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Application of Bowen Ratio Method for Estimating Fluxes of Sulfate and Nitrate Aerosols

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Abstract— **The Bowen ratio method was used to estimate dry deposition fluxes and velocities of SO_4^{2-} and NO_3^- above the Dipterocarp forest in Thailand from August 2009 – January 2010. The micrometeorological parameters for flux estimation were measured real time. The micrometeorological data showed average net radiation, sensible heat, latent heat and soil heat in the wet season higher than the dry season. The concentration of SO_4^{2-} ranged between 1.62 – 9.34 μg m^{-3} and NO_3^- ranged between 3.61– 22.90 μg m^{-3}. The dry deposition flux of SO_4^{2-} was evaluated to be 0.0023 μg m^{-2} s^{-1} – 0.0083 μg m^{-2} s^{-1} and NO_3^- to be 0.0078 μg m^{-2} s^{-1} – 0.0533 μg m^{-2} s^{-1}. The dry deposition velocities of SO_4^{2-} and NO_3^- found high in August (wet season) and the dry deposition velocity of NO_3^- was higher than SO_4^{-2} for all months.**

Keywords-Bowen ratio; Fluxes; Nitrate; Sulfate

I. INTRODUCTION

Ambient aerosols play an important role in many atmospheric processes affecting air quality poor visibility degradation, and climatic changes. Atmospheric reactions modify the physical and chemical properties of emitted materials, changing removal rates and exerting a major influence on acid deposition rates [1]. The aerosols dry deposition has effect directly to forest, agriculture area, soil and water in ecosystem. For example, SO_2 gas can dissolve into the water of lakes or streams, or it can be absorbed by the foliage of plants. This dry-deposited SO_2 is then oxidized to SO_4^{2-}, which is electrochemically balanced by H^+, so that acidity results. Dry-deposited NO_x gas can similarly be oxidized to NO_3^- and also balanced by H^+ [2, 3]. Atmospheric aerosols sulfate (SO_4^{2-}) and nitrate (NO_3^-) are secondary pollutants which result from dry deposited SO_2 is then oxidized to SO_4^{2-} and dry deposited NO_x gas can similarly be oxidized to NO_3^- that so acidity results [3, 4]. Aerosols dry deposition is affected by a multiplicity of factors that often interact in complex ways. The most important factors are the characteristics of the atmosphere, the nature of the surface, and properties of the depositing species [5, 6].

Transport of aerosols through the atmosphere depends on many meteorological variables [7, 8]. Like the transport of water vapor, heat, momentum, and gases. The movement of aerosols through the boundary layer above a plant canopy is controlled by eddy diffusion and roughness element which is difference than movement of vapor, heat, momentum, and gases. Whereas gases are transported primarily through molecular diffusion, particle transport and deposition basically take place through sedimentation, interception, impaction and Brownian diffusion [9]. Understanding of aerosol deposition is incomplete due to the complexity of the functional dependence on physical and chemical properties of the particle, surface characteristics, and atmospheric conditions and difference of techniques to estimate pollutant [10]. It is important to estimate flux and deposition velocity (V_d) of the dry deposition in specific meteorological conditions and the area of interest.

Bowen ratio is derived from the energy balance that uses time average measurements of temperature and humidity profiles in the boundary surface layer above a canopy for estimation of these fluxes. In Thailand, the flux measurements of SO_2 in several areas including both agriculture and forest have been conducted [11, 12, 13]. The purpose of this study is to apply the Bowen Ratio technique to estimate the fluxes and deposition velocities of SO_4^{2-} and NO_3^- over the Dipterocarp Forest in Thailand.

II. THEORY

The energy balance in a boundary sublayer above a forest can be defined by the following equation:

$$R_n = H+\lambda E+G+\Delta H_S \quad (1)$$

Where Rn is the net radiation which is equal to the absorbed solar radiation plus terrestrial radiation minus the terrestrial radiation emitted from the forest, H is sensible heat flux; λE is the latent heat flux, the latent heat exchange occurs not only due to evaporation or condensation at the surface, but to a large extent due to transpiration from the plant leaves. The combination of evaporation and transpiration is called evapotranspiration; it produces nearly a constant flux of water vapor above the canopy layer; G is soil heat flux; ΔH_s is the change of heat storage consist of two parts, namely, the rate of physical heat storage and the rate of biochemical heat storage as result of photosynthesis and carbon dioxide exchange. [14]

