



## A four-year investigation on wet deposition in western Thailand

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Received 10 May 2007; revised 2 July 2007; accepted 10 August 2007

### Abstract

The investigation of pH variation and the chemical composition of rainwater have been studied from April 2003 to October 2006 at a rural area of Nakhon Pathom Province, western Thailand. The pH value ranged from 4.0 to 7.8 with an average of 6.1. Out of 319 rain events, 72 events were observed in acidic range (pH < 5.6). The pH of rainwater gradually increased over the sampling period. The volume-weighted mean concentrations ( $\mu\text{eq/L}$ ) of ion species followed the order:  $\text{Ca}^{2+} > \text{NH}_4^+ > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{Na}^+ > \text{Cl}^- > \text{CH}_3\text{COO}^- > \text{Mg}^{2+} > \text{K}^+ > \text{H}^+ > \text{HCOO}^- > \text{PO}_4^{3-}$ . Neutralization factor calculations reveal that  $\text{Ca}^{2+}$  plays a major role in neutralization processes in this area. Enrichment factor calculations indicate that  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were originated from non-marine sources. The statistical measure principle component analysis indicates influence of various local emission sources e.g., soil, limestone mines, biomass burning and agricultural emissions, on the chemical composition of rainwater.

**Key words:** acid rain; wet deposition; neutralization factor; enrichment factor; factor analysis

### Introduction

Acid deposition has become a crucial problem worldwide, due to its potential transboundary effects. In Thailand, rapid growth in the economy has led to a significant increase of anthropogenic pollution emission sources some of which are precursors of acid rain phenomenon. Previous studies in different regions of Thailand, e.g., Thepanondh *et al.* (2005) and Granat *et al.* (1996) revealed that the main cause of acid depositions was due to the contribution of local atmospheric pollutants from both natural as well as anthropogenic sources. In western Thailand, a variety of both natural and anthropogenic land-use activities may be the causes of occurrences of acid deposition. The land uses include tropical rain forests in the west, dense agriculture in the rural areas in the central to the east, transitions of agriculture to urban over the rest of the areas. Thus, it is important to investigate acid deposition in this region. The study is a part of the comprehensive research on acid deposition monitoring in Thailand in cooperation with the Pollution Control Department (PCD). The Department of Environmental Science, Faculty of Science, Silpakorn University has taken part in the monitoring in the western region. This article presents the situation of acid deposition during four years study (from 2003 to 2006). Statistical analyses have been conducted to evaluate correlations among atmospheric species and to investigate the possible emission sources.

### 1 Materials and methods

#### 1.1 Sampling site

The sampling site was located at Kampangsan meteorological station (14.1°N, 99.58°E), Nakhon Pathom Province, western Thailand. The site was specified as a rural area according to the criteria defined by the Acid Deposition Monitoring Network in East Asia (EANET). The samplers were mounted at an open field of a provincial meteorological monitoring station. In the immediate vicinity of the site there is a large experimental farm of Kasetsart University. The site is surrounded by suburban and agricultural areas. Characteristics of the sampling site are shown in Fig.1. There are secondary roads nearby the site, having a low traffic density around 1,000 vehicles/day. There are tropical rain forests at distances of 10 and 50 km west from the site. The sanitary landfill and the central area of limestone mines are about 10 km north and 60 km southwest from the site, respectively.

#### 1.2 Sample collection

Rainwater was collected on a daily basis using a wet-only collector (Model 301, Aerochem Metric Inc., USA). The sampling period was 43 months, from April 2003 to October 2006. The rainwater samples were stored in polypropylene bottles in a refrigerator. To prevent the degradation of ionic species by bacterial action, the samples were preserved by thymol (2-isopropyl-5-methyl phenol). Meteorological parameters during the sampling period were also recorded.

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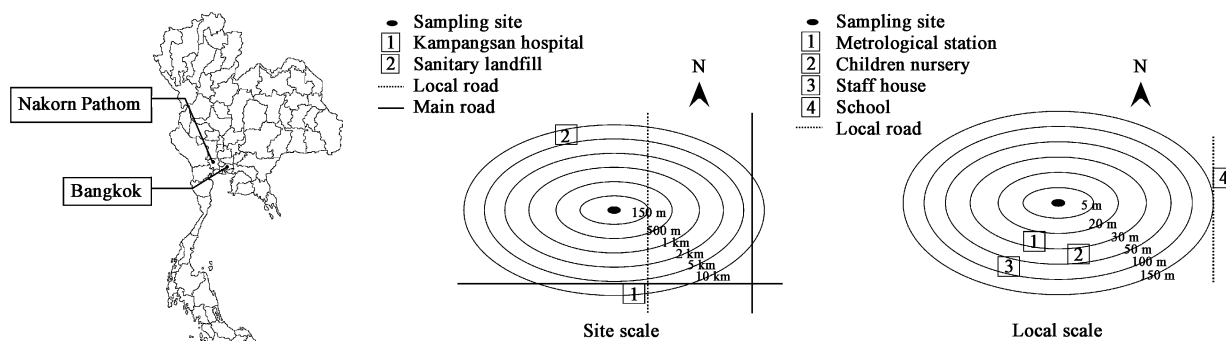


Fig. 1 Environment surrounding the sampling site.

### 1.3 Analysis

After collection, the samples were transported to the laboratory for chemical analyses. Each sample was divided into two portions. For non-filtrated portion, pH and electrical conductivity was measured using Sartorius model PP-50 and YSI model 3200, respectively. For filtrated portion, chemical species, which comprise  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{HCO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{H}^+$  were analyzed by ion chromatograph (Metrohm, model 732, Switzerland).

