SPRINGWATER CHEMISTRY AFTER RAINFALL
ON AKIYOSHI-DAI LIMESTONE PLATEAU,
WESTERN JAPAN

Toru OKAMOTO*

Abstract Springwater chemistry after rainfall were investigated at Kaerimizu, Yanaginomizu and Dekimizu springs on Akiyoshi-dai limestone plateau, western Japan. The major components, Ca\(^{2+}\) and HCO\(_3^-\) supplied by the solution of limestone, were strongly correlated, and their concentrations of Yanaginomizu and Dekimizu were higher than those of Kaerimizu. The other dissolved components were highly correlated at Kaerimizu, whereas there were no clear relationships at Yanaginomizu and Dekimizu. These facts indicate that Kaerimizu is recharged from both the subcutaneous and phreatic storage, and has relative large and long flow paths such as conduits (caves and shafts) within catchment area. In contrast, at Yanaginomizu and Dekimizu, it is probable that their water are recharged only from the subcutaneous storage, and are mostly fed through a diffuse flow system and short flow paths. It is therefore clear that the differences of springwater chemistry after rainfall among those springs reflect hydrogeological differences in karst aquifer. Furthermore, high Ca\(^{2+}\) concentration and saturation index for respect to calcite at Yanaginomizu and Dekimizu suggest that both springs have the characteristics of subcutaneous flow, which implies the solution of limestone mostly occurs in the epikarstic zone and soil-limestone interface.

Key words: Akiyoshi-dai limestone plateau, epikarstic zone, conduits, diffuse flow system, subcutaneous flow

1. Introduction

A considerable number of hydrological studies have been carried out in many karst areas. Most of those studies have been made on the basin outlets, and then their hydrogeological characteristics and net solution rates have been clarified. However, Gunn (1986) pointed out that net solution erosion rates provide a useful measure of the overall efficiency of solution processes in individual areas but are largely unrepresentative of solution at any specific location within those area. According to Gunn

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(1981a, 1986), Williams and Dowling (1979), and Ford and Williams (1989), 50–90% of solution takes place in the uppermost weathered layer 010. of limestone (termed the epikarstic or subcutaneous zone) and soil–limestone interface. This implies that the solution of limestone in the epikarstic zone contributes directly to the surface lowering. As a result, closed depressions which are common feature of temperate karst (also known as dolines) are developed by focusing of solution in the epikarstic zone (Gunn, 1986; Ford and Williams, 1989; Williams, 1983, 1985). It is therefore necessary to investigate the epikarstic zone in order to clarify the evolution of surface landforms in karst areas.

In Japan, Yoshimura and Inokura (1992) carried out the detailed studies of hydrological characteristics of springs at the foot of Akiyoshi–dai limestone plateau, Yamaguchi Prefecture. They suggested that the epikarstic zone as well as phreatic zone plays an important role as water storage in karst system and contributes to the evolution of groundwater chemistry. However, few measurements of groundwater chemistry of springs on the limestone terrain in Japan have been made, although those springs are considered to be a subcutaneous flow which is defined lateral water movement through the epikarstic zone.

The purpose of this study is to clarify the storm response of springs on Akiyoshi–dai limestone plateau. representative karst area in Japan, and estimate their aquifer and recharge type. Moreover, it is examined whether those springs have the characteristics of subcutaneous flow on the basis of their physical and chemical characteristics.

2. Study Area

Outline of Akiyoshi–dai Plateau

Akiyoshi–dai Plateau, Yamaguchi Prefecture, western Japan, is the widest limestone terrain in Japan extending over 130 km², and about 100 m to 400 m in height above sea level. The karst landforms are developed on Carboniferous–Permian Akiyoshi Limestone which is originated from seamount–associated reef complex (Sano and Kanemera, 1991). In the study area some late Quaternary tephas which were erupted from caldera volcanoes in Kyushu are deposited (Machida and Arai, 1992), which form soil parent materials. Throughout the plateau doline is distributed, especially in the central part of the plateau doline density is highest. displays 140–160/km² (Miura, 1989). Over the Akiyoshi–dai, it is recognized to be six erosion surface with low relief (Miura, 1989). At present most part of Akiyoshi–dai has been grassland by successive human agencies such as firing and deforesting from the past. Fire burns which is carried out every February, holds the vegetation in the status of the grassland for sightseeing and pasture. There are several patches of trees on the plateau, which are considered to be vestiges of the original dense. According to Shioi and Nakamura (1981), Machilus thunbergii community once covered Akiyoshi–dai. Rainfall is evenly distributed throughout the year. The mean annual precipitation is 1,974 mm and the mean annual temperature is about 14.0°C.
Spring description

