Depositions of Acid Aerosols and Black Carbon from Biomass Burning over the Sakaerat Biosphere Reserve Forest, Thailand

Phuvasa Chanonmunag, Thailand Institute of Scientific and Technological Research, Thailand
Pojanie Khummongkol, King Mongkut's University of Technology Thonburi, Thailand
Khattiya Sukprasert, King Mongkut's University of Technology Thonburi, Thailand
Yutthana Tantiwiwat, Thailand Institute of Scientific and Technological Research, Thailand
Taksin Artchwakom, Thailand Institute of Scientific and Technological Research, Thailand

The European Conference on Sustainability, Energy & the Environment 2015
Official Conference Proceedings

Abstract

Burning of biomass is an important source of acid aerosols and black carbon emissions into the atmosphere. In the tropics, the formation of secondary organic and inorganic aerosols depends on meteorological parameters. High humidity and rain washout both air borne gas and aerosol concentrations. We monitored the concentrations of aerosols associated with biomass burning from July to December 2012 at the Sakaerat Biosphere Reserve (SBR) - a UNESCO Man and Biosphere (MAB) reserve. Considerable biomass burning is known to occur in the vicinity of SBR. All meteorological instruments were installed on 36 m tower. Air samples were collected by the filter packs method. The organic acids identified samples included citrate, tartrate, malate, formate, acetate, succinate and lactate. The concentration of organic acids was 6, 27 and 100 times higher than black carbon, sulfate and nitrate, respectively. We used the inferential method to determine the deposition flux of aerosols. The deposition of organic acids was obtained in the ranges of 4.9–51.0 µg $m^{-2}min^{-1}$; black carbon, 1.2–7.8 µg $m^{-2}min^{-1}$; sulfate, 0.2–0.5 µg $m^{-2}min^{-1}$ and nitrate, 0.3–1.0 µg $m^{-2}min^{-1}$. The deposition depended on the atmospheric concentration and deposition velocity of each component. The deposition velocity also varied with season and canopy surfaces

Keywords: acid aerosol, black carbon, deposition, biomass burning, inferential method

Introduction

Biomass burning represents an important source of atmospheric aerosols and greenhouse gases (Streets, et al., 2001; Menon, et al., 2002). It is widespread, especially in the tropics (Crutzen, et al., 1990; Cao, et al., 2006). It is a common practice during the dry season in Thailand to burn crop wastes left on lands in order to promote agricultural productivity and higher crop yield. Biomass burning leads to emissions carbon monoxide (CO), hydrocarbon (HC) and soot or black carbon (BC). Further reactions in the presence of light; transform these primary gases and aerosols to secondary aerosols, including organic and inorganic acids through gas-to-particle conversion (Zhang, et al., 2010; Donahue, et al., 2011). Deposition of these primary and secondary aerosols can harm our ecosystem.

Organic acids are organic compounds consisting of low molecular weight, monocarboxylic acids (MCA) and high molecular weight, dicarboxylic acids (DCA). MCA are found in larger amounts than DCA (Keene, et al., 1988; Yu, et al., 1999b). Organic acids have acidic propertied, high water solubility, hygroscopic and cloud condensation nuclei activity (Yu, et al., 2000). Generally, organic acids are formed from products of incomplete combustion of fossil fuels and biomass. It occurs through photochemical reactions and biological processes (Kawamura, et al., 1993; Limbeck, et al., 1999; Chebbi, et al., 1996). Organic acids can be found in urban, rural and remote atmospheres around the world around the world (Kerminen, et al., 2000; Kubátová, et al., 2000; Röhrl et al., 2001; Limon-Sanchez, et al., 2002; Souza, et al., 1999).

The size of BC particles spans from a few nanometers for atmospheric aerosols (BC) to a few centimeters for charcoal fragments of combusted plant materials (Wang, et al., 2011a). Immediately after fires, emitted BC particles smaller than 1 μm may become airborne, China and India released approximately 25-35% of total global BC into the atmosphere (Ramanathan, et al., 2008) in 2006. BC concentrations were monitored every 5 minutes starting from September 2003 – August 2004 in Xi'an, China (Cao, et al., 2009). Daily average BC concentration was 2-65 μg m^{-3} with minimum concentrations occurring during summer and peak concentrations in winter. A study of BC concentration at 8 locations in India was carried out in 2009 (Beegum, et al., 2009). The BC concentration was found to vary from 27 μg m^{-3} in the urban areas to 0.065 μg m^{-3} on a rural island. Schmidt, et al., (2001), made a comparative analysis of BC in Australian soils (Schmidt, et al., 2001). They measured BC formed in eight soil samples by six established methods. All methods involved removal of the non-BC components from the samples by thermal and/or chemical means. The remaining carbon is operationally defined as BC.

