Spatio-temporal variation of phosphate concentration at a high P concentration groundwater in the Hachirogata polder

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[Aim] The present study was conducted to elucidate spatio-temporal variation of phosphate (PO\textsubscript{4}) concentration and the PO\textsubscript{4} release mechanism at a high PO\textsubscript{4} concentration groundwater in the Hachirogata polder, Akita, Japan.

[Materials and Methods] The study site was at a pristine wilderness area after the land reclamation in southwest part of the Hachirogata polder. Groundwater samples were collected once a month from December 2013 to December 2014 from seven groundwater wells at a depth of 3.1, 4.3, 5.6, 6.6, 12.4, 19.5, and 45.0 m, respectively. The 30 m ($\phi$ 5 cm) boring core sample was collected from near the wells in Feb. 2013. We measured water temperature, pH, and electrical conductivity (EC) using a pH/EC meter (D-54, Horiba, Kyoto, Japan) and measured oxidation-reduction potential (ORP) using a ORP electrode (D-55, Horiba) on site. The water samples were also filtered through a 0.45 $\mu$m membrane filter on site. The concentrations of PO\textsubscript{4} in the groundwater were determined using an autoanalyzer (QuAAtro2-HR, BLTEC, Osaka, Japan). The fresh boring sediment was extracted twice with distilled water (soil:water, 1:2.5 for pH and 1:5 for EC), and pH and EC of in the extract were determined using pH/EC meter (LAQUA F-74BW, Horiba). Water soluble P were determined using an autoanalyzer (QuAAtro2-HR, BLTEC, Osaka, Japan). Sediment samples were digested with a combination of HF-HNO\textsubscript{3}-HClO\textsubscript{4} acids in Teflon beakers at 180 $^\circ$C and element concentration in solutions were determined by ICP-OES (iCAP 6000, Thermo Fisher Scientific).

[Results and Discussion] TP content in sediments increased in clay and silt layers while PO\textsubscript{4} content increased in sandy layers. This indicated that clay and silt layers were a P sink/source and released PO\textsubscript{4} was moving in sand layers. Sediment EC increased in clay layer and drastically increased from 21 m deeper layer likely influenced by sea water. Groundwater ORP showed a moderately reducing (-113 ± 42 mV) environment in all the wells. PO\textsubscript{4} concentration in groundwater was ranged from 5.7 to 18.2 mg L\textsuperscript{-1}, and the highest concentration was observed at the well of 6.6 m depth (18.2 ± 0.7 mg L\textsuperscript{-1}) at sandy layer, the second was at the well of 12.4 m depth (10.2 ± 0.9 mg L\textsuperscript{-1}). Positive correlation was observed between PO\textsubscript{4} and F\textsuperscript{-} concentrations in groundwater ($r = 0.96$, $P <0.01$, n = 7), indicated fluorapatite would be a PO\textsubscript{4} source. At the well of 6.6 m depth, Cl\textsuperscript{-} concentration was the lowest (29.8 ± 2.9 mg L\textsuperscript{-1}) value and was similar to the lake (Lake Hachiro) water (20.6 mg L\textsuperscript{-1}), suggesting that freshwater was preferentially flowing into the land through groundwater around the depth. At the well of 6.6 m depth that had little fluctuation of water qualities all year round, Na\textsuperscript{+}, bicarbonate and carbonate ion were higher but Ca\textsuperscript{2+} concentration was lower compare to other wells. At the well of 12.4 m depth that had a large fluctuation of water qualities, PO\textsubscript{4}, pH, Na\textsuperscript{+}, bicarbonate and carbonate ion, and Fe increased while Ca\textsuperscript{2+} and ORP decreased when Cl\textsuperscript{-} concentration decreased from 72 to 33 mg L\textsuperscript{-1} during May to Oct. 2014. These phenomena indicated PO\textsubscript{4} release induced likely by Na-saturated sediment might be due to release of P associated with oxide surfaces or to dissolution Ca-P at clay layer by increasing pH and dissolution of CaCO\textsubscript{3} (from shell) by inflowing freshwater to the groundwater.

Keywords: phosphate, groundwater, polder, Na saturation, freshwater