Asian Journal of Chemistry; Vol. 33, No. 4 (2021), 892-896

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.23125

Emission of Polycyclic Aromatic Hydrocarbons in Smoke Particulates at Three Different Combustion Stages from Burning of *Rhizophora apiculate*, *Melaleuca leucadendron* and *Hevea brasiliensis* Wood

T.H. Seng[1], S. Suratman[1,*], M.R. Abas[2] and N.M. Tahir[1]

[1]Institute of Oceanography and Environment, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia
[2]Chemistry Department, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

*Corresponding author: E-mail: miman@umt.edu.my

Received: 16 January 2021; *Accepted*: 11 February 2021; *Published online*: 20 March 2021; AJC-20300

The purpose of this study was to characterize and determine the concentrations of polycyclic aromatic hydrocarbons (PAHs) emitted in smoke particulates from burning of *Rhizophora apiculata*, *Melaleuca leucadendron* and *Hevea Brasilensis* at the smouldering, flaming and charring stages. Smoke particulates were sampled using a total suspended particulate Hi-volume sampler (HVS) at a rate of 1.13 m^3/min and PAHs were extracted with a mixture of dichloromethane-methanol (3:1 v/v) using ultrasonic agitation. Fractionation of PAHs was carried out on an alumina-silica column and analysis by gas chromatography-mass spectrometry (GC-MS). The results showed that most of the samples exhibited the highest total identified PAHs in the smouldering stage with formation of PAHs with three rings or more increasing from the smouldering to flaming stages and reducing as combustion entered the charring stage. Naphthalene, phenanthrene and pyrene were the dominant PAHs detected in the wood smoke particulates, depending on combustion stage. Overall the emission and formation of PAHs are strongly dependent on combustion stage as well as other factors such as wood morphology, species, moisture content and combustion temperature.

Keywords: Smoke aerosols, Biomass burning, Combustion process, Polycyclic aromatic hydrocarbons.

INTRODUCTION

Biomass burning is a process related to any burning of organic matter and can happen through manmade fires or natural processes (lightning-induced fires, volcanoes, *etc.*). The practice of biomass burning in clearing forest and savanna grassland is an easy method and widely applied for land clearing and agricultural purposes. Biomass burning can also result from the burning of agricultural waste and stubble after harvesting as well as the use of biomass for fuel [1]. The use of biomass as fuels is a common practice especially in developing countries as it is cheap, easily obtained and there is often an abundance of raw biomass materials. The most common choices of biomass material used as fuel are wood, charcoal, pellets and sawdust as well as animal dung. Soot and organic particulate matter are the main by-products from biomass burning and these substances are reactants that greatly influence atmospheric chemical as well as radiative and optical properties through direct and indirect mechanisms. All biomass fires are dominated by incomplete combustion processes which produce polycyclic aromatic hydrocarbons (PAHs) and other organic compounds in the smoke particulate matter released. Several studies [2-9] have been carried out on PAH compounds emitted from the combustion of biomass materials and it has been found that biomass burning contributes diverse classes of hydrocarbon groups to the atmosphere, among them the carcinogenic and mutagenic benzo[*a*]pyrene. Thus, it is important to characterize the organic substances contained in smoke particulate matter for a better understanding of their concentrations and possible effects on human beings.

In Malaysia, biomass burning is practiced through the clearing of agricultural wastes, garden refuse, forest clearing and for many more purposes. Surprisingly, in rural or suburban areas, biomass burning is normally practiced for the purpose of cooking (*e.g.* biomass fuel), waste disposal and for aesthetic reasons such as indoor fireplaces or campfires. For instance, in Terengganu, Malaysia, the charcoal processing industry found in the coastal area uses paper bark tea tree wood (*Melaleuca leucadendron*) for charcoal making. In contrast, a similar industry on the west coast of Peninsular Malaysia uses mangrove trees (*Rhizophora apiculata*) as the raw material for charcoal making. Terengganu is also popular with the 'keropok lekor' or fish cake industry which can be found along coastal areas (*e.g.* Penarik, Merang, Batu Rakit, Chendering); 'keropok lekor' require boiling before being sold or eaten. The result from a survey carried out to determine the type of wood used as fuel in this industry showed that *Hevea brasiliensis* wood was the most common and popular biofuel among 'keropok lekor' manufacturers for boiling 'keropok lekor' due to its low cost and abundant supplies. This study presents the identification and yields of PAHs emitted in the smoke particulate matter at different combustion stages (smouldering, flaming and charring) from the burning of *Rhizophora apiculata*, *Melaleuca leucadendron* and *Hevea brasiliensis* wood.

