Chemical Composition and Component Analysis of Atmospheric Wet Deposition in Chiang Mai Province

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Abstract

This study examined the chemical composition and sources of atmospheric wet deposition collected for 16 months from September 2006 to December 2007 at Mea Hia Research Center, Chiang Mai University, Chiang Mai Province. Total precipitation was 1219.0 mm. Mean Electro conductivity and pH values were 0.62 mS/m and 5.93, respectively. The relative volume weight mean concentrations eq/L of anions in a descending order were $SO_4^{2-}(11.94) > NO_3^{-}(8.13) > CI^{-}(5.31) > CH_3^{-}COO^{-}(3.72) > HCOO^{-}(2.61) > PO_4^{-3-}(0.32)$ and those of cations were $NH_4^{+}(17.29) > Ca^{2+}(12.89) > Mg^{2+}(5.77) > Na^{+}(3.63) > H^{+}(1.17) > K^{+}(1.93)$. The dominant ions for cations and anions are NH_4^{+} and SO_4^{-2-} , respectively. Results of a component analysis highlighted the influence of various sources, such as combustion fuel, agricultural activity, photochemical processes, soil resuspension and marine source on the chemical composition of the rainwater collected at this study site.

Keywords: Chemical composition, Wet deposition, Component analysis

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Introduction

Acid deposition is a serious environmental problem which has caused by incorporation of anthropogenic emissions of main acid forming gases, e.g. SO₂ and NO₂ (Brimblecombe, 2001; Das et al., 2005) Sulfur dioxide is the most important form of sulfur compound because it can be reacted with moisture in air to form sulfuric acid (Radojecvic and Harrison, 1992). Nitric acid, one of the major constituent of acid rain, is formed by reaction of NO, with hydroxyl radical in daytime and by reaction with ozone in nighttime (Richards, 1983). The potential for air pollution problems is due to high population and the consequent upward trend in agricultural production, industrialization, transport, energy consumption, biomass burning, etc. (Hu et al., 2003).

Acid deposition can be deposited into two forms which are wet and dry deposition. The first is wet deposition which sulfuric and nitric acids are incorporated into the clouds, and fall onto the ground in the form of rain, snow and mist. The second process, called dry deposition, occurs on fine and cloudy days. Airborne acids come directly through wind which can be transported thousands of kilometers. Consequently, the environmental effects of these pollutants are associated with the acidification of precipitation, visibility reduction and a general deterioration of human health (Goldberg et al., 2003). The resulting acid deposition cause serious environmental damage to aquatic, terrestrial and estuarine ecosystems.

The acid deposition monitoring program in Thailand had experienced about harmful of acid deposition due to SO_2 emitted from the Mae Moh lignite-fired power plant in Lampang Province (Thepanondh et al., 2005). Acid deposition in

Khon Kaen and Nakhon Ratchasima were high at the beginning of the rainy season and the first rainfall after a dry spell, due to more pollutants in the air. It was found that NH_4^+ , NO_3^- , and SO_4^{2-} were the main chemical components of rainwater (Luangjame et al., 2005). Monitoring and analysis of acid deposition in Chiang Mai during 2003-2004 showed that the dominant constituent detected in wet samples was NO₃⁻ and the highest deposition in dry samples in forms of particles were NH_4^+ and SO_4^{2-} (Chirasathaworn, 2005). After that, during August 2005 to July 2006 the rainwater samples have been collected by both bulk and wet-only collectors. The result showed that NH_4^+ and SO_4^{2-} were the dominant cation and anion, respectively. It can be assumed that sources of acid pollutants in Chiang Mai could be from vehicle internal combustion, agricultural activities and fuel burning in industrial processes for NO, NH, and SO, respectively (Chantara and Chunsuk, 2008). In the dry period of the year 2007, air pollution presented in form of haze occurs in Northern part of Thailand. Source of pollutant was claimed to be open burning including agricultural activities and forest fire. Data analysis might help in identifying possible sources of emission by factor analysis.

The aims of this study are to monitor and analyze chemical composition of wet deposition collected by wet-only collector, and to identify potential sources of the wet deposition in Chiang Mai by factor analysis.

