

Levoglucosan as an Indicator of Biomass Burning from Selected Tropical Plants

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Abstract

South East Asia has been recognised as one of the region most affected by atmospheric haze from biomass burning due to combustion of various plants. The distribution of atmospheric aerosols from biomass burning itself can be determined through the level of levoglucosan found in the atmosphere. In this study, the amount of levoglucosan produced by five selected tropical plants after combustion processes was determined using the modified anthrone-sulfuric colorimetric method. The results showed that the concentration of levoglucosan in the plant soot (after combustion) ranged from 0.49 ± 0.28 mg/g to 10.51 ± 4.47 mg/g. Among the five plants, *Oryza sativa* was found to have the highest levoglucosan content and the amount of levoglucosan produced by biomass burning was found to be influenced by the photo oxidation processes e.g. by ultra violet radiation and ozonization.

Keywords: levoglucosan; biomass burning; tropical plants; indicator; air pollution

1. Introduction

Biomass burning is the major source of particulate matter emissions. To the order of 104 Tg/yr in the world (Zamperlini *et al.*, 1997), haze episodes are a common phenomenon in South East Asia. This is particularly the case during the south-west monsoon season which runs from July to September and is fundamentally the result of biomass burning from agricultural activities (Abas *et al.*, 2004). These burning activities usually involve different plant species and emit and trap smoke in the troposphere for a certain period of time. The varying temperature and conditions during burning determine the molecular alteration and transformation of the organic compounds emitted as a consequence of biomass burning. The heat intensity, aeration and duration of smoldering and flaming conditions shape the distribution and ratio of the natural versus altered compounds in the smoke (Simoneit *et al.*, 2004; Simoneit *et al.*, 1999; Abas *et al.*, 2004).

Levoglucosan (1,6-anhydro- β -D-glucopyranose) is an organic molecule that can be used as an indicator for biomass burning (Abas *et al.*, 1995; Elias *et al.*, 2001; Abas *et al.*, 2004; Engling *et al.*, 2006; Wang *et al.*, 2007; Puxbaum *et al.*, 2007; Bergauff *et al.*, 2008). It is formed through the thermal breakdown alteration of

the cellulose present in vegetation (Dos Santos *et al.*, 2002). Levoglucosan has been reported to be present in the fine particle phase of residential wood smoke and has been found to have an emission rate with a range of 2-18 mg/min from a typical wood stove (Simoneit, 2002). It is stable in the atmosphere, showing no decay over an 8 hour exposure to ambient conditions and sunlight (Larsen III *et al.*, 2006; Puxbaum *et al.*, 2007). According to Schkolnik and Rudich (2006), in acidic conditions, levoglucosan showed no decay over 10 days, which compares with those of atmospheric liquid droplets. Its stability and occurrence in large quantities in the atmosphere, specifically from cellulose containing substances, means that it meets the criteria as an ideal molecular marker for biomass burning (Simoneit *et al.*, 1999; Fraser and Lakshmanan, 2000; Simoneit *et al.*, 2004; Holmes and Petrucci, 2007; Puxbaum *et al.*, 2007).

As atmospheric tracer, levoglucosan represents a simple, cheap and readily accessible means for quantifying the contribution of wood smoke to the atmosphere. Levoglucosan is always accompanied by other stereo isometric monosaccharides anhydrides (mannosan and galactosan) (Medeiros *et al.*, 2006). The existence of mannosan and galactosan due to the combustion process results from the pyrolysis of

hemicellulose, although their emitted amounts from previous studies are substantially lower than those of levoglucosan (Shafizadeh, 1984; Abas *et al.*, 2004; Hsu *et al.*, 2007; Puxbaum *et al.*, 2007).

This study aims to determine the amount of levoglucosan from several tropical species to determine the suitability of it as a biomarker of biomass burning in the tropical areas of South East Asia.

