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title: **Use of 15N and 222Rn to identify sources of groundwater nitrates in the Ryukyu Limestone aquifer of Okinawa Island, Japan**

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INTRODUCTION

Recently, increasing nitrate concentrations in groundwater have been of worldwide concern. Nitrates are implicated in methemoglobinemia and may be a causative factor in other health disorders such as cancer, though at present the evidence is inconclusive. In general, nitrate pollution is considered to be caused by nitrogen loading as a result of human activities such as increased use of chemical fertilizers, inappropriate management of livestock manure, and emission of effluents from septic tanks. Groundwater in karst aquifers is particularly vulnerable to chemical pollution because water moves rapidly through fractures and fissures of an aquifer. Nitrogen loading processes in karst aquifers are considerably influenced by the characteristics of groundwater flow that are closely related to hydrogeological features such as caves and caverns. To control nitrates in groundwater, we must understand the dominant sources and transport processes of nitrates, regarding the impacts of karstic features on nitrogen loading processes.

The Ryukyu Islands, are a chain of southwestern Japanese islands. The largest is Okinawa Island. The Ryukyu Limestone, of the Quaternary age, is extensively distributed on these islands. Recently rising concentrations of nitrates in groundwater have become a problem. The southern part of Okinawa Island is a suburban region with many farms where mainly vegetables and sugarcane are cultivated and numerous livestock farms exist. Nitrate concentrations in groundwater had increased until the mid-1990s, which was believed to be caused by chemical fertilizer applied to upland fields.

In this study, we examined the fate and transport of groundwater nitrates in the Ryukyu Limestone aquifer. The sources of nitrogen affecting the groundwater quality were estimated by analyses of a ratio of two stable isotopes of nitrogen in nitrates, ^{14}N and ^{15}N. In addition, radon (^{222}Rn) were used to clarifying rapid groundwater flow in caves and caverns and its influence to transportations of nitrates in groundwater. ^{222}Rn is useful as an indicator to distinguish the impacts of the caves and caverns, because ^{222}Rn concentrations in groundwater of caves and caverns are relatively low.

STUDY AREA

The study area was located at the southern tip of Okinawa Island. A hydrogeological map of the study area is shown in Fig. 1. The basement rocks in the study area belong to the Shimajiri Group, of the Neogene age, which consists mainly of alternating layers of sandstone and mudstone. The Shimajiri Group is relatively impermeable with a hydraulic conductivity of less than 2.0×10^{-7} m s^{-1}. The Ryukyu Limestone that overlies the Shimajiri Group over most of the study area is thick (generally 30–40 m thick) and porous and contains well-developed cracks and caves that give it high permeability with a hydraulic conductivity of about 1.0×10^{-4} m s^{-1} and effective porosity of 9%. Groundwater in this region flows mainly in the pores of the Ryukyu Limestone above the impermeable Shimajiri Group. Groundwater basins are formed by one or two tectonic blocks where groundwater flows through buried valleys in the upper surface of the Shimajiri Group. Karst terrains are characterized by landforms such as sinkholes and caves, and continuously evolve by dissolution of calcite and dolomite into the groundwater. The study area is a typical karst terrain containing many caves and caverns (Fig. 1; Imaizumi et al., 2003). Two large caverns in the Komesu Basin connect some of the caves to the seashore (Fig. 1), and in these caverns, the groundwater flows preferentially. In addition, springs are also common in the study area.

The study area is a suburban agricultural area. It consists mainly of upland fields of sugarcane and vegetables, but several residential areas are situated among the upland fields. In 2005, acreage of upland field in Itoman City was 15.90 km^2, and sugarcane acreage 5.30 km^2. Population in Itoman City in 2005 was 55,816. Moreover, livestock operations such as hog farms have been established in the residential areas. Most of the livestock farms are located in the residential areas. In 2005, the numbers of beef cattle, cows, hogs and chickens in Itoman City were 1,620, 310, 20300 and 104,000, respectively.

