



## Composition of Levoglucosan and Surfactants in Atmospheric Aerosols from Biomass Burning

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### ABSTRACT

Biomass burning contributes to various organic substances in the atmosphere. Levoglucosan has been recognised as one of the indicators of biomass burning and surfactants are a group of molecules which can be distributed through biomass burning. This research aims to determine the composition of levoglucosan and surfactants in agricultural areas and the several tropical plant species which can contribute to a high amount of levoglucosan and surfactants in the atmosphere. Suspended particulate matter in the atmosphere (fine and coarse mode) was collected in the agricultural areas (paddy fields) during the dry season and compared to samples collected at the Universiti Kebangsaan Malaysia (UKM), Bangi. The soot samples were prepared through the burning of several tropical plant species, namely: *Oryza sativa*, *Rhizophora spp.*, *Elaeis guineensis* and *Saccharum officinarum* at 300°C in a furnace. This allowed for the levels of levoglucosan and surfactants such as MBAS and DBAS to be determined using the colorimetric method. Oxidation and UV radiation were also used to examine the impact of photo-oxidation on the concentration of levoglucosan and surfactants in soot. The results showed that the concentration of levoglucosan in the agricultural areas during harvesting season is significantly higher compared to the levoglucosan recorded at UKM Bangi (semi-urban areas). The concentration of surfactants is dominated by anionic surfactants, particularly in fine mode aerosols. Soot from leaves was found to contribute a high amount of levoglucosan when compared to wood and straw. There are indications that biomass burning can contribute to a large quantity of polar group molecules which behave like anionic surfactants and correlate to the amount of surfactants.

**Keywords:** Surfactants; Levoglucosan; Biomass burning.

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### INTRODUCTION

Biomass burning provides a substantial contribution to carbonaceous particles in the atmosphere (Simoneit, 2002; Abas *et al.*, 2004; Zhang *et al.*, 2008, Hennigan *et al.* 2010; Saarnio *et al.*, 2010). Numerous studies have suggested that open burning is a major source of hazardous emissions and this has prompted some countries to impose stringent restrictions on such activities. Volatile organic carbons (VOC), semi-volatile organic carbons (SVOC), carbonyls and chlorobenzenes are among the groups of noxious gaseous emissions resulting from open burning (Estrellan and Iino,

2010). In South East Asia, biomass burning takes place most of the year due to agricultural activities (Lee *et al.*, 2008; Fartas *et al.*, 2009; Anwar *et al.*, 2010). Malaysia, which is in the centre of South East Asia, is commonly affected by biomass emissions from Sumatra and Kalimantan during the southwest monsoon, and Indochina (particularly the Malaysian Peninsular) as a result of the northeast monsoon. Fire from peat land during the southwest monsoon often creates haze episode in South East Asia and contributes significantly to carbon emissions (Anwar *et al.*, 2010; Hyer and Chew, 2010; Md Yusof *et al.*, 2010; Miettinen *et al.*, 2010). For the other seasons, post-harvest combustion, particularly of paddy straw, was found to dominate the biomass burning. Previous studies (Simoneit *et al.*, 2002; Lee *et al.*, 2008; Gonçalves *et al.* 2011; Wang *et al.*, 2011) have demonstrated that organic carbon (OC) was the dominant composite of the aforementioned burning and that the heat intensity, aeration and duration of smouldering

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and flaming conditions were responsible for shaping the distribution and ratio of the natural versus altered compounds in the smoke (Abas *et al.*, 2004; Simoneit *et al.*, 2004).

Levoglucosan and related saccharidic compounds are increasingly employed as biomass burning tracers (Simoneit *et al.*, 1999; Fraser and Lakshmanan, 2000; Simoneit, 2002; Zhang *et al.*, 2008; Kumagai *et al.*, 2010; Kim Oanh *et al.*, 2011). Levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) is a product of cellulose combustion (Dos Santos *et al.*, 2002; Jordan *et al.*, 2006). When cellulose is heated over 300°C, it undergoes various pyrolytic processes, yielding a highly combustible tar, a major constituent of which is levoglucosan, a dehydrated glucose. Levoglucosan is relatively stable in the atmosphere, showing no decay over 10 days in acidic conditions (Simoneit, 2002; Schkolnik and Rudich, 2006). Levoglucosan can be detected in most oceanic aerosols samples, which confirms the long-range transport of biomass burning plume (Fraser and Lakshmanan, 2000; Simoneit and Elias, 2000, 2001; Wang *et al.*, 2007).