Little data exist on organic acids in tropical climates. The purpose of this study was to characterize the types and concentrations of organic acids derived from biomass burning around the United Nations Educational, Scientific and Cultural Organization (UNESCO) designated Sakaerat Biosphere Reserve (SBR) forest in the Northeast Thailand. We monitored concentrations of the organic acids: citrate, tartrate, malate, formate, acetate, succinate and lactate as well as the inorganic acids, sulfate, nitrate and nitric acid. We also monitored BC. Deposition rates of aerosols were also estimated.

Materials and Methods

Site description

The experiments were conducted in the forests of the UNESCO designated Sakaerat Biosphere Reserve at an elevation of 300 m above sea level in the Northeast of Thailand (14°30′13.68"N, 101°57′8.67"E). The area is mainly covered by two major species types: Dry Evergreen Forest (DEF) and Dry Dipterocarp Forest (DDF). This study conducted in DDF. The heights of trees vary between 20-27 m. The climate is tropical (warm and humid) and is affected by an annual monsoons, with a rainy season from June to October and a dry season for the rest of the year. Temperatures at SBR averaged 24-33 $^\circ C$. In the dry season, slashing and burning of biomass are a common practice in the area and emission of smokes (Figure 1) can be seen from the 36 m tall micrometeorological tower. This tower was established to install meteorological instruments to monitor: 3-D ultrasonic anemometer, ambient temperature, relative humidity and net radiation recorders to monitor variation of climate around the area. The tower and attachment of 3-D anemometer and filter packs to collect air samples are shown in Figure 2.

Figure 1: Forest fire and emission of smoke in the vicinity of Sakaerat forest

All samples were collected simultaneously during July to December 2012. This period covered the wet (July–September) and the dry (October–December) climate conditions. The collection procedures and concentration analyses were performed as follows;

Black Carbon

Two sets of a two-stage filer pack were used to collect BC. They were placed on the tower at 34 m above the ground and 6 m above the tree canopy. The filter papers were made of cellulose. The air suction was set at a constant flow rate of 10 L min^{-1}. In order to investigate the diurnal variation of aerosol formation sample collection was split into daytime (6:00-18:00 hrs) and nighttime (18:00-6:00 hrs). The thermal heating method was used to determine BC. The samples collected on cellulose papers were heated to 105 °C for 1 hr to dry up the water content and then burned at 375 °C for 24 hr. The weighted differences determined the amount of BC.

Figure 2: Aerosol and Black Carbon collectors on a 36 m- high tower at SBR

Organic Acids

Air samples were collected by a 3-stage filter pack. The first and second filters were made of Teflon and nylon. The third filter was cellulose paper impregnated with 6% K_2CO_3 and 2% glycerin. The air flow rate was controlled at 10 L min^{-1}. Collection was made for 7 days per month from July to December 2012. The substances collected on filters were extracted with deionized water and analyzed by ion chromatography (Khlystov, et al., 1995; Orsini, et al., 2003).

Sulfate and Nitrate

The procedures used to collect samples for inorganic acids sulfate (SO_4^{2-}) and nitrate (NO_3^-) were the same as those used for organic acids.

Particle Size Distribution

An electrical low pressure impactor (ELPI) ELPIVI 4.0: DEKATI was used to determine the atmospheric particle number per volume with size distribution over the area of study. The air sample was drawn in by a pump at a constant flow rate of 40 L min^{-1}. Aerosols were classified by size interval and the cut diameters (size of particles collected with 50% efficiency) of stages 1–13 were 0.03, 0.06, 0.11 0.17, 0.27, 0.41, 0.66, 1.02, 1.66, 2.52, 4.49, 6.80, and 10.0 µm, respectively.

