

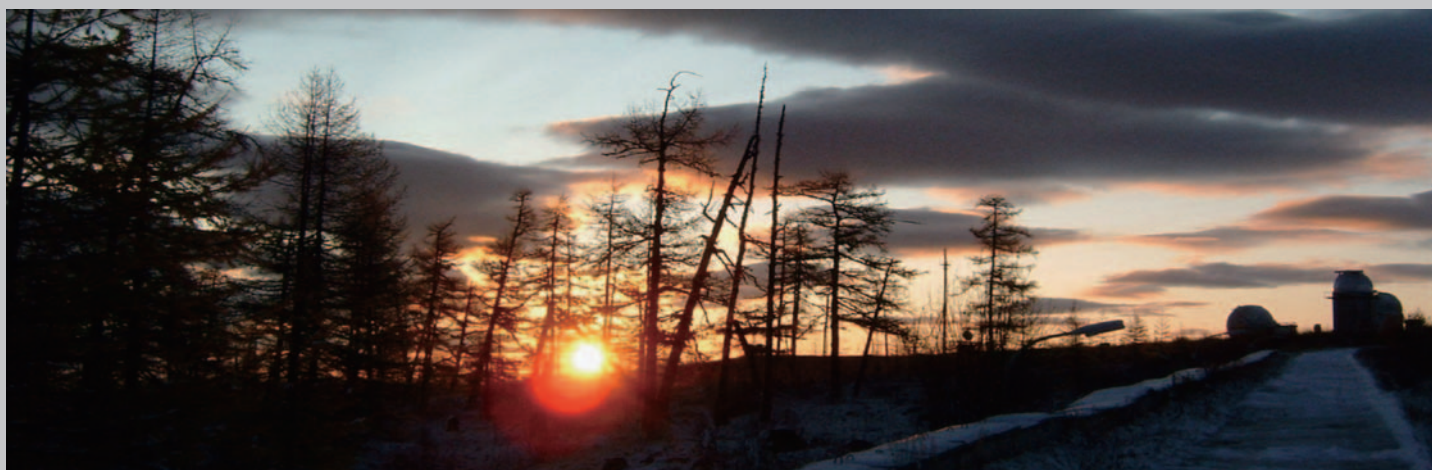
*Volume 1*

*November 2008*

ISSN 1883-3608

*Acid Deposition Monitoring Network in East Asia (EANET)*

# *EANET Science Bulletin*



*Network Center for EANET*

*<http://www.eanet.cc>*

## **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 1**

The EANET Science Bulletin is published by the Network Center for EANET once every two years. The Network Center is located at the Acid Deposition and Oxidant Research Center in Niigata, Japan.

### **Editorial Board**

|   |             |
|---|-------------|
| Leong Chow Peng (Deputy Director General)     | - Chair     |
| Jiro Sato (Assistant Deputy Director General) | - Secretary |
| Akira Nitta (Deputy Director General)         |             |
| Ken Yamashita (Planning and Training)         |             |
| Hiroaki Yago (Atmospheric Research)           |             |
| Shinji Nakayama (Data Management)             |             |
| Hiroyuki Sase (Ecological Impact Research)    |             |
| Keiichi Sato (Data Management)                |             |

### **Adviser**

Hiromasa Ueda (Director General)

**Endorsed at the Eighth Session of the Scientific Advisory Committee of EANET**

## ***Preface***

### ***Objectives of EANET Research Activities***

*The Acid Deposition Monitoring Network in East Asia (EANET) 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 monitoring and research activities of EANET are of great importance to achieve a better understanding of the extent of atmospheric acidification and impacts on the environment of the vast East Asian region, which includes some of the fastest growing economies in the world. Research activities are also necessary for improving current methodologies for monitoring acid deposition and related air pollutants and adapting them to suit the diverse topographical and climate conditions within the region. For these purposes, the Network Center for EANET, which is responsible for handling of scientific and technical matters of the network, has been conducting joint research projects with governmental agencies and research institutions in countries with sensitive ecosystems or severe climate conditions to better understand the factors affecting the measurements so as to develop improved methodologies for monitoring and evaluating the data collected.*

*In addition, since 2005 the Network Center has been implementing the EANET Research Fellowship Program whereby each year two young scientists from participating countries are invited to spend two months at the Acid Deposition and Oxidant Research Center to carry out research activities related to the EANET objectives under the guidance of senior researchers from the Network Center. The research fellows are required to submit a report in the form of a research paper at the end of their attachment period.*

*Researchers from the participating countries are also encouraged to use the growing high quality EANET database to conduct national studies that could advance knowledge on air pollution and their impacts to the countries. Such information are very useful to assist policy makers in planning air pollution control and mitigative measures.*

*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. Abstracts of published papers on issues relevant to EANET activities are also included for the information of the scientific community.*

***Hiromasa Ueda***  
***Director General***  
***Acid Deposition and Oxidant Research Center***  
***Network Center for EANET***

## Contents

### Preface

Objectives of EANET Research Activities  
*Hiromasa Ueda, Director General ADORC*

### Reports of the EANET Research Fellowship Program (2005-2007)

|   |    |
|---|----|
| Assessment of Ozone Variability in East Asia during Recent Years<br><i>Eyi Wang, Tatsuya Sakurai and Hiromasa Ueda</i>                                    | 3  |
| Determination of Unanalyzed Components in Rainwater<br><i>Arcely Candelario Viernes and Jun Nagata</i>  | 21 |
| Determination of Unanalyzed Components in Precipitation Water<br><i>Bulgan Tumendemberel</i>  | 37 |
| Application of a Scientific Climatological Approach and Statistical Method for EANET Network Optimization<br><i>Elena V. Gritsan and Sergey A. Gromov</i> | 49 |
| Comparison of Air Pollution and Acid Deposition between Two Mega-Cities<br><i>Yibing Lu and Hiroaki Yagoh</i>   | 57 |
| Assessment of Ozone and Other Gaseous Concentrations in East Asia<br><i>Truong Anh Son, Tatsuya Sakurai and Hiromasa Ueda</i>                             | 77 |

### Joint Projects of EANET with Participating Countries

|   |     |
|---|-----|
| Joint Research Project with Mongolia on Plant Sensitivities to Acid Deposition            | 93  |
| Joint Research Project with Russia on Evaluation of East Siberian Atmospheric Environment | 97  |
| Joint Research Project with Thailand on Dry Deposition Flux                               | 101 |
| Joint Research Project with Thailand on Dry Deposition Monitoring                         | 107 |

|  |     |
|--|-----|
| Joint Research Project with Republic of Korea on Dry Deposition (aerosol concentration) Monitoring     | 111 |
| Joint Research Project with Thailand on the Catchment Analysis   | 115 |
| Joint Research Project with Japan on the Catchment Analysis  | 119 |
| Joint Research Project on Model Simulation Works<br>(Model Intercomparison Study – MICS-Asia Phase II) | 125 |

### **Scientific and Technological Research Papers from Participating Countries**

|   |     |
|---|-----|
| Concentration and Isotopic Ratio of Lead in Wet Depositions in Several Regions of East Asian Russia<br><i>Natalia A. Onischuk, Tamara V. Khodzher, Eugeny P. Chebykin, Hiroaki Yagoh, Tsuyoshi Ohizumi and Sergey A. Gromov</i> | 133 |
| Russian Governmental Monitoring Networks Related to Acid Deposition and Results of their Activities over East Asian Territory<br><i>Sergey A. Gromov, Veronika A. Ginzburg and Sergey G. Paramonov</i>                          | 141 |
| Long Term Acidification of Upstream River and Lake Water in Central Japan<br><i>Hidemi Kurita, Leong Chow Peng and Hiromasa Ueda</i>  | 153 |

### **Abstracts of Published Papers related to EANET**

|  |     |
|--|-----|
| Establishing an Acid Deposition Monitoring Network in East Asia<br><i>Masaharu Yagishita</i>   | 175 |
| Model Intercomparison Study of Long Range Transport and Sulfur Deposition in East Asia (MICS-ASIA)<br><i>Gregory R. Carmichael, Hiroshi Hayami, Giuseppe Calori, Itsushi Uno, Seog-Yeon Cho, Magnuz Engardt, Seung-Bum Kim, Yoichi Ichikawa, Yukoh Ikeda, Hiromasa Ueda and Markus Amann</i> | 176 |
| Step-by-Step Approach to Establish Acid Deposition Monitoring Network in East Asia (EANET): Thailand's Experience<br><i>Supat Wangwongwatana</i>   | 177 |
| Quality Control and its Constraints during the Preparatory-phase Activities of the Acid Deposition Monitoring Network in East Asia (EANET)<br><i>Tsunehiko Ootshi, Norio Fukuzaki, Hu Li, Hiroshi Hoshino, Hiroyuki Sase Masashi Saito and Katsunori Suzuki</i>                              | 178 |

|   |     |
|---|-----|
| The MICS-Asia Study: Model Intercomparison of Long-Range Transport and Sulfur Deposition in East Asia<br><i>Gregory R. Carmichael, Giuseppe Calori, Hiroshi Hayami, Itsushi Uno, Seog-Yeon Cho, Magnuz Engardt, Seung-Bum Kim, Yoichi Ichikawa, Yukoh Ikeda, Jung-Hun Woo, Hiromasa Ueda and Markus Amann</i> | 179 |
| Simulations of Monthly Mean Nitrate Concentrations in Precipitation over East Asia<br><i>Junling An, Hiromasa Ueda, Zifa Wang, Kazuhide Matsuda, Mizuo Kajino and Xinjin Cheng</i>  | 180 |
| Neutralization of Soil Aerosol and its Impact on the Distribution of Acid Rain over East Asia: Observations and Model Results<br><i>Zifa Wang, Hajime Akimoto and Itsushi Uno</i>   | 181 |
| Simulated Impacts of SO <sub>2</sub> Emissions from the Miyake Volcano on Concentration and Deposition of Sulfur Oxides in September and October of 2000<br><i>Junling An, Hiromasa Ueda, Kazuhide Matsuda, Hisashi Hasome and Motokazu Iwata</i>   | 182 |
| High-resolution Model Simulations of Anthropogenic Sulphate and Sulphur Dioxide in Southeast Asia<br><i>Urban Siniarovina and Magnuz Engardt</i>  | 183 |
| Ozone Dry Deposition above a Tropical Forest in the Dry Season in Northern Thailand<br><i>Kazuhide Matsuda, Ichiro Watanabe, Vitsanu Wingpud, Phunsak Theramongko, Pojanie Khummongkol, Supat Wangwongwatana, Tsumugu Totsuka</i>   | 184 |
| Tree Decline and its Possible Causes around Mt. Bogdkhan in Mongolia<br><i>Hiroyuki Sase, Bulgan Tumendemberel, Tseveen Batchuluun, Hideyuki Shimizu and Tsumugu Totsuka</i>  | 185 |
| Response to O <sub>3</sub> and SO <sub>2</sub> for Five Mongolian Semi-arid Plant Species<br><i>Hideyuki Shimizu, Ping An, Yuanrun Zheng, Lijun Chen, Hiroyuki Sase, Tsumugu Totsuka, Bulgan Tumendemberel and Youbin Zheng</i>   | 186 |
| Model Study on Acidifying Wet Deposition in East Asia During Wintertime<br><i>Zhiwei Han, Hiromasa Ueda and Tatsuya Sakurai</i>   | 187 |
| Deposition Velocity of O <sub>3</sub> and SO <sub>2</sub> in the Dry and Wet Season above a Tropical Forest in Northern Thailand<br><i>Kazuhide Matsuda, Ichiro Watanabe, Vitsanu Wingpud, Phunsak Theramongkol and Tsuyoshi Ohizumi</i>  | 188 |

|   |     |
|---|-----|
| Modeling Study of Ozone Seasonal Cycle in Lower Troposphere over East Asia<br><i>Jie Li, Zifa Wang, Hajime Akimoto, Chao Gao, Pakpong Pochanart and Xiquan Wang</i>   | 189 |
| Spatial Distribution and Source Identification of Wet Deposition at Remote EANET Sites in Japan<br><i>Sinya Seto, Manabu Sato, Tsutomu Tatano, Takashi Kusakari and Hiroshi Hara</i>  | 190 |
| Modeling Study of Long-range Transport of SO <sub>2</sub> , NO <sub>x</sub> and O <sub>3</sub> over Northeast Asia in March 2002<br><i>Zhiwei Han, Hiromasa Ueda, Yu Hozumi and Tatsuya Sakurai</i>   | 191 |
| Cost-effectiveness Analysis of Reducing the Emission of Nitrogen Oxides in Asia<br><i>Ken Yamashita, Fumiko Ito, Keigo Kameda, Tracey Holloway and Matthew Johnston</i>   | 192 |
| Influence of Vertical Eddy Diffusivity Parameterization on Daily and Monthly Mean Concentrations of O <sub>3</sub> and NO <sub>y</sub><br><i>Junling An, Xinjin Cheng, Yu Qu and Yong Chen</i>  | 193 |
| Secondary Acidification: Changes in Gas-aerosol Partitioning of Semivolatile Nitric Acid and Enhancement of its Deposition due to Increased Emission and Concentration of SO <sub>x</sub><br><i>Mizuo Kajino, Hiromasa Ueda and Shinji Nakayama</i>   | 194 |
| MICS-Asia II: The Model Intercomparison Study for Asia Phase II Methodology and Overview of Findings<br><i>Gregory R. Carmichael, Tatsuya. Sakurai, David Streets, Yu Hozumi, Hiromasa Ueda, Soon-Ung Park, Christopher Fung, Zhiwei Han, Mizuo Kajino, Magnuz Engardt, Cecilia Bennet, Hiroshi Hayami, Karine Sartelet, Tracey Holloway, Zifa Wang, Akiyoshi Kannari, Joshua Fu, Kazuhide Matsuda, Narisara Thongboonchoo and Markus Amann</i> | 195 |
| MICS-Asia II: Model Intercomparison and Evaluation of Ozone and Relevant Species<br><i>Zhiwei Han, Tatsuya. Sakurai, Hiromasa Ueda, Gregory R. Carmichael, David Streets, Hiroshi Hayami, Zifa Wang, Tracey Holloway, Magnuz Engardt, Yu Hozumi, Soon-Ung Park, Mizuo Kajino, Karine Sartelet, Christopher Fung, Cecilia Bennet, Narisara Thongboonchoo, Youhua Tang, Alick H. Y. Chang, Kazuhide Matsuda and Markus Amann</i>                  | 196 |

|  |     |
|--|-----|
| MICS-Asia II: Model Intercomparison and Evaluation of Particulate Sulfate, Nitrate And Ammonium  | 198 |
| <i>Hiroshi Hayami, Tatsuya. Sakurai, Zhiwei Han, Hiromasa Ueda, Gregory R. Carmichael, David Streets, Tracey Holloway, Zifa Wang, Narisara Thongboonchoo, Magnuz Engardt, Cecilia Bennet, Christopher Fung, Alick H. Y. Chang, Soon-Ung Park, Mizuo Kajino, Karine Sartelet, Kazuhide Matsuda and Markus Amann</i>                                   |     |
| MICS-Asia II: Model Inter-comparison and Evaluation of Acid Deposition   | 200 |
| <i>Zifa Wang, Fuying Xie, Tatsuya. Sakurai, Hiromasa Ueda, Zhiwei Han, Gregory R. Carmichael, David Streets, Magnuz Engardt, Tracey Holloway, Hiroshi Hayami, Mizuo Kajino, Narisara Thongboonchoo, Cecilia Bennet, Soon-Ung Park, Christopher Fung, Alick H. Y. Chang, Karine Sartelet and Markus Amann</i>   |     |
| MICS-Asia II: Impact of Global Emissions on Regional Air Quality in Asia   | 201 |
| <i>Tracey Holloway, Tatsuya Sakurai, Zhiwei Han, Susanna Ehlers, Scott N. Spak, Larry W. Horowitz, Gregory R. Carmichael, David G. Streets, Yu Hozumi, Hiromasa Ueda, S.U. Park, Christopher Fung, Mizuo Kajino, Narisara Thongboonchoo, Magnuz Engardt, Cecilia Bennet, Hiroshi Hayami, Karine Sartelet, Zifa Wang, K. Matsuda and Markus Amann</i> |     |
| MICS Asia Phase II – Sensitivity to the Aerosol Module   | 202 |
| <i>Karine Sartelet, Hiroshi Hayami and Bruno Sportisse</i>   |     |
| MICS-Asia II: Modeling Gaseous Pollutants and Evaluating an Advanced Modeling System over East Asia  | 203 |
| <i>Joshua S. Fu, Carey J. Jang, David G. Streets, Zuopan Li, Roger Kwok, Rokjin Park and Zhiwei Han</i>  |     |
| MICS-Asia II: An Inter-comparison Study of Emission Inventories for the Japan Region   | 204 |
| <i>Akiyoshi Kannari, David G. Streets, Yutaka Tonooka, Kentaro Murano and Tsuyoshi Baba</i>  |     |
| Seasonal Variation in the Atmospheric Deposition of Inorganic Constituents and Canopy Interactions in a Japanese Cedar Forest  | 205 |
| <i>Hiroyuki Sase, Akiomi Takahashi, Masahiko Sato, Hiroyasu Kobayashi, Makoto Nakata and Tsumugu Totsuka</i>   |     |
| Seasonal and Annual Fluxes of Inorganic Constituents in a Small Catchment of a Japanese Cedar Forest near the Sea of Japan   | 206 |
| <i>Masato Kamisako, Hiroyuki Sase, Taeko Matsui, Hiroko Suzuki, Akiomi Takahashi, Takuji Oida, Makoto Nakata, Tsumugu Totsuka and Hiromasa Ueda</i>  |     |



***Reports of the EANET Research Fellowship  
Program (2005-2007)***

## **Assessment of Ozone Variability in East Asia during Recent Years**

Eyi Wang<sup>1)\*</sup>, Tatsuya Sakurai<sup>2)</sup> and Hiromasa Ueda<sup>2)</sup>

*1) Division of Air Polluting Monitoring, China National Environmental Monitoring Center*

*\*Contact address: No.1 Yuhuinanlu, Beisihuandonglu, Beijing, 100029, China [email: wang.eyi@sepa.gov.cn]*

*2) Acid Deposition and Oxidant Research Center (ADORC)*

The variability of ozone observed at sixteen sites in East Asia during recent years were investigated in this paper. The yearly and monthly/ daily /hourly behaviors of ozone were examined and compared, then the spatial-temporal variation of ozone and its sources were discussed.

1) Stations over mid-latitudes have high ozone concentrations, and the differences between yearly mean concentrations are small (within 10%). Good correlations can be seen between every two stations for monthly value; Ozone concentrations are low in mid-low latitudes, but they have large variations between yearly mean values, up to 24%; the tropic sites have the lowest ozone level, and the monthly variation in Thailand is much different from other sites in EANET.

2) Both Happono (Japan) and Mondy (Russia) sites are located on high mountains, Good correlations can be seen between Happono and Mondy for monthly ozone concentrations, the correlation exceeds 90%; In spring and winter, the daily mean ozone concentrations of the two stations has similar variations, but it appears that Happono has a 3-6 days delay. Similar daily ozone concentrations shows that the atmospheric transport of ozone may be an important cause of high ozone concentrations in Happono. However, the mean ozone in Happono is about 28% higher than that of Mondy, which implies that there must be other causes: In Happono, there are no evidences for hourly concentrations between the high ozone concentrations and photochemical reactions (sunlight, temperature, local NO<sub>x</sub> etc.). But the ozone concentrations have negative correlation with humidity. Sinking of high-level dry air from stratosphere and atmospheric transport may be important causes of high ozone in Happono. According to Backward trajectories at Mondy for high daily ozone concentration, Long range EURO-ASIA transport from Europe may be a likely reason for high ozone concentrations at Mondy. And the positive correlation between ozone and wind speed implies that transport is an important factor of high-concentration ozone at Mondy.

3) There are two stations with obvious variations during recent 5 years, which are both located in the islands of southern Japan. At two inland sites, there is negative-correlation between the ozone concentration and the temperature, which is associated with clean marine air mass, which has lower ozone levels; The ozone concentrations of two sites also have negative correlation with humidity. However, they result from different reason. For Mondy and Happono, the correlation may be caused by the sinking of high-level dry air with high ozone concentration. While at Japan sites, it's because of the transport by wet flow from the ocean with low-concentration ozone.

4) Ozone in Thailand is not higher than 20ppb for yearly mean and 40 ppb for monthly mean. Humidity, cloud cover, and precipitation are possible factors to influence ozone concentration in Thailand.

## 1. Introduction

Ozone is a reactive gas produced naturally both in the Earth's upper atmosphere and at ground level. It is also a photochemical oxidant formed by a series of chemical reactions in the presence of sunlight and high temperature. Volatile organic compounds (VOCs) and oxides of nitrogen ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) are involved in the photochemical reactions. High concentration of ground level ozone is known to have detrimental effects on human health and vegetations (NRC, 1991). It is of great importance to study the ozone pollution.

The East Asian region faces increasing risks of problems related to ozone pollution as a result of enforced industrialization for last decades. There are many studies focusing on ozone measurement and analysis in East Asia Region (Akimoto, 1994; 1996; Kajii, 1997; Pochanart, 1999; Lam, 2001; Wang, 1997; Chan, 1998; Buhr, 1996). It is clear now that both transport and photochemistry are important sources of surface ozone. However, much attention has been paid on the variability of surface ozone at single or several sites. More studies are necessary to compare the signatures of surface ozone at different sites as a whole in the East Asian region.

Acid Deposition Monitoring Network in East Asia (EANET) was initiated in 1998. Since the start of EANET, monitoring of ozone has been implemented in some participating countries in order to observe concentrations and to evaluate fluxes of ozone in East Asia. The participating countries submitted their data and related information obtained through the monitoring activities of EANET. In this paper, Monitoring data from EANET from 2000 to 2004 were used to explore the main characters of ozone at different sites over East Asia.

## 2. Methodology

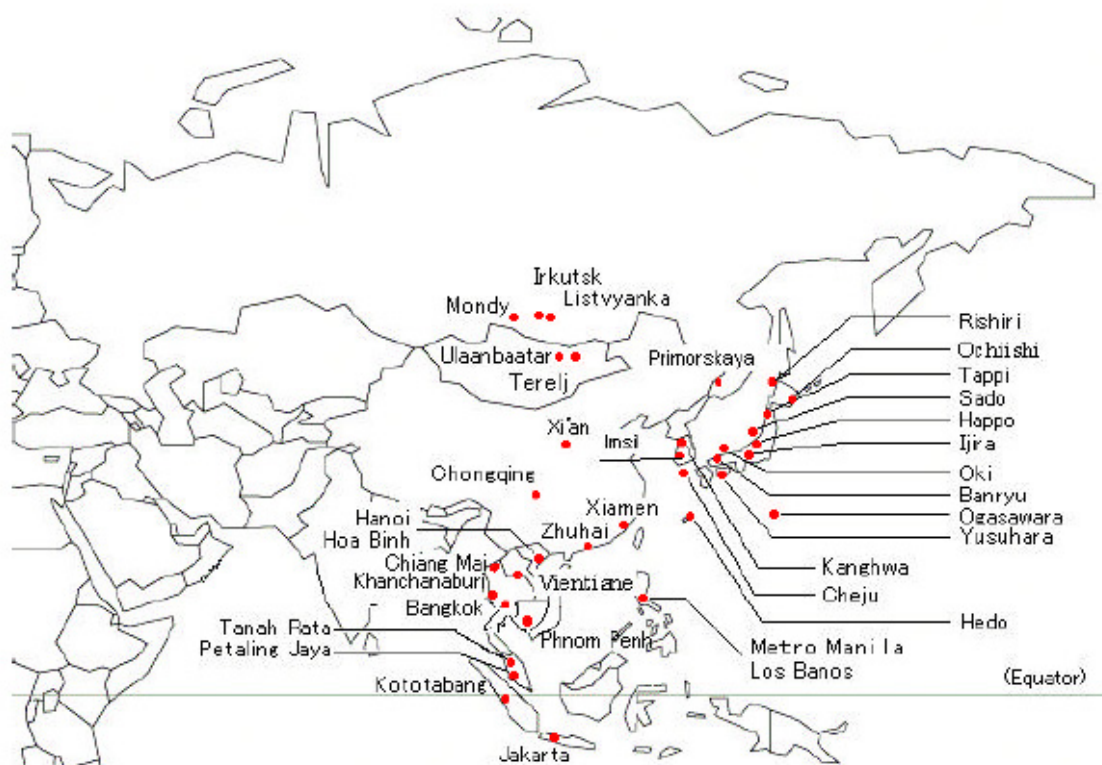
### 2.1. Monitoring sites

Sixteen monitoring sites with ozone concentration including Rishiri, Ochiishi, Tappi, Ogasawara, Sado-seki, Happo, Oki, Yusuhara, Hedo, Ijira, Banryu (Japan), Kanghwa, Cheju and Imsil (Korea), Mondy (Russia), Samutprakarn and Chiangmai (Thailand) were considered in EANET. The geographical locations of the monitoring sites were listed in Table 1 with detail information. Except Six sites (Banryu and Samutprakarn are urban stations, Ijira, Chiangmai, Kanghwa and Imsil act as rural stations), the other sites are set up as the regional background stations in East Asia. These stations with criteria presented in Fig. 1.1 are located from local pollution sources so that the signatures of regional ozone concentration can be captured.

**Table 1 Description of ozone monitoring sites and data sets**

| Country | Name of sites | Characteristics of sites | Latitude  | Longitude  | Height above sea | Measurement period |
|---------|---------------|--------------------------|-----------|------------|------------------|--------------------|
| Japan   | Rishiri       | Remote                   | 45° 07' N | 141° 14' E | 40m              | 2000-2004          |
|         | Tappi         | Remote                   | 41° 15' N | 141° 21' E | 105m             | 2000-2004          |
|         | Ogasawara     | Remote                   | 27° 50' N | 142° 13' E | 230m             | 2000-2004          |
|         | Sado-seki     | Remote                   | 38° 14' N | 138° 24' E | 110m             | 2000-2004          |
|         | Happo         | Remote                   | 36° 41' N | 137° 48' E | 1,850m           | 2000-2004          |
|         | Oki           | Remote                   | 36° 17' N | 133° 11' E | 90m              | 2000-2004          |
|         | Yusuhara      | Remote                   | 33° 22' N | 132° 56' E | 225m             | 2000-2004          |
|         | Hedo          | Remote                   | 26° 51' N | 128° 15' E | 50m              | 2000-2004          |

|                   |              |        |           |            |       |           |
|-------------------|--------------|--------|-----------|------------|-------|-----------|
| Republic of Korea | Ijira        | Rural  | 35° 43' N | 136° 41' E | 140m  | 2000-2004 |
|                   | Banryu       | Urban  | 34° 40' N | 131° 48' E | 60m   | 2000-2004 |
|                   | Kanghwa      | Rural  | 37° 42' N | 126° 17' E | 150m  | 2002-2004 |
|                   | Cheju        | Remote | 33° 18' N | 126° 10' E | 72m   | 2002-2004 |
|                   | Imsil        | Rural  | 35° 36' N | 127° 11' E |       | 2002-2004 |
| Russia            | Mondy        | Remote | 51° 40' N | 101° 0' E  | 2000m | 2002-2004 |
| Thailand          | Samutprakarn | Urban  | 13° 44' N | 100° 34' E | 2m    | 2001-2003 |
|                   | Chiangmai    | Rural  | 18° 46' N | 98° 56' E  | 350m  | 2003-2004 |



**Figure 1** Locations of EANET sites.

## 2.2. Method and data

Monitoring of ozone and related parameters were conducted at 16 sites from 2000 to 2004. All stations measured ozone with UVP photometric analyzer. The list of monitoring data at different stations was presented in Table 2. There were hourly data of ozone, NO<sub>x</sub>, NO and meteorological data at ten Japanese stations, daily ozone and meteorological data for Thailand and Russia stations, and only daily ozone concentration for three Korean stations. As described in Table 2 with 16 sites presented ozone data meteorological conditions such as wind speed, wind direction, air temperature, relative humidity, and solar radiation were measured by equipments installed at the sites or nearby at the meteorological observatories.

**Table 2 Outline of ozone monitoring data sets**

| Country           | Name of sites | Ozone  | NOx/NO | meteorological | Measurement period |
|-------------------|---------------|--------|--------|----------------|--------------------|
| Japan             | Rishiri       | Hourly | ○      | ○              | 2000-2004          |
|                   | Tappi         | Hourly | ○      | ○              | 2000-2004          |
|                   | Ogasawara     | Hourly | ○      | ○              | 2000-2004          |
|                   | Sado-seki     | Hourly | ○      | ○              | 2000-2004          |
|                   | Happo         | Hourly | ○      | ○              | 2000-2004          |
|                   | Oki           | Hourly | ○      | ○              | 2000-2004          |
|                   | Yusuhara      | Hourly | ○      | ○              | 2000-2004          |
|                   | Hedo          | Hourly | ○      | ○              | 2000-2004          |
|                   | Ijira         | Hourly | ○      | ○              | 2000-2004          |
|                   | Banryu        | Hourly | ○      | ○              | 2000-2004          |
| Republic of Korea | Kanghwa       | Daily  | ○      | none           | 2002-2004          |
|                   | Cheju         | Daily  | ○      | none           | 2002-2004          |
|                   | Imsil         | Daily  | ○      | none           | 2002-2004          |
| Russia            | Mondy         | Daily  | none   | ○*             | 2002-2004          |
| Thailand          | Samutprakarn  | Daily  | ○      | ○*             | 2002-2003*         |
|                   | Chiangmai     | Daily  | ○      | ○*             | 2003-2004          |

○\* means WMO data; In 2001, Percentage of period of available data in Thailand is low (deleted data)

### 3. Results and discussion

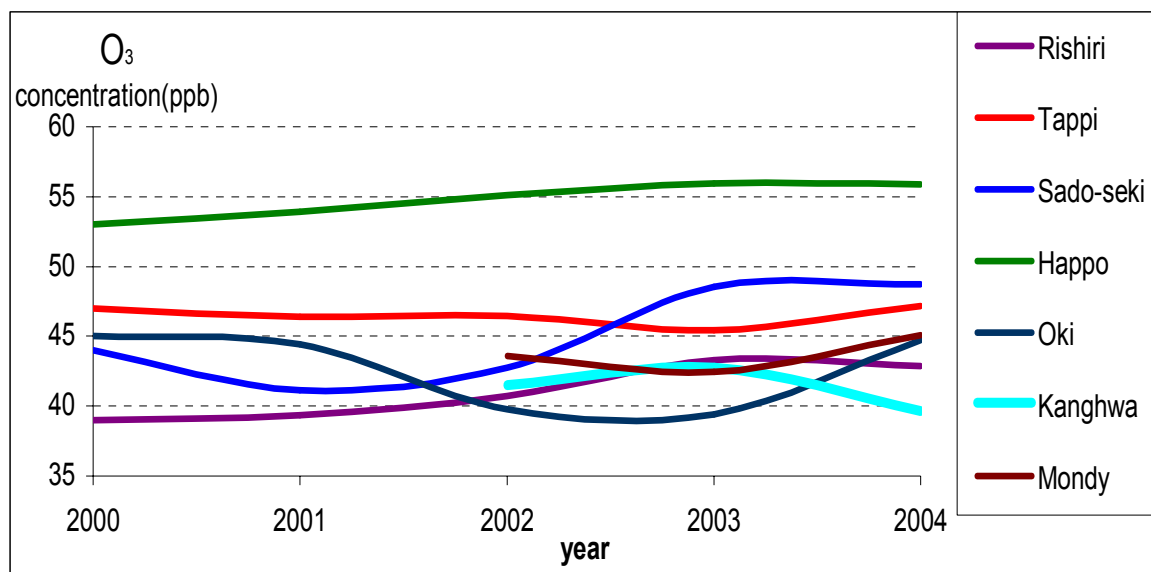
#### 3.1. Annual changes of ozone concentration in EANET

The annual average values of ozone pollutants were illustrated in Fig.2. The annual means were listed in Table 3. As shown by Fig 2, stations with high ozone concentrations were located in northern Japan, Mondy of Russia and Kanghwa of Korea, these stations had means no more than 40ppb over recent 5 years, which indicated higher ozone concentration over the whole mid-latitudes, with highest mean up to 56 ppb (Happo site, 2003~2004). However, considering the trend multiyear variation (Table 3), the differences between yearly mean concentrations at mid-latitude site were within 10%. (Notes: in this study, the area north of 36°N is regarded as mid-latitudes while low-mid latitudes as south of 36°N)

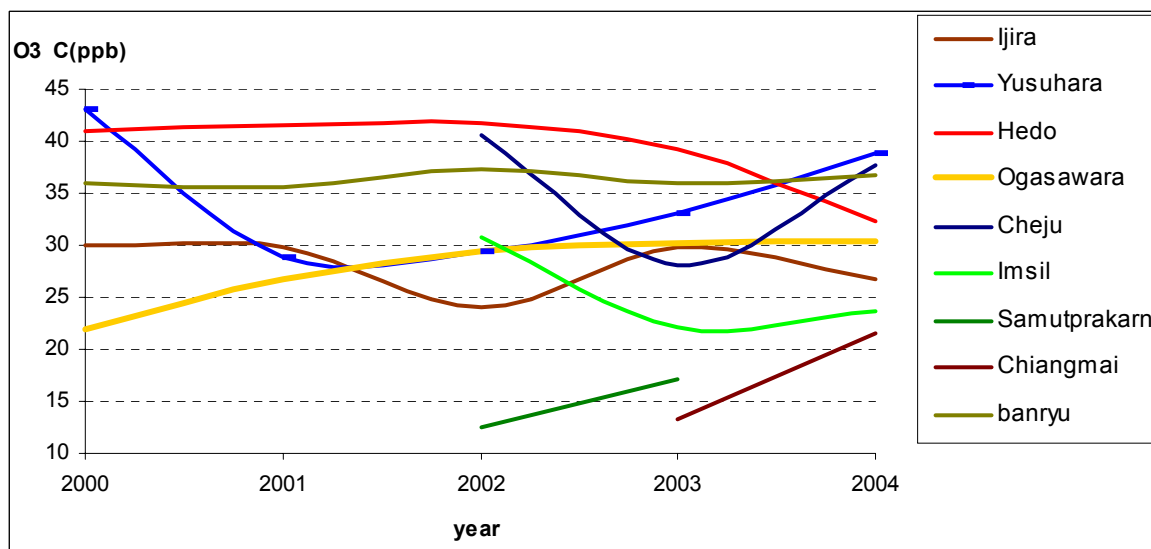
Lower ozone concentrations existed over the most mid-low latitudes with multiyear mean lower than 35 ppb except Hedo (an island to the east of Euro-Asian Continent) and Banryu (an urban site) of 35~40ppb. Samutprakarn and Chiangmai (in Thailand) have the lowest ozone concentration, which was lower than 20ppb. Ozone concentrations were low in Thailand, but they had large variations between yearly mean values, up to

24%. Highest annual averaged ozone level was found at Happo site of Japan and lowest ozone level was observed at the urban site in Thailand. Ozone concentration at Banryu city station of Japan had small yearly variations within 3%, and it was lower than the mean value of 10 stations of Japan. There were two stations with obvious variations during recent 5 years, they were both located in the islands of southern Japan. One was Hedo station, its ozone decreases generally year by year, and the other was Ogasawara station, which had a trend of increase. (Notes: in this study, the area north of 36°N is regarded as mid-latitudes while low-mid latitudes as south of 36°N)

(a)



(b)



**Figure 2 Annual ozone concentration in EANET: (a) Annual variations in mid-latitudes East Asia, (b) Annual variations in low-mid latitudes.**  
(The area north of 36°N is regarded as mid-latitudes while low-mid latitudes as south of 36°N.)

**Table 3 Annual change of ozone concentration from 2000 to 2004**

| Name of sites                  | Mean value during recent years (ppb) | Annual change |      |      |      |      |
|--------------------------------|--------------------------------------|---------------|------|------|------|------|
|                                |                                      | 2000          | 2001 | 2002 | 2003 | 2004 |
| Rishiri                        | 41                                   | -5%           | -4%  | -1%  | 5%   | 4%   |
| Tappi                          | 46                                   | 1%            | 0%   | 0%   | -2%  | 1%   |
| Sado-seki                      | 45                                   | -2%           | -9%  | -5%  | 8%   | 8%   |
| Happo                          | 55                                   | -3%           | -2%  | 1%   | 2%   | 2%   |
| Oki                            | 43                                   | 5%            | 4%   | -7%  | -8%  | 5%   |
| Kanghwa *                      | 41                                   | /             | /    | 0%   | 4%   | -4%  |
| Mondy *                        | 44                                   | /             | /    | 0%   | -3%  | 3%   |
| Hedo<br>(island site)          | 39                                   | 5%            | 6%   | 6%   | 0%   | -18% |
| Banryu<br>(urban site)         | 36                                   | -1%           | -2%  | 3%   | -1%  | 1%   |
| Yusuhara                       | 34                                   | 15%           | -15% | -13% | -2%  | 15%  |
| Ijira                          | 28                                   | 7%            | 6%   | -14% | 6%   | -5%  |
| Ogasawara<br>(island site)     | 28                                   | -21%          | -4%  | 6%   | 9%   | 9%   |
| Cheju *                        | 35                                   | /             | /    | 15%  | -21% | 6%   |
| Imsil *                        | 26                                   | /             | /    | 21%  | -13% | -7%  |
| Samutprakarn**<br>(urban site) | 14                                   | /             | /    | -16% | 16%  | /    |
| Chiangmai**                    | 14                                   | /             | /    | ¥    | -24% | 24%  |

\* Mean value of three years, \*\* Mean value of two years.



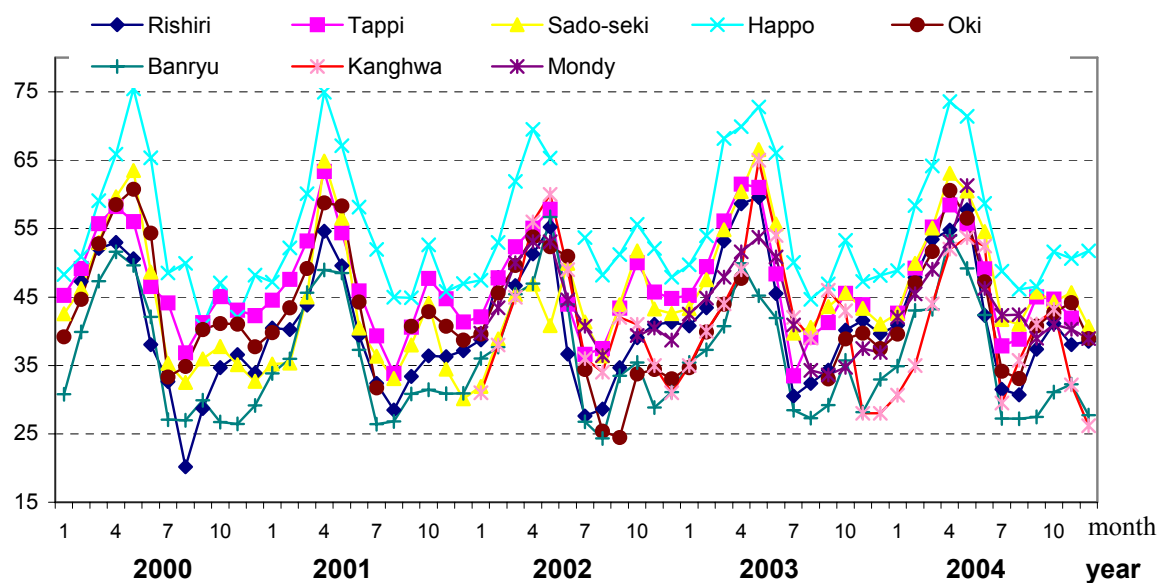
### 3.2. Monthly changes

Fig. 3 indicates the stations at mid-latitudes have similar mean variation of ozone concentration. In mid-latitudes, Ozone showed clear seasonal cycles. In general, ozone concentration was high in spring and low in summer. In autumn, there was another peak of ozone which was smaller than that in spring. The highest monthly concentration was as high as 75ppb, appeared in May 2000 at Happono. Ozone concentrations in summer were lower, and the possible reason is most of Japanese sites are affected by clean marine air mass, which have lower ozone levels. The autumn maximum of ozone had also been found in other studies, it is caused by both the transport of higher ozone and its precursors from the polluted continent/ marine air masses and the stronger photochemical production in a dry and sunny weather (Ishino, 2001).

Over low-mid latitudes, monthly variations were different for different stations. There were always more peaks in a year. A common thing was that there existed low value periods in summer, the other season had evidently higher monthly means. The lowest monthly means appeared at urban station in Thailand. Another possible reason may be associated with more water vapor and more strong solar radiation, which yields more radicals ( $\text{HO}_2$ ) and cause more depletion of ozone. (Liu, 1980) As depicted by Table 4.1, Good correlations could be seen between stations with high monthly mean ozone in northern parts of Japan. The correlation coefficients between every two stations exceeded 70%. Ozone concentrations at two stations, Mondy in Russia and Happono in Japan, were closely correlated with those of other Japanese stations (except two island stations and the southeast station-Yusuhara) and of the Korea. It was found that the correlation between Mondy and Happono exceeded 90%, including a very similar seasonal variation between 2 sites, which shows high value in spring and low in summer. The two stations in Japan islands had well-correlated monthly ozone concentrations. However, it showed no significant correlations with those of other stations. In contrast to other sites, Monthly ozone concentrations in Thailand were the lowest, and the monthly variation of Thailand was much different from that of other area.

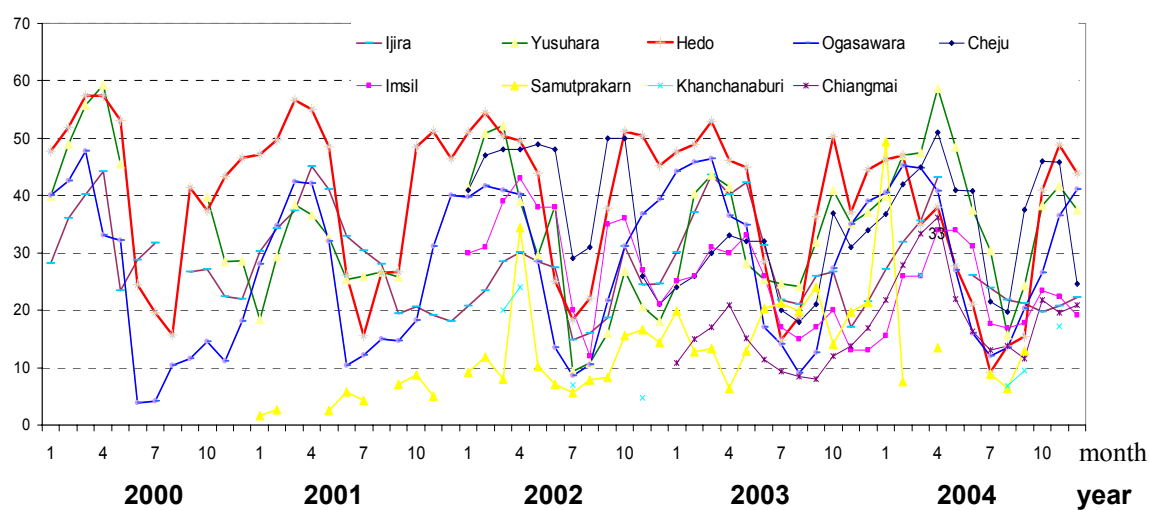
**(a)**

Ozone c(ppb)



**(b)**

Ozone c(ppb)



**Figure 3 Monthly ozone concentrations for respective sites.**  
**(a) in mid-latitudes; (b) in low-mid latitudes**

**Table 4.1 Correlations coefficient between stations for monthly mean ozone from 2000 to 2004 (Japanese sites)**

| Correlation | Rishiri | Tappi | Sado-seki | Happo | Oki  | Banryu | Ijira | Yusuhara | Hedo | Ogasawara |
|-------------|---------|-------|-----------|-------|------|--------|-------|----------|------|-----------|
| Rishiri     | 1.00    | 0.94  | 0.78      | 0.81  | 0.76 | 0.87   | 0.72  | 0.64     | 0.56 | 0.68      |
| Tappi       | 0.94    | 1.00  | 0.80      | 0.85  | 0.80 | 0.88   | 0.76  | 0.59     | 0.57 | 0.60      |
| Sado-seki   | 0.78    | 0.80  | 1.00      | 0.86  | 0.70 | 0.75   | 0.65  | 0.47     | /    | 0.35      |
| Happo       | 0.81    | 0.85  | 0.86      | 1.00  | 0.80 | 0.88   | 0.68  | 0.46     | /    | 0.35      |
| Oki         | 0.76    | 0.80  | 0.70      | 0.80  | 1.00 | 0.86   | 0.59  | 0.71     | 0.34 | 0.34      |
| Banryu      | 0.87    | 0.88  | 0.75      | 0.88  | 0.86 | 1.00   | 0.70  | 0.61     | 0.44 | 0.48      |
| Ijira       | 0.72    | 0.76  | 0.65      | 0.68  | 0.59 | 0.70   | 1.00  | 0.50     | 0.37 | 0.41      |
| Yusuhara    | 0.64    | 0.59  | 0.47      | 0.46  | 0.71 | 0.61   | 0.50  | 1.00     | 0.51 | 0.60      |
| Hedo        | 0.56    | 0.57  | /         | /     | 0.34 | 0.44   | 0.37  | 0.51     | 1.00 | 0.78      |
| Ogasawara   | 0.68    | 0.60  | 0.35      | 0.35  | 0.34 | 0.48   | 0.41  | 0.60     | 0.78 | 1.00      |

Test with significance level at 0.05,  $r \geq 0.29$

**Table 4.2 Correlations between stations for monthly mean ozone from 2002 to 2004 (all sites)**

| Correlation coefficient | Rishiri | Tappi | Sado-seki | Happo | Ijira | Oki  | Banryu | Yusuhara | Hedo | Ogasawara | Kanghwa | Cheju | Imsil | Mondy | Samutprakarn |
|-------------------------|---------|-------|-----------|-------|-------|------|--------|----------|------|-----------|---------|-------|-------|-------|--------------|
| Rishiri                 | 1.00    | 0.96  | 0.72      | 0.86  | 0.80  | 0.80 | 0.86   | 0.62     | 0.51 | 0.62      | 0.61    | 0.43  | 0.61  | 0.81  | /            |
| Tappi                   | 0.96    | 1.00  | 0.76      | 0.88  | 0.83  | 0.75 | 0.87   | 0.56     | 0.50 | 0.59      | 0.69    | 0.47  | 0.70  | 0.79  | /            |
| Sado-seki               | 0.72    | 0.76  | 1.00      | 0.82  | 0.82  | 0.62 | 0.65   | 0.38     | 0.08 | 0.19      | 0.67    | /     | 0.46  | 0.70  | /            |
| Happo                   | 0.86    | 0.88  | 0.82      | 1.00  | 0.80  | 0.80 | 0.88   | 0.47     | /    | /         | 0.79    | 0.45  | 0.73  | 0.90  | /            |
| Ijira                   | 0.80    | 0.83  | 0.82      | 0.80  | 1.00  | 0.58 | 0.73   | 0.50     | 0.39 | 0.50      | 0.57    | /     | 0.51  | 0.71  | /            |
| Oki                     | 0.80    | 0.75  | 0.62      | 0.80  | 0.58  | 1.00 | 0.84   | 0.79     | /    | 0.36      | 0.64    | 0.56  | 0.58  | 0.82  | /            |
| Banryu                  | 0.86    | 0.87  | 0.65      | 0.88  | 0.73  | 0.84 | 1.00   | 0.60     | /    | 0.39      | 0.74    | 0.60  | 0.79  | 0.85  | /            |
| Yusuhara                | 0.62    | 0.56  | 0.38      | 0.47  | 0.50  | 0.79 | 0.60   | 1.00     | 0.46 | 0.60      | /       | 0.51  | 0.39  | 0.43  | /            |
| Hedo                    | 0.51    | 0.50  | /         | /     | 0.39  | /    | /      | 0.46     | 1.00 | 0.84      | /       | 0.36  | 0.40  | /     | /            |
| Ogasawara               | 0.62    | 0.59  | /         | /     | 0.50  | /    | 0.39   | 0.60     | 0.84 | 1.00      | /       | /     | /     | /     | /            |
| Kanghwa                 | 0.61    | 0.69  | 0.67      | 0.79  | 0.57  | 0.64 | 0.74   | /        | /    | /         | 1.00    | 0.38  | 0.67  | 0.72  | /            |
| Cheju                   | 0.43    | 0.47  | /         | 0.45  | /     | 0.56 | 0.60   | 0.51     | /    | /         | 0.38    | 1.00  | 0.68  | 0.44  | /            |
| Imsil                   | 0.61    | 0.70  | 0.46      | 0.73  | 0.51  | 0.58 | 0.79   | 0.39     | 0.40 | /1        | 0.67    | 0.68  | 1.00  | 0.73  | /            |
| Mondy                   | 0.81    | 0.79  | 0.70      | 0.90  | 0.71  | 0.82 | 0.85   | 0.43     | /    | /         | 0.72    | 0.44  | 0.73  | 1.00  | /            |
| Samutprakarn            | /       | /     | /         | /     | /     | /    | /      | /        | /    | /         | /       | /     | /     | /     | 1            |

Test with significance level at 0.05,  $r \geq 0.37$ .

### 3.3. The correlation between monthly O<sub>3</sub> and meteorological factor at every station.

Table 5 gives the correlation coefficients between monthly ozone and meteorological data at every monitoring station. It can be concluded that, for every station, ozone concentration had no significant relationships with corresponding meteorological factors although it was quite well correlated with the concentrations of other stations. At two island sites, there was negative-correlation between the ozone concentration and the temperature, which suggested that the relative roles of transport and photochemistry were different at island sites. In general, water vapor was negatively correlated with ozone, implying that humidity influence the ozone concentration at monitoring sites over mid-latitudes.

The ozone concentrations of Mondy and Japan sites had negative correlation with humidity. However, they result from different reason. To Mondy, the correlation may be caused by the sinking of high-level dry air with high O<sub>3</sub> concentration while at Japan sites, it's for the transportation by wet flow from the ocean with low-concentration ozone. The positive correlation between ozone and wind speed at Mondy indicates that transportation is an important factor of high-concentration ozone at Mondy.

The negative correlation between ozone and temperature at Hedo and Ogasawara site is associated with clean marine air mass, which has lower ozone levels

In summary, there were higher ozone concentrations during the transition seasons over mid-latitude East Asian, especially in spring. The possible reasons may be as below:

(1) the boreal ozone columns often increase with latitude and are highest in spring, lowest in winter. Its seasonal variation increases with latitude. The maximum ozone concentration in spring occurs first in the upper troposphere and then propagates down to the surface later.

(2) At mid-latitudes, there exists more cyclone activity in spring which can transport ozone from the higher latitudes; There are more west and north wind components in spring that can bring higher-concentration O<sub>3</sub> from Euro-Asia transport while more south wind components in summer that may bring low-concentration ozone from low-latitudes.

(3) The high system that controls the East Asia during winter and transiting seasons is dry, which benefits the transport of the ozone concentration, while the high/low system during summer is wet and warm, which goes against the increase of ozone concentration.

**Table 5 Correlations between monthly mean ozone and meteorological parameters at monitoring site**

**Correlation coefficient between monthly mean ozone and meteorological parameters from 2000 to 2004**

| items                           | Rishiri        | Tappi | Sado-seki | Happo | Ijira | Okii  | Banryu | Yusu-hara | Hedo  | Ogasa-wara | Kang-hwa | Cheju | Imsil | Mondy | Samut prakarn |
|---------------------------------|----------------|-------|-----------|-------|-------|-------|--------|-----------|-------|------------|----------|-------|-------|-------|---------------|
| Temperature (°C)                | monthly mean   | -0.44 | -0.39     | /     | /     | /     | /      | -0.43     | -0.79 | -0.72      | 0.40     | /     | /     | /     | /             |
|                                 | max.daily mean | -0.43 | -0.32     | /     | /     | /     | /      | -0.40     | -0.75 | -0.78      | 0.39     | /     | /     | /     | /             |
|                                 | min.daily mean | -0.44 | -0.37     | /     | /     | /     | /      | -0.45     | -0.75 | -0.65      | 0.41     | /     | /     | /     | /             |
| Humidity (%)                    | monthly mean   | -0.43 | -0.34     | -0.43 | -0.67 | -0.56 | -0.35  | /         | -0.68 | /          | /        | /     | -0.55 | -0.72 | /             |
|                                 | max.daily mean | /     | /         | /     | /     | -0.37 | -0.05  | /         | /     | /          | /        | /     | /     | /     | /             |
|                                 | min.daily mean | -0.50 | -0.60     | -0.68 | -0.38 | -0.45 | -0.66  | -0.63     | -0.82 | /          | /        | -0.63 | -0.53 | -0.70 | /             |
| Mean wind speed (m/s)           | /              | /     | /         | /     | 0.62  | /     | /      | 0.35      | 0.38  | /          | 0.47     | /     | 0.52  | 0.60  | /             |
| Precipitation amount (mm/month) | -0.32          | -0.43 | /         | /     | /     | /     | /      | -0.41     | -0.31 | /          | /        | /     | -0.37 | /     | /             |
| sunshine duration (hours/month) | /              | /     | /         | /     | /     | /     | /      | /         | /     | /          | 0.68     | /     | 0.58  | 0.62  | /             |
| Solar radiation (MJ/m2/month)   | /              | /     | /         | 0.46  | /     | /     | /      | /         | /     | -0.31      | /        | /     | /     | /     | /             |

Student Test with significance level at 0.05

### 3.4. Happo and Mondy sites

Both Happo and Mondy sites are located on high mountains in middle latitude regions (the altitude of Happo is 1850m, and Mondy, 2000m). The monthly and yearly mean ozone in Happo were the highest among all stations, and it had a good correlation with the Mondy station (>90%, as shown in Table 5). Good correlations for monthly mean ozone were also shown between these two stations and other stations in Japan (not include the southern stations and island stations) and in Korea.

The variations of ozone in Happo and Mondy were analyzed to investigate the relationships between ozone, NO<sub>x</sub> and meteorological conditions. It showed that the ozone in Happo and Mondy had the similar seasonal variations (high in spring and low in Summer), but the monthly mean ozone of Happo was about 28% higher than that of Mondy. In spring and winter, the daily mean ozone at the two stations has similar variations, but it appears ozone at Happo had a 3-6 days delay (as shown in Table 6). There was no obvious relationship between the high ozone in Happo and local NO<sub>x</sub> and temperature. Atmospheric transport and diffusion from stratosphere may be important causes of high ozone in Happo. The low ozone in summer is relative to transport from the Western Pacific ocean.

#### 3.4.1. Comparisons between ozone of the two stations

The Monthly ozone concentrations at Happo and Mondy site can be seen in Fig 4. Similar features were shown, with high ozone in spring and low ozone in summer, while in autumn there were small peaks. However, the monthly mean ozone of Happo (45-74ppb) was typically 4-20ppb higher than that of Mondy (34-61). In the past 3 years, the monthly mean ozone of Happo was 28% higher than that of Mondy. In October 2003, the difference was 53%.

Daily ozone concentrations at Happo and Mondy are showed in Fig.5. Rapid daily variations were found at Happo site, with the highest daily mean of 94ppb that appeared in spring (May 7th), which was five times of the lowest value of 18ppb (September 7th). Compared to Happo, ozone concentration at Mondy did not exhibit strong daily cycle, spring maximum daily value (84ppb) was three times of the lowest value (27ppb).

The daily cycle of ozone are shown in Fig.6. The daily variations in Happo were rapid in summer while slow in other seasons. In July, the daily highest value was twice of the lowest. However the variation was weaker than Happo. In July of summer, fluctuation in Happo (23-74ppb) was 1.6 times of Mondy (27-58). Daily variations of Happo were relatively weak in winter, with a fluctuation of 15%, and were rapid in the other seasons, with fluctuations of about 30%.

Although daily fluctuations were different, the two stations showed similar daily cycles. Correlation coefficients are shown in Table 6. In autumn and spring, there were good correlations between daily mean of Mondy and that of Happo 3-6 days later, which implies long range transport of ozone could be a contributing factor to both sites, ozone concentration in Happo was about 28% higher than that of Mondy, which implies that there must be other contributing sources, such as northeast Asia continent or stratospheric air mass intrusion. In summer, there were no obvious correlations between the two stations, and low ozone value in Happo was even lower than that of Mondy, which may be explained as transport of ozone from ocean. The second maximum of ozone in autumn is possibly caused by both the transport of higher ozone and its precursors from the polluted continent/ marine air masses.

#### 3.4.2. Ozone analysis in Happo

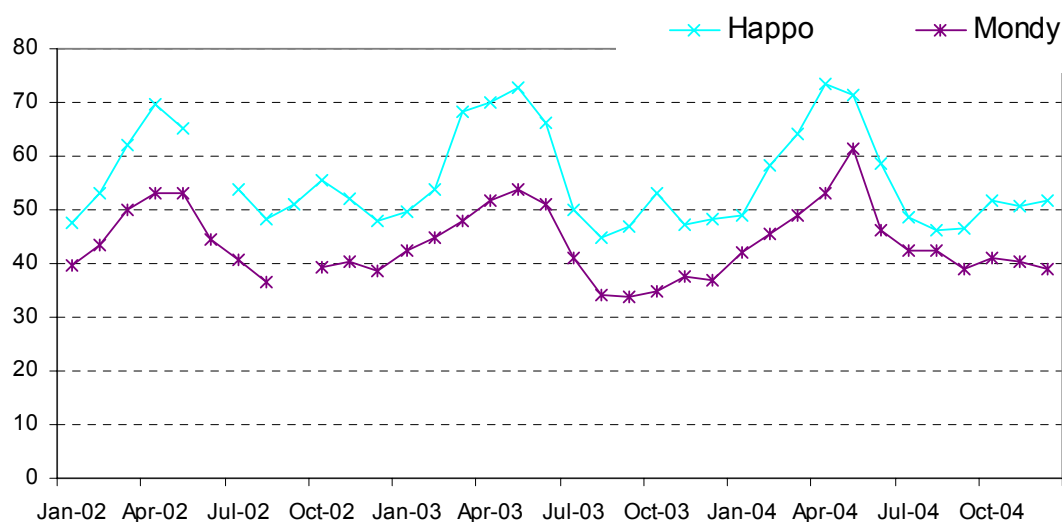
With respect to high ozone during 24 hours of a day at Happo, there appeared no obvious regularities in hourly variations for spring high ozone: no evidences of photochemical reactions (no obvious relationships between ozone and sunlight, temperature, etc.), little relationships between ozone and weather conditions. However, correlations were high between ozone and NO<sub>2</sub>, SO<sub>2</sub> or NO<sub>x</sub> in some cases, implying photochemistry. Several



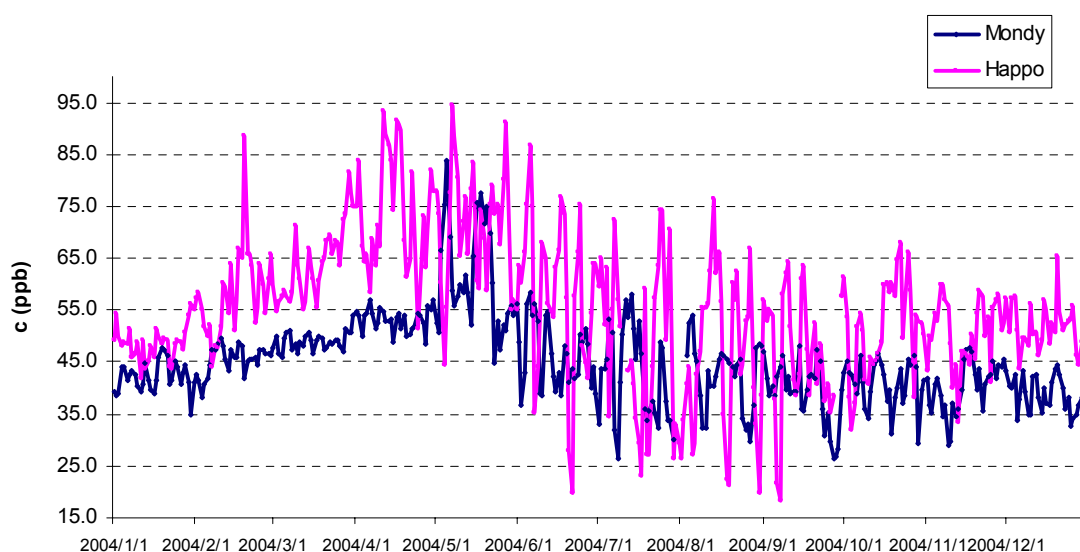
peaks appeared in April may be related to atmospheric transport from Mondy. And another cause of high ozone may be the transport from stratospheric ozone. This may explain the high value on 11, 16 and 18, April but not for 17 April, which had high moist and the stratospheric transport is not important.

### 3.4.3. Backward trajectories at Mondy site

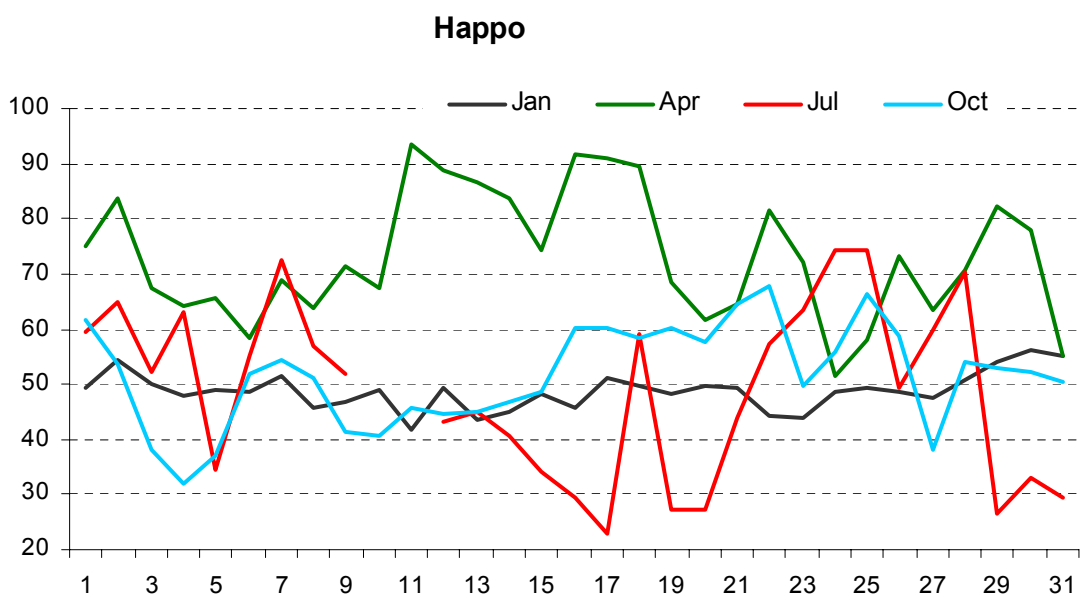
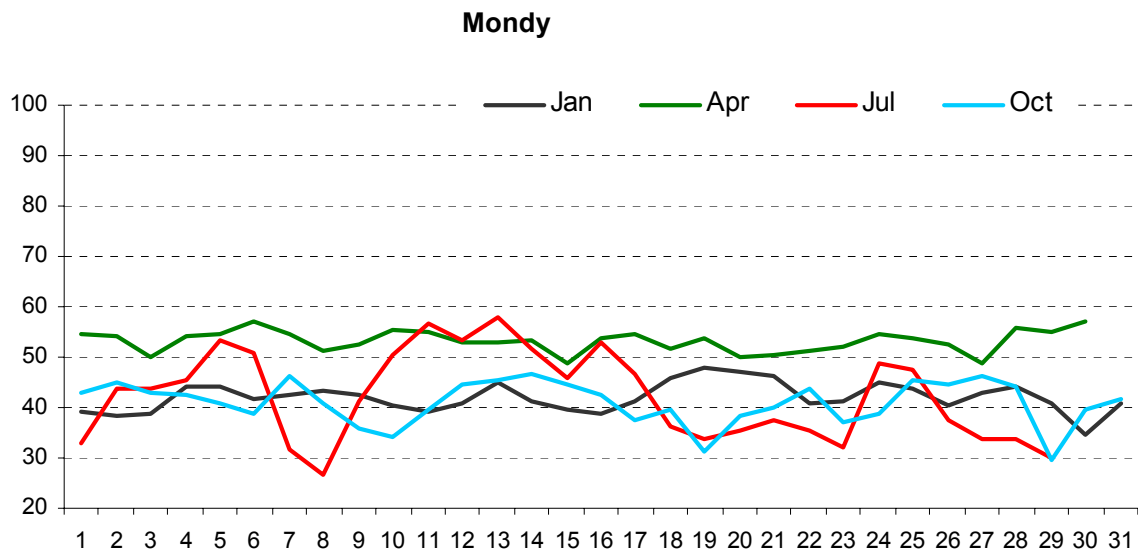
Backward trajectories at Mondy for the highest daily ozone concentration (5 May) was calculated. Three-days backward trajectory arriving at 50, 500 and 1000m above ground level are shown in Fig 8. According to the trajectories, the high ozone high may be caused by the subsiding and mixing of the ozone from the upper atmosphere. But the humidity on 5th is high, so it appears that the high ozone is not caused by dry air stratosphere intrusion, long range EURO-ASIA transport from Europe may be a likely reason for high ozone at Mondy during this day.



**Figure 4 Monthly ozone concentration at Mondy site and Haplo site.**



**Figure 5 Daily ozone concentration at Mondy site and Haplo site in 2004.**

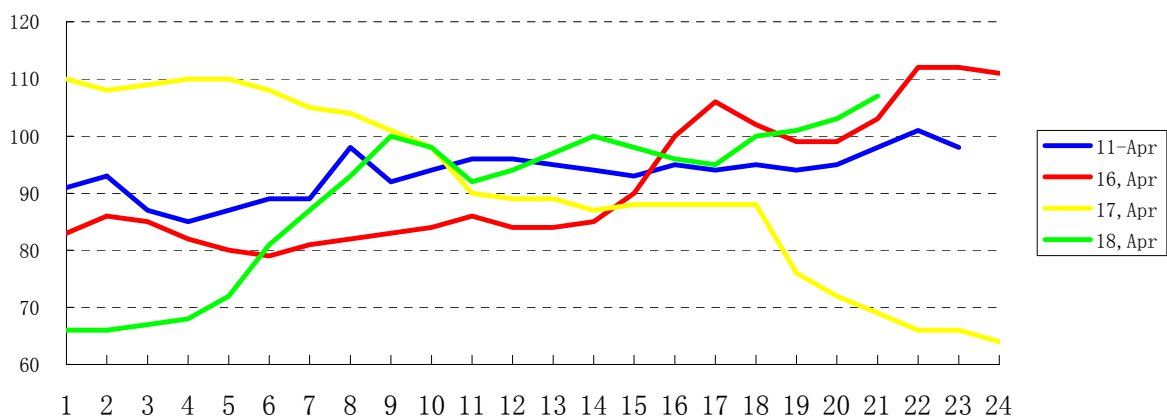


**Figure 6** Daily ozone concentration in different seasons at Mondy and Happo site of 2004.

**Table 6 Correlations between Happo and Mondy with daily mean ozone**

| Correlation coefficient |              | Mondy                                |                                |                                |
|-------------------------|--------------|--------------------------------------|--------------------------------|--------------------------------|
|                         |              | Form Dec,2003 to May 2004 (183 days) | Form Jun to Aug 2004 (93 days) | Form Sep to Nov 2004 (91 days) |
| Happo                   | Same period  | 0.52                                 | /                              | /                              |
|                         | After 1 day  | 0.57                                 | /                              | /                              |
|                         | After 2 day  | 0.63                                 | /                              | /                              |
|                         | After 3 day  | 0.65                                 | /                              | /                              |
|                         | After 4 day  | 0.63                                 | /                              | /                              |
|                         | After 5 day  | 0.63                                 | /                              | /                              |
|                         | After 6 day  | 0.65                                 | /                              | /                              |
|                         | After 7 day  | 0.61                                 | /                              | /                              |
|                         | After 8 day  | 0.59                                 | 0.26                           | /                              |
|                         | After 9 day  | 0.56                                 | 0.40                           | /                              |
|                         | After 10 day | 0.54                                 | 0.45                           | /                              |
|                         | After 11 day | 0.51                                 | 0.30                           | /                              |

Student Test with significance level at 0.05



**Figure 7 Twenty four hours change of high daily ozone concentration at Happo.**

**Table 7 Correlations between daily mean O<sub>3</sub> and meteorological parameters at Happo**

| Correlation coefficient | WS(m/s) | TEMP(°C) | HUM(%) | SUN<br>(cal/cm <sup>2</sup> h) | NO | NOx* | NO <sub>2</sub> |
|-------------------------|---------|----------|--------|--------------------------------|----|------|-----------------|
| A year (366 days)       | /       | /        | /      | /                              | /  | 0.39 | 0.42            |
| Mar-May (92 days)       | /       | /        | /      | /                              | /  | 0.52 | 0.54            |
| April (30 days)         | /       | /        | /      | /                              | /  | 0.66 | 0.67            |

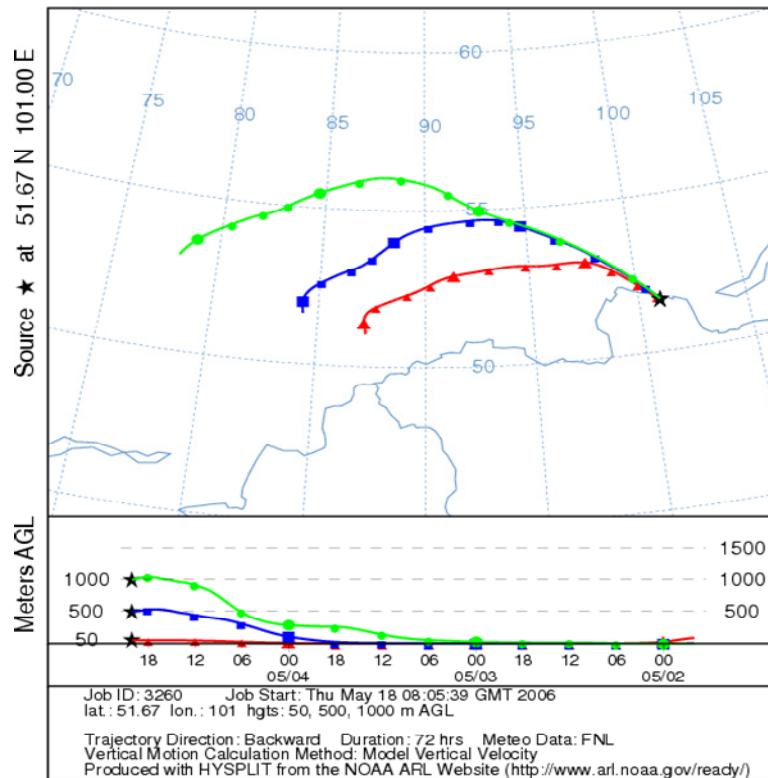
Student Test with significance level at 0.05

**Table 8 Correlations between hourly O<sub>3</sub> and other parameter at Happo with high concentration**

| Correlation coefficient | WS(m/s) | TEMP(°C) | HUM(%) | SUN<br>(cal/cm <sup>2</sup> h) | SO <sub>2</sub> | NO | NOx* | NO <sub>2</sub> |
|-------------------------|---------|----------|--------|--------------------------------|-----------------|----|------|-----------------|
| 11, Apr (24 hours)      | /       | /        | 0.62   | /                              | /               | /  | 0.86 | 0.85            |
| 16, Apr (24 hours)      | 0.65    | /        | /      | /                              | 0.90            | /  | /    | /               |
| 17, Apr (24 hours)      | -0.78   | /        | /      | /                              | 0.95            | /  | 0.68 | 0.70            |
| 18, Apr (24 hours)      | /       | 0.78     | /      | 0.46                           | 0.80            | /  | 0.92 | 0.91            |
| 16-18, Apr (72 hours)   | /       | /        | /      | /                              | 0.82            | /  | 0.54 | 0.55            |

Student Test with significance level at 0.05

NOAA HYSPLIT MODEL  
Backward trajectories ending at 20 UTC 04 May 04  
FNL Meteorological Data



NOAA HYSPLIT MODEL  
Backward trajectories ending at 12 UTC 05 May 04  
FNL Meteorological Data

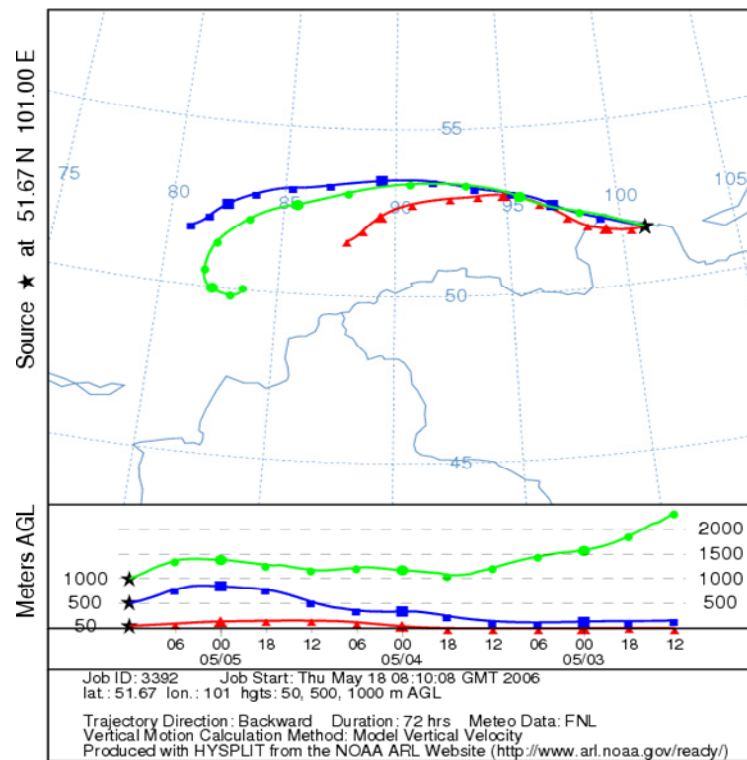


Figure 8 Backward trajectories at Mondy site during 5 May, 2004.

## Determination of Unanalyzed Components in Rainwater

Arcely Candelario Viernes<sup>1)\*</sup> and Jun Nagata<sup>2)</sup>

*1) Research and Development Division, Environmental Management Bureau (EMB),  
Department of Environment and Natural Resources (DENR)*

*\*Contact address: DENR Compound, Visayas Avenue, Diliman, Quezon City 1101,  
Philippines [e-mail: cely\_emb@yahoo.com]*

*2) Acid Deposition and Oxidant Research Center (ADORC)*

The determination of unanalyzed components in rainwater was conducted to assess which of these components are required for inclusion in the ionic balance in order to generate good quality data. Hydrogen carbonate ( $\text{HCO}_3^-$ ) and other minor anions fluoride ( $\text{F}^-$ ), bromide ( $\text{Br}^-$ ), nitrite ( $\text{NO}_2^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), hydrogen phosphate ( $\text{H}_2\text{PO}_4^-$ ), formate ( $\text{HCOO}^-$ ) and acetate ( $\text{CH}_3\text{COO}^-$ ) were determined in addition to the ten major parameters – EC, pH, sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), chloride ( $\text{Cl}^-$ ), ammonium ( $\text{NH}_4^+$ ), sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ) and calcium ( $\text{Ca}^{2+}$ ) in rainwater samples collected from the wet deposition monitoring sites of the Acid Deposition Monitoring Network in East Asia (EANET) in the Philippines. It was found that hydrogen carbonate has contributed a significant fraction to the major anions for the calculation of acceptable values of  $R_1$  and  $R_2$ . Nitrite, bromide and phosphate ions were also found to have concentrations that contributed to such values that were acceptable. The concentrations of eight species of heavy metals (Al, Cd, Cr, Cu, Pb, Mn, Ni and Zn) were likewise determined in the samples for future reference.

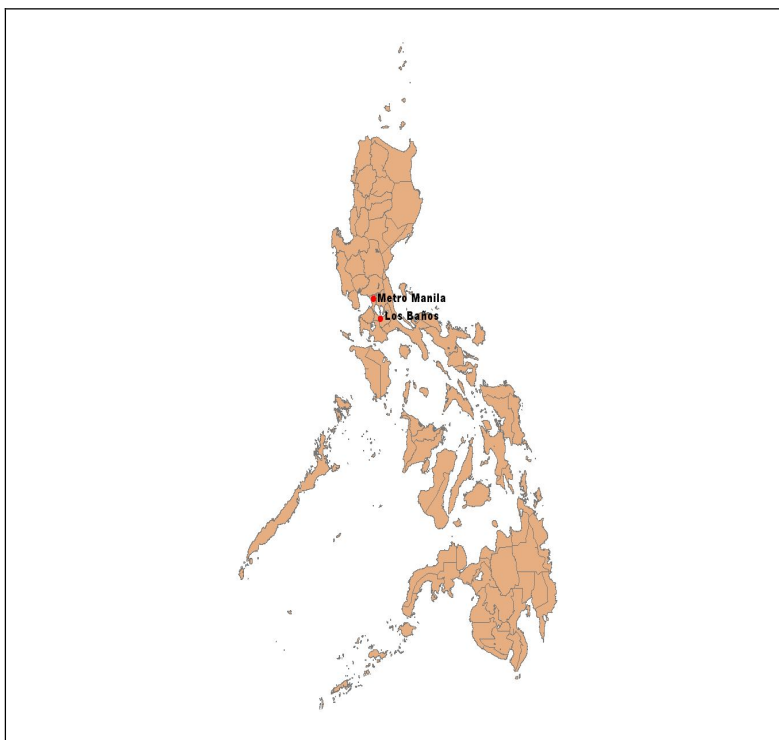
### 1. Introduction

As one of the ten countries that first established the Acid Deposition Monitoring Network in East Asia (EANET), the Philippines started its acid deposition monitoring activities during EANET's preparatory phase in 1998 – 2000. The Philippines has collected wet deposition monitoring data according to EANET's Technical Documents for Wet Deposition Monitoring in East Asia. Measurements of the ten major parameters: electrical conductivity, pH, the anions –  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , and the cations –  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  have always been conducted on every rainwater sample, except in rare cases when a sample is insufficient for analyses of all these major parameters. However, in many precipitation samples, ion balance ( $R_1$ ) and conductivity agreement ( $R_2$ ) were not always attained.

Quality assurance / quality control (QA/QC) plays a critical role in acid deposition monitoring as well as in other environmental measurements. In wet deposition monitoring, particularly in laboratory measurements, the ion balance, which is based on the principle of electroneutrality, and the electrical conductivity agreement, are the fundamental measures of data quality. In precipitation chemistry, the negative electric charge due to anions and the positive electric charge due to cations, are in equilibrium. Equilibrium is attained when the ratio between the total cations and total anions, in their equivalent units, is 1. EANET's Technical Documents for Wet Deposition Monitoring in East Asia and for Monitoring on Inland Aquatic Environment in East Asia identify the major parameters for analysis on such samples. Tables for  $R_1$  and  $R_2$  criteria are provided. When these criteria are not met, it is possible that unanalyzed components such as  $\text{HCO}_3^-$ ,  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Br}^-$  and  $\text{F}^-$  ions are present in rainwater sample. These components should then be included in the computation of  $R_1$  and  $R_2$ .