To ensure the data quality, as according to the EANAT guideline (EANAT, 2000), cation and anion balance (R1) and comparison between calculated and measured electric conductivity (R2) were conducted. The result, depicted in Fig.2, shows that most of R1 values are in the positive direction interpreting anion deficit (total cation (TC) measured is greater than total anion (TA) measured). This may be due to the presence of volatile organic acids such as carboxylic acids generated from microbial anaerobic reaction in a sanitary landfill located about 20 km north from the sampling site. Volatile carboxylic acids are mainly found in atmosphere due to their low molecular weight and high polarity, therefore it was reported to be a major fraction of the total organic carbon in fog, cloud water and precipitation (Chebbi and Carlier, 1996). Only two dominant species of carboxylic acids—formic and acetic acids—were analyzed in terms of their anion species in this study, but other acid species such as propionic acid, butyric acid, pyruvic acid were excluded. Majority of R2 values dense in the center indicates a good agreement between

EC calculated and EC measured.

## 2 Results and discussion

### 2.1 Variation of pH value

The average pH of rainwater, calculated from volume-weighted mean concentration of  $\text{H}^+$ , equals 6.0. Fig.3 displays the percent frequency distribution of pH for 319 rain events. Most of the samples (227 events, 72.8%) indicate that the pH of the rainwater is in the alkaline range as compared to the reference pH 5.6 for cloud water at equilibrium with atmospheric  $\text{CO}_2$ . This could be due to the presence of alkaline dust suspended in the atmosphere (Kulshrestha *et al.*, 2003). These alkaline dust particles play an important role as buffering agent. An observation carried out at the site reveals that the major proportions of  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  in aerosols are 28.60 and 24.43 mmol/L, respectively (Panyakapo and Bohuwech, 2004, 2005, 2006). However, there were 72 rain events in the acidic range as shown in Fig.3. Overall, as can be observed from Fig.4, the pH of rainwater gradually increases over the sampling period. This can indicate both the decreasing of acid species and the increasing of alkali species.

### 2.2 Chemical composition of rainwater

Volume-weighted mean concentrations ( $\mu\text{eq/L}$ ) of the rainwater chemical components are summarized in Table 1. The order of major ionic species in decreasing concentrations is as follows:  $\text{Ca}^{2+} > \text{NH}_4^+ > \text{SO}_4^{2-} > \text{HCO}_3^- >$

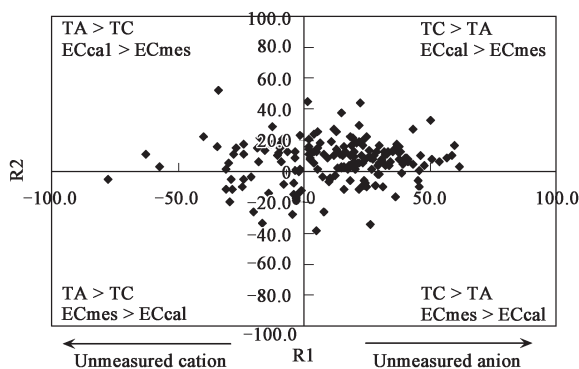


Fig. 2 Quality of analytical data.

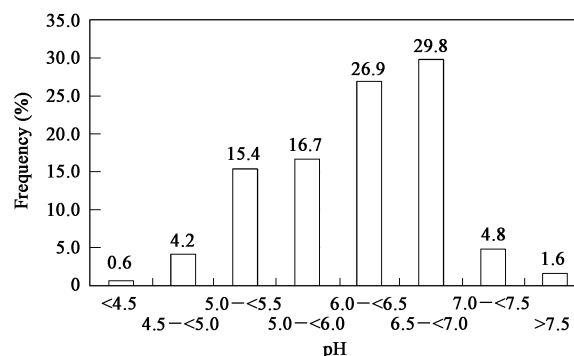
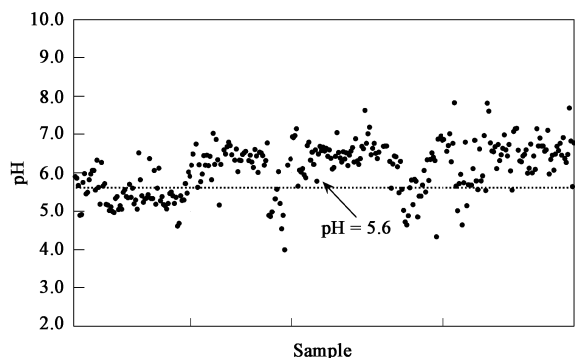


Fig. 3 Frequency distribution of pH.



