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Flow history of deep groundwater in a sedimentary basin by fluorescence EEM spectroscopy

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Recent and wider usages of deep groundwater due to increased demands for industrial water and hot spring resources require better understanding of the nature of hydrologic deep groundwater flow patterns in a sedimentary basin from the point of view of conservation of groundwater and evaluation of environmental effect as well as utilization of underground spaces such as CO_2 storage and waste disposal. Although major elements and stable isotope ratios have been employed to examine deep groundwater flows, more indices would lead to a better understanding of the groundwater flow patterns. We focused to a fluorescence excitation-emission matrix (EEM) spectroscopy, which needs only a small amount of samples, as it is highly sensitive for dissolved organic matter (DOM) with conjugated bonds at natural abundance levels. In this study, origins of DOM in groundwater samples with varying depth in the eastern Tokachi sedimentary basin were investigated with the EEM spectroscopy. EEM spectra were collected for the groundwater samples and for isolated humic acid and fulvic acid samples from the groundwater. Parallel factor analysis (PARAFAC) modeling for the corrected spectra and subsequent principal component analysis statistics of the PARAFAC data showed that they distribute within three end-members, a humic-like component originated from soil and peat, a subsurface microbial fulvic-like component and a degraded humic-like component. The difference of the DOM nature depends on origins of the aquifer, which possibly shows interaction of groundwater with surrounding rocks. This result agrees well with groundwater flow patterns in this area investigated with major elements and stable isotope ratios; thus the EEM spectroscopy combined with PARAFAC could also evaluate hydrologic behavior of deep groundwater containing DOM.

Keywords: EEM spectroscopy, sedimentary rock, groundwater flow, DOM, Humic substances