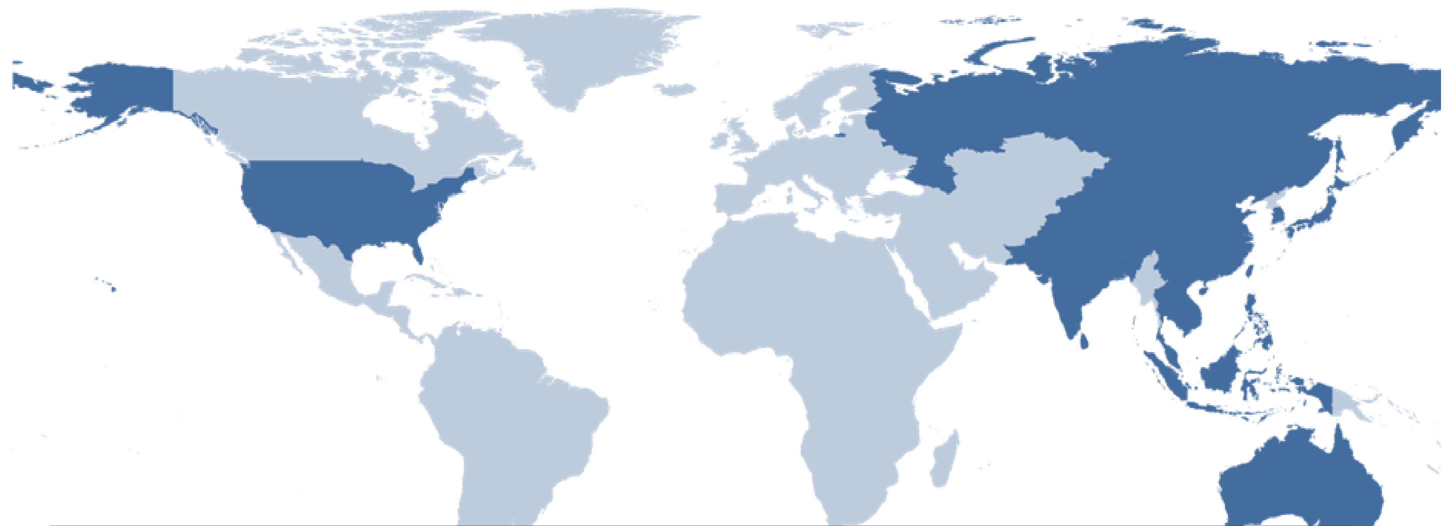
ASIA-PACIFIC NETWORK FOR
GLOBAL CHANGE RESEARCH

Project Reference Number: ARCP2013-13CMY-Sase

# *Dynamics of Sulphur Derived From Atmospheric Deposition and Its Possible Impacts on the East Asian Forests*



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ACAP

**Project Refence Number: ARCP2013-13CMY-Sase**

# *Dynamics of Sulphur Derived From Atmospheric Deposition and Its Possible Impacts on the East Asian Forests*

## Final Report Submitted to APN

## Part One: Overview of Project Work and Outcomes

### Non Technical Summary

Deposition level of sulphur (S) is high and hence the cumulative load of S is also high in Northeast and Southeast Asia. Since S deposited on ecosystems may be retained in soil and/or cycled in the soil-plant system, manifestation of its effect may be delayed. Effect of S deposition on terrestrial ecosystems is one of the important issues to be investigated in the region. The scientists from the community of Acid Deposition Monitoring Network in East Asia (EANET) investigated the dynamics of S derived from atmospheric deposition in forest catchments in Japan, Thailand, and Sabah and Sarawak, Malaysia. Field surveys and chemical analyses were conducted in cooperation with various local scientists and a new research community was formed through the activities. Two workshops were held in Malaysia in 2013 and Thailand in 2014 to share the knowledge obtained in the project with government officers, experts, and scientists in the respective countries. The knowledge will be informative for discussion on possible impacts of S deposition on the forests in the region. Moreover, research capacity of all the scientists involved in the project has been developed.

### Keywords

sulphur isotope, Japanese cedar, dry evergreen forest, tropical rainforest, rehabilitated forest

### Objectives

In the project, S dynamics in the forest ecosystems will be investigated with the following objectives:

- To determine S dynamics in ecosystems of the East Asian forests
- To evaluate the combined effects of S and nitrogen (N) on acidification and eutrophication of the East Asian forests

### Amount Received and Number of Years Supported

The Grant awarded to this project was:

US$ 44,000 for Year 1:

US$ 35,600 for Year 2:

### Activity Undertaken

- Field surveys and data analysis in four forest catchments
  The study sites were established in four forest catchments, namely Kjikawa site in Japan, Sakaerat site in Thailand and Danum Valley sites in Sabah and Bintulu sites in Sarawak,

Malaysia. In these sites, field surveys and data analysis were carried out to address the following subjects:

i) Flux determination of S and nitrogen
ii) Analysis of S isotopic ratio of rainwater and stream water
iii) Speciation of S compounds in soil layer
iv) Trial application of biogeochemical simulation model

In the field surveys, rainfall outside of forest canopy (RF), throughfall and stemflow (TF+SF) under forest canopy, stream water (SW), soil solution (SS), and soil were collected periodically or intensively. Ion concentrations including $SO_4^{2-}$ in rainwater, SW and SS were determined with S isotopic ratio. In particular, in Kajikawa and Sakaerat sites, trend analysis was also carried out using the existing flux data by the previous studies.

- Project seminars in Malaysia and Thailand
  The project seminars entitled “The APN Project Workshop on Sulphur Dynamics in East Asian Forests” were held in 2013 and 2014 in Malaysia and Thailand, respectively.

## Results

- Based on the field surveys and data analysis above, characteristics of S dynamics have been clarified in the four study forests.
  - S loads from atmosphere: The S deposition amount was larger in the following order, Kajikawa (29 kg S $ha^{-1}$ $year^{-1}$) > Bintulu (19 kg S $ha^{-1}$ $year^{-1}$) >> Sakaerat (5.8 kg S $ha^{-1}$ $year^{-1}$) > Danum Valley (3.6 S kg $ha^{-1}$ $year^{-1}$).
  - $SO_4^{2-}$ concentration in stream water (SW): The SW concentration was higher in the following order, Kajikawa (101 $\mu mol_c$ $L^{-1}$) > Bintulu (73 $\mu mol_c$ $L^{-1}$) > Danum Valley (39 $\mu mol_c$ $L^{-1}$) >> Sakaerat (6.3 $\mu mol_c$ $L^{-1}$).
  - The SW concentration in Sakaerat site was significant low compared to that of the deposition (41.9 $\mu mol_c$ $L^{-1}$, as the weighted-mean of TF+SF), suggesting retention of S in the forest ecosystems.
  - S isotopic analysis of SW suggested various possible sources of S in these forest ecosystems. Not only atmospheric deposition but also geology and biological fractionation should carefully be considered as possible S sources in SW.
  - With declining of atmospheric S deposition for the observation period, SW in Kajikawa site seemed to be recovered from acidification, while SW in Sakaerat site seemed to be acidified. Both forest ecosystems may respond sensitively to changes in atmospheric conditions but the reactions are different depending on the respective climates.
- Project seminars in Malaysia and Thailand
  Approx. 40 participants including scientists, governmental officers and experts, respectively, attended the project seminars entitled “The APN Project Workshop on Sulphur Dynamics in East Asian Forests” in Malaysia and Thailand, respectively. In addition to progress and outcomes of the project, future research topics to be promoted in these countries were discussed from various view points.

## Relevance to the APN Goals, Science Agenda and to Policy Processes

The project team consists of scientists who have been involved in the EANET, the regional initiative for acid deposition monitoring. The project was conducted in cooperation with many local scientists in Japan, Thailand and Malaysia. New scientific community has been formed through the project. Moreover, many young scientists are involved in the project and their research capacity has been enough developed. They are closely related to APN Goals 1 (Supporting regional cooperation…) and 2 (Enhancing capacities…).

The project team has been communicating with governmental officers from relevant agencies in the respective countries to provide scientific outcomes from the project. Importance of biogeochemical studies like this project has been emphasized. In the case of Japan, based on our experience, S isotopic analysis has been applied to governmental surveys for precipitation, lake water and forest catchments since 2014. This contributes to APN Goal 3 (Strengthening interactions among scientists and policy makers…).

Some of the project members are nominated as the members of Scientific Advisory Committee (SAC) of the EANET. The project leader is working at the Network Center for the EANET. The project members have presented the project progress at SAC meetings to share with scientists from 13 EANET member countries. This contributes to APN Goal 4 (Cooperating with other global change and sustainability networks and organizations).

The project studied S derived from atmospheric deposition and it dynamics in forest ecosystems. Atmospheric S pollution is still one of the important environmental issues in Asian region. The project theme was closely related to the APN Scientific Research Agenda 2 (Ecosystems, Biodiversity and Land Use) and Agenda 3 (Changes in the Atmospheric, Terrestrial and Marine Domains).

## Self-evaluation

We studied S derived from atmospheric deposition and its dynamics in forest ecosystems, utilizing S isotopic analysis, and identified possible S sources in the ecosystems. Effects of atmospheric S deposition on SW chemistry were also identified in all the sites, although magnitude and types of the effects were different between the sites. In particular, our trials in Thailand and Malaysia are the first biogeochemical catchment studies using isotopic analysis in Southeast Asia. The project outcomes will contribute to development of biogeochemical studies in Asia. Moreover, the data will be utilized for modeling, which may contribute to policy making in future.

Field surveys, data analysis including existing and new data, and communications among contributors were relatively smooth and fruitful. However, soil S analysis is still on going in some sites. Some more detailed data in soil S may be produced in near future. Trial application of the data to biogeochemical models is also still under discussion. In near future hopefully, the data may be applied to such models. Moreover, only one paper is published in an international journal, although one paper is under review and several papers are under preparation. It can be expected that some more papers will be published as outputs from the project in near future.

## Potential for further work

In Northeast and Southeast Asia, in addition to acidic pollutants including S and N, other types of air pollutants, such as ozone and particulate matters (PM), have been highlighted recently. S is also important as a component for forming fine PM (e.g. $PM_{2.5}$). These are also raised as important research topics in the project workshop, which was held in Thailand in December 2014. Effects of multi pollutants, including S, N, ozone and PM, and climate change should be studied in near future in the region.

Consequently, based on the community formed by the APN project, a new joint study has just started in December 2014:

- *The effects of ozone and aerosols on physiological characteristics of urban and suburban forests in Malaysia* (Project Leader, Dr. Roland Kueh Jui Heng): funded by Fundamental Research Grant Scheme (FRGS), Ministry of Education, Malaysia.
  The study is carried out in Bintulu, Sarawak, Malaysia. Dr. Hiroyuki Sase and Prof. Nik Muhamad Majid are involved in the new study as major collaborators.

Not only in Malaysia, in Japan also, a similar study on PM has just started by Dr. Tsuyoshi Ohizumi and Dr. Hiroyuki Sase. Outcomes of both studies will be informative each other. In Thailand, in near future, similar new studies should be promoted.

Moreover, in near future, the current project members would like to start a new international project, in which three or four countries are involved, hopefully with support from APN.

## Publications [please write the complete citation]

Yamashita, N., Sase, H., Kobayashi, R., Leong, K-P., Hanapi, J.M., Uchiyama, S., Urban, S., Toh, Y-Y., Muhamad, M., Gidiman, J., Chappell, N.A. 2014. Atmospheric deposition versus rock weathering in the control of streamwater chemistry in a tropical rain-forest catchment in Malaysian Borneo. *Journal of Tropical Ecology*, 30: 481-492. doi:10.1017/S0266467414000303

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# Preface

Atmospheric deposition of S compounds is still one of the important environmental issues in Northeast and Southeast Asian countries. To tackle this scientific issue, scientists from the community of Acid Deposition Monitoring Network in East Asia (EANET) investigated S dynamics in forest catchments in Japan, Thailand and Malaysia. This is the first international project on S dynamics in Asian forests. We are sure that our findings will contribute to evaluation of atmospheric S impacts and further development of biogeochemistry in this region.

# Table of Contents



## 1. Introduction

Deposition level of sulphur (S) is high and hence the cumulative load of S is also high in East Asia. Emissions of $SO_2$ in Asia increased by 119% from 1986 to 2003 (Ohara et al. 2007). Although $SO_2$ emissions in China peaked in 2006 and have decreased gradually thereafter (Lu et al. 2011), emission levels remain high in the region. Since S deposited on ecosystems may be retained in soil and/or cycled in the soil-plant system, manifestation of its effect may be delayed (e.g. Mitchell and Likens 2011; Kobayashi et al. 2012). Moreover, several rivers/lakes for monitoring on inland aquatic environment in the East Asian countries showed pH-declining trend with $SO_4^{2-}$-increasing trend (EANET 2011). Effect of S deposition on terrestrial ecosystems is one of the important current issues to be investigated in East Asia. However, effects of S were mostly ignored as a scientific subject, since S emission had already been reduced in developed countries, while nitrogen (N) deposition and its biogeochemistry had been well studied in context of N saturation (Aber et al. 1989; Stoddard 1994). Moreover, biogeochemical studies on the catchment scale, which is an effective approach to evaluating the effects of S and N, had not been enough promoted in Southeast Asia.

The scientists from the community of Acid Deposition Monitoring Network in East Asia (EANET) investigate the dynamics of S derived from atmospheric deposition in forest catchments in Niigata Prefecture, Japan, Nakhon Ratchasima Province, Thailand, and Sabah and Sarawak States, Malaysia. In order to determine S dynamics in the forest ecosystems, analysis of S isotopic ratio was applied for rainwater, soil water and stream water in addition to measurement of the fluxes. The data obtained in the project may explain the possible impacts of S deposition on the forests. Since N deposition is also quite high in the region, its relation to acidification/eutrophication could also be discussed in the part of the sites.

In this project, S dynamics in the forest ecosystems were investigated to determine S dynamics in ecosystems of the East Asian forests and to evaluate the combined effects of S and nitrogen on acidification and eutrophication of the East Asian forests.

## 2. Methodology

Study sites:

The study sites were established in four forest catchments in Japan, Thailand and Malaysia (Fig. 1). Fluxes of ions including $SO_4^{2-}$ had been studied by previous projects since 2002, 2005 and 2008 in Kajikawa, Sakaerat and Danum Valley sites, respectively (Table 1). However, the surveys in these sites were mostly finished in 2010/2011. In 2012, the study sites were reactivated for the APN project and the rehabilitated forest in Bintulu was added as a new site for the APN project.

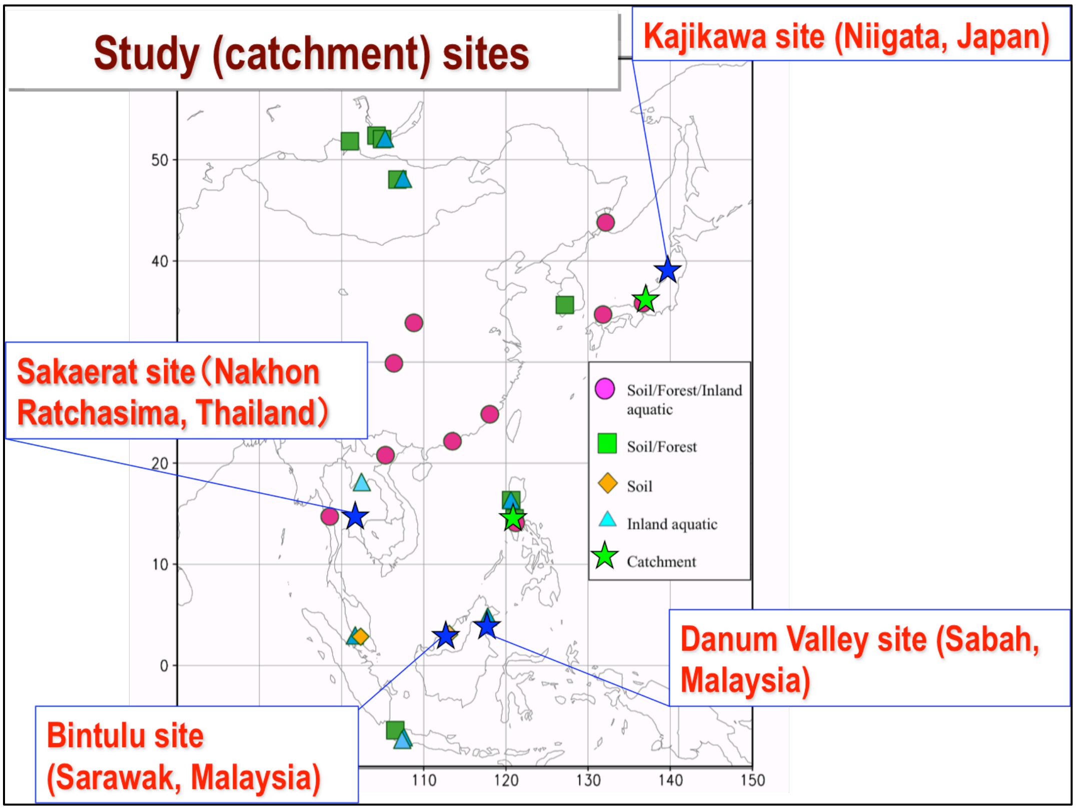



Fig. 1 Locations of the existing EANET ecological monitoring sites and study catchments. In the EANET sites marked with circle, square, diamond, and triangle indicates sites for

monitoring on soil, forest vegetation and inland aquatic environment, on soil and forest vegetation, on soil only, on inland aquatic environment only, respectively. Stars colored with green and blue indicates catchment sites on regular basis and research basis, respectively.

Table 1. Study sites and applied methods

| Site | Kajikawa | Sakaerat | Danum Valley | Bintulu |
|---|---|---|---|---|
| Country | Niigata, Japan | Nakhon Ratchasima, Thailand | Sabah, Malaysia | Sarawak, Malaysia |
| Forest type | Japanese cedar | DEF | Tropical rainforest | Rehabilitated Forest |
| Applied methods for deposition | Bulk sampling of rainwaters from RF, TF, and SF | Bulk sampling of rainwaters from RF, TF, and SF<br>IER sampling<br>(see Fig. 2) | IER sampling | IER sampling |
| Applied methods for soil solution | Water sampling using the porus cup | IER sampling | IER sampling | IER sampling |
| Applied methods for stream water | Water sampling | Water sampling<br>IER sampling for S isotopic analysis | Water sampling<br>IER sampling for S isotopic analysis | Water sampling<br>IER sampling for S isotopic analysis |
| Start year | 2002 | 2005 | 2008 | 2012 |

Note. DEF, dry evergreen forest;RF, rainfall outside forest canopy; TF, throughfall; SF, stemflow; IER, ion-exchange resin

Flux determination:

Field surveys were conducted to determine the fluxes of ion constituents by rainfall outside forest canopy (RF), throughfall (TF) and stemflow (SF), and stream water (SW). The sampling methods applied for the respective sites were summarized in Table 1. In addition to water sampling, the data obtained from the ion-exchange resin (IER) sampling (Fig. 2) were also be used for this purpose. Ion concentrations in the water samples and extract samples from IER were determined using ion chromatograph. The ionic analysis was carried out in ACAP, Japan or ERTC, Thailand.

In the case of Kajikawa, Sakaerat and Danum Valley sites, fluxes of ion constituents were determined by the previous projects. The existing data were utilized to summarize the fluxes in these sites.

S isotopic analysis:

To obtain enough amounts of the samples for S isotopic analysis, “IER sampling” was applied in Sakaerat, Danum Valley and Bintulu sites (see Table 1). In the case of rainwater, the IER column, in which the IER was packed, was installed with a plastic funnel to collect RF and TF below the canopy (Fig. 2). The IER in the column can trap $SO_4^{2-}$ in rainwater. The IER sampling was also applied for collection of SS and SW, for which plastic rings and mesh bags were used for packing the IER, respectively. The IER ring samplers for SS were installed in different depths in soil to collect $SO_4^{2-}$ in water vertically passed through each depth. The resin samplers for rainwater and SS were installed in the fields for several months to obtain enough amounts of $SO_4^{2-}$ for isotopic analysis. The IER bags for SW were placed in the center of the stream flow for several hours. In the case of Kajikawa site, water samples are also used for S isotopic analysis.

The $SO_4^{2-}$ extracted from the resin samplers or that in water samples were concentrated by evaporating water on hot plate and then precipitated as $BaSO_4$ by using $BaCl_2$. The S isotopic ratio in the powdered $BaSO_4$ is analyzed by using the Elemental analyzer (EA) - Mass Spectrometer (MS). The S isotopic analysis was carried out in ACAP, while the pre-treatment was carried out partly in UPM, too. Isotopic ratio of S compounds ($^{34}S/^{32}S$) may be changed by biological process (isotope fractionation). S isotopic ratio of rainwater and SW was measured to discriminate origin of S (atmospheric, biological or geological origin) and to discuss retention time of S in the ecosystems. S isotopic ratio is expressed as:

$$\delta^{34}S\ (‰) = \{(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{CDT} - 1\} \times 1000$$

where, $(^{34}S/^{32}S)_{sample}$ and $(^{34}S/^{32}S)_{CDT}$ were isotopic ratios of sample and Canyon Diablo troilite (standard substance), respectively.

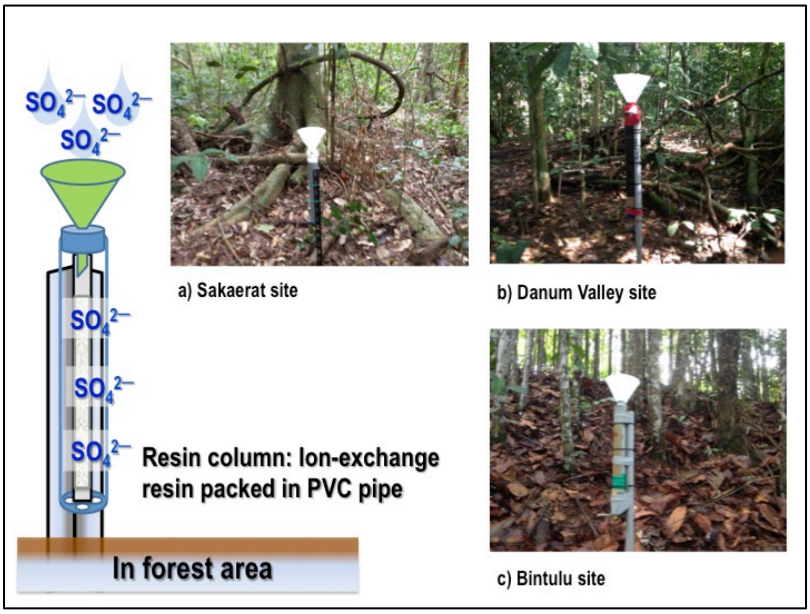



Fig. 2. Ion-exchange resin (IER) samplers for S isotopic analysis

Speciation of S compounds in soil layer:

In Bintulu site, $NaHCO_3$-extractable fraction was measured in UPM according to the EANET technical manual (EANET 2000). This fraction may include $SO_4^{2-}$ and some organic S. In other sites, $CaHPO_4$-extractable fraction was measured in ACAP according to Tabatabai (1996). This fraction may include both adsorbed $SO_4^{2-}$ and soluble $SO_4^{2-}$.

Trial application of biogeochemical simulation model:

We have been discussing possibility of utilizing a biogeochemical model, which was developed by Prof. Junko Shindo, University of Yamanashi. Prof. Shindo was the project leader of the previous projects, in which the catchment plots in Sakaerat and Danum Valley sites were established. So far, the data in Kajikawa and Sakaerat sites have been applied to the model to simulate soil solution concentrations in the previous project. However, utilization of the new data on S dynamics is still under discussion.

Project seminars in Malaysia and Thailand:

The project seminars entitled "The APN Project Workshop on Sulphur Dynamics in East Asian Forests" were held in 2013 and 2014 in Malaysia and Thailand, respectively, in order to share outcomes from the project and discuss future research topics in the region.

## 3. Results & Discussion

Fluxes of S and N:

Inputs of S and N by TF (+SF) under forest canopy and the outputs by SW in the study catchments were summarized in Table 2. The mean $SO_4^{2-}$ concentrations in SW were 101, 73, 39, and 6.3 $\mu mol_c\ L^{-1}$ in Kajikawa, Bintulu, Danum Valley, and Sakaerat sites, respectively.

The atmospheric inputs of S and N were significantly large in Kajikawa site, where long-range transport of air pollutants from the Asian Continent was suggested (Sase et al. 2012). The inputs in Bintulu site were also large, which is one of the most industrialized cities in Malaysia. The inputs in Sakaerat and Danum Valley sites were relatively small, although the inputs of Sakaerat site showed a distinct seasonality and high peaks were observed in the beginning of wet season as described below.

The outputs of S and N in Kajikawa site were approx. 75% and 56% of the inputs, respectively. Even though a relatively large portion of the S input was discharged from SW, it seemed that the S input was not directly discharged into SW, as discussed in the section for S isotopic analysis. As already discussed by Stoddard (1994), $NO_3^-$ concentration in SW in healthy forests should be low, since N is an important nutrient and normally limited in temperate forests. The large N output as $NO_3^-$ suggested possible N saturation, as shown in the long-term data.

The outputs in Sakaerat site were significantly smaller than the inputs. The catchment is under tropical savanna climate, which has distinct dry and wet seasons. There was a large uncertainty of the water balance. Even though the uncertainty was taken into account, the outputs were significantly small. The $SO_4^{2-}$ concentration in SW was significant low compared to that of the input (41.9 $\mu mol_c\ L^{-1}$, as the weighted-mean of TF+SF), suggesting retention of S in the forest ecosystems, as discussed below. Although $NO_3^-$ concentration (6.3 $\mu mol_c\ L^{-1}$) was also low compared to those of $NO_3^-$ (24.4 $\mu mol_c\ L^{-1}$) and $NH_4^+$ (31.4 $\mu mol_c\ L^{-1}$), the N may be effectively used in the large internal N cycle as suggested by Yamashita et al. (2010).