Methodology

Sampling Site

A sampling site (Figure 1) is located at meteorological station in the area of Mea Hia



Figure 1. Location of sampling site

Research Center, Chiang Mai University, Muang District, Chiang Mai Province, which is in agricultural area and an opening in a large open meadow close to the reservoir. This site was classified as rural site based on Acid Deposition Monitoring Network in East Asia (EANET) criteria. It is located at latitude 18° 45′ 40.3″ N and longitude 98° 55′ 54.3″ E. Its elevation is 334 meter above sea level.

Sampling and analysis

Rain samples were collected on a daily basis by using a wet only collector with an automatic lid. Sampling has been collected at 9.00 am local time. De-ionized water with conductivity < 0.15 mS/m was used for cleaning a sampling bucket after sample collection even in case of no rain. Sampling period was 16 months started from 1 September 2006 to 31 December 2007. The sampling period has been divided into four sub-periods; Wet I (September–October 2006), Dry I (November 2006–April 2007), Wet II (May – October 2007), Dry II (November–April 2007). The rainwater sample was weighed and divided into two parts. The first part was for electo–conductivity (EC) and pH measurement under controlled temperature at 25 °C using conductivity and pH meters, respectively. The second part of the sample was filtered through 0.45

m cellulose acetate filter paper and stored in the dark at 4 °C until ion analysis was performed, typically within a week after sampling. The Metrohm ion chromatograph was used for determination of major cations (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) and major anions (HCOO⁻, CH₃COO⁻, Cl⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻). Hydrogen ion (H⁺) concentration was

derived from pH value (EANET,2000). A varimax rotation with Kaiser Normalization of Principle Components Analysis by SPSS program (version 15) was used for determination of factors underlying the inter-correlations between the measured species. In order to identify relationships between the various ionic species in rainwater precipitation, Pearson correlation (r) was carried out on wet deposition ion data.

Result

Rain precipitation amount

The number of wet precipitation samples collected by wet only collector was 125 samples. Precipitation data recorded by The Mae Hia Research Center Office and Chiang Mai Meteoro-logical Center were 119 days and 127 days, respectively, which equal to 98 % and 105% respectively, in comparison to the sample number collected this study. There was no precipitation occurred for 5 months (November 2006-March 2007) of the study.

pH Measurement of rain water samples

The acid precipitation refers to any precipitate form which has pH lower than 5.6. The distribution of pH values are illustrated in Figure 2.



Figure 2. Frequency distribution of precipitation pH values (n=120)

The distribution of pH values of wet samples was made from 120 samples (precipitation amount > 4 mm). Figure 2 shows the non-normal distribution (skewed to the left) which is the character of rain samples in clean area. Monthly mean pH values are shown in Figure 3. The precipitation was found to be slightly acids (pH<5.6) in April 2007. The changing of meteorological condition was affected to sample concentrations. The monthly volume weight mean (VWM) pH ranged from 4.80 to 6.95 and the VWM of pH values was 6.18. There was approximately 10% of rain samples which have pH values lower than 5.60. In the dry I period, that was no precipitation between November 2006 to March 2007. The amount of rain precipitation affected to the pH values of the samples. It can be seen that low amount of precipitation resulted in low pH values, while high amount of those resulted in opposite. The mean of pH values were lowest in April 2007 which has the lowest amount of precipitation. Apart from that, low pH value is properly from pollutants deposited in the atmosphere after long period of dry season.



Figure 3. Variation of monthly amount of precipitation and mean values of pH

Measurement of Electro Conductivity (EC)

EC value indicates level of ionic contamination in precipitation. High EC value indicates high ionic contamination. EC value of deionized water is normally less than 0.15 mS/m. Number of rain water samples measured for EC were 120. The VWM EC values of the rain samples were 0.62 mS/m. The maximum detected EC values were in April 2007 whereas the minimum of those were in August 2007 (see Figure 4). Amount of rain precipitation affected to the EC values of the samples, low amount of precipitation resulted in high EC values, while high amount of those resulted in low EC values.



Figure 4. Variation of monthly amount of precipitation and mean values of EC

In dry I period, there was almost no rain excepted in April 2006, which consequently presented high EC values. It can be from the large amount of pollutants in the atmosphere such as biomass burning in the area around the sampling site. When it started to rain again, these pollutants were scavenged from the atmosphere. Consequently, in the rain itself contains high concentrations of the pollutants. Figure 4 reveals that amount of precipitation is inverted with EC values, which means that high precipitation, results in low EC value. On the other hand, low precipitation, causes high EC value due to dilution effect.