## 2. Experimental method

The rainwater samples used in this study were collected with the wet-only samplers installed at the EANET monitoring sites in the Philippines – Los Baños (LB) and Metro Manila (MM). Figure 1 shows the two monitoring sites, which represent rural site and urban site, respectively. Each sample was preserved in an ice chest after collection through transport to the Environmental Management Bureau Laboratory. A total of 35 samples, 20 from Los Baños and 15 from Metro Manila, these were unfiltered excesses of samples (each around 100 mL), collected from May 2005 to March 2006. These samples were preserved in the laboratory refrigerator. The samples were kept cool during transport from the EMB Laboratory to the Acid Deposition and Oxidant Research Center (ADORC) in Niigata, Japan, where the research fellowship was undertaken.



**Figure 1 Wet Deposition Monitoring Sites of EANET in the Philippines.**

Observing the EANET's Technical Documents for Wet Deposition Monitoring in East Asia, the determination of EC and pH were conducted prior to the measurements of the other parameters. Conductivity measurement was done with conductivity meter model EC Horiba DS-15 and the pH measurement was with pH meter model Horiba F-23. Then, an ample amount of each sample was filtered for the measurements of the other parameters by Ion chromatography (IC) method. The IC model DX-500 by Dionex Co. was used in the analyses of the cations  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The same IC model was used in the determination of the major anions  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  as well as of the following minor anions:  $\text{HCO}_3^-$ ,  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{F}^-$  and  $\text{Br}^-$ .

In the measurement of  $\text{HCO}_3^-$  by IC method, DX-500 was used with the ion-exchange-separation mode. With the good separation condition in the ion-exchange mode, simultaneous measurement of  $\text{HCO}_3^-$  and other inorganic anions were done. The  $\text{OH}^-$  eluent system with an anion self-regeneration suppressor (Dionex ASRS-2) was used for the analysis. In addition, freshly prepared standard solutions were used in the calibration of the instrument. Low concentration values could be easily affected by ambient air because dissolved ambient  $\text{CO}_2$  usually influences samples results in any batch of analysis. It was therefore necessary to get the instrument



determination limit.

In the EANET's Technical Document on Wet Deposition Monitoring in East Asia, the following formula shows the mole ratio of dissociated ion and not-dissociated ion in a sample:

$$\begin{aligned} [A^-] &= [HA] / [H^+] \times K_a \\ &= [H^+] \times 10^{pH - pK_a} \end{aligned} \quad (1)$$

where:

$$\begin{aligned} [A^-] &= \text{concentration of dissociated ion in sample} \\ [HA] &= \text{concentration of not-dissociated ion in sample} \\ K_a &= \text{dissociation coefficient.} \end{aligned}$$

But, in ion chromatography, the instrument is usually calibrated with total acid concentration. Thus, the determination value obtained is the total acid concentration of the sample. Following is the derivation of the equation used for the calculation of concentration of hydrogen carbonate. Similarly, this applies to phosphate and organic acids:

$$[A^-]_i = [A^-] + [HA] \quad (2)$$

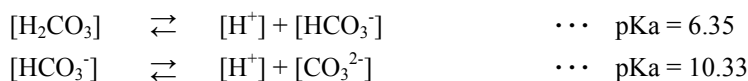
where:

$$[A^-]_i = \text{result of ion chromatograph (mol/L)}$$

From equations (1) and (2) the concentration of dissociated ions become,

$$[A^-] = 10^{pH} / (10^{pH} + 10^{pK_a}) \times [A^-]_i \quad (3)$$

The carbonates concentrations by IC method were calculated using Equation (10) below which is derived as follows:



$$[H_2CO_3]_{\text{total}} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (4)$$

The concentration of each component in sample would be calculated through the following Equations:

$$\begin{aligned} [H_2CO_3] &= [1 / \{1 + 10^{-6.35} / [H^+] + 10^{-16.68} / [H^+]^2\}] \times [H_2CO_3]_{\text{total}} \\ &= f_0 [H^+] \times [H_2CO_3]_{\text{total}} \end{aligned} \quad (5)$$

$$\begin{aligned} [HCO_3^-] &= [1 / \{[H^+] / 10^{-6.35} + 1 + 10^{-10.33} / [H^+]\}] \times [H_2CO_3]_{\text{total}} \\ &= f_1 [H^+] \times [H_2CO_3]_{\text{total}} \end{aligned} \quad (6)$$

$$\begin{aligned} [CO_3^{2-}] &= [1 / \{[H^+]^2 / 10^{-16.68} + [H^+] / 10^{-10.33} + 1\}] \times [H_2CO_3]_{\text{total}} \\ &= f_2 [H^+] \times [H_2CO_3]_{\text{total}} \end{aligned} \quad (7)$$

The equivalent concentration of carbonate in sample would then be,

$$\begin{aligned}
[\text{H}_2\text{CO}_3]_{\text{sample}} &= [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] \\
&= (f_1 [\text{H}^+] + 2 \times f_2 [\text{H}^+]) \times [\text{H}_2\text{CO}_3]_{\text{total}}
\end{aligned} \quad (8)$$

$$[\text{H}_2\text{CO}_3]_{\text{total}} = [\text{H}_2\text{CO}_3]_i \quad (9)$$

By substitution, Equation (8) becomes,

$$[\text{H}_2\text{CO}_3]_{\text{sample}} = (f_1 [\text{H}^+] + 2 \times f_2 [\text{H}^+]) \times [\text{H}_2\text{CO}_3]_i \quad (10)$$

Hydrogen carbonate determination was also conducted using the Total Organic Carbon (TOC) method for the purpose of comparison. TOC 5000A analyzer (Shimadzu) was used for the measurement. TOC analyzer is usually used for the measurement of inorganic carbon or total carbonate, which comprises  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . In the TOC method, inorganic carbon is acidified, purged, and finally changed to  $\text{CO}_2$ , and then detected by non-dispersive infrared gas detector. In the conduct of the analysis, the contamination of ambient  $\text{CO}_2$  to the standard solution was minimized through the use of freshly prepared standard solutions for calibration. In addition, the regression line of calibration was shifted to the zero intercept to deduct the amount of  $\text{CO}_2$  contamination from the calibrated value. TOC analyzer generates  $\text{CO}_2$  concentration equivalent to total carbonate in a sample. Thus, the concentration of  $\text{HCO}_3^-$  was calculated using the following equation:

$$[\text{HCO}_3^-] (\text{mgL}^{-1}) = C \times b \times 1.387 \quad (11)$$

where:

C = concentration of  $\text{CO}_2$  ( $\text{mgL}^{-1}$ )

b = mole ratio of  $\text{HCO}_3^-$  to total carbonate

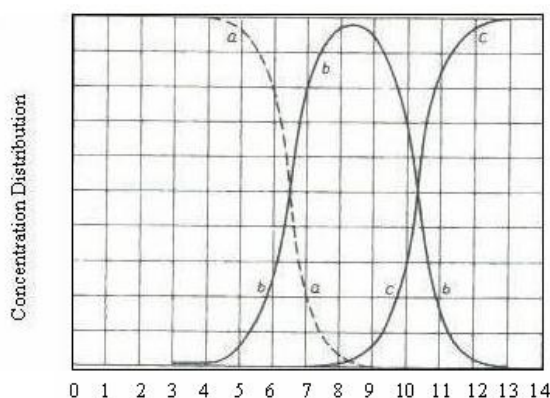
1.387: coefficient of conversion of the total carbonate to hydrogen carbonate ion equivalent, (61.02/44.01).

The concentration distribution of carbonate relative to pH is shown in Table 1. Figure 2 indicates the respective mole ratios of carbonic acid, hydrogen carbonate ion and carbonate ion relative to total carbonate in Table 1 (Japanese Industrial Standards (JIS) K0101 25.1 (Japanese Standard Association, 1998), Table 25.1 and Figure 25.2).

**Table 1 Concentration distribution of total carbonate relative to pH**

| PH  | Concentration distribution (25°C) |                        |                          | PH   | Concentration distribution (25°C) |                        |                          |
|-----|-----------------------------------|------------------------|--------------------------|------|-----------------------------------|------------------------|--------------------------|
|     | a ( $\text{H}_2\text{CO}_3$ )     | b ( $\text{HCO}_3^-$ ) | c ( $\text{CO}_3^{2-}$ ) |      | a ( $\text{H}_2\text{CO}_3$ )     | b ( $\text{HCO}_3^-$ ) | C ( $\text{CO}_3^{2-}$ ) |
| 2.0 | 1.000 0                           | –                      | –                        | 8.0  | 0.022 6                           | 0.972 8                | 0.004 6                  |
| 2.5 | 0.999 9                           | 0.000 1                | –                        | 8.5  | 0.007 2                           | 0.978 3                | 0.014 5                  |
| 3.0 | 0.999 6                           | 0.000 4                | –                        | 9.0  | 0.002 2                           | 0.953 0                | 0.044 8                  |
| 3.5 | 0.998 6                           | 0.001 4                | –                        | 9.5  | 0.000 6                           | 0.870 1                | 0.129 3                  |
| 4.0 | 0.995 7                           | 0.004 3                | –                        | 10.0 | 0.000 2                           | 0.680 1                | 0.319 7                  |
| 4.5 | 0.986 6                           | 0.013 4                | –                        | 10.5 | 0.000 0                           | 0.402 2                | 0.507 8                  |
| 5.0 | 0.958 7                           | 0.041 3                | –                        | 11.0 | –                                 | 0.175 4                | 0.824 6                  |

|     |         |         |         |      |   |         |         |
|-----|---------|---------|---------|------|---|---------|---------|
| 5.5 | 0.880 0 | 0.120 0 | –       | 11.5 | – | 0.063 0 | 0.937 0 |
| 6.0 | 0.698 8 | 0.301 2 | 0.000 0 | 12.0 | – | 0.020 8 | 0.979 2 |
| 6.5 | 0.423 2 | 0.576 7 | 0.000 1 | 12.5 | – | 0.006 7 | 0.993 3 |
| 7.0 | 0.188 3 | 0.811 3 | 0.000 4 | 13.0 | – | 0.002 1 | 0.997 9 |
| 7.5 | 0.068 3 | 0.930 3 | 0.001 4 |      |   |         |         |



**Figure 2** Curve on mole ratios of carbonic acid, hydrogen carbonate ion and carbonate ion relative to total carbonate in Table 1 and of pH (25°C) of a sample. a:  $\text{H}_2\text{CO}_3$ , b:  $\text{HCO}_3^-$ , c:  $\text{CO}_3^{2-}$

For additional comparison purposes, the determination of hydrogen carbonate by titration method was also conducted. The Gran's Plot titration method was used instead of the alkalinity method (the end-point, pH4.8) because the former method requires a smaller amount of sample for analysis than the latter one. Similar to alkalinity method, the Gran's plot method is also a kind of potentiometric titration method, but the difference is the way to get the volume of acid added. In the Gran's plot method, a high precision pH meter and a micropipette are required. The pH and potential inclination of a 10-mL of sample were first determined. Then a 0.05 mL of 0.02N  $\text{H}_2\text{SO}_4$  was added to the sample and the corresponding potential inclination was recorded. The same addition of acid 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  $[\text{H}^+]$  was prepared for every sample. The volume of sulfuric acid added was determined at the x-intercept of the regression line. As the linearity of regression line is most important in this method, the selection of plot points could give large difference for determination values. 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.

The concentrations of 8 species of heavy metals (aluminum, cadmium, chromium, copper, lead, manganese, nickel and zinc) were also determined on the rainwater samples with the use of Inductively Coupled Plasma-Mass Spectrometer model SPQ 9000 Plasma Quadrupole Mass Analyzer. The standard solutions for calibration of the instrument were freshly prepared. Optimization of the instrument was done before the analysis of the filtered samples.

### 3. Results and discussion

#### 3.1. Major parameters

Of the total thirty-five samples determined for the ten major parameters – EC, pH,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$ , five did not meet the ion balance ( $R_1$ ) and six did not meet the electrical conductivity agreement ( $R_2$ ). Repeat measurements on the samples with unacceptable  $R_1$  and  $R_2$  were done, and still two samples had unacceptable  $R_1$  (one in each site) and with one unacceptable  $R_2$  in Metro Manila. Table 2 shows the data on the ten major parameters. EC values ranged from 0.324 – 3.56 and 0.526 – 6.570 in Los Baños and Metro Manila, respectively. The values of pH were of the range 4.269 – 6.378 and 4.675 – 6.900 in Los Baños and Metro Manila, respectively. It is noticeable from the Table that Metro Manila, an urban site, has generally higher mean concentrations of the major ions, except for  $\text{Cl}^-$  and  $\text{Na}^+$ , as compared with those of Los Baños.

It could be observed that the unacceptable  $R_1$  have values significantly greater than zero and pH greater than 6. With this information, the ion imbalance was indicative of the presence of some significant but undetermined ionic species in the samples. A calculated concentration of hydrogen carbonate based on the equilibrium between ambient  $\text{CO}_2$  and dissolved  $\text{HCO}_3^-$  using the equation  $[\text{HCO}_3^-](\text{neq/mL}) = 1.24 \times 10^{(\text{pH}-5.35)}$  (EANET 2000a, 2000b, 2000c; Noguchi and Hara 2004) is integrated in the computation of the ion balance,  $R_1$  in the EANET Data Reporting Procedures and Formats, Form (Wet A). However, this calculation does not always apply especially for samples with pH value of 6.000 or greater. It is therefore important to evaluate the  $\text{HCO}_3^-$  concentration with actual determination. If the determined concentration differs from the calculated value, the former should be included in the computation of  $R_1$  and  $R_2$  in order to obtain values within the EANET's required criteria for  $R_1$  and  $R_2$  (EANET 2000a, 2000b). Likewise,  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{F}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{H}_2\text{PO}_4^-$  may be considered in the evaluation of  $R_1$  and  $R_2$ .

**Table 2 Values/concentration of major parameters in Los Baños and Metro Manila**

| Sample | Sampling period |          | Precipitation | EC,<br>mS/m   | pH    | SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | Cl <sup>-</sup> | NH <sub>4</sub> <sup>+</sup> | Na <sup>+</sup> | K <sup>+</sup> | Mg <sup>2+</sup> | Ca <sup>2+</sup> | Anions | Cations | R <sub>1</sub> | R <sub>2</sub> |
|--------|-----------------|----------|---------------|---------------|-------|-------------------------------|------------------------------|-----------------|------------------------------|-----------------|----------------|------------------|------------------|--------|---------|----------------|----------------|
|        |                 |          |               |               |       |                               |                              |                 |                              |                 |                |                  |                  |        |         |                |                |
|        | Code            | Start    | End           | Amount,<br>mm |       |                               |                              |                 |                              |                 |                |                  |                  |        |         |                |                |
| LB 01  | 05/25/05        | 06/01/05 | 41.6          | 1.985         | 4.576 | 20.6                          | 29.4                         | 8.69            | 29.7                         | 8.05            | 2.15           | 1.48             | 1.04             | 79.3   | 71.5    | -5.2           | -3.9           |
| LB 02  | 9/14/05         | 09/22/05 | 106.9         | 0.488         | 5.195 | 5.40                          | 0.92                         | 5.13            | 0.78                         | 3.96            | 1.61           | 1.23             | 1.77             | 16.9   | 18.7    | 5.3            | -6.7           |
| LB 03  | 9/22/05         | 09/28/05 | 50.0          | 0.611         | 5.276 | 7.65                          | 5.26                         | 7.02            | 10.4                         | 6.26            | 1.59           | 1.40             | 1.92             | 27.6   | 30.2    | 4.5            | -4.7           |
| LB 04  | 9/28/05         | 10/05/05 | 37.2          | 0.982         | 5.717 | 11.0                          | 8.82                         | 33.0            | 16.9                         | 29.5            | 10.3           | 2.59             | 3.22             | 63.9   | 70.2    | 4.7            | -0.5           |
| LB 05  | 10/5/05         | 10/12/05 | 43.4          | 1.091         | 4.795 | 11.8                          | 12.2                         | 3.70            | 11.3                         | 2.65            | 0.793          | 1.48             | 2.22             | 39.5   | 38.2    | -1.6           | -3.9           |
| LB 06  | 10/19/05        | 10/27/05 | 71.5          | 0.594         | 5.480 | 4.84                          | 3.13                         | 21.3            | 4.21                         | 18.5            | 2.05           | 2.26             | 2.12             | 34.1   | 36.8    | 3.9            | -2.4           |
| LB 07  | 10/27/05        | 11/03/05 | 91.8          | 0.388         | 5.532 | 2.57                          | 1.05                         | 11.2            | 2.38                         | 9.66            | 0.921          | 1.32             | 0.649            | 17.4   | 19.8    | 6.5            | -7.7           |
| LB 08  | 10/27/05        | 11/03/05 | 91.8          | 0.394         | 5.518 | 4.08                          | 2.50                         | 4.74            | 2.77                         | 4.39            | 0.665          | 1.44             | 1.82             | 15.4   | 17.4    | 6.1            | -12.0          |
| LB 09  | 11/23/05        | 11/30/05 | 62.9          | 1.143         | 4.806 | 15.2                          | 1.42                         | 13.6            | 5.16                         | 13.5            | 0.844          | 2.14             | 3.17             | 45.4   | 45.7    | 0.4            | -3.1           |
| LB 10  | 11/30/05        | 12/07/05 | 126.8         | 0.324         | 5.760 | 3.06                          | 1.29                         | 6.69            | 5.71                         | 6.18            | 1.23           | 1.32             | 1.25             | 14.1   | 20.0    | 17.3           | -7.1           |
| LB 11  | 11/30/05        | 12/07/05 | 126.8         | 0.360         | 5.918 | 3.25                          | 1.42                         | 7.95            | 5.04                         | 9.70            | 1.07           | 1.44             | 1.77             | 15.9   | 23.4    | 19.3           | -10.0          |
| LB 12  | 12/7/05         | 12/14/05 | 214.0         | 0.431         | 5.776 | 2.48                          | 1.13                         | 17.8            | 3.27                         | 15.7            | 0.665          | 1.97             | 1.25             | 23.9   | 27.8    | 7.6            | -5.4           |
| LB 13  | 12/14/05        | 12/23/05 | 52.3          | 0.997         | 6.378 | 4.28                          | 2.79                         | 46.8            | 6.65                         | 68.3            | 1.59           | 3.66             | 1.55             | 71.4   | 87.4    | 10.1           | -0.8           |
| LB 14  | 12/28/05        | 01/11/06 | 33.8          | 0.729         | 5.821 | 3.48                          | 2.52                         | 34.4            | 3.27                         | 31.0            | 1.27           | 3.97             | 3.52             | 43.9   | 52.0    | 8.4            | -4.8           |
| LB 15  | 1/11/06         | 01/18/06 | 26.4          | 1.426         | 6.063 | 7.92                          | 3.61                         | 55.3            | 10.8                         | 49.1            | 3.12           | 6.09             | 4.80             | 81.1   | 85.6    | 2.7            | -12.7          |
| LB 16  | 1/18/06         | 01/25/06 | 44.0          | 0.532         | 5.906 | 4.54                          | 2.98                         | 15.0            | 3.84                         | 13.6            | 0.995          | 2.64             | 4.42             | 27.1   | 33.8    | 11.1           | -10.1          |

|       |          |          |       |       |       |      |       |       |       |      |       |      |      |       |       |      |       |
|-------|----------|----------|-------|-------|-------|------|-------|-------|-------|------|-------|------|------|-------|-------|------|-------|
| LB 17 | 1/25/06  | 02/01/06 | 36.1  | 0.541 | 5.442 | 6.61 | 2.21  | 11.5  | 7.21  | 9.79 | 0.665 | 1.77 | 1.72 | 26.9  | 28.3  | 2.4  | -5.8  |
| LB 18 | 2/1/06   | 02/08/06 | 19.8  | 3.560 | 4.269 | 14.7 | 6.16  | 120.5 | 7.66  | 72.0 | 3.08  | 6.36 | 3.90 | 156.0 | 157.1 | 0.4  | 1.1   |
| LB 19 | 2/8/06   | 02/15/06 | 9.8   | 1.402 | 6.008 | 6.93 | 3.30  | 70.1  | 9.70  | 70.9 | 3.20  | 6.58 | 4.42 | 92.9  | 106.7 | 6.9  | -3.6  |
| LB 20 | 3/7/06   | 03/15/06 | 32.7  | 0.663 | 5.363 | 8.30 | 5.14  | 12.0  | 10.6  | 13.4 | 1.51  | 1.73 | 1.77 | 33.8  | 36.8  | 4.3  | -4.3  |
| MM 01 | 5/26/05  | 06/02/05 | 110.1 | 2.530 | 4.677 | 36.6 | 42.6  | 12.4  | 56.5  | 9.22 | 2.66  | 2.47 | 12.1 | 128.2 | 118.6 | -3.9 | -3.5  |
| MM 02 | 6/2/05   | 06/09/05 | 255.9 | 0.751 | 5.281 | 9.32 | 4.14  | 13.3  | 10.7  | 11.8 | 2.07  | 1.85 | 2.40 | 36.1  | 38.3  | 2.9  | -6.1  |
| MM 03 | 8/4/05   | 08/12/05 | 143.0 | 1.347 | 5.745 | 16.3 | 4.32  | 51.6  | 22.01 | 44.4 | 4.04  | 5.14 | 3.79 | 88.6  | 90.1  | 0.8  | -3.1  |
| MM 04 | 8/18/05  | 08/24/05 | 41.9  | 2.470 | 4.675 | 38.2 | 32.4  | 10.2  | 58.8  | 7.05 | 2.92  | 2.02 | 8.43 | 119.1 | 110.8 | -3.6 | -4.4  |
| MM 05 | 9/14/05  | 09/22/05 | 130.1 | 0.855 | 5.229 | 14.4 | 2.64  | 10.3  | 11.5  | 9.70 | 5.65  | 1.48 | 3.49 | 41.7  | 42.7  | 1.2  | -5.7  |
| MM 06 | 9/14/05  | 09/22/05 | 130.1 | 0.526 | 5.310 | 8.36 | 2.06  | 4.99  | 9.65  | 5.48 | 2.02  | 1.48 | 2.40 | 23.8  | 29.8  | 11.2 | -1.1  |
| MM 07 | 9/22/05  | 09/28/05 | 32.4  | 1.749 | 5.160 | 31.6 | 15.8  | 24.6  | 50.4  | 21.7 | 5.06  | 3.21 | 6.89 | 103.7 | 104.3 | 0.3  | -2.1  |
| MM 08 | 10/20/05 | 10/28/05 | 143.4 | 0.579 | 5.263 | 7.07 | 0.435 | 8.07  | 0.83  | 3.65 | 4.53  | 1.44 | 4.84 | 22.6  | 27.0  | 8.8  | -7.8  |
| MM 09 | 10/28/05 | 11/03/05 | 62.6  | 1.695 | 6.258 | 24.2 | 33.9  | 9.62  | 75.4  | 7.13 | 5.70  | 1.89 | 12.5 | 101.8 | 117.6 | 7.2  | -4.3  |
| MM 10 | 11/3/05  | 11/10/05 | 20.6  | 1.641 | 6.000 | 28.9 | 18.5  | 31.6  | 40.2  | 17.6 | 5.68  | 3.74 | 23.9 | 108.0 | 119.7 | 5.1  | -1.4  |
| MM 11 | 11/24/05 | 12/01/05 | 39.8  | 2.040 | 5.053 | 32.5 | 45.0  | 8.29  | 64.3  | 3.35 | 2.89  | 2.39 | 16.6 | 118.2 | 117.3 | -0.4 | -2.8  |
| MM 12 | 12/8/05  | 12/15/05 | 52.1  | 0.799 | 6.030 | 14.8 | 6.45  | 8.66  | 22.9  | 7.39 | 1.33  | 2.14 | 9.21 | 50.6  | 55.3  | 4.4  | -3.4  |
| MM 13 | 12/22/05 | 12/28/05 | 11.2  | 0.736 | 5.855 | 9.30 | 6.69  | 11.8  | 1.27  | 11.8 | 2.46  | 3.95 | 10.5 | 37.1  | 45.8  | 10.5 | -11.8 |
| MM 14 | 1/25/06  | 02/02/06 | 7.0   | 1.181 | 5.513 | 25.0 | 9.85  | 8.35  | 36.8  | 6.66 | 2.25  | 1.56 | 9.13 | 68.2  | 70.1  | 1.4  | -4.6  |
| MM 15 | 3/10/06  | 03/16/06 | 33.6  | 6.57  | 6.900 | 40.6 | 17.9  | 41.2  | 302.1 | 37.6 | 79.5  | 19.5 | 72.6 | 184.3 | 603.6 | 53.2 | -10.8 |

### 3.2. Hydrogen carbonate ion

In order to improve the ion balance, hydrogen carbonate was determined. With the IC method, the concentrations were found to range from 0.043 to 15.12  $\mu\text{mol/L}$  and 0.000 to 351.20  $\mu\text{mol/L}$  in Los Baños and Metro Manila, respectively. Table 3 shows the concentrations of the minor ions determined. The highest concentration in Metro Manila was extremely high as compared to all the other concentrations. It had also the highest pH value at 6.900. It was observed that samples with low pH have lower concentrations than those with high pH.

By the TOC method,  $\text{HCO}_3^-$  concentrations were of the range 0.340 – 16.0  $\mu\text{mol/L}$  and 0.659 – 327.41  $\mu\text{mol/L}$  in Los Baños and Metro Manila, respectively. The extremely high concentration was the same sample as that determined with the IC method.

A plot of the  $\text{HCO}_3^-$  concentrations determined by IC of the 6 samples with pH values of 6.000 and greater versus their corresponding calculated values (Figure 3), shows a slope that is remarkably greater than 1. Similar slope is attained with the plot of  $\text{HCO}_3^-$  concentrations by TOC method versus the calculated values (Figure 4). The slopes indicate that the calculated values were extremely low compared with the determined concentrations. It is therefore necessary to conduct an actual  $\text{HCO}_3^-$  determination on samples with high concentration, generally on samples with pH values towards 6.000 and greater.

With the plot of all the samples' concentrations of TOC versus those of IC,  $R^2 = 0.9983$  (Figure 5). Plotting the same but excluding the extremely high concentration Figure 6,  $R^2 = 0.6506$ . Furthermore, the percent difference of TOC and IC versus the pH values were plotted (Figure 7). It is observed that samples with pH near the value of 6.000 had low differences in their concentrations. Of the eight samples with pH ranging from 5.906 to 6.900, seven were within the percent difference range of -3 to 19. The samples with pH lower than 5.906 had high percent differences with the range of 30 – 100 %. It is also observed in Table 3 that almost all the  $\text{HCO}_3^-$  concentrations by TOC method are higher than those by IC method. Possible reasons of the differences in concentrations determined between the methods IC and TOC are: 1) possible high or low estimates of the mole

ratios based on curve b in Figure 2 and 2) ambient CO<sub>2</sub> contamination. The percent difference in concentrations between IC and TOC methods is low when pH value is near towards 6.000 or greater. Thus, depending on the availability of instrument, either the IC method or the TOC method is applicable in the determination of hydrogen carbonates on samples with pH values around 6.000.

**Table 3 Concentrations of minor anions in Los Baños and Metro Manila**

| Sample Code | PH    | HCO <sub>3</sub> <sup>-</sup><br>μmol/L (TOC) | HCO <sub>3</sub> <sup>-</sup><br>μmol/L (IC) | HCOO <sup>+</sup><br>μmol/L | CH <sub>3</sub> COO <sup>+</sup><br>μmol/L | NO <sub>2</sub> <sup>-</sup><br>μmol/L | PO <sub>4</sub> <sup>3-</sup><br>μmol/L | Br <sup>-</sup><br>μmol/L | F <sup>-</sup><br>μmol/L |
|-------------|-------|---|--|-----------------------------|--|--|---|---------------------------|--------------------------|
| LB 01       | 4.576 | 0.60  | 0.043  | *                           | *  | 0.152                                  | 0.28                                    | 0.11                      | *                        |
| LB 02       | 5.195 | 2.59  | 0.34   | *                           | *  | *                                      | *                                       | 0.10                      | *                        |
| LB 03       | 5.276 | 2.63  | 0.42   | *                           | *  | 0.24                                   | *                                       | 0.10                      | *                        |
| LB 04       | 5.717 | 4.45  | 1.45   | 0.44                        | *  | 0.17                                   | 0.32                                    | 0.13                      | *                        |
| LB 05       | 4.795 | 0.92  | 0.09   |                             | *  | 0.28                                   |   | 0.10                      | *                        |
| LB 06       | 5.480 | 2.77  | 0.84   | 0.33                        | *  | 0.23                                   | 0.28                                    | 0.13                      | *                        |
| LB 07       | 5.532 | 2.92  | 0.75   | *                           | *  | *                                      |   | 0.11                      | *                        |
| LB 08       | 5.518 | 3.19  | 0.8  | *                           | *  | 0.13                                   | 0.32                                    | 0.10                      | *                        |
| LB 09       | 4.806 | 0.72  | 0.08   | *                           | *  | 0.11                                   | *                                       | 0.11                      | *                        |
| LB 10       | 5.760 | 4.22  | 1.83   | *                           | *  | 0.20                                   | *                                       | 0.10                      | *                        |
| LB 11       | 5.918 | 2.53  | 2.7  | *                           | *  | 0.26                                   | *                                       | 0.10                      | *                        |
| LB 12       | 5.776 | 4.67  | 1.45   | *                           | *  | 0.20                                   | *                                       | 0.12                      | *                        |
| LB 13       | 6.378 | 15.96   | 15.12  | *                           | *  | 0.17                                   | *                                       | 0.15                      | *                        |
| LB 14       | 5.821 | 9.08  | 2.55   | *                           | *  | 0.20                                   | *                                       | 0.14                      | *                        |
| LB 15       | 6.063 | 4.00  | 3.98   | *                           | *  | 0.50                                   | *                                       | 0.18                      | *                        |
| LB 16       | 5.906 | 4.40  | 3.22   | *                           | *  | 0.24                                   | *                                       | 0.11                      | *                        |
| LB 17       | 5.442 | 2.29  | 1.12   | *                           | *  | 0.15                                   | *                                       | 0.13                      | *                        |
| LB 18       | 4.269 | 0.34  | 0.08   | *                           | *  | 0.37                                   | *                                       | 0.18                      | *                        |
| LB 19       | 6.008 | 5.49  | 3.72   | *                           | *  | *                                      | *                                       | 0.26                      | *                        |
| LB 20       | 5.363 | 2.95  | 0.24   | *                           | *  | 0.26                                   | *                                       | 0.11                      | *                        |
| Minimum     | 4.269 | 0.34  | 0.043  | 0.33                        |  | 0.11                                   | 0.28                                    | 0.10                      |                          |
| Maximum     | 6.378 | 15.96   | 15.12  | 0.44                        |  | 0.50                                   | 0.32                                    | 0.26                      |                          |
| Mean        | 5.480 | 3.84  | 2.04   |                             |  | 0.23                                   | 0.30                                    | 0.13                      |                          |
|             |       |   |  |                             |  |  |   |                           |                          |
| Sample Code | PH    | HCO <sub>3</sub> <sup>-</sup><br>μmol/L (TOC) | HCO <sub>3</sub> <sup>-</sup><br>μmol/L (IC) | HCOO <sup>+</sup><br>μmol/L | CH <sub>3</sub> COO <sup>+</sup><br>μmol/L | NO <sub>2</sub> <sup>-</sup><br>μmol/L | PO <sub>4</sub> <sup>3-</sup><br>μmol/L | Br <sup>-</sup><br>μmol/L | F <sup>-</sup><br>μmol/L |
| MM 01       | 4.677 | 0.66  | 0.00   | *                           | *  | 0.4129537                              | 0.28                                    | 0.11                      | *                        |
| MM 02       | 5.281 | 2.49  | 0.24   | *                           | *  | 0.28                                   | *                                       | 0.11                      | *                        |
| MM 03       | 5.745 | 7.75  | 0.21   | *                           | *  | 0.63                                   | *                                       | 0.16                      | *                        |
| MM 04       | 4.675 | 0.91  | 0.00   | *                           | *  | 0.63                                   | 0.38                                    | 0.11                      | *                        |
| MM 05       | 5.229 | 2.60  | 0.10   | *                           | *  | 0.48                                   | *                                       | 0.11                      | *                        |
| MM 06       | 5.310 | 2.43  | 0.11   | 0.28                        | *  | 0.50                                   | *                                       | 0.10                      | *                        |
| MM 07       | 5.160 | 2.76  | 0.12   | *                           | *  | 1.22                                   | *                                       | 0.14                      | *                        |

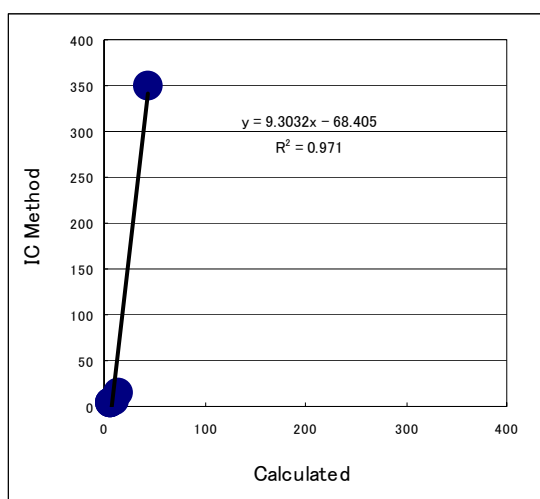
|         |       |        |        |       |   |       |      |      |   |
|---------|-------|--------|--------|-------|---|-------|------|------|---|
| MM 08   | 5.263 | 2.44   | 0.19   | *     | * | *     | *    | 0.10 | * |
| MM 09   | 6.258 | 16.65  | 5.56   | *     | * | 1.87  | 1.29 | 0.10 | * |
| MM 10   | 6.000 | 9.30   | 9.60   | *     | * | 1.72  | 0.35 | 0.13 | * |
| MM 11   | 5.053 | 1.42   | 0.08   | *     | * | 1.24  | *    | 0.11 | * |
| MM 12   | 6.030 | 6.77   | 3.68   | 0.47  | * | 1.93  | *    | 0.11 | * |
| MM 13   | 5.855 | 5.51   | 1.90   | *     | * | 0.13  | *    | 0.10 | * |
| MM 14   | 5.513 | 3.27   | 0.43   | *     | * | 1.26  | *    | 0.11 | * |
| MM 15   | 6.900 | 327.41 | 351.20 | *     | * | 1.80  | 50.6 | 0.13 | * |
| Minimum | 4.675 | 0.66   | 0.00   | 0.284 |   | 0.130 | 0.28 | 0.10 |   |
| Maximum | 6.900 | 327.4  | 351.2  | 0.47  |   | 1.9   | 50.6 | 0.2  |   |
| Mean    | 5.530 | 26.2   | 24.9   |       |   | 1.0   | 10.6 | 0.12 |   |

\* Less than the determination limit

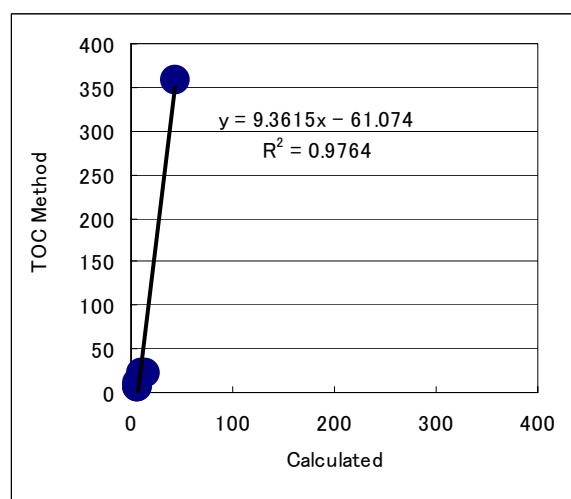
The values of  $\text{PO}_4^{3-}$  and  $\text{HCOO}^-$  were calculated through dissociated ions by pKa and pH.

Computing for the values of  $R_1$  and  $R_2$  with the inclusion of the results of bicarbonate ion of either method gave better results but unacceptable values still existed. This condition indicates that there are other minor anions that should be determined.

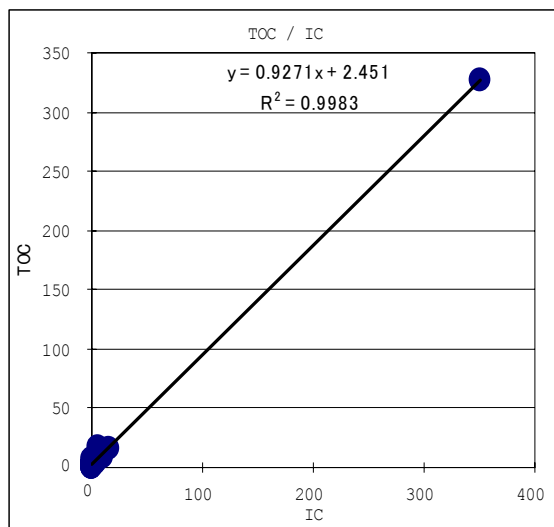
With the Gran's Plot method, overall hydrogen carbonate concentrations were found to range from 0.000 to 293.7  $\mu\text{mol/L}$ . The sample (MM-15) with the highest concentration (data is shown in Table 4 and Figure 8) was the same sample as that in the other two methods but of lower value. The rest of the determined concentrations were not comparable to the results of either IC or TOC. When a sample has a high pH value, say 6 or greater, this method could be used to determine the  $\text{HCO}_3^-$  concentration. The Gran's Plot method is not recommended for bicarbonate determination on samples of low pH, which would yield unreliable results. It is therefore better to use alkalinity method than Gran's Plot method when sample amount is sufficient (Ochiai et al., 2001).



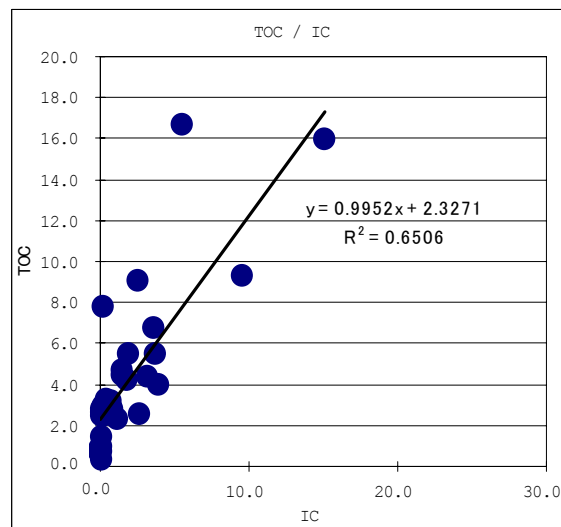
**Figure 3**  $\text{HCO}_3^-$  IC determined values versus calculated values.



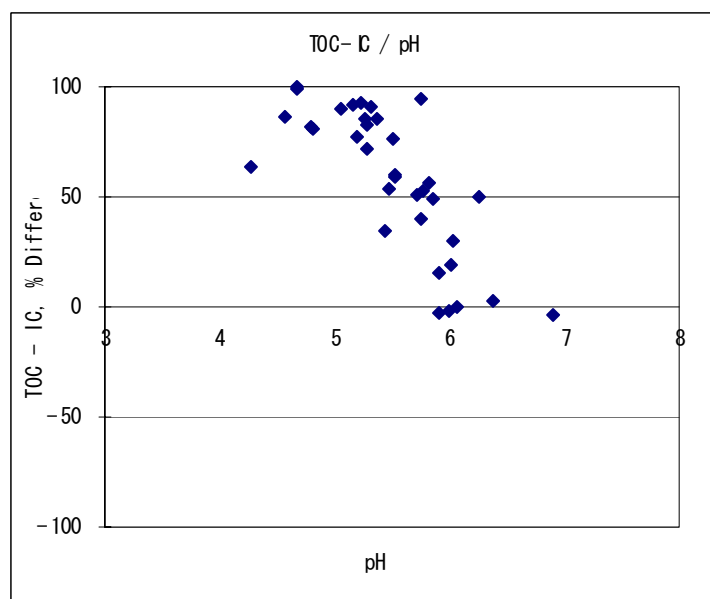
**Figure 4**  $\text{HCO}_3^-$  TOC determined values versus calculated values.



**Figure 5 TOC versus IC (all concentrations).**



**Figure 6 TOC versus IC (extremely high concentration excluded)**



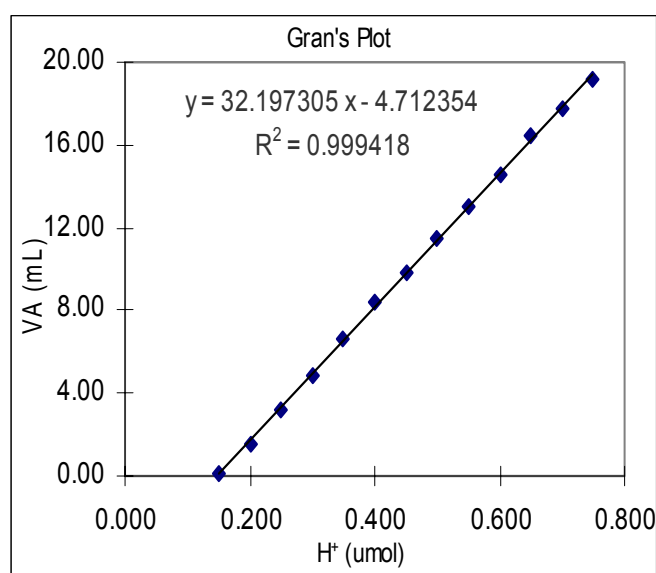
**Figure 7 Percent concentration difference of TOC and IC versus pH**

**Table 4 Potential values (E, mV) of sample MM-15 per addition of 0.05 mL 0.02N H<sub>2</sub>SO<sub>4</sub>**

| VA (mL) | E (mV) | pH      | H <sup>+</sup> (μmol/L) | H <sup>+</sup> (μmol) |
|---------|--------|---------|-------------------------|-----------------------|
| 0.00    | -25    | 7.11863 | 0.07610                 | 0.00152               |
| 0.05    | -2     | 6.72728 | 0.18738                 | 0.00375               |
| 0.10    | 36     | 6.08072 | 0.83039                 | 0.01661               |



|      |     |         |           |          |
|------|-----|---------|-----------|----------|
| 0.15 | 90  | 5.16191 | 6.88794   | 0.13776  |
| 0.20 | 152 | 4.10699 | 78.16547  | 1.56331  |
| 0.25 | 170 | 3.80072 | 158.22809 | 3.16456  |
| 0.30 | 181 | 3.61355 | 243.47129 | 4.86943  |
| 0.35 | 189 | 3.47743 | 333.09427 | 6.66189  |
| 0.40 | 195 | 3.37534 | 421.36331 | 8.42727  |
| 0.45 | 199 | 3.30728 | 492.85188 | 9.85704  |
| 0.50 | 203 | 3.23922 | 576.46921 | 11.52938 |
| 0.55 | 206 | 3.18818 | 648.36699 | 12.96734 |
| 0.60 | 209 | 3.13713 | 729.23192 | 14.58464 |
| 0.65 | 212 | 3.08609 | 820.18240 | 16.40365 |
| 0.70 | 214 | 3.05206 | 887.03407 | 17.74068 |
| 0.75 | 216 | 3.01803 | 959.33469 | 19.18669 |



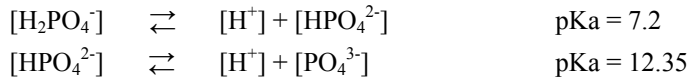
**Figure 8 Gran's Plot of sample MM-15**

### 3.3. Other minor anions

Acceptable results of  $R_1$  and  $R_2$  were attained with the inclusion of the other minor anions which concentrations are also shown in Table 3. Thirty-one of the samples had  $\text{NO}_2^-$  concentrations. Samples collected from Los Baños had concentrations of the range 0.000 – 0.500  $\mu\text{mol/L}$  and at an average of 0.197  $\mu\text{mol/L}$  while those from Metro Manila had a range of 0.000 – 1.93  $\mu\text{mol/L}$  and at an average of 0.940  $\mu\text{mol/L}$ . It can be noticed that samples from Metro Manila, an urban site, had significantly higher concentrations than those of Los Baños.

Phosphate was determined in nine samples, 4 from Los Baños and 5 from Metro Manila. Concentrations were of the range 0.284 – 50.59  $\mu\text{mol/L}$ , the highest of which was from Metro Manila. Phosphate concentrations were computed based on the equation of the total dissociation of anions, which was derived from the following equations:





$$[\text{H}_3\text{PO}_4]_{\text{total}} = [\text{H}_3\text{PO}_4] + [[\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]] \quad (12)$$

From (12), the following equations (components concentration) could be formed:

$$\begin{aligned}
[\text{H}_3\text{PO}_4] &= [1 / \{1 + 10^{-2.15} / [\text{H}^+] + 10^{-9.35} / [\text{H}^+]^2 + 10^{-21.7} / [\text{H}^+]^3\}] \times [\text{H}_3\text{PO}_4]_{\text{total}} \\
&= f_0 [\text{H}^+] \times [\text{H}_3\text{PO}_4]_{\text{total}} \quad (13)
\end{aligned}$$

$$\begin{aligned}
[\text{H}_2\text{PO}_4^-] &= [1 / \{[\text{H}^+] / 10^{-2.15} + 1 + 10^{-7.2} / [\text{H}^+] + 10^{-19.55} / [\text{H}^+]^2\}] \times [\text{H}_3\text{PO}_4]_{\text{total}} \\
&= f_1 [\text{H}^+] \times [\text{H}_3\text{PO}_4]_{\text{total}} \quad (14)
\end{aligned}$$

$$\begin{aligned}
[\text{HPO}_4^{2-}] &= [1 / \{[\text{H}^+]^2 / 10^{-9.35} + [\text{H}^+] / 10^{-7.2} + 1 + 10^{-12.35} / [\text{H}^+]\}] \times [\text{H}_3\text{PO}_4]_{\text{total}} \\
&= f_2 [\text{H}^+] \times [\text{H}_3\text{PO}_4]_{\text{total}} \quad (15)
\end{aligned}$$

$$\begin{aligned}
[\text{PO}_4^{3-}] &= [1 / \{[\text{H}^+]^3 / 10^{-21.7} + [\text{H}^+]^2 / 10^{-9.35} + [\text{H}^+] / 10^{-12.35} + 1\}] \times [\text{H}_3\text{PO}_4]_{\text{total}} \\
&= f_3 [\text{H}^+] \times [\text{H}_3\text{PO}_4]_{\text{total}} \quad (16)
\end{aligned}$$

The equivalent concentration of phosphate in a sample is calculated using Equation 19, as follows:

$$\begin{aligned}
[\text{H}_3\text{PO}_4]_{\text{sample}} &= [\text{H}_2\text{PO}_4^-] + 2 [\text{HPO}_4^{2-}] + 3 [\text{PO}_4^{3-}] \\
&= (f_1 [\text{H}^+] + 2 \times f_2 [\text{H}^+] + 3 \times f_3 [\text{H}^+]) \times [\text{H}_3\text{PO}_4]_{\text{total}} \quad (17)
\end{aligned}$$

$$[\text{H}_3\text{PO}_4]_{\text{total}} = [\text{H}_3\text{PO}_4]_i \quad (18)$$

Finally, by substitution, Equation (17) becomes,

$$[\text{H}_3\text{PO}_4]_{\text{sample}} = (f_1 [\text{H}^+] + 2 \times f_2 [\text{H}^+] + 3 \times f_3 [\text{H}^+]) \times [\text{H}_3\text{PO}_4]_i \quad (19)$$

Results of formate ion were less than the determination limit, except for four samples, two from both stations. The concentrations were 0.329 and 0.441 in Loa Baños and 0.284 and 0.465  $\mu\text{mol/L}$  in Metro Manila. Concentrations were likewise computed based on the total dissociation of ions based on Equation (3), from which the following Equation was derived:

$$[\text{HCOO}^-] = 10^{\text{pH}} / (10^{\text{pH}} + 10^{3.55}) \times [\text{HCOO}^-]_i \quad (20)$$

Similarly, the equation for the calculation of acetate ion concentration follows as:

$$[\text{CH}_3\text{COO}^-] = 10^{\text{pH}} / (10^{\text{pH}} + 10^{4.56}) \times [\text{HCOO}^-]_i \quad (21)$$

It was found that no acetate ion was determined because the results were all less than the determination limit. Of the chromatograms of some samples previously analyzed at the EMB Laboratory had a peak of minor anion, possibly  $\text{F}^-$ ,  $\text{CH}_3\text{COO}^-$ , or  $\text{HCOO}^-$ , which indicates that there was a possible degradation of samples.

Concentrations of  $\text{Br}^-$  were determined in all samples and the concentrations were equable and had averages at 0.128 and 0.116  $\mu\text{mol/L}$  in Los Baños and Metro Manila, respectively. For fluoride ion ( $\text{F}^-$ ), no

concentrations were determined for the results were all found to be less than the instrument determination limit.

### 3.4. Heavy Metals

The results of metals determination in the rainwater samples are shown in Figures 9 and 10. For both sites, zinc had the highest concentration. The mean concentration in Metro Manila was almost five times higher than the mean concentration in Los Baños. In Metro Manila, next to zinc was aluminum with its mean concentration also almost five times higher than that in Los Baños. This was likewise true of the manganese mean concentrations. Only twelve of the samples from Los Baños though had manganese concentrations higher than the determination limit.

Lead concentrations had averages of 2.90 and 0.337  $\mu\text{g/L}$  in Metro Manila and Los Baños, respectively. As urban site, Metro Manila's arithmetic mean concentration was 88% higher than the mean concentration in Los Baños. Data gathered from the Air Quality Monitoring Stations in Metro Manila during the months of April through June 2005 had a mean concentration of 0.097  $\mu\text{g/Ncm}$  (EMB-NCR Ambient Air Quality Monitoring). For Los Baños site, during the period January 2005 to March 2006, mean concentration of 0.05  $\mu\text{g/Ncm}$  was determined from the Air Quality Monitoring Station in Batangas City, the nearest Air Quality Monitoring Station to the site (EMB-Region 4A Ambient Air Quality Monitoring).

For both sites, copper was of comparable concentration levels. Metro Manila had a mean concentration of 2.91  $\mu\text{g/L}$  while Los Baños had it at 2.19  $\mu\text{g/L}$ . Nickel concentrations were determined on ten samples in each site with mean concentrations of 1.02 and 0.318  $\mu\text{g/L}$  in Metro Manila and Los Baños, respectively. Only one sample in Metro Manila had a cadmium concentration, 2.32  $\mu\text{g/L}$ . All the other samples had concentrations less than the determination limit. This was also true of chromium in all samples.

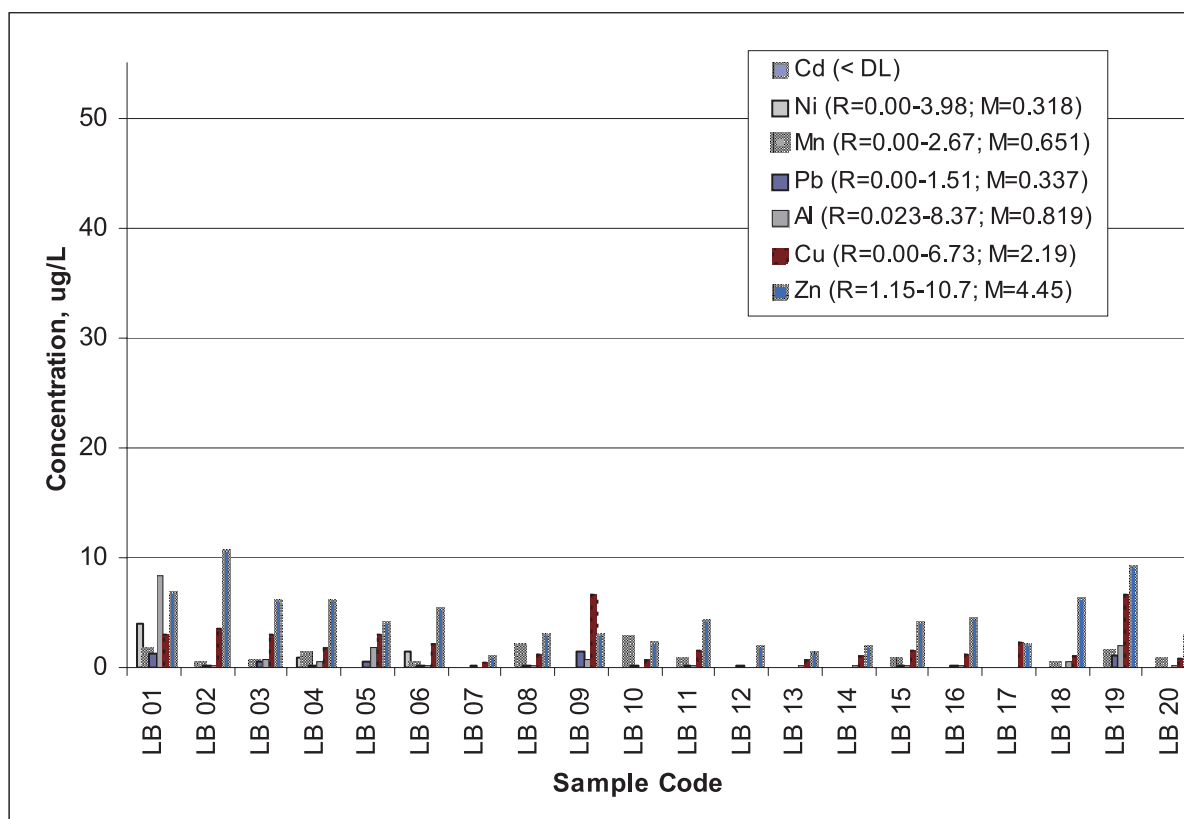
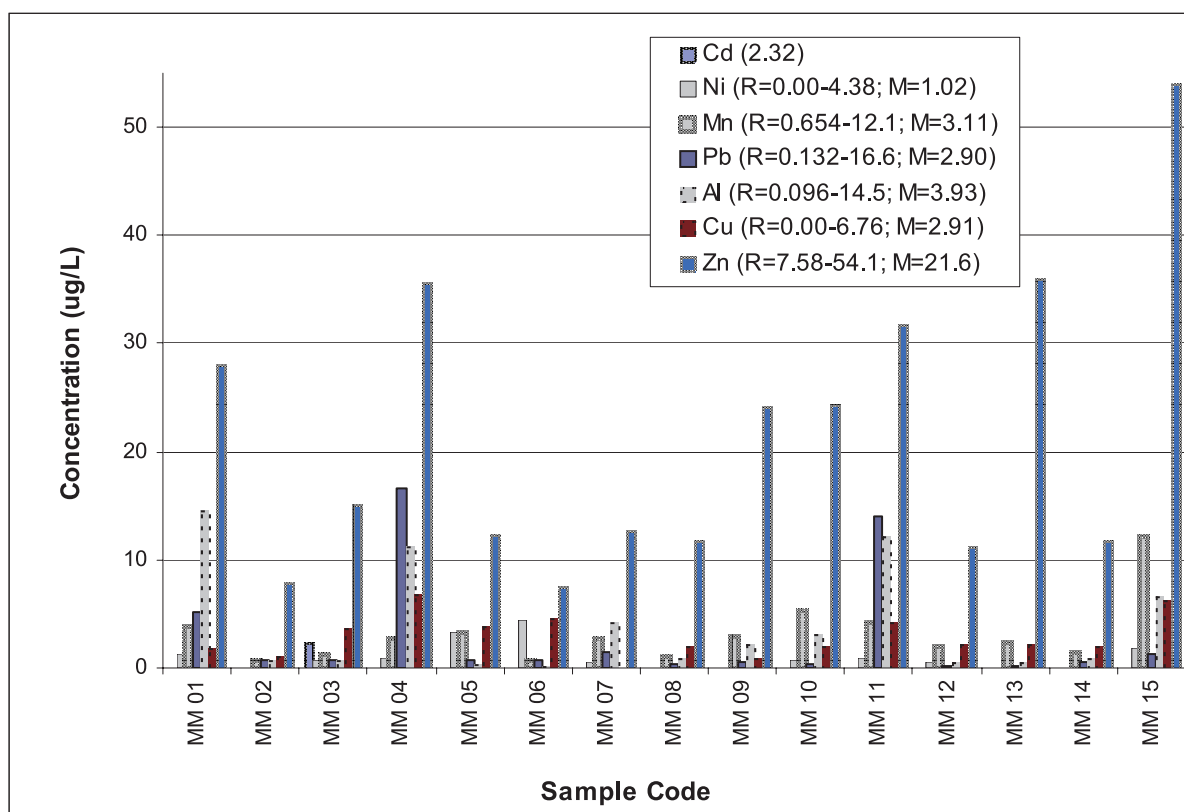


Figure 9 Concentrations of Metals in Los Baños.



**Figure 10 Concentrations of Metals in Metro Manila.**

#### 4. Conclusion and Recommendations

If re-measurements of a rainwater sample still do not give acceptable results of  $R_1$  and  $R_2$ , it is recommended that the determination of other components is necessary in order to meet the  $R_1$  and  $R_2$  criteria. When  $R_1$  value of a sample is significantly greater than zero or does not meet the criteria and its pH is greater than 6.000, it is possible that the other minor anions are also present in that sample so these anions should also be determined. In particular, a sample with pH around 6.000 indicates the presence of hydrogen carbonate ion. In this study, the best results of  $\text{HCO}_3^-$  were generated through the TOC method, but the IC method also gave good results. Depending on the availability of instrument for determination, either TOC or IC method can be used. The other anions such as  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$  and  $\text{F}^-$  may likewise be determined by IC. Determination of these additional anions is being recommended for the purpose of generating a reliable wet deposition monitoring data.

The determination of  $\text{HCO}_3^-$  through the Gran's Plot method was conducted in this study but results were not comparable to the results of TOC and IC methods. Further comparison study is thus recommended.

#### Acknowledgements

We gratefully acknowledge the generous support provided for by the Acid Deposition and Oxidant Research Center, the Network Center of EANET through which this research fellowship was made possible. We would like to express our deepest gratitude to Dr. Tsuyoshi Ohizumi for his technical guidance and supervision, to Ms. Tomomi Kominami for her technical assistance, and to everyone in ADORC who had extended his/her help during the conduct of this research fellowship.

## References

- Acid Deposition Monitoring Network in East Asia (EANET) 2000a. Technical Documents for Wet Deposition Monitoring in East Asia. Acid Deposition and Oxidant Research Center (ADORC), Niigata, Japan.
- Acid Deposition Monitoring Network in East Asia (EANET) 2000b. Technical Documents for Monitoring Inland Aquatic Environment in East Asia. Acid Deposition and Oxidant Research Center (ADORC), Niigata, Japan.
- Acid Deposition Monitoring Network in East Asia (EANET) 2000c. Data Reporting Procedures and Formats for Acid Deposition Monitoring in East Asia. Acid Deposition and Oxidant Research Center (ADORC), Niigata, Japan.
- Japanese Standard Association 1998. Japanese Industrial Standard K0101 Testing Methods for Industrial Water, Japanese Standard Association, Tokyo, pp. 23-327.
- Environmental Management Bureau – National Capital Region 2005. Ambient Air Quality Monitoring, Environmental Management Bureau, Manila, Philippines.
- Environmental Management Bureau – Region 4A 2006. Ambient Air Quality Monitoring, 2005 and 1st Quarter, Environmental Management Bureau, Manila, Philippines.
- Nogushi I. & Hara H. 2004. Ionic imbalance due to hydrogen carbonate from Asian dust, In ELSEVIER website (Atmospheric Environment) [www.elsevier.com/locate/atmosenvi](http://www.elsevier.com/locate/atmosenvi).
- Ochiai, S., Miyakita, A., Kawakami, T. 2001. Application of Gran's Plot Method to Measurement of Surface Water ANC. Journal of Environmental Systems and Engineering, 685: 157-164.

# Determination of Unanalyzed Components in Precipitation Water

Bulgan Tumendemberel\*

*Central Laboratory of Environment and Metrology*

*\*Contact address: POBox-150, Ulaanbaatar-36, Mongolia [e-mail: bnbm@magicnet.mn]*

This report consists of 2 parts as follows: I. Determination of unanalyzed ions in precipitation water and II. Determination of heavy metals and Pb isotopic ratios in precipitation water of Mongolia.

## I. Determination of unanalyzed ions in rain water of Mongolia

### 1. Introduction

In Mongolia, the acid deposition monitoring was initiated in August 1998 for two sites of wet and dry deposition that were equipped within the EANET activities. Based on experience of acid deposition monitoring in Mongolia during the last period, we have been facing poor ion balance problem in rainwater chemistry although all procedures of site selection, sampling, chemical analysis, and implementation of QA/QC activities are carried out in accordance with the Guidelines and Technical Manuals for the EANET. There were as many as 100-70% of measurements of rainwater have not met the required criteria for R1. Referring to the data reports of the EANET, 82% and 71% of all samples at Terelj (TR) (MN11032) did not meet the R1 criteria in 2004 and 2005, respectively. In Ulaanbaatar (UR), all rain samples in 2004, 91% of all samples in 2005 did not meet the criteria.

Therefore, laboratory exercise on determination of unanalyzed components in rain water using sophisticated analytical tools is very important and valuable in order to discriminate cause of such uncertainty in analytical practice and define it whether analytical mistake or some rooms for undetermined components in precipitation water.

### 2. Methodology

Rain samples in remote site Terelj (TR) and urban site Ulaanbaatar (UB) were collected with a wet-only sampler on daily bases and snow samples in TR were collected with bulk sampler on event bases for 2006. After collection, the samples were kept in a refrigerator.

Concentration of major ions including previously undetermined ions such as  $\text{HCO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{F}^-$  and  $\text{Br}^-$  were analyzed in 30 rain samples of the 42 samples collected at UB, from April to October 2006, 33 rain and snow samples of the 44 samples collected at TR, from December 2005 to October 2006 using the Acid Deposition and Oxidant Research Center (ADORC) facilities.

The anions were determined by IC (IC) with Eluent Generator Cartridge (EGC) 23mM KOH system, Dionex DX-500. In order to shorten a retention time of  $\text{H}_3\text{PO}_4$ , a step gradient mode was chosen. For cation analysis, IC with Eluent Generator Cartridge (EGC) 20mM MSA system, Dionex DX-500 was used.

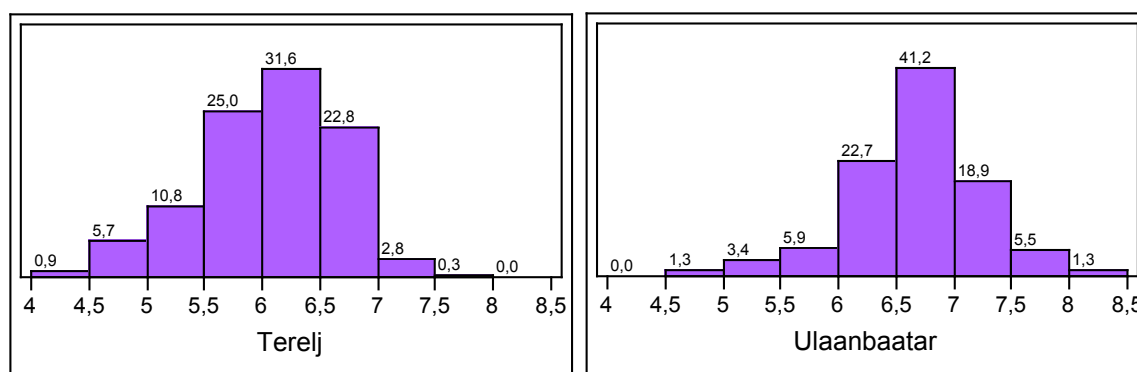
In fact that ion chromatograph is usually calibrated with total acid concentration, thus determined value obtained from IC shows total acid concentration in the samples. Therefore, concentrations of hydrogen carbonate and phosphate in the samples were recalculated by modifying IC results using equations suggested by Technical Document on Wet Deposition Monitoring in East Asia and Atmospheric Research Department, ADORC (Atmospheric Research Department, ADORC, 2006a and 2006b).

In line with IC, the alkalinity method was applied for determination of hydrogen carbonate concentration

in the samples. A pH meter HM-60G, TOA and burette with 0.05 precision, filled with 2mM H<sub>2</sub>SO<sub>4</sub> solution were used for potentiometric titration.

### 3. Results and discussion

According to the monitoring data for 2000-2005, pH of rainwater was in the range from 4.3 to 7.8 in remote site TR, while it varied from 4.8 to 8.3 at urban site UR. The volume-weighted annual average of rainwater pH was 5.6 for TR and 6.1 for UR. The frequency distribution of the rainwater pH is presented in Fig. 1.



**Figure 1** Frequency distribution of the rainwater pH.

The main fraction of pH values was between 5.5 and 7.0 at the remote site, while it was shifted to range between 6.0 and 7.5 at the urban site. There are many factors to neutralize pH and increased concentrations of the major ions in rainwater at both sites, among them there are presences of not only acidic species but also alkaline species such as calcium carbonates, ammonium associated salts in the air.

Since the CLEM is being equipped with dual columns IC, the only 3 major anions such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> were determined previously by the IC and therefore there were observed substantial lack of HCO<sub>3</sub><sup>-</sup> or other anions in ion balance of precipitation water of Mongolia.

#### 3.1. Ionic composition

Originally, after analysis at the CLEM, 23 samples of the 30 samples in UB, 31 samples of the 33 samples in TR did not meet the ion balance criteria (R1) and 1 and 4 samples did not meet the electrical conductivity criteria (R2), respectively. After analysis at the ADORC, 2 samples of UB, 10 samples of TR didn't meet R1 and only 1 sample of TR did not meet R2 criteria (Table 1) and reason of such dispersion is being discussed later.

**Table 1** Compliance of required criteria for R1, R2

| Site             | Sample number | CLEM |    | ADORC |    |
|------------------|---------------|------|----|-------|----|
|                  |               | R1   | R2 | R1    | R2 |
| Ulaanbaatar (UB) | 30            | 7    | 29 | 28    | 30 |
| Terelj (TR)      | 33            | 2    | 29 | 23    | 32 |

Referring to analytical results of anions which were analyzed at the ADORC, there were detected HCO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and F<sup>-</sup> in most samples along with the 3 previously measured major anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>), however Br<sup>-</sup> was detected only in a few samples although its standard was also included in the standard mixture.

Table 2 shows the concentration ranges and number of samples (in brackets) in which previously undetermined anions were detected.

**Table 2 Concentration range of previously undetermined components, mg/L**

|         | F <sup>-</sup>     | PO <sub>4</sub> <sup>3-</sup> | NO <sub>2</sub> <sup>-</sup> | HCO <sub>3</sub> <sup>-</sup> |
|---------|--------------------|-------------------------------|------------------------------|-------------------------------|
| UB (30) | 0.001-0.06 (24smp) | 0.14-0.22(8smp)               | 0.03-0.32(27)                | 0.06-26 (30)                  |
| TR (33) | 0.001- 0.06(19smp) | 0.15-1.22(18smp)              | 0.02-0.04(17)                | 0.32-6.49(31)                 |

Within these anions, concentration of HCO<sub>3</sub><sup>-</sup> was considerable as expected before and it was detected in all samples of UB, in case of TR, only 2 samples (where pH were below 4.0) did not contain hydrogen carbonate ion. Most (90%) of UB samples contained NO<sub>2</sub><sup>-</sup>, while considerable number (54%) of TR samples had PO<sub>4</sub><sup>3-</sup> and concentrations of those ions were quite high. It is still unclear potential source of these 2 ingredients and need further research on identification of their sources. F<sup>-</sup> was included almost in same number samples of both sites, however its concentrations were negligible.

Comparison of measurement results of 3 previously measured anions at 2 institutions (CLEM and ADORC) shows a variation of NO<sub>3</sub><sup>-</sup> concentrations in some samples. Therefore, cation reanalysis was taken at the ADORC in order to clarify if there are any possible chemical conversions of ingredients during sample storage. Result of the cation analysis at the ADORC has confirmed the oxidation of reduced nitrogen compounds at different stages (NH<sub>4</sub> – NO<sub>2</sub> – NO<sub>3</sub>) whereas with increased nitrate concentration, the ammonium concentration has decreased up to zero in some samples or quite high concentration of nitrite has occurred also in some samples. So now it can be assumed that there were 2 samples of UB (9 Apr, 23 Jun) and 10 samples of TR (19 Dec, 2 Feb, 23 Feb, 9 Mar, 9 Apr, 1 May, 8 May, 29 May, 7 Jun, 10 Jun, 23 Jun) effected by the conversion and ion balance of those samples was out of the required criteria. Cause of such phenomena should be studied also in future.

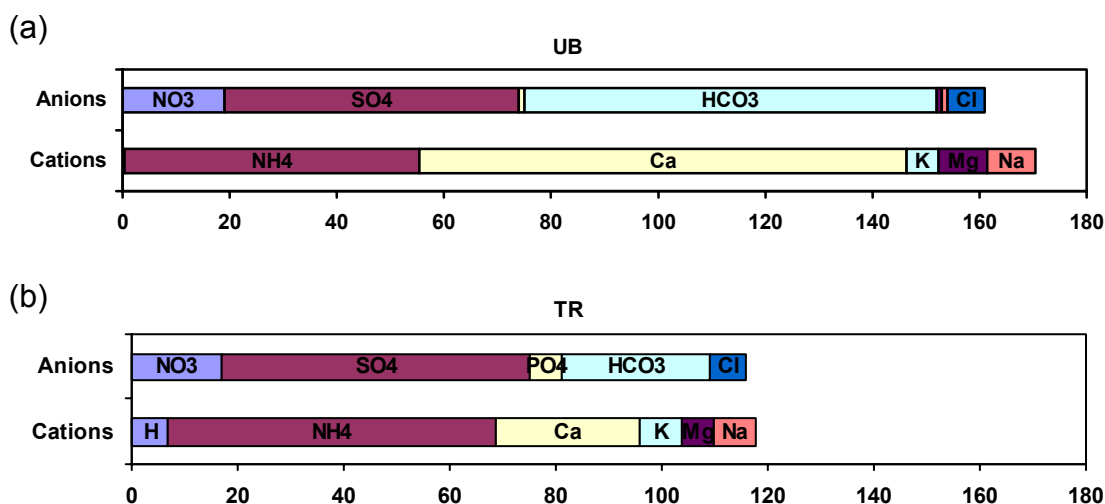
The ion balance was recalculated using the all data set including newly measured anions except high concentration of NO<sub>2</sub><sup>-</sup> referring to NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> results. If omit the data which were subjected to chemical conversion of N compounds, so all data met the required criteria of R1 and R2.

Average concentrations of all measured ions were calculated for comparison of ionic composition ratio and presented in the Table 3. Ionic composition ratio of precipitation water of both sites for 2006 is shown in Fig.2.

**Table 3 Average concentrations of ions, µeq/L**

|           | H   | HCO <sub>3</sub> | F | Cl | NO <sub>3</sub> | SO <sub>4</sub> | PO <sub>4</sub> | NO <sub>2</sub> | Na | NH <sub>4</sub> | K | Mg | Ca |
|-----------|-----|------------------|---|----|-----------------|-----------------|-----------------|-----------------|----|-----------------|---|----|----|
| <b>UB</b> | 0.4 | 77               | 1 | 7  | 19              | 55              | 1               | 1               | 9  | 55              | 6 | 9  | 91 |
| <b>TR</b> | 6.7 | 28               | 0 | 7  | 17              | 58              | 6               | 0               | 8  | 62              | 8 | 6  | 27 |





**Figure 2 Ionic composition ratio of precipitation water, µeq/L.**  
**(a) Ulaanbaatar (UR) site, (b) Terelj (TR) site**

Referring to the Table 3 and Fig.2, hydrogen carbonate and sulfate ions have predominated within anions of precipitation water of UB and TR, respectively. However, contribution of  $\text{SO}_4^{2-}$  to precipitation acidity of UR was still significant and it predominated in several cases while contribution of  $\text{HCO}_3^-$  had a similar picture in precipitation composition of TR. As seen at the Fig.2, concentrations of  $\text{NO}_3^-$  and  $\text{Cl}^-$  were comparable at both sites and their contributions to precipitation acidity were not so considerable.

Ammonium and calcium ions mostly have predominated among the cations in the precipitation water. In the TR,  $\text{NH}_4^+$  was the dominant cation, which accounts on average for 52 of its cation total while in UR,  $\text{Ca}^{2+}$  was the predominant with 53% accounts due to alkaline dust effects. These major cations neutralize the original acidity and provide relatively high pH of rainwater at both sites, especially in UR in spite of a high concentration of acidic constituents.

### 3.2. Hydrogen carbonate ion

Since hydrogen carbonate ion plays important role in precipitation chemistry of Mongolia, its determination in rainwater is essential for good ion balance. As mentioned above,  $\text{HCO}_3^-$  was examined by 2 methods namely by IC and alkalinity method at the ADORC. The Fig.3 presents a comparison of  $\text{HCO}_3^-$  concentrations determined by 2 different methods.

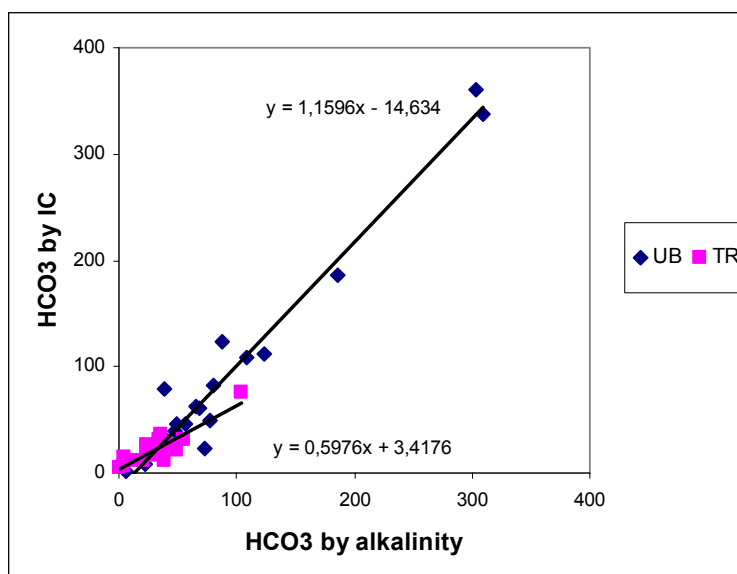
The results of UB samples by both methods were more identical with each other, but it was overestimated by alkalinity method than IC method for TR. Therefore, selection of analytical method for determination of  $\text{HCO}_3^-$  and its operational procedure should be examined carefully.

## 4. Conclusion and recommendations

The results of analysis of undetermined components at ADORC have suggested that in order to improve ion balance, the measurement of hydrogen carbonates is essential in precipitation water samples when pH is higher than 5.5 at both sites and some other components such as  $\text{PO}_4^{3-}$  and  $\text{NO}_2^-$  can be analyzed if there is any significant peak occurred after  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , respectively, especially  $\text{PO}_4^{3-}$  at remote site and  $\text{NO}_2^-$  at urban site. But further research is needed for identification of  $\text{PO}_4^{3-}$  sources.

There is a prepared procedure on determination of hydrogen carbonate in rainwater taking into account country's precipitation features and technical availability. However, there is still need some additional facilities such as digital pH-meter, high grade stock acid, precise micro burette to facilitate introducing of the procedure

into the monitoring practice successfully.



**Figure 3 Comparison of HCO<sub>3</sub><sup>-</sup> concentrations.**

## II. Determination of heavy metals and Pb isotopic ratios in precipitation water of Mongolia

### 1. Introduction

Concentration of 13 heavy metals and lead isotopic compositions were determined in Mongolian precipitation water and aerosol samples in order to know magnitude of the soluble metals in water, its enrichment factors, and relationship between metal concentrations and lead isotopic compositions, source identifications as well as comparison of those values in remote and urban sites.

Since there are no any significant heavy industries in the country, the heavy metals are mainly contributed by coal burning, leaded petrol, and waste incineration. Long range transportation of such components may take place.

### 2. Methodology

Rain samples in remote site TR and urban site UB were collected with a wet-only sampler on daily bases and snow samples in TR were collected with bulk sampler on event bases for 2006. After collection, the samples were kept in a refrigerator. Concentration of heavy metals and lead isotopic compositions were analyzed in 23 rain samples of the 42 samples collected UB, from April to October 2006, 24 rain & snow samples of the 44 samples collected TR, from December 2005 to October 2006.

Particle samples were collected with the four-stage filter pack sampler (1 l/min flow rate) in biweekly bases at TR and weekly in UB. The water extract of 6 samples of TR, 8 samples of UB were analyzed for heavy metals.

The heavy metal concentrations and lead isotopic composition were determined by inductively coupled plasma mass spectrometry (ICP-MS), SPQ 9000, SII Seiko Instruments Inc. The lead isotopic ratios were corrected for fractionation by the Standard Reference Material (SPM) 981.

Statistical calculation was carried out by SPSS 13.0 for Windows. The Hysplit 4.5 model from NOAA was used for back trajectory analysis of air mass pattern. (<http://www.arl.noaa.gov/ready>)

### 3. Results and discussion

#### 3.1. Concentration of heavy metals

In general, concentrations of water soluble heavy metals in Mongolian precipitation water were low except Al, Mn, and Zn (Table 4). Al and Mn concentrations were relatively high, probably because those have presented in the earth crust (Al – 40200ppm, Mn – 770ppm). But Zn arises from man made sources.

