Research article

Quantification and health impact assessment of polycyclic aromatic hydrocarbons (PAHs) emissions from crop residue combustion

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A B S T R A C T

Emission of Polycyclic Aromatic Hydrocarbon compounds from combustion of crop residue was investigated. Crop residues comprising maize cobs, maize husks, rice husks and bean chaff were burnt in a furnace at a temperature of 400 °C and the emissions from the combustion process were characterized using standard methods. Health risk through inhalation was assessed using toxic equivalent factors and excess lifetime cancer risk. The results showed the detection of 16 PAH compound which included: Benzo[ghi]perylene, Naphthalene, Acenaphthene, Anthracene, Phenanthrene, Fluorene, Fluoranthene, Acenaphthylene, Pyrene, Benzo[a]anthracene, Dibenzo[a,h]anthracene, Benzo[b]fluoranthene, Chrysene, Benzo[a]pyrene, Indene[1,2,3-cd]pyrene and Benzo [k]fluoranthene. Benzo[b]fluoranthene had highest mean concentration of 1.30 µg/mg while Dibenzo[a,h] anthracene had the lowest mean concentration of 0.01 µg/mg. It was also revealed that the toxicity of PAHs was due to the presence of Benzo[b]fluoranthene for all the samples except for sample 4 for which the main contribution to toxicity was emission from benzo(a)pyrene, while the cancer risk assessment estimated to be 1.2×10^{-1} was far above the acceptable carcinogenic risk limit of 1×10^{-6}. This study concluded that, more efforts are needed to reduce emission of PAHs from the combustion of crop residues into the ambient air otherwise, human health could be under threat especially if exposed for a long period.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are compounds with two or more bonded benzene rings and are produced when organic materials such as wood, coal or oil undergo incompletely combustion (Vichi et al., 2005; Haritash and Kaushik 2009; Jiang et al., 2014; Kim et al., 2016). They are compounds containing only carbon and hydrogen, bonded in simple ring structures to more complex ones and can either be light or heavy (depending on the number of the rings). PAHs have been described as harmful persistent organic pollutants; which are detrimental to the environment and human health (Lawal, 2017). Many PAH compounds are not only cancer-causing and poisonous for production, but they also have potentials to cause permanent changes in the DNA sequence (Crone

and Tolstoy, 2010). Apart from the fact that they stay long in the atmosphere and barely disintegrate, they are also bio-accumulative.

PAHs can be released into the atmosphere naturally or through anthropogenic means. Natural emission sources of PAHs include hydrothermal processes, forest fires and volcanoes, while waste or biomass burning, burning of fossil fuel and automobile exhausts are some of the anthropogenic sources (Li et al., 2015). Apart from these, PAHs can be emitted from other sources. For instance, emissions from hazardous waste sites, industries, cigarette smoking, as well as burn pits have been identified as some of the emitters of PAHs (White et al., 2016; Lawal, 2017).

The emission of particles and all other toxic vapour pollutants resulting from the combustion of agricultural residues is a major global

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concern as it affects climate and human health (Guoliang et al., 2008). In developing countries, burning of crop residues has become a common practice as a means of disposal, possibly because of lack of awareness or due to technological backwardness. Despite the fact that crop residues left in the field after grain harvests have great potentials as a feedstock for bioenergy and possess nutrient, erosion, and soil carbon characteristics that should not be ignored, many farmers in developing nations still consider them as by-products. In developing nations, combustion of crop residues is considered as the most suitable and economical in managing agricultural wastes (Cheewaphongphan et al., 2011).

According to Gurjar et al. (2016), farmers practice combustion of crop residue to dispose heaps of agricultural wastes and this operation releases volatile organic compounds (VOCs), carbon monoxide, hydrocarbons, nitrogen oxide and PAHs. Apart from green-house gas emissions (CH_4, N_2O, CO_2), air contaminants (non-methane hydrocarbons, smoke, volatile organic compounds, CO, SO_2, PAHs, NO_x, particulate matter, NH_3), agricultural waste burning also causes severe land and water contamination at the local as well as national levels, thereby posing a danger to public human health (Sahai et al., 2007; Gadde et al., 2009; Cheewaphongphan et al., 2011). Gadde et al. (2009) reported annual estimates of concentration of air pollutants emissions from open field combustion of rice straws in three different countries as 16, 253, 012; 779; 144,719 and 207 Mg of CO_2, CO, Total Particulate Matter (TPM) and PAHs respectively, from India; 12,206,603; 290,116; 108,689 and 156 Mg of CO_2, CO,TPM and PAHs respectively, from Thailand and 11,850, 034; 281, 641; 105,514 and 151Mg of CO_2, CO, TPM and PAHs respectively, from Philippine. This is considered to increase the atmospheric pollution loads of the respectively regions and thus severely impacts both human and environmental of the countries.

Resulting effects of crop residues combustion can be detrimental to both mankind and environment. For example, the short term/acute health effects include eye irritation, nausea, vomiting, diarrhea, skin irritation and inflammation (Abdel-Shafy and Mansour, 2016; Lawal., 2017). The long term/chronic health effects include decreased immune functions, cataracts, kidney and liver damage, asthma-like symptoms and lung function abnormalities (Abdel-Shafy and Mansour, 2016). Besides, black soot contributes to the rise in the concentration of particulate in the air thereby leading to poor visibility (Cheewaphongphan et al., 2011). Likewise, generation of these vapor pollutants indirectly leads to high concentration of ozone gases, a major contributor of air pollution. Also, destruction of soil texture and eventual loss of soil minerals which subsequently affect productivity in the subsequent cultivating years is also one of the dangers of burning agricultural residues.