Biomass burning can also contribute to a large quantity of water soluble organic compounds (WSOC), which consist of high molecular weight molecules or humic-like substances and behave like surface active agents or surfactants (Latif *et al.*, 2005; Asa-Awuku *et al.*, 2007; Asa-Awuku *et al.*, 2008). Surfactants often found in tropospheric aerosols can affect the onset and development of clouds (Taraniuk *et al.*, 2008). The surface active agent can generate more cloud water due to the reduction of surface tension in a droplet and behave like cloud condensation nuclei (CCN) in the atmosphere. The amount of CCN increases the albedo effect and influences climate change in certain areas (Ellison *et al.*, 1999; Roberts *et al.*, 2002; Tabazadeh, 2005).

This study aims to determine the concentration of levoglucosan and surfactants in atmospheric aerosols in agricultural areas where open burning occurs. The study also intends to determine the composition of levoglucosan and surfactants from the soot of several tropical plants, as well as examine how they are affected by oxidation and UV-radiation.

## METHODS

### Sampling Location

The sampling station in Sekincan, Selangor is located in the middle of the western coast of the Malaysian Peninsular (Fig. 1). This area is an agricultural and a great distance from local roads and urban areas. Samples for suspended particulate matter (coarse and fine mode) were collected at two sampling sites in the paddy field areas where biomass burning occurred for the burning of paddy straw after harvesting. The samples were collected between 7th and 13th January, 2009. In order to compare suspended particulate matter with biomass burning, samples of suspended particulate matter were also collected at the Universiti Kebangsaan Malaysia (UKM), Bangi from 15th to 17th January, 2009. UKM Bangi is located in a suburban area south of Kuala Lumpur. Being in a tropical area, the temperatures measured in the sampling locations were between 24°C and 32°C with a wind speed of 2–4 m/s. The northeast monsoon dominates

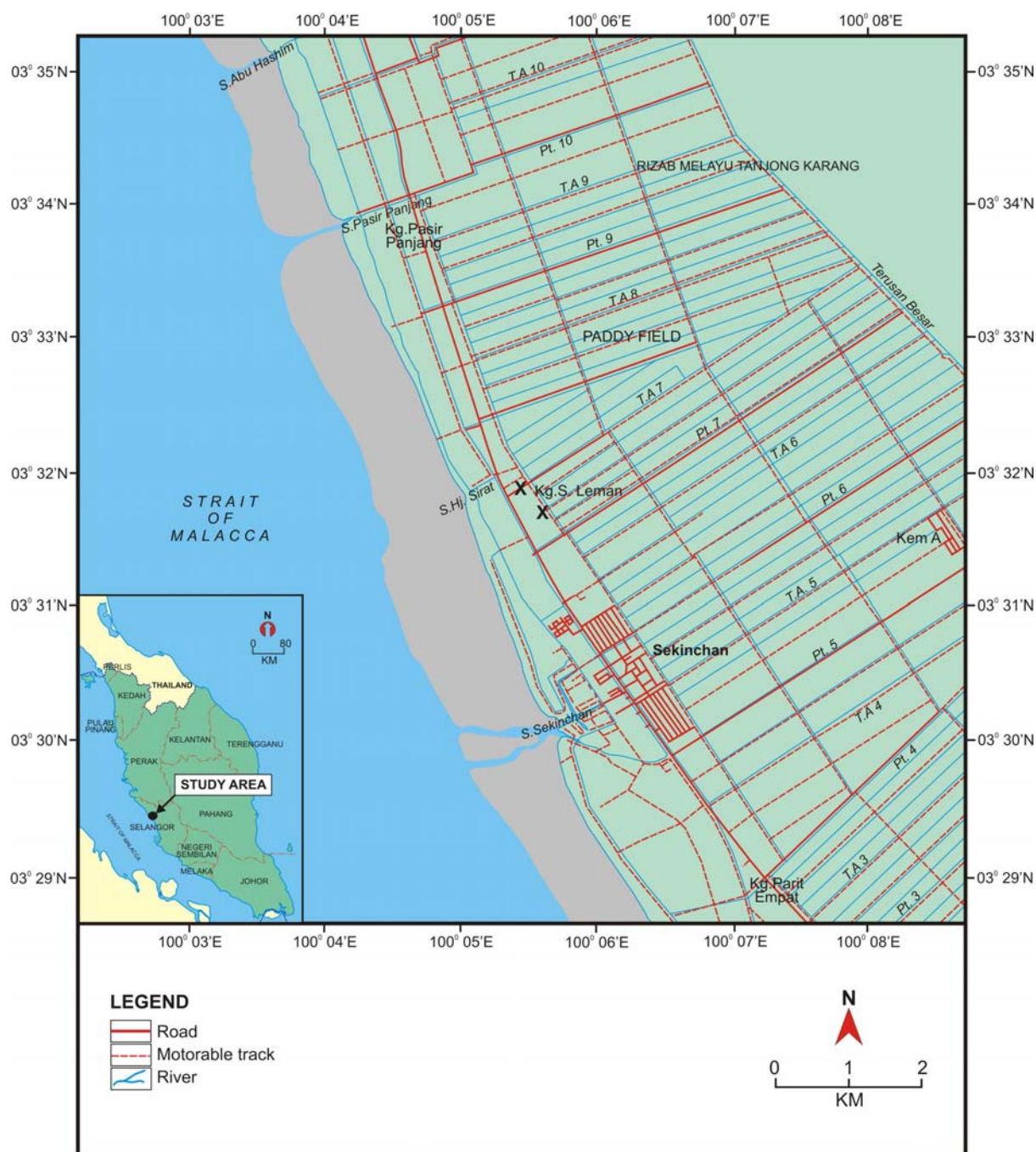
the wind directions in the study areas between November and March. For each sampling location, two replicates ( $n = 2$ ) for total suspended solids were collected.