Results and Discussion

Climate Condition

Meteorological parameters are important factors influencing atmospheric formation of aerosols and later their depositions onto the earth surfaces (Mcmurry, et al., 1989; Vasconcelos, et al., 1994). This study monitored the ambient temperature, wind speed, humidity and net radiation real time. With the tropical climate, the ambient temperatures did not vary significantly (Figure 3) and the average ambient temperature ranged from 25 °C during the wet season (July–September) to 20 °C in the dry season (October–December). The wind speed varied between 0.7–1.5 m/s. Due to the low wind speeds throughout the experimental period (July–December), transport of the aerosols to locations more than 10 km from the emission sources was unlikely. Hence, the aerosols collected in our samples were probably from biomass burning sources. Relative humidity reached the highest value of 87% in September concurrent with the peak rainfall (97 mm). Precipitation was minimal in November and December in the area. Relative humidity decreased to 77% in the dry season.

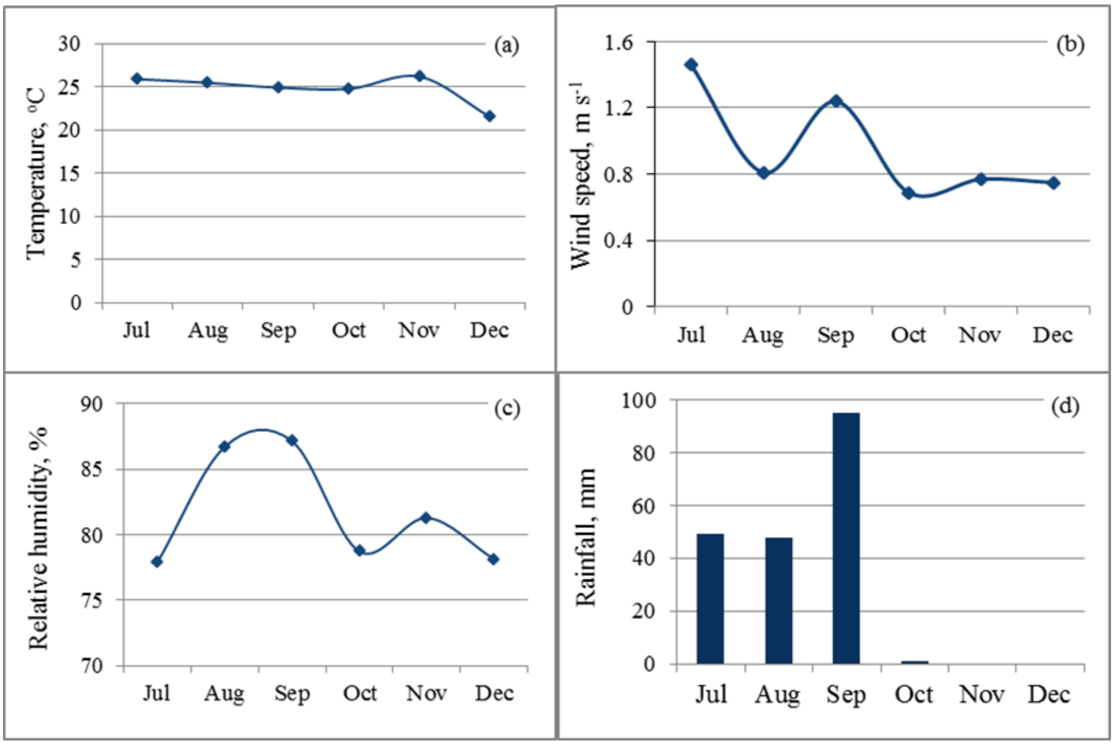

Figure 3: Climate conditions at the experimental area in the SBR forest

Particle Size Distribution

Most of particulates collected were smaller than 1 µm (Figure 4) with the most particles 0.1 µm in size. In wet season, only 4,000 particles per cm^3 were detected due to the effect of rain wash out (Figure 4). The highest concentrations 10,000 per cm^3 occurred in the dry season with the peak of 20,000 particles per cm^3 were being observed in July. The peak occurred during a transitional period from dry to wet season. However, peaks in particulate concentrations in the dry season were probably associated with three types of biomass burning which occurred at that time agricultural land preparation for the next-crop; fires set illegally in the forest to catch wildlife, and naturally occurring forest fires caused by very dry weather conditions.

