# COMPOSITIONS OF RAINWATER AND AEROSOLS AT GLOBAL ATMOSPHERIC WATCH IN DANUM VALLEY, SABAH

# (Komposisi Air Hujan dan Aerosol di Stesyen Atmosferik Global, Lembah Danum, Sabah)

S.Mariam Sumari<sup>1\*</sup>, Fairus Muhamad Darus<sup>1</sup>, Nesamalar Kantasamy<sup>1</sup>, Nurrul Izza Taib<sup>1</sup>, Siniarovina ak Urban Sinyaw<sup>2</sup>, Ida Rosmini Othman<sup>3</sup>

<sup>1</sup>Faculty of Applied Sciences, Universiti Teknologi MARA, 40450, Shah Alam, Selangor
<sup>2</sup>The Malaysian Meteorological Services Department, Petaling Jaya, Selangor, Malaysia
<sup>3</sup>Faculty of Information Technology and Quantitative Science, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia

\*Corresponding author: sitim007@salam.uitm.edu.my

#### Abstract

Weekly wet rainwater and dry deposition samples were separately collected for 12 months from January to December 2007 in Danum Valley, Sabah. Rainwater samples were determined for rainfall volume, pH, conductivity, and major ions composition. The dry deposition samples were analysed for ions and reactive gases. The average pH of rainwater was 5.17, below 5.6, the limiting value for clean rainwater. The dominant species were  $SO_4^{2-}$  and  $CI^-$  in wet sample where  $SO_4^{2-}$  and  $NO_3^-$  were well correlated. The buffering system to acidity was mainly due to Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> for wet deposition (rainwater). In dry deposition sample, NH<sub>3</sub> was the major component (50 %).

Keywords: Danum Valley, wet deposition, dry deposition, conductivity, buffering system

#### Abstrak

Penyampelan pemendapan basah dan kering telah dilakukan berasingan secara mingguan untuk Stesyen Atmosferik Global di Lembah Danum, Sabah selama 12 bulan dari Januari hingga Disember 2007. Pengukuran isipadu air hujan, pH dan konduktiviti serta analisa untuk kandungan ion utama telah dilakukan untuk sampel air hujan. Nilai purata pH air hujan adalah 5.17, iatu kurang dari nilai pH untul air hujan tak tercemar, 5.6. Spesis yang dominan ialah  $SO_4^{2-}$ , Cl<sup>-</sup> dalam air hujan, di mana  $SO_4^{2-}$  dan  $NO_3^{-}$  mempunyai korelasi yang baik. Sistem peneutralan keasidan dalam sampel basah adalah  $Na^+$  dan  $NH_4^+$ . Untuk sampel kering, komponen utama adalah  $NH_3$  (50 %).

Kata kunci: Lembah Danum, pemendapan basah, pemendapan kering, konduktiviti, sistem penimbal

### Introduction

Air pollution is due to contamination of the air by noxious gases and minute solid particles and liquid matter(particulates) in concentrations that pose health risk. Air pollutants are emitted into the atmosphere from anthropogenic sources primarily from the burning of fossil fuels [1], which have precursors from industrial sources, power and heat generators, waste disposal and internal combustion engines. In addition, large scale biomass burning and forest fires release organic and inorganic air pollutants which can travel across national boundaries. Natural sources like volcanoes, sea sprays and forests also release pollutants including biogenic volatile organic compounds [2]. Although they are not very significant contributors to air pollution and do not generally cause as much problem as anthropogenic sources do, they are nevertheless important air pollutiont sources, especially on a global scale.

Once in the atmosphere, these pollutants undergo chemical and physical transformation through complex atmospheric processes to form secondary pollutants as particulates or aerosols (sulfates, nitrates, trace metals), and related gases ( $NO_x$ , eg. nitrogen dioxide;  $SO_x$ , eg.sulfur dioxide and nitric acid,  $HNO_3$ ) [3]. The nature of these pollutants and meteorological conditions influence the way atmospheric pollutants are eventually sequestered via wet or dry deposition [4]; some are deposited close to the source while others are transported over longer distances before being deposited [5] onto surfaces.

The chemical composition of atmospheric deposition, therefore, is a signature of several interacting physical and chemical processes including emission and sources; transport and dynamics of the atmosphere; and removal processes involved. The effects of atmospheric deposition include acidification of lakes and streams, nutrient enrichment of coastal waters and large river basins, soil nutrient depletion and decline of sensitive forests, agricultural crop damage, and impacts on ecosystem biodiversity [3,6].

Recognizing the importance of atmospheric chemistry in weather and climate processes towards understanding and controlling the increasing influence of human activity on the global atmosphere. The World Meteorological Organization (WMO) have initiated long-term Global Atmospheric Watch (GAW).

monitoring program in 1989. Among its main objectives is to make systematic monitoring of atmospheric chemical composition and related physical parameters on a global to regional scale over decades for the purpose of monitoring and predicting changes in atmospheric composition and its impacts. Presently there is a network of 22 GAW Global stations worldwide, the latest addition being the Danum Valley (DV) in Sabah, Malaysia.