Measurement of Ion Concentration in Rainwater Samples

Monthly VWM concentrations of the major chemical components are illustrated in Figure 5. It was found that most of ion concentrations were high in the dry I period due to low amount of rain precipitation and early of rainy, while low concentrations were found in the wet periods. Most of the highest concentrations of anions and cations were found in April 2007. On the other hand, most of the lowest concentrations of anions and cations were found in June to July 2007. The relative volume weight mean concentrations eq/L of anions in a descending order were $SO_4^{2-}(11.94) > NO_3^{-}(8.13)$ > Cl⁻ (5.31) > CH₃COO⁻ (3.72) > HCOO⁻ (2.61) > PO_{A}^{3-} (0.32) and those of cations were NH_{A}^{+} $(17.29) > Ca^{2+} (12.89) > Mg^{2+} (5.77) > Na^{+}$ $(3.63) > H^+ (1.17) > K^+ (1.93)$. The dominant ions for cations and anions are NH_{4}^{+} and SO_{4}^{2-} , respectively. The relative of percentage of total caions and anions were NH_4^+ (23%) > SO_4^{2-} (17%) > Ca^{2+} (16%) > NO_{3}^{-} (11%) > Mg^{2+} (8%) > Cl^{-} (7%) > CH_oCOO⁻ (5%) > Na⁺(5%) > HCOO⁻ $(4\%) > K^{+}(3\%) > H^{+}(2\%) > PO_{4}^{3-}(0.4\%)$ (shown in Figure 6). The ratio between total cations and total anions is 51:49 in the unit of eq/L.

Comprehensive analysis

Data screening

Comprehensive analysis such as neutralization factor (NF), correlation and principle component analysis was processed. In order to get high precision and correct data, it is necessary to do quality control. Data quality of rainwater samples was checked by ionic balance (R_1) and conductivity balance (R_2) . The data was rejected if it was not met

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Figure 5. Monthly average variability of rain precipitation; (A) major anion concentrations and (B) cation concentrations



Figure 6. Relative of percentage of total caions and anions base on unit of eq/L

the quality criteria. R_1 and R_2 values illustrate the accuracy of ion analysis and EC measurement, respectively. The calculated values were then compared with the criteria set up by the EANET. In wet-only samples, about 42% of R_1 and 73% of R_2 were accepted. While 36% of both R_1 and R_2 were accepted and used for statistic analysis.

Acid neutralization

In case that all the nss-SO₄²⁻ and NO₃⁻ existed in the form of free acid forms, the summation of those should equal to H⁺ (Hu et al.,2003). VWM concentrations of nss-SO₄²⁻ and NO₃⁻ were 11.90 and 8.10 eq/L, respectively. Therefore, the summation was 20.00 eq/L. From this figure, the pH should be 5.93, but from the measurement it was 6.18 which are lower by 0.25. It indicated that the rainwater precipitation had some neutralization. From previous studies (Das et al., 2005;Saxena et al., 1996), NH₄⁺, Ca²⁺, K⁺ and Mg²⁺ have been used to validate by calculating neutralization factor .Neutralization factors (NF) in this study for those mentioned ions are shown in Table 1.

Table 1. Neutralization factors of Ca^{2+} , NH_4^+ , Mg^{2+} and K^+

	NH_4^+	CA^{2+}	MG^{2^+}	K^{+}
NF	0.86	0.64	0.29	0.10

Table 1 illustrates order of NF, which was $NH_4^+ > Ca^{2+} > Mg^{2+} > K^+$. This feature suggests that in rain water samples, the acidity is mainly neutralized by NH_4^+ based on the fact that NH_4^+ concentration was the highest cation concentrations, which probably resulted from agricultural activities surrounded the sampling area. However, the NF values of Ca^{2+} were higher than Mg^{2+} and K^+ that indicating the influence of soil resuspension.