EXPERIMENTAL

Collection of samples: *Melaleuca leucadendron* and *Rhizophopra apiculate* woods were collected from a bush forest located a few kilometres from a major roadside in Kg. Bukit Berangan and a mangrove area in the estuary of Kg. Merang, Setiu, Terengganu, Malaysia, respectively. For both wood samples, only the trunk part was taken for the burning process. *Hevea brasiliensis* wood was collected from a 'keropok lekor' shop located in Kg. Batu Rakit, Kuala Nerus, Terengganu, Malaysia. All the sampled woods were kept separately in aluminium lined boxes and cleaned from unwanted debris. The woods were then air dried for a period of two to three weeks before subjected to the burning process.

Sampling of wood smoke particulate: Each type of wood sample was burnt and the smoke particulates emitted were collected using a high-volume air sampler (HVS) fitted with a pre-cleaned glass fibre filter, placed approximately 1 m diagonally above and to the side of the flames in the smoke plume. The HVS was calibrated and its suction rate was adjusted to 1.13 m^3/min before the sampling commenced. Wood smoke particulates were sampled at three different stages, *i.e.* smouldering, flaming and charring, where a new glass fibre filter was placed into the sampler at each stage. Fig. 1 shows the combustion stages for the collection of smoke particulates. Sample filters were then wrapped with aluminium foil and kept in a desiccator until further analysis.

Extraction and fractionation: PAH compounds were extracted with dichloromethane-methanol (3:1 v/v) using ultrasonic agitation for a period of 30 min. For recovery assessment, predeuterated perylene-*d*12 ($C_{12}D_{12}$) was spiked onto filter paper. Agitated extracts obtained were then concentrated using a rotary evaporator and pre-concentrated to about 1 mL using a gentle stream of nitrogen gas (purity ≈ 99.999%). PAHs were then eluted on a silica-alumina column (silica: 5% deactivated (230-400 mesh); alumina: 2% deactivated (70-230 mesh) using a combination of 10% dichloromethane in hexane followed by 50% dichloromethane in hexane.

Gas chromatography-mass spectrometry (GC-MS) analysis: The identification and quantification of naphthalene (Naph), acenaphthylene (Acena), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phen), anthracene (Anth), fluoranthene (Flan), pyrene (Py), benz[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), benzo[*e*]pyrene (BeP), indeno[1,2,3-*cd*]-pyrene (Indeno), dibenz[*a,h*]anthracene (Dibenz), benzo[*g,h,i*]-perylene (BgP) compounds were carried out using a Shimadzu-QP2010 gas chromatography-mass spectrometry (GC-MS) in EI mode (70 eV). The sum of 17 United State Environmental Protection Agency (USEPA) priority PAH compounds as listed above is known as Total Identified PAHs (TIPAH). The GC-MS was used in splitless mode using helium as the carrier gas at a rate of 1.20 mL/min. The column temperature was programmed at 70 ºC (held for 2 min) to 180 ºC (25 ºC/min) then ramped to 280 ºC (6 ºC/min) and held for 10 min. Verification of peaks was carried out based on key fragment ions, retention times compared to those of external PAHs standards and/or mass spectra.

Recovery blanks: Procedural blanks as well as solvent blanks were analyzed and quantified and no PAH compounds of interest were detected in these blanks. Recovery of perylene-*d12* accessed during the multi-step procedure ranged from 68 to 95%. Appropriate corrections were made to the measured concentrations.

