

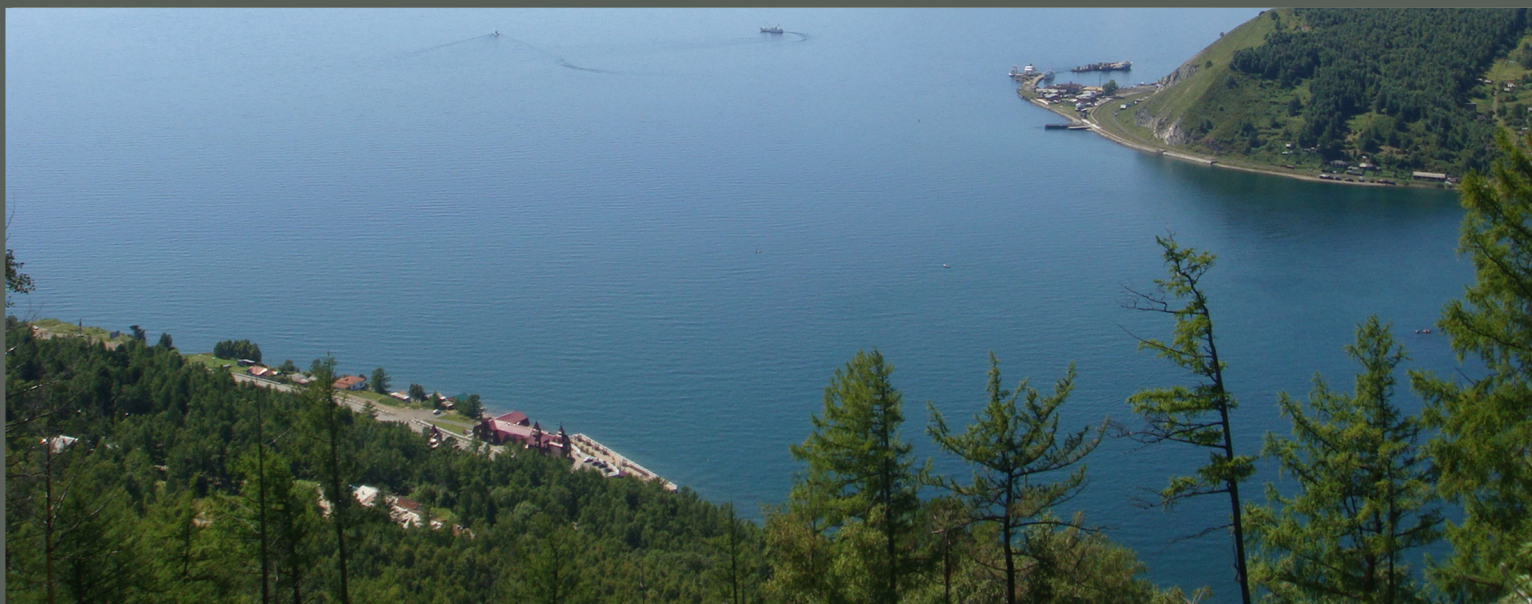
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Acid Deposition Monitoring Network in East Asia (EANET)

EANET Science Bulletin



Network Center for EANET

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Acid Deposition Monitoring Network in East Asia (EANET)

Objectives

- *Create a common understanding of the state of acid deposition in East Asia.*
- *Provide useful inputs for decision making at local, national and regional levels with the aim of preventing or reducing adverse impacts on the environment caused by acid deposition.*
- *Contribute to cooperation on issues related to acid deposition among the participating countries.*

EANET Science Bulletin

Volume 2

The EANET Science Bulletin is published by the Network Center for EANET once every two years. The Network Center is located at the Asia Center for Air Pollution Research (ACAP) in Niigata, Japan.

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Endorsed at the Tenth Session of the Scientific Advisory Committee of EANET

Preface

The EANET Science Bulletin

The objective of the EANET Science Bulletin is to share the research findings from the EANET Research Fellowship Program and Joint Research Projects among the EANET community. The Bulletin can also provide a platform for scientists from participating countries to publish their science and technology research results that are relevant to EANET. List of published papers on issues relevant to EANET activities are also included for the information of the scientific community.

This is the Volume 2 of the Science Bulletin of the Acid Deposition Monitoring Network in East Asia (EANET) that was formally established in 2000 as a cooperative regional initiative to promote efforts for environmental sustainability and protection of human health. Currently 13 countries in Northeast and Southeast Asia are participating in EANET activities.

The research activities of EANET are of the great importance to achieve a better understanding of the extent of atmospheric pollutants and impacts on the environment of the East Asian region which is the fastest economic growth in the world. Research activities are, therefore, very important and necessary for improving the situation of the air pollutants. The Network Center for EANET is also responsible for handling of scientific and technical matters of the participating country members. Therefore, the fellowship research, joint research projects with governmental agencies and research institutions and national research papers in the member countries are included in this bulletin.

Research materials from EANET database are encouraged to use in growing the high quality to conduct national studies and advance knowledge of air pollution and their impacts to the countries. Such information is very useful to assist policy makers in planning air pollution control and mitigation measures.

Finally, hopefully, this science bulletin will be useful for all researchers and people who obtained this knowledge and could achieve in successful environmental integrity.

Hajime Akimoto
Director General
Asia Center for Air Pollution Research
Network Center of EANET

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Reports of the EANET Research Fellowship Program (2008-2009)

The EANET Science Bulletin is issued every two-year period. While the Research Fellowships are obtained every year, sometimes, there was a person or two persons per year that was depended on budget availability. Therefore, the reports of two-year programs are included in the bulletin. This bulletin is the EANET Science Bulletin Volume 2 that collected the research results of the year 2008-2009 programs.

Short-Term Changes in River Water Chemistry in Niigata

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Abstract

In the study aimed to examine water chemistry and to compare the rivers of Niigata prefecture (Japan), the physical characteristics (pH, electric conductivity, water flow, and rainfall) and water chemistry (concentration of cations and anions as well as the silicon content) were examined during different seasons. The following are major objectives of the study:

1. River water measurement at clarification of short-term changes in river water chemistry during meteorological events such as heavy rain.
2. Clarification of seasonal (autumn to winter) changes in river water chemistry.

This work was made on good analytical level by means of modern methods of sampling and subsequent analysis using the ion chromatograph (DX-500, Dionex Corp., CA, USA) and other types of modern equipment. The interesting approach is application of a multi sensor probe (HORRIBA W-23 XD) that allow to determine pH, electrical conductivity (EC), concentrations of the NO_3^- and Cl^- ions, and water temperature with 30 minutes interval. This equipment allows to trace in details the fluctuations in the river water chemistry caused by the changes in water flow depending on the amount of incoming precipitation. These studies are important when studying the waters characterized by low buffer capacity (low electrical conductivity, low alkalinity, etc.), since they are sensitive to acidification. This type of water bodies is exemplified by the Araya River. The river located in granite area is one of the most sensitive to acid deposition in Niigata. Its water is characterized by low alkalinity and shows trend of pH to decrease. The chemical properties and physical parameters of the river water were studied since June 15, 2006 till November 11, 2008. The results obtained show the changes in the content of acid components (the NO_3^- concentration and some other parameters) due to increased water flow during intense rainfall. The report also included the data on underlying bedrock in the river basin, which is important when study the water bodies subjected to acidification. At the end of report, a comparative analysis of the chemical properties of the Araya River with those of the other rivers in Niigata prefecture is presented.

Key word: Araya river, acidification, river water chemistry, low buffer capacity.

1 .Introduction

1.1. Background

Acid rain has probably been observed for centuries, although acidity was not measured until about 100 years ago. The problem has, however, increased during the last decades due to man-made emission. Emissions of natural and anthropogenic acidic gases on global basis are about equal, but in the more industrial Northern Hemisphere, man-made emission account for 90% or more of total emission of acidic substances (Anonymous,1992).

The increase of population, industries, forest fire and transportation in East Asia region had given negative impacts to ecosystems and environment. The negative impacts to ecosystems of lake and stream may include degradation of its water quality and disturbance of its ecosystems. The industry's activities need fossil fuel. Combustions of fossil fuel, forest fire, and transportation cause emission of SO₂ and NO_x. The sulfate and nitrate derived from the acidic gases cause acidification in lakes, reservoirs, stream and even the land. The acidification may cause increase of the soluble metal and disturbance of the ionic balance, and inhibit metabolism cycle of microorganism or biota aquatic (Sutamihardja, 2006).

In Japan, the cumulative acid loading from the atmosphere to the terrestrial ecosystems must be huge because of the development of the Japanese economy during the last several decades. The estimated accumulated emission of sulfur in Japan from 1850 to 1990 was almost the same as that in Europe in the 1960s (175 metric ton S km⁻²; Lefohn *et al.*, 1999). In addition to the domestic emissions, rapid industrialization in East Asia has increased emissions of acidic substances. Therefore, it may be possible that impacts of acid deposition become obvious in Japan in regions with sensitive geology and high acid loading.

Yamada *et al.* (2007) recently reported that river and lake waters had been acidified since the mid-1990s in the Lake Ijira catchment, in Gifu Prefecture; Chubu region (central region) of Japan, the amount of acid substances deposited is the largest among acid-deposition monitoring site in Japan. The committee for Acid Deposition Measures of Japan (2004) reported that the highest deposition of inorganic nitrogen (NO₃⁻ + NH₄⁺) among 56 monitoring stations in the Japanese Acid Deposition Survey from 1988 to 2002 was 18 kg N ha⁻¹ yr⁻¹ (data were obtained with a wet-only sampler), which was recorded in 2000 at the Lake Ijira station in Gifu Prefecture. The wet deposition of non-sea salt (nss)-SO₄²⁻, 17 kg S ha⁻¹ yr⁻¹ in 2000, at the Lake Ijira station was the second highest among these stations (Ministry of Environment of Japan, 2004; Committee of Acid Deposition Survey, 2005). The values correspond to 90% and higher than 90% for nitrogen and nss - sulfur respectively, on the distribution of wet deposition in Japan.

Niigata Prefecture, where Acid Deposition and Oxidant Research Center (ADORC) is located, can also be characterized as areas with high acid loading from the atmosphere. The wet deposition at the Nagaoka station which is located almost center of Niigata Prefecture, was 19 kg N ha⁻¹ yr⁻¹ and 18 kg S ha⁻¹ yr⁻¹, respectively. The values are comparable to those of the Lake Ijira station. In fact, Matsubara *et al.* (2008) found that pH has declined significantly for the last 15 years in many rivers in Niigata Prefecture based on the data analysis of

“Public Water Body”¹. Moreover, all of the rivers showing the pH-declining trend were located in the northern part of Niigata Prefecture, which was dominated by granite, an acid-sensitive rock.

In acid-sensitive regions, not only long-term acidification of the river water but also short-term changes in water chemistry could be seen during periods of high hydrologic loading, including during snowmelt (Suzuki, 1991) and rainfall (Komai *et al.*, 2001). Therefore, we focused on Araya river, one of the most sensitive rivers to acid deposition in Niigata, whose water shows trend of pH decrease and low alkalinity and which is located in granite area (Matsubara *et al.*, 2008). The river catchment may have minimum effect of hot spring and local human activities. Deposition amount is relatively large in the area along the Sea of Japan, including Niigata Prefecture. Therefore, short-term acidification may also occur in such a sensitive river.

1.2. Scope

The fellowship study was conducted in particular for the following scope:

- Clarification of short-term changes in river water chemistry during meteorological events such as heavy rain.
- Clarification of seasonal (autumn to winter) changes in river water chemistry.

2. Methods

2.1. Characterization of the sampling site, Araya river

Araya river is located in granite area in “Kaetsu area”, the northern part of Niigata Prefecture. The mountainous area of Kaetsu area is mostly covered by granitic rocks. On the other hand, “Joetsu area”, the southern part of Niigata Prefecture is covered by andesite or limestone, which may have high acid neutralizing capacity. Geological map of Niigata Prefecture presented in Figure 1.

¹ Each local government in Japan monitors several parameters related to water pollution in public water bodies such as river or reservoirs for the continuous assessment of “Public Water Body” areas as specified by the Water Pollution Control Law of 1970. Therefore, the historical data on river water quality in Japan is available for several decades. Fortunately, pH is one of the monitored parameters, but no other parameters are directly related to acid deposition.

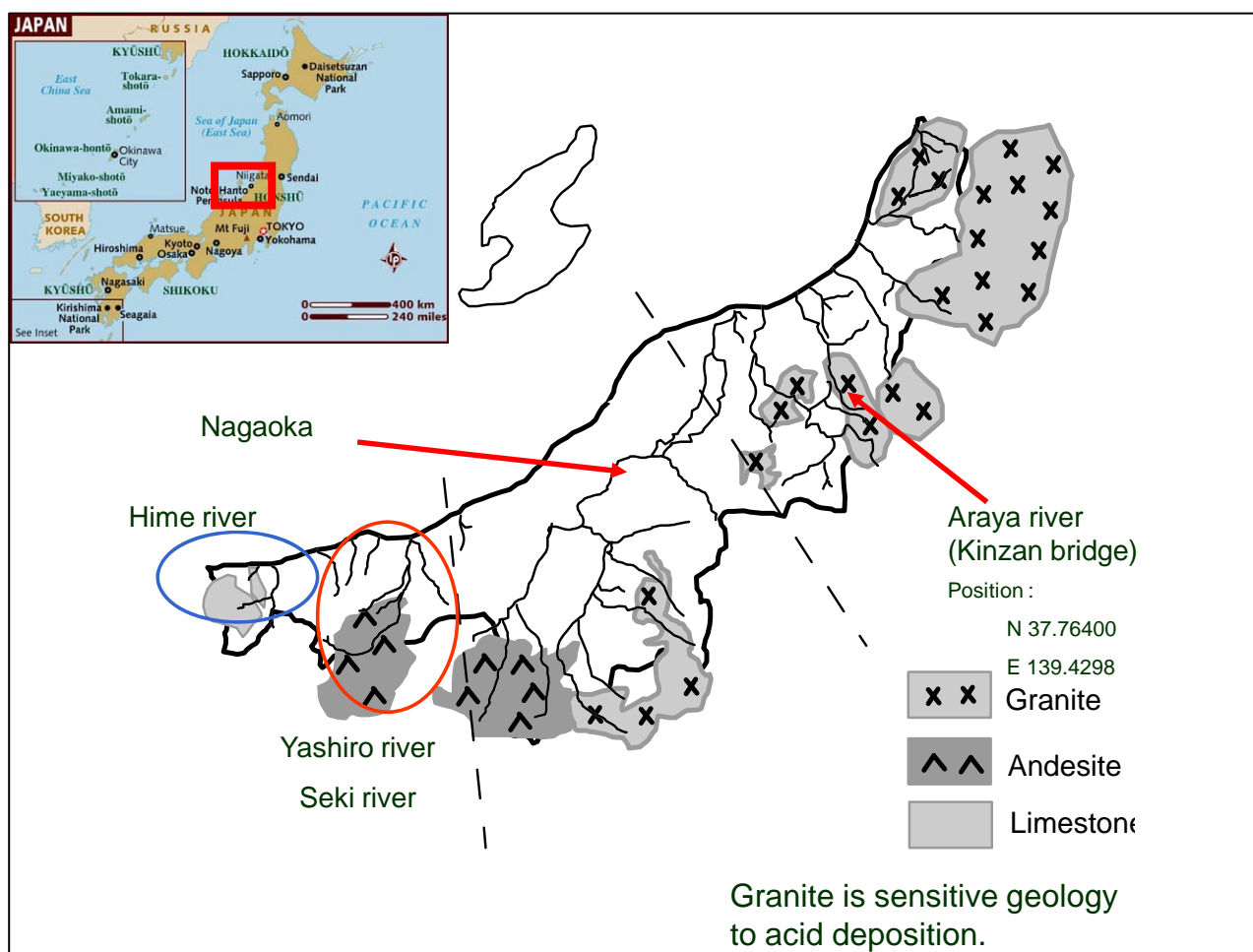


Figure 1. Geological map of Niigata Prefecture in Japan.

To clarify characteristics of the sampling site, Araya river, we investigated the rivers in Joetsu area, too. River water was collected in the Hime river, Seki river upstream, Seki river downstream and Yashiro river by using a plastic bucket one time at December 17, 2008 for comparison of water chemistry in different geology area. Description of river water site and data sets were listed in Table 1.

Table 1. Description of river water site and data sets.

No	Name of rivers	Characteristic of sites	Latitude	Longitude	Measurement period
1	Araya (at Kinzanbashi bridge)	Remote(Granite area) Regular Sampling	N 37°. 7640'	E 139°. 4298'	June 2006 to November 2008
		Remote (Granite area) Intensive Survey			- October, 28-30, 2008 - November, 18-20, 2008 - November, 26-28, 2008
2	Hime	Remote(Limestone)	N 36°. 9784'	E 137°. 8713'	December, 17, 2008
3	Seki upstream	Remote (Andesite)	N 36°. 8539'	E 138°. 1956'	December, 17, 2008
4	Seki down stream	Rural (Andesite)	N 36°. 9872'	E 138°. 2745'	December, 17, 2008
5	Yashiro	Remote (Andesite)	N 37°. 0018'	E 138°. 2013'	December, 17, 2008

2.2. River water measurement at Araya river

2.2.1. Regular sampling

The water sample is taken from Araya river at Kinzanbashi bridge using a plastic bucket. See Figure 2(b). The survey was carried out every two weeks from June 15, 2006 to November 11, 2008. The river water samples were collected in polyethylene bottles, kept cool in a cooler box during transport to the ADORC laboratory, and stored in a refrigerator until analysis. Chemical analyses were carried out always within two weeks.

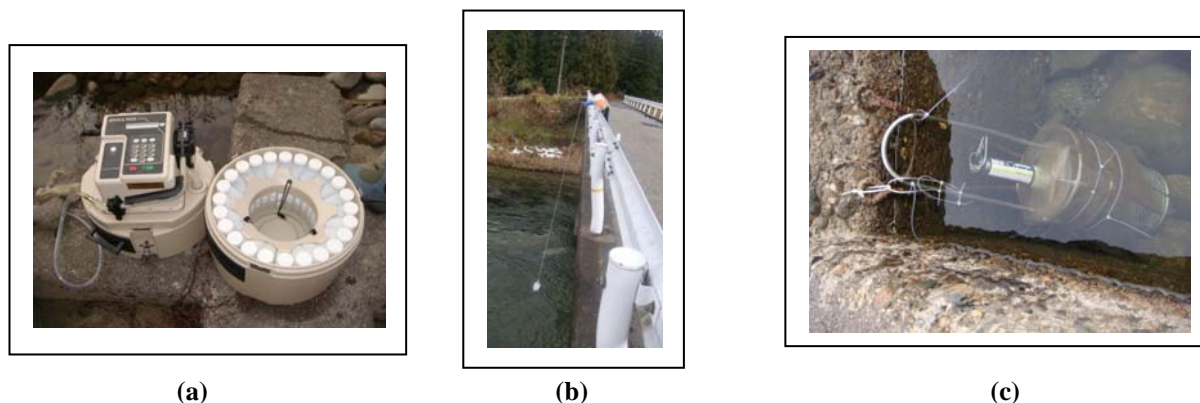


Figure 2. Sigma Model 900 (a); Sampling by a plastic bucket (b); Multi sensor probe (c), Horiba W-23 XD.

2.2.2. Intensive survey

Intensive surveys were carried out at Araya river during three periods. The first sampling was conducted from 28 to 30 October 2008, the second sampling was from 18 to 20 November 2008 and the third sampling was from 26 to 28 November 2008. The river water samples are taken from Araya river near Kinzanbashi bridge by Sigma Model 900 (Automatic liquid sampling device) in heavy rain days (See Figure 2(a)). In this tool, there are 24 plastics bottles used to take samples of river water every 2 hours for 2 days. For detail data analysis, the water - level logger was installed, which interval was every 5 minutes.

2.2.3. Sensor probe

The pH, electrical conductivity (EC), concentrations of NO_3^- and Cl^- , and water temperature were measured by using a multi sensor probe, HORRIBA W-23 XD (See Figure 2(c)). The interval was 30 minutes. Every 2 weeks sensor probe was exchanged to the new one for calibration.

2.3. Analysis

For analyses of EC, pH and alkalinity, unfiltered samples should be used. For analyses of ionic components, filtered sample should be used. (Whatma GF/C or Millipore GF filter which pore size is about $1\mu\text{m}$ with 47 mm diameter, dried at $100\pm 5^\circ\text{C}$ for 2 hours).

Concentration of anions (SO_4^{2-} , NO_3^- , Cl^-), cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), SiO_2 , pH, and EC were measured according to methods in the EANET Technical Manual (Second ISAG Meeting 2000). The pH was measured with a glass electrode (HM-60G, TOA- Electronics Ltd, Tokyo, Japan). When measuring pH, pH meter must be calibrated using a standard solution. There are five kinds of standard solution specified in “JIS 28802 pH measurement”. For normal measurement, two of standard solution with pH 4, 7 and 9 are sufficient to

accurately calibrate the meter. EC was measured with a conductivity cell (CM-60G, TOA - Electronics Ltd, Tokyo, Japan). See Figure 3(a).



(a)



(b)

Figure 3. pH meter and Conductivity meter (a); Ion chromatography DX-500, DIONEX (b).

Alkalinity was determined by the Gran's Plot method. For the Gran's plot method, a high precision pH meter and a micropipette are required. In the calibration of pH meter, pH potential of pH 4 and 7 should be record for pH potential inclination. And 20 mL of sample was prepared with 25°C. Then a 0.05 mL of 0.02 N H₂SO₄ was added to the sample by micropipette and the corresponding potential inclination was recorded. The same addition of acid and the record was continued, taking note of the potential inclination after every addition until pH value reached around 3.0. A plot between the titrated volume and the corresponding [H⁺] was recorded for every sample. The volume of sulfuric acid added was determined at the x-intercept of the regression line is most important in this method, the selection of plot points could give large difference for determination value. It is for this reason that a high precision pH meter (with three- decimal points) was used. Gran's Plot method can be done easily but long time of measurement is required (Arcely Candelareo Viernes *et al.*, 2005).

The concentration of SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺ were determined by ion chromatography (DX-500, Dionex Corp., CA, USA: See Figure 3(b)). The concentration of SiO₂ was measured by Molybdenum-yellow spectrophotometry. Detection limit of the anions and cations are made from the mix solution 0.06 mg/L were measured 8 times, is shown in Table 2.

Table 2. Detection limit of anion and cation by Ion Chromatography, Silica by spectrophotometer.

Data	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Silica
STDEV	0.000668	0.000411	0.000286	0.000422	0.000732	0.000945	0.00142	0.00087	0.00055
Detection Limit (3×STDEV)	0.002	0.001	0.001	0.001	0.002	0.003	0.004	0.003	0.002

2.4. Data management

All measured data were checked for R_1 and R_2 values. If necessary, remeasurement was carried out and the adequacy of data was checked. If the concentration or standard deviation of concentration of anion differed greatly from the long term average concentration or standard deviation of concentration, respectively, during a given period, the cause was carefully considered.

To find out the relationship between pH, Alkalinity, Electric conductivity and cation or anion in river water chemistry, correlation coefficient (r) was calculated between them.

3. Results and Discussion

3.1. Characteristics of the sampling site, Araya river

The comparison data of pH, alkalinity, EC at Araya river, Hime river upstream, Yashiro river upstream, Seki river upstream and Seki river downstream were shown in Figure 4. The pH, EC and alkalinity of the Araya river were less than those in Hime river, Yashiro river, Seki river upstream and its downstream. The EC at Seki river upstream or downstream, Yashiro river upstream and Hime river upstream were more than 10 mS/m.

It seemed that the high values of EC were caused by the condition of the river catchment area. Hime river is located in limestone area while Seki and Yashiro rivers are located in andesitic area. Yashiro river is located near the cement factory of using the limestone. Thus the Araya river located granite area can be characterized as the most sensitive river to acid deposition among these 5 rivers.

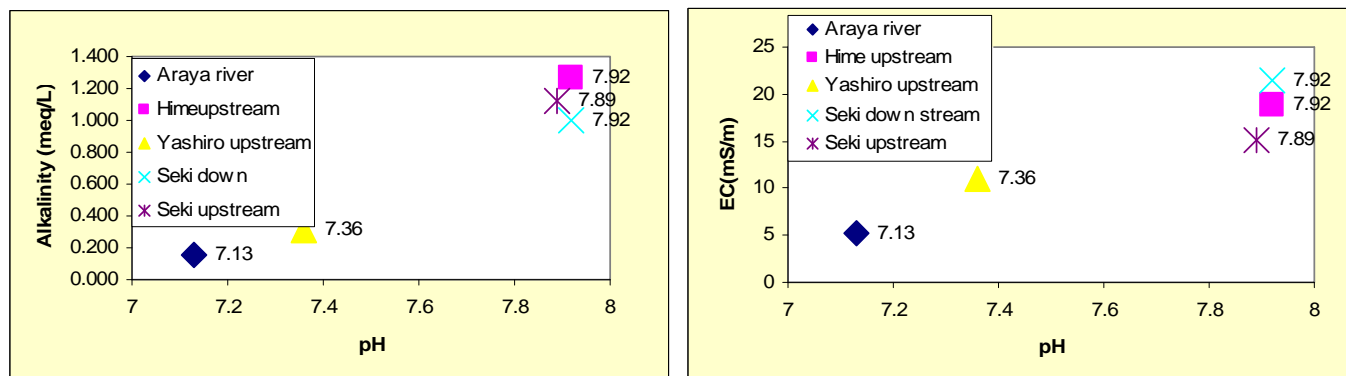


Figure 4. The data of pH, alkalinity and electric conductivity at Araya river, Hime upstream, Yashiro upstream, Seki down and Seki upstream on December 17, 2008.

3.2. Regular sampling

According to the monitoring data at Kinzanbashi bridge in the Araya river from June 15, 2006 - November 11, 2008 ($n = 30$), pH of the river water was in the range from 6.66 to 7.48, the average pH was 7.15 and the standard deviation (Stdev) was 0.18. The EC was in the range from 3.26 to 7.75 mS/m, the average EC was 5.21 mS/m and the Stdev was 0.89. The alkalinity was in range from 0.06 to 0.24 meq/L, the average alkalinity was 0.15 meq/L and the Stdev was 0.05.

The precipitation amount (monthly) was in the range from 57.0 to 735.0 mm in Tsugawa weather station 8 km south of Araya river, the average precipitation (monthly) was 214.65 mm and the Stdev was 131.7.

Analysis of SiO₂ in river water carried out from April 2008 to November 11, 2008 (n = 15). The concentration of SiO₂ was in the range from 2.36 to 3.42 mg/L, the average concentration was 2.92 mg/L and the Stdev was 0.42. Data is shown in Table 3.

Table 3. Data of pH, EC and alkalinity at Kinzanbashi bridge in Araya river and rainfall in Tsugawa weather station From June 15, 2006 to November 11, 2008 (Regular sampling).

Data	Rainfall monthly (mm)	pH	EC (mS/m)	Alkalinity (meq/LHCO ₃ ⁻)	SiO ₂ (mg/L)
Average	214.7	7.15	5.21	0.15	2.03
Minimum	57.00	6.66	3.26	0.006	2.36
Maximum	735.00	7.48	7.75	0.24	3.42
Stdev	133.83	0.18	0.89	0.05	0.42

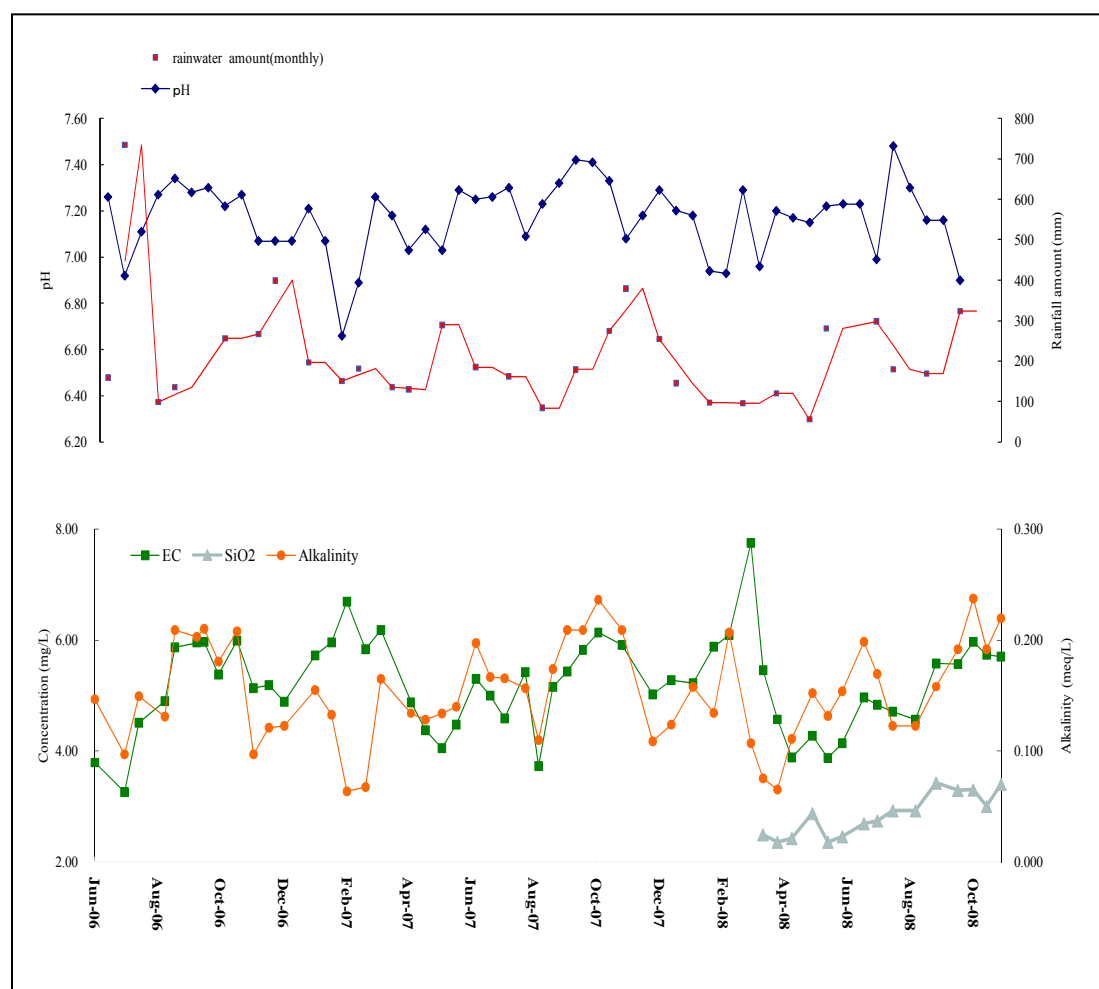


Figure 5. Trends of pH, electrical conductivity, alkalinity and rainfall in Araya river 2006 -2008.

Based on the regular sampling at Kinzanbashi bridge in the Araya river made from June 15, 2006 until November 11, 2008, pH, EC, alkalinity and rainfall data showed seasonal changes (Figure 5). In February 2007 and in the period from February to March 2008, the same trends occurred, in which the pH, rainfall, alkalinity decreased but EC increased. It was suggested that temporary acidification occurred by input of high

concentration (high EC) water to the river. It may be possible that so-called “acid shock” phenomenon occurred in the periods by snow melting in the Mountainous area.

In the periods from December 2007 to January 2008 and from August to September 2008, pH, alkalinity and EC increased while rainfall decreased. Concentration of SiO₂ was a little bit increased but relatively stable. It seemed that the river water was concentrated and enough neutralized in the catchment because of low rainfall.

In July 2006, August 2007, and the period from July 2008, pH, EC, and alkalinity decreased mostly simultaneously. In August 2008, the significant pH increase was accompanied by decreased EC and alkalinity.

In the period, the area seemed to have much rainfall, although the case of August 2007 is not clear probably because of the monthly data. It may be possible that pH and EC decreased with dilution of the water by rainfall in summer.

There are many factors to decrease or increase of pH, EC, and alkalinity in river water. In the water, there are not only acidic species but also alkaline species. The pH of solution is the negative common logarithm of the hydrogen ion activity, a_{H^+}

$$pH = -\log_{10} (a_{H^+}).$$

In a dilute solution, the hydrogen ion activity is approximately equal to the concentration of hydrogen ion. The pH is one of the chemical nature of water is quite important. The pH value of water can affect the usefulness of the water, both for irrigation, fisheries, agriculture, and also the needs of others. The pH of natural water is usually neutral and value pH about 7. The impact of acidification will increase soluble metals (i.e., Pb, Zn, Cu) and disturb of the ionic balance, inhibit metabolism cycle of microorganism or biota aquatic. The significantly high or low pH values indicate the deviation from the water (Anonymous, 1984).

Based on the data analysis of the regular sampling above, it was suggested that the seasonal changes in water chemistry of Araya river occurred in particular in snow-melting season or rainy season in summer. However, the regular sampling at two-week interval cannot detect mechanism in these seasons. Therefore, the intensive sampling with automatic sampling device was applied as described below.

3.3. Intensive sampling

Intensive sampling at Araya river was carried out at three periods. The first sampling was on 28 – 30 October 2008, the second sampling was on 18 – 20 November 2008 and the third sampling was on 26 -28 November 2008.

3.3.1. First intensive sampling

Concentrations of anion, cation, and SiO₂, water level, EC, and alkalinity at the first sampling were shown in Table 4.

Table 4. Anion, cation, alkalinity, pH and EC during the heavy rain event on 28 – 30 October 2008 (First sampling).

No	Parameter	Minimum	Max	Average	Standard Deviation
1	Water level (cm)	97.7	131,3	111.6	10.79
2	SiO ₂ (mg/L)	2.37	3.2	2.81	0.277
3	pH	6.96	7.2	7.10	0.0875
4	EC(mS/m)	4.42	5.8	5.12	0.5211
5	Alkalinity (meq/L)	0.11	0.2	0.15	0.0313
6	SO ₄ ²⁻ (mg/L)	4.92	6.9	5.98	0.7699
7	NO ₃ ⁻ (mg/L)	0.76	1.2	0.94	0.1635
8	Cl ⁻ (mg/L)	4.31	5.0	4.62	0.2160
9	Na ⁺ (mg/L)	3.01	4.1	3.65	0.3558
10	K ⁺ (mg/L)	0.47	0.60	0.52	0.0239
11	Ca ²⁺ (mg/L)	2.6	4.0	3.3	0.4507
12	Mg ²⁺ (mg/L)	1.5	2.0	1.8	0.1530
13	NH ₄ ⁺ (mg/L)	0	0	0	0

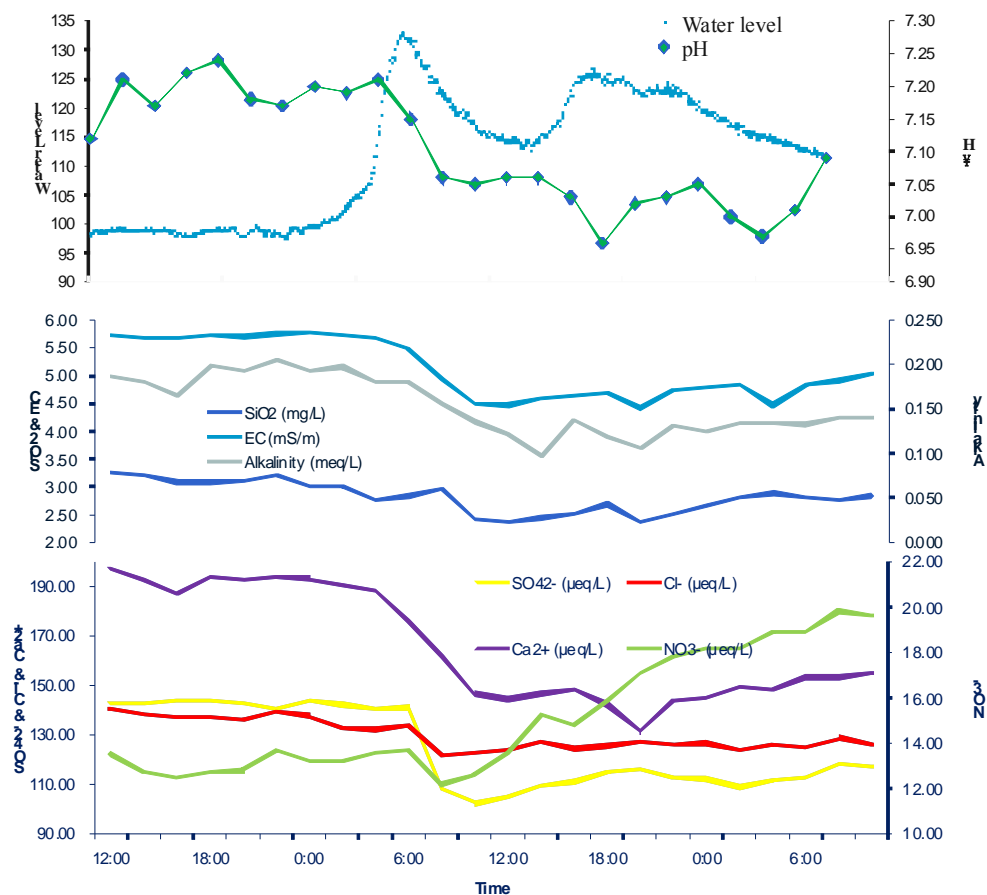


Figure 6. Changes in the concentrations of various chemical components in Araya river during the heavy rain event in October 28 -30, 2008 (First Sampling).

When the water level rapidly increased from around 06:00 hr October 29, 2008 to the second day, concentrations of most ions in Araya river including SiO_2 , SO_4^{2-} , Ca^{2+} , and Cl^- decreased, whereas the NO_3^- concentration increased (Figure 6). The pH, EC and alkalinity also decreased during the event. The lowest pH was accompanied by increase of NO_3^- from 08:00 to 24:00 hr.

Correlation coefficients between water level, Si, H^+ , EC, alkalinity, SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} presented in Table 5. The NO_3^- and H^+ showed significant positive correlation ($r = 0.8$, $p < 0.05$). The NO_3^- was negatively correlated with EC, alkalinity and Ca^{2+} ($r = -0.6$, $p < 0.05$), with K^+ ($r = -0.9$, $p < 0.05$), and with Cl^- and SO_4^{2-} ($r = -0.5$, $p < 0.05$). The H^+ was negatively correlated with EC, Alkalinity, and Ca^{2+} ($r = -0.9$, $p < 0.05$), with SO_4^{2-} , and Mg^{2+} ($r = -0.8$, $p < 0.05$), and with Cl^- , Na^+ , and K^+ ($r = -0.7$, $p < 0.05$).

Table 5. Correlation coefficients between water level Si, H^+ , EC, alkalinity, cation and anion at Araya river in Niigata Japan from October 28 to 30, 2008).

	Water level	Si	H^+	EC	Alk	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
Water level	1.0												
Si	-0.7	1.0											
H^+	0.7	-0.7	1.0										
EC	-0.9	0.8	-0.9	1.0									
Alk	-0.8	0.8	-0.9	0.9	1.0								
SO_4^{2-}	-0.9	0.8	-0.8	1.0	0.9	1.0							
NO_3^-	0.5	-0.3	0.8	-0.6	-0.6	-0.5	-1.0						
Cl^-	-0.9	0.8	-0.7	0.9	0.8	1.0	-0.5	1.0					
NH_4^+	0.2	-0.4	0.2	-0.3	-0.2	-0.1	0.0	-0.2	1.0				
Na^+	-0.8	0.8	-0.7	0.9	0.9	0.9	-0.4	0.9	-0.1	1.0			
K^+	-0.3	0.2	-0.7	0.5	0.5	0.5	-0.9	0.5	0.1	0.4	1.0		
Ca^{2+}	-0.9	0.9	-0.9	1.0	1.0	0.9	-0.6	0.9	-0.3	0.9	0.6	1.0	
Mg^{2+}	-0.9	0.8	-0.8	1.0	0.9	1.0	-0.4	0.9	-0.2	0.9	0.4	0.9	1.0

Blue = significant positive, Yellow = significant negative, White = non significant

In the first sampling when the water level rapidly increased, EC decreased. The EC is a measure of the electric current in the water sample carried by the ion substances, and therefore contains a dissolved salt in the water. A high conductivity value indicates a relatively large salt content; on the contrary, a small conductivity value is related to a small salt content (Ratna H, 2007). In fact, The EC was significantly positively correlated with SO_4^{2-} , Ca^{2+} , and Mg^{2+} ($r = 1.0$, $p < 0.05$), with Cl^- , and Na^+ ($r = 0.9$, $p < 0.05$) and with K^+ ($r = 0.5$, $p < 0.05$). On the other hand, the EC was negatively correlated with the water level and NO_3^- ($r = -0.9$ and -0.6 , respectively, $p < 0.05$). It was suggested that most ion concentrations were diluted during the heavy rain event, while only NO_3^- was leached significantly by increasing water level.

In this event alkalinity decreased when the pH decreased. Relationship between alkalinity and H were significantly negative ($r = -0.9$, $p < 0.05$). Alkalinity is the capacity of water to neutralize a strong acid pH values, expressed in units of meq/L or mg/L. In natural water, alkalinity is largely caused by the bicarbonate and the rest by carbonic and hydroxide. In certain circumstances the algae in the water cause a reduction in carbon dioxide content, increased content and carbonic hydroxide and raise pH (reference). The alkalinity was significantly

positively correlated with SO_4^{2-} , Cl^- , Na^+ , Ca^{2+} , and Mg^{2+} ($r = 0.8$ to 1.0 , $p < 0.05$) and with K^+ ($r = 0.5$, $p < 0.05$).

The SiO_2 showed significant positive correlation with EC, alkalinity, SO_4^{2-} , Cl^- , Na^+ , Ca^{2+} , and Mg^{2+} ($r = 0.8$ to 0.9 , $p < 0.05$.) while SiO_2 was significantly negatively correlated with H^+ ($r = -0.7$, $p < 0.05$).

3.3.2 Second intensive sampling

Concentrations of (minimum, maximum, average and standard deviation) of anion, cation, SiO_2 , EC, alkalinity and the water level at the second sampling, 18 – 20 November 2008 were shown in Table 6. Changes in the concentrations during the second sampling were presented in Figure 7.

Table 6. Data of anion, cation, alkalinity, pH and Electrical conductivity during heavy rain event on November 18 – 20, 2008 (Second sampling).