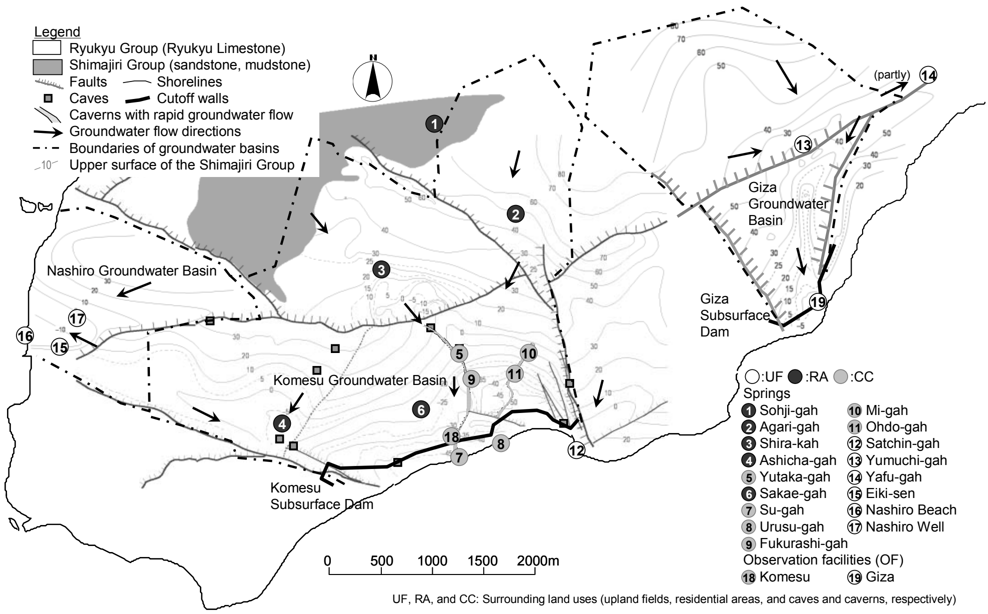

Figure 1. Geological settings and sampling sites of the study area.

METHODS

Sallow groundwater samples were collected in February 2007, March 2008 and January 2009 from 17 springs and from observation facilities of the two subsurface dams in the study area (Fig. 1). The sampling sites were categorized into three types: upland field (UF), residential area (RA), and cave and cavern (CC).

Concentrations of nitrate nitrogen (NO_3-N) in the collected samples were analyzed by ion chromatography (ICA-2000, TOA-DKK, Japan).

For isotopic analyses, nitrate samples were enriched by the freeze-drying method (Böhlke and Denver, 1995) and then converted to N_2 gas by quartz tube combustion for mass spectrometry (FlashEA 1112, Thermo Fisher Scientific, USA). The N_2 gas was analyzed for $\delta^{15}N$ by an isotope ratio mass spectrometer (Delta V Advantage, Thermo Fisher Scientific, USA) with a reproducibility of 0.15‰. Here, the value of $\delta^{15}N$ is defined by the following equation:

$$\delta^{15}N = ({}^{15}N_{sample}/{}^{14}N_{sample} - {}^{15}N_{air}/{}^{14}N_{air}) / {}^{15}N_{air}/{}^{14}N_{air} \times 1000 \; [‰], \quad (1)$$

where $^{15}N_{sample}/^{14}N_{sample}$ is the ratio in samples, and $^{15}N_{air}/^{14}N_{air}$ is the ratio in air.

Radon (^{222}Rn) concentrations in water samples collected in 2007 and 2009 were measured with a liquid scintillation counter (Tri-Carb 2250 CA, Packard BioScience, United States) after in situ extraction with toluene by the methods of Hamada and Komae (1998). The total error was less than 0.05 Bq L^{-1}. The NO_3-N concentration and the $\delta^{15}N$ value in the sample collected at Nashiro Beach in 2009 could not be analyzed because of high salinity.

