. Combustion air is drawn from a bottle of synthetic air and passed continuously through the reactor at a pressure slightly above atmospheric pressure. Total airflow is 0.6 L min⁻¹.

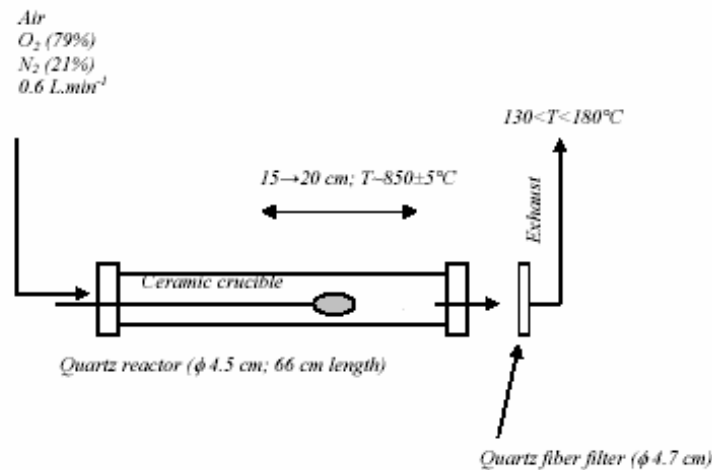


FIGURE 1 - A schematic diagram of the quartz tube of the horizontal combustor

The reactor is heated to a temperature of 850°C, the recommended temperature for the total destruction of sludge organic matter [39] under constant airflow to remove the by-products of combustion. During operation, the tubular reactor has a hot isothermal over a length of 15 to 20 cm. The residence time of flue gas in the hot zone is greater than 2 s and is therefore in agreement with values required by Directive 89/369/EEC for which gases from combustion are heated to a temperature of at least 850°C in the presence of at least 6% oxygen.

Samples of 1 g of fuel in the form of a thin layer (2-3 mm) were placed in the crucible. The temperature in the vicinity of the sample was measured by K-type thermocouple (850±5°C), and the time lag between the introduction of the sample and combustion self-ignition is a few seconds.

In order to cut down external contamination, all devices were carefully cleaned. Glassware (Petri dish, test tube, quartz tube, etc...), the pliers and the ceramic crucible were washed with ether (to eliminate all residual hydrocarbons). Finally, the devices were washed with a special alkaline soap (labwash), and then rinsed with water, deionized water, acetone and dichloromethane.

2.5. Sample collection and analysis

The emitted particulates were collected on quartz fiber filters (diameter 47 cm, Schleicher & Schuell) at a flow rate of 0.6 L min⁻¹. Prior to sampling, filters were kiln-fired at 500°C overnight. Then, the dishes were wrapped in aluminium foil and stored in a desiccator. Laboratory blanks were used for correcting possible contamination from the quartz tube, solvents and storage, for every experimental set. PAH extractions were made within two days. Extractions of blank filters showed no PAH contamination above the quantification limits.

After sampling, a deuterated PAH solution was added on the filters. PAHs eluting between naphthalene and pyrene (low PAHs) were corrected by anthracene-d10 and compounds eluting between benzo(a)anthracene and benzo(ghi)perylene (heavy PAHs) by benzo(a)pyrene-d12.

The particulates on the filter were extracted at 25°C for 1h with dichloromethane in an ultrasonic bath. The extract was concentrated to 1 mL by evaporation under nitrogen flow. Finally, a fluoranthene-d12 solution was added to each sample in micro test tubes which were hermetically sealed and stored at -28°C until analysis. Fluoranthene-d12 was used as internal standard.

Analyses were performed by High Resolution Gas Chromatography (Agilent 6890 Serie GC System) coupled with a Low Resolution Mass Spectrometer (Agilent 5973 Network Mass selective detector) provided with a chromatographic column DB5 MS (30 m × 0.25 mm ×

0.30 µm thickness) (J&W Scientific). Chromatographic conditions were as follows : injector temperature 300°C; injection in splitless mode (1 min); thermal program: 5 min at 100°C, ramp 20°C.min⁻¹ up to 180°C (3 min), ramp 15°C.min⁻¹ up to 260°C (5 min), ramp 10°C.min⁻¹ up to 300°C (10 min); carrier gas helium, 1.4 mL.min⁻¹, injection volume 0.5 µL, temperature transfer line 300°C. The chromatogram was obtained in the Selected Ion Monitoring (SIM) mode from characteristics shown in Table 3.

To study the repeatability of the analysis, a standard solution containing PAH concentrations (1 µg mL⁻¹) was injected 10 times. The relative standard deviation determined for each PAH (from 4% for ACE to 9% for PHE) is less than 10%. The reproducibility and the PAH recovery have been evaluated using the different experiments shown in Table 4. The reproducibility concerning the total PAH concentrations ranged between 16% and 38% for oak and fry-drying respectively; recoveries ranged from 78% for the low molecular weight PAHs to 85% for those with high molecular weight.

