

## Qualitative Analysis of Dominant Organic Compounds in PM<sub>10</sub> and Burning Residue of Selected Plants

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**Abstract:** A study of atmospheric particulate matter PM<sub>10</sub> was conducted in a semi-urban area from three locations in Malaysia namely Universiti Kebangsaan Malaysia (UKM), Bangi, Simpang Empat (SE), Penang and Bandar Baru Nilai (BBN). Samples were acquired using a standard high-volume air sampler (HVAS) equipped with glass fiber filter paper with the flow rate of 1.13 m<sup>3</sup> per minute for 24 hours. Ultrasonic agitation technique was carried out to extract the organic compounds from the PM<sub>10</sub> using the mixture of dicloromethane and methanol (3/1 v/v). In order to identify the sources of organic compounds in PM<sub>10</sub>, residue samples were prepared by burning of biomass, pine (leaves), palm oil and rubber (stem bark) plants. Residue sample obtained from the burning was then extracted using Soxhlet extraction method to extract the selected organic compounds from the residue. Both extracts were then injected into gas chromatography and gas chromatography mass spectrometry. Polar and non-polar fractions were then identified by their molecular weight. Compounds such as 2-ethylbutyl acetate, Methyl palmitate and methyl octadec-6-enoate were found in the polar fractions while trans-squalene in the aliphatic fractions. The result obtained shows that all identified organic compounds were detected in PM10 collected in SE and BBN, while only two out of four compounds were detected (i.e. 2-ethylbutyl acetate and methyl palmitate) in UKM. While for residue samples methyl palmitate was detected in all samples except pine burning residue, methyl octadec-6-enoate detected in all samples except palm oil, 2-ethylbutyl acetate was detected in palm oil residue samples only and trans-squalene was detected in pine residue samples only. Therefore, the burning of biomass, pine (leaves), palm oil and rubber (stem bark) plants are the major sources of atmospheric organic pollutant in these areas.

**Key Words:** Biomass burning, PM<sub>10</sub>, organic aerosols, molecular markers

### INTRODUCTION

Biomass combustion is an important primary source of particles in the global atmosphere. It contributes many trace substances which are reactants in atmospheric chemistry and soot particulate matter that decreases visibility and absorbs incident radiation [8,19]. Thus, there is a need to characterize additional specific tracers for this input process, although various molecular markers have already been proposed [6,25]. Biomass burning used as a method for clearing vegetated (forest and grassland) areas and wild fires significantly increases the input of organic aerosol components to the atmosphere. Chemical signatures of emission sources have commonly been utilized to distinguish specific inputs from point sources rather than correlation of an air parcel to its regional source.

Most urban/industrial regions produce a similar suite of organic compounds associated with

atmospheric particulate matter (i.e., combustion products, vehicular exhaust plus a variety of industrial emissions, mainly from fossil fuel use [13,21]. Regional vegetation cover also produces distinct signatures and molecular markers by direct blow-off [23,22,20].

Chemical composition data of smoke particulate matter is important for understanding the organic component contribution of biomass burning emissions to atmospheric chemistry and complements existing data on the signatures of direct organic emissions (i.e., particulate matter) from biomass sources [31,32,6,13,14,25,26,27,1,15,104]. Wood combustion has been identified in earlier studies as a non-fossil fuel source (biofuel) that can contribute appreciably to the deterioration of both outdoor and indoor air quality [2,3,5,6,7,11,14,18,31]. Previous studies were either focused on the characterization of wood smoke emissions from wild fires or on indoor wood burning in stoves or fireplaces.

In the present paper atmospheric particulate matter  $PM_{10}$  were collected at three sites in Malaysia, and burning residue samples from the burning of specific plant species (i.e. palm oil (stem bark), rubber, pine (leaves) and biomass), allowed to identify and qualify of some polar and non-polar compounds. Thus, the objectives of this study were to qualify of selected dominant organic compounds in these atmospheric particulate matters by gas chromatography–mass spectrometry (GC–MS), to indicate these OCs (e.g. 2-ethylbutyl acetate, methyl palmitate, trans-squalene and methyl octadec-6-enoate) in these three different polluted sites and to verify if selected plants burning would be a significant source of OCs to the studied of respected areas.

## MATERIAL AND METHODS

### Sampling:

**Atmospheric Particulate Matter ( $PM_{10}$ ):** Atmospheric particulate matter samples with a diameter less than  $10\mu m$  ( $PM_{10}$ ) were collected at ground level from three locations namely Universiti Kebangsaan Malaysia (UKM) Bangi, Penang (SE) and Nilai (BBN), Malaysia by using high volume air sampler (HVAS) model Staplex completed with a pre-treated glass-fiber filter paper (GFFs) (20.3cm x 25.4cm) at flow rate of  $1.13 m^3/min$  for a total period of 24 hours (temperature 25–33 °C and humidity 58–93%).