**Fig. 4** Variation of pH of rainwater at Nakhon Pathom, western Thailand. From April 2003 to October 2006.

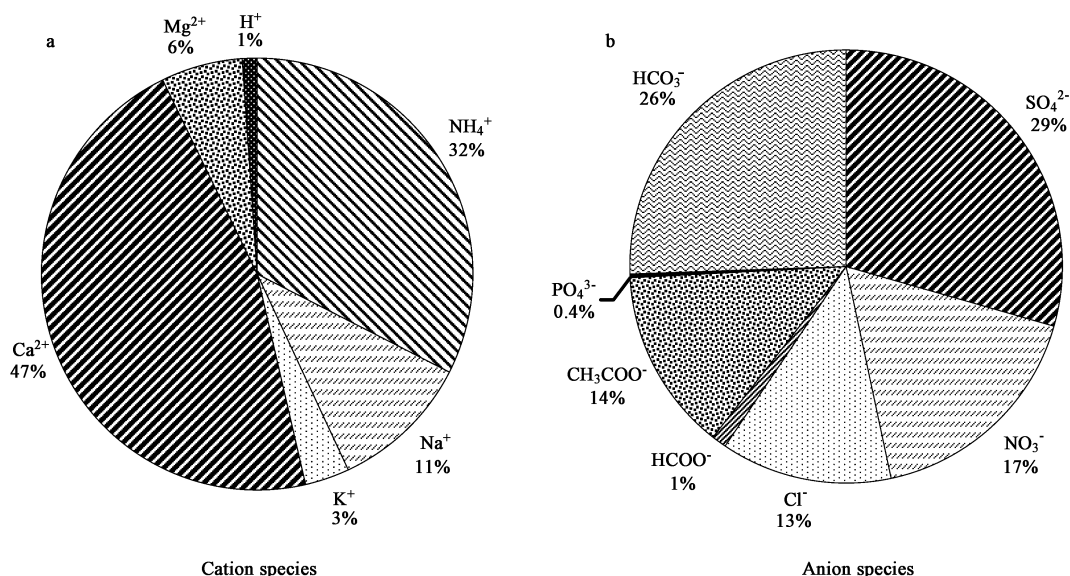
**Table 1** Concentrations of chemical components in rainwater

Chemical species*	Min.–max. ( $\mu\text{eq/L}$ )	Arithmetic mean ( $\mu\text{eq/L}$ )	Volume-weighted mean concentration ( $\mu\text{eq/L}$ )
$\text{SO}_4^{2-}$	nd–317.5	40.2	28.1
$\text{NO}_3^-$	nd–591.4	23.6	15.2
$\text{Cl}^-$	1.1–697.0	27.7	12.4
$\text{HCOO}^-$	nd–14.7	0.8	0.6
$\text{CH}_3\text{COO}^-$	nd–158.7	13.6	7.8
$\text{PO}_4^{3-}$	nd–17.4	0.4	0.1
$\text{HCO}_3^-$	5.7–374.5	29.8	16.4
$\text{NH}_4^+$	nd–347.6	49.1	36.6
$\text{Na}^+$	nd–836.9	34.4	13.9
$\text{K}^+$	nd–538.1	7.9	3.6
$\text{Ca}^{2+}$	9.0–1802.4	77.8	51.3
$\text{Mg}^{2+}$	nd–186.0	9.9	6.6
$\text{H}^+$	nd–102.3	2.8	2.7
Precipitation (mm)	0.2–124.3	10.6	
pH	4.0–7.8	6.1	6.0

\*Organic ion species ( $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{PO}_4^{3-}$ ) were started to analyze at November 2004, nd: not detected.

$\text{NO}_3^- > \text{Na}^+ > \text{Cl}^- > \text{CH}_3\text{COO}^- > \text{Mg}^{2+} > \text{K}^+ > \text{H}^+ > \text{HCOO}^- > \text{PO}_4^{3-}$ .

Figure 5 displays the fractional contributions of cation and anion species. As for cation,  $\text{Ca}^{2+}$  is the majority



**Fig. 5** Fractional contributions of cation (a) and anion (b) species.

species (concentration of  $55.1 \mu\text{eq/L}$  accounting for 47% of total cations). Main sources of  $\text{Ca}^{2+}$  can be the crusting processes and wind-blown soil (Kulshrestha *et al.*, 2003; Okay *et al.*, 2002). A current study carried out at surrounding areas of the site reveals that the highest concentration of ion composition in soil is  $\text{Ca}^{2+}$  (Sanmanee *et al.*, 2007). In addition, contribution of  $\text{Ca}^{2+}$  at sampling sites can be originated from a group of limestone mines located about 60 km southwest from this site. This potentially contributes  $\text{CaCO}_3$  dust to the atmosphere by local wind systems.

$\text{NH}_4^+$  is the second highest cation species. Previous studies revealed that the use of fertilizers as well as wastes from agricultural and domestic activities are the main sources of gaseous ammonia emissions (Dianwu and Anpu, 1994; Fujita *et al.*, 2000; Kulshrestha *et al.*, 2003; Thepanondh *et al.*, 2005). Such activities seem to explain the high  $\text{NH}_4^+$  precipitation in the sampling site, where a sanitary landfill and farm produces are adjoining.

As for anion species,  $\text{SO}_4^{2-}$  has the highest proportion (volume-weighted mean concentration of  $29.3 \mu\text{eq/L}$ , accounting for 29% of total anions), while  $\text{HCO}_3^-$  is the second highest anion species accounting for 26% of total anions.  $\text{NO}_3^-$  and  $\text{Cl}^-$  have shares of 17% and 13%, respectively.  $\text{CH}_3\text{COO}^-$  and  $\text{HCOO}^-$  contribute approximately 15%. This may be due to the presence of precursors like acetic acid ( $\text{CH}_3\text{COOH}$ ) and formic acid ( $\text{HCOOH}$ ) in the atmosphere. Such organic acids are produced from microbiological anaerobic digestion processes in the sanitary landfill. The high value of  $\text{SO}_4^{2-}$  was contributed by emissions from fossil-fuel combustion (Thepanondh *et al.*, 2005; Okay *et al.*, 2002). Major activities consuming fossil-fuel found surrounding the site consist of a rice mill, vehicles driving and household cooking stoves.

