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Tidal Freshwater Zones as Hotspots for Biogeochemical Cycling: Sediment Organic Matter Decomposition in the Lower Reaches of Two South Texas Rivers

Xin Xu[1] · Hengchen Wei[1] · Grayson Barker[1,2] · Kylie Holt[1] · Spyder Julian[1] · Tricia Light[1,3] · Sierra Melton[1,4] · Ana Salamanca[1,5] · Kevan B. Moffett[6] · James W. McClelland[1] · Amber K. Hardison[7]

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Abstract

While organic and inorganic nutrient inputs from land are recognized as a major driver of primary production in estuaries, remarkably little is known about how processes within the tidal freshwater zones (TFZs) of rivers modify these inputs. This study quantifies organic matter (OM) decomposition rates in surface sediment layers in the lower reaches of two south Texas river channels and identifies key parameters that influence sediment decomposition rates. Sediment cores were collected from non-tidal and tidal freshwater sites in the Mission and Aransas rivers during two summers (June 2015 and June 2016) and two winters (February 2016, January 2017). We measured oxygen consumption rates, organic carbon and nitrogen content, stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$ of OM), and sediment porosity. O_2 consumption rates in TFZ sediments were 385 ± 88 μmol O_2 m^{-2} h^{-1} (summer) and 349 ± 87 μmol O_2 m^{-2} h^{-1} (winter) in the Aransas River and 767 ± 153 μmol O_2 m^{-2} h^{-1} (summer) and 691 ± 95 μmol O_2 m^{-2} h^{-1} (winter) in the Mission River. These rates in TFZs were similar to rates in estuaries and higher than rates at non-tidal riverine sites. Rates of sediment O_2 consumption were primarily controlled by OM content and temperature. Sediment OM was dominated by algal biomass from in situ production in both TFZs. We hypothesize that algal production and sinking within TFZs is a major pathway for translocation of watershed-derived nutrients from the water column to the sediments within TFZs. Further work is needed to quantify linkages between decomposition, nutrient remineralization, and potential removal through processes such as denitrification.

Keywords Tidal freshwater zone · Organic matter decomposition · Oxygen consumption · Diffusive oxygen uptake

Introduction

While rivers are recognized as important conduits for the transport of organic and inorganic nutrients from watersheds to estuaries, processes occurring within river networks can substantially alter the forms and quantities of watershed-derived nutrients that are delivered to estuaries. Nutrient dynamics in stream networks have been studied intensively since the 1980s, following the emergence of the concepts of nutrient spiraling (Newbold et al. 1982; Newbold 1992) and the river continuum (Vannote et al. 1980). Early work emphasized inorganic nutrients such as nitrogen (N) and phosphorus (P), but river networks have been increasingly recognized as globally significant sites of organic matter (OM) processing and removal as well (Cole et al. 2007). However, tidal freshwater zones (TFZs) in rivers, bounded by the inland extent of salinity intrusion at their downstream end and by tidal influence on water stage at their upstream end (Jones et al. 2017, 2020), have received much less

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✉ Amber K. Hardison
akhardison@vims.edu

[1] University of Texas at Austin Marine Science Institute, 750 Channel View Dr, Port Aransas, TX, USA

[2] Appalachian State University, Boone, NC, USA

[3] Scripps College, Claremont, CA, USA

[4] Colorado College, Colorado Springs, CO, USA

[5] Texas A&M University – Corpus Christi, Corpus Christi, TX, USA

[6] Washington State University Vancouver, Vancouver, WA, USA

[7] Virginia Institute of Marine Science, College of William & Mary, Gloucester Point, VA, USA

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attention in terms of their function in transforming OM and inorganic nutrients.

Conditions within TFZs are often lentic, with slow or even reverse flow that is conducive to extended water residence times (Jones et al. 2017, 2020). This makes it possible for TFZs to have distinct biogeochemical features compared to faster-flowing, unidirectional upstream reaches of rivers, such as greater phytoplankton production and higher rates of particulate OM (POM) deposition to the sediment surface. For example, chlorophyll *a* concentration increased from nearly zero in the non-tidal river to 2–12 μg L^{-1} at the beginning of the tidal freshwater reach of the Hudson River (Lampman et al. 1999). Thus, TFZs may be hotspots for biogeochemical processing within the river continuum that may exert a particularly strong influence on nutrient/OM loadings to estuaries.

Previous studies have reported inorganic N and P retention by primary producers in TFZs of the Hudson River, New York, USA (Lampman et al. 1999); Rio de la Plata River, South America (Nagy et al. 2002); and James River, Virginia, USA (Bukaveckas and Isenberg 2013). While long residence times in TFZs can promote phytoplankton growth and thus retain inorganic nutrients as biomass (Bukaveckas and Isenberg 2013), some TFZs have high turbidity and allochthonous OM input that facilitate more OM remineralization than production, such as in the Hudson River TFZ (Cole et al. 1992; Findlay et al. 1991; Howarth et al. 1996). In addition, anthropogenic impacts play an important role in changing biogeochemical processes in TFZs. For example, increasing OM input from agricultural lands over the past century drove the Hudson River TFZ from a net autotrophic to a net heterotrophic state, and the trend was interrupted by the introduction of invasive zebra mussels in the 1990s (Howarth et al. 1996). In recent years, upstream nutrient load reductions have limited phytoplankton growth in some TFZs (e.g. Mattawoman Creek, Maryland, USA, Boynton et al. 2014; James River, Virginia, USA, Wood and Bukaveckas 2014).

Despite their prevalence and potential importance in modifying nutrient transport from land to sea, relatively few studies have investigated benthic OM processing and inorganic nutrient dynamics in TFZs. High rates of POM deposition to sediments in TFZs due to long residence times may fuel a productive benthic community and high levels of OM decomposition. Sediments are critical zones of OM cycling, including recycling and removal of carbon and nutrients (Burdige 2007). This paper focuses on aerobic OM decomposition rates in surface sediments and associated sediment characteristics in the TFZs of two rivers (Mission and Aransas) in south Texas, USA. We hypothesized that (1) OM decomposition rates within the TFZ sediments would vary as a function of sediment OM quantity and quality, and (2) TFZ-wide removal of OM due to aerobic decomposition would be enhanced compared to upstream river reaches due to the TFZs' long residence times and would be sufficient to substantially modify watershed-to-estuary OM transport.