2. Materials and Methods

2.1. Preparation of residue (burned) selected plants samples

Several tropical plants e.g. *Asystasia nemonum*, *Cocos nucifera*, *Elaeis guineensis*, *Saccharum officinarum* and *Oryza sativa* were selected for levoglucosan analysis. Residue samples were prepared by the cutting selected parts of each plant i.e. leaves (L) and wood (W) to small pieces. The samples then were placed in an iron dish, wrapped in aluminum foils, burned completely up to 300°C in the furnace for 3 hours and then sieved (0.6 mm) to remove coarse particles after 24 hours cooling period.

2.2. Determination of levoglucosan through the anthrone colorimetric method

The levoglucosan analysis from plant extractions (burned samples) was itself conducted through the use of the anthrone-sulphuric colorimetric method as used by Laurentin and Edwards (2003), Fartas *et al.* (2009) and Latif *et al.* (2011). Each step in this breakdown of glucose (I) to 5-(hydroxymethyl)-2-furaldehyde (IV) 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 was dependent on the presence of 5-(hydroxymethyl)-2-furaldehyde, or a similar furfural compound, as formed by the action of the sulfuric acid on the carbohydrate.

2.3. Levoglucosan Analysis

The anthrone reagent was prepared by dissolving of 0.2 g of anthrone (9,10-dihydro-9-oxoanthracene) in 100 ml of concentrated sulfuric acid H₂SO₄ 97%. The reagent was left to stand for 45 minutes until it was perfectly clear. Each day, the reagent was freshly prepared and used within 12 hours (Yemm and Willis, 1954). After that, the anthrone reagent (10 ml) was pipetted into thick-walled Pyrex tubes (150 x 25 mm) against 5 ml of Levoglucosan standard solutions (0.1, 0.2, 0.3, 0.4, 0.5, 1, 1.5, 2, 2.5 and 3 mg/L). The solutions were then transferred to a 100°C water bath for

10 minutes to produce the green dye, followed by 4°C for 5 minutes, and, to prevent condensation of moisture on the optical tubes during reading, 5 minutes in water at 20°C. All samples were read in a calorimeter at 620 nm against the deionised water. Then, the calibration curve (levoglucosan concentration vs. absorbance) obtained from data for standard glucose solutions (0.1-3.0 mg/L) was drawn. The method employed was based on improved techniques in which the order of the addition of the reagent proved to be essential, for reproducibility corrections are made for noncarbohydrate materials that may be present in the sample.

2.4. Exposure towards UV radiation

Soot samples (50 mg) were placed in a beaker and were exposed to high intensity UV light (Erlan Model 2002087) for two hours to determine any impact of photodegradation. The samples were then fan-cooled to maintain a temperature of 50-55°C. Subsequently, exposed samples were dissolved in deionised water and ready for extraction. The concentration of levoglucosan in the solutions was analysed after exposure and compared to the level of levoglucosan in each solution prior to exposure.

2.5. Exposure towards O₃ radiation

Soot samples (50 mg) were exposed to O₃ in a Dreschel bottle. The O₃ was generated from pure oxygen in a laboratory ozoniser (FS-106 AWR) inside a fume cupboard. The flow rate of O₃ from the generator was controlled at 1 L per minute, which gave a concentration of 20 g/L in the solution. The extracts were shaken and filtered using 0.2 µm pore size 47 mm diameter cellulose acetate filter papers (Whatman) and a vacuum pump.

2.6. Comparison with soot from motor vehicles

For the purpose of comparison, soot from petrol and diesel car exhaust was also collected for levoglucosan analysis. Soot was collected from vehicles' exhaust pipes using a soft paint brush. Aqueous extracts were obtained from small quantities of each material (50 mg) and extracted separately into 100 ml of ultra pure water in a volumetric flask. The extracts were shaken and filtered using 0.2 µm 47 mm cellulose acetate filter papers (Whatman) and a vacuum pump.