In Akiyoshi-dai, there are several springs at the foot of the plateau. The hydrology of those springs was described by Fujii (1980), Inokura et al. (1985), and Yoshimura and Inokura (1992). Here, there follows a detailed description of springs which water samples were taken. Kaerimizu, Yanaginomizu and Dekimizu, on Akiyoshi-dai, as shown Fig. 1.

Kaerimizu Spring is the largest spring on Akiyoshi-dai and located at northern part of the plateau. A stream rises from the talus of northwestern base of the closed depression, called Kaerimizu Doline, and flows about 20m as a surface stream before

![Location map of springs on Akiyoshi-dai Plateau](image-url)

Fig. 1 Location map of springs on Akiyoshi-dai Plateau
water sinks at the southeastern base of the doline. Kaerimizu is considered to reach the water table (Fujii, 1980), and their mean discharge is 5.6 l/s (Yoshimura and Inokura, 1992). During and after intense rainfall "temporary doline pond" is formed, which returns prestorm condition within several days.

Dekimizu and Yanaginomizu Springs are located at the western part of Akiyoshi-dai. At Dekimizu waters slightly emerge from fissure in the limestone throughout the year and usually form small permanent pond which is about 80cm in diameter. During and after intense rainfall water level in pond rises and overflows. Yanaginomizu rises from the base of depression and flows about 10m before waters sink into fissure in the limestone. Both Yanaginomizu and Dekimizu are considered to be recharged by the epikarstic aquifer above the water table (Fujii, 1980).

Discharge of Kaerimizu is much higher than that of Yanaginomizu and Dekimizu. Moreover, Kaerimizu is not only recharged from the saturated (phreatic) zone but also the unsaturated (vadose) zone, whereas Yanaginomizu and Dekimizu are recharged only from the unsaturated zone above the water table (Fujii, 1980). Thus these springs are classified into two types. Kaerimizu and Yanaginomizu–Dekimizu.

3. Experimental Method

The water samples were collected at Kaerimizu, Yanaginomizu, Dekimizu Springs on Akiyoshi-dai between 18 and 25 July, 1993. Temperature, electrical conductivity and pH were measured at the sampling site. Water level of springs was measured at the time of water sampling, in order to estimate spring discharge. Because of imprecise measurement of flow velocity, water levels were only used to estimate physically change of each springs. The water samples were passed through 0.45μm filter at the sampling site, stored in a 30ml polyethylene bottle. Dissolved matters of water samples were analyzed in the laboratory by Professor Kazuisha Yoshimura of the Kyushu University. The determination of Na⁺, K⁺, Mg²⁺ and Ca²⁺ were carried out by atomic absorption spectrometry. Cl⁻, NO₃⁻ and SO₄²⁻ were determined by ion chromatography. SiO₂ were determined by absorption spectrometry with molybdisilic acid. HCO₃⁻ was determined by titration with H₂SO₄ or mass balance between cation and anion. Saturation index for respect to calcite (Slc) was calculated by methods described by Yoshimura and Tarutani (1982), and defined as:

$$Slc = \log \left( \frac{a_{Ca} a_{CO3}}{K_{CaCO3}} \right)$$

where a and K is. activity and solubility product, respectively.

4. Results

Precipitation and water level
The hydrological investigation was carried out 18–25 July, 1993. Before and during
investigation. three rainfall events were observed, 54, 155 and 9 mm of total rainfall on 13–14, 16–18 and 24–25, respectively. At Kaerimizu it was impossible to obtain water sample because doline pond was formed owing to rapid rise of water level associated with intense rainfall on 16–18.