Methods

Study Area

The Mission River (MR) and the Aransas River (AR) are adjacent rivers in south Texas (Fig. 1). These rivers provide the majority of freshwater inflow to Copano Bay (Evans et al. 2012; Mooney and McClelland 2012). They are located in a sub-humid to semi-arid subtropical climate that exhibits highly variable precipitation (Fulbright et al. 1990). As a consequence, the flow regimes of the MR and AR are characterized by low baseflow with occasional stormflow pulses. During the study period (June 2015 – February 2017), daily mean flow rates of the MR (USGS gage 08189500, Mission River at Refugio, TX) ranged from 0.03 to 104.49 m^3s^{-1}, with an overall mean flow rate of 1.70 m^3s^{-1} and median of 0.20 m^3s^{-1}. Daily mean flow rates of the AR (USGS gage 08189700, Aransas River near Skidmore, TX) ranged from 0.06 to 17.44 m^3s^{-1}, with an overall mean flow rate of 0.37 m^3s^{-1} and median of 0.16 m^3s^{-1}. The combination of climate, hydrology, and tides in the study area is conducive to the existence of extended TFZs (Jones et al. 2017). In addition, neither of these rivers is dammed, maintaining a natural flow regime. Previous studies found that water residence times in the tidal reaches of these two rivers can be several months during the low-flow period (Johnson 2009; Mooney and McClelland 2012). During and shortly after occasional storm events, the entire TFZ disappears and is converted to a fast-flowing river (Jones et al. 2017). With this in mind, all four sampling trips for this study were conducted under baseflow conditions when discharge in the TFZs was slowed by tidal forces. Mean flow rates at the river gages on the sampling dates were 0.33 ± 0.13 m^3 s^{-1} in the AR and 0.73 ± 0.53 m^3 s^{-1} in the MR. The salinity of bottom water at all of our TFZ sites was below 1.5 during the duration of the study.

The MR and AR watersheds are similar in size (MR 2675 km^2 and AR 2146 km^2) but differ in land use (Fig. 1) and anthropogenic impact on water flow and quality. The MR watershed mainly consists of shrub and grassland and contains three municipal wastewater treatment plants (WWTPs) with a combined discharge of 1.9 million L per day (mld). In contrast, a large proportion of the AR watershed is covered with cultivated crops and contains 10 WWTPs, which contribute to a combined discharge of 14.4 mld (Mooney and McClelland 2012; US EPA 2008). Research conducted during 2007 and 2008 showed that inorganic nutrient concentrations above tidal influence were 10- to 60-fold higher in the AR than in the MR, whereas POC concentrations were relatively similar

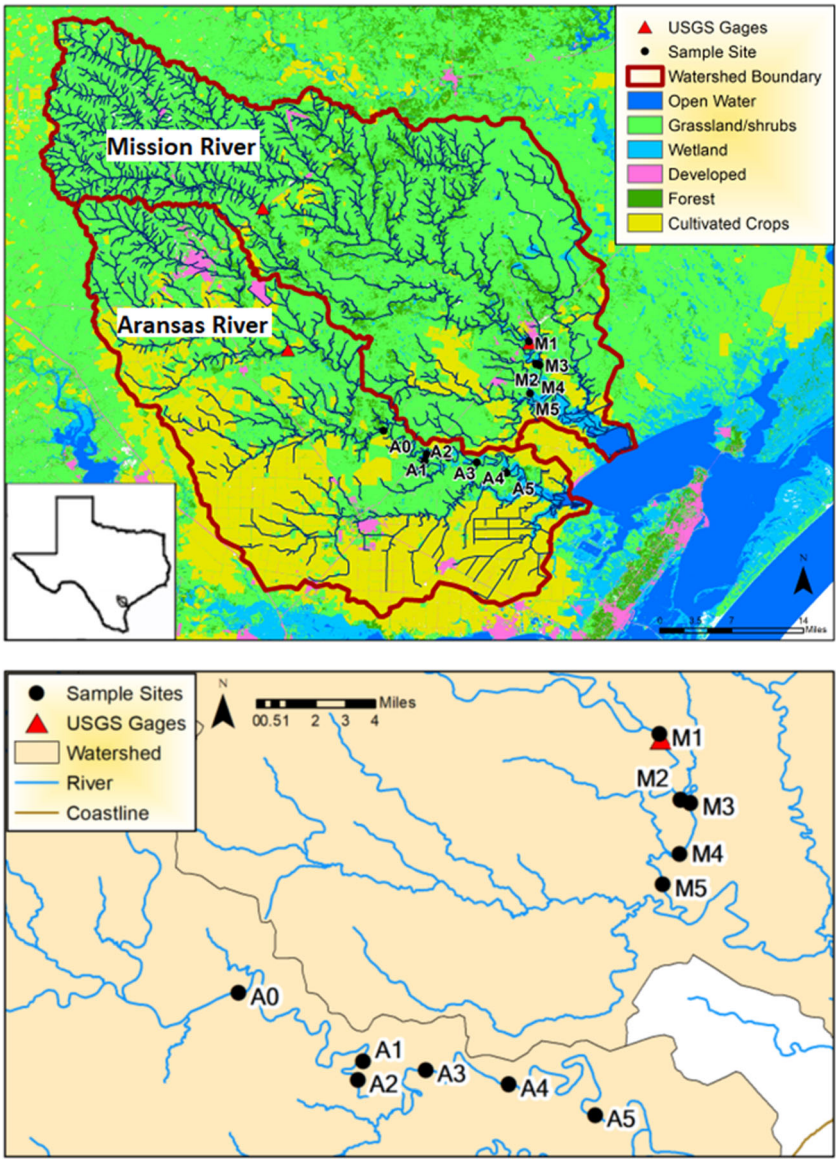

Fig. 1 Study area and sampling sites. A0 and M1 are non-tidal riverine sites, and A1–A5 and M2–M5 are the TFZ sites. Inset map shows the location of the Mission and Aransas watersheds within Texas. Colors on the map indicate land use (see legend)

(Mooney and McClelland 2012). Annual exports of POC from the non-tidal river reaches to the TFZs during baseflow conditions were 33,284 kg year^{-1} in 2007 and 6629 kg year^{-1} in 2008 in the MR and 10,055 kg year^{-1} in 2007 and 4733 kg year^{-1} in the AR (Mooney and McClelland 2012).