2.7. Determination of anions concentration

In order to compare the amount of levoglucosan to other combustion products, the composition of anions e.g. nitrate and sulphate were analysed using ion

Table 1. Composition of levoglucosan in the soot from plant and motor vehicles exhaust

Soot from	Levoglucosan (mg/g)
<i>Asystasia nemonum</i> (W)	2.43 ± 0.49
<i>Asystasia nemonum</i> (L)	3.81 ± 0.73
<i>Cocos nucifera</i> (W)	0.67 ± 0.23
<i>Cocos nucifera</i> (L)	1.27 ± 0.28
<i>Elaeis guineensis</i> (W)	1.94 ± 0.23
<i>Elaeis guineensis</i> (L)	0.49 ± 0.28
<i>Saccharum officinarum</i> (L)	1.16 ± 0.17
<i>Oryza sativa</i> (L)	10.51 ± 4.47
Motor vehicles	Ud

Ud = undetected, L= leaf, W = wood

chromatography (DIONEX 4000i Ion Chromatograph). Ion chromatography is a separation technology which utilises an anion exchange column to separate anions moving through the column. These are then measured using a detector system at the column outlet (Jeffery et al., 1989).

3. Results and Discussion

3.1. Levoglucosan in soot from plant

Results in Table 1 show the concentration of levoglucosan in the plants after burning. Levoglucosan in *Oryza sativa*, was found to have the highest concentration (10.51 ± 4.47 mg/g) of the samples of biomass burning, followed by *Asystasia nemonum* (L), *Asystasia nemonum* (W), *Elaeis guineensis* (W), *Cocos nucifera* (L), *Saccharum officinarum* (L), *Cocos nucifera* (W) and

Elaeis guineensis (L). The different concentrations of levoglucosan found in the plant matter is expected to be due to the cellulose content of the plants (Elias et al., 2001). According to Engling et al. (2006), the product of levoglucosan also relates to combustion efficiency because of the ability of primary organic compounds, such as anhydrosugars, to decompose into smaller secondary species. In the case of *Asystasia nemonum* and *Cocos nucifera* the composition of levoglucosan was found to be higher in the soot from leaf (L) compared to the soot generated from wood (W).

Soot collected from petrol and diesel exhaust did not indicate any source of levoglucosan (Table 1). This corresponds to the studies by Schneider et al. (2006) and Schkolnik and Rudich (2006) which indicated that levoglucosan is source-specific to the burning of any fuel containing cellulose. The combustion of other materials (e.g., fossil fuels) or biodegradation and hydrolysis of cellulose do not produce levoglucosan. The data from Kuo et al. (2008) also confirm that levoglucosan occurs exclusively in biomass combustion residues and is absent from petroleum combustion byproducts or coal materials.

3.2. Exposure of soot to UV and O₃

Overall, the elevated amount of levoglucosan in plant soot exposed to UV light and O₃ (Fig. 1) shows that the oxidation agent was able to increase the level of levoglucosan present. Base on Figs 2 and 3, the strong positive correlation between the concentration of levoglucosan in soot samples before and after exposure to UV ($r = 0.99$, $p < 0.05$) and O₃ ($r = 0.87$, $p < 0.05$) shows that photo-oxidation processes are likely to influence the high molecular weight molecules and