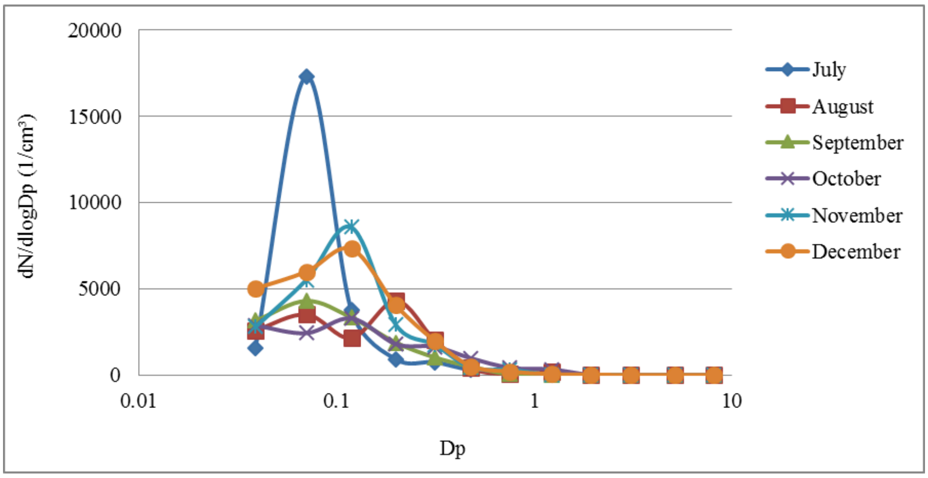

Figure 4: Size distribution of aerosols from biomass burning

Black Carbon

Atmospheric concentrations of BC were observed to vary seasonally condition (Figure 5). BC decreased to the lowest value in the wet season due to washout effect by rainfall and increased in the dry season due to more biomass burning. BC concentrations ranged from 4–17 µg m^{-3}. Time of day also influenced BC concentrations with higher values occurring during the daytime. Most biomass burning activities were carried out during the day.

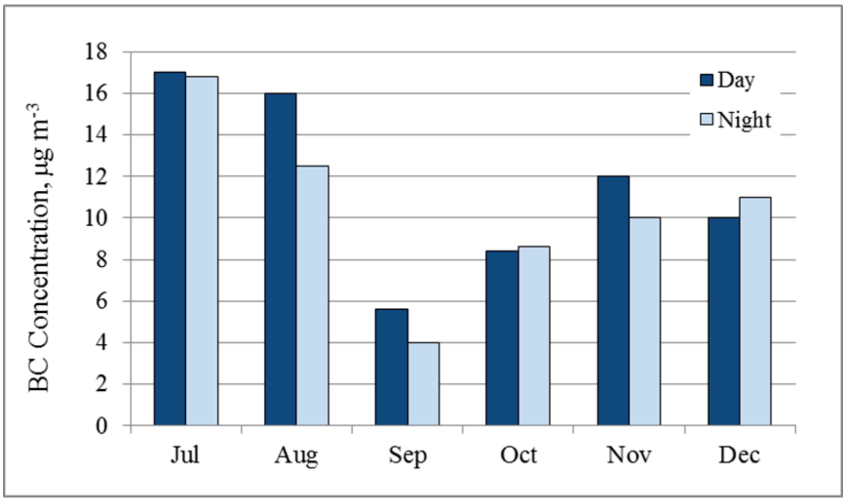

Figure 5: Diurnal variation of BC concentrations over the SBR forest

Organic Acid

The important organic acids comprised mainly citrate ($C_3H_5O(COO)_3^{3-}$, tartrate ($C_4H_4O_6^{2-}$), malate ($C_4H_4O_5^{2-}$), formate ($CHOO^-$), acetate (CH_3COO^-) succinate ($C_4H_4O_4^{2-}$) and lactate ($C_3H_5O_3^-$). Organic acid in the atmosphere are subsequently deposited on the earth's surface as acid rain which can be determined to ecosystems (Dolske, et al., 1985; Galloway, et al., 2004). Our analyses showed lactate occurred in the highest concentrations (~14 µg m^{-3}), followed by acetate (~11 µg m^{-3}) and citrate (~9 µg m^{-3}) (Figure 6a). The overall concentration of organic acids was as 110 µg m^{-3} which was 6 times higher than BC. Organic acids are formed though transformation of primary gases (hydrocarbon group of alkane, alkene and alkine) by photochemical reactions with hydroxyl radical (•OH) (Sander, et al., 1976; Richards, et al., 1983; Huntzicker, et al., 1984). The hydroxyl radical is the main oxidant in forming or deforming the organic acids in the atmosphere. It should be noted that citrate and tartrate concentrations were lower in the dry season compared with others.

