A Case Study on the Input-Output Balance of Sulfur in a Catchment Area in Japan

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The input-output balance of sulfur was studied in a catchment area in Japan. Precipitation (collected using a wet-only sampler), cloud water, and sulfur dioxide (SO₂(g)) and particulate sulfate (SO₄²⁻(p)) in ambient air were considered agents providing input to the catchment area, while stream water was considered an agent carrying output from the catchment area. The input amounts of sulfur by precipitation, cloud water, and SO₂(g) and SO₄²⁻(p) in ambient air were approximately 1900, 5100, and 270 and 80 kgS during the survey period, respectively, equivalent to 6.2, 23.2, and 1.5 and 0.45 kgS/ha/year, respectively. However, the output amount of sulfur by the stream water was approximately 5900 kgS for the period from April 21st 1999 to April 22nd 2000, equivalent to 13.7 kgS/ha/year. The input was approximately 2 times greater than the output, showing that the excessive load and the accumulation of the sulfur are advanced around the catchment area.

Key words: Cloud water, Dry deposition, Input-output balance, Precipitation, Stream water, Sulfur

1. Introduction

When studying the forest ecosystem and the mechanism for recovery from acidification in forests, it is important to consider the input-output balance of materials. Precipitation is one of the most important agents providing nutrients to forest ecosystems (Ukonmaanaho and Starr 2002; Laclau et al. 2003). Recently, throughfall, stemflow, cloud water, stream water, groundwater, and dry deposition have been investigated in regard to the estimation of the input-output balance and the study of forest ecosystems (Fenn and Kiefer 1999; Castro et al. 2000; Marcos and Lancho 2002; Quilchano et al. 2002; Stachurski and Zimka 2002; Rodrigo et al. 2003). Precipitation is a major vehicle for the input of materials to forest ecosystems. However, cloud water and dry deposition also play important roles in the supply of materials. It has been reported that the input of chemical species into a forest ecosystem by cloud water is equal to or larger than that by precipitation at mountain sites (Kobayashi et al. 1999). In the study at two different sites with different site classifications, Aikawa et al. (2006) investigated the chemistry of precipitation (wet-only and bulk), throughfall, stemflow, cloud water, and atmospheric aerosol and gases that can provide the input of materials to the forest ecosystem. Taking the comprehensive investigation into account, the current study was carried out with the primary objective of studying the input-output balance of sulfur in a catchment area.

2. Experimental

2.1 Study site

A field study was carried out at Mt. Awaga (elevation at the summit: 962 m above sea level (a.s.l.)) in the town of Aogaki, Hyogo Prefecture, Japan. A location map of the monitoring site and Aogaki is shown in Fig. 1. Mt. Awaga is located inland, where there are few industrial companies. Because commerce is limited, Mt. Awaga is unlikely to be highly influenced by anthropogenically derived pollutants. A 4.28-km² catchment area is located in Mt. Awaga. Geologically, Mt. Awaga is mainly athrogenic dacite. The soil of the catchment area is brown forest soil.
The F layer and H layer can scarcely be observed, whereas the thickness of the A layer is approximately 30 cm and the boundary between the A layer and the B-C layers is clear. The vegetation is mainly Cryptomeria japonica, Chamaecyparis obtuse, and Quercus serrata, and it is partially Lindera umbellata. The elevation of the catchment area is 280 m to 962 m a.s.l. The slope is 20 to 30%.

2.2 Sample collection
2.2.1 Method and period
Precipitation samples were collected by using a wet-only sampler. Cloud-water deposition amount was estimated by considering throughfall, stemflow, bulk...
precipitation, and evapotranspiration (Kobayashi et al., 2000). Cloud-water was collected by using an active string-fog collector to measure the \( \text{SO}_4^{2-} \) concentration of cloud-water. The four-stage filter pack method was used to collect sulfur dioxide (\( \text{SO}_2(g) \)) and particulate sulfate (\( \text{SO}_4^{2-} \) (p)) in ambient air (Karakas and Tuncel 1997; Matsumoto and Okita 1998; Sickles et al. 1999). The details on the methodology for sample collection are described in the previous manuscript (Aikawa et al., 2006). Sample collection was performed from May to November 1999. Because of heavy snow, samples could not be collected from December to April.