**Table 4 Concentration of water soluble heavy metals in precipitation water (enrichment of metals), ppb (a) Ulaanbaatar (UB), (b) Terelj (TR)**

(a) Uraanbaatar

| <b>UB</b> | Al          | V             | Cr         | Mn            | Co            | Ni          | Cu            | Zn            | As            | Cd         | Sb            | Pb         | Bi         |
|-----------|-------------|---------------|------------|---------------|---------------|-------------|---------------|---------------|---------------|------------|---------------|------------|------------|
| Av.       | <b>5.6</b>  | <b>0.4</b>    | <b>0.6</b> | <b>5.6</b>    | <b>0.2</b>    | <b>2.6</b>  | <b>1.3</b>    | <b>4.9</b>    | <b>0.8</b>    | <b>0.2</b> | <b>0.2</b>    | <b>0.9</b> | <b>0.8</b> |
| STD       | <b>5.3</b>  | <b>0.5</b>    | <b>0.2</b> | <b>5.1</b>    | <b>0.2</b>    | <b>2.4</b>  | <b>1.1</b>    | <b>5.8</b>    | <b>0.8</b>    | <b>0.1</b> | <b>0.1</b>    | <b>0.3</b> | <b>0.1</b> |
| Max       | <b>27.5</b> | <b>1.5</b>    | <b>1.1</b> | <b>22.3</b>   | <b>0.8</b>    | <b>10.7</b> | <b>5.6</b>    | <b>23.6</b>   | <b>4.2</b>    | <b>0.4</b> | <b>0.4</b>    | <b>1.9</b> | <b>0.9</b> |
| Min       | <b>2.3</b>  | <b>&lt;DL</b> | <b>0.4</b> | <b>&lt;DL</b> | <b>&lt;DL</b> | <b>0.8</b>  | <b>&lt;DL</b> | <b>&lt;DL</b> | <b>&lt;DL</b> | <b>0.1</b> | <b>&lt;DL</b> | <b>0.6</b> | <b>0.7</b> |

(b) Terelj

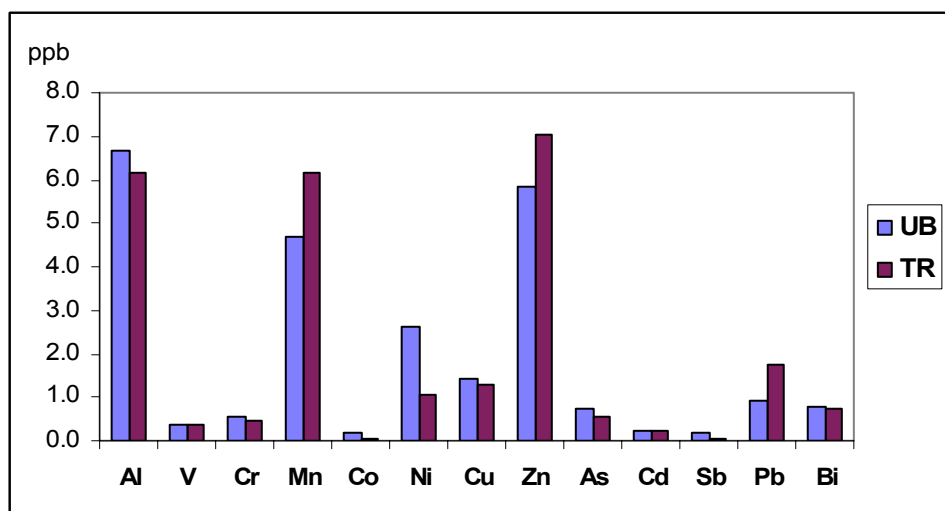
| <b>TR</b> | Al          | V             | Cr         | Mn            | Co            | Ni         | Cu            | Zn            | As            | Cd         | Sb            | Pb          | Bi         |
|-----------|-------------|---------------|------------|---------------|---------------|------------|---------------|---------------|---------------|------------|---------------|-------------|------------|
| Av.       | <b>4.8*</b> | <b>0.4</b>    | <b>0.6</b> | <b>7.3</b>    | <b>0.1</b>    | <b>1.3</b> | <b>1.4</b>    | <b>8.9</b>    | <b>0.7</b>    | <b>0.3</b> | <b>0.1</b>    | <b>2.9</b>  | <b>0.8</b> |
| STD       | <b>33.0</b> | <b>0.5</b>    | <b>0.6</b> | <b>6.7</b>    | <b>0.3</b>    | <b>0.9</b> | <b>2.2</b>    | <b>103</b>    | <b>0.5</b>    | <b>0.2</b> | <b>0.2</b>    | <b>6.1</b>  | <b>0.1</b> |
| Max       | <b>164</b>  | <b>1.7</b>    | <b>3.3</b> | <b>27.1</b>   | <b>1.4</b>    | <b>3.4</b> | <b>10.9</b>   | <b>451</b>    | <b>2.6</b>    | <b>1.1</b> | <b>0.6</b>    | <b>30.2</b> | <b>0.9</b> |
| Min       | <b>1.3</b>  | <b>&lt;DL</b> | <b>0.4</b> | <b>&lt;DL</b> | <b>&lt;DL</b> | <b>0.3</b> | <b>&lt;DL</b> | <b>&lt;DL</b> | <b>&lt;DL</b> | <b>0.1</b> | <b>&lt;DL</b> | <b>0.6</b>  | <b>0.7</b> |
| Av.*      |             |               |            |               |               |            | <b>1.0</b>    | <b>6.3</b>    | <b>0.6</b>    | <b>0.2</b> |               | <b>1.4</b>  |            |

\* High concentration on 22 September 2006 was omitted for calculation.

Comparing the heavy metals concentrations between 2 sites, there was observed a strange thing that average concentrations of Mn, Pb and Zn in TR were higher than those the urban site. In TR site, there were observed several episodes (6 Feb, 9 Jun, 22 Sep. 2006) that had higher concentrations of those metals, while in UR were not observed such events at all. Distance between 2 sites is about 50km. Totally, 12 samples pair were collected in same time at both sites in 2006. Table 5 and Fig. 4 show an average concentration of metals in the samples which were collected same days at both sites.

**Table 5 Average concentration of the samples taken at same time, ppb**

|           | Al         | V          | Cr         | Mn         | Co         | Ni         | Cu         | Zn         | As         | Cd         | Sb         | Pb         | Bi         |
|-----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| <b>UB</b> | <b>6.7</b> | <b>0.4</b> | <b>0.6</b> | <b>4.7</b> | <b>0.2</b> | <b>2.6</b> | <b>1.4</b> | <b>5.8</b> | <b>0.7</b> | <b>0.2</b> | <b>0.2</b> | <b>0.9</b> | <b>0.8</b> |
| <b>TR</b> | <b>6.2</b> | <b>0.4</b> | <b>0.5</b> | <b>6.2</b> | <b>0.0</b> | <b>1.0</b> | <b>1.3</b> | <b>7.0</b> | <b>0.5</b> | <b>0.2</b> | <b>0.1</b> | <b>1.7</b> | <b>0.7</b> |



**Figure 4 Average concentration of the samples taken at same time, ppb.**

The result shows same phenomena as higher concentrations of those metals in TR site. That implies there are different sources of heavy metals in those sites.

It can be assumed that there are no significant local sources of such metals that contribute their high water soluble concentrations in precipitation water in both sites. In UR, population of automobile is relatively low about 100.000 compare with mega cities even though leaded petrol is used and its contribution as water soluble form is not significant. Therefore, relatively high concentration of some metals such as Pb, Al, Zn, As, Cu, and Cd in TR site suggests their origin can be long-range transportation of the pollutants.

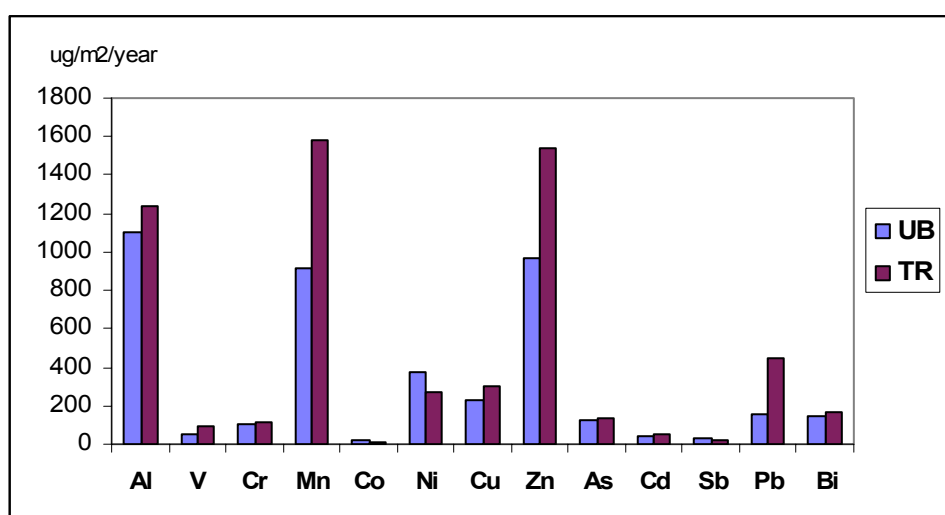
There is an example, one particular extreme episode occurred in 22 September 2006 at TR site when the pH of rain was 3.80, electric conductivity 123  $\mu\text{S}/\text{cm}$ . This rain sample contained considerably high concentration of heavy metals (Al – 164ppb, Cu – 11ppb, Zn – 64ppb, As – 2.6ppb, Cd – 1.1ppb, Pb – 30ppb) in line with high concentration of acidic substances. This acidic nature of sample can digest original content of heavy metals during transportation. That period, there was no rain in UR. In the next day, 23 September rain was at both sites most probably from frontal origin (because precipitation amount was quite enough), however looking at the back trajectories and lead isotopic signatures there was some differentiation (same initial origin but different height and mixtures). In this day, the concentrations of heavy metals in TR were much lower than in previous day but those were still higher than in UR (see isotope ratio).

Isentropic 3-day back trajectories were calculated by using the Hysplit 4.5 model to examine the origins of air parcels arriving at the site at 00:00UTC (09:00 local time) during the episodes, for three altitudes (1000, 2000, and 2500m above ground level (AGL)).

Depositions of such heavy metals were calculated using an average concentration and precipitation amount for 2006 and it is shown in Table 6 and Fig. 5. Since the precipitation amount was higher at TR (229mm) than in UR (188mm), wet deposition amount of heavy metals was higher in TR, especially such metals as Mn, Zn, Pb because of their higher concentrations comparing with the urban site.

**Table 6 Depositions of water soluble heavy metal for 2006,  $\mu\text{g}/\text{m}^2/\text{year}$**

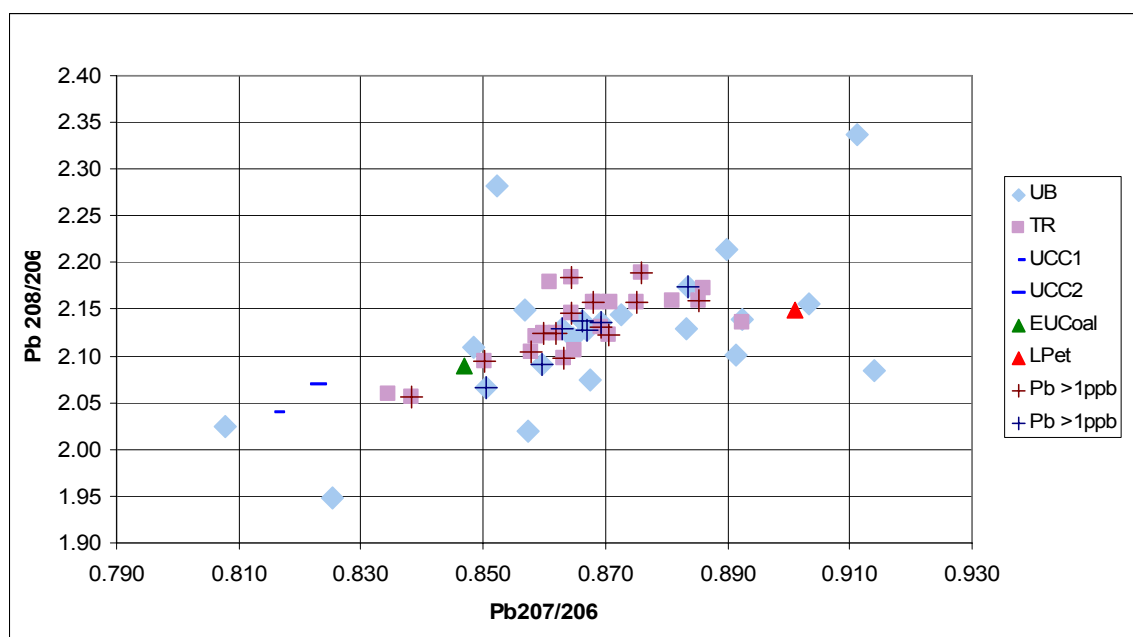
|    | Al   | V  | Cr  | Mn   | Co | Ni  | Cu  | Zn   | As  | Cd | Sb | Pb  | Bi  |
|----|------|----|-----|------|----|-----|-----|------|-----|----|----|-----|-----|
| UB | 1100 | 55 | 107 | 917  | 24 | 379 | 226 | 968  | 122 | 42 | 32 | 155 | 145 |
| TR | 1235 | 95 | 113 | 1579 | 12 | 271 | 302 | 1543 | 140 | 52 | 17 | 451 | 168 |



**Figure 5** Deposition of heavy metals for 2006,  $\mu\text{g}/\text{m}^2/\text{year}$ .

### 3.2. Lead isotopic ratios

Lead isotopic ratios in precipitation water were analyzed in same samples of heavy metals and are shown in Fig. 6. For comparison, the figure includes the ratios of upper continental crust (UCC1, UCC2), leaded petrol (LPet), and European coal (EUCoal). All analyzed data are plotted in the same figure and the ratios which have Pb concentration more than 1ppb are marked with (+).



**Figure 6**  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{207}\text{Pb}/^{206}\text{Pb}$  of precipitation water.

There was not only different isotopic composition but also different distribution of isotopic ratios in 2 sites. More linear distribution was at TR than at UR even though Pb concentration was higher. After elimination of the data with Pb concentration is below 1 ppb, the distribution of UR ratio was more linear almost in same line as the TR trend line. However, if analyze particular samples collected in same day in both sites, there were still quite enough differences existing. For instance, looking at previously mentioned episodes on 22, 23 September

2006, the isotope signatures ( $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$ ) of TR samples in 22 and 23 September were similar each other 0.863; 0.860 and 2.10; 2.12 respectively, but in case of UR sample in 23 September there are different ratios than in TR samples, they were 0.883 and 2.17 (see Fig. 6). Therefore, this differentiation suggests also on different sources of lead contents in rainwater at 2 sites. There were only 3 cases of the 8 sample pairs on same day collection in 2 sites that had similar isotopic ratios.

### 3.3. Correlation matrices

Correlations of heavy metals in rainwater with pH, EC, and lead isotope ratios  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$  for both sites were calculated. In TR, most of metals such as Al, Cu, As, Cd, and Pb correlate negatively with pH and positively with EC and each other at the 0.01 significant level because of the episodes on 22, 23 September 2006. In case of UR, there were no such strong correlations as in TR, but positive correlations between pH, EC and Cr, Co, Ni as well as between the ratios  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  have existed at the 0.01 significant level. The lead isotopic ratios have not had any correlations with concentrations of heavy metals in both sites.

### 3.4. Heavy metals in water extract of filter pack

Concentration of heavy metals in water extract of filter pack (FP) is shown in Table 7 and comparison of average concentrations of heavy metals at both sites shown in Fig. 7. There was distinctive picture of heavy metals in water extract of FP than heavy metals in rainwater. Concentration of all analyzed heavy metals in UR was higher than TR samples indicating influence of local sources. If there is acid digestion of samples, obviously there will be more heavy metals in particles.

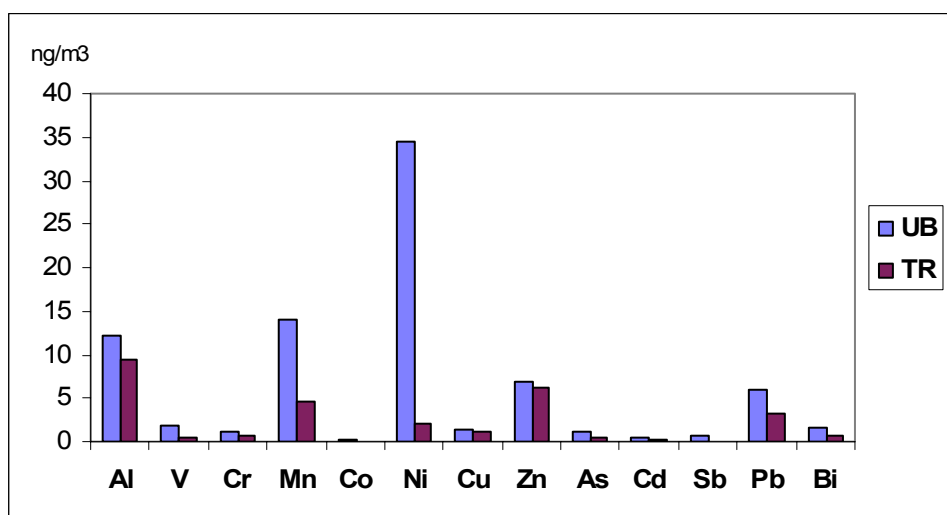
The Fig.8 shows the lead isotopic ratio of the water extract of particles. Pb isotopic ratios are more common in both sites, the ratio was less radiogenic in TR site. Correlations of heavy metals in particles with lead isotope ratios  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$  for both sites were calculated also. In TR, Al correlates positively with Zn, Bi and Pb with V. In UR, Al correlates positively with most metals except V, Pb at the 0.01, and 0.05 significant levels thus indicate the same source of those metals, probably soil source. The lead isotopic ratios have not had any correlations with others in both sites.

**Table 7 Concentration of heavy metals in particles, ngm<sup>-3</sup>**

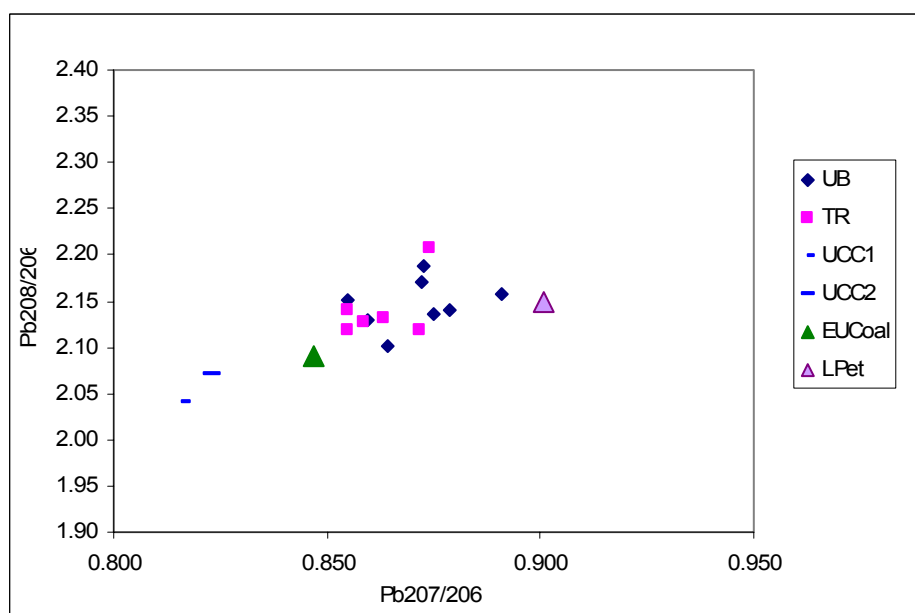
| <b>UB</b> | <b>Al</b>     | <b>V</b>      | <b>Cr</b>  | <b>Mn</b>   | <b>Co</b>     | <b>Ni</b>   | <b>Cu</b>     | <b>Zn</b>     | <b>As</b>     | <b>Cd</b>  | <b>Sb</b>     | <b>Pb</b>   | <b>Bi</b>  |
|-----------|---------------|---------------|------------|-------------|---------------|-------------|---------------|---------------|---------------|------------|---------------|-------------|------------|
| Av.       | <b>12.1</b>   | <b>1.9</b>    | <b>1.1</b> | <b>14.2</b> | <b>0.1</b>    | <b>34.4</b> | <b>1.4</b>    | <b>6.8</b>    | <b>1.2</b>    | <b>0.4</b> | <b>0.7</b>    | <b>5.9</b>  | <b>1.5</b> |
| STD       | <b>12.3</b>   | <b>1.2</b>    | <b>0.6</b> | <b>17.5</b> | <b>0.3</b>    | <b>84.1</b> | <b>1.9</b>    | <b>4.2</b>    | <b>0.5</b>    | <b>0.2</b> | <b>0.9</b>    | <b>3.2</b>  | <b>0.3</b> |
| Max       | <b>40.9</b>   | <b>3.5</b>    | <b>2.5</b> | <b>56.9</b> | <b>0.8</b>    | <b>243</b>  | <b>6.0</b>    | <b>15.4</b>   | <b>1.9</b>    | <b>0.8</b> | <b>2.8</b>    | <b>11.4</b> | <b>2.1</b> |
| Min       | <b>&lt;DL</b> | <b>&lt;DL</b> | <b>0.7</b> | <b>2.6</b>  | <b>&lt;DL</b> | <b>1.3</b>  | <b>&lt;DL</b> | <b>&lt;DL</b> | <b>&lt;DL</b> | <b>0.3</b> | <b>&lt;DL</b> | <b>1.5</b>  | <b>1.1</b> |

| <b>TR</b> | <b>Al</b>   | <b>V</b>      | <b>Cr</b>  | <b>Mn</b>  | <b>Co</b>     | <b>Ni</b>  | <b>Cu</b>     | <b>Zn</b>   | <b>As</b>     | <b>Cd</b>  | <b>Sb</b>     | <b>Pb</b>  | <b>Bi</b>  |
|-----------|-------------|---------------|------------|------------|---------------|------------|---------------|-------------|---------------|------------|---------------|------------|------------|
| Av.       | <b>9.4</b>  | <b>0.4</b>    | <b>0.8</b> | <b>4.8</b> | <b>0.0</b>    | <b>2.1</b> | <b>1.1</b>    | <b>6.1</b>  | <b>0.5</b>    | <b>0.2</b> | <b>&lt;DL</b> | <b>3.2</b> | <b>0.8</b> |
| STD       | <b>8.5</b>  | <b>0.4</b>    | <b>0.4</b> | <b>3.7</b> | <b>0.0</b>    | <b>1.7</b> | <b>0.8</b>    | <b>4.9</b>  | <b>0.3</b>    | <b>0.1</b> |               | <b>2.4</b> | <b>0.1</b> |
| Max       | <b>26.4</b> | <b>0.9</b>    | <b>1.3</b> | <b>9.9</b> | <b>0.1</b>    | <b>4.9</b> | <b>2.2</b>    | <b>15.3</b> | <b>0.9</b>    | <b>0.3</b> |               | <b>6.9</b> | <b>1.0</b> |
| Min       | <b>3.4</b>  | <b>&lt;DL</b> | <b>0.4</b> | <b>1.5</b> | <b>&lt;DL</b> | <b>0.7</b> | <b>&lt;DL</b> | <b>1.7</b>  | <b>&lt;DL</b> | <b>0.1</b> |               | <b>0.8</b> | <b>0.7</b> |



**Figure 7** Concentration of heavy metals in water extract of particles.



**Figure 8**  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{207}\text{Pb}/^{206}\text{Pb}$  of particles.

### Acknowledgements

I am grateful to the NC of EANET for giving me chance to have such fruitful research fellow and providing of technical supports, guidance for its successful implementation. I would like to especially thank to Mr. J. Nagata, Dr. T. Ohizumi, Ms. T. Kominami, and other staffs of ADORC for their kind assistance and advices.

### References

Atmospheric Research Department, ADORC 2006a. Determination of organic acid, carbonate, and phosphate in rain water by ion chromatograph. Acid Deposition and Oxidant Research Center (ADORC), Niigata, Japan.  
 Atmospheric Research Department, ADORC 2006b, Determination of hydrogen carbonate in rain water. Acid Deposition and Oxidant Research Center (ADORC), Niigata, Japan.

- Takeuchi H. 2002. Encyclopedia of measurements and analysis on global environment, Vol.1, Terrestrial Environment (1). Fuji Techno System, Inc., Tokyo.
- Noguchi, I. & Hara H. 2004, Ionic imbalance due to hydrogen carbonate from Asian dust. *Atmospheric Environment* 38: 6969-6976.
- ISAG Meeting of EANET 2000. Technical Documents on Acid Deposition Monitoring in East Asia. Acid Deposition and Oxidant Research Center (ADORC), Niigata, Japan.
- Weiss, D., Shotyk, W., Krames, J. D. & Gloor, M. 1999. Sphagnum mosses as archives of recent and past atmospheric lead deposition in Switzerland. *Atmospheric Environment* 33:959-972



# Application of a Scientific Climatological Approach and Statistical Method for EANET Network Optimization

Elena V. Gritsan<sup>1)\*</sup> and Sergey A. Gromov<sup>2)</sup>

*1) Institute of Global Climate and Ecology, Roshydromet  
and the Russian Academy of Science (RAS)*

*\*Contact address: 20-b Glebovskaya str., Moscow, 107258, Russia [e-mail:  
gritsan@gmail.com]*

*2) Acid Deposition and Oxidant Research Center (ADORC)*

Precipitation chemistry measurements of the EANET network were analyzed using a statistical approach. Spatial representativeness, which is a condition of data spreading throughout the site surrounding area with the certain accuracy, was defined for each station. Areas that are not covered with the EANET network observations were evaluated on the basis of the obtained results.

## 1. Introduction

One of the main goals of an atmospheric monitoring network is to obtain data for appropriate and adequate evaluation of the deposition process under different geographical or climate conditions. From this point of view, information on measurements' representativeness is of great importance. Representativeness is a condition of spreading measurements at a single station throughout its surrounding area with the certain accuracy. In this paper, an attempt to identify such areas for each station of the EANET network was made. Approach applied in the study reveals "measurement gaps", i.e. territories to which measurements of any station can not be spread. These territories should be regarded as the first-priority areas under organization of new stations.

## 2. Description of the method

The most vital question in measurement representativeness estimation is choice of a representativeness criterion. One of the wide spread approaches is assumption an interpolation error or an error of spatial average value estimation at one station over a region as the representativeness criterion. An interpolation error is used for parameters with relatively low temporal and spatial variability. In case of precipitation chemistry we have a discrete field in time and space, so we should consider spatial averaged values and error of spatial average value estimation at one station over a region should be used as the representativeness criterion.

Assuming the exponential form of the correlation function, the error of estimation of the spatial average value at one station over region with area  $S$  can be calculated by the observations from the following expression (Kagan and Gushchina, 1966).

$$E = \sigma(1 - r(0) + 0.23 r(0) \frac{\sqrt{S}}{l_0})^{\frac{1}{2}} \quad (1),$$

where  $\sigma$  is the standard deviation,  $r(0)$  and  $l_0$  are parameters of the correlation function  $r(l)$ , which reflects the dependence of the correlation coefficient from distance, and  $S$  is an area to which measurements at a station can be spread.  $r(0)$  is a value of the correlation coefficient under zero distance. Theoretically,  $r(0)$  should equal to 1 as it is correlation of observations at a station with themselves. However, it is smaller then 1 in practice due to the measurement error and influence of some other factors. Thus, a value of  $1-r(0)$  characterizes an input of the

stochastic errors to element variability.  $l_0$  is a correlation radius, i.e. it is a distance at which the correlation coefficient decreases in  $e$  times

Expression (1) is written in absolute values, but it is more convenient to deal with non-dimensional values. Both parts of (1) must be divided by the multiyear mean concentration ( $C$ ) to obtain the non-dimensional form

$$\frac{E}{C} = \frac{\sigma(1 - r(0) + 0.23r(0)\frac{\sqrt{S}}{l_0})^{\frac{1}{2}}}{C} \quad (2).$$

$E/C$  varies from 0 to 1. It's a natural requirement  $E/C$  to be as small as possible. However, in practice it can not be so. In this investigation,  $E/C$  was accepted to be equal to the DQO (0.15).

Transforming (2), we obtain  $S$ . After it, we should decide what shape to choose for approximation of the area  $S$ . Generally, it can be any shape with the area  $S$ . In this paper, it was assumed to be a circle with the radius  $(S/\pi)^{1/2}$ . So, the final expression for calculation of the representativeness is as following

$$R = \frac{l_0}{0.23r(0)\pi^{\frac{1}{2}}} \left[ \left( \frac{0.15C}{\sigma} \right)^2 - 1 + r(0) \right] \quad (3).$$

Mapping of the calculated radiuses shows the representativeness areas for all stations and makes possible to see "measurement gaps".

So, the method is based on calculating correlation function characteristics for the precipitation chemistry fields. Then, obtained results are used to find areas of representativeness for each station.

### 3. Data and procedure

The monthly averaged data on precipitation chemistry in 2000-2005 were used for the first approach and the weekly averaged data were used for more detailed investigation. The weekly averaged data were regarded separately for the climatic regions and only for the summer period (June-August) as data completeness during this time is very high. The set of stations, which data were used, are shown in Annex 1.  $\text{nss-SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{nss-Ca}^{2+}$ ,  $\text{H}^+$  were chosen among all the measured components as they are priority pollutants of the rain water.

On the first step, correlation matrices were calculated for the every pair of stations and for the each parameter on the basis of the monthly and weakly averaged data. On the second step, dependences of the correlation coefficients from a distance were found and approximated by analytical expressions, i.e. the correlation functions were obtained. The correlation coefficients were averaged per distance's gradations beforehand. As a result, the shape of function was defined more evidently. It's necessary to note that only correlation coefficients for stations outlying from each other for no more than 1000 km were used for investigation. This is the scale of the regional atmospheric processes and along it correlation can be considered as nonrandom one.

### 4. Results

The correlation functions and its parameters  $r(0)$  and  $l_0$ , which were obtained on the first step, are presented in Table 1.

The minimum value of  $l_0$  is typical for  $\text{NO}_3^-$ . This fact probably is connected with the  $\text{NO}_3^-$  formation process. It is formed during the reactions of oxidation of  $\text{NO}_x$ , which passes relatively fast, so  $\text{NO}_3^-$  spreads to smaller distances. Some statistical characteristics of the radiuses, which were calculated according to (3), are presented in Table 2.

**Table 1 Correlation function and its parameters, calculated on the base of the monthly data**

|                                   | Correlation function   | $r(0)$ | $l_0$ , km |
|-----------------------------------|------------------------|--------|------------|
| nss-SO <sub>4</sub> <sup>2-</sup> | $y=0.5398e^{-0.0009x}$ | 0.5398 | 1111       |
| NO <sub>3</sub> <sup>-</sup>      | $y=0.5263e^{-0.002x}$  | 0.5263 | 500        |
| NH <sub>4</sub> <sup>+</sup>      | $y=0.4101e^{-0.0011x}$ | 0.4101 | 909        |
| nss-Ca <sup>2+</sup>              | $y=0.2759e^{-0.0015x}$ | 0.2759 | 667        |
| H <sup>+</sup>                    | $y=0.3853e^{-0.0011x}$ | 0.3853 | 909        |

**Table 2 Statistical characteristics of radiuses for the monthly averaged data**

|                        | nss-SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | NH <sub>4</sub> <sup>+</sup> | nss-Ca <sup>2+</sup>  | H <sup>+</sup>       |
|------------------------|-----------------------------------|------------------------------|------------------------------|-----------------------|----------------------|
| Mean value, km         | 2112                              | 1030                         | 3025                         | 4198                  | 3303                 |
| Standard deviation, km | 122                               | 50                           | 98                           | 60                    | 201                  |
| Maximum value, km      | 2281<br>(Jiwozi)                  | 1097<br>(Kototabang)         | 3151<br>(Tappi)              | 4278<br>(Tanah Rata)  | 3539<br>(Weishuiyan) |
| Minimum value, km      | 1734<br>(Ijira)                   | 833<br>(Ijira)               | 4051<br>(Listvyanka)         | 2794<br>(Primorskaya) | 2878<br>(Tappi)      |

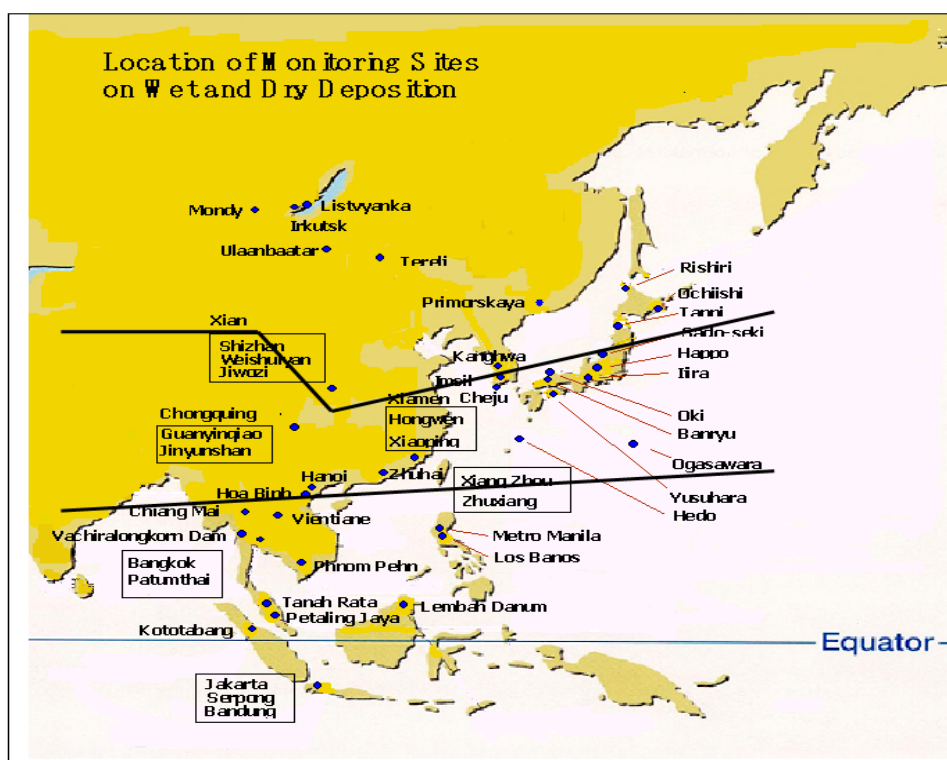
This result lets us see that statistics of precipitation chemistry from the existent stations may be applied for the first-order evaluation of acid deposition throughout the whole territory for all considered parameters from the certain point of application under the condition of 15%-error concentration determination. However, such high values of the representativeness radiuses are due to the suggestion about similarity of the correlation functions for the whole territory and for the whole year.

The second-order approach, which is based on the weekly averaged data, is more accurate definition of the correlation functions. Three climatic regions were separated on the investigated territory, which are, namely, the middle latitudes region (30 – 55° N), the subtropical region (22 – 30° N), and the tropic region (10° S – 22° N). The regions are presented in Fig.1. Only 2 stations are situated in the subtropical region, so none calculations can be done for it.

The calculated parameters of the correlation functions and the values of  $r(0)$  and  $l_0$  are shown in Table 3. In some cases, available data didn't let to disclose the dependence of the correlation coefficient from distance.

The radiuses calculated on the base of the weekly averaged data for the summer period are smaller then radiuses calculated on the base of the monthly averaged ones. It means that correlation of the weekly averaged concentrations decreases faster with distance, so weekly measurement data of sites can be spread to smaller area than monthly ones.

The statistical characteristics of the calculated radiuses are presented in Table 4.



**Figure 1** Locations of the middle latitudes region (30 – 55° N), the subtropical region (22 – 30° N), and the tropic region (10° S – 22° N).

**Table 3** Correlation function and its parameters, calculated on the base of weekly data

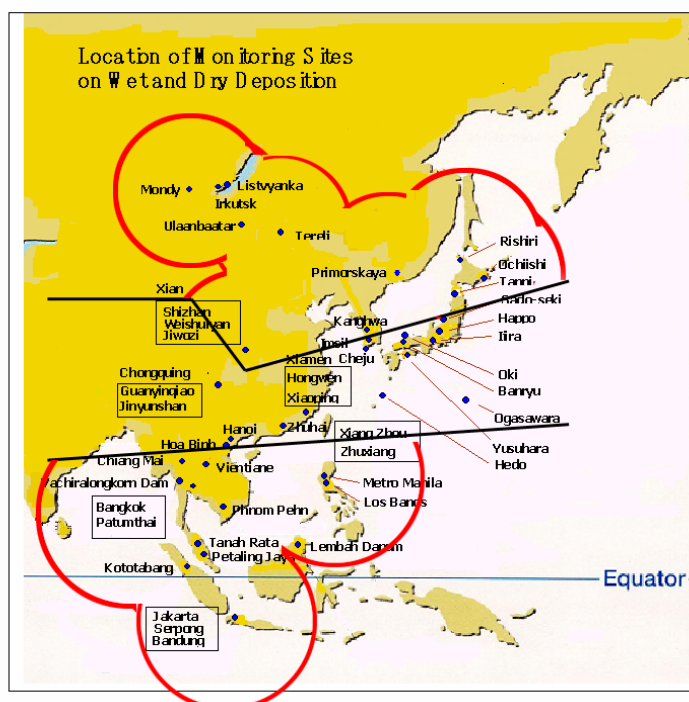
|                                   | Correlation function   | $r(0)$ | $l_0$ , km |
|-----------------------------------|------------------------|--------|------------|
| Middle latitudes region           |                        |        |            |
| nss-SO <sub>4</sub> <sup>2-</sup> | $y=0.619e^{-0.0016x}$  | 0.619  | 625        |
| NO <sub>3</sub> <sup>-</sup>      | $y=0.6137e^{-0.0021x}$ | 0.6137 | 476        |
| nss-Ca <sup>2+</sup>              | $y=0.4829e^{-0.0025x}$ | 0.2759 | 400        |
| Tropical region                   |                        |        |            |
| nss-SO <sub>4</sub> <sup>2-</sup> | $y=0.6536e^{-0.0011x}$ | 0.6536 | 909        |
| NO <sub>3</sub> <sup>-</sup>      | $y=0.6626e^{-0.0016x}$ | 0.6626 | 625        |
| NH <sub>4</sub> <sup>+</sup>      | $y=0.3872e^{-0.002x}$  | 0.3872 | 500        |

**Table 4 Statistical characteristics of radiuses for the weekly averaged data**

|                         | nss-SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | NH <sub>4</sub> <sup>+</sup> | nss-Ca <sup>2+</sup> | H <sup>+</sup>      |
|-------------------------|-----------------------------------|------------------------------|------------------------------|----------------------|---------------------|
| Middle latitudes region |                                   |                              |                              |                      |                     |
| Mean value, km          | 828                               | 646                          |                              | 3013                 |                     |
| Standard deviation, km  | 70                                | 54                           |                              | 91                   |                     |
| Maximum value, km       | 923<br>(Jiwozi)                   | 719<br>(Jiwozi)              |                              | 3151<br>(Happo)      |                     |
| Minimum value, km       | 654<br>(Ijira)                    | 513<br>(Ijira)               |                              | 2800<br>(Kanghwa)    |                     |
| Tropical region         |                                   |                              |                              |                      |                     |
| Mean value, km          | 1061                              | 853                          | 1344                         |                      | 594                 |
| Standard deviation, km  | 55                                | 60                           | 43                           |                      | 44                  |
| Maximum value, km       | 1137<br>(Chiang Mai)              | 923<br>(Kototabang)          | 1403<br>(Chiang Mai)         |                      | 655<br>(Chiang Mai) |
| Minimum value, km       | 972<br>(Kototabang)               | 774<br>(Hoa Binh)            | 1275<br>(Kototabang)         |                      | 523<br>(Kototabang) |

The smallest radiuses are typical for NO<sub>3</sub><sup>-</sup> in the middle latitudes region and for H<sup>+</sup> in the tropical region. Radiuses for NO<sub>3</sub><sup>-</sup> in the tropical region are also not so large, thus it confirms the fact that the densest network is required for adequate evaluation of the deposition process for this compound.

The maps of the representativeness areas for nss-SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, H<sup>+</sup>, which were obtained on the base of the weekly averaged data, are presented in Figs. 2-4.



**Figure 2 The representativeness areas for nss-SO<sub>4</sub><sup>2-</sup>, obtained on the base of weekly data.**

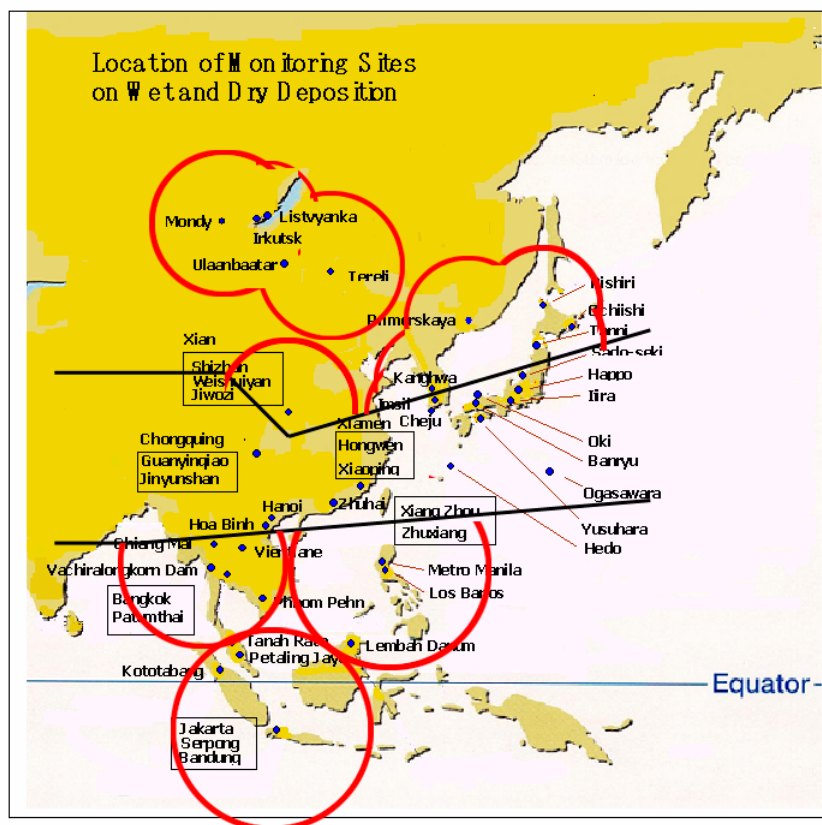


Figure 3 The representiveness areas for  $\text{NO}_3^-$ , obtained on the base of weekly data.

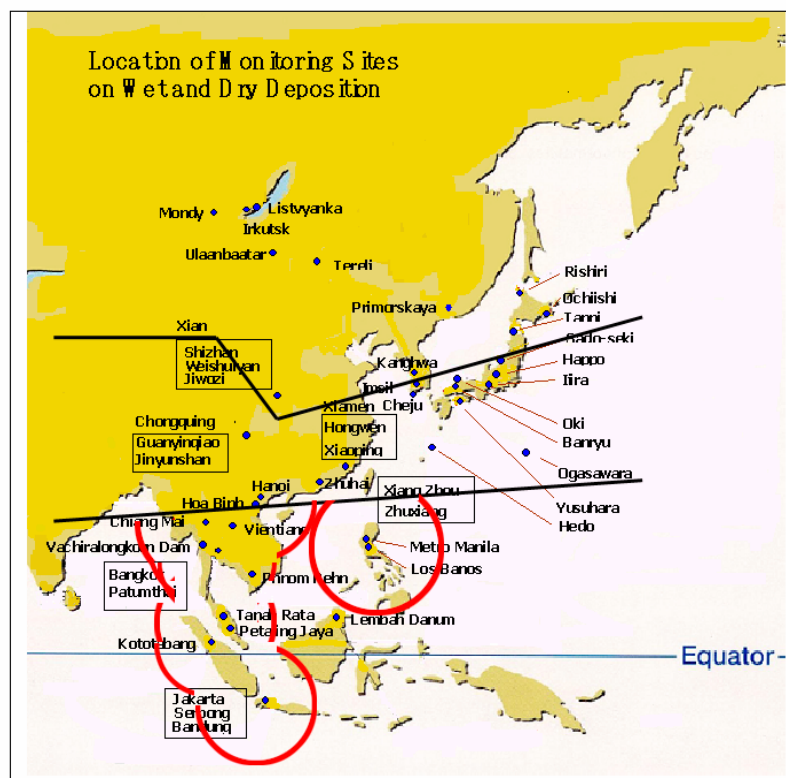


Figure 4 The representiveness areas for  $\text{H}^+$ , obtained on the base of weekly data.

Some important remarks should be done after the analysis of Figs. 2-4:

- there were no calculations for the subtropical region because only two stations belong to it (Xiaoping and Jinyunshan). Thus, it's the first area where new stations should be organized;
- for  $\text{nss-SO}_4^{2-}$ , the most part of the territory both in the middle latitudes and in the tropical region is covered by the observations. There are no suitable sites for the southwestern part of China, south part of Siberia, Russian Far East and east part of Indonesia;
- for  $\text{NO}_3^-$ , the gaps are more considerable. In addition to the same territories as for  $\text{nss-SO}_4^{2-}$ , the north and northeast parts of China are out of measurements network;
- for  $\text{H}^+$ , which was investigated only for tropical region, there are gaps in the east parts of Indonesia and Malaysia.

Summarizing this all we can say that densest network should be created for measuring  $\text{NO}_3^-$ , what is in good correspondence with the scientific conception of its cycle in the atmosphere. The gaps in the precipitation measurements are detected in the subtropical region ( $22 - 30^\circ \text{ N}$ ) for all parameters; in the southwestern part of China, south part of Siberia, Russian Far East, and east part of Indonesia for  $\text{nss-SO}_4^{2-}$ ; the southwestern, north and northeast parts of China, south part of Siberia, Russian Far East, and east part of Indonesia for  $\text{NO}_3^-$ ; the east parts of Indonesia and Malaysia for  $\text{H}^+$ .

These results are preliminary ones. It's evident that additional data in term of spatial resolution and temporal continuance is necessary to define the correlation functions and its parameters more precise and appropriate for evaluation of the representativeness areas. Experiments with the data of modeling will be very useful for this purpose. Also additional data let to identify variability of the correlation function in the different directions, for example, to evaluate whether the representativeness areas will be an ellipse or a round circle.

## References

- Isaev A. A. 1988. Statistics in meteorology and climatology. Moscow University, Moscow, Russia, pp. 209-218.
- Kagan R. L. 1966. Towards representativeness estimation of the precipitation data. Trudy MGO, 191: 22-34.
- Kagan R. L. & Gushchina M. V. 1966. On the statistical structure of the precipitation fields. Trudy MGO, 191: 35-47.
- Vitvitskii G. N., 1960. The Foreign Asia climates. Gosud. Isd. Geogr. Lit., Moscow, Russia, 399 p.

**Annex 1    Sets of stations, which data were used for calculations on the first-order and second-order approaches**

|                   |             |             |                               |
|-------------------|-------------|-------------|-------------------------------|
| China             | Jinyunshan  | Indonesia   | Serpong                       |
|                   | Weishuiyuan |             | Kototabang                    |
|                   | Jiwozi      | Malaysia    | Tanah Rata                    |
|                   | Xiaoping    | Philippines | Los Banos                     |
| Japan             | Rishiri     | Thailand    | Patumthani                    |
|                   | Tappi       |             | Chiang Mai (Mae Hia)          |
|                   | Sadoseki    |             | Kanchanaburi (Vachiralongkorn |
|                   | Happo       |             | Dam)                          |
|                   | Oki         |             |                               |
|                   | Yusuhara    |             |                               |
|                   | Ogasawara   |             |                               |
|                   | Hedo        |             |                               |
|                   | Ijira       |             |                               |
|                   | Ochiishi    |             |                               |
| Mongolia          | Terelj      | Viet Nam    | Hoa Binh                      |
| Republic of Korea | Kanghwa     | Russia      | Mondy                         |
|                   | Cheju       |             | Listvyanka                    |
|                   | Imstil      |             | Primorskaya                   |



# **Comparison of Air Pollution and Acid Deposition between Two Mega-Cities**

Yibing Lu<sup>1)\*</sup> and Hiroaki Yagoh<sup>2)</sup>

*1) Dept. of Analysis Technology, China National Environmental Monitoring Center (CNEMC),*

*\*Contact address: No.1 Yuhuananlu, Beisihuandonglu, Chaoyang District,  
Beijing 100029, P. R. China [e-mail: lvyb@cnemc.cn]*

*2) Acid Deposition and Oxidant Research Center (ADORC)*

About the acid deposition, precipitation with a pH of less than 3, which may cause acute damage to plants, was not observed in the two mega-cities. However, studies carried out at Chongqing from 2000 to 2006 indicated that about 76.2% of the samples had a pH of less than 5.0 and 2.4% less than 4.0. For Kawasaki from 1988 to 2005, the pH varied from 3.8–6.6 and the rain with pH below 5.0 was 75.1%. Compared with the urban sites, the acid deposition seemed serious in rural areas of Chongqing and that may be caused by lower neutralization function.

Though the social-economic developed with a dramatic speed, the emission of SO<sub>2</sub> from industrial in Chongqing didn't increase at all. Sulfate and nitrate deposition varied with season and the maximum value was observed in winter. Apart from SO<sub>2</sub>, TSP is still a problem in Chongqing. In Japan, the concentration of SO<sub>2</sub>, SPM met the standards in 1979 and 2004 respectively.

There is little reason to believe that vegetation damage attributable to acid deposition has been widespread and it is difficult to conclude that ecological damage of ecosystem caused by acid deposition has become obvious in Japan. The effects of acid deposition on soil, plant and ecosystem were interested in Chongqing. The exact reasons for the forest damage in 1982 remain to be determined but acid deposition due to SO<sub>2</sub> may have been the major cause.

Since that the concentration of organic substances was rather low and sometimes the ion balance can be obtained, most of the researchers thought that the functions of the organic substances could not be taken into consideration. However, in the south China, the relative contribution of organic acidic substances to acid rain was over 10%. Compared with Kawasaki, the metals existed with higher concentrations in the atmosphere. Apart from industrial influences, the automobile exhaust and the landforms of the area may be responsible for the pollution in Chongqing.

Special attention was given to the countermeasures against global warming, energy measures, chemical substance control, fine particles control and Photo-chemical fog recently in Kawasaki. Generally speaking, the Kawasaki City played vital roles in creating and implementing these solutions on air pollution. They enacted laws and formulated measures that have stimulated their efforts. Companies have made efforts to comply with governmental measures and policies at the same time. Kawasaki City is continuing to evolve, becoming an information base that will diffuse the city's experiences and technologies to other parts of the world.

## **1. Introduction**

Acid deposition was drawing considerable concern in Europe and North America during the 1970s and 1980s. Rapid population growth, industrial activities and high fuel consumption in the East Asian countries have created increasing threat of air pollution, which can cause damaging effects on the regional environment. Acid

deposition is a significant regional environmental problem that has received much attention from scientists around the world as well as international organizations [1].

Atmospheric environmental quality in China has been improving due to a variety of programs implemented by the Chinese government in recent decades. However, air pollution is still serious because of rapid socioeconomic development and increased energy consumption. Air pollution originates from multiple sources and the effect on public human health will increase. Acid rain was recognized as a potential environmental problem in China in the late 1970s. In 2001, the Chinese state Environmental Protection Agency estimated that about one third of the Chinese territory suffers pollution from acid rain in 2003 [2,3]. In China, coal accounts for about 70% of the commercial energy production, and it is likely that coal will be the major energy carried also in the coming decades. This leads to large emissions of  $\text{SO}_2$ , which up to now has been the most important precursor of acid rain in China. Furthermore, there is a rapidly increasing  $\text{NO}_x$  emission, in addition to the increasing emission from the coal combustion.

Just like North America and Europe, in Japan, the emission of  $\text{SO}_2$  has decreased substantially the last decades. The long-term monitoring networks that traditionally have served the acid rain issue are now also very valuable for eutrophication, climate and aerosol research. Nevertheless, acid rain is still a major environmental problem, but the focus is more on nitrogen species because of their increased relative importance in creating acid rain. In addition, nitrogen is important for eutrophication and formation of ozone. The situation is quite different in China where  $\text{SO}_2$  is still a major problem.

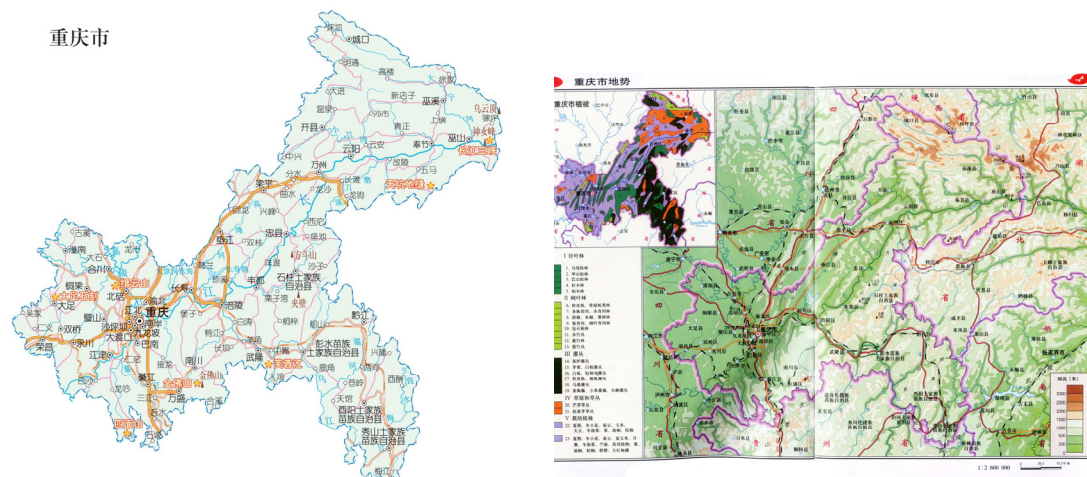
In this report, the air pollution and acid deposition in the two selected mega-cities, including Chongqing in China and Kawasaki in Japan was discussed. Chongqing is among the heaviest polluted cities in China and combustion of coal with relatively high sulfur contents causes high sulfur emission and deposition in the area. And in Japan, Kawasaki was selected because kinds of data can be found and it always the serious polluted city historically. Rich experiences in controlling the air pollution and acid deposition as well may be beneficial to the other mega-cities facing the similar problems.

## **2. Air pollution and acid deposition in the mega-cities**

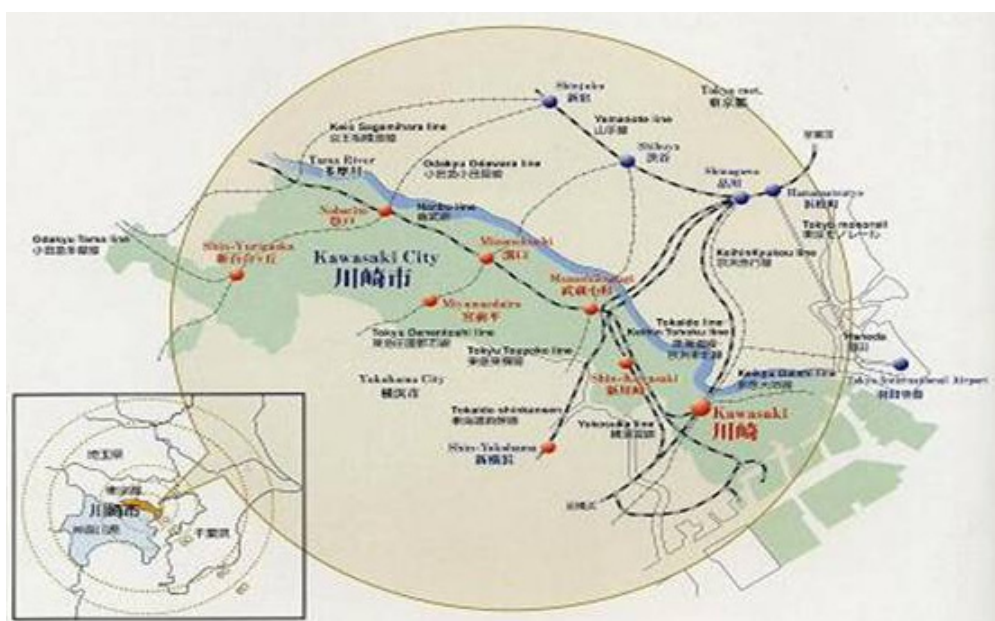
### **2.1. Introduction of the two mega-cities**

Widely acknowledged as the largest industrial and economic center in southwestern China, Chongqing was founded in 1997. Prior to then, it was a city in Sichuan Province. Of all the municipalities, Chongqing has the largest area, covering 82,400  $\text{km}^2$  and the highest proportion of peasants. At the end of 1997, 30.429 million people lived in Chongqing, however, more than 80 percent of the population is rural, a figure far higher than in the other municipalities. Chongqing City spreads across a number of low hills (average elevation of 400 meters), surrounded by mountains, and straddling the Yangtze River (Fig. 1).

Kawasaki City, just south of Tokyo, has a population of 1.3 million (Fig. 2). The city has been the basic engine of Japan's economic development for decades, particularly during the last half century. In the process of economic expansion and development, however, its environment was rapidly polluted by expanding industrial activities. This phenomenon was very evident in the 1960s and 1970s, when Kawasaki City became known as a "polluted city". Many citizens suffered from the effects of air pollution, resulting in serious social and political problems. In recent years, Kawasaki has been changing its identity significantly into a high-tech industrial technology and research and development functions gather.



**Figure 1** Location and topography of Chongqing.



**Figure 2** Location of Kawasaki-City.

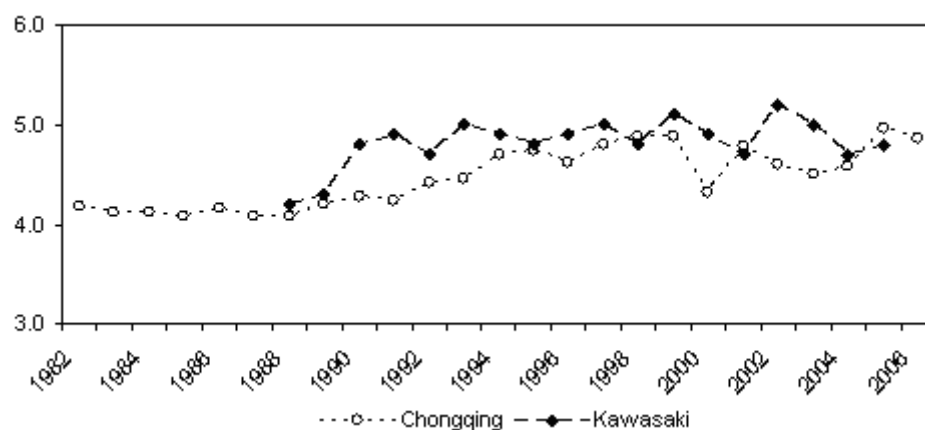
Due to the diversity of geography and climatic regimes throughout the two regions, differences in specific meteorological conditions can be expected in each city. Since no corrected data could be found in Kawasaki, meteorological conditions of Chongqing and Yokohama, neighboring Kawasaki-city, were shown in Table 1.

**Table 1** Multi-year average monthly meteorological condition at Chongqing and Yokohama

| City      | Temperature, | Humidity, | Wind speed m.sec <sup>-1</sup> | Precipitation, mm | Years of data |
|-----------|--------------|-----------|--------------------------------|-------------------|---------------|
|           |              | %         |                                |                   |               |
| Chongqing | 18.7         | 80        | 1.6                            | 1212              | 2002-2004     |
| Yokohama  | 16.2         | 64        | 3.7                            | 1901              | 2004-2004     |

## 2.2. Acid deposition in the two mega-cities

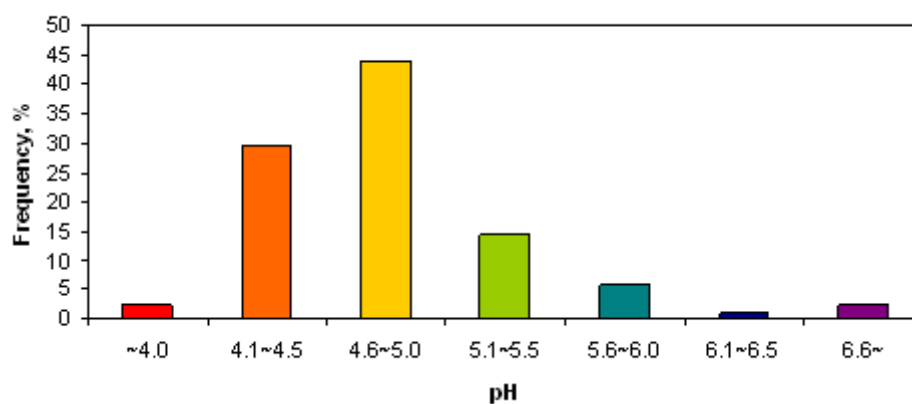
### 2.2.1. Wet deposition



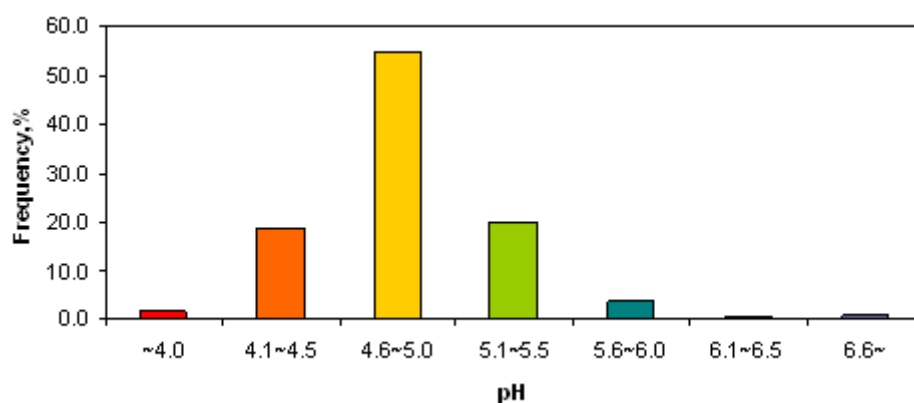
**Figure 3 Annual average changing tendency of pH.**

There was observed a slight increase in rainwater pH for the whole assessment period in Chongqing and Kawasaki (Fig. 3) [4-6]. The volume-weighted annual average of rainwater pH values were 4.5 for Chongqing from 1982 to 2006 and 4.8 to Kawasaki from 1988 to 2005. The frequency distributions of the rainwater pH in the two selected mega-cities were presented in Fig. 4 and Fig. 5.

The pH of rainwater was in the range from 3.8~7.6 in urban area of Chongqing, however, considerable part of measurements, about 76.2% of all samples had a pH of less than 5.0 and 2.4% less than 4.0. For Kawasaki, the pH varied from 3.8~6.6 and the rain with pH below 5.0 was 75.1% and 1.5% less than 4.0. Precipitation with a pH of less than 3, which may cause acute damage to plants, was not observed in the two mega-cities.

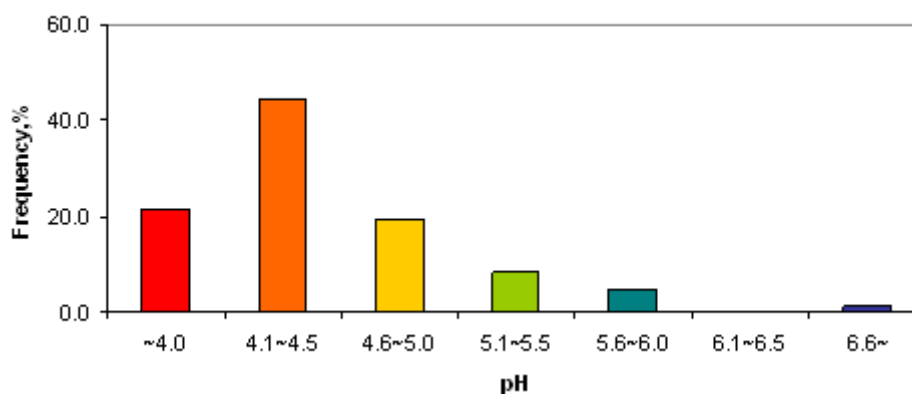


**Figure 4 Precipitation frequency and amount classified by pH in Chongqing, 2000-2006.**



**Figure 5** Precipitation frequency and amount classified by pH in Kawasaki, 1988-2005.

Compared with the urban sites, the acid deposition seemed serious in rural areas of Chongqing now (Fig. 6) and maybe higher concentration of cations such as  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  had larger neutralization function at the urban sites (Table. 2). The pH of rainwater was in the range from 3.7~6.7 in rural area, however, considerable part of measurements, about 85.6% of the samples had a pH of less than 5.0 and 21.7% had less than 4.0.



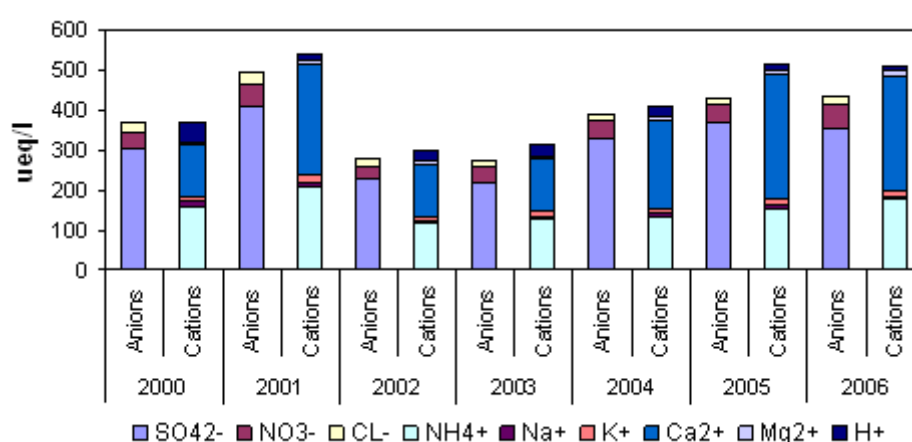
**Figure 6** Precipitation frequency and amount classified by pH in rural areas of Chongqing, 1988-2005.

**Table 2** Concentrations of  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  in Chongqing

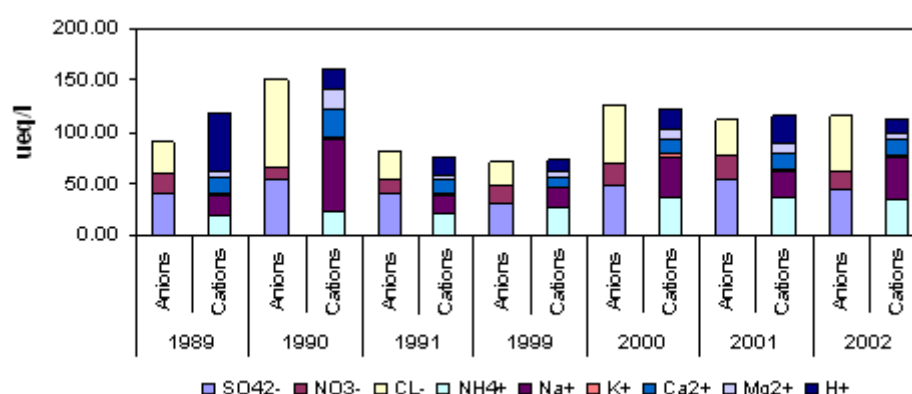
|                  |       | (μmol/L) |      |      |      |      |      |      |
|------------------|-------|----------|------|------|------|------|------|------|
| Year             |       | 2000     | 2001 | 2002 | 2003 | 2004 | 2005 | 2006 |
| $\text{Ca}^{2+}$ | Urban | 63       | 137  | 65.4 | 65.4 | 110  | 156  | 143  |
|                  | Rural | 55.2     | 44.9 | 29.7 | 30.7 | 70.2 | 57.4 | 98.2 |
| $\text{NH}_4^+$  | Urban | 161      | 211  | 120  | 132  | 137  | 157  | 179  |
|                  | Rural | 105      | 111  | 83.5 | 85.6 | 105  | 105  | 121  |

Rainwater contains various dissolved anions and cations after incorporating gaseous and aerosol species from the ambient air. The anions and cations usually measured were  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{H}^+$ . The volume-weighted, averaged compositions of directly measurable cations and anions were calculated and shown in Figs. 7 and 8 to exhibit the characteristics of ionic species in precipitation at Chongqing and Kawasaki.

The major anion at Chongqing was found to be  $\text{SO}_4^{2-}$ , and the major cations were  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ . Kawasaki, located in coastal areas, was greatly affected by sea salt input and the major anion and cation were  $\text{Cl}^-$  and  $\text{Na}^+$ , respectively. It was discovered that the  $\text{Cl}^-$  concentration was equal to  $\text{Na}^+$  concentration, because they were incorporated into cloud or rain droplets in the form of salts. Besides  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  also appeared to be a major anion, followed by  $\text{NO}_3^-$ . Note that  $\text{Ca}^{2+}$  appeared to be negligible at Kawasaki.

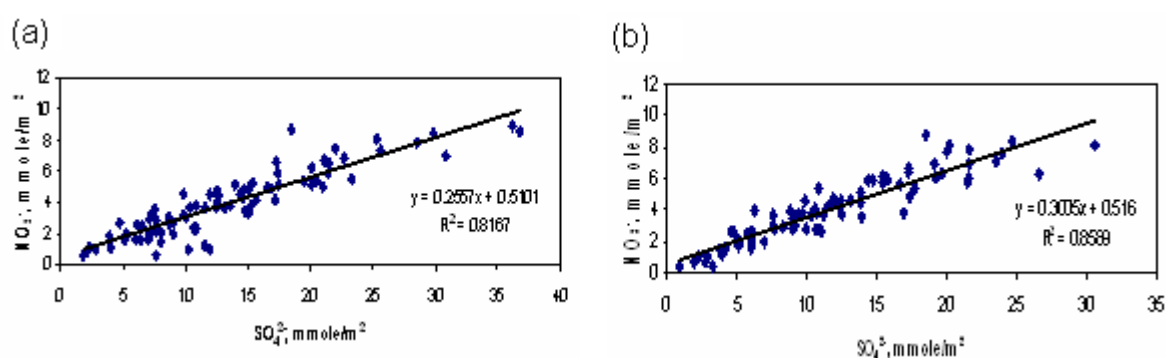


**Figure 7** Concentrations of main anions and cations in precipitation collected at Chongqing.



**Figure 8** Concentrations of main anions and cations in precipitation collected at Kawasaki.

The correlation of ions in rainwater may reveal source characteristics as well as precipitation chemistry. And, the correlations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were often analyzed, because knowing the ratio of the two is useful in identifying major acidifying substances. The monthly averaged amount of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  correlated very well (Fig. 9 (a) and (b)). The slope lines in Figures were derived by linear regression analysis and could be interpreted as a molar ratio of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in precipitation. The  $R^2$  values were 0.81 and 0.86 in urban and rural areas of Chongqing, respectively, implying a statistically significant level of correlation. The molar ratios of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in Chongqing were 2.97 and 3.64. Therefore,  $\text{SO}_4^{2-}$  may be regarded as a major acid ion in rainwater in Chongqing, surpassing  $\text{NO}_3^-$ , and its molar ratios were higher than Kawasaki and other parts of the EANET region (Table 3).



**Figure 9** Monthly averaged wet deposition amount of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in (a) urban and (b) rural areas of Chongqing (2000-2006).

**Table 3** Ratios of sulfate and nitrate estimated by linear regression analysis

| Cities             | Monitoring site | $R^2$ | $\text{SO}_4^{2-}/\text{NO}_3^-$ |
|--------------------|-----------------|-------|----------------------------------|
| Chongqing, China   | Urban           | 0.81  | 2.97                             |
|                    | Rural           | 0.86  | 3.64                             |
| Kawasaki, Japan    | Urban           | 0.54  | 0.78                             |
| Jakarta, Indonesia | Urban           | 0.74  | 0.68                             |
| Hanoi, Vietnam     | Urban           | 0.47  | 0.73                             |
| Bangkok, Thailand  | Urban           | 0.91  | 0.74                             |

### 2.2.2. Dry deposition

With the economic development in China, the coal production and consumption amount have rapid increased, amounting to 136 billion tons in 1998, which accounted for over 70% of the total. The air pollutants from burning the coal with high sulfur and high ash content without any treatment have become the source of the serious air pollution. Especially, Chongqing City in southwest area which has suffered from serious air pollution and acid rain is well known as a typical city polluted by the coal combustion in the world [7]. Moreover, special natural circumstances resulted in serious air pollution, which is rarely nation-wide.

The emission of  $\text{SO}_2$  during 1998-2005 was shown in Table 4 (Chongqing Environmental Protection Bureau) [8]. For residential, the emission of  $\text{SO}_2$  decreased since then because the civilian fuel for cooking, space heating etc. was gradually replaced with natural gas. Though the social-economic developed with a dramatic speed, the emission of  $\text{SO}_2$  from industrial didn't increase at all because the height of the chimney for



factory boilers increased in urban area and the desulphurization equipments for flue gas were established on the power plants for recent years. For example, Chongqing government invested 182 million-yuan for the project removing the waste gas in 1998 and established the control area of SO<sub>2</sub> emission in urban where the use of the raw coal without any treatment was banned. However, the concentrations of SO<sub>2</sub> exceed the National Standard 3 times in 1998 and 0.22 in 2005 (Fig. 9). The annual average wind is low, only 1.3m/s and the annual calm frequency amounted to 60-80% in urban area. Thus, a large fraction of emissions from the coal combustion is deposited directly as the gaseous and particulate sulfur due to the complicated terrain and unfavorable meteorological condition for diffusion of air pollutants.

Heavy oil and coal were mainly used as fuel from 1960s to 1970s in Kawasaki (Table 5). During that period, SO<sub>2</sub> emission was so serious that the citizens suffered from diseases caused by the air pollution. The situation changed since the improvement of technology and use of natural gas. In Kawasaki, the concentrations of SO<sub>2</sub> met the environmental standard in the entire city in 1979 (Fig. 10).

**Table 4 Emission amounts of SO<sub>2</sub> in Chongqing City**

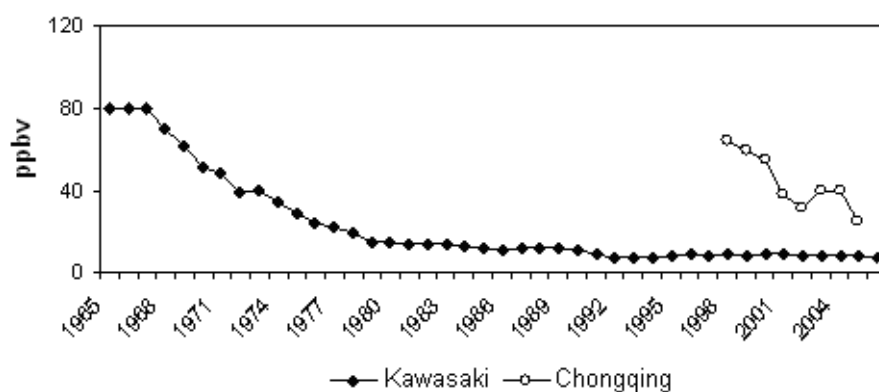
| year | Industrial, ×10000t | Residential, ×10000t | Total, ×10000t |
|------|---------------------|----------------------|----------------|
| 1998 | 73.64               | 19.43                | 93.07          |
| 1999 | 75.88               | 18.24                | 94.11          |
| 2000 | 66.42               | -                    | 83.94          |
| 2001 | 56.94               | 19.00                | 72.20          |
| 2002 | 55.18               | 14.75                | 69.93          |
| 2003 | 61.31               | 15.32                | 76.63          |
| 2004 | 64.11               | 15.42                | 79.53          |
| 2005 | 68.32               | 15.39                | 83.71          |

**Table 5 Usage of materials and the emission of SO<sub>2</sub> from industries in Kawasaki [9]**

|      | Heavy oil |                     | Coal    |                     | Gas                              |                     | Fe <sub>2</sub> O <sub>3</sub> |                     | Total               |
|------|-----------|---------------------|---------|---------------------|----------------------------------|---------------------|--------------------------------|---------------------|---------------------|
|      | ×10000kl  | SO <sub>2</sub> , t | ×10000t | SO <sub>2</sub> , t | ×10 <sup>7</sup> Nm <sup>3</sup> | SO <sub>2</sub> , t | ×10000t                        | SO <sub>2</sub> , t | SO <sub>2</sub> , t |
| 1965 | 174       | 82000               | 470     | 47000               | -                                | -                   | 430                            | 24900               | 152100              |
| 1966 | 165       | 74800               | 201     | 20100               | -                                | -                   | 430                            | 23200               | 118100              |
| 1967 | 214       | 88600               | 210     | 21000               | -                                | -                   | 430                            | 21500               | 131100              |
| 1968 | 233       | 80900               | 273     | 27300               | -                                | -                   | 436                            | 20100               | 128300              |

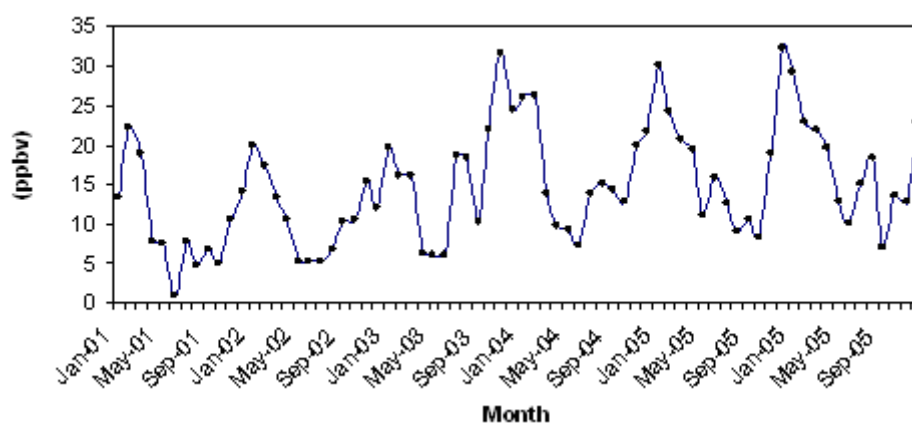


|      |     |       |     |       |      |      |     |       |        |
|------|-----|-------|-----|-------|------|------|-----|-------|--------|
| 1969 | 312 | 86000 | 176 | 17600 | -    | -    | 456 | 14600 | 118200 |
| 1970 | 415 | 98300 | 109 | 8800  | -    | -    | 449 | 13500 | 120600 |
| 1971 | 385 | 69300 | 90  | 6400  | -    | -    | 414 | 10800 | 86500  |
| 1972 | 364 | 47600 | 39  | 2700  | -    | -    | 310 | 6300  | 56600  |
| 1973 | 430 | 34500 | 2   | 100   | 423  | 4500 | 305 | 4700  | 43800  |
| 1974 | 404 | 15900 | -   | -     | 426  | 3700 | 164 | 1600  | 21200  |
| 1975 | 332 | 12900 | -   | -     | 450  | 3700 | 156 | 1300  | 17900  |
| 1976 | 365 | 8700  | -   | -     | 478  | 1600 | 217 | 900   | 11200  |
| 1977 | 387 | 8800  | -   | -     | 907  | 2000 | 659 | 1100  | 11900  |
| 1978 | 380 | 7400  | -   | -     | 932  | 1900 | 591 | 800   | 10100  |
| 1979 | 368 | 6300  | -   | -     | 927  | 1900 | 490 | 400   | 8600   |
| 1980 | 322 | 5100  | 2   | -     | 1224 | 2000 | 606 | 100   | 7200   |
| 1981 | 284 | 3900  | 12  | -     | 1274 | 2200 | 644 | 100   | 6200   |
| 1982 | 239 | 3100  | 11  | -     | 1233 | 2000 | 612 | 100   | 5200   |
| 1983 | 210 | 2600  | 18  | -     | 1270 | 2000 | 637 | 100   | 4700   |

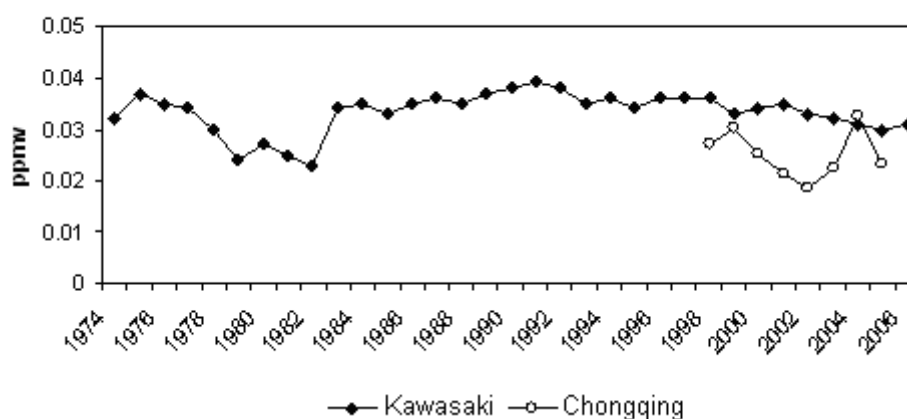


**Figure 10 Annual change of SO<sub>2</sub> concentration in Kawasaki and Chongqing.**

The monthly average concentrations of the SO<sub>2</sub> in the Jiyunshan Mountain are plotted in Fig. 11. There was a clear seasonal variation with highest concentrations during the winter. Most researches were carried on the air pollution at urban sites, however, the higher concentration of SO<sub>2</sub> in the rural areas showed that the results will necessarily have large impact on the air quality. The monitoring of acid and entrophying pollutants needs to be extended to cover larger areas in China and especially more rural sites. Although sulphur is the dominant acidification precursor at the sites, the concentration and deposition of nitrogen is considerable recently (Fig. 12). And it is necessary to increase focus on nitrogen and base cations in addition to pH and sulphate, which have the main attention at present.