No	Parameter	Minimum	Maximum	Average	Standard Deviation
1	Water level (cm)	94.2	123.0	109.4	7.15
2	SiO_2 (mg/L)	2.6	3.2	2.9	0.14
3	pH	6.9	7.3	7.1	0.09
4	EC(mS/m)	5.5	6.2	5.8	0.27
5	Alkalinity (meq/L)	0.1	0.2	0.2	0.04
6	SO_4^{2-} (mg/L)	5.9	7.3	6.4	0.52
7	NO_3^- (mg/L)	0.8	1.3	1.1	0.17
8	Cl^- (mg/L)	5.0	7.5	6.3	0.71
9	Na^+ (mg/L)	4.0	4.4	4.2	0.10
10	K^+ (mg/L)	0.5	0.7	0.6	0.06
11	Ca^{2+} (mg/L)	3.1	4.4	3.5	0.42
12	Mg^{2+} (mg/L)	1.9	2.1	2.0	0.08
13	NH_4^+ (mg/L)	0	0	0	0

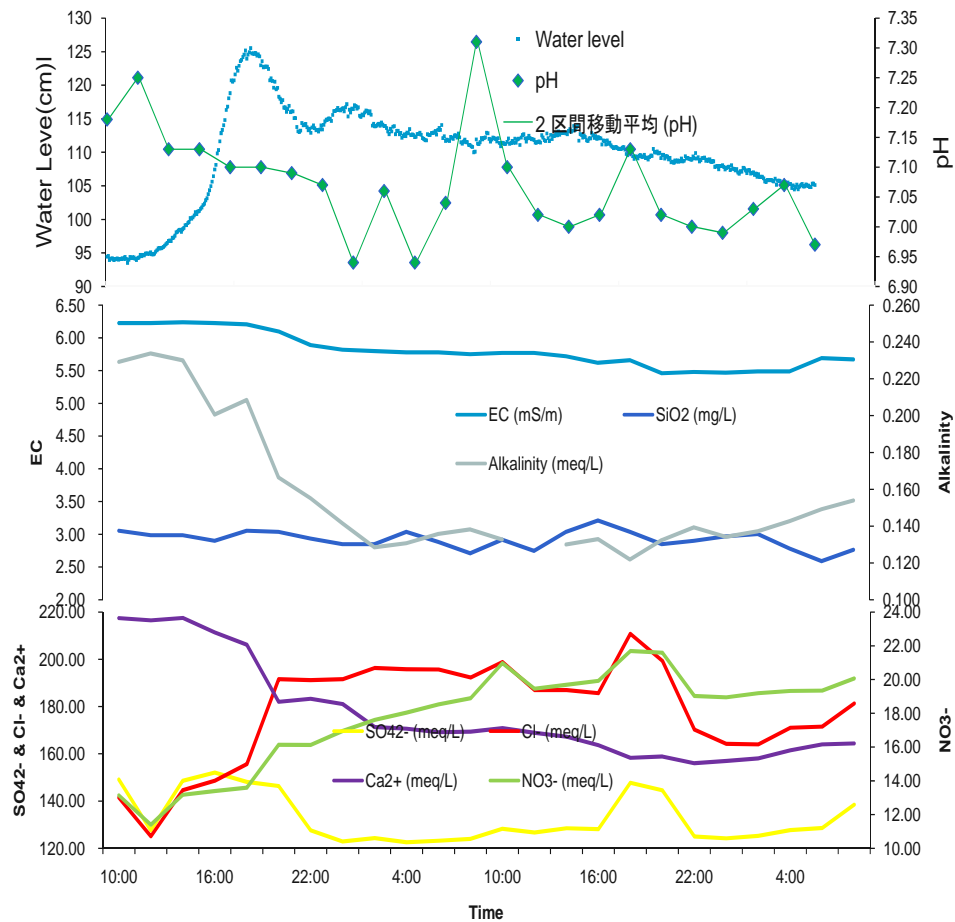


Figure 7. Changes in the concentrations of various chemical components in Araya river during heavy rainfall event on November 18 – 20, 2008 (Second sampling).

When the water level rapidly increased from 04:00 hr, November 18, 2008 to second day, concentration of most ions including pH, alkalinity, and SO_4^{2-} decreased, while the concentrations of Cl^- and NO_3^- increased. The EC and SiO_2 almost did not change. The lowest pH was accompanied by increasing NO_3^- concentration.

Correlation coefficient between the water level Si, H^+ , EC, alkalinity, cation and anion at Araya river from November 18 to 20, 2008) is shown in Table 7. The Cl^- was positively correlated with the water level, NO_3^- , and K^+ ($r = 0.50$ to 0.70 , $p < 0.05$), while the relationship with EC, SO_4^{2-} , Ca^{2+} , and alkalinity was significant negative correlation ($r = -0.5$ to -0.8 , $p < 0.05$). Sea salts in the precipitation may lead to a short term acidification of the runoff natural catchments due to ion exchange reaction (Christophersen *et al.*, 1982). Although contribution of sea salt to the temporary acidification was not clear, it seemed that effects of sea salts were relatively large in this event.

Table 7. Correlation coefficients between water level Si, H⁺, EC, alkalinity, cation and anion at Araya river in Niigata, Japan from November 18 to 20, 2008 (Second sampling).

	Water level	Si	H ⁺	EC	Alk	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
Water level	1.0												
Si	0.1	1.0											
H ⁺	0.4	-0.1	1.0										
EC	-0.3	0.3	-0.5	1.0									
Alk	-0.6	0.2	-0.6	0.9	1.0								
SO ₄ ²⁻	-0.4	0.3	-0.5	0.7	0.7	1.0							
NO ₃ ⁻	0.4	-0.3	0.4	-0.9	-0.9	-0.5	1.0						
Cl ⁻	0.7	-0.1	0.3	-0.5	-0.8	-0.5	0.7	1.0					
NH ₄ ⁺	-	-	-	-	-	-	-	-	1.0				
Na ⁺	-0.3	0.1	-0.3	0.5	0.5	0.5	-0.3	-0.2	-	1.0			
K ⁺	0.6	0.2	0.0	0.4	-0.1	-0.1	-0.2	0.5	-	0.0	1.0		
Ca ²⁺	-0.5	0.3	-0.6	1.0	0.9	0.7	-0.9	-0.7	-	0.4	0.2	1.0	
Mg ²⁺	-0.1	0.3	-0.5	0.9	0.8	0.6	-0.8	-0.4	-	0.6	0.4	0.9	1.0

Blue = significant positive, Yellow = significant negative, White = non significant

3.3.3. Third intensive sampling

Data of cation and anion on November 26-28, 2008 are shown in Table 8.

Table 8. Data of anion, cation, alkalinity, pH and Electrical conductivity during heavy rain event on November 26–28, 2008 (Third sampling).

No	Parameter	Minimum	Maximum	Average	Standard Deviation
1	Water level (cm)	103.4	117.6	106.7	3.1
2	SiO ₂ (mg/L)	0.6	3.2	1.2	0.8
3	pH	6.9	7.1	7.0	0.1
4	EC(mS/m)	4.9	5.4	5.3	0.1
5	Alkalinity (meq/L)	0.01	0.03	0.1	0
6	SO ₄ ²⁻ (mg/L)	5.69	6.93	5.92	0.31
7	NO ₃ ⁻ (mg/L)	1.2	1.48	1.33	0.07
8	Cl ⁻ (mg/L)	5.0	6.31	5.62	0.23
9	Na ⁺ (mg/L)	4.1	4.22	4.11	0.08
10	K ⁺ (mg/L)	0.60	0.59	0.51	0.02
11	Ca ²⁺ (mg/L)	4.0	3.20	3.07	0.11
12	Mg ²⁺ (mg/L)	2.0	1.88	1.83	0.03

In this event, the water level rapidly increased from 01:00 hr of the 3rd day, the most of parameters were decreased but SiO₂ almost no change (Figure 8). In this event, unfortunately we couldn't catch the peak of water level.

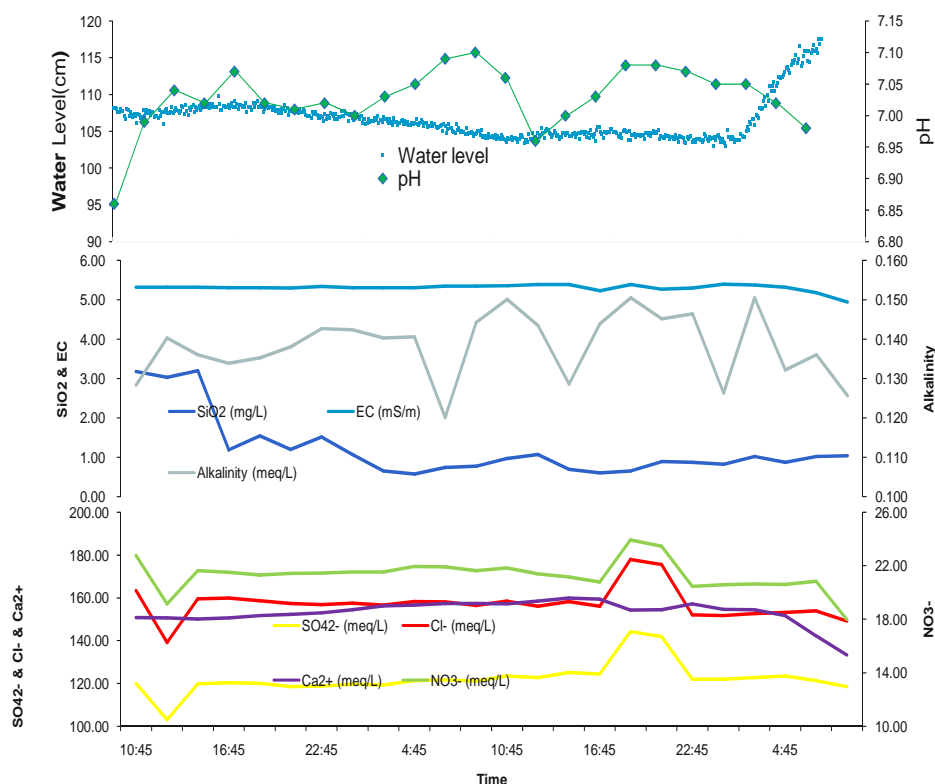


Figure 8. Change in the concentrations of various chemical components in Araya river during snow season on November 26 – 28, 2008 (Third sampling).

Correlation coefficients of the water level were mostly negative with most parameters including pH, EC, alkalinity, cations and anions, ranging from -0.89 to -0.25 (Table 9), while SiO₂ had the positive correlation.

Table 9. Coefficient correlation between water level Si, H⁺, EC, alkalinity, cation and anion at Araya river in Niigata Japan from November 26 to 28, 2008).

	Water Level	SiO ₂	pH	EC	ALK	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
Water Level	1.0											
SiO ₂	0.24	1.0										
pH	-0.36	-0.45	1.0									
EC	-0.86	0.01	0.2	1.0								
ALK	-0.42	-0.16	0.4	0.3	1.0							
SO ₄ ²⁻	-0.36	-0.47	0.3	0.1	0.3	1.0						
NO ₃ ⁻	-0.48	-0.08	0.1	0.5	0.3	0.7	1.0					
Cl ⁻	-0.25	-0.08	0.1	0.2	0.2	0.9	0.9	1.0				
Na ⁺	-0.58	0.16	-0.1	0.6	0.2	-0.2	0.3	0.0	1.0			
K ⁺	-0.25	-0.04	0.1	0.0	0.2	0.0	-0.1	-0.1	0.3	1.0		
Ca ²⁺	-0.89	-0.29	0.3	0.8	0.4	0.2	0.5	0.2	0.8	0.2	1.0	
Mg ²⁺	-0.85	-0.36	0.3	0.7	0.4	0.2	0.4	0.2	0.8	0.2	1.0	1.0

3.4. Comparison between sensor probe and intensive observation data

Figure 9 presents comparison between the sensor probe and laboratory analysis (Intensive survey) for parameters pH, Cl^- , EC and NO_3^- .

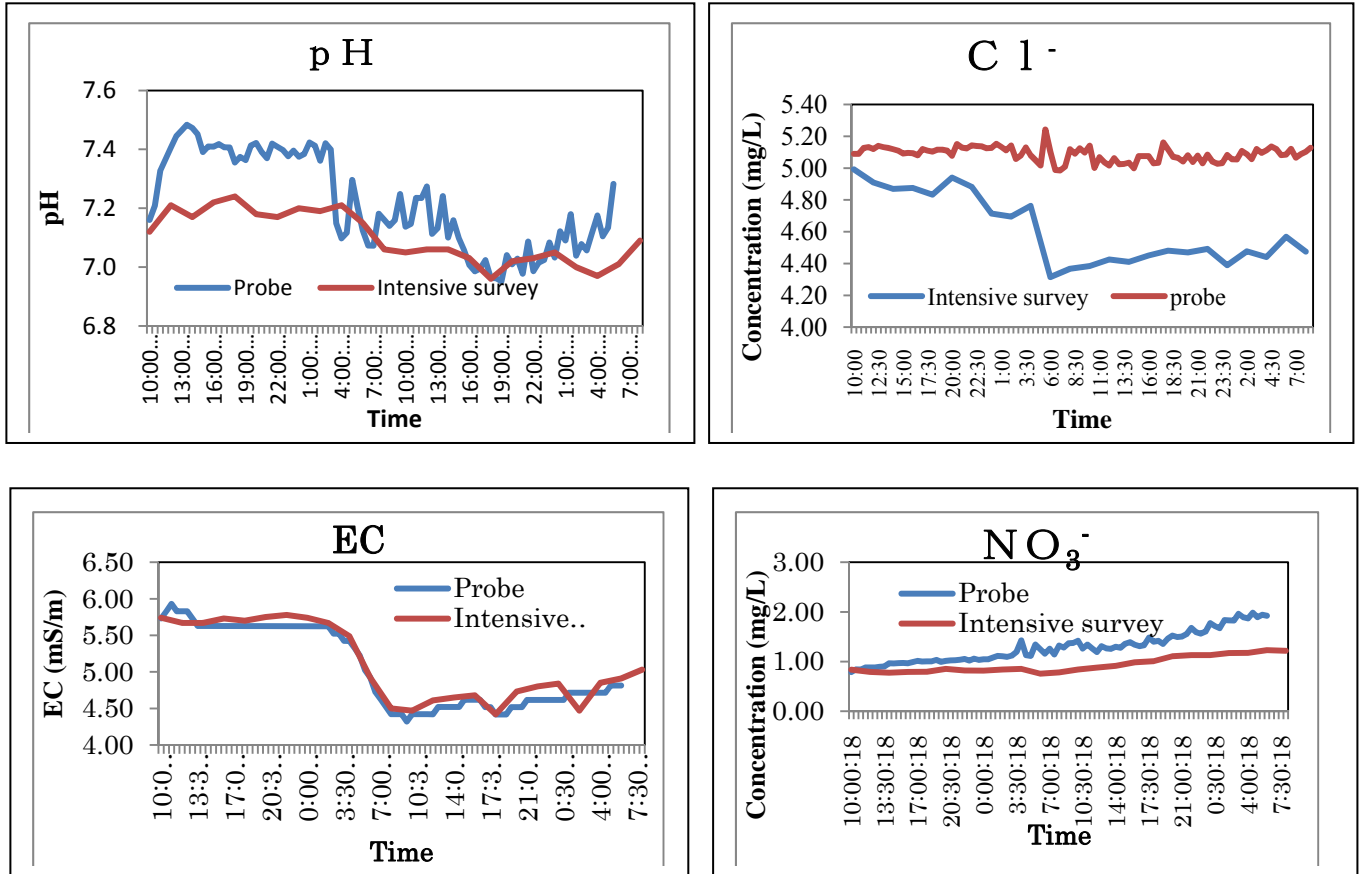


Figure 9. Comparison between the sensor probe and laboratory (Intensive survey) analysis for parameter pH, EC, Cl^- and NO_3^- .

The pH by the probe method showed higher values than that by the laboratory analysis. The average pH was 7.22 and 7.10 by the probe and the laboratory analysis, respectively. The difference was 1.66%. Moreover, the values of the sensor probe were significantly fluctuated. It seemed that small diurnal and/or shorter-term changes were detected by the sensor probe. The sensor probe was unable to reproduce changes in concentration of Cl^- at all.

The EC values by the sensor probe and by the laboratory analysis showed the similar pattern during the event. The average of EC by the probe was 5.04 mS/m and the average by the laboratory analysis was 5.12 mS/m. The difference was 1.56%.

The NO_3^- values by the probe method were higher than those by the laboratory analysis, showing a steeper slope. Average of NO_3^- by the probe was 1.29 mg/L and the average by laboratory was 0.94 mg/L. The difference was 27.06%.

As possible causes of the difference between the values by the sensor probe and the laboratory analysis, not only calibration of the probe but also changes in equilibrium with atmosphere during the transport, measurement temperature and other factors should be considered. For different values between the sensor probe and the laboratory analysis, we need the data verification more carefully.

3.5. Comparison between Kajikawa rainfall and Araya river

The Kajikawa catchment site is located 20 km north from Kinzan bridge. And the stream water, rainfall outside canopy, throughfall and stemflow were collected every 2 weeks. Rainfall chemistry could be considered almost the same between Kajikawa and Araya river. The data of pH, EC and rainfall at Kajikawa is presented in Figure 10. Compared with summer, the EC increased in winter. This phenomenon may be caused by change of monsoon wind direction and in winter the wind with sea-salt blows to the area along the Sea of Japan including Niigata prefecture. And the phenomenon could affect the water chemistry of Araya river, as seen in the 2nd intensive survey.

The depositions by the rainfall outside the canopy at the Kajikawa site was 18 kg N ha⁻¹ yr⁻¹ and 22 kg S ha⁻¹ yr⁻¹, respectively, (Kamisako *et al.*, 2008). The values are comparable to the Ijira and Nagaoka stations, which showed the highest level of the wet deposition in Japan. The high depositions may cause the long-term decreasing trends of the river water pH in this acid-sensitive river as mentioned above.

The water chemistry at Araya river was higher than 7.0 in general. So, the acid neutralizing system may still function as appropriate.

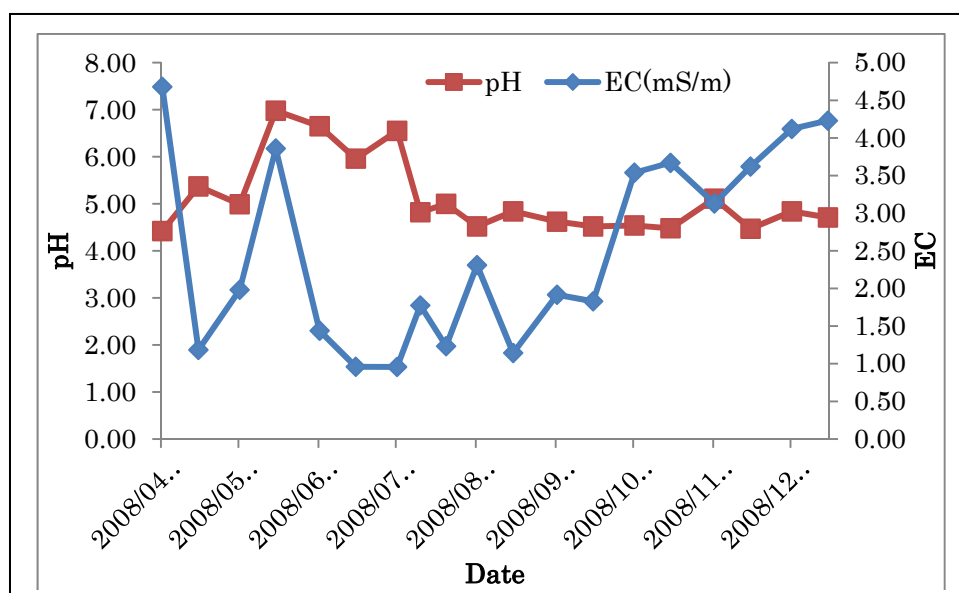


Figure 10. Data pH of Kajikawa rainfall (April –December 2008).

4. Conclusions

Araya river is acid sensitive. Its EC and alkalinity are below the recommended values for monitoring in the IAE manual (EC <10mS/m, alkalinity < 0.2meq/L). Short-term changes in water river chemistry were found in Araya river especially by heavy rain events, probably because its acid-sensitive property.

Changes in the chemical parameters of river water depend on the water level. The river water could be considered to be acidified with relatively increase of NO_3^- concentration, while the other parameters were diluted with water flow increase. These data analysis from this short-term acidification study must contribute furthermore to the studies in other rivers or streams of inland aquatic environmental monitoring site in EANET.

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Ion Chromatographic Analysis of Monocarboxylic and Dicarboxylic Acids in Rainwater at Si Racha, Thailand Compared with Ogasawara Island and Tokyo, Japan

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Abstract

Rainwater samples were collected from three different locations an industrial site of Si Racha, Thailand, a remote site of Ogasawara and an urban site of Tokyo, Japan during July and October, 2008 in order to determine chemical compositions of ionic species including organic acids. Isocratic Ion Chromatography (IC) was applied for analysis of cation (ammonium, sodium, potassium, calcium and magnesium ions) using 20 mM methanesulfonic acids as eluent. Inorganic anions (chloride, nitrate and sulfate ions) and selected monocarboxylic acids including formic, acetic, propanoic, and lactic acids and dicarboxylic acids including succinic, malonic and oxalic acids were analyzed by gradient elution IC with water and potassium hydroxide solutions. The methods provided good resolution and detection limit (0.2 – 4.8 μ M) for all anionic species. The volume-weighted averages of pH were 4.66, 5.14 and 4.42, and those of EC were 1.29, 0.96 and 3.31 for Si Racha, Ogasawara and Tokyo, respectively. Sodium ion predominated in Si Racha and Ogasawara rainwater due to marine contribution. Anthropogenic sources are most significant sources for ammonium ion in Tokyo rainwater. For industrial (Si Racha) and urban (Tokyo) sites, ammonium ion mainly contributed neutralization of acidic species but magnesium ion partly contributed neutralization in remote (Ogasawara) site. Sulfate and nitrate ions contributed as Total Free Acidity (TFA) in all rainwater samples collected at three different sites. For the industrial site (Si Racha), the contribution of monocarboxylic acids to TFA exceeded 18.68% while there were much smaller contributions in Ogasawara and Tokyo rainwater (2.3 and 1.79%, respectively).of TFA. Dicarboxylic acids contributed in trace levels in almost all sampling area. It could be summarized that chloride alkaline and chloride alkaline earth salts originated from marine source in coastal areas. At the rural and industrial sites, sulfate and nitrate ions which were originated from anthropogenic activities caused acidification

of rainwater. Thymol could be added as preservative to protect biological degradation of organic acids in rainwater prior analysis. Rainwater samples which added with thymol were able to be analyzed within 21 days after a rainy event.

Keyword: Monocarboxylic acid, Dicarboxylic acid, Ion chromatography, Rainwater, Biocide.

1. Introduction

Chemical compositions of rainwater represent an important aspect for estimation of an atmospheric air pollution level. Rainout and/or washout are the significant cleaning processes to remove pollutants from the atmosphere and transfer to other ecosystems such as soil, water reservoirs, forests and so on (Fornaro, 2003). Increasing of rainwater acidity from natural precipitation is caused by dissolution of acidic substances in the atmosphere. High emissions of sulfur and nitrogen oxides are transformed to sulfuric and nitric acids under atmospheric conditions (Morales *et al.*, 1998). Additionally, short-chain mono- and dicarboxylic acid (C_1 to C_4) compounds might cause lower pH of rain water (Willey and Wilson, 1993; Keene and Galloway, 1984; Khare *et al.*, 1997). Acetic and formic acids are dominant species of low molecular weight carboxylic acids in rainwater, followed by propanoic acid. The contribution of organic species including formic and acetic acids and their precursors; formaldehyde and acetaldehyde are primarily generated from incomplete combustion of fossil fuels in vehicles and second most from photochemical reactions of anthropogenic hydrocarbons and other atmospheric precursors (Kawamura *et al.*, 2001). Aqueous oxidation of aldehydes to carboxylic acids in the gas-phase via hydroxyl radical reactions is proposed to be another important pathway (Chameides and Davis, 1983). Formic and acetic acids are also originated from natural emissions of vegetation and microbial activities (Keene and Galloway, 1988; Talbot *et al.*, 1988; Avery *et al.*, 1991). They could be detected in rainwater and snow samples collecting at Los Angeles, California, southeastern North Carolina, USA, western Pacific Ocean, Spain, Brazil, Venezuela as well as Thailand (Kawamura *et al.*, 1996; Sempéré and Kawamura, 1996; Morales *et al.*, 1998; Kawamura *et al.*, 2001; Lara *et al.*, 2001; Kieber *et al.*, 2002; Peña, 2002; Fornaro and Gutz, 2003; Avery *et al.*, 2006). Aromatic monoacids such as benzoic acid were found in urban rainwater ranged from 0.1-0.5 μM , which was less than 4% of total aliphatic monoacids (Kawamura *et al.*, 1996).

For dicarboxylic acids, the predominant compound is the shortest-chain oxalic acid (C_2) followed by malonic and succinic acids. The high carbon numbers in long chain of dicarboxylic acids were less abundant in urban rainwater and snow/sleet samples (Sempéré and Kawamura, 1994). Dicarboxylic acids were considered to be mainly generated from secondary photochemical reactions of anthropogenic and natural organic compounds (Kawamura and Gagosian, 1990). Direct emission from incomplete oxidation of fossil fuels during combustion processes were another source of dicarboxylic acids (Kawamura and Kaplan, 1987). C_6 - C_{11} dicarboxylic acids with a predominant of C_9 compounds might be produced from photooxidation of biogenic unsaturated fatty acids in marine atmosphere (Kawamura and Gagosian, 1987).

The chemical compositions of rainwater were mostly concerned especially in China due to the severe air

pollutions in many cities including Beijing, Shanghai and Guangzhou. Rainwater samples were collected from fifty three rain events throughout the year 2003. Formate, acetate and methane sulfonic acids (MSA) were additional organic species that were quantified. The most abundance that lowered pH of rainwater were sulfate and nitrate ions and neutralized ions were ammonium and calcium ions (Tang *et al.*, 2005). Similarly, all species were analyzed in seventy-six rainwater samples collected from acid precipitation in Shanghai. Volume-weighted mean concentration of CH_3COO^- , HCOO^- and MSA were 0.66 ± 0.36 , 0.14 ± 0.06 and $0.003 \pm 0.003 \mu\text{eq l}^{-1}$, respectively. CH_3COO^- and HCOO^- ions contributed to acidity of rainwater but there were underestimation owing to the evaporation loss during measurement (Huang *et al.*, 2008).

Water-soluble organic compounds (WSOC) in the size-segregated aerosol samples, cloud water and wet depositions were collected at Jeju Island. Liquid Chromatography coupled with TOC and NMR was applied to characterize main functional groups and chemical classes of WSOC. The chemical shift in ppm of ^1H -NMR spectra of the size-aggregated samples could identify any organic functional groups. Formate, acetate, oxalate and MSA were found in active and passive collectors of cloud samples and wet deposition samples at the 100m Hill except MSA was not be found in passive collectors (Decesari *et al.*, 2005).

This research focused on investigation of the optimized conditions for analysis of mono- and dicarboxylic acids such as formic, acetic, propanoic, lactic, malonic, oxalic and succinic acids in rainwater by Ion Chromatography. Then, concentrations of mono- and dicarboxylic acids were compared among three different sampling sites; Si Racha site (industrial site), Ogasawara Island (remote site) and Tokyo (urban site) during July to October, 2008. The impacts of anthropogenic activities on organic acid concentrations in rainwater were determined. The appropriate concentration of thymol used for storage of rainwater samples and the storage time before analysis was also evaluated.

2. Experimental methods

2.1 Reagents and standards

Oxalic acid anhydrous (AR grade) was obtained from Wako Pure Chemical Wako Pure Chemical (Osaka, Japan); acetic, propanoic, malonic and succinic acids and thymol from Kanto Chemical (Tokyo, Japan); formic and lactic acids from Fisher Scientific. Standard inorganic anions (chloride, nitrate and sulfate) and standard cation solutions were prepared from each standard solution (Japan Calibration Service System (JCSS) certified, Kanto Chemicals). Repeatability of cation measurement was confirmed by two concentration levels of reference materials used in Acid Deposition Monitoring Network in East Asia (EANET) (Network Center for EANET, 2008). Deionized water filtered through a $0.2 \mu\text{m}$ Whatman membrane cartridge in a Millipore Water Purification Systems (Millipore Co., Billerica, MA) was used to prepare all aqueous solution. The concentrations of standard solutions which are closed to natural concentration levels in rainwater were prepared once a week from a concentrated stock.

2.2 Rainwater collection and storage

Rainwater samples were collected from three monitoring sites with different climates and geographical locations: Si Racha as an industrial site, Ogasawara Island as a remote site and Tokyo as an urban site. The Si Racha monitoring site ($13^\circ 07' 05.38'' \text{ N}$, $100^\circ 55' 20.26'' \text{ E}$, 53 m above sea level) is located in the campus of

Kasetsart University, Si Racha, Chonburi, Thailand. This station is defined as an industrial site as well as hilly topography with heights between 80–180 m and hemicycle of the Gulf of Thailand (http://en.wikipedia.org/wiki/Eastern_Thailand). It is surrounded by Eastern Seaboard as well as petrochemical, consumer products, automobile and shipping industries (http://en.wikipedia.org/wiki/Amphoe_Si_Racha). The eastern part of this area is regarded as potentially sources of various atmospheric pollutants. In terms of rainfalls, a rainy season starts from June to October and a dry one between November to May. The Ogasawara monitoring site (27° 05' 30'' N, 142° 12' 58'' E, 230 m above sea level) is located in an archipelago of over 30 subtropical and tropical islands in the Pacific Ocean. It is located about 1,000 km directly south of Tokyo, Japan. The Tokyo monitoring site (35° 41' 18'' N, 139° 45' 22'' E, 47 m above sea level) is located at the rooftop of Science Museum, Tokyo in Kitanomaru Park near the Imperial Palace. Surrounding of the Tokyo site is business area and heavy traffic environment. Rainwater samples were collected in a pre-cleaned polyethylene bucket (surface area 0.06 m²) using wet-only collector. The samples from three sites were continuously collected within 24 hr during July to October, 2008. The biocide; thymol (isopropylmethylphenol, IPMP) was added in rainwater samples for biodegradable protection. Rainwater samples were stored in darkness at 4°C and filtered through a 0.22 µm pore size Millipore filter prior to Ion Chromatographic analysis.

2.3 Analytical procedures

Amounts of daily precipitations were recorded followed by pH and electrical conductivity (EC) of rainwater. pH was measured with F55 Navi pH/electrical conductivity meter (Horiba, Japan); electrical conductivity was determined with DS-15 conductivity meter (Horiba, Japan) at 25°C. Concentration of inorganic cations (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) were analyzed with Dionex Ion Chromatographic system equipped with an IP25 isocratic pump, a EG40 eluant generator, a CD20 conductivity detector, a LC25 chromatographic oven, and a AS3500 autosampler with 100 µl of injection loop. The separation procedure was performed by Dionex IonPac CS12A (4 x 250 mm) separation column, CG12A (4 x 50 mm) guard column coupled with a cation self-regenerating suppressor (CSRS-ULTRA II, 4mm). An isocratic system consisted of 20 mM methanesulfonic acid (MSA) as an eluant at 1.0 ml min⁻¹.

All carboxylic acids were identified and analyzed in their anionic form (formate, acetate, propanonate, lactate, succinate, malonate and oxalate) by the same setup of Dionex Ion Chromatographic system. Inorganic anions (chloride, nitrate and sulfate) were analyzed at the same time. An IonPac AS11-HC anion exchange column (4 x 250 mm) coupled with a anion self-regenerating suppressor (ASRS-300, 4 mm) was used as an analytical column. The gradient profile was modified from the Dionex recommended condition in order to configure appropriate conditions and high separation resolution. A gradient profile consisted of 1 mM potassium hydroxide at the beginning and exponentially increased to 5 mM from 0 to 7 min. From 7 to 10 min, the eluant concentration was exponentially increased to 8 mM and then continuously exponentially increased to 25 mM from 10 to 35 min from 35 to 40 min, it linearly decreased from 25 to 1 mM. The eluant flow rate was 1.0 ml min⁻¹. The separation column for anionic species consists of cross-linked polystyrene-divinylbenzene resin with a functional group of alkanol quaternary ammonium as the stationary phase where all organic and inorganic species could be separated. (<http://www.dionex.com/en-us/columns-accessories/ion-chromatography/hydroxide/cons3609.html>).

Standard solutions containing known anionic species were individually analyzed to identify the retention time. The quantification was calculated from linear regression lines of mixed anionic standards, detection limits and relative error of measurement were calculated from calibration lines of each anion. All calculations for electroneutral and non-seasalt species were provided by Technical Manual for Wet Deposition Monitoring in East Asia (Network Center for EANET, 2000).

The various concentrations of thymol ranged from 25 – 400 ppm were added in mixed anionic solutions to determine the appropriate amount with different storage times.

3. Results and Discussion

3.1 Optimization and calibration of Ion chromatographic analysis

An analytical condition of Ion Chromatography for organic species were modified and optimized from the Dionex recommended conditions (<http://www.dionex.com>). The gradient profile started from 1 mM at the beginning and exponentially increased to 5 mM in 7 min. The concentration of potassium hydroxide was then continuously increased to 8 mM within 10 min. and immediately increased to 10 mM at 10.01 min. The increasing concentration in potassium hydroxide from 0 to 10 mM was appropriated for completely separation for monocarboxylic acids. The obtained chromatogram of organic and inorganic species is shown in Figure 1. The peaks of lactate (9.40 min), acetate (9.65 min), propanoate (10.27 min) and formate (10.67 min) ions were separated with high resolution time. Chloride, nitrate and sulfate ions showed high electrical conductance and could be eluted at 14.92, 23.56 and 30.59 min, respectively. Dicarboxylate ions were eluted with high concentration of potassium hydroxide in order of succinate (25.28 min), malonate (27.09 min) and oxalate (33.24 min) ions.

The retention time, calibration curves of all species determined by linear regression as well as correlation coefficients and detection limits of the appropriate methods were summarized in Table 1.

The appropriate chromatographic methods provided very good precision and repeatability, the standard deviations ranged from 0.01 – 0.55 μM for all concentration levels. The method mostly provided the relative error within the accepted limit ($\pm 10\%$).

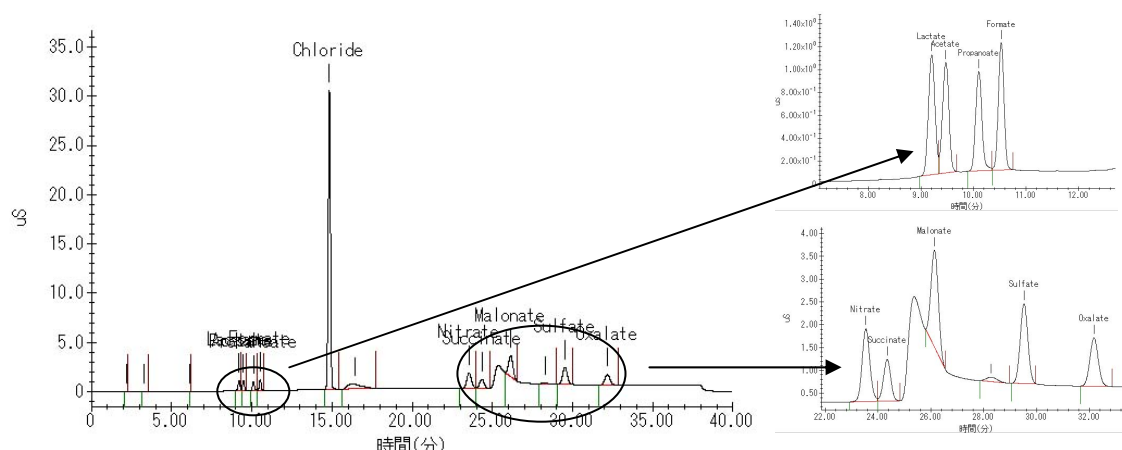


Figure 1. Chromatogram of mixed organic and inorganic species.

Table 1. Retention time, linear regression lines, correlation coefficients and detection limits of the measurement for anionic species.

Anions	Retention time (min)	Calibration curve	Correlation coefficient	Detection limit (μM)
Lactate	9.40	$x = 5.238 \times 10^{-5}y - 0.0795$	0.999857	0.25
Acetate	9.65	$x = 6.895 \times 10^{-5}y - 0.4818$	0.998963	0.67
Propanoate	10.27	$x = 8.118 \times 10^{-5}y - 0.6673$	0.999091	0.37
Formate	10.67	$x = 5.978 \times 10^{-5}y - 0.3432$	0.999445	0.20
Chloride	14.92	$x = 1.669 \times 10^{-6}y - 0.002$	0.999997	0.46
Nitrate	23.56	$x = 2.993 \times 10^{-6}y - 0.02577$	0.999862	0.38
Succinate	25.28	$x = 4.79 \times 10^{-5}y - 0.1306$	0.999386	0.78
Malonate	27.09	$x = 6.404 \times 10^{-5}y + 3.793$	0.999118	4.85
Sulfate	30.59	$x = 2.465 \times 10^{-5}y$	0.998762	1.55
Oxalate	33.24	$x = 3.149 \times 10^{-5}y$	0.998868	0.93

x and y denote concentrations of ions (mg l^{-1}) and represented peak area (arb. unit), respectively.

3.2 pH and EC of rainwater collected at the three monitoring sites during June and October, 2008

Volume-weighted mean (VWM) pH and EC of rainwater collected at the three monitoring sites during June and October, 2008 were given in Table 2. The results showed that the VWM-pH of Ogasawara rainwater was closed to the pH of natural unpolluted rainwater (5.6). The lowest EC in the Ogasawara site indicated the lower concentrations of ionic species which were also observed in Table 3 and 5. Low VWM-pH and high VWM-EC of rainwater in the Tokyo site was attributed to the anthropogenic activities, especially automobile emissions. The data of Si Racha monitoring site suggested that ionic species derived from industrial activities caused lower pH of rainwater. The results were clearly indicated that anthropogenic activities of both transportation and industry cause d lower pH of rainwater than natural activities.

Table 2. VWM-pH and EC of rainwater samples collected at the three monitoring sites during June and October, 2008.

Station	pH	EC (mS m^{-1})
Si Racha	4.66	1.29
Ogasawara	5.14	0.96
Tokyo	4.42	3.31

3.3 Concentration of cationic species in rainwater collected at the three monitoring sites.

VWM concentrations of cations in rainwater collected at the three monitoring sites were shown in Table 3. For metropolitan city as Tokyo, ammonium ion was dominated followed by sodium ion. The Ogasawara and Si

Racha sites were located near the coastal line; sodium ion originated from seasalt particles dominated as well as cluster elements such as calcium and magnesium ions. Tokyo site is also closed to the sea (Tokyo bay), high sodium concentration was the second most ion that contributed from seasalt compared to other species. Si Racha site was also located closed to petrochemical plants and many industrial estates, and thus those emission sources might generate ammonium ion as the second most abundant ion. Non-seasalt (nss) calcium ion could be calculated from Eq. (1), the nss-calcium in Ogasawara rainwater (remote site) was lower compared with the seasalt fraction. It could be considered that most of calcium ions originated from the seawater while this cluster ion in Tokyo rainwater (urban site) and Si Racha rainwater (industrial site) was considered to be mainly originated from anthropogenic activities. VWM of cations were given in Table 3.

The non-seasalt (NSSF) or seasalt fractions (SSF) of one component (X) were calculated by the following equations:

$$NSSF_X = [X_{\text{rain}}] - [(Na_{\text{rain}}) * (X/Na_{\text{seawater}})] \quad (1)$$

$$SSF_X = [Na_{\text{rain}}][X/Na_{\text{seawater}}] \quad (2)$$

Table 3. Volume-weighted mean concentrations of cations in rainwater.

Station	Volume-weighted mean concentrations (μM)					
	Ammonium	Sodium	Potassium	Magnesium	Calcium	nss-Calcium
Si Racha, Thailand	15.43	19.07	3.95	1.33	10.10	9.69
Ogasawara, Japan	1.21	37.26	0.91	5.39	0.88	0.13
Tokyo, Japan	47.32	17.14	1.65	2.60	6.25	5.88

3.4 Neutralization of acidic species in rainwater

Ammonium ion and various anion oxides, carbonate and bicarbonate of basic cations such as Ca^{2+} , Mg^{2+} and K^+ were able to neutralize protons from sulfuric, nitric and other organic acids in rainwater. The degree of neutralization of acids, which are mainly considered for nitrate and sulfate ions were calculated as neutralization factors (NF) expressed by the below equation:

$$NF_X = [X]/[\text{NO}_3^- + \text{SO}_4^{2-}] \quad (3)$$

Where X denotes the respective cation concentrations (μM) of interest species (NH_4^+ , Ca^{2+} and Mg^{2+}). Table 4 demonstrates that ammonium ion is considered as the major neutralizing ions followed by K^+ and Ca^{2+} . The high concentration of ammonium ion in rainwater corresponds with the high amount of ammonia gas in ambient air. From the neutralization factors in Table 4, ammonium ion provided the highest NF in Si Racha and Tokyo sites. This ion obtains from aqueous dissolution of ammonia which is mainly emitted from fertilizer application, biomass burning and animal breeding (Bouwman *et al.*, 1997).. Ammonium ion partly neutralized acid species in Tokyo and Si Racha rainwater. Calcium ion which was originated from anthropogenic activities

(Table 3) was the second most neutralization ion in Si Racha rainwater. Magnesium ion as cluster ion from natural sources was the most neutralization ion in Ogasawara rainwater

Table 4. Neutralization factors for NH_4^+ , Ca^{2+} , Mg^{2+} , and K^+ .

Station	Neutralization factors			
	Ca^{2+}	Mg^{2+}	NH_4^+	K^+
Si Racha, Thailand	0.32	0.04	0.48	0.12
Ogasawara, Japan	0.13	0.82	0.18	0.14
Tokyo, Japan	0.07	0.03	0.57	0.05

3.5 Contribution of anionic species to ion concentrations in rainwater.

The concentrations of anions in rainwater and their total free acidities are shown in Table 5. The most abundant anion in rainwater collected at both Ogasawara (remote) and Si Racha (industrial) sites was chloride ion, which infers that marine contribution is significant. Nitrate was dominated in Tokyo rainwater, which infers that nitrate was supposed to originate from automobiles, and sulfate was the second most abundant and also originated from anthropogenic sources. Among organic species, lactate was the most abundant in Ogasawara rainwater while formate was the most dominant species in Tokyo and Si Racha rainwater followed by acetate ion. Formate ion is considered to originate from oxidation of formaldehyde. Aqueous and atmospheric oxidation of aldehydes to carboxylic acids (Chameides and Devis, 1983) by oxidants such as hydroxyl radical and oxidation of ethanol in gasohol were the major sources of acetic acid in Si Racha rainwater.

Volume weighted mean (VWM) concentration and volume weighted standard deviation were calculated using the following equations (Huang *et al.*, 2008):

$$\text{VWM concentration} = \frac{\sum x_i p_i}{\sum p_i} \quad (4)$$

$$\text{VWMSD} = \sqrt{\frac{N \sum p_i^2 [x_i]^2 - (\sum p_i [x_i])^2}{(\sum p_i)^2 (N-1)}} \quad (5)$$

VWM concentrations and VWMSD of anions and their acidities are shown in Table 5. An acidity of anion, $[\text{A}^-]$ is an amount of dissociated acid and determined by the following acid-base equilibrium equation (4). In addition to acidities, a total free acidity (TFA) can be expressed by total free anion concentration determined by the Eq. (5) (Keene *et al.*, 1983; Peña *et al.*, 2002):

$$[\text{A}^-] = \frac{K_a [\text{M}]}{K_a + [\text{H}^+]} \quad (6)$$

$$\text{Total Free Acidity} = 2[\text{nss-SO}_4^{2-}] + [\text{NO}_3^-] + \Sigma[\text{Formate, Acetate, Propanoate}] + 2\Sigma[\text{Lactate, Succinate, Oxalate}] \quad (7)$$

Where $[\text{M}]$ denotes the concentrations of anionic species, K_a denotes the acid dissociation constant and $[\text{H}^+]$ denotes the hydrogen ion concentration. For Si Racha rainwater, total free organic acids exceeded up to

20.94% of total free acids which was almost ten times higher than those in the other two locations. The acidity of rainwater was generated from nitrate and nss-sulfate that acidified pH Tokyo rainwater while organic acids were not much affect in pH of Tokyo rainwater. Difference from Tokyo rainwater, Ogasawara rainwater presented very low acidity and mostly contributed from sulfate and nitrate ions.