The stream water samples were full-year collected once a week from April 21st 1999 to April 22nd 2000 at the middle point of a stream in the watershed, usually on a Monday, or, if that was impossible, on a Sunday or Tuesday. The discharge was calculated based on either actual measurements or an H-Q equation. The discharge calculated by actual measurements was based on the flow rates measured monthly by a flow-rate meter. The discharge calculated by using the H-Q equation was based on the actually measured discharge and the water depth measured by the water gage.

### 2.2.2 Chemical analysis

The pH values were measured with a flow-analysis reference unit. Electric conductivity was measured with a conductivity meter. Concentrations of anions and cations were measured with an ion chromatograph. The details on the chemical analysis are also described in the previous manuscript (Aikawa et al., 2006).

### 2.3 Calculation of input and output amount of sulfur

The input and output amount of sulfur was calculated as follows:

- **Input by precipitation:**
  
  \[
  \text{Input amount of sulfur (kgS)} = \sum_{i=1}^{n} \left( \text{precipitation amount}_i \right) \times \text{SO}_4^{2-} \text{concentration}_i \times \text{catchment area} \times 32/96
  \]
  
  \( n \): Number of sample collections (\( n = 14 \))

- **Input by cloud water:**

  \[
  \text{Input amount of sulfur (kgS)} = \sum_{i=1}^{n} \left( \text{cloud-water deposition amount}_i \right) \times \text{SO}_4^{2-} \text{concentration of cloud water}_i \times \text{catchment area} \times 32/96
  \]
  
  \( n \): Number of sample collections (\( n = 14 \))

- **Input by dry deposition from ambient air:**

  \[
  \text{Dry deposition amount of sulfur (kgS)} = \sum_{i=1}^{n} \left( \text{SO}_2(g) \text{concentration in ambient air}_i \right) \times \text{SO}_2(g) \text{deposition velocity} \times 32/64 + \left( \text{SO}_4^{2-}(p) \text{concentration in ambient air}_i \right) \times \text{SO}_4^{2-}(p) \text{deposition velocity} \times 32/96) \times \text{(sampling duration)} \times \text{catchment area}
  \]
  
  \( n \): Number of sample collections (\( n = 14 \))

- **Output of sulfur by stream water:**

  \[
  \text{Output of sulfur by stream water (kgS)} = \sum_{i=1}^{n} \left( \text{streamflow rate}_i \times \text{(sampling duration)} \times \text{SO}_4^{2-} \text{concentration in stream water}_i \right) \times 32/96
  \]
  
  \( n \): Number of sample collections (\( n = 56 \))

### 3. Results and discussion

#### 3.1 Input

**3.1.1 Precipitation**

The survey of the precipitation was carried out for 7 months (from May to November), not full-year. The annual input amount of sulfur was, therefore, estimated by using a correction coefficient (\( f \)) obtained by taking into account the seasonal variations of the precipitation amounts measured at a meteorological station about 18 km southeast of the survey site. On the other hand, while there was snowfall from December to April at the survey site (near the summit), there was little snowfall at the meteorological station, suggesting that the estimated annual input amount of sulfur at the survey site was underestimated. This will be mentioned in detail later. The \( \text{SO}_4^{2-} \) mean concentration observed at the survey site was 12 \( \mu\text{mol/L} \) during the survey period, i.e., for 7 months (Aikawa et al. 2006); the annual mean \( \text{SO}_4^{2-} \) concentration measured by Hyogo Prefecture near the survey site in the survey year was similar, at 13 \( \mu\text{mol/L} \) (Hyogo Prefecture, 2004). Therefore, the seasonal variations of the \( \text{SO}_4^{2-} \) concentrations were not taken into account when considering the correction coefficient.

The precipitation amount observed at the survey site was 1124 mm during the survey period, i.e., for 7 months (Aikawa et al. 2006). Taking into account the seasonal variations of the precipitation amounts measured at the meteorological station, the precipitation amount (1124 mm/survey period, i.e., 7 months) was equivalent to 1611 mm/year. The precipitation amount measured at the meteorological station was approximately 1800 mm/year.
in the survey year. Observations conducted by Hyogo Prefecture (2004) approximately 22 km southeast of the survey site showed a precipitation rate of approximately 1600 mm/year. The estimated precipitation amount (1611 mm/year) at the survey site seems to be comparable to those measured at the meteorological station and by Hyogo Prefecture. However, there was snowfall from December to April at the survey site (near the summit), while there was little snowfall at the meteorological station and at the Hyogo Prefecture observation site, suggesting that the estimated precipitation amount (1611 mm/year) at the survey site was underestimated.

