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SOURCE IDENTIFICATION AND POTENTIAL RISK OF HUMAN HEALTH OF *PM_{10} - BOUND* POLYCYCLIC AROMATIC HYDROCARBONS FROM RICE STRAW OPEN BURNING IN MEKONG, VIETNAM

Pham Thi Hong Phuong, Pham Thi Mai Thao, Nguyen Thi Linh Giang
Hanoi University of Natural Resources and Environment, Vietnam

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Abstract

In this study, we dealt with variations of PM_{10} - bound polycyclic aromatic hydrocarbons (PAHs) to estimate the human health risk and identify their possible sources from rice straw open burning (RSOB). Field experiments were conducted in the middle of the rice fields, away from roads, residential and industrial activities, to collect particle-bound PAHs emitted from rice straw open burning in the Mekong Delta. 16 PAHs in extracted solution samples were quantified using GC/MS - MS Thermo TSQ9000. The results showed that the ratio of B[a]P/B[k]F, B[a]P/∑COMB and Fth/(Fth + Pyr) could be used as diagnostic ratios for the identification of sources from RSOB. In addition, the carcinogenic risk of PAHs on PM_{10} (ECR - $B[a]P_{TEQ}$) on burning samples was 238 times higher than the ECR index (10^{-4} ng.m^{-3}). These results prove that the RSOB emitted PAHs compounds on PM with a high risk to human health. ECR - $B[a]P_{MEQ}$ emitted from RSOB have a very high potential for mutagenicity. These results can be used to make a scenario about the risk of PAHs arising from RSOB for policymaking in air quality management.

Keywords: Rice straw; Open burning; Polycyclic aromatic hydrocarbons (PAHs); Marker; Risk; Human health.

Corresponding author. Email: phphuong@hunre.edu.vn

1. Introduction

Rice straw open burning (RSOB) is a popular method to treat rice straw because it helps to clear the fields quickly and remove harmful organisms for new seasons. Uncontrolled burning of rice straw emits huge amounts of toxic air pollutants, contributes to the increase of greenhouse gases and seriously affects air quality and human health [1 - 5]. Polycyclic Aromatic Hydrocarbons (PAHs) are produced from the combustion of RSOB by incomplete combustion and pyrolysis of organic matter. Hundreds of single PAH are released into the atmosphere from biomass combustion, but 18 PAHs are commonly studied because of their superior carcinogenicity and mutagenicity [6, 7]. According to the recommendations of the US Environmental Protection Agency (US. EPA), there are 16 PAHs that are of most

concern including: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fth), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (I(1,2,3-c,d)P), dibenzo[a,h] anthracene (DahA) and benzo[g,h,i] perylene (BghiP).

Each PAH can exist in the air in the gas phase or adsorb on dust particles (particle phase) depending on their physical and chemical characteristics. They can be divided into two categories: low-molecular-weight compounds consisting of PAHs with less than four benzene rings, found mainly in the gas phase and macromolecular compounds with four or more benzene rings and most are adsorbed on the dust phase [8, 9]. The International Agency for Research on Cancer (IARC) classified several PAHs as potentially carcinogenic to humans (Group 1, 2A or 2B). Among these are some congeners including benzo[a] pyrene (group 1), naphthalene, chrysene, benz[a] antracene, benzo[k] fluoranthene and benzo[b] fluoranthene (Group 2B) [10]. The carcinogenic potential of PAHs can be expressed by the Carcinogenic Equivalency Factor (CEF). PAHs with 2 to 3 benzene rings in their molecules are less likely to cause cancer and genetic mutations. PAHs with 4 to 5 aromatic rings or more have strong carcinogenic and mutagenic potential. However, the carcinogenic activity usually focuses only on PAHs with 4, 5 and 6 aromatic rings. PAHs with complex spatial molecular structures often have more aggressive oncogenic activities than planar structures [11].

PAH diagnostic ratios may provide an important tool for identifying pollution emission sources. They can be used to differentiate emissions from engine combustion, crude oil processing products and biomass combustion processes. The calculated PAH rates for each source are unknown and each pair of rates may be specific to a different discharge source (Table 1).