Sampling and Analytical Procedures

We collected four sediment cores per site from five sites on the MR and six sites on the AR (Fig. 1). The most upstream sampling site on each river was above tidal influence. All other sites were located within the MR and AR TFZs. These sites were separated by 2–10 km intervals that spanned from the upper third to the lower third of each TFZ. Summer samplings were conducted in June 2015 and June 2016 and winter samplings in February 2016 and January 2017. Salinity of bottom water at all sites was below 1.5 when samples were collected. For each sampling date, four intact sediment cores with ~ 10 cm sediment depth and ~ 10 cm overlying water depth (core tube 7.6 cm I.D. × 30 cm length) were taken at each site and transported back to the lab in the dark under in situ temperature within 2–8 h for further analyses. Sampling occurred in water that was < 2 m deep. The water was always turbid with phytoplankton and suspended particles. The bottom water was well oxygenated, but no active microphytobenthic community was observed at the sediment surface, likely due to the turbid overlying water.

Two sediment cores from each site were used for sediment porosity and sediment organic matter (SOM) determination. The top 1 cm section was weighed before and after drying at 60 °C to determine water content as a measure of porosity. The dried sediment was then homogenized and analyzed on a

Carlo Erba NC 2500 Elemental Analyzer coupled to a Finnigan MAT Delta^{PLUS} IRMS in continuous-flow (He) mode for sediment total organic carbon (SOC), sediment total nitrogen (SN), $\delta^{13}C$, and $\delta^{15}N$. Calibration of $\delta^{13}C$ to VPDB and $\delta^{15}N$ to air was achieved using USGS-40 ($\delta^{13}C = -26.39$ ‰; $\delta^{15}N = -4.52$ ‰) and USGS-41a ($\delta^{13}C = +37.63$ ‰; $\delta^{15}N = +47.57$ ‰) standards. Accuracy was evaluated using an in-house OM standard (peach leaves). For SOC content and $\delta^{13}C$ analyses, dried sediments were acidified with 6% H_2SO_3 to remove carbonates prior to analysis (Verardo et al. 1990).

The other two sediment cores per sampling site were used for dissolved O_2 (DO) profiling. DO profiles were measured using a Clark-type microelectrode (OX-50, Unisense) on intact cores from the well-oxygenated overlying water to anoxic sediments at depth. Sediment cores were placed in the dark with gentle stirring of overlying water, mimicking the in situ light condition and mixing regime. Each measurement was completed within 10 min and produced a vertical DO profile with 250 μm increments (Fig. S1). Diffusive O_2 consumption rates (μmol O_2 m^{-2} h^{-1}) were determined by applying a classical steady-state one-dimension diffusion-reaction model to the DO profiles (Boudreau 1997; Soetaert and Meysman 2009; Brin et al. 2014; Hardison et al. 2017):

$$\varphi\left(D_{O2}/\theta^2\right)\left(d^2O_2/dt^2\right) = v_{\max}(O_2)/(O_2 + k_{O2}) \quad (1)$$

where φ is the sediment porosity, D_{O2} is the diffusion coefficient for O_2 for the given temperature and salinity, θ^2 is the tortuosity determined by $\theta^2 = (1 - \ln(\varphi^2))$ (Boudreau 1997), and $v_{\max}$ and k_{O2} are Monod-type kinetic parameters describing sediment O_2 consumption. The model was set up in R (version 3.4.3, www.r-project.org) using the reactive transport (ReacTran, Soetaert and Meysman 2009) and flexible modeling environment (FME, Soetaert and Petzoldt 2010) packages. O_2 consumption rates normalized to SOC (C-specific O_2 consumption rate, in μmol O_2 (g OC)$^{-1}$ h^{-1}) were then calculated by dividing the O_2 consumption rate by the mass of SOC in the top 1 cm of each sediment sample.

Statistical Analyses

All statistical analyses were run in R (version 3.4.3). The dataset was verified to have a normal distribution with Shapiro-Wilk tests. A two-sample Welch's *t* test was used to test for differences in sediment O_2 consumption rates and other sediment properties between the MR and AR TFZs on annual bases. Because summer and winter measurements within the same TFZ were collected at the exact same sites, seasonal differences were tested with a paired *t* test to gain more statistical power.

A multiple linear regression analysis was used to identify factors influencing sediment O_2 uptake. A priori, we selected several measures of OM quality and quantity to use in our analysis as well as an environmental variable (temperature) that is a known control on biogeochemical rates in most sediments (Arndt et al. 2013). Areal O_2 consumption rate was treated as the dependent variable, while temperature, SOC, C/N, $\delta^{13}C$, and $\delta^{15}N$ were treated as independent variables. Percent SN was excluded because SOC and SN are tightly linked, and SOC alone provides a sufficient representation of sediment OM content. We used three different indicators of OM quality (C/N, $\delta^{13}C$, and $\delta^{15}N$) because each has the potential to provide unique information about OM sources and degradation states (Peterson and Fry 1987; Teeri and Stowe 1976).

Four parameters were used to evaluate each independent variable: slope, i.e., the estimated regression coefficient of each variable in the linear regression; the *p* value of each regression coefficient; the relative importance, i.e., the proportion of variance in O_2 consumption explained by each independent variable; and the variance inflation factor (VIF), a measurement of collinearity among independent variables. The metric lmg was used to represent the relative importance, which was calculated with the R package relaimpo (Groemping 2006). lmg was calculated as the proportional contribution of each variable to the coefficient of determination (R^2) of the entire regression. VIFs were calculated with the R package car (Fox and Weisberg 2011). A VIF equal to 1 indicates no collinearity and that the independent variable is orthogonal to the other independent variables. A VIF greater than 4 indicates collinearity large enough to require further investigation.