The Global Atmospheric Watch (GAW) Stations are normally located in remote locations within a pristine environment with very low background levels of pollutants. It is intended to continuously measure a broad range of atmospheric parameters which can be used to assess the relationship between regional pollution and changes in regional patterns in deposition. The GAW station in DV is equipped with a range of monitoring instruments and an automatic weather station to carry out measurement for greenhouse and reactive gases, meteorological parameters and wet precipitation. Data from these observations provide means to assess and predict early warning system for changes in atmospheric concentrations affecting climate change and related environmental issues.

Atmospheric monitoring is essential in detecting signs of changing trend and hence any plausible air pollution and atmospheric acidification. Air quality and pollution may be partly assessed by examination of compositions in both wet and dry deposition. The objective of this study is to analyze the wet precipitation and aerosol composition in this remote DV and to evaluate the anthropogenic and natural influences on the chemical composition of rainwater (wet deposition) and aerosols (dry deposition) in this area.

# Experimental

#### Sampling Site

The GAW Station atop Bukit Atur in the DV, Sabah is among 24 GAW stations operating worldwide and was commissioned in 2004. The GAW station includes a 100m tall sampling tower and facilities for climate and atmospheric research, a core activity in DV, where international scientists from UK, Japan, Sweden, Australia and Singapore collaborate with local researchers. It is about 10 km from Danum Valley Field Centre (DVFC), a globally known research site within a 438 km<sup>2</sup> of Danum Valley Conservation Area (DVCA). The station has an altitude above mean sea level at approximately 426 metres with a latitude and longitude at 04° 58' 53" N (4.95 deg. N) and 117° 50' 37"E (117.85 deg. E) respectively. The climate of DV is equatorial and generally seasonal with a mean annual temperature of 26.8°C. Except during prolonged dry periods, temperatures in excess of 34°C are rare. Figure 1 shows the location of GAW station near DVCA.

Mean annual rainfall (1985-2006) recorded was 2,825 mm with mean monthly rainfall ranging from 153mm in April to 309 mm in January and tends to be highest in the transition months following the equinoxes (May-June and October-November) and also during the northerly monsoon months of December-January. Rainfall is generally lowest during March and April, which are the most drought-prone months during ENSO (El Niño Southern Oscillation) events, and in August and September when the south-westerly monsoon is at its height [7]. DVCA, set up by Sabah Foundation is a protected zone with an undisturbed primary forest conservation reserve which has been recognized as one of the world's most complex ecosystems comprising a vast reserve of lush lowland tropical forest rich in flora and fauna in its original natural environment [8]. The nearest town is Lahad Datu, 70 km away or about 3 hours drive on logging roads. Even though the main activities in the DVCA are nature-related research, logging activities are still taking place in the surrounding forest outside the protected area, mainly from the Ulu Segama and Malua forest reserves that circle the DVCA.. Log laden heavy vehicles plying the dust-laden log trail, the land route into the DVCA and the GAW station are common sights in this area. In the case of DV, logging activities would constitute a conspicuous anthropogenic polluting activity contributing emissions into the atmosphere. In the absence of human settlement except for limited human activities mentioned above, DV is considered a remote site.



Figure 1: GAW Station near DVFC and DVCA

# Sampling and Analysis

Rainwater was collected using a wet only sampler placed on a platform of a GAW building atop Bukit Atur. The rainwater collection was programmed to be carried out weekly over a period of 12 months from January 2007 to December 2007. The volume of rainwater was recorded using a rain gauge. 4% thymol was added to the samples to prevent degradation of organic acids. The samples were sent to the Department of Chemistry Malaysia (DOC) in Petaling Jaya in the mainland Malaysian West Coast by fast-delivery mail for laboratory chemical analysis. Composition of wet deposition was determined for major cations (H<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>) and major anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> SO<sub>4</sub><sup>2-</sup>, CH<sub>3</sub>COO<sup>-</sup> and HCOO<sup>-</sup>) by ion chromatography. In addition, the pH and electrical conductivity of rainwater were also determined using pH meter (Mettler Toledo) and conductivity meter (Mettler Toledo) respectively.



Figure 2 (a)-(b): Four-stage filter pack arrangement for dry deposition sampling

For dry deposition sampling, a four-stage filter pack method (Figure 2) was used. As air was drawn in through the filter unit using a pump, aerosols and reactive gases (HCl,  $NH_3$  and  $SO_2$ ) were trapped selectively by specially treated filters as indicated in Figure 2a. The filter pack containing air samples were collected weekly after 7–day exposure to be sent to the DOC for analysis for major ions in aerosols as well as for quantification of HCl,  $NH_3$  and  $SO_2$ .

#### **Results and Discussions**

# Quality Assurance

Analysis of samples were done in duplicate. For rainwater, measured data were checked for R1 and R2 values. Basically R1 refers to ionic balance (ratio of sum cations, C/sum anions, A) whilst R2 refers to a comparison between calculated and measured electrical conductivities (Meas mS/m). For the range of concentration measured, deviation of  $\pm 30\%$  was allowed for R1 and  $\pm 20\%$  for R2 as specified in the data quality control criteria of EANET [9]. Compliance would mean that most of the major ions have been analyzed and accounted for. In this study compliance of ion balance (R1) and conductivity balance (R2) has been observed to be 72% and 90% respectively (Figures 3a and 3b).