### Preparation of Aerosols Samples

Sample of aerosols were collected using a high volume air sampler (HVAS) with a five-stage Cascade Impactor (Staplex). Only for stage 3 and 4 were slotted filter papers (Westech Instrument) used to collect coarse mode aerosol samples (diameter size  $> 1.5 \mu\text{m}$ ). For the backup stage, a backup filter paper (Whatman EPM 2000) was used to collect fine mode aerosol samples (diameter size  $< 1.5 \mu\text{m}$ ). In order to remove organic matter, slotted filter papers and backup filter papers were packed in aluminium foil and pre-fired at 500°C in a muffle furnace for 4 hours prior to use. The filter papers were then conditioned in a desiccator for 24 hours before being weighed with an electronic balance and stored in a refrigerator (4°C) until analysis. The high volume air sampler, with prepared filter papers, was placed in an open field to avoid any disturbance of material to the flow of aerosols entering the instrument. The sampling was carried out for 24 hours with a flow rate of 1.13 m<sup>3</sup>/min. After the aerosol sampling, the filter papers were once again carefully packed in aluminium foil and conditioned in a desiccator prior to weighing. The blank filter papers were treated in the same manner as the filter paper used to collect aerosol samples. The filter paper was fitted to the high volume air sampler for 24 hours without the high volume sampler being switched on. To extract the aerosol samples from the filter paper, a quarter of the filter paper containing aerosol particles was cut into small pieces (1 cm  $\times$  1 cm) with cleaned scissors and forceps. 40 mL of deionised water was measured into the centrifuge tube with the filter paper and sonicated for 45 minutes. The mixed solution was then filtered through Whatman 0.45  $\mu\text{m}$  GF/C glass microfibre filters by using a vacuum pump (850 Air Compressor). The resulting filtered solution was diluted to 100 mL in a volumetric flask and kept at 4°C until analysis. The above extraction procedure was replicated three times.

### Preparation of Residue (Soot) from Selected Plants Samples

Several tropical plants, e.g. *Oryza sativa*, *Rhizophora spp.*, *Elaeis guineensis* and *Saccharum officinarum* were selected for levoglucosan and surfactants analysis. A variation of plants, in addition to *Oryza sativa* were selected so as to compare and determine whether those containing wood are able to produce greater quantities of levoglucosan and surfactants. Soot samples were prepared by cutting selected parts of each plant (namely leaves (L), bunches (B) wood (w) and straws (W)) into small pieces. The samples were then placed in an iron dish and wrapped in aluminium foil before being completely burned at 300°C in the furnace for 3 hours. After which they were sieved (0.6 mm) to remove debris and large particles. For every sample, there were three replications ( $n = 3$ ) for each analysis. This experiment compared the amount of levoglucosan from *Oryza sativa*, taken as the main source of biomass burning in the study area, to the other tropical species which produce levoglucosan from biomass burning.



**Fig. 1.** Sampling locations in Sekinchan, Selangor, Malaysia.

### ***Levoglucosan and Surfactants Analysis***

The determination of levoglucosan and surfactants in aerosols and soot extractions was based on the formation of coloured ion-association complexes. The levoglucosan analysis from the aerosols and soot extractions was conducted using the anthrone-sulphuric colorimetric method, as utilised by Laurentin and Edwards (2003) and Fartas *et al.* (2009). Each step in this breakdown of glucose to 5-(hydroxymethyl)-2-furaldehyde represents dehydration with either double bond or ring formation. Sattler and Zerban (1948) suggest that the development of the green dye in the anthrone reaction is dependent on the presence of 5-(hydroxymethyl)-

2-furaldehyde, or a similar furfural compound, as formed by the action of the sulphuric acid on the carbohydrate.