The internal standard quantification method was performed for each compound for the 0-100 µg mL⁻¹ linear domain. The analytical quantification limits (S/N=10) for individual PAH compounds were between 0.3-0.7 ng (Table 3). Limits of quantification for the emission rates are between 0.6 and 1.4 µg g⁻¹ for all fuels except fry-dried sludge and used cooking oils (1.8-4.2 µg g⁻¹).

2.6. Emission rates

The emission rate τ_{PAH} expresses the ratio between the mass of PAHs collected on the filter and the total fuel mass. It is calculated according to relationship 3.

$$\tau_{\text{PAH}} = [\text{PAH}]_f \frac{m_c m_i}{\rho m_p} \quad (3)$$

where, m_i is the mass of dichloromethane used for extraction by ultrasound, m_p is the mass of a sample taken for concentration, m_c is the mass of extract obtained after concentration, ρ is the density of dichloromethane and $[\text{PAH}]_f$ is the concentration of final extract obtained by chromatographic analysis (µg mL⁻¹).

3. RESULTS AND DISCUSSION

The total emissions of PAHs (particulate phase) vary depending on the fuel sample (Table 4). The emission rate varies between 123 and 45455 µg g⁻¹ for air-dried sludge and used cooking oils respectively. Emission from fry-dried sludge is in the region of 5000 µg g⁻¹ thus 10 times higher than those for wood and 10 times lower than those for oils.

TABLE 3 - Nomenclature, number of aromatic rings, retention time, m/z of specific fragments used in SIM data acquisition mode, limit of detection⁽¹⁾, limit of quantification⁽²⁾.

PAH	Nomenclature	Number of aromatic rings	Particle/gas phase distribution [40]	Retention time (min)	Quantification ion	Confirmation ion	LOD ⁽¹⁾ (ng)	LOQ ⁽²⁾ (ng)
Naphthalene	NAP	2	Gas phase	6.7	128	126	0.09	0.3
Acenaphthylene	ACY	2	Gas phase	10.1	152	150	0.09	0.3
Acenaphthene	ACE	2	Gas phase	10.4	154	151	0.09	0.3
Fluorene	FLR	2	Gas phase	11.7	166	165	0.09	0.3
Phenanthrene	PHE	3	Particle Gas phase	14.4	178	176	0.09	0.3
Anthracene	ANT	3	Particle Gas phase	14.6	178	176	0.10	0.3
Anthracene d10	ANT-d10	3	Particle Gas phase	14.6	188	186	0.10	0.3
Fluoranthene	FTN	3	Particle Gas phase	17.2	202	200	0.12	0.4
Fluoranthene d10	FTN-d10	3	Particle Gas phase	17.2	212	210	0.12	0.4
Pyrene	PYR	4	Particle Gas phase	17.7	202	200	0.12	0.4
Benzo(a)anthracene	B[a]A	4	Particle phase	21.1	228	226	0.14	0.5
Chrysene	CHR	4	Particle phase	21.2	228	226	0.14	0.5
Benzo(b)fluoranthene	B[b]F	4	Particle phase	25.3	252	250	0.16	0.5
Benzo(k)fluoranthene	B[k]F	4	Particle phase	25.4	252	250	0.16	0.5
Benzo(a)pyrene	B[a]P	5	Particle phase	26.3	252	250	0.18	0.6
Benzo(a)pyrene d10	B[a]P-d10	5	Particle phase	26.3	264	262	0.18	0.6
Indeno(1,2,3,cd)pyrene	IND	5	Particle phase	30.2	276	277	0.25	0.7
Dibenzo(a,h)anthracene	D[ah]A	5	Particle phase	30.3	278	279	0.25	0.7
Benzo(g,h,i)perylene	B[ghi]P	6	Particle phase	31.3	276	277	0.25	0.7

TABLE 4 - PAH particulate emission rates ($\mu\text{g g}^{-1}$) of dried sludge, woody biomass, used cooking oil and oil shale

