

Shift in phosphorus cycles coupled to iron- and sulfate reduction in the sediments separated by large-scale dyke in the Yeongsan River estuary, Yellow Sea

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In Korea, to ensure the demand for freshwater for agriculture and industry, over 18,000 dams, dykes and weirs have been constructed during the last four decades. To elucidate the changes and controls of Fe, S and P cycles associated with major organic carbon (C_{org}) oxidation pathways, we investigated sediment geochemistry, iron- and sulfate reduction rate and benthic P release, together with the P-speciation at both limnetic and estuarine sections separated by the dyke in the Yeongsan River estuary in the Yellow Sea. At both sections, the sediments near the dyke were characterized by highly reduced condition and high organic carbon content (1.4–1.7%, dry wt.). The limnetic sediments were characterized by high CH_4 accumulation, whereas the C_{org} oxidation in estuarine sediments near the dyke was dominated by the sulfate- ($47.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$) and iron reduction ($13.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$), comprising 68 % and 19 % of total C_{org} oxidation, respectively. In the limnetic sediment (St. YL), most of the P were bound to Fe and Al, comprising respectively 43 % and 37 % of total P in sediment, and only small amounts of the P ($0.03 \text{ mmol m}^{-2} \text{ d}^{-1}$) were released to the overlying water column. In contrast, in the estuarine sediment (St. YE1), H_2S derived from high SO_4^{2-} reduction quickly reacts with $FeOOH$ to form Fe-sulfides ($3H_2S + 2FeOOH \rightarrow FeS + S^0 + 4H_2O$), which ultimately releases the P into the pore-water. Furthermore, high Fe(III) reduction (i.e., $CH_2O + 4FeOOH + 8H^+ \rightarrow CO_2 + 4Fe^{2+} + 7H_2O$) may stimulate the dissolution of Fe(III) bound P, which enhances the release of P into the pore-water. Consequently, the enhanced mobility of P in the estuarine sediments stimulated the benthic P release ($0.24 \text{ mmol m}^{-2} \text{ d}^{-1}$) into bottom water. Overall results indicated that the construction of dyke that enhances the retention time of the river water in the freshwater reservoir plays a significant role inducing P sink (i.e., adsorption of P) in the limnetic sediment. Therefore, the slow discharge of the relatively P-depleted fresh water may deepen the P-limiting condition for primary production in estuarine ecosystem. In such condition, benthic P release from the sediment, rather than the riverine supply, play a significant internal source of P in estuarine ecosystem.