RESULTS AND DISCUSSION

It must be conceded that the distribution and abundances of *n*-alkanes and PAHs quantified from *Rhizophopra apiculate*,

Fig. 1. Photo of combustion stages, (a) smouldering combustion; (b) flaming combustion and (c) charring combustion

Melaleuca leucadendron and *Hevea brasiliensis* wood smoke particulate matter were strongly based on the smoke particulates that were trapped on the glass fibre filter and are strongly dependent on combustion conditions (*e.g.* smouldering *versus* flaming duration). Although an attempt has been made to sample aerosols during both flaming and smouldering conditions, uncertainty remains with respect to the duration of each combustion phase. Since the wood burning was not carried out in a controlled combustion chamber, the values reported should not be used as absolute values but as relative chemical fingerprints for each wood sample. Fig. 2 shows TIPAH concentrations obtained according to the respective combustion stages of wood samples studied, with most samples exhibiting highest TIPAH concentrations in the smouldering stage except for *Melaleuca leucadendron*. TIPAH concentrations calculated from all wood smoke particulates ranged from 113 to 1740 μg/g. The identities and yields of each PAH compound obtained from wood smoke particulates at different combustion stages are shown in Table-1. The most dominant PAH compounds emitted were naphthalene, phenanthrene and pyrene, depending on

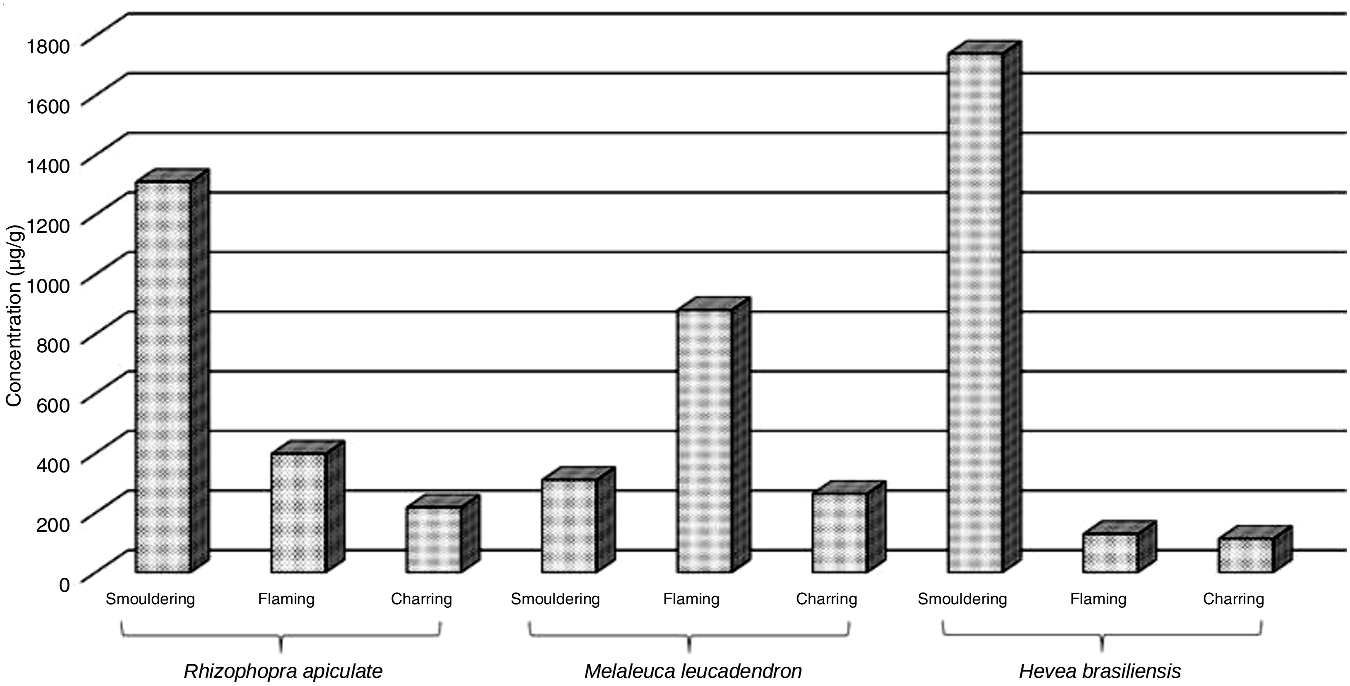

Fig. 2. Concentration of TIPAH in wood smoke particulates according to combustion stage