Diurnal variation on organic acid concentrations was observed with concentrations of all species decreasing at nighttime. This was due to the fact that the photochemical reaction was less active and the biomass burning activities were reduced at nighttime (Figure 6b).

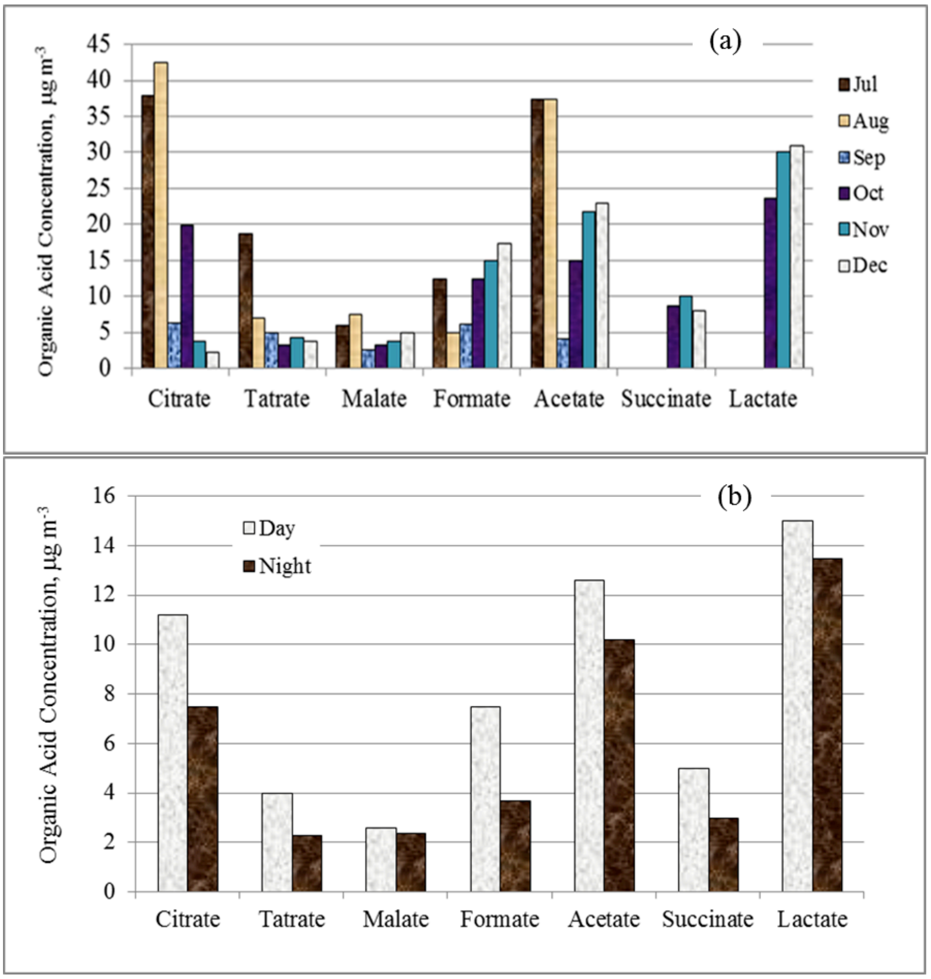

Figure 6: Organic acid concentrations over the SBR forest
(a)Types of organic acids and (b) Diurnal variation of organic acid concentrations

Sulfate and Nitrate

The primary pollutants (SO_2 and NO_x) generated from biomass combustion (in this study) were slowly oxidized with the presence of water in atmosphere to form Sulfuric and nitric acids. Upon further reaction with cation mediums, they eventually transform to sulfate and nitrate aerosols (Matsumoto, et al., 1996; Matsumoto, et al., 1998). However, only a small concentration of sulfate and nitrate was obtained by this study (Figure 7). Low concentrations of sulfate were found in the ambient environment because of the low sulfur content in the biomass being burned (less than 1%) (Tillman, et al., 2012). Nitrate concentrations were also very low because biomass burning in the open air provided low combustion efficiency. In practice, the combustion temperature for biomass burning is around 700–800 °C. The formation of

NO_x is slow when the combustion temperature is below 800 °C. There were no distinguishable differences between daytime and nighttime concentrations of these acid compounds (Figure 8).

