

Phosphorus Retention Linked to Vivianite in Hamilton Harbour, Lake Ontario

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Sediments critically regulate phosphorus (P) availability in the water column. Legacy P in sediments can be released to water column, contributing to eutrophication, which has significant economic and public health issue on a worldwide scale. Sediment can also serve as a long-term sink that permanently sequestering P. Thermodynamic analyses indicate vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), a stable iron-phosphate mineral, forms preferentially in anaerobic sediments as a permanent P sink. However, the extent of vivianite contribution to P retention in freshwater systems remains poorly quantified.

To address this, Hamilton Harbour (HH), a eutrophic and anthropogenically impacted site in Lake Ontario, was studied. Sediment cores were collected in July and October 2023 and August 2024 using a UWITEC gravity corer. Porewater and sediment were analyzed for soluble reactive phosphorus (SRP), phosphorus-binding forms, methane (CH_4) concentrations, isotopic ($\delta^{13}\text{C}-\text{CH}_4$) composition, and microbial community structure. Vivianite was extracted from sediments via density separation and confirmed through X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). The redox-sensitive P fraction (BD-P) dominated total sediment P, increasing from 36% at the surface to 50% in deeper layers at station HH1001. Vivianite accounted for around 20% of total sediment P, highlighting its role as a stable sink. Vivianite formation in deep sediment was confirmed by XRD. CH_4 concentrations peaked at 906.9 μM at 24 cm depth in August 2024 but decreased sharply below this depth. Concurrently, $\delta^{13}\text{C}-\text{CH}_4$ values exhibited isotopic enrichment, shifting from -73.1‰ to -69.9‰ between 24 and 28 cm, a pattern consistent with microbial CH_4 oxidation. Vivianite formation can reduce P bioavailability, potentially mitigating eutrophication by limiting P release into water columns. These findings underscore the role of vivianite in P sequestration and provide a new prospective of Fe capacity to regulate P retention in freshwater sediments.