TABLE-1
IDENTITIES AND YIELDS OF POLYCYCLIC AROMATIC HYDROCARBONS (μg/g) OBTAINED IN AROMATIC FRACTION OF WOOD WITH BARK SMOKE PARTICULATE STUDIED

Compound	Target ion	*Rhizophora apiculata*			*Melaleuca leucadendron*			*Hevea brasiliensis*			ID basis
		SmL	Flm	Chr	SmL	Flm	Chr	SmL	Flm	Chr	
Naphthalene	128	3.5	19.4	43.6	12.3	46.5	74.2	68.0	19.9	bdl	A
Acenaphthylene	152	bdl	bdl	bdl	1.0	3.4	1.8	15.7	0.5	bdl	A
Acenaphthene	154	bdl	bdl	bdl	bdl	bdl	bdl	116	bdl	bdl	A
Fluorene	166	bdl	bdl	bdl	3.7	3.7	2.5	66.2	bdl	bdl	A
Phenanthrene	178	137	62.2	25.7	85.6	221	69.1	323	11.6	6.5	A
Anthracene	178	40.5	21.4	5.0	32.3	59.2	10.9	122	4.2	bdl	A
Fluoranthene	202	295	80.3	49.0	43.6	158	31.2	268	25.9	46.0	A
Pyrene	202	324	106	80.1	55.0	295	66.7	274	28.6	52.3	A
Benz[*a*]anthracene	228	86.1	20.1	9.5	15.5	28	7.5	120	7.5	8.3	A
Chrysene	228	89.7	17.8	5.0	23.1	22.9	bdl	73.1	8.7	bdl	A
Benzo[*b*]fluoranthene	252	87.3	12.8	bdl	11.1	21.6	bdl	78.1	6.5	bdl	A
Benzo[*k*]fluoranthene	252	28.9	2.2	bdl	4.2	6.5	bdl	29.5	2.0	bdl	A
Benzo[*e*]pyrene	252	40.7	5.7	bdl	3.9	8.5	bdl	32.5	3.1	bdl	S
Benzo[*a*]pyrene	252	83.9	11.3	bdl	11.0	20.6	bdl	76.4	6.2	bdl	A
Indeno[1,2,3-*cd*]pyrene	276	41.2	38.7	bdl	3.5	7.1	bdl	33.9	1.9	bdl	A
Dibenz[*a,h*]anthracene	278	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	A
Benzo[*g,h,i*]perylene	276	52.9	bdl	bdl	4.5	8.3	bdl	43.9	2.4	bdl	A
TIPAH (μg/g)		1310	398	218	310.3	880.3	263.9	1740	129	113	

SmL: Smouldering; Flm: Flaming; Chr: Charring; A = matches with authentic standard; S = interpolated from homologues series fragmentation pattern; bdl = below detection limit; detection limit: 0.045 μg/g.

combustion stage, for all wood smoke particulates. Fig. 3 shows an example of the GC-MS total ion chromatogram (TIC) for *Melaleuca leacadendron* at smoldering, flaming and charring stages. Although there are several factors that could influence the combustion process, the main parameters that control the efficiency of combustion are combustion temperature, the oxygen content during burning and also the moisture content of the biomass fuel. These parameters will also influence the organic aerosol output released and at the same time determine the dominant species of organic constituents in organic aerosol [4,10-14]. It was observed that naphthalene concentrations increased from the smouldering to the charring stage, except for *Hevea brasiliensis* wood which showed the reverse, whilst other PAHs exhibited a decrease in concentrations as the burning proceeded to the flaming and charring stages. This trend is the opposite to previous findings by other researchers [4,15] who carried out their combustion experiments in temperature controlled combustion chambers but is similar to other findings from uncontrolled combustion [6,7,14]. Since the wood burning in this study was carried out resembling open air combustion and not in a combustion chamber, the burning temperature and oxygen content during burning were not controlled and monitored, which in hand affected the burning efficiency as well as the formation of high molecular weight PAH compounds.