In an effort to evaluate the impacts of human related activities on the ambient air quality, this study investigated PAHs emission from combustion of agricultural waste residue. Previous studies have reported various pollutants emitted from biomass burning along with their resulting concentrations and possible impacts. A Study by Awasthi et al. (2011) shows that the concentration of the different size fraction of particulate emitted during combustion depends on the types of the agricultural crop residue. Investigation of emissions from the combustion of barley straw and oats by Calvo et al. (2011) shows that burning barley straw generates more of fine particles as compared to that of oats. Emission of gaseous pollutants such as carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), CO, non-methane hydrocarbons, NOx, SO_2, and particulate matter (PM) were reported by Gadde et al. (2009). Impact of the burning of rice crop residue on the levels of suspended particulate matter (SPM), SO_2 and NO_2 in the ambient air of Patiala (India) was investigated by Singh et al. (2010). The study reported that the concentration of SPM, SO_2 and NO_2 rise in rice residue combustion period which is between September–January. Study by Shen et al. (2011) evaluated the emission factor and size distribution of PAHs from indoor crop residue burning in a typical rural stove. It was reported that the PAHs emission factors from selected crop residues burnt in a typical Chinese cooking stove were higher compared to those from experimental chamber. In specific terms, critical review of literature revealed that

previous studies have concentrated on the assessment of emission of inorganic pollutants generated from biomass burning but there is existence of major data gaps on PAHs emission from burning of agricultural residues.

Generally, polycyclic aromatic hydrocarbons have received research attention in some developed nations due to its negative effects on environment (Kanzari et al., 2012), animals (Qi et al., 2013) and public health (Kannan et al., 2005). Likewise, there have been emerging research attentions being given to health risk assessment of PAHs in few Asian countries in recent years. For instance, in Southwest Iran, Doroodzani et al. (2021) investigated effects of exposure to PAHs on pregnant women and their fetuses. The study showed that mothers who live in industrial areas and consume PAHs-containing foodstuffs are at high risk of transmitting PAHs to the fetuses. Also, potential carcinogenic risk of exposure to PM_{10}-bound PAHs by residents of three major cities in Iran has also been reported (Goudarzi et al., 2021). Several other health risk assessment studies on exposure to PAHs have been carried out in China (Wang et al., 2020), Iran (Raeisi et al., 2016; Akhbarizadeh et al., 2021) and in Germany (Dobaradaran et al., 2019, 2020) as against dearth of reported information on PAHs sources and levels in emergent nations, especially African countries. Moreover, while few reported studies have focused on PAHs present in soil from industrial and residential regions (Nieuwoudt et al., 2011), there is a limited knowledge of the contribution of PAHs emission from combustion of crop residue/agricultural wastes to the ambient air quality in developing nations (Okedeyi et al., 2013).

Therefore, going by the common practice of burning, as a strategy for disposing large heaps of agricultural wastes/residue in developing nations and the potential of such practice to emit hydrocarbon-based pollutants such as VOCs and PAHs, coupled with the threat that PAHs could pose to the ambient air quality, there is the need for the assessment of these emissions from combustion of variety of crop residues. This study investigated PAHs emissions emanating from the burning of crop residue and their impacts on ambient air quality as well as associated health risks that could result from exposure to the vapor emission. This study will provide information on PAHs emission from burning of agricultural waste.

2. Methodology

2.1. Experimental set-up

The experimental set-up is furnace coupled with a thistle tube. The furnace made up of a combustion chamber, thermostat, an ignition source and an in-built heat exchanger. Samples were fed into the combustion chamber where they were ignited by the ignition source at a controlled temperature. The heat exchanger in the furnace absorbed heat from the combustion process. A thistle tube loaded at the round neck/ reservoir with activated carbon (adsorbent) was tightly inserted into the opening/vent/flue collar at the top of the furnace to trap the emission from the combustion process. The insertion was made possible by first passing the tube through a hole drilled in a stopper and inserting the stopper into the flue collar of the furnace. The mouth of thistle tube was closed, air tightly with a rubber cork to prevent escape.

2.2. Experimental procedure

For this study, the crop residues (Maize cobs, Maize Husk, Rice Husks and Beans chaff) used were collected from Landmark University Teaching and Research Farm. The selected crop residues chosen represent three major agricultural crops in Nigeria. The crop residues selected were then dried thoroughly to remove the moisture content that may affect the rate of combustion before being crushed to increase the surface area and weighed. The representation of the samples is as shown in Table 1. The pre-determined quantity of the crushed crop residues was then fed into the furnace and burnt at a temperature of 400 °C (combustion temperature of the residue) while the emissions from the combustion process was trapped in thistle tube covered with a rubber cork.

Table 1. Representation of the samples.

Sample Number	Crop Residue	Denotation
1	Maize Cobs	AQ1
2	Maize Husks	AQ2
3	Rice Husk	AQ3
4	Bean Chaff	AQ4
5	Equal quantity of maize cobs + maize husks + rice husks + bean chaff	AQ5

The rubber cork covered the larger end of the thistle tube. The emission vented out was trapped from the flue collar into the thistle tube containing adsorbent (activated carbon) where the pollutants were collected on the surface of the adsorbent in 5 min. A muslin cloth was placed inside the thistle tube to serve as a filter medium due to its high capacity for particle retention. The thistle tube was half-filled with activated carbon (previously baked prior to sampling at 300 °C for about 2 h to remove any trace of organic) which weighed 4g for each sample and then sealed with a glass rod attached to a rubber cork for escape of the emissions. The pollutants-rich-sorbent was quickly poured into a rubber container and refrigerated before PAHs extraction, characterization and quantification.

2.3. Extraction of PAHs from pollutants-rich-sorbent

Extraction of PAHs for the sorbent followed method described and employed by previous researchers (Lai et al., 2009; Sadowska-Rociek et al., 2014), using a centrifuge (MPW 380, Germany) and T25 digital disperser to prepare the samples. Preparation of standard solutions in pure solvent was done for all procedures by diluting solution of the standard mixture in hexane in the following ranges: 0.1, 1, 5, 10, 40, 70 and 100 ng mL^{-1} and each made in triplicate, contained 100μL of anthracene-d$_{10}$ solution. For the extraction of PAHs, A standard solution was made to cover (up to 20 μg/kg) 1 g of each sample earlier weighed into a 50- ml centrifuge tube. This was thoroughly shaken for proper mixing and allowed to settle for 15 min at room temperature. This was then followed by the addition of 10 ml of hot (boiled) water to the sample for the improvement of the yield, the solution was then cooled to ambient temperature. After cooling was the addition of 10 ml of ethyl acetate and vigorous shaking of the mixture for 1 min. This was followed by addition

of 1 and 4 g of NaCl and MgSO$_4$, respectively. Apart from immediate shaking after the addition of the salt, the tube and the contents (for each sample) were shaken thoroughly for 1 min to ensure homogeneity, before centrifuging at 8,700 RCF for 15 min. Into a 15 ml tube holding an adequate amount of 0.9 g MgSO$_4$ and tested sorbent, a 6 ml of supernatant was transferred, the tube was then shaken for 2 min before centrifuging at 5,000 RCF for 5 min. Extract of about 4 ml was taken into a screw cup vial and then mixed with 100 μL of the anthracene-d10 solution. Evaporation of the solvent and concentration of the extracts were done under a stream of nitrogen. The analysis of the extracts was then performed using GC-MS.

