Journal of Water Resource and Protection, **2013, 5, 511-519**
http://dx.doi.org/10.4236/jwarp.2013.55051 Published Online May 2013 (http://www.scirp.org/journal/jwarp)

Quantitative Analysis of the Rate of Geochemical Weathering of Sulfur from Sedimentary Rocks Using Atmospheric Deposition, Concentration and River Discharge Data

—A Case Study of the Mountainous Basin of the Tedori River, Japan, over a 16-Year Period

Toshisuke Maruyama[1], Masashi Yoshida[1], Keiji Takase[1],
Hiroshi Takimoto[1], Shigeo Ishikawa[2], Sadao Nagasaka[2]
[1]Faculty of Environmental Science, Ishikawa Prefectural University, Ishikawa, Japan
[2]College of Bioresource Science, Nihon University, Kanagawa, Japan
Email: maruyama@ishikawa-pu.ac.jp

Received March 5, 2013; revised April 7, 2013; accepted April 27, 2013

ABSTRACT

Quantitative analysis of the rate of geochemical weathering of sulfur (*S*) from sedimentary rocks (*GeoS*) was conducted using concentration (*Cs*) and discharge (*Qs*) data from the Tedori River and atmospheric deposition (*AtdepS*) in the basin. First, *S* fluxes were calculated using 16 years of *Cs* and *Qs* data. The annual average discharge of *S* (*TotalS*) was estimated at 8597 ton·year^{-1} (117.3 kg·ha^{-1}·year^{-1}). Of this, 1331 ton·year^{-1} was *AtdepS* (18.2 kg·ha^{-1}·year^{-1}) and another 7266 ton·year^{-1} was *GeoS* (99.1 kg·ha^{-1}·year^{-1}). Monthly changes in *TotalS* were investigated, which showed that *GeoS* was highest in summer, because of the air temperature, while *AtdepS* peaked in winter because of seasonal wind. Using *Qs* and *AtdepS* corrected for altitude, *TotalS*, *AtdepS* and *GeoS* were estimated at six sites, and among these sites we found that the *TotalS* per unit area values were random, depending on the site characteristics. In particular, the discharge from the Kuwajima site was remarkably high suggesting that the sedimentary rocks at this site had higher pyrite content than at the other sites. Finally, we also assessed the relationship between the characteristics of sedimentary rocks and *GeoS* in a range of rivers in the Hokuriku Region, and found that there was a close relationship between concentrations of SO_4^{2-} greater than 10 mg·l^{-1} and sedimentary rocks containing the pyrite group. In addition, we estimated that the influence of *GeoS* was present when the concentration of SO_4^{2-} in river water was greater than 2 - 3 mg·l^{-1} in the Hokuriku region.

Keywords: Sulfur Balance; Wet and Dry Deposition; Sulfur Concentration; Altitude Dependence; Sulfur Discharge from Pyrite

1. Introduction

There is great concern about sulfur (*S*) cycling in a river basin because it is closely related to acid deposition in soil, leads to sulfate contamination of irrigation water and has possible damaging consequences for human health. The *S* cycle in a mountainous river basin is governed by atmospheric deposition (*AtdepS*) and geochemical weathering of sedimentary rocks (*GeoS*). The annual average discharge of *S* (*TotalS*) from a basin can be estimated by taking the product of the discharge (*Q*s) and the concentration of *S* (*Cs*) in the river.

Based on the above, the objectives of this research were as follows: 1) to establish weathering rates of the sulfur mineral defined as *GeoS* using *Qs* and *Cs* of the river and *AtdepS* in the study area; 2) to estimate *TotalS* discharge from a river basin at various sites both within and beyond the study area; and 3) to investigate the effect of *GeoS* from sedimentary rocks on different sulfate concentrations in river.

Many studies on geochemical cycling of *S* have been conducted, including large-scale marine studies. Jamieson *et al.* carried out a study on the concentrations of sulfate in seawater from sulfur isotopes in sulfide ore [1], while Newton *et al.* reported large shifts in the isotopic composition of seawater sulfate across the Permian-Triassic boundary in northern Italy [2]. Ooki reported size resolved sulfate and ammonium measurements in marine boundary layer from November 2001 to March 2002 over the North and South Pacific [3].

Much research has also been carried out on sulfur cycling in river basins. For example, Norman *et al.* examined the biogenetic contribution to aerosols and precipitation using isotopes and oxygen [4]. Elimaers *et al.* investigated the effects of climate on sulfate fluxes from forested catchments in south-central Ontario [5]. William *et al.* investigated the change in ion outputs from watersheds resulting from acidification of precipitation [6]. Beaulieu *et al.* modeled the interactions between water and rocks in the Mackenzie Basin; and highlighted the competition between sulfuric and carbonic acid [7]. Huang *et al.* investigated weathering and soil formation rates based on geochemical mass balances in a small forested watershed [8].

Mine drainage water has also been studied by many researchers. Budakoglu *et al.* investigated the distribution of, and contamination from, sulfur-isotopes related to the Baya Pb-Zn mine in Turkey [9], while Edraki *et al.* investigated the hydrochemistry, mineralogy and sulfur isotope geochemistry of acid mine drainage at the Mt. Morgan mine, Australia [10].

This study differs from those documented above, in that it reports the results of quantitative analysis of *TotalS* in a river, in which *GeoS* has been estimated quantitatively by analysis of *Qs*, *Cs* and *AtdepS* data. To date, there have been very few studies of quantitative analysis of *S* discharges from river basins [11].

2. Methods

2.1. Fundamental Concept of Our Research

We collected *Qs* and *Cs* data of river water and the *AtdepS* (wet and dry) in a mountainous basin, to estimate fluxes of *GeoS* quantitatively, and analyzed the relationships among them. The relationship is relatively simple in mountainous basins when compared with lowland basins, as land use is generally more complicated in lowland basins and may include agricultural land, residential and industrial areas.