The formation of PAH compounds happened in the pyrolysis environment with temperatures ranging from 350 ºC to more than 1200 ºC [16] especially in the case of high molecular weight PAH compounds (five aromatic rings and above), which usually form at temperatures of greater than 500 ºC [6,17,18]. However, studies by Hall *et al*. [6], Wiriya *et al*. [7], Olsson and Kjällstrand [19] and Olsson [20] showed that the biomass materials generally combusted with temperatures ranging from 400 to 500 ºC and the PAH compounds emitted were dominated by three to four aromatic ring PAH, which is very similar with the results obtained in this study (Table-2). The lower combustion temperature may also be due to the moisture content. In this study, wood samples were air dried for a period of three weeks in the laboratory before the combustion experiment. This might result in higher moisture contents in the internal part of wood compared to the surface area. When wood is burnt, the upper surface of the wood will be the first to burn before the burning proceeds into the internal part of the wood. This could explain the increase in the concentrations of naphthalene and the decrease in concentrations of PAHs with three, four, five and six aromatic rings. Jauhiainen *et al*. [15] stated that in the smouldering stage, the wood surface burnt at lower temperatures thus leading to higher levels of formation of two aromatic ring PAHs. During the flaming stage, the high moisture content in the internal part of wood tends to limit the combustion efficiency resulting in lower temperature burning which reduces the formation of three aromatic ring PAHs and above, whilst in the charring stage, as the flame ceases, the burning temperature drops to a minimum, which means larger molecular weight PAHs are unable to form. Though the individual PAH concentrations emitted at each combustion stage exhibited differently the emission of PAH compounds by ring number did correlate with previous literature. From the results obtained