2.4. Quality control/quality assurance (QC/QA)

For each compound, Detection limits were estimated as three the noise. For the calibration and spiking of the matrix, an external standard (USA. EPA 525 PAH Mix-B) containing the 16 compounds was used. This involves addition of a pre-known concentrations of the analytes to be determined to the sample aliquots. Volumetric dilution was employed to prepare the matrix spike solution form stock standards, followed by subsequent injection on the cleaned filters. Removal efficiency of the PAHs was determined by sampling the flue gas containing the fly ash and the PAHs simultaneously before and after the activated carbon adsorption. The recovery efficiency varied between 65 and 98%. For the field blank, a clean filter was exposed to the same sampling environment. For each of the five samples, two blanks were obtained. All the concentrations of the PAH compounds were found to be below the limits of detections of the field blank.

2.5. PAHs characterization and quantification

To carry out the analysis, standard methods and procedures described by earlier researchers (Lai et al., 2009; Sadowska-Rociek et al., 2014) are also followed in this study. Gas Chromatography- Mass Spectrometer (Varian 4000) was employed. The injection was done in triplicate by utilizing mass spectrometer of a single CP-1117 split or splitless injector at 270 °C and injection volume of 1.0 μL. Using nitrogen as a carrier gas at 1.0 ml/min, the GC was run at these initial conditions:50 °C (1.0 min) –15 °C min^{-1} –320 °C (6.0 min). The internal ionization with mas to charge ratio from 45 to 500 was chosen as the operation mode for the ion trap mass spectrometer, setting the ionization filament dwell time to 80

Table 2. Concentrations (μg/mg) of the detected PAHs.

S/No	PAHs Detected	Concentration (μg/mg)				
		AQ1	AQ2	AQ3	AQ4	AQ5
1	Naphthalene	1.05 ± 0.42	0.01 ± 0.08	1.02 ± 0.43	0.01 ± 0.11	0.82 ± 0.34
2	Acenaphthylene	1.02 ± 0.31	0.09 ± 0.10	1.00 ± 0.26	ND	0.77 ± 0.27
3	Acenaphthene	0.03 ± 0.11	0.31 ± 0.16	0.03 ± 0.10	0.03 ± 0.15	0.83 ± 0.21
4	Phenanthrene	1.00 ± 0.25	1.00 ± 0.20	0.26 ± 0.09	ND	1.00 ± 0.33
5	Anthracene	0.04 ± 0.10	1.21 ± 0.43	0.32 ± 0.12	0.02 ± 0.10	0.84 ± 0.29
6	Fluorene	0.02 ± 0.10	0.11 ± 0.13	0.03 ± 0.12	0.49 ± 0.23	1.02 ± 0.28
7	Fluoranthene	0.04 ± 0.13	0.15 ± 0.23	0.04 ± 0.10	0.61 ± 0.28	1.00 ± 0.36
8	Pyrene	0.13 ± 0.26	0.13 ± 0.10	0.63 ± 0.35	0.83 ± 0.30	0.03 ± 0.10
9	Benzo[a]anthracene	0.02 ± 0.14	1.02 ± 0.37	0.67 ± 0.31	0.82 ± 0.30	1.22 ± 0.31
10	Benzo[b]fluoranthene	1.32 ± 0.37	1.36 ± 0.34	1.40 ± 0.41	1.32 ± 0.38	1.10 ± 0.33
11	Chrysene	0.96 ± 0.46	0.56 ± 0.10	1.37 ± 0.46	0.82 ± 0.19	0.98 ± 0.26
12	Benzo[a] pyrene	0.02 ± 0.15	0.02 ± 0.11	0.03 ± 0.21	0.74 ± 0.20	0.02 ± 0.08
13	Indene[1,2,3-cd] pyrene	0.01 ± 0.12	0.02 ± 0.10	0.01 ± 0.06	1.18 ± 0.37	0.01 ± 0.01
14	Benzo[k]fluoranthene	1.06 ± 0.31	0.03 ± 0.2	0.01 ± 0.02	0.54 ± 0.22	0.72 ± 0.19
15	Benzo[ghi]perylene	1.47 ± 0.18	0.02 ± 0.13	ND	0.58 ± 0.26	0.55 ± 0.22
16	Dibenzo[ah] anthracene	ND	ND	ND	0.01 ± 0.03	ND

ND = not detected.

Table 3. Number of rings, molecular weight, LOD, recovery efficiency and P-values showing significant difference between samples of PAHs.

S/No	PAHs Compounds	No of ring	Molecular weight	LOD Limits	Recovery %	P-value showing significant difference between samples
1	Naphthalene	2	128	0.014	73	0.014
2	Acenaphthylene	2	152	0.010	85	0.013
3	Acenaphthene	2	154	0.017	90	0.001
4	Phenanthrene	3	178	0.026	98	0.010
5	Anthracene	3	178	0.013	68	0.014
6	Fluorene	2or3	166	0.016	65	0.011
7	Fluoranthene	3or4	202	0.023	70	0.011
8	Pyrene	4	202	0.018	82	0.001
9	Benzo[a]anthracene	4	228	0.013	63	0.012
10	Benzo[b]fluoranthene	4/5	252	0.028	95	0.003
11	Chrysene	4	228	0.018	80	0.008
12	Benzo[a] pyrene	5	252	0.010	88	0.009
13	Indene[1,2,3-cd] pyrene	5/6	276	0.013	96	0.014
14	Benzofluoranthene	4/5	252	0.019	91	0.012
15	Benzoghiperylene	5/6	276	0.004	76	0.016
16	Dibenzoahanthracene	5	278	0.022	94	

