

Introduction

Progress has been made in quantifying major terms in the carbon budget of the coastal ocean but gaps remain in quantifying carbon fluxes at key interfaces such as the marsh-estuary interface. Exchange of carbon at this interface remains one of the least-constrained fluxes in carbon budgets for tidal wetlands and the coastal margin. This study measured concentrations of dissolved and particulate pools of carbon (POC, DOC and DIC) concurrently over a range of timescales. Sources of particulate organic carbon (POC) were further evaluated using stable isotopes and lipid biomarker composition. **The specific objectives of this project were to:**

1. Measure concentrations of POC, DOC and DIC over tidal, monthly and seasonal timescales.
2. Use stable carbon isotope values ($\delta^{13}\text{C}$), chlorophyll-a and lipid biomarker composition to understand the sources of POC at the marsh-estuary interface.
3. Use structural equation modeling (SEM) to examine the effects of physical and biological processes on [POC].

Study Sites

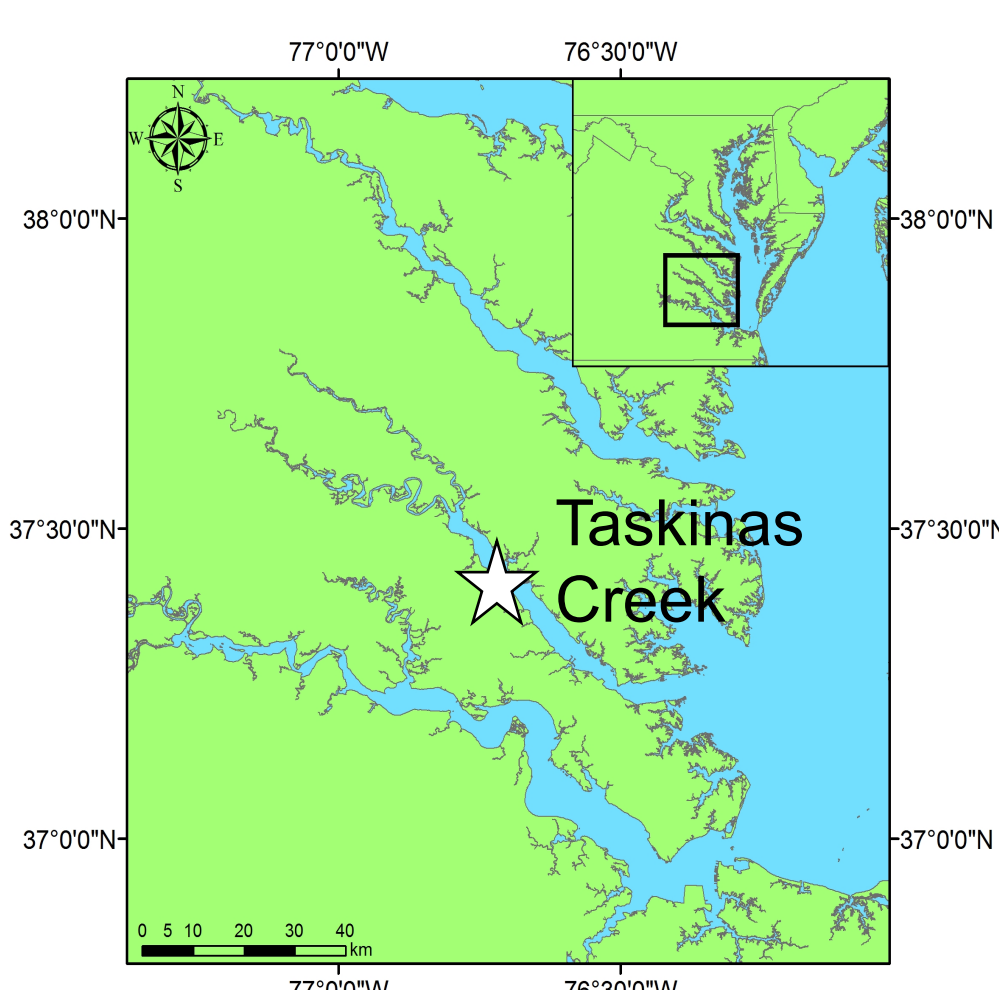


Figure 1. POC, DOC and DIC were measured over a tidal cycle on a monthly basis at Taskinas Creek (TC, white star), located along the York River, a sub-estuary of Chesapeake Bay in VA. Long-term water quality and meteorological data are available for TC through the Chesapeake Bay National Estuarine Research Reserve (CBNERR). Lipid biomarker composition of POC was evaluated at high vs. low tide at the Kirkpatrick Marsh and TC, representing two temperate marshes in the Chesapeake Bay (photos below).