We considered chemical fertilizer application, livestock and human wastes, and soil (natural) nitrogen as nitrogen sources having a major effect on groundwater quality. Contribution ratios from these nitrogen sources, denoted as R_{CF}, R_{LH} and R_{SN}, were estimated from the observed NO_3-N concentrations C_{obs} and the $\delta^{15}N$ values X_{obs} by the following simultaneous equations (Nakanishi et al., 1995);

$$1 = R_{CF} + R_{LH} + R_{SN}, \quad (2)$$

$$X_{obs} \approx X_{CF}R_{CF} + X_{LH}R_{LH} + X_{SN}R_{SN}, \quad (3)$$

$$R_{SN} = C_{SN} / C_{obs}, \quad (4)$$

where X_{CF}, X_{LH} and X_{SN} are representative $\delta^{15}N$ values in groundwater nitrates derived solely from fertilizer application, livestock and human wastes, and soil nitrogen, and C_{SN} a concentration of groundwater nitrates from soil nitrogen were assumed to be always constant. The values of X_{CF}, X_{LH} and X_{SN} were set to 3‰, 15‰ and 4‰ from literature values (Fig. 2). In addition, because of absence of spring or well free from impacts of human activities, 1.4 mg L^{-1} (Nakanishi et al., 1995) was employed as the value of C_{SN}.

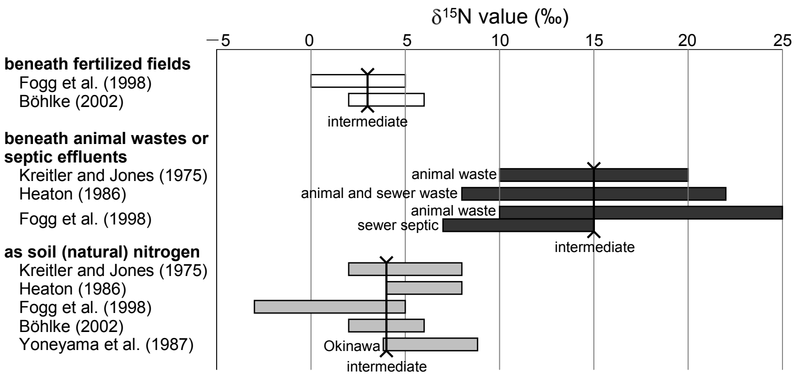

Figure 2. Ranges of δ15N values in the literatures and the applied values in this study.

RESULTS

Nitrate was found in all groundwater samples from the study area. The average NO_3-N concentration was 10.4 mg L^{-1}, and the range was 5.5–18.9 mg L^{-1} (Fig. 3).

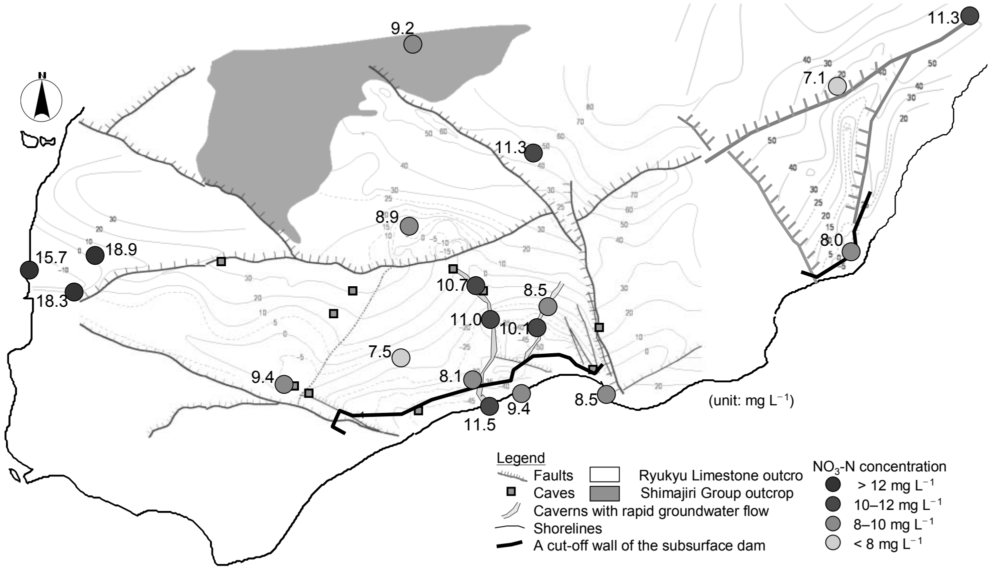

Figure 3. NO3-N concentrations in groundwater in February 2007.