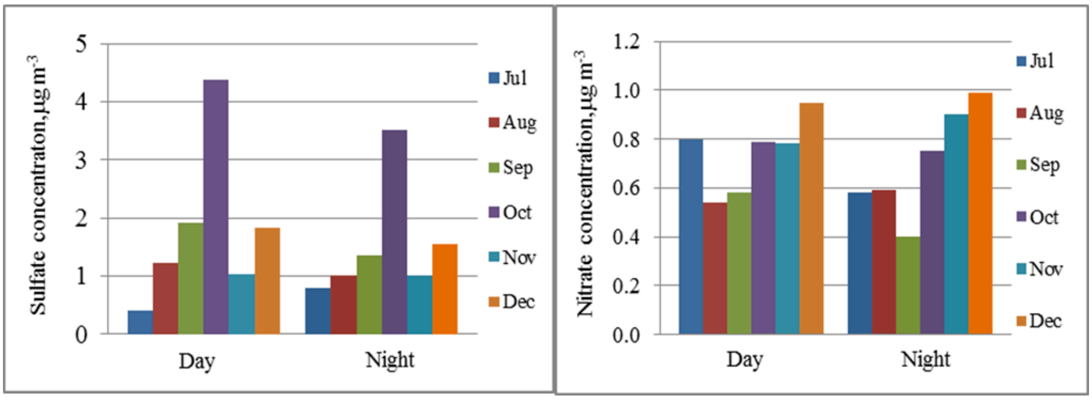

Figure 7: Diurnal variation of sulfate and nitrate concentrations over the SBR forest

Aerosol Deposition

Deposition of aerosols onto the earth's surface can cause damage to terrestrial ecosystems including forests. Although it is a slow accumulation process, damage to forests will ensure when the amount of aerosol deposition exceeds the soil's critical load (Galloway, et al., 2004). The quantity of aerosol deposition or flux (F) generated through biomass burning can be estimated using the inferential method, $F = V_dC$. Where V_d is deposition velocity in cm s^{-1} and C is average local concentration, µg m^{-3}. The monthly measured concentrations of aerosols and V_d used for each category calculations are shown in Figures 8a and 8b. The total organic acid concentrations were observed to be 6 times higher than BC, 27 times higher than sulfate and 100 times higher than nitrate at peak values. A large seasonal difference in concentration was seen in the case of organic acid in which the lowest concentration has occurred when the rainfall reached the highest millimeter reading (see also Figure 3d).

The deposition velocity, V_d varied with meteorological conditions (Figure 8b). The monthly V_d values varied between 0.26–0.76 cm s^{-1} for organic acid, 0.24–0.77 cm s^{-1} for BC, 0.18–0.85 cm s^{-1} for sulfate and 0.34–0.95 cm s^{-1} for nitrate. A difference in V_d was occurred between the wet and the dry seasons (Figure 8b). A study by Matsuda (2012) at SBR forest concluded that V_d was high in the leafless season (dry season) and low in leafy season (wet season) (Matsuda, et al., 2012).

Figure 8c shows variation in aerosol deposition. Deposition increased during the period of October to December when both the concentration and V_d were high and decreased during the period of August to September when the concentration and V_d were low. Deposition of aerosol in July was also high due to the transitional period from wet to dry season. The low deposition rates were observed in wet season due to atmospheric wash out by rain. Deposition of organic acids ranged from 4.9–51.0 µg $m^{-2}min^{-1}$; BC, 1.2–7.8 µg $m^{-2}min^{-1}$; sulfate, 0.2–0.5 µg $m^{-2}min^{-1}$ and nitrate, 0.3–1.0 µg $m^{-2}min^{-1}$. The results of this study show that organic acids from biomass burning are more important contributors of acid components to forests than sulfate and nitrate.