Figure 3: Quality control for rainwater analysis (a) Ion balance (R1) and (b) Conductivity balance (R2)

### Variations of pH in Rainwater

Figure 4(a) shows the temporal variation of pH of rainwater at DV during January to December 2007. It is observed that pH for DV rainwater during the study period ranged from 4.89 to 5.90, with an average of 5.17. This means, overall, pH for DV was still within the range of unpolluted rainwater, pH 5.6 being the limiting pH value of clean rainwater, which is slightly acidic as a result of dissolution of  $CO_2$  in water. This average value was also well above 4.3, the mean pH for urban Petaling Jaya [10] or areas subjected to acidic precipitation (pH 4.7 in North eastern China) [11]. The frequency distribution of pH as shown in Figure 4b shows about 17% of the total rainfall in DV can be considered acidic (<5.0), whereas 75% of rainwater accounted for mildly acidic (5.0-5.6). Only 8.3% of the precipitation recorded can be categorized as slightly alkaline (5.6-6.0). Samples with very alkaline (>7.0) was not observed, indicating the absence of strong influence of basic species, notably  $Ca^{2+}$ . These results demonstrated that strong influence of neither strong acids nor alkaline components was impacting DV area resulting in volume weighted mean (VWM) pH of 5.17, slightly below 5.6. Thus even remote areas like DV, which is regarded as pristine with limited human activities, impact from some acidic influence created elsewhere cannot be totally ruled out.

Rainfall amount can affect rainwater acidity and pH due to dilution effect, as illustrated by some selected data in Table 1. The effect on pH is closely related to the concentration of acidic species, notably  $NO_3^-$  and  $SO_4^{2^-}$ . The highest pH was pH 5.90 coinciding with high rainfall (280 mm) in July with total sum of  $NO_3^-$  and  $SO_4^{2^-}$  concentrations of 5.35 of  $\mu$ eq/L. The lowest pH was 4.89 with a recorded lower rainfall amount of 211 mm, and with corresponding  $NO_3^-$  and  $SO_4^{2^-}$  concentrations equivalent to 6.26  $\mu$ eq/L for August. Other examples of dilution effect by rainfall amount are the pH values and rainfall volumes for June (5.24, 337 mm) and May (5.16, 283.6 mm).

However, in instances where changes in rainfall volume did not necessarily match expected changes in pH, the influence of neutralizing ions (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) in reducing acidity have to be considered. An examples of this neutralizing effect is illustrated by comparing the pH values for June and July. Even though rainfall for July (280 mm) was less than that for Jun (337 mm), the pH for July (5.90) was greater than that of June (5.24); in spite of the total amount of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> being greater (5.35 ueq/L) for July than for June (3.13 µeq/L). The explanation for this is, the concentration of neutralizing ions (16.28 µeq/L) in particular NH<sub>4</sub><sup>+</sup> (not shown), was much greater for July than for June (2.20 µeq/L); and the effect of the subsequent partial neutralization that had resulted in residual acidity was more apparent for July than for June. Similar explanation holds true for pH pair for April-August. Thus, to understand the overall acidification effect, there is a need to understand the complex chemistry of the various chemical species in the atmosphere, neutralization and buffering reactions being the simplest examples.



Figure 4: Temporal variation of pH (a) and percent pH distribution for rainwater (b)

Month	pН	Rainfall mm	SO <sub>4</sub> <sup>2-</sup> μeq/L	NO <sub>3</sub> <sup>-</sup> μeq/L	$(NH_4^+ + Na^+ + K^+ + Ca^{2+} + Mg^{2+})$ $\mu eq/L$
Apr	4.97	89.5	11.95	7.08	17.61
May	5.16	283.6	2.49	0	2.16
June	5.24	337.5	2.62	0.51	2.20
July	5.9	279.7	3.46	1.89	16.28
August	4.89	211.2	5.71	0.55	10.29

Table 1: Selected data of rainfall, acidic and basic components of rainwater

### Temporal Variation of Ions with Rainfall

The temporal variation of ions with rainfall is shown in Figure 5(a)-(b). Rainfall has a dilution effect on the compositions of ions in rainfall; the greater the rainfall the lower the concentrations of species and the higher the acidity [10] as explained previously. This was illustrated in April during the lowest rainfall seasons when the concentration of ions were higher compared to the following wetter season with increased rainfall amount between May to November. The decrease in ion concentration during the period of decreased rainfall reflects the dissolution and scavenging action of rainwater, this effect being more pronounced with the ions of crustal elements associated with road dust and surface sediment (K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>) compared with acidic species (SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>). However during another high amount of rainfall in July, some ions notably K<sup>+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and especially CH<sub>3</sub>COO<sup>-</sup> showed marked increase in concentration. The concentrations of these ions especially NH<sub>4</sub><sup>+</sup> posed a leverage effect on acidification by strong acid (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>) and weak acid (CH<sub>3</sub>COO<sup>-</sup>) precursors, culminating in the highest recorded pH 5.90 in July. These ions with the exception of CH<sub>3</sub>COO<sup>-</sup> bore the hallmark of haze constituents originating from forest fires or biomass burning, whose most probable source was neighboring Indonesia. Biomass burning whereby farmers slash and burn their agricultural

waste is a common practice in Indonesia; the aftermath of such practice has been the recurring haze episodes especially so during the dry months, brought about by long-range transport of aerosol and fine particulate laden air mass across the Indian Ocean by the prevailing south westerly wind from the direction of Sumatra, across the Straits of Malacca sweeping into the land mass of Peninsular Malaysia [10]. Meanwhile, the most probable source of CH<sub>3</sub>COO<sup>-</sup> was from local industries. Hence even though DV is a clean background site, anthropogenic activities created elsewhere can impact this area as a result of local and long range airborne transport.