The *S* cycle in this study is based on the hypothesis that the *TotalS* (the product of *Qs* and *Cs*) is consist of *AtdepS* and *GeoS* in locations where there is little artificial disturbance (**Figure 1**). Among them, *GeoS* is a source of *S* from inside and *AtdepS* is an input of *S* from outside of the basin. The hypothesis contains the change in storage of *S* in the basin is negligible small due to *AtdepS* without including *GeoS*, In other words, this study assumes a steady state, in which the effect of *AtdepS* in the study area remained constant during the study period. On the other hand, river basin usually has sedimentary rock layers, which sometimes contain *S* compounds. These layers will have been subject to long-term weathering, resulting in the release of SO_4^{2-} into the river.

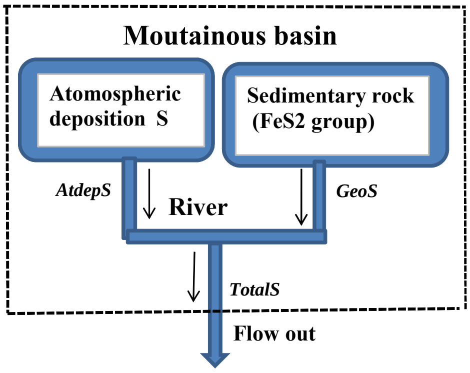

Figure 1. Flow of sulfur (*S*) in mountainous basin.

This research procedure consists of the three following steps:

1) Estimation of the total outflow of *S* (*TotalS*) from a test basin using *Qs* and *Cs*;
2) Estimation of *AtdepS* using SO_4^{2-} atmospheric deposition data measured near the test basin;
3) Estimation of *GeoS* by subtracting the *AtdepS* from the *TotalS*.

To verify the relationships mentioned above, long-term data are required to 1) eliminate the short-term variation in stored *S* inside of the basin, and 2) minimize the influence of high flows through flooding periods on *Cs* concentrations. In other words, the *S* cycle is assumed to be in a dynamic steady state as follows: If *AtdepS* is deposited into a basin, the *S* will be distributed throughout the soil, water, grass, trees and wild animals. The forest (basin) will gradually become saturated with *S*, and the excess *S* from *AtdepS* will then flow out to the river. If this *S* cycle continues over a prolonged period, the flow of *S* in the forest will approach a steady state. Based on the above hypothesis, *AtdepS* data for a 16-year period (divided into yearly intervals) were analyzed. We applied the approach which has been taken in the nitrogen balance analysis already [12,13]. Because the sulfur and nitrogen ions may behave in a similar manner, we applied the same procedure to sulfur analysis.

2.2. Research Site

The research site is located in the southern part of Ishikawa prefecture, Japan. The research river is the Tedori River which has an area of 809 km^2, as shown in **Figure 2**. The source of the river is at Mount Hakusan, which has an altitude of 2702 m, and flows down a ravine between mountains to Nakajima point (at which point the basin area is 733 km^2), from where the river flows

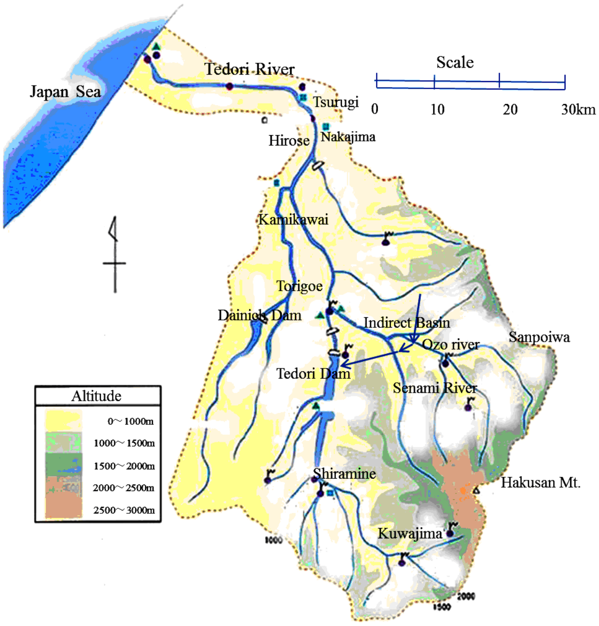

Figure 2. The upland area of the Tedori river basin and the discharge (*Qs*) and total nitrogen concentration (*Cs*) monitoring sites.

through an alluvial fan into the Sea of Japan. The alluvial area comprises developed fertile agricultural land and important industrial and residential areas, all of which are supported by surface water and groundwater from the Tedori River.

Plant cover in the basin varies according to the altitude. There is a mountainous belt (altitude 400 - 1500 m), a semi-high mountain belt (1500 - 2000 m) and a high mountain belt (>2000 m). The upstream area belongs to the high mountain belt, is dominated by the Hakusan National Park and is covered with low height pine trees. In the semi-high mountain belt there is high mountain grass, known as flower meadow. *Betula Ermanii Chanisso* and *Abies Mariesii Mast* are typical of this area, with the former tree more common in higher areas than the latter. In the mountainous area, there are mature high quality beech trees, while *Quercus Crisoula Blume* and *Japan Marple* are found in the lowland areas. Red pine trees are found on ridges and cedars are found in the valley areas of mountains [14-16].

The catchment is in an area of high precipitation, and the annual average precipitation recorded at Kanazawa is 2348 mm. Of this total, 1059 mm falls between April and September, while 1289 mm falls from October to May, including much snowfall. The average temperature is 14.9˚C, with an average maximum of 26.1˚C recorded in August and an average minimum of 4.0˚C recorded in January.

2.3. Investigation of *AtdepS*, *Cs* and *Qs*

The *AtdepS* was monitored weekly by the Ishikawa prefectural government over a 16 year period at the Taiyougaoka site, located at an altitude of 120 m and at a distance of 10 km from the study area [17]. The samples were collected by a 20 cm diameter rain gauge. The *S* in *AtdepS* was analyzed by the ion chromatograph method.