The comparative study of chemical composition revealed an exciting similarity to previous work. Thepanondh *et al.* (2005) reported the ionic species concentrations observed at an industrial site in northern Thailand following the order  $\text{HCO}_3^- > \text{NH}_4^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Na}^+ > \text{Cl}^- > \text{NO}_3^- > \text{K}^+ > \text{Mg}^{2+} > \text{H}^+ > \text{PO}_4^{3-} > \text{F}^-$ .

Granat *et al.* (1996) observed the chemical compositions at two rural sites in the Northwest (Srinakarini dam) and Northeast (Nampong dam) at distances of about 100 and 400 km from the site of this study, respectively. At the first site, ionic species concentrations followed the order  $\text{SO}_4^{2-} > \text{Ca}^{2+} \sim \text{NH}_4^+ > \text{H}^+ > \text{Cl}^- > \text{Na}^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+$ , similar to the second site which had the order  $\text{NH}_4^+ > \text{SO}_4^{2-} > \text{H}^+ > \text{Ca}^{2+} \sim \text{NO}_3^- > \text{Cl}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ . These are also comparable to an observation by Thepanondh (2004) performed between 1999 and 2001 at the remote site of Kanchanaburi province, which is approximately 60 km northwest of the site of this study. Results of this study showed the order of ionic species concentration as follows:  $\text{Cl}^- > \text{Ca}^{2+} > \text{Na}^+ > \text{SO}_4^{2-} \sim \text{NH}_4^+ \sim \text{K}^+ > \text{NO}_3^- > \text{H}^+ > \text{Mg}^{2+}$ . On the contrary, this study presented the concentration of ionic species, observed at the urban site of Bangkok, capital of Thailand, having the order as  $\text{SO}_4^{2-} > \text{NH}_4^+ > \text{Ca}^{2+} > \text{NO}_3^- > \text{Na}^+ > \text{Cl}^- > \text{H}^+ > \text{Mg}^{2+} > \text{K}^+$ . These remarkably suggest the effect of urban traffic and industry induced emissions of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  precursors like  $\text{SO}_2$  and  $\text{NO}_x$ .

Table 2 shows the matrix of Pearson correlation coefficients ( $p < 0.05$ ) among the major ions analyzed in rainwater. Several ions were highly interrelated. A high correlation between  $\text{Cl}^-$  and  $\text{Na}^+$  in rainwater was found with high level of significance ( $r = 0.96$ ) suggesting a marine origin.  $\text{Cl}^-$  had also a strong correlation with  $\text{K}^+$  ( $r = 0.96$ ). This indicates that part of the  $\text{Cl}^-$  is originated from a specific source.  $\text{K}^+$  is associated with airborne particles generated by biomass burning (Khare *et al.*, 2004). As from the observation, utilization of charcoal as household cooking fuel as well as burning of agricultural residuals preparing for cultivation by farmers could be the main source of  $\text{K}^+$  emission in this area. Strong relationships are also found between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ( $r = 0.92$ ), and between  $\text{Na}^+$  and  $\text{K}^+$  ( $r = 0.95$ ). These again may be owing to the effect of the local limestone mines. The observation reveals that there is a group of limestone mine in Ratchaburi Province far from the site about 60 km in direction to the southwest. In addition, the influence of local road traffic, which enhances the suspension of soil derived particles into the air, may be a factor contributing to such particles (Tanner and Wong, 2000).

The moderate correlation between  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ( $r = 0.75$ ) suggests that precursors of both species, i.e.,  $\text{SO}_2$  and  $\text{NO}_x$  were generated from the same sources like fossil fuel burning. The fairly significant relationships between  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  ( $r = 0.75$ ), and between  $\text{NO}_3^-$  and  $\text{NH}_4^+$

( $r = 0.71$ ) reveal co-occurrence of  $\text{NH}_4^+$  with  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in precipitation. This may be caused by dissolution of aerosols/secondary pollutants in rainwater containing  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  (Khare *et al.*, 2004). In addition, utilization of ammonium sulfate as fertilizer (formula of 21-0-0) in local plantation may be a further source of such components as well (Kampangsan District Agricultural Office, 2005).

### 2.3 Neutralization factor

Neutralization factor (NF) is a parameter used for indicating degree of neutralization of cations by specific anion species in the precipitation. The role of  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  are validated by calculating neutralization factors using the following equation:

$$\text{NF}(x) = \frac{C_x}{C_{\text{NO}_3^-} + C_{\text{SO}_4^{2-}}} \quad (1)$$

where,  $C_x$  is the concentration of cation ( $x$ ) of interest.

In the above equation, volume-weighted mean concentrations of  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  were utilized. The average values of NF over period of the study for  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  are 1.68, 0.93 and 0.21, respectively. As mentioned earlier, as Ca aerosols are released from limestone mines and natural soil, the highest NF value for  $\text{Ca}^{2+}$  was therefore attained. This indicates that major neutralization occurs due to  $\text{Ca}^{2+}$ , while  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  play minor roles.

### 2.4 Variation with deposition

Monthly variation of volume-weighted mean concentration of measured ionic species with respect to occurrences of precipitation during four years is given in Fig.6. As expected, concentration of ionic species appeared to have an inverse relationship with the precipitation as they were dissolved in the precipitation by means of rain-out and wash-out mechanisms. This is a crucial phenomenon for maintaining neutralization process in this site.