Results

Spatial Variability Within TFZs

Sediment properties varied among sampling sites, but no consistent upstream-downstream trends were observed within the Mission and Aransas TFZs. For example, while O_2 consumption rates increased steadily from upstream to downstream sites in the MR during summer (Fig. 2c), this was not observed during winter (Fig. 2d), nor was it observed in the AR during either season (Fig. 2a, b). O_2 consumption rates at non-tidal river sites were near the lower end of the range observed within TFZs, and O_2 consumption rates at the most downstream stations within the TFZs tended to be highest, but patterns for intermediate sites were less consistent (Fig. 2). Upstream-downstream patterns in other sediment properties were similarly variable/inconsistent among sampling sites. Therefore, subsequent results focus on comparisons of TFZ-wide averages between seasons and rivers. TFZ-wide averages are also compared to averages for non-tidal sites.

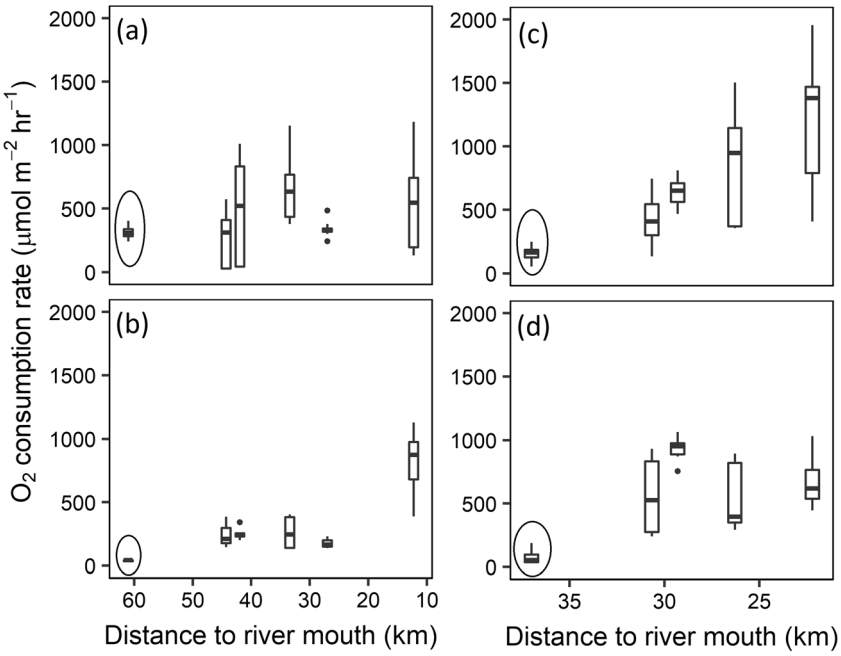

Fig. 2 Areal O_2 consumption rates (μmol m^{-2} h^{-1}) by site in the Aransas River in summer (**a**) and winter (**b**), and in the Mission River in summer (**c**) and winter (**d**). The most upstream non-tidal riverine sites are circled. Boxes represent 25% and 75% quanrtiles, horizontal bars represent median, whiskers represent maximum and minimum values, and dots represent outliers

Sediment O_2 Consumption

Seasonally-averaged areal O_2 consumption rates ranged from 268 to 589 μmol O_2 m^{-2} h^{-1} within TFZ sediments (Table 1; Fig. 3a). Areal O_2 consumption rates were twice as high in the MR TFZ as the AR TFZ ($p = 0.002$ for annual averages, Tables 2 and 3). In both rivers, summer rates were ~10% higher than winter rates ($p = 0.909$ for the AR TFZ, $p = 0.721$ for the MR TFZ, Tables 1 and 3), suggesting a potential seasonal effect. This seasonal effect becomes more evident when values are normalized to SOC content (Table 1; Fig. 3b). In particular, C-specific O_2 consumption rates were ~80% higher in summer than in winter in the AR TFZ ($p = 0.030$, Tables 1 and 3), and ~25% higher in the MR TFZ ($p = 0.093$, Tables 1 and 3). Annual average C-specific O_2 consumption rates were ~35% higher in the AR TFZ than that in the MR TFZ (t test, $p = 0.098$, Table 3).

Comparisons of annually averaged areal O_2 consumption rates within the TFZs to averages for non-tidal sites show a consistent pattern for both rivers (TFZ > non-tidal), but these differences are more pronounced for the MR (Tables 2 and 3). Uncertainty associated with individual averages (as reflected by standard errors in Table 2) is similar in both rivers. However, the difference between TFZ and non-tidal values in the MR is substantially greater than the difference between TFZ and non-tidal values in the AR.

Sediment Porosity and OM Characteristics

Porosity was ~30% higher in the MR TFZ than the AR TFZ (Tables 2 and 3), and there were minimal seasonal differences in porosity within either TFZ (Tables 1 and 3). Average annual values showed a consistent pattern of lower porosity in non-tidal as compared to TFZ sediments, but differences were more pronounced within the MR (Tables 2 and 3). Porosity was highly correlated with sediment grain size (% fine grain, < 63 μm) at all sampling sites ($R^2 = 0.86$, $p < 0.001$; Fig. S2).

Table 1 Sediment O_2 consumption rates, sediment organic carbon (SOC) and nitrogen (SN) content, C to N molar ratio (C/N), $\delta^{13}C$, $\delta^{15}N$, and porosity. Values are means of sites within the TFZs with S.E. in parentheses ($n = 10$ for the Aransas River; $n = 8$ for the Mission River). Carbon (C)-specific O_2 consumption rates were calculated using the mass of organic carbon in surface sediments (0–1 cm)

River	Season	Areal O_2 consumption rate (μmol O_2 m^{-2} h^{-1})	C-specific O_2 consumption rate (μmol O_2 (g OC)$^{-1}$ h^{-1})	SOC (% dry wt)	SN (% dry wt)	C/N	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	Porosity
Aransas	Summer	385 (88)	11.0 (1.9)	0.5 (0.1)	0.06 (0.02)	7.5 (0.6)	−24.1 (0.5)	7.3 (0.5)	0.45 (0.06)
Aransas	Winter	349 (87)	6.2 (0.9)	0.7 (0.1)	0.10 (0.02)	8.2 (0.6)	−25.6 (0.3)	8.2 (0.2)	0.50 (0.05)
Mission	Summer	767 (153)	7.0 (0.9)	1.3 (0.2)	0.12 (0.02)	10.2 (0.4)	−26.6 (0.4)	7.0 (0.2)	0.57 (0.04)
Mission	Winter	691 (95)	5.6 (0.5)	1.4 (0.2)	0.21 (0.03)	7.2 (0.6)	−27.3 (0.3)	7.9 (0.5)	0.64 (0.04)