**Figure 11 Monthly averaged concentration of SO<sub>2</sub>.**



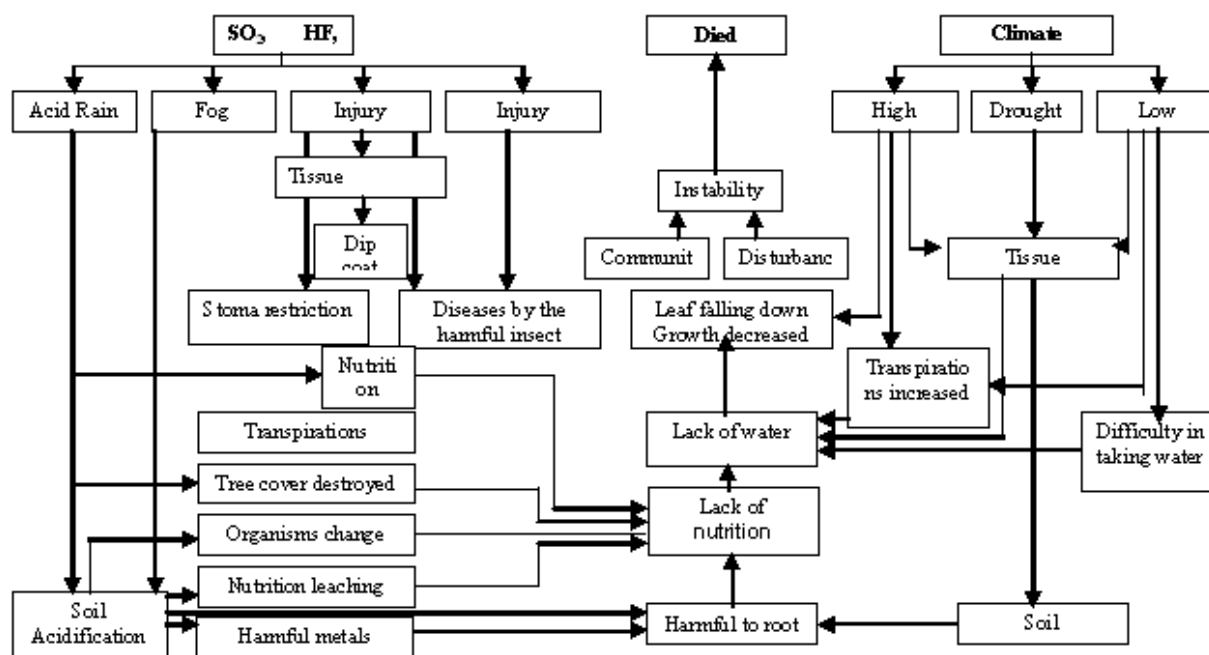
**Figure 12 Annual change of NO<sub>2</sub> concentration in Kawasaki and Chongqing.**

### 2.2.3. Effect on ecosystem

No correlated report can be found about the effect on the ecosystem in Kawasaki City. However, in Japan, no major changes in the chemical components of soil were observed yet; suggesting that, by the large, there has been no drastic development in the acidification of soil in Japan. However, the level of tree damage was monitored at about 120 sites from 1988 to 2002. As a result, damaged trees were found at 55 sites, almost half of all the observation sites. In most cases, the cause of tree damage can be specified, for example, as damage by disease and pests (such as pine wilt disease), and there were no damaged trees for which the primary causes of damage were definitely considered to be acid deposition and acidified soil. For example, when the cause of

damage to an Erman's birch forest was discussed, the concentration of rain and fog and the level of  $\text{NO}_2$  and  $\text{SO}_2$  in the atmosphere were low; and according to the observation of the atmosphere,  $\text{NO}_2$  was between 2 and 4 ppb, and  $\text{SO}_2$  was between undetectable and 2.5 ppb, the levels of such substances were too low to have caused the damage, and acidified soil was also considered unlikely to have caused the damage (typical relationship is depicted in Fig. 13). That's mean, in Japan there is little reason to believe that vegetation damage attributable to acid deposition has been widespread and it is difficult to conclude that ecological damage of ecosystem cause by acid deposition has become obvious [10]. No correlated data can be found about Kawasaki City.

The effects of acid deposition on soil, plant and ecosystem were interested in Chongqing City [11-15]. The  $\text{Al}/(\text{Ca}^{2+}+\text{Mg}^{2+})$  molar ratio has been suggested used as an acidification indicator in Europe and North America. The concentration of inorganic aluminum in soil water must be characterized as high and possible toxic effects on plant roots may be expected. However, it is assumed that high concentration of bivalent cations (i.e.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) counteract the toxic effect of Al. At Tieshanping, high concentration of calcium keeps the  $\text{Al}/(\text{Ca}^{2+}+\text{Mg}^{2+})$  ratio moderately low. The sources for the calcium deposition is not known clearly, but if a significant part originates from combustion sources it important to take this into consideration when setting emission reduction measures [16]. However, some stress symptoms at the forest in the area and severe forest damage has been reported at Nanshan, closer to Chongqing Center. Especially, on the night of 18 June, 1982, the amount of precipitation was 14mm in Baxian located in the south of Chongqing. The following day was clear, and the leaf color was noted to have faded and to be red in the afternoon. Lightly damaged leaves had red spots, as many as 15-20cm spots in chains in the worst cases. In a few days, plants died, as if by burning and the damaged areas were about 667 ha where the heavily damaged areas covered 467 ha. Up to July 1983, dead forest area was as much as 754 ha. The exact reasons for the forest damage remain to be determined but acid deposition due to  $\text{SO}_2$  may have been the major cause [17].

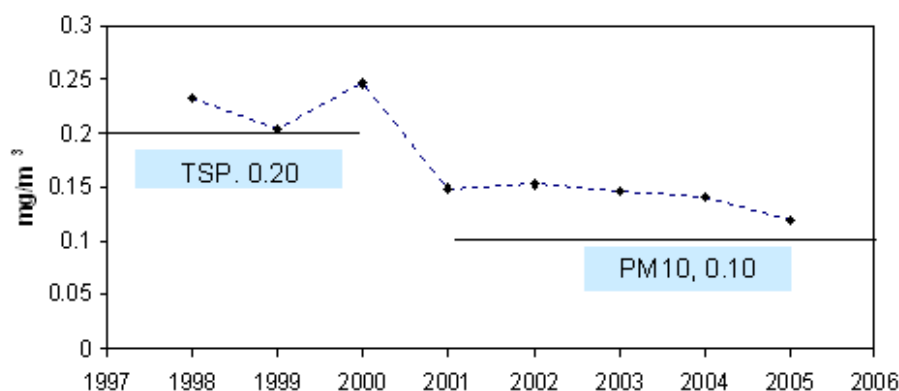


**Figure 13 Relationship between trees damages and environmental elements.**

## 2.3. Other pollutants

### 2.3.1. TSP in Chongqing City

Apart from  $\text{SO}_2$ , particles such as TSP and  $\text{PM}_{10}$  are still a problem in Chongqing (Fig. 14). Early research showed that the main TSP in Chongqing was coal soot, steel and iron soot, street soil soot, building material soot and the secondary aerosol. Results indicated that construction activities enhanced the pollution level of particulate matter. Compared with the roadway sections without construction activity, the section with construction activity had higher dust load 8.76 times. With the increase of distance, concentration of atmospheric particulates decreased [18]. Soil, coal burning vehicle and metallurgy are main sources of the traffic dust. Soil is found to contribute about half of the traffic dust, while another came from human activities [19].



**Figure 14 The changing tendency of particles in Chongqing.**

The dominant cation in the fall dust is calcium and it can absorb  $\text{SO}_2$  and not acidify itself. Calculation indicated fall dust can neutralize 11.8% of the amount of hydrogen in precipitation in maximum in urban area and 6.2% at four side mountain background regions. Compared with the north cities in China, particulates in Chongqing have higher acidity and much lower buffering capacity. Along with decreasing in size, the acidity of particles is increasing while buffering capacity decreasing. This is due to the fact that  $\text{SO}_4^{2-}$  content is higher and  $\text{Ca}^{2+}$  content is lower in fine particles than in coarse particles. Experiments on buffering capacity of airborne particles and below-cloud scavenging of  $\text{SO}_2$  in air showed that atmospheric particulates are able to neutralize near half of the acid in precipitation. Washout of particulates is the major source of  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$  in precipitation [20].

### 2.3.2. Organic substances in southwest China

While during precipitation, rainwater dissolves and scavenges from the atmosphere gases as well as aerosols that contain a large array of inorganic and organic materials. Although numerous studies have recently been conducted on the inorganic chemistry of rainwater, little attention has so far been paid to the organic compounds. Lunde *et al.* have provided the most detailed report on aliphatic aromatic hydrocarbons, ketones, aldehydes, phthalates, fatty acid ethyl esters, free fatty acids, and other acids in rain water and snow samples in Norway and discussed their origin and transport through the atmosphere [21]. Matsumoto and Hanya [22] reported nonvolatile organic constituents in atmosphere fallout (dry fallout plus rain) in the Tokyo area and discussed the fluxes of n-alkanes, fatty acids, phenols, and bisphenol A. Hydrocarbons were, on the average, twice as abundant as fatty acids and 12~130 times as abundant as phenols. Also, other miscellaneous reports have appeared on specific organic compounds in rain the U.S. In 1986 to 1989 and organic compounds in the rainwater of Los Angeles were analyzed by Kimitaka Kawamura [23,24].

Since that the concentration of organic substances was rather low and sometimes the ion balance can be obtained, most of the researchers thought that functions of the organic substances could not be taken into consideration. However, in the south China, the relative contribution of organic acidic substances to acid rain was over 10%. Organic and acidic substances in the atmospheric environment and rain were continuously and systematically monitored in Southwest China (Guiyang, Chongqing and Chengdu) for four years [25]. Results showed that the organic chemicals especially the aldehydes have the promoting function on  $\text{SO}_2$  transformation into  $\text{SO}_3$  and then to form  $\text{H}_2\text{SO}_4$ , and the effect of hydrocarbon on the formation of organic acids by photochemical reaction in the atmosphere are described. The atmospheric chemical reaction processes were simulated the model verified with data of field measurement. The relative contribution of major acidic substances ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and organic acid) to acid rain was 75.2-81.5%, 5.9-6.1% and 12.4-18.9% respectively. Since the ion balance couldn't be met in some places in south China, further research should be carried on whether the organic substances will affect the acid deposition. No VOCs data can be found in Chongqing China. And in Kawasaki, EPA TO-14 method was used and 44 kinds of VOCs were determined from 2002 to 2006.

### 2.3.3. Heavy Metal in the two mega-cities

Once anthropogenic and natural emissions are released into the atmosphere, a complex mix of physical and chemical processes redistributes them locally, regionally and globally. The measurement of emissions from either individual or multiple sources is very important to understand and predict the present and future status of the air quality. Concerning this interest, studies on the transport and deposition of atmospheric trace elements have received increasing attention, especially with regard to the issue of long range transport. Most of the measurements were done for several years or only for a short time based on seasonal changes of the certain area due to limitations of equipment, personnel and funds. However, the National Air Surveillance Network in Japan has sequentially collected air quality data including aerosol particles without interruption for a long time on many measured items by almost the same methods of collection and analysis. The data from National Air Surveillance Network (NASN) for selected crustal elements (Al, Ca, Fe, Mn, Sc and Ti), anthropogenic elements (As, Cu, Cr, Ni, Pb, V and Zn) and a marine element (Na) in atmospheric particulate matter have been evaluated over Japan from 1974 to 1996 [26]. The highest average concentrations (Fe, Ti, Mn, Cu, Ni and V) could be seen in the industrial city Kawasaki.

Concentration of kinds of metal elements in the atmospheric TSP was analyzed in the urban district of Chongqing in 1992. Results indicated the concentrations of metals in Chongqing were higher than Beijing, Shanghai [27]. In 2001, the concentration of Pb decreased greatly to  $289.2 \text{ ng/m}^3$ , may be affected by the use of improved oil (Table 6). The source of crustal-derived elements in the atmosphere is mainly wind-blown soil particle; however, in industrial and/or urban areas, human activities such as metal industry and fuel combustion can be origins of soil-derived elements in the atmosphere. Based on the method of enrichment factor, the results showed that the enrichment coefficient of 5 kinds of heavy metals in the TSP greatly higher than 10, even 1-3 number grade and can conclude that the pollution of heavy metals in the TSP of Chongqing mainly come from the human activities [28].

Compared with Kawasaki, the metals existed with higher concentrations in the atmosphere. For example, concentration of Pb, derived principally from the combustion of petrol containing lead additives and from smelting, nearly 5 times higher than Kawasaki. Apart from industrial influences, the automobile exhaust and the landforms of the area may be responsible for the air pollution.

**Table 6 Annual concentrations of the elements in atmospheric particulate matter in Chongqing and Kawasaki**

| Elements | Chongqing(1992)*      | Kawasaki(1974-1996) |
|----------|-----------------------|---------------------|
| Al       | 4802                  | 586.1±195.9         |
| Fe       | 1020                  | 1246.1±316.9        |
| Mn       | 401.1                 | 70.2±36.3           |
| Cu       | 144.1, 109.6 (2001)** | 100.5±76.7          |
| Cr       | 53.2, 471.9 (2001)**  | 19.3±4.79           |
| Ni       | 42.2                  | 13.6±3.79           |
| Pb       | 872.2, 289.2 (2001)** | 146.1±94.1          |
| V        | 13.9                  | 14.9±7.81           |
| Zn       | 1022, 921.6 (2001)**  | 190±34.3            |

\*Data on 1992 from reference 22 and on 2001 from 23 respectively.

\*\* Data on 2001 cited from Jiangbei District.

#### 2.3.4. Other pollutants in Kawasaki

In Kawasaki, much attention is paid to the air quality. 9 general stations and 9 roadside stations are set up for monitoring the air pollution. The monitoring items, measuring methods and environmental quality standards are shown in Table 7.

**Table 7 Monitoring items of Kawasaki City**

| Monitoring items  | Measuring methods                        | Environmental quality standards   |  |
|-------------------|--|---|--|
|                   |  | Environmental target value  | Measure target value   |
| NO                | JIS B 7953                               |   |  |
| NO <sub>2</sub>   | JIS B 7953                               | 0.02 ppm, daily average   | 0.04 ppm, daily average  |
| SPM               | JIS B 7954                               | 0.075 mg/m <sup>3</sup> , daily average; 0.0125 mg/m <sup>3</sup> , trend of annual average | 0.1 mg/m <sup>3</sup> , daily average; 0.2 mg/m <sup>3</sup> , hourly values |
| Ox                | JIS B 7957                               | 0.06 ppm, hourly values   |  |
| SO <sub>2</sub>   | JIS B 7952                               | 0.04 ppm, daily average; 0.1ppm, hourly values  | 0.04 ppm, daily average; 0.1 ppm, hourly values                              |
| CO                | JIS B 7951                               | 10 ppm, daily average; 20ppm, hourly values   | 10 ppm, daily average; 20 ppm, hourly values                                 |
| NMHC              | JIS B 7956                               |   |  |
| CH <sub>4</sub>   | JIS B 7956                               |   |  |
| PM <sub>2.5</sub> | Tapered Element Oscillating Microbalance |   |  |

|           | method                          |
|-----------|---------------------------------|
| Acid Rain | Glass electrode method          |
| WD        | Windmill type                   |
| WS        | Windmill type                   |
| TEMP      | Platinum resistance thermometer |
| HUM       | Hair type, Capacitance method   |
| SUN       | Duplication glass dome method   |
| RAIN      | Tipping bucket method           |

Special attention was given to the countermeasures against global warming, energy measures, chemical substance control, nanoparticles control and Photo-chemical fog recently. Especially, information on Announcement Situation of Photochemical Smog Warnings can be offered to the citizens by the telephone and the Internet in Kanagawa Prefecture on the day from April to October of period. Moreover, 234 kinds of chemicals were defined to “hazardous atmospheric substances” and among which 22 should be determined priority. 19 kinds of pollutants were analyzed in Kawasaki every year. Most of the results were lower than the standards except for the concentrations of benzenes and Ni (Table 8).

**Table 8 Average concentration of hazardous atmospheric substances in Kawasaki, 2006**

| Pollutants          | Monitoring Sites |          |         |         | Standards |
|---------------------|------------------|----------|---------|---------|-----------|
|                     | Daishi           | Nakahara | Tama    | Ikegami |           |
| Benzene             | 2.6              | 2.1      | 2.2     | 3.2     | 3         |
| Trichloroethylene   | 2.1              | 2.6      | 1.6     | 2.6     | 200       |
| Tetrachloroethylene | 0.72             | 0.87     | 0.77    | 0.65    | 200       |
| Dichloromethane     | 3.1              | 3.2      | 3.2     | 3.2     | 150       |
| Acrylonitrile       | 0.63             | 0.23     | 0.14    | 0.65    | ( 2 )     |
| Vinyl chloride      | 0.057            | 0.059    | 0.021   | 0.14    | ( 10 )    |
| Hg                  | 0.0026           | 0.0021   | 0.0022  | 0.0032  | ( 0.040 ) |
| Ni                  | 0.029            | 0.010    | 0.0046  | 0.035   | ( 0.025 ) |
| trichloromethane    | 0.26             | 0.23     | 0.24    | 0.23    | (18)      |
| 1,2-Dichloroethane  | 0.17             | 0.20     | 0.16    | 0.19    | (1.6)     |
| 1,3-Butadiene       | 0.84             | 0.39     | 0.32    | 1.5     | (2.5)     |
| Ethylene oxide      | 0.52             | 0.33     | 0.31    | 0.60    | —         |
| Benzo(a)pyrene      | 0.00054          | 0.00041  | 0.00035 | 0.00070 | —         |

|              |          |          |          |          |   |
|--------------|----------|----------|----------|----------|---|
| formaldehyde | 3.7      | 3.6      | 3.1      | 4.5      | — |
| acetaldehyde | 4.0      | 3.5      | 3.2      | 4.9      | — |
| Be           | 0.000021 | 0.000014 | 0.000011 | 0.000035 | — |
| Mn           | 0.12     | 0.053    | 0.043    | 0.16     | — |
| Cr           | 0.018    | 0.0043   | 0.0028   | 0.024    | — |
| As           | 0.0012   | 0.0011   | 0.0010   | 0.0014   | — |

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

## 2.4. Rules to control the air pollution in Kawasaki

Kawasaki has been polluted seriously in 1960s and now it's a high-tech industrial city (Fig.15).



**Figure 15 Outlook of Kawasaki in 1960s and recently.**

Usually, rapidly industrializing nations occasionally face a host of environmental concerns ranging from the more “traditional” type of pollution to global environmental challenges. In particular, the urban air pollution levels in industrializing nations match those of Japan during its most polluted period in the past. For each nation can apply lessons learned from the Japan’s and other developed nations’ successes and failures in environmental measures to avoid the occurrence of pollution-related tragedies such as Minamata Diseases and Yokkaichi Asthma as experienced in Japan. Moreover, by taking advantage of the positions as “late-starters”, one should be able to prevent pollution and pollution-inspired illness at lower economic and social cost than predecessors. Main progresses of Kawasaki’s efforts are list in Table 9.

The role of the administration in overcoming pollution in Kawasaki included several steps, such as clarification of health hazards to determinate the causality of the diseases, and then maintenance of the air pollution monitoring systems to confirmation of the spread of air pollution and recognition of the necessity for countermeasures. The administration would issue regulations by ordinances based on scientific evidence and including the pollution control in cooperation with other organizations. Environmental technology has been developed through these processes.

General Speaking, the Kawasaki City and national governments played vital roles in creating and implementing these solutions. They enacted laws and formulated measures that, although later than the companies’ initiatives, have stimulated their efforts. Companies have made efforts to comply with governmental



measures and policies and at the same time. In addition to companies in the coastal Area, high-tech industries are located in the inland part of Kawasaki. These industries have endeavored to develop highly eco-efficient production methods and to disseminate products that are environmental sound during use. What has been happening in Kawasaki shows that the “eco-industrial revolution” is under way. Kawasaki City is continuing to evolve, becoming an information base that will diffuse the city’s experiences and technologies to other parts of the world [29].

**Table 9 Progress of the Kawasaki city’s efforts**

| Year | Pollution-related events in Kawasaki City   | Related events  |
|------|---|---|
| 1950 | Complains about air pollution increased   |   |
| 1956 | Measurement of dust fall amount started   |   |
| 1957 | Measurement of SO <sub>2</sub> concentration started  |   |
| 1960 | Kawasaki-city Pollution Control Ordinance (old ordinance) was issued  | Petrochemical industrial complexes were formed  |
| 1964 | Automatic measurement of SO <sub>2</sub> concentration started  | Kanagawa Prefecture’s “Pollution Control Ordinance” was issued  |
| 1968 | The city council submitted to the prime minister an opinion brief about antipollution measures for Kawasaki-City  | “Air Pollution Control Law” was issued; “Noise Regulation Law” was issued   |
| 1970 | First photochemical smog was observed for the first time in the city;<br>Kawasaki-city concluded an “Agreement Concerning Air Pollution Control” with 39 factors in the   | Photochemical smog was observed around Suginami-city in Tokyo and 6000 people suffered from pain in eyes and throats<br>14 laws related to environmental pollution have been established in the Diet (thus this is called the “Pollution Diet”) |
| 1972 | Kawasaki-city Pollution Control Ordinance” was issued; Kawasaki Pollution Monitoring Center” was completed  |   |
| 1973 | Kawasaki-city Pollution Research Center” was completed  | The first oil crisis occurred   |
| 1974 | The regulatory standards for total emissions of SO <sub>2</sub> and particulate were applied based on the city’s ordinance  |   |
| 1976 | “Kawasaki-city Ordinance on Environmental Impact Assessment” was issued   |   |
| 1978 | “Automatic Monitoring System of Nitrogen Oxides at Emission Source” was completed (32 large factories in the city)<br>The regulatory standard for total emissions of nitrogen oxides was applied based on the “Kawasaki-City Pollution Control Ordinance” |   |
| 1979 | The concentration of SO <sub>2</sub> meets the environmental standard in the entire city  |   |
| 1982 |   | Patients with pollution-related diseases  |

|      |   |  |
|------|---|--|
|      |   | instituted a suit demanding pollution prohibition and loss compensation                      |
| 1983 | “Water Quality Automatic Monitoring System” were completed  |  |
| 1996 |   | The plaintiffs and the accused companies of Kawasaki Pollution Lawsuits came to a settlement |
| 1999 | “Kawasaki-city Ordinance Concerning Living Environmental Preservation Such as Pollution Control” was enacted and issued                       | “Law Concerning Special Measures against Dioxins” was issued                                 |
| 2003 | “Diesel Vehicle Travel Control” was started in cooperation with municipal governments of Tokyo and Kanagawa                                   | “Soil Contamination Countermeasures Law” was enforced  |
| 2004 | The amount of SPM met environmental standard at all General Environmental Measuring stations and Vehicle Exhaust Emissions Measuring Stations |  |

---

### 3. Conclusions

About the acid deposition, precipitation with a pH of less than 3, which may cause acute damage to plants, was not observed in the two mega-cities. There was observed a slight increase in rainwater pH for the whole assessment period in Chongqing and Kawasaki. During 2000 to 2006, the pH of rainwater was in the range from 3.8~7.6 in urban area of Chongqing, however, considerable part of measurements, about 76.2% of all samples had a pH of less than 5.0 and 2.4% had less than 4.0. For Kawasaki from 1988 to 2005, the pH varied from 3.8~6.6 and the rain with pH below 5.0 was 75.1% and 1.5% less than 4.0. Compared with the urban sites, the acid deposition seemed serious in rural areas of Chongqing and that may be caused by lower neutralization function.  $\text{SO}_4^{2-}$  may be regarded as a major acid ion in rainwater in Chongqing, surpassing  $\text{NO}_3^-$ , and its molar ratios were higher than Kawasaki and other parts of the EANET region.

Though the social-economic developed with a dramatic speed, the emission of  $\text{SO}_2$  from industrial didn't increase at all. Apart from  $\text{SO}_2$ , Total Suspended Particulates is still a problem in Chongqing. In Japan, the concentration of  $\text{SO}_2$ , SPM met the standard in 1979 and 2004 respectively. There is little reason to believe that vegetation damage attributable to acid deposition has been widespread and it is difficult to conclude that ecological damage of ecosystem caused by acid deposition has become obvious. The effects of acid deposition on soil, plant and ecosystem were interested in Chongqing City. The exact reasons for the forest damage in 1982 remain to be determined but acid deposition due to  $\text{SO}_2$  may have been the major cause.

Since that the concentration of organic substances was rather low and sometimes the ion balance can be obtained, most of the researchers thought that functions of the organic substances could not be taken into consideration. However, in the south China, the relative contribution of organic acidic substances to acid rain was over 10%. Compared with Kawasaki, the metals existed with higher concentrations in the atmosphere. Apart from industrial influences, the automobile exhaust and the landforms of the area may be responsible for the pollution in Chongqing.

Compared with Kawasaki, the metals existed with higher concentrations in the atmosphere. For example, concentration of Pb, derived principally from the combustion of petrol containing lead additives and from smelting, nearly 5 times higher than Kawasaki. Apart from industrial influences, the automobile exhaust and the landforms of the area may be responsible for the air pollution.

Special attention was given to the countermeasures against global warming, energy measures, chemical substance control, nanoparticles control and Photo-chemical fog recently. Moreover, 234 kinds of chemicals were defined to “hazardous atmospheric substances” and among which 22 should be determined priority. 19 kinds of pollutants were analyzed in Kawasaki every year. Most of the results were lower than the standards except for the concentrations of benzenes and certain heavy metals.

General Speaking, the Kawasaki City and national governments played vital roles in creating and implementing these solutions on air pollution. They enacted laws and formulated measures that have stimulated their efforts. Companies have made efforts to comply with governmental measures and policies at the same time. The high-tech industries have endeavored to develop highly eco-efficient production methods and Kawasaki shows that the “eco-industrial revolution” is under way. Kawasaki City is continuing to evolve, becoming an information base that will diffuse the city’s experiences and technologies to other parts of the world.

## References

- [1] Network Center of EANET 2006. Periodic report on the state of acid deposition in East Asia. (Part 1: regional assessment). Acid Deposition Monitoring Network in East Asia (EANET), Bangkok.
- [2] Network Center of EANET 2006. Periodic report on the state of acid deposition in East Asia. (Part 2: National assessment). Acid Deposition Monitoring Network in East Asia (EANET), Bangkok.
- [3] Wenche, A., Min, S., Lei, J. *et al.* 2007. Air concentrations and wet deposition of major inorganic ions at five non-urban sites in China, 2001-2003. *Atmospheric Environment*. 41: 1706-1716.
- [4] 徐龙均 & 兰劲涛 2005. 重庆市酸雨规律分析及防治对策. *矿业安全与环保*, 32: 16-19.
- [5] 陈桂元 1991. 重庆地区污染源及其对酸雨的影响. *重庆环境科学*. 13: 2-5, 10.
- [6] 王玮, 王文兴, 全浩等. 我国酸性降水来源探讨.
- [7] Gao, S., Sakamoto, K., Wang, D. *et al.* 2001. Studies on atmospheric pollution, acid rain and emission control for their precursors in Chongqing, China. *Water, air and soil pollution*. 130: 247-252.
- [8] Communiqué on the state of the environment in Chongqing. 1993-2005
- [9] Terabe, M. 1984. The progress of air pollution problem in Keihin industrial area in Japan. *Journal of Japan Society for Safety Engineering*, 23: 1-9.
- [10] The committee on acid deposition 2004. Comprehensive summary report on acid deposition monitoring survey.
- [11] Li, J., Liu, Z., Shu, J. *et al.* 2005. Analysis on the forest soil acidification status in typical acid rain areas of central and south China. *China Environmental Science*, 25: 77-80.
- [12] 孟小星, 姜文华, 张卫东 2003. 重庆酸雨地区森林生态系统土壤、植被与地表水现状分析. *重庆环境科学*, 25: 71-73.
- [13] Quan, H. & Zheng Y. Air pollution and its effects on the system in Chongqing.
- [14] Tao, F. & Feng, Z. 2003. Critical loads of acid deposition for ecosystem in south China- derived by a new method. *Water, air and Soil Pollution*, 130: 1187-1192.
- [15] Iang, D. Lydersen, E., Seip, H. M. *et al.* Integrated monitoring program on acidification of Chinese terrestrial system (IMPACTS)-a Chinese-Norwegian cooperation project.
- [16] Zhao, D., Larssen, T., Zhang, D. *et al.* 2001. Acid deposition and acidification of soil and water in the Tieshanping area, Chongqing, China. *Water, air and soil pollution*, 130: 1733-1738.
- [17] 余叔文, 俞子文, 马光靖等. 重庆南山马尾松林衰亡原因初步探讨. *环境科学*, 9: 77-81.
- [18] Zhou Y. 2004. Effect of construction activities on particulate matter pollution along roadways. *Journal of southwest agricultural university (natural science)*. 26: 518-520.
- [19] Zhang, Y. & Hu, K. 1993. Identification of the sources of traffic dust in Chongqing. *Research of Environmental Sciences*, 6: 20-24.

- [20] Zhao, D., Liu, H., Xiong, J. *et al.* 1987. Atmospheric particulates and acid rain. *China Environmental Science*. 7: 1-8
- [21] Gulbrand, L., Jorgen, G., Nina, G. *et al.* 1977. Organic micropollutants in precipitation in Norway. *Atmospheric Environment*, 11: 1007-1014.
- [22] Matsumoto, G. & Hanya, T. 1980. Organic constituents in atmospheric fallout in the Tokyo area. 14: 1409-1419.
- [23] Kawamura, K. & Kaplan I. R. 1984. Capillary gas chromatography determination of volatile organic acids in rain and fog samples. *Analytical Chemistry* 56: 1616-1620.
- [24] Kawamura, K. & Kaplan, I. R. 1983. Organic compounds in the rainwater of Los Angeles. *Environmental Science & Technology*, 17: 497-501.
- [25] Chen, Z., Wang, Y., Lu M. *et al.* 1991. The role of atmospheric organic compounds in the formation of acid rain. *Environmental Chemistry*. 10: 1-13.
- [26] Var F., Narita, Y. & Tanaka, S. 2000. The concentration, trend and seasonal variation of metals in the atmosphere in 16 Japanese cities shown by the results of National Air Surveillance Network (NASN) from 1974 to 1996. *Atmospheric Environment*, 34: 2755-2770.
- [27] 陈思龙, 郑有斌, 赵琦 1997. 重庆城区大气悬浮颗粒物金属元素特征. *重庆环境科学*, 19: 370-374.
- [28] 杨三明, 陈刚才, 赵琦等 重庆市大气总悬浮颗粒物的重金属的分布特征.
- [29] Kato S. 2004. Kawasaki's eco-industrial revolution. *Sustainable consumption and production*. UNEP Industry and Environment.

## **Assessment of Ozone and Other Gaseous Concentrations in East Asia**

Truong Anh Son<sup>1)\*</sup>, Tatsuya Sakurai<sup>2)</sup> and Hiromasa Ueda<sup>2)</sup>

*1) Center for Environmental Research, Vietnam Institute of Meteorology  
Hydrology and Environment,*

*\*Contact address: 5/62 Nguyen Chi Thanh, Hanoi, Vietnam [e-mail: trsonimh@yahoo.com]*

*2) Acid Deposition and Oxidant Research Center (ADORC)*

The Models-3/Community Multi-scale Air Quality (CMAQ) modeling system, driven by WRF/NCEP reanalysis data as the meteorology was applied to simulate the O<sub>3</sub>, and other gaseous concentrations (SO<sub>2</sub> and NO<sub>2</sub>) in East Asia. Comparison of hourly mean simulated concentrations of O<sub>3</sub>, NO<sub>2</sub> and SO<sub>2</sub> with those obtained by surface observations of EANET's sites in March, July and December 2001 shows that the modeled concentrations of these gases are generally in good agreement with their observed ones. They simulated the overall trends of the O<sub>3</sub>, NO<sub>2</sub> and SO<sub>2</sub> concentrations obtained by the surface observations.

The spatial distribution of monthly mean concentrations for SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub> in March, July and December 2001 and March 2002 shows that high SO<sub>2</sub> and NO<sub>2</sub> concentration areas matched well with areas having high emissions such as Chongqing, Beijing, east China, Pusan, Bangkok, south Malaysia and some areas in Japan. Simulated SO<sub>2</sub> and NO<sub>2</sub> concentrations also have a seasonal variation. The mean concentrations were low in summer (July) but higher in winter (in March and December). Unlike the SO<sub>2</sub> and NO<sub>2</sub> concentrations, the high value of O<sub>3</sub> concentration appeared at the remote sea areas, far away from the large-scale emission region. Furthermore, it exhibited apparent seasonal variation. In winter, high O<sub>3</sub> area appeared much far away from the heavy emission area than that in summer. Moreover, spatial distribution of monthly amount of acid deposition in March, July and December 2001 was also presented in this study. However, because of insufficient validation by observed data, this result is only for reference and need to be studied more deeply.

### **1. Introduction**

Air pollution is damaging public health, environmental quality, agriculture industry etc., and it will deteriorate the economy and health conditions. In order to maintain its public health and realize its sustainable development of energy, all countries in the region must control their air quality, study the health impact of air pollutants, and grasp the ability to study and forecast air pollutant parameters. Effective energy and environmental policies can play active roles for the air quality in the future and public health improvements by legislative and regulatory controls over energy consumption and air pollutant emissions, while modeling and simulation studies can provide opportunities to look into the future environmental situation and provide helpful information for the government to take legal steps for better air quality controls and better public health.

In recent years, the economy of countries in East Asia in general and Vietnam in particular has been developing rapidly. Besides economic achievements, rapid economic development has imposed a great threat to the environment. The change of agricultural structure and development of the industrial sector including heavy and energy industries have resulted in consumption of a large amount of fossil fuel that emits air pollutants causing air quality degradation in the region. In consequence, air environment pollution and acid deposition have been widespread.

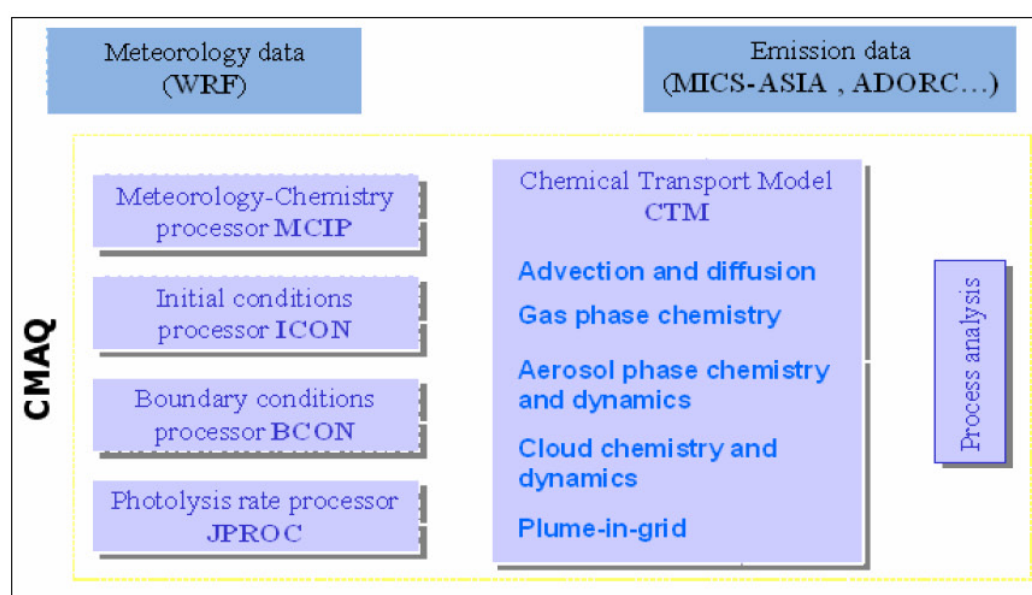
The rate of success to prevent avoidable health disaster can be enhanced by close collaboration between public health and energy policy with the help of modeling studies. Using an air quality model to assess the impact of air quality from these gaseous pollutants is critical for atmospheric chemistry studies and for the development of environmental management strategies (National Research Council- NRC) and play a role for the decision makers. In this study, The Model-3/ Community Multi-scale Air Quality (CMAQ) modeling system (Byun and Ching, 1999) was used to simulated and evaluate the distribution of ozone and other gaseous concentrations in East Asia region.

## 2. Overview of Model and its parameterization

### 2.1. USEPA's Model-3/CMAQ modeling system

The U.S. Environmental Protection Agency Community Multiscale Air Quality (CMAQ) model (Byun and Ching, 1999; Byun and Chere, 2006) is a three-dimensional eulerian (i.e., gridded) atmospheric chemistry and transport modeling system that simulates ozone, acid deposition, visibility, and fine particulate matter throughout the troposphere. Designed as a one-atmosphere model, CMAQ can address the complex couplings among several air quality issues simultaneously across spatial scales ranging from local to hemispheric. The CMAQ source code is highly transparent and modular to facilitate extensibility through community development.

CMAQ is a third-generation air quality model that is designed for applications ranging from regulatory and policy analysis to understanding the complex interactions of atmospheric chemistry and physics. First-generation air quality models simulated air quality using simple chemistry at local scales, and Gaussian plume formulation was the basis for prediction. Second-generation models covered a broader range of scales (local, urban, regional) and pollutants, addressing each scale with a separate model that often focused on a single pollutant (e.g., ozone). Third-generation models, like CMAQ, treat multiple pollutants simultaneously up to continental or larger scales, often incorporating feedback between chemical and meteorological components. The Model-3/CMAQ system was first released to public in July 1998 and had a recent update release in October 2006. The model structure and input data treatment processes of CMAQ were presented at Fig. 1 below.



**Figure 1 Conceptual diagram of CMAQ model structure.**

As a framework for simulating the interactions of multiple complex atmospheric processes, CMAQ thus



requires two major types of inputs: meteorological information and source emissions rates.

With weather conditions contributing the primary physical driving forces in the atmosphere (such as the changes in temperature, winds, cloud formation, and precipitation rates), representative gridded meteorology forms the basis of all 3-D air quality model simulations. The Fifth-Generation Pennsylvania State University/National Center for Atmospheric Research Mesoscale Model (MM5) (Grell et al., 1994) and the Weather Research and Forecasting (WRF) model Advanced Research WRF (WRF-ARW) (Skamrock et al., 2005) are two meteorological models that are compatible with CMAQ.

For inputs on emissions, CMAQ uses an emissions model to estimate the magnitude, location, and temporal variability of pollution sources. Open-source models such as the Sparse Matrix Operator Kernel Emissions (SMOKE) model (CEP, 2006) and the Consolidated Community Emissions Processing Tool (CONCEPT) (<http://www.conceptmodel.org/>) are available for computing emissions inputs to CMAQ from annual, county-level emissions inventories. CMAQ emissions inputs must be on the same horizontal and vertical spatial scales and cover the same time period used in the air quality model simulation. The emissions inputs to CMAQ must also represent volatile organic compound (VOC) emissions using a chemical parameterization supported by CMAQ; currently supported photochemical mechanisms are the Carbon Bond IV (CB IV) mechanism (Gery et al., 1989; Dodge, 1989; Carter, 1996), the 2005 update to the Carbon Bond mechanism (CB05) (Yarwood et al., 2005), and the Statewide Air Pollution Research Center (SAPRC- 99) mechanism (Carter, 1990, 2000). Additional details about the gas-phase chemistry in CMAQ are provided by Byun and Ching (1999). Those two sources also describe the primary aerosol emissions species that are supported by CMAQ. It is possible to add new emission species to CMAQ that are not supported in the distributed version of the software using the chemical mechanism compiler CHEMMECH.

## **2.2. Model parameter description**

### **2.2.1. Model domain**

In this Model-3/CMAQ application, the model domain covered all most of East Asia region (China, Mongolia, Korea, Japan) and a path of South East Asia (Viet Nam, Laos, Cambodia, Thailand, Myanmar, Malaysia, Singapore, Indonesia, Brunei, Philippines) showed in Fig. 2, 55 km x 55 km grid resolutions set up by CMAQ/WRF in this study.

The domain for WRF larger than that of CMAQ, with the center located at (240 N, 1150 E). There are 103 x 98 horizontal grid cells using a 55 km resolution base on Lambert Conformal map projection, and 31  $\sigma$ -layers from surface up to 100 hPa, while the domain for CMAQ had 100 x 95 horizontal grid cells resolution, and 16  $\sigma$ -layers as below: 1.0 (0 m), 0.994 (55 m), 0.983 (150 m), 0.975 (220 m), 0.960 (350 m), 0.940 (500 m), 0.915 (750 m), 0.880 (1000 m), 0.840 (1500 m), 0.800 (2000 m), 0.740 (2500 m), 0.650 (3500 m), 0.550 (4800 m), 0.400 (7000 m), 0.200 (11000 m), 0.000 (20000 m).

### **2.2.2. Input data**

#### **(a) Meteorology data**

The three-dimensional meteorological fields for wind, temperature, water mixing ratio, precipitation, surface variables required by CMAQ, and these were provided by Weather Research Forecasting (WRF) model with version 2.2. The initial and boundary condition of meteorological data were derived from analyzed datasets of NCEP, with 10 x 10 resolution and 6 hrs interval.

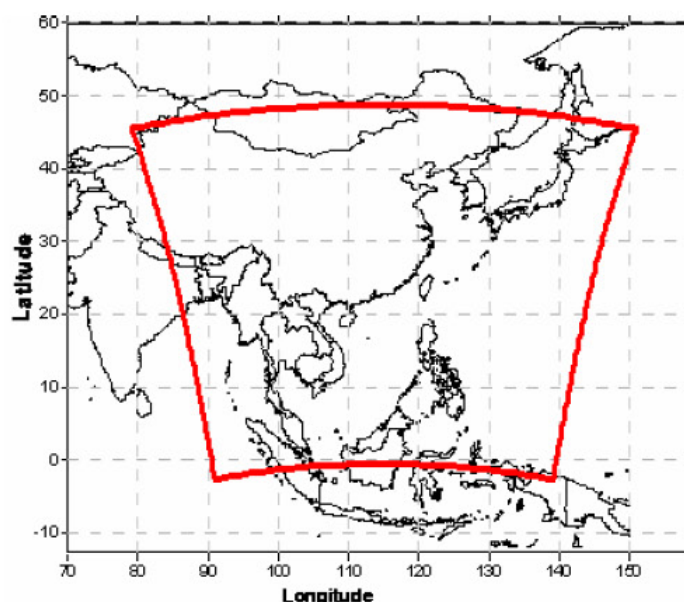
#### **(b) Initial and boundary condition**

The background initial condition is based on the results to wash out the first 5 days during the model runs. Boundary condition was taken from observations and references for East Asia in recent years (Carmichael et al., 1998; Luo et al., 2000). Ozone concentration in the northern boundary is set from 40 ppb for the first layer to 95

ppb near the model top, 20-80 ppb in the southern boundary; the top boundary condition for Ozone is taken as 100ppb. Boundary conditions for other species are generally taken as clean back-ground to highlight any changes in this study domain.

(c) Emission data

Emission inventories of SO<sub>2</sub>, NO<sub>x</sub>, CO, CO<sub>2</sub>, OC, CH<sub>4</sub>, VOC, BC, NH<sub>3</sub>, PM<sub>10</sub>, PM<sub>2.5</sub> and NMVOC were derived from those obtained by the MICS-ASIA II studies (Carmichael et al. 2007). Such data set include area source, point and biomass burning source sector in a grid resolution of 0.50 x 0.50 on monthly basis. All the area sources were allocated to the middle of the first model layer above the ground (55 m). Large point sources are assigned into a height of approximately 300 m. Volcanic emission was taken into account at its releasing height of about 1500m. Biogenic VOCs and soil NO<sub>x</sub> emissions were neglected since they are much smaller than the anthropogenic emissions in winter. Slitting factors of NMVOC are from Camichael et al. (1998) for East Asia.



**Figure 2 CMAQ modeling domain (100 x 95 cells).**

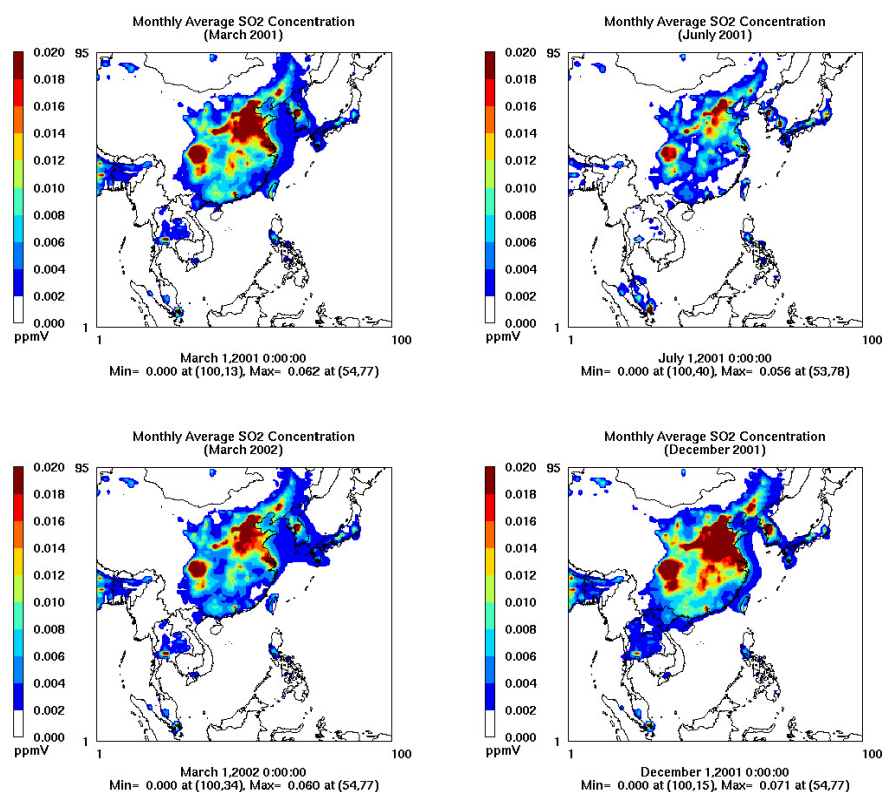
### 3. Results and discussion

#### 3.1. Monthly mean concentration

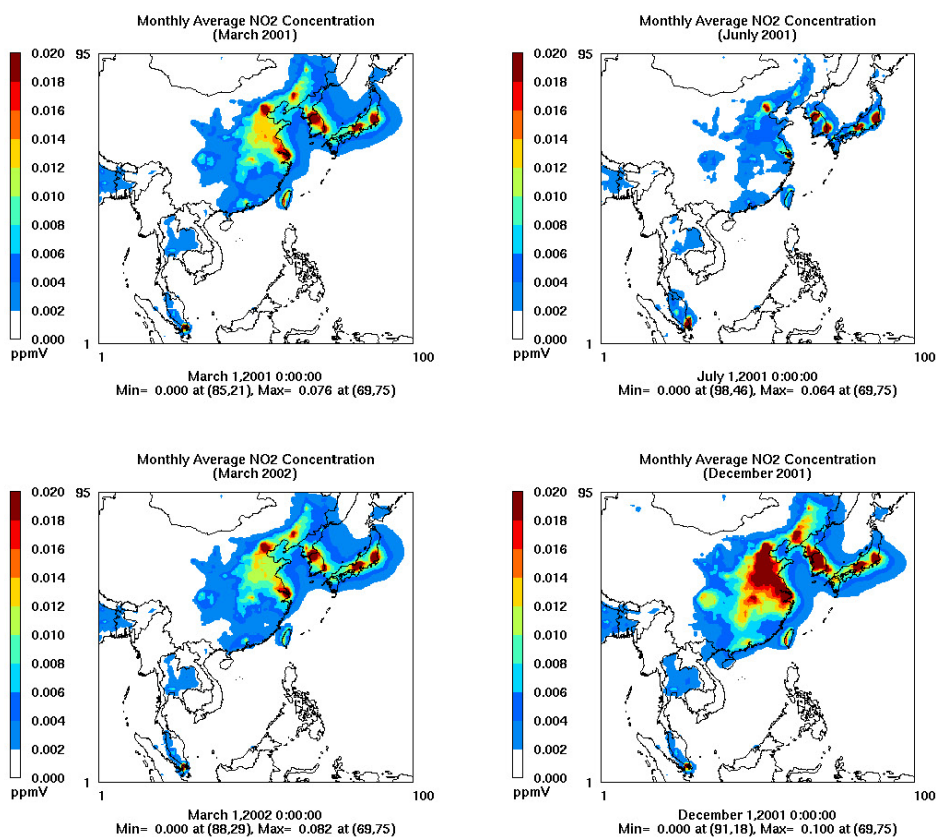
The spatial distributions of monthly average near surface concentrations for SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub> in the 4 periods (March, July and December, 2001 and March, 2002) were presented in Fig. 3 to Fig. 5.

The distribution of monthly average concentration for SO<sub>2</sub> was showed in Fig. 3. The high value areas matched well with areas having high SO<sub>2</sub> emission in each simulated month. Peak concentrations showed at Chongqing, Beijing and east China. High SO<sub>2</sub> concentration area condensed in mainland China. There was just a relatively high concentration zone in suburb Pusan, Bangkok and south Malaysia. The max value of SO<sub>2</sub> concentration showed up to 0.082 (ppmV) in March, 0.056 (ppmV) in July and 0.071 (ppmV) in December, 2001 in some areas in China. Simulated SO<sub>2</sub> concentration had a seasonal variation. The mean concentration was low in summer (July), while it had a higher level in winter (in March and December). The distribution of high SO<sub>2</sub> concentration spreads out in most of China in winter in comparison with that in summer.





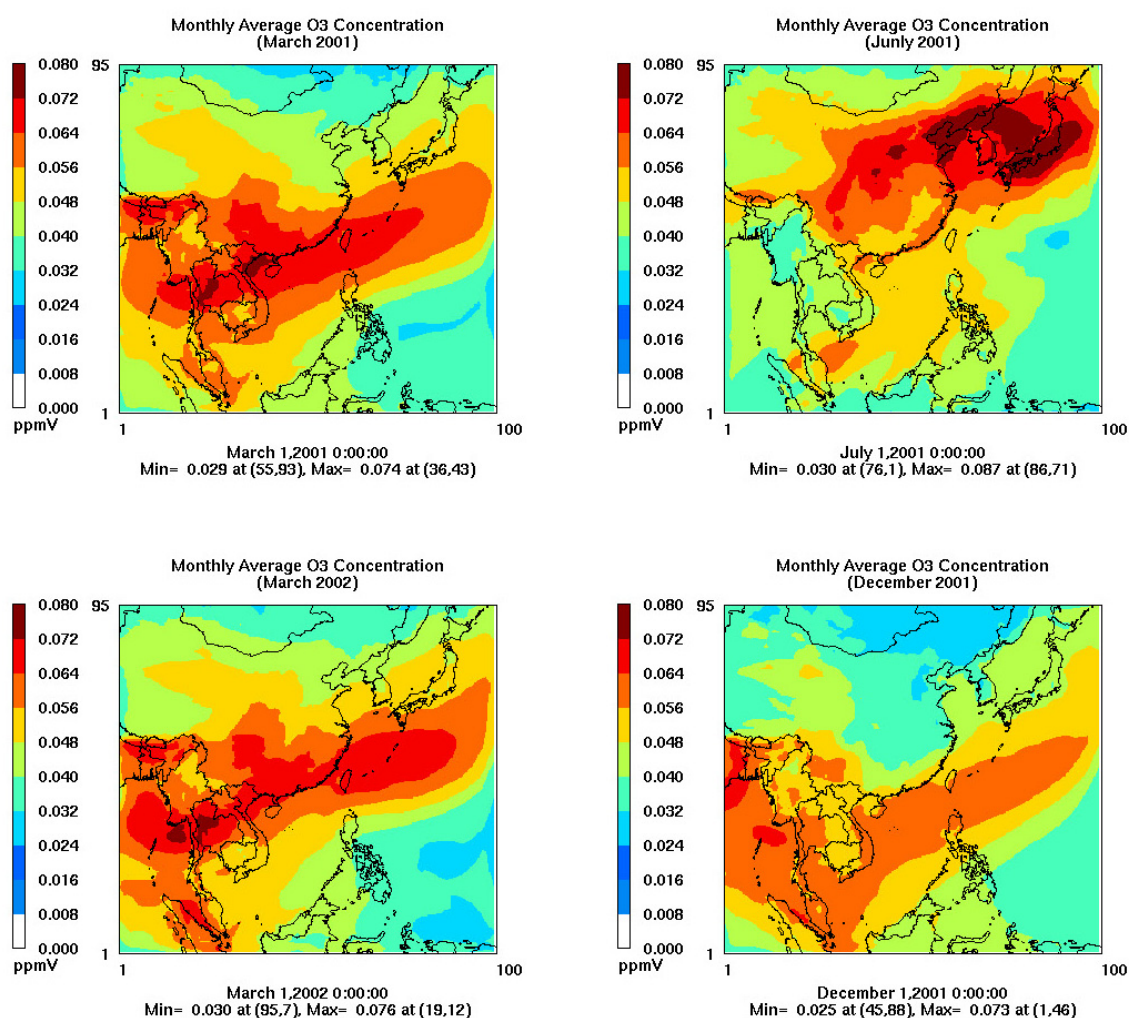
**Figure 3** Spatial distribution of monthly average SO<sub>2</sub> concentration in 4 periods (March, July, December 2001 and March 2002).



**Figure 4** Spatial distribution of monthly average NO<sub>2</sub> concentration in 4 periods (March, July, December 2001 and March 2002).

Figure 4 shows the spatial distributions of monthly average concentration for  $\text{NO}_2$ . The areas having high  $\text{NO}_2$  concentration occurred almost at the same location with  $\text{SO}_2$  in mainland China. But, for Korea, Japan and Malaysia areas, the concentration was at the same level as in mainland China, unlike the  $\text{SO}_2$  status. These high concentration areas located at Pusan, Tokyo, Osaka and south Malaysia. In general,  $\text{NO}_2$  distribution pattern resembled with that of emission pattern. Furthermore, it exhibited a seasonal variation of  $\text{NO}_2$  concentration as same as that of  $\text{SO}_2$ .

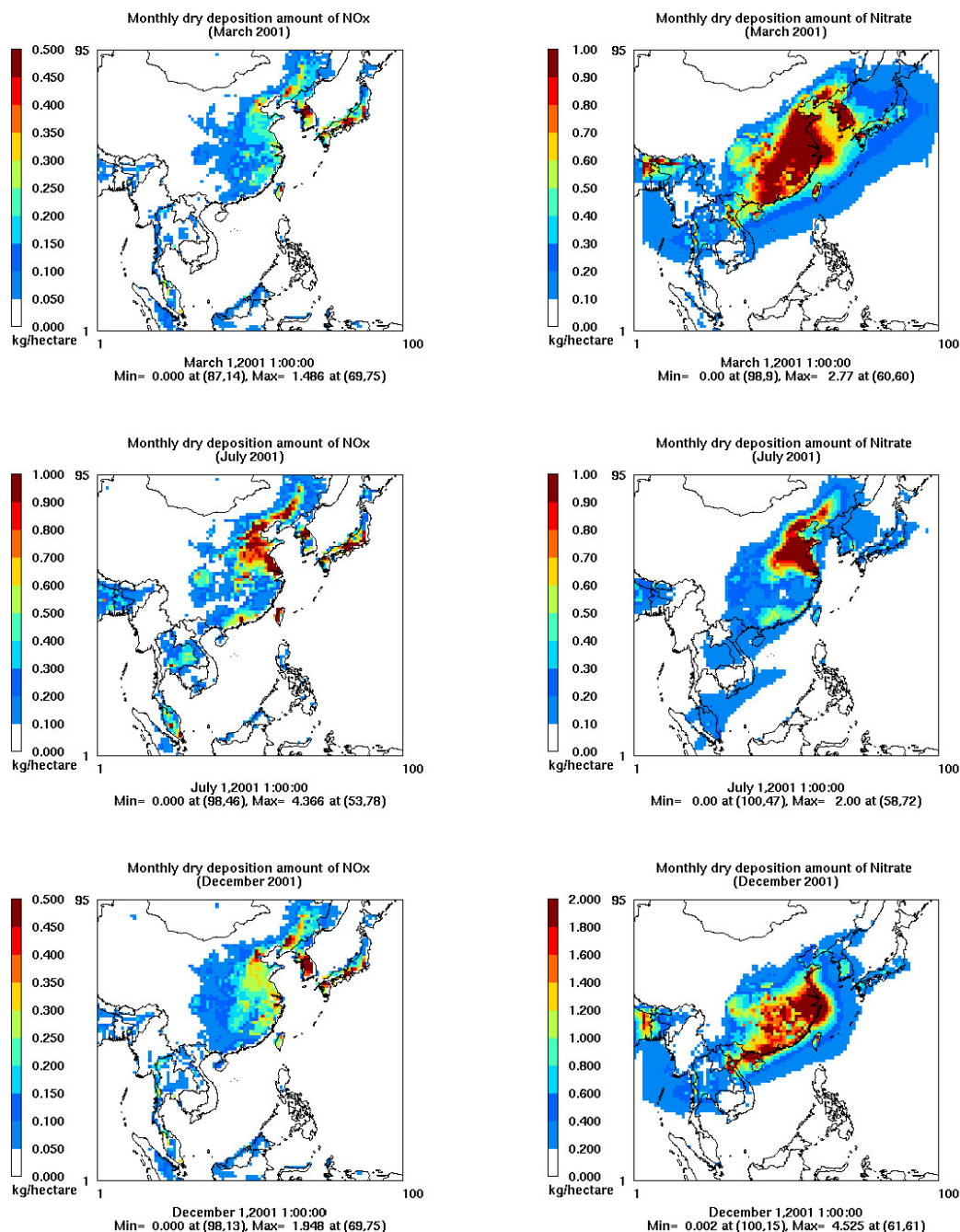
For the simulated  $\text{O}_3$  monthly mean concentration as shown in Fig. 5, the high value usually appear at the remote sea areas, far away from the heavy emission region. Furthermore, it exhibited apparent seasonal variation. In winter, high  $\text{O}_3$  area appeared farther away from the heavy emission area than in summer. The strong transportation effects by active passages of cold front in winter make the pollutants advecting much far away from the emission area. In winter, the mean  $\text{O}_3$  concentration at the heavy emission area was lower than that in summer. Because the weak UV radiation and strong ventilation effect make the weak photochemistry in winter compared with that in summer, it produced less  $\text{O}_3$  near the emission area.



**Figure 5** Spatial distribution of monthly average  $\text{O}_3$  concentration in 4 periods (March, July, December 2001 and March 2002).

### 3.2. Monthly amount of dry-deposition

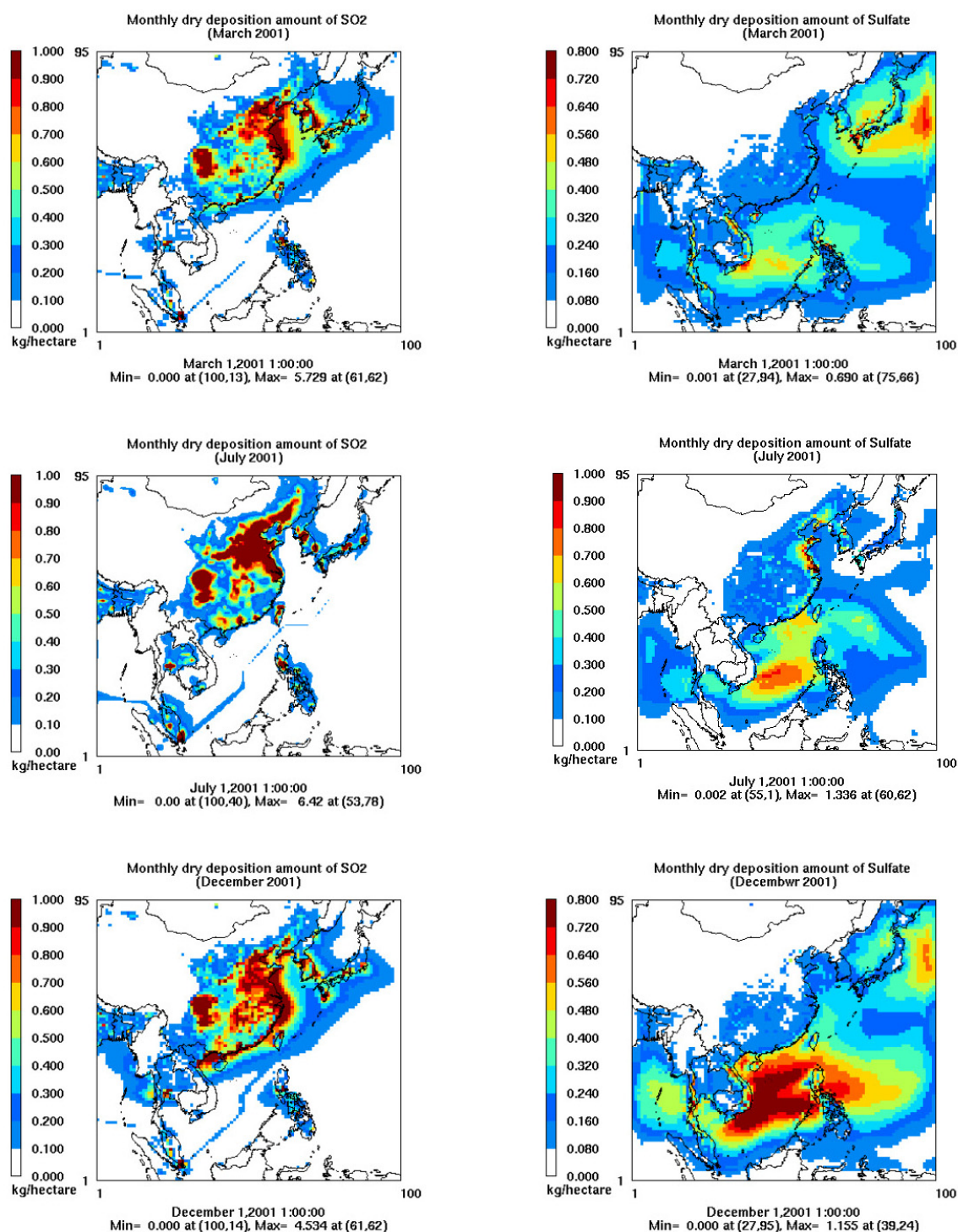
It is easy to realize that accumulated NO<sub>x</sub> dry deposition amount in March and December distributes rather conformably to the distribution of NO<sub>2</sub> concentration. However, the dry deposition distribution of NO<sub>x</sub> was relatively different. Moreover, NO<sub>x</sub> dry deposition amount in July was twice as high as it in March and December while rainfall in July was higher than it in other months (Fig. 6). On the other hand, the deposition processes can occur over relatively short distance from the primary pollutant sources or at distance of 1000km or more. Thus both short-range and long-range transport must be considered. Dry deposition amount of nitrate was highest in December. In July, the area having high dry deposition of nitrate located in whole China but its range trended to spread Vietnam due to effect of northeast monsoon in March and December (Fig. 6).



**Figure 6** Spatial distribution of monthly amount for NO<sub>x</sub> and Nitrate dry-deposition in 3 periods (March, July, December 2001).



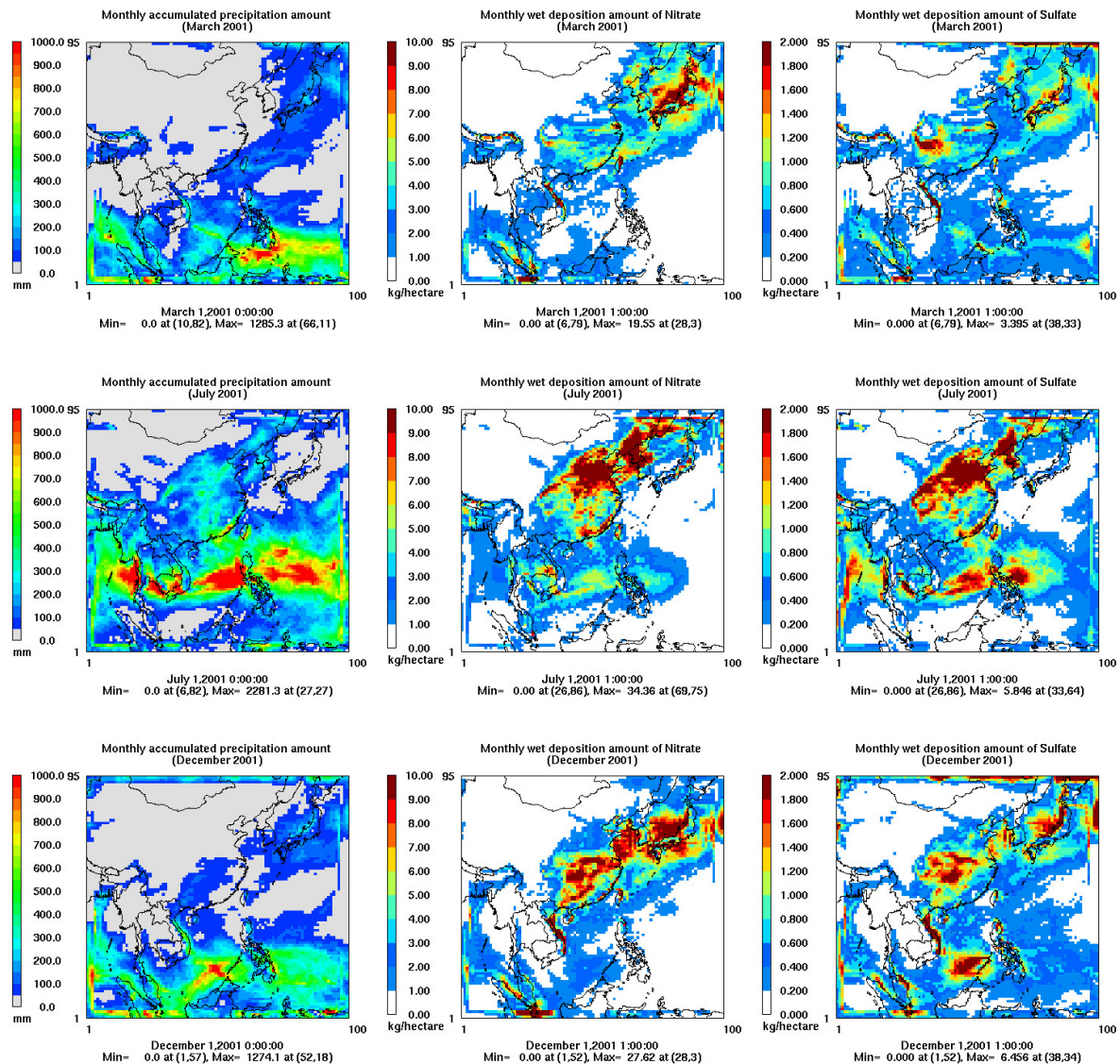
In case of dry deposition of  $\text{SO}_2$ , the high value appeared in northeastern and northern of China, some areas in South Korea and Japan. The amount of sulfate deposition in July and December were higher than it in March. It is noted that the distribution of high sulfate deposition located above the sea, especially relatively high deposition of sulfate on South China Sea in December. Dry deposition of sulfate and nitrate show opposite seasonal variation, with higher amount of sulfate and lower amount of nitrate in summer (July) and lower amount of sulfate and higher amount of nitrate in winter (March and December) (Fig. 7).



**Figure 7** Spatial distribution of monthly amount for  $\text{SO}_2$  and Sulfate dry-deposition in 3 periods (March, July, December 2001).

### 3.3. Monthly amount of wet-deposition

Figure 8 presents spatial distribution of monthly amount of precipitation and nitrate and sulfate wet deposition in March, July and December 2001. In comparison with March and December, the precipitation was higher and covered most of China in July. As a result, wet deposition amount of nitrate and sulfate reached the high values in July and mostly located in China. Wet deposition of nitrate was significantly higher wet deposition of sulfate. It is relative to chemical processes in atmosphere that result in high wet deposition of nitrate despite less NO<sub>x</sub> emission.



**Figure 8 Spatial distribution of monthly amount precipitation and monthly amount for SO<sub>2</sub> and Sulfate wet-deposition in 3 periods (March, July, December 2001).**

### 3.4. Model Validation

To assess the accuracy of model, we usually validate used-model by comparing computed results to observed data in the same location and at the same time. In this paper, the model validation is presented in Table 1, and Figs. 9 to 11.

Table 1 shows the statistics for comparison of hourly monitoring results of SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> in 3 periods (March, July and December, 2001) at EANET's stations. In the table, N is the number of paired samples, R is the correlation coefficient, MBE is the mean bias error and RMSE is root mean square error. The model simulated

hourly O<sub>3</sub> concentration well with correlation coefficient 0.64 in March but unwell in December with R of -0.12. Regarding the average value, R of SO<sub>2</sub> was the highest value with 0.68. While most values of exhibit positive mean biased errors MBE, the value of O<sub>3</sub> in March and SO<sub>2</sub> in December had small negative MBE, implying underprediction. RMSE was also in a lower range among these months. Table 1 also indicates that model of prediction skill is quite good compared with other models in MICS ASIA II studies (Han, et al., 2007 and Fu et al., 2007). In general, O<sub>3</sub> well agreed with the observation data with correlation of 0.64, 0.52, - 0.12, MBE was -3.95, 1.54, 3.17 and RMSE was 6.7, 9.7, 3.6 in March, July and December respectively. Compared to O<sub>3</sub>, the NO<sub>2</sub> concentrations were simulated less well. The MBE and RMSE were not high.

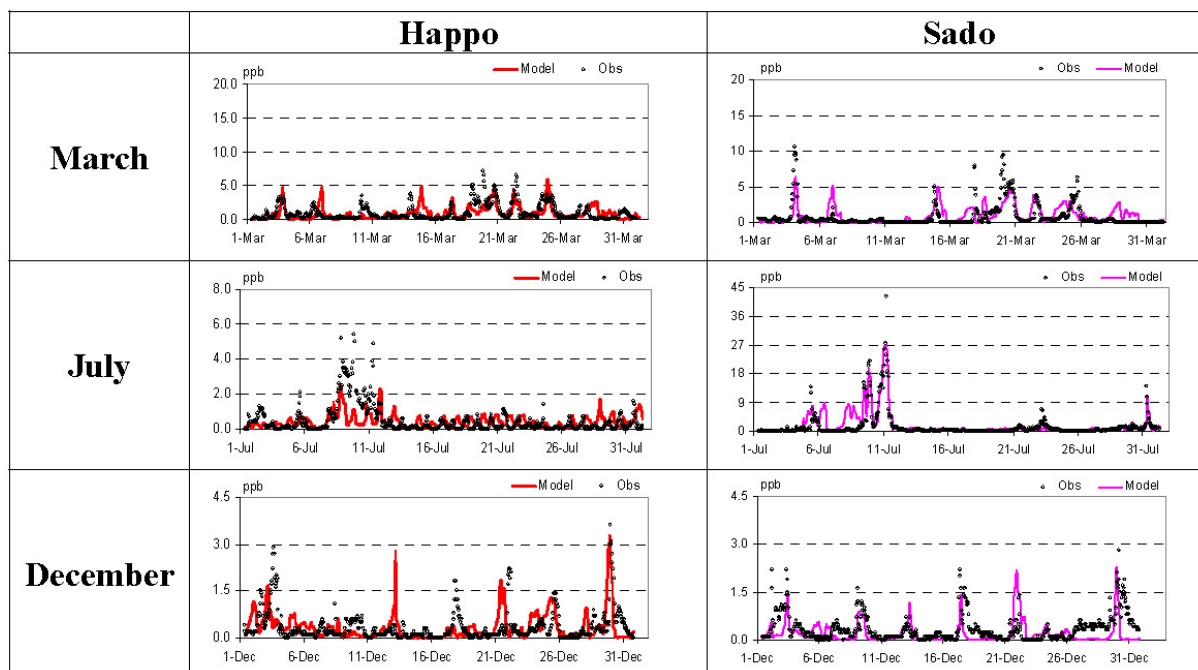
**Table 1 Statistics for comparison of hourly monitoring results**

|                 |                             | <b>R</b> | <b>MBE</b> | <b>RMSE</b> | <b>N</b> |
|-----------------|-----------------------------|----------|------------|-------------|----------|
| <b>March</b>    | <b>SO<sub>2</sub> (0.7)</b> | 0.58     | 0.22       | 0.80        | 731      |
|                 | <b>NO<sub>2</sub> (1.3)</b> | 0.56     | 0.45       | 1.15        | 731      |
|                 | <b>O<sub>3</sub> (45.2)</b> | 0.64     | -3.95      | 6.70        | 731      |
| <b>July</b>     | <b>SO<sub>2</sub> (1.3)</b> | 0.68     | 0.46       | 0.97        | 733      |
|                 | <b>NO<sub>2</sub> (0.8)</b> | 0.19     | 0.08       | 0.87        | 733      |
|                 | <b>O<sub>3</sub> (49.1)</b> | 0.52     | 1.54       | 9.70        | 733      |
| <b>December</b> | <b>SO<sub>2</sub> (0.3)</b> | 0.41     | -0.12      | 0.29        | 723      |
|                 | <b>NO<sub>2</sub> (1.1)</b> | 0.57     | 0.03       | 0.69        | 723      |
|                 | <b>O<sub>3</sub> (30.2)</b> | -0.12    | 3.17       | 3.67        | 723      |

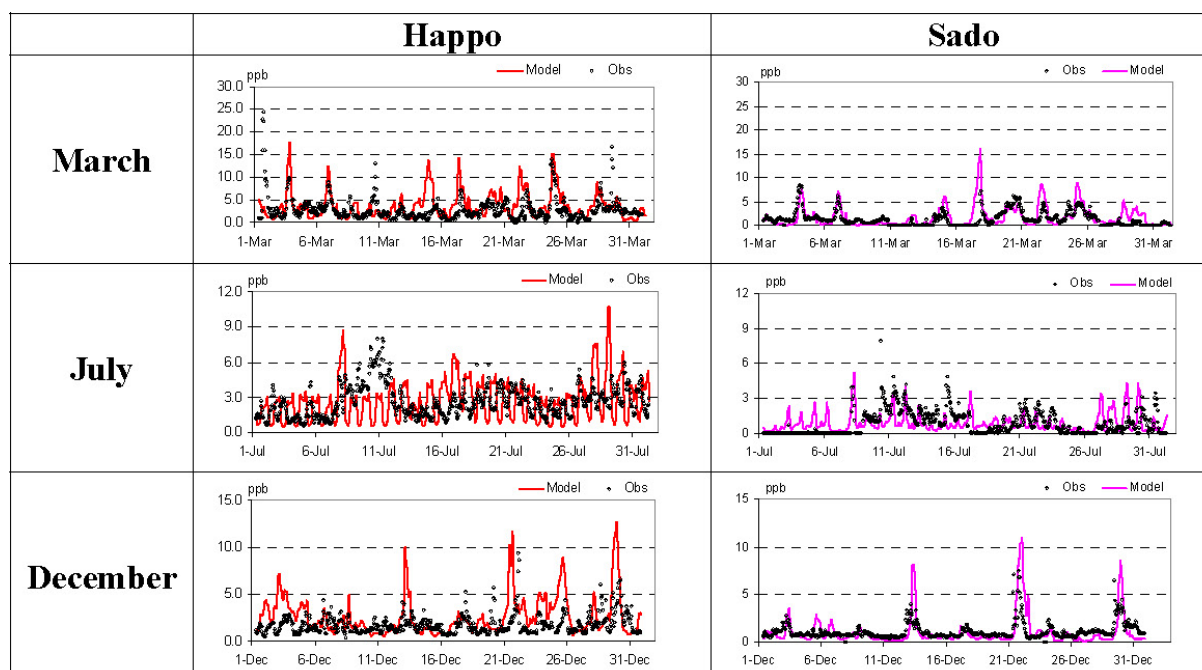
Unit: ppbv, Values in parentheses denote observed data.

Figures 9 to 11 shows the hourly variation for observed and calculated concentration of NO<sub>x</sub>, SO<sub>2</sub> and O<sub>3</sub> in 3 periods (March, July and December, 2001) at Sado and Happo sites. Complementary to the statistical descriptions in Table 1, the model time series (red solid line) in the figures well agreed with the overall trend of the observations. They also peaked up to the 28 ppb of NO<sub>x</sub>, 9 ppb of SO<sub>2</sub> and 90 ppb of O<sub>3</sub> peak on July 11 and March 5 at Sado. Ability to simulate NO<sub>x</sub>, SO<sub>2</sub> and O<sub>3</sub> peaks is important because without that, it is difficult to highlight which emitting species to be reduced so that a control strategy can be effectively carried out. The different dips from the July 11 and March 5 episode were also followed closely by our model up to around December for NO<sub>x</sub>, from March 7 to the end of the month for SO<sub>2</sub>, and from 16 to 25 July for O<sub>3</sub>. During the July 11-21 period, the formation of the O<sub>3</sub> peak is more likely caused by regional transport or local production by VOCs imported from the Asian continent. In any cases the mesoscale meteorology definitely plays the essential part. In general, the model trend is in phase with the observations throughout the months. In comparison with Sado station, the modeled results in Happo did not showed a good agreement. The location of this station can be one of the reasons for this disagreement because Happo is located on the high mountain, at 1840 (m) in height from sea water level.

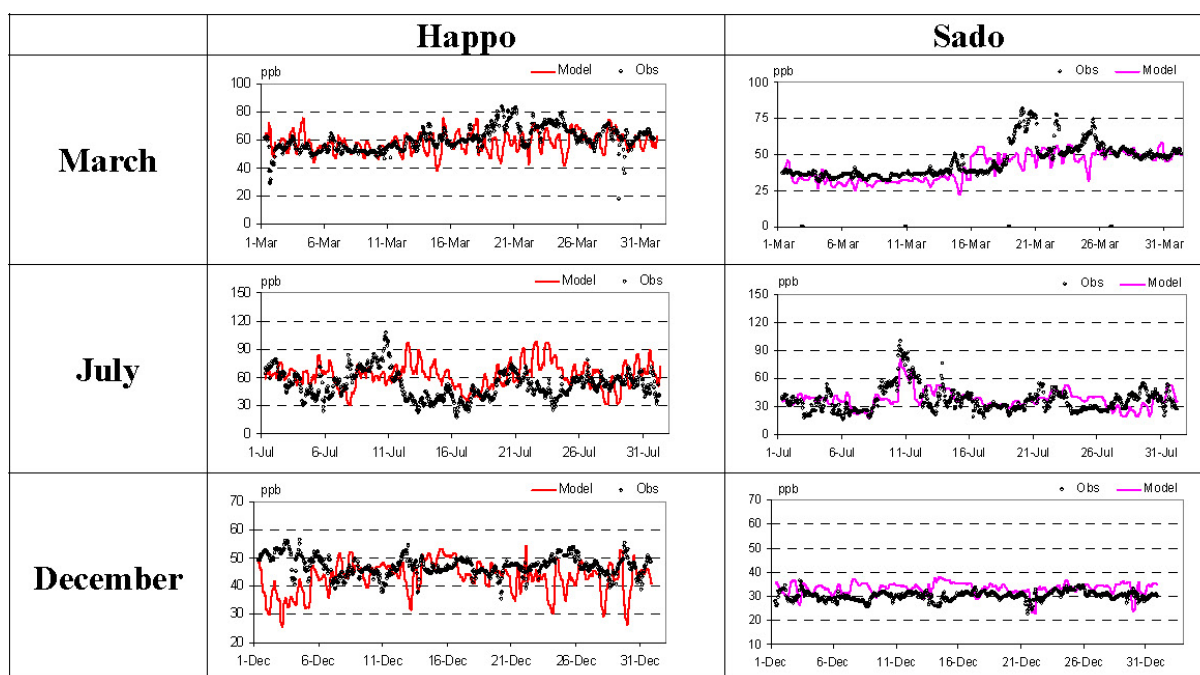




**Figure 9** The hourly variation for observed and calculated concentration of NO<sub>2</sub> in 3 periods (March, July, December 2001).



