A Study on the dynamics of various phosphate forms in soil and groundwater in Ryukyu limestone regions

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Phosphorus in water environment exists in various forms and size, such as dissolved, particulate, organic and inorganic forms. However, there are many unclear points in Phosphorus in groundwater. In this study, we tried to understand the dynamics of various phosphate forms in soil and groundwater in Ryukyu limestone regions by combining Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and ^{31}P Nuclear Magnetic Resonance (^{31}P-NMR), in addition to Colorimetric (molybdenum blue method). From August 2017 to August 2018, we took groundwater samples in southern part of Okinawa, Japan, with Ryukyu limestone distribution on a monthly basis. We measured pH, electronic conductivity (EC), Oxidation-Reduction Potential (ORP), dissolved oxygen (DO) and alkalinity (HCO_3^-) on site, and analyzed major dissolved ion (Cl^-, HCO_3^-, NO_2^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}), suspended solid (SS) and phosphorus concentration. Phosphorus concentration analyzed 3 different method to molybdenum blue method (Col-P), ICP-AES (ICP-P) and Total P (T-P). Phosphate form analysis used ^{31}P-NMR.
We compared Col-P and ICP-P in order to understand dissolved phosphorus spatial distribution. The results show that ICP-P is 1.06˜49.24 times larger than Col-P. It is inferred that ICP-P is also measuring fine particulate phosphorus and organic phosphorus. As a result, several forms of phosphate without orthophosphate were found in groundwater. Particulate phosphorus was determined by subtracting ICP-P from T-P. A positive correlation (r= 0.78) was found between P-P and SS. According to these results, it is thought that PP adsorbs various forms of phosphate including orthophosphate. We analyzed the correlation between dissolved phosphorus (Col-P, ICP-P) and all measured value in order to understand the characteristics of seasonal variation to dissolved phosphorus. There was a negative correlation between Col-P to water temperature. When focusing on seasonal variation of Col-P, we found that Col-P concentration decreases when water temperature increases. Moreover, Col-P concentration increases as water temperature increases. Through the analysis of various forms of phosphate in soil and SS by using ^{31}P-NMR, along with orthophosphate, pyrophosphate, pyrophosphate ester, orthophosphate monoester were also detected. It is thus suggested that the phosphate of polymeric or organic forms other than orthophosphate are from plant origin, as a result of microbial activities and microorganism decomposition.

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