Prior sampling, the GFFs were wrapped with aluminium foil and combusted at 550 °C for three hours to remove trace organic background contaminants. The GFFs were weighed under controlled temperature and humidity conditions (25 °C, 50% RH) before and after the sampling in order to determine the concentrations of particulate matter ( $PM_{10}$ ). The exposed filters were removed from the sampler after 24 hours and folded into half, face to face, and again placed in a plastic bag and wrapped in aluminium foil. After  $PM_{10}$  collection, all filters were conditioned and re-weighed. The difference in weight before and after sampling and the total volume of air sample were used to calculate the  $PM_{10}$  concentration ( $\mu g m^{-3}$ ). All filter papers were stored in a freezer (-5 °C) for further analysis.

**Extraction of Organic Compounds (OCs) in  $PM_{10}$  Sampling:** The extraction of organic compounds OCs from exposed quartz fiber filters consisted of two steps before qualitatively analysis using GC-MS. First, the OCs fractions were extracted by using ultrasonic agitation and then concentrated by using rotary evaporation.

Half of aerosol samples quartz fibre filter paper was cut into  $1cm^2$  squares by using cleaned scissors

and forceps. The cutting process was done in the laminar flow chamber (clean air station). The pieces were transferred to a 250 ml flask (Schott, Germany) and it follows the method first used by [20] including some modifications for data comparison purposes. Samples of smoke particles are taken by filtration (quartz or glass fiber) were typically extracted using ultrasonic agitation for three 20-min periods using 100 ml a mixture of dichloromethane ( $CH_2Cl_2$ ) and methanol ( $CH_3OH$ ) (3:1 v/v). Solvent extracts were filtered using a filtration unit to remove all insoluble particles [20]. Filtrates were concentrated by rotary evaporation to 5ml and then clean up by a stream of filtered nitrogen gas before qualitatively analysis using gas chromatography mass spectrometry (GC– MS)

### Burning Residue Preparation and Extraction:

Residue samples were prepared by a cut of selected types of wood (pine, rubber, biomass and palm oil) to small pieces, drying, placed in iron dish, wrapped in aluminum foils, burned completely up to 300°C in the furnace for 3 hours and then sieved (0.6mm) to remove coarse particles.

### Extraction of Organic Compounds (OCs) from

**Burning Residue Samples:** About 5 g of residue samples were accurately weighed, placed in a 3 mm Pyrex glass thimble and inserted in a “Soxhlet” apparatus. Extraction of OCs was done for 6 hours using 250 ml mixture of dichloromethane (DCM) and *n*-Propanol as the extracting solvents. The condenser was passed with ice cold water to ensure that all the OCs in the DCM and Propanol will not evaporate. The OCs in DCM+Propanol solution was filtered using whatman glass fibre; r filters to removal of insoluble particles[20]. The mixture was filtered over 0.5 g anhydrous sodium sulfate ( $Na_2SO_4$ ) as a dehydrating agent (to adsorb water and moisture). Filtrates were concentrated using rotary evaporator until 5 ml of mixture and then clean up by a stream of filtered nitrogen gas. Aliquots are then taken for direct gas chromatography–mass spectrometry (GC– MS) analysis.

## RESULTS AND DISCUSSION

The results of the qualitative analysis of dominant organic compounds from burning residue of selected plants showed that the OCs pollutant are mostly those that come from natural and anthropogenic sources at a selected areas, as there are no other possible sources of OCs that were observed around those areas.

Results obtained for the analysis of individual organic compounds present in the various polarity and non polarity fractions separated from the extract of  $PM_{10}$  and burning residue samples are summarized in

Table 1 and Table 2. Particulate matter PM<sub>10</sub> samples and burning residue extracted for qualitative analysis of OCs to identify the possible sources of OCs in PM<sub>10</sub>. The characterizations of the organic compounds in the samples as listed and categorized in Table 1.

The possible organic marker tracers in the particulates matter PM<sub>10</sub> and residue of the biomass burning samples for selected plants are (i.e. 2-thyl butyl acetate C<sub>8</sub>H<sub>16</sub>O<sub>2</sub> and methyl palmitate C<sub>17</sub>H<sub>34</sub>O<sub>2</sub>) as these markers were detected at all stations although at trace qualities (UKM, BBN and SE) as well as in the residue from palm oil (seed shell) burning. However, 2-thyl butyl acetate was not detected in biomass residue, pine (leaves) and rubber (stem bark) burning while, Methyl palmitate was detected in the biomass residue burning and rubber burning but was not indicated in the pine residue burning (Table .1). These compounds could be the oxidation products from unsaturated lipids or incomplete combustion products, again indicating aging or long-range transport [1,9]. On the other hand trans-squalene C<sub>30</sub>H<sub>50</sub> and methyl octadec-6-enoate C<sub>19</sub>H<sub>36</sub>O<sub>2</sub> markers were detected at BBN and SE sites except UKM as well as in the residue from pine (leaves) burning. Methyl octadec-6-enoate was detected also in the burning residue of the biomass and rubber (stem bark). Long chain alkanes (trans-squalene C<sub>30</sub>H<sub>50</sub>) are interpreted to be the high

molecular weight (410 g/mol). As these compounds are found in emissions from other sources such as automobiles [17] and vascular plant wax [24].