**Figure 10** The hourly variation for observed and calculated concentration of SO<sub>2</sub> in 3 periods (March, July, December 2001).



**Figure 11 The hourly variation for observed and calculated concentration of O<sub>3</sub> in 3 periods (March, July, December 2001).**

#### 4. Summary and conclusions

The Models-3 CMAQ modeling system with meteorology fields calculated by the Weather Research Forecasting (WRF) model was investigated to simulate O<sub>3</sub> and other gaseous concentrations (NO<sub>2</sub> and SO<sub>2</sub>) in East Asia.

Comparison of hourly mean simulated concentrations of O<sub>3</sub>, NO<sub>2</sub> and SO<sub>2</sub> with surface observations of EANET' sites in March, July and December 2001 showed that the modeled concentrations of these gases were generally in good agreement with their observed ones. They simulated the overall trend of the observed data. Among these species, O<sub>3</sub> is well simulated while the evaluation of NO<sub>2</sub> is not in good agreement. Statistics of monthly means showed that the model skill was very good in reproducing O<sub>3</sub> and SO<sub>2</sub>.

The spatial distributions of monthly average near surface concentrations for SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub> were also performed in 4 periods (March, July and December 2001 and March 2002). The high SO<sub>2</sub> and NO<sub>2</sub> concentration areas matched well with areas having high emissions such as Chongqing, Beijing, east China, Pusan, Bangkok, south Malaysia and some areas in Japan. Simulated SO<sub>2</sub> and NO<sub>2</sub> concentrations had a seasonal variation. The mean concentration was low in summer (July), while they have a higher level in winter (in March and December). Unlike the SO<sub>2</sub> and NO<sub>2</sub>, the high value of O<sub>3</sub> concentration areas usually appear at the remote sea areas, far away for the heavy emission region, and it exhibited apparent seasonal variation. In winter, high O<sub>3</sub> area appeared farther away from the heavy emission area than in summer.

In addition to the assessment and simulation of air pollutant concentration distribution, evaluation of acid deposition is also one result of this study. However, because of insufficient validation by observed data, this result is only for reference and need to be studied more deeply.

#### Acknowledgements

The study has conducted with the support by Acid Deposition and Oxidant Research Center (ADORC), Japan through Research Fellowship Program. The authors wish to thank Prof. Dr. Itsushi Uno (Research Institute of Applied Mechanics, Kyushu University), Dr. H. Hayami (Center Research Institute of Electric Power



Industry) and all staffs of ADORC for providing highly valuable advices in order to help us to complete this study.

## References

- Byun, D. W. & Ching, J. K. S. (Eds) 1999. Science algorithms of the EPA Model-3 community Multi-scale Air Quality (CMAQ) modeling system. NERL, Research Triangle Park, NC, USA.
- Byun, D. W. & Schere, K. L. 2006. Review of the governing equations, computational algorithms, and other components of the Model-3 Community Multi-scale Air Quality (CMAQ) modeling system. *Applied Mechanics Review* 59: 51-77.
- Carmichael, G. R., Sakurai, T., Streets, D., Hozumi, Y., Ueda, H., Park, S.U., Fung, C., Han, Z., Kajino, M., Engardt, M., Bennet, C., Hayami, H., Sartelet, K., Holloway, T., Wang, Z., Kannari, A., Fu, J., Matsuda, K., Thongboonchoo, N. & Amann, M. 2007. MICS-Asia II: the model intercomparison study for Asia phase II methodology and overview of findings. *Atmospheric Environment*, 42: 3468-3490.
- Carmichael, G. R., Uno, I., Phadnis, M. J., Zhang, Y. & Sunwoo, Y. 1998. Tropospheric Ozone production in the springtime in east Asia. *Journal of Geophysical Research* 103: 10649-10671.
- Carter, W. P. L. 1990. A detailed mechanism for the gas-phase atmospheric reactions of organic compounds. *Atmospheric Environment*, 24A: 481-518.
- Carter, W. P. L. 1996. Condensed atmospheric mechanisms for isoprene. *Atmospheric Environment*, 30: 4275-4290.
- Carter, W. P. L. 2000. Implementation of the SAPRC-99 chemical mechanism into the Models-3 Framework. U.S. Environmental Protection Agency, Washington, DC, USA [Available online at <http://pah.cert.ucr.edu/~carter/reactdat.htm> .]
- Dodge, M. C. 1989. A comparison of photochemical oxidant mechanisms. *Journal of Geophysical Research*, 94: 5121-5136.
- Grell, G. A., Dudhia, J. & Stauffer, D. R. 1994. A Description of the Fifth Generation Penn State/NCAR Mesoscale Model (MM5). In NCAR Technical Note NCAR/TN-398+STR. National Center for Atmospheric Research, Boulder, USA, 138 pp.
- Grell, G., Dudhia, J. & Stauffer, D. R. 1995. A description of the fifth-generation Penn State/NCAR mesoscale model (MM5). In NCAR Tech. Note NCAR/TN-398+STR. National Center for Atmospheric Research, Boulder, USA, 117 p.
- Gery, M. W., Whitten, G. Z., Killus, J. P. & Dodge, M. C. 1989. A photochemical kinetics mechanism for urban and regional scale computer modeling. *Journal of Geophysical Research*, 94: 12925-12956.
- Holloway, T., Levy, H. & Carmichael, G. 2002. Transfer of reactive nitrogen in Asia: development and evaluation of a source-receptor model. *Atmospheric Environment* 36: 4251-4264.
- Luo, C., Jonh, J. C. S., Zhou, X. J., Lam, K. S., Wang, T. & Chameides, W. L. 2000. Nonurban ozone air pollution episode over eastern China: observation and model simulations. *Journal of Geophysical Research* 105: 1889 -1908.
- Skamarock, W. C., Klemp J. B., Dudhia J., Gill, D. O., Barker, D. M., Wang, W. & Powers, J. G. 2005: A Description of the Advanced Research WRF Version 2. In NCAR Technical Note NCAR/TN-468+STR. National Center for Atmospheric Research, Boulder, USA, 88 p.
- Son, T. A & Son, D. H. 2005. Experimental applying of the community multi-scale air quality (CMAQ) modeling system in North VietNam. *Proceedings of Science Reports of Institution of Hydro and Meteorology*.
- Son, T. A & Son, D. H. 2007. Preliminary Study on applying Community Multi-scale air quality (CMAQ) modeling system in Vietnam. *Scientific and Technical Hydro-Meteorological Journal*.
- Son, T. A & Son, D. H. 2008. Study on assessment of air pollution transboundary. *Scientific and Technical*

Hydro-Meteorological Journal.

Streets, D. G., Bond, T. C., Carmichael, G. R., Fernandes, S. D., Fu, Q., He, D., Klimont, Z., Nelson, S. M., Tsai, N. Y., Wang, M. Q., Woo, J.-H. & Yarber, K. F. 2003. An Inventory of Gaseous and Primary Aerosol Emissions in Asia in the Year 2000. *Journal of Geophysical Research*, 108: DOI 10.1029/2002JD003093.

Wang, W., D. Barker, C., Bruy`ere, J. D. Gill, D. D. & Michalakes, J. 2004. WRF Version 2 modeling system user's guide. [http://www.mmm.ucar.edu/wrf/users/docs/user\\_guide/](http://www.mmm.ucar.edu/wrf/users/docs/user_guide/).

Yarwood, G., Rao, S., Yocke, M. & Whitten, G. 2005. Updates to the Carbon Bond chemical mechanism: CB05. In Final Report to the U.S. EPA, RT-0400675. U.S. Environmental Protection Agency, Washington, DC, USA [Available online at [www.camx.com](http://www.camx.com).].

***Joint Projects of EANET with Participating  
Countries***

# **Joint Research Project with Mongolia on Plant Sensitivities to Acid Deposition**

## **Lead organization:**

- Acid Deposition and Oxidant Research Center

## **Organizations in the participating countries:**

- Central Laboratory of Environment and Metrology, Mongolia
- National University of Mongolia
- National Institute for Environmental Studies, Japan

## **1. Introduction**

Sensitivity and/or physiological response of plants to acid deposition/ air pollution have not been enough studied in most part of East Asia including the (sub-) arid zone. Decline of larch trees (*Larix sibirica*) has been reported in Bogdkhan Mountain near the city of Ulaanbaatar, Mongolia, and it was suggested that air pollution derived from the thermal power plants might be one of the possible causes. Effects of air pollution on plant species including the larch trees were studied in this project. The project was supported financially by the Global Environmental Research Fund of the Ministry of the Environment of Japan, and Sumitomo Foundation. This report was prepared based on two scientific papers published in international journals.

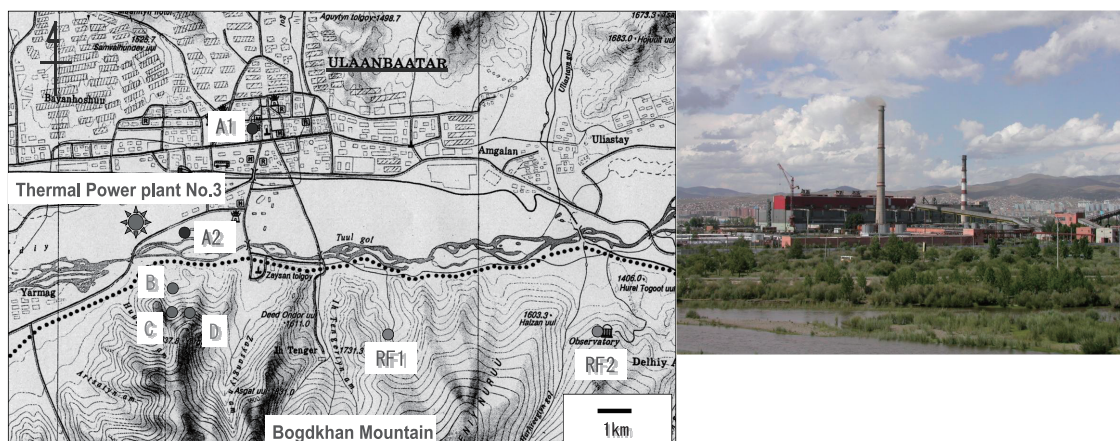
## **2. Objectives**

The project was carried out with the following final objectives:

- To discuss implication between air pollutions derived from a thermal power plant and chemical/ (eco-) physiological properties on plant and soil
- To accumulate basic information on Mongolian plant sensitivities

## **3. Methods**

Surveys on air concentrations by passive samplers, field observation of tree decline and chemical properties of needles/soils were carried out in 2001 and 2003 at Bogdkhan Mountain near the city of Ulaanbaatar (Fig 1). To study sensitivities of Mongolian plant species to air pollution, five semiarid species, whose seeds were collected in the Bogdkhan Mountain, were exposed to either O<sub>3</sub> (50 ppb average, 100 ppb maximum) or SO<sub>2</sub> (100 ppb constant) for 4 weeks in controlled environment chambers.

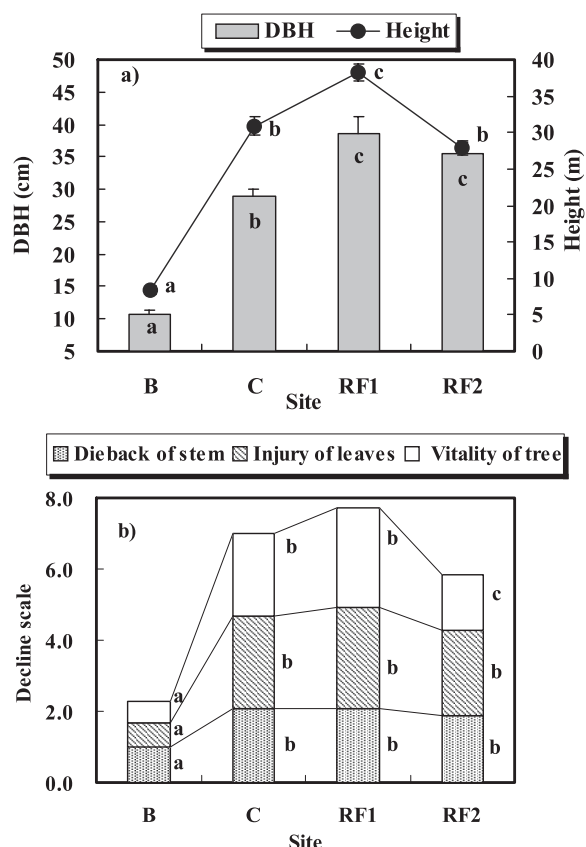


**Figure 1** Study plots around the Bogdkhan Mountain near Ulaanbaatar City (left) and the photo of the Thermal Power Plant No. 3 (right).

#### 4. Outcomes of the project

Tree sizes of *Larix sibirica* were shown in Fig. 2 a). At site B in the bottom of the slope facing the power plant, only young trees were observed and the sizes were three times smaller than trees in the other sites. Trees at site C were significantly smaller than trees at sites RF1 and RF2 in DBH, while they were not different from trees at RF2 in height. Decline classes by the representative observation parameters were shown in Fig. 2 b). Larger values of these parameters indicate more severe decline. Trees at site B were healthier than trees at the other sites. Trees at sites C and RF1 were worse than those at RF2 in vitality of trees.

Severe forest decline by insect attack was observed near RF1. Trees attacked by insects in this area showed severe defoliation not only on the crown but also in lower branches. Tree decline observed in site RF1 and RF2 may be mainly caused by the insect attack. However, trees at B and C on the slope facing the thermal power plant showed typical dieback symptoms mainly on the crown, which were different



**Figure 2** Tree size (a) and decline condition (b) of *Larix sibirica* in Mt. Bogdkhan (Sase et al., 2005).

symptoms observed in site RF1 and RF2. Other effects than insect attack should be considered as possible causes for the decline of trees on the slope.



**Figure 3 Typical dieback of larch trees near the site B.**

O<sub>3</sub> concentration was relatively high (ca. 40ppb) in summer. Mean concentrations of SO<sub>2</sub> and O<sub>3</sub> were higher at the sites on the slope than those at the other sites (Table 1). Sulfur contents of larch needles were also higher on the slope than other sites. The slope facing the thermal power plant might suffer more negative effects than the other areas.

**Table 1 Concentrations of SO<sub>2</sub> and O<sub>3</sub> and sulfur concentrations of *Larix sibirica* (Sase et al. 2005)**

| Site | Passive sampling (from July to November, 2003) |      |                      |      | S conc. of needles<br>(mg-S/g-dry needles) |
|------|--|------|----------------------|------|--|
|      | SO <sub>2</sub> (ppb)                          |      | O <sub>3</sub> (ppb) |      |  |
|      | Mean   | Max. | Mean                 | Max. |  |
| A1   | 1.0 (0.4) ac                                   | 4.0  | 16.0 (1.8) a         | 27.4 | 1.5  |
| A2   | 0.5 (0.2) a                                    | 1.6  | 21.7 (1.6) b         | 32.1 | -  |
| B    | 1.7 (0.4) bc                                   | 3.8  | 27.2 (1.5) c         | 35.1 | 1.8  |
| C    | 1.6 (0.5) bc                                   | 3.9  | 30.8 (2.0) d         | 40.5 | 2.2  |
| RF1  | 0.4 (0.1) a                                    | 1.1  | 22.1 (2.1) b         | 32.3 | 1.2  |
| RF2  | 0.8 (0.2) ac                                   | 2.0  | 27.4 (1.8) c         | 34.5 | 1.1  |

Soil chemical properties were measured near several study sites. Soil pH and contents of exchangeable base cations were high (Table 2), suggesting high acid neutralizing capacity (ANC). The high ANC may suppress soil acidification buffering acids derived from atmospheric deposition. It seemed that soil acidification or nutrient deficiency were not main factors related to the tree decline. Accumulation of heavy metals, such as Pb, Cu and Zn, cannot be detected in soil samples on the slope, too.

**Table 2 Soil chemical properties in Bogdkhan Mountain**

| Sampling points |                | pH(H <sub>2</sub> O) | Ex-Na      | Ex-K | Ex-Mg | Ex-Ca |
|-----------------|----------------|----------------------|------------|------|-------|-------|
|                 |                |                      | cmol(+)/kg |      |       |       |
| A2              |                | 7.8                  | 0.2        | 0.9  | 1.0   | 24.8  |
| B               |                | 6.7                  | 0.3        | 0.9  | 7.1   | 46.1  |
| C               | C <sub>1</sub> | 5.9                  | 0.2        | 0.8  | 5.4   | 21.9  |
|                 | C <sub>2</sub> | 5.8                  | 0.2        | 0.9  | 3.9   | 23.4  |
|                 | Av.            | 5.9                  | 0.2        | 0.9  | 4.6   | 22.6  |
|                 |                |                      |            |      |       |       |
| D               | D <sub>1</sub> | 5.9                  | 0.2        | 1.3  | 7.3   | 34.4  |
|                 | D <sub>2</sub> | 5.7                  | 0.4        | 1.1  | 8.5   | 34.5  |
|                 | Av.            | 5.8                  | 0.3        | 1.2  | 7.9   | 34.5  |

## 5. Conclusion

It was clarified that air pollutions such as SO<sub>2</sub> and O<sub>3</sub> were transported to the Bogdkhan Mountain, and the slope facing the thermal power plant suffered more negative effects of the pollution than the reference forests. Direct effects of air pollution may be one of the possible causes for the tree decline on the slope as well as natural environmental factors such as insect attack (Sase et al., 2005).

Moreover, by the exposure test, several sensitive species to O<sub>3</sub> or SO<sub>2</sub>, such as *Carex* spp., *Polygonum alopecuroides*, and *Sanguisorba officinalis*, were identified (Shimizu et al., 2005). The sensitive species, which were identified in this study, should be monitored carefully in the future monitoring for early detection of possible impacts of air pollution in this area.

## References

- Sase, H., Bulgan, T., Batchuhuluun, T., Shimizu, H. & Totsuka, T. 2005. Tree decline and its possible causes around Mt. Bogdkhan in Mongolia. *Phyton* (Horn, Austria) 45: 583-590.
- Shimizu, H., An, P., Zheng, Y. R., Chen, L. J., Sase, H., Totsuka, T., Bulgan, T. & Zheng, Y. 2005. Response to O<sub>3</sub> and SO<sub>2</sub> for five Mongolian semiarid plant species. *Phyton* (Horn, Austria) 45: 601-607.



# **Joint Research Project with Russia**

## **on Evaluation of East Siberian Atmospheric Environment**

### **Lead organization:**

- Acid Deposition and Oxidant Research Center

### **Organizations in the participating countries:**

- Limnological Institute, Russian Academy of Science, Siberian Branch, Russia
- Primorsky Center for Environmental Monitoring, Russia

### **1. Introduction**

In order to obtain basic information for improving monitoring methodologies applicable to a frigid zone, the joint research project was started in 1998 with the Limnological Institute, Russian Academy of Science, Siberian Branch (LIN/RAS/SB). The next phase project on “Evaluation of Atmospheric Environment in East Siberia and Primorsky Region” with same counterpart was started in 2002 to obtain basic information on atmospheric environment in East Siberia and Primorsky Region and on the trans-boundary air pollution over North East Asian/Pacific part in Northern Hemisphere. Acid deposition data monitored in East Siberia and Primorsky Region have been analyzed to evaluate atmospheric environment in those region and to provide useful information on the long-range transportation of air pollutants on the hemispheric scale.

### **2. Objectives**

The project was carried out with the following objectives:

- To clarify the atmospheric environment in East Siberian and Primorsky regions
- To evaluate the long-range transportation of air pollutants on the hemispheric scale

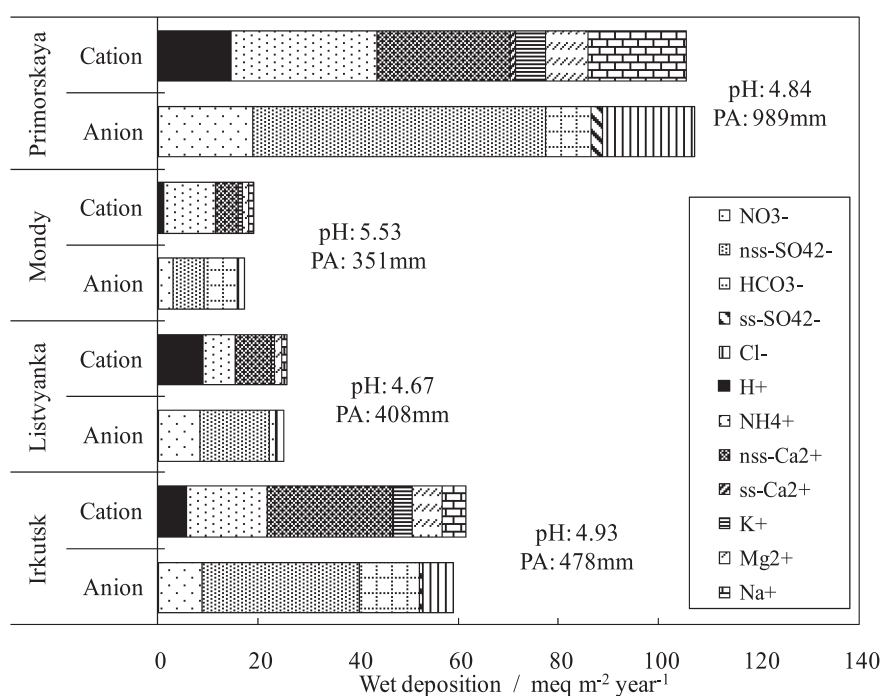
### **3. Methods**

The atmospheric environment in Russian East Siberia and Primorsky region may be influenced by air pollution in Europe and affect air quality in East Asia. In order to evaluate the atmospheric environment annually in these regions, wet deposition and gas/aerosol concentrations have been monitored at 3 sites (Irkutsk, Listvyanka, and Mondy) in East Siberia and 1 site (Primorskaya) in Primorsky region which are in transition area on the long-range transportation of air pollutants. Moreover, lead concentrations and lead isotopic composition of samples have been also monitored in those regions as tracers of long-range transportation of air pollutants.



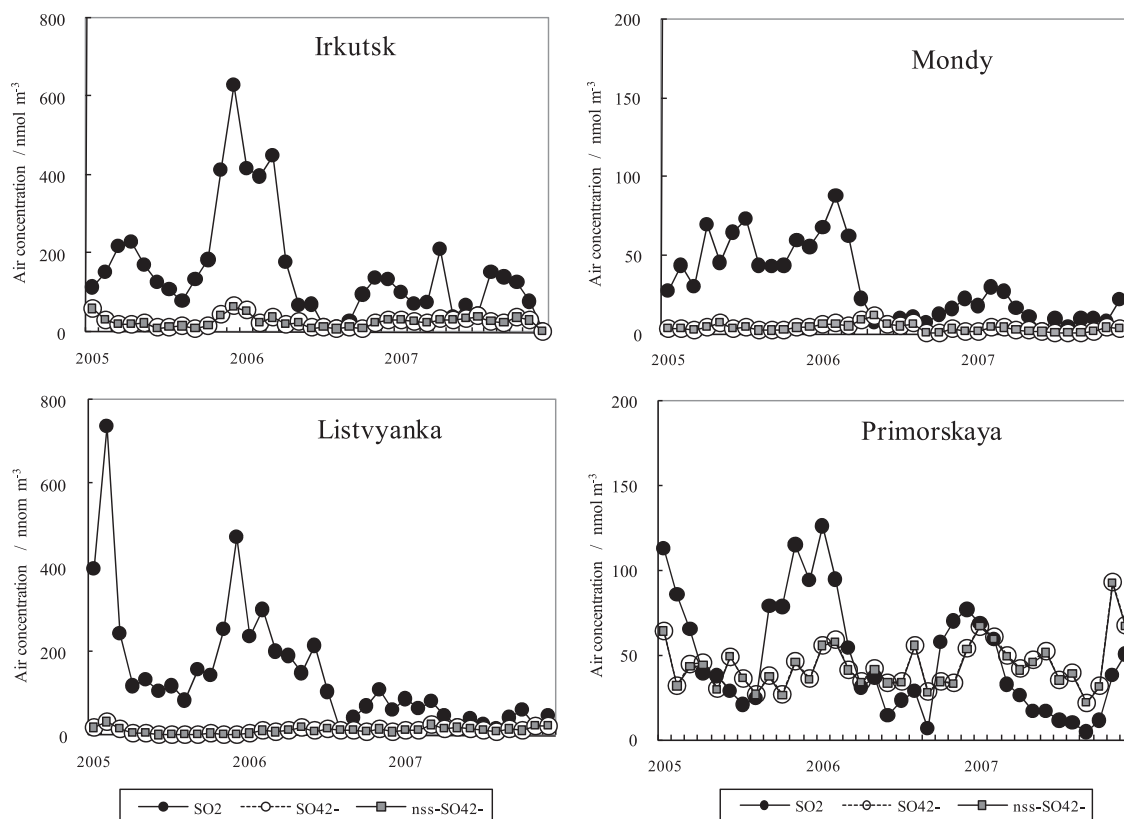
#### 4. Outcomes of the project

Annual precipitation amounts at 4 sites in those regions ranged from 351mm to 989mm with seasonal variation, high in summer and low in winter in 2007. Annual mean pH in wet deposition ranged from 4.67 through 5.53 in 2007. Precipitations were acidified mainly by sulfuric acid. Non-sea-salt sulfate was one of major components of acidic substances, and non-sea-salt Calcium ion and Ammonium ion were major components of basic substances in precipitation. Wet deposition amounts of major components varied with season being large in summer and small in winter harmonizing with variation of precipitation amount.



**Figure 1 Wet deposition amounts of major components in 2007.**

SO<sub>2</sub> and NH<sub>3</sub> gas concentrations were highest at Listvyanka. HNO<sub>3</sub> gas concentration was highest at Primorskaya. Mondy was the cleanest site among 4 sites from the point of view of the concentrations of aerosols. Sulfur dioxide and sulfate aerosol were major components of acidic substances and ammonia gas and ammonium aerosol were major components of basic substances in the atmosphere in those regions. Sulfur dioxide concentration was high in winter in all sites. Figure 2 shows variations of sulfur dioxide, sulfate and non-sea-salt sulfate concentrations at 4 sites. As shown in this figure, large difference was observed in the concentration of sulfur dioxide from 2005 to 2006. Research has been continued taking the possibilities of the increased concentrations into account, for example; 1) Cold winter (especially in 2006); 2) Smaller precipitation; 3) Large area and continuance of forest fire; and 4) Increase of SO<sub>2</sub> emitted in Siberian region or transported from European part of Russia.



**Figure 2** Monthly variation of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{nss-SO}_4^{2-}$  concentrations.

Annual mean concentrations of acidic and basic substances were on the same level or lower than those of low concentration sites in Japan except ammonia gas concentration at Primorskaya. The composition of acidic components in precipitations was almost similar to that in aerosols.

The concentrations of lead at 4 sites were lower than those of the previous year. The ratio of sulfate and nitrate concentrations was almost same between the particulate matter and the precipitations.

Moreover, the lead isotopic ratios in the samples measured in these regions were similar to those in Japan, and it was confirmed that the atmospheric environment of those regions and Japan were closely related to each other.

## 5. Conclusion

Significant differences were not observed on wet deposition of major components between the monitoring results in previous years and 2007. Wet deposition amount of these components increased in summer and decreased in winter, so it depended on the fluctuation of precipitation amount. Sulfate deposition was largest at Primorskaya and smallest at Mondy in 4 monitoring sites in Russia. Precipitations in East Siberia and Primorsky Region were acidified mainly by sulfuric acid and

neutralized by calcium aerosol and ammonia gas.

Moreover, bicarbonate concentrations were larger than nitrate concentrations in wet deposition in East Siberia area where hydrogen ion concentrations were high. The sulfur dioxide and ammonia gas concentrations in the atmosphere fluctuated during the year. The monitoring of atmospheric environment should be continued in the future to estimate these factors.



**Location of Irkutsk site**



**Location of Listvyanka site**



**Location of Primorskaya site**



**Location of Mondy site**

**Figure 3 Locations of observation sites in Russia.**

# **Joint Research Project with Thailand on Dry Deposition Flux**

## **Lead organization:**

- Acid Deposition and Oxidant Research Center

## **Organizations in the participating countries:**

- Pollution Control Department (PCD), Thailand
- Meisei University, Japan

## **1. Introduction**

In order to investigate on dry deposition flux and deposition velocity above specific surfaces typical in East Asia, the Network Center for EANET (NC) promoted a joint research project on dry deposition flux with Pollution Control Department (PCD), Thailand from January 2000 (JFY1999). The program is one of the activities proposed in the Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET that was endorsed by the Interim Scientific Advisory Group (ISAG) through the diplomatic channel in September 1999.

The experiments were performed in a teak forest in Mae Moh (18.28°N, 99.72°E) in Lampang Province, Thailand located about 550 km north of the Bangkok metropolitan area. The climate of northern Thailand is classified as tropical savannah with an evident dry and wet season each year. The vegetation of this region is mainly subtropical deciduous forest, and forested teak is a typical tree species in this area.

An observational station was established with a flux measurement system that used micrometeorological techniques. Observations of O<sub>3</sub> and SO<sub>2</sub> concentrations, and the meteorological parameters, were regularly conducted from December 2001 up to 2005 and calculation of the deposition velocities was made. After accumulating data for more than four years, both organizations decided to terminate the project in December 2005. Data evaluation was conducted by NC and Japanese experts from Meisei University, Japan in cooperation with the experts in Thailand.

The data from the dry season of 2002 was mainly analyzed to obtain the ozone dry deposition in 2003. This result was summarized and published (Matsuda et al., 2005). In 2004, the ozone analysis continued and a preliminary analysis on SO<sub>2</sub> dry deposition was also carried out. The results were reported at the EANET Fifth Senior Technical Manager's Meeting (STM5) and Fourth Session of the Scientific Advisory Committee (SAC4). In 2005, the seasonal change of O<sub>3</sub> dry deposition between wet and dry seasons was analyzed. The progress of this project was reported at EANET meetings.

## **2. Objectives**

The project was carried out with the following final objectives:

- To estimate the dry deposition velocities of ozone and sulfur dioxide in a teak forest site in Thailand

using field observations

- To develop a suitable direct method for estimating dry deposition flux in the tropical region for future EANET monitoring

### 3. Methods

#### 3.1. Experiment description

The study field is located approximately 5 km south from Mae Moh Thermal Power Plant (Fig. 1). An observational station was constructed in a teak (deciduous) forest in the area. The forest canopy is flat and uniform as far as a distance of 1 km in main upwind directions. Density of the forest is about 625 trees/ha, and its height is about 12 meters. An observational tower (24 meters) is constructed within the forest.

The measurement system consists of an ultrasonic anemometer, radiometers, ventilated wet and dry thermometers (for temperature difference measurement), soil heat flux meters, a SO<sub>2</sub> monitor (UV fluorescence method), an O<sub>3</sub> monitor (UV photometric method) and a sampling changer. Differences of concentrations for SO<sub>2</sub> and O<sub>3</sub> were measured by using the sampling changer. In the system, Bowen ratio and gradient methods are applied to output the fluxes.

#### 3.2. Computation of fluxes and deposition velocities

The gradient method introduced below was used for result calculations:

All measured parameters were averaged every 30 min, and then fluxes,  $F$ , were computed, using the following equation (Erisman and Draaijers, 1995):

$$F = -u_* c^*, \quad (1)$$

where  $u_*$  is the friction velocity, and  $c^*$  is the eddy concentration. The  $c^*$  is expressed by the following equation (Feliciano et al., 2001):

$$c^* = k \Delta c / [\ln(z_2 - d / z_1 - d) - \Psi_h(z_2 - d / L) + \Psi_h(z_1 - d / L)], \quad (2)$$

where  $\Delta c$  is the differences of O<sub>3</sub> concentrations at a height between  $z_2$  (23 m) and  $z_1$  (15 m),  $d$  is displacement height,  $k$  is the Von Karman constant,  $L$  is the Monin-Obukhov length and  $\Psi_h$  is the integrated stability correction function for heat defined by Erisman and Draaijers (1995).

The deposition velocity,  $V_d$ , is determined by the following equation:

$$V_d = -F / C, \quad (3)$$

### 4. Outcomes of the project

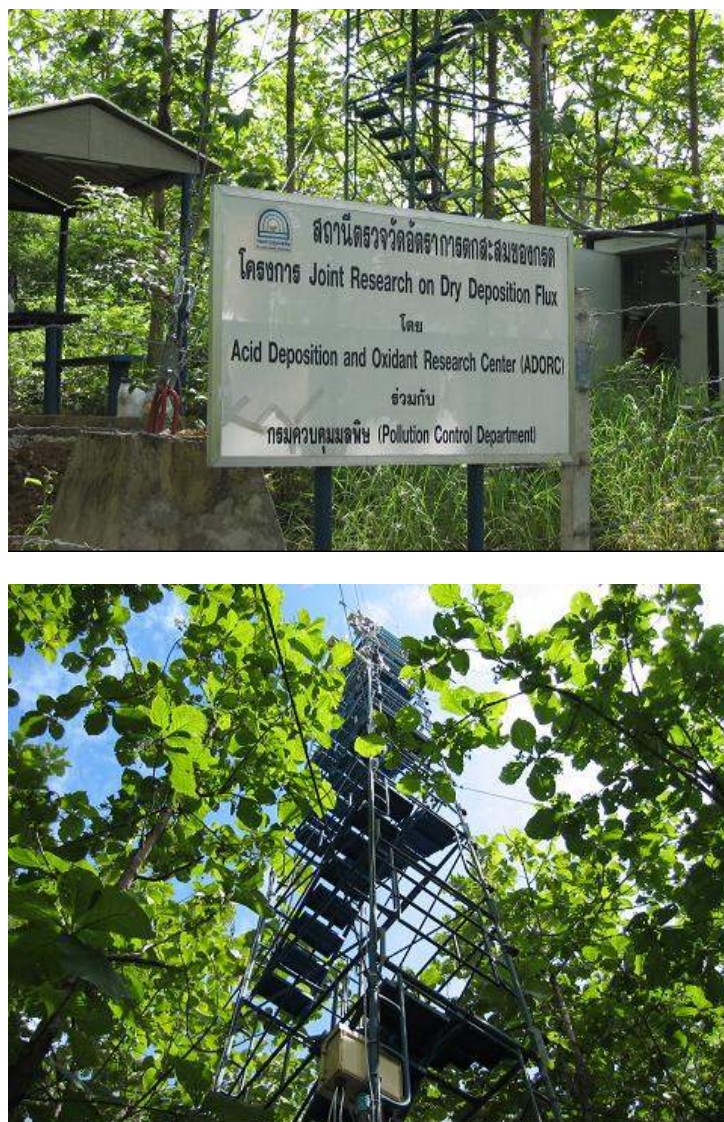
In order to analyze the seasonal change, the dry season from January to April in 2002 and the wet season from June to September in 2003 were selected taking into account conditions of the instruments



and data completeness.

Figure 2 shows median diurnal variation of  $O_3$  fluxes in the dry and wet seasons. Seasonal change with the dry season high and the wet season low in the daytime was clearly observed. Figure 3 and 4 show median diurnal variations of  $O_3$  concentration and deposition velocity respectively. The concentration in the dry season was higher than that in the wet season. On the other hand, seasonal change of the deposition velocity was not clearly observed. It means that the high flux in the dry season was mainly caused by the high concentration in the season.

In general, low concentration produces large errors of flux and deposition velocity. The flux and deposition velocity in the wet season seems to have large errors because of the low concentration. Accumulation of a large number of data sets for wet season analyses was required.



**Figure 1** Photographs taken at the monitoring site in Lampang Province.

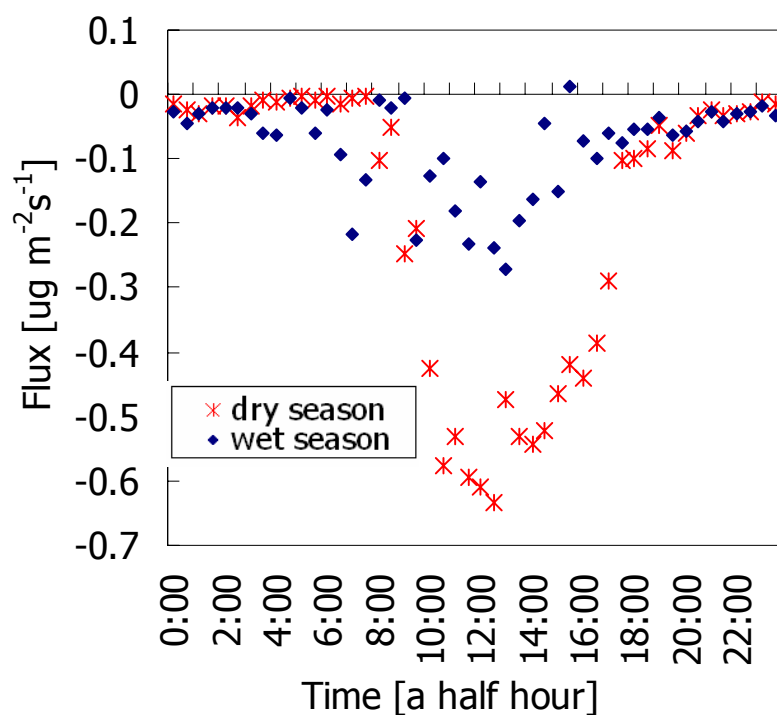


Figure 2 Median diurnal variation of O<sub>3</sub> fluxes in the dry and wet seasons.

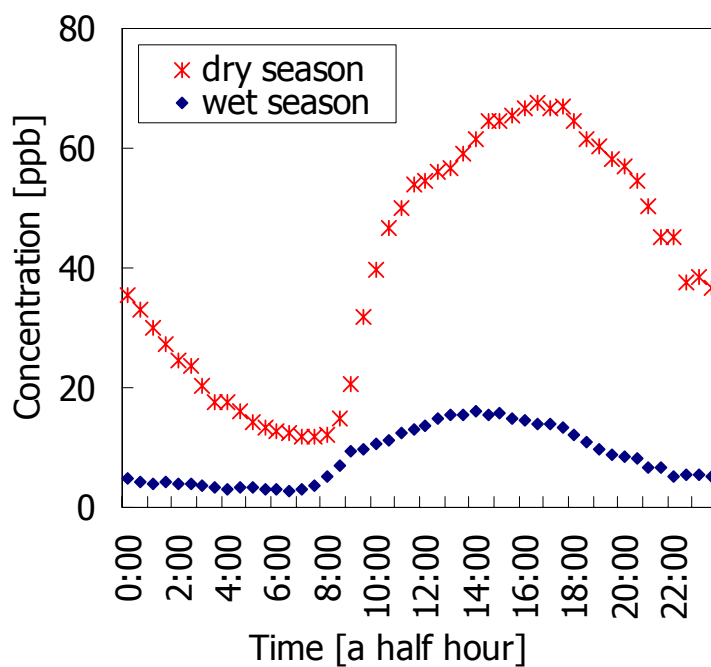
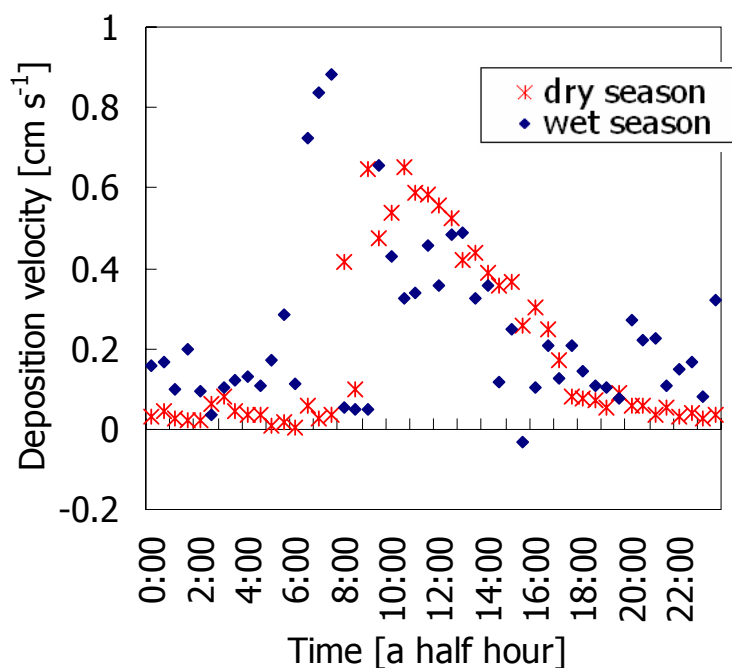


Figure 3 Median diurnal variation of O<sub>3</sub> concentrations in the dry and wet seasons.



**Figure 4 Median diurnal variation of O<sub>3</sub> deposition velocities in the dry and wet seasons.**

## 5. Conclusion

The Joint Research Project on dry deposition flux is the first phase of the joint research collaboration between ADORC and Thailand for improvement of EANET monitoring methodologies. Phase 1 was implemented from January 2000 to December 2005. The results from this project will be applied in the activity of the Strategy on EANET Development (2006-2010) on development of a Technical Manual on dry deposition flux estimation.

Phase 2 of this joint collaboration started in August 2005 focusing on QA/QC of gas concentration monitoring methods in a tropical region. Various monitoring methods of gas concentrations (automatic monitor, filter-pack method, and passive sampling method) are used at sites in southern Thailand and the data will be compared and evaluated jointly by ADORC, PCD in cooperation with Meisei University, Japan.

## References

- Erisman, J. W. & Draaijers, G. P. J. 1995. Atmospheric deposition in relation to acidification and eutrophication. In *Studies in Environmental Research* 63. Elsevier, the Netherlands, 405 p.
- Matsuda, K., Watanabe, I., Vitsanu, W., Phunsak, K., Pojanie, K., Supat, W. & Totsuka, T. 2005. Ozone dry deposition above a tropical forest in the dry season in northern Thailand. *Atmospheric Environment* 39: 2571-2577.



# Joint Research Project with Thailand on Dry Deposition

## Monitoring

### Lead organization:

- Acid Deposition and Oxidant Research Center, Japan

### Organizations in the participating countries:

- Pollution Control Department, The Ministry of Natural Resources and Environment, Thailand
- Asian Center for Environmental Research, Meisei University, Japan

### 1. Introduction

Acid Deposition and Oxidant Research Center (ADORC), Network Center of EANET (NC) has been promoting a Joint Research program with Pollution Control Department (PCD), Thailand since January 2000 (Japanese fiscal year (JFY) 1999). Following the termination of the Joint Research on dry deposition flux (Phase I) from January 2000 to December 2005, NC and PCD agreed to establish Phase II of the Joint Research focusing on QA/QC of Filter-pack method in tropical region in August 2005. In Phase II, Asian Center for Environmental Research, Meisei University (ACER) newly joined the study with contributions of human resources.

### 2. Objectives

To inter-compare gaseous measurements using several different types of monitoring methods i.e. Filter-pack method, Automatic monitor, and Passive Sampler method.

### 3. Methods

#### 3.1 Comparison study

Measurements of gas concentrations by using different types of monitoring methods were carried out at Bangkok EANET station from December 2006. Table 1 shows the monitoring methods and the parameters measured in the joint research project.

Table 1. Monitoring methods and Parameters

| Monitoring methods (Manufacturer)             | Parameters      |                |    |                 |                 |
|---|-----------------|----------------|----|-----------------|-----------------|
| Automatic monitor (Nippon Thermo Co., Ltd.) * | SO <sub>2</sub> | O <sub>3</sub> | NO | NO <sub>x</sub> | NO <sub>2</sub> |
| Passive sampler (Ogawa & Co., USA, Inc.)      | SO <sub>2</sub> | O <sub>3</sub> | NO | NO <sub>x</sub> | NO <sub>2</sub> |

\*: The Automatic monitor was used in the Joint Research on Dry Deposition Flux (Phase I).

Automatic monitor was already installed at the station and Filter-pack monitoring data were also used for the research. PCD staff carried out routine maintenance of the Automatic monitor newly installed at the station following procedures of the measurements for the research. PCD collected and analyzed samples from Passive sampling following the procedures that were developed based on the discussion among three parties.



Photo of Bangkok EANET station

#### **4. Outcomes of the comparison study**

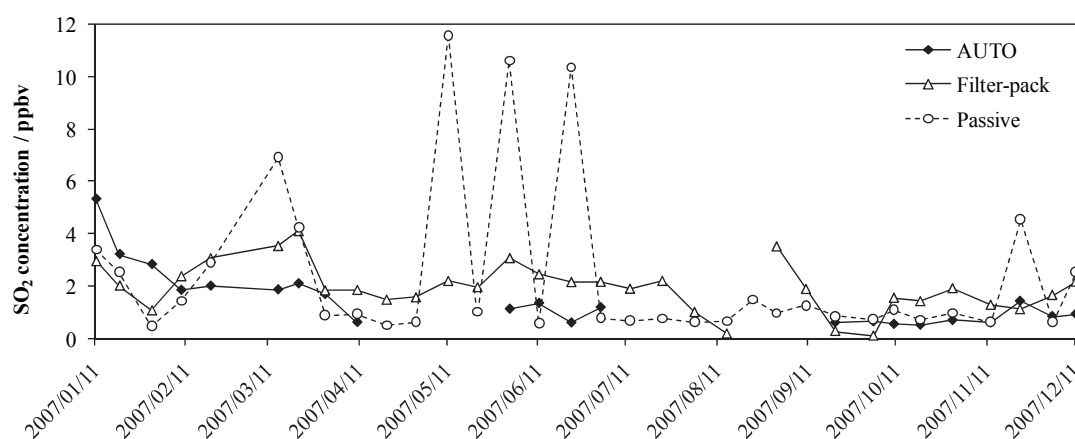
SO<sub>2</sub> concentrations measured by Filter-pack method and Automatic monitor shows difference (Fig.1). The concentration by Filter-pack method was approximately twice higher from Feb. 2007 to Dec. 2007. The difference of the concentration by each methodology did not show the relationship with meteorological parameters. This suggests that there could be issues (sampling system etc.) for the difference.

SO<sub>2</sub> concentration measured by Passive method and Automatic monitor is shown in Fig. 1. The collected amounts of passive filters during the same sampling period sometimes showed big differences. Except the big difference data, the concentration by the each methodology shows weak correlation (Correlation coefficient: Corr. = 0.62, n=38). The difference was not influenced by the meteorological parameters (Relative humidity etc.). This could possibly be due to the influence from emission sources around the station, therefore it needs further investigation.

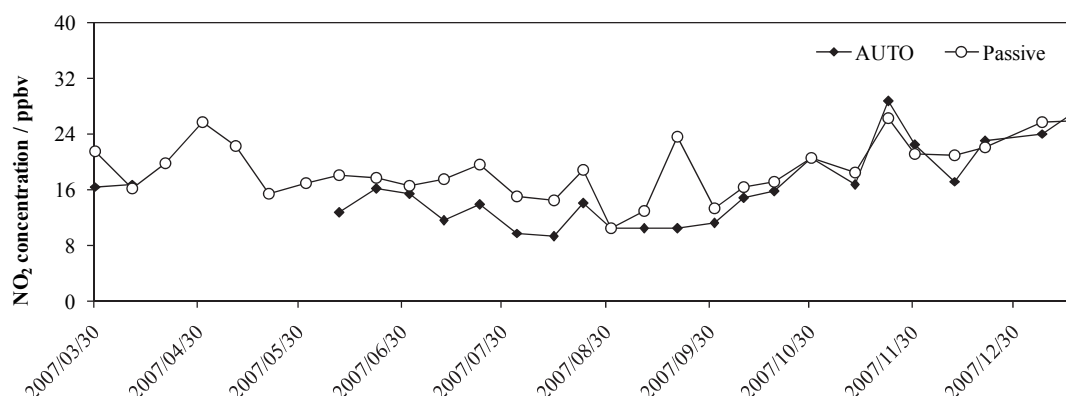
O<sub>3</sub> concentration by Passive method could not be compared with the data at the Bangkok EANET station, because the Automatic monitor which was newly installed was not functioning well. In the future, it will be estimated the O<sub>3</sub> concentration by Passive method and compared with the meteorology parameters.

NO<sub>2</sub> concentration by Passive method shows good correlation (Fig.2, Corr. = 0.79, n=24) with Automatic monitor. The concentration by each methodology shows good agreement except the period from Jun. 2007 to Oct. 2007, rainy season, in Bangkok. The difference of the concentration between each methodology showed weak correlation with relative humidity (Corr. = 0.45, n=24). It is possible that the NO<sub>2</sub> concentration was influence by relative humidity.

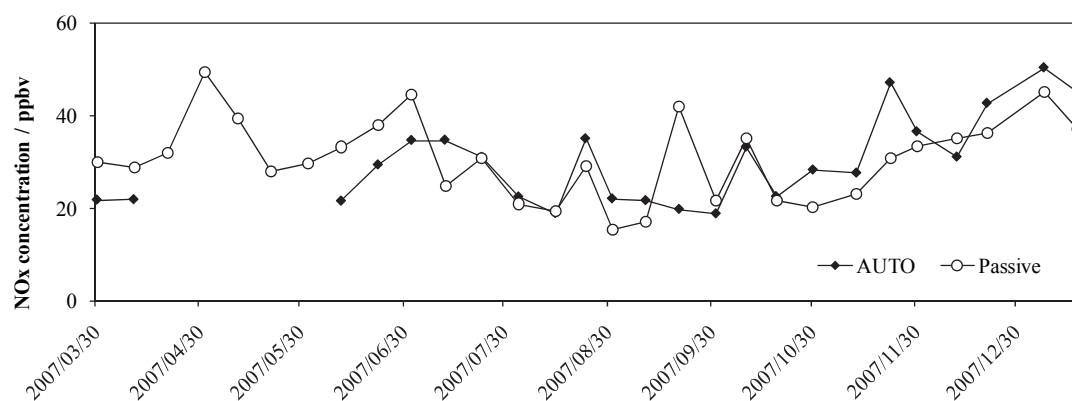
NO<sub>x</sub> concentration by Passive method shows weak agreement with Automatic monitor (Fig. 3, Corr. = 0.57, n=23). The difference of the concentration by each methodology did not correlate with meteorological parameters. The passive filters of NO<sub>x</sub> were easy to react with the solar radiation, therefore it is necessary to compare the solar radiation data and improve the sample filters of NO<sub>x</sub>.



**Figure 1 Comparison of SO<sub>2</sub> concentration by Filter-pack method, Passive method and Automatic monitor (from Jan. 2007 through Dec. 2007).**



**Figure 2 Comparison of NO<sub>2</sub> concentration by Passive method and Automatic monitor (from Mar. 2007 through Jan. 2008).**



**Figure 3 Comparison of NO<sub>x</sub> concentration by Passive method and Automatic monitor (from Mar. 2007 through Jan. 2008).**

## 5. Discussion

A comparison of SO<sub>2</sub> concentration by Filter-pack method and Automatic monitor showed that the concentration by Filter-pack method was consistently higher throughout the period monitored. Steps are being taken by the participating organizations to address these issues such as improving the sampling system, checking the chemical analysis procedures (leak, filter blank etc.).

The monitoring data is also being analyzed with the meteorological data to check for meteorological influences and more information on sources of pollution around the site location will be collected.

Further investigations and more comparison studies are necessary before it can be confirmed that the Ogawa Passive samplers can be applied for monitoring ambient air in the tropical region, particularly for monitoring of SO<sub>2</sub>, NO<sub>x</sub>.

This project will continue in JFY 2008 (until March 2009). A more comprehensive report will be made at the end of the project.

# **Joint Research Project with Republic of Korea**

## **on Dry Deposition (aerosol concentration) Monitoring**

### **Lead organization:**

- Acid Deposition and Oxidant Research Center (ADORC)

### **Organizations in the participating countries:**

- National Institute of Environmental Research (NIER), Ministry of the Environment, Republic of Korea

### **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 PM<sub>10</sub>, PM<sub>2.5</sub> 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). Preliminary research was implemented in October 2005 and a workshop to discuss the results was held in February 2006 in the Republic of Korea. 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 site and Japanese site on 12-27 October 2006 and 16-31 May 2007. Several methods for aerosol monitoring including PM<sub>2.5</sub> (PM<sub>10</sub>) collection were implemented simultaneously in both sites. The progress of the project and preliminary results from the intensive monitoring were discussed during small one-day workshops held at NIER during the NC technical missions to Republic of Korea every year since 2005.

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<sub>2.5</sub> measured in Republic of Korea and Japan will be evaluated through this joint research project.

### **1. Objectives**

The project is being carried out with the following final objectives:

- To compare 3-stage filter pack method with 4-stage filter pack method in Korea and Japan.
- To compare PM<sub>2.5</sub> (cyclone and impactor) with open face type of filter pack method in Korea and

Japan.

## 2. Methods

The intensive monitoring was conducted at Cheju in Korea and ADORC, Niigata in Japan during the period from 16 through 31 May 2007. Aerosol was observed by parallel measurement of the following 4 kinds of method:

**Table 1 Summary of sampling methods of aerosol monitoring**

|                                       |                        |
|---------------------------------------|------------------------|
| 1) PM 2.5 (cyclone) + 3-stage filter  | Daily sampling, 15days |
| 2) PM 2.5 (impactor) + 3-stage filter | Daily sampling, 15days |
| 3) Open face + 4-stage (2LPM)         | 5days sampling x 3     |
| 4) Open face + 4-stage (1LPM)         | 5days sampling x 3     |



**Figure 1 Pictures of the intensive monitoring at Cheju in Korea.**



**Figure 2 Pictures of the intensive monitoring at ADORC, Niigata in Japan.**

### **3. Outcomes of the project**

The results of the intensive monitoring are now being analyzed and discussed, and outcomes of the project will be published in the future.

# **Joint Research Project with Thailand**

## **on the Catchment Analysis**

### **Lead organization:**

- Acid Deposition and Oxidant Research Center

### **Organizations in the participating countries:**

- Royal Forest Department, Thailand
- Environmental Research and Training Center, Department of Environmental Quality Promotion, Thailand
- Kyoto University, Japan

### **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 been sufficiently promoted in the tropical region. The project was carried out as a part of the project supported by the Global Environment Research Fund (GERF, C-052: Project Leader, Dr. Junko Shindo, National Institute for Agro-Environmental Sciences: NIAES), the Ministry of the Environment of Japan. This report was prepared by the Acid Deposition and Oxidant Research Center as the lead organization of the project.

### **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**

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.

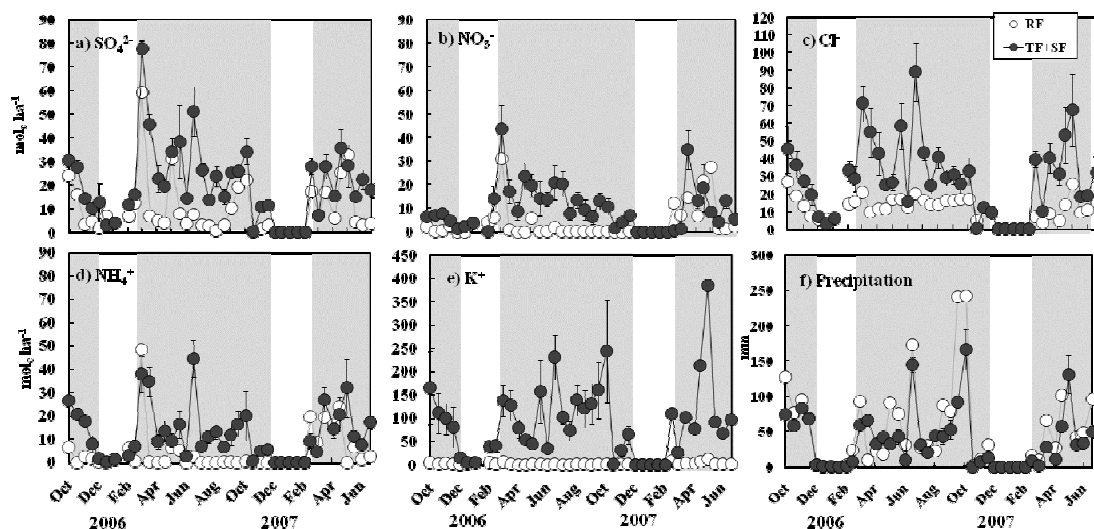
In addition to these continuous surveys, to clarify the seasonal and spatial variation of soil acidity, soil sampling plot (40 m × 350 m) was set up crossing the stream in the catchment. Soil samples were collected in October 2005 (the end of rainy season) and March 2006 (dry season). To clarify the soil mineral-nitrogen fluxes, soil pit was set up in the upper, middle and lower slopes. In 0-5, 5-20, 20-40 and 40-60 depth, the nitrogen (N) mineralization, nitrification and input-output fluxes of related elements as N were determined using in situ incubation method and ion exchange resin method.

#### **4. Outcomes of the project**

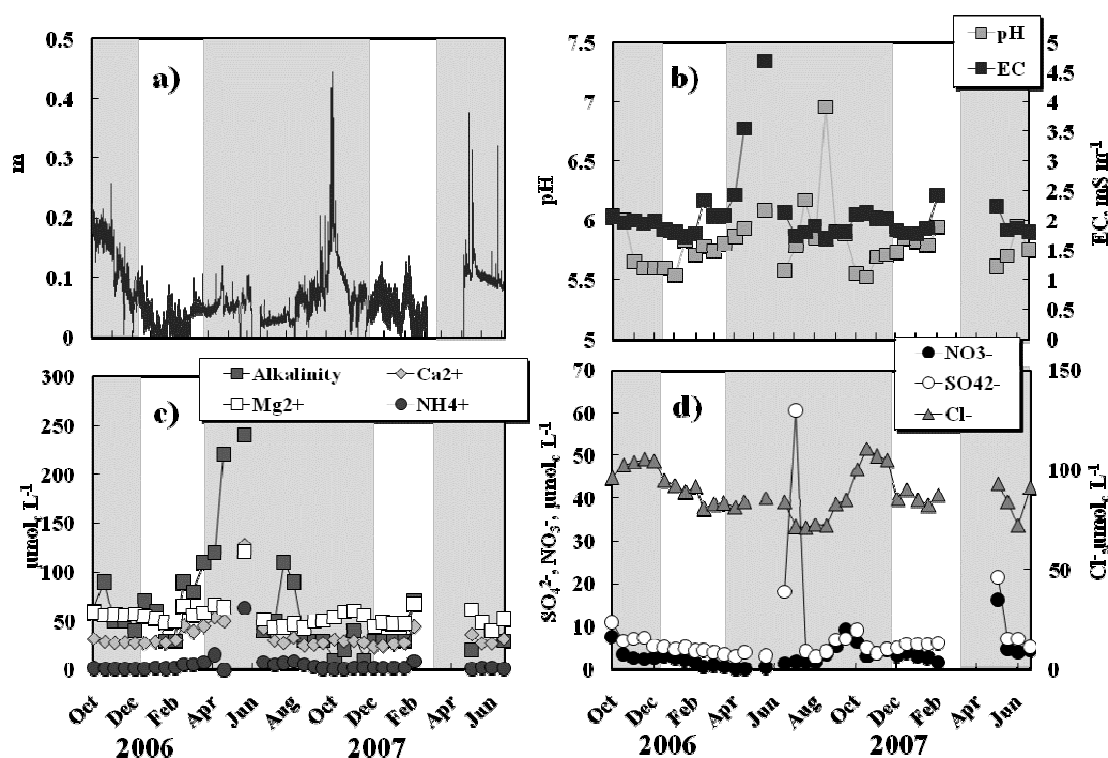
##### **4.1. Atmospheric deposition and stream water chemistry**

Deposition amounts of all ions by TF+SF significantly increased in the middle of March, in the beginning of the wet season (Fig. 1). Especially,  $\text{SO}_4^{2-}$  showed the largest amounts in this season. As for the output from the stream, in the early wet season, specific phenomena could be seen in the stream water chemistry (Fig. 2). The pH and EC increased with alkalinity and concentrations of cations from May to June 2006. Then, the concentration of  $\text{SO}_4^{2-}$  increased significantly in July. The pH and alkalinity decreased with increase of  $\text{SO}_4^{2-}$ . Moreover, pH decreased with increase of EC and concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  in the late wet season.

It was suggested that air pollutants including much  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were suspended in the atmosphere during dry season and washed out by the first precipitations in the beginning of the wet season in the Sakaerat SRS site. As for the output from the stream, high-weathered acidic soil distributed in the tropical region may affect the stream water chemistry. The pH-dependent charge of high-weathered soil in this area may be related to retention/ release of  $\text{SO}_4^{2-}$ , resulting in temporary acidification of the stream water, since the soil pH was significantly higher in wet season than in dry season as mentioned below. Moreover, activated uptake of plants in the early wet season may affect the stream water chemistry. Further analysis is necessary to clarify the seasonal changes.



**Figure 1** Deposition amounts by the throughfall-stemflow method (TF+SF) and the rainfall outside the canopy (RF). Error bar indicates the standard error. Shadow part represents wet season.



**Figure 2** Seasonal changes of the water depth (a), pH and EC (b), alkalinity and cations (c), and anions in the stream water. Shadow part represents wet season.

#### **4.2. Soil acidity and nitrogen flux in soil**

Pronounced spatial variation in soil pH was observed in a surface soil, but not in a deeper soil for each season. Large-scale and small-scale fluctuations were observed in centerline (350 m) of the plot. In all depths, pH (H<sub>2</sub>O) in wet season was significantly higher than in dry season. However, seasonal difference was not found in exchangeable cations. Small-scale spatial variation in soil pH was correlated with exchangeable cation concentrations and large-scale spatial variation might be associated with the difference in the surface-soil structure derived from topographic factor.

The N budget was much larger in the internal circulation than in external budget. An input from Ao layer to mineral soil surface and a supply with mineralization or nitrification may assimilate mostly into the vegetation because the leaching from the soil was very few in comparison with input and supply. Spatial-seasonal variation in nitrogen fluxes was also observed. A supply was higher in lower slope than in other slopes. An input significantly increased in the beginning of wet season and a supply increased in the middle of wet season.

#### **5. Conclusion**

In general, the forest catchment in the East Asian region is largely influenced by seasonal changes caused by the monsoons. Seasonal changes of atmospheric deposition were very clear in Thailand. Moreover, the stream water chemistry may depend on soil characteristics and nutrient fluxes in the ecosystem.

Experience gained through the project suggested that new technical issues should be considered in catchment-scale monitoring. For example, it may be necessary to consider spatial and seasonal variation in soil pH and mineral-nitrogen fluxes in the tropical seasonal forest. The information will be compiled and utilized for preparation of the guidelines for the future catchment-scale monitoring in EANET.

The phase II project will be carried out from JFY 2008 to JFY 2010 (until March 2011) as a part of the project supported by the GERP (C-082, Dr. Junko Shindo, NIAES). Further analysis of the obtained data will be implemented and surveys in Sakaerat SRS will be continued for a while. Collaboration with biogeochemical model simulation is also planned in the new GERP project. More comprehensive outcomes can be expected.

# Joint Research Project with Japan on the Catchment Analysis

## Lead organization:

- Acid Deposition and Oxidant Research Center

## Organizations in the participating countries:

- Niigata University, Japan
- Niigata Prefectural Institute of Public Health and Environmental Sciences, Japan

## 1. Introduction

The data of the catchment-scale analysis has not been enough accumulated even in Japan, especially in the area along the Sea of Japan, which receives a high level of atmospheric deposition and shows its clear seasonality. A project was started in 2002 to accumulate experience and knowledge on the catchment-scale analysis in this area. Moreover, the experience may be informative for implementation of similar projects in Thailand and Malaysia and for the future catchment-scale monitoring in EANET. This report was prepared based on two scientific papers published in international journals.

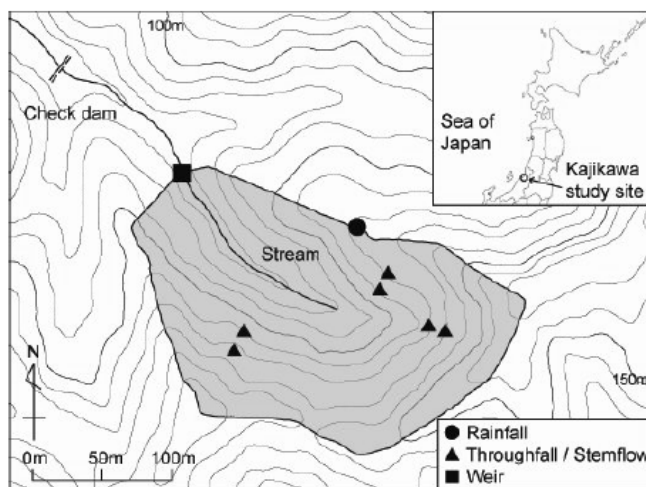
## 2. Objectives

The project was carried out with the following final objectives:

- To estimate effects of acidic deposition on the forested catchment in the area along the Sea of Japan
- To develop a monitoring guideline for the catchment analysis for future EANET monitoring

## 3. Methods

The study site was established in 2002 in a small forested catchment (approximately 3.84 ha) near the Sea of Japan in the northern part of Shibata City (the former Kajikawa Village), Niigata Prefecture, Japan (Fig. 1). Rainfall (RF), throughfall (TF) and stemflow (SF) collectors were installed in the study site as shown in Fig. 1. Rainwater samples were collected at intervals of about 4 weeks until 2007 and then ever 2 weeks thereafter. A weir was installed at the bottom of the catchment, where the stream water (SW) was collected at intervals of roughly 2 weeks.

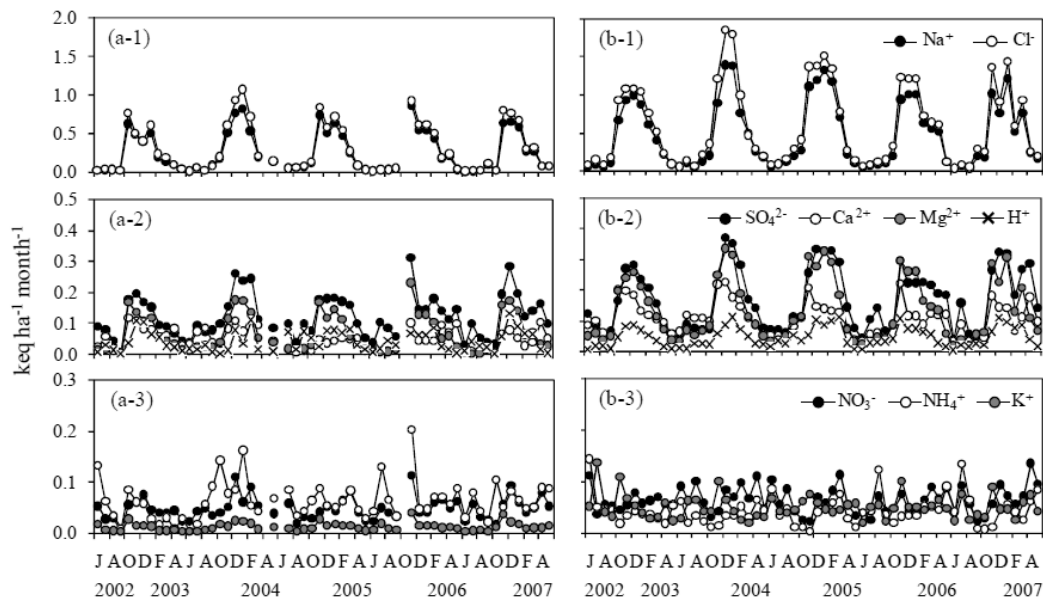


**Figure 1 Study site and layout of the collectors.**

Inorganic constituents in the water samples were determined by ion chromatography. Intensive sampling of soil, Japanese cedar leaves, and SW was carried out occasionally.

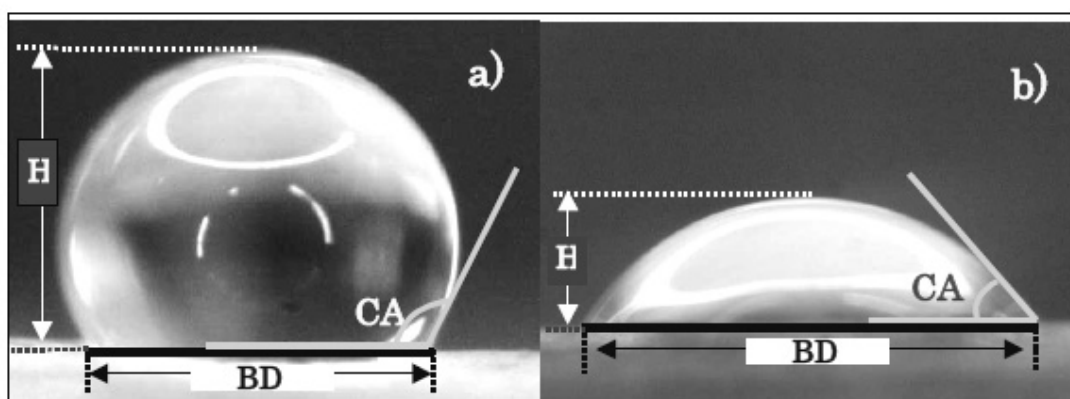
#### 4. Outcomes of the project

The study catchment exhibited distinct seasonality in atmospheric deposition (Fig. 2). The fluxes for  $\text{Na}^+$  and  $\text{Cl}^-$  from RF increased from late autumn to midwinter, and then decreased in the spring. Seasonal trends were observed for the fluxes of  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , which were comparable to those of  $\text{Na}^+$  and  $\text{Cl}^-$  (Sase et al., 2008; Kamisako et al., in press). Fluxes of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{K}^+$  did not show clear seasonal trends, especially for TF and SF, suggesting canopy interactions, while those of  $\text{NO}_3^-$  and  $\text{K}^+$  showed weak trends (Sase et al., 2008).



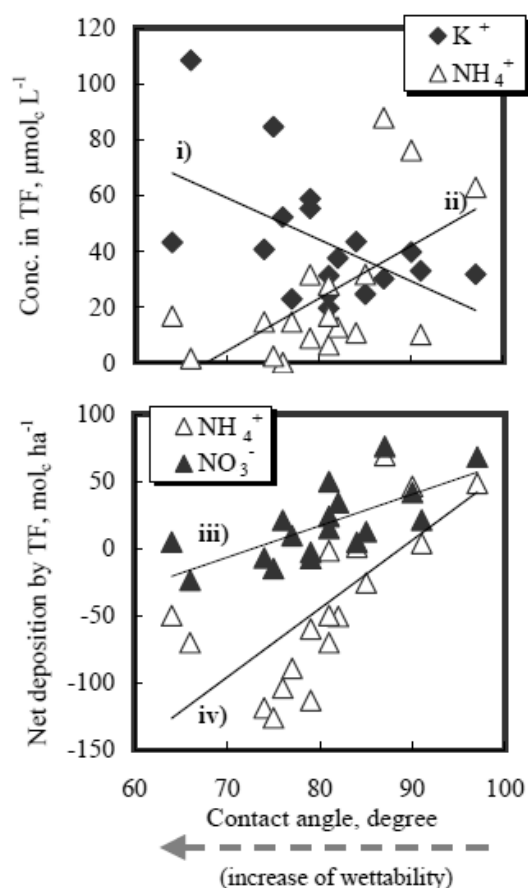
**Figure 2** Seasonal changes of atmospheric depositions from rainfall outside the canopy (a) and from throughfall and stemflow (b) (Kamisako et al. in press).

Leaf surface properties deteriorated gradually with leaf aging. The amount of epicuticular wax increased during the development of the leaves, and then decreased gradually with leaf age. The contact angle (CA) of water droplets on the leaf surface decreased gradually after leaf expansion/growth in both 0-y and 1-y leaves, as shown in Fig.3, but the decrease in CA for 0-y leaves was greater. The CA of 0-y leaves was higher than the 1-y leaves ( $p < 0.001$ ). The leaching rate of  $\text{K}^+$  by the exposure test to artificial fog water was significantly higher in 1-y leaves than in 0-y leaves ( $p < 0.001$ ). Changes of leaf surface properties may affect canopy interactions (Sase et al., 2008).



**Figure 3** A sample measurement of the contact angles (CAs) of a water droplet on the surface of a 0-y leaf in June (a) and a 1-y leaf in November (b). CA was calculated based on the height (H) and basal diameter (BD) of the droplet according to the following equation.  $CA = 2\tan^{-1} [H/(BD/2)] \cdot (180/\pi)$ . (Sase et al., 2008).

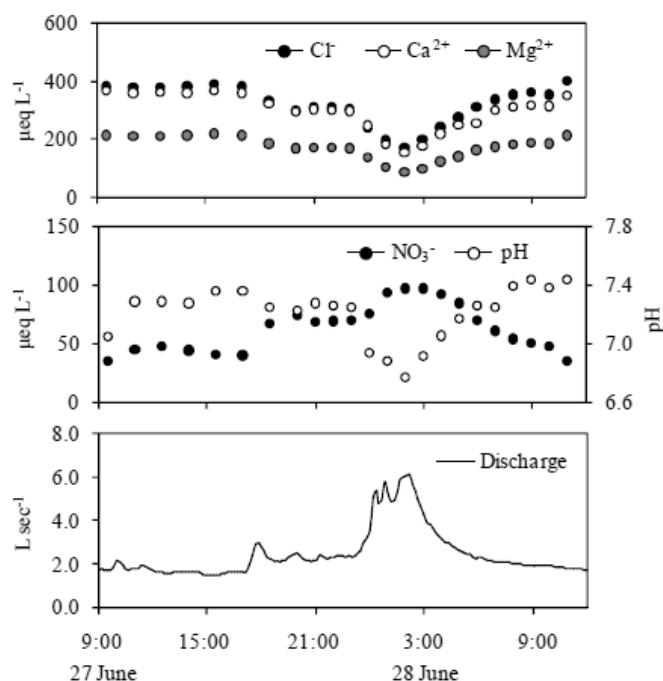
The concentrations and fluxes of ions from TF in the snow-free seasons were compared with CA to elucidate the effects of leaf wettability on ion transport between droplets of rainwater and the surface of the leaf. The concentration of  $K^+$  increased with increase of wettability, while the concentration of  $NH_4^+$  decreased (Fig. 4a). The net fluxes of  $NO_3^-$  and  $NH_4^+$  from TF decreased with increase of wettability (Fig. 4b), but the correlation coefficient was larger for  $NH_4^+$  than for  $NO_3^-$ . Similar correlations were also observed with the CA of 0-y leaves, showing slightly weaker correlations for  $NO_3^-$  ( $r = 0.582$ ,  $p = 0.011$ ) and  $NH_4^+$  ( $r = 0.702$ ,  $p = 0.001$ ). Leaf surface properties, leaf wettability in particular, may be one of regulatory factors for the leaching of  $K^+$  and uptake and/or consumption of nitrogen compounds on the forest canopy, which



**Figure 4** The relationship between contact angle and concentrations of  $K^+$  and  $NH_4^+$  in throughfall (a) and net flux of nitrogen compounds by throughfall (b) (Sase et al., 2008).

accelerates ion exchange on the surface (Sase et al., 2008).

Annual dissolved inorganic nitrogen inputs in RF and in TF + SF were 17.7 and 17.9 kg N ha<sup>-1</sup> y<sup>-1</sup>, respectively, which exceeded previously published thresholds in Europe and the U.S. (i.e., the values at which these inputs increased NO<sub>3</sub><sup>-</sup> levels in SW) and equaled the highest level of nitrogen deposition previously reported in Japan. The NO<sub>3</sub><sup>-</sup> concentration in SW decreased slightly in summer, indicating biological uptake of N during the growing season. However, the lowest NO<sub>3</sub><sup>-</sup> concentrations observed in the summer were still relatively high, equaling approximately 30 µeq L<sup>-1</sup>. Moreover, temporary acidification of SW was observed with high NO<sub>3</sub><sup>-</sup> concentrations during heavy rain events (Fig. 5).



**Figure 5** Changes in the stream water properties during a heavy rainfall event in June 2005 (Kamisako et al., in press).

**Table 1** Annual fluxes of inorganic constituents in the study site (Kamisako et al. in press)

|         | Water<br>(mm y <sup>-1</sup> ) | Annual flux (keq ha <sup>-1</sup> y <sup>-1</sup> ) |                              |                   |                               |                              |                   |                   |                   |                   |                   |
|---------|--------------------------------|---|------------------------------|-------------------|-------------------------------|------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|         |                                | SO <sub>4</sub> <sup>2-</sup>                       | NO <sub>3</sub> <sup>-</sup> | Cl <sup>-</sup>   | HCO <sub>3</sub> <sup>-</sup> | NH <sub>4</sub> <sup>+</sup> | Na <sup>+</sup>   | K <sup>+</sup>    | Ca <sup>2+</sup>  | Mg <sup>2+</sup>  | H <sup>+</sup>    |
| RF      | 2371                           | 1.38 <sup>a</sup>                                   | 0.54 <sup>a</sup>            | 3.32 <sup>a</sup> | -                             | 0.72 <sup>a</sup>            | 2.87 <sup>a</sup> | 0.13 <sup>a</sup> | 0.56 <sup>a</sup> | 0.73 <sup>a</sup> | 0.45 <sup>a</sup> |
| TF + SF | 1959                           | 1.94 <sup>b</sup>                                   | 0.76 <sup>b</sup>            | 6.60 <sup>b</sup> | -                             | 0.52 <sup>b</sup>            | 5.31 <sup>b</sup> | 0.60 <sup>b</sup> | 1.27 <sup>b</sup> | 1.55 <sup>b</sup> | 0.51 <sup>a</sup> |
| SW      | 1439                           | 1.53 <sup>a</sup>                                   | 0.64 <sup>a</sup>            | 5.55 <sup>c</sup> | 5.15                          | 0.01 <sup>c</sup>            | 5.20 <sup>b</sup> | 0.30 <sup>c</sup> | 4.76 <sup>c</sup> | 2.74 <sup>c</sup> | 0.00 <sup>b</sup> |

The H<sup>+</sup> inputs were well neutralized in the soil, whereas significant quantities of base cations, such as Ca<sup>2+</sup> and Mg<sup>2+</sup>, were leached into SW (Table 1), suggesting that the acid neutralizing capacity of the soil has gradually decreased as a result of H<sup>+</sup> consumption in the soil.

## 5. Conclusion

The study area may experience a relatively direct effect of seasonal winds from the Sea of Japan.



However, seasonal changes in the flux and net flux of TF+SF suggest that the leaching of  $K^+$  and uptake and/or consumption of nitrogen compounds, especially  $NH_4^+$ , is occurring on the forest canopy. Estimation of dry deposition fluxes is necessary for precise discussion of total deposition in the forest area, taking the canopy interactions into account. Moreover, N deposition in the study site equaled the highest level observed in Japan, which would cause unused N to leach into SW even during the growing season. The magnitude of the N deposition would certainly contribute to the high  $NO_3^-$  concentrations observed in SW and the temporary acidification that was observed during intense rainfall events.

## References

- Kamisako, M., Sase, H., Matsui, T., Suzuki, H., Takahashi, A., Oida, T., Nakata, M., Totsuka, T. & Ueda, H. 2008. Seasonal and annual fluxes of inorganic constituents in a small catchment of a Japanese cedar forest near the Sea of Japan. *Water, Air, & Soil Pollution*, doi: 10.1007/s11270-008-9726-8.
- Sase, H., Takahashi, A., Sato, M., Kobayashi, H., Nakata, M. & Totsuka, T. 2008. Seasonal variation in the atmospheric deposition of inorganic constituents and canopy interactions in a Japanese cedar forest. *Environmental Pollution* 152: 1-10.