Table 5. Concentrations of anionic species and total free acid of anionic species in rainwater.

Species	Si Racha		Tokyo		Ogasawara	
	Conc. (μM)	Acidity (μM)	Conc. (μM)	Acidity (μM)	Conc. (μM)	Acidity (μM)
Sulfate	10.06 ± 1.550	10.06	31.02 ± 0.197	31.02	4.03 ± 1.314	4.03
Nitrate	8.87 ± 1.970	8.87	45.88 ± 14.997	45.88	2.06 ± 0.338	2.06
Formate	5.35 ± 3.433	4.71	1.49 ± 0.651	1.61	0.17 ± 0.048	0.16
Acetate	1.90 ± 0.327	0.80	1.23 ± 0.475	0.32	0.09 ± 0.066	0.06
Propanoate	3.41 ± 1.773	1.21	0.05 ± 0.037	0.01	4.96 x 10 ⁻⁵ ± 9.46 x 10 ⁻⁵	9.6 x 10 ⁻¹¹
Lactate	0.99 ± 0.271	0.85	0.04 ± 0.024	0.03	0.26 ± 0.076	0.02
Succinate	-	-	0.02 ± 0.023	3.54 x 10 ⁻⁸	-	-
Oxalate	0.20 ± 0.055	0.11	0.18 ± 0.084	0.007	0.01 ± 8.276 x 10 ⁻³	0.008
TFA		36.67		109.90		10.37

For all rainwater samples, monocarboxylic acid anions such as formate, acetate, propionate were most abundant, especially in Si Racha rainwater (18.68%) followed by 2.3% and 1.7% for Ogasawara and Tokyo rainwater respectively. Dicarboxylic acid anions such as lactate, succinate and oxalate were very low contribution in all sites (0.09, 0.003 and 0.3% for Ogasawara, Tokyo and Si Racha rainwater, respectively). It could be concluded that organic acids in Si Racha rainwater originated from anthropogenic activities. Sulfate and nitrate ions were acidic anions from anthropogenic activities in Tokyo and Ogasawara rainwater. Since Ogasawara is located in a remote site, the impact of these two acidic anions might be transformed from washed out not originated from the sampling station itself. They might be no sources of acidic pollutants so that rainwater probably dissolved all acidic species from polluted cloud.

The ionic neutralization in rainwater is expressed by the following equation:

$$R_1 = (C - A)/(C + A) \times 100\% \quad (8)$$

Where R_1 , C and A represent an ionic balance of rainwater and equivalent concentrations of cations and anions, respectively. Figure 2 shows ionic balances of rainwater including organic anions and those without organic anions. Total equivalent concentrations of cations could be balanced with those of anions in Ogasawara and Tokyo rainwater, which could be concluded that all ionic species in rainwater were analyzed. On the other

hand, some Si Racha rainwater samples without organic anions are highly rich in cation ($R_1 > 20\%$). When organic species were added to total equivalent concentrations of anionic species (A) in equation (8) for Si Racha rainwater samples, the ionic balances were improved to fall within the range of acceptance limit ($\pm 20\%$). This results suggests that organic ionic species must be considered when ionic balance of Si Racha rainwater is focus on.

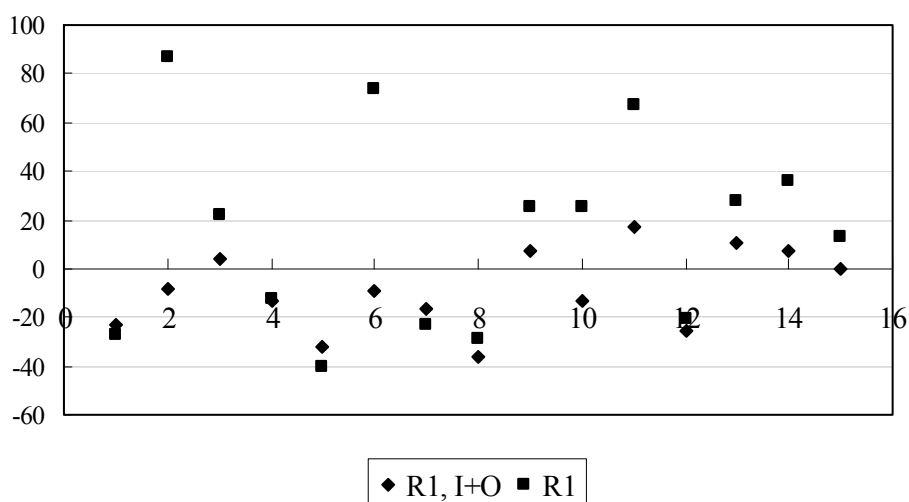


Figure 2. Ionic balances of rainwater including organic anions and those without organic anions.

3.6 Correlation coefficients between ionic species

The correlation coefficients between any ionic specie concentrations in Ogasawara rainwater in Table 6 showed strong correlations between sodium, potassium calcium and magnesium ions ($r > 0.7$). It could be concluded that these ions are suspected to originate from the marine natural sources. Sodium, potassium, calcium and magnesium ions were assumed to be dominantly found in chloride salts and some were in sulfate salts because of considerably high correlation with chloride ($r > 0.72$) and high correlation with sulfate ($r > 0.59$). Acetate ion highly correlated with proton as well as ammonium and calcium ions, which implies that acetate existed as acetic acid, ammonium salt or calcium salt. Strong correlation between nitrate and acetate ions ($r = 0.788$) indicated the same origin from anthropogenic activities possibly vehicle and industrial sources..

In Tokyo rainwater, strong correlation between sodium and magnesium ions with chloride was found (Table 7), which suggests that these cations existed as chloride salts. Nitrate and sulfate ions were assumed to originate in ammonium salts because of high correlation coefficients. Formate strongly correlated with acetate and lactate ions due to the anthropogenic activities. The minus signs of lactate and oxalate ions with sodium and potassium ions indicated these compounds were in acidic forms. It could be summarized that the causes of acidity in Tokyo rainwater generating from nitrate and sulfate ions in acid and ammonium salts on the basis of high correlation coefficients.

Table 6. Correlation coefficients between ionic species in Ogasawara rainwater.

	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Formate	Acetate	Lactate
H ⁺	1	0.002	0.244	0.02	0.048	4 x 10 ⁻⁵	0.006	0.280	0.165	0.049	0.417	0.201
Na ⁺		1	0.006	0.947	0.711	0.985	0.970	-0.015	0.617	0.0523	0.152	0.011
NH ₄ ⁺			1	0.046	0.216	0.007	0.007	0.390	0.012	0.067	0.658	0.049
K ⁺				1	0.739	0.928	0.926	-0.007	0.669	0.301	0.006	-0.004
Ca ²⁺					1	0.706	0.725	0.062	0.447	0.213	0.944	-0.026
Mg ²⁺						1	0.957	-0.024	0.590	0.481	-0.270	0.019
Cl ⁻							1	-0.013	0.591	0.147	-0.072	-0.002
NO ₃ ⁻								1	0.040	0.039	0.788	0.032
SO ₄ ²⁻									1	0.014	-0.000	0.011
Formate										1	*	0.059
Acetate											1	-0.098
Lactate												1

Table 7. Correlation coefficients between ionic species in Tokyo rainwater.

	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Formate	Acetate	Lactate	Oxalate
H ⁺	1	0.187	0.529	-0.070	-0.034	0.192	0.237	0.734	0.793	-0.200	-0.157	-0.105	0.003
Na ⁺		1	-0.001	0.325	0.019	0.927	0.989	-0.031	0.067	-0.029	-0.087	-0.650	-0.462
NH ₄ ⁺			1	0.078	0.341	0.006	-0.001	0.820	0.625	-0.002	0.0213	0.016	0.3697
K ⁺				1	0.1153	0.202	0.253	0.049	0.113	0.246	0.097	-0.112	-0.711
Ca ²⁺					1	0.089	0.016	0.308	0.061	0.013	0.006	0.085	0.0663
Mg ²⁺						1	0.945	-0.005	0.089	0.112	-0.137	-0.479	0.280
Cl ⁻							1	-0.027	0.081	-0.065	-0.120	-0.810	-0.376
NO ₃ ⁻								1	0.552	2 x 10 ⁻⁵	0.030	0.087	0.228
SO ₄ ²⁻									1	-0.032	-0.011	0.027	0.045
Formate										1	0.772	0.789	-0.049
Acetate											1	0.066	0.000
Lactate												1	*
Oxalate													1

* Very small no. of data.

In Si Racha rainwater (Table 8), sodium ion strongly correlated ($r = 0.983$) with chloride ion, they might be affected by marine contributions. Potassium and ammonium ions were also considered to originate from the same sources because of high correlation ($r = 0.713$). From the same reasons, acetate and formate ions were probably found in ammonium acetate and calcium formate salts, respectively. Propanoate might be originated with formate ion while lactate and oxalate were generated together with nitrate and acetate ions. The last four ions (lactate, oxalate, succinate and malonate) could be classified as artificial anions especially nitrate from combustion in vehicles. Oxidation of aldehydes (formaldehyde and acetaldehyde) and ethanol from gasohol were the main sources of formate and acetate ions.

Table 8. Correlation coefficients between ionic species in Si Racha rainwater.

	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Formate	Acetate	Propanoate	Lactate	Oxalate
H ⁺	1	0.004	-0.043	-0.032	-0.055	-0.001	0.013	0.325	0.275	-0.210	0.001	-0.021	0.146	0.042
Na ⁺		1	0.128	-0.008	-0.017	0.407	0.983	-0.075	-0.015	-0.233	-0.080	0.015	-0.081	-0.353
NH ₄ ⁺			1	0.713	0.037	0.001	0.095	0.157	0.034	0.172	0.517	0.024	0.348	0.315
K ⁺				1	0.081	0.003	-0.002	0.067	0.053	0.066	0.137	-0.033	0.394	0.312
Ca ²⁺					1	0.009	-0.018	0.028	0.032	0.726	-0.037	-0.009	0.027	0.073
Mg ²⁺						1	0.431	-0.014	0.025	0.176	0.022	0.000	-0.043	-0.081
Cl ⁻							1	0.048	-0.002	-0.248	-0.058	0.000	0.048	0.239
NO ₃ ⁻								1	0.089	0.075	0.272	-0.027	0.527	0.523
SO ₄ ²⁻									1	-0.007	0.005	-0.037	0.031	0.016
Formate										1	0.305	-0.729	0.061	0.266
Acetate											1	-0.073	0.795	0.576
Propanoate												1	-0.078	-0.228
Lactate													1	0.616
Oxalate														1

3.7 Time variation of organic acid concentrations with addition of thymol as preservative

Concentrations of organic acids in rainwater are significantly decreased with the elapsed time in a room temperature because microorganisms could assimilate them after collection. Various kinds of biocides such as chloroform, mercuric chloride, phosphoric acid and thymol were applied as preservative (Kawamura *et al.*, 1996; Sempéré and Kawamura 1996; Morales *et al.*, 1998; Kawamura *et al.*, 2001; Lara *et al.*, 2001; Peña *et al.*, 2002 and Avery *et al.*, 2006), while Fornaro and Gutz (2003) stored all rainwater samples in a freezer (-18 °C). In this research work, thymol was selected as preservative of rainwater. Time variation of seven kinds of mono- and di-carboxylic acid concentrations (formic, acetic, propanoic, lactic, succinic, maleic and oxalic acids) and two levels of the initial concentrations (10 and 50 µM) with a storage time were presented in Figure 3. Increasing of thymol concentrations did not significantly result in decrease of organic acid concentrations. For various concentrations of thymol, the two initial levels of all organic acid concentrations were mostly stable until 21 days and then continuously decreased. Among organic acids, a concentration of lactic acid with the initial concentration of 50 µM rapidly decreased within 21 days and slightly decreased after the day 21. It might be attributable that lactic acid was one of fruit acids that could be served as nutrient, and thus it was more suitable for microorganism than the other kinds of organic acids. For the high level of the initial concentrations (50 µM), all acids decreased more rapidly than those with the lower initial concentrations after 21 days. It could be explained that the degradation rate was dependent on the initial concentrations of organic acids. For high precision analysis, these results suggest that the rainwater samples have to be measured within three weeks.

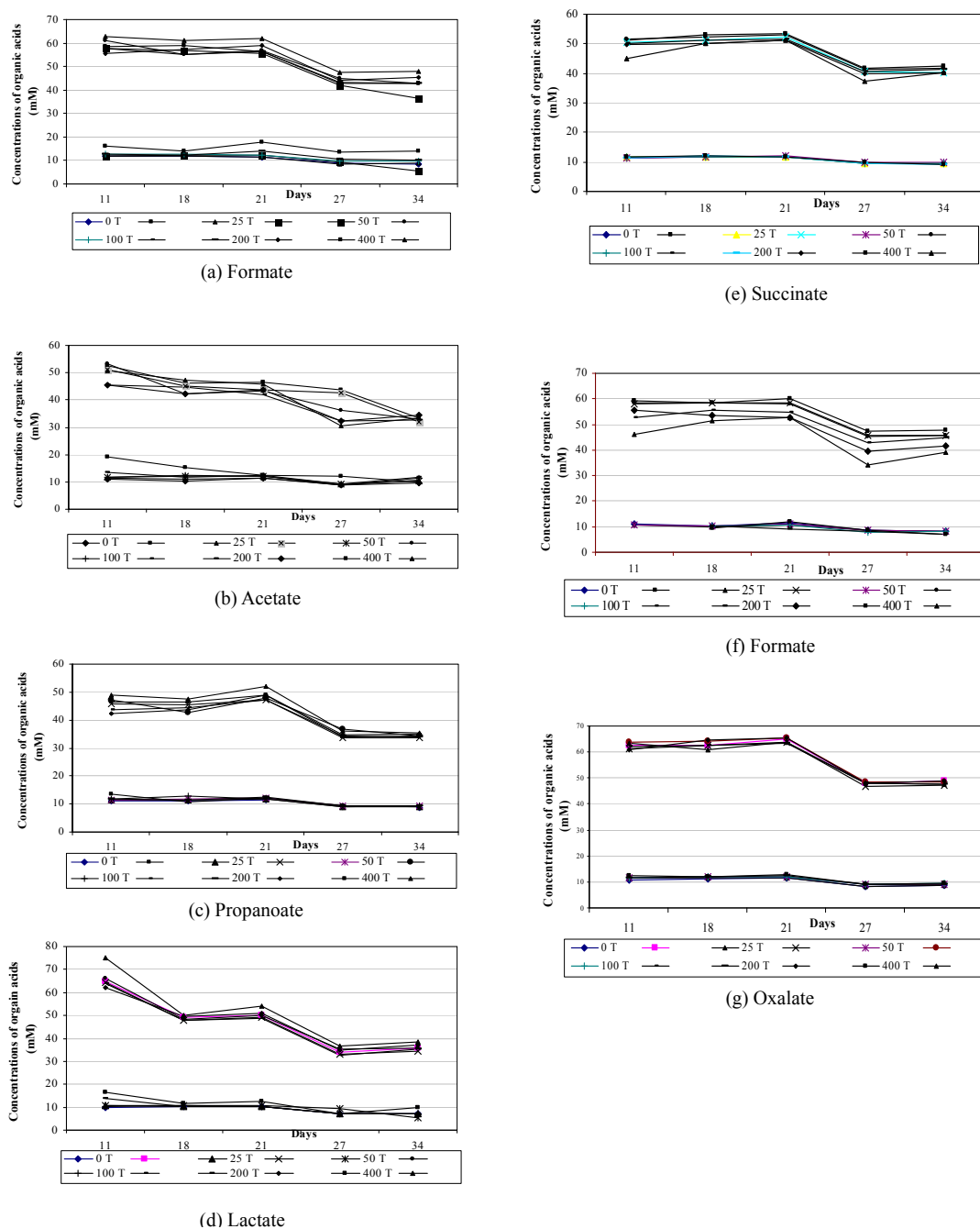


Figure 3. Time variation of organic acid concentrations when a prepared organic acid solution was added with various amount of thymol. Initial concentrations of organic acids were 10 and 50 μ M, and thymol concentrations in the sample solutions were 0, 25, 50, 100, 200, 400 ppm, respectively.

4. Conclusions

Mono- and di- carboxylic acids in rainwater samples could be analyzed by ion chromatographic technique without sample preparation. The samples were measured for pH, EC, ion concentrations, sample volume and amount of precipitations. Among cations, sodium was the most abundant in Si Racha and Ogasawara rainwater, whereas ammonium ion was the most abundant in Tokyo rainwater. Cluster ions such as magnesium are

considered to play an important role in neutralization of acidity in remote site of Ogasawara. For Tokyo (urban site) and Si Racha (industrial site) rainwater, ammonium ion strongly neutralized acid anions and cause decrease in the acidity of rainwater.

Contribution of organic acid ions to total acidity was only 21% while inorganic acids such as sulfuric and nitric acids contributed lower pH of Si Racha rainwater samples. Different from Si Racha, acidity of Tokyo and Ogasawara rainwater were contributed from inorganic species (almost 98%). Both cationic and anionic species in Ogasawara rainwater were mostly originated from natural sources. Concentrations of monocarboxylic acids were higher than dicarboxylic acids in rainwater samples collected in all three sampling locations. Besides three different locations, mono- and di- carboxylic acids were more significantly contributed in industrial site than in rural and remote sites. Addition of organic species could be improved the ionic neutralization of Si Racha rainwater. From the correlation coefficients, it could be found the cluster ions were associated with chloride and sulfate salts. It could be found that the acidity of rainwater in Tokyo caused by ammonium sulfate and nitrate.

Sodium chloride was the most abundant and organic acids were strongly contributed to lower pH of Si Racha rainwater.

Concentrations of organic acids were sustained by addition of various amounts of thymol as preservatives. Addition of thymol could maintain concentrations of organic acids within 21 days and then continuously decrease after the day 21. Contribution of organic acids should be considered for lower pH of rainwater especially in industrial and heavy traffic areas.

5. Acknowledgements

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Effect of Haze Episodes on Chemical Composition of Wet and Dry Depositions at Monitoring Sites in Thailand

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Abstract

This study investigated contribution of haze episode to depositions of chemical species of dry (aerosol) and wet depositions in Northern and Southern Thailand. Variations of PM₁₀ caused by haze episodes were investigated. Air mass trajectory analysis using HYSPLIT model with related fire hotspot data was also carried out. In the case of “Northern haze”, daily PM₁₀ concentrations at 5 monitoring sites around Chiang Mai and Lampang showed a maximum value (up to 396 µg/m³) in the 13th of March 2007. Since a heavy haze was observed during March and April, 2007, the peaks of PM₁₀ concentration may be associated with the haze event. Factor analysis of ionic species of aerosol and precipitation performed for the samples collected at the Chiang Mai EANET (Acid Deposition Monitoring Network in East Asia) monitoring sites indicated aerosol species: NO₃⁻, K⁺ and Ca²⁺ associated with biomass burning. Their factor scores were relatively high during the heavy haze even in March 2007 as compared to other years. Although there was no rainfall during February and March, 2007, NH₄⁺, CH₃COO⁻ and HCOO⁻ of the first rainfall (April, 2007) even were enriched, which may be associated with the haze event. Furthermore, trajectory analysis has proved that air masses which passed through hot spot area arrived at the northern Thailand during the occurrence of high PM₁₀ concentration day. In the case of “Southern haze”, daily PM₁₀ concentrations at three monitoring sites in southern Thailand were of a maximum value (up to 108 µg/m³) in 16th August 2005, which was corresponded to the haze event. However, the extent of haze was less than that of the “Northern haze”. The factor analysis of ionic species of precipitation and aerosol collected at the Songkla site in southern Thailand and the Tanah Rata EANET site in Malaysia revealed that presence of SO₄²⁻, NO₃⁻ and NH₄⁺ in aerosol may be associated with the haze period, and NH₄⁺, NO₃⁻ and HCOO⁻ in precipitation at Songkla and NH₄⁺, NO₃⁻ and K⁺ in precipitation at Tanah Rata enriched and showed large factor loadings during the haze period. Increments of their factor scores were also detected in the heavy haze period of August 2005 as compared to other years.

Key words: Haze episode, wet and dry depositions, trajectory analysis, factor analysis

1. Introduction

In recent years, there have been two significant higher pollution episodes that cause vast effects on atmospheric environment in Thailand. “Northern haze”, occurs in northern region from March to April, originates from open biomass burning activities (burning up open field agricultural residuals as well as forest fires) both in northern Thailand and adjacent countries (Myanmar and Laos). Another haze episode called as “Southern haze”, frequently occurs during August to September, is caused by transport of contaminated air masses to southern Thailand from areas of biomass burning in Indonesia. These episodes have been recognized as potential long-range transport of air pollution in the ASEAN region (Qadri, 2001; Pongkiatkul & Kim Oanh, 2007). Air quality monitoring revealed that PM₁₀ concentrations were frequently exceeded the national ambient air quality standard during these haze events. In particular, the strong Northern and Southern haze episodes were recognised as producing very high PM₁₀ concentrations in the period of March 2007 and August 2005, respectively (Pengchai *et al.*, 2009; Pentamwa & Kim Oanh, 2008). These significantly affected not only on public health but may be potentially responsible for increasing deposition of chemical species in the regions. Previous studies reveal that biomass burning activity contributes a higher number of chemical species, e.g., K⁺, CH₃COO⁻, HCOO⁻, NO₃⁻, NH₄⁺ and SO₄²⁻ (Whitlow *et al.*, 1994; Dibb *et al.*, 1996; Pengchai *et al.*, 2008), which may cause large effect on sensitive terrestrial and aquatic ecosystems.

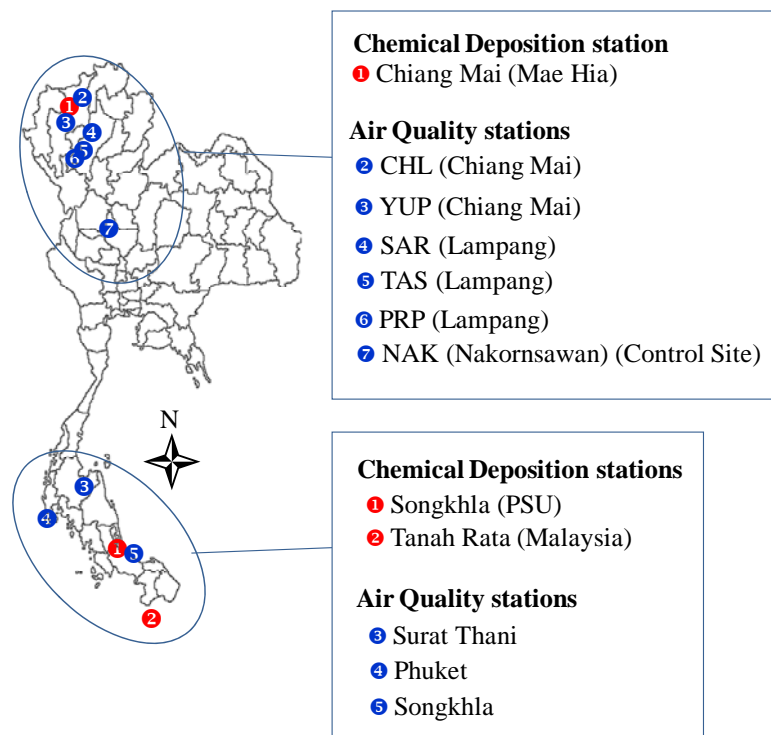
This study aims to evaluate the impact of these two haze episodes on the chemical composition of wet and dry depositions by means of the following 3 subjects using monitoring data from 2005 to 2008 for “Northern haze” and 2004 to 2006 for “Southern haze”; (1) PM₁₀ concentration variations at monitoring sites in Thailand during haze events, (2) source identification of chemical species of wet and dry depositions in northern and southern Thailand between severe-haze and non-haze situations by using factor analysis, and (3) investigation of air masses transport to Thailand during the haze episodes.

2. Methods

2.1 PM₁₀ measurements

In this study, we considered the air quality during heavy haze episodes in comparison with the non haze periods. Collection of the data therefore covered the years before and after the years that the heavy haze events were reported, i.e., 2007 for Northern region and 2005 for Southern region. In the case of “Northern haze”, hourly PM₁₀ data were collected at the national ambient air quality monitoring stations of Pollution Control Department (PCD) of Thailand during the periods of 2005 to 2008. Data from two automatic monitoring stations located in Chiang Mai province: (1) Yuparaj Witayalai School, (2) City hall and the three stations in Lampang province: (1) Sarn Lag Muang, (2) Tar-se sub-district, (3) Prapa (Water Supply Local Office) were selected. Additionally, the station located at Nakornsawan province, central Thailand was also selected as a control site because it had no report on the effect of the heavy haze episode. For “Southern haze”, the data gathered from the PCD’s automatic monitoring stations during the years 2004 to 2006 in three southern cities: (1) Surat Thani, (2) Phuket and (3) Songkla (Hat Yai district) were used. Locations of these stations are displayed in Figure 1. Concentration of PM₁₀ is measured using either Beta Attenuation or Tapered Oscillated Micro Balance (TEOM)

systems, depending on the stations. As for QA/QC consideration, the day that has missing measured hourly PM₁₀ concentrations over than 20% of all 24 hourly data were not used to calculate the daily mean concentration.



(CHL: Chiang Mai's City Hall, YUP: Yuparaj Witayalai School, SAR: Sarn Lag Muang, TAS: Tar-se Sub-district, PRP: Prapa (Water Supply Local Office), NAK: Nakornsawan, PSU: Prince of Songkla University)

Figure 1. Locations of chemical deposition and air quality monitoring stations.

2.2 Chemical depositions measurements

Dataset of wet and dry depositions from monitoring sites located in Northern and Southern regions of Thailand were selected at the same periods of PM₁₀ data as described earlier. An Acid Deposition Monitoring Network in East Asia (EANET)'s site located in Chiang Mai province (Mae Hia) of Northern Thailand and another two southern sites: (1) Songkhla (Prince of Songkla University, PSU) and (2) EANET's site at Tanah Rata (located in Malaysia) were selected for this study. The measured concentrations of ion components in aerosol, namely, SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺ were used as the parameters of dry deposition data for this study. Aerosols were collected by using the four-stage filter pack method which applies an ensemble of four filters in line with the air stream. The first filter made of polytetrafluoro-ethylene (PTFE); pore size 0.8 μm and diameter 47 mm, mounted in front of the other filters was used for collecting the aerosols while others are for collecting gases. The filters were contained in the filter pack holder which was connected to sampling pump with the flow rate ranged from 1 to 2 liter/min. Air volumes counted by mass flow meters or gas volume meters were used for calculation of ambient air concentration. Shelter was also mounted above the filter pack holder for rain protection. The sampling period was ten-daily basis. After sampling, the filter pack was sealed into a polyethylene bag covering further with an aluminum-coated bag. The sealed filter pack was kept in a refrigerator and transported to the laboratory. The chemical components were analyzed by ion chromatography (EANET, 2003).

For wet deposition, twelve chemical species: SO_4^{2-} , NO_3^- , Cl^- , HCOO^- , CH_3COO^- , PO_4^{3-} , NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and H^+ were included in this study. Rainwater was collected on a daily basis using a wet-only collector. The rainwater samples were stored in polypropylene bottles in a refrigerator. Meteorological parameters during the sampling periods were also recorded. After collection, the samples were transported to the laboratory for chemical analysis using ion chromatograph. pH and electrical conductivity were also determined with a pH electrode and an electric conductance meter, respectively (EANET, 2000). All wet deposition datasets were compiled into volume weight mean (VWM) concentration.

2.3 Factor Analysis

Factor analysis (Principle Component Analysis-PCA) is a statistical method which attempts to explain given datasets by a small number of underlying factors. This method has been widely used in previous studies to identify the number of possible sources having a major influence on air pollution problems (for example, Tanner & Wong, 2000; Astel *et al.*, 2004; Khare *et al.*, 2004; Thepanondh *et al.*, 2005; Seto *et al.*, 2007; Panyakapo & Onchang, 2008). In this study, factor analysis (Principle Component Matrix) was applied to ten-daily aerosol components data and daily wet deposition data of chemical species to identify their sources affecting air quality at chemical deposition sites. Initial factors were extracted from a matrix of correlations. Factors with eigenvalues over than one were considered for varimax rotation to obtain the final factor matrix. Factor scores were estimated by regression method, which is one of the most popular method (Seto *et al.*, 2007). Factor analysis was carried out by the principle component method using the statistical package – SPSS version 18 for Windows.

2.4 Trajectory analysis

In order to identify the relationship between the possible distant source areas and the pathways that give raise to the observed high PM_{10} concentration in the study areas, backward trajectory analysis was conducted by the NOAA HYSPLIT4 (Hybrid Single Particle Lagrangian Integrated Trajectory Model Version 4) model (Draxler & Rolph, 2003) together with the MODIS's satellite images of fire hotspots corresponded to open burning activities covering parts of Southeast Asia provided by the Fire Information for Resource Management System (FIRMS). The model performed a 3-days back-trajectory calculation at starting levels of 100, 500 and 1,000 m (above ground level) from the selected monitoring stations presenting highest PM_{10} concentrations. The starting time of a back-trajectory was started at 0.00 UTC.

3. Results and Discussion

3.1 Northern haze

3.1.1 PM_{10} variation

Monthly mean concentrations of PM_{10} at five monitoring stations and amount of rainfalls collected at the EANET site (Mae Hia) in North Thailand during the years 2005 to 2008 are presented in Figure 2. The variation of rainfall indicated wet and dry seasons in the area. Monthly variation of PM_{10} concentration detected at all stations shared the same pattern, in which it increased at beginning of dry season (December) and reached its peak in March before decreased by the end of April. This unique seasonal pattern of PM_{10} concentration was found only in Northern part of Thailand and it was suggested due to the influence of temporary source of PM_{10} as well as the occurrence of an inversion layer in the intermountain basin of Chiang Mai and Lampang areas during the dry period (Pengchai *et al.*, 2008). The distinctly highest PM_{10} concentrations over four years were

detected in March 2007 at Chiang Mai's stations (YUP and CHL). This may be due to the presence of an unusually long drought period which was no rainfall recorded since the end of December 2006 until mid of March 2007, with the consequence of possible enhancing biomass open burning activities and inactivating rain-out and wash-out processes. Figure 3 displays daily PM_{10} concentrations during dry season (February to April) 2007, when the possible severe haze episode was detected in Chiang Mai, at YUP and CHL stations with a comparison to the control site (NAK) at Nakornsawan province. Please note that the data were missing in some days during this period. Highest daily PM_{10} concentrations were detected on 13th March 2007 at both Chiang Mai's stations YUP and CHL, the figures were $396 \mu g/m^3$ and $317 \mu g/m^3$, respectively –being three times higher than Thailand National Ambient Air Quality Standard (NAAQS) of $120 \mu g/m^3$, while there were no significant increment of PM_{10} been detected at the control site. Pengchai *et al.* (2008) revealed that during the first two weeks of March 2007 air pollution in Chiang Mai and the surrounding provinces was raised steadily above the safety limit and produced a yellow-tinged haze with cutting visibility down to less than 1,000 m. The daily PM_{10} concentration variation in Lampang, depicted in Figure 4, indicates an increase of PM_{10} at the same period with evidence that values were also higher than ones at the control site. However, PM_{10} concentrations in Lampang's stations (SAR, TAS and PRP) seemed to be lower than in Chiang Mai stations (YUP and CHL). This may be due to different contribution of local emission sources and various role of local geographical feature. Chiang Mai is the second largest province with a population of about 1.6 million, whereas Lampang had only about 0.7 million in 2009. Both Chiang Mai and Lampang are located within an adjoined intermountain basin. The mountains act as a barrier which impedes polluted air parcels to move from Chiang Mai and further areas to Lampang. In overall, the analysis of PM_{10} variation indicated the increasing of PM_{10} concentration during dry periods in Northern Thailand, especially in the year 2007, which were possible related to biomass burning activities.

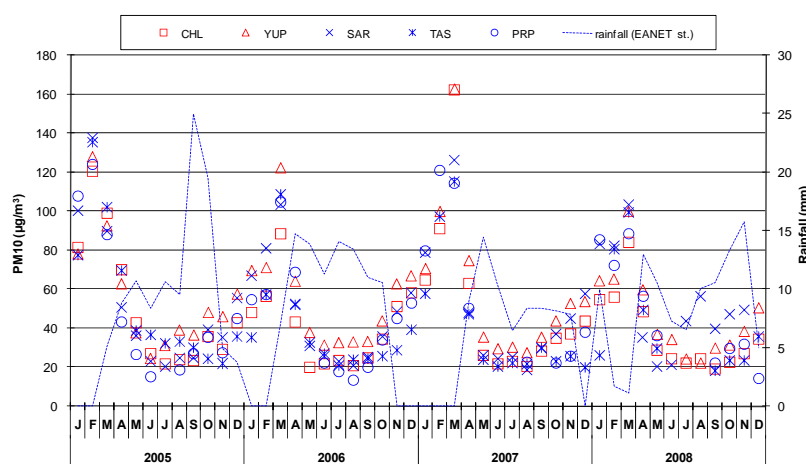


Figure 2. Monthly means PM_{10} and rainfall during 2005 – 2008 at five northern stations.

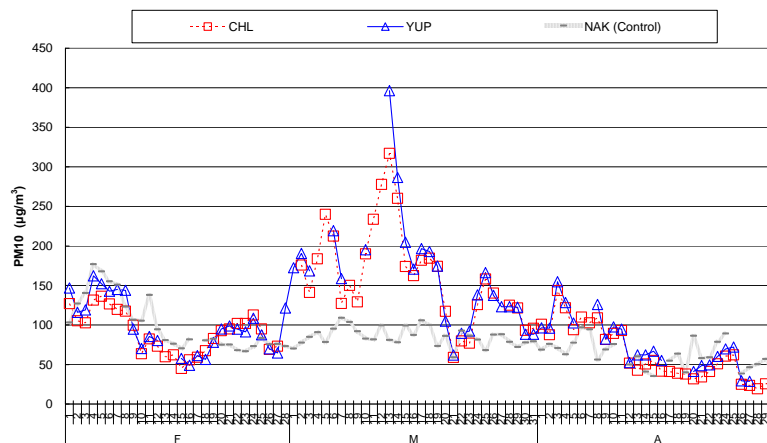


Figure 3. Daily mean PM₁₀ during dry season (February to April) 2007 at the stations located in Chiang Mai.

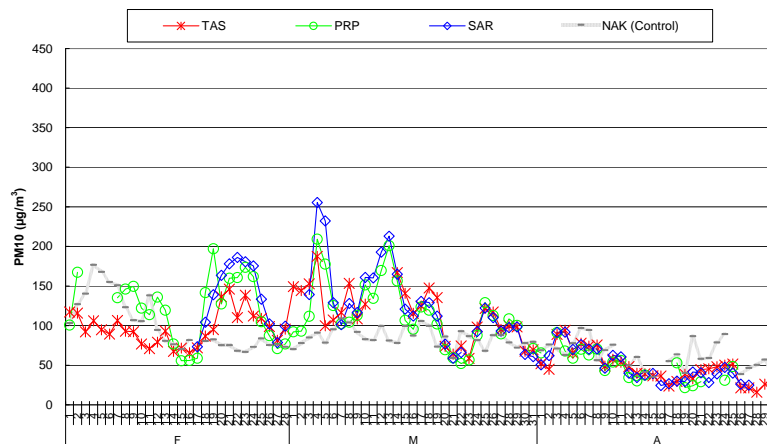
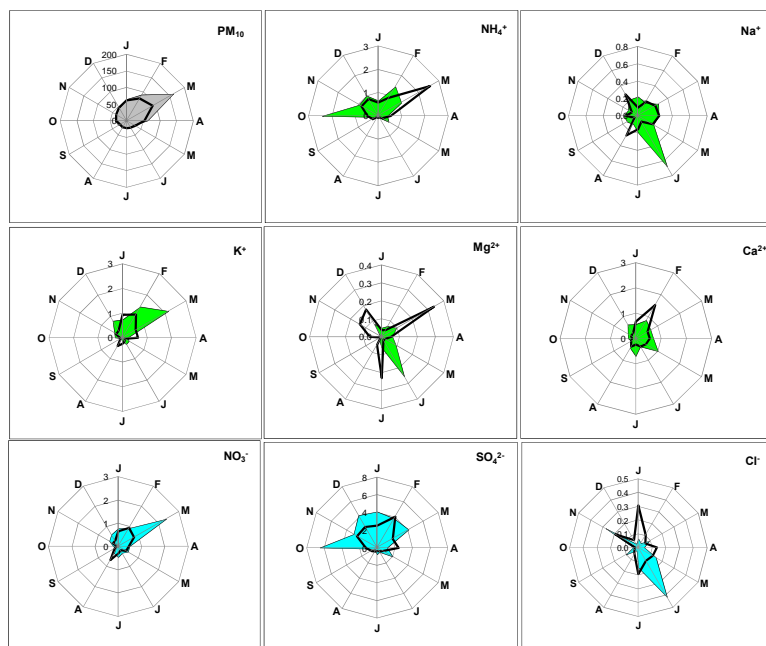


Figure 4. Daily mean PM₁₀ during dry season (February to April) 2007 at the stations located in Lampang.

3.1.2 Aerosol compositions and PM₁₀ concentration

Since the EANET site used for collecting chemical deposition species (Mae Hia) is located close to the PM₁₀ monitoring station at CHL (see Figure 1) at the distance about 6 km, this makes possible to compare the results of aerosol species and PM₁₀ concentrations to review its relationship. Monthly mean concentrations of PM₁₀ and aerosol species calculated from the data of the non-haze years of 2005, 2006 and 2008 are displayed in Figure 5 with the comparison to the severe haze year of 2007. It can be seen that PM₁₀ variation was in a unique pattern, while aerosol species relatively scattered over the months. K⁺ and NO₃⁻ likely followed the similar pattern of PM₁₀ in which the monthly mean concentrations within the severe haze period of March 2007 was higher than similar mean monthly values of non-haze years. This indicated a possible relationship between ionic aerosol species and PM₁₀, in particular during the severe haze episode. However, it should be remarked that filter pack method does not ensure completely precise measurement due to possibility of artifact problems. For example, volatilization of particulate NH₄NO₃ and NH₄Cl after collected on a filter, caused by increase of temperature during sampling period, could be occurred (EANET, 2003). This may result lower measuring values of relevant ionic species and therefore affecting this relationship analysis.



Unit: $\mu\text{g}/\text{m}^3$

Figure 5. Monthly means of PM_{10} (at CHL) and aerosol species (at Mae Hia) of non-haze years (2005, 2006 and 2008) (line) and haze year of 2007 (shaded area).

3.1.3 Wet deposition

Monthly weighted mean concentrations of measured ionic species with respect to occurrences of precipitation averaged over the years 2005, 2006 and 2008 compared with the value in 2007 collected at EANET (Mae Hia) site are given in Figure 6a and Figure 6b, respectively. As expected, concentration of ionic species showed inverse relationships with the precipitations as they were dissolved in the precipitation by means of rain-out and wash-out mechanisms. There was no rainfall during the whole period from December 2006 to March 2007 (Figures 6b and 2). That occurrence was an unusual in comparison with the mean values of those in the year 2005, 2006 and 2008 (Figure 6a) when there were some rainfalls even in dry seasons. Figure 7 illustrates monthly fractional contributions of cation and anion species in comparison with mean values over the three years and the year 2007. Interestingly, the percent shares of NH_4^+ , CH_3COO^- and HCOO^- were higher in April 2007 than those of the three yearly mean at the same month. This indicates the heavy haze episode possibly related to redistribution of compound inputs in precipitation.

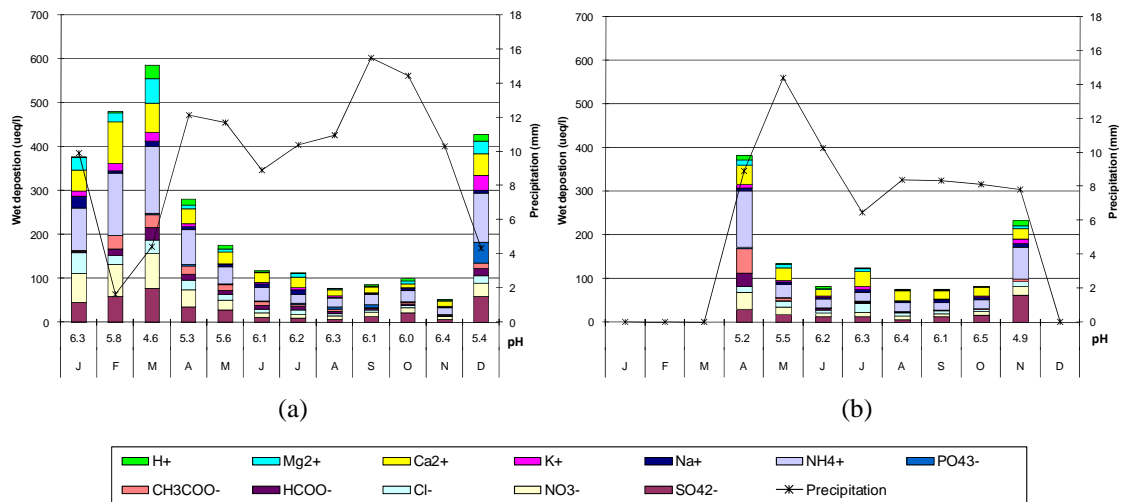


Figure 6. Monthly weighted average concentrations compared with occurrences of precipitation at Mae Hia over the years 2005, 2006 and 2008 (averaged) (a) and 2007 (b).