Figure 5: Temporal variation of ions in rainwater for (a) anions (b) cations

# **Ionic Composition of Rainwater**

A statistical summary of VWM concentrations of major ions, as well as rainwater amount and pH is presented in Table 2. The percentage contribution of each ion to either anion or cation and also total ion is given in Figure 6. The results show that the average relative abundance of ionic species in the wet precipitation followed the order:  $H^+ > CI^- > SO_4^{2-} > Na^+ > HCOO^- > NH_4^+ > CH_3COO^- > NO_3 > K^+ > Mg^{2+} > C_2O_4^{2-} > Ca^{2+}$ . To estimate the marine and non-marine contribution, ratios of ions to Na<sup>+</sup> were compared with established sea salt ratio [13] as shown in Table 3.

Parameter	Unit	Average	S.D.	Max	Min
Rainfall amount	mm	233.34	± 96.54	424.20	89.50
pH		5.17	± 0.26	5.90	4.89
EC	mS/m	0.83	± 3.11	2.10	0.30
$\mathrm{H}^+$	µeq/L	7.68	$\pm 0.60$	12.87	1.25
$SO_4^{2-}$	µeq/L	5.22	± 2.69	11.95	2.49
NO <sub>3</sub> <sup>-</sup>	µeq/L	1.10	± 1.99	7.08	0.00
Cl	µeq/L	5.64	$\pm 4.86$	16.62	2.05
$\mathrm{NH_4}^+$	µeq/L	1.74	$\pm 2.88$	7.86	0.00
Na <sup>+</sup>	µeq/L	4.85	$\pm 4.75$	15.82	1.04
Ca <sup>2+</sup>	µeq/L	0.61	$\pm 0.60$	2.09	0.01
Mg <sup>2+</sup>	µeq/L	1.03	$\pm 0.77$	2.34	0.10
$K^+$	µeq/L	1.23	$\pm 0.70$	2.68	0.36
CH <sub>3</sub> COO <sup>-</sup>	µeq/L	1.47	$\pm 3.90$	13.67	0.00
HCOO	µeq/L	1.86	± 3.94	13.49	0.00
$C_2 O_4^{2-}$	µeq/L	0.66	± 1.44	4.99	0.00
nss-SO4 <sup>2-</sup>	µeq/L	4.92	± 2.56	11.61	2.43

Table 2: Chemical composition of rainwater at Danum Valley

Among these anions, chloride Cl<sup>-</sup> was the leading acid contributor with the greatest average concentration of 5.64  $\mu$ eq/L, contributing 35.4% to this group and 17% to total ion composition. (SO<sub>4</sub><sup>2-</sup>) was the second most abundant anion (5.22  $\mu$ eq/L) followed by HCOO<sup>-</sup> (1.86  $\mu$ eq/L), while the concentration of NO<sub>3</sub><sup>-</sup> was notably much less (1.1  $\mu$ eq/L). Since DV is neither densely populated nor industrialized, vehicles are few and far between; hence as this study shows, NO<sub>3</sub><sup>-</sup> contribution from exhaust emission was low resulting in only 3.3% to overall total ions. For DV the ratio of Cl<sup>-</sup>/Na<sup>+</sup> is 1.16 (Table 3), which equals to sea salt ratio of 1.16 [14]. Hence marine contribution is a major acid contributor to this region. On the other hand, the ratio of SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup> is 1.08, greater than sea salt ratio 0.125, suggesting that the source of SO<sub>4</sub><sup>2-</sup> was mostly from anthropogenic origin of which the biomass burning from Indonesia was one likely source.

Quantitatively, values for conventional acid rain precursors,  $SO_4^{2^-}$  and  $NO_3^-$  for remote site DV showed sharp deviation from typical higher values of  $SO_4^{2^-}$  and  $NO_3^-$  in urban areas; for example, 21.39 µeq/L and 26.54 µeq/L for Petaling Jaya [10], 14.29 µeq/L and 13.41 µeq/L for India [15] and, 79.50 µeq/L and 22.34 µeq/L for Singapore [16]. The obvious explanation for the foregoing pattern is the different landuse types of these monitoring sites;  $SO_4^{2^-}$  is formed from  $SO_2$  released from industrial sources such as coal-burning power plants, smelters, and oil refineries, while  $NO_3^-$  is formed from  $NO_2$  released from combustion activities, especially those involving cars, trucks, and motors such as those in power plants and other industrial sources. Such diversified activities are only expected in populous and industrialized urban sites. In contrast, acidic emissions are expected to be low in DV since it is a forested, nature-conservation remote site, lacking in industries. Another feature of  $SO_4^{2^-}$  and  $NO_3^-$  pattern is from their ratio ( $SO_4^{2^-}/NO_3^-$ ); this value is 4.74 for DV, that is contribution by  $SO_4^{2^-}$  to total acidity far outweighs contribution by  $NO_3^-$  (almost 5 times). This feature is similar with other urban sites; the explanation being the contribution by  $SO_2(SO_x)$  emission primarily from

industries and other anthropogenic activities seemed much greater than  $NO_2(NO_x)$  emission, mostly from vehicles.