The material budgets in Danum Valley have been published by Yamashita et al. (2014), as one of the project outputs. The S output was larger than the input in Danum Valley, while the N output was smaller than the input. The similar discrepancy of S budget was observed also in Sarawak in the same island (Gomyo et al. 2012). Since Danum Valley site is located in remote area in Borneo Island, other sources than atmospheric deposition, such as sulfide minerals in geology, was suggested. This was also suggested by S isotopic analysis, as discussed below.

In Bintulu site, the material budget has not been estimated because water discharge was not measured precisely. However, both inputs of S and N were relatively large. Since Bintulu is famous for industrial area, further investigation of atmospheric impacts may be necessary.

Table 2. Fluxes of S and N in the study catchments

| Site | | Kajikawa | Sakaerat | Danum Valley*4 | Bintulu |
|---|---|---|---|---|---|
| Country | | Niigata, Japan | Nakhon Ratchasima, Thailand | Sabah, Malaysia | Sarawak, Malaysia |
| Forest type | | Japanese cedar | Dry evergreen forest | Tropical rainforest | Rehabilitated Forest |
| Annual precipitation (mm) | | 2,281 | 1,488 | 2,700 | 3,500 |
| S | Input*1 | 28.5*2 | 5.76*2 | 3.6*3 | 19*3 |
| (kg S $ha^{-1}$) | Output | 21.6 | 0.16 | 6.0 | NA |
| N | Input | 16.6*2 | 7.9*3 | 6.2*3 | 11.8*3 |
| (kg N $ha^{-1}$) | Output | 9.3 | 0.1 | 1.6 | NA |

Note. *1 Input by TF (+SF) under forest canopy; *2 By water sampling of TF+SF; *3 By IER sampling of TF; *4 After Yamashita et al. (2014).

Analysis of the long-term data in Kajikawa and Sakaerat sites:

As shown in Table 1, the surveys in Kajikawa and Sakaerat sites started in 2002 and 2005, respectively. Relatively long-term data have been accumulated in these sites. Based on the analysis of the long-term data, sensitive responses to changes in atmospheric conditions have been found in both catchments.

In Kajikawa site, Japan, atmospheric deposition of S increased significantly in winter due to seasonal west winds from the Sea of Japan, as already reported by the previous studies (Ohizumi et al. 2001; Kamisako et al. 2008; Sase et al. 2008; 2012). The forest largely suffered from transboundary air pollution from the Asian Continent. According to Lu et al. (2011), S emission in China peaked in 2006 and gradually declined thereafter. Similarly, non-sea salt (nss) $SO_4^{2-}$ deposition by TF+SF in Kajikawa site peaked in 2006 and started declining (Fig. 3). The total $SO_4^{2-}$ deposition (including sea salt) also significantly declined during the observation period (detailed data is not shown here).

Accordingly, $SO_4^{2-}$ concentration in SW declined with increase of its alkalinity, while $NO_3^-$ concentration increased continuously (Fig. 4). In fact, as shown in Fig. 5, the weighted mean $SO_4^{2-}$ concentration in SW was significantly correlated with the annual $SO_4^{2-}$ deposition ($p$ = 0.00194). It was suggested that the SW in Kajikawa site recovered from acidification due to decline of $SO_4^{2-}$ deposition. Moreover, since $NO_3^-$ concentration in SW increased continuously, it was suggested that N saturation in Kajikawa forest progressed gradually. Currently, relationship between recovery from acidification due to the reduction of S input and N saturation was not clear. The discussion above is under preparation for publication (Sase et al. in preparation).

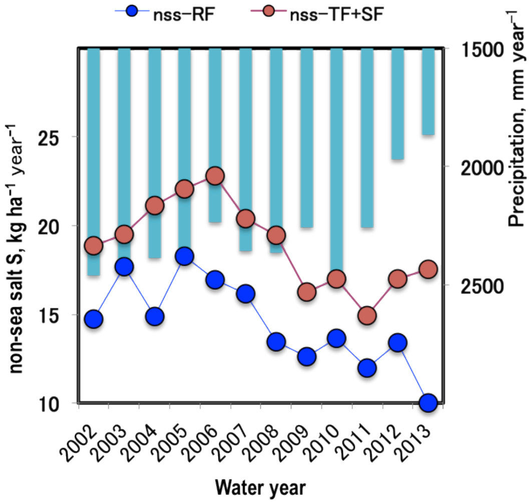



Fig. 3. Changes in annual S deposition by TF+SF and RF in Kajikawa site

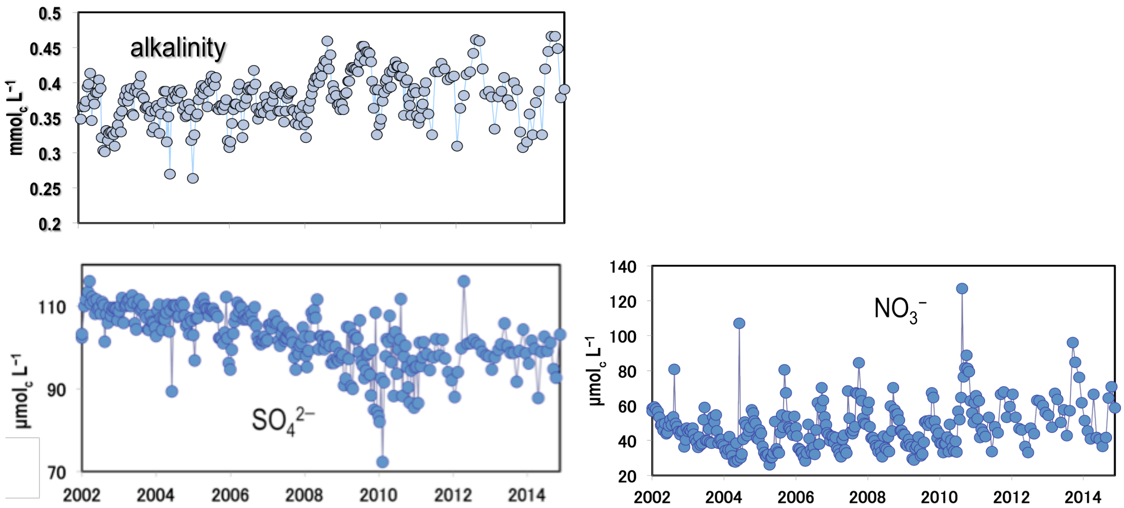



Fig. 4. Long-term changes in stream water chemistry in Kajikawa site.

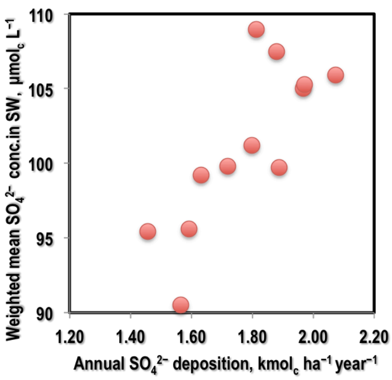



Fig. 5. Relationship between annual $SO_4^{2-}$ deposition and mean $SO_4^{2-}$ concentration of SW in Kajikawa site.

In Sakaerat site, Thailand, atmospheric deposition showed distinct seasonality as shown in Fig. 6. There is a clear dry season from November to February. In March or April in the beginning of the wet season, deposition of all ion constituents from both RF and TF+SF increased significantly. In general, canopy exchange, such as leaching and uptake, is limited in $SO_4^{2-}$ and $Cl^-$. In these ions, the deposition by TF+SF can be considered as total deposition, including wet deposition by rainfall and dry deposition of gaseous and particulate matters. Gaseous and particulate pollutants suspended in the air and plant body during the dry season may be washed out by the first precipitation (Sase et al. 2012). In the later wet season, the deposition increased again with increase of precipitation.

The SW chemistry showed very unique seasonality as shown in Fig. 7. In the early wet season, pH and EC of the SW increased with increase of base cations and alkalinity (Fig. 7a and b). It was suggested that mineralization of organic matters on forest floor was enhanced by the first precipitation in the beginning of wet season (Lodge et al. 1994) and that base cations and $NH_4^+$ derived from the mineralization leached into the SW in the early wet season. According to Yamashita et al. (2010), the soil pH also showed the seasonality, declining during the dry season and increasing during the wet season. Since anion exchange capacity (AEC) in soil is derived from pH-dependent charge, higher AEC with lower pH in the beginning of the wet season may effectively trap anions derived from atmospheric deposition as well as mineralization of organic matters. Therefore, leaching of anions was limited in the early wet season, resulting in 'alkalinization' observed here. After this alkalinization, suddenly pH dropped with the peak of $SO_4^{2-}$ (Fig. 7b and c). With increase of the soil pH during the wet season, AEC decreased, and therefore anions including $SO_4^{2-}$ may be released. However, only $SO_4^{2-}$ was observed as clear peaks, although sometimes $NO_3^-$ showed peaks. Dissolved inorganic nitrogen (DIN) such as $NO_3^-$ was effectively used in the plant-soil system (Yamashita et al. 2010). Moreover, compared with $Cl^-$ and $NO_3^-$, $SO_4^{2-}$ is strongly adsorbed on soil surface (Kamewada and Takahashi 1996). This may be the reason why only $SO_4^{2-}$ was observed as clear peaks. In fact, the magnitudes of the peaks clearly reflected the deposition amounts in the early wet season (Fig. 8), which indicated sensitive responses of the SW to atmospheric deposition.

During the observation period, as clearly shown in Fig. 7b, the pH of the SW has been declining significantly with increase of $SO_4^{2-}$. On the other hand, the $SO_4^{2-}$ deposition has been declining. The trends on the deposition and the SW chemistry were summarized in Table 3. According to the EANET data (EANET 2013), The nss-$SO_4^{2-}$ deposition and/or concentrations declined significantly for the last decade from 2000 to 2012 in Bangkok ($p$ = 0.002, since 2005, and $p$ = 0.004, respectively) and Pathumtani ($p$ = 0.03 and 0.0002, respectively) in Thailand. The latest emission inventory (Kurokawa et al. 2013) is corresponded to the trends above. The $SO_4^{2-}$ deposition/concentration seemed to be declining for the last decade at the regional scale. Decline of the $SO_4^{2-}$ deposition/concentration may accelerate release of $SO_4^{2-}$ adsorbed on soil. Moreover, precipitation pattern changed slightly such that the relative contribution of precipitation in the middle-late wet season has increased recently. This may also accelerate leaching of $SO_4^{2-}$ from the ecosystems. Release of $SO_4^{2-}$ might cause acidification observed here. Therefore, retention and release of $SO_4^{2-}$ largely contributed to both seasonal changes and trends during the observation period.

The discussion above is under submission for publication (Sase et al. submitted).

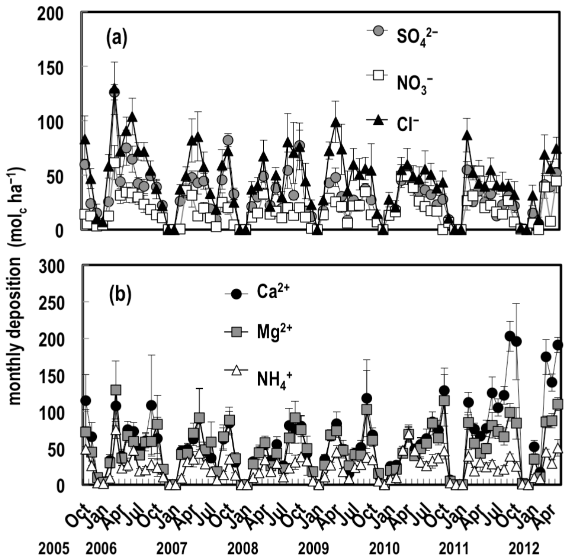



Fig. 6. Changes in monthly deposition of major anions (a) and cations (b) by throughfall and stemflow in Sakaerat site. Plots and error bars show mean values and standard errors of five collectors (Sase et al. submitted)

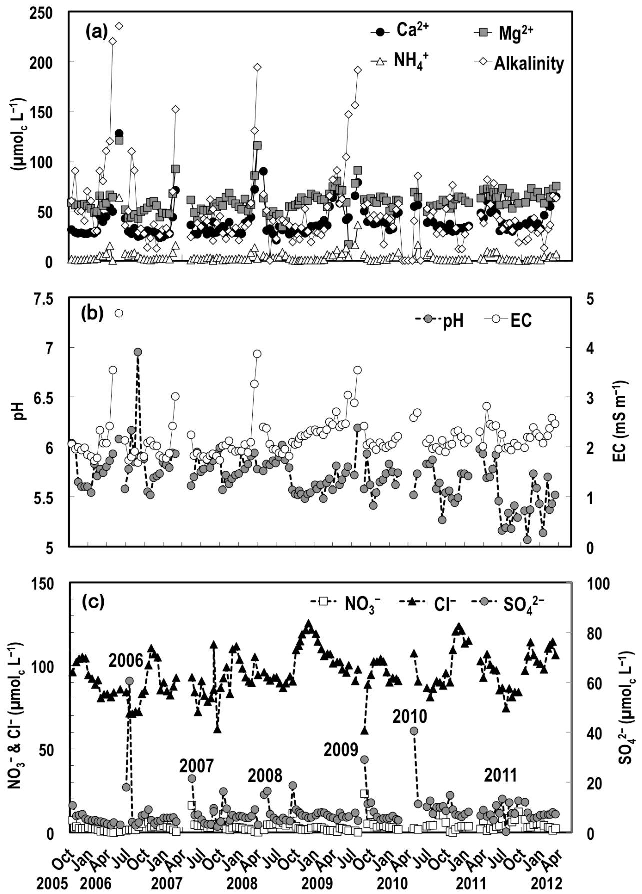



Fig. 7. Changes in stream water chemistry in Sakaerat site. The data collected at approx. 15-day intervals were shown. The year number in (c) indicates the first $SO_4^{2-}$ peak in each water year (Sase et al. submitted)

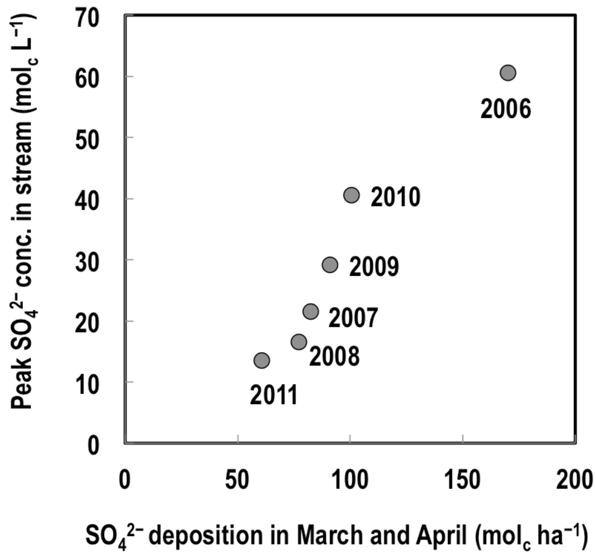



Fig. 8. Relationship between the first $SO_4^{2-}$ deposition in March and April in the beginning of wet season and the peak $SO_4^{2-}$ concentration in each water year in Sakaerat site (Sase et al. submitted)

Table 3 Trends of atmospheric depositions and stream water chemistry during the observation period in Sakaerat site (Sase et al. submitted)

| Variable | TF+SF | | SW | |
|---|---|---|---|---|
| | Concentration | Deposition | Concentration | Flux |
| $SO_4^{2-}$ | − | −− | ++ | ns |
| $NO_3^-$ | ns | ns | ++ | ns |
| $Cl^-$ | ns | −− | ++ | ns |
| $NH_4^+$ | ns | ns | − | ns |
| $Na^+$ | ns | ns | ++ | ns |
| $K^+$ | ns | ns | ns | ns |
| $Ca^{2+}$ | ns | ns | ++ | ns |
| $Mg^{2+}$ | ns | ns | ++ | ns |
| $H^+$ | ns | ns | ++ | + |
| Alkalinity | ns | ns | ns | ns |

Note. − and −−, declining at $p < 0.05$ and $p < 0.01$, respectively; + and ++, increasing at $p < 0.05$ and $p < 0.01$, respectively; ns, no significant trend. TF+SF, volume-weighted mean concentrations and atmospheric depositions by throughfall and stemflow; SW, concentrations and chemical fluxes by stream water.

S isotopic ratio of rainwater, soil solution and stream water:

The S isotopic ratio ($\delta^{34}S$, ‰) of RF, SS and SW was summarized in Table 4. The $\delta^{34}S$ values of RF were quite different among the sites. Since the study sites were located in different countries, sources of atmospheric S might also be different. Even within Borneo Island, the values are slightly different between those at Danum Valley sites, Sabah and Bintulu sites, Sarawak. The $\delta^{34}S$ values of SW may be informative to discuss dynamics of S in ecosystems and its origin. In Kajikawa site, the annual weighted mean $\delta^{34}S$ value of SW was mostly similar to that of RF. As a possible source of S, atmospheric deposition can be considered. In Sakaerat, the $\delta^{34}S$ values of SW were sometimes significantly larger than those of RF. In addition to effects of atmospheric deposition, effects of biological fractionation (bacterial dissimilatory S reduction, BDSR) can be considered. On the other hand, in the $\delta^{34}S$ values of SW in Danum Valley and Bintulu were sometimes significantly smaller than those in RF. In addition to effects of atmospheric deposition, effects of geology (rock weathering) can be considered. The $\delta^{34}S$ values of SS were basically in between those of RF and SW. Possible sources of $SO_4^{2-}$ in SW are discussed below.

Table 4. S isotopic ratios in the study catchments

| Site | | Kajikawa | Sakaerat | Danum Valley | Bintulu |
|---|---|---|---|---|---|
| Country | | Niigata, Japan | Nakhon Ratchasima, Thailand | Sabah, Malaysia | Sarawak, Malaysia |
| S isotopic ratio ($\delta^{34}S$, ‰) | RF | 8.83 (2.3 – 12.3) | 4.1 | 10.1 | 7.9 |
| | SS | 6.7 – 10.5 | 2.0 – 9.3 | 6.5 – 9.6 | 4.4 – 11.7 |
| | SW | 9.28 (8.4 -10.0) | 2.6 – 10.4 | 2.6 – 8.2 | –4.1 – +14.3 |
| Possible source of S in SW | | AD (including sea salt) | BDSR<br>AD (seasonally) | Rock weathering<br>AD (high flow period) | Rock weathering<br>AD (seasonally) |

Note. RF, Rainfall outside forest canopy; SS, soil solution; SW, stream water; AD, atmospheric deposition; BDSR, bacterial dissimilatory S reduction

In Kajikawa site, the $\delta^{34}S$ values of RF showed distinct seasonality, low in summer and high in winter, suggesting different emission sources. Effects of transboundary air pollution as well as sea salts were suggested as reported by Ohizumi et al. (2001). On the other hand, the values of SW were very stable, approx. 9‰. In winter, the values of SW were significantly smaller than those of RF. Since biological fractionation cause increase of the $\delta^{34}S$ values in the ecosystems, the fractionation cannot explain all of the phenomena. As described above, the $SO_4^{2-}$ deposition in Kajikawa site was quite large and especially increased in winter. Therefore, the large input of $SO_4^{2-}$ from the continent may affect the SW chemistry through a year. In fact, the annual weighted mean $\delta^{34}S$ value of RF was mostly similar to that of SW. According to the input-output budget in Table 2, 75% of the S deposition was released to SW. But the S isotopic analysis indicated that $SO_4^{2-}$ derived from atmospheric deposition was not directly flowed into SW. It was suggested that $SO_4^{2-}$ deposited from atmosphere was once retained in the ecosystem and released with the averaged $\delta^{34}S$ value into SW gradually. Detailed retention mechanisms, such as adsorption of $SO_4^{2-}$ to soil surface and S uptake by plants, should be investigated. The discussion above is under preparation for publication (Saito et al. in preparation).

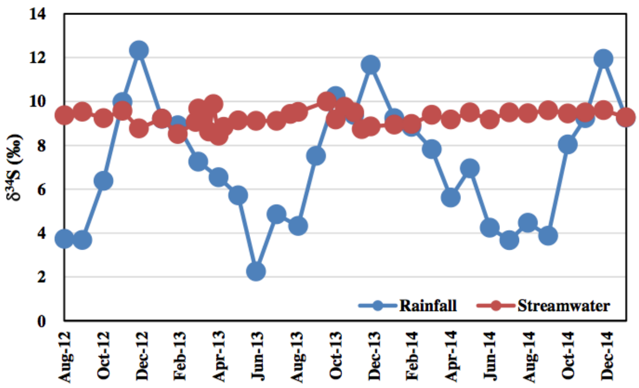
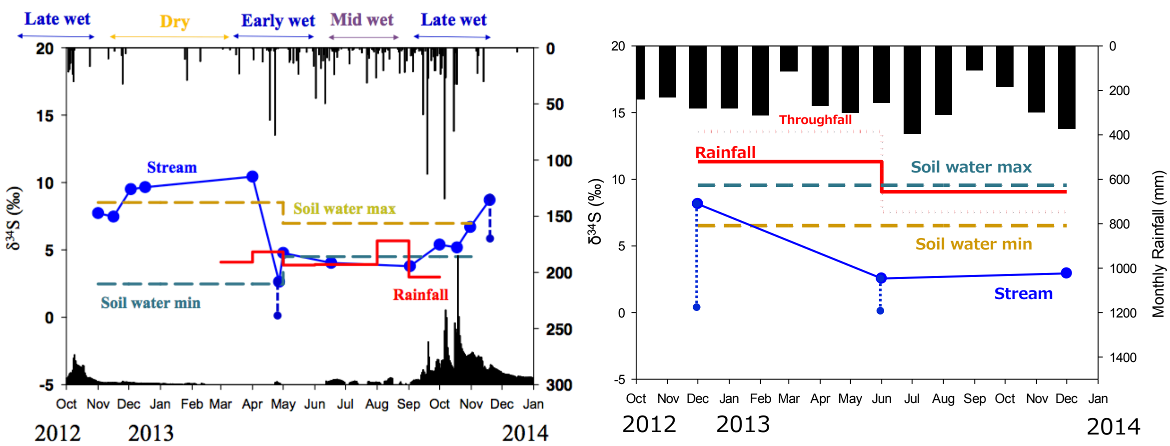



Fig. 9. Seasonal changes in the S isotopic ratio of rainwater and stream water in Kajikawa site (Saito et al. in preparation)

In tropical forest sites also, seasonal effects of atmospheric S were suggested. In Sakaerat site (Fig. 9 upper left), the $\delta^{34}S$ values of SW were significantly higher than those of RF during the dry season. However, with the first precipitation in the early wet season, the value suddenly decreased to the same level with those of RF and keeps the level from the early to middle wet seasons. The $\delta^{34}S$ values increased gradually again from the late wet season to the dry season. It was suggested that atmospheric S contributed to SW chemistry from the early to middle wet seasons, while the $SO_4^{2-}$ derived from biological fractionation (BDSR) was leached out by high water flow in the late wet season. Detailed mechanisms on BDSR in Sakaerat site should be investigated.



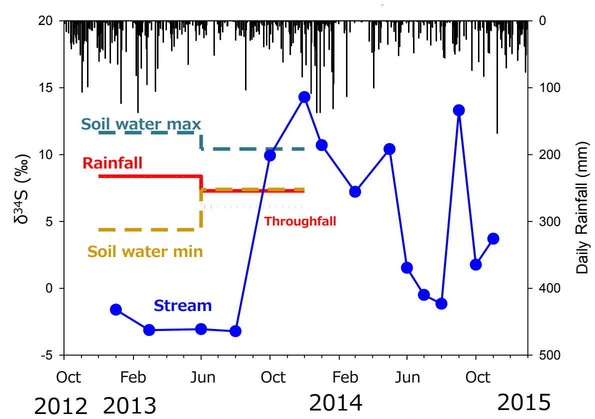




Fig. 9. Seasonal changes in the S isotopic ratio of rainwater, soil solution (soil water) and stream water in Sakaerat (upper left), Danum Valley (upper right), and Bintulu (lower left). Dotted lines of SW in Skaerate and Danum Valley sites indicate the range of $\delta^{34}S$ values among different points in the streams (Yamashita et al. in preparation)

In Bintulu site (Fig. 9 lower left), the $\delta^{34}S$ values of SW were significantly lower than those of RF in the low-precipitation period. The $\delta^{34}S$ values increased to the same level with RF in the high-precipitation period, although the detailed seasonal changes in RF were not measured. It was suggested that the $SO_4^{2-}$ derived from geology with low $\delta^{34}S$ values contributed to the SW chemistry during the low-precipitation period. On the other hand, direct effects of atmospheric S to the SW chemistry were observed in the high-precipitation period.

In Danum Valley site (Fig. 9 upper right), the data is very limited. In general, the $\delta^{34}S$ values of SW were significantly lower than those of RF. As described above, the S output in Danum Valley site was significantly larger than the input (Table 2). It was suggested that the $SO_4^{2-}$ derived from geology with low $\delta^{34}S$ values contributed to the SW chemistry in the Danum Valley site. However, the $\delta^{34}S$ value in December 2012 was significantly large and relatively close to that of RF. Since the water discharge was significantly large at that time (detailed data is not shown here), direct flow of atmospheric S may contribute to increase of the $\delta^{34}S$ value of SW.

The discussion in tropical forests is under preparation for publication (Yamashita et al. in preparation).

Extractable $SO_4^{2-}$ in soil:

S analysis in soil is still on going. The first data of extractable S in Bintulu and Sakaerat sites were shown in Fig. 10 and Fig. 11, respectively. In Bintulu site, extractable $SO_4^{2-}$ in soil was determined in different slope positions, namely upper, middle and lower positions. The content of $SO_4^{2-}$ increased with soil depth and declined with decline of the slope position (Fig. 10). The storage estimated on a unit area basis showed the similar tendency (detailed data is not shown here).