The Bowen ratio, β, is expressed in the form

$$\beta = \frac{H}{\lambda E} = \gamma \frac{\Delta T}{\Delta q} = \frac{C_p \rho_{a \cdot h} D_{2-1}(T_1 - T_2)}{\rho_a \lambda_w (e_2 - e_1)(0.622/P)} \quad (2)$$

The sensible heat flux and latent heat flux can be expressed as

$$H = C_p . \rho_{a \cdot h} D_{2-1}(T_2 - T_1) \quad (3)$$

$$\lambda E = \rho_a . \lambda_{.w} (e_2 - e_1) 0.622/P \quad (4)$$

Replacing equations 3 and 4 into equation 1, we can calculate the transfer coefficient, D in the following

$$D_{2-1} = \frac{R_n - G}{\rho_a \lambda (e_2 - e_1)(0.622/P) + C_p \rho_a (T_2 - T)_1} \quad (5)$$

where C_p is the heat capacity of air (0.24 kcal/kg/^{o}C); ρ_a is density of air (g/cm^3); λ is latent heat of vaporization of water (cal/g); P is pressure (kPa); T is temperature (^{o}C); e is vapour pressure (kPa); γ is the psychrometric constant (0.4 g/kg K^{-1}); q is specific humidity. The subscript 1, 2 are referred to the data taking at two vertical distance above a canopy. The flux of dry deposition is applied by Fick's Law

$$F = D \times \Delta C \quad (6)$$

where D is the transfer coefficient (cm/s) and ΔC is an average vertical concentration gradient (μg/m^3). The deposition velocity (Vd) is an engineering factor defined as the ratio of vertical flux (F) to concentration (C)

$$Vd = F/C \quad (7)$$

III. Sampling Site and Laboratory Analysis

The experiment was conducted above the Dipterocarp planted trees which is located adjunction to the King Mongkut's University of Technology Thonburi, Ratchburi province in Thailand at latitude 13^o 35' 13.3"N, Longitude 99^o 30' 3.9"E. The height of the tree was approximately 5 m. The experiment covered a period of August 2009 – January 2010. The climatic condition can be classified as wet season (August - October) and dry season (November - January). The aerosol concentrations were collected by two four – stage filter packs at which one filter was installed at 5 m and the other one was set at 10 m on the micrometeorological tower (see Figure 1). The vacuum pump (GAST model DOA – P504- BN) was used to draw in the air simple. The temperature and relative humidity were measured by Wisco-HT120 sensor at two positions, 6 m and 10 m. The solar radiation and the net radiation were measured at 7 m above the ground level using the solar radiometer (LSI DPA568) and the net radiometer (LSI DPA548). The soil heat flux was measured by EKO MF-81 using the heat flux plate buried at a depth of 8 cm and 4 m away from the tower. The assembling of the micrometeorological instrument is shown in Fig. 1.

The flow rate of 20 L min^{-1} of air sample was drawn by a vacuum pump continuously for 6 hours through the filter pack. The air sample was collected for every 6 hours for three days in each month. The 4-stage filter pack, starting from the inlet consisted of a Teflon filter (Pall) to collect SO_4^{2-} and NO_3^-, the second filter was nylon membrane to collect gas species the third filter was potassium carbonate impregnated cellulose (Whatman, No. 41) to collect remaing gas species and the fourth filter was phosphoric acid impregnated paper to collect NH_3. The collected filters were then placed in a polyester bag and preserved in a refrigerator. To analyze the chemical species, each filter was separately put in 50 ml polypropylene tubes and filled with distilled water up to 20 ml. For the second stage filter, 20 ml of 0.1%V/V H_2O_2 was added. The tubes were shaken for 20 minutes in an ultrasonic shaker. The solution was then filtered using membrane 0.45 micrometer filter and preserved in a refrigerator at 4 ºC. The ion chromatography was used to analyze the anion species of SO_4^{2-} and NO_3^-

Figure 1. Assembling of the micrometeorological instruments at the tower

IV. Results and Discussion

A. Micrometeorological parameters

All measured micrometeorological parameters i.e. temperature, relative humidity, wind speed, net radiation and soil heat flux are shown in Table 1. The calculated sensible heat and the latent heat were also included in Table 1.

