

## Original article

# Evaluation of the environmental condition of Submarine Groundwater Discharge (SGD) by using nitrate stable isotope ratio recorded in sea lettuce (*Ulva* sp.)

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## Introduction

Submarine Groundwater Discharge (SGD) is a flow of groundwater in the sea. SGD contains high nutrients through the underground flow from rainfall area to coastal area. In Mediterranean Sea, SGD is thought as a major source of nutrient fluxes [1]. The high nutrients derived by SGD increase biological productivity in the coastal area.

On the other hands, nutrients of SGD may cause eutrophication. In Monterey Bay, CA, nitrate and silicate derived from SGD make phytoplankton increasing rapidly [2]. Therefore, it is important to understand an ecological role of SGD. In this study, we estimated how much SGD contributes to biological production in the coastal area where fresh groundwater inputs, by using nitrogen stable isotope ratio of *Ulva* sp.

## Materials and methods

Yuza town (Fig. 1) in Yamagata prefecture is characterized by a lot of SGD flow. There is Yuza town in the foot of Mt. Chokaisan which is a volcano and the volcanic formations have permeability [3]. Thus, groundwater topically gushes out in Yuza. In Kamaiso and Mega coast, there is a lot of SGD flow in the sea. We analyzed salinity, the concentration of dissolved inorganic nitrogen (DIN), radon (<sup>222</sup>Rn) and nitrate stable isotope ratio ( $\delta^{15}\text{N}_{\text{NO}_3^-}$ ) of ambient water in the 5 coast, Nishihama, Kamaiso, Torisaki, Takinoura, and Mega.

Salinity was measured by YSI Pro 30 (YSI Pro 30, YSI Nanotech Inc.:  $\pm 0.2^\circ\text{C}$ ,  $\pm 0.1$  ppt). The concentration of DIN was measured by the autoanalyzer (TRAACS-800, BRAN LUEBBE

Company Inc.). <sup>222</sup>Rn was measured by RAD7 (RAD7, DURRIGE Company Inc.).

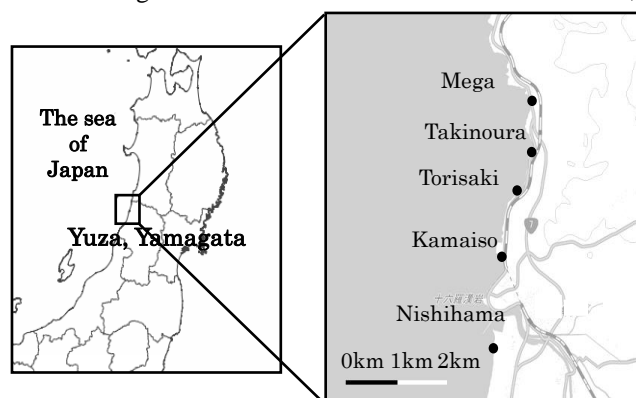
We also collected *Ulva* sp. in the study area in 2016. *Ulva* sp. were dried and grinded to analyze  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  using isotope ratio mass spectrometer (DELTA V advantage, Thermo-Fisher Scientific).

We used  $\delta^{15}\text{N}_{\text{NO}_3^-}$  values and  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of *Ulva* sp. in 2015 from unpublished data.

## Results

Kamaiso and Mega were high SGD areas and Torisaki and Nishihama were low SGD areas judging from the <sup>222</sup>Rn concentration. The  $\delta^{15}\text{N}_{\text{NO}_3^-}$  values of groundwater collected at land ranged from 1.7 to 2.5‰. The  $\delta^{15}\text{N}_{\text{NO}_3^-}$  values of ambient water in high SGD areas and low SGD areas ranged from 2.2 to 4.5‰ and from 5.6 to 8.6‰, respectively.

The  $\delta^{15}\text{N}$  of *Ulva* sp. collected in 2015 in high SGD areas ranged from -0.3 to 1.5‰. On the other hands,



**Fig. 1.** This is a figure which shows study sites in Yuza, Yamagata. We collected water and *Ulva* sp. in 5 coast Mega, Takinoura, Torisaki, Kamaiso and Nishihama.

those in low SGD areas ranged from 1.6 to 1.9‰. The  $\delta^{15}\text{N}$  of *Ulva* sp. in 2016 ranged from -0.1‰ to 3.2‰ in high SGD areas, and from 4.5‰ to 7.0‰ in low SGD areas.