This paper discusses PAH diagnostic rates used to identify sources of pollutant emissions from RSOB. It focuses primarily on the diagnostic rates of parental PAHs because these rates are less variable. In addition, the paper presents a discussion of the health risks of PAH compounds from RSOB.

Table 1. Diagnostic ratios used with their typically reported values for particular processes [12]

PAH ratio	Value Range	Source
∑COMB/∑PAHs	~ 1	Combustion
Flt/ (Flt + Pyr)	< 0,4	Petrogenic
	0,4 - 0,5	Fossil fuel combustion
	> 0,5	Grass, wood, coal combustion
Ant/ (Ant + Phe)	< 0,1	Petrogenic
	> 0,1	Pyrogenic
BaA / (BaA + Chyr)	< 0,2	Petrogenic
	0,2 - 0,35	Coal combustion
	> 0,35	Vehicular emissions
Ind / (Ind + BghiP)	< 0,2	Petrogenic
	0,2 - 0,5	Petroleum combustion
	> 0,5	Grass, wood and coal combustion

∑COMB - (FLA, PYR, BaA, CHR, BkF, BbF, BaP, IcdP and BghiP); ∑PAHs - the sum of total non - alkylated PAHs

2. Methodology

2.1. Study areas and sampling sites

Mekong delta is the largest rice - producing area in Vietnam and is referred to as Vietnam's rice bowl. With a total area of 40,548.2 km^2 (accounting for 13 % of the country's area), rice production accounts for 55.3 % and contributes more than 90 % of annual rice exports [13]. Meteorological conditions in the Mekong delta are hot all year round with an average temperature of 20 - 35 ^oC [22]. There are three main rice crops in the southwestern region, including: Winter - Spring, Summer - Autumn and Autumn - Winter. This study was conducted in the Winter - Spring crop because this is considered the crop with the highest rate of outdoor burning of straw compared to the other two crops. This study was conducted in 2 representative provinces of the Southwest region, including Vinh Long (VL) and Can Tho (CT) (Figure 1). In Can Tho city, rice is cultivated twice a year, while in Vinh Long province, rice is usually grown in 3 main crops a year, even seven crops in 2 years. In Can Tho city, the study was monitored at three different locations, while in Vinh Long province, the study was carried out at four different locations. The selected monitoring locations are not affected by industrial and residential activities and are far from roads (the minimum distance recorded is about 2 km). The distance between locations in a province is about 700 m - 3 km apart. For each site, one background sample and two burning samples were collected on the same day, starting from 6:00 am to 9:00 pm. In each field experiment, all samplers and measuring devices were placed at the fixed downwind site, about 5 m away from the downwind edge of the burning paddy field.