	Used cooking oil (UCO)	Fry-drying (FDS)	Air-drying (ADS)	Oak (OW)	Beech (BW)	Oil Shale (OS)
n	5	8	5	5	5	5
Naphthalene	22967 ± 7754	1758 ± 448	3.8 ± 0.8	129 ± 75.3	15.4 ± 3.1	14.9 ± 6.7
Acenaphthylene	529 ± 200	80 ± 18	1.1 ± 0.2	14.8 ± 3.9	16.2 ± 3.2	6.3 ± 4.2
Acenaphthene	395 ± 128	62 ± 17	3.3 ± 0.7	30.8 ± 13.2	32.8 ± 6.6	19.1 ± 8.6
Fluorene	945 ± 396	142 ± 42	3.5 ± 0.7	57.5 ± 20.6	51.0 ± 10.2	3.4 ± 1.6
Phenanthrene	5661 ± 2433	782 ± 174	4.4 ± 0.9	71.1 ± 17	68.5 ± 13.7	72.1 ± 33.0
Anthracene	1525 ± 702	335 ± 137	46.2 ± 9.2	127.4 ± 53.2	61.3 ± 12.3	54.3 ± 23.4
Fluoranthene	3005 ± 1305	516 ± 73	18.4 ± 3.7	46.4 ± 10.6	45.9 ± 9.2	48.0 ± 10.6
Pyrene	2786 ± 1169	495 ± 70	25.8 ± 5.2	54.3 ± 12.2	73.9 ± 14.8	46.3 ± 5.8
Benzo(a)anthracene	330 ± 130	56 ± 22	1.2 ± 0.2	9.1 ± 2.2	9.4 ± 1.9	8.8 ± 2.7
Chrysene	683 ± 394	183 ± 40	7.2 ± 1.4	17.6 ± 4.9	15.7 ± 3.1	12.7 ± 1.6
Benzo(b)fluoranthene	1386 ± 472	<5	5.2 ± 0.4	10.4 ± 3.4	18.0 ± 3.6	38.7 ± 16.3
Benzo(k)fluoranthene	2605 ± 836	250 ± 63	2.1 ± 0.4	16.5 ± 16.2	21.5 ± 4.3	13.9 ± 1.3
Benzo(a)pyrene	522 ± 182	123 ± 60	1.2 ± 0.2	17.4 ± 4.0	25.6 ± 5.1	13.0 ± 5.9
Indeno(1,2,3,c,d)pyrene	723 ± 562	99 ± 40	1.1 ± 0.2	3.1 ± 1.2	2.8 ± 0.6	<1.4
Dibenzo(a,h)anthracene	28 ± 12	<5	<1.4	<1.4	2.6 ± 0.5	<1.4
Benzo(g,h,i)perylene	1366 ± 983	141 ± 52	1.6 ± 0.3	3.9 ± 1.4	3.0 ± 0.6	0.8 ± 0.1
Total ($\mu\text{g g}^{-1}$)	45455	5023	123	605	463	339
$\frac{\mu\text{g} \times \text{g}^{-1}}{100 - \text{Ash}(\%)}$	457	68	3	6	5	9
$\frac{\mu\text{g} \times \text{g}^{-1}}{\text{LHV}(\text{MJ} \times \text{kg}^{-1})}$	1206	196	16	80	20	15

n: number of replicate experiments, $p < 0.05$

The PAH molecules responsible for at least 10% of emissions are (Figure 2):

fry-dried sludge: NAP, PHE, FTN

used cooking oil: NAP, PHE

beech: NAP, PHE, ANT

oak: FLR, PHE, ANT, PYR

oil shale: PHE, ANT, FTN, PYR

air-dried sludge: ANT, FTN, PYR

Indeno(1,2,3,c,d)pyrene and dibenzo(a,h)anthracene molecules were emitted at relatively low levels.

The frequent presence of naphthalene and other light particulate PAHs is the result of adsorption/absorption, because these low molecular weight molecules are more abundant in the gas phase.

A higher fraction of carbon (Figure 3) contained in the combustion fuel resulted in a higher total-PAH concentration in the particulate phase.

Human toxicity was evaluated using benzo(a)pyrene as equivalent carcinogenic toxicity (EQT). The toxic equivalent was calculated using formula 4.

$$PAH_{EQT} = \sum \tau_{PAHi} * TEF_i \quad (4)$$

Where TEF are the toxic equivalence factors [41] and τ_{PAHi} the PAH emission rates.

The toxic equivalents are listed in Table 5. The toxicity of particulate phases was mainly due to the presence of benzo(a)pyrene and indeno(1,2,3,cd)pyrene for all fuels except the oil shale for which the main contributions were from emissions of benzo(a)pyrene and benzo(b)fluoranthene. Although there are high emissions of light PAHs, their contribution to the global toxicity is a minor one.