Characterized Polycyclic Aromatic Compounds
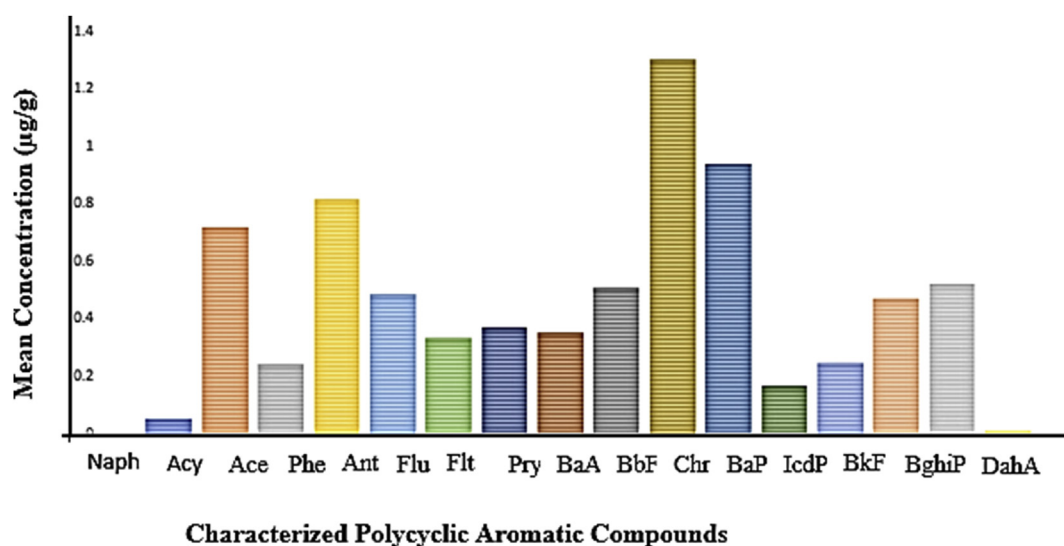
Naph= Naphthalene; Acy= Acenaphthylene; Ace=Acenaphthene; Phe= Phenanthrene Ant= Anthracene; Flu= Fluorene; Flt= Fluoranthene; Pry = Pyrene; BaA= Benzo[a]Anthracene BbF= Benzo[b] Fluoranthene; Chr= Chrysene; BaP= Benzo [1,2,3]pyrene; IcdP= Indene [1,2,3-cd] pyrene; BkF= Benzo[k] Fluoranthene; BghiP= Benzo[ghi]perylene; DahA= Dibenzo[ah]anthracene

Figure 1. Mean Concentration of the characterized polycyclic aromatic hydrocarbons.

min and the current to 15 μA (Sadowska-Rociek et al., 2014). Ions were qualitatively analyzed in the selected ion monitoring mode at 8.0 min solvent delay and 220 and 180 °C as transfer line and trap temperatures, respectively.

2.6. Health impact assessment

The three major routes through which humans are exposed to emissions of PAH compounds include ingestion, dermal and inhalation (Edokpayi et al., 2016). In man, the harmful effects of PAH are largely dependent on the route of exposure (Diggs et al., 2011). The most significant health impact to be expected from its inhalational exposure is an excess risk of lung cancer (Kim et al., 2013). Its exposure may also pose a risk for cardiovascular diseases, including atherosclerosis, hypertension, thrombosis and myocardial infarction (Holme et al., 2019). In this study, health risk through inhalation contact route was also estimated. With the knowledge that each of PAH compounds has varying degree of carcinogenic effects, therefore to assess the risk of PAH mixture and at the same time, guide against overestimation of the cancer-causing (carcinogenic) risk, two approaches were employed. These approaches are toxicity potential using toxic equivalent factors (TEFs) and excess lifetime cancer risk. The toxicity potential was employed for the five samples while excess lifetime cancer risk was used for PAH mixture using the mean concentration.

An estimate of the Toxicity potential of PAHs was made based on the most carcinogenic PAH compound-benzo[a]pyrene, using Eq. (1) (Simon et al., 2012; Nekhavhambe et al., 2014, Edokpayi et al., 2016).

$$\sum TEQ = TEF_i \times \sum C_i \qquad (1)$$

C_i = concentration level of individual PAH compound;
TEQ = toxic equivalent quotient,
TEF_i = toxic equivalent factor relative to benzo[a]pyrene.

TEFs used were obtained from US EPA (2010) and Nekhavhambe et al. (2014).

According to previous reports, health risk assessment can also be estimated for inhalation contact route using excess lifetime cancer risk (ELCR) (Wu et al., 201; Odekanle et al., 2020). Excess lifetime cancer risk is given by Eq. (2) (Wu et al., 2014)

$$ELCR = CDI \ (mg/kg/d) \times CSF \ (mg/kg/d)^{-1} \qquad (2)$$

CDI (Chronic daily intake) was estimated from Eq. (3) (Gungormus et al., 2014);

$$CD\ I = \frac{(C \times IR \times ED \times EF)}{(BW \times AT)} \qquad (3)$$

Where C = concentration of the PAH compound ($\mu g/m^3$); IR = rate of inhalation (m^3/day) which was taken as the daily BaP_{eq} inhalation rate (20 m^3/day) (Wu et al., 2014); ED is the exposure duration(year) which was taken as 50 years, assumed to be active years for farming; EF, the exposure frequency was taken as 180 days/year (Gungormus et al., 2014); BW is the body weight, taken as 62.8 kg (Odekanle et al., 2020) and AT, the averaging time was taken as 70 years (EPA, 2009). CSF is cancer slope factor was estimated applying Eq. (4) (Odekanle et al., 2020).

$$CSF = UR/(BW \times IR) \qquad (4)$$

UR, unit risk value of 0.008 $\mu g/m^3$ was chosen as previously used elsewhere (Greene and Morris, 2006).