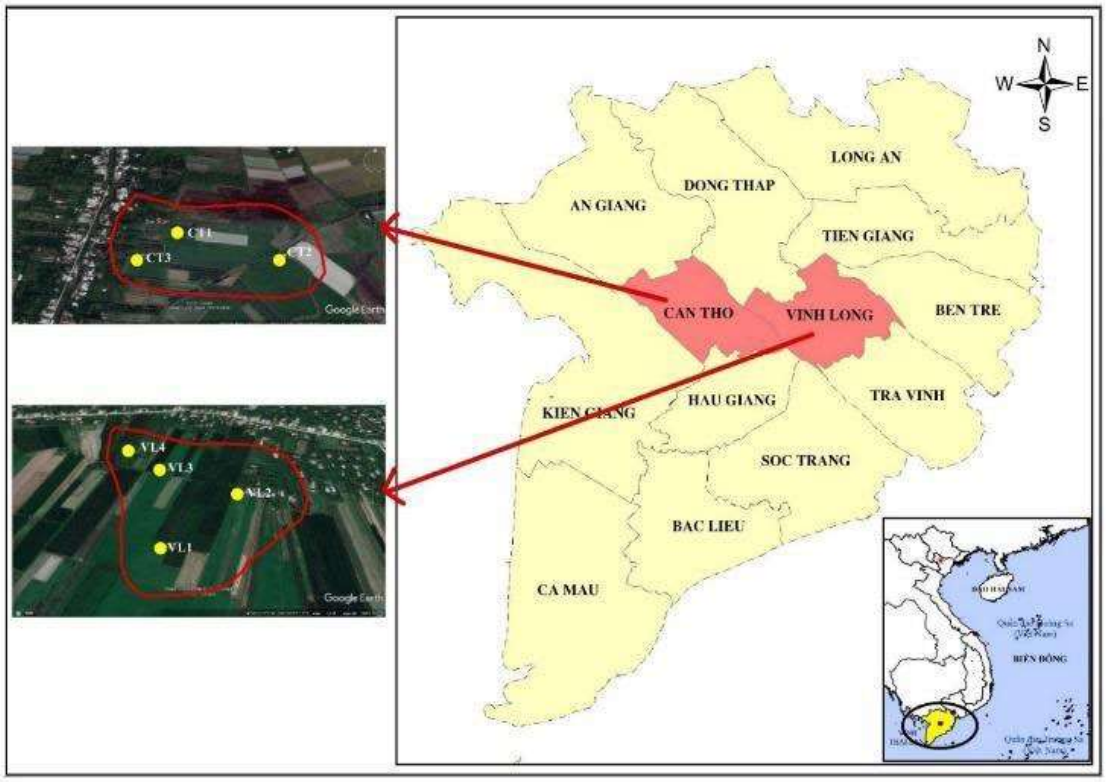

Figure 1: Sampling locations in the Mekong delta of Vietnam

The experiments were carried out on the Winter - Spring crops in 2019, which were taken place in May because the Winter - Spring crop has the highest burning ratio compared with other crops in the year.

An Andersen high - volume sampler (Model SA 1200, USA) was used to collect PM_{10} at a flow rate of 800 L.min - 1. The sampling duration for background samples is 2 hours, while the sampling duration for burning samples depends on the rice straw's burning duration [14]. After sampling, samples were wrapped in prebaked aluminum foil, sealed with clean Teflon bags and stored at -20 ^{o}C for further analysis.

2.2. Analysis

The mass of PM_{10} was analyzed by the gravimetric method. Then each filter was extracted with 100 ml dichloromethane (DCM) using the Soxhlet extraction system. The extract was concentrated and transferred to the multi - layer SPE cartridge. After eluting by 20 ml solvent mixture DCM: acetone (1:1), the solution was concentrated by gentle nitrogen flow to 1 ml. PAHs in samples were analyzed using TSQ 9000 triple quadrupole GC - MS/MS system (Thermo Scientific) with a capillary column (30 m × 0.25 mm internal diameter × 0.25 μm film thickness, 5 % methyl phenyl polysiloxane stationary phase). A standard of 16 PAHs including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fth), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene(BkF), benzo[a] pyrene (BaP), indeno[1,2,3-c,d]pyrene (I(1,2,3-c,d)P), dibenzo[a,h]anthracene (DahA) and benzo[g,h,i]perylene (BghiP) was used for quantification. The detection of PAHs was done based on positive electron ionization (EI-MS/MS) and the multiple reaction monitoring (MRM) mode [15, 16].

2.3. Equations

$$B[a]P - TEQ = B[a]P_{eq} = \sum_{i}^{n=1} [C_i \times TEF_i] \quad (1)$$

$$B[a]P - MEQ = B[a]P_{eq} = \sum_{i}^{n=1} [C_i \times MEF_i] \quad (2)$$

Carcinogenicity - equivalent concentrations (B[a]P - TEQ) and mutagenicity equivalent concentrations (B[a]P - MEQ) were calculated using the formula below [17]:

- B[a]P - TEQ is the concentration equivalent to carcinogenicity.

- B[a]P - MEQ is the concentration equivalent to mutagenicity.

- B[a]Peq is the carcinogenicity of a congener assessed based on the benzo[a] equivalent pyrene concentration. B[a]Peq was used as an indicator of the risk of toxicity from exposure to PAHs (WHO, 1987).

- TEFi are the toxic equivalence factors of individual PAHi.

- MEFi are mutagenic equivalence coefficients of individual PAHi.

- Ci is the concentration of individual PAHi.

Table 2 presents the TEF and MEF values for the individual PAHs according to the published study by US EPA (1993) [17].