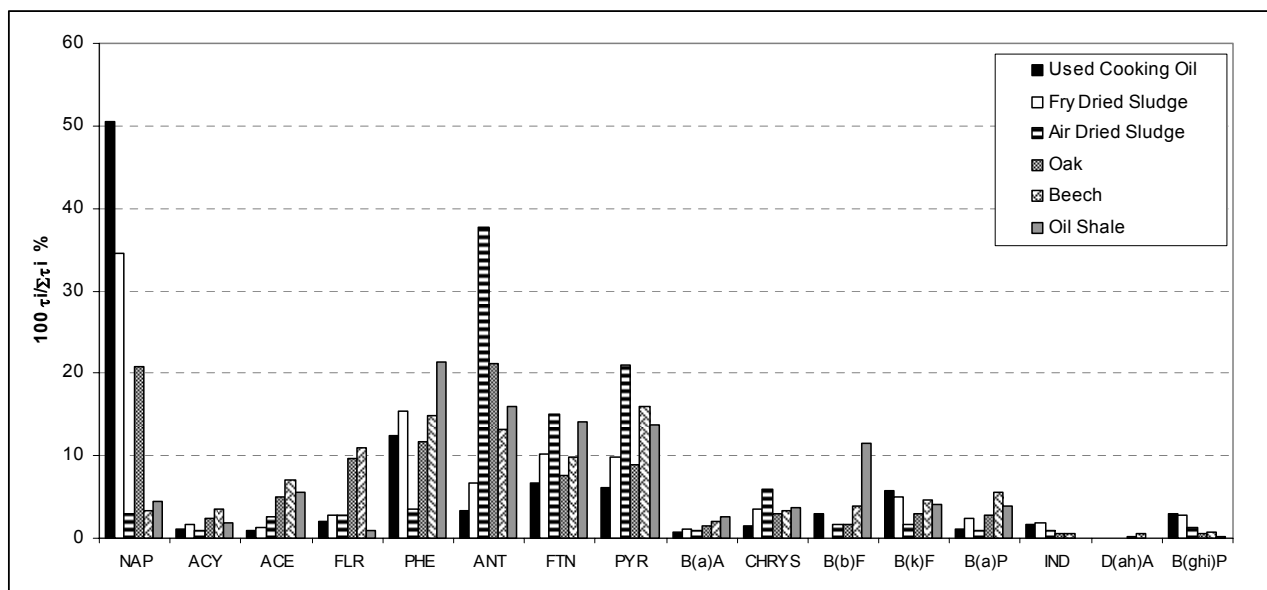


FIGURE 2 - Amount of 16 PAH emissions (%) from combustion

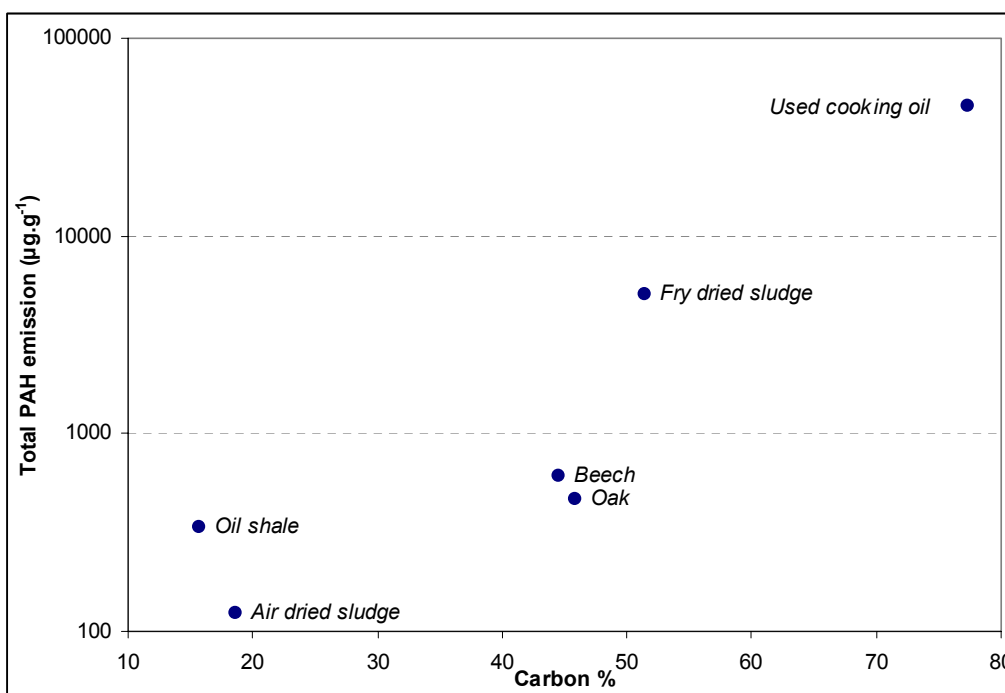


FIGURE 3 - Total PAH emission ($\mu\text{g g}^{-1}$) as a function of the carbon content of the fuel

TABLE 5- Toxic equivalent percentages of B(a)P for each PAH

	Used cooking oil (UCO)	Fry- drying (FDS)	Air-drying (ADS)	Oak (OW)	Beech (BW)	Oil Shale (OS)
Naphthalene	0.5	0.3	0.0	0.3	0.0	0.1
Acenaphthylene	0.0	0.0	0.0	0.0	0.0	0.0
Acenaphthene	0.0	0.0	0.0	0.1	0.1	0.1
Fluorene	0.0	0.0	0.0	0.2	0.1	0.0
Phenanthrene	0.1	0.1	0.0	0.2	0.1	0.3
Anthracene	0.3	5.9	0.1	3.4	1.3	2.6
Fluoranthene	0.1	0.2	5.8	0.1	0.1	0.2
Pyrene	0.1	0.3	0.2	0.1	0.2	0.2
Benzo(a)anthracene	0.7	1.5	1.5	2.4	2.0	4.2
Chrysene	0.1	0.9	0.9	0.5	0.3	0.6
Benzo(b)fluoranthene	2.9	2.5	2.5	2.7	3.9	18.5
Benzo(k)fluoranthene	5.5	2.7	2.6	4.6	4.7	6.6
Benzo(a)pyrene	10.9	15.5	15.0	45.4	56.1	62.3
Indeno(1,2,3,c,d)pyrene	75.9	68.1	68.9	39.0	30.1	3.7
Dibenzo(a,h)anthracene	0.0	0.0	0.0	0.0	0.1	0.0
Benzo(g,h,i)perylene	2.9	2.1	2.0	1.0	0.7	0.4
Total émission rates of toxic equivalents $\sum_i \tau_i \times TFE_i$	4765	669	8	43	46	21