TABLE I. The Micrometeorological Parameters

Factors	Wet season	Dry season
Temperature (^{0}C)	29.13	26.89

Relative Humidity (%)	76.02	71.73
Wind speed (m s^{-1})	1.40	1.21
Net radiation(W m^{-2})	287.15	254.65
Sensible heat (W m^{-2})	81.16	72.55
Latent heat(W m^{-2})	197.98	176.92
Soil heat(W m^{-2})	8.01	3.63

Note: the values are average and for the daytime (6 a.m. to 6 p.m.)

The average ambient temperature in the wet season was higher than the dry season because there was a higher intensity of sunlight in the day time. The net radiation was about 287 W m^{-2} in the wet season and 254 W m^{-2} in the dry season. The average relative humidity in the wet season was 76% which is 5% higher than the dry season (Table 1). Figure 2 shows a monthly variation of the temperature and the relative humidity which tends to decrease for both micrometeorological parameters toward the dry season. The climate in the tropical forests is very humid due to the warm sunlight, rain and the canopy shading over the plants that keep the moisture in. The average wind speed in the wet season was slightly higher than the dry season (1.4 and 1.2 m/s, respectively). July to October lie in the monsoon season where the region receives heavy rainfall. The average net radiation, sensible heat, latent heat and soil heat in the wet season were all higher than the dry season. These micrometeorological parameters are used in the Bowen ratio method to determine the SO_2 flux. Their seasonal variations which expected to affect the deposition velocity were investigated.

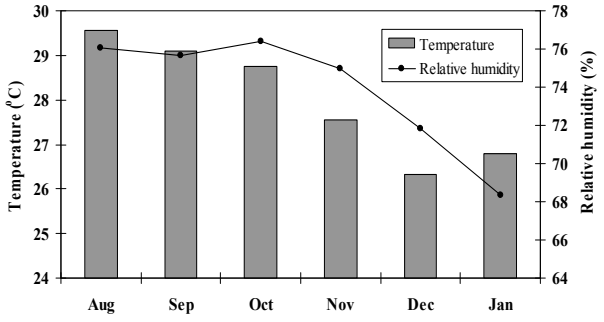

Figure 2. The monthly variation of temperature and relative humidity

B. Concentrations, fluxes and deposition velocities

The atmospheric concentrations of SO_4^{2-} and NO_3^- were calculated in μg m^{-3} by multiplying the concentrations obtained in μg L^{-1} (by Ion chromatography) with the volume extracted (L) and dividing by the air volume drawn (m^3) during sampling period. The monthly average concentration of SO_4^{2-} and NO_3^- above the Dipterocarp forest is shown in Fig. 3. These monthly values are represented for the wet season (Aug – Oct) and the dry season (Dec - Jan). The concentrations were found to be in ranges of 1.62 – 9.34 μg m^{-3} for SO_4^{2-} and 3.61– 22.90 μg m^{-3} for NO_3^-. The concentration of SO_4^{2-} and NO_3^- in the wet season was smaller than the dry season due to some wash away of both chemicals by the precipitation. In addition, the open burning for the agricultural land clearing which is a common practice in Thailand during the dry season (Nov - Dec) [15] may contribute significantly to the ambient. The ambient SO_4^{2-} may evolve from the long rang transport contributing from the local industrial combustion sources. The average NO_3^- concentration was found to be higher than SO_4^{2-} for both wet season and dry season. It is known that there are farming activities and animal husbandry such as swine production and dairy production that produce animal waste which produces NH_3. The NO_3^- can be produced by the gas phase reaction of $NHO_3$with NH_3 to ~~e~~ form NH_4NO_3 [16]. The aerosol NO_3^- exists in the atmosphere may not only dissolved in droplets, but also in the form of particulate matter such as NH_4NO_3 and as NHO_3vapor [4].

The dry deposition fluxes were calculated to be in a range of 0.0023 μg m^{-2} s^{-1} – 0.0083 μg m^{-2} s^{-1} for SO_4^{2-} and 0.0078 μg m^{-2} s^{-1} – 0.0533 μg m^{-2} s^{-1} for NO_3^-. The monthly variation of dry depositions of SO_4^{2-} and NO_3^- are shown in Fig.4. The dry deposition flux of NO_3^- was higher than SO_4^{2-} in both wet and dry seasons. This indicated NO_3^- is an important acid species over this ecosystem. When nitrogen input is in excess of the system neutralization capacity, it can induce environmental stresses such as soil acidification, forest decline, eutrophication of surface water [17].