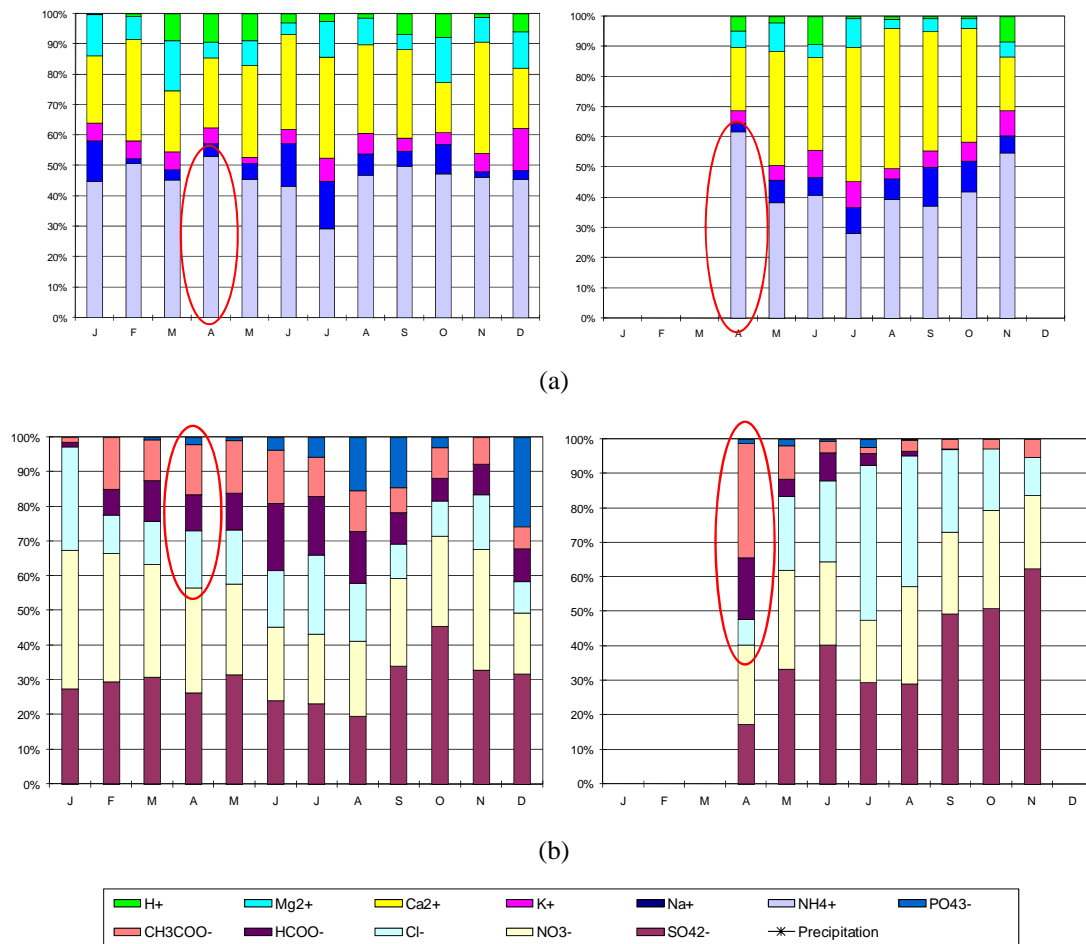


Figure 7. Monthly fractional contributions of cation (a) and anion (b) species measured at Mae Hia, compared between mean values over the three years (left) and the year 2007 (right), circles indicate remarked comparisons between percent shares of ionic species changed in the month of April.

3.1.4 Source identification

The results of factor analysis of ionic species in aerosol and in precipitation are presented in Table 1 and Table 2, respectively, for the data collected during 2005-2007. Underlined values express species of interest for its depositions. For aerosol species, this analysis identified three factors with explained about 69% of the data variance as well as factor loading with eigenvalues over than 1. Communalities, which indicate the explained fraction of the variability of the measured chemical species, are large enough for most of chemical species except SO_4^{2-} , NH_4^+ and Mg^{2+} . The first factor displays high loading level, accounting for 32.7%, of NO_3^- , K^+ and Ca^{2+} , indicating the influences of a combine source of biomass burning, combustion process. Factor 2 explains 20.8% of the variance providing correlation of SO_4^{2-} , NH_4^+ and Mg^{2+} components. This indicates the contribution of combustion process with the combination of agriculture (e.g., reaction between industrial exhaust gas and vegetative burning) and soil sources. Furthermore, dissolution of aerosols/secondary pollutants, e.g., $(\text{NH}_4)_2\text{SO}_4$ in rainwater, can cause the presence of co-occurrence of NH_4^+ with SO_4^{2-} . Such secondary aerosols are formed in the atmosphere through chemical processes. Ammonium sulfate, originating from reactions between ammonia and sulfuric acid, are major secondary aerosols (Harrison *et al.*, 1997; Chang *et al.*, 2007). The third factor contributes 15.6% of the variance and shows large loadings on Cl^- and Na^+ indicating the influence of long-range transport of sea salt.

Monthly means of factor scores of the first factor are displayed in Figure 8 as compared between two periods – non-haze (years of 2005, 2006 and 2008) and heavy-haze year of 2007. The 10-days concentrations of aerosol species fall on the first factor – NO_3^- , K^+ and Ca^{2+} – in 2007 are displayed in Figure 9. It can be seen that during the heavy haze observed in March 2007, factor scores of the first factor which includes biomass burning source were relatively high corresponding to the markedly increase of concentrations of such species. These facts clearly indicate that dry deposition of aerosol species in Chiang Mai is largely attributed to haze episode. However, Ca^{2+} may not be related to biomass burning being, instead, caused by soil source which is more pronounce in dry season than during other period in this area (Pengchai *et al.*, 2009). NO_3^- and K^+ in aerosol during the haze episode also agree with the study of Dibb *et al.* (1996). In particular, K^+ is well known as the marker of vegetative burning such as forest fires, filed crop burning and other agricultural waste combustion (Watson *et al.*, 2001; Muraleedharan *et al.*, 2000; Wangkiat *et al.*, 2004; Cachier *et al.*, 1995).

Table 1. Rotated varimax factor matrix of factor analysis for measured ionic aerosol species at Mae Hia

Component	Factor loadings			Communality
	1	2	3	
SO ₄ ²⁻	0.413	<u>0.583</u>	-0.166	0.538
NO ₃ ⁻	<u>0.796</u>	0.216	0.089	0.688
Cl ⁻	0.074	-0.244	<u>0.816</u>	0.730
NH ₄ ⁺	0.099	<u>0.751</u>	-0.135	0.591
Na ⁺	0.043	0.142	<u>0.877</u>	0.791
K ⁺	<u>0.753</u>	0.517	0.140	0.855
Mg ²⁺	-0.068	<u>0.747</u>	0.104	0.574
Ca ²⁺	<u>0.836</u>	-0.258	0.003	0.765
Eigenvalue	2.1	1.9	1.5	
Variance (%)	32.7	20.8	15.6	
Cumulative (%)	32.7	53.5	69.1	
Possible Source	Biomass burning Combustion process	Combustion process Agriculture Soil re-suspension	Marine contribution	

Table 2. Rotated varimax factor matrix of factor analysis for measured ionic species in precipitation at Mae Hia.

Component	Factor loadings			Communality
	1	2	3	
SO ₄ ²⁻	<u>0.733</u>	0.386	-0.104	0.697
NO ₃ ⁻	<u>0.707</u>	0.582	-0.001	0.838
Cl ⁻	0.265	<u>0.734</u>	-0.043	0.611
HCOO ⁻	<u>0.812</u>	0.165	0.120	0.702
CH ₃ COO ⁻	<u>0.816</u>	0.150	0.071	0.694
PO ₄ ³⁻	0.010	0.000	<u>0.928</u>	0.862
NH ₄ ⁺	<u>0.776</u>	0.503	0.134	0.873
Na ⁺	0.027	<u>0.833</u>	-0.064	0.698
K ⁺	0.231	<u>0.669</u>	0.415	0.673
Ca ²⁺	0.303	<u>0.806</u>	-0.033	0.742
Mg ²⁺	0.180	<u>0.555</u>	0.326	0.447
H ⁺	0.791	0.019	0.011	0.626
Eigenvalue	3.8	3.4	1.2	
Variance (%)	32.0	28.6	10.0	
Cumulative (%)	32.0	60.6	70.6	
Possible Source	Biomass burning Combustion process Agriculture	Biomass burning Soil re-suspension Marine contribution	Isolated unknown source	

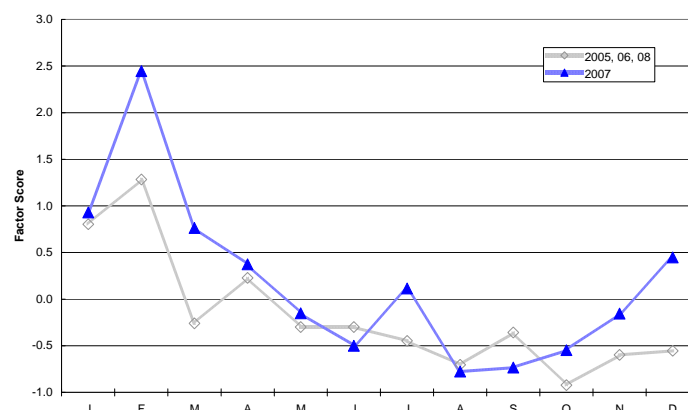


Figure 8. Monthly means factor scores of aerosol species in relation to biomass burning and other sources compared between non-haze years of 2005, 2006 and 2008 and a heavy-haze year of 2007.

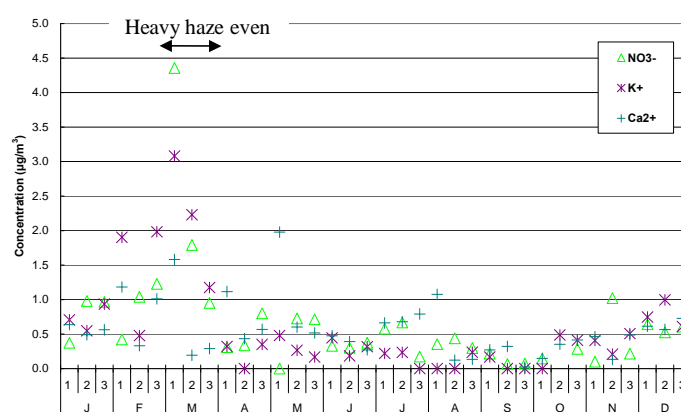


Figure 9. 10-days concentrations of aerosol species fall on the first factor (indicating biomass burning and other sources), from January to December 2007.

For wet deposition, factor analysis was conducted with the results displayed in Table 2. It can be seen that biomass burning is the emission source of ionic species in the first and second factors. Figure 10 indicates variation of monthly mean factor scores of the first factor with comparison between the non-haze years and the heavy-haze year. Although, as mentioned earlier, there was no rainfall during the heavy haze period, if consider the factor score of the first rainfall month of April 2007, the value is markedly higher than that of in April in non-haze years. This indicates that the heavy haze episode may cause redistribution of components fall on the first factors, in particular, NH_4^+ , CH_3COO^- and HCOO^- . This finding agrees with the previous studies (i.e., Legrand *et al.*, 1992; Whitlow *et al.*, 1994 and Dibb *et al.*, 1996). However, previous papers revealed that K^+ is one of the common biomass burning's signatures but in this study it was excluded from the factor indicating biomass burning for wet deposition. It may be explained by that the most of K^+ was fallen out rapidly with aerosols after heavy haze event by means of dry deposition process and in consequence there was less of K^+ remaining for rain-out and wash-out processes.

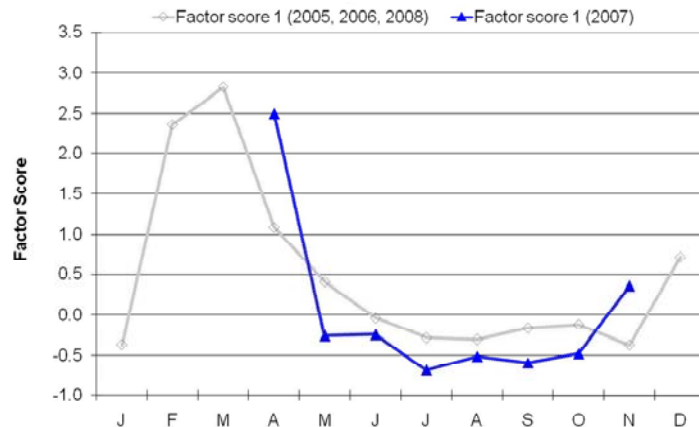


Figure 10. Monthly means factor scores of aerosol species in relation to biomass burning and other sources compared between non-haze years of 2005, 2006 and 2008 and a heavy-haze year of 2007.

3.2 Southern haze

3.2.1 PM₁₀ variation

The serious southern haze episode was observed from the beginning of August 2005 until the end of the month. The haze affected areas in Indonesia, Malaysia and Southern Thailand. The local authorities in Southern Thailand issued the warning on poor visibility and respiratory difficulties (Pentamwa & Kim Oanh, 2008). Figure 11 illustrates daily PM₁₀ measured at three southern monitoring sites (Phuket, Songkla and Surat Thani) in August 2005 and the months before and after July and September. Higher PM₁₀ levels in Phuket, Songkla and Surat Thani were observed during the haze period (1st - 31st of August) and reached its peak in the 16th of August (108 $\mu\text{g}/\text{m}^3$), the 13th of August (92 $\mu\text{g}/\text{m}^3$) and the 17th of August (43 $\mu\text{g}/\text{m}^3$), respectively, which all were not exceeding NAAQS. Figure 12 displays the PM₁₀ daily means in July - September 2005 being compared with the year 2004 and 2006 when severe haze was not explored. This reveals that the increment of PM₁₀ appeared to be the most significant in the haze days in August 2005 as compare to other periods. However, strength of the Southern haze was lesser than the Northern one due to lesser increment of PM₁₀ with shorter period of its occurrence and no exceeding NAAQS.

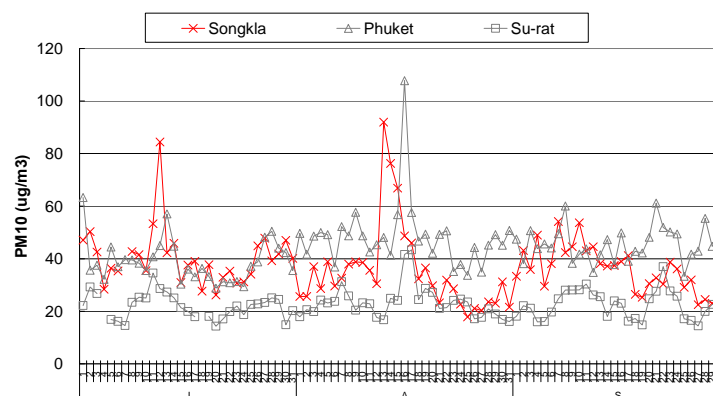


Figure 11. Daily PM₁₀ variations from July to September 2005 at the three Southern stations.

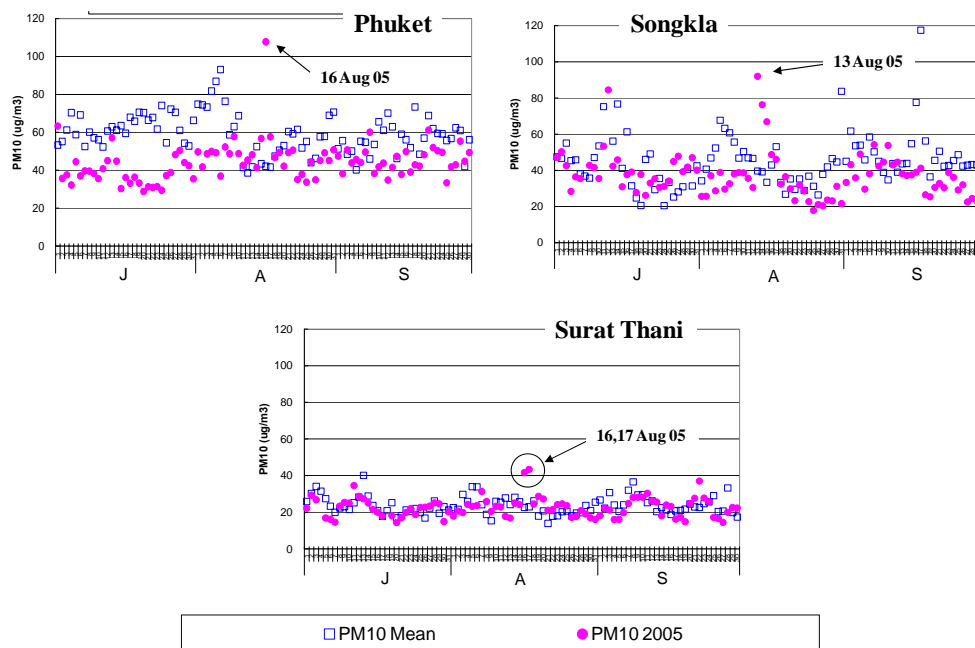
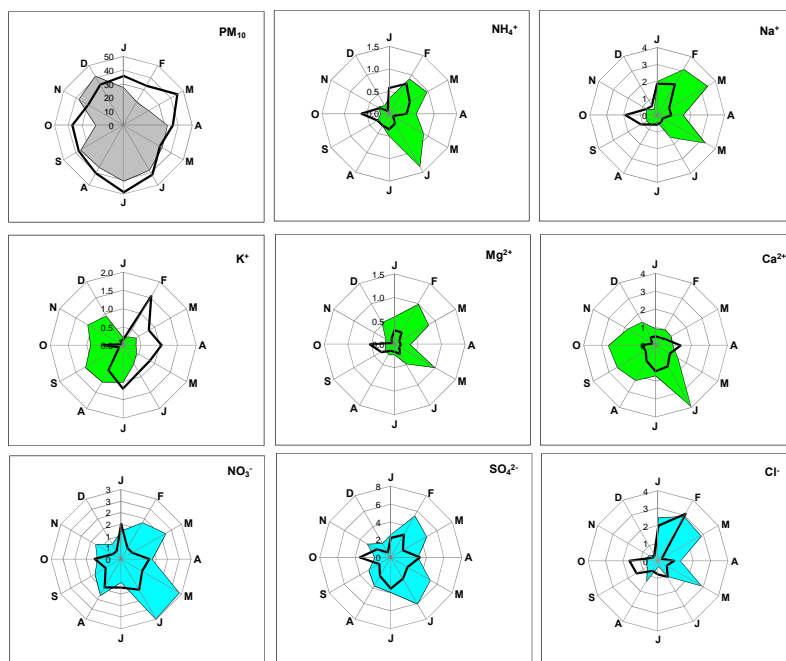


Figure 12. PM₁₀ daily means in July - September 2005 compared with the 2004 and 2006 mean at three southern stations.

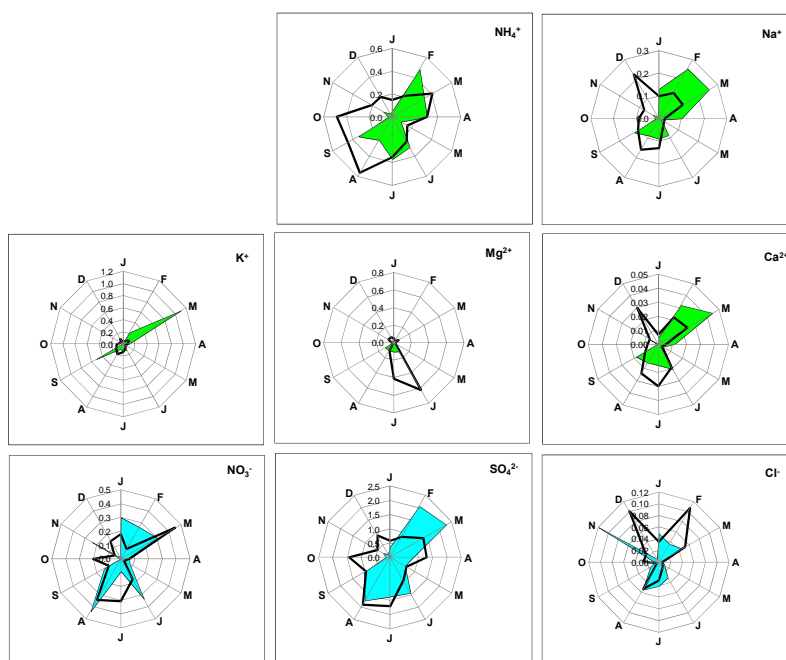
3.2.2 Aerosol compositions and PM₁₀ concentration

Figure 13 shows the variation of aerosol species collected at two chemical deposition stations: Songkla (PSU) and Tanah Rata. Monthly means PM₁₀ measured at Songkla (Hat Yai district) were also possible to be compared with aerosol species collected at the station of Songkla (PSU) due to their neighborhood (within 5 km). Aerosol species at the both stations and also PM₁₀ were varied over the years.

During the heavy haze month of August 2005, lower PM₁₀, as compare to its two-year mean value, is suggested to be under the influence of wet removal due to heavy rainfall of about 200 mm recorded in this month. However, some aerosol species, i.e., K^+ , Ca^{2+} , NO_3^- , SO_4^{2-} and Cl^- , remained chiefly higher than their monthly mean values of non-haze period. This suggests a possible increase in source intensity of haze. However this phenomenon was not clearly found in Tanah Rata where only NO_3^- was higher than its monthly mean value of non-haze period.



(a) Songkla (PSU)



(b) Tanah Rata

Unit: $\mu\text{g}/\text{m}^3$

Figure 13. Monthly means aerosol species of non-haze years (2004 and 2006) (line) and haze year of 2005 (shaded area) at Songkla (PSU) (a) (PM_{10} were collected from Songkla (Hat Yai district) station) and Tanah Rata (Malaysia) (b).

3.2.3 Wet deposition

The concentrations of ionic species compared with occurrences of precipitation at Songkla (PSU) and Tanah Rata are illustrated in Figure 14 and Figure 16, respectively. It can be seen that concentrations of ionic

species showed inverse relationships with the precipitations indicating an effect of wet removal mechanism, similar to the northern haze as mentioned earlier. However, in the case of southern region, higher precipitation was typically occurred, in terms of amount and frequency, as compared to other areas of Thailand. The southwest monsoon season, which last from May to October, brings rain and squalls to the coastal area of the Andaman Sea. There is another rainy period caused by the northeast monsoon during November to December, which brings heavy rain to the coastal areas along the Gulf of Thailand (Pentamwa & Kim Oanh, 2008). Songkla located on the Gulf of Thailand has higher rainfall in November-December (see Figure 14 (a)), while Tanah Rata (washed by the Andaman Sea) has higher rainfall in August-October (see Figure 16 (a)). Therefore, dissolving of ionic species by precipitation is different at these two sites. During the heavy haze period in August 2005, higher occurrence of precipitation was detected at Tanah Rata, in consequence, lower ionic species concentration than that of in Songkla. Moreover, it is also possible that the different in local emission sources play an important role in different contribution of ionic species. Songkla is an urban area where local sources such as traffic and industry are presence, while the intensity of the local sources is possibly lesser in Tanah Rata because it is defined as remote area (EANET, 2006). Figure 15 and Figure 17 display seasonally fractional contributions of ionic species at Songkla (PSU) and Tanah Rata, respectively. Conclusively, contribution of ionic species in wet deposition caused by southern haze episode is not clearly seen yet by means of this general examination. This suggests further statistical analysis to indentify its source relationship with haze episode by means of source identification which is given in Table 5 and Table 6 in section 3.2.4.

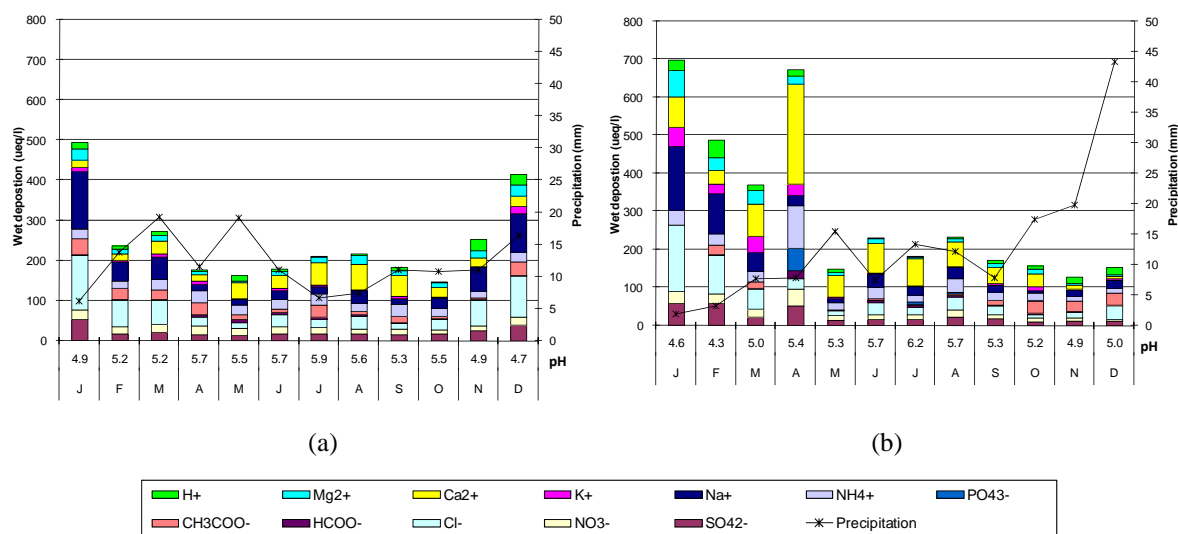
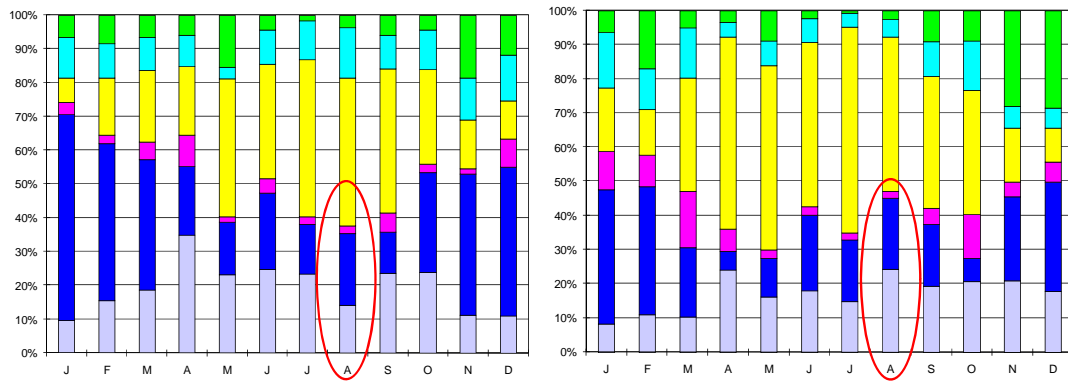
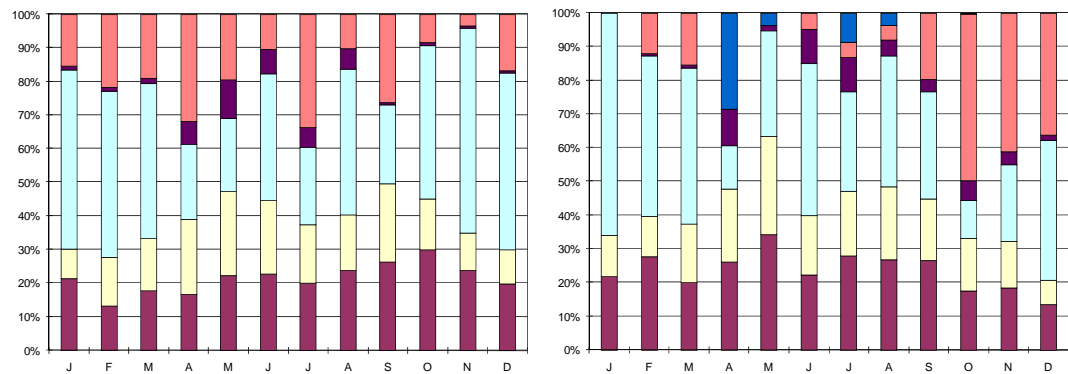


Figure 14. Monthly weighted average concentrations compared with occurrences of precipitation at Songkla (PSU) over the years 2004 and 2006 (averaged) (a) and year of 2005 (b).



(a)



(b)

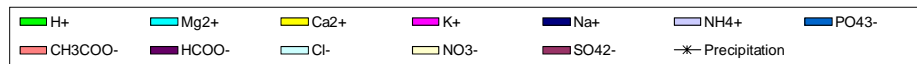


Figure 15. Monthly fractional contributions of cation (a) and anion (b) species measured at Songkla (PSU), compared between mean values over the two years (left) and the year 2007 (right), circles indicate remarked comparisons between percent shares of ionic species changed in the month of August.

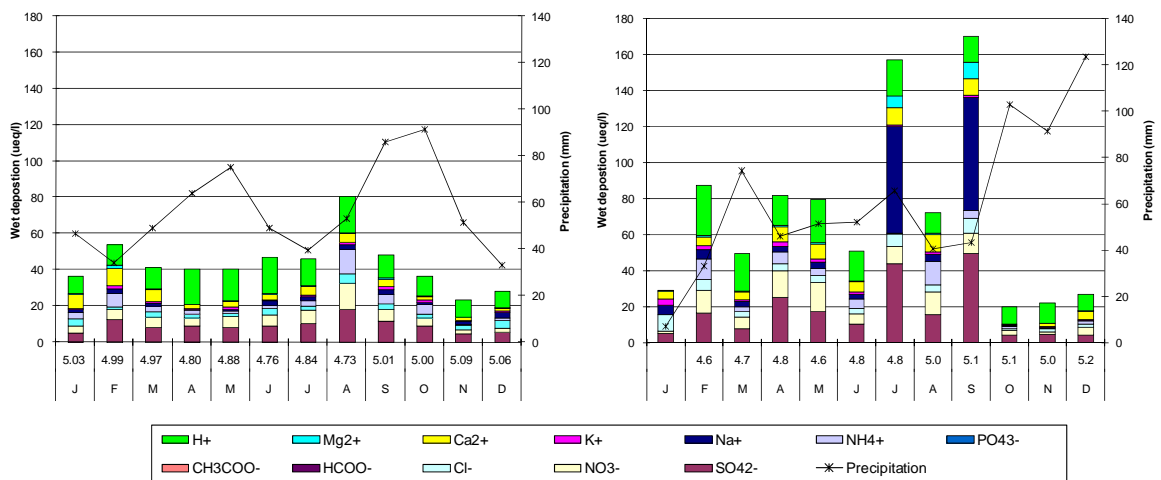


Figure 16. Monthly weighted average concentrations compared with occurrences of precipitation at Tanah Rata over the years 2004 and 2006 (averaged) (a) and year of 2005 (b).

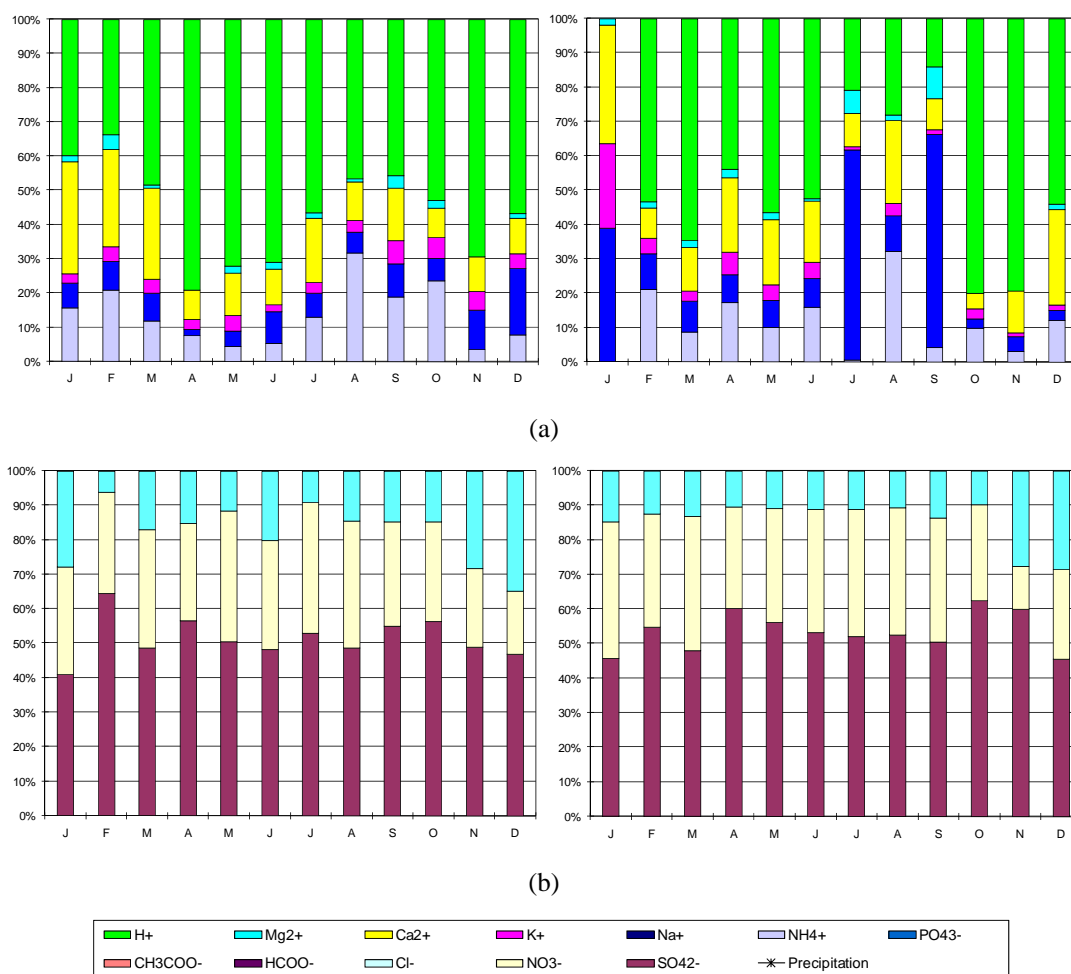


Figure 17. Monthly fractional contributions of cation (a) and anion (b) species measured at Tanah Rata, compared between mean values over the two years (left) and the year 2007 (right), circles indicate remarked comparisons between percent shares of ionic species changed in the month of August.

3.2.4 Source identification

Table 3 and Table 4 display the results of factor analysis of ionic species in aerosol collected from 2004 to 2006 at chemical deposition stations of Songkla (PSU) and Tanah Rata, respectively. Underlined values express species of interest for its depositions. It can be seen that aerosol species at the both stations were influenced by the mixture of emission sources. If factor scores are considered to belong to the first factor (Figure 18), the small elevated factor scores were observed in the period of August 2005 as compared to the mean values of the years 2004 and 2006 at the both stations. This indicated a possible impact of haze episodes on the enrichment of aerosol species at the both stations. Figure 19 illustrates variations of the aerosol species during the haze episode of August 2005 at Songkla (PSU) and Tanah Rata. If the aerosol species: Na^+ , Cl^- and Mg^+ , falling into the first factor, are believed to be originated from marine, increment of the remaining aerosols in this factor, i.e., SO_4^{2-} , NO_3^- and NH_4^+ at Songkla (PSU); and NO_3^- at Tanah Rata are therefore possibly attributed to haze episode. This finding agrees with the study of Dibb *et al.*, (1996) where such ionic aerosol species were enriched during haze event.

Table 3. Rotated varimax factor matrix of factor analysis for measured ionic aerosol species at Songkla (PSU).

Component	Factor loadings		Communality
	1	2	
SO ₄ ²⁻	<u>0.733</u>	0.427	0.719
NO ₃ ⁻	<u>0.707</u>	0.313	0.598
Cl ⁻	<u>0.774</u>	-0.382	0.745
NH ₄ ⁺	<u>0.669</u>	0.203	0.488
Na ⁺	<u>0.897</u>	-0.317	0.905
K ⁺	-0.128	<u>0.682</u>	0.481
Mg ²⁺	<u>0.838</u>	-0.080	0.709
Ca ²⁺	0.168	<u>0.776</u>	0.630
Eigenvalue	3.6	1.6	
Variance (%)	45.4	20.5	
Cumulative (%)	45.4	65.9	
Possible Source	Biomass burning Combustion process Marine contribution	Soil re-suspension	

Table 4. Rotated varimax factor matrix of factor analysis for measured ionic aerosol species at Tanah Rata.

Component	Factor loadings			Communality
	1	2	3	
SO ₄ ²⁻	0.282	<u>0.879</u>	0.190	0.888
NO ₃ ⁻	<u>0.642</u>	0.431	0.290	0.682
Cl ⁻	<u>0.898</u>	-0.146	-0.113	0.841
NH ₄ ⁺	0.162	<u>0.852</u>	0.137	0.771
Na ⁺	<u>0.827</u>	0.367	0.007	0.819
K ⁺	0.049	<u>0.664</u>	-0.068	0.447
Mg ²⁺	<u>0.786</u>	0.375	0.356	0.886
Ca ²⁺	0.057	0.057	<u>0.976</u>	0.959
Eigenvalue	2.6	2.4	1.2	
Variance (%)	32.9	30.3	15.4	
Cumulative (%)	32.9	63.2	78.6	
Possible Source	Biomass burning Combustion process Marine contribution	Biomass burning Combustion process Agriculture	Soil re-suspension	

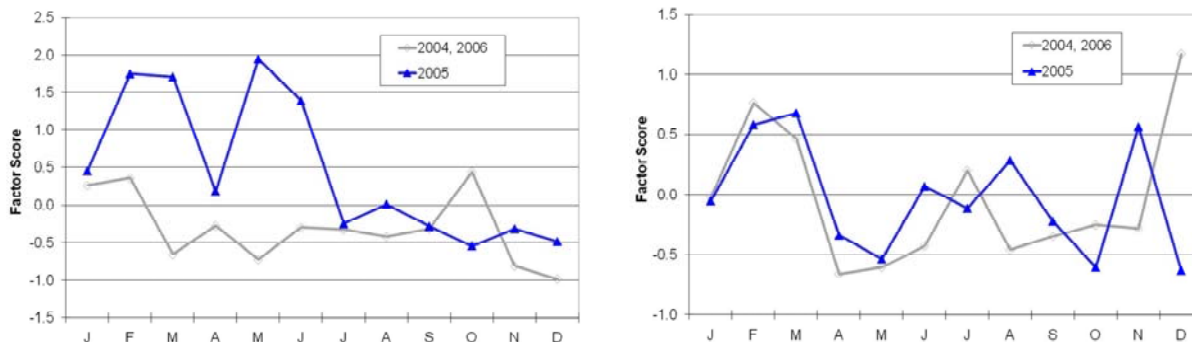


Figure 18. Monthly means factor scores of aerosol species in relation to biomass burning and other sources (Factor 1) for non-haze years of 2004 and 2006, with comparison to heavy-haze year of 2005 at Songkla (PSU) (left) and in Tanah Rata (right).

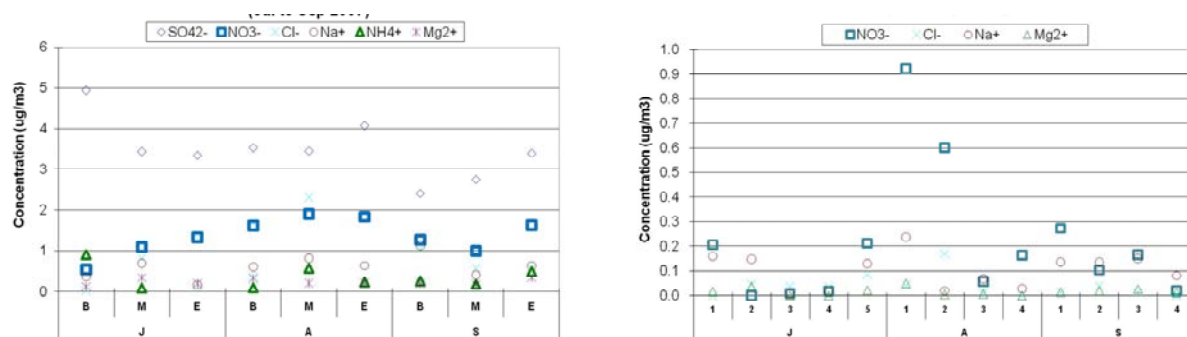


Figure 19. Concentrations of aerosol species during July to September 2005 (B: Beginning of the month, M: Middle of the month, E: End of the month) at Songkla (PSU) (left) and at Tanah Rata (right).

In the case of wet deposition, as seen in Table 5 and Table 6, the factor analysis provides the combination of emission sources with including the biomass burning in the factor 2 and 3 at chemical deposition station of Songkla (PSU) and in factor 2 at the chemical deposition station of Tanah Rata. Similar to the result of those aerosol species, small peaks of factor scores belonging to factor 2 (as illustrated in Figure 20) at the both stations were detected in August 2005 as compared to the mean values of the years 2004 and 2006. This reveals also the possible contribution of haze episodes on wet deposition of chemical species in the group of factor 2. Figure 21 indicates the variations of the chemical species of precipitations fall in this group at the both stations. An increasing of NO_3^- , HCOO^- and NH_4^+ at Songkla (PSU); and NO_3^- , NH_4^+ and K^+ at Tanah Rata (note that HCOO^- was not measured at Tanah Rata) was found during the heavy haze period of August 2005 indicating the possible effect of haze episode on such species.

Table 5. Rotated varimax factor matrix of factor analysis for measured ionic species in precipitation at Songkla (PSU).

Component	Factor loadings			Communality
	1	2	3	
SO ₄ ²⁻	<u>0.805</u>	0.406	0.272	0.887
NO ₃ ⁻	0.544	<u>0.647</u>	0.191	0.751
Cl ⁻	<u>0.789</u>	0.009	0.402	0.784
HCOO ⁻	-0.192	<u>0.693</u>	0.032	0.518
NH ₄ ⁺	0.321	<u>0.822</u>	0.151	0.802
Na ⁺	<u>0.815</u>	0.058	0.435	0.858
K ⁺	0.232	0.162	<u>0.713</u>	0.589
Ca ²⁺	-0.187	<u>0.577</u>	0.555	0.676
Mg ²⁺	0.186	0.083	<u>0.861</u>	0.784
H ⁺	<u>0.627</u>	-0.163	-0.200	0.460
Eigenvalue	2.9	2.1	2.1	
Variance (%)	28.9	21.4	20.8	
Cumulative (%)	28.9	50.3	71.1	
Possible Source	Combustion process Marine contribution	Biomass burning Agriculture Soil re-suspension	Biomass burning Soil re-suspension	

Table 6. Rotated varimax factor matrix of factor analysis for measured ionic species in precipitation at Tanah Rata.

Component	Factor loadings		Communality
	1	2	
SO ₄ ²⁻	<u>0.905</u>	0.314	0.919
NO ₃ ⁻	0.031	<u>0.886</u>	0.787
Cl ⁻	<u>0.751</u>	0.377	0.706
NH ₄ ⁺	0.068	<u>0.725</u>	0.530
Na ⁺	<u>0.982</u>	-0.112	0.978
K ⁺	0.298	<u>0.635</u>	0.492
Ca ²⁺	0.237	<u>0.636</u>	0.461
Mg ²⁺	<u>0.978</u>	-0.039	0.958
H ⁺	-0.096	<u>0.585</u>	0.352
Eigenvalue	3.4	2.7	
Variance (%)	38.5	30.2	
Cumulative (%)	38.5	68.7	
Possible Source	Combustion process Soil re-suspension Marine contribution	Biomass burning Marine contribution Agriculture Soil re-suspension	

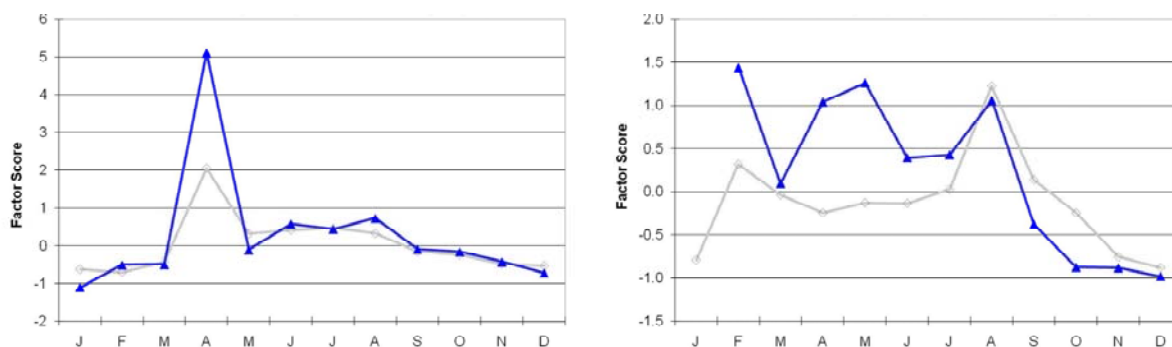


Figure 20. Monthly means factor scores of wet deposition species in relation to biomass burning and other sources (Factor 2) in comparison between non-haze years of 2004 and 2006 and a heavy-haze year of 2005 at Songkla (PSU) (left) and in Tanah Rata (right).