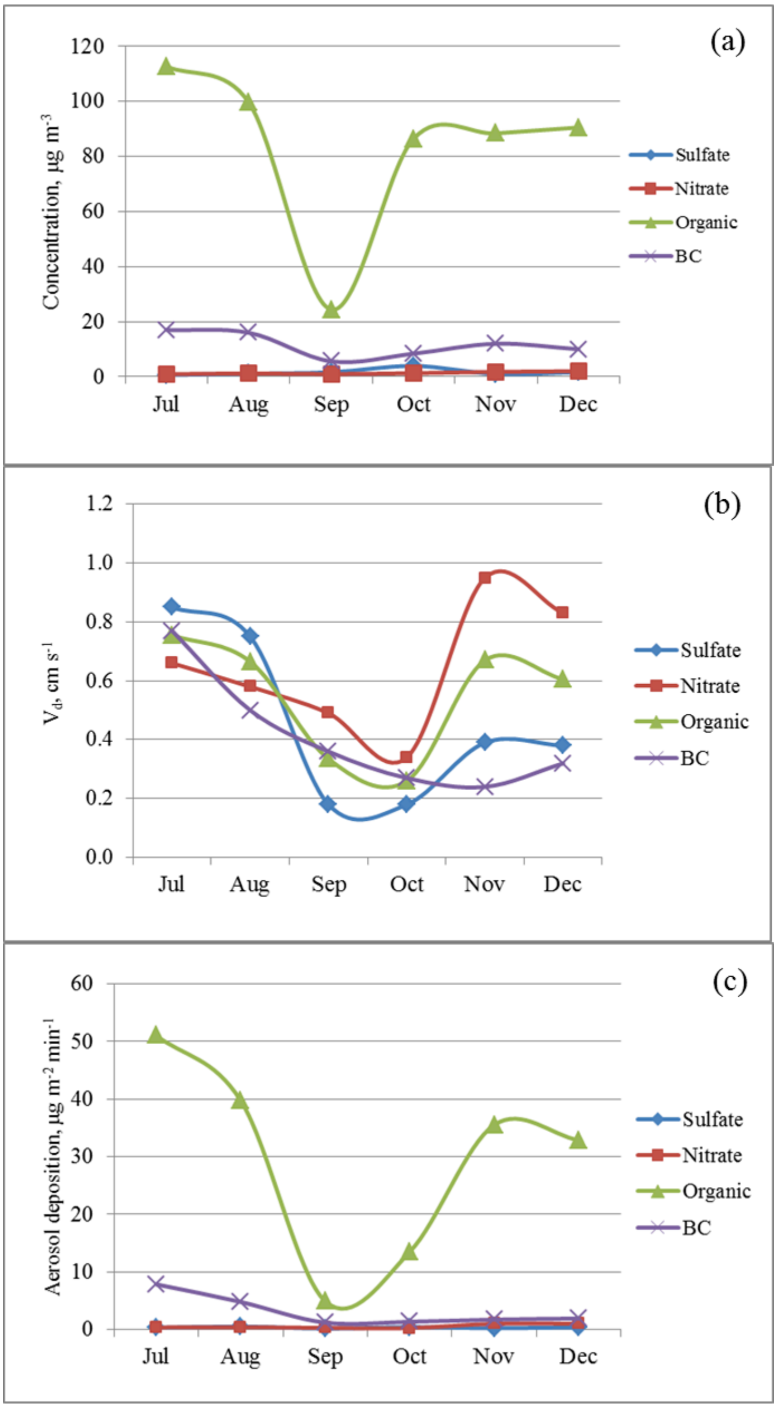

Figure 8: Comparison of aerosol (sulfate, nitrate, organic acid and BC) over the SBR forest
(a) Monthly concentration, (b) Monthly variation of deposition velocity and
(c) Deposition comparison of aerosol from biomass burning

Conclusions

Aerosols from biomass burning constituted a substantial amount of organic acids. It was found that the concentration of organic acids was 6, 27 and 100 times higher than black carbon, sulfate and nitrate, respectively. Hence, the organic acids should be placed as a priority constituent of our ecosystem. Deposition of aerosols determined by the inferential method varied with atmospheric concentration and deposition velocity. The deposition velocity also varied with local conditions, i.e. meteorological parameters, season and canopy surfaces. Reports on deposition velocity of aerosols are very few, especially in tropical climate. More researches on deposition flux and deposition velocity are needed.

Acknowledgements

The authors wish to thank Dr. Kazuhide Matsuda, Tokyo University of Agriculture and Technology, Faculty of Agriculture Field Science, Japan for his support on use of the micrometeorological tower in Sakaerat Biosphere Reserve forest.

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Contact email: phuvasa@tistr.or.th