Determination of anionic surfactants such as methylene blue substances (MBAS) and cationic surfactants like disulphine blue substances (DBAS) has been widely used and is described in the Standard Method for the Examination of Water and Wastewater (APHA, 1992). The principal of this methodology is based on the formation of a chloroform extractable ion-association complex between the anionic or cationic surfactants and cationic (disulphine blue) or anionic (methylene blue) dyes, followed by a spectrophotometric measurement of the intensity of the

extracted coloured complex as applied by Chitikela (1995), Oppo *et al.* (1999), Latif and Brimblecombe (2004), Hanif *et al.* (2009) and Roslan *et al.* (2010).

#### **Determination of Levoglucosan through the Anthrone Colorimetric Method**

The anthrone reagent was prepared by dissolving 0.2 g of anthrone (9,10-dihydro-9-oxoanthracene) in 100 mL of concentrated sulphuric acid H<sub>2</sub>SO<sub>4</sub> 97% which was left to stand for 45 minutes until perfectly clear. Each day, the reagent was freshly prepared and used within 12 hours (Yemm and Willis, 1954). The anthrone reagent (10 mL) was pipetted into thick-walled Pyrex tubes (150 × 25 mm) with 5 mL of Levoglucosan standard solutions (0.1–1 mM). The solutions were then transferred to a 100°C water bath for 10 minutes to produce the green dye, followed by a 4°C one for 5 minutes, and, to prevent condensation on the optical tubes during reading, 5 minutes in water at 20°C. The absorbance of all samples was determined through the use of a colorimeter with a wavelength of 620 nm and deionised water as blank. The lower limit of detection for levoglucosan is 7 µM, which was calculated using the mean and standard from the blank samples.

#### **Determination of Anionic Surfactants such as Methylene Blue Active Substances (MBAS)**

The sample solution (20 mL), an alkaline buffer (2 mL) of an aqueous solution of 24 g/L sodium hydrogen carbonate and 27 g/L sodium carbonate) and 1 mL of neutral methylene blue solution (0.35 g/L) followed by chloroform (5 mL) were added to a 40 mL vial in that order. The vial was tightly closed using a holed screw-cap and Teflon liner and vigorously shaken for one minute in a vortex mixer. It was then left to stand until the phases had separated, after which the chloroform layer was transferred to a new vial (vial B) containing Milli Q water (22 mL) and 1 mL of acid methylene blue solution (0.35g methylene blue + 6.5 mL H<sub>2</sub>SO<sub>4</sub>/L) using a Pasteur pipette. Vial B was shaken and the separated chloroform was collected through the Teflon liner of the holed screw-cap with a syringe equipped with a metal needle, while the vial was inverted. The absorbance of the chloroform phase was measured spectrophotometrically at 650 nm. A calibration curve with a concentration range 0–2 µM was established using sodium dodecyl sulphate, SDS as the reference compound. The lower limit of detection for anionic surfactant analysis was 0.05 µM. This was estimated using the mean and standard deviation of the blank value.

#### **Determination of Cationic Surfactants as Disulphine Blue Active Substances (DBAS)**

The sample solution (20 mL), acetate buffer pH 5 (2.0 mL) and 1 mL of disulphine blue solution (2.58 g/L mixture of 90:10 water ethanol solution) and chloroform (5 mL) were added to the solution. The solution was vigorously shaken for one minute using a vortex mixer. The cap was loosened for a few second to release the pressure, and then re-tightened. The vial was inverted and left until the two phases had completely separated. Some of the chloroform layer was removed using a syringe and its absorbance was measured at

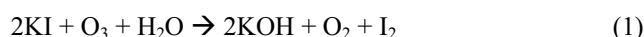
wavelength 628 nm. A calibration curve, with a concentration range 0–1.5 µM, was constructed using zephiramine as a reference compound. The lower limit of detection for anionic surfactant analysis was 0.04 µM. This was estimated using the mean and standard deviation of the blank value.

#### **Exposure of Soot Towards UV Radiation**

Soot samples (1.0 g) were placed in a beaker and exposed for two hours to UV light (40 W) generated from a UV lamp (Philips) in order to determine any photo degradation. The intensity of the UV light used in the experiment, however, is quite low compared to the intensity of cumulative radiation of sunlight to the Earth's surface, which is 120 W/m<sup>2</sup>. After exposure, the samples were fan-cooled to maintain a temperature of 50–55°C. The exposed samples were then dissolved in deionised water (100 mL) and ready for extraction. The extracts were shaken and filtered using 0.2 µm pore size 47 mm diameter cellulose acetate filter papers (Whatman) and a vacuum pump. The concentration of levoglucosan and surfactants in the solutions were analysed in the same way as the determination of levoglucosan and surfactants in atmospheric aerosols.