The input amount of sulfur by precipitation was estimated at 1895 kgS during the survey period, i.e., for 7 months (Table 1), equivalent to 6.2 kgS/ha/year. Hyogo Prefecture (2004) reported that the flux of sulfur by precipitation near the survey site was 6.6 kgS/ha/year. These values are comparable to each other. However, because the snowfall may have been underestimated, the annual input amount was presumably underestimated.

### 3.1.2 Cloud water

Kobayashi et al. (2000) reported the cloud-water deposition to the canopy of some coniferous trees at the same survey site and during the same survey period. In their method, the cloud-water deposition amount was estimated by considering throughfall, stemflow, bulk precipitation, and evapotranspiration. They investigated the frequency of fog occurrence at the survey site and assumed that the evapotranspiration amount was zero based on the frequent fog occurrence, which resulted in the underestimation of the cloud-water deposition. The assumption of the evapotranspiration amount has little influence on the evaluation of the input amount of sulfur because the sulfur material remains even if the fog water evaporates.

In the case of precipitation, when the annual input of sulfur was estimated, the seasonal variation of the precipitation amounts measured at the meteorological station was taken into account. In contrast, the seasonal variations of cloud-water deposition amounts had no statistically significant correlation with the seasonal variations of other parameters such as the precipitation amounts at the present survey site or the cloud-water depositions at other survey sites. A correction coefficient ($f^*$) based on the number of days in survey period was, therefore, applied in estimating the annual input of sulfur.

Kobayashi et al. (2000) estimated and discussed the input amount of sulfur by cloud water using the cloud-water deposition amount measured at an elevation of 900 m a.s.l. On the other hand, the cloud-water deposition amount is dependent on the elevation (Kobayashi et al. 2000; Kobayashi and Nakagawa 2001), with a higher elevation providing a larger cloud-water deposition amount. Lindberg and Owens (1993) and Shubzda et al. (1995) also reported that a higher elevation provided a greater input flux of sulfate due to higher cloud-water interception. When the cloud-water deposition amount measured at an elevation of 900 m a.s.l. is applied to the whole catchment area, the input amount of sulfur will be overestimated. Therefore, in the current analysis, to estimate the input amount of sulfur more precisely, the difference in the elevation was taken into account. The relation between the cloud-water deposition amount and the elevation obtained in the current survey area was used to estimate the cloud-water deposition amount at a specific elevation. The cloud-water deposition amounts at elevations of 300, 600, and 800 m to the canopy of Cryptomeria japonica were 195, 200, and 362 mm/year, respectively (Kobayashi et al. 2000). Based on the result, an exponential approximation,

\[
\text{Cloud-water deposition amount} = 126 \times \exp(0.0011 \times \text{Elevation}) \quad (R^2 = 0.68),
\]

was obtained. The catchment area was fractionated into $< 400$ m a.s.l., 400 m $\leq < 600$ m, 600 m $\leq < 800$ m, and 800 m $\leq$ based on the elevation, and then the cloud-water deposition amount was re-estimated at each elevation. On the basis of the re-estimated cloud-water deposition amount, the input amount of sulfur was re-estimated. By the re-estimation of cloud-water deposition amount, the possibility of error in the estimation of the input amount of sulfur by the elevation became low.

The same concentration of SO$_4^{2-}$ measured near the summit was used in the re-estimation of the input amount of sulfur. Igawa et al. (1998) showed that the concentration of chemical species in the cloud water was dependent on the cloud-base altitude. The use of the SO$_4^{2-}$ concentration

<table>
<thead>
<tr>
<th>Wet deposition</th>
<th>Dry deposition</th>
<th>Percent contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation</td>
<td>Cloud water</td>
<td>SO$_4^{(g)}$</td>
</tr>
<tr>
<td>1895</td>
<td>5119</td>
<td>271</td>
</tr>
</tbody>
</table>

Note: 1.Unit is kgS except percent contribution.
measured near the summit in the re-estimation of the input amount of sulfur suggests the possibility of underestimating the input amount of sulfur.