# **Joint Research Project on Model Simulation Works**

## **(Model Intercomparison Study – MICS-Asia Phase II)**

### **Lead organization:**

- Acid Deposition and Oxidant Research Center

### **Organizations in the participating countries:**

- Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences, Beijing, China
- Central Research Institute of Electric Power Industry (CRIEPI), Tokyo, Japan
- Disaster Prevention Research Institute (DPRI), Kyoto University, Japan
- Center for Global and Regional Environmental Research, (CGRER), University of Iowa, USA
- International Institute for Applied System Analysis (IIASA), Laxenburg, Austria

### **1. Introduction of MICS-Asia**

In order to help develop a better common understanding of the performance and uncertainties of chemical transport models (CTMs) in East Asia applications and to help build a modeling community, a model intercomparison study on long-range transport and deposition of sulfur, i.e., MICS-Asia Phase I, was carried out during the period from 1998 to 2002. A primary focus of this study was to better understand the capabilities of regional models in predicting source-receptor (S/R) relationships for sulfur deposition in East Asia. In 2003 this initiative was expanded and focused on:

- Long-term simulation and source-receptor analysis;
- Expanding the chemical species such as sulfur, nitrogen, aerosols, ground-level ozone and
- Individual episodes that are of special interest for gaining insights into important conditions in Asia (e.g., yellow-sand and high ozone episodes).

This broader collaborated study, MICS-Asia Phase II, examined four different periods, encompassing two different years and three different seasons (i.e., March, July, and December in 2001, and March in 2002). Nine different regional modeling groups simulated chemistry and transport of O<sub>3</sub>, precursors, sulfur dioxide, and secondary aerosols, using common emissions and boundary conditions derived from the global models of ozone and related tracers. (MOZART, vol. 2.4).

### **2. Publishing the results of MICS-Asia Phase II**

According to the outline of Phase II, participants prepared necessary common data and then carried out preliminary model simulations after the 5th Workshop. At the 6th Workshop held at IIASA in February 2004, the specifics of Phase II was discussed, taking into account the preliminary results

reported by the participants. From the 7th (February, 2005) to 9th (February, 2007) Workshop, the Working Group members had been preparing their scientific papers regarding each topics, and then the final drafts of scientific papers had been submitted in March, 2007. In May 2008, these papers were published as the Special Issue: MICS-ASIA II of *Atmospheric Environment*.

### **3. Simulation works using Regional Air Quality Model(RAQM)**

#### **3.1. Introduction**

RAQM, developed by the Acid Deposition and Oxidant Research Center (ADORC), is a three-dimensional eulerian model including some key processes of chemical species in atmosphere such as transport, diffusion, chemistry, wet and dry deposition, and it has been used to simulate species of SO<sub>2</sub>, sulfate, NO<sub>x</sub>, NO<sub>y</sub> and O<sub>3</sub>. MICS-Asia has been contributed greatly to the development of this numerical model and the promotion of EANET modeling activities described in the Strategy on EANET Development which was adopted in 8<sup>th</sup> Intergovernmental Meeting. In this project, model validation and Source-Receptor analysis in Northeast Asia in March, July and December 2001 were conducted using RAQM as a supplementary study of MICS-Asia Phase 2.

#### **3.2. Objectives**

The project was carried out with the following final objectives:

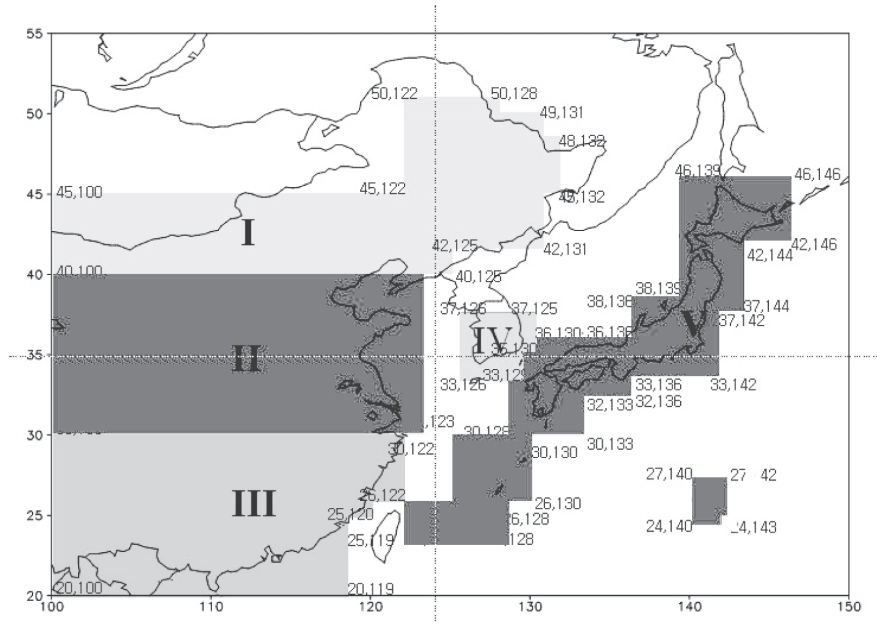
- To validate the Regional Air Quality Model (RAQM) developed by ADORC using EANET data (SO<sub>2</sub>, NO<sub>x</sub>/NO<sub>x</sub>\* and O<sub>3</sub>)
- To determine the relationship between air concentrations and emissions
- To determine the source-receptor relation for sulfur
- To contribute to the MICS-Asia studies

#### **3.3. Results**

Model validation and Source-Receptor analysis in Northeast Asia in March, July and December 2001 were conducted using Regional Air Quality Model (RAQM). Figure 1 shows a domain for this simulation works, and this domain is used also in the Long-range Transboundary Air Pollutants in Northeast Asia (LTP) project participated by 3 countries in Northeast Asia, namely, Japan, Korea and China.

In RAQM, 12 layers stretch vertically from surface to about 10km (50, 150, 300, 500, 750, 1500, 2500, 3500, 4500, 6000, 7500, 8950m) with a horizontal resolution of 0.5 degree. Initial and boundary conditions were taken as the lower end of available observations from recent studies for East Asia (Carmichael et al., 1998; Luo et al., 2000). Side boundary conditions are held fixed during simulation, whereas top boundary condition for O<sub>3</sub> is taken as a constant level with seasonal variation. Emission inventories of SO<sub>2</sub>, NO<sub>x</sub>, CO, NH<sub>3</sub>, and VOCs are derived from MICS-Asia Phase 2 emission data. MM5

v3.7 is used to prepare meteorological inputs. NCEP FNL reanalysis data with 1.0 degree resolution were used to provide initial and boundary conditions for meteorological fields.



**Figure 1 Study domain for simulation works and Source-Receptor relationship analysis.**

Table 1 shows the statistics for comparison of hourly SO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> monitoring results at Rishiri and Sado stations in March, July and December 2001. Predicted concentrations generally showed a reasonable agreement with hourly monitoring data at both of Rishiri and Sado in every period, and it seems that RAQM has a good skill in simulating level and trend of each concentration.

Table 2-4 present dry, wet and total depositions of sulfur in respective regions for the 3 periods. Total deposition amount of sulfur is highest in July over every region except for region V. Table 5-7 show the source-receptor relationship for total sulfur deposition, which is defined as contribution rate to  $j^{\text{th}}$  receptor by  $i^{\text{th}}$  source according to the “reverse method”. The reverse method evaluates the contribution from  $i^{\text{th}}$  domain by a difference between a simulation result with all emissions and a simulation result with all emission except for  $i^{\text{th}}$  domain. “Others” in tables includes the contribution from boundary/initial conditions. Although region V includes large ocean area, contributions to the total deposition amount from outside are 48%, 22% and 64% for March, July and December, respectively. The outside contribution to region V considerably decreases in summer season because of the prevailing winds from Pacific Ocean which is caused by the existence of high atmospheric pressure around region V in summer season.

**Table 1 Statistics for comparison of hourly monitoring results in the 3 periods**

|     |      | Rishiri         |                                    |                | Sado            |                                    |                |
|-----|------|-----------------|------------------------------------|----------------|-----------------|------------------------------------|----------------|
|     |      | SO <sub>2</sub> | NO <sub>x</sub> /NO <sub>x</sub> * | O <sub>3</sub> | SO <sub>2</sub> | NO <sub>x</sub> /NO <sub>x</sub> * | O <sub>3</sub> |
| Mar | n    | 247             | 247                                | 247            | 702             | 702                                | 700            |
|     | r    | 0.54            | 0.68                               | 0.10           | 0.34            | 0.50                               | 0.01           |
|     | MBE  | 0.07            | 0.61                               | 5.35           | 0.12            | 0.39                               | 6.74           |
|     | RMSE | 0.26            | 0.80                               | 7.94           | 2.07            | 1.92                               | 14.86          |
| Jul | n    | 708             | 708                                | 708            | 700             | 703                                | 670            |
|     | r    | 0.30            | 0.03                               | 0.33           | 0.47            | 0.36                               | 0.58           |
|     | MBE  | -0.01           | 0.85                               | 0.84           | 0.79            | 0.00                               | 6.20           |
|     | RMSE | 0.20            | 1.42                               | 10.57          | 3.64            | 1.60                               | 13.13          |
| Dec | n    | 708             | 708                                | 708            | 699             | 699                                | 697            |
|     | r    | 0.02            | 0.23                               | 0.25           | 0.09            | 0.40                               | 0.08           |
|     | MBE  | 0.23            | 0.85                               | 0.62           | 0.22            | 1.25                               | -8.26          |
|     | RMSE | 0.43            | 1.08                               | 3.50           | 0.47            | 1.70                               | 9.40           |

**Table 2 Deposition amount of sulfur at each region for March 2001 (unit: kton)**

| Region | I    | II    | III   | IV   | V     |
|--------|------|-------|-------|------|-------|
| Dry    | 28.8 | 241.0 | 213.9 | 18.8 | 104.9 |
| Wet    | 35.2 | 49.6  | 376.6 | 6.5  | 270.0 |
| Total  | 64.0 | 290.6 | 590.5 | 25.3 | 374.9 |

**Table 3 Deposition amount of sulfur at each region for July 2001 (unit: kton)**

| Region | I     | II    | III   | IV   | V     |
|--------|-------|-------|-------|------|-------|
| Dry    | 42.3  | 231.3 | 135.8 | 14.4 | 61.0  |
| Wet    | 117.9 | 538.8 | 614.3 | 28.4 | 207.7 |
| Total  | 160.2 | 770.1 | 750.0 | 42.8 | 268.7 |

**Table 4 Deposition amount of sulfur at each region for December 2002 (unit: kton)**

| Region | I    | II    | III   | IV   | V     |
|--------|------|-------|-------|------|-------|
| Dry    | 33.2 | 342.9 | 269.4 | 21.9 | 66.8  |
| Wet    | 24.4 | 283.2 | 346.0 | 18.0 | 186.2 |
| Total  | 57.6 | 626.0 | 615.4 | 39.9 | 253.0 |

**Table 5 Contribution of source to receptor for sulfur deposition in March 2001**

| S \ R  | I   | II  | III | IV  | V   |
|--------|-----|-----|-----|-----|-----|
| I      | 57% | 1%  | 0%  | 5%  | 2%  |
| II     | 18% | 87% | 11% | 22% | 16% |
| III    | 0%  | 6%  | 75% | 3%  | 11% |
| IV     | 1%  | 0%  | 0%  | 56% | 2%  |
| V      | 1%  | 0%  | 0%  | 2%  | 52% |
| Others | 24% | 6%  | 14% | 13% | 17% |

**Table 6 Contribution of source to receptor for sulfur deposition in July 2001**

| S \ R  | I   | II  | III | IV  | V   |
|--------|-----|-----|-----|-----|-----|
| I      | 32% | 1%  | 0%  | 1%  | 1%  |
| II     | 50% | 76% | 5%  | 16% | 6%  |
| III    | 1%  | 18% | 82% | 8%  | 2%  |
| IV     | 2%  | 0%  | 0%  | 62% | 3%  |
| V      | 0%  | 0%  | 0%  | 6%  | 78% |
| Others | 14% | 5%  | 13% | 8%  | 9%  |

**Table 7 Contribution of source to receptor for sulfur deposition in December 2001**

| S \ R  | I   | II  | III | IV  | V   |
|--------|-----|-----|-----|-----|-----|
| I      | 51% | 2%  | 0%  | 5%  | 4%  |
| II     | 23% | 83% | 18% | 23% | 21% |
| III    | 0%  | 7%  | 72% | 2%  | 8%  |
| IV     | 0%  | 0%  | 0%  | 48% | 3%  |
| V      | 0%  | 0%  | 0%  | 2%  | 36% |
| Others | 26% | 8%  | 10% | 20% | 28% |

***Scientific and Technological Research Papers  
from Participating Countries***

# Concentration and Isotopic Ratio of Lead in Wet Depositions in Several Regions of East Asian Russia

Natalia A. Onischuk<sup>1)\*</sup>, Tamara V. Khodzher<sup>1)</sup>, Eugeny P. Chebykin<sup>1)</sup>, Hiroaki  
Yagoh<sup>2)</sup>, Tsuyoshi Ohizumi<sup>3)</sup> and Sergey A. Gromov<sup>4)</sup>

*1) Limnological Institute SB RAS,*

*\*Contact address: Ulan-batorskaya st. 3, Irkutsk, Russia (email: onischuk@lin.irk.ru)*

*2) Acid Deposition and Oxidant Research Center (ADORC)*

*1182 Sowa, Nishi-ku, Niigata-shi, 950-2144, Japan*

*3) Niigata Prefectural Institute of Public Health and Environmental Sciences*

*Sowa 314-1, Nishi-ku, Niigata, 950-2144, Japan*

*4) Institute of Global Climate and Ecology Roshydromet and RAS,*

*Glebovskaya st. 20-B, Moscow, 107258 Russia*

## 1. Introduction

The lead is considered by environmentalists and health protection authorities to be a cumulative poisoning substance same as mercury. Its organic compounds are more toxic than oxides and elemental form. Main causes of atmospheric lead pollution are fuel burning (consumption of oil and gasoline provided up to 50% of lead anthropogenic emission (Bashkin & Kasimov, 2004), nonferrous and ferrous metal production, treatment of complex ores and other industrial activities. The intensity of anthropogenic lead emission to the atmosphere was of the highest level on the late 1970s, when it significantly exceeded natural emission. After the implementation of mitigation measures to use lead contained gasoline the total lead emission was reduced by 2-3 times. However, until now auto transport is the major source of atmospheric lead emission in developing countries, where restriction of ethylated gasoline utilization was not applied or not performed (Bashkin & Kasimov, 2004).

Last years many developed countries totally refused from utilization of lead compounds in gasoline production. The restriction of lead utilization had been significantly done in Germany since 2000, in the Netherlands since 2002, whereas such European countries as Denmark, Austria, and Switzerland completely prohibited the use of lead for the relevant industrial processes. According to some decisions this will become a rule for all countries of European Union since 2015. The technologies aimed to find an alternative way to using lead in industry are also developed in USA and Russia. Under the laws in Russia, it had been prohibited to produce and utilize ethylated lead gasoline since July 1, 2003. However, the evaluation of the atmospheric heavy metal balances for Russia demonstrated that the lead air concentration in the background territories has increased during recent years from 1-3 ng/m<sup>3</sup> up to 9 ng/m<sup>3</sup> (Ginzburg, 2005).

The lead in the environment is composed by a mixture of four isotopes <sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb, <sup>208</sup>Pb. Among them, <sup>204</sup>Pb is not related to radioactive decay only, whereas the other isotopes are formed due to radioactive decay of uranium and thorium. There are substantial variations in the lead isotopes in natural media (rocks, soils, frozen solids, etc) caused by interference of several reasons such as rather high geochemical mobility of U and Pb (mainly, uranium); by formation of a range of intermediate products during decay of U and Th; by different values of half-life period of parent elements (Anonymous author, 1988).

The lead isotopic ratios in solid rocks and minerals have been investigated since 1960s and correspondent

results have been presented in extensive literature on this topic (Shevchenko, 2006; Vladykin *et al.*, 2002). During recent decades, the investigation of lead isotopic ratios in aerosols and atmospheric depositions became of great interest for scientists due to increased emissions of lead-containing substances to the atmosphere and also because they are tracers of long-range transportation of anthropogenic pollutants in the environment.

Using the approach based on the lead isotopic ratio, Hopper and coauthors (Hopper, 1991) made a conclusion on air quality deterioration in Sweden caused by transport of polluted air masses from Russia. The major sources of lead and its isotopes in Russia were explored by Mukai and coauthors (Mukai, *et al.*, 2001) with an aim to examine a long-range transport of these compounds towards East Asian countries.

There were no detailed studies in Russia on lead isotopic ratios in air in spite of the evidences that lead polluted air masses from the regions may affect the air quality of the other territories both inside Russia and abroad (Mukai, *et al.*, 2001; Shevchenko, 2006). The new results of examination of lead isotopes in soluble fraction of the depositions and in aerosols are presented in this paper for the Baikal region and the area in Far East territory with different physical and geographical features. Potential sources of these components and possible effects of their transportation in the atmosphere are also discussed.

## 2. Area of studies

Measurements of lead concentration and its isotopic ratio were performed for the samples collected in four atmospheric deposition monitoring sites which are operating in the frame of EANET Program. Irkutsk (52.3° N, 104.4° E) is located within a large industrial center of South Eastern Siberia with population of around 600 thousand. Listvyanka (51.9° N, 104.7° E) is on rural place located 70 km far from Irkutsk city to east at the shore of southern Baikal Lake. Listvyanka village has 5 thousand inhabitants and recently become a tourism center on Lake Baikal. Mondy (52.0° N, 103° E) is the background (remote) one located on the mountain area Chasovye Sopki (a plateau between the Eastern Sayan and the Khamar-Daban Ridges) at the altitude of 2005 m above sea level. Primorskaya (43.4° N, 132° E) is rural site located 150 km north-west from the city of Vladivostok.

## 3. Materials and methods

During the period from November 2005 to January 2007, 80 samples of the atmospheric depositions (rain and snow) and 20 samples of snow cover were collected and analyzed for the lead concentration and its isotopic ratio. The wet only sampler was equipped for collecting rain samples and plastic containers were utilized to collect snow-falls.

Snow cover sample was taken through whole snow column excluding its lowest part in order to avoid influence of soil. Snow cover in Irkutsk city was sampled multitudinously at the monitoring site and its surrounding area with different anthropogenic impact or deposition loading.

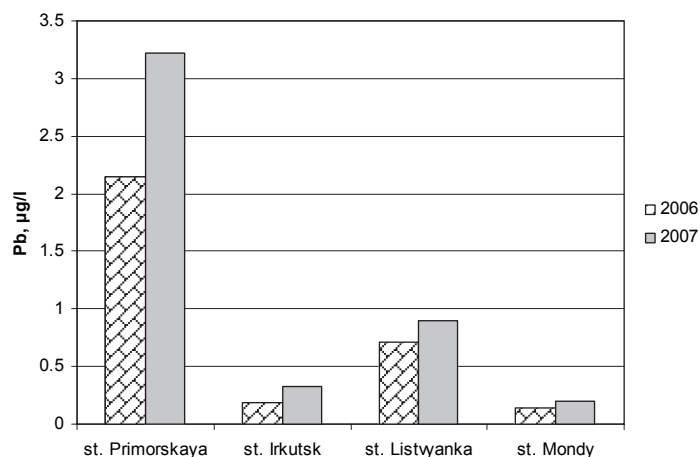
The rain and snow water was filtered through the membrane filter paper with 0.45 µm pore size and preserved by 1% nitric acid (extra pure grade). Lead concentrations were determined by using quadrupole mass spectrometer, Agilent 7500 ce. High sensitivity of this instrument allowed examining samples without preliminary solution concentrating.

Lead isotopes with 204, 206, 207, and 208 masses were determined by ICP-MS realizing the *Isotope analysis* method. The NBS SRM 981 reference solution was used as external isotopic standard for the determination for the concentration range from 0.2 to 10 µg Pb/L. The integrating time was selected for 5 minutes, point number on mass was 20, and scans number (repeating) was 1000 per measurement. Taking the instrument's background and the isobaric interferences of  $^{204}\text{Hg}$ – $^{204}\text{Pb}$  into account, the intensity signals of 202 and 220 masses were measured. The errors didn't exceed 10% in the analysis of lead concentration and were 1% or less for determination of lead isotopic ratios.



#### 4. Results

Dynamics of the lead concentrations in the atmosphere during the period of experimental observations is presented on Figure-1. At Primorskaya site, the lead concentration in the atmospheric depositions varied widely within the range from 0.2  $\mu\text{g/L}$  to 12.5  $\mu\text{g/L}$ , with the average of 3.22  $\mu\text{g/L}$  in 2007. Substantial range of lead concentrations at this area is caused by considerable difference of synoptic processes provided precipitation events (see discussion below). In the Baikal region, there were no significant variations in spatial distribution of lead concentrations in 2007 with the averages of 0.22, 0.33, and 0.9  $\mu\text{g/L}$  for Mondy, Irkutsk, and Listvyanka, respectively.



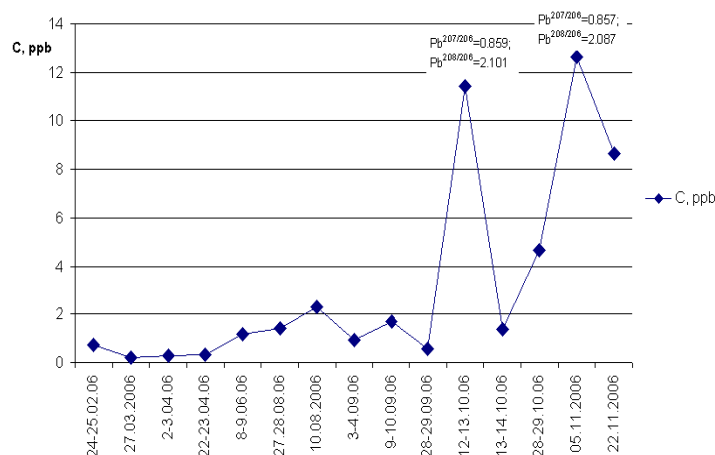
**Figure 1 Inter-annual dynamics of mean lead concentrations in the atmospheric depositions at Russian EANET monitoring sites,  $\mu\text{g/L}$ .**

It is important to mention that mean lead concentration at Listvyanka (for the entire observation period) is higher than that in Irkutsk. The low level of lead concentration in the atmospheric depositions in Irkutsk was probably related to the lead sorption on alkali ashes which are emitted from coal power plants.

The lead concentrations in snow cover were observed rarely over other territories of Russia and demonstrated a considerable diversity with the values from 0.010.20  $\mu\text{g/L}$  in the background Arctic regions to 8.4-81.7  $\mu\text{g/L}$  in Norilsk city (Shevchenko, 2006). According to the results of measurements, lead concentration in the atmospheric depositions at Mondy site is close to the value of background regions, e.g. the Arctic region of Russia (Fig.1).

Seasonal variation of lead concentration and its isotopes in the atmospheric deposition was traced in details at Primorskaya site (Fig.2, Table 1). Due to increasing amount of burning fuel in cold season, the lead concentrations in the atmosphere might be higher in winter whereas the isotopic ratios might be lower than those in warm season. This is supported by the report that coal has high isotopic ratio (on average),  $^{207}\text{Pb}/^{206}\text{Pb}=0.859-0.857$  and  $^{208}\text{Pb}/^{206}\text{Pb}=2.101-2.087$  (Anonymous author, 1988). Actually during the experimental period the lead concentrations in the atmospheric depositions at Primorskaya site in cold season exceeded those in warm one. However, the lead isotopic ratio was not changed significantly and decreasing isotopic ratios were not observed in cold season. On the contrast, the highest ratios ( $^{207}\text{Pb}/^{206}\text{Pb}=0.887$  and  $^{208}\text{Pb}/^{206}\text{Pb}=2.136$ ) were registered in single sample (13-14.10.2006) which had relatively low lead concentration. Such isotopic ratios scattering may be caused by influence of other sources, in particular, by transboundary transport of air pollutants from the industrial centers of China. Mukai and coauthors (Mukai *et al.*, 2001) didn't reveal both seasonal variation of the lead isotope and relevant correlation with winter usage of fossil fuel in East Asian cities as well.

As a result of substantial isolation in the territories surrounded Southern Lake Baikal from other parts of Irkutsk district, there are some specific peculiarities of climatic conditions on lake shores including Listvyanka place compared to other land areas which have effect on precipitation chemistry. The lead isotopic ratios observed in atmospheric deposition at Listvyanka are within relatively narrow range:  $^{206}\text{Pb}/^{204}\text{Pb}=17.81-17.93$ ;  $^{207}\text{Pb}/^{206}\text{Pb}=0.862-0.878$ ;  $^{208}\text{Pb}/^{206}\text{Pb}=2.089-2.122$ .



**Figure 2 Seasonal variation of lead concentration in the atmospheric deposition at Primorskaya EANET monitoring sites with the lead isotopic ratios of high concentration samples.**

**Table 1 The concentration of lead (ppb) and its isotopic ratio in the atmospheric depositions (rain, snow fall, snow cover) at Russian EANET monitoring sites during 2006-2007.**

| №  | Site       | Date of sampling | Type of sample | Pb conc., ppb | lead Isotopic ratio |         |         |
|----|------------|------------------|----------------|---------------|---------------------|---------|---------|
|    |            |                  |                |               | 206/204             | 207/206 | 208/206 |
| 1  | Mondy      | 22/05/2006       | Snow           | 0.39          | 17.61               | 0.882   | 2.148   |
| 2  | Mondy      | 23/05/2006       | Snow           | 0.23          | 17.44               | 0.878   | 2.118   |
| 3  | Mondy      | 23/11/2006       | Snow           | 0.30          | 18.01               | 0.876   | 2.118   |
| 4  | Mondy      | 1-2/01/-2007     | Snow           | 0.11          | 18.30               | 0.879   | 2.118   |
| 5  | Mondy      | 20/01/2007       | Snow cover     | 0.11          | 18.00               | 0.871   | 2.086   |
| 6  | Mondy      | 20/01/2007       | Snow cover     | 0.11          | 18.39               | 0.882   | 2.133   |
| 7  | Mondy      | 20/01/2007       | Snow cover     | 0.14          | 17.86               | 0.882   | 2.101   |
| 8  | Lystvyanka | 21/12/2006       | Snow           | 0.46          | 17.93               | 0.869   | 2.107   |
| 9  | Lystvyanka | 13-15/02/2006    | Snow           | 0.80          | 17.84               | 0.871   | 2.115   |
| 10 | Lystvyanka | 5-6/03/2006      | Snow           | 1.77          | 17.88               | 0.868   | 2.108   |
| 11 | Lystvyanka | 23-24/03/2006    | Snow           | 0.64          | 17.90               | 0.867   | 2.106   |
| 12 | Lystvyanka | 26-28/10/2006    | Snow           | 0.27          | 17.78               | 0.878   | 2.118   |
| 13 | Lystvyanka | 11-13/11/2006    | Snow           | 1.54          | 17.85               | 0.870   | 2.113   |
| 14 | Lystvyanka | 10/01/2007       | Snow           | 0.84          | 17.81               | 0.876   | 2.122   |
| 15 | Irkutsk    | 2-3/12/2006      | Snow           | 0.28          | 17.85               | 0.877   | 2.112   |
| 16 | Irkutsk    | 2-3/01/2007      | Snow           | 0.24          | 17.74               | 0.876   | 2.113   |
| 17 | Irkutsk    | 15/01/2007       | Snow cover     | 0.11          | 17.53               | 0.865   | 2.103   |
| 18 | Irkutsk    | 15/01/2007       | Snow cover     | 0.25          | 17.62               | 0.872   | 2.110   |
| 19 | Irkutsk    | 15/01/2007       | Snow cover     | 0.15          | 17.69               | 0.869   | 2.103   |

|    |             |               |            |       |       |       |       |
|----|-------------|---------------|------------|-------|-------|-------|-------|
| 20 | Irkutsk     | 15/01/2007    | Snow cover | 0.41  | 17.99 | 0.869 | 2.115 |
| 21 | Irkutsk     | 15/01/2007    | Snow cover | 0.31  | 18.03 | 0.862 | 2.096 |
| 22 | Irkutsk     | 15/01/2007    | Snow cover | 1.17  | 17.93 | 0.864 | 2.107 |
| 23 | Irkutsk     | 15/01/2007    | Snow cover | 0.49  | 18.15 | 0.866 | 2.102 |
| 24 | Irkutsk     | 15/01/2007    | Snow cover | 0.05  | 17.66 | 0.870 | 2.099 |
| 25 | Irkutsk     | 15/01/2007    | Snow cover | 0.17  | 17.59 | 0.872 | 2.116 |
| 26 | Primorskaya | 24-25/02/2006 | Snow       | 0.71  | 17.83 | 0.871 | 2.105 |
| 27 | Primorskaya | 27/03/2006    | Snow       | 0.18  | 17.75 | 0.873 | 2.099 |
| 28 | Primorskaya | 2-3/04/2006   | Rain       | 0.27  | 18.17 | 0.870 | 2.118 |
| 29 | Primorskaya | 22-23/04/2006 | Rain       | 0.31  | 18.20 | 0.867 | 2.107 |
| 30 | Primorskaya | 8-9/06/2006   | Rain       | 1.18  | 17.78 | 0.874 | 2.118 |
| 31 | Primorskaya | 27-28/08/2006 | Rain       | 1.42  | 17.75 | 0.876 | 2.121 |
| 32 | Primorskaya | 10/08/2006    | Rain       | 2.29  | 17.94 | 0.870 | 2.111 |
| 33 | Primorskaya | 3-4/09/2006   | Rain       | 0.91  | 17.65 | 0.877 | 2.122 |
| 34 | Primorskaya | 9-10/09/2006  | Rain       | 1.70  | 17.79 | 0.874 | 2.118 |
| 35 | Primorskaya | 28-29/09/2006 | Rain       | 0.56  | 17.76 | 0.876 | 2.122 |
| 36 | Primorskaya | 12-13/10/2006 | Rain       | 11.42 | 18.06 | 0.859 | 2.101 |
| 37 | Primorskaya | 13-14/10/2006 | Rain       | 1.38  | 17.44 | 0.887 | 2.136 |
| 38 | Primorskaya | 28-29/10/2006 | Rain       | 4.66  | 17.83 | 0.874 | 2.125 |
| 39 | Primorskaya | 05/11/2006    | Snow       | 12.65 | 18.06 | 0.857 | 2.087 |
| 40 | Primorskaya | 22/11/2006    | Snow       | 8.64  | 17.87 | 0.873 | 2.120 |

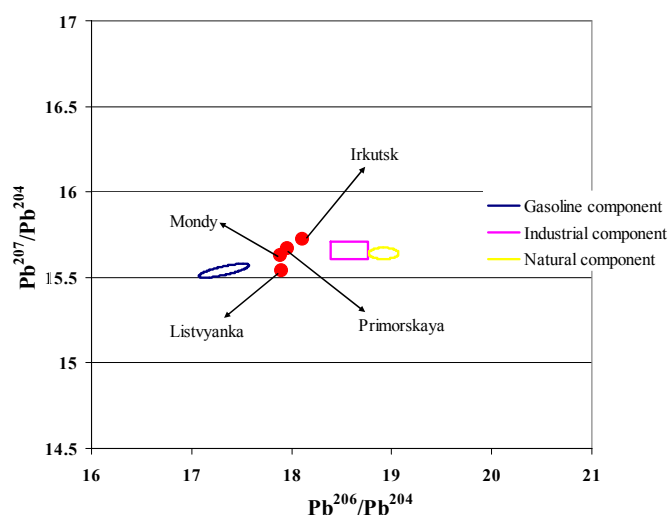
The mean isotopic ratios for the atmospheric deposition at Mondy were  $^{206}\text{Pb}/^{204}\text{Pb}=17.894$ ;  $^{207}\text{Pb}/^{206}\text{Pb}=0.879$ ;  $^{208}\text{Pb}/^{206}\text{Pb}=2.117$  which might be attributed to the continental background levels. However, it should be noted that low lead concentrations in the deposition at Mondy were accompanied with higher measurement errors on the determination of lead isotopic ratios. Such measured isotopic ratios were close to those detected in alkali rocks of the PreHovsgol region in Siberia (Vladykin *et al.*, 2002). According to published data, the lead isotopic ratio of ore deposits in Eastern Sayan mountains varies widely in the ranges:  $^{206}\text{Pb}/^{204}\text{Pb} = 15.38-18.48$ ;  $^{207}\text{Pb}/^{206}\text{Pb} = 0.87-0.90$ ;  $^{208}\text{Pb}/^{206}\text{Pb} = 2.19-2.33$  (Anonymous author, 1988. This doesn't allow recognizing the distinguishing specific features of the lead isotopic ratio to be typical for this region.

The lead isotopic ratios of the deposition at Irkutsk varied in relatively wider ranges (Table 1):  $^{206}\text{Pb}/^{204}\text{Pb} = 17.53-18.15$ ;  $^{207}\text{Pb}/^{206}\text{Pb} = 0.862-0.877$ ;  $^{208}\text{Pb}/^{206}\text{Pb} = 2.096-2.115$  being probably affected by intensive industrial emissions in this region. The aluminum production plant "IrkAZ-SUAL" located 20 km far from Irkutsk is considered to be a large source of industrial lead emissions (Vladykin *et al.*, 2002). The other sources of the lead and its isotopes in the atmosphere are large power plants located both Irkutsk inside and nearby cities in Priangarie (the cities along the Angara river: Angarsk, Usol'e-Sibirskoe, and Shelekhov). Auto transport is also a significant source provided mostly extended lead deposition along the roads. The isotopic ratios in the samples of snow cover collected near intercity roads during the experimental period were:  $^{206}\text{Pb}/^{204}\text{Pb}=17.53-17.69$ ;  $^{207}\text{Pb}/^{206}\text{Pb}=0.869-0.872$ ;  $^{208}\text{Pb}/^{206}\text{Pb}=2.115-2.116$ . However, these values were much higher compared to those for the samples collected in the Irkutsk Park (forested resort area within city).

## 5. Discussion

The visual comparison of mean isotopic ratios  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  determined in Russian EANET monitoring sites are presented on Fig. 3 with the isotopic ratios of possible emission sources (Cocherie *et al.*, 1998). The data observed during this project occupy the intermediate field between typical domains of different

natural and anthropogenic lead sources. Similar values of isotopic ratios dominate in Russian Siberia because they reflect the impact of industrial processing of Kazakhstan lead ores. The lead isotopic ratio in the deposition over Baikal region and Far East is close to that determined for the Kazakhstan lead ore.

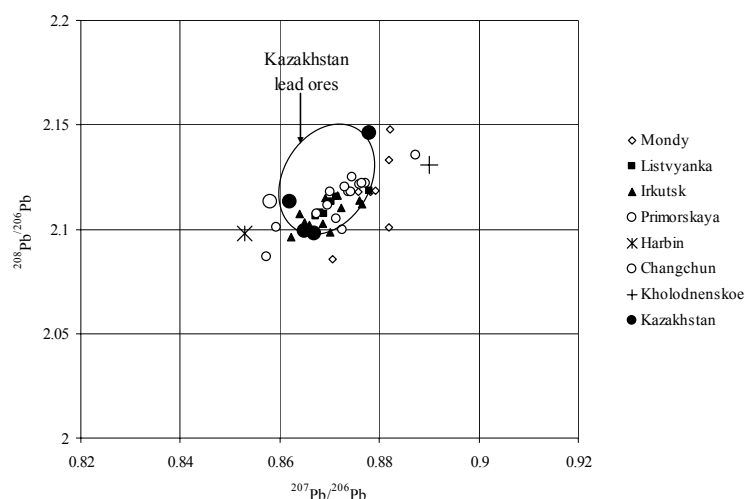


**Figure 3 The mean lead isotopic ratios in the atmospheric depositions at Russian EANET monitoring sites and distinctive ranges for general source types (Cocherie *et al.*, 1998).**

To identify possible sources of lead detected in the atmosphere of Baikal region and the Far East (Primorskaya site) the comparison was explored between the isotopic ratios determined with the typical signatures of some ore deposits in Asia (Fig. 4). Russian industry imports a lot of lead ores from Kazakhstan and Uzbekistan. There are two large ore deposit fields in the east of Baikal region, Buryatia also (Ozernoe and Kholodnenskoe in Eravninskiy and Severobaikalskiy districts, respectively) which are not exploited until now. The ores from Kholodnenskoe field have the isotopic ratios  $^{207}\text{Pb}/^{206}\text{Pb}=0.890$  and  $^{208}\text{Pb}/^{206}\text{Pb}=2.131$  to be slightly higher comparing with typical values of Kazakhstan ores (Karpenko *et al.*, 1981). Kazakhstan ores are characterized by ratios of  $^{207}\text{Pb}/^{206}\text{Pb}=0.87$  and  $^{208}\text{Pb}/^{206}\text{Pb}=2.12$  on the average whereas the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of Russian ores which are mined and treated near Salar and Zmeinogorsk is equal to 0.84 and even lower (Brown, 1962). Figure 4 demonstrated that the most of presented data on isotopic ratios are within the range of typical Kazakhstan ores. This fact indicates that lead from Kazakhstan ore is a major source of the atmospheric lead in Russian region of East Asia.

There are some specific features in the results obtained at Primorskaya site. The high lead concentration (up to  $12.65 \mu\text{g/L}$ ) and low isotopic ratios ( $^{207}\text{Pb}/^{206}\text{Pb}=0.857\text{--}0.859$  and  $^{208}\text{Pb}/^{206}\text{Pb}=2.087\text{--}2.101$ ) were periodically registered in the deposition during late autumn (Table 1). In accordance with published investigation on urban environment in China data the lead isotopic ratios in the atmosphere in Harbin and Changchun cities at the north east of China are also rather low in winter being 0.853 and 0.858 for  $^{207}\text{Pb}/^{206}\text{Pb}$  as well as 2.098 and 2.113 for  $^{208}\text{Pb}/^{206}\text{Pb}$  in those cities, respectively (Mukai *et al.*, 2001). The high average lead concentrations were measured also in air of those cities. The measurements at Primorskaya site proved that the mean lead concentration in the atmospheric aerosol in Russian Far East ( $4.58 \text{ ng/m}^3$ ) is of two times lower than that of Chinese cities mentioned.

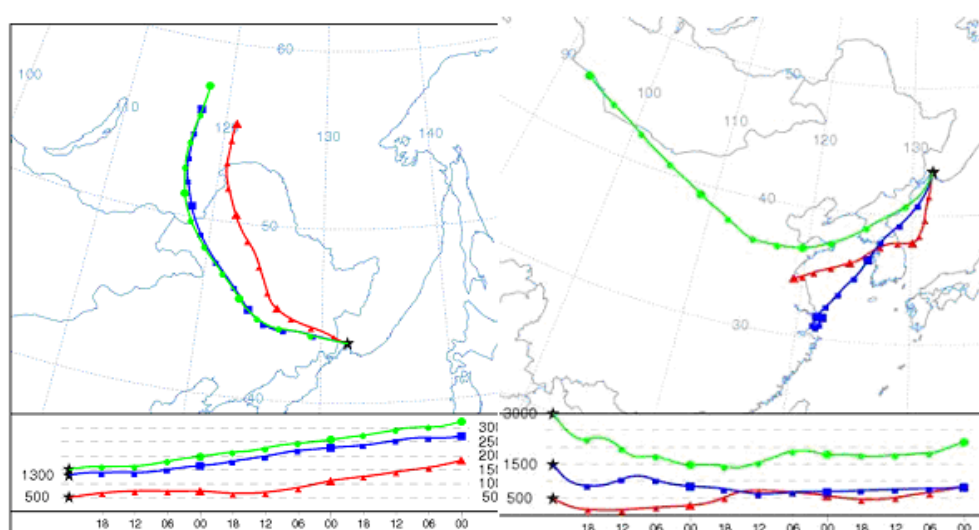
Besides these an effect of long range transport of polluted air masses is periodically recorded at rural Primorskaya site among collected data. The atmospheric precipitation events sampled at Primorskaya site on October 12-13 and October 28-29, 2006 may be exemplified as well as on November 5 and November 22, 2006



**Figure 4 The lead isotopic ratios in the atmospheric depositions at the Russian EANET monitoring sites and some cities (Mukai *et al.*, 2001) in comparison with those for ores from different Asian regions.**

(Table 1). The analysis of these samples detected the increased lead concentrations and their isotopic ratios had the similar values to be also close to those in air of Chinese cities (Mukai *et al.*, 2001). This is a point to assume the evidence of influence by possible same sources on precipitation chemistry in those cases.

To confirm this potential effect the backward trajectories of air masses were re-constructed for these cases of the precipitation events using the HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) (Draxler & Hess, 1997). Evaluation of air masses back trajectories on October 12, 2006 and November 5, 2006 (Fig. 5) disclosed that the atmospheric wet depositions were caused during pass of the frontal zone in the cyclone with air passed and transformed above China and South Korea. Thus, the deposition collected at Primorskaya site was affected by pollution transport with air masses coming from the territories of China, and such occurrence might be come into existence periodically with similar synoptic processes.



**Figure 5 Backward trajectories of air masses transport to Primorskaya site for October 12, 2006 (on the left) and November, 5, 2006 (on the right).**

## 6. Conclusion

The original data on the lead isotopic ratios in the atmospheric deposition and snow cover were obtained during the period of 2006-2007 at both the urban and the remote areas of the Baikal region and Russian Far East territory. Scientific evaluation was demonstrated that these ratios may serve as tracers for long range transportation of air pollutants including their soluble fraction in precipitation. There were small differences among the mean lead isotopic ratios in all the regions of measurements, and their levels are close to typical lead isotopic ratio of the Kazakhstan ores. The processing of Kazakhstan lead ores using widely and everywhere by industries over former Soviet Union territory was suggested to serve exactly as a major source type of the atmospheric lead in Eastern Siberia. However, any specific sources of lead air pollution and their location were not revealed in the Baikal region. According to comparative and meteorological analysis of data at Primorskaya site, the composition of precipitation during the cold season is affected by transport of atmospheric pollution from China. This is proved by specific signature of certain samples with the increased lead concentrations and the isotopic ratio to be similar to that for aerosols in some cities in north-east China.

## Acknowledgements

This study was funded by the Russian Science Support Foundation and MOEJ (Japan).

## References

- Anonymous author. 1988. The lead isotopes and questions of ore genesis. Nedra, Leningrad, 243 pp. (in Russian).
- Bashkin, V. N. & Kasimov, N. S. 2004. Biogeochemistry. M.: Nauchnyi mir, 648 pp. (in Russian).
- Belozertseva, I. A., 1999. Man-caused influence on snow cover in Upper Priangarie. In *Geografiya i prirodnye resursy*, N 2, pp.46-51 (in Russian).
- Brown, J. S. 1962. Ore lead and isotopes. *Economic Geology* 57: 673-720.
- Cocherie, A., Negrel, P. H., Roy, S. & Guerrot C. 1998. Direct determination of lead isotope ratios in rain water using inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 13: 1069-1073
- Draxler, R. R. & Hess G. D. 1997. Description of the Hysplit\_4 modeling system. In NOAA Tech Memo ERL ARL-224. National Oceanic and Atmospheric Administration, U. S. A., 24 pp.
- Ginzburg V. A. 2005. The formation of the components of lead balance in the atmosphere above territory of Russia. Ph D Thesis abstract. Moscow, Russia, 27 pp. (in Russian).
- Hopper J. F., Ross H. B., Sturges W. T. & Barrie L. A. 1991. Regional source discrimination of atmospheric aerosols in Europe using the isotopic composition of lead. *Tellus B*, 43, 45-60.
- Karpenko S., Delevaux M N. & Doe B.R. 1981. Lead isotope analyses of Calanas from selected ore deposits of the U.S.S.R. *Economic Geology*, 76: 716-742.
- Mukai H., Machida T., Tanaka A., Vera Y. P. & Uematsu M. 2001. Lead isotope ratios in the urban air of eastern and central Russia. *Atmospheric Environment*, 35: 2783-2793.
- Mukai H., Tanaka A., *et al.* 2001. Regional Characteristics of Sulfur and Lead Isotope Ratios in the Atmosphere at Several Chinese Urban Sites. *Environmental Science & Technology*, 35: 1064-1071.
- Shevchenko V. P. 2006. Aerosols influence on the environment and marine sedimentation in Arctics. Lisitsyn, A.P. & Nauka, M. (eds.), 226 pp. (in Russian).
- Vladykin, N. V., Isakov, Y. A., Sandimirova, G. P., Vladimirova T. A. & Tatarnikov S. A. 2002. Lead isotope composition of alkali rocks in Siberia and Mongolia. In *Geochemistry of magmatic rocks, Materials of annual session*. Moscow, (in Russian).

# **Russian Governmental Monitoring Networks Related to Acid Deposition and Results of their Activities over East Asian Territory**

Sergey A. Gromov\*, Veronika A. Ginzburg and Sergey G. Paramonov

*Institute of Global Climate and Ecology (IGCE) Roshydromet and the Russian Academy of Science (RAS)*

*\*Contact address: Glebovskaya street 20-B, Moscow, 107258 Russian Federation  
[e-mail: Sergey.Gromov @igce.ru]*

## **1. Introduction**

The monitoring activities on environmental pollution and its impact on natural ecosystem had started in the territory of the former Soviet Union (USSR) from 1960s when the first measurements on chemical composition of precipitation were organized by Russian scientists. Their results provided a basis to create an extensive governmental network on precipitation chemistry in close cooperation with other countries and international organizations (WMO, OECD, etc) as well as to make the first scientific assessments on the nature and state of chemical composition of rain water and snow (Drozdova *et al.*, 1964).

There are other several networks created during 1970s-1980s in the territory of the former Soviet Union whose programs include the measurements of pollution in atmospheric air and precipitation in regions far from considerable emission sources. One of them was exclusively designated to monitoring and evaluation of transboundary atmospheric transport of acidified compounds (Izrael *et al.*, 1987) developed under pan-European cooperation and with support of UN Economic Commission for Europe. Another network was aimed to trace and evaluate the sensitivity and long-term changes of natural environment (or so-called “background state”) under the anthropogenic impact of global and inter-regional scales (Izrael and Rovinsky, 1990) with common efforts of several countries and under the umbrella of UNEP-GEMS. Unfortunately, the capacities of these networks decreased during 1990s due to both destruction of established international cooperation and general economic depression in participating countries.

As one of the new efforts to improve environmental monitoring, Russian Federation has been participating in EANET since the start of Network activities of the preparatory phase in 1998. The national experts from governmental authorities and research institutes being responsible for environmental monitoring took part in expert meetings and workshops on establishing the Network. They also contributed to the preparation of technical documents and guidelines for monitoring operation and laboratory analysis.

There are a large number of monitoring stations of several national networks operated under the management of the Russian Federal Service for Hydrometeorology and Environmental Monitoring (Roshydromet), and IGCE being the coordinating centre for monitoring activities provides them various scientific and methodological supports together with some other institutes. Their programs include the sampling and measurement of atmospheric concentrations and deposition of airborne pollutants with including acidified compounds among others.



Periodical reporting on environmental quality and assessments is provided by governmental authorities with help and contribution of research institutes as well as by some regional offices. However, the screening and integrating of monitoring data from different networks is one of the important problems in the field of environmental evaluation. This is caused by the difference of initial goals and tasks of networks, certain diversity of equipment and methodologies applied, variety of priorities for measured pollutants and target environmental objects as well as of output results.

A group of scientists in IGCE have raised the problems of data comparability and integration among national networks based on their experience on preparation of annual environmental Reports (Review, 2007; Review, 2008). The special two-year project was initiated to explore the possibilities for network data aggregation and common use in provision of environmental information and evaluation for public and relevant authorities. The review of all national monitoring activities related to regional acid deposition over the whole Asian part of Russia is presented below together with the first attempt on deeper scientific overview of respective national monitoring results on precipitation chemistry and acid depositions for these regions.

## **2. General information on national monitoring activities related to acid deposition**

### **2.1. Outline of the national monitoring systems**

The Russian Federal Service for Hydrometeorology and Environmental Monitoring (Roshydromet) is a governmental agency under the Ministry of Natural Resources and Ecology to be responsible for monitoring of environmental pollution in Russia. There are different key monitoring activities performed including measuring precipitation chemistry and evaluating acid depositions and their effects, contamination of the atmosphere and other related environmental media by toxic pollutants and anthropogenic persistent compounds as well as climate changes and its factors.

There are several governmental monitoring networks in Russia related to acid deposition problems that were developed as relatively independent environmental quality control systems:

- Urban air quality control;
- Precipitation chemistry monitoring network over urban and rural territories;
- Russian EMEP monitoring network;
- Russian EANET monitoring sites,
- Monitoring of chemical pollution of snow cover;
- Monitoring network of surface water quality near the cities and far from towns;
- Integrated background monitoring network.

Most of these networks were designed to cover the whole territory of Russia, while EMEP sites were established along the western border of Russia (or of the former Soviet Union, for example, in Byelorussia, Ukraine or Baltic countries) and EANET sites are located only in eastern Asian part of the country. All of the mentioned networks conduct measurements under monitoring programs related or immediately concerned to acid deposition problems. However, comparative analysis of their approaches and applied methodologies demonstrated that there are six national subsystems which monitoring activities of the most correspondent to regional atmospheric pollution problems and their experience and capacities could be useful to each other:

***Urban air quality control network*** was developed at the beginning of 1960s for measuring air pollutant concentrations in inhabited areas. For the period after year 2000 there are about 600 measurement sites in 230-260 cities/towns in Russia. Being partly operating subsystem the methodology of short-time (20 minutes)



sampling have been applied for detection of SO<sub>2</sub>, NO<sub>2</sub>, CO, SPM and other specific pollutants in ambient air three or two times per day.

***Precipitation chemistry monitoring network*** was established as the subsystem of urban and rural sites since the end of 1960s. Nowadays, the Russian national monitoring system on acidity and chemical composition of atmospheric precipitations consists of about 130 sites. All major ions, conductivity and pH are determined in fall-out atmospheric water after collection of samples in bulk samplers during a week or month. Some of these stations were selected to be included into WMO-GAW precipitation network with the goal to trace background state of precipitation chemistry

***EMEP monitoring*** network are operated along the north-western boundary of Russia from 1980s according to the same principles and analytical procedures as for most of European Evaluation and Monitoring Programme (EMEP) countries. The sulfur and nitrogen atmospheric compounds are measured in air and precipitation on the daily basis as well as ozone (continuously). The ion chromatography and AAS are used for analysis by national operational laboratory in Institute of Global Climate and Ecology (IGCE, Moscow).

***Russian EANET monitoring*** stations were established in the South-Eastern Siberia and Far East region. They provide the measurement data in accordance with unified EANET programs using the Network manuals and technical documents. Roshydromet was designated as the National Focal Point at the regular phase of EANET and had conducting all relevant activities as well as took responsibility on necessary communication and coordination among national contributors. Institute of Global Climate and Ecology (IGCE) of Roshydromet and Russian Academy of Sciences (RAS), Moscow was designated as Russian National EANET Center with support to NFP on network development at national and international levels. Limnological Institute (LIN) of Siberian Branch RAS, Irkutsk operates as National EANET Data Center to organize and conduct monitoring activities and data acquisition in Asian part of Russia. Chemical analysis of samples is carried out by two laboratories within regions mentioned above with the general quality assurance/quality control and data management by LIN.

***Network of snow cover chemical pollution*** was established over the whole Russian territory with seasonal snow cover to evaluate deposition of major ions and specific pollutants with help of analysis of snow samples gathered through whole layer of snow accumulation every year before melting. Up to 1000-1200 sampling sites provide spatial information on integrated dry and wet deposition fluxes during snow season. All major ions and pH are determined by wet chemistry analytical methods in regional laboratories.

***Integrated Background Monitoring Network (IBMoN)*** was established in the former Soviet Union as a specific observation system realizing an integrated approach to the assessment of re-distribution and cycling of environmental pollutants. In accordance with principles of IBMoN design it was considered as a part of UNEP Global Environmental Monitoring System (UNEP/GEMS). The monitoring programs at the sites include measurements of pollutant concentrations in different environmental media such as air, precipitation, surface water, bottom sediments, soil, snow cover, and biota in the areas away from direct anthropogenic influence (far from main urban, industrial centers or highways). The initial design project suggested opening at least 16 stations over the territory of Russia to provide comprehensive information on the state of each type of large-scale bio-geographical ecosystems over Russia under the closer cooperation with a number of biosphere reserves (Izrael, 1989). However, there were 9 stations as a maximum really operated in Russia during the whole period of the network activity and now there are 5 sites only conducting sampling and measurements.

## 2.2. National environmental monitoring program over the Asian territory of Russia for 2001-2005

There are about 70 precipitation chemistry monitoring sites established over the Asian territory of Russia (ATR). The list of the sites within regions eastward from 80°E meridian is presented in Table 1 and their location is presented at the schematic map on Fig.1. The sites established in background areas are highlighted in Bold in Table and green color at the map.

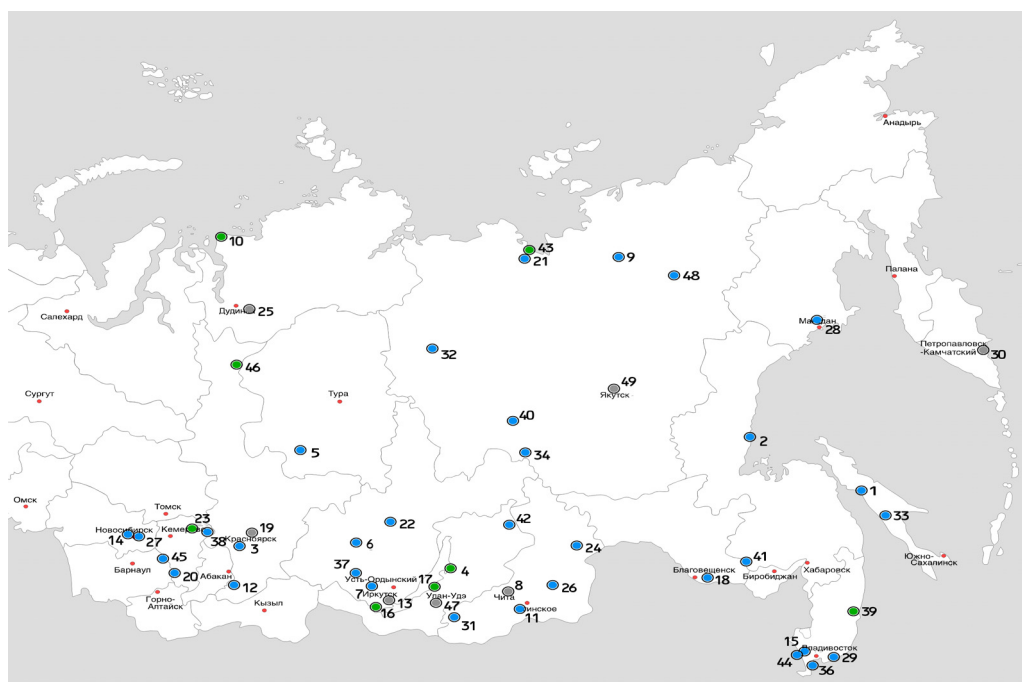
Unfortunately, the IBMoN sites in Barguzin BR (Baikal region) and in Sikhote-Alin BR were closed down due to constraints in technical supply and finance. And nowadays there are no integrated monitoring sites any more which operate at the Asian territory of Russia (ATR) with complete program of measurements.

Snow monitoring network covers Asian territory of Russia also with the sites of different spatial density. However, the stable snow cover extends to southern areas farther than on the European part of Russia, and potentially the more detail information could be obtained there.

**Table 1 Regional and background monitoring sites on precipitation chemistry located on the Asian territory of Russia in 2001-2005**

| <i>Station</i>         | <i>Latitude, deg</i> | <i>Long, deg East</i> | <i>Station</i>             | <i>Latitude, deg</i> | <i>Long, deg East</i> |
|------------------------|----------------------|-----------------------|----------------------------|----------------------|-----------------------|
| Alexandrov             | 50.9                 | 142.2                 | Ogurtcovo                  | 55.1                 | 83                    |
| Ayan                   | 56.5                 | 138.2                 | Palatka                    | 60.1                 | 150.9                 |
| Balakhat               | 55.4                 | 91.7                  | Partizansk                 | 43.2                 | 133                   |
| <b>Barguzinskiy BR</b> | 54.3                 | 109.5                 | <i>Petropavlovsk-Kamch</i> | 52.9                 | 158.6                 |
| Baykit                 | 61.7                 | 96.4                  | Petrovskiy Zavod           | 51.3                 | 108.9                 |
| Bratsk                 | 56.3                 | 101.7                 | Polyarniy                  | 66.7                 | 112.4                 |
| Cheremkhovo            | 53.2                 | 103                   | Poronaysk                  | 49.2                 | 143.1                 |
| <i>Chita</i>           | 52.1                 | 113.5                 | Preobrazhenka              | 60.1                 | 108.1                 |
| Deputatskiy            | 69.3                 | 139.7                 | Romanovka                  | 53.2                 | 112.8                 |
| <b>Dikson</b>          | 73.5                 | 80.4                  | Sad-gorod                  | 43.3                 | 132.1                 |
| Duldurga               | 50.7                 | 113.6                 | Sayansk                    | 54.0                 | 102                   |
| Ermakovskoe            | 53.3                 | 92.4                  | Sharipovo                  | 56.0                 | 89                    |
| <i>Irkutsk</i>         | 52.3                 | 104.3                 | <b>Sikhote-Alinskiy BR</b> | 45.0                 | 136.6                 |
| Iskitim                | 54.7                 | 83.3                  | Suntar                     | 62.2                 | 117.7                 |
| Khalkidon              | 44.3                 | 132.4                 | Sutur                      | 50.1                 | 132.1                 |
| <b>Khamar-Daban</b>    | 51.9                 | 103.6                 | Taksimo                    | 56.4                 | 114.8                 |
| <b>Khuzhir</b>         | 53.2                 | 107.3                 | <b>Tiksi</b>               | 71.6                 | 128.9                 |
| Konstantinovka         | 49.6                 | 128                   | Timiryarevskiy             | 43.9                 | 131.9                 |
| <i>Krasnoyarsk</i>     | 56.0                 | 92.9                  | Togul                      | 53.5                 | 85.9                  |
| Kuzedeevo              | 53.3                 | 87.2                  | <b>Turukhansk</b>          | 65.8                 | 87.9                  |
| Kyusyur                | 70.7                 | 127.4                 | <i>Ulan-Ude</i>            | 51.8                 | 107.6                 |
| Maksimovo              | 57.1                 | 104.9                 | Ust-moma                   | 66.5                 | 143.2                 |
| <b>Mariinsk</b>        | 56.1                 | 87.8                  | <i>Yakutsk</i>             | 62.0                 | 129.7                 |
| Mogocha                | 53.7                 | 119.8                 | <b>Yailu</b>               | 51.8                 | 87.6                  |
| Nerchinsk              | 52.0                 | 116.5                 | <b>Zhigansk</b>            | 66.8                 | 123.4                 |

\* Background sites are shown by **Bold**, urban sites are shown by *Italic*.



**Figure 1** Precipitation chemistry sites in ATR (area: *grey*—urban, *blue*—rural, and *green*—remote).

### 2.3. Principles of data interpretation and publications

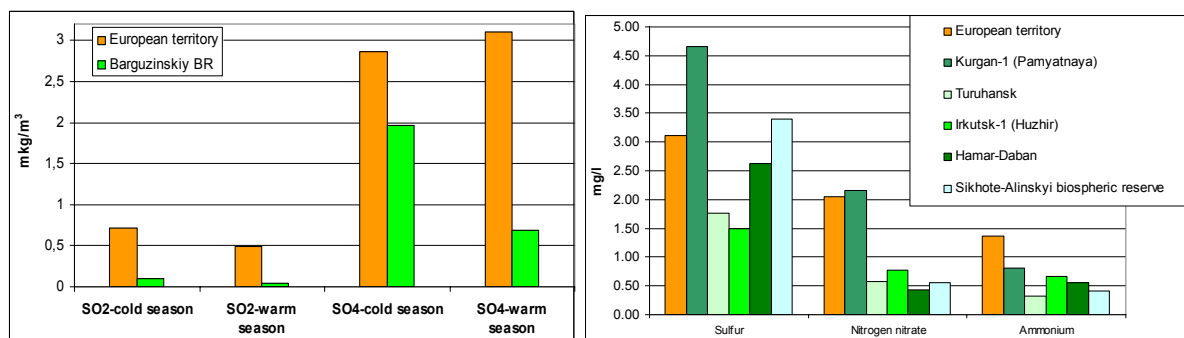
Analysis and generalization of data, their interpretation and evaluation of the state of the environment and its pollution are annually published in a number of governmental and international issues based on these information. Annual national publications are “Review of the environmental pollution in Russian Federation” and “Review of the background state of natural environment on the territory of CIS countries”. Some reports on the state of the environment are also annually prepared and published separately for regions of Russia.

The system of the data availability and their usage by different environment stakeholders is not developed well enough. Currently, copies of each annual review are sent to libraries and all regional centers of Roshydromet based on prepared distribution lists. The numbers of copies are also available free upon the request. The public interest to such publication is quite high and obviously much higher than printing easy available because of very limited number of copies is usually published. Reviews of last years are also prepared to be accessible in the Internet.

## 3. Review of the state of acid deposition over the Asian part of Russia with national monitoring data

### 3.1. The state of the environment before millennium and long term concentration tendency

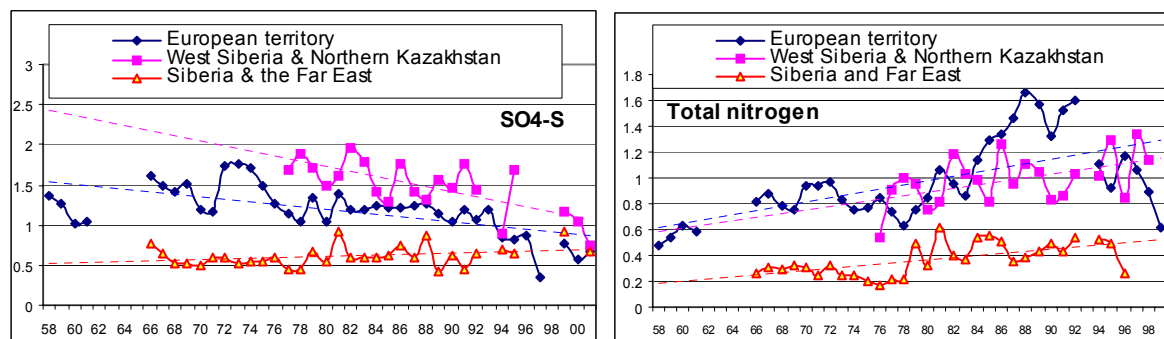
This retrospective analysis is based on almost all data from the background monitoring sites operated over the territory of Russia for the period from the end of 1980s to 2000. Evaluation of a spatial distribution of sulfur and nitrogen compounds both in the air and precipitations proved that their maximums were observed over the western part of Russia with a general decreasing of magnitude toward inner regions eastward (Figure 2). Comparison of measurements in Asian and European part of the country demonstrates that average concentration of sulfur dioxide was less than  $0.1 \mu\text{g}/\text{m}^3$  in background territories of Baikal Lake region while one was 5-6 times higher over the European territory of Russia. Sulfate concentration in air was generally higher than  $\text{SO}_2$  with average values around  $2 \mu\text{g}/\text{m}^3$  during cold seasons and about  $0.7 \mu\text{g}/\text{m}^3$  in warm seasons at the Asian region of Russia.



**Figure 2 Comparison of levels of acidic compounds concentrations in air (left) and precipitation (right) over European and Asian parts of Russia in 1990-2000.**

Concentrations of nitrogen compounds in precipitation were also generally decreased along the West-East direction with higher values over the central regions of Russia. Annual average concentrations of sulfur over the Asian part of Russia were varied during the period of 1990-2000 from 1.5 mg/L at Khuzhir to 4.0 mg/L in Sikhote-Alinskiy BR, meanwhile the average value for European territory of Russia was 3.1 mg/L for the same period.

Long term monitoring data obtained from the background monitoring stations over Russia shows that generally there was a tendency of decreasing sulfur and increasing nitrogen compounds in precipitation (Figure 3). Sulfur concentrations in precipitations of Siberian and Far East background regions were of the lowest level among regions of Russia at the beginning of measurement period. However, they remained practically stable there and even increases a bit for more than 30-year period while sulfur contents had decreased significantly in other regions.



**Figure 3 Long-term trends of sulfur (left) and nitrogen (right) concentrations in precipitations (mg/L) over Russian territory.**

### 3.2. Wet deposition during 2000-2004

Initial monitoring data gathered from the monitoring network of precipitation chemistry and rain acidity were averaged over the following regions: Central and Northern Siberia, Southern Siberia, Baikal Lake region and Far East region. In order to compare the levels of pollution in precipitation at Asian and European territories of Russia, the average data for both these regions are also presented below. Such information is annually prepared by the Main Geophysical Observatory (St. Petersburg, Russia) and published in the issues of "Review of the environmental pollution in Russian Federation" (Chistyakova, 2002; Shalamanskiy *et al.*, 2002; Chistyakova *et al.*, 2003; Svistov *et al.*, 2004, 2005).

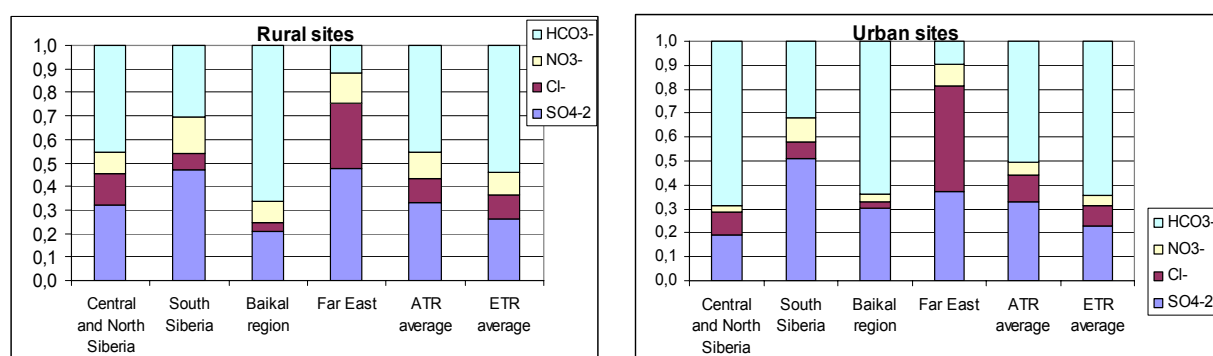
Average weighted data on ions concentrations in the precipitations of the regions are presented in the Table 2. Predominant ions in the precipitation of Russian Asia are sulfate and bicarbonates. Bicarbonates are

mostly predominant in Baikal Lake region (more than 60% of ion balance), Central and Northern Siberia, while sulfate is a major ion in precipitation over Southern Siberia and Far East region contributed of 33-40% to ion sums (Fig. 4). Baikal Lake region is distinguished by the highest values of mineralization ( $M=30.5 \text{ mg/L}$ ) of precipitations among all regions.

**Table 2 Average weighted concentrations of major ions in the precipitations in 2004, mg/L**

| Region                       | $\text{SO}_4^{2-}$ | $\text{Cl}^-$ | $\text{NO}_3^-$ | $\text{HCO}_3^-$ | $\text{NH}_4^+$ | $\text{Na}^+$ | $\text{K}^+$ | $\text{Ca}^{+2}$ | $\text{Mg}^{+2}$ | M           | pH         |
|------------------------------|--------------------|---------------|-----------------|------------------|-----------------|---------------|--------------|------------------|------------------|-------------|------------|
| Central and Northern Siberia | 2.9                | 1.2           | 0.8             | 4.1              | 0.6             | 1.0           | 0.4          | 0.6              | 0.6              | 12.2        | 6.3        |
| Southern Siberia             | 6.1                | 0.9           | 2.0             | 3.9              | 0.8             | 0.5           | 0.4          | 0.6              | 0.4              | 15.6        | 6.4        |
| Baikal region                | 5.1                | 0.9           | 2.2             | 16.2             | 0.4             | 1.2           | 0.7          | 1.4              | 2.4              | 30.5        | 6.4        |
| Far East                     | 4.1                | 2.4           | 1.1             | 1.0              | 0.4             | 1.5           | 0.5          | 1.0              | 0.3              | 12.3        | 5.3        |
| <b>ATR average</b>           | <b>4.6</b>         | <b>1.4</b>    | <b>1.5</b>      | <b>6.3</b>       | <b>0.6</b>      | <b>1.1</b>    | <b>0.5</b>   | <b>0.9</b>       | <b>0.9</b>       | <b>17.7</b> | <b>6.1</b> |
| <b>ETR average</b>           | <b>3.3</b>         | <b>1.3</b>    | <b>1.2</b>      | <b>6.8</b>       | <b>0.6</b>      | <b>0.6</b>    | <b>0.5</b>   | <b>2.0</b>       | <b>0.7</b>       | <b>17.0</b> | <b>6.1</b> |

Minimum and maximum concentrations of sulfur and nitrogen compounds in precipitations measured in 2004 are presented in Table 3. Generally maximum values of sulfur, nitrate and ammonium concentrations are of 4-6 times higher than average ones for Asian territory. However in Central and Northern Siberia region the maximum concentration of ammonium recorded is 11 times higher than average while in Far East maximum nitrate concentration prevailed average one by factor of 9.



**Figure 4 Anion ratios in precipitation at urban and rural sites of the Asian territory of Russia.**

Rain waters in Far East region is characterized by the lowest pH value on average (5.3, Table 2) which can be comparable only with precipitation acidity over north-western European territory of Russia. It should be noted that both mentioned regions are characterized by sulfate type of precipitations. Precipitations on all over the regions of Russia are almost neutral ( $\text{pH} = 6.1-6.4$ ). Acidic minimum pH value of precipitations (3.5) was observed in Central and Northern Siberia region. Acidic precipitation events with pH around 4.5 were registered also over all the Asian territory of Russia, however, the frequency of such events is less than 5%.

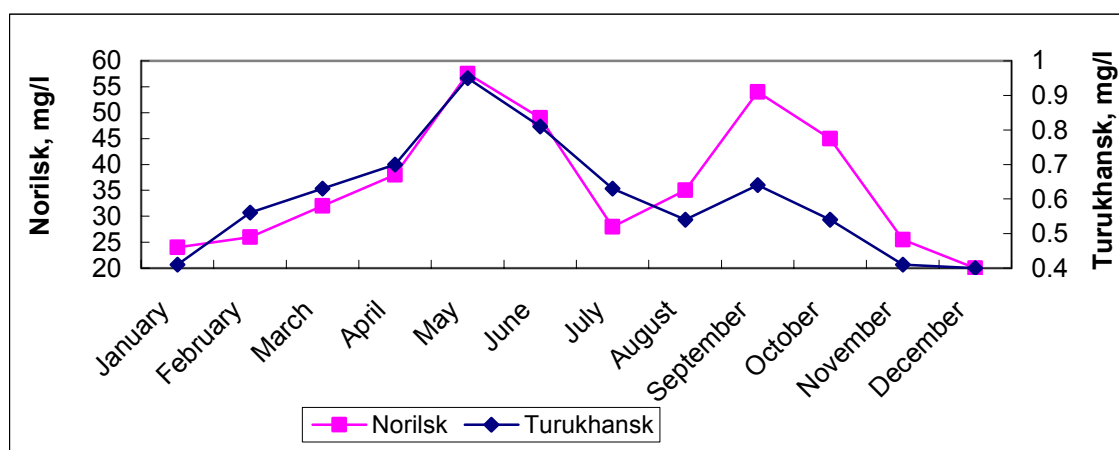
Detail evaluation of mineralization and acidity of precipitation in Asian Russia demonstrates that distribution of ions in urban regions is almost the same as for rural regions (Figure 4). The predominant anion in rain over urban places of Central, Northern Siberia and Baikal region is bicarbonate, while sulfate is a main acidic ion in precipitation over Southern Siberia. In Far East region main anions in urban precipitations are  $\text{SO}_4^{2-}$  and marine  $\text{Cl}^-$ . Average concentrations of main ions in urban sites are about 2-2.5 times higher than in rural ones. There is no big difference in urban and rural levels of sulfate concentrations during summer months. They did not exceed  $2 \text{ mg/L}$  over Baikal Lake region. Otherwise, the influence of urban and industrial centers on precipitation chemistry could be traced clearly during winter when sulfate concentrations of snow waters in

Irkutsk increase up to 15-23 *mg/L*, while at regional level in Baikal region values of this parameter are almost 3 times lower. The influence of air quality conditions in urban and industrial centers at the territory of Siberia and the Far East region is peeped in increasing of sulfate ion concentrations in precipitation and sulfur dioxide concentrations in air at urban and regional sites comparing with background level.

**Table 3 Minimum and maximum values of sulfur and nitrogen compounds and pH in 2004**

| Region                       | SO <sub>4</sub> |             | NO <sub>3</sub> |            | NH <sub>4</sub> |             | pH         |            |
|------------------------------|-----------------|-------------|-----------------|------------|-----------------|-------------|------------|------------|
|                              |                 |             | <i>mg/L</i>     |            |                 |             |            |            |
|                              | min             | max         | min             | max        | min             | max         | min        | max        |
| Central and Northern Siberia | 0.07            | 16.4        | 0.04            | 3.8        | 0.02            | 6.80        | 3.5        | 7.1        |
| Southern Siberia             | 0.10            | 22.9        | 0.10            | 5.1        | 0.05            | 2.80        | 5.0        | 7.5        |
| Baikal region                | 0.40            | 28.4        | 0.05            | 5.5        | 0.02            | 2.20        | 4.8        | 8.4        |
| Far East                     | 0.30            | 16.8        | 0.10            | 10.3       | 0.10            | 2.30        | 4.1        | 7.4        |
| <b>ATR average</b>           | <b>0.22</b>     | <b>21.1</b> | <b>0.07</b>     | <b>6.2</b> | <b>0.05</b>     | <b>3.53</b> | <b>4.4</b> | <b>7.6</b> |
| <i>Standard deviation</i>    | <i>0.16</i>     | <i>5.7</i>  | <i>0.03</i>     | <i>2.8</i> | <i>0.04</i>     | <i>2.20</i> | <i>0.7</i> | <i>0.6</i> |
| <b>ETR average</b>           | <b>0.18</b>     | <b>16.5</b> | <b>0.03</b>     | <b>6.1</b> | <b>0.10</b>     | <b>3.45</b> | <b>4.5</b> | <b>7.1</b> |
| <i>Standard deviation</i>    | <i>0.10</i>     | <i>8.7</i>  | <i>0.01</i>     | <i>4.0</i> | <i>0.13</i>     | <i>1.30</i> | <i>0.6</i> | <i>0.4</i> |

According to the information prepared for AMAP assessment report (Hole *et al.*, 2006), concentrations of sulfate sulfur over the Northern Siberian region ranged from almost zero in remote place to 143 *mg/L* in industrial area of Norilsk (where the highest concentrations were observed throughout Russia). The average level of SO<sub>4</sub><sup>2-</sup>S for the region, excluding Norilsk, did not exceed 0.89 *mg/L* and there was a maximum concentration of 16.8 *mg/L*. Background concentrations, characterized by data from measurement points in Urengoy, Turukhansk, Polyarniy, and Zhigansk, were in range from 0.2 to 1.2 *mg/L* with the minimum values in warm or spring months. In contrast, average monthly sulfur concentrations at Norilsk were 50 to 60 times higher than at remote site Turukhansk. Precipitation at Norilsk was the most polluted conditions in May and September (Figure 5). Seasonal variation of sulfate sulfur concentration in precipitations at the background station in Turukhansk had followed the same pattern traced at Norilsk but with different order of magnitudes.



**Figure 5 Seasonal distribution of sulfate sulfur concentration in precipitations over Norilsk industrial area and at background site Turukhansk**

Average wet depositions of sulfur, nitrogen and sum of ions presented in the Table 4 were dependent on the ion concentrations and precipitation amounts. Annual sulfur deposition fluxes are varied over Asian part of Russia from 0.3 to 1.1 *t/km<sup>2</sup>* with highest values in Southern Siberia and Far East meanwhile average total

nitrogen deposition is about  $0.4 \text{ t/km}^2$  per year. Average total wet deposition of all measured elements over Asian territory was about 1.5 times less than ones for European territory of Russia.

**Table 4 Average annual wet deposition of sulfur, nitrogen and ion sum ( $\text{t/km}^2$  per year)**

| Regions                      | S ( $\text{SO}_4^{2-}$ ) | N ( $\text{NO}_3^-$ ) | N ( $\text{NH}_4^+$ ) | $\Sigma \text{ N}$ | M    | S/ $\Sigma \text{ N}$ | $\frac{\text{N} (\text{NH}_4^+)}{\text{N} (\text{NO}_3^-)}$ |
|------------------------------|--------------------------|-----------------------|-----------------------|--------------------|------|-----------------------|---|
| Central and Northern Siberia | 0.36                     | 0.07                  | 0.18                  | 0.24               | 4.6  | 1.5                   | 2.6   |
| Southern Siberia             | 1.11                     | 0.25                  | 0.34                  | 0.58               | 8.5  | 1.9                   | 1.4   |
| Baikal region                | 0.49                     | 0.14                  | 0.09                  | 0.23               | 8.8  | 2.1                   | 0.6   |
| Far East                     | 1.00                     | 0.18                  | 0.23                  | 0.41               | 9.0  | 2.4                   | 1.3   |
| <b>ATR average</b>           | 0.70                     | 0.16                  | 0.20                  | 0.36               | 7.1  | 2.0                   | 1.2   |
| <b>ETR average</b>           | 0.70                     | 0.16                  | 0.30                  | 0.46               | 10.8 | 1.5                   | 1.8   |

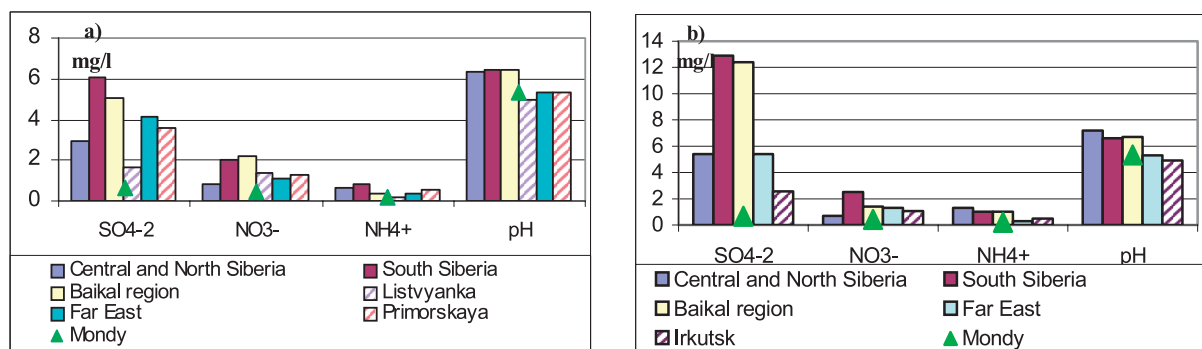
There was no clear tendency observed in total mineralization of precipitation at Asian territory of Russia during the last 5 years period (2000-2005) while it had significantly decreased over European territory for these years. The similar feature was observed for sulfur concentrations that varied within 3 to 8 mg/l with maximum values for all regions over Asian territory in 2000. Chlorine concentration shows clear tendency to decrease almost in all regions except of Northern and Central Siberia. Nitrogen concentrations had increased in precipitation over Far East region.