Principally,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are produced by means of oxidation reactions of  $\text{NO}_x$  and  $\text{SO}_x$ , respectively. Once they are released from emission sources to the atmosphere, their residence times in air, before deposition to the ground, are 10 and 1.8 d, respectively (Meszaros, 1992). During dry season, both  $\text{SO}_x$  and  $\text{NO}_x$  deposit to the ground as dry deposition with different deposition rates. Due to  $\text{NO}_x$  having relatively higher residence time in the air than  $\text{SO}_x$ , dry deposition of  $\text{NO}_x$  is slower. This gives a higher opportunity for  $\text{NO}_x$  remaining in the air

**Table 2** Pearson correlation coefficients ( $r$ ) between major ionic concentrations in rainwater

	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{Cl}^-$	$\text{HCO}_3^-$	$\text{NH}_4^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$
$\text{NO}_3^-$	<u>0.75</u>							
$\text{Cl}^-$	0.22	0.06						
$\text{HCO}_3^-$	0.11	0.15	0.31					
$\text{NH}_4^+$	<u>0.75</u>	<u>0.71</u>	-0.01	0.07				
$\text{Na}^+$	0.18	0.03	<u>0.96</u>	0.30	-0.05			
$\text{K}^+$	0.13	0.00	<u>0.96</u>	0.30	-0.07	<u>0.95</u>		
$\text{Ca}^{2+}$	0.67	0.67	0.25	0.08	0.45	0.23	0.20	
$\text{Mg}^{2+}$	0.63	0.62	0.21	0.04	0.44	0.21	0.15	<u>0.92</u>

The underline data are the significant Pearson correlation coefficients indicating high and moderate correlations. Significance level of 0.05.

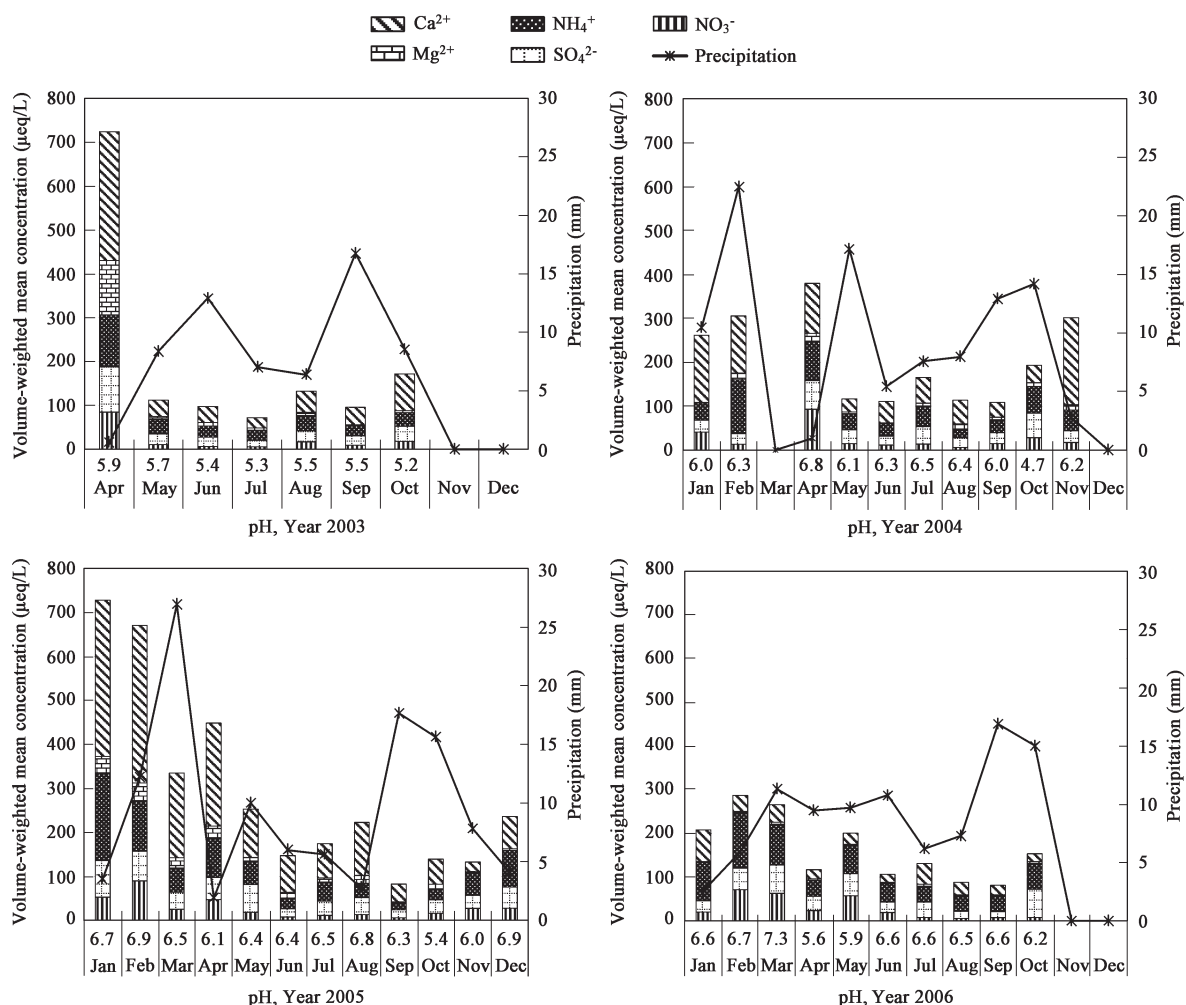


Fig. 6 Monthly weighted average concentrations compared with occurrences of precipitation during the year 2003 to 2006.

and playing a major role as a precursor causing acidity of rainwater during the dry season.