From the summation of the non sea salt nss-SO₄²⁻ and NO₃⁻, it was indicated that acid neutralization was occurred (Hu et al., 2003). Normally, neutralization is frequently reported and attributed to NH₄⁺ and Ca²⁺ (Vong et al., 1990). Consequently, it was expected that the summation of concentrations of H⁺, NH₄⁺ and Ca²⁺ correlated with summation of concentrations of nss-SO₄²⁻ and NO₃⁻ in the even that the acidity of the rainwater precipitation is mainly neutralized by NH₄⁺ and Ca²⁺. This hypothesis was confirmed by the scatter plots between those two summation values (Figure 7).



Figure 7. Correlation of $([H^+] + [NH_4^+] + [Ca^{2+}])$ and $(nss-[SO_4^{2-}] + [NO_3^-])$ (N=44)

Source analysis of major ion composition

In order to find possible association sources of ions in rainwater precipitations, component analysis was carried out in order to determine the factors underlying the inter-correlations between the measured species. The method used was principle component analysis (PCA). A varimax rotation with Kaiser Normalization of Principle Components Analysis by SPSS program (SPSS for Windows version 15) was applied and the results are shown in Tables 2.

The principle component analysis identified that there was three factors contributed about 92 % of the variance to the log transformed dataset. Given observation that only factor loadings higher than 0.5 are deem to be statistically significant (Vong, 1990; Ungvari et al., 2007). For component 1, wet log transformed datasets provided high loading on the SO_4^{2-} , NO_3^{-} , NH_4^{+} and Mg^{2+} . It associated reasonably with combustion process $(SO_4^{2-} \text{ and } NO_3^{-})$ and neutralization components (NH₁⁺ and Mg²⁺), which indicated that they come from agricultural area. The variables of the component 2 were Cl⁻, Na⁺, Ca²⁺ and K⁺, hereafter referred to as the marine source (Cl⁻, Na⁺ and K⁺) (Hu et al., 2003) and soil resuspend for Ca²⁺ (Saxena et al., 1996). Component 3 shows high loading on HCOO⁻, CH₂COO⁻ and H⁺, which can be indicates a prevalence of its photochemical production (Ungvari et al., 2007).

Conclusion

Investigation of chemical composition of rainwater was carried out from September 2006 to December 2007. The results showed that the mean EC and pH values were 5.93 mS/m and 0.62, respectively. During November 2006 to March 2007 there was no precipitation, therefore high ions

concentration was detected in rain water samples collected in April 2007, which is in the first period of rain. The relative percentage of total caions and anions in the unit of eq/L were $NH_4^+ > SO_4^{2-} > Ca^{2+}$ $>NO_{q}^{-}>Mg^{2+}>Cl^{-}>CH_{q}COO^{-}>Na^{+}>HCOO^{-}>K^{+}>COO^{-}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>COO^{-}>K^{+}>COO^{-}>K^{+}>COO^{-}>COO^{-}>K^{+}>COO^{-}>COO^{-}>COO^{-}>COO^{-}>COO^{-}>K^{+}>COO^{-}$ $H^+ > PO_A^{3-}$. NH_A^+ and SO_A^{2-} are dominant ions for cations and anions, respectively. 120 rain samples of this study, 43 samples were qualified for both R (ion balance) and R_{a} (conductivity balance). The dominating neutralizing components in the collected samples were NH_{4}^{+} and Ca^{2+} . R₁ (ion balance) and R₂ (conductivity balance). The dominating neutralizing components in the collected samples were NH⁺ and Ca²⁺. Enrichment factor analysis based on Na^{+} indicated that SO_{4}^{2-} , K^{+} and Ca^{2+} were enriched, revealing significant influences of local sources with exception more than half of Cl⁻ content which came from marine source. Sea salt fraction calculation for rain water samples revealed that about 80% Cl⁻ were from marine origin.

The factor analysis was also determined to explain the sources of the pollutants in acid deposition. There were three factors contributed about 92 % of the variance to the log transform dataset. For component 1, that indicated the contribution of combustion process ($SO_4^{2^-}$ and NO_3^-) and agricultural activities (NH_4^+ and Mg^{2^+}). The variables of the component 2 were referred to as the marine source (CI^- , Na^+ and K^+) and soil resuspension for Ca^{2^+} . Component 3 represented the photochemical production ($HCOO^-$, CH_3COO^- and H^+).

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