The weak organic acids contributors, formate, acetate and oxalate contributed 25 % of the total anions or 12% of total ions, indicating significant contribution from biogenic emission to acidity in this forested area. Quantitatively, the total mean concentration of these weak acids was significantly higher (3.99  $\mu$ eq/L) than the value at urban site Petaling Jaya (2.35  $\mu$ eq/L)[10] at which they made up less than 3% of total ion [3]. This finding is in agreement with certain finding that biogenic acids are important sources of acidity in pristine area [7] not greatly impacted by strong acids (SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>).



Figure 6: Distribution of ions in rainwater

Among the cations,  $H^+$  was the most abundant with an average concentration of 7.68 µeq/L, making up about more than 43% of total mass of cations, followed by Na<sup>+</sup> (28%), NH<sub>4</sub><sup>+</sup> (10%) K<sup>+</sup> (7%), Mg<sup>2+</sup> (6%) and Ca<sup>2+</sup> (4%). The presence of these basic ions neutralized acidic components and effectively prevented acidification. The most dominant basic ionic species contributing to the buffering system to potential acidity are Na<sup>+</sup>, which was a marine source as explained previously, followed by NH<sub>4</sub><sup>+</sup>, and with Ca<sup>2+</sup> the least. Ca<sup>2+</sup>, mostly of crustal origin and present in airborne dust is normally among the biggest contributors to alkalinity in rainwater. Hence the little presence of Ca<sup>2+</sup> in rainwater helps explains why pH for DV was never more than 6, indicating no significant neutralization in rainwater. Table 3 shows that Ca<sup>2+</sup>/Na<sup>+</sup> ratio is higher than sea water ratio (0.04) indicating the influence of non-marine source. Besides soils and windblown dust of crustal origin (Mg<sup>2+</sup>, Ca<sup>2+</sup>), other most likely anthropogenic sources for basic ions in DV rainwater would be biomass burning since among the main aerosol compositions from biomass burning are basic ions (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>,Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>) as well as acidic ions (H<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and NO<sub>3</sub><sup>-</sup>) [16,17]

The ratio of  $Mg^{2+}/Na^+$  is 0.21, less, but almost the same as sea salt ratio (0.23) indicating that  $Mg^{2+}$  was more likely to be of marine origin rather than crustal or anthropogenic sources. This relationship is further strengthened by the correlation between sea salt marker ions,  $Mg^{2+}$  and  $Na^+$  (0.74) as shown in Table 3. As for  $NH_4^+$ , this basic ion is normally associated with agricultural activities involving the use of fertilizers, livestock farming and biomass burning, as well as decomposition of animal/human waste, all of which create volatilization of  $NH_3$  and subsequent formation  $NH_4^+$  and incorporation into wind blown dust.

	Cl <sup>-</sup> /Na <sup>+</sup>	SO42-/Na+	K <sup>+</sup> /Na <sup>+</sup>	Ca <sup>2+</sup> /Na <sup>+</sup>	Mg <sup>2+</sup> /Na <sup>+</sup>
Seawater	1.16	0.125	0.02	0.04	0.23
DV	1.16	1.08	0.25	0.13	0.21

Table 3: Equivalent concentration ratios of ionic components to Na in rainwater

# **Statistical Analysis for Rainwater**

A statistical evaluation of relations between major component concentrations in rainwater was done using Pearson correlation coefficients using statistical software, SPSS. The results are summarized in Table 4. The high correlation between NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> (0.62), Mg<sup>2+</sup> (0.64), K<sup>+</sup>(0.68), nss-SO<sub>4</sub><sup>2-</sup>(0.84) suggests a common origin with a specific source, most probably, biomass burning as these ions are major aerosol components of biomass burning explained previously. Recent finding also showed that K<sup>+</sup> is released during transpiration and accumulate on plants' leaves to be dispersed by wind into the atmosphere [13]. The correlation between combination process with the formation of NH<sub>4</sub>(NO<sub>3</sub>), Mg(NO<sub>3</sub>)<sub>2</sub> and, KNO<sub>3</sub>. Good correlation between combination pairs Mg<sup>2+</sup>-Na<sup>+</sup> (r=0.74), Mg<sup>2+</sup>-Cl<sup>-</sup> (r=0.76) and Na<sup>+</sup>-Cl<sup>-</sup> (r=1.00) implies that these ions were from marine source. The fact that Mg<sup>2+</sup> was of marine origin was supported by earlier finding that the equivalent ratio of Mg<sup>2+</sup>/Na<sup>+</sup> was 0.21 which correlates well with seawater ratio as explained previously. However moderate correlation between Mg<sup>2+</sup> and Ca<sup>2+</sup>(r= 0.49) also indicates some crustal contribution to Mg<sup>2+</sup>. In addition, equivalent ratio of Ca<sup>2+</sup>/Mg<sup>2+</sup> (0.59) is more than that of seawater, which is about 0.19 [17], further implying that Mg<sup>2+</sup> originated from multiple sources including marine and crustal or anthropogenic. Similarly, the close association between ion pairs NH<sub>4</sub><sup>+</sup> -Ca<sup>2+</sup> (r=0.85), NH<sub>4</sub><sup>+-</sup> K<sup>+</sup>(r=0.77), Ca<sup>2+</sup>-K<sup>+</sup> (r=0.88), Mg<sup>2+-</sup>K<sup>+</sup>(r=0.67) and Mg<sup>2+-</sup>SO<sub>4</sub><sup>2-</sup> (r=0.78), again indicates anthropogenic contribution from biomass burning either due to local or long range transport as explained previously.