During wet season, there is frequently rain and having sufficient volume of rainwater, this gives a high opportunity for SO<sub>x</sub> to be dissolved as bisulphite (HSO<sub>3</sub><sup>-</sup>) and H<sup>+</sup>. Bisulphate is then oxidized continuously to SO<sub>4</sub><sup>2-</sup> and more H<sup>+</sup> (Howells, 1995). A comparative field study into SO<sub>2</sub> and NO<sub>2</sub> oxidation to SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, respectively has concluded that, whereas droplet-phase reactions are important for SO<sub>2</sub> oxidation, gas-phase reactions are predominant for the oxidation of NO<sub>2</sub> (Radojevic, 1992). These, therefore, draw a conclusion that during the wet season SO<sub>4</sub><sup>2-</sup> is major species playing a role causing acidity in rainwater, while NO<sub>3</sub><sup>-</sup> plays only a minor role. On the contrary, during the dry season NO<sub>3</sub><sup>-</sup> plays a major role.

In Fig.6, pH values measured during wet season are likely lower than dry season. This may be due to following reasons: firstly, as observed at this site (Fig.5), SO<sub>4</sub><sup>2-</sup> has higher proportion than NO<sub>3</sub><sup>-</sup>; secondly, as mention earlier, SO<sub>4</sub><sup>2-</sup> plays a major role in inducing acidification of rainwater during wet season.

The relationship between individual ionic species and precipitation can be considered by *r* values given in Table 3. The precipitation had negative correlations with almost

Table 3 Correlation of components with precipitation

	<i>r</i> value		<i>r</i> value
Precipitation	1		
pH	-0.13	NH <sub>4</sub> <sup>+</sup>	-0.15
SO <sub>4</sub> <sup>2-</sup>	-0.20	Na <sup>+</sup>	-0.14
NO <sub>3</sub> <sup>-</sup>	-0.06	K <sup>+</sup>	-0.08
Cl <sup>-</sup>	-0.16	Ca <sup>2+</sup>	-0.12
PO <sub>4</sub> <sup>3-</sup>	-0.08	Mg <sup>2+</sup>	-0.12
HCO <sub>3</sub> <sup>-</sup>	-0.004	H <sup>+</sup>	0.21

all species except H<sup>+</sup>. The increasing of H<sup>+</sup> suggests that the greater the rainfall, the lower the concentrations of species but the higher the acidity (Khare *et al.*, 2004).

Figure 7 depicts the monthly neutralization factors during period of the study. A high degree of neutralization occurred during the dry season, when there was low precipitation. Among the considered cation species, Ca<sup>2+</sup> plays an important role in neutralization reaction over entire period of the time. This agrees with the results of neutralization factor as explained earlier.

The presence of high amount of Ca<sup>2+</sup> and Mg<sup>2+</sup> during dry season is related to the higher limestone mine's activities in dry season compared to the wet season. Moreover, during the dry season, when the amount of rainfall is relatively low, the cation species originated from those