Kirkpatrick Marsh (GCREW)
Rhode River MD



Taskinas Creek
York River VA

Methodology

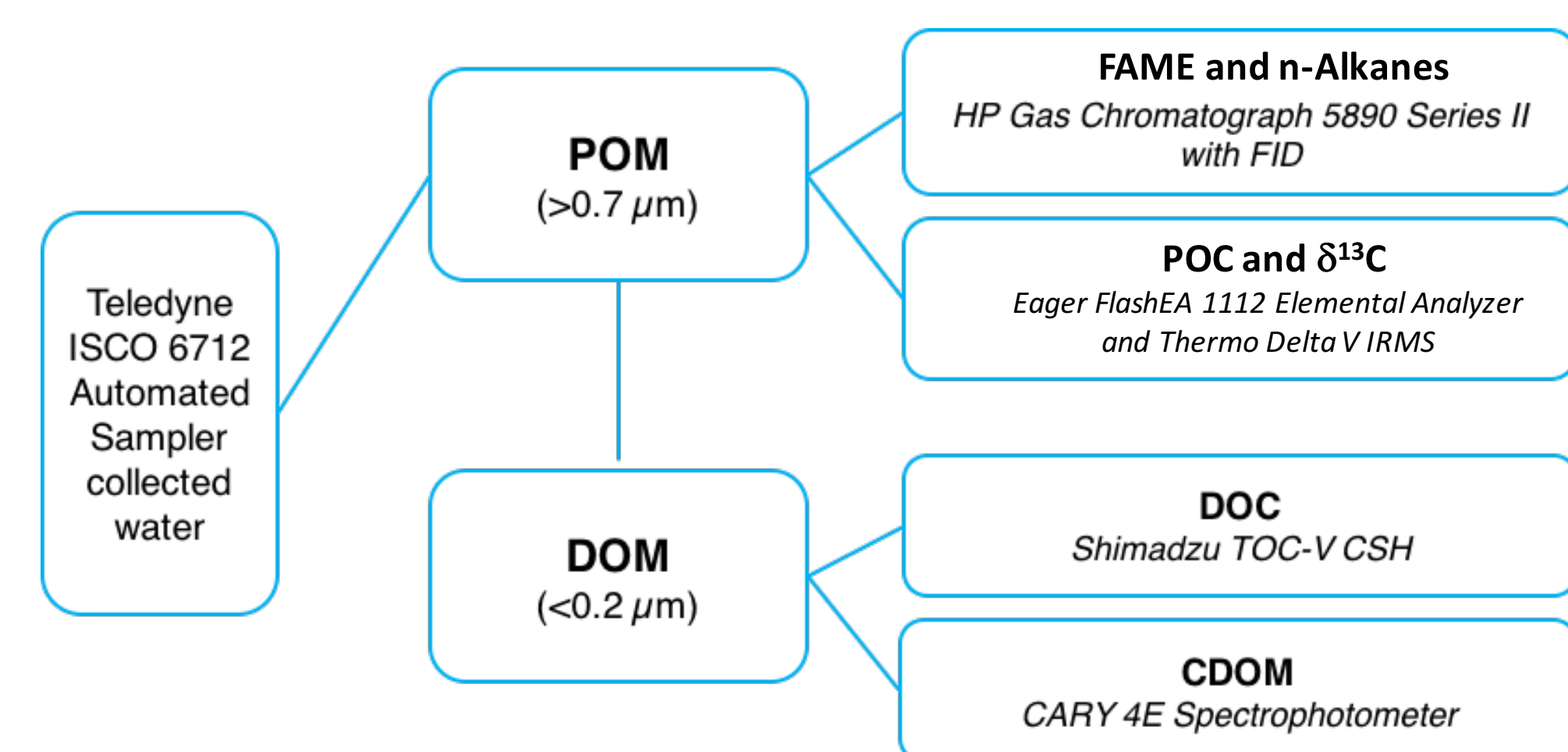


Figure 2. Water samples were collected from TC every 2.5 hours over a 25-hour tidal cycle on a monthly basis and separated into particulate and dissolved organic matter (POM and DOM) by filtration. Samples were analyzed for POC, DOC and DIC concentration. Sources of POM were assessed using $\delta^{13}\text{C}$, C:N ratio and chlorophyll a. Large volume samples were collected concurrently at high and low tide and analyzed for lipid biomarker composition to provide additional information about POM sources.