Good correlation between NO<sub>3</sub><sup>-</sup> and nss-SO<sub>4</sub><sup>2-</sup>(0.84) suggests they were from the same source namely fossil fuel, and having a common transport mechanism [18]. Weak correlation between H<sup>+</sup> and Cl<sup>-</sup> (r=0.2) may be attributed to little acidity contribution by this ion. On the other hand SO<sub>4</sub><sup>2-</sup> which was moderately correlated (r=0.54) with H<sup>+</sup> evidently had more influence to acidity to rainwater than any other ion present. Although this ion had more influence to acidity to rainwater than any other ion, the effect was neutralized by the basic species resulting in moderate acidity with a mean pH of 5.12.

	$\mathrm{H}^{+}$	NO <sub>3</sub> <sup>-</sup>	CI	$\mathrm{NH_4}^+$	$Na^+$	Ca <sup>2+</sup>	$Mg^{2+}$	$K^+$	nss-SO4 <sup>2-</sup>
$\mathrm{H}^+$	1								
$NO_3^-$	0.16	1							
CI	0.2	0.2	1						
$\mathrm{NH_4}^+$	-0.05	0.62	-0.1	1					
Na <sup>+</sup>	0.2	0.19	1	-0.13	1				
Ca <sup>2+</sup>	-0.18	0.49	0.04	0.84	-0.01	1			
$Mg^{2+}$	0.28	0.64	0.76	0.4	0.74	0.49	1		
$K^+$	-0.09	0.68	0.26	0.77	0.21	0.88	0.67	1	
nss-SO42-	0.54	0.84	0.42	0.41	0.42	0.36	0.78	0.52	1

Table 4: Correlation coefficients between major ionic concentrations in rainwater

Bold text shows significant correlations.

0.60-1.00=strong correlation; 0.50-0.59=moderate; 0.40-0.49=weak; 0.00-0.39=little or no association

# **Composition of Aerosols in Dry Deposition**

Table 5 shows the mean values of dry deposition compositions of aerosol expressed as nmolm<sup>-3</sup>. The percentage contribution of each component to either ion or gas or total aerosols is given in Figure 7. The concentration followed the order:  $NH_3 > SO_4^{2-} > HCl > Na^+ > SO_2 > NH_4^+ > K^+ > HNO_3 > Mg^{2+} > Ca^{2+} > NO_3^-$ . The basic specie NH<sub>3</sub> was the most dominant constituting about 50% of total composition, followed by acid species  $SO_4^{2-}$  (10%), and HCl (9%). NO<sub>3</sub><sup>-</sup> was the least with only 1% of total aerosol content. Ammonia is present in the atmosphere as NH<sub>3</sub> incorporated in dry fallout, and as NH<sub>4</sub><sup>+</sup> in wet precipitation and in aerosols. The presence of NH<sub>3</sub> indicates the importance of this basic specie in the neutralizing or buffering any acid precursor species, mainly  $SO_4^{2-}$  and  $NO_3^-$ . The presence of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> was indicators of available sources which include livestock manure (beef cattles, dairy cows, laying hens), synthetic fertilizers and some automobile exhaust. NH<sub>3</sub> vapor and ammonium ion are scavenged by wet deposition. NH<sub>3</sub> may also form due to bacterial activity in the soil. NH<sub>3</sub> produced from these sources become airborne and transported and deposited elsewhere. In addition the biomass smoke from neighboring Indonesia is also a factor to be reckoned with as indicated by the rainwater analysis. Its contribution to NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> helped elevate these ions to be dominant species in the dry deposition.

The next dominant specie,  $SO_4^{2^-}$  showed similar feature with rainwater in its  $SO_4^{2^-}/NO_3^-$  ratio, the equivalent ratio of  $SO_4^{2^-}/NO_3^-$  is about 26; which means the contribution to acidity by  $SO_4^{2^-}$  was more significant than  $NO_3^-$ . The result also means that while contribution of  $NO_x$  by automobile was kept at minimum in this restricted area, the contribution by anthropogenic activities leading to  $SO_x$  emission was significant. In the absence of industries associated with  $SO_2/SO_x$  emission and  $SO_4^{2^-}$  production in this region, the likely source of  $SO_4^{2^-}$  was mostly from the contribution by Indonesian biomass burning via long range airborne transport.

Comparison between rainwater and aerosol components reveals some information about common sources of these components. As Figure 8 shows, similar pattern in is depicted by  $SO_4^{2^-}$ ,  $NH_4^+$ ,  $K^+$ ,  $Na^+$ ,  $Mg^{2^+}$  and  $Ca^{2^+}$ .  $Na^+$  and  $Mg^{2^+}$  are sea salt elements in both rain and aerosol.  $Mg^{2^+}$ ,  $Ca^{2^+}$ , and  $Na^+$  are associated with crustal origin. Similarly the anthropogenic constituents  $SO_4^{2^-}$ ,  $NH_4^+$  and  $K^+$  indicate similar source of origin, namely, they were incorporated into cloud droplet and transported to other location (eg. the Indonesian biomass smoke). Some of these were particles which were removed effectively onto surfaces by dry deposition.