In addition to wet deposition, there is dry deposition of *S* from the atmosphere, which was investigated only for 5 years from 2003 to 2007 [18-21]. To account for dry deposition in other years, the average of the dry deposition of *S* data collected was added to wet deposition of the other years because the ratio of dry deposition to wet deposition was very small.

Furthermore, the *AtdepS* (wet deposit) was investigated at Torigoe, located close to the center of the study area, over 7-year period (1997 and 1999-2004) [17]. When compared with the Taiyougaoka and Taiyougaoka data, similar trends are apparent; therefore we considered that the Taiyougaoka data was sufficiently reliable to be used for estimating the quantity of sulfur even though the observation site was located outside of the study area.

To assess the *TotalS* in the study area, *Cs* data (as SO_4^{2-}) was collected at the following six sites (**Figure 2**): the Hirose site located near the Nakajima discharge observation site, the Tedori dam site located at the No. 1 Hydroelectric Power Generation Station just downstream of the Tedori dam, and the Kamikawai site located downstream of the Dainichi dam. The Senami site is located at the water outlet of the Senami and the Ozo rivers because the basin was changed so that it flows into the Tedori dam. The Shiramine site is located in the upstream section of the Tedori River and the Kuwajima site is at the intake for the Kuwajima Hydroelectric Power Generation Station.

Cs was sampled monthly from 1994 to 2003 and quarterly after 2004 (May, August, November, February), except at the Tedori dam site, where monthly sampling continued after 2004. SO_4^{2-} was measured by the ion chromatograph method. The data were reported in an Annual Report by the Ishikawa Water Supply Office of the Tedori River [21].

The *Qs* was recorded at the Nakajima site, which is located in the lower reaches of the basin near the Hirose site (**Figure 2**). The *Qs* data were supplied by the Hokuriku Hydroelectric Company. The *TotalS* outflow from the basin was estimated by multiplying the *Qs* and *Cs*.

2.4. Altitude Correction for *Qs* and *AtdepS*

To estimate the *TotalS* at the above six sites, *Qs* and *AtdepS* had to be corrected for *Qs* and *AtdepS* based on the altitude because both are strongly affected by basin height. Full details of how we analyzed the altitude dependence of *Qs* and *AtdepS* are available elsewhere [12, 13], but brief details of the procedure are as follows:

The altitude correction was conducted at 200 m intervals. To make the calculation simple, the weighted central height of the basin was obtained previously by the following formula.

$$Hc = \frac{1}{A}\sum_{i=1}^{n}\left(Hi \times Ai\right) \quad (1)$$

Here, *Hc*(m) *i*s the central altitude within the 200 m belt weighted area, *Hi*(m) is the central altitude of the each belt, *Ai* (ha) is the area of the belt, *n* is the number of belts and *A* (ha) is the total area of the test basin sites.

The *Hc* for relevant test sites is shown in **Table 1**.

2.4.1. Altitude Dependence of *Qs*

Qs in the Tedori River basin at Kanazawa was not recorded, but was estimated using precipitation minus evapotranspiration. The evapotranspiration was estimated by complementary relationship using the Penman equation. The result was obtained using 16 years data.

The relationship between the two sites is:

$$Qs(\text{Nakajima}) = 1.153Qs(\text{Kanazawa}) + 1406$$
$$\left(R^2 = 0.689, p = 0.0007\right) \quad (2)$$

Here, the unit of *Qs* is mm·year^{-1}.

The altitude dependence of *Qs* between sites at Kanazawa (*Qs* is 1603 mm·year^{-1} and *Hc* is 7 m) and Nakajima (*Qs* is 3299 mm·year^{-1} and *Hc* is 943 m) was determined by a straight line passing through the altitude and the *Qs* of two sites **Figure 3**. The following experimental formula was obtained:

$$Qs = 1.757Hc + 1594 \quad (3)$$

To estimate *Qs* at relevant sites, the experimental Formula (3) was rewritten by standardization with Nakajima site which have investigated *Qs* data.

$$\frac{Qs}{Qs(\text{Nakajima})} = 0.000540Hc + 0.4908 \quad (4)$$

The relative *Qs* [*Qs*/*Qs* (Nakajima)] was shown in **Table 1** for estimation of *Qs* at the relevant sites.

2.4.2. Altitude Dependence of *AtdepS*

The altitude dependence of *AtdepS* between Taiyougaoka and Sanpoiwa was based on the average of 7 years' data from June to October as shown in **Figure 4** (1995-2001) [17]. The relationship is:

$$AdepS(\text{Sanpoiwa}) = 0.554AtdepS(\text{Taiyougaoka}) \quad (5)$$

where, unit of *AtdepS* is kg·ha^{-1}·5 month^{-1}.

The experimental formula was applied for entire year. The average of observed *AtdepS* at Taiyougaoka was 25.08 kg·ha^{-1}·year^{-1} and the *AtdepS* of Sanpoiwa was 13.89 kg·ha^{-1}·year^{-1} estimated by Equation (5), then, the altitude dependence was determined by a straight line passing through the above two *AtdepS* values and each altitude (Taiyougaoka altitude *Hc is* 120 m and Sanpoiwa altitude *Hc* is 1450 m above sea level respectively). The experimental formula was obtained as follows:

$$AtdepS = 26.09 - 0.00841Hc \quad (6)$$

where, the unit of *AtdepS* is kg·ha^{-1}·year^{-1} at any altitude *Hc* (m).

To estimate *AtdepS* at relevant sites, the experimental Formula (6) was rewritten by standardization with Taiyougaoka site which have investigated *AtdepS* data.

$$\frac{AtdepS}{AtdepS(\text{Taiyougaoka})} = 1.040 - 0.000335Hc \quad (7)$$

The relative *AtdepS* [*AtdepS*/*AtdepS* (Taiyougaoka)] was shown in **Table 1** for estimation of *AtdepS* at relevant sites.

