Enhanced riverine carbon flux in carbonate catchment area: a comparative hydrogeochemical study in Ishigaki and Iriomote Islands.

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Reaction rate of carbonate dissolution is in two to four orders of magnitude higher than that of aluminosilicate dissolution. Thus, rivers with carbonate watershed could have large carbon flux even if the catchment size is small. In this study, the influence of rock-water interactions within the catchment area is evaluated comparing chemical compositions of river waters from two neighboring islands: Iriomote and Ishigaki Islands, which have typical lithological characters of aluminosilicate sandstones and carbonate reef sediments (Ryukyu-Limestones), respectively.

Low pH and alkalinity observed in rivers in Iriomote Island indicate a large contribution of surface runoff (direct discharge of precipitations). In contrast, as a result of carbon-rich groundwater discharge near the river mouth, rivers in Ishigaki Island exhibited high alkalinity and P_{CO2} (up to 2.5 mmol/kg and 7,000 ppm, respectively). Despite the small size of catchment area (less than 50 km2), concentrations of dissolved matters of Miyara River in Ishigaki were higher than the mean value of world major rivers and in comparable range of those of rivers such as Mississippi or Rio Grande.

In the processes of such carbon-rich groundwater formation, soil layer plays an important role as a CO_2 source to groundwater aquifer, along with the carbonate rocks. Stable carbon isotopic ratio ($d^{13}C$) of DIC basically agreed that the riverine DIC source in Ishigaki Island was dissolution of carbonate by soil CO_2, but certain inconsistency between the observed $d^{13}C$ and predicted values indicate that acid deposition may have some contribution to enhance carbonate dissolution.

In addition to DIC, high DIN concentration due to agricultural activities was also observed in river water and groundwater in Ishigaki. As a result, river water in Ishigaki had high C:P and N:P ratios of 330-4,680 and 33-130, respectively. Under strong influence of this terrestrial water, surrounding coral reefs could become potential sources of CO_2 for the atmosphere, while the coastal ecosystem has been considered as a CO_2 sink due to terrestrial nutrient input. Such situation could be occurring elsewhere in the coastal area and continental shelf, with the combined contribution of carbonate dissolution and groundwater discharge near the river mouth.