Table 2. Coefficient of TEF, MEF

Sign	Number of benzene rings	TEF [17]	MEF [18]
Nap	2		
Acy	3	0.001	
Ace	3	0.001	
Flu	3	0.001	
Phe	3	0.01	
Ant	3	0.001	
Fth	4	0.001	
Pyr	4	0.001	
B[*a*]A	4	0.1	0.082
Chry	4	0.1	0.017
B[*b*]F	5	0.1	0.25
B[*k*]F	5	0.1	0.11
B[*a*]P	5	1	1
*D[a,h]*A	5	1	0.29
*B[g,h,i]*P	6	0.01	0,19
I[1,2,3-cd]P	6	0.1	0.31

3. Results and discussion

3.1. PM_{10} - bound polycyclic aromatic hydrocarbons profiles

The average concentrations of PM_{10}-bound polycyclic aromatic hydrocarbons in the Mekong delta in the background (BG) were 2.55 ± 0.940 ng.m$^{-3,}$ while it in the burning areas was 2479.6 ± 447.3 ng.m^{-3} (Figure 2). The average concentrations of the Σ 16PAHs on PM_{10} during RSOB are 974 times higher than those in the background, which used the "reference samples". The average concentrations of cPAHs and ncPAHs in the background were 0.54 ± 0.250 (21 %) and 2.01 ± 0.700 (79 %), respectively. However, the average concentrations of cPAHs and ncPAHs in the burning areas were 825.7 ± 171.6 ng.m^{-3} (33 %) and 1653.9 ± 275.7 ng.m^{-3} (67 %), respectively. The concentrations of the cPAHs group increased significantly during burning, from 21 % in BG to 33 % in RSOB. In the cPAHs group, B[b]F and B[a]P concentrations dominate. B[b]F accounted for 38 % of the cPAHs group, while B[a]P accounted for 32 %.

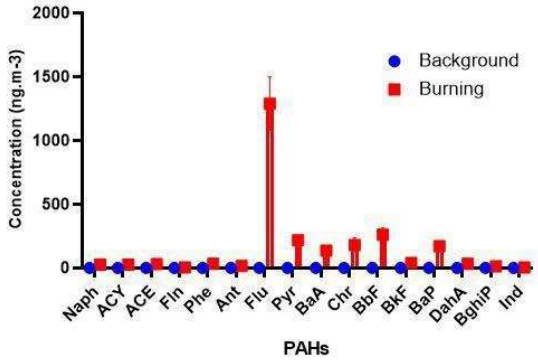

Figure 2: The average concentration of individual PAHs (ng.m^{-3}) in the background and burning in PM_{10}

3.2. PAHs diagnostic ratios for source identification of rice straw open burning

PAHs can be emitted from a variety of sources and their concentrations can be varied depending on the process in which the PAHs are generated. Combustion sources have a significantly higher capacity to form individual PAHs than the other sources. Therefore, the PAH diagnosis ratios are considered an indicator contributing to identifying combustion source characteristics.

The ratio of Fth/(Fth + Pyr) was 0.47 ± 0.06 in the background sample, which is close to the fossil fuel burning ratio (0.4 - 0.5) [19]. Meanwhile, the burning sample was 0.93 ± 0.004, which was larger than the range determined from biomass burning (> 0.5) [12, 19]. In addition, the ratio of B[a]P/B[k]F in burning samples (4.3 ± 1.2) was higher than in motorcycle

exhaust (2.6 ± 1.1) [20]. Furthermore, the contribution of BaP to the total content of Σ 9PAHs (Fth, Pyr, B[*a*]A, Chr, B[*b*]F, B[*k*]*F*, B[*a*]P, B[*ghi*]P, I[1,2,3-*cd*]P) was 7.1 ± 2.6 %, while it is 2.2 ± 1.6 % in PM from motorcycle exhaust [20]. This means that the contribution of B[a]P to total PAHs in RSOB is significantly higher than in vehicle exhaust. Thus, the ratios Fth/(Fth + Pyr), B[a]P/B[k]F and B[a]P/∑ 9 PAH can be used as diagnostic rates to identify emitted from RSOB.

