

Fractionation behaviors of Cu, Zn, and S isotopes in groundwater contaminated with petroleum and treated by oxidation

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Fractionation behaviors of Cu and Zn isotopes have been increasingly studied at the field scale, but those in various redox conditions of groundwater contaminated with petroleum and treated by oxidation have not been assessed. In this study, $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ as well as $\delta^{34}\text{S}_{\text{SO}_4}$ and $\Delta\delta^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$ were assessed in wells undergoing contamination by TPH (total petroleum hydrocarbon) and oxidation using H_2O_2 in 2021 and 2022. High $\delta^{34}\text{S}_{\text{SO}_4}$ and relevant parameters (e.g., dissolved sulfide and HCO_3^-) indicated the occurrence of sulfate reduction. The plot of $\delta^{65}\text{Cu}$ versus $\delta^{34}\text{S}_{\text{SO}_4}$ effectively indicated precipitation of Cu sulfides and their reoxidation at oxidation wells. Although the plot of $\delta^{66}\text{Zn}$ versus $\delta^{34}\text{S}_{\text{SO}_4}$ could also indicate reoxidation of Zn sulfides, the Zn isotopic fingerprint of sulfide precipitation may have been diminished by fractionation by sorption. The advantage of using $\delta^{65}\text{Cu}$ in the redox reactions resulted from the wider range of $\delta^{65}\text{Cu}$ owing to the redox behavior of Cu. Using the plot with isotopic fractionations of Cu and S will assist in assessing precipitation of sulfides and oxidative treatment in TPH-contaminated groundwater.

Acknowledgement: This research was partly supported by Korea Environmental Industry and Technology Institute (KEITI) through the project (Integrated environmental forensic approaches to trace source and pathways of subsurface contaminants) funded by Korea Ministry of Environment (MOE) (2021002440003). This research was also partly supported by the Development of Source Identification and Apportionment Methods for Toxic Substances in Marine Environments Program of the Korea Institute of Marine Science & Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries (KIMST-20220534).