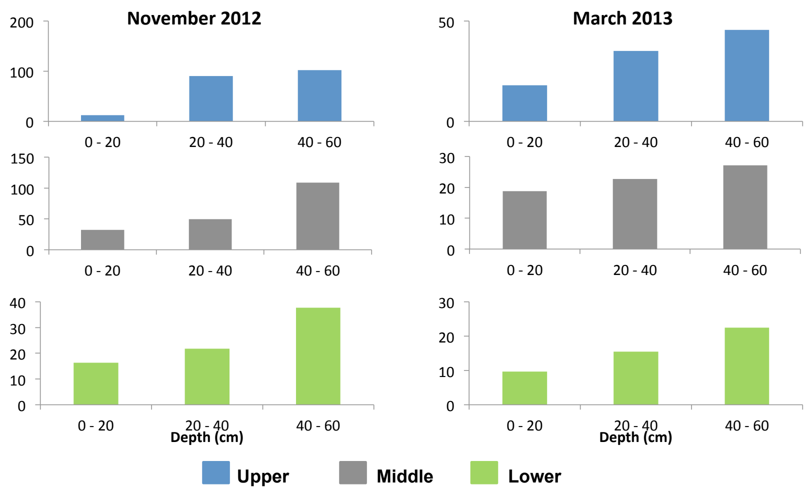



Fig. 10. $NaHCO_3$-extractable $SO_4^{2-}$ in soil (mg $kg^{-1}$) in different slope positions in Bintulu site. (Ahmed et al. in preparation)

On the other hand, in Sakaerat site, the content of $SO_4^{2-}$ was larger in 5 cm than in 50 cm (Fig. 11), although the extraction method is different. However, the storage on a unit area basis must be larger in deeper soil layers than in shallow soil layers due to high density in deeper soil.

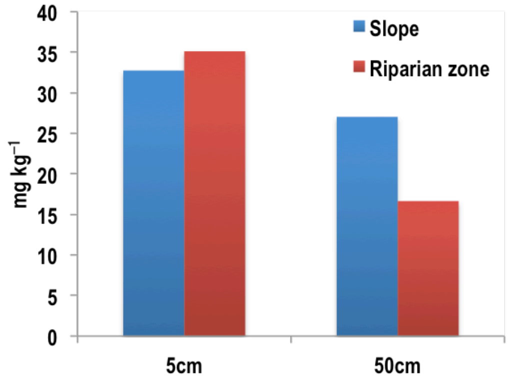



Fig. 11. $CaHPO_4$-extractable $SO_4^{2-}$ in soil (mg $kg^{-1}$) in different slope positions in Sakaerat site. (Yamashita et al. in preparation)

Extractable $SO_4^{2-}$ in soil in other sites will be determined in near future. Moreover, S isotopic ratio of extractable $SO_4^{2-}$ may be measured for some samples, if the S contents are high enough for the isotopic analysis.

Trial application of biogeochemical simulation model:

We have just clarified some unique characteristics S dynamics and their possible origins in the study sites. However, the detailed mechanisms of S dynamics are still under investigation. We may need some more data analysis and also additional surveys to clarify the mechanisms. Therefore, application of the data to biogeochemical model is still under discussion. Hopefully in near future, with accumulation of the data and analysis, application of the model can be considered.

Project seminars in Malaysia and Thailand:

"The APN (Project) Workshop on Sulphur Dynamics in East Asian Forests" was held in Malaysia and Thailand in 2013 and 2014, respectively, as follows:

- In Selangor, Malaysia: 24 June 2013 (with the field trip on 25 June)
- In Bangkok, Thailand: 18 December 2014 (with the field trip on 19 December)

The 40 - 45 participants from universities, institutes and governmental agencies attended the respective workshops. Progress and outcomes of the project were presented and active discussion was made. Moreover, possible future research topics were discussed. The workshop summaries were attached in the Appendix.

Several papers are under preparation for publication based on the data obtained in the project. Most of the project data will be disclosed in the papers. The project data may also be disclosed on the ACAP website after publication of the papers.

## 4. Conclusions

Atmospheric deposition of S compounds is still one of the important environmental issues in Northeast and Southeast Asian countries. We conducted field surveys and data analysis in four forest catchments in Japan, Thailand and Malaysia to clarify dynamics of S in the ecosystems and to evaluate possible combined effects of S and N on acidification and eutrophication. As a new trial, S isotopic analysis was also applied in this study. Fluxes of S and N were significantly large in Kajikawa site, Japan, and Bintulu site, Sarawak, Malaysia, where transboundary air pollution and effects of local industrial area were suggested, respectively. In particular, it was suggested that Kajikawa site has been recovering from acidification due to reduction of S input, while N saturation has been progressing gradually. Currently, relationship between the recovery from acidification and N saturation was still not clear. Further investigation is necessary for combined effects of S and N inputs on the ecosystems. The fluxes in other two sites are relatively low. However, it was clarified that SW chemistry responded sensitively to changes in atmospheric conditions in Sakaerat site, Thailand. Based on the S isotopic analysis, dynamics of S in the ecosystems and possible sources of S in SW were clarified in the respective sites, although characteristics of S dynamics were quite different among the sites and the detailed mechanisms should be investigated more. Effects of atmospheric S on SW chemistry were certainly suggested in Kajikwa and Sakaerat site, while effects of geological sources (such as rock weathering) on SW chemistry were suggested in Danum Valley and Bintulu sites. In particular, the S output significantly exceeded the input in Danum Valley probably due to S leaching derived from rock weathering. Moreover, biological fractionation of S (BDSR) may occur from the late wet season to the dry season in Sakaerat site. We found certain effects of atmospheric S on the ecosystems through the project. However, we also found that climate, geology and feature of the ecosystems should carefully be taken into consideration for evaluation of S dynamics in Northeast and Southeast Asia. Our findings will be shared with the EANET community and will contribute to evaluation of atmospheric S impacts and further development of biogeochemistry in this region.

## 5. Future Directions

We found possible S sources for SW and possible processes of S dynamics in the ecosystems. In particular, biological S fractionation (BDSR) observed in Sakaerat site is a very important process in the S dynamics. Detailed mechanisms should be investigated. Moreover, geological S suggested in Danun Valley and Bintulu sites may also be important for nutrient dynamics at the watershed scale. Changes in precipitation amount and its pattern due to climate change may affect significantly S weathering in such watersheds, as Mitchell and Likens (2011) suggested. Further studies on such S sources and processes in the ecosystems should be promoted in Northeast and Southeast Asia. Relationship between cycles of S and N in the ecosystems should also be investigated.

Currently, deposition as particulate $SO_4$ (such as $(NH_4)_2SO_4$) is one of the major processes on atmospheric S input in ecosystems. The $(NH_4)_2SO_4$ is a major component of fine aerosols, so-called '$PM_{2.5}$'. Problem on particulate matters (PM) is a big issue in Northeast and Southeast Asia. Many possible S sources, such as power plants, industry, vehicle, and biomass burning, have been discussed in the region. Our trial on S isotopic analysis may contribute to identify possible sources of $PM_{2.5}$.

Moreover, as suggested in Sakaerat site, biomass burning is a possible large source of pollutants. Not only S-containing PM but also other types of PMs such as black carbon (BC) should be investigated. Ozone may also be produced. Forest canopy effectively trap PM on the surface, and this can be considered as a removal process of PM from atmosphere. This process should be investigated in detail as one of ecological functions of forest canopy.

Taking the subjects into accounts, effects of multi pollutants, including S, N, ozone and PM, and climate change should be studied in the region. In any types of the studies above, our experience in the project will be utilized effectively.

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## Appendix

Conferences/Symposia/Workshops

- The APN Workshop 2013 on Sulphur Dynamics in East Asian Forests
  Venue: Residence Hotel, UNITEN, Selangor, Malaysia
  Date: 24 June 2013 (with the field trip on 25 June)

  - List of speakers invited by the project budget
    Project members:
    - Dr. Hiroyuki Sase, ACAP
    - Dr. Tsuyoshi Ohizumi, ACAP
    - Dr. Naoyuki Yamashita, ACAP
    - Mr. Bopit Kietvuttinon, RFD
    - Dr. Hathairatana Garivait, ERTC

    Collaborators:
    - Mr. Tatsuyoshi Saito, ACAP, tsaito@acap.asia
    - Dr. Seca Gandaseca, UPM Bintulu Campus (UPMKB), seca@upm.edu.my
    - Dr. Ahmed Osumanu Haruna, UPMKB, osumanu@upm.edu.my
    - Mr. Mohamad Hilmi bin Ibrahim, UPMKB, mohamadhilmiibrahim@gmail.com

  - Local project member
    - Prof. Nik Muhamad Majid, UPM

  - Relevant scientists, experts, and officers from universities, institutes and governmental agencies attended the Workshop.
    - UPM
    - Institute of Tropical Forestry and Forest Product (INTROP), UPM
    - Malaysian Meteorological Department (MMD)
    - Department of Chemistry (DOC)
    - Other universities

- The APN Project Workshop 2014 on Sulfur Dynamics in East Asian Forests
  Venue: H. Slade Meeting Room, Department of National Park, wildlife and Plant, Bangkok, Thailand
  Date: 18 December 2014 (with the field trip on 19 December)

  - List of speakers invited by the project budget
    Project members:
    - Dr. Hiroyuki Sase, ACAP
    - Dr. Tsuyoshi Ohizumi, ACAP
    - Dr. Naoyuki Yamashita, ACAP
    - Prof. Nik Muhamad Majid, UPM

    Collaborators:
    - Mr. Tatsuyoshi Saito, ACAP, tsaito@acap.asia
    - Dr. Yayoi Inomata, ACAP, inomata@acap.asia
    - Dr. Seca Gandaseca, UPM, seca@upm.edu.my

- Dr. Ahmed Osumanu Haruna, UPMKB, osumanu@upm.edu.my

- Local project member
  - Mr. Thiti Visaratana, RFD
  - Mr. Bopit Kietvuttinon, RFD
  - Dr. Hathairatana Garivait, ERTC

- Guest speakers by their own budget
  - Dr. Kazuhide Matsuda, Tokyo University of Agriculture and Technology, kmatsuda@cc.tuat.ac.jp
  - Mr. Tatsuya Yamazaki, student, Meisei University

- Relevant scientists, experts, and officers from universities, institutes and governmental agencies attended the Workshop.
  - ERTC
  - RFD
  - Pollution Control Department (PCD)
  - Japan International Research Center for Agricultural Sciences (JIRCAS)
  - Other universities

The workshop summaries including the detailed presentation program are attached as PDF file (Appendix 1).

# Workshop Summary

# APN Workshop 2013 on Sulphur Dynamics in East Asian Forests

Hiroyuki Sase[1] and Nik Muhamad Majid[2]

[1] Asia Center for Air Pollution Research (ACAP), [2] Universiti Putra Malaysia (UPM)

## I. Background

1. Effect of sulfur deposition on terrestrial ecosystems is one of the important issues to be investigated in the East Asia region. Since sulfur deposited on ecosystems may be retained in soil and/or cycled in the soil-plant system, manifestation of its effect may be delayed. In fact, in US and Europe, it was reported that sulfur accumulated in the past has been leaching to streams in forest area recently. Moreover, several rivers/lakes for monitoring on inland aquatic environment in the East Asia countries showed pH-declining trend with $SO_4^{2-}$-increasing trend.

2. Scientists from the Acid Deposition Monitoring Network in East Asia (EANET) have been promoting the catchment-scale analysis in different types of forests, namely in Kajikawa site, Niigata, Japan, in Sakaerat site, Nakhon Ratchasima, Thailand and in Danum Valley site, Sabah, Malaysia. The research team is now studying sulfur dynamics in the forest catchments. The location of the study sites were shown in Fig. 1.


**Fig. 1. Location of the study sites for APN Project**

3. The project is supported by Asia Pacific Network on Global Change Reearch (APN). Part of the surveys in Sakaerat site and Bintulu site is financially supported by KAKENHI from Ministry of Education, Culture, Sports, Science & Technology in Japan and Mitsubishi Corporation, Japan, respectively.

## II. Outline of the workshop

4. The APN Workshop 2013 on Sulphur Dynamics in East Asian Forests was held on 24 June 2013 in Selangor, Malaysia, by ACAP in cooperation with UPM. The workshop objectives are:

   i) To discuss effects of sulphur derived from atmospheric deposition on East Asian forest ecosystems.

   ii) To share outcomes/progress of the projects with relevant agencies.

   iii) To chart future directions of the project.

5. The workshop was attended by the project members, researchers on relevant study fields, and experts from the EANET relevant organizations, including Malaysian Meteorological Department (MMD), Department of Chemistry (DOC), Universiti Putra Malaysia (UPM), etc.

6. The workshop was opened by Prof. Paridah MD Tahir, Director of Institute of Tropical Forestry and Forest Product (INTROP), UPM.

7. Following the introduction of the APN project by Dr. Hiroyuki Sase, Project Leader, eight speakers presented outcomes from relevant studies in Japan, Thailand and Malaysia as well as progress of the project.

8. The workshop program, including names of the speakers and presentation titles, is shown in the Appendix.

## III. Outcomes from the workshop

9. The presentations in the workshop included the latest scientific knowledge on catchment-scale analysis in the EANET countries and new trials in the project, such as sulfur isotopic analysis and use of the rehabilitated forests for acid deposition study. The information above may be informative for understanding possible mechanisms of acid deposition impacts on forest ecosystems and considering future direction of the EANET monitoring and relevant studies.

10. In the panel discussion on future direction of the project, several suggestions were made:

- The project studies in Japan, Thailand and Malaysia produced valuable scientific data and findings. The experience in the three countries should also be shared with other ten countries in the EANET.

- The catchment-scale analysis is a useful methodology to discuss effects of acid deposition on forest ecosystems more precisely. Investigation of material flow/cycle in the unit area is informative to discuss the effects quantitatively. The methodology should be promoted in the EANET community. Moreover, in the APN Project, sulfur isotopic analysis was adopted as a new tool for tracing material flow in the ecosystems. Outcomes from the project will contribute to more precise understanding of acid deposition impacts on ecosystems in the region.

- The rehabilitated forests could be utilized for acid deposition studies, since they are quasi-natural forest and their growth/management records were fully compiled. Use of the rehabilitated forests for the future EANET monitoring should be considered.

- The project approach may be informative to understand sulfur cycle in forest ecosystems. In addition to this, effects of sulfur compounds on plant nutrition should also be studied in future.

- Atmospheric deposition may affect plant physiology such as transpiration rate, which may also be related to climate. Synergistic effects of atmospheric deposition and climate change on forest ecosystems should also be taken into consideration.

- MMD informed that new project on long-range transport of air pollutants from Southern part of China to the peninsula part of Malaysia would start soon.

- Some more relevant agencies in Malaysia, such as Department of Forestry, should be involved in the EANET activity.

## IV. Acknowledgements

- The workshop participants thank Asia Pacific Network on Global Change Research (APN, ARCP2012-18NMY-Sase) and Universiti Putra Malaysia (UPM) for sponsoring this workshop.

**Appendix : Program of the APN Workshop**

**Workshop (June 24, 2013)**

| Time | Speaker | Topics |
|---|---|---|
| 09.00 | Prof. Dr. Paridah Md. Tahir | Opening |
| 09.15 | Dr. Hiroyuki Sase | Introduction of the APN Project, "Dynamics of sulphur derived from atmospheric deposition and its possible impacts on the East Asian forests" |
| 09.30 | Dr. Tsuyoshi Ohizumi | Utilization of stable S isotope analysis for atmospheric science |
| 10.00 | Mr. Tatsuyoshi Saito | Seasonal variation of sulfur isotope ratio in a small catchment of a Japanese cedar forest in Kajikawa, Niigata prefecture, Japan |
| 10.30 | Coffee break | |
| 10.45 | Dr. Hathairatana Garivait | Precipitation chemistry and the potential impact on soil acidification in Sakaerat forested catchment in Thailand |
| 11.15 | Dr. Hiroyuki Sase | Seasonal changes in stream water chemistry in Sakaerat site in Thailand |
| 11.45 | Assoc. Prof. Dr. Seca Gandaseca | Water Quality on Rehabilitated Forest in UPM Bintulu, Sarawak |
| 12.15 | Assoc. Prof. Dr. Ahmed Osumanu Haruna | Soil chemistry of a rehabilitated forest |
| 12.45 | Lunch | |
| 14.00 | Dr. Naoyuki Yamashita | Neutralisation of dissolved materials in a tropical rainforest catchment near Danum Valley, Malaysian Borneo |
| 14.30 | Mr. Mohamad Hilmi bin Ibrahim | Evaluation of deposition amounts of ion constituents at different forest stands of a rehabilitated forest in Malaysia |
| 14.45 | Coffee break | |
| 15.15 | Prof. Dr. Nik Muhamad Nik Ab. Majid (Facilitator) | Panel Discussion facilitated by Prof. Nik<br>Panelists:<br>i) Dr. Hiroyuki Sase, ACAP, Japan<br>ii) Assoc. Prof. Dr. Ahmed Osumanu, UPM<br>iii) Dr. Hathairatana Garivait, Environmental Research and Training Center (ERTC), Department of Environmental Quality Promotion (DEQP), Thailand<br>iv) Ms. Maznorizan Muhamad, MMD |
| 16.00 | Dr. Hiroyuki Sase | Closing |

**Field Trip (June 25, 2013)**

| Time | Activities |
|---|---|
| 09.00 | Assembly – Hotel Lobby |
| 09.30 | Briefing – Forest Rehabilitation Project |
| 10.00 | Site visit |
| 11.00 | End of program |

# Chairpersons' Summary

## APN Project Workshop 2014 on Sulfur Dynamics in East Asian Forests

## I. Background

1. Deposition level of sulfur is still high and a cumulative load of sulfur is quite large in East Asia. Since sulfur deposited on ecosystems may be retained in soil and/or cycled in the soil-plant system, manifestation of its effect may be delayed. Moreover, several rivers/lakes for monitoring on inland aquatic environment in the East Asian countries showed pH-declining trend with $SO_4^{2-}$-increasing trend. Effect of sulfur deposition on terrestrial ecosystems is one of the important issues to be investigated in the region.
2. Consequently, the research project started in 2012 with financial support of the Asia Pacific Network for Global Change Research (APN) (ARCP2012-18NMY-Sase & ARCP2013-13CMY-Sase, Dynamics of Sulphur Derived from Atmospheric Deposition and its Possible Impacts on East Asian Forests). In the project, dynamics of sulfur derived from atmospheric deposition have been investigated in forest catchments in Niigata, Japan, Nakhon Ratchasima, Thailand, and Sabah and Sarawak, Malaysia. The APN Workshop 2013 on Sulphur Dynamics in East Asian Forests was held in Selangor, Malaysia, to share the progress of the project.
3. The APN Project Workshop 2014 on Sulphur Dynamics in East Asian Forests was held on 18-19 December 2014 in Bangkok, Thailand, to share the outcomes from the project and discuss current environmental issues and future research topics in the region. The workshop was organized by the Asia Center for Air Pollution Research (ACAP) in cooperation with the Royal Forest Department (RFD) of Thailand.

## II. Schedule and Venue

4. The workshop on 18 December was held in the H. Slade Meeting Room, Department of National Park, Wildlife and Plant, Bangkok, Thailand. Moreover, the workshop fieldtrip to the forest park in Samutprakarn Province was carried out on 19 December to learn the forest management in the province.

## III. Outline of the workshop

5. The workshop was attended by approx. 45 scientists/experts from institutes, universities or agencies in Thailand, Malaysia and Japan.
6. The workshop was moderated by Mr. Bopit Kietvuttinon, Director and Mrs. Suwanna Umphauk, Silvicultural Research Division, RFD.
7. The sessions were chaired by Dr. Hiroyuki Sase, ACAP or Prof. Nik Muhamad Majid, Universiti Putra Malaysia (UPM).
8. The timetable of the workshop is shown in the following table.

| Time | Speaker | Possible topics |
|---|---|---|
| 9:00 | Mr. Thiti Visaratana, Acting Director of Forest Research and Development Bureau, Royal Forest Department (RFD) | Opening remarks |
| 9:15 | Dr. Hiroyuki Sase, ACAP | Introduction of the APN Project |
| **Session 1: Utilization of stable S isotope analysis for atmospheric and biogeochemical sciences in Japan (Chaired by Prof. Nik)** | | |
| 9:30 | Dr. Tsuyoshi Ohizumi, ACAP | Utilization of stable S isotope analysis for atmospheric science |
| 9:50 | Dr. Yayoi Inomata, ACAP | Seasonal variation of sulfur isotopic ratio in precipitation in coastal region of Sea of Japan |
| 10:10 | Mr. Tatsuyoshi Saito, ACAP | Seasonal variation of sulphur isotopic ratio in a small catchment of a Japanese cedar forest in Kajikawa, Niigata prefecture, Japan |
| 10:30-11:00 | Coffee break | |
| **Session 2: Atmospheric depositions of sulfur in Japanese forests (Chaired by Dr. Sase)** | | |
| 11:00 | Dr. Kazuhide Matsuda, Tokyo University of Agriculture and Technology | Sulfur dry deposition on forests in East Asia |
| 11:20 | Mr. Tatsuya Yamazaki, Meisei University | Vertical profiles of sulfate and nitrate aerosols in a forest canopy |

| | | |
|---|---|---|
| | | in suburban Tokyo |
| **11:40-13:00** | **Lunch break** | |
| **Session 3: Soil and stream water chemistry in Sarawak, Malaysia (Chaired by Dr. Sase)** | | |
| 13:00 | Dr. Ahmed Osumanu Haruna, Universiti Putra Malaysia (UPM) | Sulphur storage in soil of a rehabilitated forest at Bintulu, Sarawak |
| 13:20 | Dr. Seca Gandaseca, UPM | Stream water chemistry in the rehabilitated forest in Bintulu, Sarawak, Malaysia |
| **Session 4: Atmospheric depositions of sulfur and its dynamics in Thai forests (Chaired by Prof. Nik)** | | |
| 13:40 | Dr. Hathairatana Garivait, Environmental Research and Training Centre (ERTC), Department of Environmental Quality Promotion (DEQP) | Precipitation chemistry in Sakaerat forest, Nakhon Ratchasima Province |
| 14:00 | Dr. Naoyuki Yamashita, ACAP | Vertical distribution of sulfur isotopic ratio in rainfall, throughfall, soil and streamwater in Thai and Malaysian tropical forest |
| 14:20 | Dr. Hiroyuki Sase, ACAP | Alkalinization and acidification of stream water in Sakaerat forest |
| 14:40-15:15 | Coffee break | |
| **Session 5: Panel discussion** | | |
| 15:15 | Panel discussion | Dr. Sase (Moderator), Prof. Nik, Mr. Bopit, and Dr. Hathairatana. |
| 16:30 | Mr. Bopit Kietvuttinon | Closing remarks |

## IV. Major outcomes

9. The project members and cooperative researchers presented progress of the studies on sulfur dynamics in forest ecosystems in Thailand, Malaysia and Japan, which included topics on various media in the ecosystems, such as rainwater, soil, soil solution and stream water.
10. Moreover, the atmospheric scientists from Japan introduced studies on dry

deposition processes onto/in forest canopy.

11. In the panel discussion, the following two themes were discussed by four panelists and the participants:

i) Current atmospheric environmental issues

- In addition to acid deposition and nitrogen deposition, ozone and particulate matters (PM) should be taken into consideration as the important atmospheric pollutants in the region, which may cause reduction of plant growth/yields as well as harmful effects on human health.
- However, tropospheric ozone has not been well recognized as a harmful pollutant by the general public. Public awareness should be promoted furthermore.

ii) Future research topics and collaboration

- It was introduced that new joint research projects on ozone and/or PM have already been planned in Malaysia and Thailand:
  - Malaysia: December 2014 – November 2016
    The effects of ozone and aerosols on physiological characteristics of urban and suburban forests in Malaysia (by Roland Kueh Jui Heng, Nik Muhamad Majid, Ahmed Osumanu Haruna, Franklin Raai Kundat, and Hiroyuki Sase)
  - Thailand: *April 2015 – March 2018 (under application)*
    Removal process of biomass-origin black carbon by forest canopy in dry forests in Northeast Thailand (by Hiroyuki Sase, Kazuhide Matsuda, Naoto Murao, T. Ohizumi, T. Fukazawa, and N. Yamashita with B. Kietvuttionon, H. Garivait, and T. Artchawakom)
- In addition to the research topics above, the various research ideas were raised by the participants as follows:
  - Next generation of the inferential method with meteorological model, multi-layer and multi-pollutant models
  - Unknown processes in tropical region, such as nitrogen dynamics and processes in deeper soils, to contribute to development of biogeochemical model
  - Effects on local community
  - More direct relations to the EANET stations and utilization of the

EANET data

- S isotopic ratio in $PM_{2.5}$ in the northeast Asian countries
- Relations to climate change

12. During the fieldtrip to the forest park in Samutprakarn Province on 19 December, the workshop participants realized that a relatively large green area has been conserved and still enlarged year by year just next to the megacity, Bangkok, by efforts of the RFD and local community. It was suggested that such a large green area in urban area had an important role to remove air pollutants from the atmosphere. The participants planted native tree species in the forest park to contribute to rehabilitation of the forest.

*Funding sources outside the APN*

- In-kind support for the project
  - ACAP: supporting the surveys in Kajikawa site, including use of laboratory instruments, etc.
  - RFD: supporting the surveys in Sakaerat site, including use of facilities, field workers for sampling, etc. and preparation of the workshop
  - ERTC: supporting the chemical analysis in Sakaerat site, including use of laboratory instruments, laboratory staff, etc.
  - UPM: supporting the field surveys and chemical analysis in Bintulu site, including laboratory instruments, laboratory staff, etc. and preparation of the workshop
  - Danum Valley Field Centre: supporting the field surveys in Danum Valley

- Co-funding for the project
  - Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan: Grant-in-Aid for Scientific Research on Innovative Areas (20120012)
    The project was finished in the end of March 2013. Sample collection/analysis for RF and TF+SF in Sakaerat site was supported by the project. Grant in JFY 2012: 3,800,000 JPY

- The previous project, in which the relevant data was accumulated.
  - Ministry of the Environment of Japan (MOEJ): Environment Research and Technology Development Fund (C-052, C-082 and B-0801), from 2005 to 2010 in Sakaerat and Danum Valley sites
  - Mitsubishi Corporation: the Malaysian Experimental Project in Tropical Forest Regeneration, since 1990 in Bintulu site
  - MOEJ: Kajikawa site was originally established for the surveys of the MOEJ in 2001 and has been operated as the research site of ACAP thereafter. Surveys on multi-isotopic analysis (S, Sr, Pb, N and O of $NO_3^-$ etc.) started by MOEJ in several sites including Kajikawa site in 2014.