#### 4. Comparison of the Russian EANET and national monitoring data on precipitation chemistry

The use of different sampling and analytical methodology at national monitoring network and at EANET sites does not allow to make comprehensive representative comparison of their results. This should be a subject of separate detail investigation. Some preliminary attempts to compare these data were made in Russian National EANET Center - IGCE (Ginzburg *et al.*, 2006). Generally, it could be noted that according to the results from both networks the predominant ions in precipitations over Asian part of Russia are sulfate and bicarbonates. However, according to the measurements at background sites of national precipitation monitoring network, average contribution of bicarbonates to ion content is 30% (in particular, more than 50% in Baikal region) as well as one of sulfate is 25%. Based on data from Listvyanka (EANET) the content of sulfate ion consists of more than 50% of anions.

Comparison of average levels of major ion concentrations in precipitation of Russia regions and at Russian EANET sites is presented at Figure 6 for rural and urban areas. According to Russian EANET monitoring data the precipitation in Far East region is characterized by the higher level of sulfur, while higher levels of nitrogen compounds are measured in Baikal region. In the contrast according to long-year measurements at the national precipitation monitoring network, sulfate concentrations in precipitation is lower in Far East region than in Southern Siberia and Baikal region. It also can be noted that concentrations of all major ions at Listvyanka site was measured as lower than averages for Baikal region (in particular, sulfate is 3 times less, nitrogen – 1.5 times less, ammonium – 2.5 times less). At the same time, measurements at Primorskaya EANET site correlated quite well with average data of precipitation chemistry network over Far East region.





**Figure 6 Comparison of average region concentrations of sulfate, nitrate and ammonium ions in precipitations (according to national monitoring network) with background levels (Mondy) and EANET data (Listvyanka, Primorskiy) in 2004 for rural (a) and urban (b) sites.**

Differences in concentration levels at different monitoring networks could be explained by different sites location and sampling methodology. An appropriateness of mentioned reasons and detail comparison of monitoring methodologies and results should be made in the future.

## 5. Monitoring data on chemical composition of snow cover

This overview was prepared based on the data from the snow chemistry monitoring network (Nazarov *et al.*, 2002; Artemov *et al.*, 2005). Some results were also compared with the data obtained from the sites of precipitation chemistry and acidity monitoring.

Snow cover chemical pollution monitoring network is operated in Russia since 1980 on the basic infrastructure of meteorological monitoring network conducted observation on snow cover. Its main goal is the evaluation of atmospheric pollution loads. Designed density of snow monitoring network should be 1 site per 36 thousand  $\text{km}^2$  for Asian part of Russia (that is about 360 sites per whole territory with seasonal snow layer). Results of measurements allow evaluating seasonal loads of sulfate sulfur, nitrate and total nitrogen as well as to estimate their annual depositions. The suite of analysis included also measurements of snow pH and content of anthropogenic pollutants such as heavy metals and POPs.

Average annual values of estimated atmospheric loads over Asian territory of Russia are: sulfate sulfur - 210  $\text{kg}/\text{km}^2$ , nitrate nitrogen – 60  $\text{kg}/\text{km}^2$ , total nitrogen – 175  $\text{kg}/\text{km}^2$ . Average annual data for administrative regions of Russian Asian territory are presented in Table 5.

The most intensive deposition of sulfur was recognized at the Southern and Central part of West Siberia region (547 and 344  $\text{kg}/\text{km}^2$  per year) and Sakhalin and Primorskiy region (397  $\text{kg}/\text{km}^2$  per year). The highest values of nitrogen and total nitrate deposition were also observed at the Southern and Central part of West Siberia region. The intensities of sulfur and nitrogen deposition measured by estimation of snow monitoring data were much lower in comparison with the results obtained at the precipitation chemistry network.



**Table 5 Deposition of sulfur and nitrogen at Asian territory of Russia in 2000-2004 (kg/km<sup>2</sup> per year)**

|                        | Region   | Square, km <sup>2</sup> | Sulfur | Nitrogen nitrate | Total nitrate |
|------------------------|--|-------------------------|--------|------------------|---------------|
| Western Siberia        | Tumen region   | 1435                    | 212    | 83               | 294           |
|                        | Omsk, Tomsk and Novosibirsk regions                    | 635                     | 344    | 168              | 346           |
|                        | Khemerovo region, Altay                                | 265                     | 547    | 207              | 372           |
|                        | Republic of Altay                                      | 93                      | 220    | 63               | 293           |
| Eastern Siberia region |  | 4123                    | 269    | 55               | 174           |
| Far East               | Yakutiya   | 3103                    | 60     | 21               | 95            |
|                        | Khabarovsk, Amur, Kamchatka, Magadan, Chukotka regions | 2860                    | 143    | 34               | 104           |
|                        | Primorskiy kray, Sakhalin                              | 237                     | 397    | 83               | 318           |
|                        |  |                         |        |                  |               |

## 5. Conclusions based on the results of national monitoring

Russian national acid deposition monitoring system over the Asian territory consists of network with sites to measure precipitation chemistry and acidity of rain at the regional and background levels; urban sites where pollutant concentrations are measured in both ambient air and precipitation; and snow chemistry monitoring network. Analysis and generalization of monitoring results, their interpretation, and evaluation of the state of the environment based on results of observations are annually published in a number of issues. The most complete of them is "Review of the environmental pollution in Russian Federation" which is printed with a very limited number of copies, but the issues of last years are available in the Internet.

Long term monitoring data obtained from the background monitoring stations over Russia shows that generally there is a tendency for decreasing of sulfur and increasing of nitrogen concentrations over Russian territory. At the same time, sulfur concentration in precipitations around Siberian and Far East regions stays practically stable at the background level and even slightly increases a bit during the measurement period of more than 30 years.

Sulfate and bicarbonates are dominant ions in the precipitation chemical composition over Russian Asia. Bicarbonates are predominant in Baikal region, Central and Northern Siberia, while sulfate is a major ion in precipitation of Southern Siberia and Far East region. Baikal region is also characterized by the highest mineralization of precipitations among all mentioned regions.

The lowest average pH (5.3) was detected in Far East region with minimum values up to 4 that can be comparable with remarkable acidic precipitation at north-western territory of European Russia. All precipitation over the territory of Asian Russia were almost neutral (pH = 6.1- 6.4) on average.

Average concentrations of main ions in urban sites are about twofold higher than in rural ones. The influence air quality of urban and industrial centers can mostly be seen during winter time when sulfate concentration in urban regions increase significantly. Concentrations of nitrogen compounds in urban sites were almost the same or 1.5 times higher than in rural ones.

Different sampling and analytical methodology used at national monitoring network and at EANET sites do not allow making a representative comparison of results. However, some preliminary attempts show that there was some discrepancy in the measurement results of these networks. To disclose reasons of such divergence and further detail comparison of monitoring methodology and relevant results should be a subject for a separate investigation.

## References

- Artemov, Y. M., Belikova, T. V., Vasilenko, V. N., & Nazarov, I. M., 2005. Atmospheric deposition of sulfur and nitrogen over the territory of Russia (based on snow monitoring data). In Review of the environmental pollution in Russian Federation in 2004, Moscow. (in Russian)
- Chistyakova, M. V., 2002. Acidity and chemical composition of precipitations. In Review of the environmental pollution in Russian Federation in 2001, Moscow. (in Russian)
- Chistyakova, M. V., Pavlova, M. T., Sokolova & O. I., 2003. Acidity and chemical composition of precipitation. In Review of the environmental pollution in Russian Federation in 2002, Moscow. (in Russian)
- Drozdova V. M., Petrenchuk O. P., Selezneva E. S. & Svistov P. F., 1964. Chemical composition of atmospheric precipitation over European part of the USSR. Gidrometeoizdat, Leningrad, 209 p. (in Russian)
- Ginzburg, V. A., Paramonov, S. G., Alekseeva, L. I. & Sokolova, O. A., 2006. Complex assessment of sulfur and nitrogen pollution over Asian territory of Russia (according to the monitoring data). In Proceedings of the Second All-Russian Conference "Scientific aspects of environmental problems in Russia". May 29-30, Moscow, Russia (in Russian)
- Hole L. R., Christensen J., Ginzburg V. A., Makarov V., Pershina N.A., Polischuk A.I., Ruoho-Airola T., Ph. Svistov P. & Vasilenko V. N., 2006. Concentrations and deposition of acidifying pollutants. In AMAP assessment 2006: Acidifying Pollutants, Arctic Haze, and Acidification in the Arctic. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, pp. 11-30.
- Izrael Y. A., Nazarov I. M., Fridman S. D., *et al.* 1987. Monitoring of the transboundary air pollutant transport. Gidrometeoizdat, Leningrad, 302 p. (in Russian)
- Izrael Y. A., Nazarov I. M., Pressman A. Y., *et al.* 1989. Acid Rains. Gidrometeoizdat, Leningrad, 269 p. (in Russian)
- Izrael Y. A. & Rovinsky F. Y. 1990. Integrated Background Monitoring of Environmental Pollution in Mid-Latitude Eurasia. WMO GAW No 72, WMO-TD-434, 72 p.
- Nazarov, I. M., Vasilenko, V. N. & Belikova, T. V. 2002. Atmospheric loads of sulfur and nitrogen over the territory of Russia. In: Review of the environmental pollution in Russian Federation in 2001, Moscow. (in Russian).
- Review, 2007. Review of the environmental pollution in Russian Federation in 2006. Roshydromet, Moscow, 162 p. (in Russian).
- Review, 2008. Review of the background state of natural environment on the territory of CIS countries in 2006. Roshydromet, N.Novgorod, 85 p. (in Russian).
- Shalamyanskiy, A. M., Romashkina, K. I. & Chistyakova, M. V. 2002. Acidity and chemical composition of precipitation. In Review of the environmental pollution in Russian Federation in 2001, Moscow. (in Russian).
- Svistov, P. P., Pershina, N. A., Pavlova, M. T. & Polishok, A. I. 2004. Acidity and chemical composition of precipitation. In Review of the environmental pollution in Russian Federation in 2003, Moscow. (in Russian).
- Svistov, P. P., Pershina, N. A., Pavlova, M. T. & Polishuk, A. I., 2005. Acidity and chemical composition of precipitation. In: Review of the state of the environmental pollution in Russian Federation in 2004, Moscow. (in Russian).

# Long Term Acidification of Upstream River and Lake Water in Central Japan

Hidemi Kurita<sup>1)</sup>, Leong C. Peng<sup>2)</sup> and Hiromasa Ueda<sup>2)</sup>\*

1) *Nagano Women's Junior College, 9-11-29 Miwa, Nagano 380-0803, Japan*

2) *Acid Deposition and Oxidant Research Center, Sowa 1182, Nishi-ku,  
Niigata 950-2144, Japan*

*\*Contact address: Acid Deposition and Oxidant Research Center, Sowa 1182, Nishi-ku,  
Niigata 950-2144, Japan  
[e-mail: ueda@adorc.gr.jp]*

Long term acidification of the upstream river and lake water in the mountainous region in central Japan was investigated in relation to acid deposition. Using the 32-years (1972-2003) records of monthly pH values from 79 water quality monitoring points in Nagano prefecture (area 13,600 km<sup>2</sup>), 27 points were selected as unpolluted ones and their data were analyzed statistically along with the precipitation pH from 21 air pollutions monitoring sites to determine long term trend and relation with the geology and geography.

It was found that the precipitation was acidic in the pH range between 4.8 to 5.3 and remaining almost at the same acidic levels throughout the 32 years, while the annual mean values of upstream river and lake water at 14 out of the 27 points showed significant decrease with  $\Delta$ pH ranging from 0.3 to 0.7 within 5% risk in the 30 years. Moreover, the annual means of water pH have become acidic at the levels of pH 7.0 or lower with a minimum pH 6.3 in the Yomase-river. In addition, remarkable decline of the pH down to 5.0 was observed in the early snow-melting season in recent years in the case of the Yomase-river where inflow of hot spring water with low alkalinity had reduced the acid neutralization capacity.

The acidification trend of the upstream river and lake water is considered to be caused by acid deposition, and it is not only confined to the acidic bedrock watershed areas but it has spread gradually to the neighboring areas.

## 1. Introduction

The adverse impacts of acid deposition on ecosystems are of great concern to national and regional environments. It is well known that Europe and North America have experienced serious damages to their inland aquatic environment, forests and vegetations in the past due to acid deposition. East Asia also has a high potential for such damages to ecosystems because of the rapid industrialization and motorization. Recently, a regional acid deposition monitoring network, the Acid Deposition Monitoring Network in East Asia (EANET), has been started, initially on a preparatory basis in 1998 and on a regular basis from 2001. Currently 13 countries in the East and Southeast Asia are participating in EANET activities and soil-vegetation monitoring and inland water monitoring are conducted at 24 and 15 sites, respectively (Network Center for EANET, 2007). In Japan, national acid rain monitoring was started in 1983. It was reported that the annual mean precipitation pH was 4.77 and had remained almost at the same level for the past 20 years (MOEJ, 2004). The deposition of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> ions were almost at the same levels as those in Europe and North America. However, since

Japan had experienced serious air pollution due to SO<sub>x</sub> and NO<sub>x</sub> in the 1960s, the continuation of acid rain monitoring and investigations on the integrated acid deposition effects on soil are of great importance.

The acid deposition effects might appear in various ecosystems. Of such effects, soil acidification is important and substantial because it in turn causes the decline of forests and crops and the acidification of inland aquatic environment. Soil acidification may be reflected directly to the long term records of river and lake water quality in the uppermost stream part of mountainous regions. Water quality monitoring has been carried out for several decades for the purpose of public water use. In the present study long term monitoring records of water quality were analyzed statistically, together with the records of air quality and acid deposition, to investigate to what extent acidification is proceeding in the upstream river and lake water and which areas are affected.

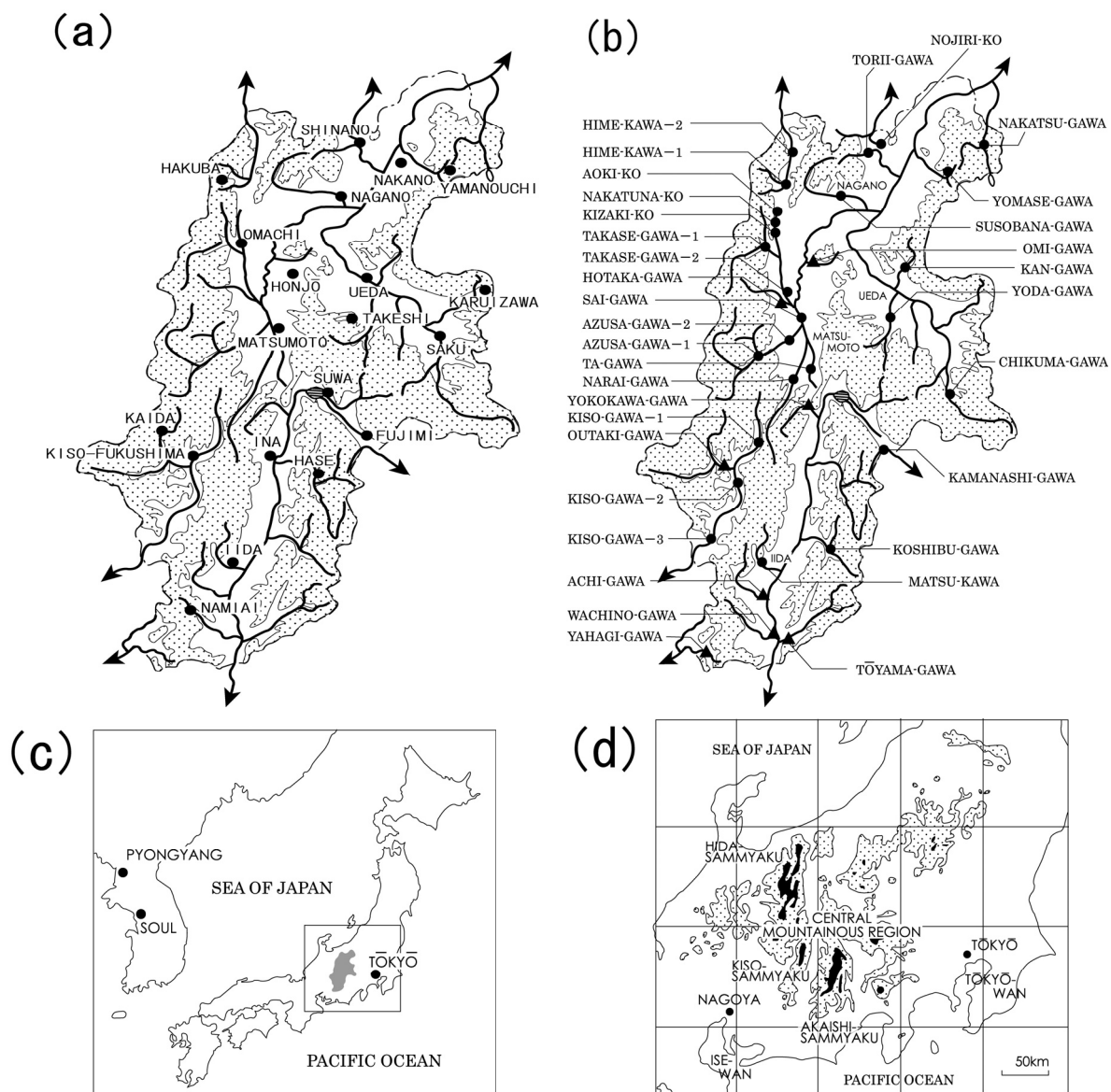
As for the long term trend of inland water acidification in Japan, the present authors (1993) were the first to discover the acidification of upstream river and lake water in the mountainous region in central Japan. This effect was limited to the watershed areas on the acidic bedrock with low buffering capacity to acid deposition. Such a trend was detected in the river water and dam-lake water in the Gotoh Islands in Kyushu district (Mori *et al.*, 1999) and in Nara prefecture (Matsumoto *et al.*, 2003). It was also observed in a high-land lake at the summit of Mt. Norikura in central Japan (Kawakami, 1998). Recently significant acidification of the Ijira lake and its inflow water in the Central District was recognized in the report of Japanese Acid Deposition Survey (MOEJ, 2004).

On the other hand, short term acidification and its effects on aquatic life in North Europe have been revealed in snow-melted stream water (e.g., Leivestad & Muniz, 1976). Even in Japan the decline of river water pH in heavy snow areas was detected in the early and middle snow-melting seasons (e.g., Miyanaga & Ikeda, 1994). Run-off of the snow-melted water with high ion-concentrations was also observed in early spring. Apart from the snow melting season, a significant decrease of pH in the mountain streams in a catchment was detected when the water flow rate peaked after rainfall (Ebise, 1996; Katsuno *et al.*, 1998). This acidification is also reflected on river water with low acid neutralizing capacity.

From these facts acidification of the inland aquatic environment occurred in Japan, particularly in the acidic bed-rock watersheds in central Japan. However more extensive and longer term analyses are necessary to conclude the long term and short term acidification. The objective of the present study is to reveal the long term acidification of the upstream river and lake waters in Japan systematically, from the 32-year records of water quality monitoring, together with those of air quality and acid deposition monitoring.

## **2. Geographical and Geological Features of Objective Area**

The target area was whole of Nagano prefecture located in central Japan that has a total area of 13600 km<sup>2</sup>. As shown in Fig. 1, it is in the mountainous region far from large emission sources. Distances from Tokyo metropolitan area and Nagoya industrial area to the nearest prefectural border are about 150km and 100km, respectively. Geographically the Nagano area is composed of three mountain ranges of more than 2000 m above MSL, namely the Hida, Kiso and Akaisi mountain ranges and basins surrounded by them. Geologically the bed-rocks in the southern and western part are mainly acidic ones such as granite and rhyolite that have low acid neutralizing capacity to acid deposition. Moreover, the highland areas are mostly covered by highland lithosols that is one of the most sensitive soils to acid deposition (MOEJ, 1983). Because of these geographical and geological features, the upstream river and lake water was expected to reflect the adverse effects of the acid deposition if any.



**Figure 1** Location of (a) sampling sites of air pollution denoted by black circles (dotted areas represent land higher than 1000m MSL), (b) water quality monitoring points (black circles denote long-term monitoring points and black triangles denote short-term monitoring points), (c) situation of region where precipitation and water pH was analyzed. (d) Geographical features of the region: dotted areas and black areas represent land higher than 1000m and 2000m MSL respectively

In this central mountainous region westerly or northwesterly winds prevail in winter and spring time, which cause the long-range transboundary transport of acidic pollutants from the Asian continent and substantial wet deposition in the form of acidic snow. On the other hand, in summer time it is exposed sometimes to the long range transport of acidic pollutants from Tokyo metropolitan area and from Nagoya industrial area (Kurita *et al.*, 1985; Kitada *et al.*, 1986). These features suggested that Nagano prefecture had a high potential to experience the adverse impacts of acid deposition on the ecosystems.

### 3. Data sets

Each local government in Japan monitors water quality in rivers or reservoirs for assessment of "public water body" continuously according to the Water Pollution Control Law in 1970, and therefore, the long term monitoring records of river or lake water quality are available for several decades. The long term monitoring records of water quality were analyzed statistically, together with those of air quality and acid deposition. Water quality monitoring was conducted once or three times per month at 79 points in total in the whole Nagano prefecture and their locations are indicated in Fig. 1 (b). The pH was measured on-site by means of glass electrode pH meters. Of the total 79 points, 21 unpolluted points were selected based on the criterion of BOD values less than 1 mg/liter. Of these 21 points, 19 were river water monitoring points and 2 were lake water monitoring points. In addition, 6 more points, 3 points for river water and 3 for lake water were selected as moderately-polluted ones. They were located in upper- or mid-streams but the BOD values were slightly higher ranging from 1 to 3 mg/liter. Thus, in total 27 sets of records of water quality monitoring for 32 years (1973 to 2004) were extracted out of 79 records and used for the long term acidification analyses.

In addition, in order to study the detailed spatial distribution and seasonal variation of the acidification, 7 sets of river water quality monitoring data were used starting from 1995, in addition to the routine monitoring data sets mentioned above.

Long term air quality monitoring and acid deposition monitoring were also performed in Nagano prefecture, of which acid deposition monitoring were conducted at 5 sites from 1986. The precipitation pH was measured monthly using pH meters for samples collected from wet-only samplers. Trend analysis was then made on the long term records of 18 years. The same procedure was also carried out for the Ohmachi site data but for total deposition starting 13 years earlier than for the wet-only deposition monitoring. To investigate the detailed spatial distribution of precipitation pH and its seasonal change, records from additional 15 sites for 5 years from 1993 to 1998 obtained especially from an acid rain research project in Nagano prefecture were also used. These observation sites were distributed uniformly in the whole area of Nagano, as indicated in Fig. 1 (a).

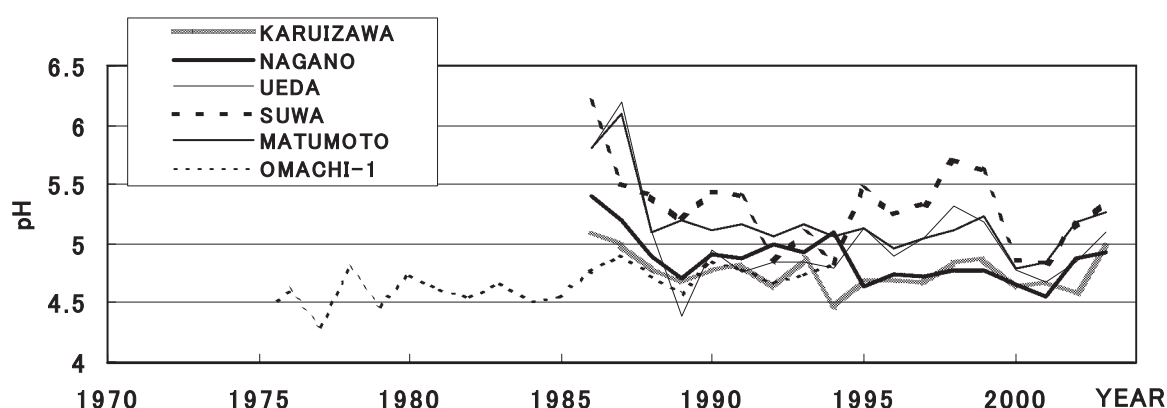
## 4. Results and discussion

### 4.1. Acid deposition

#### 4.1.1. Long term trend of acid deposition

Long term records of precipitation pH measured at 6 sites in Nagano prefecture were presented in Fig. 2. Bulk sampling of wet and dry deposition was made at Ohmachi while wet-only sampling was done at the other 5 sites. The precipitation pH appeared to be almost constant for this long period. However, anomalous pH peaks observed during a two-year period (1986 - 1987) obscured the long term trend at a few points. Thus, regression analysis was made for these long term records, excluding the data in the anomalous two-year period. The long term trend of the precipitation pH was listed in Table 1. Although a slightly increasing trend in the precipitation pH was detected at Ohmachi over 23 years from 1972 to 1994 with a statistical significance of 1% risk ( $p < 0.01$ ), and an average value of 4.6 was obtained, however this result should be treated with caution as the observation was made by a bulk sampler for total deposition including dustfall during non-rainy periods. The precipitation pH values at the other 5 wet-only sampling sites remained unchanged for the period from 1988 to 2003 at a 5 % risk level, and ranged from pH 4.8 to 5.3. From these results, it is concluded that the precipitation pH values in the central mountainous region in central Japan were about 5.0 and remained almost at the same levels for the 32 years. These pH values were slightly higher than pH 4.77 of the whole of Japan averaged over 20 years from 1983 (MOEJ, 2004). It was considered that Nagano prefecture is less severely influenced by domestic large emission sources than other areas in Japan, since it is in the mountainous region far from these source areas.





**Figure 2** Changes of annual mean pH of precipitation in the mountainous region in central Japan.

**Table 1** Regression analysis of annual mean pH values of precipitation

| Location  | Regression equation* <sup>1</sup> | Slope                      |                            | Trend toward decline* <sup>3</sup> | Average | r* <sup>4</sup> | Period  | n  |
|-----------|-----------------------------------|----------------------------|----------------------------|------------------------------------|---------|-----------------|---------|----|
|           |                                   | Upper 95% CI* <sup>2</sup> | Lower 95% CI* <sup>2</sup> |                                    |         |                 |         |    |
| Matsumoto | $y = 5.17 - 0.006x$               | -0.021                     | 0.010                      |                                    | 5.2     | 0.19            | '88-'03 | 16 |
| Nagano    | $y = 4.97 - 0.010x$               | -0.026                     | 0.006                      |                                    | 4.9     | 0.33            | '88-'03 | 16 |
| Karuizawa | $y = 4.71 + 0.015x$               | -0.014                     | 0.017                      |                                    | 4.8     | 0.05            | '88-'03 | 16 |
| Suwa      | $y = 5.37 - 0.007x$               | -0.039                     | 0.024                      |                                    | 5.3     | 0.13            | '88-'03 | 16 |
| Ueda      | $y = 4.72 + 0.012x$               | -0.014                     | 0.038                      |                                    | 5.0     | 0.26            | '88-'03 | 16 |
| Omachi-1  | $y = 4.59 + 0.012x$               | 0.005                      | 0.020                      | S**                                | 4.6     | 0.61            | '72-'94 | 21 |

\*<sup>1</sup> y: pH, x: year - 1980

\*<sup>2</sup> Confidence limit

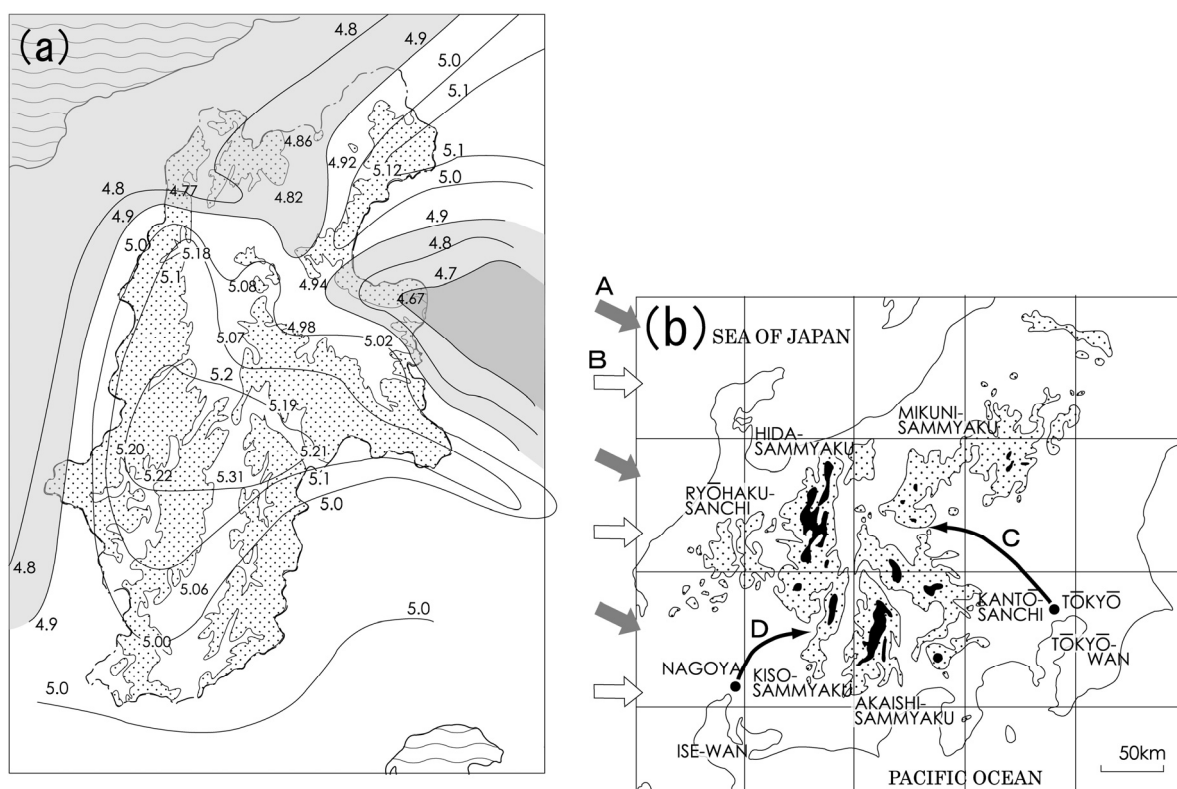
\*<sup>3</sup> S: Decrease in pH is significant (\* level of significance 0.05, \*\* level of significance 0.01)

\*<sup>4</sup> Correlation coefficient

Preliminary analysis was also made for sulfate, nitrate and ammonium in precipitation and in particulate matters monitored at the same time at these 6 sites. The wet deposition of sulfate decreased by 1/1.50 for the period from 1988 to 2003, while that of nitrate increased by 1.5 times and that of ammonium remained constant. Thus, it was found that the total wet deposition of sulfate and nitrate, as well as that of ammonium did not change significantly at a 5 % risk level. It was also in case for dry deposition of those species in particulates and gas phase. Although more detailed data analyses should be made for deposition, in particularly for dry deposition, here we assumed that both the wet and dry deposition of the species did not change significantly for these 30 years.

#### 4.1.2 Spatial distribution and seasonal change of acid deposition

Spatial distribution and seasonal change of the precipitation pH were investigated for the data obtained from the 20 observation sites in the acid deposition research project for years 1993 to 1998. The spatial distribution of the precipitation pH averaged over this period was presented in Fig. 3. These 5-year data records also indicated that the precipitation pH ranged from 4.7 to 5.3 and the average was 5.0. Lower pH values appeared for sites in the eastern part facing the Tokyo metropolitan area and in the northern part facing the Japan Sea.



**Figure 3** (a) Distribution of mean precipitation pH averaged over 1993 to 1997 in the mountainous region in central Japan, (b) Long-range transport routes of acidic pollutants to the central mountainous region. A: acidic pollutants from the Asian Continent, B: Kosa (the Asian dust) from the Asian Continent, C: acidic pollutants from the Tokyo metropolitan area, D: acidic pollutants from the Ise-Bay area.

Seasonal variation of the precipitation pH was presented in Fig. 4. At 5 sites in the eastern part, low precipitation pH was observed during the warm season. Particularly it was significant at Karuizawa which was located on the prefectural border 150-200 km downwind of the Tokyo metropolitan area. Thus, the low precipitation pH was considered to be the result of long range transport from the Tokyo metropolitan area by a large-scale wind system blowing into the thermal low created in the daytime with its center in the mountainous region (Kurita *et al.*, 1985). Since this wind system was created by the interaction of several local wind systems such as extended sea breezes, anabatic winds and plane/plateau winds, the pollutant transport occurred very frequently in the warm season and along almost the same route (Kurita *et al.*, 1985; Kurita and Ueda, 1990). The long range transport of gaseous and particulate air pollution were reported by Sasaki *et al.* (1988) and Chang *et al.* (1989) and acid rain by Carmichael *et al.* (1990). A large amount of particulates were produced in photochemical reactions during the long-range transport and partitioned in the aerosol phase in the thermodynamic equilibrium under low temperature and high relative-humidity conditions. These particulate matters were very acidic with high concentrations of  $\text{SO}_4^{2-}$  ions and sometimes  $\text{HSO}_4^-$  ions also (Sasaki *et al.*, 1988; Ueda *et al.*, 2000). Moreover, they made the cloud and rain droplets very acidic. Thus, higher amount of acid deposition through both wet and dry deposition processes occurred in the eastern part of Nagano prefecture. Seasonal variation of the precipitation pH in the northern part of Nagano was presented in Fig. 4 (b). The precipitation pH decreased both in summer and in winter. In summer the pollutants transported in the air from both Tokyo metropolitan area and Nagoya industrial area caused the acidified precipitation. Thus, although



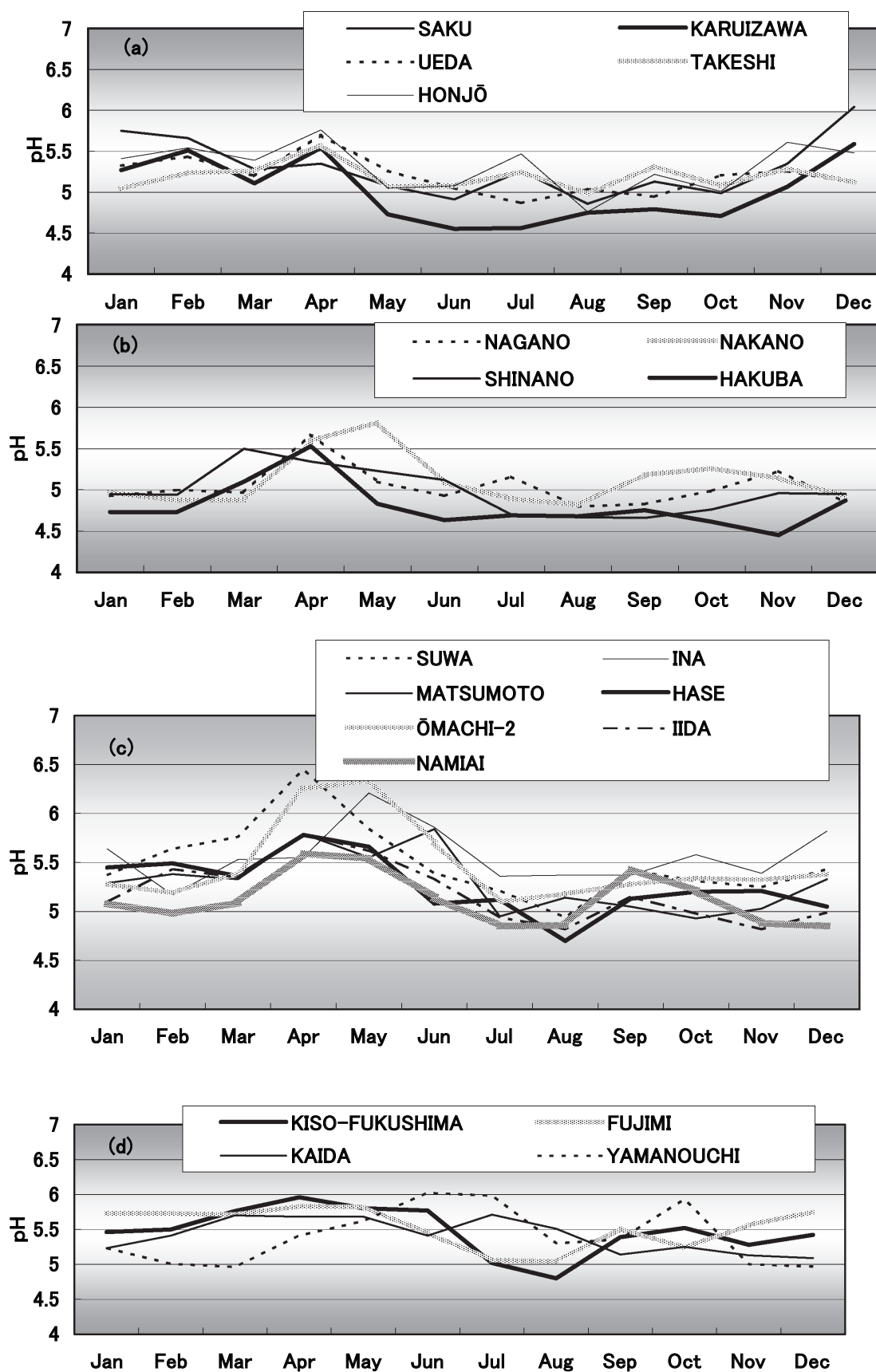
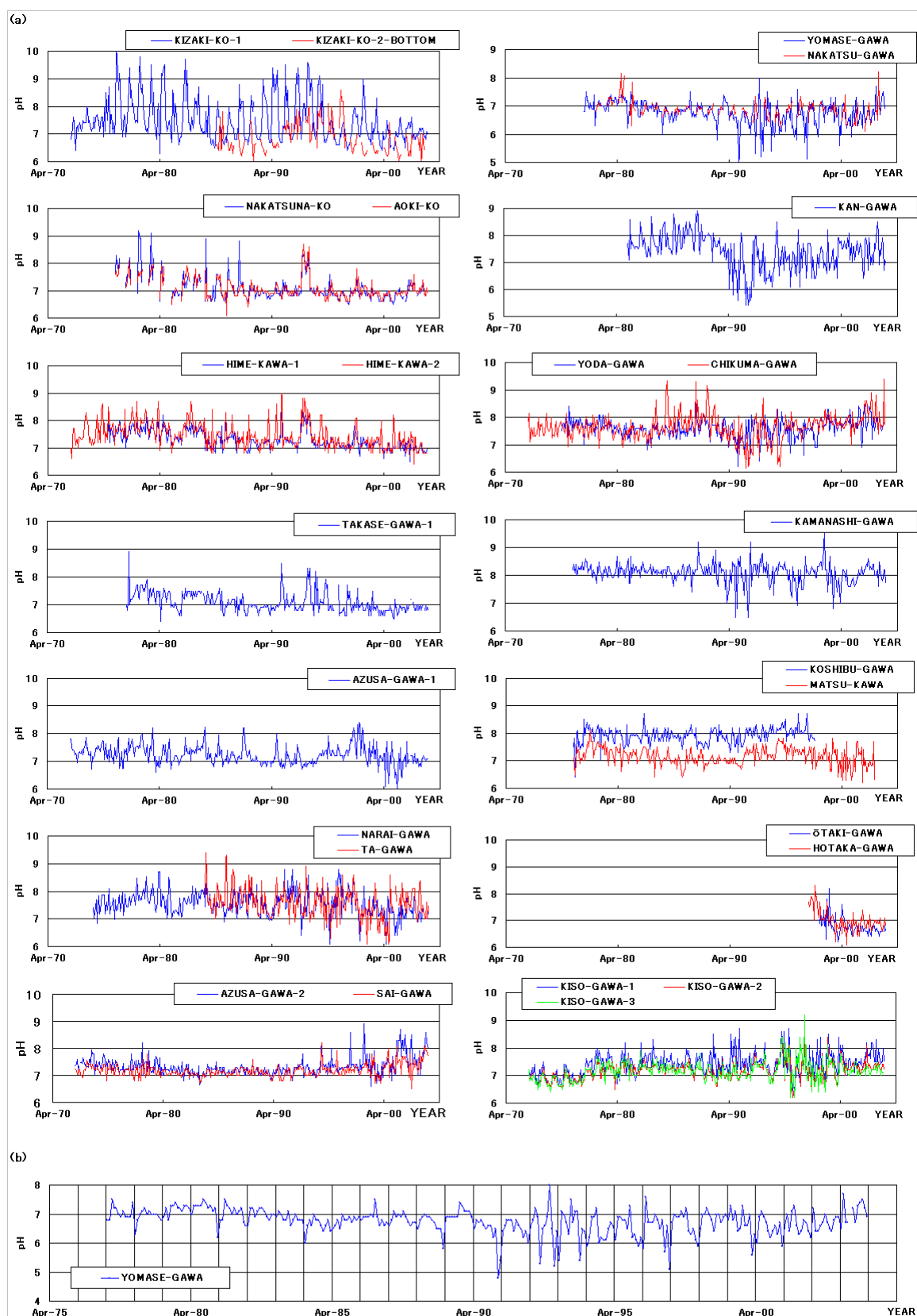


Figure 4 Seasonal change of precipitation pH in the mountainous region in central Japan.  
(a) east, (b) north, (c) middle and south, (d) plateau areas far from urban.



**Figure 5** Change of monthly pH of river and lake water in the mountainous region in central Japan.

**Table 2 Regression analysis of pH values of river and lake water from 1972 to 2003**

(a) Annual mean pH values

| Location           | Regression equation* <sup>1</sup> | Slope                      |                            | Trend toward decline* <sup>3</sup> | Fall in pH in thirty years* <sup>4</sup> | pH at 2003* <sup>4</sup> | r* <sup>5</sup> | Period | n  |
|--------------------|-----------------------------------|----------------------------|----------------------------|------------------------------------|--|--------------------------|-----------------|--------|----|
|                    |                                   | Lower 95% CI* <sup>2</sup> | Upper 95% CI* <sup>2</sup> |                                    |  |                          |                 |        |    |
| Hime-kawa-1        | $y = 7.44 - 0.022x$               | -0.028                     | -0.015                     | S**                                | 0.7                                      | 6.9                      | 0.78            | 75-'03 | 29 |
| Nakatsuna-ko       | $y = 7.23 - 0.021x$               | -0.030                     | -0.012                     | S**                                | 0.6                                      | 6.7                      | 0.68            | 76-'03 | 28 |
| Hime-kawa-2        | $y = 7.48 - 0.019x$               | -0.027                     | -0.011                     | S**                                | 0.6                                      | 7.0                      | 0.68            | 72-'03 | 32 |
| Aoki-ko            | $y = 7.22 - 0.019x$               | -0.028                     | -0.009                     | S**                                | 0.6                                      | 6.8                      | 0.62            | 76-'03 | 28 |
| Takase-gawa-1      | $y = 7.19 - 0.017x$               | -0.025                     | -0.009                     | S**                                | 0.5                                      | 6.8                      | 0.65            | 77-'03 | 27 |
| Narai-gawa         | $y = 7.51 - 0.017x$               | -0.026                     | -0.008                     | S**                                | 0.5                                      | 7.1                      | 0.58            | 74-'03 | 30 |
| Kizaki-ko-1        | $y = 7.28 - 0.015x$               | -0.023                     | -0.007                     | S**                                | 0.5                                      | 6.9                      | 0.56            | 72-'03 | 32 |
| Yomase-gawa        | $y = 6.82 - 0.023x$               | -0.039                     | -0.006                     | S*                                 | 0.7                                      | 6.3                      | 0.48            | 77-'03 | 27 |
| Nakatsu-gawa       | $y = 6.99 - 0.015x$               | -0.024                     | -0.006                     | S**                                | 0.5                                      | 6.6                      | 0.58            | 78-'03 | 26 |
| Ta-gawa            | $y = 7.65 - 0.025x$               | -0.044                     | -0.005                     | S*                                 | 0.8                                      | 7.1                      | 0.53            | 84-'03 | 20 |
| Azusa-gawa-1       | $y = 7.21 - 0.011x$               | -0.018                     | -0.004                     | S**                                | 0.3                                      | 7.0                      | 0.52            | 72-'03 | 31 |
| Kizaki-ko-2-bottom | $y = 6.59 - 0.010x$               | -0.016                     | -0.003                     | S**                                | 0.3                                      | 6.4                      | 0.75            | 85-'03 | 11 |
| Matsu-kawa         | $y = 7.17 - 0.010x$               | -0.020                     | -0.001                     | S*                                 | 0.3                                      | 6.9                      | 0.40            | 76-'03 | 28 |
| Kan-gawa           | $y = 7.53 - 0.032x$               | -0.064                     | 0.001                      |                                    |  | 6.8                      | 0.40            | 81-'03 | 23 |
| Takase-gawa-2      | $y = 7.07 - 0.007x$               | -0.015                     | 0.001                      |                                    |  | 6.9                      | 0.34            | 77-'03 | 27 |
| Susobana-gawa      | $y = 7.33 - 0.002x$               | -0.006                     | 0.002                      |                                    |  | 7.3                      | 0.24            | 78-'03 | 26 |
| Nojiri-ko          | $y = 7.23 - 0.001x$               | -0.004                     | 0.002                      |                                    |  | 7.2                      | 0.11            | 72-'03 | 32 |
| Kamanashi-gawa     | $y = 8.07 - 0.010x$               | -0.023                     | 0.003                      |                                    |  | 7.8                      | 0.31            | 76-'03 | 28 |
| Kiso-gawa-3        | $y = 7.18 - 0.004x$               | -0.013                     | 0.005                      |                                    |  | 7.1                      | 0.19            | 77-'03 | 27 |
| Azusa-gawa-2       | $y = 7.23 + 0.000x$               | -0.006                     | 0.006                      |                                    |  | 7.2                      | 0.01            | 72-'03 | 31 |
| Kiso-gawa-2        | $y = 7.15 + 0.000x$               | -0.008                     | 0.009                      |                                    |  | 7.2                      | 0.01            | 77-'03 | 27 |
| Yoda-gawa          | $y = 7.50 - 0.001x$               | -0.011                     | 0.010                      |                                    |  | 7.5                      | 0.02            | 75-'03 | 29 |
| Sai-gawa           | $y = 7.11 + 0.005x$               | 0.000                      | 0.010                      |                                    |  | 7.2                      | 0.37            | 72-'03 | 32 |
| Torii-gawa         | $y = 7.49 + 0.002x$               | -0.008                     | 0.012                      |                                    |  | 7.5                      | 0.10            | 83-'03 | 21 |
| Kiso-gawa-1        | $y = 7.32 + 0.003x$               | -0.007                     | 0.012                      |                                    |  | 7.4                      | 0.11            | 77-'03 | 27 |
| Chikuma-gawa       | $y = 7.44 + 0.008x$               | -0.005                     | 0.020                      |                                    |  | 7.6                      | 0.23            | 72-'03 | 32 |
| Koshibu-gawa       | $y = 7.82 + 0.008x$               | -0.004                     | 0.020                      |                                    |  | 8.0                      | 0.31            | 77-'96 | 20 |

\*<sup>1</sup> y: pH, x: year - 1980\*<sup>2</sup> Confidence limit\*<sup>3</sup> S: Decrease in pH is significant (\* level of significance 0.05, \*\* level of significance 0.01)\*<sup>4</sup> Estimated from regression equations\*<sup>5</sup> Correlation coefficient

**Table 2 Continued**

(b) Mean pH values in winter months (from December to March).

| Location                         | Regression equation <sup>*1</sup> | Slope                      |                            | Trend toward decline <sup>*3</sup> | Fall in pH in thirty years <sup>*4</sup> | pH at 2003 <sup>*4</sup> | r <sup>*5</sup> | Period | n  |
|----------------------------------|-----------------------------------|----------------------------|----------------------------|------------------------------------|--|--------------------------|-----------------|--------|----|
|                                  |                                   | Lower 95% CI <sup>*2</sup> | Upper 95% CI <sup>*2</sup> |                                    |  |                          |                 |        |    |
| Hime-kawa-1                      | $y = 7.42 - 0.024x$               | -0.033                     | -0.015 S**                 |                                    | 0.7                                      | 6.9                      | 0.73            | 75-'03 | 28 |
| Nakatsuna-ko                     | $y = 6.98 - 0.014x$               | -0.024                     | -0.004 S**                 |                                    | 0.4                                      | 6.7                      | 0.55            | 76-'03 | 22 |
| Hime-kawa-2                      | $y = 7.54 - 0.023x$               | -0.035                     | -0.010 S**                 |                                    | 0.7                                      | 7.0                      | 0.57            | 72-'03 | 32 |
| Aoki-ko                          | $y = 6.86 - 0.002x$               | -0.015                     | 0.011                      |                                    |  | 6.8                      | 0.08            | 76-'03 | 22 |
| Takase-gawa-1                    | $y = 7.22 - 0.015x$               | -0.031                     | 0.001                      |                                    |  | 6.9                      | 0.36            | 77-'03 | 27 |
| Narai-gawa                       | $y = 7.55 - 0.018x$               | -0.033                     | -0.004 S*                  |                                    | 0.5                                      | 7.1                      | 0.44            | 74-'03 | 30 |
| Kizaki-ko-1                      | $y = 7.07 - 0.019x$               | -0.027                     | -0.011 S**                 |                                    | 0.6                                      | 6.6                      | 0.69            | 72-'03 | 31 |
| Yomase-gawa                      | $y = 6.73 - 0.024x$               | -0.047                     | 0.000                      |                                    |  | 6.2                      | 0.38            | 77-'03 | 27 |
| Nakatsu-gawa <sup>*6</sup>       |                                   |                            |                            |                                    |  |                          |                 |        |    |
| Ta-gawa                          | $y = 7.50 - 0.013x$               | -0.033                     | 0.006                      |                                    |  | 7.2                      | 0.32            | 84-'03 | 20 |
| Azusa-gawa-1                     | $y = 7.13 - 0.002x$               | -0.011                     | 0.007                      |                                    |  | 7.1                      | 0.09            | 72-'03 | 32 |
| Kizaki-ko-2-bottom <sup>*6</sup> |                                   |                            |                            |                                    |  |                          |                 |        |    |
| Matsu-kawa                       | $y = 7.10 - 0.009x$               | -0.021                     | 0.004                      |                                    |  | 6.9                      | 0.26            | 76-'03 | 28 |
| Kan-gawa                         | $y = 7.39 - 0.024x$               | -0.061                     | 0.012                      |                                    |  | 6.8                      | 0.29            | 81-'03 | 23 |
| Takase-gawa-2                    | $y = 7.00 - 0.003x$               | -0.010                     | 0.005                      |                                    |  | 6.9                      | 0.16            | 77-'03 | 27 |
| Susobana-gawa                    | $y = 7.31 - 0.010x$               | -0.019                     | -0.001 S*                  |                                    | 0.3                                      | 7.1                      | 0.42            | 78-'03 | 26 |
| Nojiri-ko                        | $y = 7.07 + 0.001x$               | -0.001                     | 0.004                      |                                    |  | 7.1                      | 0.18            | 72-'03 | 32 |
| Kamanashi-gawa                   | $y = 8.09 - 0.011x$               | -0.028                     | 0.005                      |                                    |  | 7.8                      | 0.28            | 76-'03 | 28 |
| Kiso-gawa-3                      | $y = 7.09 - 0.003x$               | -0.015                     | 0.009                      |                                    |  | 7.0                      | 0.10            | 77-'03 | 26 |
| Azusa-gawa-2                     | $y = 7.21 - 0.004x$               | -0.011                     | 0.003                      |                                    |  | 7.1                      | 0.22            | 72-'03 | 30 |
| Kiso-gawa-2                      | $y = 7.08 + 0.002x$               | -0.012                     | 0.017                      |                                    |  | 7.1                      | 0.07            | 77-'03 | 27 |
| Yoda-gawa                        | $y = 7.50 - 0.006x$               | -0.021                     | 0.010                      |                                    |  | 7.4                      | 0.14            | 75-'03 | 29 |
| Sai-gawa                         | $y = 7.09 + 0.002x$               | -0.003                     | 0.007                      |                                    |  | 7.1                      | 0.14            | 72-'03 | 30 |
| Torii-gawa                       | $y = 7.48 + 0.007x$               | -0.009                     | 0.022                      |                                    |  | 7.6                      | 0.20            | 83-'03 | 21 |
| Kiso-gawa-1                      | $y = 7.20 + 0.015x$               | 0.004                      | 0.027                      |                                    |  | 7.5                      | 0.49            | 77-'03 | 26 |
| Chikuma-gawa                     | $y = 7.46 + 0.010x$               | -0.002                     | 0.021                      |                                    |  | 7.7                      | 0.30            | 72-'03 | 31 |
| Koshibu-gawa                     | $y = 7.78 + 0.016x$               | 0.001                      | 0.031                      |                                    |  | 8.1                      | 0.47            | 77-'96 | 20 |

<sup>\*1</sup> y: pH, x: year - 1980<sup>\*2</sup> Confidence limit<sup>\*3</sup> S: Decrease in pH is significant (\* level of significance 0.05, \*\* level of significance 0.01)<sup>\*4</sup> Estimated from regression equations<sup>\*5</sup> Correlation coefficient<sup>\*6</sup> Not measured in winter season.

Hakuba and Shinano are far away from the large emission source areas and even far from medium-sized urban areas, the precipitation pH decreased down to 4.6 and wet deposition of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ions (not shown) increased. In contrast, in winter time the transboundary long range transport of pollutants from the Asian continent caused the low precipitation pH and large acid deposition in snow (Oizumi *et al.*, 1991, Toriyama *et al.*, 1991, Yamaguchi *et al.*, 1991).

In the central and southern parts of Nagano (Fig. 4 (c)), the seasonal variation of precipitation pH was similar to that in the northern part but the pH values were higher by about 0.5. Here, the pH decrease in summer was considered to be due to the long range transport mainly from Nagoya industrial area. In contrast, in the highland areas (Fig. 4 (d)), although pH values decreased slightly in summer and winter, their seasonal variation

was small. Moreover, their average precipitation pH was almost the same as of clean water saturated by CO<sub>2</sub>, and therefore might be considered representative of the clean air in the mid-troposphere over Nagano prefecture. Thus, the seasonal variations in Fig. 4 (a) to (c) and the spatial distribution of precipitation pH in Fig. 3 were mainly dependent on whether the air mass came from Japanese mega cities or from the Asian continent.

In Fig. 4 it should be noted that in spring time, mainly from April to May, large increase in the precipitation pH was observed at all the monitoring points over Nagano prefecture. This was commonly observed in eastern and central Japan and was caused by the so-called yellow sand storms from the Asian continent. These sandstorms transported high concentrations of Ca<sup>2+</sup> in particulates and precipitation in the lower- and middle-troposphere which have the capacity to neutralize the acidic species in precipitation (Terada *et al.*, 2002) and their effects are spread widely and rather uniformly over the whole Nagano prefecture, while anthropogenic pollutants were confined in the lower troposphere and the effects were different spatially..

## **4.2. River and lake water acidification**

### **4.2.1. Monthly pH variation**

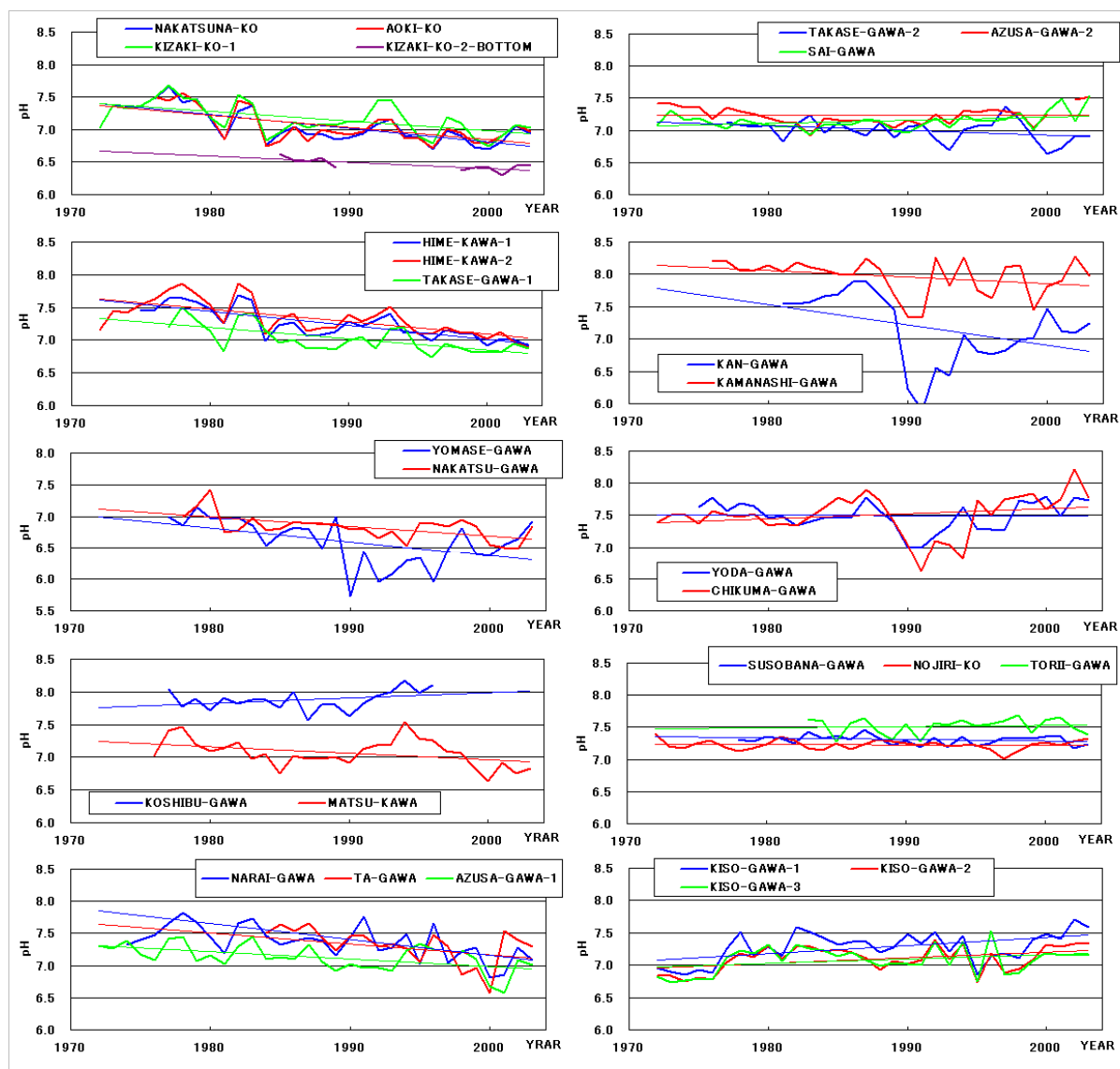
Long term records of the monthly pH variation of the upstream river and lake water were presented in Fig. 5. The length of records were 32 years (1972-2004) at 21 unpolluted points and at 6 moderately-polluted points. The long term trend of pH could be clearly seen in the pH records at unpolluted points (e.g., HIME-KAWA-1 and -2 and TAKASE-GAWA-1). In contrast, the moderately-polluted points such as KIZAKI-KO-1 and -2 had large seasonal variation of water pH with large peak values in the warm season and lesser fluctuations in the winter, obscuring its long term trend. In fact, in such a polluted aquatic environment with high BOD and SS concentrations, the photosynthesis of phytoplankton were active and increased the water pH in the warm season. The alkalization of river water was observed generally in midstream and downstream regions of Japanese main rivers and was attributed to the active biogenic activities, mainly primary algae production (Kiyono & Ishikawa, 1985). However, since its mechanism was complex and had not been explained quantitatively, in this study the data analysis was restricted mainly to the unpolluted water bodies. Here the criterion adopted for unpolluted river water was the annual mean BOD (or COD for lake) value should be less than 1 mg/litr. The records of the upstream river and lake water pH at 21 points were selected and an additional 6 moderately-polluted points in the middle stream was used for contradistinction to the unpolluted ones. In this selection the annual mean BOD was restricted to the range of 1 to 2 mg/litr.

Another important characteristic feature of the monthly pH variation detected was the sharp and strong spikes of the pH during the snow melting season in some rivers, typically in YOMASE-GAWA ( Fig. 5 (b)). It will be discussed later in section 4.2.3.

### **4.2.2 Long term trend of river and lake water pH**

Long term records of the annual mean pH at all 27 points were illustrated in Fig. 6(a). Regression analysis of the long term trend was made on these pH records and the results were presented in Table 2 (a). It was also done on the mean pH values in winter months to exclude the influences of photo phytoplankton activities, and the results were shown in Table 2 (b). In the regression analyses only the data within 3 $\sigma$  were used where  $\sigma$  was the standard deviation of the monitoring data. Out of these 27 points, a total of 14 points of which 12 are unpolluted points and 2 are moderately-polluted points, showed significant decrease in pH with 1 % risk at 10 points and 5 % risk at 4 points. The decrease was observed in the annual mean pH throughout the period at all points except one point, SUSOBANA-GAWA, where it was clearly seen only in the winter mean pH. These points were plotted in the geological map, Fig. 7, which indicated that 7 points were located in the northwestern part, 3 in the northeastern part, 3 in the central part and 1 in the southern part and thus the evidence of acidification was apparent all over Nagano prefecture. Therefore, it can be said that significant acidification had

occurred in more than half of the upstream rivers and lakes for these 30 years and had spread over the whole Nagano prefecture.



**Figure 6** Change of annual mean pH of river and lake water in the mountainous region in central Japan.

**Table 3** Regression analysis of annual mean pH values of river and lake water from 1972 to 1989

| Location      | Regression equation*1 | Slope          |            |            | Trend toward decline*3 | r*4  | Period | n  |
|---------------|-----------------------|----------------|------------|------------|------------------------|------|--------|----|
|               |                       | Lower 95% CI*2 | Upper CI*2 | 95%        |                        |      |        |    |
| Hime-kawa-1   | y = 7.45 - 0.038x     | -0.061         |            | -0.015 S** |                        | 0.70 | 75-'89 | 15 |
| Nakatsuna-ko  | y = 7.29 - 0.054x     | -0.081         |            | -0.027 S** |                        | 0.78 | 76-'89 | 14 |
| Hime-kawa-2   | y = 7.49 - 0.017x     | -0.041         |            | 0.007      |                        | 0.36 | 72-'89 | 18 |
| Aoki-ko       | y = 7.28 - 0.052x     | -0.082         |            | -0.022 S** |                        | 0.73 | 76-'89 | 14 |
| Takase-gawa-1 | y = 7.24 - 0.040x     | -0.070         |            | -0.010 S*  |                        | 0.66 | 77-'89 | 13 |

|             |                     |        |           |      |        |    |
|-------------|---------------------|--------|-----------|------|--------|----|
| Kizaki-ko-1 | $y = 7.26 - 0.022x$ | -0.043 | -0.001 S* | 0.49 | 72-'89 | 18 |
|-------------|---------------------|--------|-----------|------|--------|----|

\*1 y: pH, x: year - 1980

\*2 Confidence limit

\*3 S: Decrease in pH is significant (\* level of significance 0.05, \*\* level of significance 0.01)

\*4 Correlation coefficient

**Table 4 Regression analysis of annual mean pH values of river and lake water from 1990 to 2003**

| Location      | Regression equation* <sup>1</sup> | Slope                         |                               | Trend<br>toward<br>decline* <sup>3</sup> | r* <sup>4</sup> | Period | n  |
|---------------|-----------------------------------|-------------------------------|-------------------------------|--|-----------------|--------|----|
|               |                                   | Lower<br>95% CI* <sup>2</sup> | Upper<br>95% CI* <sup>2</sup> |  |                 |        |    |
| Hime-kawa-1   | y = 7.59 – 0.029x                 | –0.041                        | –0.016 S**                    |  | 0.82            | 90–’03 | 14 |
| Nakatsuna-ko  | y = 7.05 – 0.009x                 | –0.029                        | 0.011                         |  | 0.26            | 90–’03 | 14 |
| Hime-kawa-2   | y = 7.77 – 0.036x                 | –0.049                        | –0.023 S**                    |  | 0.86            | 90–’03 | 14 |
| Aoki-ko       | y = 7.04 – 0.006x                 | –0.025                        | 0.013                         |  | 0.20            | 90–’03 | 14 |
| Takase-gawa-1 | y = 7.20 – 0.016x                 | –0.034                        | 0.001 S <sup>†</sup>          |  | 0.51            | 90–’03 | 14 |
| Kizaki-ko-1   | y = 7.50 – 0.027x                 | –0.054                        | 0.001 S*                      |  | 0.52            | 90–’03 | 14 |

\*1 y: pH, x: year - 1980

\*2 Confidence limit

\*3 S: Decrease in pH is significant (<sup>†</sup> level of significance 0.1, \* level of significance 0.05, \*\* level of significance 0.01)

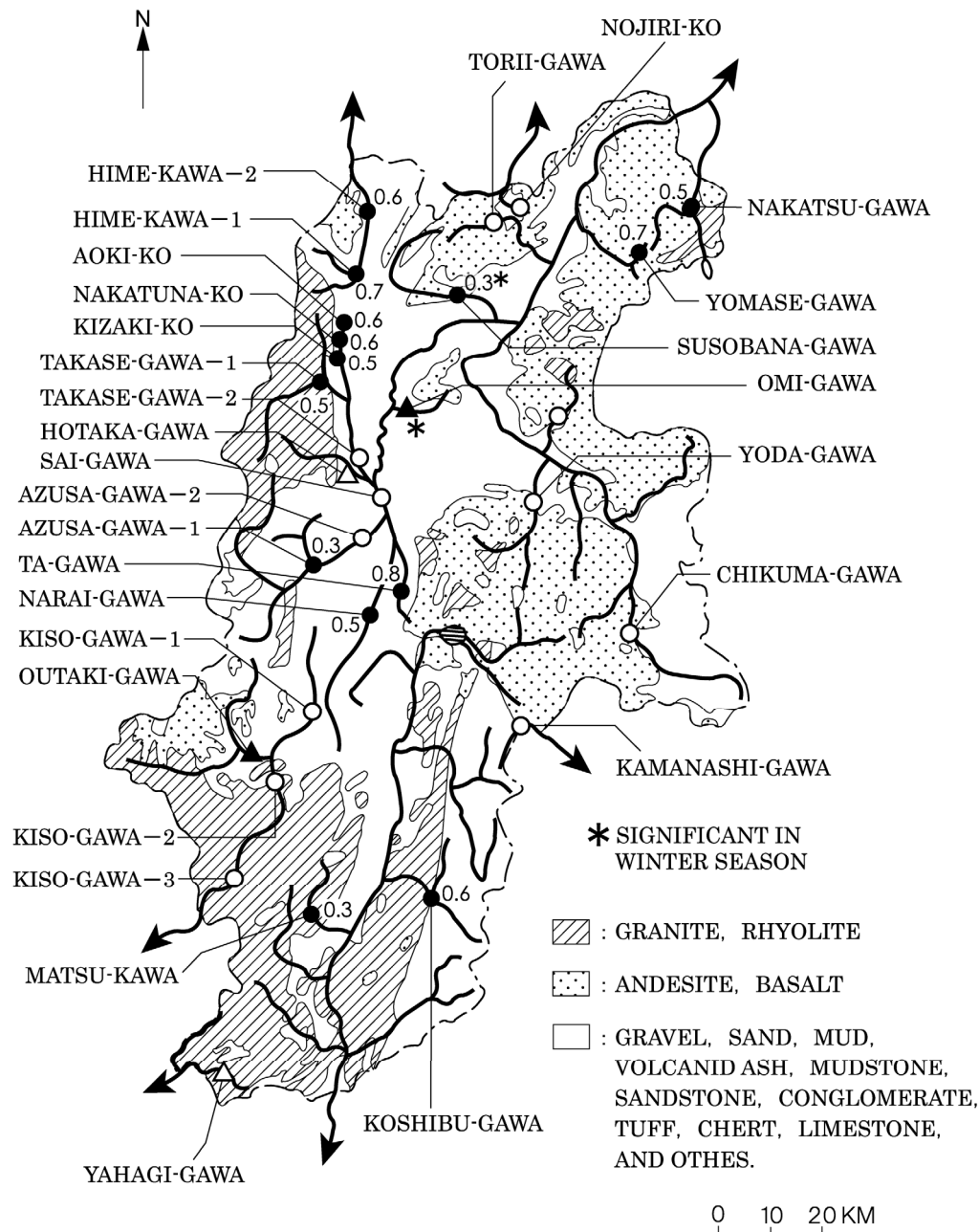
\*4 Correlation coefficient

As seen in Fig. 6(a), yearly variations of the pH were monotonic at many points, while anomalous low pH occurred at some points. In particular, at YODA-GAWA, CHIKUMA-GAWA, KAN-GAWA and YOMASE-GAWA, all of which are in the eastern part, drastic decrease of the pH occurred in the year 1990 and the streams only recovered after 4-5 years. Other two- or three-year anomalies were also seen in Fig. 6. A regression analysis was made using the data records from 6 points which showed significant acidification in the previous 30-year analysis for two periods, i.e., from 1972 to 1989 and from 1990 to 2003, and the results were listed in Tables 3 and 4. The analysis of the first 18 years period reproduced almost all the decreasing trend but the analysis of the next 14-year period just after the starting time of the pH anomaly was not conclusive. It indicated that the short term records, e.g., 10- or 15-year ones, which included large pH anomalies, were not sufficient to extract long term trends of the river and lake water pH, but the present 30-year record could give the long term trend with confidence.

#### 4.2.3 Long term pH decrease of river and lake water and its relationship to geological features

From the long term records, a decreasing trend in the annual mean or winter mean pH was detected at 14 points. The pH decrease in the past 30 years,  $\Delta\text{pH}$ , was calculated from the regression equation and presented in Table 2. It ranged from 0.3 to 0.8 and the average  $\Delta\text{pH}$  was 0.53. These  $\Delta\text{pH}$  values were inserted in the geological map, Fig. 7. It indicated that at 7 points in the northwestern part  $\Delta\text{pH}$  was quite large in the range of 0.5 and 0.7, at 3 points in the northeastern part  $\Delta\text{pH}$  was between 0.3 and 0.7, at 3 points in the central part  $\Delta\text{pH}$  was between 0.3 and 0.8 and at one point in the southern part  $\Delta\text{pH}$  was 0.3.





**Figure 7** Geological map (Geological Survey of Japan, 1987) of Nagano Prefecture and decrease of pH of river and lake water in the 30 years. Black circles denote points where the decrease of pH was significant, and open circles denote points where the decrease of pH was insignificant (level of significance  $\alpha=0.01$  or  $0.05$ ). Figures denote decrease of pH in the 30 years. Black triangles denote short-term monitoring points where the decrease of pH was insignificant (level of significance  $\alpha=0.05$  or  $0.1$ ).

As seen in the geological map, Fig. 7, these points where acidification was occurring were situated mainly in the acidic bed-rock areas that consisted of granite and rhyolite or just downstream of them. It indicated strong relationship existed between the river and lake water acidification and acidic bed-rock with low acid neutralizing or buffering capacity, as suggested by Wright *et al.* (1976) and Watt *et al.* (1983). However, at

3 points in the central part, namely, AZUSA-GAWA-2, TAKASE-GAWA-2 and SAIGAWA, the water acidification trend was not significant, although it had occurred upstream. It was considered that this could be due to water pollution since these points were located in basins (Fig. 1) with populated middle-sized urban areas.

In the southern part of Nagano prefecture the prevailing bed-rock was granite or rhyolite with low neutralizing capacity. However, the acidification trend was detected only at one point, This was due to the sparse distribution of the observation points. In fact, there were additional 2 points in OUTAKI-GAWA and YAHAGI-GAWA rivers where the water quality observation started from 1995. However, the 3 points along the KISO-GAWA river did not show any acidification. The reason was not clear but it is suspected to be due to the water pollution upstream along with the lower acid deposition in the southern part as described before. Therefore it may be concluded that significant long term acidification of the upstream rivers and lakes is progressing in the acidic bed-rock areas and their surroundings in the whole Nagano prefecture.

Exceptions were YOMASE-GAWA and NARAI-GAWA rivers in the northern and central parts, respectively. Acidic bed-rock did not exist in their watersheds, but hot spring water flowed into the streams. Such hot spring inflow caused low alkalinity in the river water. The relationship of water acidification with water alkalinity will be discussed in section 4.2.5.

#### **4.2.4. pH in acidified river and lakes**

The effects of acidic environment on aquatic organisms are well known from the experiences in Northern Europe and America, as introduced in the report of the Swedish Ministry of Agriculture and Environment Committee (1982). These effects on aquatic organisms, mainly on crustacean and upstream water fishes like salmon, char and trout begin to appear when the water is slightly-acidic. In particular, under slightly-acidic conditions abnormal oviposition behavior could be observed in salmon .

Using data from 14 points where statistically significant acidification was progressing, the water pH values in the year of 2003 were calculated from the regression equation and listed in Table 2 . It may be seen that all points had pH values less than 7.1 and would become acidic ( $\text{pH} < 7.0$ ) in a few years. The results indicated that more than a half of the unpolluted and moderately-polluted upstream rivers and lakes, i.e., 14 out of 27 points, were in the slightly-acidic state and show tendency to become more acidic. Such acidic state was observed at an EANET (Acid Deposition Monitoring Network in East Asia) monitoring site, Lake Ijira, in central Japan (MOEJ, 2004). In addition, this trend was also detected in lakes near the summit of Mt. Norikura in central Japan (Kawakami, 1998) and in rivers and dam-lakes in Gotoh Islands in Kyushu District (Mori *et al.*, 1999) and in Nara prefecture (Matsumoto *et al.*, 2003). Therefore, it can be said that acidification of the upstream rivers and lakes in Japan is already occurring in many places mainly in acidic bed-rock areas. Moreover the water pH in these places was already in the slightly-acidic state. These facts suggest the soil pH in these places are very low ( $\text{pH}$  4.5 - 4.1) and fraction of base cations absorbed on the soil particles for the cation exchange process, i.e., base saturation is also at very low level (Ulrich, 1983; Reuss, 1991). In fact, such low soil pH and base saturation were observed at the watershed of Lake Ijira nearby Nagano prefecture from the EANET soil and vegetation monitoring (Network Center for EANET, 2007). These facts raise concerns about high-concentration ionic aluminum species dissolved in the soil water and their effects on decline of plants (Ulrich, 1983). Thus, more attention should be paid on soil acidification, together with river and lake water acidification and their linkages, as well as their effects on aquatic organisms and plants.

#### **4.2.5. Relationship among water acidification, water alkalinity and acid deposition**

The relationship between water acidification and alkalinity has been investigated in the past four decades in North Europe and America. Based on the data from lakes in North America, Hendry *et al.* (1980) suggested that the sensitivity of water to acid deposition appeared in the range of alkalinity  $\text{alk} \leq 0.2$  meq/litr. The

alkalinity is the acid neutralizing or buffering capacity and is defined conceptually as the sum of base cations minus sum of strong acids, while many definitions have been proposed for it from methodological view points. In this paper it was defined simply by the  $\text{HCO}_3^-$  ion concentration, since the water pH was greater than 6 and so the  $\text{Al}^{2+}$  ion dissolved in the soil water might be precipitated when it drained into the stream water and its concentration in the stream water be small.

**Table 5 Relation among decrease of pH of river water, pH of precipitation, and alkalinity of river water ( $\text{HCO}_3^-$  concentration, inflow of hot spring water and influence of outflow of chemical fertilizer from farmland are quoted from Miyajima *et al.* (1996))**

| Location                    | Trend toward decline <sup>*1</sup> | pH at 2003 <sup>*2</sup> | Fall in pH in thirty years <sup>*2</sup> | pH of precipitation | E.C. mS/m | $\text{HCO}_3^-$ meq/l | Geologic composition <sup>*3</sup> | Inflow of hot spring water | Influence of fertilizer outflow |
|-----------------------------|------------------------------------|--------------------------|--|---------------------|-----------|------------------------|------------------------------------|----------------------------|---------------------------------|
| Hime-kawa-1                 | S**                                | 6.9                      | 0.7                                      | 4.8                 | 9.5       | 0.69                   | A                                  | ×                          | ×                               |
| Takase-gawa-1 <sup>*4</sup> | S**                                | 6.8                      | 0.5                                      | 4.8                 | 7.4       | 0.27                   | A                                  | ×                          | ×                               |
| Narai-gawa                  | S**                                | 7.1                      | 0.5                                      | 5.2                 | 6.1       | 0.42                   | O                                  | ×                          | ×                               |
| Yomase-gawa                 | S*                                 | 6.3                      | 0.7                                      | 5.0                 | 12.1      | 0.11                   | O                                  | ○                          | ×                               |
| Nakatsu-gawa                | S**                                | 6.6                      | 0.5                                      | 5.1                 | 5.8       | 0.12                   | A, O                               | ○                          | ×                               |
| Azusa-gawa-1                | S**                                | 7.0                      | 0.3                                      | 5.2                 | 5.0       | 0.33                   | A, O                               | ×                          | ×                               |
| Matsu-kawa                  | S*                                 | 6.9                      | 0.3                                      | 5.0                 | 3.9       | 0.25                   | A                                  | ×                          | ×                               |
| Kan-gawa                    |                                    | 6.8                      |  | 4.9                 | 12.8      | 0.76                   | A, O                               | ×                          | ○                               |
| Susobana-gawa               |                                    | 7.3                      |  | 4.8                 | 6.7       | 0.38                   | O                                  | ×                          | ×                               |
| Kamanashi-gawa              |                                    | 7.8                      |  | 5.2                 | 17.0      | 1.64                   | O                                  | ×                          | ×                               |
| Kiso-gawa-2                 |                                    | 7.2                      |  | 5.1                 | 5.6       | 0.29                   | A, O                               | ×                          | ×                               |
| Yoda-gawa                   |                                    | 7.5                      |  | 5.0                 | 8.0       | 0.38                   | O                                  | ×                          | ×                               |
| Torii-gawa                  |                                    | 7.5                      |  | 4.9                 | 6.2       | 0.48                   | O                                  | ×                          | ×                               |
| Kiso-gawa-1                 |                                    | 7.4                      |  | 5.2                 | 6.1       | 0.40                   | O                                  | ×                          | ×                               |
| Chikuma-gawa                |                                    | 7.6                      |  | 5.1                 | 7.6       | 0.45                   | O                                  | ×                          | ○                               |
| Koshibu-gawa                |                                    | 8.0                      |  | 5.1                 | 15.3      | 1.26                   | A, O                               | ×                          | ×                               |

<sup>\*1</sup> S: Decrease in pH is significant (\* level of significance 0.05, \*\* level of significance 0.01)

<sup>\*2</sup> Estimated from regression equations

<sup>\*3</sup> A: Acidic rock, O: Other than acidic rock

<sup>\*4</sup> The concentration of  $\text{HCO}_3^-$  became less than 0.2meq/l occurred in cases of large precipitation amount.

The alkalinity of stream water in Japan has not been measured extensively as a routine monitoring item and its information is not sufficient, but Miyajima *et al.* (1996) made alkalinity and electric conductivity measurements in 19 upstream rivers in Nagano prefecture. These results were compared with the water pH and its decrease  $\Delta\text{pH}$  in Table 5, together with the geological and inflow conditions. Those values shown were from one-time measurements in May-July 1993 or September-October 1993, except for TAKASE-GAWA-1 and HIME-KAWA-1 rivers. For these two rivers, measurements were made once a month and the values listed in Table 5 were the annual means.

Five points showed an acidification trend with significance level  $p < 0.01$  and 2 points with  $p < 0.05$ . Of these 7 points, 2 points, YOMASE-GAWA and NAKATSU-GAWA, recorded alkalinities of 0.11 and 0.12 respectively, which are lower than the critical value  $\text{alk} = 0.2$  meq/litr (Hendrey *et al.*, 1980), and thus they indicated high sensitivity of river and lake water to acid deposition. These two points were influenced largely by hot spring inflow. However, the low alkalinity suggested high sensitivity not only to acid deposition but also to the other acid inflow events. In fact, the so-called acid shock occurred in YOMASE-GAWA in the snow-melting period. It was clearly seen in Fig. 5(b) in which low pH spikes down to pH 5.0 appeared. Moreover, it occurred almost every year after 1991, while it was observed only two times before 1990. Such an acid shock

was not recorded in the NAKATSU-GAWA river as water quality monitoring was not carried out in winter and early spring, but it might have occurred in this river since it is located nearby YOMASE-GAWA and is at very low alkalinity levels.