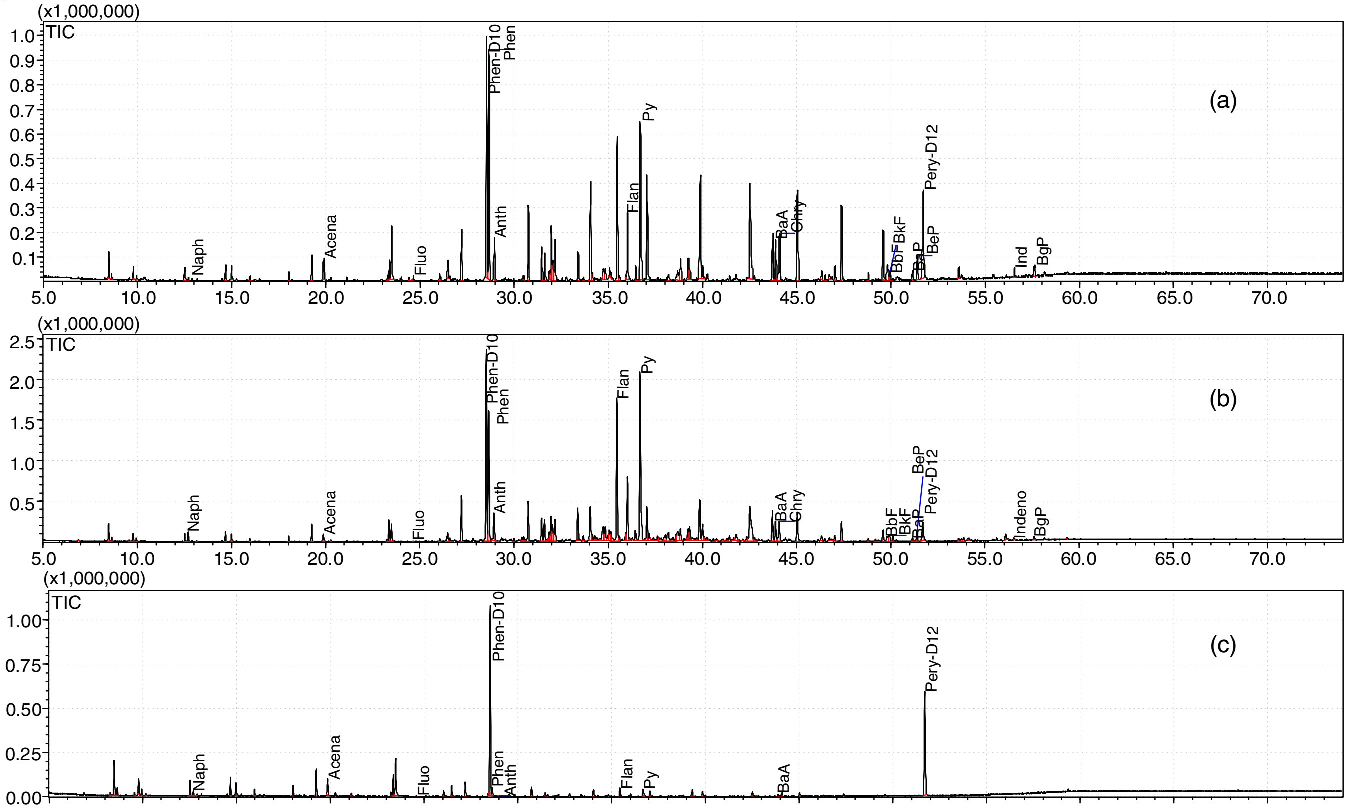

Fig. 3. GC-MS total ion chromatogram for *Melaleuca Leucadendron* at (a) smoldering, (b) flaming and (c) charring stage

TABLE-2
POLYCYCLIC AROMATIC HYDROCARBON AROMATIC RING PERCENTAGE IN DIFFERENT COMBUSTION STAGE

Wood sample	Combustion stage	PAHs aromatic ring (%)				
		2 Ring	3 Ring	4 Ring	5 Ring	6 Ring
Rhizophopra apiculate	Smouldering	0.27	36.0	47.0	12.7	4.04
	Flaming	4.87	41.2	40.0	14.0	–
	Charring	20.0	36.6	43.4	–	–
Melaleuca leucadendron	Smouldering	5.51	52.1	35.1	6.00	1.45
	Flaming	5.89	48.1	41.1	4.00	0.91
	Charring	29.8	42.1	28.1	–	–
Hevea brasiliensis	Smouldering	15.3	41.0	33.0	8.21	2.53
	Flaming	15.8	32.4	41.4	8.59	1.88
	Charring	-	46.4	53.6	–	–

2 Ring = naphthalene, acenaphthylene, acenaphthene, fluorene; 3 Ring = phenanthrene, anthracene, fluoranthene; 4 Ring = Pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene; 5 Ring = benzo[*a*]pyrene, benzo[*e*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene; 6 Ring = benzo[*g,h,i*]perylene; – = not present.

in this study, the formation of three ring and above PAHs increases from the smouldering to flaming stages and reduces as combustion enters the charring stage.

Conclusion

Naphthalene, phenanthrene and pyrene were the dominant PAHs emitted depending on combustion stage for all wood smoke particulates. Three to four aromatic ring PAHs exhibited the highest levels in the wood smoke particulates studied. Emission of PAH compounds were also strongly dependent on the combustion conditions (smouldering *versus* flaming). Beside these conditions, other parameters such as oxygen supply during burning, wood moisture content and temperature of burning during each combustion stage also play an important part in emissions of organic compounds in smoke particulates.

