

Can Superoxide Nanobubbles Inhibit the Release of Phosphorus from Reservoir with Stagnant Water?

*Qingqing Sun¹, Siliang Li¹, Jingfu Wang², Pingping Yu³

1. Institute of Surface-Earth System Science, Tianjin University, 2. State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 3. Zunyi City Drainage Limited Liability Company

Natural mineral materials (a) Calcined Organobentonite (450°C, 9.5h), (b) Organobentonite, sieving 2000 mesh, (c) Kaolinite, sieving 6000 mesh, (d) Talc Powder, sieving 5000 mesh, (f) Sericite, sieving 3000 mesh, (g) Silicone microbeads, sieving 3000 mesh, (h) biological material, Calcined Oyster Powder were firstly selected as nanobubble carriers. Then methanol, ultrapure water, and oxygen were used to generate nanobubbles. The miniature devices were used to simulate the inhibiting effect of the above agents on the sediment-water interface, and were 40 cm high, with an outer diameter of 6.5 cm. The sediment inside the simulators was 6 cm high and the lake water was 28 cm high. The sediment was collected from the front of the Dam of Hongfeng Lake. The nanobubble inactivation agents were added to the simulators and precipitated for 24 hours to form stable sediment-water interfaces as the experimental group, which was monitored continuously for 30 days and a control group (without any inactivation agents) was synchronously monitored. PO_4^{3-} -P concentrations were measured in the 21 out of 30 days. Fe^{2+} , NO_2^- -N, NH_4^+ -N contents were measured during the first 7 days. Oxidation-Reduction Potential (ORP), dissolved oxygen (DO), pH and water temperature were also measured. V, Cr, As, Se, Mo, Sb, W, Cu, Cd, Co, Ni, Pb, Zn, P, Mn and Fe in overlying water, pore water, and sediment only were monitored twice in primary sediment cores on the 0 day (without inactivation agents) and the final ones on the 30th day (with inactivation agents). Combined with the changes in phosphorus and heavy metal morphology in sediment before and after the simulation experiments, these experimental results show that (f) sericite has a better effect. Constrained by the small-scale of the exploratory simulation experiment, larger simulation experiments need to be conducted, and more demonstration work with new efficient materials and preparation methods need to be applied to the actual lake management.

Hongfeng Lake Reservoir (E106°20'10"~106°27'00", N26°24'37"~26°34'17"), a river-type and Phosphorus(P) limited reservoir in canyon rift basin, was built in 1960. Due to the domestic, industrial and agricultural pollution being discharged into the reservoir from 1988 to 2009, especially phosphogypsum piled up of phosphate fertilizer industry, environmental pollution incidents occurred frequently: dead fish incident in cages in 1994 and 1998, periodic black water in 1995, high arsenic pyrite acid wastewater pollution and blue-green algae eruption in 1996, *Aphanizomenon* bloom in 1998, and multiple algae outbreaks in 2006, 2007 and 2008. As a source of drinking water in Guiyang City, China, although exogenous pollution is well controlled and water quality is improving in the last decade, there is still a risk of secondary release. Refer to previous studies, the two-end member mixing model of $\delta^{18}\text{O}_p$, the diffusive models of the diffusive gradient in thin films (DGT) technique and the sediment core incubation method, the relative contribution of internal P released from sediments even reached 35.7%~59%. The main P forms of surface sediment also changed from organic P and Fe-P (80%~88%) to NaOH-P (Fe, Al-P) and Rest-P (67%~77%). According to the Bayesian modeling of $\delta^{18}\text{O}$ - NO_3 and $\delta^{15}\text{N}$ - NO_3 , the relative contribution of endogenous modified nitrogen (N) source (denitrification) released from sediments reached 24~38%. Especially in the stratification period (from March to August), the bottom water is anaerobic, and the release fluxes from the sediment are higher. The degradation of organic N and denitrification are closely related to the early mineralization of P. The above facts highlight the influence of the internal P and N on water eutrophication and the necessity to control the internal P pollution. Due

to the discharge of acidic coal mine wastewater near the reservoir, the release fluxes of heavy metals also cause concern, especially for geochemical cycles in which these elements are coupled with P. On 24 July 2019, sediment cores from the center of the north lake (A), Dam(B), Huayudong(C), water-intake of Xijiao Water Plant (D), Houwu(E) and hydro-fluctuation belt(F) in the shore near Xijiao Water Plant were collected. The P(V), $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$, and mean Fe(II), Mn(II), Zn(II), Pb(II), As (V) fluxes were $(0.041\sim0.136) \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, $(0.39\sim8.98) \times 10^{-3} \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, $(0.046\sim5.10) \times 10^{-3} \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, $2.20 \times 10^{-3} \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, $3.67 \times 10^{-4} \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, $3.04 \times 10^{-5} \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, $2.04 \times 10^{-5} \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, $4.53 \times 10^{-6} \text{ cm}^{-2}\cdot\text{s}^{-1}$ in sediment-water interfaces respectively, and monitored by DGT.

Keywords: superoxide Nanobubbles, phosphorus, diffusive gradient in thin-films technique, sediment-water interface