List of Young Scientists

- Mr. Tatsuyoshi Saito, Researcher, Ecological Impact Research Department, ACAP, tsaito@acap.asia
  - He joined the surveys in Kajikawa, Danum Valley and Bintulu sites.
  - Through the project, he developed his experimental skills, especially for S isotopic analysis.
  - Currently, he is also the Ph.D. student of Niigata University. It is expected that papers produced based on the project will be part of his Ph.D. Thesis.
  - Message from Mr. T. Saito: "The project was a good opportunity to challenge new scientific subjects. Especially, it was happy for me to have participated in the workshop and presented outcomes from the project."

- Students of UPM supported field surveys and chemical analysis with their supervisors:
  - Ms. Norainie Rosli, Ph.D. student, UPMKB
    - Her supervisor: Dr. Seca Gandaseca, Associate Professor, UPM, seca@upm.edu.my
  - Mr. Mohamad Hilmi bin Ibrahim, Master Course student, UPMKB, mohamadhilmiibrahim@gmail.com
    - His supervisor: Dr. Ahmed Osumanu Haruna, Associate Professor, UPMKB, osumanu@upm.edu.my

Glossary of Terms

ACAP, Asia Center for Air Pollution Research

BC, black carbon

BDSR, bacterial dissimilatory S reduction

DIN, dissolved organic nitrogen

DOC, Department of Chemistry

ERTC, Environmental Research and Training Centre, Thailand

INTROP, Institute of Tropical Forestry and Forest Product, UPM

MMD, Malaysian Meteorological Department

MEXT, Ministry of Education, Culture, Sports, Science and Technology, Japan

nss, non-sea salt

PCD, Pollution Control Department

PM, particulate matters

RF, rainfall outside forest canopy

RFD, Royal Forest Department, Thailand

S, sulphur

SF, stemflow

SS, soil solution

SW, stream water

TF, throughfall

UPM, Universiti Putra Malaysia

Abstracts, Power Point Slides of conference/symposia/workshop presentations

The following materials are attached as PDF files (Appendix 2)

- Brochure for The APN Workshop 2013 on Sulphur Dynamics in East Asian Forests
- Abstracts for The APN Workshop 2013 on Sulphur Dynamics in East Asian Forests
- Abstract Book of The APN Project Workshop 2014 on Sulfur Dynamics in East Asian Forests
- Power Point Slides of the presentation, Introduction of the APN Project, "Dynamics of sulphur derived from atmospheric deposition and its possible impacts on the East Asian forests" by Sase et al. in the workshop 2014
- Poster presentation materials in other conferences:
  - Japanese Forest Society in 2015 (by Yamashita et al.)
  - Japan Geoscience Union Meeting (JpGU meeting) 2015 (by Yamashita et al.)
  - Japan Geoscience Union Meeting (JpGU meeting) 2015 (by Saito et al.)
  - Isotope Symposium 2013 (by Sase et al.)

## Background

Effect of sulphur deposition on terrestrial ecosystems is one of the important issues to be investigated in the East Asia region. This is because the sulphur deposition level is still high and cumulative load of sulphur is quite large in this region. Since sulphur deposited on ecosystems may be retained in soil and/or cycled in the soil-plant system, manifestation of its effect may be delayed. In fact, in US and Europe, it was reported that sulphur accumulated in the past has been leaching to streams in forest area recently. Moreover, several rivers/lakes for monitoring on inland aquatic environment in the East Asia countries showed pH-declining trend with $SO_4^{2-}$-increasing trend.

Scientists from the Network Center (NC) and the East Asia countries have been promoting the catchment-scale analysis in different types of forests, namely in Kajikawa site, Niigata, Japan, in Sakaerat site, Nakhon Ratchasima, Thailand and in Danum Valley site, Sabah, Malaysia. The research team is now studying sulphur dynamics in the forest catchments.

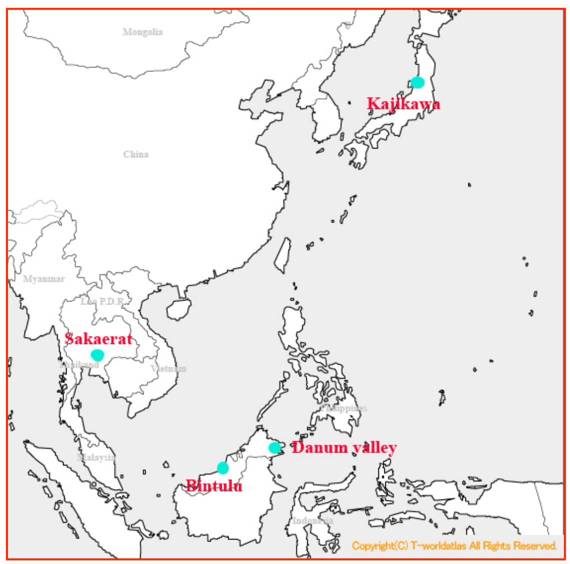
The project is supported by the Asia Pacific Network for Global Change Research (APN). Part of the surveys in Sakaerat site and Bintulu site is financially supported by KAKENHI from Ministry of Education, Culture, Sports, Science & Technology in Japan and Mitsubishi Corporation, Japan, respectively.

## Workshop Objectives

1. To discuss effects of sulphur derived from atmospheric deposition on East Asian forest ecosystems.
2. To share outcomes/progress of the projects with relevant agencies.
3. To chart future directions of the project.

## Study sites

The study sites were established in four forest catchments in Japan, Thailand and Malaysia. Fluxes of ions including $SO_4^{2-}$ were measured in previous projects since 2002, 2005 and 2008 in Kajikawa, Sakaerat and Danum Valley sites, respectively. The surveys in these sites were completed in 2010/2011. In 2012, the study sites were reactivated for the APN project and the rehabilitated forest in Bintulu was added as a new site for the project.




## Collaboration

Since the project is conducted based on the Acid Deposition Monitoring Network in East Asia (EANET) community, outcomes/progress of the project should be shared with the EANET relevant agencies in Malaysia, including Ministry of Natural Resources and Environment (NRE), Malaysian Meteorological Department (MMD), Department of Environment (DOE), Department of Chemistry (DOC), Universiti Teknologi Mara (UiTM) and Universiti Putra Malaysia (UPM).

## Members of Panel Discussion on Future Project Direction

1. Prof. Dato' Dr. Nik Muhamad Majid (Chairman)
2. Dr. Hiroyuki Sase
3. Assoc. Prof. Dr. Ahmed Osumanu
4. Assoc. Prof. Dr. Ahmad Ainuddin Nuruddin
5. Dr. Hathairatana Garivait
6. Ministry of Natural Resources and Environment
7. Malaysian Meteorological Department

## Acknowledgements

We thank Asia Pacific Network on Global Change Research (APN, ARCP2012-18NMY-Sase) and Universiti Putra Malaysia (UPM) for sponsoring this workshop.

## Workshop's Program (June 24, 2013)

| Time | Speaker | Topics |
|---|---|---|
| 09.00 | Prof. Dr. Paridah Md. Tahir | Opening |
| 09.15 | Dr. Hiroyuki Sase | Introduction of the APN Project, "Dynamics of sulphur derived from atmospheric deposition and its possible impacts on the East Asian forests" |
| 09.30 | Dr. Tsuyoshi Ohizumi | Utilization of stable S isotope analysis for atmospheric science |
| 10.00 | Mr. Tatsuyoshi Saito | Seasonal variation of sulfur isotope ratio in a small catchment of a Japanese cedar forest in Kajikawa, Niigata prefecture, Japan |
| 10.30 | Coffee break | |
| 10.45 | Dr. Hathairatana Garivait | Precipitation chemistry and the potential impact on soil acidification in Sakaerat forested catchment in Thailand |
| 11.15 | Dr. Hiroyuki Sase | Seasonal changes in stream water chemistry in Sakaerat site in Thailand |
| 11.45 | Assoc. Prof. Dr. Seca Gandaseca | Water Quality on Rehabilitated Forest in UPM Bintulu, Sarawak |
| 12.15 | Assoc. Prof. Dr. Ahmed Osumanu Haruna | Soil chemistry of a rehabilitated forest |
| 12.45 | Lunch | |
| 14.00 | Dr. Naoyuki Yamashita | Neutralisation of dissolved materials in a tropical rainforest catchment near Danum Valley, Malaysian Borneo |
| 14.30 | Mr. Mohamad Hilmi bin Ibrahim | Evaluation of deposition amounts of ion constituents at different forest stands of a rehabilitated forest in Malaysia |
| 14.45 | Coffee break | |
| 15.15 | Prof. Dr. Nik Muhamad Nik Ab. Majid | Panel discussion |
| 16.00 | Closing | |

## Field Trip Program (June 25, 2013)

| Time | Activities |
|---|---|
| 09.00 | Assembly – Hotel Lobby |
| 09.30 | Briefing – Forest Rehabilitation Project |
| 10.00 | Site visit |
| 11.00 | End of program |

## Registration Form:

Name: ______________________________

Position: ______________________________

Organization: ______________________________

______________________________

Tel.: ______________ Fax.: ______________

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# APN WORKSHOP 2013 ON SULPHUR DYNAMICS IN EAST ASIAN FOREST

JUNE 24 – 25, 2013

RESIDENCE HOTEL, UNITEN

BANGI, SELANGOR, MALAYSIA

ORGANIZERS:

# Introduction of the APN Project, "Dynamics of sulphur derived from atmospheric deposition and its possible impacts on the East Asian forests"

Sase, H.[1], Ohizumi, T.[1], Yamashita, N.[1], Visaratana, T.[2], Kietvuttinon, B.[2], Garivait, H.[3], and Majid, N.M.[4]

1. Asia Center for Air Pollution Research; 2. Royal Forest Department, Thailand; 3. Environmental Research and Training Center, DEQP, Thailand; 4. Universiti Putra Malaysia, Malaysia.

Keywords: stable isotope, biogeochemical cycle, rainwater, stream water, soil

Deposition level of sulphur is still high and a cumulative load of sulphur is quite large in East Asia. Since sulphur deposited on ecosystems may be retained in soil and/or cycled in the soil-plant system, manifestation of its effect may be delayed (e.g. Mitchell and Likens 2011; Kobayashi et al. 2012). Moreover, several rivers/lakes for monitoring on inland aquatic environment in the East Asian countries showed pH-declining trend with $SO_4^{2-}$-increasing trend (EANET 2011). Effect of sulphur deposition on terrestrial ecosystems is one of the important issues to be investigated in the region. Consequently, scientists from the community of Acid Deposition Monitoring Network in East Asia (EANET) started the new project in 2012 with financial support of the Asia Pacific Network for Global Change Research (APN). In the project, dynamics of sulphur derived from atmospheric deposition are investigated in forest catchments in Niigata, Japan, Nakhon Ratchasima, Thailand, and Sabah and Sarawak, Malaysia (Table 1).

Table 1. Study forest catchments in Japan, Thailand and Malaysia

| Site | Kjikawa | Sakaerat | Danum Valley | Bintulu |
|---|---|---|---|---|
| Country | Niigata, Japan | Nakhon Ratchasima, Thailand | Sabah, Malaysia | Sarawak, Malaysia |
| Forest type | Japanese cedar | Dry evergreen forest (DEF) | Tropical rainforest | Rehabilitated Forest |
| Start year | 2002 | 2005 | 2008 | 2012 |

Acknowledgements

The project is supported by the grant from APN (ARCP2012-18NMY-Sase) and Mitsubishi Cooperation. Field surveys and laboratory analysis were conducted by Y. Inomata, T. Saito, D. Staporn, A.O. Haruna, S. Gandaseca, J. Gidiman, Y.Y. Toh, K.P. Leong, Maznorizan Mohamad, N. Chappell and other collaborators. Authors thank them for their support and cooperation.

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Kobayashi, R. et al. 2012. Seasonal variation of water chemistry and sulphur budget in an acid-sensitive river along the Sea of Japan. Limnology 14: 195-209.

Mitchell MJ, Likens GE 2011. Watershed sulphur biogeochemistry: shift from atmospheric deposition dominance to climatic regulation. Environ Sci Technol 45: 5267–5271.

APN Workshop 2013 on Sulphur Dynamics in East Asian Forests.

# Utilization of Stable S Isotope Analysis for Atmospheric Science

Tsuyoshi Ohizumi[1], Yayoi Inomata[1], Naoko Take[1]

1. Asia Center for Air Pollution Research

Keywords: Sulfur Isotope, Northeast Asia, Anthropogenic Emission, Transboundary Air Pollution

Sulfur isotope geochemistry has been a rewarding study field because of the relatively large percentage mass difference between the two principal isotopes, the variety of chemical forms of sulfur, and their widespread occurrences in the earth's lithosphere, hydrosphere, and atmosphere. Sulfur isotope geochemistry began in the late 1940s and has been concerned with such problems as isotope fractionation in the biological sulfur cycle, the sulfur-bearing gases of volcanoes, the isotopic composition of present-day and ancient oceans, isotope distribution in coal and petroleum, etc. Sulfur isotopic ratio measurement on air pollution research was initiated by Mizutani and Rafter (1969) in Japan and Grey and Jensen (1972) in USA, etc. and has increased application in environmental studies.

We have monitored sulfur isotopic ratio of the atmospheric deposition collected in the area along the Sea of Japan since 1980s, in order to clarify the causes of obvious seasonal variation and huge amount of winter deposition of sulfur in the region (Fig. 1). As the results, we could conclude that the observed seasonal variation of the amount and isotopic ratio values of sulfate deposition can only be explained by taking a sulfur supply with high delta values into account, in addition to variation of sulfur contribution from sea salt, biogenic, volcanic and local anthropogenic origins. The contribution of high delta sulfur becomes the most significant in winter in which continental outflow becomes significant.

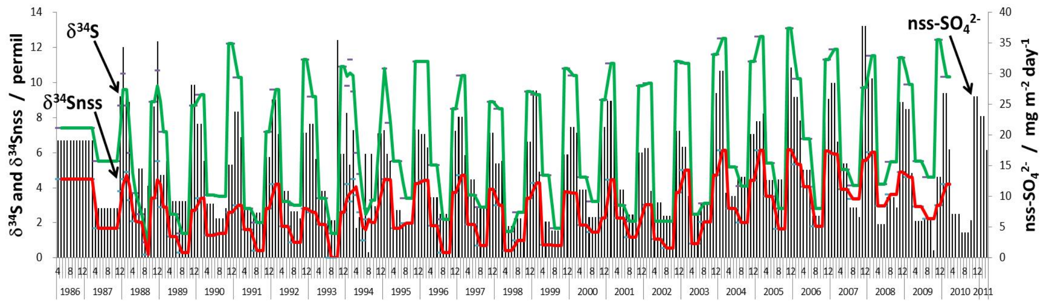


Fig.1 Variation with time in the isotopic ratio and deposition of sulfur collected in Niigata, Japan

## References

1) Mizutani, Y., and Rafter, T.A., 1969, N.Z. J. Sci., 12, 69-80. 2) Grey, D.C., and Jensen, M.L., 1972, Science, 177, 1099-1100. 3) Ohizumi, T., Fukuzaki, N., and Kusakabe, M., 1997, Atmos Environ, 31, 1339-1348.

APN Workshop 2013 on Sulphur Dynamics in East Asian Forests.

# Seasonal variation of sulfur isotope ratio in a small catchment of a Japanese cedar forest in Kajikawa, Niigata prefecture, Japan

Saito, T.[1], Yamashita, N.[1], Inomata, Y.[1], Uchiyama, S.[1], Nakata, M.[2], Ohizumi, T.[1], and Sase, H[1].

1. Asia Center for Air Pollution Research (ACAP); 2. Niigata University, Japan.

Keywords: sulfur isotope ratio, rainwater, soil water, stream water

This study is conducted to clarify the dynamics of sulfur derived from atmospheric deposition, especially the variation of sulfur isotope ratio. The study plot was selected in a small catchment of a Japanese ceder forest in Kajikawa, Niigata prefecture, Japan (Fig.1) which suffered large amount of deposition from transboundary air pollution (Kamisako et al. 2008). Rainwater, soil water (middle slope: 20 centimeters depth; lower slope: 20 and 60 centimeters depth) and stream water (upstream and downstream) were collected from the study site at least once a month (Fig. 2). In addition, throughfall and stemflow were also collected. The pH, electric conductivity, major ions and sulfur isotope ratio in these samples were determined. Water sampling and measurement began in August 2012. Sulfur isotope ratio in rainwater and stream water showed clear difference. In this presentation we discuss their seasonality.

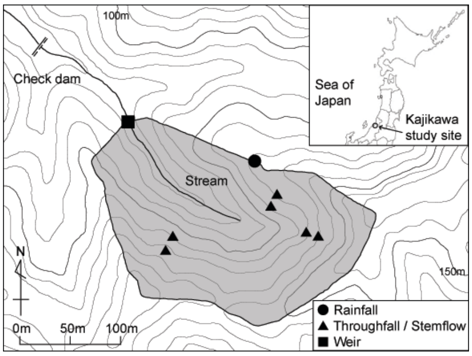


**Fig. 1. Kajikawa study site**

**Fig. 2. Collect rain, soil and stream water**

**Acknowledgements**

The study was supported by the grant from APN (ARCP2012-18NMY-Sase). Authors thank them for their support and cooperation.

**References**

Kamisako, M. et al. 2008. Seasonal and annual fluxes of inorganic constituents in a small catchment of a Japanese ceder forest. Water, Air, and Soil Pollution 195: 51-61.

# Precipitation chemistry and the potential impact on soil acidification in Sakaerat forested catchment in Thailand

Hathairatana Garivait[a], Preeda Parkpian[b], Hiroyuki Sase[c], Jessada Luangjame[c], Bopit Kievuttinon[d], Daisy Morknoy[a], Duangduean Chanatorn[a] and Chantiraporn Meepol[a]

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[b]Asian Institute of Technology (AIT), 42 Phaholyothin highway, P.O. Box 4, Klong Luang, 12120, Pathumthani, Thailand.

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[d]Royal Forest Department, 61 Phaholyothin Road, Bangkok 10900, Thailand.

## ABSTRACT

The rapid increase in developmental activities by human has given considerable rise to atmospheric pollutants which have affected the natural ecosystems severely. Among those pollutants emission of $SO_2$ and $NO_x$ have increased significantly in the East Asian region since 1990. Acid deposition has become more and more important issue in the region due to its trans-boundary nature and the impact to ecological acidification. The impact lead to soil acidification would be the most important for catchment area where water availability is defined.

Wet deposition such as rainfall (RF), stem flow (SF) and throughfall (TF) in the catchment area of SRS station has been measured since 2005 under the joint research project on catchment analysis in Thailand. Clear seasonality of atmospheric deposition and elemental flow in the forest ecosystems has been observed under the catchment study. Deposition amounts of all ions by TF+SF generally increased during the beginning of wet season, especially $SO_4^{2-}$ showed the highest concentration. As in the year 2008, the total amount of precipitation collected by RF was 1377.2 mm, while TF and SF were 863.1 mm and 34.9 mm, respectively. The volume weighted average pH of the precipitation was 5.15. Total amount of $SO_4^{-2}$ deposition in RF, TF and SF were 8.3, 87.0 and 3.0 mmol/m²/year, respectively. An attempt is made to quantify the potential effects on long-term soil acidification at a tropical forested catchment area in Thailand. The regulatory factors that govern soil sensitivity and vulnerability in the area are summarized. The modifications to soil chemical characteristics in which such changes may influence soil acidification in the area are discussed.

***Keywords:*** precipitation chemistry, tropical forested catchment, soil characteristics, soil acidification

# Seasonal changes in stream water chemistry in Sakaerat site in Thailand

Sase, H.[1], Yamashita, N.[1], Visaratana, T.[2], Kietvuttinon, B.[2], Garivait, H.[3], Junko Shindo[4] and Kazuhide Matsuda[5]

1. Asia Center for Air Pollution Research; 2. Royal Forest Department, Thailand; 3. Environmental Research and Training Center, DEQP, Thailand; 4. Yamanashi University; 5. Tokyo University of Agriculture and Technology.

Keywords: acid deposition, sulfur, dry evergreen forest, acidification, alkalinization

A small catchment plot (approx. 35 ha) was established in a dry-evergreen forest in the Sakaerat Silvicultural Research Station, Nakhon Ratchasima Province, Thailand. Field surveys on input and output are carried out in the catchment plot. As for the output, stream water at the outlet of the catchment was collected at the same interval and the discharge was continuously monitored. As for the input, precipitation samples including throughfall (TF), stemflow (SF), and rainfall outside the forest canopy were collected basically at two-week interval. Ion constituents were determined using ion chromatograph for the water samples. The regular surveys started in October 2005. Soil chemical properties and ion fluxes in soil layers were also determined intensively. In this presentation, seasonal changes in stream water chemistry will be mainly discussed. Stream water chemistry showed a distinct seasonality. The pH and EC increased simultaneously with alkalinity and base cations in early wet season. After the alkalization above, the pH and alkalinity suddenly decreased with flushing of $SO_4^{2-}$ in middle/late wet season. High mineralization rate (Yamashita et al., 2010) and high deposition amount (Sase et al. 2012) in the beginning of wet season may affect alkalization and acidification of the stream water, respectively. In particular for acidification, mechanisms on retention and release of $SO_4^{2-}$ in the catchment should be discussed.

Acknowledgements

The study was supported by the Environment Research and Technology Development Fund (B-0801), MOE and KAKENHI (20120012), MEXT, Japan, and the grant from APN (ARCP2012-18NMY-Sase). Authors thank them for their support and cooperation.

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**Yamashita, N. et al. 2010. Seasonal and spatial variation of nitrogen dynamics in the litter and surface soil layers on a tropical dry evergreen forest slope. Forest Ecology and Management 259: 1502-1512.**

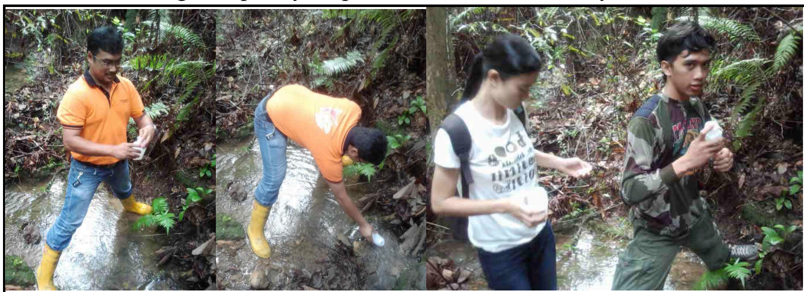
APN Workshop 2013 on Sulphur Dynamics in East Asian Forests.

# Water Quality on Rehabilitated Forest in UPM Bintulu, Sarawak

Seca Gandaseca, Noraini Rosli, Chandra Iman Ariyanto
Tropical Forest Ecosystem Science Research Centre (TROFES)
Faculty of Agriculture and Food Science
Universiti Putra Malaysia Bintulu Sarawak

*Keywords: water quality, rehabilitated forest, macroelement, National Water Quality Standard, Water Quality Index.*

This study was conducted to assess the water quality condition on stream water at Rehabilitated Forest of Universiti Putra Malaysia Bintulu Sarawak, Malaysia. A total of 144 water samples were collected from 12 stations and taken from upstream, middle stream and downstream the study area. Monitoring, field measurement and water sampling was conducted from 29$^{th}$ January until 19$^{th}$ March 2013. Twenty water quality parameters were measured and analyzed in field (*in situ*) and in laboratory (*ex situ*) according to Standard Methods APHA. According to National Water Quality Standards (NWQS) Malaysia, the water temperature was in normal ranges; electrical conductivity (EC), salinity (SAL), ammonia nitrogen ($NH_3$-N), biochemical oxygen demand (BOD), total dissolved solids (TDS) and total suspended solids (TSS) were categorized under Class I, while dissolved oxygen (DO), turbidity (TUR) and chemical oxygen demand under Class II and pH under class III. Macroelements such as potassium (K), calcium (Ca), magnesium (Mg), sodium (Na) and micronutrients include iron (Fe), zinc (Zn), manganese (Mn) and copper (Cu) was found in safe level and healthy condition. Based on Malaysia Water Quality Index (WQI) provided by Department of Environment (DOE) Malaysia, overall water quality status at the study area was categorized under Class II which represents water bodies of good quality, unpolluted and safe for body contact.



**Acknowledgment**
Thank ACAP-Japan and UPM-Mitsubishi Rehabilitated Project for support this research.

**References**

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# Soil chemistry of a rehabilitated forest

**Ahmed, O. H.[1], Ch'ng, H. Y.[1], Majid, N. M. A.[2], Susilawati, K.[1], Sase, H.[3], and Yamashita, N.[3]**

**[1]Department of Crop Science, Faculty of Agriculture and Food Sciences, Universiti Putra Malaysia Bintulu Sarawak Campus,97008Bintulu, Sarawak, Malaysia.**

[2]Department of Forest Management, Faculty of Forestry, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.