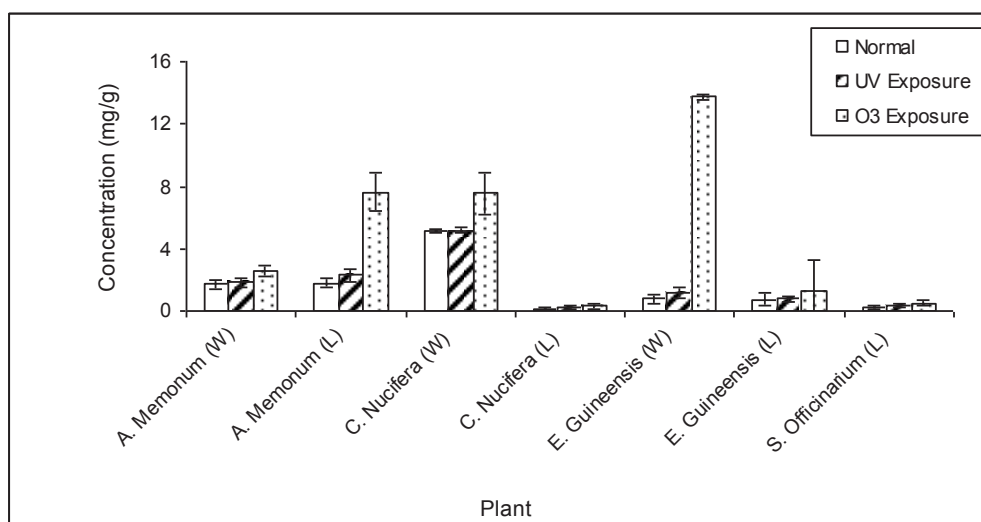


Figure 1. Concentration of levoglucosan from selected plants after being burned in the furnace (normal condition), UV and O₃ exposure

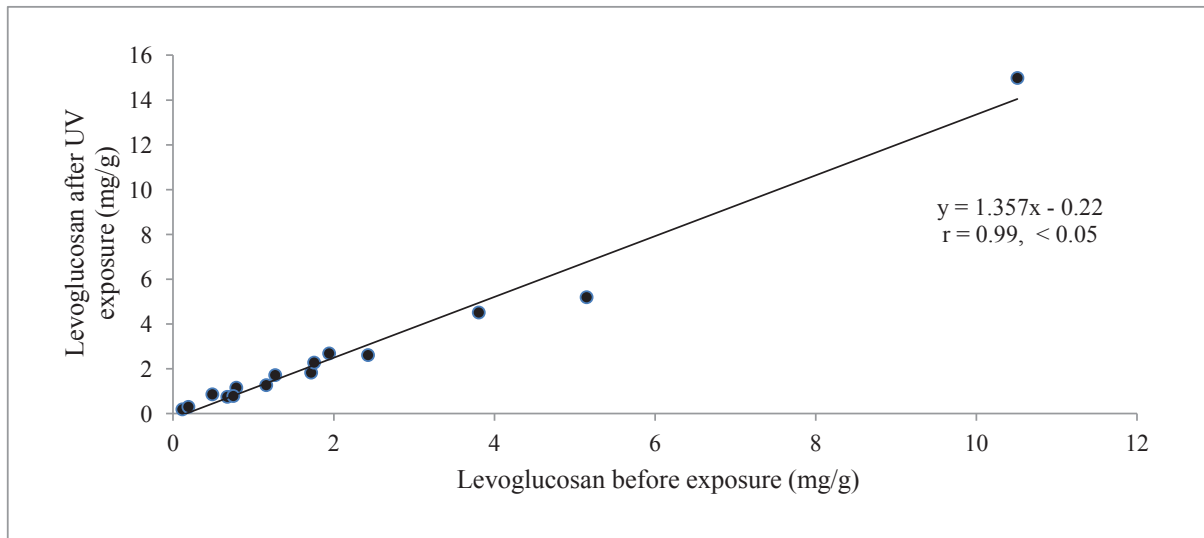


Figure 2. Correlation between concentration of levoglucosan before and after UV exposure

to produce more levoglucosan from the plant matter and soot. Plants usually consist of two types of main molecules: cellulose and hemicelluloses. A cellulose molecule is a long chain linear polymer consisting of 7000-12,000 D-glucose monomers and individual cellulose molecules which organise to form bundles (elementary fibrils) that are associated with larger parallel fibre structures (Simoneit, 2002). It is possible that levoglucosan was generated from a long chain polymer after exposure to photo-oxidation processes.

