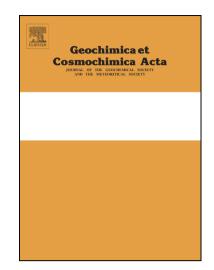
### Accepted Manuscript

Seasonality of Major Redox Constituents in a Shallow Subterranean Estuary

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## **ACCEPTED MANUSCRIPT**

#### Seasonality of Major Redox Constituents in a Shallow Subterranean Estuary

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#### Abstract

The subterranean estuary (STE), the subsurface mixing zone of outflowing fresh groundwater and infiltrating seawater, is an area of extensive geochemical reactions that determine the composition of groundwater that flows into coastal environments. This study examined the porewater composition of a shallow STE (<5 m depth) in Gloucester Point, VA (USA) over two years to determine seasonal variations in dissolved organic carbon (DOC) and the reduced metabolites Fe, Mn, and sulfide. An additional aim of this study was to investigate the relative importance of salinity gradients (which have great geochemical influence in surface estuaries) versus redox gradients on STE geochemistry. Two freshwater endmembers were identified, between which redox potential and composition varied with depth — a shallow freshwater endmember was oxidizing and high in DOC, whereas a deep freshwater endmember was reducing, lower in DOC, and high in sulfide. Results showed that dissolved Fe, Mn, and sulfide varied along a redox gradient distinct from the salinity gradient, and that threeendmember mixing was required to quantify non-conservative chemical addition/removal in the STE. In addition to salinity, humic carbon was used as a quasi-conservative tracer to quantify mixing according to a three-endmember model. The vertical distributions of DOC and reduced metabolites remained approximately constant over time, but concentrations varied with season.

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