[3]Ecological Impact Research Department, Asia Center for Air Pollution Research (ACAP), Japan Environmental Sanitation Center (JESC), 1182 Sowa, Nishi-ku, Niigata 950-2144, Japan

In recent times, concerns have been expressed about the degradation of the environmental quality. Sulphur oxides have been implicated in the air quality degradation world-wide, particularly in highly industrialized areas. Since sulphur compounds including sulphur oxides and sulphate in the atmosphere are likely to find their way to the soil in forest areas, the need for studies in sulphur dynamics is essential especially in degraded and rehabilitated forest soils which are known to be fragile. This aspect of research also calls for studies on soil fertility and soil factor evaluation *vis a vis* sulphur dynamics. In line with this, a study was carried to assess Soil Evaluation Factor (SEF) of a rehabilitated forest soil. The study was carried at the rehabilitated forest of Universiti Putra Malaysia Bintulu Campus Sarawak, Malaysia. Standard procedures were used to determine variables evaluated in this study. The SEF equation (Lu et al., 2002) was used to estimate the fertility of the soil as this method is an improvement over Soil Fertility Index (SFI).

$$SEF = [Ca + Mg + K - \log(1+Al)] \times OM + 5$$

The SEF slightly increased with increasing soil depth probably due to movement of nutrients down the soil profile. However, regardless of soil depth, the SEF was less than 5 suggesting that the fertility status of the rehabilitated forest soil was relatively poor. Among the variables evaluated in this study, the SEF related to magnesium, potassium, aluminium, and soil organic matter. This suggests that sulphur dynamics could affect soil fertility of this rehabilitated forest since sulphur interacts with soil organic matter and aluminium. This premonition is being researched in the rehabilitated forest.

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APN Workshop 2013 on Sulphur Dynamics in East Asian Forests.

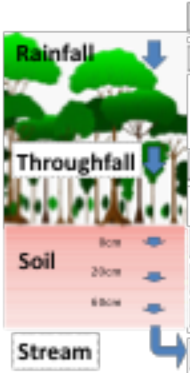
# Neutralisation of dissolved materials in a tropical rainforest catchment near Danum Valley, Malaysian Borneo

Yamashita, N.[1], Sase, H.[1], Kobayashi, R.[2], Kok-Peng, L.[3], Hanapi, J.M.[4], Uchiyama, S.[1] Urban, S[3], Ying-Ying, T.[3], Muhamad, M.[3], Gidiman, J.[4] and Nick A Chappell[5]

1. Asia Center for Air Pollution Research; 2. NSS corporation; 3. Malaysian Meteorological Department; 4. Danum Valley Field Centre, c/o Yayasan Sabah Group, Sabah, Malaysia; 5. Lancaster Environment Centre, Lancaster University

Keywords: atmospheric deposition, tropical forest catchment, streamwater, soil solution, throughfall

The neutralisation process of dissolved materials from rainfall to streams in catchments is poorly understood in tropical rainforests with complex biogeochemical and hydrological processes. The temporal variations in streamwater chemistry and vertical nutrient fluxes within plant-soil systems have been observed for about 4 years in Sabah, Malaysian Borneo. The mean precipitation pH value of 5.3 declined to 4.8 in the surface soil solution at upper slope and increased to 5.9 in the subsoil at lower slope and 7.1 in the streamwater. The $NO_3^-$, $NH_4^+$ and $K^+$ fluxes markedly decreased from the surface soil to the stream, whereas the $Na^+$, $Ca^{2+}$ and $Mg^{2+}$ fluxes remained high in the subsoil and the stream. Significant chemical weathering in deeper strata played an important role in the relatively high streamwater pH value because exports of $Na^+$, $Ca^{2+}$ and $Mg^{2+}$ to the stream greatly exceeded the input via atmospheric deposition. This tropical stream had a low acid sensitivity to the fluctuation of strong acid leaching during storms periods due to the constant high $HCO_3^-$ leaching, whereas DOC, including organic acids, may cause temporal variations in water acidification.




| | pH | $NO_3^-$ | $SO_4^{2-}$ | $NH_4^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $HCO_3^-$ | DOC |
|---|---|---|---|---|---|---|---|---|---|
| Rainfall | 5.6 | 4 | 16 | 11 | 2 | 2 | 3 | - | - |
| Throughfall | - | 4 | 22 | 40 | 87 | 9 | 11 | - | - |
| Soil | - | 469 | 194 | 204 | 778 | 267 | 214 | - | - |
| Soil | 4.8* | 710 | 129 | 96 | 194 | 123 | 166 | <0.01* | 15* |
| Soil | 5.9* | 497 | 115 | 42 | 117 | 189 | 152 | 0.14* | 3.7* |
| Stream | 7.1 | 10 | 35 | 1 | 17 | 149 | 126 | 4.9 | 3.1 |

**Fig.** Vertical changes of pH, ion-fluxes, $HCO_3^-$ and DOC through a tropical rainforest ecosystem in Danum valley

Acknowledgements

The study was supported by the Environment Research and Technology Development Fund (B-0801), MOE and the grant from APN (ARCP2012-18NMY-Sase). Authors thank them for their support and cooperation.

# Evaluation of deposition amounts of ion constituents at different forest stands of a rehabilitated forest in Malaysia

I. M. Hilmi1, Nik, M. Majid2, O. H. Ahmed1, K. Susilawati1, H. Sase3 and N. Yamashita3

[1]Department of Crop Science, Faculty of Agriculture and Food Sciences, Universiti Putra Malaysia Bintulu Sarawak Campus, 97008, Bintulu, Sarawak, Malaysia
[2]Institute of Tropical Forestry and Forest Products (INTROP), University Putra Malaysia, 43400, Serdang, Selangor, Malaysia
[3]Department of Ecological Impact Research, Asia Center for Air Pollution Research (ACAP), 1182 Sowa, Nishi-ku, Niigata, 950-2144, Japan

**Keywords**: Deposition, rainfall, throughfall, rehabilitated forest, acid rain

Malaysia as a developing country has not exceptional for experiencing acid deposition problem. Current status of rainfall and throughfall depositions is generally scarce in the humid tropical region. The objective of this study is to compare the rainfall deposition outside forest canopy with throughfall depositions for several ions at different forest stands (5, 8, 11, and 14 years) old of rehabilitated forest in Bintulu, Sarawak, Malaysia where atmospheric depositions have not reported yet. Ion exchange resin (IER) method was used for measuring rainfall and throughfall deposition. Annual rainfall depositions were 1704, 207.3, 4.9, 900, 218 and 802 mg $m^{-2}$ $year^{-1}$ for $Ca^{2+}$, $Na^{+}$, $Mg^{2+}$, $NH_4^{+}$, $NO_3^{-}$ and $SO_4^{2-}$, respectively. Depositions ions amount for throughfall were higher than rainfall in terms of $Mg^{2+}$, Fe, Zn and $NH_4^{+}$, but for $Ca^{2+}$, Cu and $NO_3^{-}$ it was lower. The study shows that a rehabilitated forest or a forest area with canopy closure significantly affects the amount of both anions and cations reaching the forest floor. Several processes on the forest canopy can be considered as possible causes of the phenomena above, which may include dry deposition of gaseous/particulate matters to the canopy, leaching/uptake of ions on leaf surface and consumption/modification of ions by microorganisms, etc. The results suggested the role of trees to change ion compositions in rainwater by such canopy interactions.

**Acknowledgements**

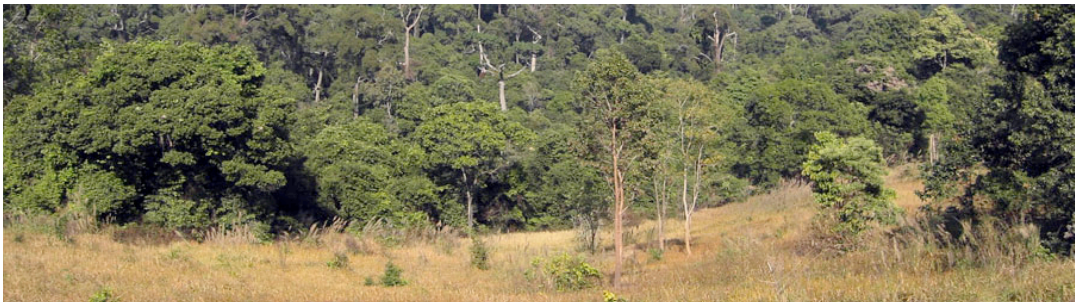
The authors would like to thank Ministry of Higher Education and Universiti Putra Malaysia for financial grant (RUGS: 9199765 and FRSG: 5523701) and Ministry of the Environment of Japan for their financial support by Environment Research and Technology Development Fund (B-0801) during the conduct of the research and preparation of this paper.

ARCP2013-13CMY-Sase

# APN Project Workshop 2014

# on Sulfur Dynamics in East Asian Forests

## Abstract book



**18-19 December 2014, Bangkok, Thailand**

# Preface

It's my great pleasure to hold the "APN Project Workshop 2014 on Sulfur Dynamics in East Asian Forests" in Bangkok, Thailand. Effect of atmospheric deposition on forest ecosystems is one of the important issues to be investigated in Asia. However, the topic has not been enough studied in the region, especially in tropical countries.

In Thailand, Royal Forest Department (RFD) has been conducting a joint research project on catchment analysis in Sakaerat Silvicultural Research Station, Nakhon Ratchasima Province, since 2005, in cooperation with Environmental Research and Training Centre (ERTC), Department of Environmental Quality Promotion (DEQP) and Asia Center for Air Pollution Research (ACAP). A lot of scientific knowledge has been obtained through the project, regarding atmospheric deposition, soil and stream water chemistry, and their biogeochemical processes in the dry forest. Several scientific papers based on the joint project have already been published in international journals.

In particular since 2012, by obtaining the research grant from Asia-Pacific Network for Global Change Research (APN), we have been studying sulfur dynamics in forest area in three countries, namely Thailand, Malaysia and Japan. This multilateral research project is an epoch-making study on atmospheric deposition and forest ecosystems in the region. The workshop will introduce major outcomes from the project and relevant research activities. I believe that fruitful discussion will be made during the workshop, which must contribute to improvement of atmospheric environment in the region.

(Thiti Visaratana)
Forest Management Expert
Acting Director of Forest Research and Development Bureau
Royal Forest Department

## 1. Background

Deposition level of sulfur is still high and a cumulative load of sulfur is quite large in East Asia. Since sulfur deposited on ecosystems may be retained in soil and/or cycled in the soil-plant system, manifestation of its effect may be delayed (e.g. Mitchell and Likens 2011; Kobayashi et al. 2012). Moreover, several rivers/lakes for monitoring on inland aquatic environment in the East Asian countries showed pH-declining trend with $SO_4^{2-}$-increasing trend (EANET 2011). Effect of sulfur deposition on terrestrial ecosystems is one of the important issues to be investigated in the region.

Consequently, scientists from the community of Acid Deposition Monitoring Network in East Asia (EANET) started the project in 2012 with financial support of the Asia Pacific Network for Global Change Research (APN) (ARCP2012-18NMY-Sase & ARCP2013-13CMY-Sase, Dynamics of Sulphur Derived from Atmospheric Deposition and its Possible Impacts on East Asian Forests, Project Leader: Dr. Hiroyuki Sase, Asia Center for Air Pollution Research, ACAP). In the project, dynamics of sulfur derived from atmospheric deposition are investigated in forest catchments in Niigata, Japan, Nakhon Ratchasima, Thailand, and Sabah and Sarawak, Malaysia. Last year, the APN Workshop 2013 on Sulphur Dynamics in East Asian Forests was held in Selangor, Malaysia, to share the progress of the project. This year, the APN Workshop 2014 is held in cooperation with Royal Forest Department (RFD) in Bangkok, Thailand, to share the outcomes from the project and discuss current environmental issues and future research topics in the region.

## 2. Schedule

17 December: Arrival in Bangkok
18 December: APN Workshop in Bangkok
19 December: Workshop fieldtrip to the forest park in Samutprakarn Province
(Some of the project members will visit Sakaerat site in Nakhon Ratchasima Province on 15-16 December.)

## 3. Venue

H. Slade Meeting Room, Department of National Park, wildlife and Plant, Bangkok, Thailand

## 4. Timetable

Moderator: Mr. Bopit Kietvuttinon / Mrs.Suwanna Umphauk

Chairs: Dr. Hiroyuki Sase, Prof. Nik Muhamad Majid

| Time | Speaker | Possible topics |
|---|---|---|
| 9:00 | Mr. Thiti Visaratana, Acting Director of Forest Research and Development Bureau, Royal Forest Department (RFD) | Opening remarks |
| 9:15 | Dr. Hiroyuki Sase, ACAP | Introduction of the APN Project |
| **Session 1: Utilization of stable S isotope analysis for atmospheric and biogeochemical sciences in Japan (Chaired by Prof. Nik)** | | |
| 9:30 | Dr. Tsuyoshi Ohizumi, ACAP | Utilization of stable S isotope analysis for atmospheric science |
| 9:50 | Dr. Yayoi Inomata, ACAP | Seasonal variation of sulfur isotopic ratio in precipitation in coastal region of Sea of Japan |
| 10:10 | Mr. Tatsuyoshi Saito, ACAP | Seasonal variation of sulphur isotopic ratio in a small catchment of a Japanese cedar forest in Kajikawa, Niigata prefecture, Japan |
| 10:30-11:00 | Coffee break | |
| **Session 2: Atmospheric depositions of sulfur in Japanese forests (Chaired by Dr. Sase)** | | |
| 11:00 | Dr. Kazuhide Matsuda, Tokyo University of Agriculture and Technology | Sulfur dry deposition on forests in East Asia |
| 11:20 | Mr. Tatsuya Yamazaki, Meisei University | Vertical profiles of sulfate and nitrate aerosols in a forest canopy in suburban Tokyo |

| | | |
|---|---|---|
| **11:40-13:00** | **Lunch break** | |
| **Session 3: Soil and stream water chemistry in Sarawak, Malaysia (Chaired by Dr. Sase)** | | |
| 13:00 | Dr. Ahmed Osumanu Haruna, Universiti Putra Malaysia (UPM) | Sulphur storage in soil of a rehabilitated forest at Bintulu, Sarawak |
| 13:20 | Dr. Seca Gandaseca, UPM | Stream water chemistry in the rehabilitated forest in Bintulu, Sarawak, Malaysia |
| **Session 4: Atmospheric depositions of sulfur and its dynamics in Thai forests (Chaired by Prof. Nik)** | | |
| 13:40 | Dr. Hathairatana Garivait, Environmental Research and Training Centre (ERTC), Department of Environmental Quality Promotion (DEQP) | Precipitation chemistry in Sakaerat forest, Nakhon Ratchasima Province |
| 14:00 | Dr. Naoyuki Yamashita, ACAP | Vertical distribution of sulfur isotopic ratio in rainfall, throughfall, soil and streamwater in Thai and Malaysian tropical forest |
| 14:20 | Dr. Hiroyuki Sase, ACAP | Alkalinization and acidification of stream water in Sakaerat forest |
| 14:40-15:15 | Coffee break | |
| **Session 5: Panel discussion** | | |
| 15:15 | Panel discussion | Dr. Sase (Moderator), Prof. Nik, Mr. Bopit, Dr. Hathairatana, etc. |
| 16:30 | Mr. Thiti Visaratana, RFD | Closing remarks |

# Introduction of the APN Project, "Dynamics of sulphur derived from atmospheric deposition and its possible impacts on the East Asian forests"

Sase, H.[1], Ohizumi, T.[1], Yamashita, N.[1], Visaratana, T.[2], Kietvuttinon, B.[2], Garivait, H.[3], and Majid, N.M.[4]

1. Asia Center for Air Pollution Research; 2. Royal Forest Department, Thailand; 3. Environmental Research and Training Center, DEQP, Thailand; 4. Universiti Putra Malaysia, Malaysia.

Keywords: stable isotope, biogeochemical cycle, rainwater, stream water, soil

Deposition level of sulphur is still high and a cumulative load of sulphur is quite large in East Asia. Since sulphur deposited on ecosystems may be retained in soil and/or cycled in the soil-plant system, manifestation of its effect may be delayed (e.g. Mitchell and Likens 2011; Kobayashi et al. 2012). Effect of sulphur deposition on terrestrial ecosystems is one of the important issues to be investigated in the region. Consequently, scientists from the community of Acid Deposition Monitoring Network in East Asia (EANET) have been conducting a research project since 2012 with financial support of the Asia Pacific Network for Global Change Research (APN). In the project, dynamics of sulphur derived from atmospheric deposition are investigated in forest catchments in Niigata, Japan, Nakhon Ratchasima, Thailand, and Sabah and Sarawak, Malaysia (Table 1).

**Table 1. Study forest catchments in Japan, Thailand and Malaysia**

| Site | Kjikawa | Sakaerat | Danum Valley | Bintulu |
|---|---|---|---|---|
| Country | Niigata, Japan | Nakhon Ratchasima, Thailand | Sabah, Malaysia | Sarawak, Malaysia |
| Forest type | Japanese cedar | Dry evergreen forest (DEF) | Tropical rainforest | Rehabilitated Forest |
| Start year | 2002 | 2005 | 2008 | 2012 |

**Acknowledgements**

The project is supported by the grant from APN (ARCP2012-18NMY-Sase: ARCP2013-13CMY-Sase) and Mitsubishi Cooperation. Field surveys and laboratory analysis were conducted by Y. Inomata, T. Saito, D. Staporn, A.O. Haruna, S. Gandaseca, J. Gidiman, Y.Y. Toh, K.P. Leong, Maznorizan Mohamad, N. Chappell and other collaborators. Authors thank them for their support and cooperation.

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Kobayashi, R. et al. 2012. Seasonal variation of water chemistry and sulphur budget in an acid-sensitive river along the Sea of Japan. *Limnology* 14: 195-209.

Mitchell MJ, Likens GE 2011. Watershed sulphur biogeochemistry: shift from atmospheric deposition dominance to climatic regulation. Environ Sci Technol 45: 5267–5271.

# Utilization of stable S isotope analysis for atmospheric science

Ohizumi, T.[1], Inomata, Y.[1] and Take, N.[1]

1. Asia Center for Air Pollution Research, Japan

Keywords: Transboundary air pollution, Rainwater, PM2.5

Rainwater has been acidified by sulfuric acid and sulfate has been main component of PM2.5 in Northeastern Asian countries including Japan. Original sulfur of those sulfuric acid and sulfate has been emitted from various sources to the atmosphere as many kinds of chemical species such as sulfur dioxide, hydrogen sulfide, dimethyl sulfide, sulfate, etc. However, since those sulfur compounds are oxidized to sulfuric acid and sulfate in the atmosphere, it is impossible to identify the sulfur sources from the chemical species in rainwater and particulate matter. Sulfur isotopic composition which is usually utilized as the ratio of second maximum ($^{34}S$) to the maximum member of sulfur ($^{32}S$) has provided useful information for identification of sulfur sources in rainwater collected in various regions of the world. In the case of Japanese rainwater collected in the area along the Sea of Japan, sulfur isotopic ratio ($^{34}S/^{32}S$) has varied with season and has increased in winter in which large amount of sulfate wet deposition is observed. In the area, sulfur sources characterized by light (oil) and heavy (coal) sulfur have been identified as constant and variable sources, respectively. We have started sulfur isotopic analysis for PM2.5 in the area since 2013 to identify the sources of sulfate in PM2.5 (Fig. 1). Different from rainwater sulfuric acid, seasonal variation of fine particulate sulfate concentration in the area is generally characterized by high in summer and low in winter. However, seasonal variation of sulfur isotopic composition comparable with rainwater can be seen from the analytical results of PM2.5 collected in Niigata-Maki station.

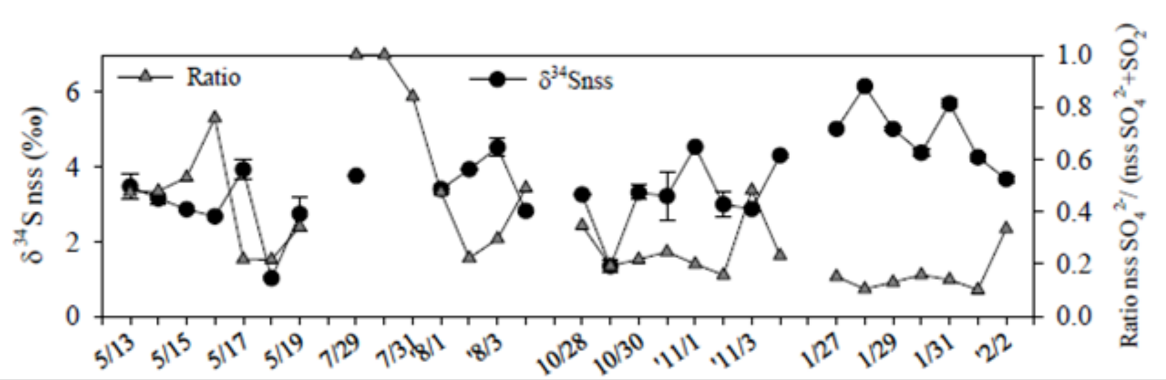


Fig.1 Sulfur isotopic compositions and particle formation rates of PM2.5 collected in Niigata-Maki station, Japan, in 2013

***References***

*Inomata, Y. et. al., 2014, Proceedings of 2014 annual conference of Japan Society for Atmospheric Environment, p.474*

# Seasonal variation of sulfur isotopic ratio in precipitation in coastal region of Sea of Japan

Inomata, Y.[1], Yamashita, N.[1], Saito, T.[1], Sase, H.[1] and Ohizumi, T.[1]
1. Asia Center for Air Pollution Research, Japan.

Keywords: Sulfur isotopic ratio, sulfate, Precipitation, Transboundary transport, Anthropogenic contribution

【Introduction】Although $SO_2$ emissions in East Asia are decreased recently, sulfate ions are one of the major species in the precipitation. It is well recognized that sulfur isotopic ratios ($\delta^{34}S$) are useful to identify the sources because the $\delta^{34}S$ have source specific values. The purpose of this study is to investigate the spatial and temporal variation of anthropogenic sulfur deposition and evaluation of effect of transboundary transport.

【Methodologies】We collected precipitation samples at 13 sites by using EANET sampling network. The sampling interval was from 2 weeks to seasonal depending on the sampling scahedule at each site. After samples were evaporated and filtered, sulfate ions were precipitated as $BaSO_4$. The $BaSO_4$ samples were analyzed by stable isotope mass spectrometer (NCS2500, Conflo II, Delta-Plus; Thermo Co. Ltd.). Canyon Diablo Troilite (CDT) is used as the reference materials. In this presentation, we focus on the results at the coastal site of Sea of Japan.

【Results and discussion】Figure 1 shows the temporal variation of $\delta^{34}S_{nss}$ at the coastal monitoring sites in Sea of Japan. There is found a seasonal variation with high in autumn-spring and low in summer. This seasonal variation is associated with the contribution of transboundary transport from the Asian Continent. The detail as well as the results with the other region will show in the presentation.

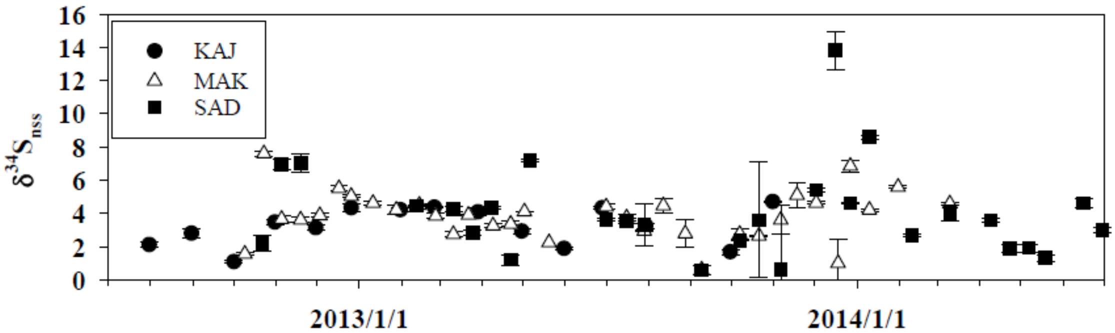


Figure 1. Temporal variation of $\delta^{34}S_{nss}$ in sulfate in precipitation at the coastal sites in Japan Sea.

**Acknowledgements**

This study is financially supported by the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT, Project No. 26340055). This study is also supported by Asia-Pacific Network for Global Change Research (ARCP2013-13CMY-Sase)

# Seasonal variation of sulphur isotopic ratio in a small catchment of a Japanese cedar forest in Kajikawa, Niigata prefecture, Japan

Saito, T.[1], Yamashita, N.[1], Inomata, Y.[1], Uchiyama, S.[2], Nakata, M.[3], Ohizumi, T.[1], and Sase, H[1].

1. Asia Center for Air Pollution Research (ACAP); Environmental Science Research Niigata, Japan;
3. Niigata University, Japan.

Keywords: sulphur isotopic ratio, rainfall, stream water, soil solution

This study is conducted to clarify the dynamics of sulphur derived from atmospheric deposition, by sulphur isotopic analysis. The study plot was selected in a small catchment of a Japanese cedar forest in Kajikawa, Niigata prefecture, Japan (Fig.1), which suffered large amount of deposition from transboundary air pollution (Kamisako et al. 2008). Rainfall, stream water and soil solution were collected from the study site at least once a month. In addition, throughfall and stemflow were also collected. Sulphur isotopic ratio($\delta^{34}S$) and also water chemicals in these samples were determined. Seasonal variation of $\delta^{34}S$ from Aug. 2012 to Aug. 2013 is shown in Fig. 2. Clear variation is shown in rainfall, but $\delta^{34}S$ in stream water is stable at 9‰. It suggests that sulphur in rainfall does not directly reach to stream. Sulphur deposition may be retained once in ecosystem and $\delta^{34}S$ changed by some processes, for example soil adsorption. We'll discuss about the data include throughfall, stemflow and soil solutions in presentation.