3.3. Correlation between levoglucosan in plant soots and other anions

The results indicated that the concentration of levoglucosan analysed from the soot did not bear any correlation to the amount of other products from the combustion processes, particularly sulphate ($r = 0.013, p > 0.05$) and nitrate ($r = 0.006, p > 0.05$) (Figs. 4 and 5). Thus, it can be suggested that both

anions are un-suitable indicators for biomass burning. According to Duan *et al.* (2004) water-soluble potassium is a common inorganic tracer for biomass burning source identification and apportionment studies. The results were able to differentiate which were products of combustion from biomass burning when compared to other man-made or anthropogenic sources, as other combustion products usually contained a high level of nitrogen and sulphur oxide as a consequence of the complete combustion processes and the amount of sulphur combustion product e.g. diesel and petrol. A study by Lestari and Mauliadi (2009) also supported the fact that the presence of sulphate was a clear fingerprint of diesel vehicle emissions.

4. Conclusions

The results of this study show that levoglucosan is a suitable molecular tracer for biomass burning of several tropical plants. Such that, the burning processes

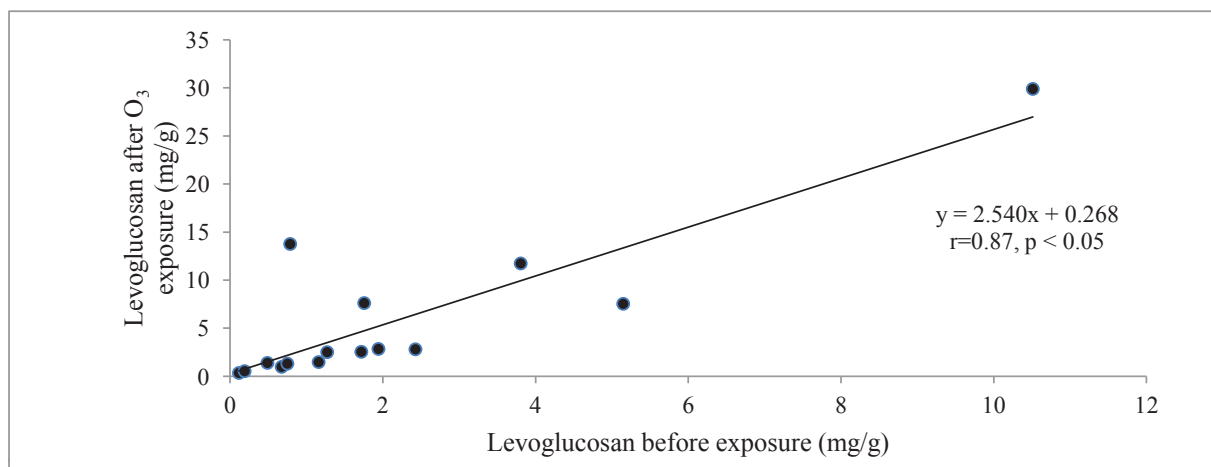


Figure 3. Correlation between concentration of levoglucosan before and after O₃ exposure