#### **Exposure of Soot Towards High Concentrations of Ozone**

Soot (1.0 g) was exposed to ozone in a dreschel bottle for 1 hour. The ozone was generated from pure oxygen in a laboratory ozoniser, MX II, in a fume cupboard. The flow rate of ozone from the ozone generator was controlled at 1 litre per minute, which gave a concentration in the solution of 20 g/L. The exposed samples were then dissolved in deionised water (100 mL) and ready for extraction. The extracts were shaken and filtered using 0.2 µm 47 mm cellulos acetate filter papers (Whatman) and a vacuum pump. Concentrations of the extracts were analysed as described in the previous section. The concentration of ozone was determined by the reaction of ozone with potassium iodide to form iodine (I<sub>2</sub>):



The concentration of ozone generated 20 g/L (around 20,000 ppm) is far higher compared to the level of ozone in the ambient air environment which is below 50 ppb. The estimated value of OH<sup>•</sup> from water, based on Eq. (1), is approximately 14 g/L. The formation of OH<sup>•</sup> from the experiment is very limited due to the low level of air humidity (below 60%) in the dreschel bottle.

The concentration of levoglucosan and surfactants in the solutions were analysed in the same way that they had been determined in atmospheric aerosols.

#### **Quality Assurance and Quality Control**

In order to reduce the likelihood of error in the results obtained, good quality control measures were implemented and maintained throughout the analysis. Prior to use, all glassware was washed with hexane, rinsed using acetone and then left to dry before being rinsed with deionized

water. The vials used were immersed in 20% nitric acid overnight before being heated in a furnace (500°C) for 24 hours. Gloves were used during all handling of filter paper to avoid any exposure to organic contamination from the hands. Detergent and soap were prohibited from use while materials were being cleaned to avoid any surfactant contamination from the detergents. As a final quality control measure, all instruments involved in the analysis were calibrated before use. All work involving the aerosol samples and filter papers was conducted in a laminar flow chamber. Ultra pure water with 18.2 MΩcm resistivity (Neptune Analytical) was used in the analysis.

## RESULTS AND DISCUSSION

### *Surfactants and Levoglucosan in Atmospheric Aerosols*

The results for suspended particulate matter concentrations as fine and coarse mode aerosols, as shown in Table 1, indicate that the concentration of total suspended particulate matter (fine and coarse mode aerosols) was recorded as being higher at the Universiti Kebangsaan Malaysia, Bangi compared to the overall levels of suspended particulate matter recorded in the agricultural areas. The concentration of suspended particulate matter recorded at all stations is dominated by fine mode aerosols (diameter size < 1.5 μm) as mentioned in several other studies, e.g. Latif and Brimblecombe (2004). The high concentration of suspended particles, particularly of fine mode aerosols ( $56.8 \pm 11.2 \mu\text{g}/\text{m}^3$ ) as recorded at UKM Bangi is expected to be the result of several contributing anthropogenic factors, such as: motor vehicles and fugitive dust, especially from bare land and road sides due to urbanization processes (Chow, 2010). On the other hand, the concentration of suspended particulate matter in the agricultural area (paddy field) during the sampling conducted was more closely related to open burning and other agricultural activities.

The concentration of levoglucosan was found at the highest concentration in the agricultural areas. The results clearly indicate that the levoglucosan in both fine mode (between  $242.12 \pm 30.40$  and  $248.40 \pm 127.02 \mu\text{mol}/\text{m}^3$ ) and coarse mode aerosol samples (between  $105.58 \pm 141.80$  and  $147.86 \pm 27.58 \mu\text{mol}/\text{m}^3$ ) collected in the agricultural areas are higher when compared to the concentration of levoglucosan taken from the samples collected in UKM Bangi. Biomass burning activities, which are the result of the burning after harvesting processes, are found to contribute to the high amount of levoglucosan in ambient air. According

to Lobert and Warnatz (1993), vegetational material is fundamentally composed of cellulose and hemicelluloses (between 50% and 75% of most dry plant materials). The pyrolysis, smouldering and glowing combustion decomposed the solid phase of plants into various inorganic and organic compositions. High-molecular weight components are decomposed to the compounds of a lower molecular weight e.g. levoglucosan and other organic substances. These are the primary sources for the flame process which contribute to the amount of gases emitted.