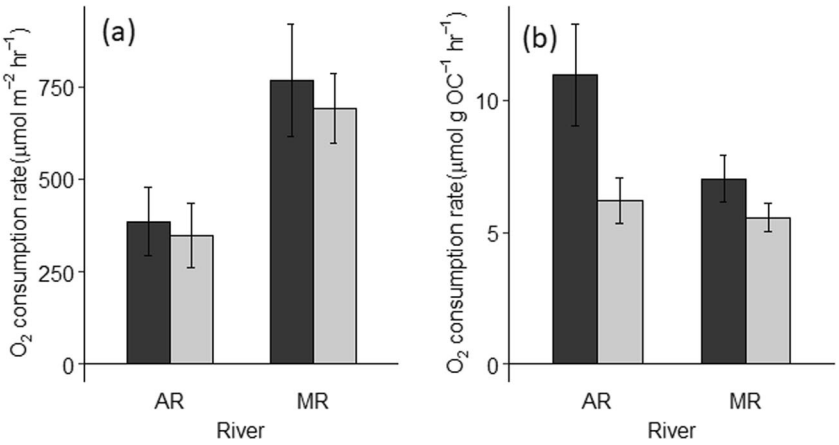

Fig. 3 **a** Areal O_2 consumption rate (μmol m^{-2} h^{-1}) and **b** carbon-specific O_2 consumption rate standardized to the mass of organic carbon (OC) in surface sediments (0–1 cm) (μmol (g OC)$^{-1}$ h^{-1}) within the Aransas River (AR) and Mission River (MR) TFZs in summer (black bars) and winter (gray bars). Error bars represent S.E. ($n = 10$ for AR; $n = 8$ for MR)

Like porosity, SOC and SN content in TFZ sediments were slightly higher in winter than in summer and were higher in the MR than AR (Fig. 4; Tables 1 and 3). Seasonal differences in SN were larger than the differences in SOC in both TFZs (Tables 1 and 3). Furthermore, annual average SOC and SN content was 3–6 times higher in the TFZs of both rivers compared to sediments at the non-tidal sites (Table 2).

In contrast with porosity and OM content, C to N ratios were similar between the AR and MR TFZs (Table 1 and 2) but did show seasonal shifts in both rivers (Table 1 and 3). However, the shifts in C/N were not consistent in the two rivers, with higher values during winter in AR and higher values during summer in MR (Table 1 and 3). C/N ratios were consistently lower in the TFZs than in non-tidal sites (Tables 2, 3).

Stable C and N isotope ratios differed between summer and winter in the AR TFZ and showed similar patterns in the MR TFZ (Tables 1 and 3). In both rivers, average values for $\delta^{13}C$ were lower in winter than summer, while average values for $\delta^{15}N$ were higher in winter than summer (Tables 1 and 3). $\delta^{15}N$ values were similar in the two TFZs, but $\delta^{13}C$ values were higher in the AR TFZ than the MR TFZ (Tables 2 and 3). There were 2–3 ‰ differences in $\delta^{15}N$ between the TFZs and non-tidal sites in both rivers, but $\delta^{15}N$ was higher in the non-tidal sites in the AR and higher in the TFZ in the MR (Tables 2 and 3). $\delta^{13}C$ did not differ between the TFZs and non-tidal sites in either river (Tables 2 and 3).

Relationship Between O_2 Consumption Rates and Environmental Parameters

Multiple regression analysis showed that SOC content is the strongest driver of O_2 consumption rates in both systems (Table 4; Fig. 5). SOC alone explained approximately half (48.7%) of the variance in O_2 consumption rates (Table 4). Temperature in water overlying the sediments (25.5 ± 0.3 °C in summer and 19.3 ± 2.3 °C in winter) was also identified as a significant factor but explained a much lower (7%) proportion of the variance (Table 4). The three source/quality indicators included in this analysis (C/N, $\delta^{13}C$ and $\delta^{15}N$) did not emerge as significant factors. Among these indicators, however, it is noteworthy that the lmg value for $\delta^{13}C$ was substantially higher than the lmg values for C/N and $\delta^{15}N$. Indeed, the lmg value for $\delta^{13}C$ was comparable to the lmg value for temperature. The variance inflation factors (VIFs) of all variables fell between 1.10 and 1.53 indicating that collinearity among variables was minimal.

Table 2 Annually averaged sediment O_2 consumption rates, sediment organic carbon (SOC) and nitrogen (SN) content, C to N molar ratio (C/N), $\delta^{13}C$, $\delta^{15}N$, and porosity. Values are means of the non-tidal or TFZ sites across both seasons with SE in parentheses. For the Aransas River, $n = 2$ (SOC, C/N, and $\delta^{13}C$) or $n = 3$ (the other variables) for the non-tidal site and $n = 20$ for the TFZ sites. For the Mission River, $n = 4$ for the non-tidal site, $n = 16$ for the TFZ sites. C-specific O_2 consumption rates were not calculated because OC content was below the detection limit for some non-tidal sites

River	Site	Areal O_2 consumption rate (μmol O_2 m^{-2} h^{-1})	SOC (% dry wt)	SN (% dry wt)	C/N	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	Porosity
Aransas	Non-tidal	221 (92)	0.1 (0.1)	0.02 (0.004)	10.8 (3.9)	− 24.7 (2.5)	10.4 (1.5)	0.26 (0.05)
Aransas	TFZ	366 (62)	0.6 (0.1)	0.08 (0.01)	7.8 (0.4)	− 24.9 (0.3)	7.7 (0.3)	0.47 (0.04)
Mission	Non-tidal	120 (38)	0.4 (0.2)	0.04 (0.01)	10.3 (1.7)	− 27.1 (0.4)	5.6 (0.7)	0.26 (0.03)
Mission	TFZ	729 (88)	1.3 (0.2)	0.17 (0.02)	8.7 (0.5)	− 26.9 (0.3)	7.5 (0.3)	0.61 (0.03)