The basin areas for relevant *Cs* observation sites, the height of the center (*Hc*) of the relevant basins, the relative discharge based on Nakajima data calculated by Equation (4) and the relative *AtdepS* based on Taiyougaoka data calculated by Equation (7) at relevant sites are shown in **Table 1**.

3. Results

3.1. Total *S* from Test Basin

Table 2 shows the statistical features of *Qs*, *Cs* and *Total S*

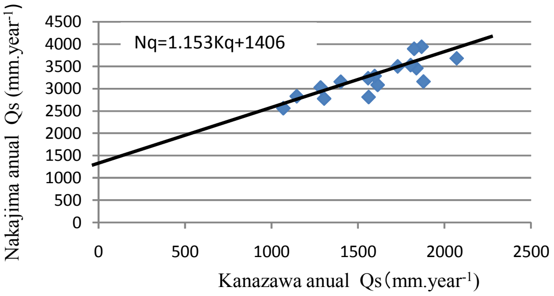

Figure 3. Relationship between *Qs* at Nakajima and Kanazawa (mm·year^{-1}).

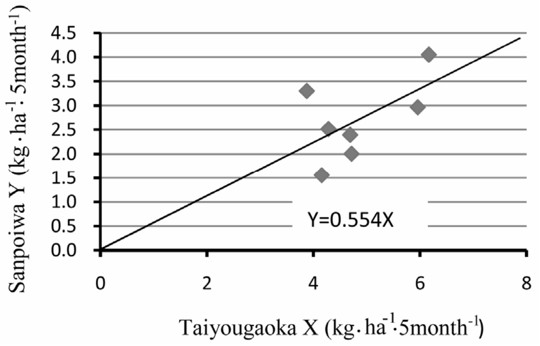

Figure 4. *AtdepS* relationship between Sanpoiwa and Taiyougaoka.

Table 1. Basin area, *Hc*, relative deposition (*AtdepS*)/*Adeps* (*Taiyougaoka*) and discharge (*Qs*)/*Qs* (*Nakajima*).

Name / Items	Nakajima (Hirose)	Tedori dam site Indirect basin	Tedori dam site Direct basine	Dainich Dam site	Shiramine	Senami (Ozo)	Kuwajima	Standard Sites
Basin area (ha)	73,307	42,836	24,723	8392	16,185	17,966	8335	
Hc (m)	943	1179	1052	733	1177	1359	1390	
Relative *AtdepS*	0.724	0.645	0.687	0.795	0.646	0.584	0.574	Taiyougaoka
Relative *Qs*	1.000	1.128	1.059	0.886	1.126	1.225	1.242	Nakajima

Table 2. Statistical features for *Qs*, *Cs*, *TotalS* and unit load at the Hirose site (Nakajima).

Items	Unit	Average	Min	Max	CV (%)
Qs	$mm \cdot year^{-1}$	3047	2445	3810	13.5
Cs	$mg \cdot l^{-1}$	3.86	2.7	4.6	12.7
TotalS	$ton \cdot year^{-1}$	8597	6436	12,046	16.6
Unit load	$kg \cdot ha^{-1} \cdot year^{-1}$	117.3	87.8	164.3	16.6

Table 3. Statistical features of monthly changes in *Qs*, *Cs* and *TotalS* at the Hirose site (Nakajima).

Items	Unit	Average	Min	Max	c.v (%)
Qs	$mm \cdot month^{-1}$	254	130	431	38.0
Cs	$mg \cdot l^{-1}$	3.97	2.15	5.25	22.4
TotalS	$ton \cdot month^{-1}$	700	387	1235	31.7
Unit load	$kg \cdot ha^{-1} \cdot month^{-1}$	9.55	5.29	16.9	31.7

Table 4. Statistical features of *AtdepS* at the Hirose site (Nakajima) ($kg \cdot ha^{-1} \cdot year^{-1}$).

Items	Average	Min	Max	c.v (%)
Wet *AtdepS*	23.1	18.5	29.5	12.2
Dry *AtdepS*	2.0	0.5	3.2	26.3
Total *AtdepS*	25.1	20.5	31.3	11.4

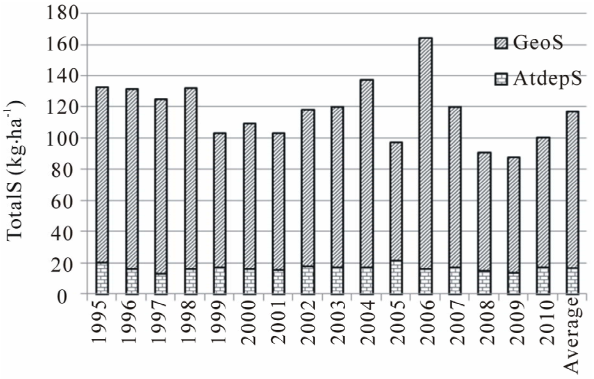

Figure 5. Temporal change in *TotalS* by unit area at the Hirose site (Nakajima).

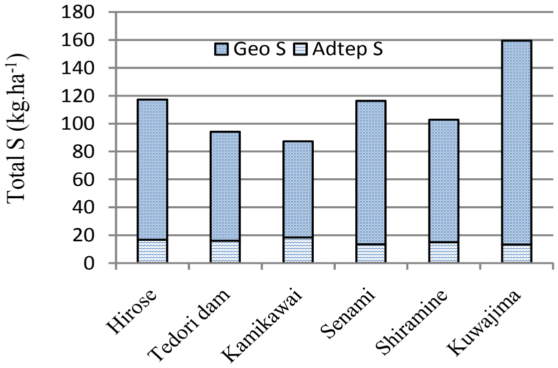

Figure 6. Comparison of *AdtepS* and *GeoS* at relevant sites.

over 16 years of the test period. *Qs* ranged from 2445 $mm \cdot year^{-1}$ to 3810 $mm \cdot year^{-1}$, with an average of 3047 $mm \cdot year^{-1}$ (coefficient of variation c.v 13.5%). The *Cs* ranged from 2.7 $mg \cdot l^{-1}$ to 4.6 $mg \cdot l^{-1}$, with an average of 3.86 $mg \cdot l^{-1}$ while *TotalS* ranged from 6436 $ton \cdot year^{-1}$ to 12,046 $ton \cdot year^{-1}$, with an average of 8597 $ton \cdot year^{-1}$.