The high concentration of levoglucosan, nevertheless, is not followed by a significantly high concentration of surface active agents (surfactants) such as methylene blue active substances (MBAS) and disulphine blue active substances (DBAS) in the atmosphere around the agricultural areas (Table 1). The concentration of surfactants, such as MBAS, are dominated in fine mode aerosols (between  $2.44 \pm 0.21$  and  $3.45 \pm 0.14 \mu\text{mol}/\text{m}^3$ ) compared to coarse mode aerosols (between  $0.55 \pm 0.47$  and  $2.44 \pm 0.21 \mu\text{mol}/\text{m}^3$ ) with the highest concentration still recorded in the agricultures areas (Table 1). These results indicate the possibility of combustion products from biomass burning containing a high amount of organic substances with the polar group, particularly in fine mode aerosols which behave like surfactants in the atmosphere. This phenomenon correlates with the results from previous studies by Latif et al. (2005), which indicated that biomass burning in South East Asia contributed to the amount of anionic surfactants, such as MBAS, in the atmosphere. The concentrations of cationic surfactants like DBAS at all stations are very low and this indicates a low contribution of cationic polar group organic molecules to the atmosphere as a result of combustion processes.

### *Levoglucosan and Surfactants in Various Type of Soot*

The concentrations of levoglucosan from soot are shown in Table 2. Overall, the concentrations of levoglucosan are dominant in soot burn from leaves. The highest concentration of levoglucosan was in soot from *Rhizophora spp.* leaves ( $70.54 \pm 3.35 \mu\text{mol}/\text{g}$ ) followed by soot from *Saccharum officinarum* leaves ( $50.47 \pm 0.46 \mu\text{mol}/\text{g}$ ) and soot from *Elaeis guineensis* leaves ( $38.34 \pm 0.74 \mu\text{mol}/\text{g}$ ). There were no significant differences ( $p > 0.05$ ) when samples were exposed to UV-radiation and high concentrations of ozone. These results indicate that levoglucosan has stable molecules and is little affected by UV radiation and high concentrations of ozone. The implication being that it can be a good indicator for biomass burning.

**Table 1.** Concentration of levoglucosan and surfactants (as MBAS and DBAS) in atmospheric aerosols collected in the study areas.

Station	Particle Size (μm)	Suspended Particulate (μg/m <sup>3</sup> )	Levoglucosan (μmol/m <sup>3</sup> )	MBAS (μmol/m <sup>3</sup> )	DBAS (μmol/m <sup>3</sup> )
Agricultural Area 1	< 1.5	31.8 ± 9.5	242.12 ± 30.40	3.40 ± 0.19	0.22 ± 0.06
	> 1.5	16.5 ± 4.8	147.86 ± 27.58	0.55 ± 0.47	0.19 ± 0.10
Agricultural Area 2	< 1.5	20.3 ± 6.2	248.40 ± 127.02	3.45 ± 0.14	0.23 ± 0.06
	> 1.5	16.5 ± 3.5	105.58 ± 141.80	1.16 ± 0.58	0.27 ± 0.13
UKM	< 1.5	56.8 ± 11.2	30.58 ± 15.73	2.44 ± 0.21	0.05 ± 0.04
	> 1.5	21.5 ± 5.1	34.38 ± 15.28	2.56 ± 0.16	0.14 ± 0.14

**Table 2.** The concentration of levoglucosan in soot before and after exposure to UV-radiation and ozone.

Sample	Plant Section	Levoglucosan		
		Normal ( $\mu\text{mol/g}$ )	Ultra-violet (UV) ( $\mu\text{mol/g}$ )	Ozone ( $\mu\text{mol/g}$ )
<i>Elaeis guineensis</i>	Leaves (L)	38.34 $\pm$ 0.74	40.36 $\pm$ 0.19	41.73 $\pm$ 0.22
<i>Elaeis guineensis</i>	Bunches (B)	2.72 $\pm$ 1.55	2.21 $\pm$ 0.20	2.38 $\pm$ 0.12
<i>Rhizophora spp.</i>	Leaves (L)	70.54 $\pm$ 3.35	61.01 $\pm$ 0.22	72.23 $\pm$ 1.32
<i>Rhizophora spp.</i>	Wood (W)	4.48 $\pm$ 0.37	8.74 $\pm$ 8.68	8.23 $\pm$ 2.13
<i>Oryza sativa</i>	Straw (S)	1.69 $\pm$ 0.45	1.86 $\pm$ 0.35	0.22 $\pm$ 0.11
<i>Saccharum officinarum</i>	Leaves (L)	50.47 $\pm$ 0.46	50.69 $\pm$ 0.21	53.43 $\pm$ 0.38

