Identification of autotrophic denitrification anomaly in the fast flowing karst aquifer using $\delta^{15}N$, $\delta^{34}S$ and $\delta^{13}C$ tracers in the Ryukyu limestone aquifers, southern Okinawa, Japan

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Nitrate contamination issue in the karst aquifer has not been observed as details, although there are a lot of contaminated mantled karst areas because of human activities and extensive agricultural practices. The complex, random and fast flowing hydrogeological system become its own challenge in discussing groundwater pollution in the karst aquifer. This also happened in the southern part of Okinawa Island, Japan. The southern part of Okinawa Island is a sea shore area where Ryukyu limestone distributes. There was not enough surface water for agricultural and domestic use, then in 2005 to meet those demands, 2 geotechnical structures which are subsurface dams were established; Komesu and Giza Subsurface Dams. Nitrate concentration in the groundwater was relatively high, NO3-N concentration was more than 10 mg/L (20 of 69 observation sites). Nitrogen and sulfur isotope analysis presented the groundwater was contaminated by chemical fertilizers, with the value of $\delta^{15}N_{NO3}$ mostly around 6-14‰ and $\delta^{34}S_{SO4}$ approximately -2 to 5‰. Carbon isotopes identified that the major source of the carbon came from terrigenous soil which were released during C4 plant decompositions with value of $\delta^{13}C_{DIC}$ around -10 to -16‰. After a 4 year’s monitoring process, we found there was a decreasing concentration of NO_3-N along the seasonal pattern (with significant plummet ±8 mg/L) in some specific wells. This anomaly can be suspected as denitrification because it was followed by an increasing value of $\delta^{15}N_{NO3}$ to reach 50 ‰. Furthermore, multiple stable isotope analysis (N, C and S isotopes) suggests that autotrophic denitrification was the dominant type that occurred across the basin. This can be seen from the stable trend of $\delta^{13}C_{DIC}$ and was followed by a decrease in the value of $\delta^{34}S_{SO4}$, while $\delta^{15}N_{NO3}$ continued to increase, although this type of denitrification has rarely been identified in the karstic aquifer with relatively fast groundwater flow regime. There are two factors that can create stagnant conditions in the study area where denitrification reaction can preferentially proceed, in lithological gap generated due to geological structures and the existence of Komesu Subsurface Dam itself.

Keywords: Subsurface dam, Karst aquifer, Denitrification, Stable isotopes