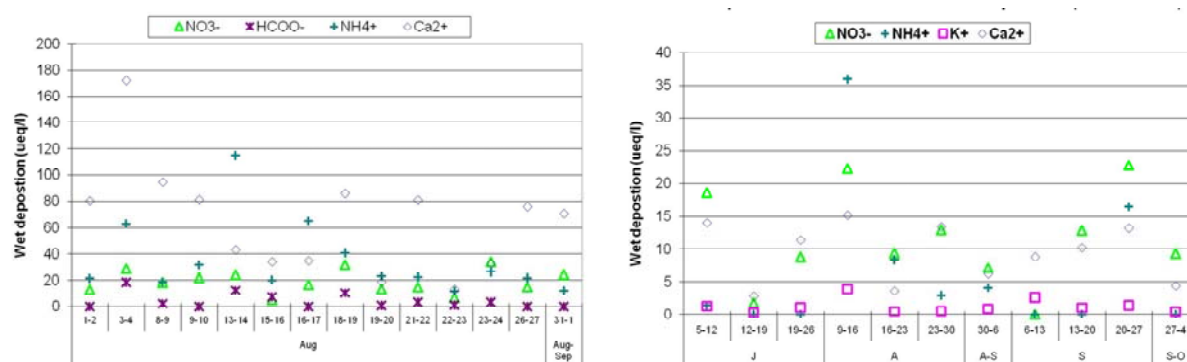


Figure 21. Concentration of aerosol species during several months with covering August 2005 at Songkla (PSU) (left) and in Tanah Rata (right).

3.3 Transport of air masses during the haze episodes

In order to explore the relationship between high PM₁₀ concentrations during the occurrence of heavy hazes and air mass transports, 72-hours back trajectory analysis was carried out for the day that significantly presented high daily PM₁₀ concentrations. Figure 22 and Figure 23 illustrate the results of air mass trajectories compared with MODIS's hotspot images at the days of peak PM₁₀ concentration observed during the haze episodes on the 13th of March 2007 for Northern and on the 13th of August 2005 for Southern Thailand. It can be seen that air masses passed through high hotspot areas may cause high PM₁₀ and ion concentrations being as biomass burning marker components.

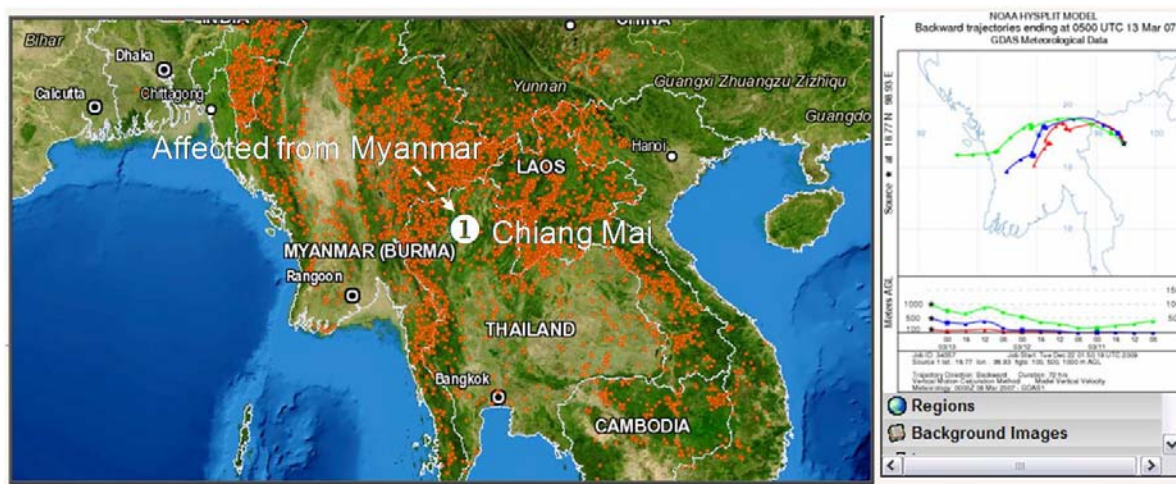


Figure 22. Hotspot (open burning and fires) distribution and 72 hrs back trajectory on the 13th of March 2007.



Figure 23. Hotspot distribution and 72 hrs back trajectory on 13th August 2005.

4. Conclusions

This study presents the effect of haze episodes on the enrichment of chemical components of wet and dry depositions. An elevated daily PM_{10} levels with maximum value up to $396 \mu g/m^3$ were detected during “Northern haze” in March 2007. Factor analysis indicates aerosol species: NO_3^- , K^+ and Ca^{2+} associated with biomass burning. There was no rainfall during February and March, 2007, NH_4^+ , CH_3COO^- and $HCOO^-$ of the first rainfall (April, 2007) even were enriched, which tend to be associated with the haze event. Trajectory analysis has proved that air masses passing through hot spot area arrived at the Northern Thailand during the presence of high PM_{10} concentration day. For “Southern haze”, daily PM_{10} concentrations at 3 monitoring sites in Southern Thailand, showed a maximum value (up to $108 \mu g/m^3$) in 16th August 2005 which corresponded to the haze event. The factor analysis of ionic species of precipitation and aerosol collected at the Songkla site in Southern Thailand and the Tanah Rata EANET site in Malaysia revealed that larger contributions of compounds, i.e., SO_4^{2-} , NO_3^- and NH_4^+ in aerosol may be associated with the haze period, and NH_4^+ , NO_3^- and $HCOO^-$ in

precipitation at Songkla and NH_4^+ , NO_3^- and K^+ in precipitation at Tanah Rata enriched and showed large factor loadings during the haze period.

5. Acknowledgements

The authors gratefully acknowledge the Asia Center for Air Pollution Research (ACAP) in Japan for providing observation data from EANET monitoring sites and giving an opportunity to conduct this research. We would like to express our thankfulness to Dr. Hajime Akimoto, Dr. Tsuyoshi Ohizumi and Dr. Sergey Gromov for their valuable comments and suggestions to develop this paper. We thank Pollution Control Department of Thailand (PCD), especially, Mr. Pichaid Atipakya and Ms. Wassana Toruksa for their kind supports regarding air quality data. We also wish to thank the NOAA Air Resources Laboratory (ARL) for the HYSPLIT model and NASA for hotspot data.

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Joint Projects of EANET with Participating Countries

EANET has also joint research projects with our participating countries on different activities, however, unfortunately, this bulletin is not available to obtain the completed results, because these projects are longer than two-year period, therefore, they are only progress reports involved included in this EANET Science Bulletin Volume 2.

Progress Report on Joint Research Project with Malaysia on the Catchment Analysis-2010

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1. Introduction

Integrated monitoring based on the biogeochemical elemental cycle should be considered for the total evaluation of ecological impacts of acid deposition. Catchment-scale monitoring is one of the solutions for this purpose but has not enough been promoted in tropical region. The project was carried out as a part of the project supported by the Global Environment Research Fund (GERF, C-052, C-082 or B-0801: Project Leader, Dr. Junko Shindo, National Institute for Agro-Environmental Sciences: NIAES), the Ministry of the Environment of Japan. Moreover, the project was conducted in collaboration with Lancaster University (Dr. Nick Chappell, hydrologist).

2. Objectives

The project was carried out with the following final objectives:

- To estimate effects of acidic deposition on tropical rainforest catchment in Malaysia
- To develop a monitoring guideline for the catchment analysis in the tropical ecosystems for future EANET monitoring

3. Methods

3.1. Surveys on a small forest catchment

A study site for the catchment-scale analysis of elemental cycle was established in 2008 in a tropical rainforest in the Danum Valley area, Tawau Division, Sabah, Malaysia. Field surveys are carried out in the Baru Catchment (approx. 45 ha), which has been studied by Lancaster University. As for the input, the data on wet deposition and dry deposition at the EANET Danum Valley station was referred basically. Additionally, ten sets of resin throughfall samplers (diameter, 120 mm) were installed under the forest canopy in the study catchment,

which could trap ion constituents in throughfall by using ion-exchange resin. The ions extracted from the exposed resin for several months were analyzed to estimate annual input. The survey was conducted twice a year in September and February/March. As for the output, the stream water at the outlet of the catchment was collected at two-week interval. Hydrological data collected by Lancaster University was referred for calculation of material flux from the catchment. Continuous surveys of input and output were started in September 2007. Soil solution, soil moisture, and ion fluxes in soil layers were measured near the throughfall samplers. A soil sampling plot with five subplots was also set up in the catchment according to the EANET method (EANET, 2000).

3.2. Regional survey on river water and wet deposition

Moreover, regional survey on river water and wet deposition was conducted in Tawau Division as shown in Figure 1. The wet deposition was estimated by using the resin samplers.

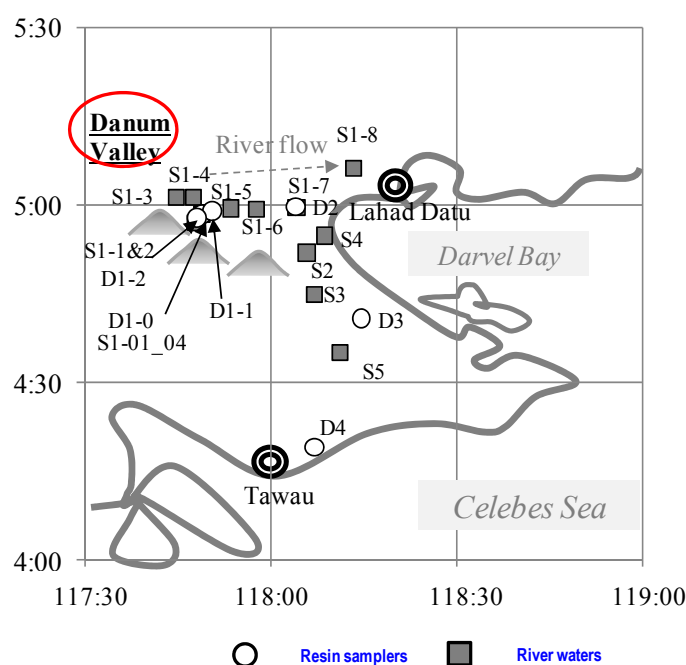


Figure 1. Map of the regional survey on river water and wet deposition using the resin sampler in Tawau Division, Sabah, Malaysia.

4. Highlighted results

4.1. Material flux in the study catchment

Table 1 shows annual vertical flux of N compounds and base cations from the forest canopy to the stream water at Baru Catchment in Danum Valley. Element fluxes in soil layers were significantly larger than in throughfall, suggesting large internal cycles. Within the soil layers, the fluxes were larger in Danum Valley site than in Sakaerat site, Thailand, suggesting larger internal cycles in Danum Valley.

Table 1. Annual material flux in Danum Valley, Malaysia and Sakaerat, Thailand

		NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
		$\text{kmolc ha}^{-1} \text{y}^{-1}$					
Danum Valley	Rainfall	0.04	0.09	nd	nd	0.03	0.06
	Throughfall	0.03	0.41	nd	nd	0.38	0.27
	Soil 0cm	6.28	0.45	1.69	14.1	15.4	7.8
	Soil 20cm	8.63	1.21	1.17	8.45	6.43	5.19
	Soil 70cm	6.56	1.12	0.96	6.77	9.64	5.44
	Stream	0.10	0.01	1.21	0.18	1.80	1.49
Sakaerat	Rainfall	0.14	0.27	nd	nd	0.11	0.04
	Throughfall	0.29	0.43	nd	nd	0.40	0.26
	Soil 0cm	1.54	3.4	0.9	11.2	7.2	6.3
	Soil 20cm	0.65	1.7	0.4	1.9	1.8	1.9
	Soil 60cm	1.70	1.4	0.6	1.8	1.9	4.1
	Stream	0.01	0.01	0.15	0.04	0.10	0.15

Note. nd, not determined. Rainfall and throughfall depositions were measured by the ion-exchange-resin sampler.

Concentration and flux of SiO_2 in the stream water in Danum Valley site were 2 times and 10 times higher than those in Sakaerat site, respectively, suggesting higher mineral weathering rate in Danum Valley. In Danum Valley site, alkalinity and pH of stream water were relatively high and pH hardly declined, while those in Sakaerat site were significantly low and both parameters often varied in response to water level, ion input etc. These phenomena could be attributed to the different mineral weathering rate in these sites.

4.2. River water chemistry in Tawau Division

The pH, EC and alkalinity in the catchment plot (Baru Catchment) were the lowest within the sampling

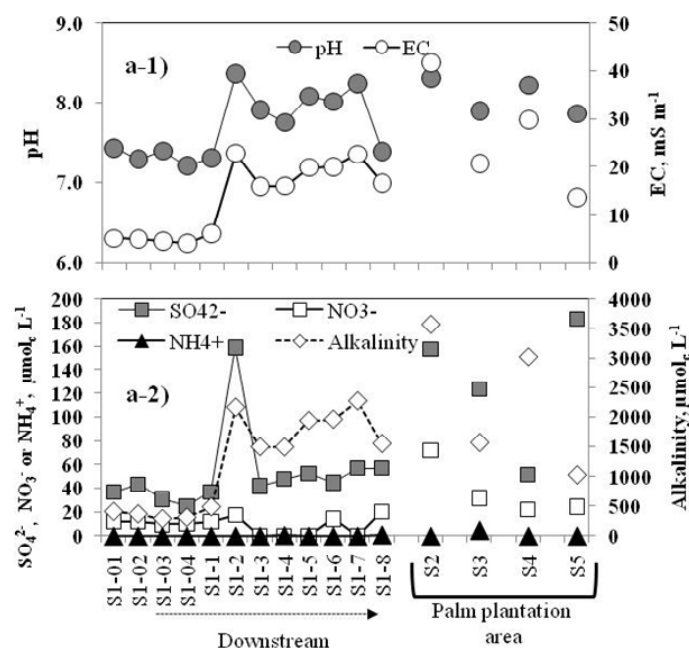


Figure 2. River water chemistry in Tawau Division.

The points, from S1-01 to S1-1, were within the study catchment.

points (Figure 2). The values were significantly lower than those at the downstream points, from S1-2 to S1-8, even in forest area. It was confirmed that the study catchment was non-polluted and relatively susceptible to acid deposition because of its low EC and alkalinity. The sampling points in palm plantation area showed relatively high pH, EC, alkalinity, and SO_4^{2-} . However, the values of NO_3^- were not quite high except the point S2, just beside the palm oil factory. Rapid denitrification rate in tropical climate may reduce the concentration of NO_3^- in the rivers.

5. Outcomes of the project

As scientific outputs from the project and relevant research activities in the study catchment, the following paper was published in international journal:

- 1) Sase, H., Nakayama, S., Leong, C.P., Kamisako, M., Luangjame, J., Garivait, H., Visaratana, T., Kietvuttinon, B., Ueda, H., 2009. QA/QC activities and ecological monitoring in the Acid Deposition Monitoring Network in East Asia (EANET). *iForest* 2: 26-29 URL: <http://www.sisef.it/iforest/show.php?id=481>

The reprint of the paper above can be obtained from the first author: sase@acap.asia.

A part of the project was also presented in the XXIII International Union of Forest Research Organization (IUFRO) World Congress, Korea in August 2010:

- 2) Sase, H., Luangjame, J., Garivait, H., Urban, S., Yamashita, N., Nakahara, O., Kietvuttinon, B., Visaratana, T., Kobayashi, R., Takahashi, M., Hakamata, T., Chappell, N., Leong, C., Ohta, S., Shindo, J., Hayashi, K., Matsuda, K. 2010. The EANET challenge on the catchment-scale analysis for the future integrated monitoring, *International Forestry Review*. 12 (5): 234.

Moreover, the experience through the project was summarized as a technical paper, Recommendations for preparation of a guideline on the future catchment monitoring in the EANET participating countries. Based on the recommendations above, the Guideline for Catchment-scale Monitoring in East Asia was developed by the Task Force on Soil and Vegetation Monitoring of EANET. The Guideline was endorsed by Scientific Advisory Committee at its Tenth Session (SAC10) in October 2010. It is expected that catchment-scale monitoring will be conducted on a regular basis using the Guideline in the EANET countries. This is the great outcome of the project, which can contribute to the future EANET monitoring and evaluation of ecosystem impacts in the region.

Progress Report on Joint Research Project with Thailand on the Catchment Analysis -2010.

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1. Introduction

Integrated monitoring based on the biogeochemical elemental cycle should be considered for the total evaluation of ecological impacts of acid deposition. Catchment-scale monitoring is one of the solutions for this purpose but has not enough been promoted in tropical region. The project was carried out as a part of the project supported by the Global Environment Research Fund (GERF, C-052, C-082 or B-0801: Project Leader, Dr. Junko Shindo, National Institute for Agro-Environmental Sciences: NIAES), the Ministry of the Environment of Japan.

2. Objectives

The project was carried out with the following final objectives:

- To estimate effects of acidic deposition on tropical seasonal forested catchment in Thailand.
- To develop a monitoring guideline for the catchment analysis in the tropical ecosystems for future EANET monitoring.

3. Methods

3.1. Surveys on a small forest catchment

A study site for the catchment-scale analysis of elemental cycle was established in 2005 in a dry-evergreen forest in the Sakaerat Silvicultural Research Station (Sakaerat SRS), Nakhon Ratchasima Province, Thailand. Field surveys on input (atmospheric deposition), output (discharge from a stream) and biogeochemical processes are carried out in the selected catchment area (approx. 35 ha). As for the input, precipitation samples including throughfall (TF), stemflow (SF), and rainfall outside the forest canopy are collected basically at two-week interval. As for the output, continuous monitoring of the discharge and measurement of the stream

water at two-week interval are also carried out. Continuous surveys of input and output were started in October 2005. Soil sampling plot (40 m × 350 m) was also set up crossing the stream in the catchment to clarify the seasonal and spatial variation of soil acidity. Soil chemical properties, flux of litterfall, and ion fluxes in soil layers have been measured in the plot.

3.2. Regional survey on river water and wet deposition

Moreover, regional survey on river water and wet deposition was conducted in Nakhon Ratchasima Province as shown in Figure 1. The river waters for chemical analysis were collected from the streams in forest area to the main rivers along the river water flow. The wet deposition was estimated by using the resin samplers, which could trap ion constituents in rainwater by using ion-exchange resin. The ions extracted from the exposed resin for several months were analyzed. The survey was conducted twice a year, in wet season and dry season.

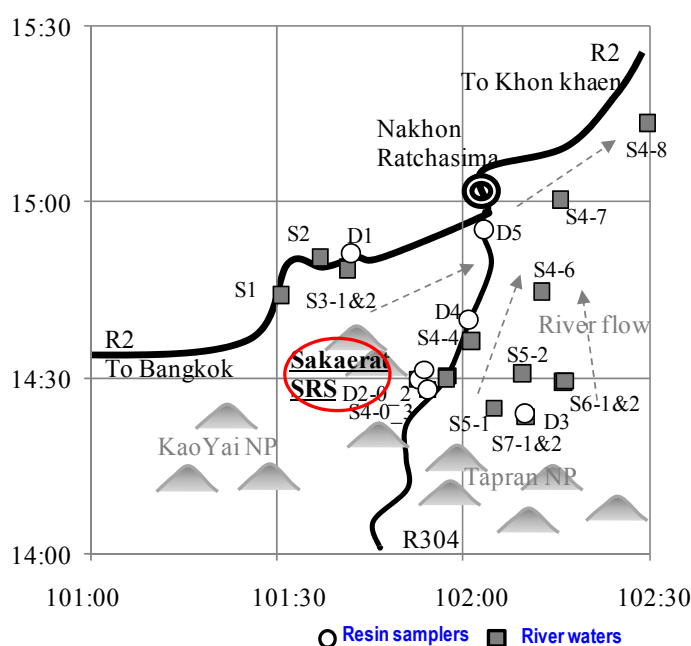


Figure 1. Map of the regional survey on river water and wet deposition using the resin sampler in Nakhon Ratchasima Province, Thailand.

4. Highlighted results

4.1. Seasonal changes in material flux in the small catchment

As reported in the EANET Science Bulletin Volume 1 in 2008, deposition amounts of all ions by TF+SF significantly increased in the middle of March, in the beginning of wet season. The similar seasonal changes were found in the later years. It was suggested that air pollutants including much SO_4^{2-} and NO_3^- were suspended in the atmosphere during dry season and washed out by the first precipitations in the beginning of wet season.

The stream water chemistry showed specific phenomena as also reported in the previous EANET Science Bulletin; the pH and EC increased with alkalinity and concentrations of cations (alkalization) in early wet season, and then, the pH and alkalinity suddenly declined with peaks of SO_4^{2-} (acidification) in middle or late wet season. As for the acidification, the flushing SO_4^{2-} may be derived from the high deposition in the beginning of wet

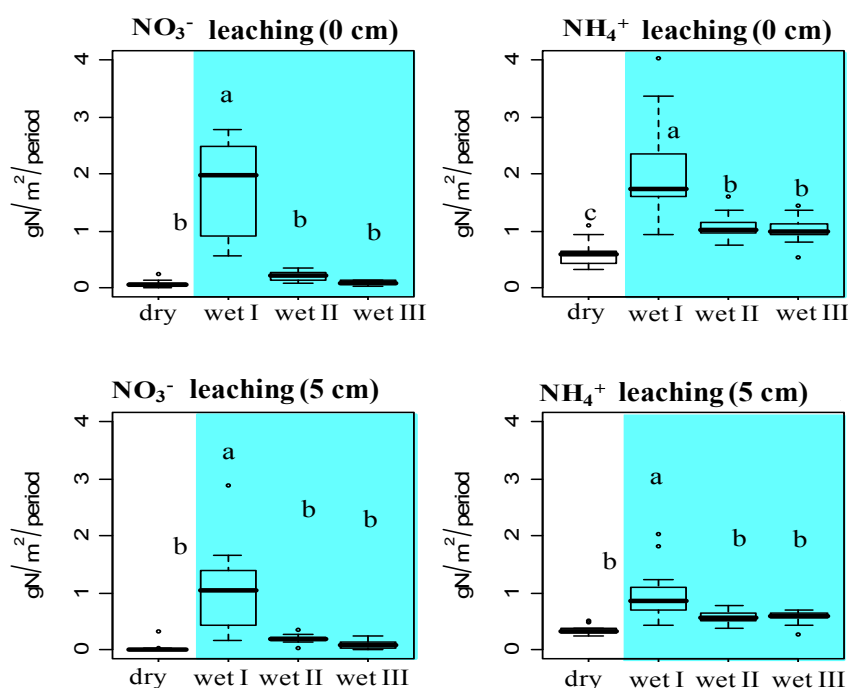


Figure 2. Seasonal changes in NO₃⁻ and NH₄⁺ in shallow soil layers.

Blue colored part represents wet season. Wet I, II, and III corresponded to early, middle, and late wet seasons, respectively.

season, while the detailed mechanism on trapping/releasing of SO₄²⁻ in the ecosystems is still under discussion. As for the alkalization in early wet season, high mineralization rate in soil may affect the stream water chemistry. Figure 2 showed seasonal changes in fluxes of NO₃⁻ and NH₄⁺ in shallow soil layers. Both NO₃⁻ and NH₄⁺ fluxes were the highest in the early wet season (wet I). Since the similar seasonal pattern was seen in the flux of base cations, it was suggested that mineralization rate of organic compounds was the highest in early wet season (Yamashita et al., 2010). The high mineralization rate in early wet season may produce much amount of base cations and NH₄⁺, resulting in alkalization of the stream water.

4.2. River water chemistry in Nakhon Ratchasima Province

The stream in the study catchment (S4-0) showed the lowest pH and EC and alkalinity among the surveyed rivers, even if compared with the streams (S7-1 & -2) in the conservation forest area of the Tapran National Park (Figure 3). At the downstream points in agricultural area or city area, the pH, EC, alkalinity, and SO₄²⁻ concentration were quickly increased along the flow. Similarly, the rivers from degraded forest area with certain area of agricultural field (S2, S3, S5 and S6) showed also relatively high values. However, NO₃⁻ concentration was not increased along with the forest degradation and/or river flow. Rapid denitrification rate in tropical climate may reduce the concentration of NO₃⁻ in the rivers. Anyway, it was confirmed that the study catchment was non-polluted and must be susceptible to acid deposition because of its low EC and alkalinity.

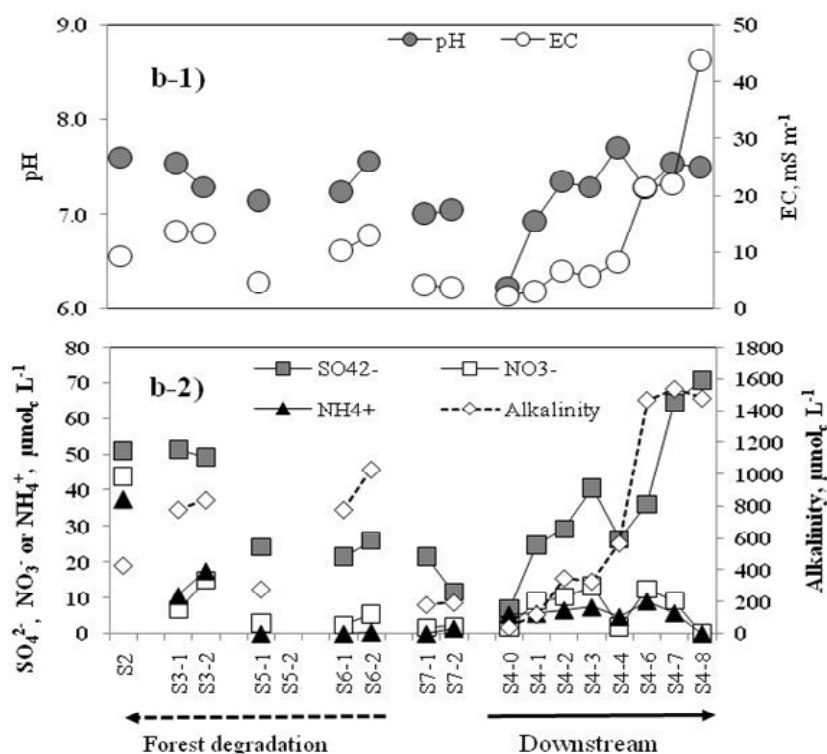


Figure 3. River water chemistry in Nakhon Ratchasima Province.

The point S4-0 was the small catchment plot.

5. Outcomes from the project

As scientific outputs from the project and relevant research activities in the study catchment, the following papers were published in international journals:

- 1) Yamashita, N., Ohta, S., Sase, H., Luangjame, J., Visaratana, T., Kietvuttinon, B., Garivait, H., Kanzaki, M. (2010). Seasonal and spatial variation of nitrogen dynamics in the litter and surface soil layers on a tropical dry evergreen forest slope. *Forest Ecology and Management*. 259: 1502-1512. doi:10.1016/j.foreco.2010.01.026.
- 2) Sase, H., Nakayama, S., Leong, C.P., Kamisako, M., Luangjame, J., Garivait, H., Visaratana, T., Kietvuttinon, B., Ueda, H., 2009. QA/QC activities and ecological monitoring in the Acid Deposition Monitoring Network in East Asia (EANET). *iForest* 2: 26-29 URL: <http://www.sisef.it/iforest/show.php?id=481>.
- 3) Murata, N., Ohta, S., Ishida, A., Kanzaki, M., Wachirinrat, C., Archawakom, T., Sase, H. 2009. Comparison of soil depths between evergreen and deciduous forests as a determinant of their distribution, Northeast Thailand. *Journal of Forest Research*. 14: 212-220. DOI10.1007/s10310-009-0127-7.
- 4) Tominaga, K., Ohta, S., Ishida, A., Kanzaki, M., Wachirinrat, C., Archawakom, T., Sase, H. 2010. Comparison of soil nutrient status between dry evergreen and deciduous forests in northeast Thailand. *Proceedings of the FORTROP II: Tropical Forestry Change in a Changing World*, 17-20 November 2008, Kasetsart University, Bangkok, Thailand. pp. 171-200.

The reprint of the papers above can be obtained from the first author: sase@acap.asia.

A part of the project was also presented in the XXIII International Union of Forest Research Organization (IUFRO) World Congress, Korea in August 2010:

5. Sase, H., Luangjame, J., Garivait, H., Urban, S., Yamashita, N., Nakahara, O., Kietvuttinon, B., Visaratana, T., Kobayashi, R., Takahashi, M., Hakamata, T., Chappell, N., Leong, C., Ohta, S., Shindo, J., Hayashi, K., Matsuda, K. 2010. The EANET challenge on the catchment-scale analysis for the future integrated monitoring, *International Forestry Review*. 12 (5): 234.

Moreover, the experience through the project was summarized as a technical paper, Recommendations for preparation of a guideline on the future catchment monitoring in the EANET participating countries. Based on the recommendations above, the Guideline for Catchment-scale Monitoring in East Asia was developed by the Task Force on Soil and Vegetation Monitoring of EANET. The Guideline was endorsed by Scientific Advisory Committee at its Tenth Session (SAC10) in October 2010. It is expected that catchment-scale monitoring will be conducted on a regular basis using the Guideline in the EANET countries. This is the great outcome of the project, which can contribute to the future EANET monitoring and evaluation of ecosystem impacts in the region.

Joint Research Project for Developing Low Cost Methodology on Gas Concentration Monitoring in East Asia

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1. Introduction

In order to evaluate the extent of acid deposition in East Asia spatially and temporally, a sufficiently long record of data on wet deposition and air concentrations from a dense network of sites distributed over the region is usually required. The data should also be acquired using reliable methods and practices. Presently, the number of EANET monitoring sites is limited and not well distributed. One of the reasons for the lack of air quality monitoring sites in some countries is the high cost of automatic instruments and recurrent costs of operating the instruments.

One of the possible ways to overcome this problem is to adopt the simpler, low cost methodologies such as filter packs, passive samplers and denuders in less accessible sites. These methodologies are used widely in monitoring networks and for field campaigns in Europe and North America. However, they have not been extensively tested in the East Asian region which may have different conditions and other unique factors.

The Strategy on EANET Development (2006-2010) included an activity to improve implementation of all required monitoring items with necessary data completeness and accuracy. One of the outputs expected from this activity is a recommendation on use of less expensive methods to reduce monitoring cost and increase the number of monitoring sites in the EANET network.

2. Objectives

The project has been carrying out with the following objectives:

- To evaluate the accuracy of measurements using passive samplers with those from the automatic instruments and filter pack methods at selected sites in the participating countries of EANET;
- To determine the suitability of applying the low cost methodologies for EANET monitoring.

3. Methods

The measurements have been conducted at selected sites in the participating countries of EANET by subjecting the samplers to a range of climate conditions to identify factors that could affect their performance and reliability. The following 4 countries are participating in the project, namely, China (Jinyunshan), Japan (Niigata-Maki), Russia (Mondy, Irkutsk, and Listvyanka), and Thailand (Bangkok).

Jinyunshan in China was selected as a site characterized by high concentration of air pollutants in the region. The monitoring is implemented as Table 1.

Table 1. Monitoring air pollutant concentration in Jinyunshan, China.

Jinyunshan	Passive (PS) method	Filter Pack (FP) method	Automatic gas monitor (AP) method
Instrument	OGAWA passive sampler	4 stage filter method	NO _x (Environnement S.A AC 32M) SO ₂ (Environnement S.A AF 22M) O ₃ (Environnement S.A O ₃ 42M)
Parameters	NO _x , NO ₂ , SO ₂ , O ₃ , NH ₃	SO ₂ , NH ₃	NO _x , NO ₂ , SO ₂ , O ₃
Sampling period	Bi-weekly 16 Dec 2009 ~	Bi-weekly Expected to start from January 2011	Hourly Data available from Dec 2009
Analytical method	Ion Chromatography	Ion Chromatography	NO _x : Chemiluminescent SO ₂ : UV fluorescent O ₃ : UV photometric

Niigata-Maki in Japan was selected as a site in warm region. The monitoring is implemented as Table2.

Table 2. Monitoring air pollutant concentration in Niigata-Maki, Japan.

Niigata-Maki	Passive (PS) method	Filter Pack (FP) method	Automatic gas monitor (AP) method
Instrument	OGAWA passive sampler	4 stage filter method	NO _x (HORIBA APNA-365) SO ₂ (HORIBA APSA-365) O ₃ (HORIBA APOA-370)
Parameters	NO _x , NO ₂ , SO ₂ , O ₃ , NH ₃	SO ₂ , NH ₃	NO _x , NO ₂ , SO ₂ , O ₃
Sampling period	Bi-weekly 4 Nov 2009 ~	Bi-weekly 4 Nov 2009 ~	Hourly Data available from 4 Nov 2009
Analytical method	Ion Chromatography	Ion Chromatography	NO _x : Chemiluminescent SO ₂ : UV fluorescent O ₃ : UV photometric

Mondy, Irkutsk and Listvyanka in Russia were selected as sites in cold and dry region. The monitoring is implemented as Table3.

Table 3. Monitoring air pollutant concentration in Mondy, Irkutsk and Litstvyanka, Russia.

Russia	Passive (PS) method	Filter Pack (FP) method	Automatic gas monitor (AP) method
Instrument	OGAWA passive sampler		O ₃ (Dasibi Model 1006-AHJ) in Irkutsk and Listvyanka O ₃ (Dasibi Model 1007-AHJ) in Mondy
Parameters	O ₃		O ₃
Sampling period	Monthly Data available from Feb 2009		Hourly Data available from Feb 2009
Analytical method	Ion Chromatography		O ₃ : UV photometric

Bangkok in Thailand was selected as a site in tropical region. The monitoring is implemented as Table 4.

Table 4. Monitoring air pollutant concentration in Bangkok, Thailand.

Bangkok	Passive (PS) method	Filter Pack (FP) method	Automatic gas monitor (AP) method
Instrument	OGAWA passive sampler	4 stage filter method	NO _x (Nippon Thermo Co., Ltd.) SO ₂ (Nippon Thermo Co., Ltd.) O ₃ (Nippon Thermo Co., Ltd.)
Parameters	NO _x , NO ₂ , SO ₂ , O ₃	SO ₂ , NH ₃	NO _x , NO ₂ , SO ₂ , O ₃
Sampling period	10 days 1 Jan 2009 ~	10 days 1 Jan 2009 ~	Hourly Data available from Jan 2009
Analytical method	Ion Chromatography	Ion Chromatography	NO _x : Chemiluminescent SO ₂ : UV fluorescent O ₃ : UV photometric

4. Progress of the project

The monitoring by using low cost methodologies such as passive method and filter-pack method have been implementing in four regions mentioned above since 2009. Obtained data by those methodologies have

been evaluated each other or in the comparison with the results of automatic air monitor in each participating organization. A part of them is introduced in this section.

4.1 Bangkok, Thailand (Tropical region)

The concentrations of NO_2 and NO_x measured by PS method are similar to those measured by AP and FP methods (Figures 1 and 2). Measurement value and fluctuation of O_3 between PS and AP method correspond well in the latter half of monitoring period (Figure 4). SO_2 correlation among 3 methods is not so strong (Figure 3).

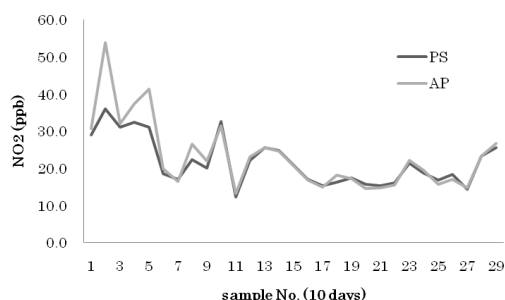


Figure 1. Average NO_2 concentration by passive and auto monitor method.

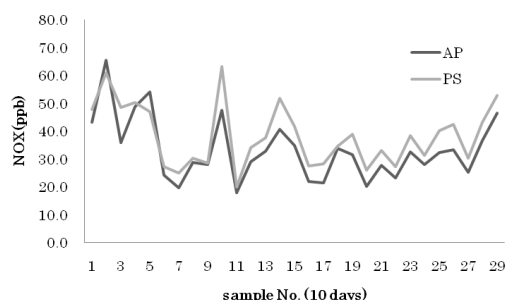


Figure 2. Average NO_x concentration by passive and auto monitor method.

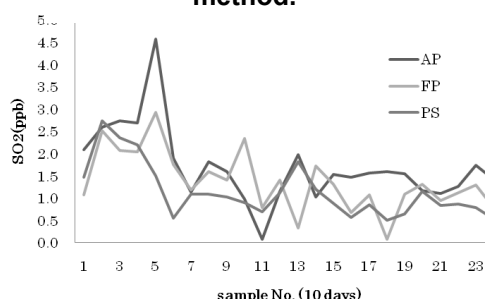


Figure 3. Average SO_2 concentration by passive, filter-pack and auto monitor method.

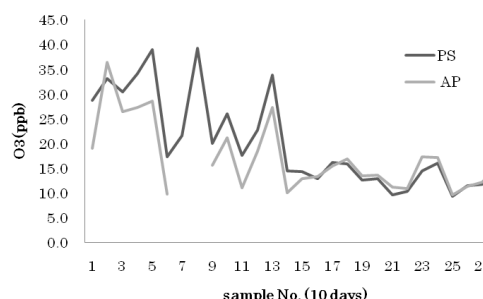


Figure 4. Average O_3 concentration by passive and auto monitor method.

4.2 Niigata-Maki, Japan (Warm region)

The concentrations of NO_2 , NO_x and NH_3 measured by PS method are similar to those measured by AP and FP methods (Figures 5, 6 and 8). SO_2 concentration measured by PS method shows different fluctuation from the other methods in the first half of the monitoring period (Figure 7). O_3 concentration has a large difference between PS and AP method (Figure 9).

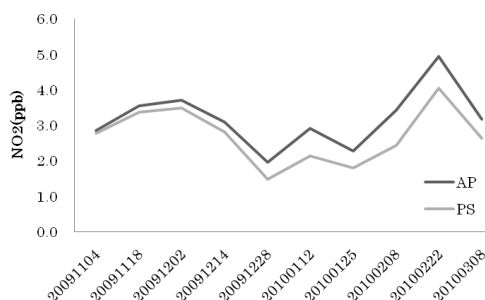


Figure 5. Average NO_2 concentration by passive and auto monitor method.

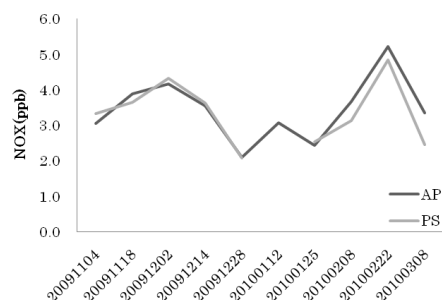


Figure 6. Average NO_x concentration by passive and auto monitor method.

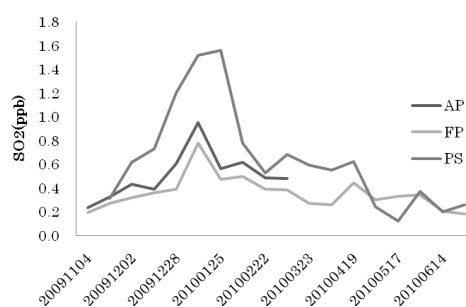


Figure 7. Average SO₂ concentration by passive, filter-pack and auto monitor method.

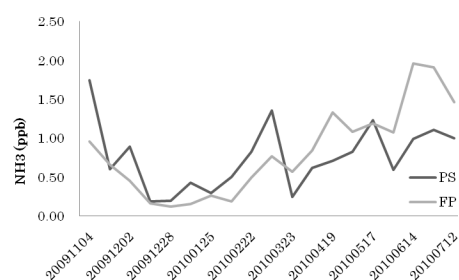


Figure 8. Average NH₃ concentration by passive and filter-pack method.

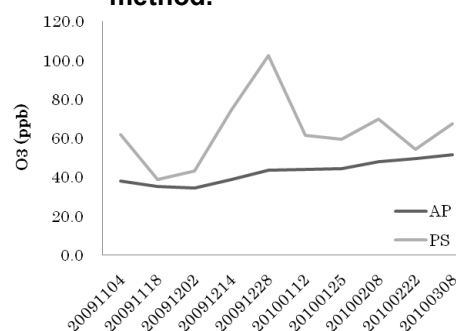


Figure 9. Average O₃ concentration by passive and auto monitor method.

4.3 Mondy, Irkutsk, and Listvyanka, Russia (Cold and dry region)

Correlation analysis showed that the ozone concentrations at the Mondy site measured by passive and automatic monitor methods are closely related. The correlation coefficient between these values is about 0.9 in linear relationship (Figure 11).

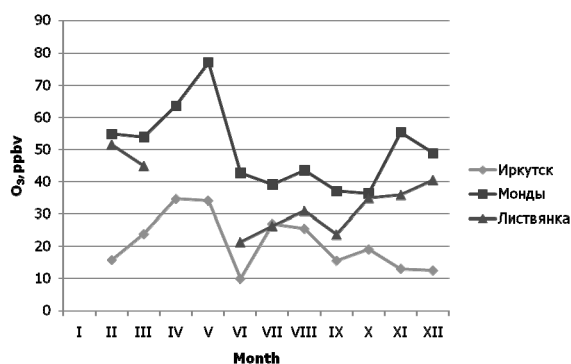


Figure 10. Average O₃ concentration by passive method at 3 sites in Russia.

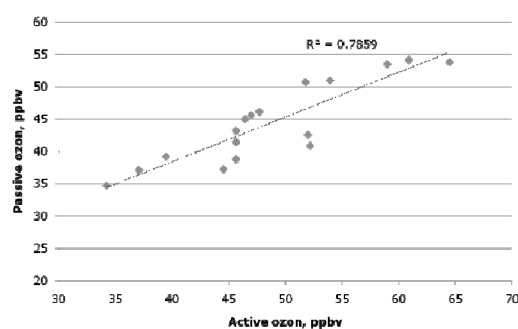


Figure 11. Relationship of O₃ concentration by passive and auto monitor method.

4.4 Chongqing, China (High concentration of air pollutants region)

The monitoring by PS method was started from 16 Dec 2009. The monitoring by FP method was started from 2010. The comparison analysis between PS, FP and AP method for NO₂, NO_x, SO₂, NH₃ and O₃ concentration will be conducted in the near future.

5. Outputs of the project

Expected outputs from the project are as follows:

- A set of data from selected sites using various monitoring methodologies, including low cost methodologies such as passive samplers, for comparison;
- An assessment report on the effectiveness of the low cost methodologies;
- Recommendations on future dry deposition monitoring methodologies to improve EANET monitoring.

The project is planned to be completed by the end of 2011. Cooperation among participating organizations is expected to achieve establishing new monitoring methodologies can be used easily for installing air concentration monitoring not only in urban area but also in remote area of EANET region.

6. References

WMO. 1997. Global Atmospheric Watch (GAW) No: 122 Report on Passive Samplers for Atmospheric Chemistry Measurements and their Role in GAW

Technical Documents for Dry Deposition Monitoring of EANET

- Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET
- Quality Assurance/Quality Control Program for Air Concentration Monitoring in East Asia
- Technical Document for Filter Pack Method in East Asia.