Figure 5 shows the temporal and yearly change of *TotalS* in unit area over the test period, which was divided into *GeoS* and *AtdepS*, ranged from 87.8 $kg \cdot ha^{-1}$ to 164.3 $kg \cdot ha^{-1}$, with an average of 117.3 $kg \cdot ha^{-1}$. *GeoS* ranged from 72.8 $kg \cdot ha^{-1}$ to 146.5 $kg \cdot ha^{-1}$ with an average of 99.1 $kg \cdot ha^{-1}$ and c.v of 20.1%. *AtdepS* ranged from 14.9 $kg \cdot ha^{-1}$ to 22.7 $kg \cdot ha^{-1}$ with an average of 18.2 $kg \cdot ha^{-1}$ and c.v of 11.4%.

Table 3 shows the average monthly changes in *Qs*, *Cs* and *TotalS* over the test period. *Qs* ranged from 130 mm to 431 mm, with an average of 254 mm (c.v is 38%). *Cs* ranged from 2.15 $mg \cdot l^{-1}$ to 5.25 $mg \cdot l^{-1}$, with an average of 3.97 $mg \cdot l^{-1}$. *TotalS* ranged from 387 ton to 1235 ton, with an average of 700 ton. Unit load ranged from 5.25 $kg \cdot ha^{-1}$ to 16.85 $kg \cdot ha^{-1}$ with an average of 9.55 $kg \cdot ha^{-1}$ (c.v is 31.7 %).

3.2. Feature of *AtdepS*

Annual *AtdepS* are shown in **Table 4**. *TotalS* ranged from 20.5 $kg \cdot ha^{-1}$ to 31.3 $kg \cdot ha^{-1}$, with an average of 25.1 $kg \cdot ha^{-1}$. Wet deposition ranged from 18.5 $kg \cdot ha^{-1}$ to 29.5 $kg \cdot ha^{-1}$, with an average of 23.1 $kg \cdot ha^{-1}$.

3.3. *TotalS* Load for Relevant Sites

The *TotalS* load of the six sites with different altitudes in the study area are shown in **Figure 6** dividing into *GeoS* and *AtdepS*, to which altitude correction had already been applied, by the relevant unit areas. The *TotalS* was based on the observed *Cs* and the estimated *Qs* data from the Nakajima site. *GeoS* occupied large part of *TotalS* of relevant sites. *TotalS* shows variation between sites, but does not show any distinct trends as were observed in nitrogen concentrations, such as upstream sites having lower concentrations than downstream sites [12,13]. The *TotalS* for the Kuwajima site are particularly high, probably attributable to geological factors.

3.4. Comparison of *AtdepS* and *GeoS*

Figure 7 shows the monthly changes in the average concentrations of *AtdepS* and *GeoS* over the test period at the Hirose site. The *GeoS* concentration was about 5.46 times greater than the *AtdepS* concentration. The maximum *AtdepS* concentration occurred in the winter season because of seasonal wind from continental Asia, while the *GeoS* had its peak in summer, however the value for *GeoS* was relatively flat compared with that of *AtdepS*. Concentrations at the remaining five sites show similar patterns to those at the Hirose site.

Figure 8 shows the monthly changes of *AtdepS* and *GeoS* loads at the Hirose site. The *AtdepS* peaks in the winter season for the same reason as *Cs*, while *GeoS* peaks in summer, because rapid chemical reactions may be caused by the high temperature. The remaining five sites in the study area show the same patterns in *TotalS* similar to those at the Hirose site.

Table 5 shows the *TotalS*, the average load by unit area and the percentage of contributions from *GeoS* and *AtdepS* over 16 years. At the Hirose site, the *TotalS* discharge was estimated at 8597 ton·year^{-1}, resulting in a unit load of 117.3 kg·ha^{-1}·year^{-1}, of which the *AtdepS* load was 18.2 kg·ha^{-1}·year^{-1} (15.5%) and the *GeoS* load was 99.1 kg·ha^{-1}·year^{-1} (84.5%).

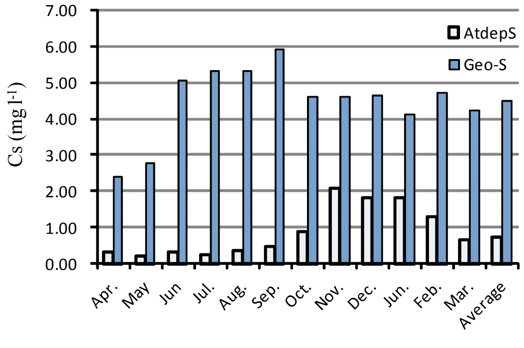

Figure 7. Monthly changes in *GeoS* and *AtdepS* concentrations at Hirose (Nakajima) site.

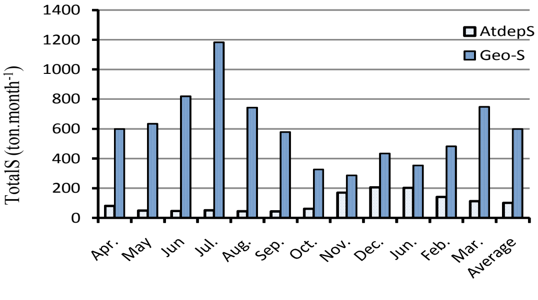

Figure 8. Monthly changes in *AtdepS* and *GeoS* loads at Hirose (Nakajima) site.