As a result, the input amount of sulfur by cloud water was estimated at 5119 kgS during the survey period, i.e., for 7 months (Table 1), equivalent to 232 kgS/ha/year. Saxena and Lin (1990) showed that the SO\(_4^{2-}\) deposition to spruce by cloud water was 22 to 32 kgS/ha/year, and Dasch (1988) reported approximately 9 kgS/ha/year in the study conducting at Mt. Mitchell (35° 44' 05" N, 82° 17' 15" W; 2038 m MSL), North Carolina, U.S. The 1.5-2 times larger SO\(_4^{2-}\) concentration was also reported in their studies. The result of the current study was within the range of these results, although the tree species were different. The percent contribution of cloud-water deposition in the wet deposition on sulfur was 73% in the current survey, while it was approximately 50% in the result obtained by Dasch (1988) and 85% in that obtained by Kobayashi et al. (1999), suggesting that the current estimation is valid.

The above-mentioned estimations were based on the data collected from May to November (summer and autumn seasons); the period from December to April (winter and spring seasons) was not considered. Aikawa et al. (2005) studied the cloud water collected in the Mt. Rokko area, approximately 50 km south of the current survey site, and clarified that the cloud water was denser and occurred more frequently in summer than in winter because in Japan the winds from the south and north are generally dominant in summer and in winter, respectively. Moreover, the wind from the south is more humid than that from the north (Aikawa et al. 2005). Taking into account the effect of characteristic seasonality on the quality and appearance of cloud water, the above-mentioned input amount of sulfur by cloud water at the current survey site may have been overestimated.

3.1.3 Ambient air

The deposition velocities of SO\(_2\)(g) (0.98 cm/sec) and SO\(_4^{2-}\) (p) (0.21 cm/sec) were applied (Kominami et al. 2005). The deposition velocity has been studied worldwide (e.g., Fujita et al. 2003; Matsuda et al. 2006). Furthermore, Schmel (1980) reviewed the deposition velocity of SO\(_4^{2-}\)(p) and showed a range of 0.1-3.0 cm/sec. As described by Kominami et al., the value of 0.21 cm/sec was low but within the range of 0.1-3.0 cm/sec, resulting in the underestimation of the dry deposition amount of sulfur in the study. The sampling duration is described in a previous manuscript (Aikawa et al. 2006). A correction coefficient (P) based on the number of days in the survey period was applied in estimating the annual input amount of sulfur in the same manner as the estimation was made for cloud water.

As a result, the dry deposition amounts of sulfur by SO\(_2\)(g) and SO\(_4^{2-}\) (p) in ambient air were estimated at 271 and 82 kgS, respectively, during the survey period, i.e., for 7 months (Table 1), which were equivalent to 1.5 and 0.45 kgS/ha/year, respectively, showing that the percent contribution of dry deposition to total deposition was 5%. Saxena and Lin (1990) showed that the percent contribution of dry deposition to total deposition was 8 to 9% on sulfur. On the other hand, Dasch (1990) demonstrated that the flux measured beneath the canopy in throughfall was approximately 9 kgS/ha/year greater than the wet deposition flux (= precipitation + cloud water), being equivalent to approximately 33% of the flux measured beneath the canopy in throughfall. Dasch noted that the difference of 9 kgS/ha/year could be the result of dry deposition input or foliar leaching.

The percent contribution of SO\(_2\)(g) to the dry deposition amount (= SO\(_2\)(g) + SO\(_4^{2-}\)(p)) in the current survey was 77% (Table 1). Kominami et al. (2005) showed the percent contribution of SO\(_2\)(g) to the dry deposition at the sites of EANET (Acid deposition Monitoring Network in East Asia) was approximately 90%. Non-sea-salt SO\(_4^{2-}\), not SO\(_4^{2-}\), was analyzed by Kominami et al., which is one of the reasons they obtained higher results for the percent contribution of SO\(_2\)(g) to the dry deposition than those obtained in the current survey.