Acknowledgements

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Carbon Concentration

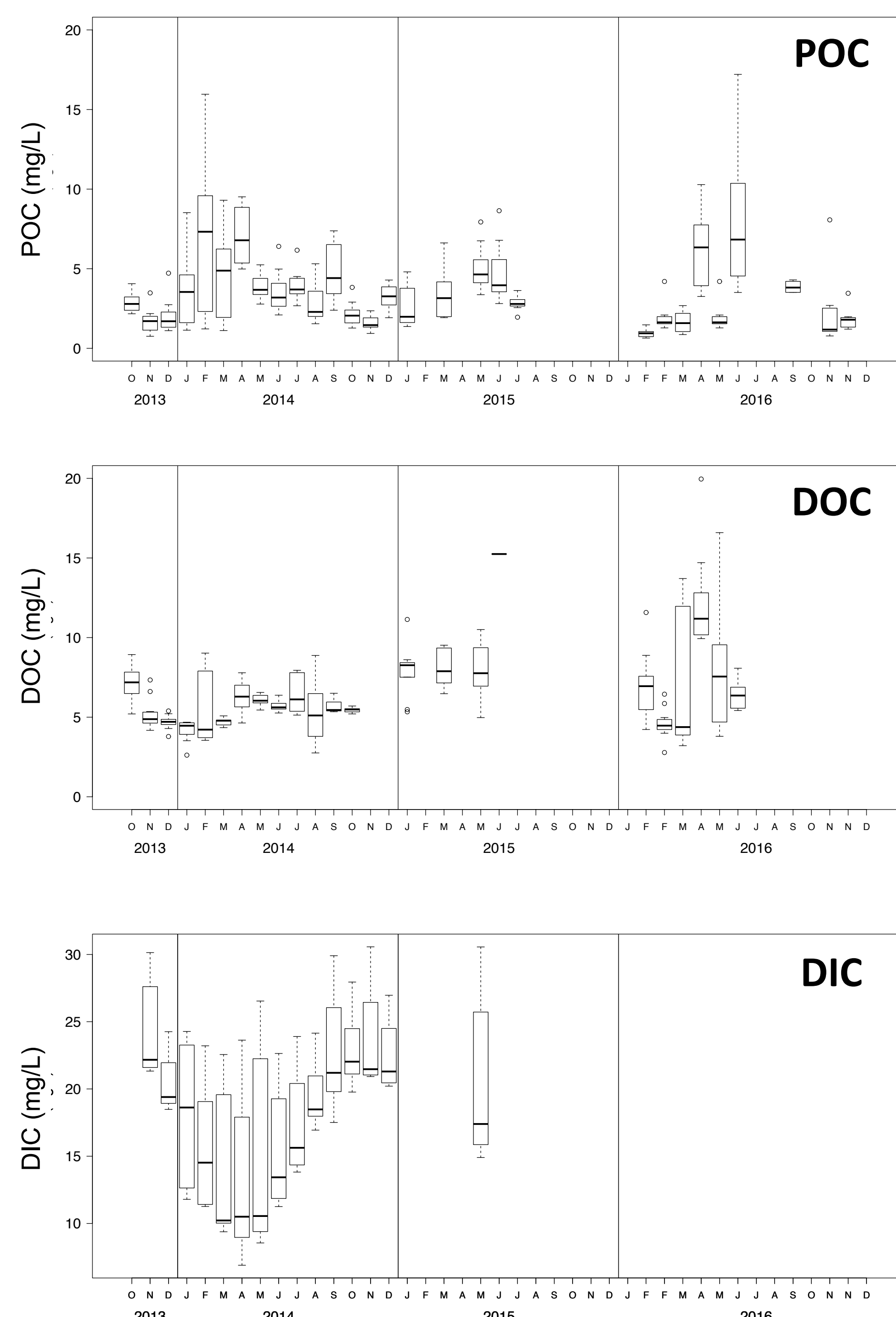


Figure 3. Boxplots showing concentrations of POC, DOC, and DIC collected over a 25-hour tidal cycle at Taskinas Creek VA between 2013-2016. POC and DIC varied seasonally with higher concentrations of POC during Spring and Summer ($p < 0.05$) and higher concentrations of DIC during Fall ($p < 0.05$). Samples collected at low tide had higher concentrations of DIC ($p < 0.05$) suggesting the marsh was a source of DIC. POC concentrations were higher during high tide and rising tide than during low tide ($p < 0.05$) suggesting that the estuary was a source for POC. Overall, concentrations of all carbon pools were highly variable over the tidal cycle and tidal variability was often comparable to, or greater than, seasonal variability.