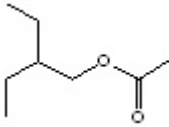
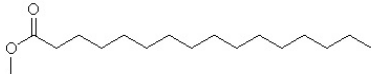
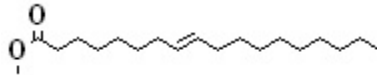
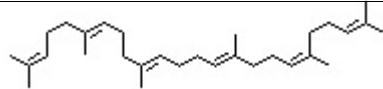
Thus, indicating the important contribution of this tracer for the particulate matter PM<sub>10</sub> derived from residue of vegetation combustion [28,27,29,30]. The results could be confirmed when the GC-MS chromatogram is compared to the selected vegetation residue chromatogram, showing very similar distribution of selected organic compounds. Fig. 1 shows an example of GC/MS total ion chromatogram, illustrating the presence of all of selected organic compounds in the polar and non-polar fraction of atmospheric particulate matter from the BBN site and the mass spectrum of selected OCs obtained at these sites. The information reported here should not be used as absolute but as relative chemical fingerprints for these sources. The molecular markers are one source of specific and might used as confirming tracers for transport and fate studies of smoke emissions from these examples of biomass fuel sources. [16] conducted a study with the ARB to characterize seven air pollution sources such as meat charbroiling, cooking with seed oils, medium-duty diesel trucks, gasoline-powered motor vehicles, fireplace combustion of wood, cigarette smoke, and industrial spray painting operations.

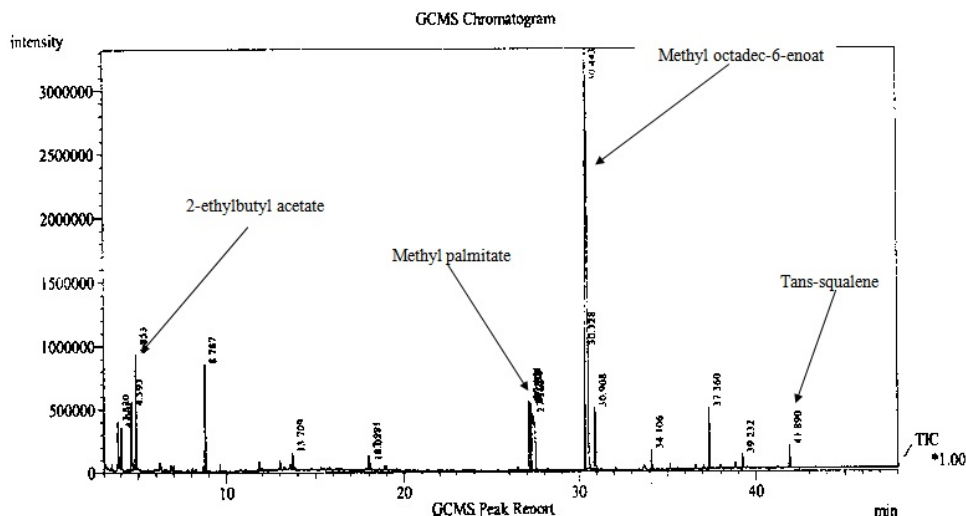
**Table 1:** Qualitative analysis of dominate organic compounds from PM<sub>10</sub> and burning residue of selected plants

Compound name	Formula	M.Wt	Structure	Location			Plants selected			
				UKM	BBN	SE	Palm oil	Biomass	Pine	Rubber
2-ethylbutyl acetate	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	144	I	✓	✓	✓	✓	ud	ud	ud
Methyl palmitate	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	270	II	✓	✓	✓	✓	✓	ud	✓
methyl octadec-6-enoate	C <sub>19</sub> H <sub>36</sub> O <sub>2</sub>	296	III	ud	✓	✓	ud	✓	✓	✓
Trans-squalene	C <sub>30</sub> H <sub>50</sub>	410	IV	ud	✓	✓	ud	ud	✓	ud

\* Undetected (ud), detected (✓)

**Table 2:** Molecular structure of selected organic compounds from PM10 and selected plants

I. 2-ethylbutyl acetate	II. Methyl palmitate
Molecular formula: C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	Molecular formula: C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>
Molecular weigh: 144	Molecular weigh: 270
	
III. methyl octadec-6-enoate	IV. Trans-squalene
Molecular formula: C <sub>19</sub> H <sub>36</sub> O <sub>2</sub>	Molecular formula: C <sub>30</sub> H <sub>50</sub>
Molecular weigh: 296	Molecular weigh: 410
	



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