3.2 Output and input-output balance

As described above, the investigation of the stream water was carried out full-year (from April 21st 1999 to April 22nd 2000), so the actual measured observation results, not the estimation, are indicated. In the equation shown in 2.3, streamflow rate × sampling duration provides the amount of stream water flowing out. The amount of stream water flowing out from April 21st 1999 to April 22nd 2000 was estimated at 6.0 million m\(^3\), equivalent to 1400 mm/year. As mentioned and discussed in 3.1.1, the estimated annual precipitation amount was 1611 mm/year. Evapotranspiration was estimated at 600 to 900 mm/year around the current survey site (Tsukamoto 1992). If 600 to 900 mm/year is applied to evapotranspiration in the current study, the amount of outflow from the catchment area can be estimated as 711 (≈ 1611-900) to 1011 (≈ 1611-600) mm/year. The actual measured amount of stream water flowing out from April 21st 1999 to April 22nd 2000 (1400 mm/year) was more than the net input amount of wet deposition (711 to 1011 mm/year), defined as precipitation – evapotranspiration.
Furthermore, the actual measured amount of stream water flowing out (1400 mm/year) from April 21st 1999 to April 22nd 2000 at the survey site corresponded to 87% (=1400/1611) for the estimated precipitation amount at the survey site (1611 mm/year). This value is too large; the estimated precipitation amount at the survey site was insufficient for the amount of stream water flowing out. Two major reasons for the insufficiency of the estimated precipitation amount are assumed: 1) the precipitation amount was underestimated because the snowfall was not evaluated and 2) the cloud-water deposition was not considered.

The precipitation flows into streams and/or rivers through several paths in the forested watershed, and the paths can be separated into various runoff processes such as surface runoff, subsurface runoff, and groundwater runoff (Chow 1964). However since all of the runoff processes ultimately flow into streams and/or rivers, it was valid and appropriate that the stream water was studied as the only agent to provide the output of sulfur in the current study.

The stream flow rate and the integral output amount of sulfur by the stream water are shown in Fig. 2. The output amount of sulfur by the stream water was estimated at 5904 kgS from April 21st 1999 to April 22nd 2000, equivalent to 13.7 kgS/ha/year.

The input amount of sulfur to the catchment area (approximately 7400 kgS / 7 months, equivalent to 31.4 kgS/ha/year) was twice or more than the output amount of sulfur (approximately 5900 kgS from April 21st 1999 to April 22nd 2000, equivalent to 13.7 kgS/ha/year).

Ukonmaanaho and Starr (2002) showed the balance of total deposition (wet + dry) input and soil water leaching output at a depth of 40 cm. They showed cases in which the total deposition input was 1.3 to 3.2 times greater than the soil water leaching output. The result in the current study was within the range of their results. The larger input amount of sulfur in the current study strongly suggests that the excessive load and the accumulation of the sulfur are advanced around the catchment area.

4. Conclusions

A case study on the input-output balance of sulfur in the catchment area was carried out in Japan. The precipitation, cloud water, and dry deposition of SO2(g) and SO42-(p) in ambient air were considered the agents providing the input of sulfur. On the other hand, the stream flow was considered the agent providing the output of sulfur. As a result, the input amount of sulfur was estimated at approximately 7400 kgS / 7 months, equivalent to 31.4 kgS/ha/year. The percent contributions of precipitation, cloud water, and dry deposition of SO2(g) and SO42-(p) in ambient air were 26%, 69%, and 5%, respectively. The large contribution of cloud water to the input of sulfur was clarified. On the other hand, the output amount of sulfur was approximately 5900 kgS from April 21st 1999 to April 22nd 2000, equivalent to 13.7 kgS/ha/year. The input was approximately 2 times greater than the output, strongly suggesting that the excessive load and the accumulation of the sulfur are advanced around the catchment area. Even taking into account the possibility of error in the measurement of each agent, a useful result is
conclusively indicated.

5. Acknowledgements

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集水域における硫黄の流入流出の収支バランス

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降水、霧水及び大気中ガス・エアロゾルによる集水域への硫黄の負荷と河川水による硫黄の流出について、その収支バランスを解析・考察した。調査は兵庫県粟鹿山（丹波市青垣町）で行った。

粟鹿山の集水域（流域面積4.28 km²）への降水、霧水及び大気中ガス（SO₂・エアロゾル（SO₄²⁻））による硫黄の負荷量は調査実施期間中それぞれ約1900 kgS, 5100 kgS, 270 kgS, 80 kgSであった。これらは、6.2 kgS/ha/year, 23.2 kgS/ha/year, 1.5 kgS/ha/year, 0.45 kgS/ha/yearに相当するものであった。

一方、1999年4月21日から2000年4月22日までの一年間の河川水による硫黄の流出量は約5900 kgSであり13.7 kgS/ha/yearに相当する量であった。

粟鹿山集水域における硫黄の収支としては、負荷量が流出量の約2倍であり、このことから、粟鹿山集水域においては硫黄成分の過度の負荷・蓄積が進んでいることが明らかとなった。