Joint Research Project with Republic of Korea on Aerosol

Monitoring Methodology

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1. Introduction

In the discussion at the Fourth Session of the Scientific Advisory Committee (SAC4) of the Acid Deposition Monitoring Network in East Asia (EANET) for the improvement of dry deposition monitoring methodologies, it was suggested that a study on PM₁₀, PM_{2.5} and their components in special sites should be considered. In line with the suggestion, the project on aerosol monitoring was planned as a joint research between National Institute of Environmental Research (NIER), Ministry of the Environment, Republic of Korea and the Network Center (NC). In order to evaluate aerosol sampling methodology and behavior of fine particles in Japan and Republic of Korea, intensive monitoring was carried out at both the Korean and Japanese sites during 2005 and 2007. Several methods for aerosol monitoring including PM_{2.5} and PM₁₀ collections were implemented simultaneously in both sites. After compiling the monitoring results, the progress of the project and preliminary results from the intensive monitoring were discussed at the small data analysis workshop each year.

The main objectives of previous joint study during 2005 and 2007 were to compare 3-stage filter pack method with 4-stage filter pack method in Korea and Japan, and to compare PM_{2.5} (separated by a cyclone and a cascade impactor) with open face type of filter pack method in Korea and Japan. For the air concentrations monitoring of EANET, there are 2 kinds of filter pack monitoring methods used. The Republic of Korea uses 3-stage filter pack monitoring method and the other countries use 4-stage filter pack monitoring method. In this context, this joint research project compares these 2 kinds of filter pack method with each other aiming at the improvement of the method of the filter pack monitoring. In addition, the behavior of PM_{2.5} measured in Republic of Korea and Japan will be evaluated through this joint research project.

The target species of the previous joint project are nitrate, sulfate, and the other cation species

which are designated as the priority dry deposition monitoring species in EANET. Recently, atmospheric behaviors of carbonaceous aerosol were one of the most interested topics in the field of atmospheric sciences because carbonaceous aerosols include potentially harmful organic components and some type of aerosol such as black carbon may affect radiative forcing and climate change. Therefore, carbonaceous components should be included in the target species in the present joint research project.

2. Objectives

The project is being carried out with the aim of the following objectives:

1. To consider a new monitoring item of carbonaceous species as the supplemental data of sulfate and nitrate aerosol
2. To compare 3-stage filter pack method with 4-stage filter pack method in Korea and Japan.
3. To compare PM_{2.5} (cyclone and impactor) with open face type of filter pack method in Korea and Japan.

3. Monitoring methods

The intensive monitoring was conducted at Jeju in Korea and the ACAP (Asia Center for Air Pollution Research), Niigata in Japan during May 11–21 and October 11–29, 2010. Aerosol was observed by parallel measurement of the following 4 kinds of method summarized in Figure 1.

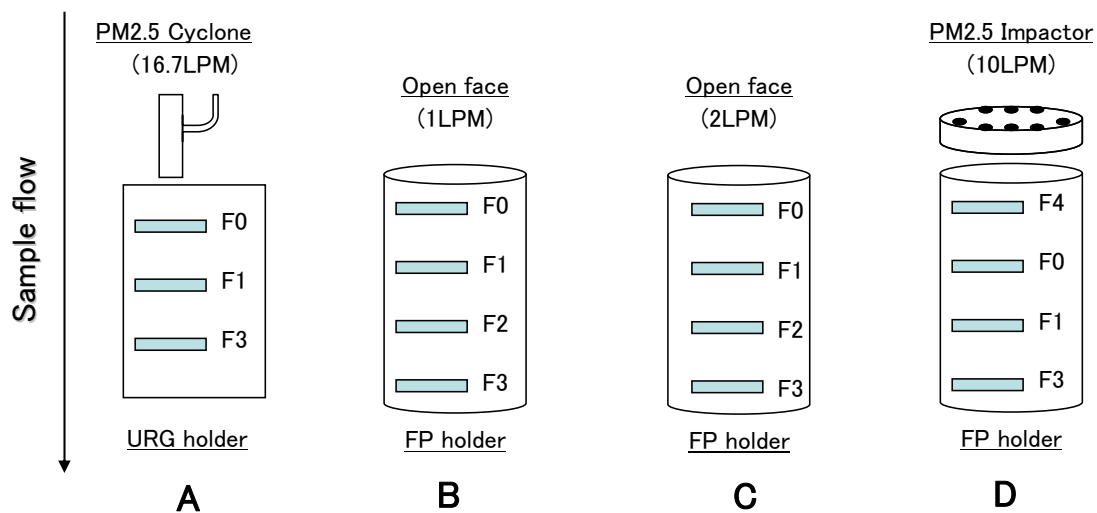


Figure 1. Summary of sampling methods of aerosol monitoring

To compare results A and D may clarify the difference between the different two aerosol separation methods. To compare results B and C may clarify the difference between the different flow rates. To

compare results of gas concentrations measured by A, B, C and D may clarify the difference between the different four sampling methods. Each sampling should be implemented on the daily basis. The analytical item should include gases (SO_2 , HNO_3 , HCl) and aerosol components (SO_4^{2-} , NO_3^- , Cl^- , Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , EC, OC, Trace elements (Optional)).

4. Current status and future works

Intensive monitoring in 2010 was conducted by the end of October, 2010, and sample analysis is promoting at present. After compiling monitoring data, the data will be exchanged between NIER and ACAP under the agreement between both institutes. Then, the discussion for the monitoring results will be implemented by a small data analysis workshop in Korea or Japan. Final outcomes are planned to publish as a peer reviewed paper.

Joint Research Project with Mongolia on Impact of Coal Burning-Derived Aerosol on Tree Decline in Ulaanbaatar

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1. Introduction

Air pollution in Ulaanbaatar, Mongolia has been in severe situation for recent years. Especially, many yurts gather around Ulaanbaatar in winter, and coal is burned for domestic use such as heating and cooking. In order to supply heat source and electricity for growing economy and population, a new coal power plant has been recently constructed. Since the temperature at Ulaanbaatar was very low (The monthly average temperature was -22.3°C in January.) in winter, a strong inversion layer forms at Ulaanbaatar, which would cause worse air pollution in addition to heavy air pollutant emissions in winter. A preceding study at Ulaanbaatar reported that tree decline was observed at some parts in Mt. Bogdkhan located in the southern Ulaanbaatar (Sase *et. al*, 2005; ADORC, 2006). The sulfur concentration in *Larix* leaves (2 mg-S g⁻¹) collected at the sites near the 3rd coal power plant in Ulaanbaatar was approximately twice as much as that collected at the reference site at Mt. Bogdkhan. This result demonstrated tree decline will be related to deposition of gaseous and particulate sulfur emitted from coal burning.

According to the preceding study, it was found that material flow of air pollutants from emission source and forest deposition would occur in the small area. This study aims to elucidate the impact of coal burning-derived aerosol on tree decline in Mt. Bogdkhan, Ulaanbaatar by the measurement of gas and particle concentration, the chemical compositions of emission finger prints in tree, soil and coal samples.

2. Methods

Because of high PM concentration, it was difficult to collect gas and aerosol sample by using a typical filterpack setup in winter Ulaanbaatar. In order to eliminate this bottleneck, we used the 5-stage filterpack equipped with a PM₁₀ impactor to measure gas and aerosol concentrations in both winter and summer in Ulaanbaatar. Soil, tree bark and leaf samples were also collected both in winter and summer, and then soil extracted and deposited substances on barks and leaves were analysed. Furthermore, some kinds of coal samples

used in coal power plants and households were collected to investigate source profiles by analysis of sulfur and trace element.

From these results of field sample analysis, the deposition amount of coal burning-derived sulfur will be estimated, and the impact of sulfur deposition on forest and other ecosystem will be evaluated. Moreover, coal burning-derived sulfate aerosol and its contribution to aerosol deposition in Mt. Bogdkhan will be determined by using the similarities of sulfur isotope ratio ($^{34}\text{S}/^{32}\text{S}$) and trace element composition among aerosol, soil, plant and coal samples.

3. Summary of intensive investigation

As a preparation of the intensive investigation, an operation check of a filterpack sampling setup was performed in a freezer at -18°C . We confirmed that the sampler was able to work more than 24 hours. Since most leaves fall in winter, staffs of Central Laboratory of Environment and Metrology, Mongolia (CLEM) collected *Larix* leaves in October, 2009. Then, the 1st intensive field investigation was conducted in January, 2010, July, 2010 and March, 2011 (planning) collaborating with the staffs of CLEM. Figure 1 shows the location map of sampling sites in Ulaanbaatar.

The gas and aerosol sampling by using filterpack was conducted at the Site A, which is located at 2 km from the 3rd coal power plant (cf. Figure 2). Soil, plant and cover snow samples were collected at the Site B, which is located at a slope of Mt. Bogdkhan and faced with the power plant, and at the Site RF, which is located at some distance of the power plant.

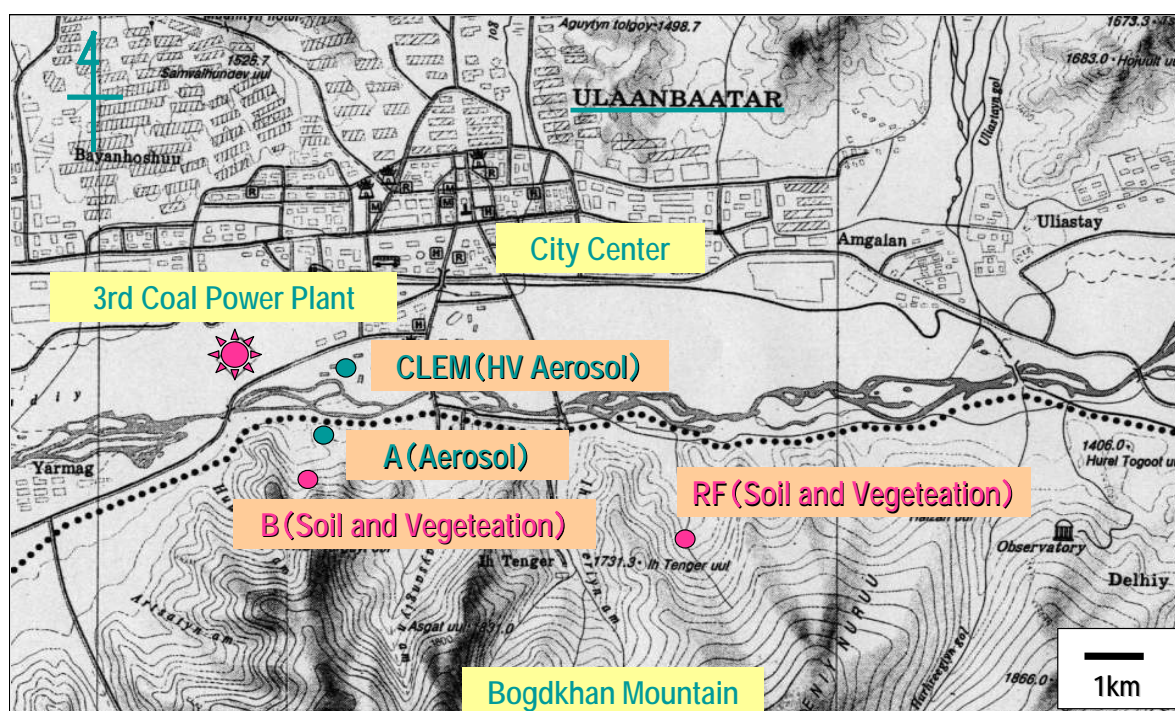


Figure 1. Location map of sampling sites in Ulaanbaatar.

Table 1 summarizes the collected samples during the field investigation. The analysis of the collected samples has not been completed by the end of February, 2011. All samples will be analyzed by the spring, 2011.



Figure 2. Picture of gas and aerosol sampling by using a filterpack method.

Table 1. List of the collected samples during the intensive field investigation in winter, 2010.

Sample	Collection period	Analytical component
Gases and aerosols	Jan., 2010	Ions, carbons, trace elements
	Jul., 2010	
	Mar., 2011	
<i>Larix</i> leaves	Jan., 2010	Sulfur, trace elements
	Jul., 2010	
	Mar., 2011	
<i>Larix</i> barks	Jan., 2010	Sulfur, trace elements
	Jul., 2010	
	Mar., 2011	
Soils	Jan., 2010	Sulfur, trace elements
	Jul., 2010	
	Mar., 2011	
Cover snow	Jan., 2010	Ions, carbons
	Mar., 2011	
Coal samples	Jan., 2010	Sulfur, trace elements

4. Interim results of the project

Figure 1 shows deposited Black Carbon (BC) amounts deposited on *Larix* leaves collected in October, 2009 and July, 2010. Deposited amounts of elementary carbon (EC) and organic carbon (OC) at the Sites B and D were higher than that at the Site RF both in autumn and summer. These results imply that carbonaceous aerosol emitted from a coal power plant will highly impact on deposited air pollutant in the tree decline area. Although the atmospheric concentration of carbonaceous aerosol at the Site A was similar level between October and July, the deposited amounts of EC and OC in October were higher than those in July. We considered the

reason of higher EC and OC depositions in July were attributable to the difference in pretreatment, namely, the July samples were not washed with ultrapure water before analysis.

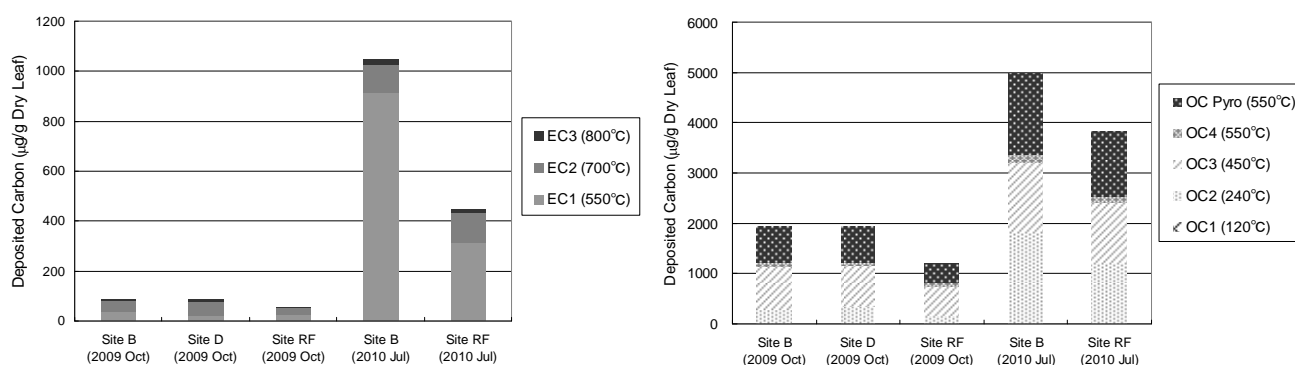


Figure 3. Deposited Black Carbon (BC) amounts (Average of 3 samples) deposited on *Larix* leaves collected at the Site B and D (Faced with the power plant) and the Site RF (Located in some distances from the power plant) in October, 2009 and July, 2010.

Soil chemical properties at the Mt. Bogdkhan were also investigated. Figure 4 shows pH and soluble sulfur concentration in depth fractionated soil collected at the Site B and Site RF in July, 2010. The Soil pH was lower and the soluble sulfur concentration was higher in the surface fraction (0-5 cm), which implies that sulfur emitted in Ulaanbaatar was accumulated on the soil surface. Moreover, the Soil pH was lower and the soluble sulfur concentration was higher at the Site B, which implies that larger amount of acidic substances may be deposited on the tree decline area. In order to clarify the effect of coal accumulation of heavy metals, such as Pb, Cu and Zn which will be fingerprint elements of coal combustion, should be investigated.

5. Future issues

For clarification of the relationship between coal burning-derived aerosol and the impact on forest ecosystem, the following issues are existing: 1) The application of the Inferential method to the boreal and mountain conditions such as Mt. Bogdkhan is not sufficient to evaluate aerosol deposition amount. 2) Since precipitation in Ulaanbaatar was very low (Annual precipitation was approximately 300 mm.), it is difficult to apply the Throughfall/Stemflow method for aerosol deposition estimation. 3) Most of trees in Mt. Bogdkhan are deciduous tree such as *Larix*, and thus it is impossible to collect aerosol sample deposited on the tree leaves.

In view of these issues, the relationship between aerosol deposition and impacts on forest ecosystem will be elucidated by using the following additional investigations: i) Material flow of coal burning-derived aerosol will be clarified by sulfur isotope ratio and trace element composition of coal, plant and soil samples. ii) The aerosol deposition amounts will be measured by using deposition of aerosol on the surrogate surface, which is made of a PTFE plate coated with plant wax.

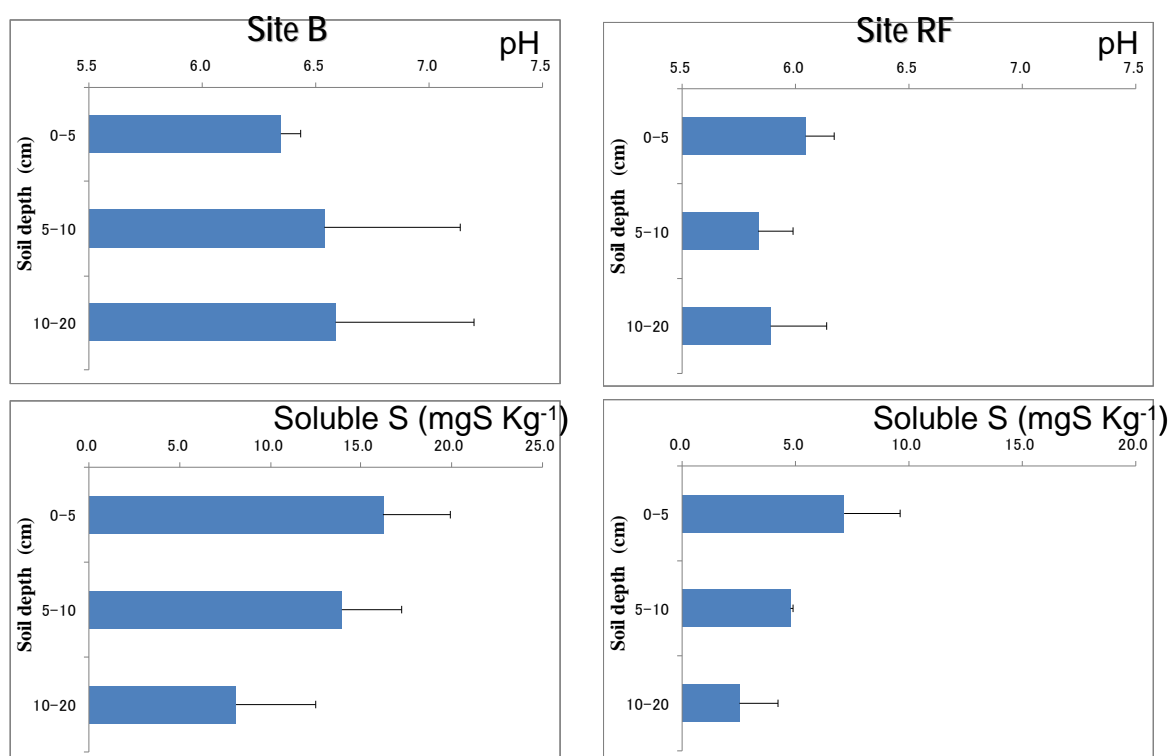


Figure 4. pH and soluble sulfur concentration in depth fractionated soil collected at the Site B and Site RF in July, 2010.

6. Acknowledgements

The authors wish to thank to Ms. Bulgan Tumendemberel at Central Laboratory of Environment and Metrology, Mongolia for supporting field investigation at Ulaanbaatar. This work is supported by Grant-in-aid for Scientific Research on innovative areas (Research in Proposed Research Area, Project No. 21120513).

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Aerosol Deposition Studies in Forests for Improvement of Estimation Method for Dry Deposition.

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1. Introduction

The process of dry deposition has been studied over decades in an attempt to estimate quantitatively the removal rate of atmospheric aerosols. Although many different turbulent and chemical mechanisms that can contribute to the processes of deposition have been discussed extensively in the literature over the years, our knowledge remains incomplete. Progress has essentially been limited to bulk estimates of the dry deposition flux. This has been mainly due to the complex interdependence of many different variables that can control the exchange process of atmospheric condensates to surfaces that are complex both at the microscale in terms of morphology and at the terrain scale. Although there have been many models that seek to explain the deposition process to complex surfaces by taking into account variables such as particle size, composition, surface morphology, meteorology, and turbulence, their predictions vary widely. The studies, although providing valuable insights into exchange processes, are not fully representative of atmospheric surface layer turbulent exchange processes, specifically the influence of atmospheric stability. The relative humidity on particle equilibrium size as a function of dry particle size and composition may also cause sizing artifacts in sample collected. This deliquescence effects on the deposition fluxes should receive attention. Buzorius *et al.* (1998) has suggested that the errors induced in deposition velocity may be large, causing an underestimate in deposition velocity under warm humid conditions.

2. Objectives

This study aims that a direct measurement method will be applied to determine the aerosol deposition flux and velocity over the forest canopy in the tropical region. The detailed scopes of this study are described as follows.

1. Direct measurement of aerosol deposition flux and velocity will be conducted in the forest in Thailand,
2. Principal aerosols to be study consist of SO_4^- and NO_3^- ,
3. Seasonal effects on the deposition velocity will be determined,
4. Seasonal differences in the tropical region will be compared with the available inferential model applied for the sub-temperate region.

3. Experimental methods

The eddy accumulation method which is a variation of the standard eddy correlation is to be applied for this study. It is a suitable technique for determining the deposition flux using the filter packs. Figure 1 shows a schematic diagram of the eddy accumulation sampling system. This system involves sampling the air onto two separate filters, with the velocity determining which filter receives the sampled air. One filter is used for positive vertical velocities and the second is used for negative vertical velocities; the instantaneous sampling rate for each filter is proportional to the magnitude of the velocity. The deposition flux of the aerosol can be calculated by

$$F = b\sigma_w (C_{\text{up}} - C_{\text{down}}) \quad (1)$$

where b is the experimental coefficient obtained from the probability distribution of vertical wind velocity, σ is the standard deviation of the vertical wind velocity and C_{up} and C_{down} are the average concentration of the pollutant depending on the wind velocity is upflow or downflow.

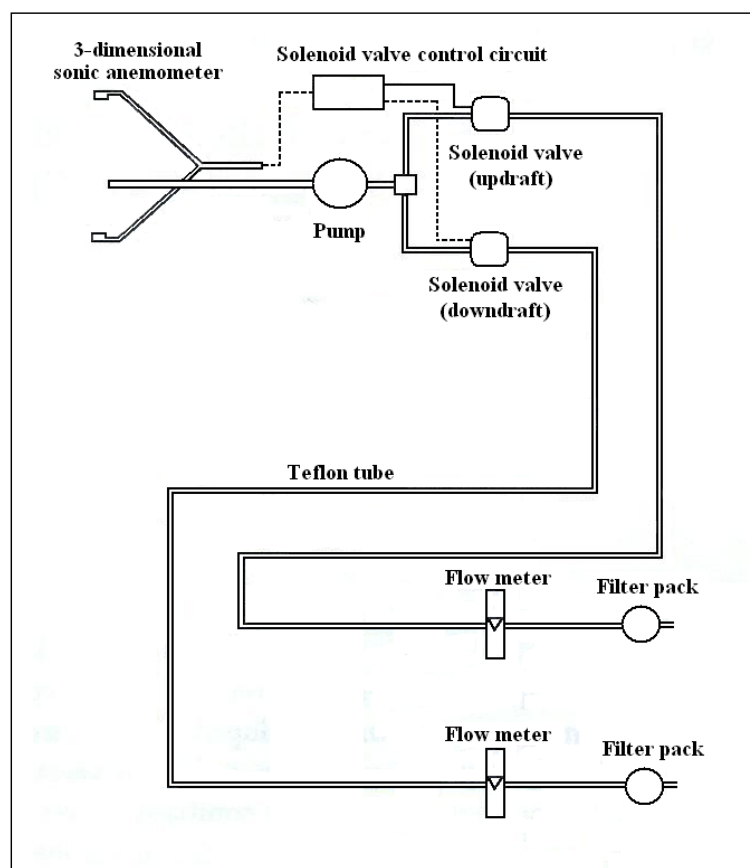


Figure 1. A schematic diagram of the eddy accumulation sampling system.

The experimental site is a forest type of Dipterocarp plantation located in Ratchaburi province (approximately 200 km away from Bangkok). Figure 2 shows the picture of experimental site.



Figure 2. The experimental site covering with Dipterocarp plantation

The micrometeorological instruments were installed on a tower 10 m high with 3 m above the trees. The climate in Thailand can be broadly classified into wet or dry. The wet season covers a period of May to October and the dry season covers a period of November to April. The 10 year average amount of rainfall from the beginning of the wet season to the peak is in the range of 60-250 mm. In the dry season, the 10 year average rainfall is in the range of 0-60 mm. The average temperature is 28.7 °C and 26.7 °C for the wet and dry seasons, respectively.

Figure 3 shows the experimental tower equipped with meteorological instruments consisting of 3D ultrasonic anemometer, filter packs, Temperature and relative humidity sensor, vacuum pump, flow meter and solenoid valves. Figure 4 shows a set of data logger and computer to record the meteorological values.

4. Results and Discussion

Figure 4 and 5 show monthly averages of ambient temperature and relative humidity as well as sulfate and nitrate concentrations, respectively. The results show the higher concentration of nitrate than sulfate (Figure 4). It is probably caused by the reaction between nitric acid and ammonia in the atmosphere. The ammonia concentration was high also in the area of measurement. The ambient temperature and the relative humidity show relative effects on the sulfate and nitrate formations. As shown in Figures 5 and 6, the measurements show that sulfate and nitrate concentrations tend to increase when the temperature and the relative humidity decrease (during the dry season).

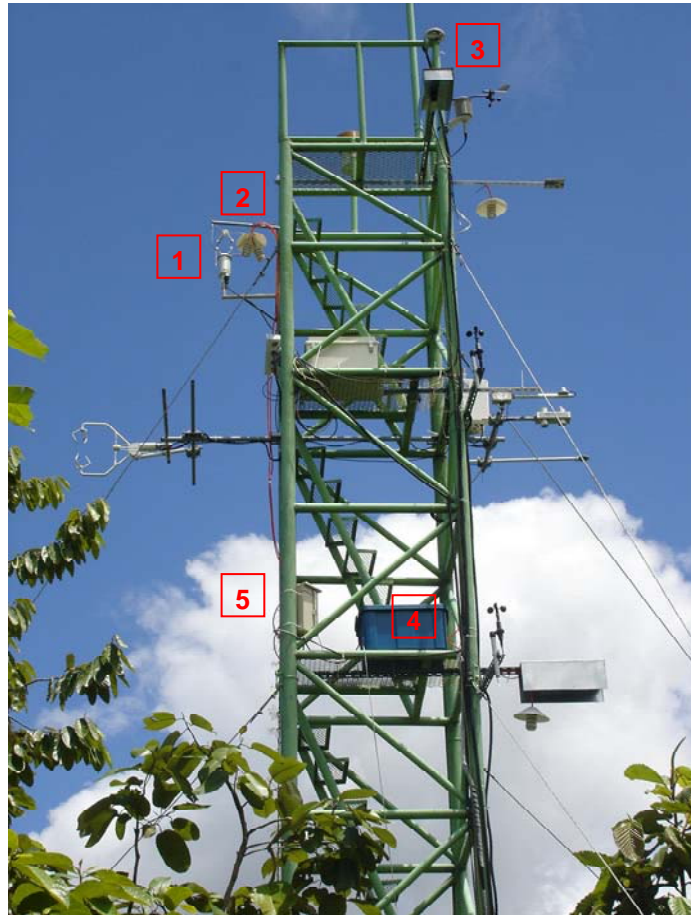


Figure 3. The experimental tower equipped with meteorological instruments, 1. 3D ultrasonic anemometer, 2. Filter packs, 3. Temperature and relative humidity sensor, 4. Vacuum pump and 5. flow meter and solenoid valves.



Figure 4. A set of data logger and computer to record meteorological values.

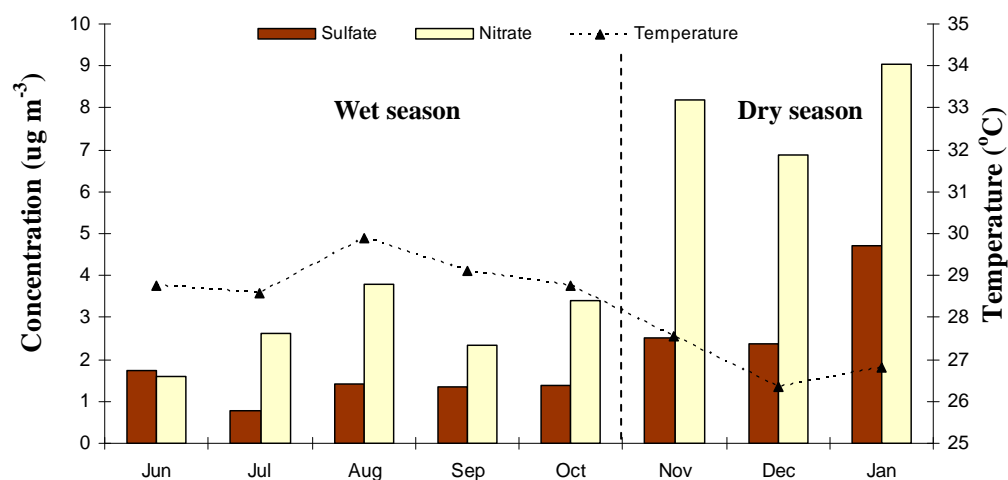


Figure 5. Measurement values of ambient temperature and monthly sulfate and nitrate concentrations.

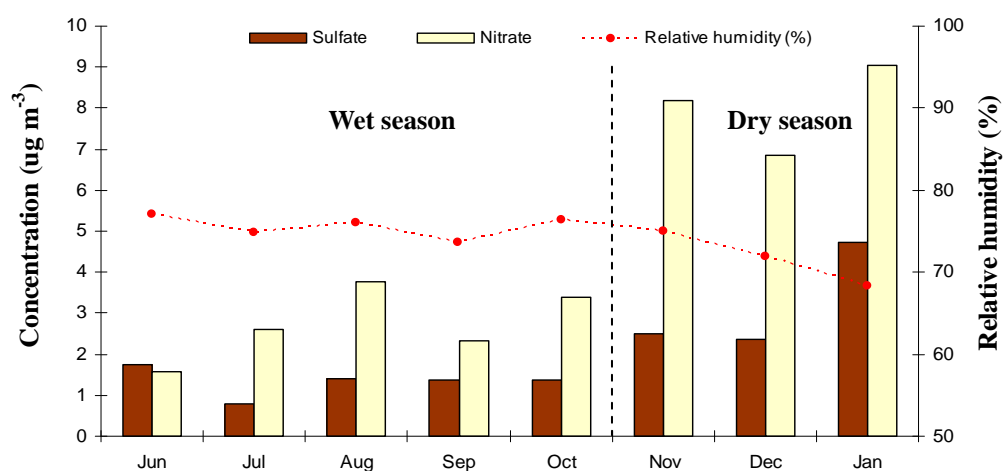


Figure 6. Measurement values of relative humidity and monthly sulfate and nitrate concentrations.

As shown in Figure 7, the dry deposition flux of sulfate tends to increase in the dry seasons. The flux values were in ranges from 0.002 to 0.011 $\mu\text{g}/\text{m}^2\cdot\text{s}$ (172.8 $\mu\text{g}/\text{m}^2\cdot\text{day}$ – 950.4 $\mu\text{g}/\text{m}^2\cdot\text{day}$). The comparison of the results of Figures 7 and 8 demonstrates that the dry deposition flux of nitrate is significantly higher than sulfate in the area of measurements. The values were found in ranges from 0.01

$\mu\text{g}/\text{m}^2.\text{s}$ to $0.10 \mu\text{g}/\text{m}^2.\text{s}$ ($864 \mu\text{g}/\text{m}^2.\text{day} - 8,640 \mu\text{g}/\text{m}^2.\text{day}$). The higher value of nitrate flux is conformed to its higher concentration comparing with sulfate. However, it should be noted that the nitrate concentration is doubling the value of sulfate concentration but the nitrate flux is 10 times higher than the sulfate flux. Further investigation on the influence of other parameters such as the molecular sizes, temperature, humidity, etc. will be carried out.

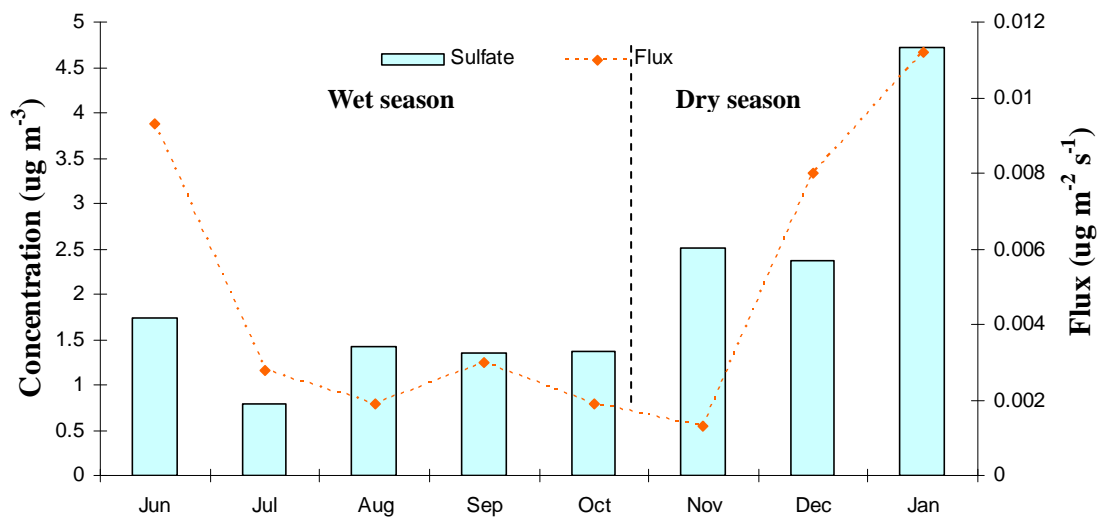


Figure 7. Dry deposition flux of sulfate in the wet and the dry seasons.

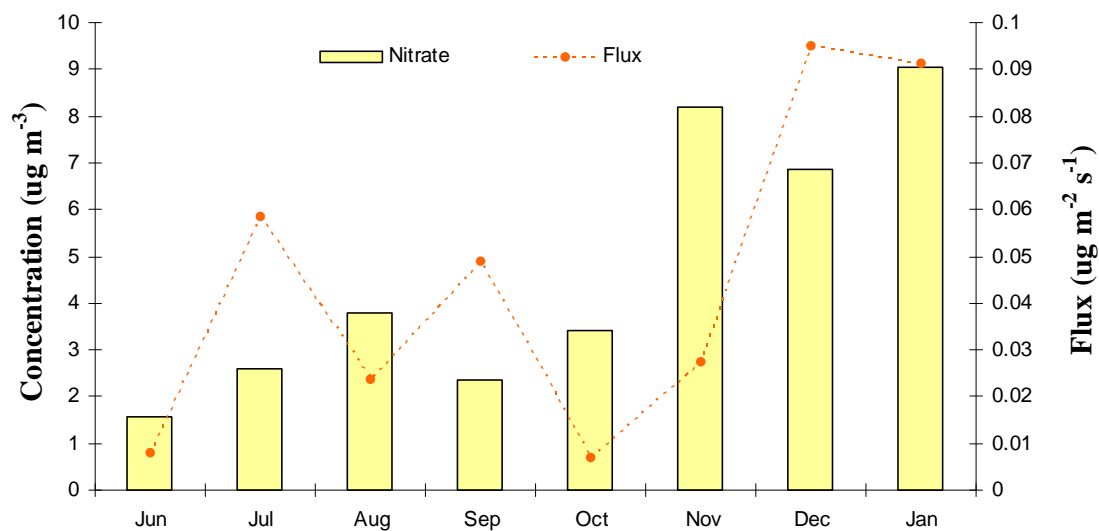


Figure 8. Dry deposition flux of nitrate in the wet and the dry seasons.

4. Future works

The work to be performed in this research project include as follows:

1. Calculate the deposition velocities of sulfate and nitrate,
2. Determine the aerosol size distribution over the forest canopy,
3. Indicate parameters affecting the aerosol fluxes and deposition velocities,
4. Fitting the Resistance model with the experimental data,
5. Paper for publication after obtaining the further results.

5. Acknowledgements

This work is partly supported by EANET High Priority Research Project from 2008 to 2010.

6. References

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Research Project on Aerosol Impacts in the East Asian Region

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1. Introduction

Aerosol in the atmosphere is closely related to global environmental problems such as global warming and acid rain. At the present time, however, information on the impacts of aerosol on plants and human health is not sufficient. The research project of “Impacts of Aerosols in East Asia on Plants and Human Health” supported by the Grant-in-Aid for Scientific Research on Innovation Areas (The Ministry of Education, Culture, Sports, Science and Technology, Japan) is in progress in 2008-2012 (fiscal year).

2. Objectives

In this research project, many scientists in the fields related to atmospheric aerosol perform their intensive investigations in collaboration with each other research group to establish "Environmental Science of Aerosols". For this purpose, this research project consists of four research items, A01: Evaluation of Aerosol Formation and the Emission Sources, A02: Elucidation of Transport and Distribution of Aerosols and Air Pollutants in East Asia, A03: Elucidation of the Impacts of Aerosols on Plants, and A04: Elucidation of the Impacts of Aerosols on Human Health. Process studies to be performed in the A01 and A02 research items and impact studies to be performed in the A03 and A04 research items will be made in closer cooperation. In the A01 and A02 research items, the processes of emission, transformation, and deposition of aerosols from East Asia will be accessed and clarified. The results are utilized in the A03 and A04 research items for investigating the present impacts. Then, their results are feed backed to the A01 research item for the evaluation of future impact. The goal is to provide scientific data that become the basis of the environmental standards for setting emission measures under international cooperation and to lead to proposals concerning those issues.

3. Outline of the Research Item A03

In the research item A03, experimental studies and field surveys in Japan and other Asian countries on possible impacts of aerosols on plants is conducting. The objective of research item A03 is to clarify the effects of aerosol on plants by experimental studies and field surveys (Figure 1). To evaluate aerosol impacts on plants in Asia, the following must be comprehensively studied: (1) the mechanism in the adsorption of aerosol on the leaves or needles of forest tree species and that in the absorption of aerosol into the leaves or needles of forest tree species by bio-imaging technique using microscopes (research group P08); (2) the effects of aerosol on growth, physiological functions such as photosynthesis, water status and nutrient status of East Asian forest tree species and its species difference (research group P09); (3) improvement of measurement techniques of aerosol deposition and application of the measurement techniques to field studies in corroboration with research group P11 (research group P10); and (4) measurements of dry deposition of aerosol components such as sulfate, nitrate and black carbon onto three forests located in tropical, temperate and frigid zones by micrometeorological measurement methods (research group P11).

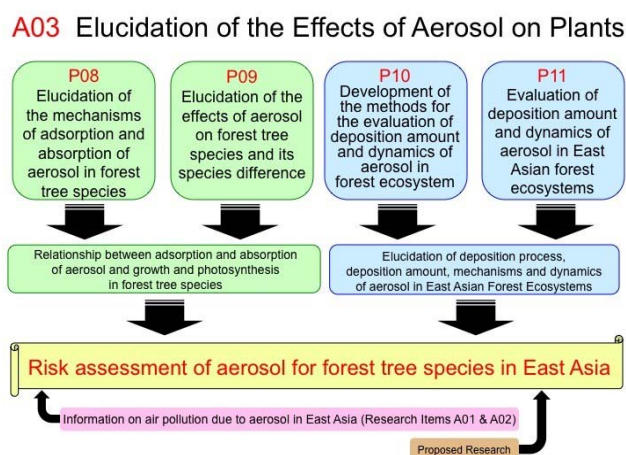


Figure 1. The objective of Research Item A03.

3.1 Experimental studies by P08 and P09

In the collaborative experimental study of research groups P08 and P09, the effects of black carbon particles with submicron size on growth and physiological functions such as photosynthesis of Japanese representative forest tree species are investigating. The seedlings of *Fagus crenata*, *Castanopsis sieboldii*, *Cryptomeria japonica* and *Larix kaempferi* were individually planted in pots filled with Kanuma pumice soil. In June 2009, the seedlings were transferred into 6 chambers (Figure 2) located at Tokyo University of Agriculture and Technology (Fuchu, Tokyo, Japan). In the chambers, air



Figure 2. Aerosol exposure chambers located at Tokyo University of Agriculture and Technology (Fuchu, Tokyo, Japan).

temperature and relative air humidity were maintained at $25.0 \pm 1.0 / 18.0 \pm 1.0^{\circ}\text{C}$ (6:00-18:00/18:00-6:00) and $70 \pm 5\%$, respectively. The seedlings of the 4 tree species were exposed to black carbon particles with submicron size generated by an electrospray aerosol generator and an ultrasonic nebulizer. The mean number concentration of black carbon particles generated by the electrospray aerosol generator was 100-200 nm. The half of the seedlings was exposed to black carbon particles every two days (black carbon treatment), and the other half of the seedlings were not exposed to the particles (control treatment). The amounts of black carbon particles deposited on the surface of the leaves or needles were measured. Gas exchange rates of the leaves or needles of the seedlings were measured using an infrared gas analyzer system. As shown in Figure 3, black carbon particles generated by the electrospray aerosol generator and ultrasonic nebulizer were observed on the surface of the leaves or needles of *F. crenata*, *C. sieboldii*, *C. japonica* and *L. kaempferi* seedlings harvested in the black carbon treatment in August and October 2009. The exposure to black carbon particles for one growing season does not significantly affect the whole-plant growth and leaf gas exchange rates of the seedlings of the 4 tree species. In 2011-2012, research groups P09 and P10 will conduct an experimental study on the effects of sulfate aerosol on growth, physiological functions such as photosynthesis and nutrient status of Japanese forest tree species such as *F. crenata*, *C. sieboldii*, *C. japonica* and *L. kaempferi*.

3.2 Field Studies by P10 and P11

In the research group P10, field experiments are conducted using experimental tower (Figure 4) to evaluate dry deposition of aerosol components on a forest-ecosystem at the research station FM Tamakyuryo (Hachioji, Tokyo, Japan), integrate different measurement methods (passive and active sampling method, open pass FTIR spectroscopy, foliar rinsing method and forest through fall method), apply the improved measurement techniques of aerosol deposition to the field surveys by research group P11, and analyze mechanisms of aerosol deposition onto leaf surface in corroboration with

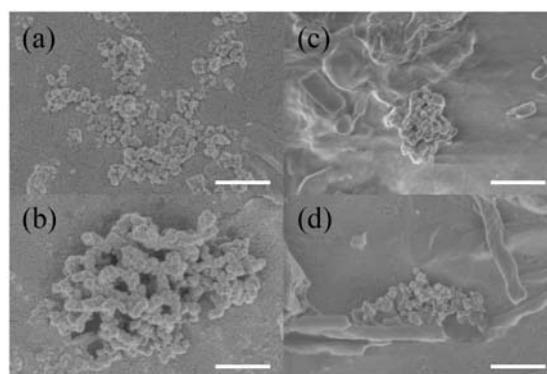


Figure 3. Field emission scanning electron microscope (FE-SEM) images of black carbon particles deposited on the leaves or needles of (a) *F. crenata*, (b) *C. sieboldii*, (c) *C. japonica* and (d) *L. kaempferi* seedlings. Bars = 500 nm.