This result is consistent with those from previous studies which have examined the stability of levoglucosan in atmospheric particles (Fraser and Lakshmanan, 2000; Simoneit *et al.*, 2004). Nevertheless, based on a laboratory kinetics study and a model simulation, Hoffmann *et al.* (2010) estimated that levoglucosan in the aqueous phase decreases to half its initial value in the atmosphere in 12.7–83.2 hours at 90% relative humidity, predominantly through its reaction with OH. Hennigan *et al.* (2010) also reported that the extent of decay ranged from 20% to 90% and was strongly correlated to the integrated OH exposure. Relative kinetics indicate that levoglucosan has an atmospheric lifetime of 0.7–2.2 days when biomass burning particles are exposed to  $1 \times 10^6$  molecules/cm<sup>3</sup> of OH, which is higher compared to the conditions of our experiment (humidity below 60%).

The concentrations of surfactants from soot are shown in Table 3. The concentration of surfactants such as Methylene Blue Active Substances (MBAS) was found to be at the highest level in the soot from *Rhizophora spp.* (leaves and wood) with the concentration of  $0.074 \pm 0.003 \mu\text{mol/g}$  and  $0.072 \pm 0.004 \mu\text{mol/g}$  respectively. Soot from *Oryza sativa* (S) was found to have the lowest concentration of MBAS. For surfactants as Disulphine Blue Active Substances (DBAS), soot from all plants showed a very low range with maximum concentration recorded at  $0.006 \pm 0.001 \mu\text{mol/g}$ . These results indicate that the concentration of surfactants from soot were dominated by anionic surfactants, as was noted in previous studies undertaken by Latif and Brimblecombe (2004). The exposure of UV radiation and ozone on the soot significantly increased the concentration of surfactants, particularly for MBAS. The results indicate that UV radiation is capable of separating the high molecular weight of surfactants into small molecules, as previously

suggested by Latif *et al.* (2007) and that oxidation processes increase the polar group of organic substances which result in a high level of surfactants in the soot.

#### Correlation between Surfactants and Levoglucosan

The correlation between surfactants such as MBAS and DBAS is shown in Fig. 2 and Fig. 3. The results demonstrate that the overall concentration of MBAS has a positive correlation to the concentration of levoglucosan. The production of surfactants and levoglucosan seem to be separated into two separate sources from different parts of the plants (leaves and the other parts of plant matter). The most positive correlation between MBAS and levoglucosan was found from the soot of leaves ( $r = 0.74$ ,  $p > 0.05$ ), which was not the case for DBAS which did not show any good correlation to levoglucosan ( $r = 0.42$ ,  $p > 0.05$ ). The organic composition of biomass burning was found to be dominated by water soluble organic compounds which have an anionic polar group (Yamasoe *et al.*, 2000; Okada *et al.*, 2001; Li *et al.*, 2010). Research undertaken by Abas and Simoneit (1996) found that the concentration of atmospheric aerosols during haze episodes resulting from biomass burning in South East Asia was dominated by n-alkanoic acids and n-alkanols as the dominant solvent-extractable components, with minor amounts of n-alkanedioic acids, n-alkanones, terpenoids, sterols, and phthalate contaminants, derived from biogenic sources (vascular plant wax); of which the majority of the molecules contain anionic group.

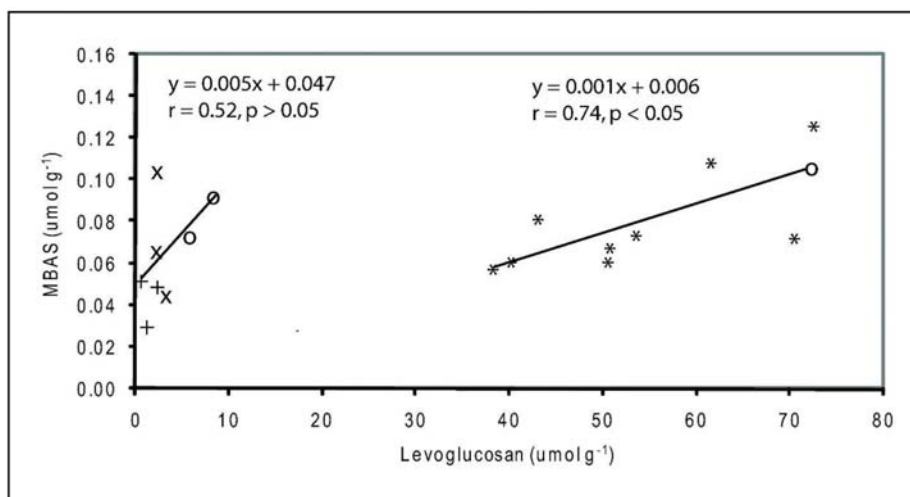
#### CONCLUSIONS

This study demonstrates there is a significant concentration of levoglucosan that is useful as a biomass burning indicator.