The emission of PAHs may also be related to the mass of fuel or the heating value. PAH composition in the particulate phase was defined as the PAH mass normalized by the total mass of fuel without the ash fraction and by the Lower Heating Value (Table 4). The trend was clearly that the emission factors from used cooking oil are 1 order of magnitude higher than fry-dried sludge and 2 orders of magnitude higher than woody biomass, oil shale and air-dried sludge.

Total PAH particulate emissions were strongly influenced by fuel type and even more strongly by burning conditions. Types of incinerator and combustion temperature are considered as the two major factors for combustion testing [14, 20]. Hence, the results were compared with emissions reported from laboratory scale studies operating in a temperature range between 800-860°C. Experiments performed in a tubular quartz reactor have been conducted for furniture wood waste [21]. Average particulate phase concentration at 800°C is about 2002 $\mu\text{g g}^{-1}$ which is 3-4 times higher than those measured for the BW and OW. However, emission of total PAHs in this study was in the range reported by [42] showing that PAHs from oak and pine were emitted between 100 and 800 $\mu\text{g g}^{-1}$ depending on the nature of wood and the altitude. Lower emission ranges varying between 126-229 $\mu\text{g g}^{-1}$ and 172-472 $\mu\text{g g}^{-1}$ for agricultural woods and forest wood respectively were also found [14].

Emissions of total PAH particulates from UCO were one order of magnitude higher than literature values for oily sludge taken from a crude oil storage tank of a petroleum refinery plant [37]. Nevertheless, the total PAH particulate emissions from oily sludge are close to the

emission from FDS. Despite the high values of emissions from FDS mainly due to the oily fraction, these values are in the same range as some agricultural biomass. Barley straw, wheat straw and corn stover yielded a higher concentration of PAH particulates (2298-3953 $\mu\text{g g}^{-1}$) [14]. The relatively lower concentration of PAHs formed under ADS combustion was also found with the combustion of coal, liquid diesel fuel and polyethylene plastic [15, 19, 37].

The spread of emissions as a function of the number of aromatic rings is shown in Figure 4. PAHs with 2 and 3 rings account for between 62 and 78% of emissions, those with 4 rings between 17 and 27% whereas the PAHs with 5 and 6-rings are in a minority (< to 10%) whatever the fuel.

The 2 and 3 ring PAHs, that are molecules generated in the gaseous phase (Table 3), are found in very high proportions in the particulate phase. In general, the concentrations in the particulate phase are overestimated for these molecules [43, 44], mainly due to sorption of gaseous compounds on the filter during sampling. For the heaviest molecules, an underestimation of the concentrations could be linked to volatilization from particulate on the filter.

Many studies have proposed that the ratios of PAH compounds can be used for source identification [16, 30, 45-47]. The calculated values for the most frequently used ratios of PAHs are listed in table 6. The B(ghi)P/IND and B(a)A/B(a)P show minimal variations and do not permit source identification. Conversely, PYR/B(a)P and B(a)P/B(ghi)P make it possible to discriminate the origins.