3. Results and discussion

In the five samples analysed, 16 PAHs were characterized using the data from the chromatographic analyses with an MS Detector. The compounds detected included; Benzo[ghi]perylene, Naphthalene, Acenaphthene, Anthracene, Phenanthrene, Fluorene, Fluoranthene, Acenaphthylene, Pyrene, Benzo[a]anthracene, Dibenzo[a,h]anthracene, Benzo[b]fluoranthene, Chrysene, Benzo[a]pyrene, Indene[1,2,3-cd] pyrene and Benzo[k]fluoranthene. Summarized in Table 2 are the concentrations ($\mu g/mg$) of PAHs in the 5 samples. The characterized PAHs had varying concentrations ranging from 1.47 to 0.01 ug/mg. Acenaphthylene and Phenanthrene were not detected for sample 4, Benzo[ghi]perylene was not detected for Sample 3 while Dibenzo[ah]anthracene was not detected for samples 1,2,3, 5 (though with a very low concentration of 0.010 $\mu g/mg$ for sample 4). The differences in the PAHs composition between the different samples were found to be statistically significant at 95 % confidence interval (p < 0.05) (Table 3).

The difference in the emission source may be responsible for the PAHs composition (Wang et al., 2020). The Mean concentration for each characterized PAHs was presented in Figure 1. Generally, PAHs with lower molecular weights were present in lower concentrations than those with higher molecular weights (except for the case of Dibenzo[a,h] anthracene with a mean concentration of 0.010 $\mu g/mg$). Benzo[b]fluoranthene and Chrysene were present in higher concentrations (1.300 and 0.938 $\mu g/mg$ respectively) when compared with other PAHs detected. Dibenzo [a,h] anthracene (0.01 $\mu g/mg$) and Naphthalene (0.052 $\mu g/mg$) are the two PAHs with lowest mean concentration. Of all the 16 PAH
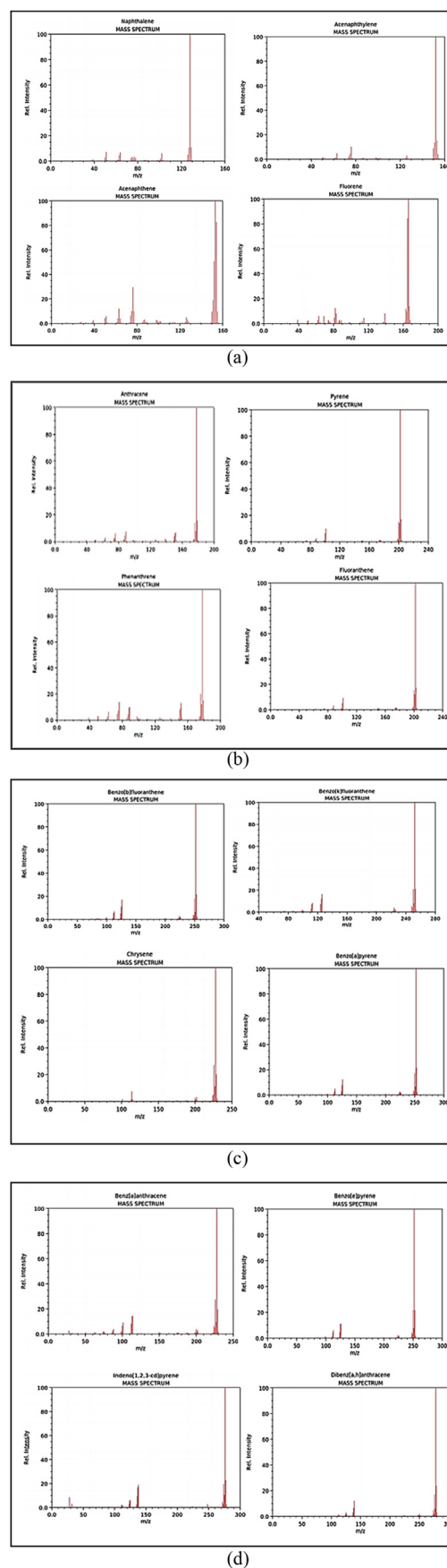

(a)

(b)

(c)

(d)

Figure 2. Mass fragmentation of the characterized PAHs.

Table 4. Characteristic diagnostic ratios values for particular emission sources.

Ratio	Petrogenic	Pyrogenic	References
Anth/(Anth + Phen)	<0.1	>0.1	Brandli et al., 2007
Fluo/(Fluo + Pyre)	<0.4	>0.4	Brandli et al., 2007
Low molecular weight/ High molecular weight	>1	<1	Nasher et al., 2013

High molecular weight = PAHs with ≥4 rings.

compounds characterized, only Naphthalene, Dibenzo[a,h]anthracene and Benzo[(a)pyrene have their mean concentrations below the 0.200 ug/mg limit set by the Occupational Safety and Health Administration (OSHA). This indicates that, human health could be under threat especially if exposed for a long period. It is thought that high molecular weight PAHs were more prevalent due to their increased weight which makes them resistant to oxidation, reduction and vaporization. The results obtained in this study were higher than most reported data by previous studies (Dhammapala et al., 2007, Lu et al., 2009, Shen et al., 2011) but comparable to the report of Simon et al. (2012). The difference could be linked to the variations in the experimental set-up. Generally, PAH emissions strongly depend on the fuel type and burning conditions which include the combustion chamber as well as the combustion temperature (Simon et al., 2012). Previous studies reported results obtained from chamber experiment while this study is based on laboratory experiment where air flow and oxygen supply are more limited, hence reduced combustion efficiency and elevated PAHs concentrations. Similarly, it is thought that combustion temperature (400 °C) in this study favoured PAHs formation due to limited heat loss during the combustion.

It has been reported that the higher the combustion temperature from 200 to 700 °C, the higher the emission of PAHs (Shen et al., 2011). Polycyclic aromatic hydrocarbons with 3 and 4 rings PAHs accounted for between 29% and 34% of the emissions, while those with 5 and 6 rings accounted for between 10% and 26% whereas, PAHs with only 2 rings are accounted for less than 1% of the emission. The mass fragmentations of the characterized PAHs were shown in Figure 2(a-d). The mass to charge ratio (m/z) ranged from 178 to 276. As the number of

the rings of molecule increased, there was also a progressive increase in the mass to charge ratios of the compounds with Naphthalene and Dibenzo[a,h]anthracene having the lowest and highest m/z ratio respectively.