Table 3 Statistical comparisons of sediment O_2 consumption rates, sediment organic carbon (SOC) and nitrogen (SN) content, C to N molar ratio (C/N), $\delta^{13}C$, $\delta^{15}N$, and porosity between seasons and sites. *p* values of paired *t* tests (e.g., within-river seasonal comparisons) and two-sample *t* tests (i.e., MR vs. AR TFZ or within-river non-tidal vs. TFZ) are presented. *AR* Aransas River, *MR* Mission River, *NT* non-tidal riverine sites, *TFZ* tidal freshwater zone sites. C-specific O_2 consumption rates were not calculated for the non-tidal sites because OC content was below the detection limit in some samples

	Areal O_2 consumption rate	C-specific O_2 consumption rate	SOC	SN	C/N	$\delta^{13}C$	$\delta^{15}N$	Porosity
AR TFZ Seasonal	0.909	0.030	0.161	0.062	0.374	0.002	0.208	0.426
MR TFZ Seasonal	0.721	0.093	0.651	0.035	0.002	0.089	0.095	0.103
AR TFZ–MR TFZ	0.002	0.098	< 0.001	0.002	0.212	< 0.001	0.507	0.008
AR NT–TFZ	0.262	–	0.009	< 0.001	0.610	0.950	0.541	0.015
MR NT–TFZ	< 0.001	–	0.002	< 0.001	0.422	0.736	0.075	< 0.001

Discussion

This study was motivated by the overarching hypothesis that tidal freshwater zones (TFZs) in rivers are important yet under-appreciated hotspots for biogeochemical cycling and storage that substantially modify organic and inorganic nutrient delivery from watersheds to estuaries. O_2 consumption rates in surface sediments are emphasized herein as an indicator of the role that TFZ sediments play in OM decomposition. Measurements of other sediment properties, including porosity, C and N content, C/N ratios, and stable isotope ratios of C and N, provide additional information about how O_2 consumption rates vary as a function of OM quality/sources.

We expected to observe clear, consistent gradients in sediment properties and associated O_2 consumption rates from upstream to downstream locations within the TFZs that would reflect gradients relative to non-tidal river inputs. The fact that no such gradients were found suggests that variable hydrologic conditions and/or smaller-scale geomorphic features within the TFZs had stronger effects on sediment characteristics than proximity to the non-tidal river. Bi-directional water flow in portions of the TFZs may also confound simple upstream-downstream interpretations, for example, when tidal force is strong enough to push water flow towards the upstream, the most downstream site is not the receiving end but being mixed with the upstream sites (Jones et al. 2017). Moreover, because of slow flow rates and tight benthic-pelagic coupling in these shallow TFZs, vertical exchange with the water column and biogeochemical processes in the sediments may be more important than longitudinal transport of materials within the TFZs. After a strong rainfall event, the entire TFZ converts to a fast-flowing, river-like system, and gradients in the water column and surface sediments are eliminated. Although it is possible that spatial gradients/heterogeneity can be established after a prolonged baseflow period, the results from our samples collected 2–7 days after storm events or > 2 weeks after storm events all showed lack of a spatial gradient. Therefore, we focus on the average conditions and sediment properties of the entire TFZ for the remaining discussion.

Below, we discuss potential reasons for differences in average O_2 consumption rates between the MR and AR TFZs, particularly as they relate to other sediment properties that

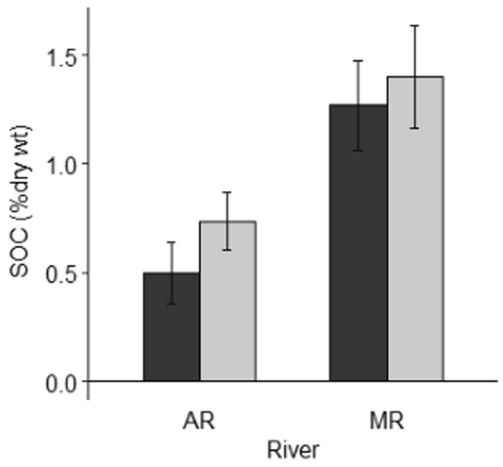

Fig. 4 Sediment organic carbon (SOC) content (% dry weight) within the Aransas River (AR) and the Mission River (MR) TFZs in summer (black bars) and winter (gray bars). Error bars represent S.E. ($n = 10$ for AR; $n = 8$ for MR)

Table 4 Multiple linear regression analysis results for variables potentially influencing areal oxygen consumption rates for both TFZs combined. In the regression, temperature was in °C, and all other parameters were in the same units as presented above. Slope is the regression coefficient of each variable in the linear regression. *p* value represents the significance of the correlation. lmg represents the relative importance of each variable. The variance inflation factor (VIF) is a measurement of collinearity among independent variables. VIF = 1 indicates no collinearity, VIF > 4 indicates collinearity large enough to require further investigation. VIF between 1 and 4 is acceptable

	Slope	*p* value	lmg	VIF
(Intercept)	− 884	0.19	NA	NA
Temperature	17	0.03	0.070	1.19
SOC	321	< 0.01	0.487	1.48
C/N	− 13	0.41	0.015	1.17
$\delta^{13}C$	− 26	0.24	0.083	1.53
$\delta^{15}N$	4	0.87	0.018	1.10

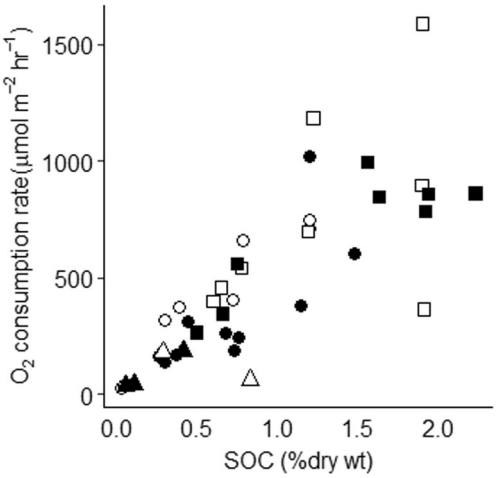

Fig. 5 Relationship between sediment organic carbon (SOC) and areal O_2 consumption rate. Circles—Aransas River TFZ; squares—Mission River TFZ; triangles —non-tidal riverine sites. Open symbols are summer measurements and filled symbols are winter measurements

were measured, and consider how rates measured within these TFZs compare to other systems.