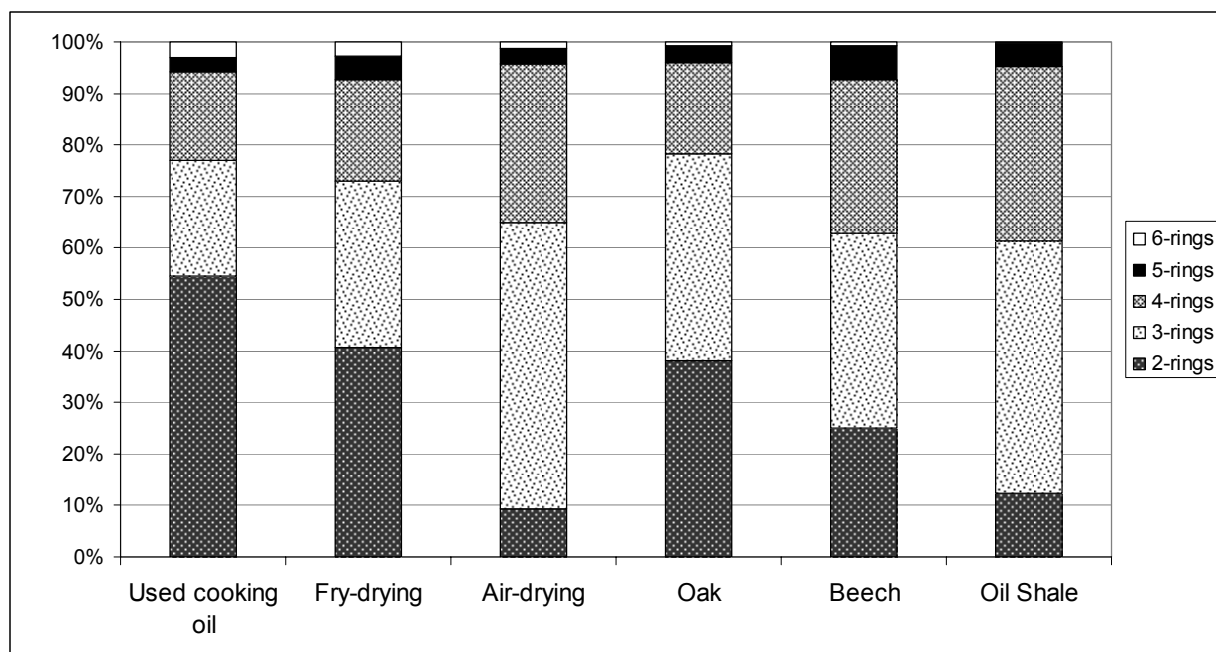


FIGURE 4 - Emissions distribution as a function of the aromatic rings number.

TABLE 6 - Comparison of PAH characteristic ratios (calculated from mean emission rates)

PAH ratios	Used cooking oil (UCO)	Fry- drying (FDS)	Air-drying (ADS)	Beech (BW)	Oak (OW)	Oil Shale (OS)
PYR/B(a)P	5.8	4.2	15.3	2.7	1.8	3.7
B(a)P/B(ghi)P	0.4	0.9	0.8	4.5	8.5	16.3
B(ghi)P/IND	1.9	1.4	1.5	1.3	1.1	>0.6
B(a)P/B(a)P	0.6	0.5	1.0	0.5	0.4	0.7

4. CONCLUSION

The objective of this work was to study the emissions of particulate PAHs in combustion of different types of fuels: used cooking oils, air-dried sludge, fry-dried sludge, woody biomass and oil shale. This work proposes an experimental protocol for combustion, the sampling of the particulate phase, and identification and quantification of the 16 priority PAH pollutants listed by the Environmental Protection Agency. The emission rates depend on the initial composition of the raw fuel, in particular the carbon and hydrogen content. Both used cooking oil and fry-dried sludge have the highest emission levels 45455 and 5023 $\mu\text{g g}^{-1}$ respectively; and these last ones are respectively 10, 15 and 40 order of magnitude higher than woody biomass, oil shale and air-dried sludge. Generally, the PAHs which contribute most significantly to the emission levels are: naphthalene, phenanthrene, fluoranthene, anthracene and pyrene. Particulate phase toxicity, calculated as benzo(a)pyrene equivalents, was essentially due to benzo(a)pyrene and benzo(b)fluoranthene. These results are an extremely useful indicator for predicting the adverse effects of this combustion on human health.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of ADEME "Agency for environment and energy management" and Midi-Pyrénées region.

REFERENCES

- [1] Liem, D.A. and Van Zorge, J.A. (1995) Dioxins and related compounds status and regulatory aspects. *Environ. Sci. & Pollut. Res.* 2(1), 46-56.
- [2] Bignal, K.L., Langridge, S. and Zhou, J.L. (2008) Release of polycyclic aromatic hydrocarbons, carbon monoxide and particulate matter from biomass combustion in a wood-fired boiler under varying boiler conditions. *Atmos. Environ.* 42, 8863-8871.
- [3] Jolliet, O., Brent, A., Geedkoop, M., Itsubo, N., Mueller-Wenk, R., Pena, C., Schenk, R., Stewart, M. and Weidema, B. (2003) Final Report of the LCIA Definition Study. Life Cycle Impact Assessment Programme of the UNEP/SETAC Life Cycle Initiative.
- [4] Werther, J. and Ogada, T. (1999) Sewage sludge combustion. *Prog. Energy. Combust. Sci.* 25, 55-116.