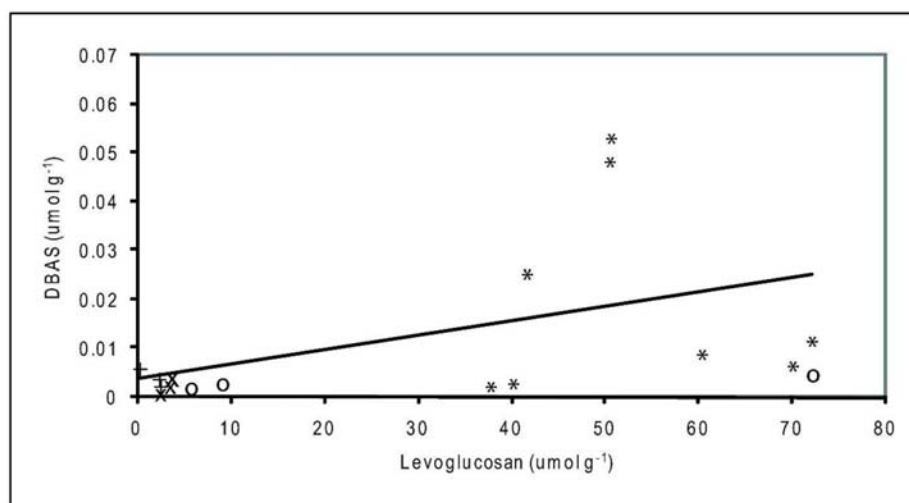
**Table 3.** The concentration of surfactants (MBAS and DBAS) in soot from plants before and after exposure to UV-radiation and ozone.

Sample	MBAS			DBAS		
	Normal ( $\mu\text{mol/g}$ )	UV ( $\mu\text{mol/g}$ )	Ozone ( $\mu\text{mol/g}$ )	Normal ( $\mu\text{mol/g}$ )	UV ( $\mu\text{mol/g}$ )	Ozone ( $\mu\text{mol/g}$ )
<i>Elaeis guineensis</i> (L)	0.056 $\pm$ 0.001	0.061 $\pm$ 0.004	0.080 $\pm$ 0.001	ud	ud	0.026 $\pm$ 0.003
<i>Elaeis guineensis</i> (B)	0.044 $\pm$ 0.002	0.068 $\pm$ 0.001	0.105 $\pm$ 0.001	ud	ud	ud
<i>Rhizophora spp.</i> (L)	0.074 $\pm$ 0.003	0.108 $\pm$ 0.0010	0.126 $\pm$ 0.011	0.006 $\pm$ 0.001	0.008 $\pm$ 0.000	0.011 $\pm$ 0.001
<i>Rhizophora spp.</i> (W)	0.072 $\pm$ 0.004	0.089 $\pm$ 0.003	0.106 $\pm$ 0.001	ud	ud	0.004 $\pm$ 0.000
<i>Oryza sativa</i> (S)	0.031 $\pm$ 0.001	0.046 $\pm$ 0.001	0.050 $\pm$ 0.001	ud	ud	0.005 $\pm$ 0.001
<i>Saccharum officinarum</i> (L)	0.059 $\pm$ 0.001	0.064 $\pm$ 0.001	0.074 $\pm$ 0.003	ud	ud	0.026 $\pm$ 0.003

\* L = Leaves, B = Bunches, W = Wood, S = Straw, ud= undetected (below detection limit).



**Fig. 2.** Correlation between MBAS and levoglucosan in leaves (\*), wood (o), bunches (x) and straw (+).



**Fig. 3.** Correlation between DBAS and levoglucosan in leaves (\*), wood (o), bunches (x) and straw (+).

The concentration of levoglucosan in the agricultural areas with biomass burning is far higher than the concentration of levoglucosan detected in atmospheric aerosols collected in semi-urban areas. Further studies show that the concentration of levoglucosan can be found in various plants, particularly in their leaves. The level of levoglucosan was found to be extremely stable and was not affected by a high concentration of ozone exposure or UV radiation. The stability of levoglucosan suggests the suitability of this compound as a tracer for the long-range transportation of aerosols from biomass burning, even though the OH in the atmosphere may reduce levoglucosan to less than 50% of its high concentration. The results from studying the quantity of surfactants in atmospheric aerosols indicate the contribution of biomass burning to the concentration of anionic surfactants, such as MBAS in fine mode aerosols. They also show a significant correlation between levoglucosan and surfactants such as MBAS, originating from specific parts of the plants which suggest the dominance of water soluble organic substances with the anionic polar group.

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