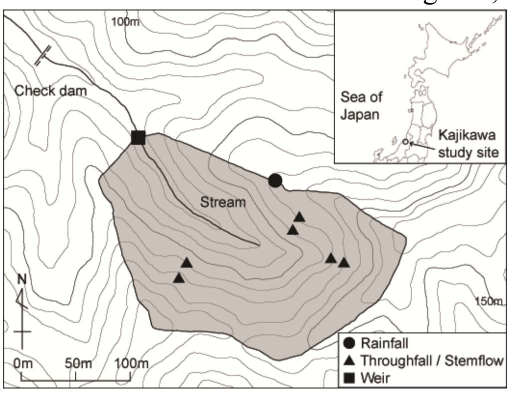


**Fig. 1. Kajikawa study site**

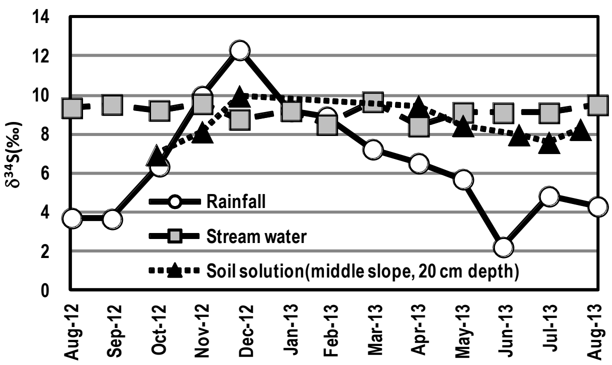


**Fig. 2. Seasonal variation of sulphur isotopic ratio**

**Acknowledgements**

The study was supported by the grant from APN (ARCP2013-13CMY-Sase). Authors thank them for their support and cooperation.

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# Sulfur dry deposition on forests in East Asia

Kazuhide Matsuda

Tokyo University of Agriculture and Technology, Japan

Keywords: deposition velocity, sulfate aerosols, sulfur dioxide, inferential method, EANET

Sulfur oxides are extremely important species in the atmospheric environment in Asia. Transboundary air pollution of sulfur and the impact of sulfur deposition on the forest ecosystem are of concern. In order to evaluate the impact, accurate estimations of deposition rate are required. Wet deposition and air concentration monitoring are carried out in EANET. We estimate sulfur dry deposition on forest surface base on the inferential method by using EANET and World Meteorological data set, and show the distribution of sulfur deposition in East Asia.

A resistance model to calculate deposition velocity of sulfur dioxide and sulfate was updated based on several field studies by direct measurements of dry deposition flux in Japan and Thailand. The model included the effect of enhancement of dry deposition due to high humidity indicated by Matsuda et al. (2006) for $SO_2$ and Matsuda et al. (2010) for sulfate. Deposition velocities were calculated from wind speed, temperature and relative humidity in 27 EANET sites from 2003 to 2008.

The estimations indicated that both $SO_2$ and sulfate deposition velocities ($V_d$) on forest surface were higher around Japan and lower around tropical area. The distribution of $V_d$ was similar to that of wind speed. Dry deposition of sulfate occupied about 30% of total sulfur dry deposition in average. Ratios of total dry deposition to wet deposition were high in high latitude and low in low latitude because of low wind speed and large precipitation amount in low latitude (Fig. 1, Fujimura et al., 2011).

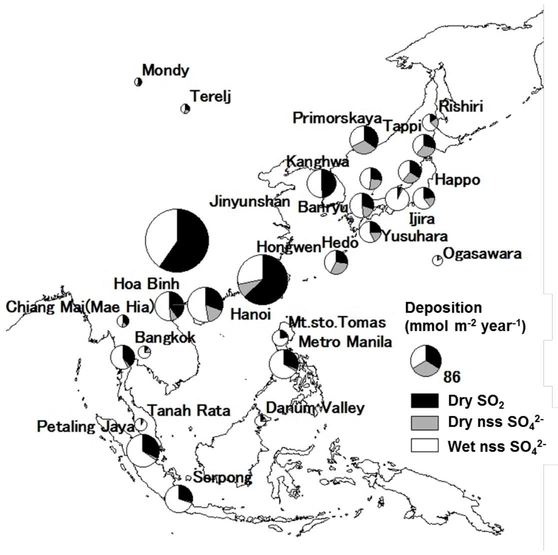


Fig. 1 Distribution of annual mean wet and dry deposition of sulfur on forest surface from 2003 to 2008.

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Matsuda et al. 2010. Deposition velocity of PM2.5 sulfate in the summer above a deciduous forest in central Japan. *Atmospheric Environment* 44, 4582-4587.

# Vertical profiles of sulfate and nitrate aerosols in a forest canopy in suburban Tokyo

Tatsuya Yamazaki[1,2] and Kazuhide Matsuda[1]

1. Tokyo University of Agriculture and Technology, Japan, 2. Meisei University, Japan.

Keywords: dry deposition, $PM_{2.5}$, ammonium nitrate, ammonium sulfate, nitric acid gas

To elucidate differences of dry deposition process in $PM_{2.5}$ components, vertical profiles of inorganic components were measured in a forest in suburban Tokyo (FM Tama site) during one year from December 2012 to November 2013. Sampling was carried out every week at 4 heights (2 heights above canopy, 2 heights below canopy) of a tower contracted in the forest. Major inorganic aerosols were $NH_4NO_3$ and $(NH_4)_2SO_4$ at the 4 heights through the year. Fig.1 shows vertical profiles of $NO_3^-$ and $SO_4^{2-}$ in $PM_{2.5}$. Significant differences between $SO_4^{2-}$ and $NO_3^-$ profiles were appeared. $NO_3^-$ relatively decreased compared with $SO_4^{2-}$ toward the forest floor through the year. Decreasing rates were high in summer and low in winter in both components. In winter and spring, temperature increased toward the forest floor. On the other hand, in summer and autumn, it was almost no difference above the canopy and decreased below the canopy. The profiles of concentration and temperature indicated that volatilization of $NH_4NO_3$ by higher temperature on the floor caused the rapid decrease of particulate $NO_3^-$ in winter and spring, and the volatilization by absent $HNO_3$ gas due to its significant removal to leaves caused the rapid decrease in summer and autumn. It indicated the removal of ammonium nitrate to forests was more efficient than that of ammonium sulfate, because of the volatilization process.

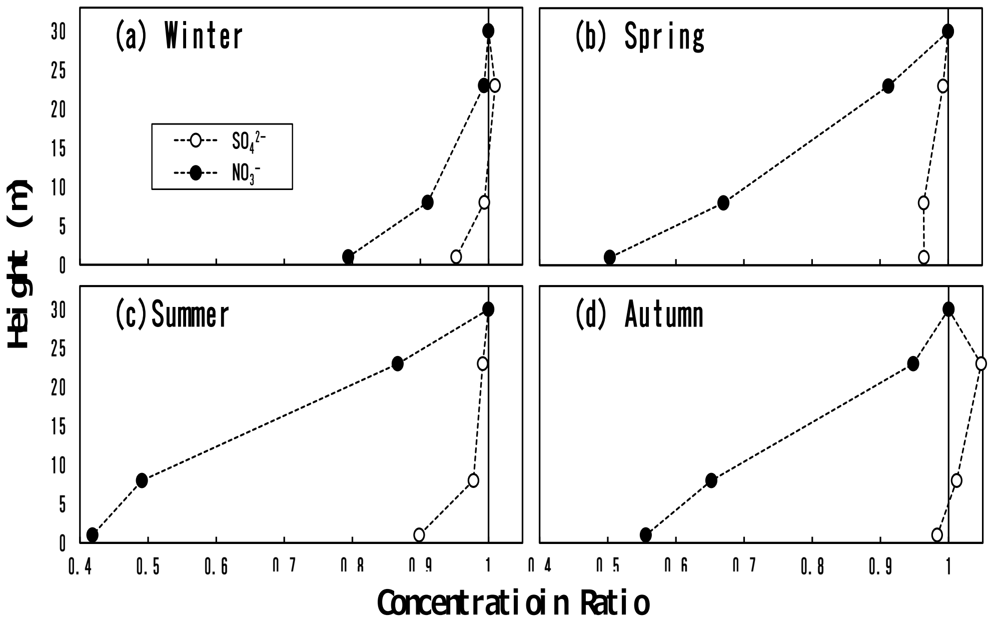


Fig.1 Normalized vertical profiles of $NO_3^-$ and $SO_4^{2-}$ concentrations in $PM_{2.5}$

# Sulphur storage in soil of a rehabilitated forest at Bintulu, Sarawak

Ahmed, O. H. [1,2], Majid, N. M. A. [3], Yamashita, N.[4] and Sase, H.[4]
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[2]Agriculture and Environment, Borneo Eco-Science Research Centre, Universiti Putra Malaysia Bintulu Sarawak Campus, 97008Bintulu, Sarawak, Malaysia.
[3]INTROP, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.
[4]Ecological Impact Research Department, Asia Center for Air Pollution Research (ACAP), Japan Environmental Sanitation Center (JESC), 1182 Sowa, Nishi-ku, Niigata 950-2144, Japan

Environmental pollution being it air, water, or soil has become a global concern. Among the chemical compounds which are likely to pollute the environment if not properly managed are sulphur oxides. Sulphur oxides pollution could be notable in highly industrialized areas and this is a cause for concern because sulphur compounds including sulphur oxides and sulphate once that are emitted into the atmosphere could be deposited in forest soils. Considering the fragile nature of rehabilitated forests in particular, the damaging effects of sulphur oxides and sulphate on this ecosystem could be significant. Therefore, there is a need for studies on sulphur dynamics of degraded and rehabilitated forest soils. Based on this rationale, a study was carried out in a rehabilitated forest of Universiti Putra Malaysia Bintulu Campus Sarawak, Malaysia to determine the soil sulphate storage of the rehabilitated forest and to also determine if the storage is related to pH, EC, acidity, and exchangeable $Al^{3+}$, $H^+$, $K^+$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$. Soil samples were taken along the gradient (upper slope, middle slope, and lower slope) of the rehabilitated forest. Standard procedures were used to determine variables evaluated in this study. As for sulphate, $NaHCO_3$ extractable fraction was measured according to the EANET technical manual. Soil $SO_4^{2-}$ storage was calculated based on the procedure of Ellert et al. (2000). The content of sulphate and storage increased with increasing soil depth suggesting trapping of $SO_4^{2-}$ in deeper soil layers. However, the $SO_4^{2-}$ storage decreased down the gradient of the rehabilitated forest indicating trapping of $SO_4^{2-}$vertically than horizontally. This is an interesting finding that should be investigated further as one would have expected more horizontal flow of $SO_4^{2}$ than vertical. Although sulphur dynamics could affect the soil fertility of this rehabilitated forests due to sulphur interaction with soil organic matter and aluminium, there was no consistent relationship between storage of $SO_4^{2-}$ and pH, EC, acidity, and exchangeable $Al^{3+}$, $H^+$, $K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$. This aspect needs to be further studied.

## Acknowledgement

We acknowledge the financial and/or technical support from Asia Center for Air Pollution Research (ACAP), Universiti Putra Malaysia and Asia Pacific Network for Global Change Research (ARCP2013-13CMY-Sase).

## References

Ellert, B.H., Jansen, H. H. and McConkey, B. G. 2000. Measuring and comparing soil carbon storage. In: Assessment methods for soil carbon. Lal, R., Kimble, J. M., Follett, R. F. and Stewart, B. A. (eds). pp:131-146. Lewis Publishers, Boca Raton, USA.

# Stream Water Chemistry in Rehabilitated Forest of Bintulu Sarawak Malaysia

Noraini, R.[1], Seca, G.[1], Yamashita, N.[2], Saito, T. [2], Sase, H.[2]

1. Universiti Putra Malaysia, Malaysia 2. Asia Center for Air Pollution Research, Japan

Keywords: water quality, water chemistry, sulphur isotope ratio, water-catchment, rehabilitated forest

Emission of pollutant gases mainly sulphur oxides causing air pollution and acid deposition particularly in highly industrialized areas. With rapid development taken place at the study area, a research was conducted to investigate the effects of the development particularly on chemical characteristics of stream water and its deposition rate. The variations in selected physico-chemical analysis were investigated to determine the water and sulphur content on water-catchment of rehabilitated forest in UPM Bintulu Sarawak Malaysia. The water chemistry was studied based on water quality variables and major ion chemistry. While, the measurement of the sulfur isotope ratios analyze and used as a tracer to identify the sources of sulphur. All analyses performed according to Standard Methods for the Examination of Water and Wastewater APHA. Twelve sampling stations were selected from upstream, middle stream and downstream of river to assess its chemical properties. Results for each physico-chemical variables are summarized as follows; pH (6.08), dissolved oxygen (7.14 mg/L), electrical conductivity (1.49 µS $cm^1$), total dissolved solids (0.03 mg/L), ammonia nitrogen (0.07 mg/L), biochemical oxygen demand (0.65 mg/L), chemical oxygen demand (2.67 mg/L), total suspended solids (20.17 mg/L), turbidity (53.01 mg/L) and alkalinity (0.82 mg/L). The major ion $NH_4^+$ (0.05 mg/L), $Na^+$ (1.99 mg/L), $K^+$ (0.5 mg/L), $Ca^{2+}$ (0.95 mg/L), $Mg^{2+}$(1.27 mg/L), $SO_4^{2-}$ (3.27 mg/L), $NO_3$ (1.05 mg/L), chloride (2.95 mg/L) and heavy metals; Mn (0.0003 mg/L), Fe (0.0024 mg/L), Cu (0.004 mg/L) and Zn (0.007 mg/L) respectively. The measurements of the sulphur isotope ratio ($\delta^{34}S$) results indicate sulphur source originated from atmosphere deposition in wetter season because the $\delta^{34}S$ in atmospheric deposition was similar to that in stream water in the season. Analysis results suggest most of the variables include the sulphate content in all samples collected across the seasons except for turbidity were not exceeded the permissible limit by the World Health Organization (WHO) water quality guidelines. Therefore, further research on continuous monitoring need to be carried out in order to validate the finding in this study and as a precautionary measure.

**Acknowledgements**

Thanks to APN and UPM Bintulu Sarawak Campus for help and support.

**References**

Shanley, J. B., Mcdowell, W. H. and Stallard, R. F. 2011. Long-term patterns and short-term dynamics of stream solutes and suspended sediment in a rapidly weathering tropical watershed. Water Resources Research 47:1-11.

# Precipitation chemistry of the Sakaerat forest catchment in the Northeastern part of Thailand.

Garivait, H.[1], Sase, H.[2], Morknoy, D.[1],Chanatorn, D.[1], Tangsuwan, C.[1], Mueanyat, T.[1], Makmai, A.[1], and Kietvuttinon, B.[3]

[1]Environmental Research and Training Centre, Thailand, [2]Asia Center for Air Pollution Research, Japan, [3]Royal Forest Department, Thailand.

Keywords: precipitation, forest catchment, ionic deposition, potential to soil acidification.

Acid deposition has become one of the most important issues in this region due to its trans-boundary nature and the impact to ecological acidification. The impact to ecology would be the most important for catchment areas where water resources availability was defined. Wet deposition of well known acidifying compounds such as nitrogen and sulfur deposition found in the catchment area through the integrated monitoring method such as rainfall (RF), throughfall (TF) and Stemflow (SF), during 2008-2014 monitoring were approximately 288, 661 mg/m²/year for nitrogen and 186, 490 mg/m²/year for sulfur, respectively. The volume weighted average pH of the precipitation, througfall and stemflow were 5.2, 6.1 and 6.3, respectively. The previous study on soil characteristics of the tropical forested catchment indicated high potential to soil acidification. Long term monitoring on the precipitation chemistry in the catchment is necessary to quantify the acidic pollutants deposition and their potential effects on long-term soil acidification at a tropical forested catchment area in Thailand.

**Acknowledgements**

We would like to acknowledge the grant from The Asia-Pacific Network for Global Change Research (APN) and the excellent collaboration of the Asia Center on Air Pollution Research (ACAP) and the Royal Forest Department, Thailand.

**References**

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Garivait, H., Parkpian, P., Sase, H., Luangjame, J., Kievuttinon, B., and Morknoy, D. *The potential impact of Sulfur deposition on soil acidification in a tropical forested catchment in Thailand.* EANET Science Bulletin 2010, volume I, Asia Center on Air Pollution Research, Niigata, Japan.

# Vertical distribution of sulfur isotopic ratio in rainfall, throughfall, soil and streamwater in Thai and Malaysian tropical forest

Yamashita, N.[1], Saito, T.[1], Rosli, N.[2], Staporn, D.[3], Gidiman, J.[4], Garivait, H.[5], Ahmed, O. H. [2], Gandaseca, S.[2], Morohashi, M.[1], Inomata, Y.[1], Kok-Peng, L.[6], Kietvuttinon, B.[3], Visaratana, T.[3], Majid, N. M. [2], Ohizumi, T.[1] and Sase, H.[1]

1. Asia Center for Air Pollution Research; 2. Universiti Putra Malaysia, Malaysia; 3. Royal Forest Department, Thailand, 4. Danum Valley Field Centre, c/o Yayasan Sabah Group, Sabah, Malaysia; 5. Environmental Research and Training Center, DEQP, Thailand; 6. Malaysian Meteorological Department.

Keywords: tropical forest, sulfur isotopic ratio, atmospheric deposition, throughfall, streamwater

In South East Asia an increase in emissions of sulfur (S) into the atmosphere may introduce new risks for the plant, soil and inland-water through acidification. However, the effect of the atmospheric S deposition on acidification by an increase in $SO_4^{2-}$ is poorly understood in tropical forests with pedogenic and lithological S sources in the internal cycles. Sulfur isotopic ratio ($\delta^{34}S$) could be a good indicator to identify the source of $SO_4^{2-}$ in soil and inland-water. Our objective is to clarify the contribution of atmospheric S deposition to S dynamics in the tropical forests by determining $\delta^{34}S$ (‰) distribution from rainfall to streamwater.

Study catchments are lowland dipterocarp forest in Danum valley, Sabah (DNV), rehabilitation forest in Bintulu, Sarawak (BTL) and dry evergreen forest in Sakaerat, Nakhon Ratchasima (SKT). Anion-exchange-resin columns were installed in each site through a year (*ca.* 6-months × 2) to collect and concentrate $SO_4^{2-}$ in the field. $SO_4^{2-}$ retained in the resin was extracted by NaCl and precipitated as $BaSO_4$. We determined $^{34}S$ / $^{32}S$ of the $BaSO_4$ by mass spectrometer and calculated $\delta^{34}S$ (‰) using the reference material (Canyon Diablo Troilite). Annual weighted-mean $\delta^{34}S$ was calculated from $SO_4^{2-}$ fluxes (kg $ha^{-1}$ 6-$month^{-1}$) and $\delta^{34}S$ in each period.

Annual weighted-mean $\delta^{34}S$ in rainfall were 10.1, 7.9 and 4.1‰ in DNV, BTL and SKT respectively, whereas S depositions were 2.6, 6.1 and 6.4 kg $ha^{-1}$ $year^{-1}$. The $\delta^{34}S$ vertically decreased from rainfall to subsoil in DNV although $\delta^{34}S$ increased in subsoil in BTL. In DNV and BTL arithmetic mean $\delta^{34}S$ in streamwater were lower than that in rainfall, which implied the existence of pedogenic or lithological S source. Those internal-S sources should be considered to examine the effect of atmospheric deposition on soil and inland-water ecosystems in this area.

**Acknowledgements**

The project is supported by the grant from APN (ARCP2012-18NMY-Sase: ARCP 2013 -13 CMY -Sase) and Mitsubishi Cooperation.

# Alkalinization and acidification of stream water in Sakaerat forest

Sase, H[1], Yamashita, N[1], Luangjame, J[1,2], Garivait, H[3], Kietvuttinon, B[2], Visaratana, T[2], Kamisako, M[1], Kobayashi, R[1], Ohta, S[4], Shindo, J[5], Hayashi, K[6], Toda, H[7] & Matsuda, K[8]

1. Asia Center for Air Pollution Research, 2. Royal Forest Department, Thailand, 3. Environmental Research and Training Center, DEQP, Thailand, 4. Kyoto University, 5. Yamanashi University, 6. National Institute for Agro-Environmental Sciences, 7. Shinshu University, 8. Tokyo University of Agriculture and Technology.

Keywords: atmospheric deposition, sulfur, dry evergreen forest, acidification, alkalinization

Stream water chemistry has not been enough investigated in tropical Asia, although emission level of air pollutants were still high in the region. Field surveys on atmospheric deposition and stream water chemistry have been carried out since 2005 in a small catchment plot, which was established in a dry-evergreen forest in the Sakaerat Silvicultural Research Station, Nakhon Ratchasima Province, Thailand. Stream water at the outlet of the catchment was collected at the same interval and the discharge was continuously monitored. Precipitation samples including throughfall (TF), stemflow (SF), and rainfall outside the forest canopy were collected twice a month. Ion constituents were determined using ion chromatograph for the water samples. Soil chemical properties and ion fluxes in soil layers were also determined intensively. Stream water chemistry showed a distinct seasonality. The pH and EC increased simultaneously with alkalinity and base cations in the early wet season. After the alkalinization above, the pH and alkalinity suddenly decreased with flushing of $SO_4^{2-}$ in the middle or late wet season. High mineralization rate (Yamashita et al., 2010) and high deposition amount (Sase et al. 2012) in the beginning of wet season may cause alkalinization and acidification of the stream water, respectively. Moreover, the trends on stream water chemistry during the observation period (6 water years) will be discussed in the presentation.

**Acknowledgements**

The study was supported by the Environment Research and Technology Development Fund (B-0801), MOE and KAKENHI (20120012), MEXT, Japan, and the grant from APN (ARCP2012-18NMY-Sase; ARCP2013-13CMY-Sase). Authors thank for their support.

**References**

Sase, H et al. 2012. Deposition process of sulfate and elemental carbon in Japanese and Thai forests. *Asian Journal of Atmospheric Environment* 6: 246-258.

Yamashita, N. et al. 2010. Seasonal and spatial variation of nitrogen dynamics in the litter and surface soil layers on a tropical dry evergreen forest slope. *Forest Ecology and Management* 259: 1502-1512.

APN Project Workshop 2014 on Sulfur Dynamics in East Asian Forests, 18-19 December 2014, Bangkok, Thailand

# Introduction of the APN Project, “Dynamics of sulphur derived from atmospheric deposition and its possible impacts on the East Asian forests”

Sase, H., Ohizumi, T., Yamashita, N., Visaratana, T., Kietvuttinon, B., Garivait, H., and Majid, N.M.

ACAP APN

## What is APN?

The Asia-Pacific Network for Global Change Research (APN) is a network of 22 member country governments that promotes global change research in the region, increases developing country involvement in that research, and strengthens interactions between the science community and policy-makers.

- The APN’s Science Agenda (2010-2015)
  - Climate Change and Climate Variability;
  - Ecosystems, Biodiversity and Land Use;
  - Changes in the Atmospheric, Terrestrial and Marine Domains; and
  - Resources Utilisation and Pathways
- Our project applied to the Annual Regional Call for Research Proposal (ARCP) was adopted at the 17th Intergovernmental Meeting of APN in March 2012.

## Outline of the project for the APN grant

- Project Title
  Dynamics of sulphur derived from atmospheric deposition and its possible impacts on the East Asian forests
- Project Leader
  Hiroyuki Sase, Head of Ecological Impact Research Department, ACAP
- Duration
  Two fiscal years 2012/2013 and 2013/2014
  (Started on 7 August 2012)
  The second year contract will continue until 17 February 2015.

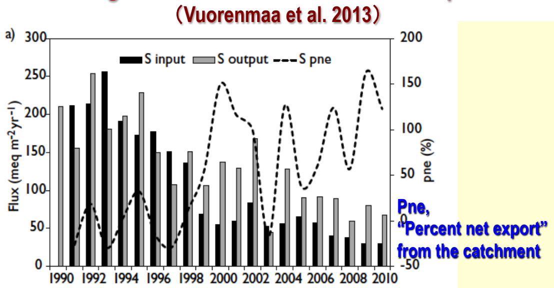
## Project members

- Applicants for the research proposal
  - Tsuyoshi Ohizumi and Naoyuki Yamashita, ACAP, Japan
  - Thiti Visaratana and Bopit Kietvuttinon, RFD, Thailand
  - Hathairatana Garivait, ERTC, Thailand
  - Nik Muhamad Majid, UPM, Malaysia
- Cooperative members
  - Yayoi Inomata and Tatsuyoshi Saito, ACAP, Japan
  - Duriya Staporn, RFD, Thailand
  - Ahmed Osumanu Haruna and Seca Gandaseca, UPM, Malaysia
  - Toh Ying Ying, Leong Kok Peng, and Maznorizan Mohamad, MMD, Malaysia
  - Nick Chappell, Lancaster University, UK

## Why sulfur is important?

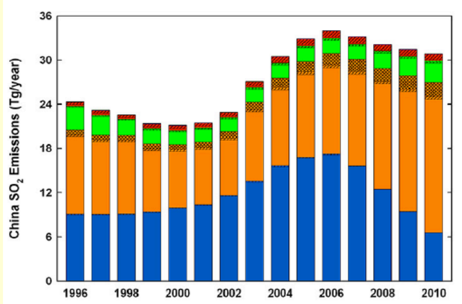
- Atmospheric deposition of sulfur compounds may gradually decrease according to the recent emission inventories in East Asia (e.g. Lu et al. 2010).
- However, the deposition level is still high in the region.
- Sulfur may be accumulated in soil, while nitrogen is cycled in soil-plant system more dynamically.
- Sulfur may be retained/released with change of the soil condition.
- The recent literatures (Mitchell et al., 2011; Mitchell & Likens, 2011) showed that the output of sulfur exceeded the input, suggesting mobilization of the sulfur accumulated in the past.

## S budget in a catchment in Czech Republic (Vuorenmaa et al. 2013)




- After reduction of the deposition amounts, S output increased。
- Similar situation in most of the sites for ICP Integrated Monitoring, CLRTAP.