- [5] Lavric, E.D., Konnov, A.A. and De Ruyck, J. (2004) Dioxin levels in wood combustion-a review. *Biomass and Bioenergy* 26, 115-145.
- [6] International Agency for Research on Cancer (1983) Evaluation of carcinogenic risk of chemicals to humans. Polycyclic aromatic compounds, Part 1, chemical, environmental and experimental data. Monograph No 32. IARC, Lyon.
- [7] Steineck, G., Plato, N., Alfredsson, L. and Norell, S.E. (1989) Industry-related urothelial carcinogens: application of a job-exposure matrix to census data. *Am. J. Ind. Med.* 16, 209-224.
- [8] Grimmer, G., Brune, H., Dettbarn, G., Jacob, J., Misfeld, J., Mohr, U., Naujaek, K.W., Timm, J. and Wenzel-Hartung, R. (1991) Relevance of polycyclic aromatic hydrocarbons as environmental carcinogens. *Fresenius J. Anal. Chem.* 339, 792-795.
- [9] Mumtaz, M.M., George, J.D. and Gold, K.W. (1996) ATSDR evaluation of health effects of chemicals. IV. Polycyclic hydrocarbons (PAHs): understanding a complex problem. *Toxicology and Industrial Health* 12(6), 742-995.
- [10] Soontjens, C.D., Holmberg, K., Westerholm, R.N. and Rafter, J.J. (1997) Characterization of polycyclic aromatic compounds in diesel exhaust particulate extract responsible for aryl hydrocarbon receptor activity. *Atmos. Environ.* 31(2), 219-225.
- [11] Pesch, B., Haerting, J., Ranft, U., Klimpel, A., Oelschlagel, B. and Schill, W. (2000) Occupational risk factors for urothelial carcinoma: agent-specific results from a case control study in Germany. *Int. J. Epidemiol.* 29, 238-247.
- [12] Pankow, J.F. (1987) Review and comparative analysis of the theories of partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.* 21(11), 2275-2283.
- [13] Hedberg, E., Kristensson, A., Ohlsson, M., Johansson, C., Johansson, P.E., Swietlicki, E., Vesely, V., Wideqvist, U. and Westerholm, R. (2002) Chemical and physical characterization of emissions from birch wood combustion in a wood stove. *Atmos. Environ.* 36(30), 4823-4837.
- [14] Jenkins, B.M., Jones, A.D., Turn, S.Q. and Williams R.B. (1996) Particle concentrations, gas-particle partitioning, and species intercorrelations for Polycyclic Aromatic Hydrocarbons (PAH) emitted during biomass burning. *Atmos. Environ.* 30(22), 3825-3835.
- [15] Mastral, A.M., Callen, M.S. and Garcia, T. (1999) Polycyclic Aromatic Hydrocarbons and Organic Matter Associated to Particulate Matter Emitted from Atmospheric Fluidized Bed Coal Combustion. *Environ. Sci. Technol.* 33(18), 3177-3184.
- [16] Cai, Q.Y., Mo, C.H., Wu, Q.T., Zeng, Q.Y. and Katsoyianis, A. (2007) Occurrence of organic contaminants in sewage sludges from eleven wastewater treatment plants, China. *Chemosphere* 68(9), 1751-1762.
- [17] Yan, J.H., You, X.F., Li, X.D., Ni, M.J., Yin, X.F., and Cen, K.F. (2004) Performance of PAHs emission from bituminous coal combustion. *Journal of Zhejiang University - Science* 5(12), 1554-1564.
- [18] Chien, Y.C., Liang, C.P. and Shih, P.H. (2009) Emission of polycyclic hydrocarbons from the pyrolysis of liquid crystal wastes. *J. Hazard. Mater.* 170, 910-914.
- [19] Mastral, A.M., Callen, M.S., Murillo, R., Garcia, T. and Vinas, M. (1999) Influence on PAH emissions of the air flow in AFB coal combustion. *Fuel* 78, 1553-1557.
- [20] Chianga, P.C., You, J.H., Chang, S.C and Wei, Y.H. (1992) Identification of toxic PAH compounds in emitted particulates from incineration of urban solid wastes. *J. Hazard. Mater.* 31(1), 29-37.
- [21] Khalfi, A., Trouve, G., Delobel, R. and Delfosse, L. (2000) Correlation of CO and PAH emissions during laboratory-scale incineration of wood waste furniture. *Journal of Analytical and Applied Pyrolysis* 56, 243-262.
- [22] Singh, S. and Prakash, V. (2007) The effect of temperature on PAHs emission from incineration of acrylic waste. *Environmental Monitoring and Assessment* 127, 73-77.
- [23] Wei, Y.L. and Wu, C.H. (1997) PAH emissions from fluidized-bed incineration of an industrial sludge. *Air & waste manage. assoc.* 47, 953,960.
- [24] Prakash, V. and Singh, S. (2010) Effect of combustion variables on PAHs emission from incineration of cellulose waste filters from acrylic industry. *Environmental Monitoring and Assessment* 163, 591-598.
- [25] You, X. (2008) Polycyclic aromatic hydrocarbon (PAH) emission from co-firing municipal solid waste (MSW) and coal in a fluidized bed incinerator. *Waste Management* 28(9), 1543-1551.
- [26] Mastral, A.M., Callen, M.S. and Murillo, R. (1996) Assessment of PAH emissions as a function of coal combustion variables. *Fuel* 75(13), 1533-1536.
- [27] Dai, J., Xu, M., Chen, J., Yang, X. and Ke, Z. (2007) PCDD/F, PAH and heavy metals in the sewage sludge from six wastewater treatment plants in Beijing, China. *Chemosphere* 66, 353-361.
- [28] Mastral, A.M., López, J.M., Callén, M.S, Garcia, T., Murillo, R. and Navarro, M.V. (2003) Spatial and temporal PAH concentrations in Zaragoza, Spain. *Sci.Total Environ.* 307(1-3), 111-124.
- [29] Karthikeyan, S., Balasubramanian, R. and See, S.W. (2006) Optimization and validation of a low temperature microwave-assisted extraction method for analysis of polycyclic aromatic hydrocarbons in airborne particulate matter. *Talanta* (69), 79-86.
- [30] Ravindra, K., Sokhi, R. and Van Grieken, R. (2008) Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmos. Environ.* (44), 2895-2921.
- [31] Dallarosa, J., Calesso Teixeira E, Meira L, WiegandF. Study of the chemical elements and polycyclic aromatic hydrocarbons in atmospheric particles of PM10 and PM2.5 in the urban and rural areas of South Brazil. *Atmos. Res.* 2008;89:76-92.
- [32] Dejean, S., Raynaud, C., Meybeck, M., Della Massa, J.P. and Simon, V. (2008) Determination of airborne polycyclic aromatic hydrocarbons in the Toulouse area (France) by Gas Chromatography – Mass Spectrometry. *Fresenius Environmental Bulletin* 17(10b), 1697-1704.
- [33] Dejean, S., Raynaud, C., Meybeck, M., Della Massa, J.P. and Simon, V. (2009) Polycyclic aromatic hydrocarbons (PAHs) in atmospheric urban area: monitoring on various types of sites. *Environmental Monitoring and Assessment* 2009;10.1007/s10661-007-0136-y.
- [34] Foan, L., Sablayrolles, C., Elustondo, D., Lasheras, E., Gonzalez, L., Ederra, A., Simon, V. And Santamaria, J.M. (2010) Reconstructing historical trends of Polycyclic Aromatic Hydrocarbons deposition in a remote area of Spain using moss material from a herbarium. *Atmos. Environ.* 44(26), 3207-3214.