POC Bulk Composition

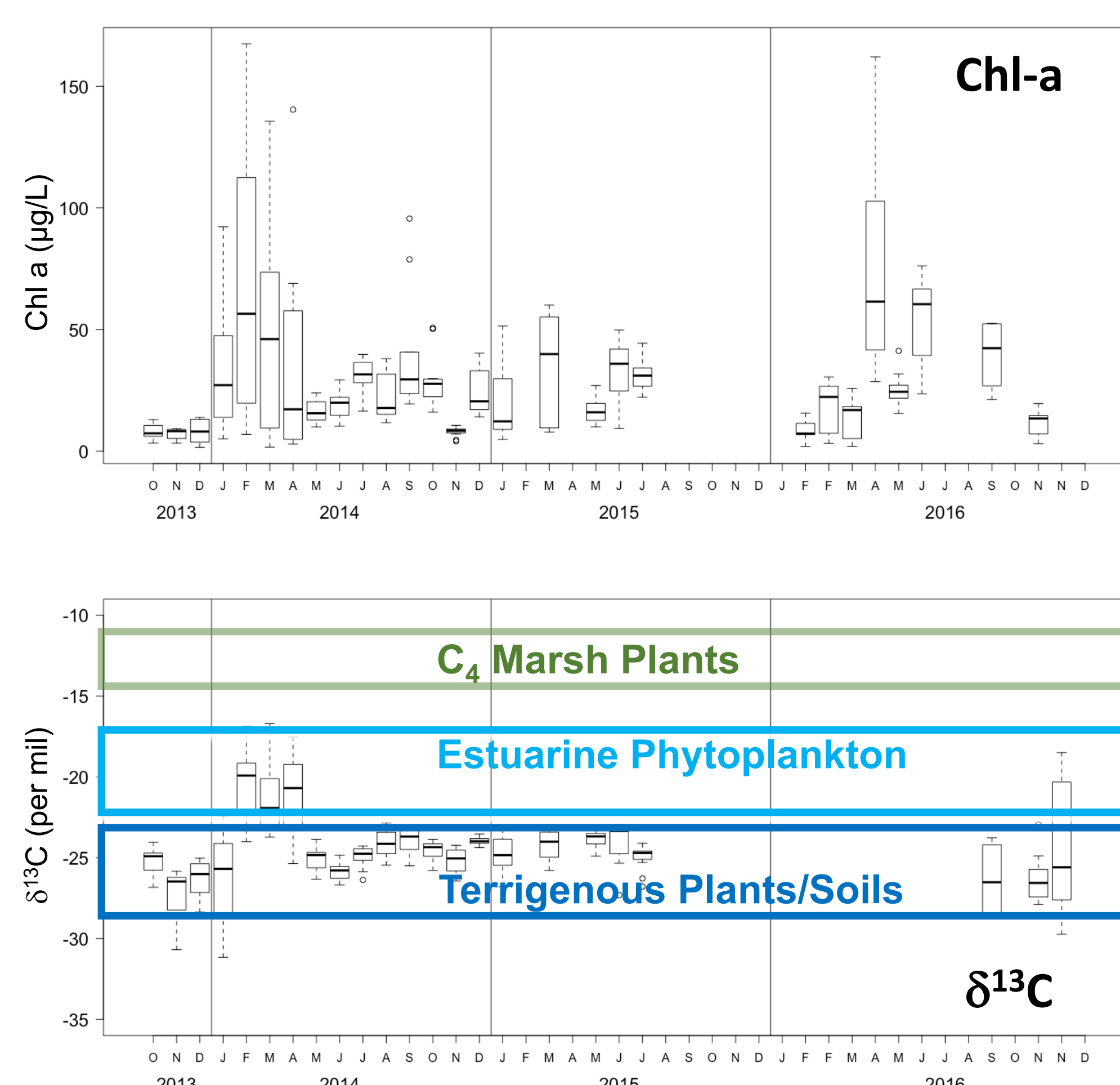


Figure 4. Boxplots showing concentrations of chlorophyll a and $\delta^{13}\text{C}$ values for POC collected over the 25-hour tidal studies at Taskinas Creek VA. Typical ranges of $\delta^{13}\text{C}$ values for C4 marsh plants, estuarine phytoplankton, and terrigenous plants/soils are provided in the colored boxes. Overall, $\delta^{13}\text{C}$ values resemble POC in the adjacent York River Estuary with estuarine phytoplankton dominating during spring and mixed sources at other times of the year. $\delta^{13}\text{C}$ values were highest during spring ($p < 0.05$) when chl a concentrations were highest. Concentrations of chl-a were higher during spring and summer (vs. fall and winter, $p < 0.005$). Like POC, chl a concentrations were lowest at low tide ($p < 0.0005$), suggesting that the York River was the primary source of phytoplankton.