The $\delta^{15}N$ values at all sites averaged 9.6‰, and ranged from 6.1‰ to 13.1‰ (Fig. 4). The average value was 8.5‰ at UF sites, 10.0‰ at RA sites, and 10.5‰ at CC sites.

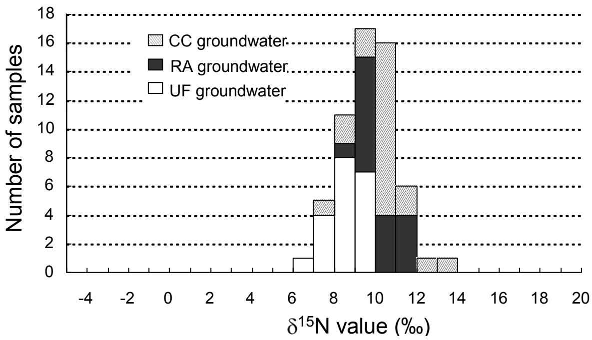

Figure 4. Frequency distribution of δ15N values of groundwater nitrates.

The average ^{222}Rn concentration was 4.4 Bq L^{-1}, and the range was 0.6–13.5 Bq L^{-1}. The ^{222}Rn concentrations at many of the CC sites were relatively low (less than 2 Bq L^{-1}) (Fig. 5).

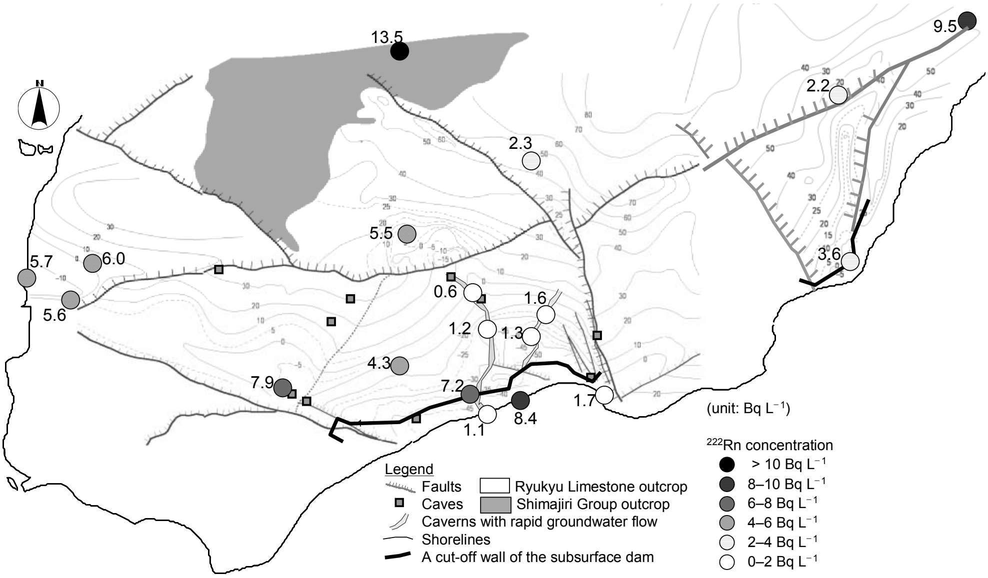

Figure 5. 222Rn concentrations in groundwater in February 2007.

The averages of R_{UF} at UF, RA and CC sites were 41%, 27% and 25%, and those of R_{LH} were 45%, 57% and 61%, respectively (Fig. 6).