Figure 4. Experimental tower located at FM Tamakyuryo of Tokyo University of Agriculture and Technology (Hachioji, Tokyo). Japan).

research groups P08 and P09.

In the research group P11, field surveys are conducting to evaluate dry deposition of aerosol components, especially sulfate, nitrate and black carbon, onto forests by micrometeorological measurement methods, improve measurement techniques of aerosol deposition and apply them to the field studies in corroboration with research group P10, analyze mechanisms of aerosol deposition onto the forests and dynamics of aerosol components in the forest ecosystems, and assess the impact of aerosol depositions to the forest



Figure 5. Experimental tower in Sakaerat,

ecosystems in corroboration with research groups P08 and P09. The observation of aerosol flux by concentration gradient method is carried out in temperate forest in Kitasaku (Nagano, Japan), frigid forest in Teshio (Hokkaido, Japan) and dry deciduous forest in Sakaerat (Nakhon Ratchasima Province, Thailand). In Sakaerat, experimental tower (Figure 5) for flux observation was constructed in the dry deciduous forest and catchment survey was started from the dry evergreen forest. At the tower, meteorological observations and aerosol sampling for the component measurements were started in December 2009. On the other hands, measurements of rainfall, throughfall and stemflow were started from January 2009 at the catchment plot. The resin-sampler was applied to the Sakaerat site in December 2009. The black carbon samplers were installed at the top of the tower in the dry deciduous forest. Moreover, to release black carbon particles strongly adsorbed on the leaf surface, epicuticular wax extracted by chloroform. Then, black carbon particles released from the leaf surface were collected on a silica filter. The chloroform extraction of black carbon particles was conducted for predominant three tree species (*Shorea henryana*, *Hopea ferrea*, and *Dipterocarpus turbinatus*) in the dry evergreen forest in December 2009 and February 2010, one of the predominant tree species (*Pterocarpus macrocarpus*) in the dry evergreen forest and a representative plantation tree species (*Acasia mangium*) in February 2010.

4. Perspective

As future framework for the elucidation of the effects of air pollutants on plants in East Asia, we must monitor not only acid deposition, but also gaseous air pollutants such as ozone and aerosol, and clarify the effects of aerosol such as black carbon particles and sulfate aerosol on plants.

Scientific and Technological Research Papers from Participating Countries

For our cooperation on research activities, we have some research papers from our participating countries that have been utilized the EANET data. Therefore, they are included in this part of the EANET Science Bulletin.

The Potential Impact of Sulfur Deposition on Soil Acidification in a Tropical Forested Catchment in Thailand

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ABSTRACT

The rapid increasing of developmental human activities has given considerable rising of the atmospheric pollutants which have severely affected the natural ecosystems. Among those pollutants emission of SO₂ and NO_x have significantly increased in the East Asian region since 1990. Acid deposition has become one of the most important issues in this region due to its trans-boundary nature and the impact to ecological acidification. The impact to ecology would be the most important for catchment areas where water resources availability was defined. An attempt to quantify the acidic pollutants deposition and their potential effects on long-term soil acidification at a tropical forested catchment area in Thailand using soil incubation method was made. Wet deposition of well known acidifying compounds SO₄²⁻ found in the catchment area through the integrated monitoring method such as rainfall (RF), throughfall (TF) and Stemflow (SF) in the year 2008 were 8.3, 87.0 and 3.0 mmol/m²/year, respectively. The volume weighted average pH of the precipitation was 5.15. The study on soil characteristics of the tropical forested catchment indicated high potential to soil acidification. The regulatory factors that govern soil sensitivity and vulnerability in the area were summarized and the possible ways in which deposition acidity may interact with these regulatory factors were examined. Aspects considered include modifications to soil chemical characteristics in which such changes may influence soil acidification in the area were critically discussed.

1. Introduction

It was recognized that Asian region is experiencing a considerable increase in pollution problem due to a rapid growth in population, economic development and industrial productivity. As the region strives to be industrialized, the environment suffers from inadequate attention. Acid deposition was considered as one of the major issues of trans-boundary air pollution in the region. The rapid increase in development of human activities has given considerable rise to atmospheric pollutants which have affected the natural ecosystems severely, as for example the forest decline (EANET, 2008). Sulfur dioxide (SO₂) and oxides of nitrogen (NO_x) are the major pollutants in industrial areas, principally as causative agents of acid deposition. Their emissions from industries, power plants and mobile sources cause the formation of H₂SO₄ and HNO₃ in precipitation (Menz and Seip, 2004) and thus affected the ecosystem by wet and dry deposition. Preliminary results from the Composition and Acidity of Asian Precipitation (CAAP) workshop held in Bangkok, in November 1998 (www.rapidc.org), clearly indicated that air pollution is severe in several areas of Asia and the levels of acid deposition received in some areas may exceed the carrying capacity to their soils. For Thailand, the relative contribution from national emission sources to the potential acidification problem has been studied in the cooperative project between Environmental Research and Training Center, Thailand and the Swedish Environmental Research Institute (IVL) and Swedish Meteorological and

Hydrological Institute (SMHI) during 2001-2003 (Technical Report on the study of possible acidification in Thailand 2003). Based on the measurement and modeling results generated in this study, we conclude that 70-80% of the anthropogenic total sulfur and oxidized nitrogen deposition in Thailand arises from sources within Thailand and the maximum amount of sulfur depositions was found in the range of 3-10 g S/m²/year. Besides, the study of world sensitivity mapping on acid deposition in 1996 has shown that soil in large parts of the country were sensitive to acidic pollution (Kuylenstierna *et al.*, 1998). However, the causes and consequences of acid deposition in the affected areas still remain unclear.

As acid rain with deposition of sulfur (S) and nitrogen (N) compounds move through the soils, it can strip away vital plant nutrients through chemical reactions, thus posing a potential threat to future forest productivity. Forest productivity is very important for the catchment areas where water resources availability is defined. Within the framework of Acid Deposition Monitoring Network in East Asia (EANET), the Acid Deposition and Oxidant Research Center (ADORC) Japan in cooperation with Environmental Research and Training Center (ERTC), the Royal Forest Department and Kyoto University have established the study on catchment analysis in Thailand since 2005. This is essential to the need of identifying and quantifying the effects of acid deposition to tropical forested catchment ecosystem where such approach has not enough promoted in the region. Several studies have attempted to determine whether naturally occurring soil acidification has been intensified as a result of acid rain and associated atmospheric depositions. So far, there was no conclusive evidence that this has occurred on a wide scale. Characterization of soil sensitivity and vulnerability is essential to understand acidification state and acidification rate of the catchment. Therefore, the study aims to assess acid deposition and the potential impact on soil acidification in the northeastern catchment area of Thailand.

2. Objective of the research

The objective of the study is to promote a comprehensive assessment of the sensitivity and vulnerability of the forest soil to acid deposition in the northeastern catchment area of Thailand using soil incubation experiment. It also aims to study the possible leachability of toxic elements due to increasing soil acidification.

3. Scope of the study

In order to assess acid deposition and the potential impact on soil acidification in the northeastern catchment area of Thailand, soil samples were collected in the Sakaerat Silvicultural Research Station (Sakaerat SRS), the sampling site of the joint research project on catchment analysis in Thailand. In cooperation with Asian Institute of Technology, soil incubation experiment was established to study soil sensitivity and vulnerability to acid deposition due to sulfur. The level of acid deposition in the area were measured by integrated monitoring, such as, throughfall (TF), stemflow (SF) and rainfall (RF) outside the forest canopy, which have been used in the joint research project on catchment analysis in Thailand to assess wet deposition input to the catchment area. Since in general H₂SO₄ is the main H⁺ in the precipitation (Verry and Harris, 1988; Galloway *et al.*, 1982; Herut *et al.*, 2000), we calculated the amount of S deposition in the catchment area and used to assess the soil acidification in this study using soil incubation experiment.

4. Research methods

In the joint research project on catchment analysis in Thailand, The study site was established in 2005 at Sakaerat Silvicultural Research Station (Sakaerat SRS); Nakhon Ratchasima Province located about 200 km in the northeast direction of Bangkok. The size of the catchment was approximately 35 hectares in the tropical dry evergreen forest with one stream flow out at the bottom. The Figure 1 showed the study area of forest catchment. The main soil type of the catchment is acrisols which is high-weathered red soil and relatively sensitive to acid deposition. The installation of 5 sets of throughfall (TF) and stemflow (SF) sampling in different places within the catchment were set to assess the wet deposition in the forest. This installation was designed to obtain the representative of deposition samples taking into account the un-homogeneity of tree species in the forest complex. In the open field of the forest, 4 rainfall (RF) samplers were also set to assess the wet deposition outside the forest canopy. The precipitation samples including TF, SF, and RF were collected basically at two-week interval for all year round. The pH, EC and Ionic composition, such as Na⁺ NH₄⁺ Ca²⁺ Mg²⁺ NO₃⁻ Cl⁻ and SO₄²⁻ of wet deposition

were analyzed according to EANET method (Technical Documents for Wet Deposition Monitoring in East Asia, EANET 2000).

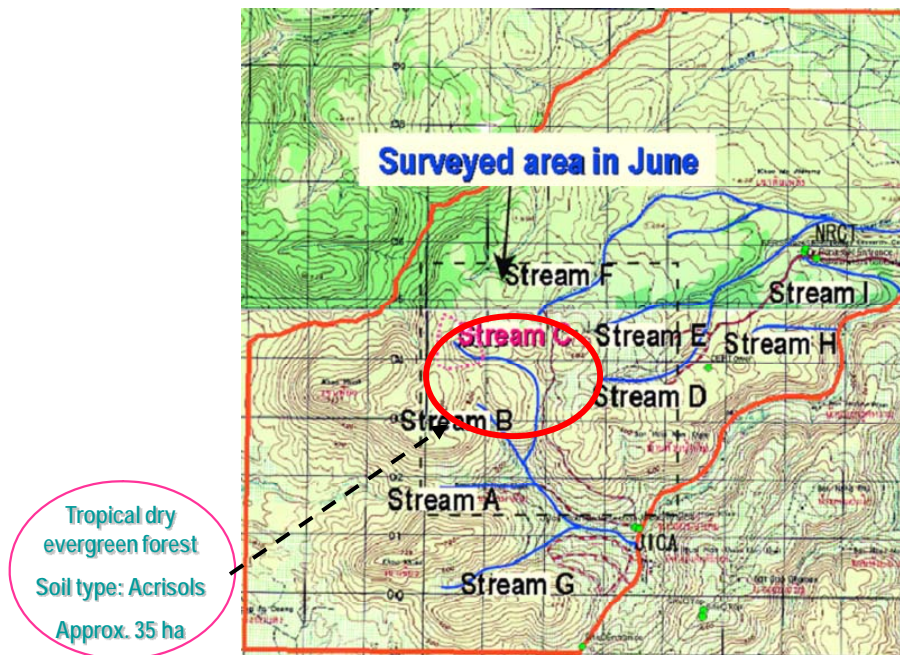
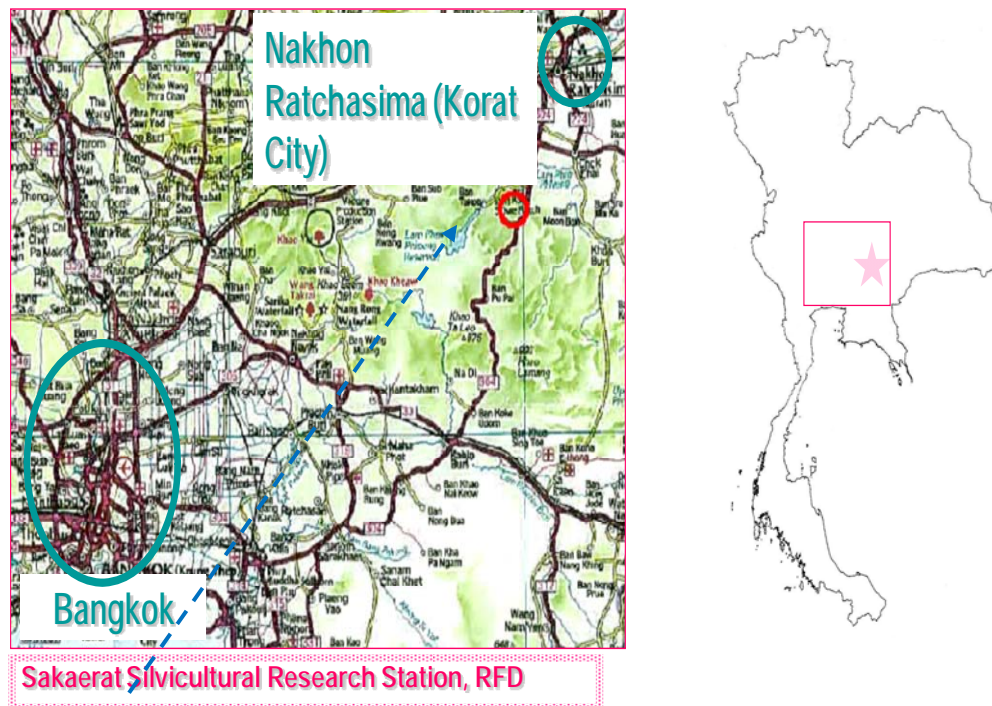


Figure 1. The location of sampling site in the catchment studied area, Sakaerat Silvicultural Research Station (SRS).

The characteristics of sensitive and vulnerable soils and their responses to acid deposition were different. The important soil parameters which play a key role on the extent of acid deposition effects on soil system are the cation exchange capacity (CEC) and soil base saturation (BS). CEC can be defined as “the number of negatively charged sites on soil particles”, while the proportion of these negative sites occupied by base cations, as opposed to aluminum or hydrogen ions, is known as the base saturation (BS).

In general, soil CEC is a measure of the soil’s capacity to buffer pH and BS is a measure of the degree to which pedogenic processes have advanced. The soils having a medium or high BS (20-60%) and low CEC are the most sensitive soils to acid deposition. Such soils are likely to exhibit accelerated acidification in response to increased inputs of H^+ from the atmosphere. The soils having already acid nature (low BS and pH below 5) are the most vulnerable soils. In this study, soil samples in the forest catchment area were collected at 6 sampling points for two different depths, e.g., 0-15 cm and 15-30 cm, the depths of active root zone which can represent soil quality and soil capacity to bare acid deposition from the atmosphere. About 50 kg of soil per sampling point were collected and put into a clean plastic bag prior to analyze in the laboratory. The Figure 2 showed the sampling points and the sample collection of forest soil samples. Soil characterization was performed based on physical and chemical properties for the soil. The Table 1 showed the parameters, analytical method and reference for soil characterization. The vulnerability and sensitivity of soils to acidification were assessed based on CEC and BS in soil with reference to the vulnerability classification of Tao *et al.*, 2000 (see Table 2) and the sensitivity classification of Bhatti and Streets, 1992 (see Table 3.).

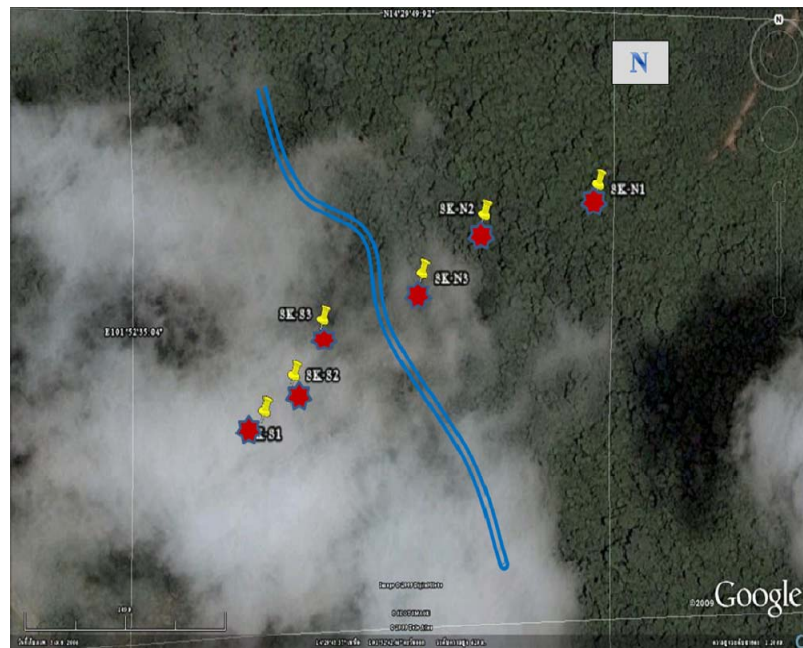




Figure 2. Location of soil sampling (upper picture) and soil sampling method (lower picture) in the SRS catchment area.

Table 1. Soil characterization methods

Physico-chemical properties	Analytical method	Reference
Particle size distribution	Hydrometer Method	Sheldrick and Wang, 1993
Soil texture class	Texture Triangle	Hillel, 1998
Bulk density (g/cm^3)	Core Method	Culley, 1993
pH	pH Meter (1:1, soil:water)	Mc Lean, 1982
EC	EC Meter (1:2.5, soil:water)	Rhoades, 1982
CEC (meq/100g soil)	1 N Ammonium Acetate	Hendershot, <i>et al.</i> , 1993
Soil organic carbon (%)	Wet Oxidation (Walkley-Bleck Method)	Nelson and Sommers, 1982
Base cations (Na, K, Ca, Mg) Soluble, Exchangeable	Saturation Extract + AAS, Ammonium Acetate Extraction + AAS	Rhoades, 1982 Thomas, 1982
Aluminum Exchangeable, Total	KCl Extraction, Dissolution Method	Barnhisel and Bertsch, 1982
Iron Exchangeable, Total	Aqua regia and HCl Extraction + AAS, Decomposition + AAS	Olson and Ellis, 1982
Manganese Exchangeable, Total	DTPA Extraction, AAS	Gambrell and Patric, 1982
Copper Total, Soluble	Digestion + AAS, Extraction + AAS	Baker and Amacher, 1982

Table 2. Types of vulnerability classes of soil series to soil acidification.

CEC (meq/100g)	Base Saturation (%)			
	0 - 20	20 - 60	60 - 80	80 - 100
< 10	I	II	III	V
10 – 25	I	III	IV	V
> 25	II	IV	V	V

Source: (Tao *et al.*, 2000)

Note: Vulnerability Classes = I, II, III, IV, V whereas I = Very severely and V = Very slightly

Table 3. Types of sensitivity classes of soil series to soil acidification.

CEC (meq/100g)	Base Saturation (%)				
	0-20	20-40	40-60	60-80	80-100
< 10	I	I	II	III	V
10 - 25	I	II	III	IV	V
> 25	II	III	IV	V	V

Source: Bhatti and Streets, 1992.

Ecosystem risk class I = Very high risk, II = High risk, III = Medium risk, IV = Low risk, V = Very low risk

In cooperation with Asian Institute of Technology, the possible impact of acid deposition to the forest catchment soil was studied using soil incubation method. The method is a common tool to characterize the dynamics and chemistry of soil organic matter and soil testing for plant nutrients. Soil samples were dried by natural air and sieved with 2 mm stainless steel mesh. Took 350 grams of the soil sample and mixed with different amount of sulfur (S) powder. The weight of S powder was approximately 6.5 g-S/m²/year by referring to the existing average amount of S deposition in Thailand (Technical report on the study of possible acidification in Thailand, 2003), then increased the weight of S to 50, 150 and 450 times of the existing level, respectively. This was done to reduce pH in soil for 2-3 units in order to assess the status of soil acidification which is directly related to the decreasing soil pH. The weight S that was mixed with 350 grams soil in each unit was calculated from the following considerations.

- Density of soil = 1.4 grams/cm²
- Weight of soil in 1 Rai (1,600 m²) with 15 cm depth = 3.36 x 10⁸ grams
- Average amount of S deposition found in the environment, 6.5 g-S/m²/year (10.4 kg-S/Rai/year).
- Weight of S that should mix with 350 grams soil
= 10.4 (kg-S/Rai) * 350 (grams soil)/3.36 x 10⁸ (grams/Rai)
= **0.01 g-S/year**

Therefore, when the amount of S increase from existing level to 50 times = 50 * 0.01 = 0.5 g-S/year, and so on. Soil samples were incubated at 60-70% relative humidity for 8 weeks. For every 1-2 weeks, soil from each unit was

randomly sampled prior to measurement of pH, Base Cations (Na, K, Ca and Mg) as well as toxic elements in soil, such as soluble Al, Mn, Fe and Cu. The soil incubation experiment is summarized in Table 4 and Figure 3.

Table 4. Soil sample and levels of S used in soil incubation experiment.

Soil sample	Depth (cm)	5 levels of S powder in 350 grams soil (g-S)	Experimental unit
Soil in the catchment area at 6 sampling points: Sakaerat SK-S1 Sakaerat SK-S2 Sakaerat SK-S3	0-15	Level 1: 0.00 Level 2: 0.01 Level 3: 0.50 Level 4: 1.50 Level 5: 4.50	6 sample x 5 levels x 3 replication = 90 units
Sakaerat SK-N1 Sakaerat SK-N2 Sakaerat SK-N3	15-30	Level 1: 0.00 Level 2: 0.01 Level 3: 0.50 Level 4: 1.50 Level 5: 4.50	6 sample x 5 levels x 3 replication = 90 units



Figure 3. Soil incubation experiments.

5. Research results

5.1 Atmospheric deposition amounts in the catchment.

Wet deposition such as rainfall (RF), stemflow (SF) and throughfall (TF) in the catchment area of SRS station has been measured since 2005 under the joint research project on catchment analysis in Thailand. Clear seasonality of atmospheric deposition and elemental flow in the forest ecosystems has been observed under the study catchment (e.g. Sase *et al*, 2008). Deposition amounts of all ions by TF+SF generally increased during the beginning of wet season, especially SO_4^{2-} showed the highest concentration. In this study the results of atmospheric deposition

measurement in 2008 was used to quantify the acidic pollutants deposition and their potential effects on long-term soil acidification at a tropical forested catchment area in Thailand. The total amount of precipitation collected by RF was 1,377.2 mm, while TF and SF were 863.1 mm and 34.9 mm, respectively. The volume weighted average pH of the precipitation was 5.15. Total amount of SO_4^{2-} deposition in RF, TF and SF were 8.3, 87.0 and 3.0 mmol/m²/year, respectively. Thus, the total amount of SO_4^{2-} deposition in the catchment area (RF+TF+SF) was 9.4 g- SO_4^{2-} /m²/year, was equal to 3.1 g-S/m²/year. This amount was used to compare with the soil incubation experiment to assess the vulnerability and sensitivity of soils to the acidification in soil.

5.2 Status of soil acidity, soil sensitivity and vulnerability of SRS soil series

The Department of Land Development has developed acid soil susceptible map using soil pH to classify the severity of acid soil in Thailand. The classification of the severity for occurrence of acid soil is shown in Table 5 and the acid soil susceptible map is illustrated in Figure 4. The map showed that one third of the total area of Thailand was susceptible to acid soil and the acid soil is mostly found in the northeastern part of the country. Forest soil from SRS located in northeastern part was classified as Chokchai soil series.

Table 5. Classification of soil susceptible to acid soil using soil pH.

Severerity to acid soil	Soil pH
very severe	< 4.5
severe	4.5-5.0
moderate	5.1-5.5
slightly	5.6-6.0
very slightly	6.1-6.5
Neutral or strong base	> 6.6

The soil pH of SRS soil series was between 4.1-4.7, which was considered as severely to very severely susceptible to acid deposition. Six soil samples were collected for both North and South sides of the stream and at two different depths (0-15 cm and 15-30 cm) of the studied catchment. Soil characteristic was analyzed for each soil sample and summarized in the Table 6 (a) and (b). The status of soil acidity as well as soil sensitivity and vulnerability were assessed preliminarily based on these characteristics. Table 6 (a) and (b) showed characteristics of forest soil with natural process of development. Forest soil was different from agricultural soil since it has never been contaminated by fertilizer or chemicals. In this regard, soluble Al^{3+} and Fe^{2+} in soil solution will increased with decreasing of soil pH. In other word for this natural soil, Al^{3+} and Fe^{2+} are the main factors that govern acidification as well as soil chemistry and soil pH control. Furthermore, the decay by natural process of soil organic matter will also produce organic acid which contribute to decrease in soil pH. Therefore, with low CEC content and percent BS, the SRS soil was considered very sensitive and vulnerable to soil acidification. From the Table 6, SRS soil was classified by types of sensitivity and vulnerability in class I-II, which would imply that the soil pH can be reduced easily with the impact of acid deposition. Moreover, soil acidification will directly affect the status of plant nutrients and the trace elements in soil. The Table 7 (a) and (b) presents the status of the nutrients and trace elements in soil in terms of exchangeable cations, bio-available trace elements and exchangeable Al^{3+} of SRS soil.

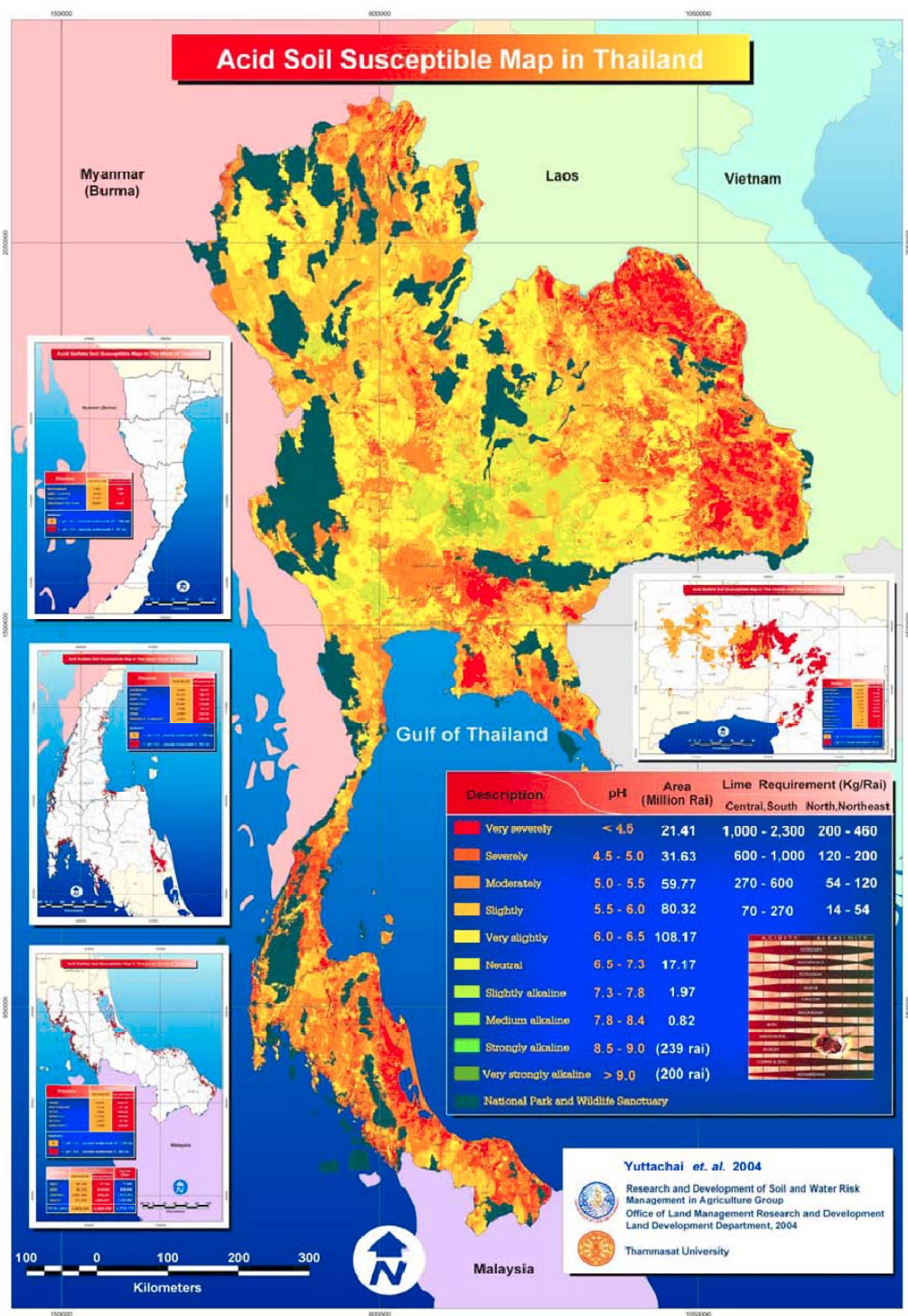


Figure 4. Acid soil susceptible map in Thailand.

Source: Anuraktiphan, 2004

Table 6. Soil Characteristics and status of soil acidity, soil sensitivity and vulnerability to soil acidification of SRS soil series.

(a) Soil samples collected from North side of the stream.

Soil parameter	Sampling points at North side of the stream					
	N1		N2		N3	
	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm
Field pH	4.45	4.36	4.10	4.21	4.38	4.73
Soil Organic Matter	3.03	2.35	2.55	1.37	3.43	1.50
Sand (%)	59.29	65.65	49.50	41.79	61.86	55.43
Silt (%)	15.01	4.79	18.79	12.72	16.58	17.15
Clay (%)	25.70	29.56	31.70	45.49	21.56	27.42
Texture	Sandy clay loam	Sandy loam	Sandy clay loam	clay	Sandy clay loam	Sandy clay loam
CEC (meq/100g)	6.52	6.92	7.55	12.12	8.65	8.62
Total Base Cation (meq/100g)	2.58	2.01	1.29	0.59	2.01	0.96
Base Saturation (BS; %)	40	29	17	5	23	11
Soil Assessment						
Acidity	Very severe	very severe	very severe	very severe	very severe	severe
Sensitivity	II	I	I	I	I	I
Vulnerability	II	II	I	I	II	I

(b) Soil samples collected from South side of the stream

Soil parameter	Sampling points at South side of the stream					
	S1		S2		S3	
	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm
Field pH	4.61	4.70	4.45	4.50	4.26	4.61
Soil Organic Matter	3.30	1.31	3.17	1.31	3.60	1.86
Sand (%)	62.08	56.08	63.79	59.86	64.93	59.00
Silt (%)	14.65	16.65	16.72	14.65	15.22	17.30
Clay (%)	23.27	27.27	19.49	25.49	19.85	23.70
Texture	Sandy clay loam	Sandy clay loam	Sandy clay loam	Sandy clay loam	Sandy clay loam	Sandy clay loam
CEC (meq/100g)	6.78	6.62	4.95	4.42	6.38	4.58
Total Base Cation (meq/100g)	2.25	0.91	2.02	0.60	1.57	1.10
Base Saturation (BS; %)	33	14	41	14	25	24
Soil Assessment						
Acidity	Severe	Severe	Very Severe	Severe	Very Severe	Severe
Sensitivity	I	I	II	I	I	I
Vulnerability	II	I	II	I	II	II

Table 7. Status of nutrients and trace elements in the SRS soil series.

(a) Soil samples collected from North side of the stream

Major and minor minerals and Trace Elements	Sampling points at North side of the stream					
	N1		N2		N3	
	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm
Exchangeable Cation (mg/kg)						
Calcium (Ca)	269.45	174.6	82.2	25.53	175.4	33.77
Potassium (K)	108.70	106.15	83.78	58.57	100.52	71.49
Magnesium (Mg)	108.00	98.01	74.57	32.40	99.44	65.91
Sodium (Na)	11.81	10.12	9.16	10.44	10.94	12.67
Total Trace Elements (mg/kg)						
Iron (Fe)	16,200	18,330	14,960	19,360	12,330	14,680
Manganese (Mn)	375.00	235.80	241.60	119.60	161.20	74.81
Zinc (Zn)	16.10	17.27	18.24	16.93	12.53	11.85
Copper (Cu)	6.68	7.39	6.26	8.30	5.50	6.00
Aluminum (Al)	139,300	148,900	136,100	168,100	104,700	125,200
Bio-available Trace Elements (mg/kg)						
Iron (Fe)	87.30	69.26	86.99	19.87	116.45	50.68
Manganese (Mn)	66.51	44.89	32.11	3.11	37.69	5.23
Zinc (Zn)	0.72	0.54	0.67	0.20	0.71	0.32
Copper (Cu)	0.64	0.83	0.75	0.31	0.66	0.48
Exchangeable Al	197.00	334.00	373.00	869.00	223.00	591.00

(b) Soil samples collected from South side of the stream

Major and minor minerals and Trace Elements	Sampling points at South side of the stream					
	S1		S2		S3	
	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm
Exchangeable Cation (mg/kg)						
Calcium (Ca)	237.25	61.58	185.85	34.58	125.50	24.60
Potassium (K)	86.21	62.92	121.05	67.9	70.06	69.07
Magnesium (Mg)	94.71	47.97	87.14	25.04	85.71	90.26
Sodium (Na)	11.34	10.56	11.68	10.8	12.34	10.25
Total Trace Elements (mg/kg)						
Iron (Fe)	12,310	14,110	11,360	12,810	11,390	11,690
Manganese (Mn)	222.20	211.00	190.10	155.90	174.70	188.90
Zinc (Zn)	16.48	16.42	13.82	14.54	15.46	14.12
Copper (Cu)	6.78	8.29	7.34	7.29	7.18	7.05
Aluminum (Al)	122,000	146,300	107,300	111,100	120,600	117,700
Bio-available Trace Elements (mg/kg)						
Iron (Fe)	64.53	27.50	99.29	40.22	159.25	44.6
Manganese (Mn)	38.41	11.60	31.64	11.70	28.41	12.30
Zinc (Zn)	0.40	0.23	0.54	0.27	0.69	0.25
Copper (Cu)	0.25	0.29	0.57	0.47	0.47	0.44
Exchangeable Al	157.00	300.00	517.00	320.00	270.00	227.00

5.3 Assessment of acid deposition impact to soil acidification by soil incubation study

The results of the soil incubation study showed that the top soil (0-15 cm) collected at north side of the stream was more sensitive and vulnerable to acid deposition than the deeper soil (15-30 cm). Simultaneously the soil pH reduced more quickly for the surface soil with the experiment with S 1-50 times of the existing level. In contrary to the soil collected at south side of the stream where the top soil and the deeper soil have same capacity to bear with soil acidification. This can be explained by the characteristics of the soil series where % BS of top soil was generally higher than the deeper soil. The result of soil incubation study confirmed that SRS soil series was severely to very severely susceptible to soil acidification. The Figures 5 and 6 showed the results of soil incubation experiment for SRS soil sample collected at the north and south sides of the stream, respectively. Decrease of soil pH would directly affect the solubility of trace elements in soil. When soil pH is less than 5.5 soluble Iron and Manganese in soil solution is important, when soil pH is between 5.0-4.5 soluble Al is significant and plays an important role to buffer the soil pH. This is the reason why soil pH of SRS soil will not decrease more than 2.5 even though we continue to increase the amount of S input for soil incubation up to 450 times of the average level. In the highly acidic soil, water soluble and exchangeable Al^{3+} and Fe^{2+} are the main factors to control the soil pH.

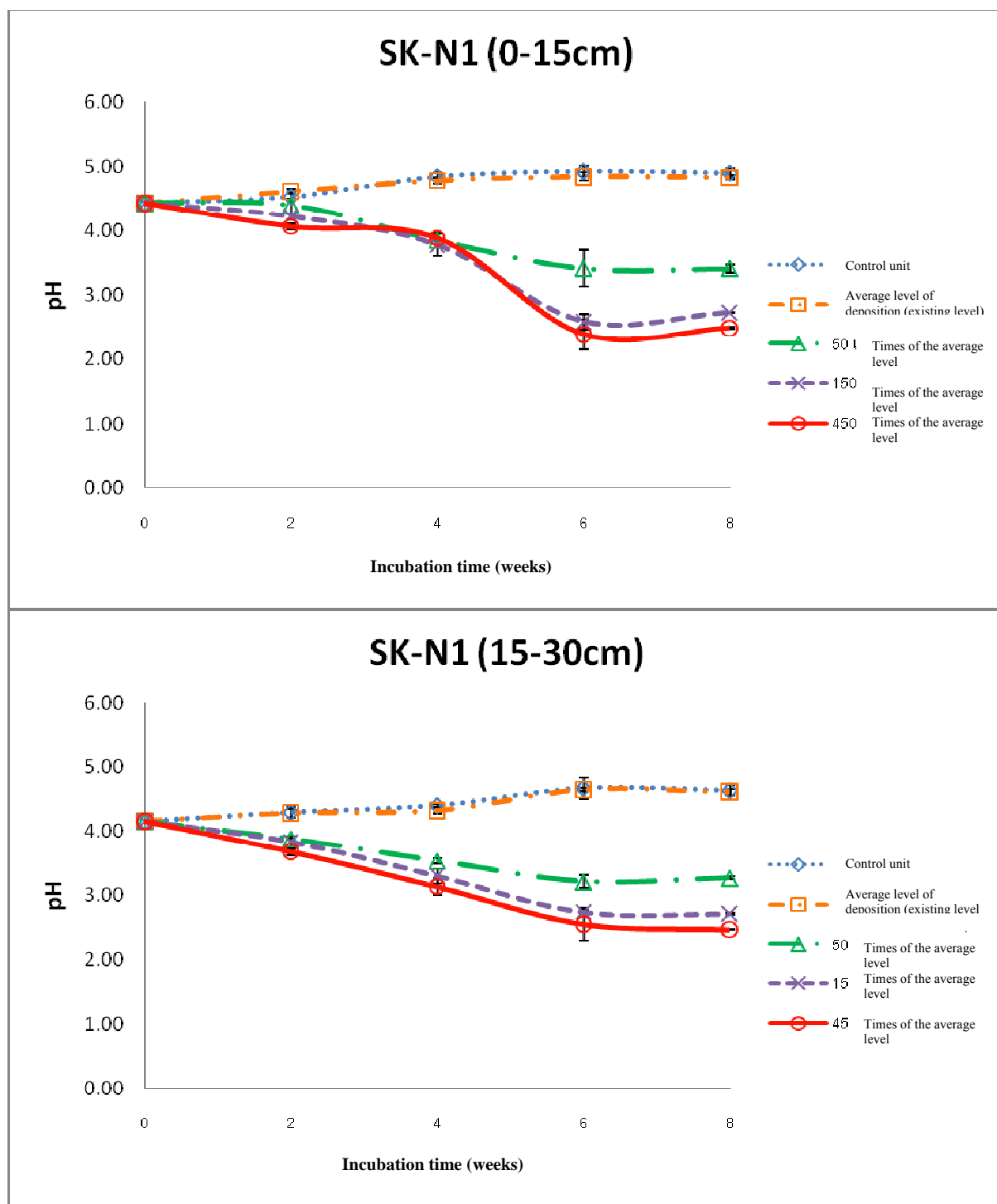


Figure 5. pH of SRS soils after incubated with different acid levels for 8 weeks North side along the stream (SK-N).

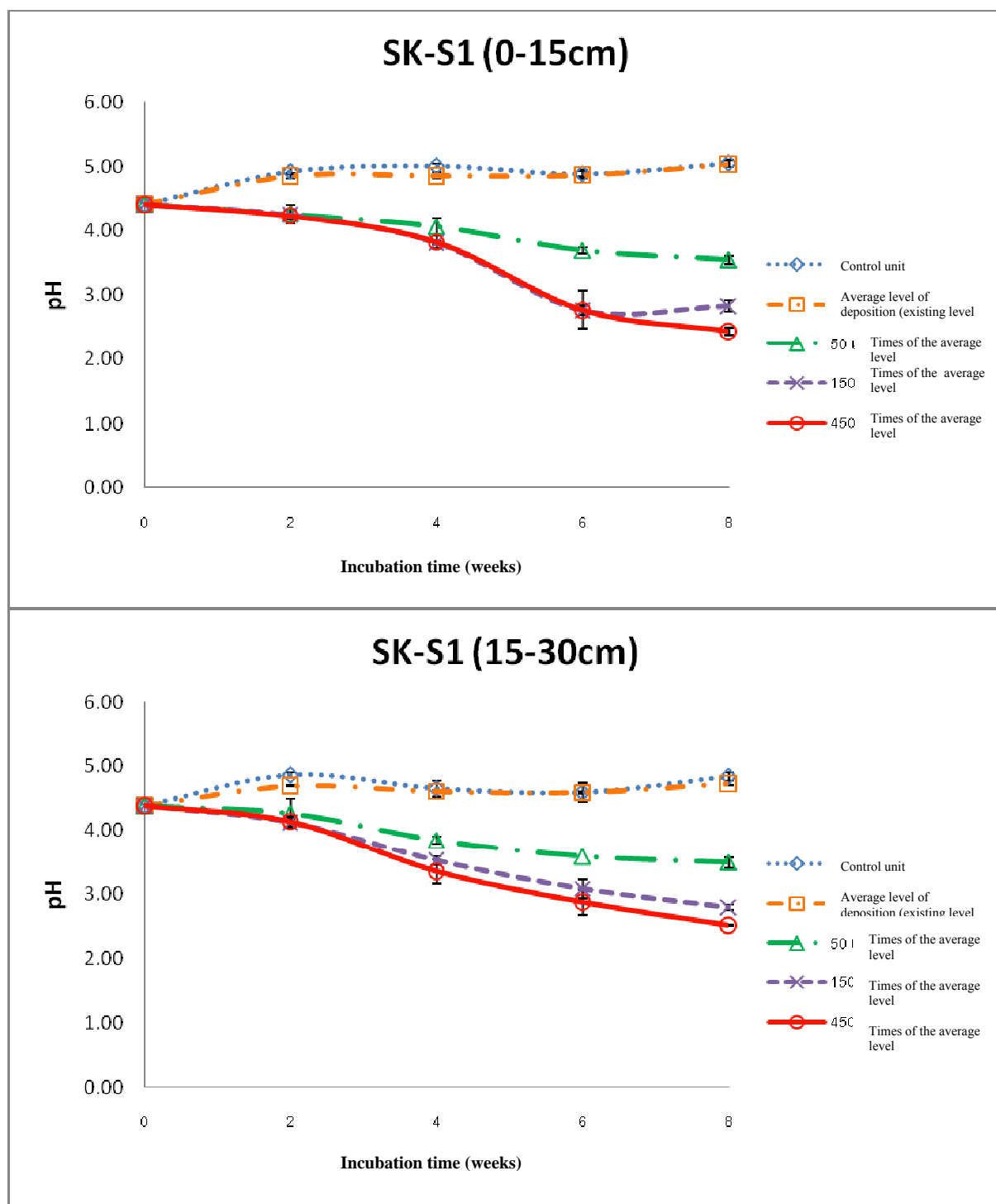


Figure 6. pH of SRS soils after incubated with different acid levels for 8 weeks South side along the stream (SK-S).