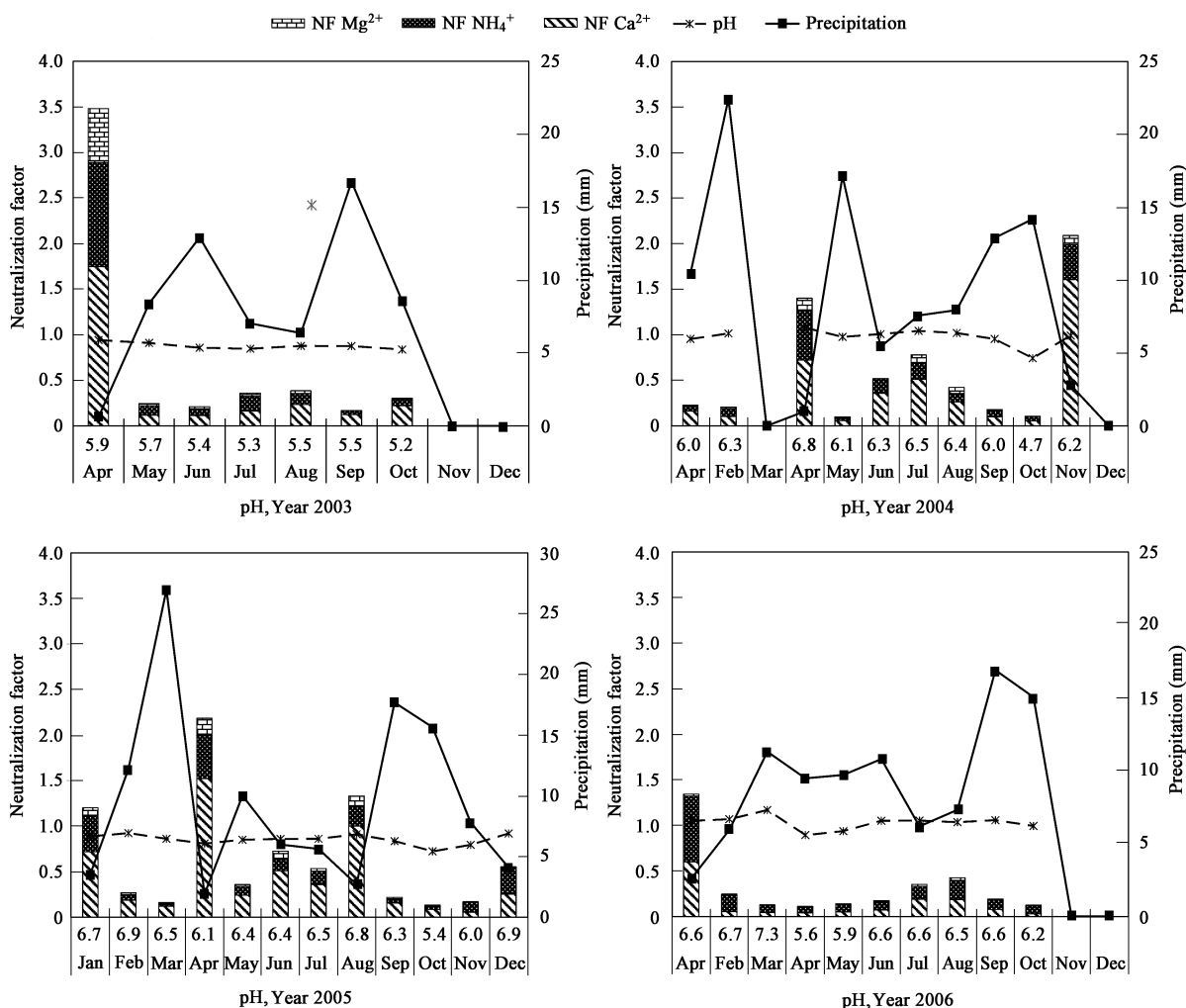


Fig. 7 Monthly neutralization factors (NF) compared with pH and occurrences of precipitation during the year 2003 to 2006.

limestone mines has a possibility to disperse in a longer distance comparing to the wet season. These draw to conclude that during the occurrences of low precipitation, the high concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are present and induce increasing of neutralization process, thus raising the pH values.

## 2.5 Marine contribution

The influence of marine on the contribution of ion species can be investigated by using ratios like sea salt fractions and enrichment factors (EF) (Ahmed *et al.*, 1990; Okay *et al.*, 2002). For this purpose,  $\text{Na}^+$  was taken as a reference element assuming that all  $\text{Na}^+$  originates from marine sources (Kulshrestha *et al.*, 1996, 2003). Table 4 shows the average ratios of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with respect to  $\text{Na}^+$ . Higher rainwater ratios of  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  than the corresponding seawater ratios suggested non-marine origin for such components. On the contrary, the close ratio of  $\text{Cl}^-$  to  $\text{Na}^+$  in rainwater (1.13) compared to the corresponding seawater ratio (1.166) indicated that greater part of  $\text{Cl}^-$  found at this site appear to be of marine contribution.

To make a distinction of aerosol sources of the elements in precipitation, the enrichment factor (EF) is calculated

using the equation:

$$EF(x) = \frac{C_x/C_{\text{Na}^+_{\text{rain}}}}{C_x/C_{\text{Na}^+_{\text{seawater}}}} \quad (2)$$

where,  $C_x$  is concentration of ion ( $x$ ) of interest.

This calculation is based on the elemental ratio found between ions collected in precipitation, compared with reference seawater, giving useful information about the sources of the elements. Principally, an EF value much smaller than 1 or much greater than 1 is considered concentrated or diluted relative to marine (Okay *et al.*, 2002).

The EF values are given in Table 4. As expected,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were enriched showing significant influence of local sources rather than marine source, while  $\text{Cl}^-$  was close to 1 due to the seashore being almost 60 km far from the sampling site.

The calculations of sea salt (SS) and non-sea salt (NSS) fractions were also conducted. The non-sea salt concentration takes into account  $\text{Na}^+$  as reference component. The non-sea salt concentration can be obtained by the equation below,

$$\text{NSS}(x) = C_T - f_x C_{\text{Na}^+} \quad (3)$$

**Table 4** Comparison of seawater ratio with rainwater components and enrichment factors

	$C_{\text{SO}_4^{2-}}/C_{\text{Na}^+}$	$C_{\text{Cl}^-}/C_{\text{Na}^+}$	$C_{\text{K}^+}/C_{\text{Na}^+}$	$C_{\text{Ca}^{2+}}/C_{\text{Na}^+}$	$C_{\text{Mg}^{2+}}/C_{\text{Na}^+}$
Seawater ratio	0.0603	1.166	0.0218	0.0219	0.1137
Ratios in rainwater	2.98	1.13	0.30	4.68	0.58
Enrichment factor	49.38	0.97	13.80	213.91	5.10

where,  $C_T$  is the total concentration of ion ( $x$ ) of interest,  $f_x$  is correction factor for concentration of ion ( $x$ ) of interest ( $X$ ) component.

Table 5 presents the NSS and SS of the important ions. The average NSS value of  $\text{SO}_4^{2-}$  was found to be 93.8%, showing the effect of non-sea sources like fossil-fuel combustion. Similarly, the high average NSS values of  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  (98.7%, 91.1% and 76.4%, respectively) suggest non-sea source contributions, which again may be the cause of earth's crust including limestone mines as well as suspension of soil due to vehicles driving.