Lipid Biomarker Composition of POC

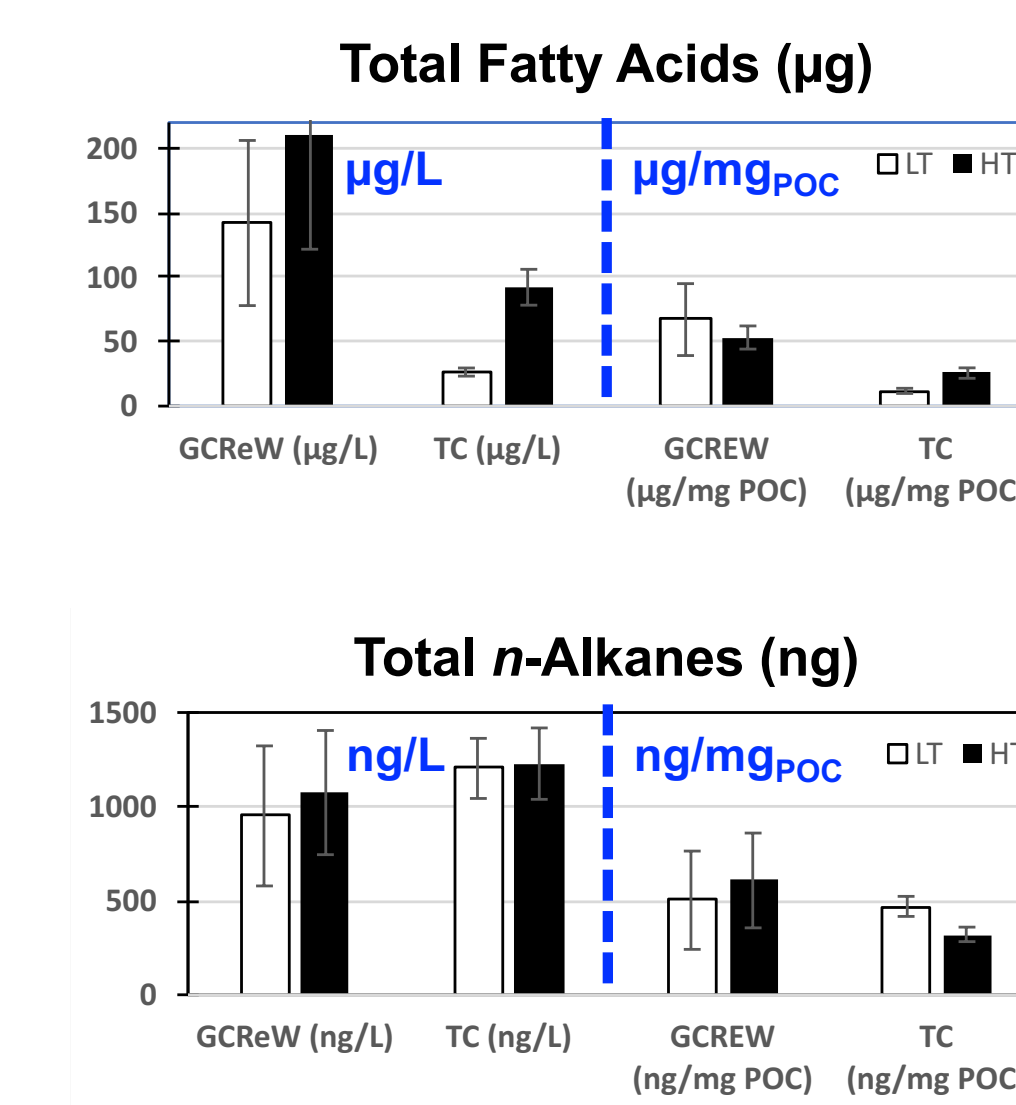


Figure 5. Two classes of lipid biomarker compounds were analyzed to compare the source composition of POM collected during low (LT) and high tide (HT) at the Kirkpatrick Marsh (GCREW) and Taskinas Creek (TC). Fatty acids (FA) and *n*-alkanes represent organic matter of different reactivities (FA=higher reactivity; *n*-alkanes=lower reactivity). Overall, FA concentrations at both marshes were higher than *n*-alkanes suggesting that POM was relatively labile. These lipid classes had similar concentrations at LT and HT.