ACKNOWLEDGEMENTS

Financial supports from FRGS fund (Vote No: 59065) is kindly acknowledged. The GC-MS analysis at the Institute of Oceanography and Environment, UMT is also acknowledged.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. I.C. Yadav and N.L. Devi, Biomass Burning, Regional Air Quality, and Climate Change; In: Earth Systems and Environmental Sciences, Encyclopedia of Environmental Health, Elsevier Inc., United States, ed. 2, p. 7 (2018).
2. B.R.T. Simoneit, W.F. Rogge, Q. Lang and R. Jaffé, *Chemosphere, Glob. Chang. Sci.*, **2**, 107 (2000); https://doi.org/10.1016/S1465-9972(99)00048-3
3. J.M. Santos Barbosa, N. Ré-Poppi and M. Santiago-Silva, *Environ. Res.*, **101**, 304 (2006); https://doi.org/10.1016/j.envres.2006.01.005
4. H. Lu, L.-H. Zhu and N.-L. Zhu, *Atmos. Environ.*, **43**, 978 (2009); https://doi.org/10.1016/j.atmosenv.2008.10.022
5. Z.-Z. Wang, X.-H. Bi, G.-Y. Sheng and J.-M. Fu, *Atmos. Environ.*, **43**, 3096 (2009); https://doi.org/10.1016/j.atmosenv.2009.03.012
6. D. Hall, C.-Y. Wu, Y.-M. Hsu, J. Stormer, G. Engling, K. Capeto, J. Wang, S. Brown, H.-W. Li and K.-M. Yu, *Atmos. Environ.*, **55**, 164 (2012); https://doi.org/10.1016/j.atmosenv.2012.03.034
7. W. Wiriya, S. Sillapapiromsuk, N.-H. Lin and S. Chantara, *Aerosol Air Qual. Res.*, **16**, 2716 (2016); https://doi.org/10.4209/aaqr.2015.04.0278
8. H. Hellén, L. Kangas, A. Kousa, M. Vestenius, K. Teinilä, A. Karppinen, J. Kukkonen and J. Niemi, *Atmos. Chem. Phys.*, **17**, 3475 (2017); https://doi.org/10.5194/acp-17-3475-2017
9. C.-T. Pham, Y. Boongla, T.-D. Nghiem, H.-T. Le, N. Tang, A. Toriba and K. Hayakawa, *Int. J. Environ. Res. Public Health*, **16**, 2343 (2019); https://doi.org/10.3390/ijerph16132343
10. D.R. Oros and B.R.T. Simoneit, *Appl. Geochem.*, **16**, 1513 (2001a); https://doi.org/10.1016/S0883-2927(01)00021-X
11. D.R. Oros and B.R.T. Simoneit, *Appl. Geochem.*, **16**, 1545 (2001b); https://doi.org/10.1016/S0883-2927(01)00022-1
12. T. Korenaga, X.-X. Liu and Z.-Y. Huang, *Chemosphere, Glob. Chang. Sci.*, **3**, 117 (2001); https://doi.org/10.1016/S1465-9972(00)00045-3
13. B.R.T. Simoneit, *Appl. Geochem.*, **17**, 129 (2002); https://doi.org/10.1016/S0883-2927(01)00061-0
14. J. Jimenez, O. Farias, R. Quiroz and J. Yañez, *J. Air Waste Manag. Assoc.*, **67**, 806 (2017); https://doi.org/10.1080/10962247.2017.1295114
15. J. Jauhiainen, I. Martin-Gullon, J.A. Conesa and R. Font, *J. Anal. Appl. Pyrolysis*, **74**, 512 (2005); https://doi.org/10.1016/j.jaap.2004.10.003
16. H.I. Abdel-Shafy and M.S.M. Mansour, *Egyptian J. Petrol.*, **25**, 107 (2016); https://doi.org/10.1016/j.ejpe.2015.03.011
17. C. Wang, Y. Wang and H.M.S.K. Herath, *Org. Geochem.*, **114**, 1 (2017); https://doi.org/10.1016/j.orggeochem.2017.09.001
18. G. Shen, W. Wang, Y. Yang, J. Ding, M. Xue, Y. Min, C. Zhu, H. Shen, W. Li, B. Wang, R. Wang, X. Wang, S. Tao and A.G. Russell, *Environ. Sci. Technol.*, **45**, 1206 (2011); https://doi.org/10.1021/es102151w
19. M. Olsson and J. Kjällstrand, *Biomass Bioenergy*, **27**, 607 (2004); https://doi.org/10.1016/j.biombioe.2003.08.018
20. M. Olsson, *Biomass Bioenergy*, **30**, 555 (2006); https://doi.org/10.1016/j.biombioe.2006.01.005