At Kaerimizu doline pond was formed from 18 to 21, but water level gradually decreased and then returned prestorm condition on 22. Moreover, water level slightly rose on 25 due to rainfall on 24–25. At Yanaginomizu water level slightly decreased during the investigation. Dekimizu overflowed during the period from 18 to 19. Then water level gradually decreased and returned prestorm condition on 22. Discharge of Kaerimizu is much higher than that of Yanaginomizu and Dekimizu.

**Water chemistry**

The change after rainfall in pH, electrical conductivity (EC), saturation index for calcite (Slc) and the concentration of dissolved components are shown in Fig. 2. Hydrological characteristics of springs during the period of investigation are also shown in Table 1.

Springwaters pH displayed 7.67–8.06, 7.08–7.46 and 7.30–7.68, at Kaerimizu, Yanaginomizu and Dekimizu, respectively. Water temperatures were in the range 14.2–14.4°C, 15.6–16.5°C and 14.2–19.8°C in Kaerimizu, Yanaginomizu and Dekimizu, respectively. The concentration of Ca²⁺ was highest among cations and HCO₃⁻ was highest among anions. Both concentrations of Yangaginomizu and Dekimizu were higher than those of Kaerimizu. Ca²⁺ and HCO₃⁻ increased with decreasing in water level at Yanaginomizu and Dekimizu, whereas at Kaerimizu they slightly decreased with falling in water level. The other dissolved components of Kaerimizu were higher than those of Yanaginomizu and Dekimizu. At Kaerimizu the concentration of Na⁺, K⁺, Cl⁻, NO₃⁻ and SO₄²⁻ decreased with falling in water level, and the opposite tendencies was shown by that of Mg²⁺ and SiO₂. On the other hand, there were no clear relationships between those ions of Yanaginomizu and of Dekimizu. All water samples were supersaturated with respect to calcite. Slc values of Kaerimizu, Yanaginomizu and Dekimizu ranged from 1.27 to 2.87, 0.53 to 1.70, and 0.83 to 2.56, respectively.

5. Discussion

**Origin of dissolved components**

Kaerimizu, Yanaginomizu and Dekimizu are likely to be autogenic system, because their catchment areas are composed entirely of limestone (Fujii, 1980: Yoshimura and Inokura, 1992). Thus it is probable that their waters are derived only from rainfall falling on Akiyoshi-dai, and dissolved components in their springwater are supplied by rainfall which contains dry fall out and the dissolution of limestone and soil minerals.

Correlation matrices of dissolved components are given in Table 2. The major components of all water samples are Ca²⁺ and HCO₃⁻, and the correlation between both ions were very high (Fig. 2). These show that Ca²⁺ and HCO₃⁻ were supplied by the solution of limestone. The relationships of other dissolved components in water
Fig. 2  Change of chemical components of the springwater

EC = electrical conductivity; SIC = saturation index for respect to calcite.

☐: Kaerlimizu, +: Yanaginomizu, ◇: Dekimizu
Table 1  Hydrological characteristics of springs on Akiyosh-dai Plateau
Concentrations of dissolved components are given in ppm.
Note: Tw = water temperature; EC = electrical conductivity;
SIC = saturation index for calcite.

<table>
<thead>
<tr>
<th></th>
<th>Tw(°C)</th>
<th>EC(μS/cm)</th>
<th>pH</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>SiO₂</th>
<th>SIC</th>
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<tbody>
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<td>0.25</td>
<td>0.94</td>
<td>56.7</td>
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<td>1.4</td>
<td>2.4</td>
<td>4.6</td>
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<td>0.1</td>
<td>17</td>
<td>0.13</td>
<td>0.2</td>
<td>0.04</td>
<td>0.06</td>
<td>0.8</td>
<td>0.3</td>
<td>2</td>
<td>0.6</td>
<td>0.1</td>
<td>0.2</td>
<td>0.53</td>
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<tr>
<td>Yanaginomizu</td>
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<tr>
<td>mean</td>
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<td>514</td>
<td>7.30</td>
<td>2.9</td>
<td>0.08</td>
<td>0.70</td>
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<td>3.2</td>
<td>242</td>
<td>0.0</td>
<td>2.4</td>
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<td>1.10</td>
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<td>0.11</td>
<td>0.1</td>
<td>0.01</td>
<td>0.03</td>
<td>4.2</td>
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<td>13</td>
<td>-</td>
<td>0.0</td>
<td>0.1</td>
<td>0.34</td>
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<td>mean</td>
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<td>0.19</td>
<td>0.67</td>
<td>75.8</td>
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<td>standard deviation</td>
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<td>36</td>
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<td>0.07</td>
<td>0.01</td>
<td>1.9</td>
<td>0.1</td>
<td>6</td>
<td>-</td>
<td>0.0</td>
<td>0.1</td>
<td>0.46</td>
</tr>
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</table>