Several factors such as the emitted concentration, meteorological conditions (temperature, windspeed, wind direction) and atmospheric oxidants determine the potential emission sources of PAH compounds (Wu et al., 2014). However, several previous studies have employed the use of diagnostic ratios for PAHs source identification (Brandli et al., 2007; Yang et al., 2007; Nasher et al., 2013). It has also been suggested that diagnostic ratios are designed to identify PAHs sources due to their stability, chemical and physical properties (Yunker et al., 2002; Nasher et al., 2013). Generally, PAHs emission can either be from petroleum origin (petrogenic source) or from the combustion of biomass (pyrogenic sources). This was assessed and ascertained using the most commonly adopted characteristic diagnostic ratio values for particular emission sources (Table 4).

The ratio of Anthracene/(Anthracene + Phenanthrene) was 0.37 (>0.1), while that of Fluoranthene/(Fluoranthene + Pyrene) was 0.51 (>0.4) and the ratio of Low molecular weight/High molecular weight gave 0.5 (<1). This was a confirmation of the pyrogenic source of the PAHs. Most PAHs in ambient air are usually from the combustion of biomass rather than petroleum origin (Edokpayi et al., 2016).

3.1. Health risk assessment

The potential toxicity of individual PAHs was presented in Table 5. The ECLR was estimated to be 1.2×10^{-1}. The toxicity of PAHs was due to the presence of Benzo[b]fluoranthene for all the samples except for sample 4 for which the main contribution to toxicity was emission from benzo[a]pyrene. Though there are emissions from light PAHs, their contribution to global toxicity could be assumed to be minor. Similarly, the inhalation risk (ECLR) calculated as 1.2×10^{-1} was higher than the generally accepted carcinogenic risk level of 1×10^{-6}.

Inhalation risks less than or equal to 1×10^{-6} are considered as being negligible or insignificant risks (Wu et al., 2014). This estimation indicates that more efforts are needed to reduce emission of PAHs from the combustion of crop residues.

Table 5. TEF and TEQ values PAHs.

PAHs Detected	TEF Values	TEQ Values				
	(10^{-2})	AQ1 (10^{-2})	AQ2 (10^{-2})	AQ3 (10^{-2})	AQ4 (10^{-2})	AQ5 (10^{-2})
Naphthalene	0.1*	0.105	0.001	0.102	0.001	0.082
Acenaphthylene	0.1*	0.102	0.009	0.10	-	0.077
Acenaphthene	1.0*	0.03	0.31	0.03	0.03	0.83
Phenanthrene	0.1*	0.10	0.10	0.026	-	0.10
Anthracene	1.0*	0.04	1.21	0.32	0.02	0.84
Fluorene	0.1*	0.002	0.011	0.003	0.049	0.102
Fluoranthene	8.0**	0.32	1.20	0.32	4.88	8.00
Pyrene	0.1**	0.013	0.013	0.063	0.083	0.003
Benzo[a]anthracene	10.0**	0.20	10.2	6.7	8.20	12.20
Benzo[b]fluoranthene	10.0**	13.2	13.6	14.00	13.20	11.00
Chrysene	1.0**	0.96	0.56	1.37	0.82	0.98
Benzo[a]pyrene	100*	2.00	2.00	3.00	74.00	2.00
Indene[1,2,3-cd]pyrene	10**	0.10	0.20	0.10	11.80	0.10
Benzo[k]fluoranthene	10**	10.6	0.30	0.10	5.40	7.20
Benzo[ghi]perylene	1.0**	1.47	0.02	-	0.58	0.55
Dibenzo[ah] anthracene	100*	-	-	-	0.01	-
∑ TEQ		29.242	29.734	26.234	120.063	44.064
ECLR = 1.2×10^{-1}						

* =US EPA (2010).
** = Nekhavhambe et al. (2014).

4. Conclusion

The analysis of the emission from the combustion of the selected crop residues for PAH compounds revealed 16 PAH compounds with varying concentrations. PAHs with lower molecular weights were present in lower concentrations than those with higher molecular weights. Health risk assessment also showed an elevated level beyond the acceptable carcinogenic threshold limit. Hence, continual exposure to the emission from these sources could endanger public health. Thus, public awareness and education on the sources and health impacts of exposure need to be improved. It is therefore concluded that more efforts are needed to reduce emission of PAHs from the combustion of crop residues into the ambient air.

Declarations

Author contribution statement

Bamidele Sunday Fakinle: Conceived and designed the experiments; Analyzed and interpreted the data.

Ebenezer Leke Odekanle: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Chika Ike-Ojukwu & Folawemi Winner Olubiyo: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Omowonuola Olubukola Sonibare: Analyzed and interpreted the data.

Olayomi Abiodun Falowo & Daniel Olawale Oke: Performed the experiments; Analyzed and interpreted the data.

Charity O. Aremu: Contributed reagents, materials, analysis tools or data.

Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Abdel-Shafy, H.I., Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt. J. Petrol. 25 (1), 107–123.

Akhbarizadeh, R., Dobaradaran, S., Torkmahalleh, M., Saeedi, R., Aibaghi, R., Ghasemi, F.F., 2021. Suspended fine particulate matter (PM2.5), microplastics (MPs), and polycyclic aromatic hydrocarbons (PAHs) in air: their possible relationships and health implications. Environ. Res. 192, 110339.

Awasthi, A., Agarwal, R., Mittal, S.K., Nirankar, N., Singh, K., Gupta, P.K., 2011. Study of size and mass distribution of particulate matter due to crop residue burning with seasonal variation in rural area of Punjab, India. J. Environ. Monit. 13, 1073.

Brandli, R.C., Bucheli, T.D., Kupper, T., Mayer, J., Stadelmann, F.X., Tarradellas, J., 2007. Fate of PCBs, PAHs and their source characteristic ratios during composting and digestion of source-separated organic waste in full-scale plants. Environ. Pollut. 148, 520–528.

Calvo, A.I., Castro, A., Pont, V., Cuetos, M.J., Sanchez, M.E., Fraile, R., 2011. Aerosol size distribution and gaseous products from the oven-controlled combustion of straw materials. Aerosol Air Qual. Res. 11, 616–629.