**Table 5** Sea salt and non-sea salt fractions of the rainwater components

	$\text{SO}_4^{2-}$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$
Concentration ( $\mu\text{eq/L}$ )	28.1	3.6	51.3	6.6
Non-sea salt ( $\mu\text{eq/L}$ )	26.4	3.2	50.7	5.1
Sea salt fraction (%)	6.2	8.9	1.3	23.6
Non-sea salt fraction (%)	93.8	91.1	98.7	76.4

## 2.6 Source analysis of major ionic composition

The statistical method, factor analysis (Principle Component Analysis-PCA), has been widely used in previous studies (Astel *et al.*, 2004; Khare *et al.*, 2004; Tanner and Wong, 2000; Thepanondh *et al.*, 2005) to investigate the number of possible sources having a major influence on the precipitation components. The method is based on mathematical modelling of the reduced factor analytical solution, to find a small number of factors from a data set of many correlated variables thereby extracting latent information. The original data matrix is decomposed into the product of a matrix of factor loading and a matrix of factor scores along with the residual matrix (containing variance of data set i.e., analytical uncertainties) (Khare *et al.*, 2004). Factor analysis was carried out by the principal component method using the SPSS PC++ version 11.5 for Windows. It was carried out on the data in an attempt to determine the factor underlying the intercorrelations between the measured species.

The major ionic species,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{H}^+$ , were taken into account in the analysis. Initial factors were extracted from a matrix of correlations. Factors with eigenvalues greater than one were considered for varimax rotation to obtain the final factor matrix. After rotation of the factor-loading matrix, the factors were interpreted as origins or common sources assuming that the intercorrelations among the original variables were generated by a smaller number of unobserved factors (Astel *et al.*, 2004; Kasseler *et al.*, 1992). In accordance with this assumption, the grouping of elements/ions in each factor was attributed to chemical, metrological and physical reasons as well as to common

sources (Khare *et al.*, 2004; Migliavacca *et al.*, 2004).

Table 6 shows the result of factor analysis. This analysis identified three factors, since in all cases, they explained about 83% of the data variance, as well as factor loading with value greater than 0.5. The first factor displays high loading level, accounting for 32.2%, of  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{K}^+$ , indicating the influences of long-range transport of sea salt and burning activities (Ayers *et al.*, 2002; Yamasoe *et al.*, 2000). Factor 2 explains 28.8% of the variance proving correlation of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  components. As mentioned earlier,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are associated reasonably with agricultural and industrial activities. Furthermore, dissolution of aerosols/secondary pollutants, e.g.,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  in rainwater, can cause the presence of co-occurrence of  $\text{NH}_4^+$  with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . Such secondary aerosols are formed in the atmosphere through chemical processes. Ammonium sulfate and ammonium nitrate, originating from reactions between ammonia and sulfuric acid or nitric acid, are major secondary aerosols (Harrison *et al.*, 1997; Chang *et al.*, 2007). Nitric acid is formed via reactions between  $\text{O}_3$  and  $\text{NO}_2$ , as well as between  $\cdot\text{OH}$  and  $\text{NO}_2$  (Emmerson *et al.*, 2004; Chang *et al.*, 2007). The third factor contributes 22.0% of the variance and shows  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as significant. This significantly indicates cations distribution from local limestone mines and soil sources.

**Table 6** Rotated varimax factor matrix of factor analysis for measured ionic species

Component	Factor 1	Factor 2	Factor 3
$\text{SO}_4^{2-}$	0.104	0.889	0.204
$\text{NO}_3^-$	0.005	<u>0.896</u>	0.109
$\text{Cl}^-$	<u>0.972</u>	0.120	0.102
$\text{NH}_4^+$	-0.045	<u>0.831</u>	0.283
$\text{Na}^+$	<u>0.975</u>	0.000	0.118
$\text{K}^+$	<u>0.976</u>	-0.043	0.062
$\text{Ca}^{2+}$	0.156	0.206	<u>0.915</u>
$\text{Mg}^{2+}$	0.111	0.156	<u>0.930</u>
$\text{H}^+$	0.024	0.476	-0.346
Eigenvalue	3.5	2.6	1.4
Variance (%)	32.2	28.8	22.0
Cumulative (%)	32.2	61.0	83.1
Possible source	Marine contribution	Combustion process	Lime stone mines; Soil re-suspension
	Biomass burning	Agriculture	

The underline data indicate significant degree of contribution of components within relevant factor loading.

## 3 Conclusions

This study presents the situation of wet deposition in a rural area in western Thailand. The pH of rainwater, ranging 4.0–7.8 with an average of 6.1, gradually increased over the sampling period. This indicates reduction of acid

deposition at this site. The analyzed ionic species indicated that  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  are the significant alkaline species for neutralization process. The enrichment factors analysis indicated that  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  originate from local sources, while  $\text{Na}^+$  and greater part of  $\text{Cl}^-$  are from the sea. The application of factor analysis reveals that crusting as well as anthropogenic activities play an important role in contributing ionic species in wet precipitation at the site.

### Acknowledgements

This work was supported by the Pollution Control Department of Thailand. As this study is part of the research on acid deposition monitoring network in Thailand, coordinated by PCD (Pollution Control Department of Thailand), the authors are thankful for the financial support and the encouragement. We would like to thank Mr. Somphon Chunngam, Head of Kampangsan meteorological station; and Assistant Professor Dr. Dirakrit Buavait Bohuwech, Department of Environmental Science, Silpakorn University for their assistance in transferring samples. We are grateful to Assistant Professor Dr. Kamolchanok Panishkan, Department of Statistics, Silpakorn University for valuable advice regarding statistical analyses.

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