samples of Kaerimizu was clearer than those of Yanaginomizu and Dekimizu as shown Table 2. At Kaerimizu, the concentration of Cl⁻ was positively correlated with that of Na⁺, K⁺, SO₄²⁻ and NO₃⁻. In general, it is well known that Na⁺ and Cl⁻ are supplied by rainfall and dry fall out mainly in the form of sea salt. Muraoka and Hirata (1988) suggested that nitrate is stored forest soil near the surface as an organic substance with years of forest activity. However, in the present study NO₃⁻ concentration in all water samples was relatively low as expected from occurrence of grassland in the drainage basin of all three springs. It is therefore likely that the change of NO₃⁻ concentration at Kaerimizu was caused by rainfall. K⁺ and SO₄²⁻ were also mostly supplied by rainfall on the basis of correlation with Na⁺, Cl⁻ and NO₃⁻. In contrast, SiO₂ is not contained in rainfall, and supplied by the dissolution of minerals at surface soil and soil–bedrock interface (Muraoka and Hirata, 1988; Shimada et al., 1992). The contents of acid insoluble residue which mostly consists of SiO₂ in Akiyoshi limestone are low (Sakae et al., 1980). It is therefore clear that SiO₂ in water samples were mainly introduced from surface soil. Mg²⁺ is also thought to be supplied by solution of soil minerals, because of high correlation with SiO₂. Due to the dissolution of the almino–silicate minerals, feldspar which is the common minerals in Akiyoshi–dai soils, Na⁺ as well as SiO₂ were introduced into groundwater. Na⁺ and Cl⁻ are also deposited on Akiyoshi–dai as a dry fall out mainly in the form of sea salt. Thus there are positive relationships between Na⁺ and SiO₂ (Yoshimura and Tarutani, 1980; 1982). Conversely, in the present study at Kaerimizu there was negative relationship between both ions. This is likely explained that dry deposits, Na⁺ and Cl⁻, had already been discharged by previous rainfall (July 13–14) at the start of water sampling.

Spring chemograph interpretation

The response of the chemical quality of karst springs to rainfall is an important index of the karst system. In particular the variation of Ca²⁺ concentration, total hardness and electrical conductivity (EC) is usually used to interpret the karst aquifer
Table 2 Correlation matrices of dissolved components of springs on Akiyoshi-dai Plateau