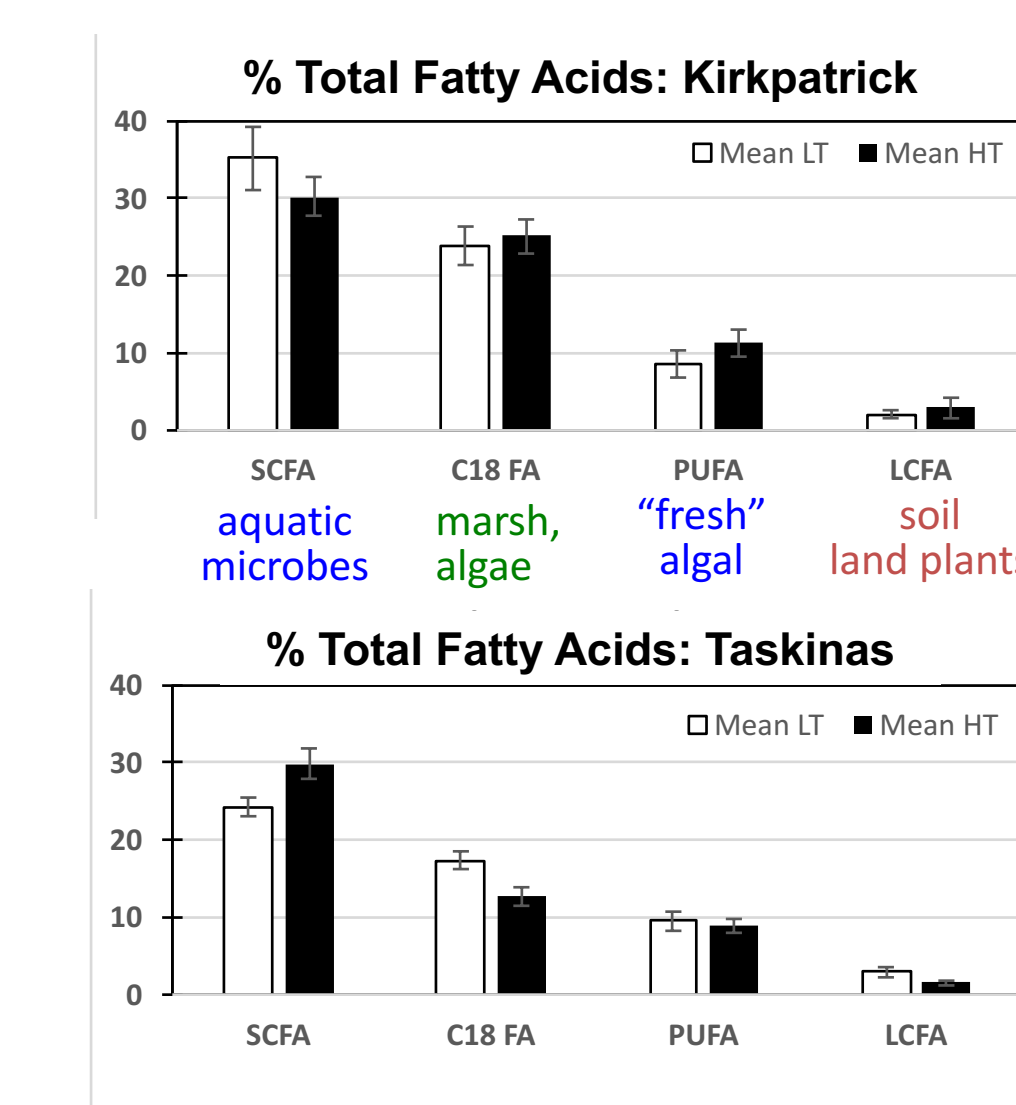


Figure 6. At both marshes, POM was dominated by short-chain fatty acids (SCFA) from aquatic microbial sources and C₁₈ fatty acids from marsh plants and microalgae. Overall, FA composition was similar at HT and LT but C₁₈ FA were more abundant at low tide at Taskinas Creek in VA ($p < 0.05$).