As shown in Table 5, other 4 acidifying rivers had alkalinities in the range of 0.25-0.42 meq/litr and another point had 0.69, which were all larger than the Hendrey's critical value, but they showed significant water acidification. Since those alkalinities were from one-time measurement except for TAKASE-GAWA and HIME-KAWA, this result should be treated with care. In fact, such low alkalinities  $\text{alk} < 0.2$  meq/litr were occasionally observed in TAKASE-GAWA in the once-a-month measurements differing from the values listed in Table 5 which were the annual means and showed alkalinities higher than 0.2 meq/litr.

Strong relationship between the long term water acidification and the alkalinity were also detected in other places in Japan. Mori *et al.* (1999) reported the ICHINO-KAWA river in the granite bed-rock area in Gotoh-islands had long term acidification trend and its alkalinity was less than the Hendrey's critical value,  $\text{alk} = 0.2$  meq/litr. In addition they showed the high sensitivity to acid deposition by means of a stepwise acid-buffering test (Satake *et al.*, 1998, Satake 2003). Matsumoto *et al.* (2003) also suggested that the significant acidification in the FUKAYA-GAWA river and SAKAMOTO-KO in Nara prefecture were associated with  $\text{alk} < 0.2$  meq/litr and electric conductivity  $< 5$  mS/m, and confirmed the high sensitivity to acid deposition by the stepwise acid-buffering test. These two works supported the applicability of the Hendrey's critical alkalinity,  $\text{alk} = 0.2$  meq/litr as a suitable index for water sensitivity to acid deposition.

However, almost all the acidification of the river and lake water in Nagano prefecture had progressed at low but higher alkalinities than the Hendrey's critical value in North America. The reason for this fact is not clear at present. However, the EANET soil monitoring carried out at Ijira site nearby Nagano prefecture showed that the major differences from North American and European soils were that larger amount of cation was supplied from the higher cation exchange capacity (Network Center for EANET, 2007) and from the higher weathering rate of the soil (Ohte *et al.*, 2001), although a large portion of cation exchange sites on the soil particle surface had been consumed by the integrated acid deposition effects. These countervailing effects might have caused the water acidification at low but larger alkalinities than the Hendrey's critical value. However, more detailed studies should be done on the geological and physical-chemical and biological processes of acid deposition in the soils in relation to the climatological and hydrological conditions.

As seen in Table 5, the long term acidification of water by acid deposition did not occur in rivers in the same range of low alkalinity which are outside the acidic bed-rock areas. Thus, it can be said that water acidification by acid deposition or by acid inflow events occurred at the water alkalinities lower than Hendrey's critical value  $\text{alk} = 0.2$  meq/litr and also at the water alkalinities that are low but higher than Hendrey's critical value  $\text{alk} = 0.2$  meq/litr when the watershed is in the acidic bed-rock areas. Low alkalinity and acidic bed-rock conditions are related to each other but both these two conditions are necessary for long term acidification to occur if the water alkalinities are relatively low but higher than 0.2 meq/litr.

## 5. Conclusion

Long term acidification of the upstream river and lake water in central Japan was investigated in relation to the acid deposition, by using 32-year (1972-2003) monthly records of water pH, together with long term records of air quality and acid deposition. From the 79 water monitoring points in the whole Nagano prefecture (area 13600 km<sup>2</sup>), 21 monitoring points were selected as unpolluted ones on the basis of a criterion of BOD or COD being less than 1 mg/liter, and additional 6 points were selected as moderately-polluted ones based on BOD or COD ranging between 1- 3 mg/liter. In total 27 sets of water pH records were analyzed statistically, along with the long term records of air quality and acid deposition at 21 air pollution monitoring sites, and the

long term trend of water acidification and its relationship with the acid deposition and geological and geographical features were discussed.

The precipitation was acidic in the range of pH between 4.8 and 5.3, and it was observed that the precipitation pH, as well as the wet- and dry- deposition of acidic species remained almost at the same levels for those 32 years. The spatial distribution and seasonal variation of the acidic species were influenced mainly by the transboundary transport from the Asian continent in winter and by the long-range transport from Tokyo metropolitan area and Nagoya industrial area in summer, in addition to the so-called yellow sand (the Asian dust) storms in springtime.

The river and lake water pH values at 14 points out of the 27 points showed a significant decreasing trend,  $\Delta\text{pH}$  ranging from 0.3 to 0.7 (10 points with the significance level  $p < 0.01$  and 4 points with  $p < 0.05$ ) in these 30 years, and thus it can be concluded that more than a half of the unpolluted and moderately-polluted rivers and lakes in the prefecture had been acidified. Moreover, the water pH in those acidifying rivers and lakes estimated for the year 2003 was almost in the slightly acidic state with a minimum pH of 6.3. These acidifying rivers and lakes were situated mainly in the acidic bed-rock areas consisting of granite and rhyolite that extended over the whole Nagano prefecture.

Close relationships of the water acidification with the water alkalinity were identified. Firstly, in the case of short term acidification, the low alkalinity is the cause of the so-called acid shock. This was observed in the snow-melting period in a river with very low water alkalinity  $\text{alk} = 0.11$  meq/litr. Low pH spikes down to pH 5.0 appeared in the pH record with an annual mean pH between 6.3-6.5. Moreover, it occurred almost every year after 1991, while it was recorded only two times before 1990. The alkalinity was lower than the critical value  $\text{alk} = 0.2$  meq/litr proposed by Hendrey *et al.* 1980 as an index for high sensitivity of water to acid deposition. Although the low alkalinity was mainly attributed to the large hot spring water inflow, the resulting high sensitivity of water is related not only to acid deposition but also to the other acid inflow events.

Secondly, it was observed that the long term water acidification by acid deposition also occurred at water alkalinities below Hendrey's critical value  $\text{alk} = 0.2$  meq/litr. Moreover, it was found that acidification occurred at low alkalinities which are higher than the Hendreys' critical value  $\text{alk} = 0.2$  meq/litr if the watershed is in the acidic bed-rock areas. Low alkalinity and acidic bed-rock conditions are related to each other, but when the water alkalinities are low but larger than 0.2 meq/litr, both of these conditions are necessary for long term acidification to occur. The acidification did not occur in rivers in the same range of low alkalinity but located outside the acidic bed-rock areas. The reason for this is not clear at present and more detailed study should be done on the geological and physical-chemical and biological processes of acid deposition in the soils in relation to the climatological and hydrological conditions.

## References

- Carmichael, G.R., Chang, Y.-S., Ravishanker, B.S., Kurita, H. & Ueda, H. 1990. Acid deposition in central Japan, *Atmos. Environment*, 24A: 2035-2049.
- Chang, Y.-S., Carmichael, G.R., Kurita, H. & Ueda, H. 1989. The transport and formation of sulfates and nitrates in central Japan, *Atmos. Environment*, 23: 1749-1773.
- Ebise, S. 1996. Estimation on effect of acid rain by observation of mountainous river waters during dry-weather day and storm event in Yakushima Island. *Environ. Science*, 9: 377-391 (in Japanese).
- Environment and Nature Conservation Div. of Nagano Prefectural Government (1973-2004). Annual Report of Air Pollution Monitoring Data in Nagano Prefecture (in Japanese).
- Environment and Nature Conservation Div. of Nagano Prefectural Government (1973-2004). Annual Report of Water Monitoring Data in Nagano Prefecture (in Japanese).



- Geological Survey of Japan 1987. 1:1,000,000 Geological Map of Japan. Geological Atlas of Japan (1982). Second Printing.
- Hendrey, G. R., Galloway, J. N., Norton, S. A., Schofield, C.L., Shaffer, P. W. & Burns, D. A. 1980. Geological and hydrochemical sensitivity of the Eastern United States to acid precipitation. EPA-600/3-80-024.
- Katsuno, T., Miyajima, I. & Shiozawa, K. 1998. Short-term effects of acid rain on mountain stream water in the granite southern area of Nagano prefecture. *Environmental Science*, 11: 131-138 (in Japanese).
- Kawakami, T. 1998. Modeling the effects of acid rain on lake Tsurugaike in the Mt. Norikura Alpine Area. *Environmental Science* 11: 65-76 (in Japanese).
- Kitada, T., Igarasi, K. & Owada, M. 1986. Numerical analysis of air pollution in a combined field of land/sea breeze and mountain/valley wind. *J. Climate and Appl. Meteorol.* 25: 767-784.
- Kiyono, M. & Ishikawa Y. 1985. Overview of river/lake water quality and limnological studies on volcanic inorganic acid lakes in Japan – Relation to the effects of acid deposition –. Report of Central Research Institute of Electric Power Industry, No. 484016, pp.14 (in Japanese).
- Kurita, H., Hori, J., Hamada, Y. & Ueda, H. 1993. Decrease of pH of river and lake water in mountainous region in central Japan and its relation to acid rain. *J. Japan Soc. Air Pollut.* 28, 308-315 (in Japanese).
- Kurita, H., Sasaki, K., Muroga, H., Ueda, H. & Wakamatsu, S. 1985. long-range transport of air pollution under light gradient wind conditions. *J. Climate and Appl. Meteorol.* 24: 425-434.
- Kurita, H. & Ueda, H. 1990. Combination of local wind system under light gradient wind conditions and its contribution to the long-range transport of air pollutants. *J. Applied Meteorology* 29: 331-348.
- Leivestad, H., Muniz, I. P. 1976. Fish kill at low pH in a Norwegian river. *Nature* 259: 391-392.
- Matsumoto, M., Asano, K., Ujike, E. & Kitada, Y. 2003. Investigation of acidification of dam lakes in Nara prefecture, *Environmental Conservation Engineering*, 32: 318-327 (in Japanese).
- Ministry of Environment, Japan (MOEJ) 1983. Map for assessing susceptibility of Japanese soils to acid precipitation 1:4,000,000.
- Ministry of Environment, Japan (MOEJ) 2004. Report of Japanese Acid deposition Survey.
- Miyajima, I., Katsuno, T., Takeda, Y. & Shiozawa, K. 1996. Survey of river water acidification in Nagano prefecture. *Bulletin of the Nagano Research Institute for Health and Pollution*, 19: 49-56 (in Japanese).
- Miyanaga, Y. & Ikeda, H. 1994. A review of surface water acidification and its prediction method. *J. Japan Society on Water Environment*, 17: 787-794 (in Japanese).
- Mori, A. & Honda, K. 1999. Effects of acid precipitation on rivers in Nagasaki prefecture. *Annual Report of Nagasaki Prefectural Institute of Public Health and Environmental Sciences*, 45: 71-74 (in Japanese).
- Network Center for EANET, 2007. Acid Deposition Monitoring Network in East Asia, Data Report 2006. Acid Deposition and Oxidant Research Center, Niigata, Japan.
- Ohizumi, T., Fukuzaki, N., Moriyama, N., Urushiyama, Y. & Kusakabe, M. 1991. Source of sulfur in the atmospheric deposits in view of sulfur isotopic variations – A case study in Niigata prefecture, Japan –. *Nippon Kagaku Kaishi* (Journal of the Chemical Society of Japan, Chemistry and Industrial Chemistry), 1991: 675-681 (in Japanese).
- Ohte, N., Tokuchi, N., Shibata, H., Tsujimura, M., Tanaka, T. & Mitchell, M.J. 2001. Hydrobiogeochemistry of forest ecosystems in Japan: major themes and research issues. *Hydrol. Process.* 15: 1771-1789.
- Reuss, J. O. 1991. The transfer of acidity from soils to surface waters, in 'Soil Acidity', ed. by B. Ulrich and M.E. Summer, Springer-Verlag, Berlin, pp.201-217.
- Sasaki, K., Kurita, H., Carmichael, G. R., Chang, Y. -S., Murano K. & Ueda, H. 1988. Behavior of sulfate, nitrate and other pollutants in the long-range transport of air pollution. *Atmospheric Environment*, 22: 1301-1308.

- Satake, K. 2003: Analysis of Environmental samples for acid Pollution Research, AICHI Shuppan Co., Tokyo, pp.81-91 (in Japanese).
- Satake, K., Inoue, T., Kasasaku, K., Nagafuchi, O. & Nakano, T. 1998. Monitoring of nitrogen compounds on Yakushima Island, a world natural heritage site. *Environmental Pollution*, 102: S1, 107-113 (in Japanese)
- Swedish Ministry of Agriculture and Environment 1982. Report of the Swedish Ministry of Agriculture and Environment Committee (1982).
- Terada, H., Ueda, H. & Wang, Z. 2002. Trend of acid rain and neutralization by yellow-sand in East Asia – A numerical study –, *Atmospheric Environment*, 36, 503-509.
- Toriyama, S., Shimada, H., Arakawa, H., Takata T. & Tohezou, Y. 1991. Precipitation chemistry in Toyama, Japan.19 *Nippon Kagaku Kaishi* (Journal of the Chemical Society of Japan, Chemistry and Industrial Chemistry) 1991: 682-689 (in Japanese)
- Ueda, H., Takemoto, T., Kim, Y.P. & Sha, W. 2000. Behavior of volatile inorganic components in urban aerosols. *Atmospheric Environment*, 34: 353-361.
- Ulrich, R. 1983., in 'Effects of Accumulation of Air Pollutants in Forest Ecosystems', eds. by B. Ulrich and J. Pankrath, Kluwer Academic Publication, Dordrecht.
- Yamaguchi, K., Tateno, T., Tanaka, F., Nakao, M. & Gomyoda M. 1991. An analysis of precipitation chemistry measurements in Shimane, Japan. *Atmospheric Environment*, 25A: 285-291
- Watt, W. D., Scott, C. D. & White, W. J. 1983. Evidence of acidification of some Nova Scotia Rivers and its impact on Atlantic Salmon. *Canadian Journal of Fisheries and Aquatic Sciences*, 40: 462-473.
- Wright, R. F., Dale, T., Gjessing, E. R., Hendrey, G., Henriksen, A., Johannessen, M. & Muniz, I. P. 1976. Impact of acid precipitation on freshwater ecosystems in Norway. *Water, Air, Soil & Pollution*, 6: 483-499.

***Abstracts of Published Papers related to  
EANET***



## **Establishing an Acid Deposition Monitoring Network in East Asia**

Masaharu Yagishita

*Ministry of the Environment, Japan*

Acid deposition is widely recognized as one of the most serious international atmospheric pollution problems. East Asian countries are currently experiencing acid deposition and have only recently begun expanding domestic research and monitoring activities. However, acid deposition is not only a domestic but also a transboundary problem. In addressing the transboundary aspect, cooperative and collaborative action will be essential. The Environment Agency of Japan is advocating the need to establish an acid deposition monitoring network in East Asia. Therefore, it is sponsoring three "Expert Meetings on Acid precipitation Monitoring Network in East Asia" between 1993 and 1995. The meetings are attended by both scientific researchers and government officials from numerous East Asian countries. At the administrative and scientific discussions of the first two meetings a consensus on the desirability of establishing a monitoring network in East Asia was obtained and a preliminary technical guideline manual for monitoring acid deposition was adopted. By the end of the third meeting it is hoped that a basic consensus can be reached on a framework for an East Asian acid deposition monitoring network. It is essential to establish such a network in order to evaluate the present state of acid deposition in the region and to reach a common scientific understanding on the acid deposition problem. This is a vital step toward promoting international cooperation on the issue.

## **Model Intercomparison Study of Long Range Transport and Sulfur Deposition in East Asia (MICS-ASIA)**

Gregory R. Carmichael<sup>1)</sup>, Hiroshi Hayami<sup>2)</sup>, Giuseppe Calori<sup>1)</sup>, Itsushi Uno<sup>3)</sup>, Seog-Yeon Cho<sup>4)</sup>, Magnuz Engardt<sup>5)</sup>, Seung-Bum Kim<sup>6)</sup>, Yoichi Ichikawa<sup>2)</sup>, Yukoh Ikeda<sup>7)</sup>, Hiromasa Ueda<sup>8)</sup> and Markus Amann<sup>9)</sup>

<sup>1)</sup> *Center for Global and Regional Environmental Research, University of Iowa, USA*

<sup>2)</sup> *Central Research Institute of Electric Power Industry, Japan*

<sup>3)</sup> *Research Institute for Applied Mechanics, Kyushu University, Japan*

<sup>4)</sup> *Dept. of Environmental Engineering, Inha University, Korea*

<sup>5)</sup> *Swedish Meteorological and Hydrological Institute, Sweden*

<sup>6)</sup> *Dept. of Atmospheric Sciences, Yonsei University, Korea*

<sup>7)</sup> *Osaka Prefecture University, Japan*

<sup>8)</sup> *Disaster Prevention Research Center, Kyoto University, Japan*

<sup>9)</sup> *International Institute for Applied Systems Analysis, Austria*

To help improve the use of models in science & policy analysis in Asia it is necessary to have a better understanding of model performance and uncertainties. Towards this goal an intercomparison exercise has been initiated as a collaborative study of scientists interested in long-range transport in East Asia. An overview of this study is presented in this paper. The study consists of a set of prescribed test calculations with carefully controlled experiments. Models used the same domain, emission inventory, model parameters, meteorological conditions, etc. Two periods (January and May 1993) were selected to reflect long-range transport conditions under two distinct seasons. During these periods measurements of sulfur concentrations and deposition were made throughout the study region using identical sampling and analysis protocols. The intercomparison activity consists of four tasks (Blind Test, Fixed Parameter Test, Source Receptor test, and Tuning Test). All participants were asked to do Task A, and as many of the other tasks as possible. To date seven different models have participated in this study. Results and key findings are presented.

## **Step-by-Step Approach to Establish Acid Deposition Monitoring Network in East Asia (EANET): Thailand's Experiences**

Supat Wangwongwatana

*Pollution Control Department (PCD), Thailand*

Recognizing the adverse effects of acid deposition and its transboundary nature, efforts have been made for the past six years by countries in the East Asian region to establish acid deposition monitoring network in the region by taking a step-by-step approach towards the formal establishment. The First Intergovernmental Meeting held in March 1998 agreed as the first step to implement preparatory-phase activities for two years with the aim to officially establish the EANET in the year 2000. With the successful implementation of the preparatory-phase activities, the Second Intergovernmental Meeting held in October 2000 subsequently agreed to start the activities of the EANET on a regular basis from January 2001.

Thailand developed and carried out the national monitoring plan for the preparatory-phase activities through the cooperation of various agencies. Four monitoring sites were included in the preparatory-phase activities of the EANET. Monitoring capacity in Thailand has been gradually built during the preparatory-phase and Thailand is now ready to start monitoring activities of the EANET on a regular basis.

Efforts should be continued to study the complex nature of acid deposition phenomena, to quantify the adverse environmental impacts of acid deposition, and to eventually reduce emissions of acid precursors. Strong supports from international and regional organizations are essential for effective implementation of the EANET activities and to address acid deposition problem in the East Asian region.

## **Quality Control and its Constraints during the Preparatory-phase Activities of the Acid Deposition Monitoring Network in East Asia (EANET)**

Tsunehiko Otoshi, Norio Fukuzaki, Hu Li, Hiroshi Hoshino,  
Hiroyuki Sase, Masashi Saito and Katsunori Suzuki  
*Acid Deposition and Oxidant Research Center (ADORC), Japan*

Participating countries of the Acid Deposition Monitoring Network in East Asia (EANET) launched the preparatory-phase activities from April 1998. For the recognition and improvement of the analytical precision and accuracy, the Interim Network Center (INC) carried out the inter-laboratory comparison on the analysis of artificial rainwater samples and soil samples. Relevant laboratories submitted their analytical data to the INC for the evaluation. Submitted data were summarized and evaluated in terms of precision and accuracy, and were compared with the Data Quality Objectives (DQOs) of EANET. These inter-laboratory comparisons made clear the present conditions of laboratories as well as the major constraints that should be solved in the future.

## **The MICS-Asia Study: Model Intercomparison of Long-Range Transport and Sulfur Deposition in East Asia**

Gregory R. Carmichael<sup>1)</sup>, Giuseppe Calori<sup>1)</sup>, Hiroshi Hayami<sup>2)</sup>, Itsushi Uno<sup>3)</sup>, Seog-Yeon Cho<sup>1)</sup>, Magnuz Engardt<sup>4)</sup>, Seung-Bum Kim<sup>5)</sup>, Yoichi Ichikawa<sup>2)</sup>, Yukoh Ikeda<sup>6)</sup>, Jung-Hun Woo<sup>1)</sup>, Hiromasa Ueda<sup>7)</sup> and Markus Amann<sup>8)</sup>

<sup>1)</sup> *Center for Global and Regional Environmental Research, University of Iowa, USA*

<sup>2)</sup> *Central Research Institute of Electric Power Industry, Japan*

<sup>3)</sup> *Research Institute for Applied Mechanics, Kyushu University, Japan*

<sup>4)</sup> *Swedish Meteorological and Hydrological Institute, Sweden*

<sup>5)</sup> *Department of Atmospheric Sciences, Yonsei University, South Korea*

<sup>6)</sup> *Osaka Prefecture University, Japan*

<sup>7)</sup> *Disaster Prevention Research Center, Kyoto University, Japan*

<sup>8)</sup> *International Institute for Applied Systems Analysis, Austria*

An intercomparison study involving eight long-range transport models for sulfur deposition in East Asia has been initiated. The participating models included Eulerian and Lagrangian frameworks, with a wide variety of vertical resolutions and numerical approaches. Results from this study, in which models used common data sets for emissions, meteorology, and dry, wet and chemical conversion rates, are reported and discussed. Model results for sulfur dioxide and sulfate concentrations, wet deposition amounts, for the period January and May 1993, are compared with observed quantities at 18 surface sites in East Asia. At many sites the ensemble of models is found to have high skill in predicting observed quantities. At other sites all models show poor predictive capabilities. Source–receptor relationships estimated by the models are also compared. The models show a high degree of consistency in identifying the main source–receptor relationships, as well as in the relative contributions of wet/dry pathways for removal. But at some locations estimated deposition amounts can vary by a factor of 5. The influence of model structure and parameters on model performance is discussed. The main factors determining the deposition fields are the emissions and underlying meteorological fields. Model structure in terms of vertical resolution is found to be more important than the parameterizations used for chemical conversion and removal, as these processes are highly coupled and often work in compensating directions.

## **Simulations of Monthly Mean Nitrate Concentrations in Precipitation over East Asia**

Junling An<sup>1),2)</sup>, Hiromasa Ueda<sup>3)</sup>, Zifa Wang<sup>2),4)</sup>, Kazuhide Matsuda<sup>1)</sup>,  
Mizuo Kajino<sup>3)</sup> and Xinjin Cheng<sup>2)</sup>

<sup>1)</sup> *Acid Deposition and Oxidant Research Center (ADORC), Japan*

<sup>2)</sup> *Institute of Atmospheric Physics, Chinese Academy of Sciences, China*

<sup>3)</sup> *Disaster Prevention Research Institute, Kyoto University, Japan*

<sup>4)</sup> *Frontier Research System for Global Change-IGCR, Japan*

Monthly mean nitrate concentrations in precipitation over East Asia (10-55 degrees N, 75-155 degrees E) in April, July, September, and December of 1999 were simulated by using a regional air quality Eulerian model (RAQM) with meteorological fields four times per day taken from National Centers for Environmental Prediction. The distribution of the nitrate concentration in precipitation depends significantly on the emission patterns of nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) and volatile organic compound (VOC) and seasonal precipitation variability. The downward trend is also revealed, particularly in July and December. Highest concentrations are found in the industrialized regions, i.e., the coastal area of the Mainland of China, the Bay of the Huanghai Sea and the Bohai Sea, Korea, and Southern Japan. Long-range transport may cause elevated concentrations in remote areas downwind of the industrialized regions under favorable meteorological conditions, e.g., low precipitation. Comparison of observations and simulations indicates that the RAQM model reasonably predicts synoptic-scale changes in different months (seasons) and simulated nitrate levels in 4 months fit observed data with the discrepancy within a factor of 2. Exclusion of liquid chemistry within clouds is feasible for regional (1degrees x 1degrees) and long-term (monthly) nitrate simulations. The uncertainty originates mainly from that of the emission data and modeled precipitation amounts and initial and boundary conditions.

## **Neutralization of Soil Aerosol and its Impact on the Distribution of Acid Rain over East Asia: Observations and Model Results**

Zifa Wang, Hajime Akimoto and Itsushi Uno

*Frontier Research System for Global Change-IGCR, Japan*

A comprehensive Air Quality Prediction Modeling System is applied to simulate the pH values in precipitation and to investigate neutralization by soil aerosols and their influence on the distribution of acid rain over east Asia. A modified deflation module is designed to provide explicit information on the soil aerosol loading. Numerical simulation was performed for 1 year, from 15 December 1998 to 31 December 1999. Wet deposition monitoring data at 17 sites of the Acid Deposition Monitoring Network in east Asia in addition to State Environmental Protection Agency data were used to evaluate the model, and a reasonable agreement was obtained. Observed evidence clearly shows that in northern China acid deposition is heavily influenced and buffered by natural soil dust from desert and semiarid areas. The observed mean rainwater pH value in northern China is the highest, between 6.0 and 7.2, while in southern China, where many areas severely impacted by acid precipitation are located, the pH value is much lower, between 3.5 and 5. In Japan the mean pH value is 4.7, significantly higher than that in southern China, while in South Korea the pH value is intermediate between those in northern China and Japan. The model is capable of reproducing this geographical distribution of rainwater pH over east Asia. The simulation results for 1999 demonstrated strong neutralization of precipitation by soil aerosols over northeast Asia, and the distribution pattern of acid rain was also altered. The annual mean pH values in northern China and Korea show a remarkable increase of 0.8-2.5, while the increase in mean pH values over southern China and Japan are less than 0.1. The neutralization effects vary by season, with the greatest influence in spring, when pH values increased by 0.1-0.4 in Japan, 0.5-1.5 in Korea, and more than 2 in northern China.

## **Simulated Impacts of SO<sub>2</sub> Emissions from the Miyake Volcano on Concentration and Deposition of Sulfur Oxides in September and October of 2000**

**Junling An, Hiromasa Ueda, Kazuhide Matsuda, Hisashi Hasome  
and Motokazu Iwata**

*Acid Deposition and Oxidant Research Center (ADORC), Japan*

A regional air quality Eulerian model was run for 2 months (September and October of 2000) with and without SO<sub>2</sub> emissions from the Miyake volcano to investigate effects of the changes in the volcanic emissions on SO<sub>2</sub> and sulfate concentrations and total sulfur deposition around the surrounding areas. Volcanic emissions were injected into different model layers in different proportions within the planetary boundary layer whereas the other emissions were released in the first model layer above the ground. Meteorological fields four times per day were taken from National Centers for Environmental Prediction (NCEP). Eight Japanese monitoring sites of EANET (Acid Deposition Monitoring Network in East Asia) were used for the model evaluation. Simulations indicate that emissions from the Miyake volcano lead to increases in SO<sub>2</sub>, and sulfate concentrations in the surrounding areas downwind in the PBL by up to 300% and 150%, respectively, and those in SO<sub>2</sub> levels in the area found similar to 390 km north away from the Miyake site in the free troposphere (FTR) by up to 120%. Total sulfur deposition amounts per month are also increased by up to 300%. Daily SO<sub>2</sub>, concentrations in different model layers display strong variability (10-450%) at sites significantly influenced by the volcano. Comparison shows that the RAQM model predicts daily SO<sub>2</sub> variations at relatively clean sites better than those at inland sites closer to volcanoes and the model well captures the timing of SO<sub>2</sub> peaks caused by great changes in SO<sub>2</sub> emissions from the Miyake volcano at most chosen sites and that monthly simulated sulfate concentrations in rainwater agree quite well with observations with the difference within a factor of 2. Improvement in spatial and temporal resolutions of meteorological data and removal of the uncertainty of other volcanic emissions may better simulations.



## **High-resolution Model Simulations of Anthropogenic Sulphate and Sulphur Dioxide in Southeast Asia**

Urban Siniarovina<sup>1)</sup> and Magnuz Engardt<sup>2)</sup>

<sup>1)</sup> *Malaysian Meteorological Service, Malaysia*

<sup>2)</sup> *Swedish Meteorological and Hydrological Institute, Sweden*

The Multiple-scale Atmospheric Transport and Chemical modeling system (MATCH)-driven by meteorological data from the ECMWF has been applied to a model domain covering Southeast Asia to complete a simulation extending over the full year of 2000. The current paper presents an evaluation of the model performance using archived chemical and meteorological data collected in the region during the year 2000. The calculated sulphate concentrations (on atmospheric aerosols and in precipitation) compare reasonably with observations while the atmospheric SO<sub>2</sub> mixing ratios show worse correspondence. This latter mismatch is attributed to local variations in the measured SO<sub>2</sub> concentrations that are not resolved in the regional model and possible miss-location of the emissions in our model. It can also be pointed out that different laboratories measuring SO<sub>2</sub> at the same site occasionally report SO<sub>2</sub> concentrations that differs by an order of magnitude or more.

The seasonal variations of the modeled species are less than initially expected but generally in accordance with the measurements available. Most of the Malaysian cities have comparatively low concentrations of sulphate in precipitation. This is supported both by the model results and by independent measurements. From the model simulations and the measurements, it is concluded that the sulphur deposition is still relatively low (i.e. < 0.5 g sulphur m<sup>-2</sup> year<sup>-1</sup>) in most of rural Malaysia. This is also the case in Myanmar, Laos, central Vietnam, Kampuchea and southern Thailand. The situation in the vicinity of the large cities in the region is, however, much worse and the deposition is similar, or larger, than estimated critical loads.

## **Ozone Dry Deposition above a Tropical Forest in the Dry Season in Northern Thailand**

Kazuhide Matsuda<sup>1)</sup>, Ichiro Watanabe<sup>2)</sup>, Vitsanu Wingpud<sup>3)</sup>, Phunsak  
Theramongkol<sup>3)</sup>, Pojanie Khummongkol<sup>4)</sup>, Supat Wangwongwatana<sup>3)</sup> and  
Tsumugu Totsuka<sup>1)</sup>

<sup>1)</sup> *Acid Deposition and Oxidant Research Center (ADORC), Japan*

<sup>2)</sup> *Japan Environmental Sanitation Center (JESC), Japan*

<sup>3)</sup> *Pollution Control Department (PCD), Thailand*

<sup>4)</sup> *King Mongkut's University of Technology (KMUTT), Thailand*

In order to investigate the ozone dry deposition above a tropical forest in Southeast Asia, the field experiments were performed in a flat deciduous (teak) forest in Mea Moh located in northern Thailand, in the dry season, from January to April 2002. The experimental period included both the leafless period and transitional period between lush and leafless. Ozone fluxes were obtained by coupling a UV photometric ozone monitor with an ultrasonic anemometer on the basis of the gradient method. Ozone concentrations exceeded 60 ppb on average in the afternoons during the experimental period. The ozone fluxes peak around noon. The daytime level of the fluxes in this study is relatively high compared with the fluxes from previous experiments over a tropical forest or a leafless deciduous forest in other regions. This high daytime flux level is mainly caused by the high concentrations in the dry season in Mae Moh. Median deposition velocities of ozone were  $0.32 \text{ cm s}^{-1}$  in daytime (6:00-17:00) and  $0.04 \text{ cm s}^{-1}$  in nighttime (18:00-5:00), respectively. The deposition velocities as well as the fluxes peak around noon. Observed surface resistances decreased in daytime. The surface resistances were found to be affected by aerodynamic process rather than stomatal process during the time from 10:00 to 2:00. Wesely's parameterization to infer surface resistance was examined to consider its applicability in the region. The observed surface resistance in the dry season is lower to the inferred surface resistance using the input resistances of transitional spring than using the input resistances of leafless seasons. This indicates that the parameterization of non-stomatal resistances needs modification above the teak forest in the dry season taking into account the influence of aerodynamic process and the specific conditions in northern Thailand.

## **Tree Decline and its Possible Causes around Mt. Bogdkhan in Mongolia**

Hiroyuki Sase<sup>1)</sup>, Bulgan Tumendemberel<sup>2)</sup>, Tseveen Batchuluun<sup>3)</sup>,  
Hideyuki Shimizu<sup>4)</sup> and Tsumugu Totsuka<sup>1)</sup>

<sup>1)</sup> *Acid Deposition and Oxidant Research Center (ADORC), Japan*

<sup>2)</sup> *Central Laboratory of Environmental Monitoring, Mongolia*

<sup>3)</sup> *National University of Mongolia, Department of Forestry, Mongolia*

<sup>4)</sup> *National Institute for Environmental Studies, Japan*

East Asian region consists of several climatic zones. Information on plant responses to acid deposition in respective climatic zones is essential for evaluating effect of acid deposition on vegetation. However, in most part of East Asia including the (semi-) arid zone, sensitivity and/or physiological response of plants to acid deposition have not been enough studied. A decline of larch trees (*Larix sibirica*) has been reported around the Bogdkhan Mountain near the city of Ulaanbaatar, Mongolia, and it has been suggested that air pollution derived from the thermal power plants was one of the possible causes. Surveys on air pollutants concentrations by passive samplers, field observations of tree decline and chemical properties of needles/soils were carried out in 2001 and 2003 at Bogdkhan Mountain in order to obtain information on relationship between air pollution and chemical/(eco-)physiological properties of plant and soil. Tree decline was observed not only on the slope facing the thermal power plant but also in reference forests because of insect attack. However, decline symptoms observed on the slope were different from those in the reference forests. In summer concentrations of all the monitored pollutants except O<sub>3</sub> were not high; less than 5 ppb (average concentration of two weeks), but O<sub>3</sub> concentration was relatively high (ca. 40 ppb). From autumn to winter, concentrations of NO<sub>x</sub> increased probably due to increasing of combustion of coal/wood in winter. Mean concentrations of SO<sub>2</sub> and O<sub>3</sub> during the sampling period of the year 2003 were higher at the sites on the slope than those at the other sites. In addition sulfur contents of larch needles were also higher on the slope than other sites. It was suggested that the slope facing the thermal power plant has received more negative effects than the other areas. Soil acidification due to acid deposition may hardly occur because of the high concentration of base cations; e.g. pH(H<sub>2</sub>O) > 5.8. exchangeable Ca > 22.6 cmol(+) / kg in sites on the slope. Direct effects of air pollution, especially effects of O<sub>3</sub>, should be considered as one of the possible causes for the tree decline on the slope as well as natural environmental factors such as insect attack.

## **Response to O<sub>3</sub> and SO<sub>2</sub> for Five Mongolian Semi-arid Plant Species**

Hideyuki Shimizu<sup>1)</sup>, Ping An<sup>1),2)</sup>, Yuanrun Zheng<sup>1)</sup>, Lijun Chen<sup>1)</sup>, Hiroyuki Sase<sup>3)</sup>, Tsumugu Totsuka<sup>3)</sup>, Bulgan Tumendemberel<sup>4)</sup> and Youbin Zheng<sup>1),5)</sup>

<sup>1)</sup> *National Institute for Environmental Studies, Japan*

<sup>2)</sup> *Global Environmental Forum, Japan*

<sup>3)</sup> *Acid Deposition and Oxidant Research Center (ADORC), Japan*

<sup>4)</sup> *Central Laboratory of Environmental Monitoring, Mongolia*

<sup>5)</sup> *Controlled Environmental System Research Facility, University of Guelph, Canada*

A regional air quality model (RAQM) has been developed and applied together with an aerosol model to investigate the states and characteristics of wet deposition in East Asia in December 2001. Model simulation is performed with monthly based emission inventory [Streets, D.G., Bond, T.C., Carmichael, G.R., Fernandes, S.D., Fu, Q., He, D., Klimont, Z., Nelson, S. M., Tsai, N.Y., Wang, M.Q., Woo, J.-H., Yarber, K.F., 2003. An inventory of gaseous and primary emissions in Asia in the year 2000. *Journal of Geophysical Research* 108(D21), 8809] and meteorological fields derived from MM5. Model results are compared with extensive monitoring data including relevant gaseous species and ions in precipitation. The validation demonstrates that this model system is able to represent most of the major physical and chemical processes involved in acid deposition and reproduces concentrations reasonably well, within a factor of 2 of observations in general. The study shows that the regions with pH less than 4.5 are mainly located in southwestern China, parts of the Yangtze Delta, the Yellow Sea and the Korean peninsula, indicating wide regions of acid precipitation in East Asia in wintertime. Japan islands mainly exhibit pH values of 4.5–5.0, whereas over wide areas of northern China, pH values are relatively high ( $\geq 5.0$ ) due to neutralization by alkaline materials such as calcium-laden particles and ammonia, which are more abundant in northern China than that in southern China. While acid rain over most of China is still characterized by sulfur-induced type, considerable areas of eastern China and the western Pacific Rim are found to be more affected by nitric acid than sulfuric acid in acidification of precipitation, which is supposed to result from a combined effect of variations in photochemistry and emission, suggesting the increasing importance of NO<sub>x</sub> emission in these regions.

## **Model Study on Acidifying Wet Deposition in East Asia During Wintertime**

Zhiwei Han<sup>1),2)</sup>, Hiromasa Ueda<sup>1)</sup> and Tatsuya Sakurai<sup>1)</sup>

<sup>1)</sup> *Acid Deposition and Oxidant Research Center (ADORC), Japan*

<sup>2)</sup> *Institute of Atmospheric Physics, Chinese Academy of Sciences, China*

Increasing air pollution level in Mongolia has caused great concerns in the stability of some of the semiarid grassland ecosystems. So far, there is not experimental datum available for assessing the effects of air pollutants on the native grass species in this region. In the present study, five Mongolian semiarid plant species (*Astragalus* spp., *Carex* spp., *Chamaeneria angustifolia*, *Polygonum alopecuroides* and *Sanguisorba officinalis*) were exposed to either O<sub>3</sub> (0.05 ppm average, 0.1 ppm maximum) or SO<sub>2</sub> (0.1 ppm constant) for 4 weeks in controlled environment chambers. To investigate the growth responses of these species to the two air pollutants, growth parameters such as leaf number, leaf area, biomass and root/shoot ratio were measured at the final harvest. Different species showed different sensitivities to the two air pollutants. O<sub>3</sub> significantly reduced leaf number of *Carex* spp., biomass and root/shoot ratio of *Polygonum alopecuroides*, root/shoot ratio of *Sanguisorba officinalis*, but had no effect on other growth parameters of these species or all the growth parameters of the other species. SO<sub>2</sub> significantly reduced leaf number and biomass of *Carex* spp., and had no effects on other growth parameters for this species and all the growth parameters of the rest of the four species.

## **Deposition Velocity of O<sub>3</sub> and SO<sub>2</sub> in the Dry and Wet Season above a Tropical Forest in Northern Thailand**

Kazuhide Matsuda<sup>1)</sup>, Ichiro Watanabe<sup>2)</sup>, Vitsanu Wingpud<sup>3)</sup>,  
Phunsak Theramongkol<sup>3)</sup> and Tsuyoshi Ohizumi<sup>4)</sup>

<sup>1)</sup> *Department of Environment Systems, Meisei University, Japan*

<sup>2)</sup> *Japan Environmental Sanitation Center (JESC), Japan*

<sup>3)</sup> *Pollution Control Department (PCD), Thailand*

<sup>4)</sup> *Acid Deposition and Oxidant Research Center (ADORC), Japan*

In order to investigate ozone (O<sub>3</sub>) and sulfur dioxide (SO<sub>2</sub>) dry deposition above a forest in a tropical savanna climate in Southeast Asia, field experiments were performed in a teak deciduous forest in Mea Moh, Lampang Province, located in northern Thailand. O<sub>3</sub> and SO<sub>2</sub> fluxes were observed on the basis of the aerodynamic gradient method. The experimental period from January to August in 2004 covered the dry (Jan-Apr) and wet (May-Aug) seasons. Both gas concentrations increased in the dry season and decreased in the wet season. Interval estimation of average with confidence interval of 95% on the deposition velocity data between 25 and 75 percentiles were performed. The intervals of average O<sub>3</sub> deposition velocity were estimated to be 0.37-0.39 cm s<sup>-1</sup> (daytime) and 0.12-0.13 cm s<sup>-1</sup> (nighttime) in the dry season; and 0.62-0.65 cm s<sup>-1</sup> (daytime) and 0.25-0.27 cm s<sup>-1</sup> (nighttime) in the wet season. The intervals of average SO<sub>2</sub> deposition velocity were estimated to be 0.10-0.31 cm s<sup>-1</sup> (daytime) and 0.08-0.11 cm s<sup>-1</sup> (nighttime) in the dry season; and 0.95-1.39 cm s<sup>-1</sup> (daytime) and 0.26-0.42 cm s<sup>-1</sup> (nighttime) in the wet season. SO<sub>2</sub> deposition velocity in the rain period was significantly higher than that in the no rain period. Higher deposition velocities in the wet season were mainly caused by non-stomatal uptake of wet canopy due to a lot of wet days, especially in the case of SO<sub>2</sub>. Much higher daytime deposition velocities in the wet season were additionally caused by stomatal uptake of leafy trees. The applicability of Wesely's parameterization of deposition velocity to a tropical savanna climate was examined. In both gases, the input resistance of transitional spring to the dry season and that of midsummer to the wet season could be applied as a first approximation, although strictly the parameterization of O<sub>3</sub> non-stomatal resistance needs modification in the dry-season daytime. The applicability of some other parameterizations was also considered. Including the enhanced effect of wet canopy uptake in the non-stomatal resistance was essential in parameterizing SO<sub>2</sub> deposition velocity in the wet season of the region.

## **Modeling Study of Ozone Seasonal Cycle in Lower Troposphere over East Asia**

Jie Li<sup>1)</sup>, Zifa Wang<sup>1)</sup>, Hajime Akimoto<sup>2)</sup>, Chao Gao<sup>1)</sup>,  
Pakpong Pochanart<sup>2)</sup> and Xiquan Wang<sup>1)</sup>

<sup>1)</sup> *Nansen-Zhu International Research Center, China*

<sup>2)</sup> *Frontier Research Center for Global Change, Japan*

On the basis of three mountain sites (Mount Tai, Hua and Huang) newly founded in east-central China and several other sites from the Acid Deposition Monitoring Network in east Asia (EANET) and WMO World Data Centre for Greenhouse Gases (WDCGG), we investigate seasonal cycle of ozone over east Asia and its budgets in east-central China by using a regional chemical transport model (NAQPMS). The observations show a striking ozone pattern of two sharp peaks in May-June and September-October at three mountain sites in east-central China which are higher than those observed at other mountain sites in Europe and North America. Ozone budgets analysis by the model confirms that maximum of net photochemical productions reaches 31.8, 15.1, and 11.4 ppbv/d at Mount Tai, Hua, and Huang, respectively. The net photochemical production dominates the formation of ozone maximums at Mount Tai and Hua in June, and the importing transport also plays a comparable importance at Mount Huang. In comparison with those in the western North Pacific, east-central China shows stronger net photochemical productions, which are comparable to anthropogenic sources regions in Europe and North America.

## **Spatial Distribution and Source Identification of Wet Deposition at Remote EANET Sites in Japan**

Sinya Seto<sup>1)</sup>, Manabu Sato<sup>2)</sup>, Tsutomu Tatano<sup>3)</sup>, Takashi Kusakari<sup>3)</sup>  
and Hiroshi Hara<sup>4)</sup>

<sup>1)</sup> *Hiroshima Prefectural Technology Research Institute, Japan*

<sup>2)</sup> *Hiroshima City University, Japan*

<sup>3)</sup> *Shimane Prefectural Institute of Public Health and Environmental Science, Japan*

<sup>4)</sup> *Tokyo University of Agriculture and Technology, Japan*

Wet deposition of major ions was discussed from the viewpoint of its potential sources for six remote EANET sites in Japan (Rishiri, Happa, Oki, Ogasawara, Yushara, and Hedo) having sufficiently high data completeness during 2000-2004. The annual deposition for each site ranged from 12.1 to 46.6 meq m<sup>-2</sup> yr<sup>-1</sup> for nss-SO<sub>4</sub><sup>2-</sup>, from 5.0 to 21.9 meq m<sup>-2</sup> yr<sup>-1</sup> for NO<sub>3</sub><sup>-</sup>. The ranges of annual deposition of the two ions for the sites were lower than those for urban and rural sites in Japanese Acid Deposition Survey by Ministry of the Environment, Japan, and higher than those for global remote marine sites. Factor analysis was performed on log-transformed daily wet deposition of major ions for each site. The obtained two factors were interpreted as (1) acid and soil source (or acid source for some sites), and (2) sea-salt source for all the sites. This indicates that wet deposition of ions over the remote areas in Japan has a similar structure in terms of types of sources. Factor scores of acid and soil source were relatively high during Kosa (Asian dust) events in spring in western Japan. Back-trajectories for high-deposition episodes of acid and soil source (or acid source) for the remote sites showed that episodic air masses frequently came from the northeastern area of Asian Continent in spring and winter, and from central China in summer and autumn. This indicates a large contribution of continental emissions to wet deposition of ions over the remote areas in Japan.



## **Modeling Study of Long-range Transport of SO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> over Northeast Asia in March 2002**

Zhiwei Han, Hiromasa Ueda, Yu Hozumi and Tatsuya Sakurai

*Acid Deposition and Oxidant Research Center (ADORC), Japan*

The characteristics of transport and transformation of SO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> in northeast Asia have been investigated by using a comprehensive regional air quality model (RAQM) driven by a meteorological model MM5. A study period of 1-15 March 2002 has been selected due to the availability of intense observation of chemical species for both ground and upper levels. Model results have been compared against observational data to provide insights into the strength and weakness of the model's ability and the evolutionary features of chemical species. Validation shows a good skill of this model system in reproducing most of the key features in long-range transport, but apparent bias still remains due to a series of uncertainties from either emission estimates, prescribed parameters, or inherent model limitations. In general, this model shows a better skill for SO<sub>2</sub> and O<sub>3</sub> than for NO<sub>x</sub>. Large discrepancy occurs between the observed and calculated NO<sub>x</sub> concentration at higher levels, with the model results being much lower. A series of sensitivity tests have been conducted to investigate the potential affecting factors and it is found that the inaccuracy or incompleteness in currently used emission inventories could be a most likely cause for such discrepancy. Long-range transport from Asian continent to the western Pacific is pronounced in springtime. Substantially high concentrations of SO<sub>2</sub> and NO<sub>x</sub> in or above the boundary layer (0.5~3.0 km) over the Yellow Sea suggest an important pathway for long-range transport in northeast Asia.

## **Cost-effectiveness Analysis of Reducing the Emission of Nitrogen Oxides in Asia**

Ken Yamashita<sup>1)</sup>, Fumiko Ito<sup>2)</sup>, Keigo Kameda<sup>2)</sup>, Tracey Holloway<sup>3)</sup>  
and Matthew Johnston<sup>3)</sup>

<sup>1)</sup> *Niigata Prefectural Government, Japan*

<sup>2)</sup> *Niigata University, Japan*

<sup>3)</sup> *Center for Sustainability and the Global Environment (SAGE), University of  
Wisconsin-Madison, USA*

The purpose of this study is to evaluate cost-effective reduction strategies for nitrogen oxides (NO<sub>x</sub>) in the Asian region. The source-receptor relationships of the Lagrangian “puff” model of long-range transportation, ATMOS-N, were used to calculate the wet/dry deposition of the nitrogen (N) in Asia. Critical loads of N deposition in Asia were calculated from the relationships between the critical load of sulfur (S) and balance of N in and out using the data of S critical load of RAINS-ASIA. The cost functions of N reduction of Asian countries were derived by the regression analysis with the data of cost functions of European countries used in RAINS. In order to assess the environmental impact, the gaps between N deposition and critical load of N were calculated. The emission of NO<sub>x</sub> was reduced in some cases of this model, and the changes of gaps between N deposition and critical load were observed as well as the changes of the reduction cost. It is shown that a uniform reduction of NO<sub>x</sub> emissions by countries in Asia is not cost-effective strategy.

## **Influence of Vertical Eddy Diffusivity Parameterization on Daily and Monthly Mean Concentrations of O<sub>3</sub> and NO<sub>y</sub>**

Junling An<sup>1)</sup>, Xinjin Cheng<sup>2)</sup>, Yu Qu<sup>1)</sup> and Yong Chen<sup>1)</sup>

<sup>1)</sup> *State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, China*

<sup>2)</sup> *Institute of Atmospheric Physics, China*

Two parameterization schemes for vertical eddy diffusivity were utilized to investigate their impacts on both the daily and monthly mean concentrations of ozone and NO<sub>y</sub>, which are the major fractions of the sum of all reactive nitrogen species, i.e., NO<sub>y</sub> = NO + NO<sub>2</sub> + HNO<sub>3</sub> + PAN. Simulations indicate that great changes in the vertical diffusivity usually occur within the planetary boundary layer (PBL). Daily and monthly mean concentrations of NO<sub>y</sub> are much more sensitive to changes in the vertical diffusivity than those of ozone and ozone and NO<sub>y</sub> levels only at or in (relatively) clean sites and areas, where long-range transport plays a crucial role, display roughly equivalent sensitivity. The results strongly suggest that a widely-accepted parameterization scheme be selected and the refinement of the model's vertical resolution in the PBL be required, even for regional and long-term studies, and ozone only being examined in an effort to judge the model's performance be unreliable, and NO<sub>y</sub> be included for model evaluations.

## **Secondary Acidification: Changes in Gas-aerosol Partitioning of Semivolatile Nitric Acid and Enhancement of its Deposition due to Increased Emission and Concentration of SO<sub>x</sub>**

Mizuo Kajino<sup>1)</sup>, Hiromasa Ueda<sup>2)</sup> and Shinji Nakayama<sup>2)</sup>

<sup>1)</sup> *Disaster Prevention Research Institute, Kyoto University, Japan*

<sup>2)</sup> *Acid Deposition and Oxidant Research Center (ADORC), Japan*

Secondary acidification, or the indirect enhancement of semivolatile air pollutant deposition associated with increased SO<sub>4</sub><sup>2-</sup> concentrations, is shown to occur in general air pollution using data collected from six stations of the Acid Deposition Monitoring Network in East Asia (EANET) in Japan. This effect was first detected as a result of volcanic SO<sub>2</sub> plumes in our previous studies. Results indicate that as SO<sub>4</sub><sup>2-</sup> concentration increases, gas-aerosol partitioning of nitric acid shifts to the gas phase, increasing the HNO<sub>3</sub> gas concentration. Since the dry and wet deposition rates of HNO<sub>3</sub> gas are very high, deposition can be enhanced even when the emission of NO<sub>x</sub> remains unchanged. In western Japan, the indirect effect for wet deposition is most apparent from spring to autumn, when the Asian continental outflow carries sulfate-rich contaminated air masses. However, it is not pronounced in air masses containing abundant sea-salt particles and related cation components in aerosols. In areas such as forests or farmlands with low surface resistance, dry deposition of nitric acid is more pronounced than wet deposition as the dry deposition velocity of HNO<sub>3</sub> gas is high. Increased dry deposition of t-NO<sub>3</sub> due to the indirect effect and consequent vegetation damage is thus of considerable concern in such regions. The deposition of other semivolatile components, such as hydrochloric acid and ammonia, can be altered and can also induce secondary acidification.

## **MICS-Asia II: The Model Intercomparison Study for Asia**

### **Phase II Methodology and Overview of Findings**

Gregory R. Carmichael<sup>1)</sup>, Tatsuya Sakurai<sup>2)</sup>, David Streets<sup>3)</sup>, Yu Hozumi<sup>2)</sup>, Hiromasa Ueda<sup>2)</sup>, Soon-Ung Park<sup>4)</sup>, Christopher Fung<sup>5)</sup>, Zhiwei Han<sup>2)</sup>, Mizuo Kajino<sup>6)</sup>, Magnuz Engardt<sup>7)</sup>, Cecilia Bennet<sup>7)</sup>, Hiroshi Hayami<sup>8)</sup>, Karine Sartelet<sup>9)</sup>, Tracey Holloway<sup>10)</sup>, Zifa Wang<sup>11)</sup>, Akiyoshi Kannari<sup>12)</sup>, Joshua Fu<sup>13)</sup>, Kazuhide Matsuda<sup>14)</sup>, Narisara Thongboonchoo<sup>1)</sup> and Markus Amann<sup>15)</sup>

<sup>1)</sup> *Center for Global and Regional Environmental Research, University of Iowa, USA*

<sup>2)</sup> *Acid Deposition and Oxidant Research Center(ADORC), Japan*

<sup>3)</sup> *Argonne National Laboratory, USA*

<sup>4)</sup> *Seoul National University, South Korea*

<sup>5)</sup> *Hong Kong Environmental Protection Department, Hong Kong SAR, China*

<sup>6)</sup> *Disaster Prevention Research Institute, Kyoto University, Japan*

<sup>7)</sup> *Swedish Meteorological and Hydrological Institute, Sweden*

<sup>8)</sup> *Central Research Institute of Electric Power Industry, Japan*

<sup>9)</sup> *Centre d'Enseignement et de Recherche en Environnement Atmospherique, France*

<sup>10)</sup> *Center for Sustainability and the Global Environment,*

*University of Wisconsin-Madison, USA*

<sup>11)</sup> *Institute of Atmospheric Physics, China*

<sup>12)</sup> *Independent Researcher, Japan*

<sup>13)</sup> *The University of Tennessee, USA*

<sup>14)</sup> *Meisei University, Japan*

<sup>15)</sup> *International Institute for Applied System Analysis, Austria*

Results from the Model Intercomparison Study Asia Phase II (MICS-Asia II) are presented. Nine different regional modeling groups simulated chemistry and transport of ozone (O<sub>3</sub>), secondary aerosol, acid deposition, and associated precursors, using common emissions and boundary conditions derived from a global model. Four-month-long periods, representing 2 years and three seasons (i.e., March, July, and December in 2001, and March in 2002), are analyzed. New observational data, obtained under the EANET (the Acid Deposition Monitoring Network in East Asia) monitoring program, were made available for this study, and these data provide a regional database to compare with model simulations. The analysis focused around seven subject areas: O<sub>3</sub> and related precursors, aerosols, acid deposition, global inflow of pollutants and precursor to Asia, model sensitivities to aerosol parameterization, analysis of emission fields, and detailed analyses of individual models, each of which is presented in a companion paper in this issue of Atmospheric Environment. This overview discusses the major findings of the study, as well as information on common emissions, meteorological conditions, and observations.

## **MICS-Asia II: Model Intercomparison and Evaluation of Ozone and Relevant Species**

Zhiwei Han<sup>1),2)</sup>, Tatsuya. Sakurai<sup>2)</sup>, Hiromasa Ueda<sup>2)</sup>, Gregory R. Carmichael<sup>3)</sup>, David Streets<sup>4)</sup>, Hiroshi Hayami<sup>5)</sup>, Zifa Wang<sup>1)</sup>, Tracey Holloway<sup>6)</sup>, Magnuz Engardt<sup>7)</sup>, Yu Hozumi<sup>2)</sup>, Soon-Ung Park<sup>8)</sup>, Mizuo Kajino<sup>9)</sup>, Karine Sartelet<sup>10)</sup>, Christopher Fung<sup>11)</sup>, Cecilia Bennet<sup>7)</sup>, Narisara Thongboonchoo<sup>3)</sup>, Youhua Tang<sup>3)</sup>, Alick H. Y. Chang<sup>11)</sup>, Kazuhide Matsuda<sup>12)</sup> and Markus Amann<sup>13)</sup>

<sup>1)</sup> *Institute of Atmospheric Physics, Chinese Academy of Science, China*

<sup>2)</sup> *Acid Deposition and Oxidant Research Center(ADORC), Japan*

<sup>3)</sup> *Center for Global and Regional Environmental Research, University of Iowa, USA*

<sup>4)</sup> *Argonne National Laboratory, USA*

<sup>5)</sup> *Central Research Institute of Electric Power Industry, Japan*

<sup>6)</sup> *University of Wisconsin-Madison, USA*

<sup>7)</sup> *Swedish Meteorological and Hydrological Institute, Sweden*

<sup>8)</sup> *Seoul National University, Korea*

<sup>9)</sup> *Disaster Prevention Research Institute, Kyoto University, Japan*

<sup>10)</sup> *Centre d'Enseignement et de Recherche en Environnement Atmospherique, France*

<sup>11)</sup> *Hong Kong Environmental Protection Department, Hong Kong SAR, China*

<sup>12)</sup> *Meisei University, Japan*

<sup>13)</sup> *International Institute for Applied System Analysis, Laxenburg, Austria*

Eight regional Eulerian chemical transport models (CTMs) are compared with each other and with an extensive set of observations including ground-level concentrations from EANET, ozone soundings from JMA and vertical profiles from the TRACE-P experiment to evaluate the models' abilities in simulating O<sub>3</sub> and relevant species (SO<sub>2</sub>, NO, NO<sub>2</sub>, HNO<sub>3</sub> and PAN) in the troposphere of East Asia and to look for similarities and differences among model performances. Statistical analysis is conducted to help estimate the consistency and discrepancy between model simulation and observation in terms of various species, seasons, locations, as well as altitude ranges. In general, all models show a good skill of simulating SO<sub>2</sub> for both ground level and the lower troposphere, although two of the eight models systematically overpredict SO<sub>2</sub> concentration. The model skills for O<sub>3</sub> vary largely with region and season. For ground-level O<sub>3</sub>, model results are best correlated with observations in July 2001. Comparing with O<sub>3</sub> soundings measured in the afternoon reveals the best consistency among models in March 2001 and the largest disparity in O<sub>3</sub> magnitude in July 2001, although most models produce the best correlation in July as well. In terms of the statistics for the four flights of TRACE-P experiment, most models appear to be able to accurately capture the variability in the lower troposphere. The model performances for NO<sub>x</sub> are relatively poor, with lower correlation and with almost all models tending to

underpredict NO<sub>x</sub> levels, due to larger uncertainties in either emission estimates or complex chemical mechanism represented. All models exhibit larger RMSE at altitudes <2 km than 2–5.5 km, mainly due to a consistent tendency of these models towards underprediction of the magnitude of intense plumes that often originate from near surface. Relatively lower correlation at altitudes 2–5.5 km may be attributed to the models' limitation in representing convection or potential chemical processes. Most of the key features in species distribution have been consistently reproduced by the participating models, such as the O<sub>3</sub> enhancement in the western Pacific Ocean in March and in northeast Asia in July, respectively, although the absolute model values may differ considerably from each other. Large differences are found among models in the southern parts of the domain for all the four periods, including southern China and northern parts of some Southeast Asia countries where the behaviors of chemical components and the ability of these models are still not clearly known because of a lack of observational databases.

## **MICS-Asia II: Model Intercomparison and Evaluation of Particulate Sulfate, Nitrate and Ammonium**

Hiroshi Hayami<sup>1)</sup>, Tatsuya Sakurai<sup>2)</sup>, Zhiwei Han<sup>2)</sup>, Hiromasa Ueda<sup>3)</sup>, Gregory R. Carmichael<sup>4)</sup>, David Streets<sup>5)</sup>, Tracey Holloway<sup>6)</sup>, Zifa Wang<sup>7)</sup>, Narisara Thongboonchoo<sup>4)</sup>, Magnuz Engardt<sup>8)</sup>, Cecilia Bennet<sup>8)</sup>, Christopher Fung<sup>9)</sup>, Alick H. Y. Chang<sup>9)</sup>, Soon-Ung Park<sup>10)</sup>, Mizuo Kajino<sup>3)</sup>, Karine Sartelet<sup>11)</sup>, Kazuhide Matsuda<sup>12)</sup> and Markus Amann<sup>13)</sup>

<sup>1)</sup> *Central Research Institute of Electric Power Industry, Japan*

<sup>2)</sup> *Acid Deposition and Oxidant Research Center(ADORC), Japan*

<sup>3)</sup> *Disaster Prevention Research Institute, Kyoto University, Japan*

<sup>4)</sup> *Center for Global and Regional Environmental Research, University of Iowa, USA*

<sup>5)</sup> *Argonne National Laboratory, USA*

<sup>6)</sup> *The University of Wisconsin-Madison, USA*

<sup>7)</sup> *Institute of Atmospheric Physics, China*

<sup>8)</sup> *Swedish Meteorological and Hydrological Institute, Sweden*

<sup>9)</sup> *Hong Kong Environmental Protection Department, Hong Kong SAR, China*

<sup>10)</sup> *Seoul National University, Korea*

<sup>11)</sup> *Centre d'Enseignement et de Recherche Eau, France*

<sup>12)</sup> *Meisei University, Japan*

<sup>13)</sup> *International Institute for Applied System Analysis, Austria*

Eight chemical transport models participate in a model intercomparison study for East Asia, MICS-Asia II. This paper analyzes calculated results for particulate matter of sulfate, nitrate and ammonium through comparisons with each other and with monthly measurements at EANET (the acid deposition monitoring network in East Asia) and daily measurements at Fukue, Japan.

To the EANET measurements, model ensemble means better agree with model individual results for sulfate and total ammonium, although total nitrate is consistently and considerably underestimated. To measurements at Fukue, the models show better agreement than for the EANET measurements. This is likely because Fukue is centered in many of the model domains, whereas the EANET stations are mostly in Southeast Asia and Russia. Moreover, it would be important that Fukue is in Northeast Asia, where the emission inventory is more reliable than Southeast Asia.

The model-model comparisons are made in view of the total amount in the atmosphere, vertical profile, coefficient of variation in surface concentrations, and transformation changes with distance. All the models show reasonable tendencies in vertical profiles and composition ratios. However, total amounts in the atmosphere are discrepant among the models. The consistency of the total amount in the atmosphere would



influence source–receptor analysis. It seems that model results would be consistent, if the models take into account the primitive processes like emission, advection/diffusion, chemical transformation and dry/wet deposition, no matter the processes are modeled simply or comprehensively.

Through the comparison study, we learned that it would be difficult to find any problems from one comparison (model-observation comparison with one data or many but at one station or in a short period). Modelers tend to examine model performances only from model-observation comparisons. However, taking budget in a certain or whole model domain would be important, before the models are applied to source–receptor analysis.

## MICS-Asia II: Model Inter-comparison and Evaluation of Acid Deposition

Zifa Wang<sup>1)</sup>, Fuying Xie<sup>1),13)</sup>, Tatsuya. Sakurai<sup>2)</sup>, Hiromasa Ueda<sup>2)</sup>, Zhiwei Han<sup>2)</sup>, Gregory R. Carmichael<sup>3)</sup>, David Streets<sup>4)</sup>, Magnuz Engardt<sup>5)</sup>, Tracey Holloway<sup>6)</sup>, Hiroshi Hayami<sup>7)</sup>, Mizuo Kajino<sup>8)</sup>, Narisara Thongboonchoo<sup>3)</sup>, Cecilia Bennet<sup>5)</sup>, Soon-Ung Park<sup>9)</sup>, Christopher Fung<sup>10)</sup>, Alick H. Y. Chang<sup>10)</sup>, Karine Sartelet<sup>11)</sup> and Markus Amann<sup>12)</sup>

<sup>1)</sup> NZC/LAPC, Institute of Atmospheric Physics, Chinese Academy of Sciences, China

<sup>2)</sup> Acid Deposition and Oxidant Research Center(ADORC), Japan

<sup>3)</sup> Center for Global and Regional Environmental Research, University of Iowa, USA

<sup>4)</sup> Argonne National Laboratory, USA

<sup>5)</sup> Swedish Meteorological and Hydrological Institute, Sweden

<sup>6)</sup> University of Wisconsin-Madison, USA

<sup>7)</sup> Central Research Institute of Electric Power Industry, Japan

<sup>8)</sup> Disaster Prevention Research Institute, Kyoto University, Japan

<sup>9)</sup> Seoul National University, Korea

<sup>10)</sup> Hong Kong Environmental Protection Department, Hong Kong SAR, China

<sup>11)</sup> Teaching and Research Center in Atmospheric Environment, France

<sup>12)</sup> International Institute for Applied System Analysis, Austria

<sup>13)</sup> Graduate University of Chinese Academy of Sciences, China

This paper focuses on the comparison of chemical deposition of eight regional chemical models used in Model Inter-Comparison Study for Asia (MICS-Asia) II. Monthly-mean depositions of chemical species simulated by these models, including dry deposition of SO<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub>, sulfate, nitrate and ammonium and wet deposition of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, have been provided for four periods (March, July, December 2001 and March 2002) in this work. Observations at 37 sites of the Acid Deposition Monitoring Network in East Asia (EANET) are compared with SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> wet deposition model results. Significant correlations appeared between the observation and computed ensemble mean of participant models. Also, differences among modeled sulfur and nitrogen dry depositions have been studied at the EANET sites. Based on the analysis of acid deposition for various species from different models, total depositions of sulfur (SO<sub>2</sub> and sulfate) and nitrogen (nitrate and ammonium) have been evaluated as the ensemble mean of the eight models. In general, all models capture the observed spatial distribution of sulfur and nitrogen deposition, although the absolute values may differ from measurements. High deposition often occurs in eastern China, Japan, the Republic of Korea, Thailand, Vietnam, Philippines and other parts of Southeast Asia. The magnitude of model bias is quite large for many of the models. In examining the reasons for model-measurement disagreement, we find that differences in chemical processes, deposition parameterization, and modeled precipitation are the main reasons for large model disparities.

## MICS-Asia II: Impact of Global Emissions on Regional Air Quality in Asia

Tracey Holloway<sup>1)</sup>, Tatsuya Sakurai<sup>2)</sup>, Zhiwei Han<sup>2),3)</sup>, Susanna Ehlers<sup>1)</sup>, Scott N. Spak<sup>1)</sup>, Larry W. Horowitz<sup>4)</sup>, Gregory R. Carmichael<sup>5)</sup>, David G. Streets<sup>6)</sup>, Yu Hozumi<sup>2)</sup>, Hiromasa Ueda<sup>2)</sup>, S.U. Park<sup>7)</sup>, Christopher Fung<sup>8)</sup>, Mizuo Kajino<sup>9)</sup>, Narisara Thongboonchoo<sup>5)</sup>, Magnuz Engardt<sup>10)</sup>, Cecilia Bennet<sup>10)</sup>, Hiroshi Hayami<sup>11)</sup>, Karine Sartelet<sup>12)</sup>, Zifa Wang<sup>13)</sup>, K. Matsuda<sup>14)</sup> and Markus Amann<sup>15)</sup>

<sup>1)</sup> *Center for Sustainability and the Global Environment (SAGE),  
University of Wisconsin-Madison, USA*

<sup>2)</sup> *Acid Deposition and Oxidant Research Center(ADORC), Japan*

<sup>3)</sup> *Institute of Atmospheric Physics, Chinese Academy of Sciences, China*

<sup>4)</sup> *NOAA Geophysical Fluid Dynamics Laboratory, Princeton, USA*

<sup>5)</sup> *Center for Global and Regional Environmental Research, University of Iowa, USA*

<sup>6)</sup> *Argonne National Laboratory, USA*

<sup>7)</sup> *Seoul National University, Korea*

<sup>8)</sup> *Hong Kong Environmental Protection Department, Hong Kong SAR, China*

<sup>9)</sup> *Disaster Prevention Research Institute, Kyoto University, Japan*

<sup>10)</sup> *Swedish Meteorological and Hydrological Institute, Sweden*

<sup>11)</sup> *Central Research Institute of Electric Power Industry, Japan*

<sup>12)</sup> *Centre d'Enseignement et de Recherche en Environnement Atmosphérique, France*

<sup>13)</sup> *Institute of Atmospheric Physics, China*

<sup>14)</sup> *Meisei University, Japan*

<sup>15)</sup> *International Institute for Applied System Analysis, Austria*

This study quantifies the seasonality and geographic variability of global pollutant inflow to Asia. Asia is often looked to as a major source of intercontinental air pollution transport with rising emissions and efficient pollutant export processes. However, the degree to which foreign emissions have been imported to Asia has not been thoroughly examined. The Model Inter-Comparison Study for Asia (MICS-Asia) is an international collaboration to study air pollution transport and chemistry in Asia. Using the global atmospheric chemistry Model of Ozone and Related Tracers (MOZART v. 2.4), and comparing results with a suite of regional models participating in MICS-Asia, we find that imported O<sub>3</sub> contributes significantly throughout Asia. The choice of upper boundary condition is found to be particularly important for O<sub>3</sub>, even for surface concentrations. Both North America and Europe contribute to ground-level O<sub>3</sub> concentrations throughout the region, though the seasonality of these two sources varies. North American contributions peak at over 10% of monthly mean O<sub>3</sub> during winter months in East Asia, compared to Europe's spring- and autumn-maxima (5–8%). In comparison to observed data from the Acid Deposition Monitoring Network in East Asia (EANET), MOZART concentrations for O<sub>3</sub> generally fall within the range of the MICS models, but MOZART is unable to capture the fine spatial variability of shorter-lived species as well as the regional models.

## MICS Asia Phase II – Sensitivity to the Aerosol Module

Karine Sartelet<sup>1)</sup>, Hiroshi Hayami<sup>2)</sup> and Bruno Sportisse<sup>1)</sup>

<sup>1)</sup> *Centre d'Enseignement et de Recherche Eau, France*

<sup>2)</sup> *Central Research Institute of Electric Power Industry, Japan*

In the framework of the model intercomparison study—Asia Phase II (MICS2), where eight models are compared over East Asia, this paper studies the influence of different parameterizations used in the aerosol module on the aerosol concentrations of sulfate and nitrate in PM<sub>10</sub>.

An intracomparison of aerosol concentrations is done for March 2001 using different configurations of the aerosol module of one of the model used for the intercomparison. Single modifications of a reference setup for model configurations are performed and compared to a reference case. These modifications concern the size distribution, i.e. the number of sections, and physical processes, i.e. coagulation, condensation/evaporation, cloud chemistry, heterogeneous reactions and sea-salt emissions.

Comparing monthly averaged concentrations at different stations, the importance of each parameterization is first assessed. It is found that sulfate concentrations are little sensitive to sea-salt emissions and to whether condensation is computed dynamically or by assuming thermodynamic equilibrium. Nitrate concentrations are little sensitive to cloud chemistry. However, a very high sensitivity to heterogeneous reactions is observed.

Thereafter, the variability of the aerosol concentrations to the use of different chemistry transport models (CTMs) and the variability to the use of different parameterizations in the aerosol module are compared. For sulfate, the variability to the use of different parameterizations in the aerosol module is lower than the variability to the use of different CTMs. However, for nitrate, for monthly averaged concentrations averaged over four stations, these two variabilities have the same order of magnitude.

## **MICS-Asia II: Modeling Gaseous Pollutants and Evaluating an Advanced Modeling System over East Asia**

Joshua S. Fu<sup>1)</sup>, Carey J. Jang<sup>2)</sup>, David G. Streets<sup>3)</sup>, Zuopan Li<sup>1)</sup>, Roger Kwok<sup>1),4)</sup>,  
Rokjin Park<sup>5),6)</sup> and Zhiwei Han<sup>7)</sup>

<sup>1)</sup> *Department of Civil and Environmental Engineering, The University of Tennessee, USA*

<sup>2)</sup> *Office of Air Quality Planning and Standards, US Environmental Protection Agency, USA*

<sup>3)</sup> *Argonne National Laboratory, USA*

<sup>4)</sup> *Department of Mathematics, Hong Kong University of Science and Technology,  
Hong Kong*

<sup>5)</sup> *Division of Engineering and Applied Science, Harvard University, USA*

<sup>6)</sup> *School of Earth and Environmental Sciences, Seoul National University, Korea*

<sup>7)</sup> *Institute of Atmospheric Physics, Chinese Academy of Sciences, China*

An advanced modeling system with a “one-atmosphere” perspective, Models-3/Community Multi-scale Air Quality (CMAQ) modeling system, driven by MM5/NCEP reanalysis data as the meteorology, and GEOS-Chem outputs as boundary values was applied to simulate the O<sub>3</sub>, and other gaseous pollutants (SO<sub>2</sub> and NO<sub>2</sub>) evolution among other atmospheric chemicals for July 2001. Comparisons had been made with other models in the MICS-II exercise for the same period. Statistics of both monthly and daily means show that the model skill is very good in reproducing O<sub>3</sub> and SO<sub>2</sub> with small to moderate RMSE. The model species capture the day-to-day and spatial variability of the observations. The same O<sub>3</sub> model concentrations that overpredict most of the EANET observations in the MICS-II study may have underpredicted ones from monitoring networks in Beijing area that is not included in this paper. Vertical O<sub>3</sub> profiles at 4 ozonesonde sites are well predicted in July 2001. In fact, our model is among the best of those MICS-II models within the 2-km surface layer. The meteorology near surface and lower troposphere is well reproduced. Compared to SO<sub>2</sub> and O<sub>3</sub>, the NO<sub>2</sub> gas concentrations are simulated less well, but the correlation coefficient is still significant.

The choice of reanalysis meteorological fields and different boundary conditions generated by different global models may result in diverse spatial patterns exhibited by MICS-II models and ours. Our spatial distributions of O<sub>3</sub> shows a high concentration patch covering Beijing, a moderate to high pattern across Korea and Japan Sea, and a low but extensive pattern enclosing southern China, Taiwan, and East Sea. Extension of the pattern to southern China coincides with the existence of pollution problems in Guangdong and Taiwan, but overprediction of O<sub>3</sub> over the region deserves further improvement by various factors. One of them can be the grid resolution to resolve the complex orography in or close to the ocean. Another factor can be the refinement of local land use data that changes the micro-meteorology in favor of more air pollution events.

## **MICS-Asia II: An Inter-comparison Study of Emission Inventories for the Japan Region**

Akiyoshi Kannari<sup>1)</sup>, David G. Streets<sup>2)</sup>, Yutaka Tonooka<sup>3)</sup>, Kentaro Murano<sup>4)</sup>  
and Tsuyoshi Baba<sup>5)</sup>

<sup>1)</sup> *Independent Researcher, Japan*

<sup>2)</sup> *Argonne National Laboratory, USA*

<sup>3)</sup> *Saitama University, Japan*

<sup>4)</sup> *National Institute for Environmental Studies, Japan*

<sup>5)</sup> *Institute of Behavioral Sciences, Japan*

For the model intercomparison study, MICS Asia phase II, standard air pollutants emission data are provided from published research results (the TRACE-P data set) and other recent work. To provide preliminary information concerning the reliability of the standard emissions data, this inventory was compared with a local emission inventory, EAGrid2000-Japan, which has been developed for detailed analyses with fine grid data resolution for the Japan region. Although these inventories are based upon different estimation methodologies, from the comparative analyses it was found that regional emissions of the standard data are consistent, with differences smaller than 10% for SO<sub>2</sub>, NO<sub>x</sub>, NMVOC and CO<sub>2</sub>, and smaller than 30% for CO and NH<sub>3</sub>. Differences for all species are smaller than the 95% confidence intervals that were estimated in the research that produced the standard emissions data. Additional information is provided regarding emissions of PM<sub>10</sub> and PM<sub>2.5</sub>, although these did not originate in the TRACE-P data. Furthermore, it was found that the 0.5°×0.5° grid-based emissions from the two inventories match well for NO<sub>x</sub>, NMVOC, CO, and PM<sub>2.5</sub>, even though the spatial allocation techniques for the local inventory are much more detailed. For SO<sub>2</sub> emissions, the differences in the grid-based inventories are greater. Although some problems still remain, such as diurnal variations that are not considered in the standard emissions data, the intercomparison analysis suggests that the standard emissions data have appropriate properties for atmospheric model simulation.

## **Seasonal Variation in the Atmospheric Deposition of Inorganic Constituents and Canopy Interactions in a Japanese Cedar Forest**

Hiroyuki Sase<sup>1)</sup>, Akiomi Takahashi<sup>1)</sup>, Masahiko Sato<sup>2)</sup>, Hiroyasu Kobayashi<sup>1)</sup>, Makoto Nakata<sup>2)</sup> and Tsumugu Totsuka<sup>1)</sup>

<sup>1)</sup> *Acid Deposition and Oxidant Research Center (ADORC), Japan*

<sup>2)</sup> *Faculty of Agriculture, Niigata University, Japan*

The seasonal changes in throughfall (TF) and stemflow (SF) chemistry and the canopy interactions of K<sup>+</sup> and N compounds were studied in a Japanese cedar forest near the Sea of Japan. The fluxes of most ions, including non-sea-salt SO<sub>4</sub><sup>2+</sup>, from TF, SF, and rainfall showed distinct seasonal trends, increasing from autumn to winter, owing to the seasonal west wind, while the fluxes of NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> ions from TF + SF might have a large effect of canopy interactions. The contact angle (CA) of water droplets on leaves decreased with leaf aging, suggesting that surface wettability increases with leaf age. The K<sup>+</sup> concentration in TF was negatively correlated with the CA of 1-year-old leaves, while the NH<sub>4</sub><sup>+</sup> concentration was positively correlated with the CA. The net fluxes of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> from TF were positively correlated with the CA. The increase in wettability may accelerate leaching of K<sup>+</sup> or uptake of NH<sub>4</sub><sup>+</sup>.

## Seasonal and Annual Fluxes of Inorganic Constituents in a Small Catchment of a Japanese Cedar Forest near the Sea of Japan

Masato Kamisako<sup>1)</sup>, Hiroyuki Sase<sup>1)</sup>, Taeko Matsui<sup>2)</sup>, Hiroko Suzuki<sup>3)</sup>,  
Akiomi Takahashi<sup>1)</sup>, Takuji Oida<sup>1)</sup>, Makoto Nakata<sup>3)</sup>,  
Tsumugu Totsuka<sup>1)</sup> and Hiromasa Ueda<sup>1)</sup>

<sup>1)</sup> *Acid Deposition and Oxidant Research Center (ADORC), Japan*

<sup>2)</sup> *Niigata Prefectural Institute of Public Health and Environmental Sciences, Japan*

<sup>3)</sup> *Graduate School of Science and Technology, Niigata University, Japan*

Fluxes of major ions in rainfall (RF), throughfall plus stemfall (TF + SF), and stream water (SW) were measured for 5 water years in a small catchment of a Japanese cedar forest near the Sea of Japan. The fluxes of most ions in RF and in TF + SF, including the non-sea-salt constituents, increased from late autumn to midwinter owing to the seasonal westerly wind. The concentrations of most ions in SW showed no obvious seasonal trend during the study period, whereas  $\text{NO}_3^-$  concentrations were lowest in summer, with a small seasonality. The  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  outputs in SW were approximately 3.7 and 1.8 times the TF + SF inputs of these cations, respectively. The large net outputs of base cations in the catchment may indicate a decrease in the soil's acid-neutralizing capacity. Annual dissolved inorganic nitrogen inputs in RF and in TF + SF were 17.7 and 17.9  $\text{kg N ha}^{-1} \text{ y}^{-1}$ , respectively, which exceeded previously published thresholds in Europe and the U.S. (i.e., the values at which these inputs increased  $\text{NO}_3^-$  levels in SW) and equaled the highest level of nitrogen deposition previously reported in Japan. The  $\text{NO}_3^-$  concentrations in SW were relatively high even in summer. During high-precipitation events,  $\text{NO}_3^-$  concentrations in SW increased with increasing water discharge, and the pH decreased simultaneously during several events. Nitrogen deposition may contribute to the high  $\text{NO}_3^-$  concentrations in SW and the temporary acidification that occurred during the rain events.





Network Center

Acid Deposition Monitoring Network in East Asia (EANET)

Acid Deposition and Oxidant Research Center (ADORC)

1182 Sowa, Nishi-ku, Niigata-shi, 950-2144 Japan

Tel: (+81) 25-263-0550

Fax: (+81) 25-263-0566