<table>
<thead>
<tr>
<th></th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>SiO₂</th>
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</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.343</td>
<td>0.835</td>
<td>0.343</td>
<td>-0.779</td>
<td>-0.678</td>
<td>0.799</td>
<td>-0.680</td>
<td>0.647</td>
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<td></td>
<td>-0.712</td>
<td>0.750</td>
<td>0.464</td>
<td>-0.946</td>
<td>0.520</td>
<td>-0.570</td>
<td>0.740</td>
<td>0.470</td>
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<td>K⁺</td>
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<td>-0.874</td>
<td>-0.649</td>
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<td>0.744</td>
<td>0.813</td>
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<td>-0.311</td>
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<tr>
<td>Mg²⁺</td>
<td>-0.896</td>
<td>-0.746</td>
<td>0.864</td>
<td>-0.935</td>
<td>0.865</td>
<td>0.366</td>
<td>0.706</td>
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<td></td>
<td>0.909</td>
<td>-0.239</td>
<td>0.929</td>
<td>-0.470</td>
<td>0.508</td>
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<td>Ca²⁺</td>
<td>-0.902</td>
<td>0.825</td>
<td>0.999</td>
<td>0.846</td>
<td>-0.811</td>
<td>0.816</td>
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<td>0.998</td>
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<td>0.284</td>
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<td>Cl⁻</td>
<td>-0.912</td>
<td>0.430</td>
<td>0.925</td>
<td>0.969</td>
<td>0.114</td>
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<td>0.899</td>
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<td>-0.562</td>
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<td>SO₄²⁻</td>
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type. According to Williams and Dowling (1979), Hess and White (1988), Ford and Williams (1989), and Yoshimura and Inokura (1992), the increase in concentration of Ca²⁺ at the start of the flood are due to the flushing out of water with a long residence time in the deeper phreatic zone and the epikarstic zone; new recharge water force 'old' water out by piston-like process. With decreasing of discharge, Ca²⁺ continues to decrease below its prestorm concentration by the dilution of the groundwater caused fresh surface water input. Then the concentration of Ca²⁺ gradually rises to its prestorm value and discharge gradually falls. A similar relationship can be seen in total hardness and EC (Williams and Dowling, 1979; Hess and White, 1988). The other chemical indicators are used to assist in the study of groundwater components.

In the present study it is probable that high concentration of Ca²⁺ had already been pushed out by two rainfall events (13–14 and 16–18 July) at the start of water sampling. However, there is a difference in the change of Ca²⁺ and HCO₃⁻ between Kaerimizu and Yanaginomizu–Dekimizu. At Kaerimizu both ions were slightly decreased with falling in water level, whereas increased at Yanaginomizu and Dekimizu. In addition, there are clear relationships among the other dissolved components in Kaerimizu, but not clear in Yanaginomizu and Dekimizu. All three springs are recharged by autogenic inputs from rainfall falling on the limestone plateau, which is supported by the fact that all water samples were supersaturated with respect to calcite in spite of collections just after rainfall. From these results, the differences between Kaerimizu and Yanaginomizu–Dekimizu are considered to be caused by aquifer type, flow path length and conduit size.

Kaerimizu is recharged by the waters from both the epikarstic and phreatic zone (Fujii, 1980). Moreover, the relationships of dissolved components show that the waters percolated through the soil and underlying bedrock has been discharged. It is therefore probable that Kaerimizu has long flow paths and large conduits in catchment area recognized as shafts and caves. On the other hand, Yanaginomizu and Dekimizu are recharged only from the epikarstic storage above the water table. Low Ca²⁺ concentrations found both springs during high water level (discharge) are thought to be the result of the short flow paths rather than of a conduit flow pattern. In the epikarstic zone the waters slowly percolate through a diffuse system which is composed of tight fissures and small porosities, so that there would be no clear relationships among dissolved components except Ca²⁺ and HCO₃⁻. Although these are consistent with observation in the Inner Bluegrass of central Kentucky (Scanlon and Thrailkill, 1987), it is necessary to monitor over extended time period in each springs in order to establish these estimates with certainty.

Significance for geomorphology of Akiyoshi–dai Plateau

The results of the present study were compared with previous analyses (Yoshimura and Inokura, 1992) of streamwater and drip water of Akiyoshi–do Cave and rain water in Akiyoshi–dai (Table 3). Akiyoshi–do Cave is located at southern foot of the plateau (Fig. 1) and its drainage basin is composed of limestone and nonlimestone rocks (Fujii, 1980; Inokura et al., 1985). Ca²⁺ concentration of Yanaginomizu and Dekimizu is significantly higher than that of rain water. streamwater of Akiyoshi–do
Table 3 Chemical characteristics of Akiyoshi-dai Plateau
* From Yoshimura and Inokura (1992). Drip water was collected from stalactite in Akiyoshi-do Cave.