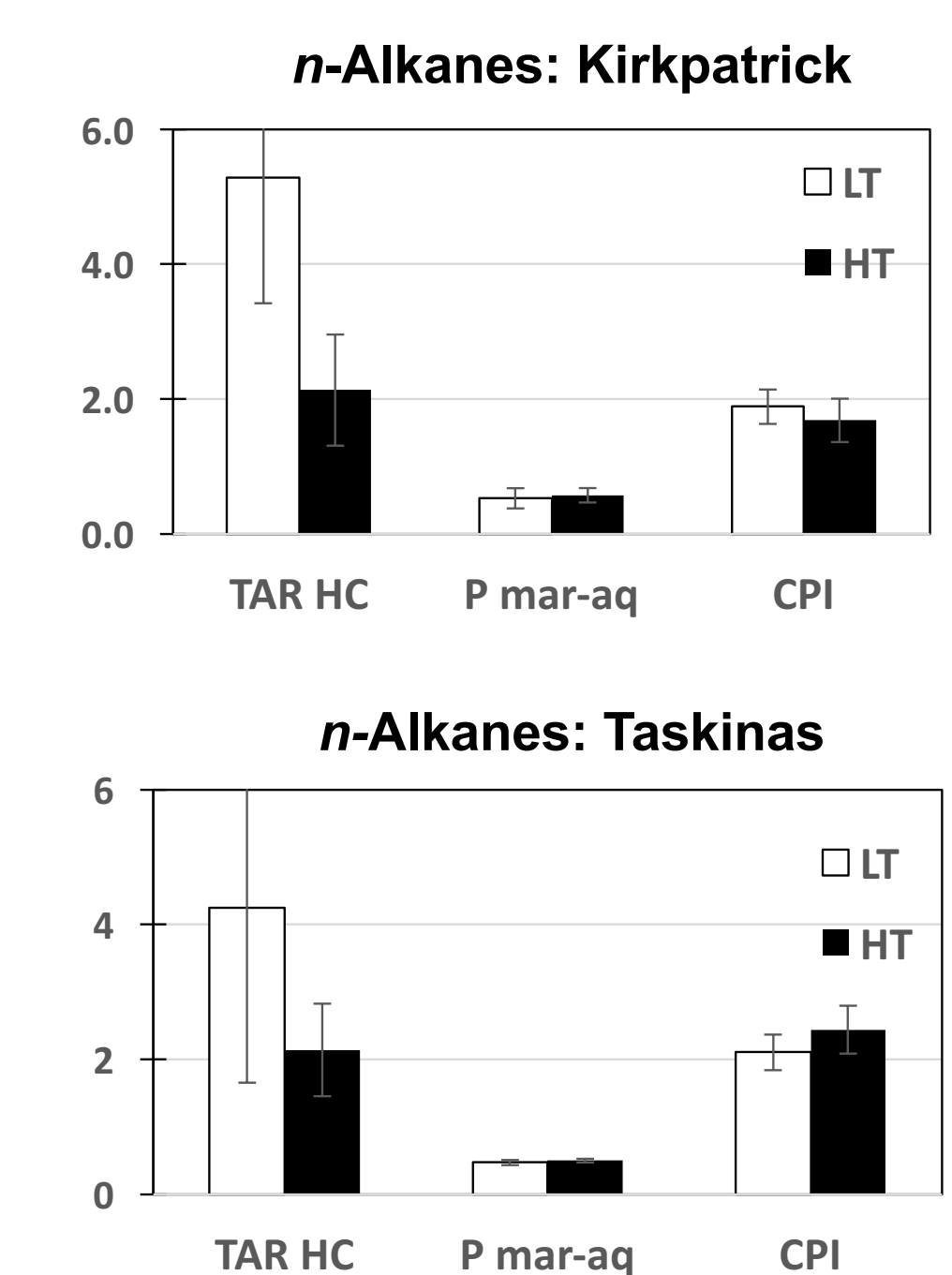


Figure 7. *n*-Alkanes associated with POM at both marshes are consistent with higher plant sources. This is reflected in terrestrial to aquatic ratios (TAR HC) > 1 , $P_{\text{mar-aq}}$ values consistent with emergent plants (0.4 to 0.6) and Carbon Preference Index (CPI) values ~ 2 .

Together higher concentrations of fatty acids relative to *n*-alkanes and the high proportion of fatty acids from aquatic sources, suggest that POC is predominantly derived from estuarine sources. Higher concentrations of POC during high/rising tide (Fig. 3) are consistent with these marshes acting as a sink for POC.