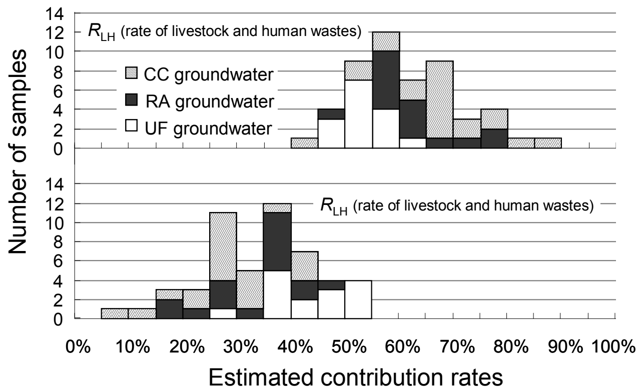

Figure 6. Frequency distribution of estimated RCF and RLH.

DISCUSSIONS

Generally, although in younger carbonate aquifers diffuse flow in matrices is dominant, caves and sinkholes are generated with evolution of karst terrains, and then in mature kasrt regions conduit flow systems with rapid groundwater flow are developed (e.g. Quinlan, Ewers, 1985). The Ryukyu Limestone aquifer can be regarded as "mixed aquifer", where slow diffuse flow in matrices and rapid conduit flow in caves and caverns exist together.

We examined the existence of preferential groundwater flow in caves and caverns from the ^{222}Rn data. In matrices of the aquifer ^{222}Rn is likely continuously supplied by the alpha decay of

^{226}Ra in the aquifer and reaches radioactively equilibrium in three weeks, whereas in caves and caverns the ^{222}Rn in the groundwater is lost through dispersion to the atmosphere and radioactive decay. Therefore, the lower ^{222}Rn concentrations at the CC sites were thought to reflect the influence of caves and caverns.

In the Ryukyu Islands, chemical fertilizer has often been considered the major cause of groundwater nitrates. Yoshimoto et al. (2008) reported that correspondence of the trend of change in NO_3-N to the variation of nitrogen emission from chemical fertilizer suggested that chemical fertilizer more strongly contributed the groundwater nitrates than other sources.

However, $\delta^{15}N$ values at all sites (Fig. 4) were higher than the literature values for $\delta^{15}N$ values in groundwater nitrates beneath fertilized upland fields (0–6‰; Fig. 2). The groundwater nitrates at the UF sites had the average $\delta^{15}N$ value of 8.5‰. It was inappropriate to regard that all groundwater nitrates beneath upland fields came from chemical fertilizer. On the other hand, the average $\delta^{15}N$ value at the RA sites was 10.0‰, which is the lowest in the range of literature values beneath animal and human waste applications (10–20‰; Fig. 2). The average at the CC sites was 10.5‰ which is quite similar to that at the RA sites. At the UF and RA sites, it was reasonable to consider that the origin of groundwater nitrates was composed of chemical fertilizer, livestock manure, domestic wastewater, and soil nitrogen in varying rates of contribution. In addition, at the CC sites, it was also a reason that nitrates were not related to surrounding land uses and carried by preferential groundwater flow in caves and caverns from upstream residential areas.

The averages of R_{CF} at UF, RA and CC sites calculated by Eqs. (2–4) were 41%, 27% and 25%. Even though these results indicated that groundwater at the UF sites were influenced by chemical fertilizer more significantly than at the RA and CC sites, the contribution of livestock manure and domestic wastewater was estimated to be much larger than chemical fertilizer (Fig. 6). This might be because the value of C_{SN} and X_{SN} were assumed to be fixed to 1.4 mg L^{-1} and 4‰ for the calculation of Eq. (2–4).

CONCLUSION

The fate and transport of groundwater nitrates in the Ryukyu Limestone aquifer were investigated. Nitrates were found in the all groundwater samples. Values of $\delta^{15}N$ in the nitrates suggested that the origin of the nitrates would be the mixture of chemical fertilizer, livestock manure, domestic wastewater and soil nitrogen. In addition, nitrates at the CC sites would be carried by preferential groundwater flow in caves and caverns from upstream residential areas.

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