4. Discussion

4.1. Geological Features of the Study Catchment and Process of SO_4^{2-} Production from Sedimentary Locks

To help explain the reason for the large percentage of *S* from *GeoS* in *TotalS*, we examined the geological map of this area (shown in **Figure 9** [22]).

The upstream area of this basin contains a sedimentary rock layer named the "Tedori sedimentary layer group", which was formed during the Cretaceous period about 180 - 110 million years ago. The layer seemed to have formed under the Sea of Japan at that time, and contained *S* compounds from the pyrite (FeS_2) group. In fact, the Ogoya mine, which was in operation until 1971 and from which chalcopyrite was extracted for about 100 years, is located outside of the test basin. The sedimentary rock layer released SO_4^{2-} by oxidation because of the presence of a canyon in the Tedori River basin.

There are three oxidation processes that produce SO_4^{2-} as following two forms [23]:

(1) Oxidation process of pyrite (FeS_2)

$$2FeS_2 + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 4S^0 + 2H_2O$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$

$$2S^0 + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+$$

The first process rapidly progresses in the presence of sulfur and iron bacteria (*Thiobacillus ferrooxidans* or *Ferrobacillus ferrooxidans*). The second process also rapidly progresses in the presence of bacteria (*Thiobacilli* containing *Thiobaccillus thiooxidans*). The third reaction will progress under acidic conditions, and as a result, SO_4^{2-} is formed.

(2) Oxidation of pyrite

$$FeS_2 + 2Fe^{3+} \rightarrow 3Fe^{2+} + 2S^0$$

$$2S^0 + 12Fe^{3+} + 8H_2O \rightarrow 12Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Table 5. *TotalS*, *AtdepS* and *GeoS* loads and unit area loads at Hirose site (Nakajima).

Items	Total	Unit area	Percentage
	ton·year^{-1}	kg·ha^{-1}·year^{-1}	(%)
TotalS	8597	117.3	100
AtdepS	1331	18.2	15.5
GeoS	7266	99.1	84.5

(3) Formation of Jarosite and goethite

In addition to the processes outlined in (1) and (2) above, the following process also occurs.

$$3\mathrm{Fe}(\mathrm{OH})_2^+ + 2\mathrm{SO}_4^{2-} + \mathrm{K}^+ \rightarrow \mathrm{KFe}_3(\mathrm{SO}_4)_2(\mathrm{OH})_6$$

$$\mathrm{KFe}_3(\mathrm{SO}_4)_2(\mathrm{OH})_6 \rightarrow 3\mathrm{FeOOH} + 2\mathrm{SO}_4^{2-} + \mathrm{K}^+ + 3\mathrm{H}^+$$

In the first reaction above, $KFe_3(SO_4)_2(OH)_6$ (Jarosite) is formed, and the Jarosite then reacts to form of SO_4^{2-} again, as shown in the second reaction, along with 3FeOOH (Goethite). Here, the SO_4^{2-} ion is indicated with an underline.

4.2. *Cs* in Rivers in the Hokuriku Region

To investigate the difference of the sedimentary rock characteristics, we investigated the *Cs* concentrations in the rivers in the Hokuriku region, which has quite similar conditions for *AtdepS* as our study area. Kobayashi reported the presence of the SO_4^{2-} ion in many rivers throughout Japan [24]. **Table 6** gives information on the SO_4^{2-} ion concentration in many rivers in Toyama, Ishikawa and Fukui prefectures. These three prefectures face toward the Sea of Japan and receive seasonal wind from the Asian Continent meaning that the conditions for *AtdepS* are quite similar.

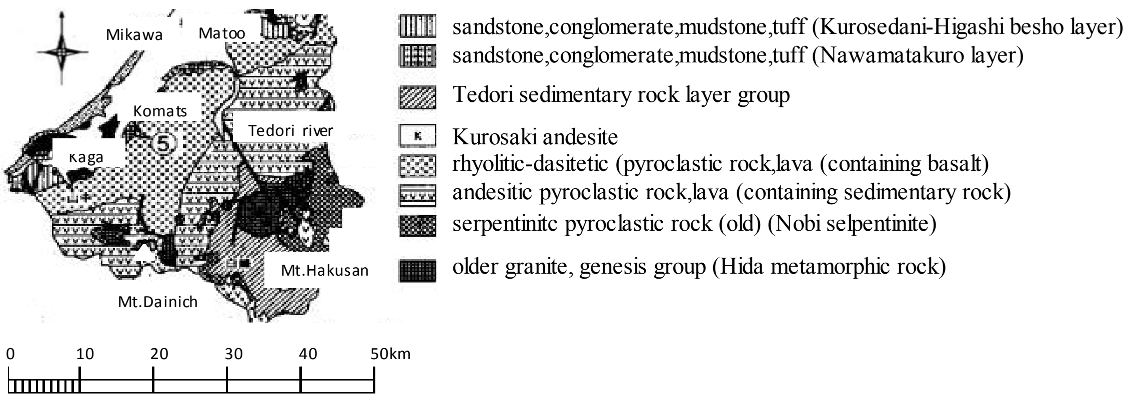

Figure 9. Geological map of study area [21].

Table 6. Sulfur concentration of river water in Hokuriku Region (Kobayashi 1971) [23].