Structural Equation Model (SEM) for POM

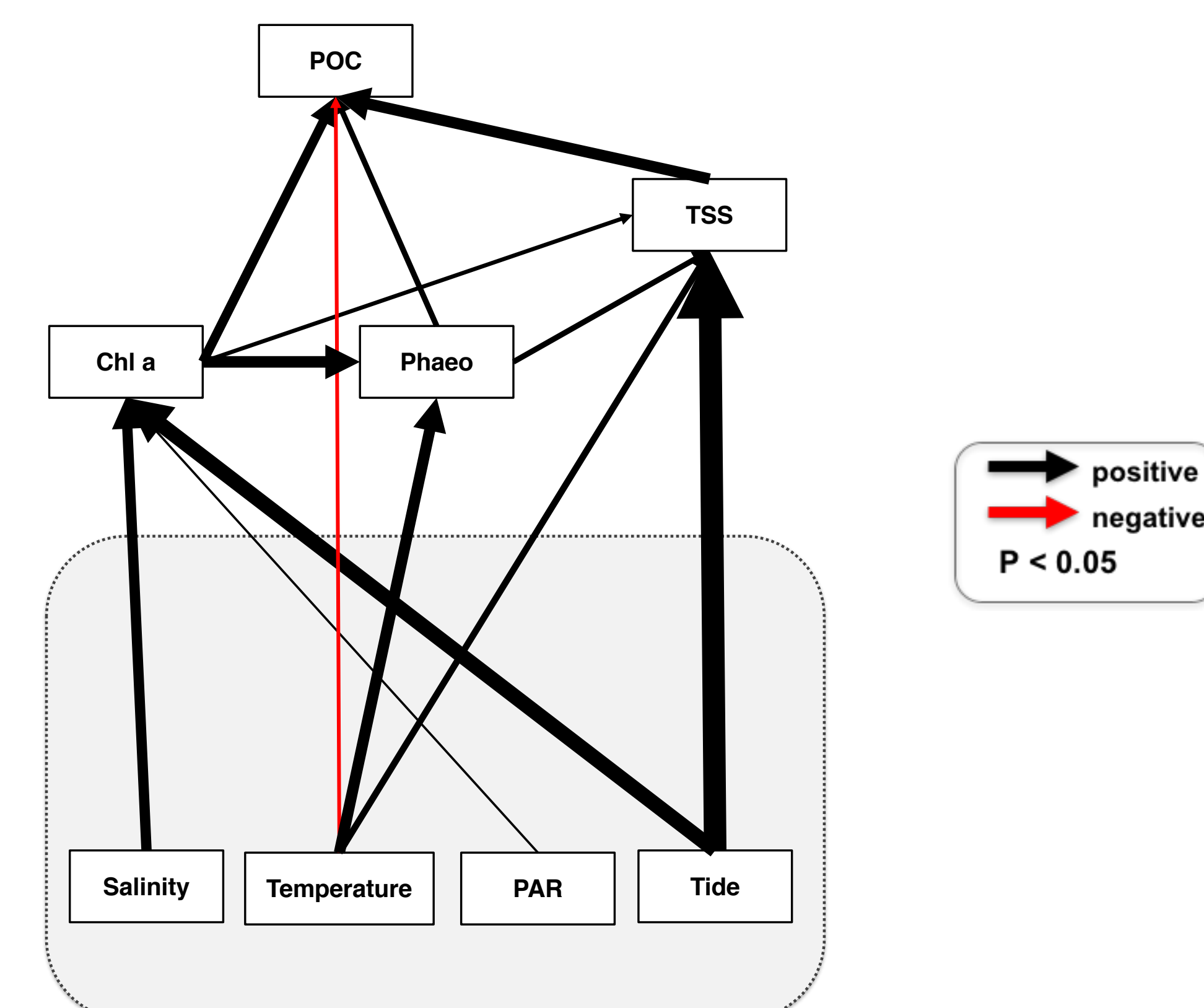


Figure 8. We used structural equation modeling (SEM) to identify the key drivers of POC concentration at Taskinas Creek. This approach illustrates that [POC] is influenced positively (black arrows) and directly by concentrations of total suspended solids (TSS), chlorophyll a and phaeopigments. There was a small negative effect of temperature on [POC] (red arrow), possibly reflecting the influence of the phytoplankton bloom in colder months February/March. [POC] was also influenced indirectly by tide, which had a positive direct effect on TSS and chlorophyll a concentrations.