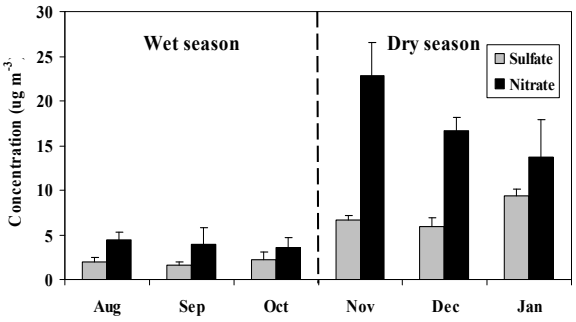

Figure 3. The monthly average concentration of SO_4^{2-} and NO_3^-

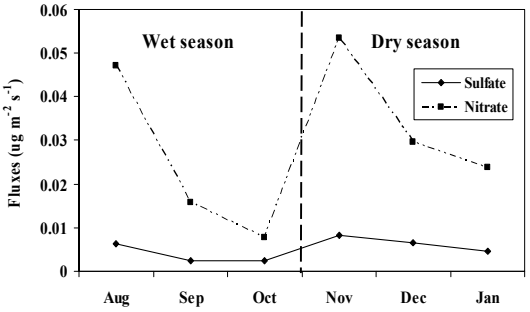

Figure 4. Monthly Variation of dry deposition of SO_4^{2-} and NO_3^- in the wet and dry seasons.

The monthly variation of deposition velocities of SO_4^{2-} and NO_3^- are shown in Fig. 5. The average deposition velocities of SO_4^{2-} in the wet and dry seasons were 0.18 and 0.09cm s^{-1}, respectively. The average deposition velocities of NO_3^- in the wet and dry seasons were 0.55 and 0.19 cm s^{-1}, respectively. The highest deposition velocity of SO_4^{2-} and NO_3^- occurred in August and found to be 0.31 and 1.04 cm s^{-1}, respectively. According to this experiment, the highest relative humidity occurred in August also. When the relative humidity increases, the hygroscopic growth on the aerosols affected the dry deposition velocity [18]. The transformation from solid particle to droplet occurs only when the relative humidity in surrounding atmosphere reaches a certain critical level corresponding to the water activity of saturated solution [4]. The dry deposition velocity of NO_3^- was higher than SO_4^2 for all month. However, the deposition velocity of aerosol also depends on other meteorological variables (e.g., wind speed, temperature, humidity, terrain, and atmospheric stability) surface variables (e.g., surface aerodynamic roughness, displacement height and canopy height, pH, wetness, hydrophobicity, porosity), and properties of the depositing material (e.g., chemical reactivity, solubility, diameter, surface charge, shape, density, diffusion coefficient, Brownian motion, impaction and interaction) [7, 8].

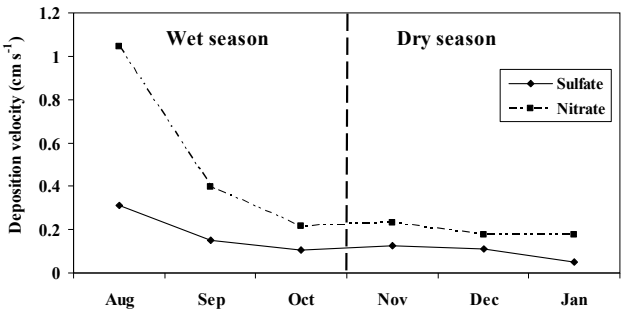

Figure 5. Monthly variation of deposition velocities of SO_4^{2-} and NO_3^- in the wet and dry seasons.

V. CONCLUDSIONS

The fluxes and dry deposition velocities of SO_4^{2-} and NO_3^- have been estimated by Bowen ratio method above the Dipterocarp forest in Thailand from August 2009 – January 2010. The concentrations of SO_4^{2-} and NO_3^- were higher in the dry season than the wet season. Particularly, the concentration of NO_3^- was significant in the dry season, due to an open burning and emission of NH_3 from the animal husbandry to the atmosphere. The minimum and maximum fluxes of NO_3^- were found to be 0.0078 μg m^{-2} s^{-1} and 0.0533 μg m^{-2} s^{-1}, respectively and SO_4^{2-} were 0.0023 and 0.0083 μg m^{-2} s^{-1}, respectively. The deposition velocities of SO_4^{2-} and NO_3^- were the highest in August which occurred in the wet season. The dry deposition velocity of NO_3^- was higher than SO_4^2 for all month.

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