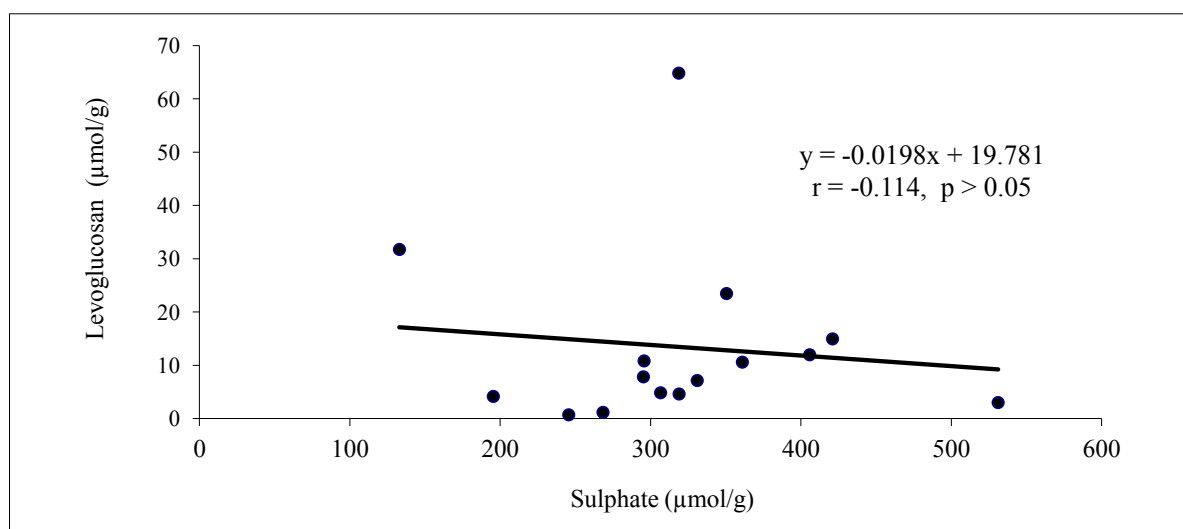


Figure 4. Correlation between levoglucosan and sulphate

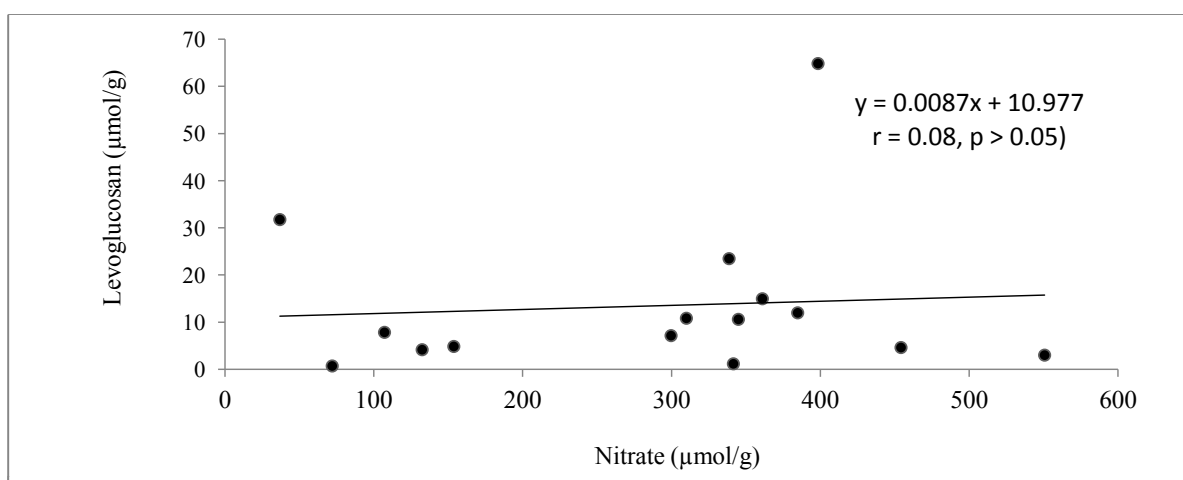


Figure 5. Correlation between levoglucosan and nitrate

of a plant e.g. *Oryza sativa*, due to agricultural activities, can be indicated through the use of levoglucosan as an indicator. The concentration of levoglucosan was found to have a higher concentration after photo-oxidation processes with UV radiation and O_3 . It was also found levoglucosan do not to have a strong correlation with sulphate and nitrate ($p > 0.05$) as an indicator of the complete combustion product from industries and motor vehicles, particularly those which predominantly used petrol and diesel as raw materials for combustion. Results from this study indicate that further research on cellulose types in different plants is required in order to determine which factors contribute to the amount of levoglucosan produced from different plant types.

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