## Emission trends in East Asia




$SO_2$ emission trend in China by Lu et al. (2011)

| Country | site | pH | EC | Alkalinity | $SO_4^{2-}$ | $NO_3^-$ |
|---|---|---|---|---|---|---|
| China | Jinyunsyan Lake | -3.34 *** | 4.34 *** | -2.69 ** | 3.44 *** | 2.50 * |
| | Xiaopin Dam | -2.35 * | 0.06 | -0.91 | 2.40 * | 0.21 |
| | Jiwozi River | -2.11 * | 2.92 ** | 3.46 *** | 3.68 *** | 0.87 |
| | Zhuxiandong Stream | 0.39 | -1.88 | -0.38 | -2.27 * | -0.09 |
| Indonesia | Patengang Lake | -2.36 * | -1.79 | -1.40 | 2.35 * | 1.23 |
| Japan | Ijira Lake | 1.49 | 0.65 | 3.19 ** | 1.06 | -3.01 ** |
| | Kamagatani River flowing river to Ijira Lake | 3.05 ** | 1.79 | 3.81 *** | 1.25 | -1.39 |
| | Kobara River flowing river to Ijira Lake | 2.47 * | 1.83 | 3.09 ** | 2.34 * | -1.70 |
| | Banryu Lake | -0.67 | 2.47 * | -0.72 | 1.17 | 2.60 ** |
| | Banryu Lake 3 | -0.67 | 2.20 * | -0.49 | 1.57 | 1.86 |
| Malaysia | Semenih Dam | -2.87 ** | 0.27 | 0.46 | 2.09 * | -1.59 |
| Mongolia | Terelj River | 0.60 | 1.53 | 2.69 ** | 1.37 | -1.04 |
| Phillipines | Pandin Lake | -1.09 | -0.89 | -1.40 | 3.27 ** | 3.91 *** |
| Russia | Pereemnaya River | -0.94 | 4.46 *** | 0.59 | 4.70 *** | 2.63 ** |
| | Komarovka River | -0.37 | 0.49 | -3.32 *** | 2.92 ** | 0.49 |
| Thailand | Vachiralongkorn Dam 1 Ban Pong Chang | 0.87 | -2.98 ** | 0.57 | -2.07 * | 1.81 |
| | Vachiralongkorn Dam 2 Ban Pang Pueng | 1.45 | -3.39 *** | 1.06 | -1.34 | 2.44 * |
| Vietnam | Hoa Binh Reservoir | 0.36 | 1.61 | -1.37 | 1.61 | 1.70 |

## Trends on inland water in the EANET sites

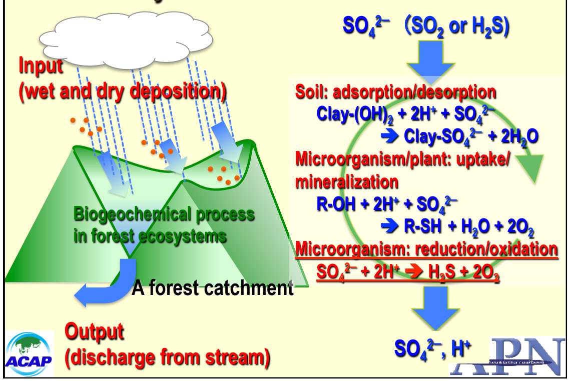
Declining trends

Increasing trends

The pH declining trend was accompanied by $SO_4^{2-}$ leaching.

(EANET, 2011. *PRSAD2*)

## Sulfur dynamics in forest catchments




## Sulfur isotopic ratio of rainwater and stream water

- Isotopic ratio ($^{34}S/^{32}S$) of sulfur compounds may be changed by biological process (isotope fractionation), mainly by sulfate reduction process.
- Isotopic ratios of atmospheric sulfur may show source specific information to identify sulfur sources, such as coal.
- Measurement of sulfur isotopic ratio of rainwater and stream water may be informative to discriminate origin of sulfur (atmospheric, biological or geological) and to discuss retention time of sulfur in the ecosystems.

$$\delta^{34}S\ (‰) = \{(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{CDT} - 1\} \times 1000$$

where, $(^{34}S/^{32}S)_{sample}$ and $(^{34}S/^{32}S)_{CDT}$ are isotopic ratio of the sample and standard substance (Canyon Diablo troilite)

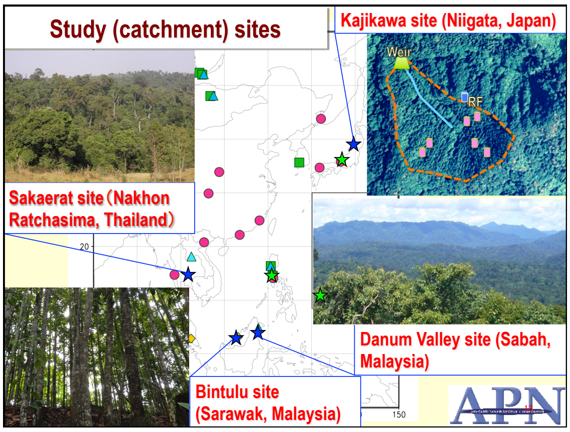
10

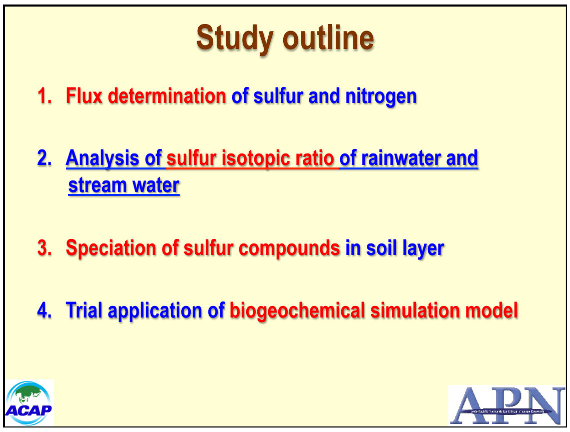
## Objectives

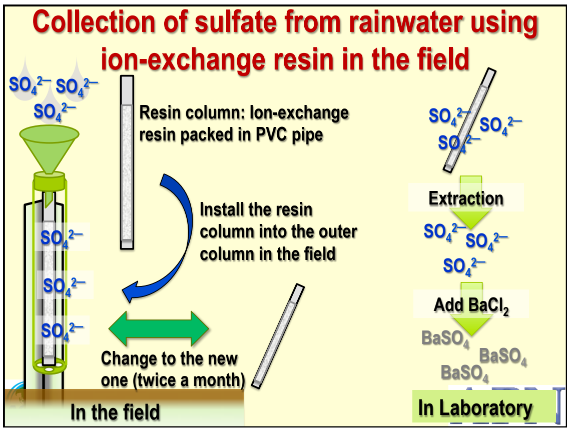
- To clarify sulfur dynamics (flux, retention time, speciation of accumulated sulfur compounds, etc.) in ecosystems of the East Asian forests
- To discuss combined effects of sulfur and nitrogen on acidification and eutrophication of the East Asian forests

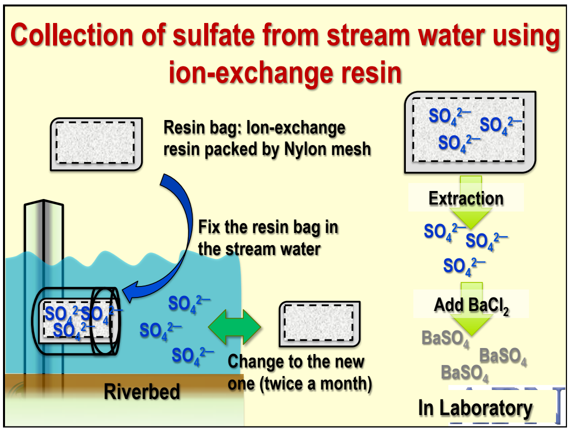
## Study sites

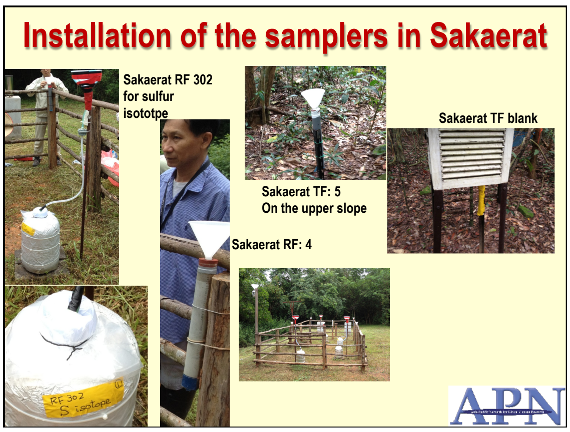
- Existing catchment study sites:
  - Kajikawa site, Niigata Prefecture, Japan: Japanese cedar forest
  - Sakaerat site, Nakhon Ratchasima Province, Thailand: Dry evergreen forest
  - Danum Valley site, Tawau Division, Malaysia: Tropical rainforest
- New site for the project:
  - Bintulu site, Sarawak, Malaysia: Rehabilitated forests

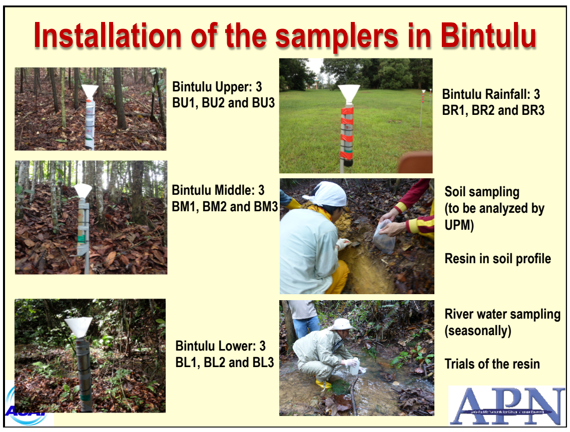

Study (catchment) sites
Kajikawa site (Niigata, Japan)
Weir
RF
Sakaerat site（Nakhon Ratchasima, Thailand）
Danum Valley site (Sabah, Malaysia)
Bintulu site (Sarawak, Malaysia)
20
150
APN


Study outline
1. Flux determination of sulfur and nitrogen
2. Analysis of sulfur isotopic ratio of rainwater and stream water
3. Speciation of sulfur compounds in soil layer
4. Trial application of biogeochemical simulation model
ACAP
APN


Collection of sulfate from rainwater using ion-exchange resin in the field
$SO_4^{2-}$
Resin column: Ion-exchange resin packed in PVC pipe
Install the resin column into the outer column in the field
Change to the new one (twice a month)
Extraction
Add $BaCl_2$
$BaSO_4$
In the field
In Laboratory


Collection of sulfate from stream water using ion-exchange resin
Resin bag: Ion-exchange resin packed by Nylon mesh
$SO_4^{2-}$
Fix the resin bag in the stream water
Change to the new one (twice a month)
Extraction
Add $BaCl_2$
$BaSO_4$
Riverbed
In Laboratory


Installation of the samplers in Sakaerat
Sakaerat RF 302 for sulfur isototpe
Sakaerat TF: 5
On the upper slope
Sakaerat TF blank
Sakaerat RF: 4
APN


Installation of the samplers in Bintulu
Bintulu Upper: 3
BU1, BU2 and BU3
Bintulu Rainfall: 3
BR1, BR2 and BR3
Bintulu Middle: 3
BM1, BM2 and BM3
Soil sampling
(to be analyzed by UPM)
Resin in soil profile
Bintulu Lower: 3
BL1, BL2 and BL3
River water sampling (seasonally)
Trials of the resin
APN

## Installation of the samplers in Danum Valley

Danum Upper: 3 DU1, DU2 and DU3

Danum Rainfall: 3 DR1, DR2 and DR3

Danum Middle: 3 DM1, DM2 and DM3

Soil sampling (in the next mission, to be analyzed by UPM)

Resin in soil profile

Danum Lower: 3 DL1, DL2 and DL3

River water sampling (during the mission)

Trials of the resin (during the mission)

APN

## Publications from the joint research projects

| Project site/ area | Atmospheric deposition | Soil and biogeochemistry | Stream/river water and biogeochemistry |
|---|---|---|---|
| Kajikawa, Niigata, Japan | • *Environmental Pollution* (2008) | | • *Water, Air and Soil Pollution* (2008)<br>• *Water, Air and Soil Pollution* (2009)<br>• *Limnology* (2013) |
| Sakaerat, Nakhon Ratchasima, Thailand | • *Atmospheric Environment* (2012)<br>• *Asian Journal of Atmospheric Environment* (2012) | • *Journal of Forest Research (2009)*<br>• *Forest Ecology and Management* (2010)<br>• *Geoderma* (2011)<br>• *Journal of Forest Research (2012)* | |
| Danum Valley, Sabah, Malaysia | | | • *Journal of Tropical Ecology* (2014) |

ACAP APN

## Possible publication plans in near future

| Project site/ area0000 | Atmospheric deposition | Soil and biogeochemistry | Stream/river water and biogeochemistry |
|---|---|---|---|
| Kajikawa, Niigata, Japan | • *ENPO* (2008) | | • *WASP* (2008)<br>• *WASP* (2009)<br>• *Limnology* (2013)<br>• Seasonal variation of S isotopic ratio by Saito et al. |
| Sakaerat, Nakhon Ratchasima, Thailand | • *AE* (2012)<br>• *AJAE* (2012)<br>• Precipitation chemistry by Garivait et al. | • *JFR (2009)*<br>• *FORECO* (2010)<br>• *Geoderma* (2011)<br>• *JFR (2012)* | • Stream water chemistry including i/o budget by Sase et al. |
| Danum Valley, abah, Malaysia | | | • *JTE* (2014) |
| Bintulu, Sarawak, Malaysia | • RF and TF by Hilmi, Yamashita et al. | • Soil sensitivities by Kasim et al.<br>• Sulfur and nitrogen in soil by Osumanu et al. | • Stream water chemistry including S isotopic ratio by Nora, Gandaseca et al. |

• Comparison study of S isotopic ratio by Yamashita et al.

ACAP APN

## Acknowledgments

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ACAP APN

# タイ・マレーシア熱帯林の降水・土壌・渓流水における $\delta^{34}S$ の地域間変動

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[*1] アジア大気汚染研究センター, [*2] Danum Valley Field Center, [*2] University Putra Malaysia, [*3] Royal Forest Department, [*4] Environmental Reserch Training Center

## はじめに

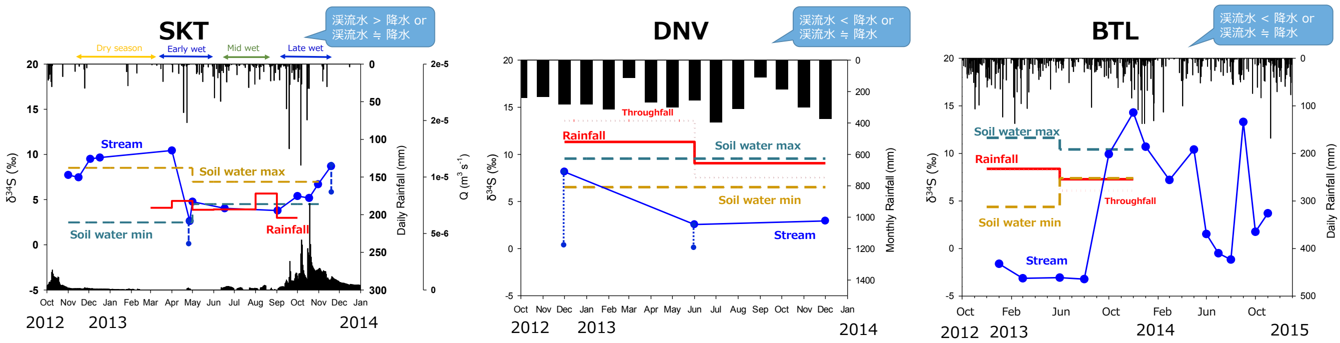
東南アジアでは硫黄酸化物の排出がいまだに増加しているが、周辺の熱帯林への硫黄沈着による影響はほとんど明らかでない。森林生態系内で循環する硫黄の安定同位体比（$\delta^{34}S$）は異化的硫酸還元を除けば顕著な分別を生じないことが知られており、大気や岩石由来の硫黄による渓流水質形成への寄与を推察できる。本研究は林外雨から林内雨、土壌水を経て渓流水に至るまでの$SO_4^{2-}$-$\delta^{34}S$の変化を、タイ・マレーシアの３つの熱帯林小集水域で明らかにすることを目的とした。

## まとめ

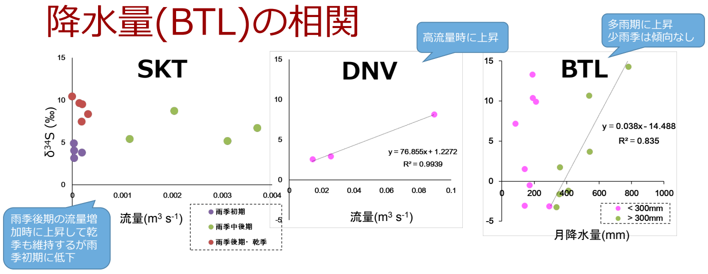
- 降水の$\delta^{34}S$は地域間で5‰程度の差が見られたが、土壌水の$\delta^{34}S$は5-10‰程度の範囲にあり、明確な地域間差は認められなかった。
- 渓流水の$\delta^{34}S$は季節性の地域間差が見られた。SKTでは雨季後期の集水域流出口近傍で降水の$\delta^{34}S$を上回っており、異化的硫酸還元による同位体分別を経た$SO_4^{2-}$が流出した可能性があった。DNV・BTLでは数回にわたって降水の$\delta^{34}S$を下回っており、岩石風化由来Sの存在が推察されたが、高流量時には（生態系内を循環する）大気由来Sの寄与が高まる可能性があった。
- 熱帯林の渓流水質形成には異化的硫酸還元や岩石風化が深く関与している可能性がある。

## 結果と考察

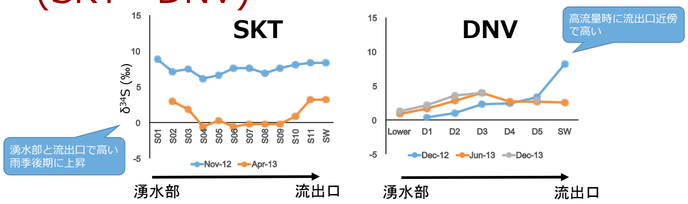
### ①降水・土壌水・渓流水における$\delta^{34}S$の季節変動



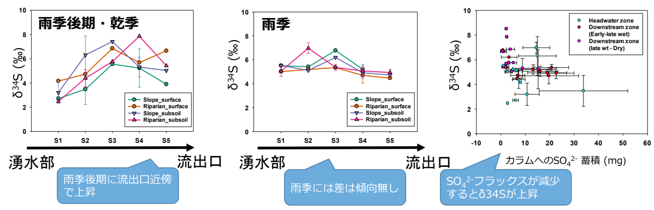

### ②渓流水$\delta^{34}S$と流量(SKT・DNV)・降水量(BTL)の相関




### ③流路沿いの渓流水$\delta^{34}S$の変動 (SKT・DNV)




### ④流路沿いの土壌水$\delta^{34}S$の変動 (SKT)




### ⑤$\delta^{34}S$の地域間差と渓流水$SO_4^{2-}$起源

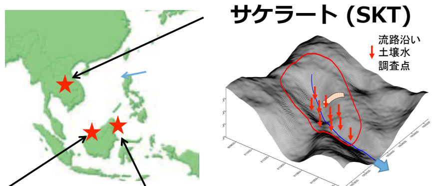
値は年間値

| | SKT | DNV | BTL |
|---|---|---|---|
| 降水 $\delta^{34}S$ | 4.1 ‰ | 10.1 ‰ | 7.9 ‰ |
| 土壌水 $\delta^{34}S$ | 2.0 – 9.3 ‰ | 6.5 – 9.6 ‰ | 4.4 – 11.7 ‰ |
| 渓流水 $\delta^{34}S$ | 2.6 – 10.4 ‰ | 2.6 – 8.2 ‰ | -4.1 – 14.3 ‰ |
| S流入量（林内雨）* S流出量* | 2.5（5.8） kg S ha$^{-1}$ 0.2 kg S ha$^{-1}$ | 2.6（3.6） kg S ha$^{-1}$ 6.5 kg S ha$^{-1}$ | 6.1（19） kg S ha$^{-1}$ NA |
| 降水34Sに対する渓流水 34S | 多い（雨季後期, 乾季） 同レベル（雨季初期） | 少ない（基底流？） 同レベル（高流量時） | 少ない（通年？） 同レベル（多雨時） |
| 渓流水$SO_4^{2-}$のソース（吸収・無機化・吸脱着プロセスは検出しない） | 異化的硫酸還元プロセスを経た$SO_4^{2-}$（雨季後期→乾季） 大気硫黄（雨季初期） | 岩石の化学風化（基底流？） 大気硫黄（高流量時） | 岩石の化学風化（通年？） 大気硫黄（多雨時） |

*SKTの流入・流出は2006-2011の平均 (Sase et al., submitted)、DNVの流入・流出は2008-2011の平均 (Yamashita et al., 2014)

## 方法

### ①調査地の概要




サケラート (SKT)
- 熱帯モンスーン気候
- 熱帯乾燥常緑林
- Acrisols
- 第三紀堆積岩(砂岩)

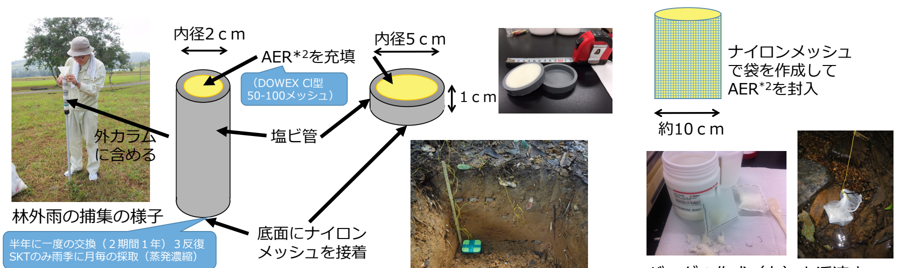
ビントゥル (BTL)
- 熱帯多雨林気候
- リハビリテーション林
- Acrisols
- 第三紀堆積岩

ダナンバレー (DNV)
- 熱帯多雨林気候
- 低地フタバガキ林
- Acrisols
- 第三紀堆積岩

水文モニタリングの実施
降雨・流量観測（SKT・DNV）
降雨のみ（BTL）

### ②陰イオン交換樹脂(AER)による$SO_4^{2-}$捕集濃縮と分析

**カラムタイプ (林外・林内雨用)**　**リングタイプ (土壌水用)**　**バッグタイプ (渓流水用)**




分析手順
① 10倍量の0.5 M NaClを加えて振とうし、抽出液をホットプレート上で100ml程度まで濃縮（一部の降水・渓流水は蒸発法で直接濃縮）
② pHを２～３に調整後に$BaCl_2$を適量加えて$BaSO_4$沈殿
③ 質量分析計(NCS2500, Conflo II, Delta-Plus)にて測定し、Canyon Diablo Troiliteを利用して$\delta^{34}S$（‰）を決定

**現地での作業を支えてくださったサケラート林業研究所、ダナンバレーフィールドセンターおよびUPMのスタッフに感謝します。本研究はAPN(ARCP2012-18NMY-Sase)で実施した。**

# タイ熱帯季節林小集水域における硫酸イオン起源の時空間異質性

# Spatial and temporal heterogeneity of the sources of streamwater sulfate in tropical dry forest catchment in Thailand

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## Introduction

In Southeast Asia an increase in emissions of sulfur (S) into the atmosphere may introduce new risks for the plant, soil and inland-water through acidification. However, the effect of the atmospheric S deposition on acidification by an increase in $SO_4^{2-}$ is poorly understood in tropical forests with possible S sources and processes in the internal cycle. S isotopic ratio ($\delta^{34}S$) could be a good indicator to identify the source of $SO_4^{2-}$ in soil and inland-water because only bacterial dissimilatory sulfur reduction (**BDSR**) results in a large fractionation of S isotope. Our objectives are to clarify the spatial and temporal variability of $\delta^{34}S$ in rainfall, throughfall, soil and stream water within the catchment and discuss the effect of the atmospheric S input on the stream in tropical dry forest.


## Summary

- Large seasonal and temporal variation in $SO_4^{2-}$-$\delta^{34}S$ was observed within the tropical dry forest catchment in Thailand.
- BDSR may play the important role for S cycle in study catchment because 1) streamwater $\delta^{34}S$ increased 4‰ in late wet season (likely to led to a reducing condition), 2) $\delta^{34}S$ in soil and soil water were higher in riparian zone and down stream area and 3) mass balance model suggested the large S sink in this system.
- Our estimation showed that the contribution of atmospheric S source to streamwater was more than 90% in early to middle wet season whereas the residues of BDSR and soil $SO_4^{2-}$ were main source for the streamwater $SO_4^{2-}$ on an annual bases.


## Seasonal variability of $\delta^{34}S$ in wet deposition and streamwater $SO_4^{2-}$

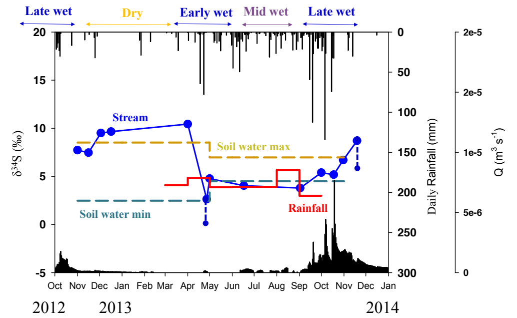



Fig. 1 Seasonal variation in wet deposition $\delta^{34}S$, streamwater $\delta^{34}S$, rainfall and discharge in SERS

Stream $\delta^{34}S$ increased in late wet - dry season

Stream $\delta^{34}S$ reduced to same level as rainfall in early – middle wet season.

Stream $\delta^{34}S$ increased with water discharge in late wet season

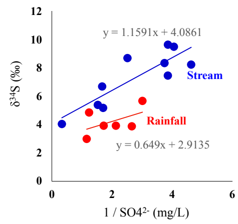



Fig. 2 $\delta^{34}S$ *vs.* $SO_4^{2-}$ concentration

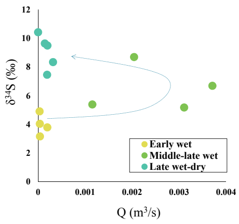



Fig. 3 Stream water $\delta^{34}S$ and instantaneous water discharge

Fig. 2 suggested a different sulfur sources between streamwater and rainfall

Enhancement of BDSR in late wet season?