Prefecture	River name	Sampling sites	SO_4^{2-} $(mg \cdot l^{-1})$	pH	Geological feature at upstrem
Toyama	Kurobe	Unatsuki Town, Shimoshinkawa Province	5.9	7.2	
	Katakai	Kurodani, Uozu City	1.9	7.2	
	Hayatsuki	Namerikawa City	3.3	7.2	
	Jougannji	Tateyama Town, Nakashinkawa Province	14.0	7.3	Tedori sedimentary rock group
	Jintsu	Oosawano Town, Kamishinkawa Province	4.6	7.3	
	Shoukawa	Shoukawa Town, Higashitonami Province	4.7	7.3	
	Oyabe	Fukumitsu Town, Nishitonami Province	3.3	6.9	
Ishikawa	Wakayama	Furukura, Wakamatsu Town, Suzu City	24.0	6.7	Diatomaceous earth area
	Nagaso	Kasai Town, Kashima Province	27.0	7.1	
	Saikawa	Hamagurisaka Town, Kanazawa City	5.9	7.1	
	Tedori	Tsurugi Town, Ishikawa Province	10.7	7.4	Tedori sedimentary rock group
	Kakehasi	Karumi Town, Komatsu City.	34.2	6.6	Tedori sedimentary rock group
	Daishoji	Yamanaka Town, Enuma Province	9.5	7.0	
Fukui	Kuzuryu	Eiheiji Town, Yoshida Province	3.3	7.2	
	Ashiba	Ashiba Town, Ashiba Province	3.3	7.2	
	Hinokawa	Nakahirabuki Town, Takefu City	3.3	7.1	
	Sasano	Tsuruga City	3.0	7.1	
	Mimikawa	Mihama Town, Mikata Province	3.7	7.1	
	Kitakawa	Miyake, Kaminaka Town, Onyu Province	3.6	7.1	
	Minamikawa	Nakai, Obama City	2.7	7.0	

In **Table 6**, we consider river basins in which the SO_4^{2-} concentrations exceeded 10 $mg \cdot l^{-1}$, and attempt to explain the elevated concentrations. The high con centration in the Jougangi, Tedori and Kakehashi rivers can be explained by the presence of the Tedori sedimentary rock layer which contains pyrite. The Kakehashi river also has a copper mine company located in its basin. There is an area of diatomaceous earth in the Wakayama which is rich in S compounds and which contributes to elevated concentrations. The reason for elevated concentrations in the Nagaso is not so clear. We can however confirm from the above that *Cs* concentrations in rivers will be quite high if the basin has a sedimentary rock layer containing *S*, such as the pyrite group.

Our research therefore demonstrates that if the concentration of SO_4^{2-} in the river water exceeds 2 - 3 $mg \cdot l^{-1}$ which may be supplied by *AtdepS* in the Hokuriku region, the river will contain *S* that originates from sedimentary rocks such as pyrite.

4.3. Further Research

There were limited data available for *Cs* due to a lack of sampling, which is of particular concern because *Cs* is strongly dependent on *Qs*. Nitrogen concentrations were also strongly dependent on discharge; however, this was mainly due to changes in organic nitrogen concentrations, while inorganic nitrogen concentrations did not change significantly. Compared with nitrogen outflow, *Cs* may not change so remarkably because the inorganic nitrogen behavior will be comparable to that of sulfate. However, to rectify the *Cs* data shortage issue, data from as long a time period as possible will be used so as to ensure inclusion of data for a wide range of discharges.

Therefore, more frequent *Cs* sampling is required in future for more reliable results. Further, this research was based on the hypothesis that the sulfur cycle was in a steady state, which is in turn based on an analogy of the nitrogen cycle, and verification of this hypothesis remains as a research issue for the future.

5. Conclusion

Based on the hypothesis that *S* in river water consists mainly of *AtdepS* and *GeoS* in mountainous basins, we carried out quantitative analysis of *TotalS* (the product of *Cs* and *Qs*) originating from *AtdepS* and *GeoS*. The Tedori River mountainous basin was chosen as a test basin, because 16 years of data for *Cs*, *Qs* and *AtdepS* were available. Furthermore, we also have experience of calculating the nitrogen balance for the same basin [19,20], thus, the procedure for which is comparable to that for the *S* analysis.

First, *TotalS* was calculated using *Qs* and *Cs* data collected over a period of 16 years. The annual average outflow of the *TotalS* was estimated at 8597 $ton \cdot year^{-1}$, which corresponds to an average of 117.3 $kg \cdot ha^{-1} \cdot year^{-1}$. Of this *TotalS*, *AtdepS* was 1331 $ton \cdot year^{-1}$, corresponding to 18.2 $kg \cdot ha^{-1} \cdot year^{-1}$, and *GeoS* was 7266 $ton \cdot year^{-1}$, corresponding to 99.1 $kg \cdot ha^{-1} \cdot year^{-1}$.

In the above analysis, *Qs* and *AtdepS* in the basin have been corrected for altitude using the limited data available, as both precipitation and *AtdepS* depend on, and vary according to the altitude.

Using the altitude correction method outlined above, the *AtdepS* was estimated at six sites, namely Kuwajima, Shiramine, Senami, the Tedori dam site, the Dainichi dam site (Kamikawai) and Hirose (Nakajima). At these six sites the *TotalS* outflow was not constant, although the *Atdep* of nitrogen showed that deposition in the upper catchment was low and that it gradually increased in the lower reaches of the catchment [19,20]. The *GeoS* load was strongly dependent on the individual site characteristics, and in particular the Kuwajima site showed a remarkably high *GeoS* load, which suggests that the sedimentary rock at this site has much higher pyrite content than at the other sites.

To help explain why *GeoS* was higher than *AtdepS*, we examined the geological map of the study basin and confirmed that the sedimentary rock layer was rich in the pyrite group. Finally, we examined the relationship between the characteristics of sedimentary rocks and *GeoS* in many rivers in the Hokuriku Region because the climate conditions for *AtdepS* in this area are quite uniform. From this examination it was clear that SO_4^{2-} concentrations greater than about 10 $mg \cdot l^{-1}$ in river water were closely related to the sedimentary layer containing the pyrite group. In addition, we estimated that SO_4^{2-} concentrations greater than 2 - 3 $mg \cdot l^{-1}$ in river water in the Hokuriku region would be influenced by *GeoS*.