- [35] Dezhi, S., Xianjin, T., Weixiang, W., Jie, F., Chaofeng, S., Murray, B. and Yingxu C. (2009) Effect of MSW source-classified collection on polycyclic aromatic hydrocarbons in residues from full-scale incineration in China. *Water Air Soil Pollut.* 198, 347-358.
- [36] Mininni, G., Sbrilli, A., Guerriero, E. and Rotatori, M. (2004) Polycyclic aromatic hydrocarbons formation in sludge incineration by fluidized bed and rotary kiln furnace. *Water Air Soil Pollut.* 154, 3-18.
- [37] Li, C.T., Lee, W.J., Mi, H.H. and Su, C.C. (1995) PAH emission from the incineration of waste oily sludge and PE plastic mixtures. *Sci.Total Environ.* 170(3), 171-183.
- [38] Romdhana, M.H., Hamasaid, A., Ladevie, B. and Lecomte, D. Energy valorization of industrial biomass: Using a batch frying process for sewage sludge. *Bioresour. Technol.* 100(15), 3740-3744.
- [39] *Mémento technique de l'eau, Dixième édition, Tome 2, Ed. Degrémont Suez, 2005.*
- [40] Ravindra, K., Bencs, L., Wauters, E., de Hoog, J., Deutsch, F., Roekens, E., Bleux, N., Berghmans, P. and Van Grieken, R. (2006) Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. *Atmos. Environ.* 40, 771-785.
- [41] Nisbet, I.C.T. and Lagoy, P.K. (1992) Toxic equivalency factors (TEFs) for polycyclic [42] McCrillis, R.C., Watts, R.R. and Warren S.H. (1992) Effects of operating variables on PAH emissions and mutagenicity of emissions from woodstoves. *J. Air Waste Manag. Assoc.* 42(5), 691-694.
- [43] Goriaux, M., Jourdain, B., Temime, B., Besombes, J.L., Marchand, N., Albinet, A., Leoz-Garziandia, E. and Wortham, H. (2006) Field comparison of PAH measurements using a low flow denudeur device and conventional sampling systems. *Environmental Sciences and Technology* 40(20), 6398-6404.
- [44] McMurry, P.H. (2000). A review of atmospheric aerosol measurements. *Atmospheric Environment* 34 (12), 1959-1999.
- [45] Guo, H., Lee, S.C., Ho, K.F., Wang, X.M. and Zuo, S.C. (2003) Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong-Kong. *Atmos. Environ.* 37, 5307-5317.
- [46] Yang, H.H., Jung, C.H., Wang, Y.F. and Hsieh, L.T. (2005) Polycyclic aromatic hydrocarbons emissions from joss paper furnaces. *Atmos. Environ.* 39, 3305-3312.
- [47] Yang, X.Y., Okada, Y., Tang, N., Matsunaga, S., Tamura, K., Lin, J.M., Kameda, T., Toriba, A. and Hayakawa, K. (2007) Long-range transport of polycyclic aromatic hydrocarbons from China to Japan. *Atmos. Environ.* 41, 2710-2718.

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