Cheewaphongphan, P., Garivait, S., Pongpullponsak, A., 2011. Inventory of pollution from rice field residue open burning based on field survey. In: 2nd International Conference on Environmental Science and Technology IPCBEE, 6. IACSIT Press, Singapore, pp. 93–97.

Crone, T.J., Tolstoy, M., 2010. Magnitude of the 2010 Gulf of Mexico oil leak. Science 330, 634.

Dhammapala, R., Claiborn, C., Simpson, C., Jimenez, J., 2007. Emission factor from wheat and Kentucky bluegrass stubble burning: comparison of field and simulated burn experiments. Atmos. Environ. 41, 1512–1520.

Diggs, D.L., Huderson, A.C., Harris, J.N., Myers, L.D., Banks, P.V., Rekhadevi, J., 2011. Polycyclic aromatic hydrocarbons and digestive tract cancers: a perspective. J. Environ. Sci. Health C Environ. Carcinog. Ecotoxicol. Rev. 29 (4), 324–357.

Dobaradaran, S., Schmidt, T.C., Lorenzo-Parodi, N., Jochmann, M.A., Nabipour, I., Raeisi, A., Stojanovic, N., Mahmoodi, M., 2019. Cigarette butts: an overlooked source of PAHs in the environment? Environ. Pollut. 249, 932–939.

Dobaradaran, S., Schmidt, T.C., Lorenzo-Parodi, N., Kaziur-Cegla, W., Jochmann, M.A., Nabipour, I., Lutze, H.V., Telgheder, U., 2020. Polycyclic aromatic hydrocarbons (PAHs) leachates from cigarette butts into water. Environ. Pollut. 259, 113916.

Doroodzani, A.K., Dorbaradaran, S., Akhbarizadeh, R., Raeisi, A., Rahmani, E., Mahmoodi, M., Nabipour, I., Keshmiri, S., Darabi, A.M., Khamisipour, G., Mamudpour, M., Keshtkar, A.M., 2021. Diet, exposure to polycyclic aromatic hydrocarbons during pregnancy, and fetal growth: a comparative study of mothers and their fetuses in industrial and urban areas in Southwest Iran. Environ. Pollut. 276, 116668.

Edokpayi, J.N., Odiyo, J.O., Popoola, O.E., Msagati, T.A.M., 2016. Determination and distribution of polycyclic aromatic hydrocarbons in rivers, sediments and wastewater effluents in vhembe district, South Africa. Int. J. Environ. Res. Publ. Health 2016 (13), 387.

Gadde, B., Bonneta, S., Menke, C., Garivait, S., 2009. Air pollutant emissions from rice straw open field burning in India, Thailand and the Philippines. Environ. Pollut. 157 (5), 1554–1558.

Goudarzi, G., Baboli, Z., Moslemnia, M., Tobekhak, M., Birgani, Y.T., Neisi, A., Ghanemi, K., Babaei, A.A., Hashemzadeh, B., Angali, K.A., Dobaradaran, S., Ramezani, Z., Hassanvand, M.S., Rad, H.D., Kayedi, N., 2021. Assessment of incremental lifetime cancer risks of ambient air PM 10-bound PAHs in oil-rich cities of Iran. J. Environ. Healt. Sci. Engineering 19 (1), 319–330.

Greene, N.A., Morris, V.R., 2006. Assessment of public health risks associated with atmospheric exposure to PM2.5 in Washington, DC, USA. Int. J. Environ. Res. Publ. Health 3, 86–97.

Gungormus, E., Tuncel, S., Tecer, L.H., Sofuoglu, S.C., 2014. Inhalation and dermal exposure to atmospheric polycyclic aromatic hydrocarbons and associated carcinogenic risks in a relatively small city. Ecotoxicol. Environ. Saf. 108, 106–113.

Guoliang, C., Xiaoye, Z., Sunling, G., Fangcheng, Z., 2008. Investigation on emission factors of particulate matter and gaseous pollutants from crop residue burning. J. Environ. Sci. 20, 50–55.

Gurjar, B.R., Ravindra, K., Nagpure, A.S., 2016. Air pollution trends over Indian megacities and their local-to-global implications. Atomspher. Environ. 142, 475–495.

Haritash, A.K., Kaushik, C.P., 2009. Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. J. Hazard Mater. 169 (1–3), 1–15.

Holme, J.A., Brinchmann, B.C., Refsnes, M., Lag, M., Ovrevik, J., 2019. Potential role of polycyclic aromatic hydrocarbons as mediators of cardiovascular effects from combustion particles. Environ. Health 18 (1), 74.

Jiang, Y., Yang, Y., Zhang, X., 2014. Review on the biodegradation and conversion mechanisms of typical polycyclic aromatic hydrocarbons. Shiyou Xuebao, Shiyou Jiagong/Acta Petrolei Sinica. Pet. Process. Sect. 30, 1137–1150.

Kannan, K., Johnson-Restrepo, Y., Yohn, S., Giesy, J., Long, D., 2005. Spatial and temporal distribution of polycyclic aromatic hydrocarbons in sediments from Michigan Inland lakes. Environ. Sci. Technol. 39, 4700–4706.

Kanzari, F., Syakti, A.D., Asia, L., Malleret, L., Mille, G., Jamoussi, B., Abderrabba, M., Doumenq, P., 2012. Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine, and organophosphorous pesticides in surface sediments from the Arc River and the Berre lagoon, France. Environ. Sci. Pollut. Res. 19, 559–576.

Kim, K., Jahan, S.A., Kabir, E., Brown, R.J.C., 2013. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. Environ. Int. 2013 (60), 71–80.

Kim, B.M., Lee, S.-B., Kim, J.Y., Kim, S., Seo, J., Bae, G.-N., Lee, J.Y., 2016. A multivariate receptor modeling study of air-borne particulate PAHs: regional contributions in a roadside environment. Chemosphere 144, 1270–1279.

Lai, C.-H., Chen, K.-S., Wang, S.-K., 2009. Influence of rice straw burning on the levels of polycyclic aromatic hydrocarbons in agricultural county of Taiwan. JES (J. Environ. Sci.) 21, 1200–1207.

Lawal, A.T., 2017. Polycyclic aromatic hydrocarbons. A review. Cogent Environmental Science 2017 (3), 1339841.