## Discussion

In order to evaluate the contribution of SGD to *Ulva* production, we used two-source model with  $\delta^{15}\text{N}_{\text{NO}_3^-}$  and nitrate concentration of groundwater and sea water, showing followed formula;

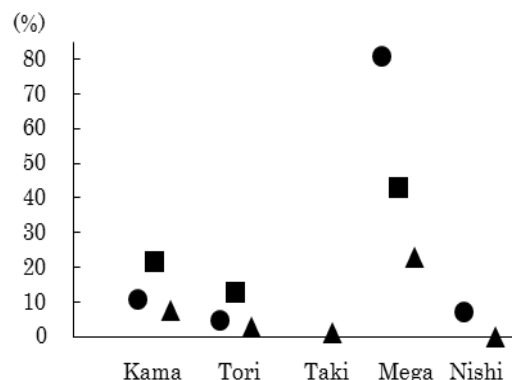
$$Rt = \left(1 - \frac{\text{NO}_3^-_{\text{GW}} \times (\delta^{15}\text{N}_{\text{NO}_3^-_{\text{GW}}} - X)}{(\text{NO}_3^-_{\text{SW}} - \text{NO}_3^-_{\text{GW}}) \times X - (\delta^{15}\text{N}_{\text{NO}_3^-_{\text{SW}}} \times \text{NO}_3^-_{\text{GW}} - \delta^{15}\text{N}_{\text{NO}_3^-_{\text{GW}}} \times \text{NO}_3^-_{\text{SW}})}\right) \times 100$$

where  $Rt$  is the value which presents the contribution of SGD to *Ulva* production,  $\text{NO}_3^-_{\text{GW}}$  is the concentration of  $\text{NO}_3^-$  of the groundwater,  $\text{NO}_3^-_{\text{SW}}$  is that of the sea water,  $\delta^{15}\text{N}_{\text{NO}_3^-_{\text{GW}}}$  is  $\delta^{15}\text{N}_{\text{NO}_3^-}$  of the ground water,  $\delta^{15}\text{N}_{\text{NO}_3^-_{\text{SW}}}$  is  $\delta^{15}\text{N}_{\text{NO}_3^-}$  of the sea water, and  $X$  is the  $\delta^{15}\text{N}$  of *Ulva* sp. or  $\delta^{15}\text{N}_{\text{NO}_3^-}$  of ambient water. We used  $\text{NO}_3^-_{\text{GW}}$  and  $\delta^{15}\text{N}_{\text{NO}_3^-_{\text{GW}}}$  value averaged from the values of groundwater, and  $\text{NO}_3^-_{\text{SW}}$  and  $\delta^{15}\text{N}_{\text{NO}_3^-_{\text{SW}}}$  value of sea water collected in Kamaiso which was not affected by fresh water.

The contribution rates of SGD estimated from  $\delta^{15}\text{N}$  of *Ulva* sp. ranged from 15.5 to 42.8% in high SGD areas, and was 12.8% in low SGD areas in 2015, and ranged from 7.7 to 22.8% in high areas, and from 0 to 2.7% in low areas in 2016 (Fig. 2). The contribution rates estimated from  $\delta^{15}\text{N}_{\text{NO}_3^-}$  of ambient water was substantially similar as that averaged from *Ulva* sp. in 2015 and 2016. The present study showed that it is possible to estimate to the contribution rate of SGD to the biological production by using the nitrogen stable isotopic signal recorded in of *Ulva* sp.

## Conclusions

We analyzed salinity, the concentration of dissolved inorganic nitrogen (DIN), radon ( $^{222}\text{Rn}$ ) and  $\delta^{15}\text{N}_{\text{NO}_3^-}$  of ambient water to estimated how much SGD contributes to biological production in the coastal area. We could distinguish high SGD areas (Kamaiso, Mega) from low SGD areas (Torisaki, Nishihama) using the values of  $^{222}\text{Rn}$ ,  $\delta^{15}\text{N}_{\text{NO}_3^-}$  and  $\delta^{15}\text{N}$  of *Ulva* sp. In order to evaluate the contribution of SGD, we used two-source model with  $\delta^{15}\text{N}_{\text{NO}_3^-}$  and nitrate concentration of groundwater and sea water. The contribution rates of SGD estimated from  $\delta^{15}\text{N}$  of *Ulva* sp. in high SGD areas were higher than those in low SGD areas. The contribution rates of SGD estimated from  $\delta^{15}\text{N}_{\text{NO}_3^-}$  of ambient water was substantially similar as that averaged from  $\delta^{15}\text{N}$  of *Ulva* sp. This study showed that it is possible to estimate to the contribution rate of SGD to the biological production using  $\delta^{15}\text{N}$  of *Ulva* sp.



**Fig. 2.** The graph presents percentages of fresh water in SGD at Kamaiso (Kama), Torisaki (Tori), Takinoura (Taki), Mega, and Nishihama (Nishi). These values were calculated from  $\delta^{15}\text{N}_{\text{NO}_3^-}$  of ambient water (●),  $\delta^{15}\text{N}$  of *Ulva* sp. in 2015 (■) or  $\delta^{15}\text{N}$  of *Ulva* sp. in 2016 (▲).

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