nmol/m <sup>3</sup>	Average	S.D	Max	Min
Cl	0.749	±0.966	2.670	0.000
NO <sub>3</sub> -	0.595	±0.417	1.36	0.110
SO4 <sup>2-</sup>	7.825	±4.227	15.06	2.820
$\mathrm{NH_4}^+$	4.433	±3.427	12.445	1.140
Na <sup>+</sup>	6.047	±3.374	12.35	1.550
$\mathbf{K}^+$	2.408	±1.643	5.93	0.660
Mg <sup>2+</sup>	1.759	±1.398	3.75	0.250
Ca <sup>2+</sup>	0.689	±0.446	1.5	0.250
SO <sub>2</sub>	4.471	±2.7419	9.25	0.770
HNO <sub>3</sub>	2.283	±1.519	6.25	0.810
HCl	6.854	±2.991	13.68	2.887
NH <sub>3</sub>	36.655	±12.185	65.71	18.950

Table 5 : Composition of aerosols in dry deposition in nmol/m<sup>3</sup> (x 10<sup>-6</sup> µmol/L)



Figure 7: Distribution of aerosol (dry) composition

### Statistical analysis for aerosol in dry deposition

Table 6 shows the correlation matrix between major component of aerosols. Good correlation between  $SO_4^{2-}$  and  $NH_4^+$  (r=0.89) suggest the fact that in the atmosphere,  $NH_3$  react with  $H_2SO_4$  to form  $(NH_4)_2SO_4$  and  $NH_4HSO_4$ , both of which are incorporated into the aerosol. The relatively moderate correlation between  $SO_4^{2-}$  and  $HNO_3$  indicates that the two species may partly have origin from similar source, i.e combustion.  $NH_4^+$  correlates well with  $K^+$  (r=0.72) indicating the biomass smoke origin.  $NH_4^+$  is also moderately correlated with  $HNO_3$  as both may be related to nitrogen oxides,  $NO_x$ . Depending on physical and chemical condition, chemical reaction of  $NO_x$  either leads to reduction to  $N_2$  and  $NH_3$  and subsequently to  $NH_4^+$  or oxidation to  $HNO_3$ . This is again supported by moderately correlated combination pair  $HNO_3$ - $NH_3$ (r=0.52). Na<sup>+</sup> correlates well with  $Mg^{2+}$  (0.63), HCl (r=0.64), and moderately with Cl<sup>-</sup> (r=0.51), implying some association with sea salt among these species. The combination pairs  $HNO_3$ - $SO_2$  (r=0.57) suggests an association with probable formation of  $NH_4$ Cl. The reason for the moderate negative correlation between the formation  $NH_4^+$ - $Cl^-$  (0.53) and  $NH_4^+$ - $NO_3^-$  (r=-0.51), however is not obvious.



Figure 8: Comparison between rainwater (wet) and aerosol (dry) composition

	CI	NO <sub>3</sub>	$SO_4^{2}$	$NH_4^+$	Na <sup>+</sup>	$K^+$	$Mg^{2+}$	Ca <sup>2+</sup>	$SO_2$	HNO <sub>3</sub>	HCI	NH <sub>3</sub>
Cl	1											
NO <sub>3</sub> <sup>-</sup>	0.53	1										
$SO_4^2$	-0.46	-0.26	1									
$NH_4^+$	-0.54	-0.51	0.89	1								
Na <sup>+</sup>	0.52	0.47	0.34	0.00	1							
$K^+$	-0.22	-0.39	0.48	0.72	-0.08	1						
$Mg^{2+}$	-0.08	0.35	0.40	-0.01	0.63	-0.42	1					
Ca <sup>2+</sup>	-0.14	0.31	0.11	0.06	-0.06	0.17	0.01	1				
$SO_2$	0.43	-0.14	0.18	0.10	0.31	-0.16	0.07	-	1			
HNO <sub>3</sub>	-0.33	-0.48	0.57	0.51	-0.08	0.08	0.18	0.31	0.57	1		
HCI	0.40	0.45	0.35	0.17	0.64	0.04	0.37	0.03	0.15	0.12	1	
NH <sub>3</sub>	0.63	0.13	-0.02	-0.13	0.43	0.17	-0.01	0.09	0.52	0.27	0.33	1
-								0.12				

Table 6: Correlation coefficients between major component of aerosols

Bold text shows significant correlations.

0.60-1.00=strong correlation; 0.50-0.59=moderate; 0.40-0.49=weak; 0.00-0.39=little or no association