Li, W., Wang, C., Shen, H., Su, S., Shen, G., Huang, Y., Tao, S., 2015. Concentrations and origins of nitro-polycyclic aromatic hydrocarbons and oxy-polycyclic aromatic hydrocarbons in ambient air in urban and rural areas in northern China. Environ. Pollut. 197, 156–164.

Lu, H., Zhu, L., Zhu, N., 2009. Polycyclic aromatic hydrocarbon emission from straw burning and the influence of combustion parameters. Atmos. Environ. 2009 (43), 978–983.

Nasher, E., Heng, L.Y., Zakaria, Z., Surif, S., 2013. Assessing the ecological risk of polycyclic aromatic hydrocarbons in sediments at Langkawi Island, Malaysia. Sci. World J. 2013, 1–3.

Nekhavhambe, T.J., Van Ree, T., Fatoki, O.S., 2014. Determination and distribution of polycyclic romatic hydrocarbons in rivers, surface runoff, and sediments in and around Thohoyandou, Limpopo Province, South Africa. WaterSA 2014 (40), 415–424.

Nieuwoudt, C., Pieters, R., Quinn, L.P., Kylin, H., Borgen, A.R., Bouwman, H., 2011. Polycyclic aromatic hydrocarbons (PAHs) in soil and sediment from industrial, residential, and agricultural areas in Central South Africa: an initial assessment. Soil Sediment Contam 2011 (20), 188–206.

Odekanle, E.L., Sonibare, O.O., Odejobi, O.J., Fakinle, B.S., Akeredolu, F.A., 2020. Air emissions and health risk assessment around abattoir facility. Heliyon 6 (2020), e04365.

Okedeyi, O.O., Nindi, M.M., Dube, S., Awofolu, O.R., 2013. Distribution and potential sources of Polycyclic aromatic hydrocarbons in soils around coal-fired power plants in South Africa. Environ. Monit. Assess. 185, 2073–2082.

Qi, W., Liu, H., Pernet-Coudrier, B., Qu, J., 2013. Polycyclic aromatic hydrocarbons in wastewater, WWTPs effluents and in the recipient waters of Beijing, China. Environ. Sci. Pollut. Control Ser. 20, 4254–4260.

Raeisi, A., Arfaeinia, H., Seifi, M., Shirzad-Siboni, M., Keshtkar, M., Dobaradaran, S., 2016. Polycyclic aromatic hydrocarbon PAHs) in coastal sediments from urban and industrial areas of Asaluyeh Harbor, Iran: distribution, potential source and ecological risk assessment. Water Sci. Technol. 74 (4), 957–973.

Sadowska-Rociek, A., Surma, M., Cieślik, E., 2014. Comparison of different modifications on QuEChERS sample preparation method for PAHs determination in black, green, red and white tea. Environmental Scienece Pollution Research 21, 1326–1338.

Sahai, S., Sharma, C., Singh, D.P., Dixit, C.K., Singh, N., Sharma, P., Singh, K., Bhatt, S., Ghude, S., Gupta, V., Gupta, R.K., Tiwari, M.K., Garg, S.C., Mitra, A.P., Gupta, P.K., 2007. A study for development of emission factors for trace gases and carbonaceous particulate species from in situ burning of wheat straw in agricultural fields in India. Atmos. Environ. 41 (39), 9173–9186.

Shen, G., Wang, W., Yang, Y., Ding, J., Xue, M., Min, Y., Zhu, C., Shen, H., Li, W., Wang, B., Wang, R., Wang, X., Tao, S., Russell, A.G., 2011. Emissions of PAHs from indoor crop residue burning in a typical rural stove: emission factors, size distributions, and gas-particle partitioning. Environ. Sci. Technol. 45, 1206–1212.

Simon, Valérie, Moreau, Lucile, Romdhana, Mohamed Hédi, Sablayrolles, Caroline, Vignoles-Montrejaud, Mireille, Lecomte, Didier, 2012. Emissions of polycyclic aromatic hydrocarbon particulates from combustion of different fuels. Fresenius Environ. Bull. 21 (4a), 946–955. ISSN 1610-2304.

Singh, N., Mittal, S.K., Agarwal, R., Awasthi, A., Gupta, P.K., 2010. Impact of rice crop residue burning on levels of SPM, SO2 and NO2 in the ambient air of Patiala (India). Int. J. Environ. Anal. Chem. 90 (10), 829–843.

US EPA, 2010. Development of a Relative Potency Factor (RPF) Approach for Polycyclic Aromatic Hydrocarbon (PAH) Mixtures, 2010. US EPA, Washington, DC, USA. EPA/635/R-08/012A.

Vichi, S., Pizzale, L., conte, L.S., Buxaderas, S., Lopez Tamames, E., 2005. Simultaneous determination of volatile and semi volatile aromatic hydrocarbons in virgin olive oil by headspace solid phase micro extraction coupled to gas chromatography/mass spectrometry. J. Chromatogr. 1090, 146–154.

Wang, S., Ji, Y., Zhao, J., Lin, Y., Lin, Z., 2020. Source apportionment and toxicity Assessment of PM2.5-bound PAHs in northeast China by PMF-ILCR. Sincen. Total Environ. 713, 136428.

White, A.J., Bradshaw, P.T., Herring, A.H., Teitelbaum, S.L., Beyea, J., Stellman, S.D., Gammon, M.D., 2016. Exposure of multiple sources of polycyclic aromatic hydrocarbons and breast cancer incidence. Environ. Int. 89–90, 185–192.

Wu, S.-P., Yang, B.-Y., Wang, X.-H., Yuan, C.-S., Hong, H.-S., 2014. Polycyclic aromatic hydrocarbons in the atmosphere of two subtropical cities in southeast China: seasonal variation and gas/particle partitioning. Aerosol Air Qual. Res. 14, 1232–1246.

Yang, X.Y., Okada, Y., Tang, N., Matsunaga, S., Tamura, K., Lin, J.M., Kameda, T., Toriba, A., Hayakawa, K., 2007. Long-range transport of polycyclic aromatic hydrocarbons from China to Japan. Atmospheric. Environment 41, 2710–2718.

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. Org. Geochem. 33, 489–515.