3.3. Toxicity of particle - bound pahs based on b[a]p equivalent

Table 3. Carcinogenicity equivalent concentrations of PAHs

PAHs *(ng.m^{-3})*	B[a]P - TEQ	ECR - B[a$_{]PT}$EQ
Nap	0.03	0.02.10^{-4}
Acy	0.03	0.02.10^{-4}
Ace	0.03	0.03.10^{-4}
Flu	0	0
Phe	0.03	0.03.10^{-4}
Ant	0.16	0.14.10^{-4}
Fth	1.29	1.13.10^{-4}
Pyr	0.22	0.19.10^{-4}
B[a]A	1.37	1.2.10^{-4}
Chry	18.07	15.88.10^{-4}
B[b]F	26.10	22.94.10^{-4}
B[k]F	3.91	3.44.10^{-4}
B[a]P	171.77	150.99.10^{-4}
D[a,h]A	33.22	29.20.10^{-4}
B[g,h,i]P	0.14	0.12.10^{-4}
I[1,2,3-cd]P	0.31	0.27.10^{-4}
Sum	256.66	224.03.10^{-4}

The toxicity of individual PAHs in the family of PAHs depends on their structural formula. PAHs containing 2 to 3 benzene rings are less likely to be carcinogenic and mutagenic, while PAHs containing more than 4 to 5 benzene rings have much greater carcinogenic and mutagenic potential. The results of equivalent carcinogenic concentrations of PAHs are presented in Table 3.

The equivalent concentration of B[a]P - TEQ carcinogenicity on PM_{10} in the burning sample was 256.66 ng.m^{-3} (Table 3). They are many times higher than the permit limit value of the UK (0.25 ng.m^{-3}), Sweden (0.1 ng.m^{-3}) and Europe (1 ng.m^{-3}).

The carcinogenic risk of PAHs on PM_{10} (ECR - $B[a]_{PTEQ}$) on burning samples was 224.03.10^{-4} ng.m^{-3}, which was 238 times higher than the ECR index (10^{-4} ng.m^{-3}). Thus, the RSOB emitted PAHs compounds on PM with a high risk to human health.

The mutagenic potential of PAHs is shown in Table 4. ECR - $B[a]P_{MEQ}$ more than 10^{-4} ng.m^{-3} indicated that PAHs emitted from RSOB have a very high potential for mutagenicity [21]. This result can be used to assist in making a scene about the risk of PAHs arising from RSOB for policymaking in air quality management.

Table 4. Mutagenic equivalent concentrations of PAHs

PAHs *(ng.m^{-3})*	B[a]P-MEQ	ECR - $B[a]P_{MEQ}$
B[a]A	0.11	0.10.10^{-4}
Chry	0.31	0.27.10^{-4}
B[b]F	6.52	5.73.10^{-4}
B[k]F	0.43	0.38.10^{-4}
B[a]P	171.77	150.99.10^{-4}
D[a,h]A	9.63	8.47.10^{-4}
B[g,h,i]P	0.03	0.02.10^{-4}
I[1,2,3-cd]P	0.10	0.08.10^{-4}
Sum	188.896	166.04.10^{-4}

4. Conclusion

PM_{10} - bound polycyclic aromatic hydrocarbons from rice straw open burning in Mekong delta, Vietnam: Potential markers for the source identification and risk of human health were studied. Field experiments were conducted for the Winter - Spring rice crops in 2019 at

Can Tho city and Vinh Long province, representing this delta.

The results showed that the RSOB was the cause of the average concentrations of total PAHs bound in PM_{10} during RSOB, 974 times higher than those in the ambient air without rice straw burning. B[a]P/B[k]F, B[a]P/∑COMB and Fth/(Fth + Pyr) can be used as diagnostic ratios for the identification of sources from RSOB. The carcinogenic risk of PAHs on PM_{10} (ECR - $B[a]P_{TEQ}$) on burning samples was 238 times higher than the ECR index, which means the RSOB emitted PAHs compounds on PM with a high risk to human health. ECR - $B[a]P_{MEQ}$ emitted from RSOB have a very high potential for mutagenicity. These results can be used to make a scenario about the risk of PAHs arising from RSOB for policymaking in air quality management.

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