Sediment O_2 Consumption in TFZs

O_2 consumption rates in the MR and AR TFZs are within the same range as published estimates of diffusive oxygen uptake (DOU) in estuaries and shallow bays. Sediment O_2 consumption is often used as a proxy for total benthic organic carbon remineralization, which is the sum of oxic and anoxic remineralization processes. However, total O_2 uptake (TOU) can be split into (1) DOU due to aerobic respiration by benthic microbes and (2) advective O_2 uptake, generally governed by benthic faunal activities. Thus, total OM decomposition, as inferred from TOU, is greater than OM decomposition estimated from DOU. TOU can be measured in many ways, including intact sediment core incubations (e.g., Archer and Devol 1992; Arrigo and van Dijken 2011; Hardison et al. 2017). On the other hand, DOU is quantified by the use of microelectrodes performed in situ or ex situ with sediment cores, as in the current study (e.g., Arrigo and van Dijken 2011; Glud et al. 1994; Hardison et al. 2017; McTigue et al. 2016). DOU has been measured extensively using microelectrodes in estuaries and shallow bays (water depth < 50 m) and can be compared directly with rates measured in the current study. In temperate to subtropical estuaries close to river mouths, system-wide average DOU rates ranged from 277 to 527 μmol O_2 m^{-2} h^{-1} (Boyko et al. 2018; Conley et al. 1997; Glud et al. 2003; Pastor et al. 2011; Rabouille et al. 2003), compared to a range of 25 to 1589 μmol O_2 m^{-2} h^{-1} in the MR and AR TFZs. Although TFZs are often overlooked portions of rivers, this study suggests that they function similarly to estuarine systems, with slow flow rates and tight benthic-pelagic coupling (in terms of microbial respiration and aerobic OM decomposition). This likely modifies OM and inorganic nutrient fluxes from watersheds to estuaries.

While there have been many studies of benthic DOU rates in estuaries, this is not the case for stream and river systems. To the best of our knowledge, the DOU rates that we report for TFZ and non-tidal river sites are the first of their kind. A survey of the literature shows that sediment O_2 consumption in non-tidal rivers and TFZs has historically been studied using sediment core or slurry incubations rather than microelectrodes (e.g., review by Boynton et al. 2018; Hill et al. 2002). This methodological choice may reflect the fact that riverine sediment grains are often coarse, making it difficult to measure vertical DO profiles with a fragile microelectrode. Higher DOU rates in the MR and AR TFZs as compared to non-tidal sites (Table 2) suggest that TFZs may be particularly important locations for biogeochemical cycling at the downstream end of river networks. These findings must be viewed with caution because our non-tidal sampling sites are not necessarily representative of the MR and AR networks as a whole. In addition, emulating in situ mixing condition is difficult to do, which adds uncertainty to the measurements (Porter et al. 2018). However, they do support our original hypothesis that TFZs serve as hotspots for biogeochemical cycling near the land-sea interface. More studies of DOU in river systems are needed to determine how generalizable this finding is, but the DOU data for TFZ and non-tidal river sediments presented herein do provide valuable benchmarks for future comparisons.

Contributing Factors to Sediment O_2 Consumption

Sediment O_2 consumption rates are controlled by environmental factors such as temperature, OM quantity, OM quality (or reactivity), OM deposition rate, benthic community composition, macrobenthic activity, and physical protection (Aller 1982; Arndt et al. 2013; Arnosti 2011; Cammen 1991; Dauwe et al. 2001; Hedges et al. 1988; Mayer 1994; Pomeroy and Deibel 1986; Sander and Kalff 1993; White et al. 1991). The amount of SOC remineralized ultimately depends on the amount of OM that settles onto the sediment surface, which is usually high in shallow coastal systems compared to the open ocean. The longer residence times of TFZs relative to faster-flowing unidirectional upstream river reaches likely enhance the deposition of OM. The source of SOM in TFZs may also influence remineralization rates. OM in sediments is composed of various groups of compounds that have different reactivities with regard to mineralization (Arndt et al. 2013; Burdige 1991; Middelburg 1989). In general, terrestrial OM, which is dominated by structural compounds such as cellulose and lignin, is considered more difficult to degrade relative to algal biomass (Hedges et al. 2000). As a result, algal-derived OM is usually remineralized more readily than terrestrial material. Riverine SOM is often a mixture of terrestrial and algal

sources. Thus, we expected sediment O_2 consumption to be related to both SOM quantity and quality in this study.

Generally, in marine and freshwater systems, higher SOC levels lead to higher O_2 consumption because OM fuels aerobic respiration (Arndt et al. 2013). Accordingly, in this study, SOC explained the largest proportion (48.7%) of the variance in O_2 consumption rates (Fig. 5; Table 4). Although SOC was higher in the MR TFZ than the AR TFZ, average water column POC concentrations were 194 ± 18 μmol L^{-1} in the AR and 196 ± 18 μmol L^{-1} in the MR, suggesting that the pools of water column POC with the potential to settle onto the sediment surface were similar for both rivers (Wei et al. under review). Thus, the SOC difference between rivers was more likely related to differences between sediment physical characteristics, rather than the productivity of the water column. Within the TFZs, SOC content correlated strongly with porosity ($R^2 = 0.69$, $p < 0.001$), which was strongly correlated with proportion of fine sediment grains ($R^2 = 0.86$, $p < 0.001$, Fig. S2). A positive correlation between fine grain size (clay and/or silt), and SOC is well established (Mayer 1994; Tyson 1995). This relationship is likely due to (1) the capacity of finer particles to slow diffusion of O_2 into sediments, thus slowing aerobic remineralization and enhancing preservation of OM, and (2) adsorption of organic particles onto charged surfaces of clay minerals (Mayer 1994; Tyson 1995). The AR TFZ sediments had lower porosity (i.e., larger sediment grain size), leading to less mineral-associated SOC.