## Inter-catchment variability of $\delta^{34}S$ in soil water $SO_4^{2-}$ and exchangeable soil $SO_4^{2-}$

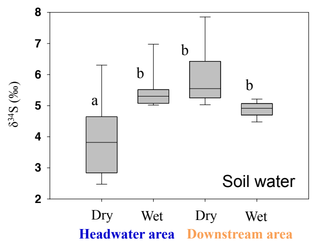



Fig. 4 Distribution of soil water $SO_4^{2-}$-$\delta^{34}S$ within study catchment

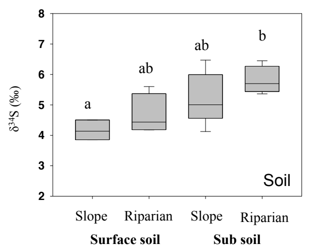
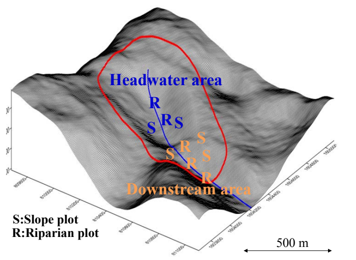



Fig. 5 Distribution of soil exchangeable $SO_4^{2-}$-$\delta^{34}S$ within study catchment




Soil water $\delta^{34}S$ in downstream was significantly higher than in headstream area

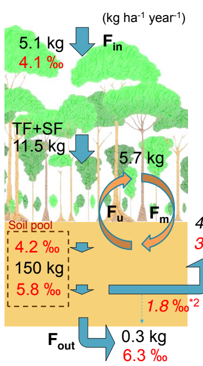
↓

Sub-soil $\delta^{34}S$ in riparian area was significantly higher than surface soil on the slope.

↓

Enhancement of BDSR in riparian area of down stream?

## Estimation of the sulfur budget




$$F_{in} + F_m = F_u + F_{bdsr} + F_{out} \quad \text{(Eq. 1)}$$

$$\frac{(F_{in}\delta^{34}S_{in} - F_{bdsr}\delta^{34}S_{bdsr})}{(F_{in} - F_{bdsr})} = \delta^{34}S_{out} \quad \text{(Eq. 2)}$$

$$\delta^{34}S_{bdsr} = \delta^{34}S_{soil} - \varepsilon_{bdsr} \quad \text{(Eq. 3)}$$

$F_{in}$: Bulk deposition, $F_m$: Mineralization rate, $F_u$: Plant uptake, $F_{bdsr}$: Bacterial dissimilarly sulfur reduction, $F_{out}$: Discharge to the stream,

BDSR might be needed to meet the simple mass balance model and high streamwater $\delta^{34}S$. Atmospheric source could be the main source of streamwater in early wet season.

Fig. 5 Estimation of annual S budget in study catchment. BDSR flux (*1) was estimated by Eq.1. Isotope fractionation ration by BDSR (*2) was estimated by Eq. 2 and Eq. 3. $F_m$ and $F_u$ are assumed to be equal.

## Contribution of different sulfur sources to stream water $SO_4^{2-}$

$$f_{in}\delta^{34}S_{in} + f_{soil}\delta^{34}S_{soil} + fb_{dsr.rd}\delta^{34}S_{bdsr.rd} = \delta^{34}S_{out} \quad \text{(Eq. 4)}$$

$$f_{in} + f_{soil} + fr_{ed.res} = 1 \quad \text{and} \quad 0 \le f \le 1 \quad \text{(Eq. 5)}$$

$$\delta^{34}S_{bdsr.rd} = \delta^{34}S_{soil} + \varepsilon_{bdsr} \quad \text{(Eq. 6)}$$

f indicates the fraction of each contributor to stream $SO_4^{2-}$. Subscripts "in", "soil" and "bdsr.rd" stand for the atmospheric input, the $SO_4^{2-}$ retained in the soil and the $SO_4^{2-}$ residues of BDSR.

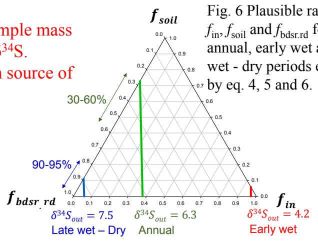



Fig. 6 Plausible range of $f_{in}$, $f_{soil}$ and $f_{bdsr.rd}$ for annual, early wet and late wet - dry periods estimated by eq. 4, 5 and 6.

## Comparison with other tropical site

| | Sakaerat *1 (This study) | Danum valley*2 (Sabah, Borneo) | Bintulu*2 (Sarawak, Borneo) |
|---|---|---|---|
| Vegetation | Tropical dry forest | Tropical rainforest | Tropical rainforest (Rehabilitation forest) |
| Type | Rural | Remote | Rural/urban |
| Annual precipitation | 1488 mm | 2700 mm | 3500 mm |
| S input (kgS $ha^{-1}$)<br>S output<br>Output – input | 5.1<br>0.3<br>- 4.8 | 2.6<br>6.5<br>+ 3.9 | 6.1<br>NA<br>NA |
| Input $\delta^{34}S$ | 4.1‰ | 10.1‰ | 7.9‰ |
| Soil water $\delta^{34}S$ | 2.0 – 9.3 ‰ | 6.5 – 9.6 ‰ | 4.4 – 11.7 ‰ |
| Output $\delta^{34}S$ | 2.6 – 10.4 ‰ | 2.6 – 8.2 ‰ | -4.1 – 14.3 ‰ |
| Output $\delta^{34}S$ – Input $\delta^{34}S$ | 2.2 ‰ | -7.4‰ | -3.9‰ |
| Possible source/sink | **BDSR** | **Rock weathering** | **Rock weathering** |

*1: Input/output data were cited from Sase et al., submitted. *2: Yamashita et al., unpublished

## Materials and methods

**[Site information]**

- Study site: Sakaerat environmental research station (SERS) located in North eastern Thailand, 350 km far from Bangkok
- Area size and altitude: 35 ha and 250-650m
- Annual precipitation and Climate: 1200 mm and Tropical savanna (Aw)
- Forest type: Tropical dry evergreen forest (DEF),
- Soil and Rock type: Acrisols (FAO) and Tertiary sand stone

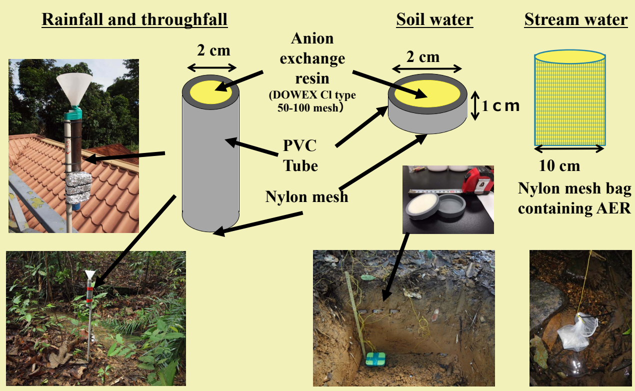
**[Sampling and analysis]**

- Anion-exchange-resin columns were installed for rainfall (N=3×2 periods), throughfall (N=15×2 periods), soil-water (10 plots×2 depth×2 periods, N=40) and stream-water (N=2×13 periods) through a year to collect and concentrate $SO_4^{2-}$ in the field (see right box).
- Monthly bulk deposition was collected from March to October 2013.
- Soils were taken from 10 plots ×2 depth (same as soil-water) to measure the exchangeable $SO_4^{2-}$ .
- The $SO_4^{2-}$ retained in the resin and soils was extracted by NaCl and CaHPO4, respectively, and precipitated as $BaSO_4$. Bulk precipitation was directly precipitated $BaSO_4$.
- $^{34}S/^{32}S$ of the $BaSO_4$ was determined by mass spectrometer (IR-MS) and $\delta^{34}S$ was calculated by the reference (Canyon Diablo Troilite).

**[Calculation]**

- Annual or periodic weighted mean $\delta^{34}S$ was calculated for rainfall and stream water by hydrological monitoring data (Sase et al., submitted)
- Significant differences for soil and soil-water $\delta^{34}S$ within the cacthmet were checked by Two-way ANOVA.
- We estimated BDSR flux and isotope fractionation ratio of BDSR ($\varepsilon_{bdsr}$) by simple mass balance equation (see above).
- We estimated the relative contribution of different sulfur sources to stream water $SO_4^{2-}$ using sulfur isotope mixture model (see above, e.g. Novak et al., 2013).

## Collecting / concentrating $SO_4^{2-}$ by anion exchange resin




We thank people in Sakaerat environmental station for their kind support in the field. The project is supported by the grant from APN (ARCP2012-18NMY-Sase: ARCP 2013 -13 CMY -Sase).

# 同位体比測定を用いた森林小集水域における硫黄動態の推定
# Estimation of sulfur dynamics in a small forest catchment by isotopic ratio analysis

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**T. Saito[1)2)], N. Yamashita[1)], Y. Inomata[1)], S. Uchiyama[3)], M. Nakata[4)], T. Ohizumi[5)], H. Sase[1)]**
[1)]Asia Center for Air Pollution Research, [2)]Graduate School of Science and Technology, Niigata University, [3)]Environmental Science Research Niigata, [4)]Faculty of Agriculture of Niigata University, [5)]Niigata Prefectural Institute of Public Health and Environmental Sciences

## はじめに Introduction

生態系内における硫黄化合物の同位体比は、生物学的プロセス等により変動することが知られており、その変化は硫黄の起源や生態系内での保持時間を議論するのに有効であると考えられる。本研究は、同位体比測定を用いて大気沈着由来の硫黄の動態を明らかにすることを目的としており、越境大気汚染由来の硫黄沈着量の多い新潟県北部の小集水域において、硫黄同位体比について調査を行ったので、その結果について論ずる。

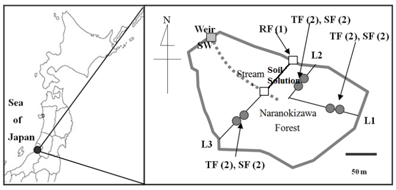
**It is known that isotopic ratio of sulfur compounds in ecosystems is changed by biological processes, and so on. These changes are useful to discuss about S origin and their retention time. This study is conducted to clarify the dynamics of S derived from atmospheric deposition by isotopic ratio analysis. We'll discuss about the results determined in a small catchment located in northern part of Niigata Prefecture, Japan which suffered from many of S deposition from transboundary air pollution.**

## まとめ Summary

林外雨の硫黄同位体比は、明確な季節変動を示すのに対し、渓流水は、9‰付近で安定していた。これに加えて、調査期間中の硫黄同位体比の加重平均では林外雨が8.8‰に対し渓流水が9.3‰であり、大きく違わない事から、大気から沈着した硫黄は、直接河川に流出するのではなく、一旦、土壌・植物系で保持され、平均化された後、渓流に流出している可能性が考えられた。

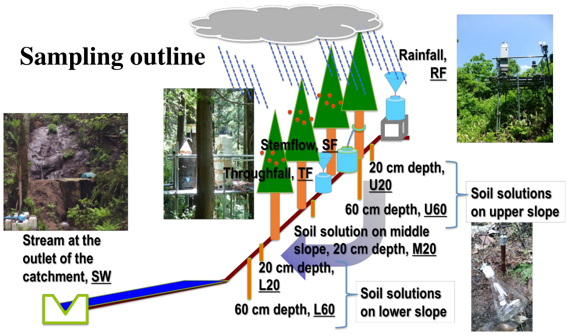
**S isotopic ratio of rainfall showed clear seasonal variation, whereas streamwater was stable at around 9 ‰. In addition to this, mean $\delta^{34}S$ of rainfall was 8.8 ‰, whereas streamwater was 9.3‰. There was not significant difference. These suggested that S deposited from the atmosphere not reach into stream directly, after once retained by slope soil or plant systems, and averaged, finally reach into stream.**

## 調査地 Study site




所在地：新潟県新発田市加治川地区
　　　　櫛形山脈山麓　楢ノ木沢団地
集水域面積：3.84ha　植生：42年生スギ森林
地質：花崗閃緑岩　土壌：褐色森林土
**Location: Kajikwa, Shibata city, Niigata Pref.**
**Catchment area: 3.84ha**
**Vegetation: 42-year old Japanese cedar forest**
**Geology: Granodiorite Soil: Brown forest soil**

## 方法 Method

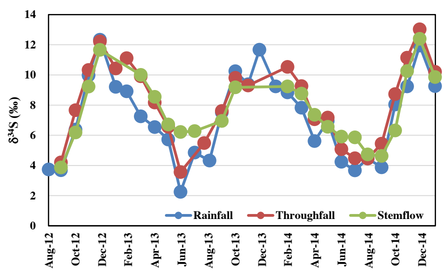



サンプル：林外雨、林内雨、樹幹流、土壌溶液、渓流水
調査期間：2012年8月～　頻度：月1回ないし2回調査
測定：pH、EC、アルカリ度、
主要イオン（イオンクロマト）、雨量（捕集量から算出）、
流量（量水堰を設置、10分間隔）、
硫黄安定同位体比（$\delta^{34}S$、StdはCanyon Diablo troiliteを使用）

**Sample: Rainfall, Throughfall, Stemflow, Soil solution, Streamwater**
**Period: Aug. 2012– Frequency: Once or twice a month**
**Measurement: pH, EC, alkalinity, major ions (by ion chromatography), Precipitation amount (calculated from the collection amount), Discharge (measured on the weir, per 10-minute), Sulfur isotopic ratio ($\delta^{34}S$, use Canyon Diablo troilite for standard)**

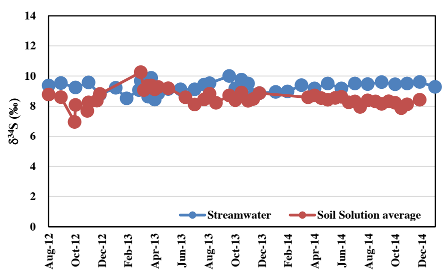
$$\delta^{34}S\ (‰) = \{(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{CDT} - 1\} \times 1000$$

## 硫黄同位体比の変動 Variation of S isotopic ratio




林外雨、林内雨及び樹幹流、いずれも夏季から冬季にかけて上昇し、その後下降するという傾向を示した。冬期以降、林内雨及び樹幹流が遅れて下降する傾向は、樹木表面への吸着、もしくは積雪による保持の可能性が考えられる。

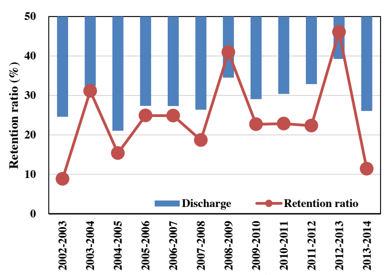
**S isotopic ratio of rainfall, throughfall and stemflow increased from summer to winter, and after that they decreased until summer. After winter season throughfall and stemflow decreased later than rainfall. It may caused by the adsorption of the tree surface or holding by the snow.**

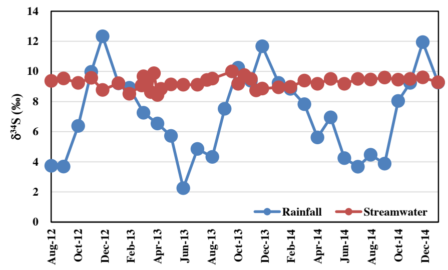



林外雨とは対照的に、渓流水硫黄同位体比では明確な季節性は見られず、9‰付近で安定していた。土壌溶液でも林外雨のような変動は見られず、概ね渓流水よりも低い値であった。林外雨にみられる同位体比の変動は、斜面土壌を通過する段階で、かなりの割合、緩和されているようである。

**In contrast to rainfall, S isotopic ratio of streamwater did not show clear seasonality, it was stable at around 9 ‰. S isotopic ratio of soil solutions were also stable. These were almost all lower than streamwater. Variation of S isotopic ratio of rainfall was almost all buffered at the time passing through the slope soil.**

## 硫黄収支との比較 Comparison with S budget



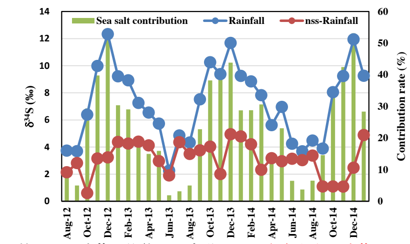

| | $\delta^{34}S$ mean |
|---|---|
| Rainfall | 8.83 |
| Throughfall | 9.83 |
| Stemflow | 9.15 |
| Streamwater | 9.28 |

Aug. 2012 – Jan. 2015

加治川集水域に沈着した硫黄は、平均で24%保持されているようである。ただし、同位体比測定の結果により、林外雨に含まれる硫黄はそのまま渓流に流出しているわけではなく、生態系内で何らかの過程で一旦平均化された後、流出しているという事が示唆された。

**S deposition in Kajikawa catchment were retained 24% on average. However, results of S isotopic ratio analysis suggested that S in rainfall did not directly reach to stream, it reached after once averaged by some processes in the ecosystem.**

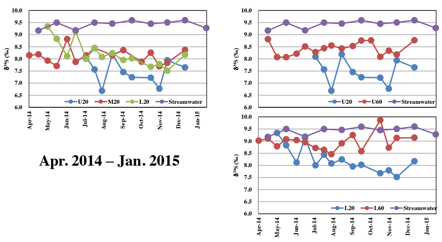
## 海塩の寄与 Sea salt contribution




林外雨の硫黄同位体比の変動には、海塩由来の硫黄（$\delta^{34}S$=20.3）が大きく影響していることが示唆された。

**It suggested that the variation of S isotopic ratio of rainfall is strongly affected by sea salt S ($\delta^{34}S$ = 20.3).**

## 土壌溶液 Soil solution



Apr. 2014 – Jan. 2015

土壌溶液の硫黄同位体比は、斜面下部、土壌深部ほど、渓流水に近い値となっていた。

**S isotope ratio of soil solutions, in lower slope or in deeper soil, became more close to streamwater.**

## 今後の展望 Future work

硫黄の内部循環過程を明らかにするため、土壌及び植物系の硫黄同位体比測定を予定している。
**To clarify the internal S circulation processes, we'll determine S isotopic ratio of soil and plants.**

**本研究はアジア太平洋地球変動研究ネットワーク（Asia Pacific Network on Global change Research, APN: ARCP2013-13CMY-Sase）の支援により実施した。**
**また、調査地の設定・利用に関し、新潟県林業振興課、県行造林地管理者の船山鋼平氏、船山武雄氏のご協力をいただいた。ここに感謝いたします。**
**This study was supported by the grant from APN (ARCP2013-13CMY-Sase). Authors thank them for their support and cooperation.**

# P5
# 東アジアの森林集水域における大気沈着由来の硫黄動態

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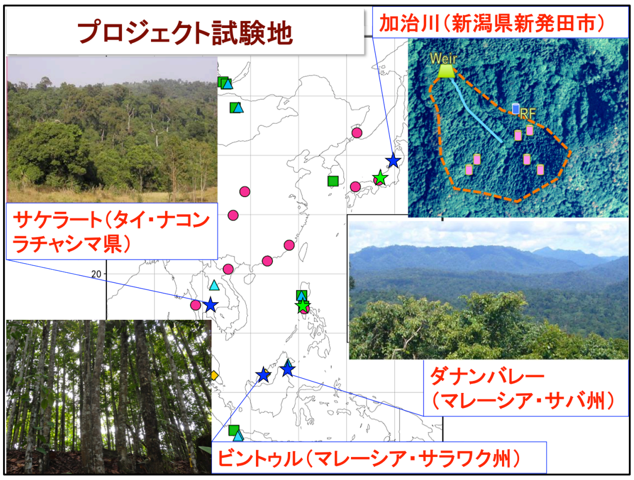
## はじめに

北東アジア及び東南アジアを含む東アジア地域では、最大排出国である中国における硫黄酸化物($SO_2$)の排出量が2006 年をピークに低下し始めたと推計されているが、依然としてその排出量は極めて多く、硫黄汚染は、まだ今日的課題である。生態系内で循環・蓄積すると考えられる硫黄は、欧米の事例が示すように長期に渡り環境に影響を及ぼす可能性がある。そこで本研究では、日本、タイ、マレーシアの森林集水域試験地において、大気沈着由来の硫黄動態を明らかにするために、硫黄安定同位体比測定も含むフィールド観測を2012 年から開始した。

## まとめ（主に加治川試験地の観測結果から）

- 加治川における降水試料の δ$^{34}$S は、夏季に低く、冬季にかけて高くなった。日本海側からの冬季季節風により、海塩に加え越境大気汚染の影響が大きくなるからであると考えられた。
- 河川の δ$^{34}$S は、夏季には降水より高いが、冬季には低く、測定期間を通じて、常に9‰付近で安定していた。
- 大気から流入した硫黄は、直接河川に流出するのではなく、一旦、生態系内に（恐らく土壌における吸着により？）保持された後、均質化され流出している可能性が示唆された。

## プロジェクト概要

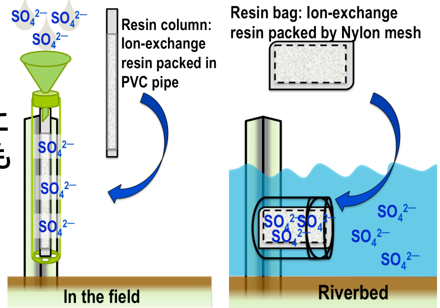



試験地の概要

| 試験地 | 加治川 | サケラート | ダナンバレー | ビントゥル |
| --- | --- | --- | --- | --- |
| 森林タイプ | スギ人工林 | 乾燥常緑林 (DEF) | 熱帯多雨林 | 再生林 (熱帯多雨林) |
| 観測開始年 (主要イオン等) | 2002 | 2005 | 2008 | 2012 |

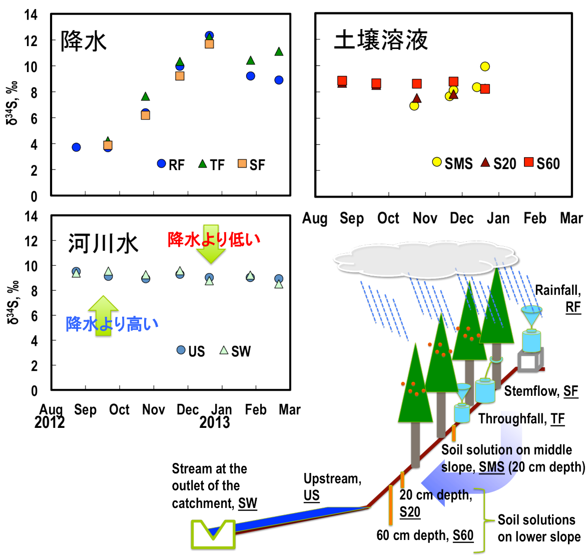
1. 主要イオンのフラックス測定（ビントゥルを除く）
   1) 林外雨（RF）
   2) 林内雨・樹幹流（TF・SF）
   3) 土壌溶液（SS）
   4) 河川水（SW）
2. 硫黄安定同位体比測定（2012年に開始）
   1) 林外雨
   2) 林内雨・樹幹流（樹幹流は加治川のみ）
   3) 土壌溶液
   4) 河川水

- 熱帯サイトでは、イオン交換樹脂による$SO_4^{2-}$捕集法も活用（右図）。



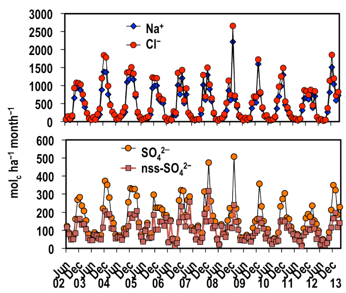

- バリウム沈殿後、サーモフィッシャー製質量分析計（NCS2500 - Conflo II - DELTA-Plus）でδ$^{34}$Sを測定。
- 標準物質：CDT（Canyon Diablo Troilite）
- 分析精度（標準偏差）：± 0.16‰

## 加治川試験地におけるδ$^{34}$Sの季節変化

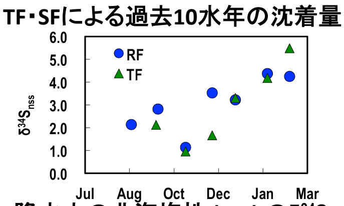



- 大気から流入した硫黄が直接河川に流出する訳ではない。

## 冬季季節風による沈着量増大



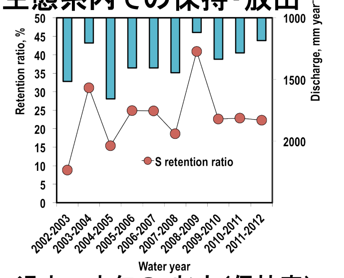

TF・SFによる過去10水年の沈着量




降水中の非海塩性 (nss) のδ$^{34}$S

- 冬季季節風により、海塩だけでなく、起源の異なるSが大量に流入する。
- 越境大気汚染の影響が示唆される。

## 生態系内での保持・放出




過去10水年のS収支（保持率）

- 少なくとも一部（平均23%）は保持される。

流入・流出物質量で加重した平均δ$^{34}$S（8月～翌年2月）

| | |
| --- | --- |
| RF | 9.8 |
| TF（9月～） | 10.7 |
| SW | 9.1 |

- 平均的には大きく変わらない？
- 一旦（恐らく土壌で吸着）保持され、均質化してから流出？
- 年間データを取得後、さらに議論。

本研究はアジア太平洋地球変動研究ネットワーク（Asia Pacific Network on Global change Research, APN: ARCP2012-18NMY-Sase）の支援により実施した。また、調査地の設定・利用に関し、新潟県林業振興課、県行造林地管理者の船山鋼平氏、船山武雄氏のご協力をいただいた。ここに感謝いたします。Project Homepage: http://www.apn.acap.asia

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Head, Communications and Scientific Affairs Division

APN Secretariat

4F East Building

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