6. Acknowledgements

We sincerely thank Professor Okazaki of Ishikawa Prefectural University for commenting on the geochemical reaction of sedimentary rocks and for providing adequate references, and Professor Emeritus Kyuma of Kyoto University for kindly commenting. We also express sincere thanks to the government of Ishikawa Prefecture for providing valuable data. We also express thanks to the co-researchers of a study entitled "Normal hydrologic cycle as a core of irrigation water in the Tedori River basin" at Ishikawa Prefectural University, supported by the Ministry of Agriculture, Forests and Fishery, for their many valuable comments.

REFERENCES

[1] J. W. Jamieson, B. A. Wing, J. Farquhar and M. D. Hannington, "Neoarchaean Seawater Sulphate Concentrations

from Sulphur Isotopes in Massive Sulphide Ore," *Nature Geosciene*, Vol. 6, No. 1, 2013, pp. 61-64.

[2] R. J. Newton, E. L. Pevitt, P. B. Wignall and S. H. Bottrell, "Large Shifts in the Isotopic Composition of Seawater Sulphate across the Permo-Triassic Boundary in Northern Italy," *Earth and Planetary Science Letters*, Vol. 218, No. 3-4, 2004, pp. 331-345. doi:10.1016/S0012-821X(03)00676-9

[3] A. Ooki, "Size-Resolved Sulfate and Ammonium Measurements in Marine Boundary Layer over the North and South Pacific," *Japanese Institutional Repositories*, Vol. 41, No. 1, 2007, pp. 81-91.

[4] A. L. Norman, W. Belzer and L. Barrie, "Insights into the Biogenic Contribution to Total Sulphate in Aerosol and Precipitation in the Fraser Valley Afforded by Isotopes of Sulphur and Oxygen," *Journal of Geophysical Research-Atmospheres*, Vol. 109, No. D5, 2004. doi:10.1029/2002JD003072

[5] M. C. Eimers and P. J. Dillon, "Climate Effects on Sulphate Flux from Forested Catchments in South-Central Ontario," *Biogeochemistry*, Vol. 61, No. 3, 2002 pp. 337-355. doi:10.1023/A:1020261913618

[6] W. M. Lewis Jr. and M. C. Grant, "Changes in the Output of Ions from a Watershed as a Result of the Acidification of Precipitation," *Ecology*, Vol. 60, No. 6, 1979, pp. 1093-1097.

[7] E. Beaulieu, Y. Godderis, D. Labat, C. Roelandt, D. Calmels and J. Gaillardet, "Modeling of Water-Rock Interaction in the Mackenzie Basin; Competition between Sulfuric and Carbonic Acids," Elsevier, Amsterdam.

[8] L.-M. Hang, G.-L. Zhang and J.-L. Yang, "Weathering and Soil Formation Rates Based on Geo Chemical Mass Balance in a Small Forested Watersheds under Acid Precipitation in Subtropical China Catena," *CATENA*, Vol. 105, 2013, pp. 11-20.

[9] M. Budakoglu, "Sulfur-Isotope Distribution and Contamination Related to the Balya Pb-Zn Mine in Turkey," *Environmental Geology*, Vol. 47, No. 6, 2005, pp. 773-781. doi:10.1007/s00254-004-1202-1

[10] M. Edraki, S. D. Golding, K. A. Baublys and M. G. Lawrence, "Hydrochemistry, Mineralogy and Sulfur Isotope Geochemistry of Acid Mine Drainage at the Mt. Morgan Mine Environment, Queensland, Australia," Pergamon Oxford, New York and Beijing, International, GeoRef.

[11] M. Aikawa, T. Hiraki, Y. Komai, U. Satoshi and N. Tokuch, "A Case Study on Input-Output of Sulfur in a Catchment Area in Japan," *Journal of Atmosphere Environment*, Vol. 43, No. 1, 2008, pp. 23-30.

[12] T. Maruyama, M. Yoshida, K. Takase, H. Takimoto, S. Ishikawa and S. Nagasaka, "Relationship between Nitrogen Atmospheric Deposition, Discharge and Concentration, and Monthly Change of Those in a River, Japan," *Journal of Water Resources and Protection*, Vol. 5, No. 3, 2013, pp. 283-293. doi:10.4236/jwarp.2013.53029

[13] T. Maruyama and M. Yoshida, "Relation between Rainfall Deposit, Nitrogen Concentration and Discharge Height," *Applied Hydrology*, 2013, pp. 1-14.

[14] Shiramine, "History of Shiramine," Vol. 1, 1961, pp. 18-20.

[15] Oguch, "History of Oguch," *Ishikawa Prefecture*, Vol. 1, 1978, pp. 66-74.

[16] Construction Bureau of Hokuriku Region, "Kanazawa Office of Construction Works, History of Flood Control," 1985, pp. 13-15.

[17] Ishikawa Prefecture, "Investigation Report on Environment and Air. 2006-2010," Research Institute of Ishikawa Environment and Health, 2007-2011.

[18] Japanese Association of Environment, "Forth Report of Acid Rainfall in Japan 2005," Environment Research Committee, 2007.

[19] Japanese Association of Environment, "Forth Report of Acid Rainfall in Japan, 2006," Environment Research Committee, 2008.

[20] Japanese Association of Environment, "Forth Report of Acid Rainfall in Japan, 2007," Environment Research Committee, 2009.

[21] Ishikawa Prefecture Water Supply Office of Tedori River, "Annual Report of Water Quality, 1977-2011,"

[22] "Geological Map of Ishikawa Prefecture," www.jisuberi-kyokai.or.jp/kobetu/isikawa/okada/12.html

[23] Tropical Agricultural Center, "Swampy Lowland in South-Asian Countries," Tropical Agricultural Center, 1986.

[24] J. Kobayashi, "Health Examination of River Water, Iwanami Series," 1971.