# Conclusion

A one-year study on rainwater and aerosol components at DV reveal that the concentration of both basic and acidic species were much less than that found on urban areas. The mean concentrations of major ions in wet precipitation followed the order:  $H^+ > CI^- > NO_3^- > SO_4^{2-} > Na^+ >$ formate  $> NH_4^+ > K^+ > NO_3^- > Mg^{2+} >$ acetate > Ca<sup>2+</sup> > oxalate. Among the aerosol components, the order was: NH<sub>3</sub> > SO<sub>4</sub><sup>2-</sup> > HCl > Na<sup>+</sup> > SO<sub>2</sub> > NH<sub>4</sub><sup>+</sup> > K<sup>+</sup> > HNO<sub>3</sub> > Mg<sup>2+</sup> > Ca<sup>2+</sup> > NO<sub>3</sub><sup>-</sup>. The acid rain precursors; SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were well correlated and so were the sea salt species,  $Mg^{2+}$ ,  $Na^+$  with Cl<sup>-</sup>. The  $SO_4^{2-}$ - $NO_3^-$  system responsible for acidification was significantly much reduced compared to values in urban areas. The buffering system to potential acidity was mainly due to Nspecies,  $NH_3$  and  $NH_4^+$  which may be associated with anthropogenic activities especially related to biomass burning in Indonesia. Na<sup>+</sup> ion associated with sea salt was also a major contributing basic ion with neutralizing effect potential. However the crustal element  $Ca^{2+}$  did not play a major role to the buffering system. The biogenic emission producing organic weak acids indicated quite significant contribution to overall composition in rainwater. The mean pH of rainwater was 5.17 which was below 5.6, the limiting value for clean rainwater. Thus, the rainwater may be considered mildly acidic. Further acidification though, was hindered by the buffering system led by  $NH_3$ - $NH_4^+$  system Like rainwater, the characteristics of aerosols were also influenced by anthropogenic species such as  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$  and  $NO_3^-$ . As such continuous monitoring is needed to detect changes in rainfall and aerosol patterns as indicators of air pollution which can be damaging to the ecosystem in Danum Valley.

#### References

- Mouli, P.C., Mohan, S.V., and Reddy, S.J. 2005. Rainwater Chemistry at A Regional Representattive Urban Site: Influence of Terrestrial Sources on Ionic Composition. Atmospheric Environment. 39: 999 – 1008
- Geron, C., Guenther, A., Greenberg, J., Loescher, H. W., Clark, D. and Baker, B. 2002. Biogenic volatile organic compound emissions from a lowland tropical wet forest in Costa Rica. Atmospheric Environment. 46 : 3793–3802.
- Polkowska, Z., Astel, A., Walna, B., Malek, S., Medrzcka, K., Gorecki, T., Siepak, J., and Namiesnik, J. 2005. Chemometric Analysis of Rainwater and Throughfall at Several Sites in Poland. Atmospheric Environment. 39: 837 – 855.
- Baez, A., Belmont, R., Gracia, R., Padilla, H., and Torres, M.C. 2007. Chemical Composition of Rainwater Collected at A Southwest Site of Mexico City, Mexico. Atmospheric Research. 86: 61 – 75.
- Hedge, P. Sudheer, A.K., Sarin, M.M., and Manjunatha, B.R. 2007. Chemical Characteristics of Atmospheric Aerosols Over Southwest Coast of India. Atmospheric Environment. 41: 7751 – 7766.
- Zhao, Z., Tian, L., Ficher, E., Li, Z., and Jiao, K. 2008. Study of chemical composition of precipitation at an alpine site and a rural site in the Urumqi River Valley, Eastern Tien Shan, China. Atmospheric Environment. 42: 8934 – 8942.
- Chappel, N. 2007. DVFC Rainfall, http://www.es.lancs.ac.uk/people/nickc/raindvfc.htm, retrieved on 16<sup>th</sup> January, 2008.
- SEARRP (South East Asia Rainforest Research Program). http://www.searrp.org/danum climate.cfm, retrieved on 25<sup>th</sup> November 2007.

- 9. EANET (Acid Deposition Monitoring Network in East Asia), 2000, Technical Documents for Monitoring on Inland Aquatic Environment in East Asia.
- 10. Siti Mariam, S., Rusdin, L., Urban Sinyaw, S., Roslin, A.B., 2005. Rainwater characterization at an urban site in the Klang Valley, Malaysian Journal of Analytical Science, Vol.9, No.2: 254-266.
- 11. Wang Y, Ming Wai, K, Gao, J., Liu, X., Wang, T., Wan, W., (2008). The impacts of anthropogenic emissions on the precipitation chemistry at an elevated site in North-eastern China Atmospheric Environment 42: 2959–2970.
- Kulshrestha, U.C., Kulshrestha, M.J., Sekar, R., Sastry, G.S.R. and Vairamani, M. 2003. Chemical characteristics of rainwater at an urban site of south-central India. Atmospheric Environment 37: 3019– 3026.
- 13. Thepanondh, S., Ayers G.P. and Hooper, M.A., 2005. Analysis of Precipitation Chemistry in Northern Thailand, Clean Air and Environmental Quality Volume 39, No.4. November: 43-47.
- 14. Park, C.J., Noh, H.R., Kim, B.G., Kim., S.Y., Jung, I.U., Cho, C.R., Hsn, J.S., 2001. Evaluation of acid deposition in Korea. Water, Air and Soil Pollution. 130:445-450.
- 15. Khare, P, Goela, A., Patelb, D. and Beharib, J., 2004. Chemical Characterization of Rainwater at A Developing Urban Habitat of Northern India, Atmospheric Research. 69 : 135–145.
- 16. Siti Mariam, S., Rusdin, L., Urban Sinyaw, S., Roslin, A.B., 2005. Rainwater characterization at an urban site in the Klang Valley, Malaysian Journal of Analytical Science, Vol.9, No.2: 254-266.
- 17. Jacobson, M.Z., 2004: The ShortTerm Cooling, but Long-Term Global Warming due to Biomass Burning, American Meteorological Society 17, 2909-2926.
- 18. Millero, F.J., 1996. Chemical Oceanography, second ed. CRC Press, Boca Raton, FL, Comment: 66.