<table>
<thead>
<tr>
<th></th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaerimizu</td>
<td>3.2</td>
<td>0.25</td>
<td>0.94</td>
<td>56.7</td>
<td>5.5</td>
<td>173</td>
<td>2.4</td>
<td>4.6</td>
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<tr>
<td>Yanaginomizu</td>
<td>2.9</td>
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<td>0.70</td>
<td>78.5</td>
<td>3.2</td>
<td>242</td>
<td>2.4</td>
<td>3.1</td>
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<tr>
<td>Dekimizu</td>
<td>2.6</td>
<td>0.19</td>
<td>0.67</td>
<td>75.8</td>
<td>3.6</td>
<td>233</td>
<td>2.3</td>
<td>3.0</td>
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<tr>
<td>Akiyoshi-do Cave*</td>
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<td>0.51</td>
<td>1.21</td>
<td>54.7</td>
<td>7.1</td>
<td>158</td>
<td>5.2</td>
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</tr>
<tr>
<td>Drip Water*</td>
<td>2.4</td>
<td>0.17</td>
<td>1.07</td>
<td>65.6</td>
<td>5.3</td>
<td>198</td>
<td>4.2</td>
<td>3.5</td>
</tr>
<tr>
<td>Rain Water*</td>
<td>0.8</td>
<td>0.1</td>
<td>0.11</td>
<td>0.2</td>
<td>1.6</td>
<td>-</td>
<td>2.1</td>
<td>-</td>
</tr>
</tbody>
</table>

Cave and springwater of Kaerimizu. It is relatively similar to that of drip water in Akiyoshi-do Cave. All water samples of Yanaginomizu and Dekimizu were supersaturated with respect to calcite (Fig. 2), although both springs are located above water table. These indicate that most of solution takes place in the uppermost weathered limestone termed the epikarstic (subcutaneous) zone. Moreover, it is clear that the epikarstic zone is a important storage together with the phreatic zone. because it is required the time for chemical reactions between water and limestone bedrock to reach

\[
Y = 3.14X - 5.04 \\
(r = 0.998)
\]

Fig. 3 Relationships between Ca²⁺ and HCO₃⁻ concentration
equilibrium.

Gunn (1981b, 1983) carried out detail studies of the hydrological function of closed depressions in the Waitomo district, New Zealand, and proposed a model incorporating three concentration mechanisms (overland flow, throughflow and subcutaneous flow) and three input mechanisms (shaft flow, vadose flow and vadose seepage). He clarified that the subcutaneous flow defined as any water flowing laterally through the epikarstic zone is high Ca$^{2+}$ concentration. From the results in the present study, it is probable that Yanaginomizu and Dekimizu would have the characteristics of subcutaneous flow. On the other hand, Kaerimizu is a phreatic spring which is recharged by both the epikarstic and phreatic storage. The subcutaneous flow presents the consequence of solution in the epikarstic zone, which contributes directly to surface lowering. It is therefore expected that the actual surface lowering in Akiyoshi-dai can be estimated by studying the hydrochemistry of Yanaginomizu and Dekimizu in more detail.

6. Conclusions

Springwater chemistry after rainfall in the karst area provides significant information on the recharge, storage and structural characteristics of aquifer in the karst system. Springs on Akiyoshi-dai Plateau whose catchment area are composed entirely of limestone, are recharged by autogenic water derived from rainfall falling on the plateau. Yanaginomizu and Dekimizu springs are located above the water table, suggesting that they are recharged only from the epikarstic storage. In addition, the correlation of dissolved matters except Ca$^{2+}$ and HCO$_3^-$ was not clear. These indicate that Yanaginomizu and Dekimizu are mostly composed of a diffuse flow system and short flow paths. On the other hand, Kaerimizu is recharged from both the epikarstic and phreatic storage, since it reaches to the water table. There were clear relationships among dissolved components in their water samples, which implies that Kaerimizu have relative large and longer flow paths such as conduits (caves and shafts).

The high Ca$^{2+}$ concentration and saturation index for respect to calcite at Yanaginomizu and Dekimizu suggest that both springs have the characteristics of subcutaneous flow. Kaerimizu is recognized as a phreatic spring. Consequently, results in the present study will support the previous studies that most solution of limestone takes place at soil-limestone interface and in the epikarstic zone which is an important storage of waters.

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I wish to dedicate this paper to Professor Hiroshi Kadamura on the occasion of his retirement from Tokyo Metropolitan University.

Reference Cited


61. 45–67.


(• in Japanese, •• in Japanese with English abstract)