While O_2 consumption rates commonly increase with temperature (Alsterberg et al. 2011; Arndt et al. 2013), the small temperature effect (7%) that we observed in this study reflects the mild winter climate and relatively narrow range in water temperatures that were encountered during the study period. The lowest temperature in this study was 14 °C, and half of the winter samples collected in late February experienced temperatures > 20 °C. Summer temperatures (averaging 25 °C) were certainly higher, but the swing between summer and winter temperatures was not large.

Although $\delta^{13}C$, a proxy for OM source, was not identified as a significant factor driving variations in O_2 consumption rates, the values do provide useful information about the composition of SOC within the TFZs. In both rivers, values ranging from approximately − 27 to − 24 ‰ (Table 1) point to a mixture of freshwater algae (− 27 to − 45 ‰) and terrestrial C_4 plant material (− 11 to − 14 ‰) contributing to sediment OM stocks (Mooney and McClelland 2012; Peterson and Fry 1987; Teeri and Stowe 1976). Terrestrial C_3 plants also have $\delta^{13}C$ values around − 28 ‰, but C_4 grasses and crops are the dominant vegetation type in these two watersheds, and large amounts of C_4-dominated OM are delivered to the TFZs during storm events (Mooney and McClelland 2012). Considerably higher $\delta^{13}C$ values for SOC in the AR as compared to the MR (Tables 2 and 3) may reflect a higher contribution from agriculture (C_4 crops). However, the fact that this difference in OM source contributions does not translate into a difference in O_2 consumption rates suggests that contributions from in situ algal production are largely driving O_2 consumption.

The molar C/N ratios in SOM are consistent with this interpretation, although it can be challenging to resolve OM sources based on C/N. Average C/N ratios of ~ 8 (Table 1) suggest that fresh vascular plant material is not a major source of SOM in the TFZs; the C/N of vascular plants is typically > 20 (Meyers and Ishiwatari 1993). It is difficult to distinguish between other potential SOM sources using C/N alone because soil OM stocks (including processed parent material and microbial biomass) and phytoplankton can both have C/N values ranging from 4 to 10 (Meyers and Ishiwatari 1993). In addition to the source-related uncertainties in C/N, processing effects can make interpretation of C/N data challenging. In particular, the N content of SOM can either increase or decrease depending on the initial C/N ratio of the parent material and the needs of the microbial community (Aerts 1997).

Implications of O_2 Consumption in TFZ Sediments

Based on a sediment area of 1.5×10^6 m^2 (calculated using TFZ boundaries defined in Jones et al. 2020), we estimate that aerobic respiration consumes 4.0×10^6 mol C $year^{-1}$ in the AR TFZ. This number was determined using a respiratory quotient of 1.2 mol of O_2 consumed for each mole of OC respired (Rabouille et al. 2009). POC inputs into the AR TFZ under baseflow conditions were 8.4×10^5 mol C $year^{-1}$ in 2007 (wet year) and 3.9×10^5 mol C $year^{-1}$ in 2008 (dry year) according to previous model estimates (Mooney and McClelland 2012). Consumption of OC in the AR TFZ exceeds POC input from the upstream watershed by nearly an order of magnitude, again suggesting that in situ algal production must primarily fuel sediment OC consumption. This is also consistent with findings in previous studies that particulate OM concentration was higher at the end of the TFZs compared to the upstream portion (Mooney and McClelland 2012). Although sediments in these TFZs do not appear to be processing large amounts of terrestrial OM, we hypothesize that algal production and sinking within TFZs is a major pathway for translocation of watershed-derived inorganic nutrients from the water column to the sediments within TFZs. In this manner, TFZs may substantially alter the forms and quantities of watershed-derived nutrients that are delivered to estuaries.

While the above comparison of OM inputs to sediment respiration rates points to the importance of in situ production and benthic-pelagic coupling, we do not yet know whether TFZs act as an overall source or sink for OM. Total OC decomposition includes more than just microbial aerobic respiration and could be 2 to 4 times higher when considering faunal activities and anaerobic respiration (Archer and Devol 1992; Glud 2008). Therefore, it is difficult to determine the

balance between primary production of OC and respiratory loss of OC. Furthermore, the estimates presented here are for baseflow conditions and do not account for mobilization and advective losses during storm flow. Previous studies of the Mission and Aransas rivers have shown that 85–98% of annual riverine POC export occurs during a few storm events each year (Mooney and McClelland 2012). These TFZs may have acted as OC sources rather than OC sinks in the land-ocean continuum over annual timeframes if large quantities of OC were flushed out from the TFZ sediments during storm events. However, our results are consistent in the same season over different years, suggesting that the TFZs are stable and homogenous under baseflow conditions. In any case, our calculations suggest that there must be large amounts of phytoplankton-derived OM decomposed within TFZ sediments between storm events.

Conclusions

O_2 consumption rates within TFZs of the Mission and Aransas rivers are similar to rates found in estuaries and higher than O_2 consumption rates at non-tidal sites within the rivers. In terms of sediment O_2 uptake and OM decomposition, TFZs behaved more like estuarine systems with slow flow rates and tight benthic-pelagic coupling rather than fast-flowing riverine systems. Sediment O_2 consumption rates were mainly related to SOM content. Watershed characteristics such as land use likely influenced TFZ sediment properties such as porosity, SOC and SN concentrations, and stable C and N isotope values, but, overall, TFZ SOM was dominated by algal biomass from in situ production. We hypothesize that algal production and sinking within TFZs is a major pathway for translocation of watershed-derived nutrients from the water column to the sediments within TFZs. Under baseflow conditions, long residence times in TFZs are sufficient to allow for intense biogeochemical processing of OM and inorganic nutrients. Further work is needed to quantify linkages between decomposition, nutrient retention, and removal through processes such as denitrification and dissimilatory nitrate reduction to ammonium (DNRA). Studies of how TFZs function under environmental stressors such as eutrophication and changing storm frequency and intensity related to climate change are also needed.

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