6. Conclusions

The forest catchment area is very important to define water resources availability. Acid deposition is an important international issue to give potential impact on the catchment ecosystem through soil acidification. The study applied soil incubation method to address the evidence of soil acidification due to S deposition in the

catchment area. Amount of S deposition in the catchment area was obtained from the integrated ecological monitoring under the joint research project on catchment analysis in Thailand. Soil characterization has been performed and the result showed the forest soil pH was 4.1-4.7, which was considered very severely susceptible to acid soil. Low CEC and % BS have been observed to demonstrate that the forest soil with natural process of development based on the type of soil sensitivity and vulnerability was classified I-II, which implies that the soil pH will easily decrease with the impact of acid deposition. However, the soil incubation experiment showed that with soil pH less than 4.5 soluble Iron, Manganese and Aluminum will be transferred to soil solution, especially Al that play an important role in buffering the soil pH. Furthermore, the observation of pH reduction in the soil incubation experiment showed that the forest soil can bear the acidification up to 50 times of the average existing amount of S deposition. Nevertheless, preventive action needs to be promoted to conserve healthy ecological catchment. If the forest catchment was damaged by soil acidification, the time taken for ecosystems to reach equilibrium may be in order of decades or may never be restored back to its original condition again.

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Seasonal Variation of Atmospheric Dry Deposition (2006 to 2007) in Chiang Mai, Thailand

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Abstract

Gases and particulate ions in atmospheric dry deposition had been collected from January 2006 to December 2007 at Mae Hia Research Center, Chiang Mai University, Chiang Mai Province, Thailand. The relative volume weight mean concentrations of pollutant gases in a descending order were $\text{NH}_3 > \text{HCl} > \text{SO}_2 > \text{HNO}_3$ in 2006 and $\text{NH}_3 > \text{HNO}_3 > \text{SO}_2 > \text{HCl}$ in 2007. The concentrations of ions in descending order were $\text{NH}_4^+ > \text{SO}_4^{2-} > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{NO}_3^- > \text{Na}^+ > \text{Cl}^-$ in 2006 and $\text{NH}_4^+ > \text{SO}_4^{2-} > \text{K}^+ > \text{Ca}^{2+} > \text{NO}_3^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Cl}^-$ in 2007. The dominant pollutants found in the atmospheric dry deposition in the area were NH_3 and SO_4^{2-} . The highest concentration of gaseous was detected in March of both years. Concentrations of particulate ion and gases species were high in dry season. High correlations between NH_4^+ and SO_4^{2-} were found in both years, which suggested the interaction in form of $(\text{NH}_4)_2\text{SO}_4$. The data collected was analyzed by principle component analysis in order to find out possible sources of atmospheric dry deposition in the area. The main component of atmospheric dry deposition 2006 and 2007 illustrated agriculture activity, combustion fuel and biomass burning.

Keywords: Air pollution; Chemical composition; Dry deposition; Pollutant sources; Seasonal variation.

1. Introduction

The Asian region is currently undergoing a dramatic industrial and economic expansion, which is accompanied by large, and sharply increasing, emissions from stations (power plants, factories, etc.) as well as mobile sources (cars, trucks, etc.) (Streets *et al.*, 2000). Biomass burning, which comprises open vegetation fires and domestic biofuel use, is one of the largest sources of aerosol particles worldwide. Pyrogenic aerosols consist predominantly of carbonaceous material with a minor component of various inorganic materials (Andreae *et al.*, 2004). In general, numerous particulates (*e.g.*, polycyclic aromatic hydrocarbons and other organics) and gaseous compounds (*e.g.*, carbon monoxide (CO) and volatile organic compounds) that come from biomass burning are known to be hazardous to human health (Torrigio *et al.*, 2000). Metzger and researchers reported that mass concentrations of CO, Nitrogen dioxide (NO_2), $\text{PM}_{2.5}$, organic carbon (OC) and elemental carbon (EC) in $\text{PM}_{2.5}$ were significantly associated with emergency department visits at hospitals due to cardiovascular diseases (Metzger *et al.*, 2004). The most important gaseous which effected to acidic dry deposition are HNO_3 , HCl and H_2SO_4 . Those gaseous can be transformed into aerosols by neutralization reactions (Semi-volatile NH_4NO_3 and NH_4Cl are formed via reversible phase equilibrium with NH_3 , HNO_3 and HCl (Pio and Harrison, 1987). Understanding the formation of secondary particulate species SO_4^{2-} , NO_3^- and NH_4^+ formation, requires investigation of the atmospheric concentration levels for HNO_3 , HCl and SO_2 and related aerosol ions. The inorganic component is made up of some insoluble dust and ash material, and soluble salts, in which potassium, ammonium, sulfate and nitrate are the most important species (Fuzzi *et al.*, 2007).

Chiang Mai Province has been annually facing air pollution during the dry season. This pollution has been recorded as a serious problem for well over 10 years. Recently, the problem has become worse than ever. Chantara *et al.* (2009) studied chemical composition of PM_{10} samples collected in Chiang Mai and Lamphun, Thailand from June 2005 to June 2006. Both anions (SO_4^{2-} , NO_3^- , and Cl^-) and cations (NH_4^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+}) were significantly higher in dry period (December-March) and transition period I (October-November) than those in other seasons. The dominant anion and cation were SO_4^{2-} and NH_4^+ , respectively. In our study, sampling of dry deposition has been carried out using the filter pack method at the rural site in Chiang Mai

Province. The aims of this study were to analyze the chemical composition of atmospheric dry deposition and to find out possible sources of air pollutants in different periods. The information obtained is expected to be useful for air quality management in the area.

2. Methods

2.1 Sampling Site and Sampling Period

The sampling site was at the meteorological station in the area of Mae Hia Research Center, Chiang Mai University, Muang District, Chiang Mai Province (Figure 1). This site was classified as rural site based on Acid Deposition Monitoring Network in East Asia (EANET) criteria since 2000. It is located at latitude 18° 45' 40.3" N and longitude 98° 55' 54.3" E. The sampling had been done within 2 years from 1st January, 2006 to 31st December, 2007.

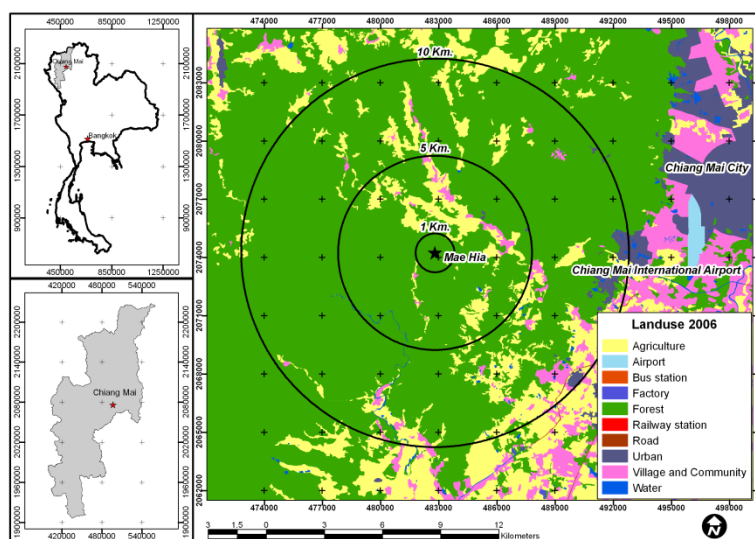


Figure 1. Sampling site location and its surroundings.

2.2 Sample analysis

A dry deposition sample is proposed to measure the level of air pollution in atmosphere. The main pollutants such as SO₂, HNO₃, NH₃, HCl, and acid aerosols were collected by a four-stage filter pack. The first two layers are polytetrafluoro ethylene filter; F0 and polyamine filter; F1. The other two layer filters are cellulose acetate filter (F2, F3), which impregnated with potassium carbonate and phosphoric acid and glycerin solution. Prior to sampling, a filters pack was connected to a sampling set at the monitoring site. Flow rate of air input was 1 L/min. Sampling was operated for 10 days long, 3 times a month. F0, F2 and F3 filter papers were extracted with 20 ml Milli Q water, while F1 was extracted with 20 ml 0.05% H₂O₂ by ultrasonication for 30 minutes. After extraction process, insoluble matters were filtered by cellulose acetate membrane (EANET 2002). Ion chromatograph (Metrohm, Switzerland) was used for determination of major cations (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) and major anions (Cl⁻, NO₃⁻ and SO₄²⁻). Analytical columns for anions and cations were Metrosep A Supp 5 (5x250 mm) and Metrosep C2 150 (4x150 mm), respectively.

2.3 Statistical analysis

Pearson correlation and principle component analysis (PCA) was used for data analysis. A varimax rotation with Kaiser Normalization of Principle Components Analysis by SPSS program was used for determination the factors underlying the inter-correlations between the measured species.

3. Results and discussions

The concentrations of gaseous and particulates ions of atmospheric acid deposition in 2006-2007 are presented in Table 1. Total number of samples in each year was 36. The main gas found in the atmospheric dry deposition was NH₃. Its annual average was 2.23±2.50 µg/m³ and 3.32±2.99 µg/m³ in 2006 and 2007, respectively. Other gases were not much different. Their concentrations in descending order were HCl > SO₂ > HNO₃ in 2006, while those of 2007 were HNO₃ > SO₂ > HCl. SO₄²⁻ was the main particulate ion found in this study. Its annual average was 2.20±0.30 µg/m³ and 2.60±0.21 µg/m³ in 2006 and 2007, respectively. The

concentrations of particles in a descending order were $\text{NH}_4^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{NO}_3^- > \text{Na}^+ > \text{Cl}^-$ in 2006, while those of 2007 were $\text{NH}_4^+ > \text{K}^+ > \text{Ca}^{2+} > \text{NO}_3^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Cl}^-$.

Table 2 shows comparison of gaseous and ionic concentrations in various areas from all over the world. The highest concentrations of gas in particularly SO_2 as well as SO_4^{2-} were found in October 2004 at the Pearl River Delta (PRD), which has high population density and rapid urbanization. The PRD is one of major cities in this china, which is the largest light industrial base. The highest concentrations of NH_3 and NH_4^+ were in Lahore, Pakistan. The main local sources of air pollution in this industrial city are vehicular emissions from motorways, emissions from coal combustion and biomass burning (Husain et al, 2007). In Taichung and Taiwan have the highest concentrations of Cl^- , NO_3^- and K^+ . The study was carried out during agricultural waste burning which regenerated K^+ as tracer in the air. The concentrations of Ca^{2+} and Mg^{2+} were highest in our study in Chiang Mai, Thailand. These ions might be released from soil and cement used in construction of the By-pass road in front of our study site (about 500 m in distance). However, most of the gaseous and particulate ions concentrations in this study were lower than other areas. The main reason was that our sampling site is situated in sub-urban area with lower human activities in comparison with other studies.

Table 1. Concentrations of gases and particulate ions of atmospheric dry deposition in 2006 and 2007.

Sampling date		Gases($\mu\text{g}/\text{m}^3$)				Particulate ions($\mu\text{g}/\text{m}^3$)							
		HCl	SO_2	HNO_3	NH_3	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
Annual (N=36) 2006	Mean	0.71	0.65	0.47	2.23	0.19	0.53	2.20	0.67	0.19	0.56	0.58	0.22
	S.D.	0.68	0.67	1.19	2.50	2.42	0.49	0.30	0.77	0.28	0.58	0.34	1.06
	Max	4.87	3.06	2.34	8.69	0.96	1.86	9.19	2.96	1.28	2.74	6.23	1.43
	Min	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Annual (N=36) 2007	Mean	0.37	0.72	1.26	3.32	0.11	0.62	2.60	0.74	0.23	0.58	0.57	0.07
	S.D.	0.77	1.11	0.27	2.99	2.81	0.75	0.21	1.04	0.31	0.70	0.12	0.41
	Max	1.47	3.62	4.16	12.46	1.08	4.36	13.29	5.07	1.87	3.08	1.58	0.19
	Min	0.05	0.08	0.01	0.26	N.D.	N.D.	0.04	N.D.	0.04	N.D.	0.02	N.D.

N.D. = non detected

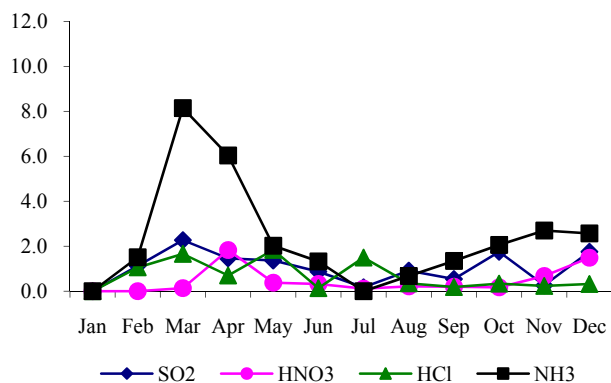
3.1 Seasonal variation of atmospheric dry deposition

Figure 2 illustrates mean concentrations of gases and particulate ions in different periods during 2006 and 2007. Seasonal variation of gaseous and particulate ions concentrations were almost the same. Their concentrations were highest in dry I period, decreasing in wet period and increasing again in dry II period. The highest concentrations of gases and particulate ion were NH_3 and SO_4^{2-} , respectively. From December 2006 to March 2007 there was no rain in the sampling area, which leads to high accumulation of pollutants in the atmosphere. The highest concentration of SO_2 was therefore detected in March, 2007. The main source of SO_2 was fossil fuel combustion. Traffic congestion is probably one of the important sources of air pollutants. During November, 2006 to January, 2007 there was an event of international flora festival held in the area closed to our sampling site. Almost 4 millions of visitors were reported. Consequently traffic congestion was therefore high during these 3 months. The highest concentrations of HNO_3 , HCl, and NH_3 (g) were detected in March, 2007. Another important source was open burning including forest fire, agricultural waste and garbage burning in communities. They were assumed to be the main sources of nitric acid in this period. In addition, high frequency of forest fire was observed via number of hot spots detected by satellite between 1-19 March, 2007 (<http://maps.geog.umd.edu>). Most of gaseous concentrations in dry II period of 2007 were higher than those of 2006 due to no precipitation and high biomass burning activities at the beginning of the year 2007. In case of ion concentrations both in 2006 and 2007, they had similar variation throughout the year. High concentrations of Ca^{2+} were found in dry I period of 2006, while K^+ were high in the same period in 2007.

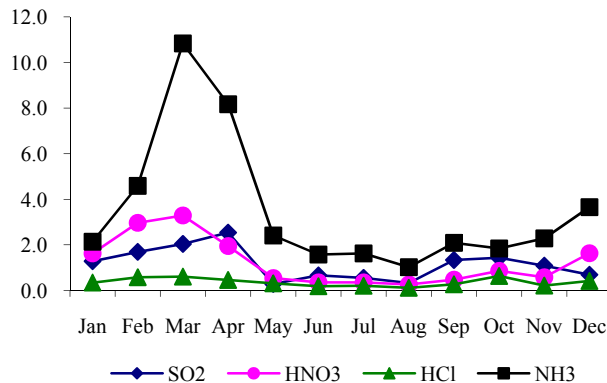
Table 2. Mean concentrations ($\mu\text{g m}^{-3}$) of gases and particulate ion composition found in this study and another parts of the world.

Sampling sites	Sampling site category	period	Gases					Particulate ions						References	
			HCl	SO ₂	HNO ₃	NH ₃	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺		Mg ²⁺
Beijing, China	urban	Jul and Aug 2002-2003	0.60	14.10	1.90	16.60	2.20	14.60	19.30	8.90					Wu <i>et al.</i> , 2009
Taichung, Taiwan	urban(AWB)	27, Nov 2002					9.90	19.10	12.20	8.70	0.40	5.60	0.40		Cheng <i>et al.</i> , 2009
		29,Jun 2004					1.10	5.40	21.50	7.60	0.30	2.50	0.40		
		25-27, Nov 2005					1.60	8.20	17.00	8.40	0.40	1.90	0.30		
	urban(NAWB)	30-31, Oct 2002					0.30	1.30	5.70	2.60	N.D.	0.50	N.D.		
		24,26,27, Jun 2004					0.20	1.00	4.30	1.30	0.50	0.50	0.30		
Gwangju, Korea	suburban	24,27, Oct 2005					0.40	2.60	6.90	2.70	0.20	0.40	0.10		Hong <i>et al.</i> , 2008
		5-3, Oct 2003					0.75	2.68	5.06	3.15		0.80			
		12-19, Nov 2003					1.53	3.08	2.70	2.08		0.51			
The Pearl River Delta, China	suburban	4 Oct- 4 Nov 2004	2.80	55.40	6.30	7.30	2.40	7.20	24.10	9.20					Hu <i>et al.</i> , 2008 Koulouri <i>et al.</i> , 2008
Crete Island	remote	Jul 2004 –Jul 2006													
Seoul, Korea	urban	(Coarse)					1.43	1.63	1.08	0.17	1.33	0.07	1.22	0.18	Song <i>et al.</i> , 2009
		(Fine)					0.08	0.10	4.40	1.45	0.05	0.12	0.07	0.01	
		May-Jul 7 ,2005						5.01	8.20	8.38					
Lahore, Pakistan	urban	Dec 2005 - Feb 2006	1.16	19.40	1.00	50.10	7.43	18.90	19.20	16.10					Biswas <i>et al.</i> , 2008 Saarikoski <i>et al.</i> , 2007
Helsinki, Finland	urban	24-29 Apr 2006							2.40			0.30			Kumagai <i>et al.</i> , 2009
Maebashi, Japan	suburban	15, May 2006							4.90			0.30			
		Apr 2005 – Mar 2006					0.19	2.66	5.07	2.47	0.08	0.21	0.07	0.02	
Akagi, Japan Chiang Mai, Thailand	rural	Apr 2005 – Mar 2006					0.00	0.45	3.87	1.41	0.03	0.10	0.03	0.01	This study
	suburban	Jan – Dec 2006	0.71	0.65	0.47	2.23	0.19	0.53	2.20	0.67	0.19	0.56	0.58	0.22	
		Jan – Dec 2007	0.37	0.72	1.26	3.32	0.11	0.62	2.60	0.74	0.23	0.58	0.57	0.07	

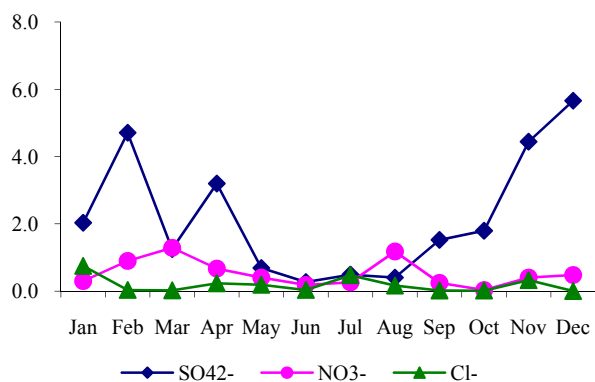
AWB = agriculture waste burning periods, NAWB = non agriculture waste burning periods.



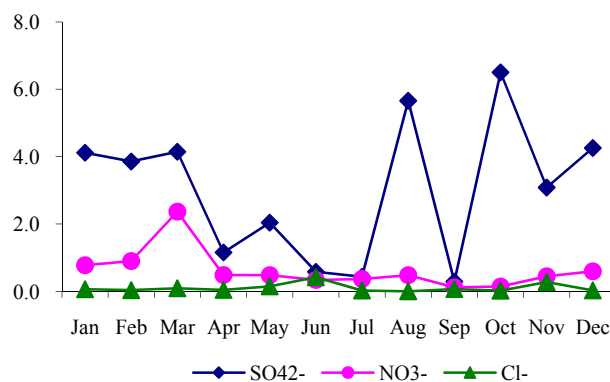
Gaseous (2006)



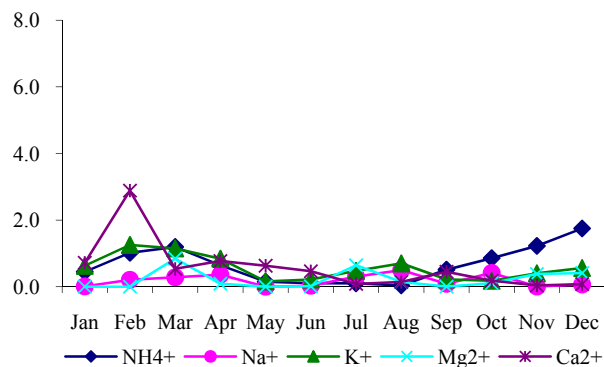
Gaseous (2007)



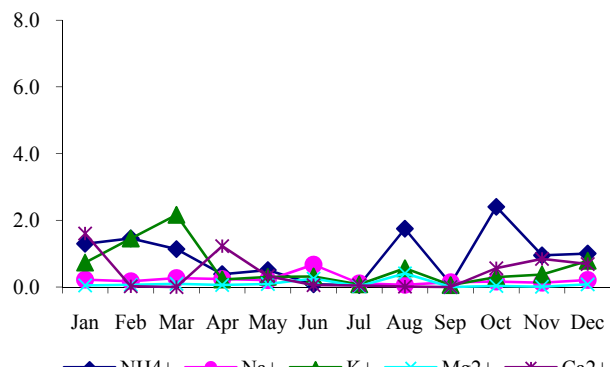
Particulate anions (2006)



Particulate anions (2007)



Particulate cations (2006)



Particulate cations (2007)

Figure 2. Seasonal variations of gases and particulate ions in 2006 and 2007.

3.2 Relative distribution of dry deposition

The relative percentage of total dry deposition in the unit of $\mu\text{g}/\text{m}^3$ is shown in Figure 3. In 2006, the percentage of particulates (53%) was higher than gases (47%), while the ratio was reversed in 2007. Gas with the highest contribution in the atmosphere was NH_3 for both 2006 (24%) and 2007 (30%), while SO_4^{2-} was the major particulate ions for both years (22-23%).

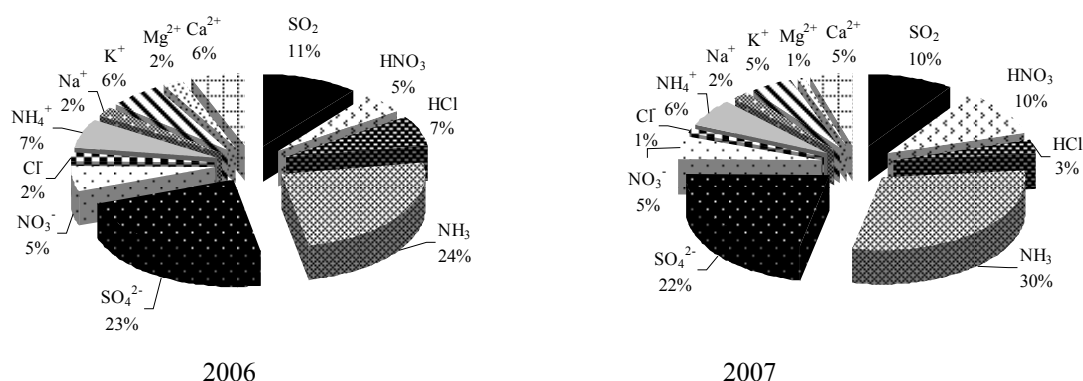


Figure 3. Percentage of gases and ions of atmospheric dry deposition in 2006 and 2007.

3.3 Pearson correlation

The ion concentrations were log-transformed ($\log(N+1)$) to achieved normal distribution. Pearson correlations (r) between pairs of ion were calculated as shown in Table 3. It was found that correlation between NH_4^+ and SO_4^{2-} were high in 2006 ($r = 0.701$) and 2007 ($r = 0.902$). The ammonium compounds applied to soil can escape into atmosphere by means of gaseous NH_3 or as NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles. When NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles were incorporated in rain, they change NO_3^- and SO_4^{2-} concentrations, but do not affect the pH. However, when ammonium was incorporated in rain, it can neutralize the acidity of rainwater (Al-Khashman, 2009).

Table 3. Correlation of ion species for 2006 and 2007.

Year	Ions species	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
2006	SO_4^{2-}	1.000							
	NO_3^-	0.059	1.000						
	Cl^-	-0.141	-0.010	1.000					
	NH_4^+	0.701	0.086	-0.304	1.000				
	Na^+	-0.051	0.329	-0.057	0.023	1.000			
	K^+	0.310	0.556	-0.017	0.466	0.279	1.000		
	Mg^{2+}	-0.011	0.295	-0.125	.341*	0.208	.359*	1.000	
	Ca^{2+}	0.236	0.229	-0.007	0.024	-0.106	0.228	-.400*	1.000
2007	SO_4^{2-}	1.000							
	NO_3^-	0.292	1.000						
	Cl^-	-0.217	-0.085	1.000					
	NH_4^+	0.902	0.157	-0.178	1.000				
	Na^+	0.013	0.168	0.638	0.025	1.000			
	K^+	0.624	0.693	0.011	0.578	0.161	1.000		
	Mg^{2+}	0.100	0.077	-0.111	0.064	-0.033	0.108	1.000	
	Ca^{2+}	0.190	0.207	0.087	0.222	-0.052	.399*	0.032	1.000

3.4 Principal component analysis

The log transformed ($\log(N+1)$) particulate ion concentrations ($\mu\text{g}/\text{m}^3$) were analysed using the principal component analysis (PCA), given observation that only factor loading higher than 0.5 are deemed to be statistically significant (Ungvari *et al.*, 2007). The PCA extracted that there was three factors contributed in each year (Table 4). The factors with high loading in the first component were NO_3^- , Na^+ , and K^+ (2006) and SO_4^{2-} and NH_4^+ (2007). The result illustrated that the main pollutant sources were biomass burning (NO_3^-), marine source (Na^+ , and K^+) (Hu *et al.*, 2003), combustion fuel (SO_4^{2-}), agricultural activities (NH_4^+) (Andreas *et al.*, 2006) and soil resuspension (Ca^{2+} and Mg^{2+}) (Xu *et al.*, 2007).

Table 4. Component loading of ions from dry deposition in 2006 and 2007.

Ions species	Component loading					
	2006			2007		
	1	2	3	1	2	3
SO ₄ ²⁻	0.041	0.825	0.305	0.943	0.187	-0.080
NO ₃ ⁻	0.856	-0.024	0.133	0.150	0.824	0.083
Cl ⁻	0.076	-0.480	0.205	-0.172	-0.030	0.887
NH ₄ ⁺	0.172	0.918	-0.074	0.963	0.087	-0.048
Na ⁺	0.616	-0.134	-0.255	0.055	0.072	0.888
K ⁺	0.779	0.378	0.120	0.577	0.716	0.146
Mg ²⁺	0.454	0.257	-0.697	-0.095	0.407	-0.251
Ca ²⁺	0.182	0.080	0.883	0.136	0.557	0.037
Eigenvalue	2.469	1.609	1.407	2.855	1.712	1.058
%Variance	30.863	20.109	17.590	35.689	21.398	13.221
Probable Sources	Biomass	Combustion		Combustion	Biomass	
	burning and sea salt	Fuel and Agricultural activity	Soil resuspension	Fuel and agricultural activity	burning and Soil resuspension	Sea salt

4. Conclusion

Analysis of chemical composition of atmospheric pollutant gases and particulate ions had been carried out during 2006-2007. The highest concentration of pollutant gas was NH₃, while that of particulate ion was SO₄²⁻. The main possible sources of atmospheric pollutants in years 2006 and 2007 were agriculture activity, combustion fuel and biomass burning.

5. Acknowledgements

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Effects of Simulated Acid Rain on Growth of Kelat (*Syzygium campanulatum*) and Selected Soil Chemical Properties

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ABSTRACT

Acid deposition is one of the major issues of transboundary air pollution in East Asia. Acid rain is fast becoming an environmental problem and Malaysia might experience detrimental effects of acid rain similar to industrialized countries. This study reports the results of a greenhouse experiment conducted to assess the effects of simulated acid rain (SAR) at different pH levels i.e. 6.0 (control), 2.0, 3.0, 4.0 and 5.0 on the growth performance of Kelat seedlings (*Syzygium campanulatum*). Fifteen seedlings were used for each of the five treatments over a period of three months. Captured rainwater was mixed with H_2SO_4 and HNO_3 to produce SAR. The plants were applied with SAR and captured rainwater was irrigated to avoid water deficit. SAR was applied only in early morning (7-8 am) to avoid exposure to high temperature during mid day and early afternoon. The experiment was conducted in a Randomized Completely Block Design (RCBD). Plant height, chlorophyll, and leaf area were measured for morphological characteristics every 14 days. Selected soil chemical properties (K^+ , Ca^{2+} , Na^+ , Mg^{2+} and N) were analyzed before planting and after harvest. The results showed that plant height decreased with decreasing pH. For example, for pH 6.0 (control) and 5.0 the average plant height increment was 3.3 cm whereas for pH 2.0 the height increment was only 1.6 cm. There was no significant difference ($P \leq 0.05$) for chlorophyll and leaf area values for the treatments. The soil chemical properties before treatment (pH 4.38) for K^+ , Ca^{2+} and Na^+ were 151.7, 196.5, and 145.4 ppm respectively, whereas for pH 2.0 the corresponding values for the above properties were significantly lower (80.17, 47.33 and 34.83 ppm), respectively. There was no significant difference for Mg^{2+} and N values before and after treatment. The study showed that *Syzygium campanulatum* is sensitive to acid rain and can be used as an indicator species to detect changes in acid deposition in Malaysia. However a field study in areas likely to be affected by acid deposition should be carried out to confirm the findings of this greenhouse study.

Key words: Simulated acid rain, *Syzygium campanulatum*, soil chemical properties

1. Introduction

Acid deposition is one of the major issues of transboundary air pollution in East Asia. Acid rain is a collective term used to describe acids falling out of the atmosphere. Acid deposition includes both wet and dry depositions (US-EPA 2004). Uncontrolled use of fossil fuels in industries and the transport sector have led to an increase in the concentrations of gaseous pollutants such as sulphur dioxide (SO_2), nitrogen dioxide (NO_2), their derivatives and ozone (O_3). It is comprised of sulfuric and nitric acids and ammonium derived from atmospheric emissions of sulfur dioxide, nitrogen oxides and ammonia, respectively. These compounds are emitted by the burning of fossil fuels and agricultural activities. Once these compounds enter an ecosystem they will acidify soil and surface waters and bring about a series of ecological changes (Driscoll *et al.*, 2005). It causes serious environmental problems particularly on human health, soil, aquatic life, water quality and vegetation. Atmospheric wet deposition has been a causal factor of crop loss and forest health deterioration in many European countries, Canada, United States and Japan (Likens *et al.*, 1996). Effects of acid rain on plant growth are often species specific; but some plants show growth enhancement (Wood and Bormann, 1977). Lee *et al.*, (1980) studied the effects of simulated acid rain (SAR) on different crops and reported yield reduction for radish, carrot, beet, mustard green and broccoli at lower pH and growth stimulation for tomato, green pepper, strawberry, alfalfa and timothy.

2. Materials and methods

An experiment was conducted to determine the effects of SAR on the growth of *Syzygium campanulatum* and selected soil chemical properties. The combination of topsoil, sand and organic matter was used as a planting medium in this study in the ratio of 3:2:1. The experiment was conducted under controlled conditions in Universiti Putra Malaysia Bintulu Campus Sarawak. *S. campanulatum* seedlings were selected based on height (24 cm-36 cm, 37 cm-47 cm, 48-72 cm) and were arranged in three separate blocks according to their height classes. SAR was prepared by mixing captured rainwater with different combinations of nitric acid (HNO₃) and sulphuric acid (H₂SO₄). There were five treatments (T) of SAR: T1 (pH 2.0), T2 (pH 3.0), T3 (pH 4.0), T4 (pH 5.0) and T5 (pH 6.0-control treatment containing captured rain water). The seedlings were applied with SAR and captured rainwater was irrigated to avoid water deficit. SAR was applied only in early morning (7 to 8 am) to avoid exposure to high temperature during mid day and early afternoon. The experiment was conducted in a Randomized Completely Block Design (RCBD). Fifteen seedlings were used for each of the five treatments over a period of three months. Each treatment was replicated three times to reduce the standard error. Plant height was measured weekly at the beginning of the experiment until 10 weeks. Leaf area measurements were monitored together with the chlorophyll content using Leaf Area Meter (L1-3100) and SPAD-502 chlorophyll meter, respectively. Soil pH was analyzed using Standard Procedure (Peech, 1965) in water and KCL. Determination of exchangeable K⁺, Ca²⁺ and Mg²⁺ content in the soil was done using double acid method.

Total N was analyzed by using Kjeldahl method. The data was analysed using SAS version 9.2. ANOVA was used to test the treatments effect while Duncan's Multiple Range Test was used to compare means of the treatments.

3. Results and Discussion

The soil characteristics analysed in this study are shown in Table 1. The pH of the soil was acidic [4.91(water), 4.38(KCL)] with 0.027% of total N. Exchangeable K⁺, Ca²⁺ and Na⁺ were 151.7, 196.5, and 145.4 ppm respectively, whereas for pH 2.0 the corresponding values for the above properties were significantly lower (80.17, 47.33 and 34.83 ppm), respectively. However there was no significant difference ($P \leq 0.05$) for Mg²⁺ and N for all treatments.

K⁺ was affected by SAR treatments and it showed significant difference during 8 weeks of analysis. Wesley *et al.*, (1988) found similar results on the growth of seedlings in an orchard. K⁺ is the one of the cations that was replaced most easily by H⁺ on their exchange sites (Binkley and Richter, 1987).

Both Ca²⁺ and Na⁺ showed significant differences in week 2, however there was no significant difference after week 2 for all treatments. This happened because nutrients were leached out exponentially from week 4 to week 8. In general, concentrations of exchangeable Ca²⁺ and Na⁺ decreased with time for all pH levels. According to Ling *et al.*, (2007) more Ca²⁺ ions were displaced by the H⁺ ions under such strong acidic conditions. Juxiu *et al.*, (2007) also reported that acidification led to the higher leaching because available Ca was higher than available Mg.

For Mg²⁺, only T1 shows decreasing concentration within 8 weeks of study period and showed no differences for all treatments. Ling *et al.*, (2007) reported that Mg²⁺ was leached slower than Ca²⁺ when exposed to SAR.

Table 1. Soil chemical properties before treatment.

Soil Properties	Value
pH _w	4.91
pH _{KCl}	4.38
Exchangeable K ⁺ (ppm)	151.7
Exchangeable Ca ²⁺ (ppm)	196.5
Exchangeable Mg ²⁺ (ppm)	8.75
Exchangeable Na ⁺ (ppm)	145.4
Total Nitrogen (%)	0.03

Table 2 shows that total nitrogen concentration in the soil after harvesting shows no significant difference in all treatments at week 2, 4, 6 and 8. According to (Francis *et al.*, 1982), N mineralization is inhibited following the addition of concentrated H₂SO₄. It is important because inorganic N often limit plant growth in forest ecosystem (Auchmoody and Filip, 1973).

Table 2. Nitrogen concentration (%) in soil 8 weeks after treatment.

Treatment	Week 2	Week 4	Week 6	Week 8
T1	0.09	0.07	0.07	0.09
T2	0.07	0.08	0.08	0.07
T3	0.08	0.07	0.03	0.03
T4	0.08	0.06	0.07	0.32
T5	0.09	0.07	0.06	0.10

Figure 1 shows that at week 8, T5 was significantly different ($P \leq 0.05$) in soil pH as compared to the other treatments (5.33), where T1 recorded the lowest soil pH (4.97). Richard (1998) stated that soil pH decreases with increasing rate of SAR application. Therefore, SAR could cause toxicity problems in soil when the aluminum solubility increases dramatically. However, soil pH from 6.5 to 7.0 provides the most suitable condition for optimum plant growth (Mengel *et al.*, 2001). Therefore, T5 with soil pH at 5.3 has the highest plant height compared to the other treatments. Dennis (2005) stated that soil pH near neutral is important to ensure proper plant growth because most essential elements reach near maximal availability and most toxic elements become unavailable in this pH range.

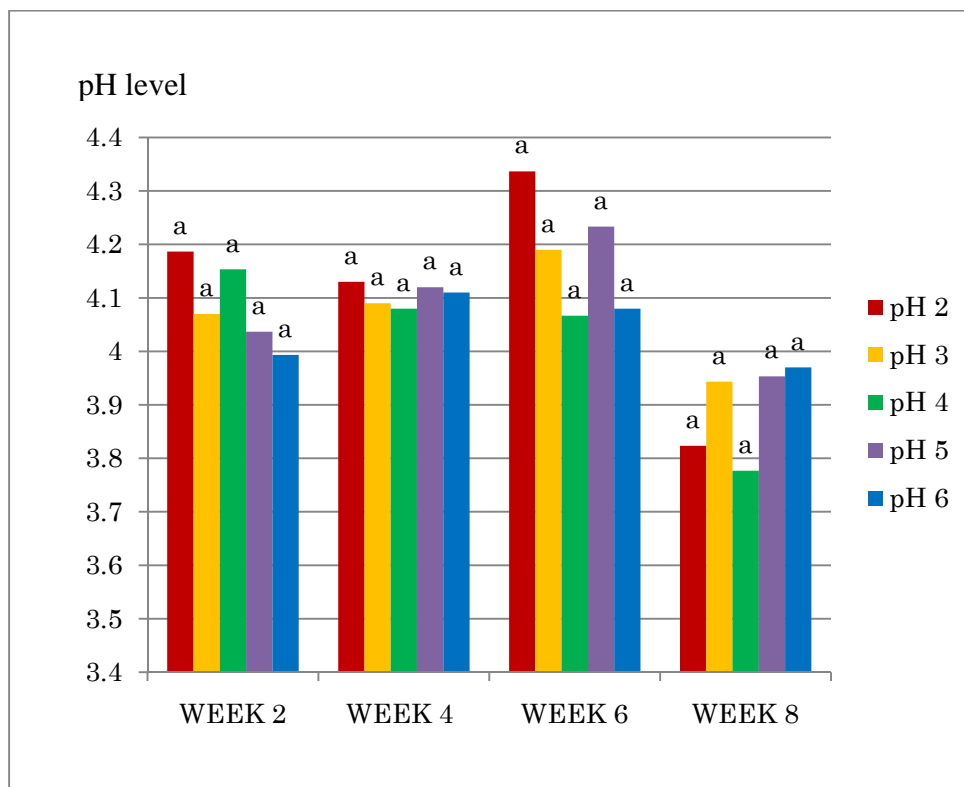


Figure 1. Soil pH value 8 weeks after treatment.

Table 3: Effect on height of *Sygyzium campanulatum* with time.

Treatment	Height increment (cm) by period			
	Week 2	Week 4	Week 6	Week 8
T1	0.73b	1.30ab	2.96a	1.73a
T2	0.93b	2.00ab	4.46a	0.26a
T3	0.80b	2.1b	1.76a	2.53a
T4	2.23a	2.63a	3.40a	6.03a
T5	2.23a	1.73a	4.66a	3.46a

Note: Means with the same letter are not significantly different at $p=0.05$ using Duncan's Multiple Range Test

The results above (Table 3) showed that plant height decreased with decreasing pH. At pH 6.0 (control) and 5.0 the average plant height increment was 3.3 cm whereas for pH 2.0 the height increment was only 1.6 cm. The increment in plant height was significantly different between treatments at week 2, but there were no significant differences in week 4, 6, and 8. The highest increment in plant height was shown in T5 (4.66 cm) while T1 has the lowest height increment (0.73 cm). According to Santi *et al.*, (2008) plant height increased with increase of pH from 2.0 to 3.0, then it was relatively stable. Even though growth was inhibited at pH 2.0 and 2.5, the plant was still able to survive.

The plant height reduced proportionately as pH was reduced from 6.0 to 2.0 over a period of 8 weeks. Generally, plants exposed to SAR at pH 5.0 were significantly higher in height compared to pH 2.0, 3.0 and 4.0. SAR significantly affected plant height in T2 and T3 in week 2 and week 4. Wood and Bormann (1974), and Ferrenbaugh (1976) reported similar results where the plants could not attain normal height growth when treated with SAR below pH 3.0.

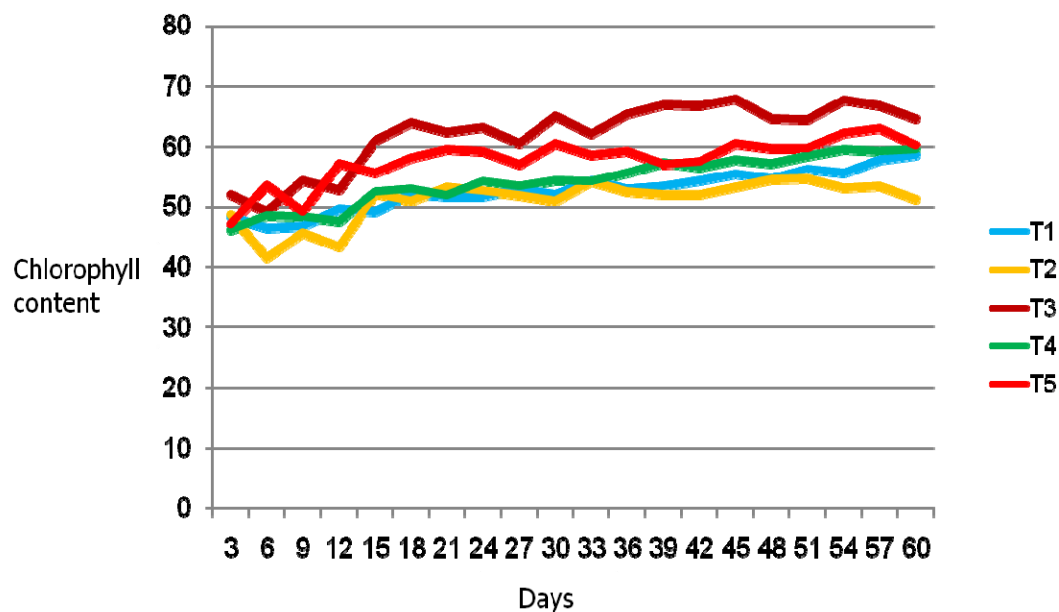


Figure 2. Chlorophyll content in *Sygyzium campanulatum* 60 days period.

Figure 2 shows that seedlings exposed to SAR at T3 showed the highest chlorophyll content (67.8) on day 45, while T2 on day 6 showed the lowest value (41.4). There was no significant difference ($P \leq 0.05$) in chlorophyll and leaf area index for all treatments. According to Shan (1998) the N content in rain water was adequate to stimulate chlorophyll production which might reduce the effect of H^+ from rain water.

Leaf area index (Table 4) was not significantly different ($P \leq 0.05$) among treatments throughout the study period. Plants exposed to SAR at T4 were higher in leaf area index (1498.21 cm^2) at week 8, while T2 in week 2 showed the lowest leaf area (616.3 cm^2). According to (Victor *et al.*, 1993) effects of acid rain on aboveground biomass and leaf area were a consequence of increasing concentration of soil N. This happened because acid rain

causes an increase concentration of nitrates provided through these treatments. In other cases, total N in the soil was converted to available N or nitrate with decreasing of pH. There was no deleterious effect of decreasing pH noted in short term, but on a long term basis, the effect on soil chemistry might affect plant nutrition.

4. Conclusions

The study showed that acid rain affected the growth of plants and selected soil chemical properties (K⁺, Ca²⁺ and Na⁺). pH 2.0 decreased height of *Syzygium campanulatum* seedlings. However a longer study period and a field study in areas affected by acid deposition should be carried out to confirm the findings of this study.

5. Acknowledgements

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List of Published Papers related to EANET

There are some research papers that are related the EANET data from our participating countries, however, these research papers were already published in some journals, therefore, they are no need to reprint as well as avoiding the copyright. Hence, they are listed in this section for further information.

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