



Development and initial application of $\delta^{18}\text{O}_p$ to understand phosphorus cycling in river, lake and groundwater ecosystems

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Variation in the stable isotope composition of oxygen within dissolved phosphate ($\delta^{18}\text{O}_p$) represents a novel and potentially powerful environmental tracer. In freshwater, marine and terrestrial ecosystems, $\delta^{18}\text{O}_p$ can act as an inherent label for the sources of phosphorus and the extent to which phosphorus from different sources is metabolised. This paper focuses on the methodological development and initial application of $\delta^{18}\text{O}_p$ across a range of freshwater ecosystems. Initially, we report modifications to the analytical protocol for $\delta^{18}\text{O}_p$ that are designed to minimise incorporation of contaminant oxygen in the final silver phosphate precipitate prior to pyrolysis. This is critical given the range of possible sources of contaminant oxygen within freshwater matrices. Subsequently, we consider the potential utility of $\delta^{18}\text{O}_p$ through application of the technique within a range of freshwater ecosystems in England, UK. Firstly, we characterise $\delta^{18}\text{O}_p$ in river water and effluents from Sewage Treatment Works (STW), and examine the opportunity to use the $\delta^{18}\text{O}_p$ of STW effluents to trace the entry and downstream fate of phosphorus from these point sources in rivers. Secondly, we analyse $\delta^{18}\text{O}_p$ to gain insights into variations in the sources and biological cycling of phosphorus in a seasonally-stratified lake ecosystem. Thirdly, we characterise $\delta^{18}\text{O}_p$ in shallow and deep groundwater samples, considering whether $\delta^{18}\text{O}_p$ might provide evidence for variation in source and extent of metabolism for phosphorus in groundwater ecosystems. Taken together, these data extend the catalogue of $\delta^{18}\text{O}_p$ in freshwater ecosystems, and further the scope of $\delta^{18}\text{O}_p$ as a tool to better understand phosphorus biogeochemistry.