

## Chapter 19. Biogeochemistry of Tidal Freshwater Wetlands

### Authors:

J. Patrick Megonigal  
Smithsonian Environmental Research Center  
647 Contees Wharf Road  
Edgewater, MD 21037  
Voice: (443) 482-2346  
Fax: (443) 482-2380  
E-mail: [megonigalp@si.edu](mailto:megonigalp@si.edu)

Scott C. Neubauer  
Virginia Commonwealth University  
Department of Biology  
1000 West Cary St.  
Richmond, VA 23284  
Voice: (804) 827-2794  
Fax: (804) 828-0503  
Email: [sneubauer@vcu.edu](mailto:sneubauer@vcu.edu)

Abbreviations: BSi, biogenic silica; CDOM, chromophoric dissolved organic matter; DIC, dissolved inorganic carbon; DIN, dissolved inorganic nitrogen; DNRA, dissimilatory nitrate reduction to ammonium; DOC, dissolved organic carbon; DSi, dissolved silica; EU, European Union; GPP, gross primary production; NPP, net primary production; POC, particulate organic carbon; ROL, root oxygen loss; TFW, tidal freshwater wetland; USA, United States of America.

### 1.0 Introduction

Biogeochemical cycles in tidal freshwater wetlands (TFWs) are regulated by many of the same factors that operate in saline tidal wetlands, yet the interplay among element cycles in TFWs is unique due to their position at the interface of nontidal rivers and brackish estuaries. Here we focus on the exchanges, transformations, and storage of the major elements, recognizing that these processes govern the contribution of TFWs to the metabolism of coastal landscapes.

TFWs and tidal saline wetlands share ecological characteristics that ultimately regulate element cycles. TFW ecosystems support the full range of plant functional types that occur in saline tidal wetlands, including herbaceous species, trees and shrubs, which differ with respect to primary productivity, root-leaf-wood C allocation, and C quality. As with tidal saline wetlands, TFWs occur in geomorphic settings that promote high rates of element sequestration in biomass and soils, but also high exchange rates of water, solutes, solids, and gases with terrestrial and aquatic ecosystems, groundwater, and the atmosphere. Tidal freshwater and tidal saline systems both develop on mineral and organic soils, the chemical composition of which is expected to affect a variety of ecosystem processes, including the contribution of

Fe(III) to anaerobic microbial respiration, and both are found on eutrophic and oligotrophic rivers that place limits on nutrient availability and productivity.

TFW biogeochemistry differs fundamentally from wetlands that are either freshwater and nontidal, or tidal and saline. Compared to nontidal freshwater wetlands, TFW hydrology is predictable and aseasonal. Also, tidal hydrology drives more open element cycles in TFWs than nontidal freshwater wetlands, an observation that inspired the Outwelling Hypothesis (Kalber, 1959; Odum, 1968) and contemporary research on import, export and chemical transformation in tidal wetlands.

Compared to tidal saline wetlands, TFW plant and microbial activity is less influenced by salts and sulfate. Low concentrations of sulfate in fresh water tend to make TFWs stronger CH<sub>4</sub> sources than saline tidal wetlands. The influence of alkalinity exported from TFWs on adjacent estuarine waters is relatively dramatic in TFW rivers because they are relatively poorly buffered compared to saline waters closer to oceans (Stets et al., 2017). Thus, the biogeochemistry of TFWs is unique in the coastal landscape due to a combination of flushing by tides, the chemical milieu of freshwater, and position at the limit of tidal influence.

## 2. Carbon Biogeochemistry

Carbon cycling is a fundamental driver of biogeochemical transformations in ecosystems. Gross primary production (GPP) largely establishes the upper limit of heterotrophic activity, including the secondary productivity of consumers. Decomposition and microbial respiration (R) releases or sequesters nitrogen and other nutrients, depending on the chemical characteristics of the detritus. The chemical composition of organic carbon compounds and interactions with mineral surfaces regulate microbial transformations such as denitrification. The capacity of ecosystems to sequester CO<sub>2</sub> in biomass or soil organic matter represents an imbalance between GPP and R (i.e., net ecosystem production, NEP), and the net exchange of particulate and dissolved organic carbon with adjacent ecosystems.

The most complete C budget of a tidal freshwater wetland completed to date concerned Sweet Hall marsh, located on the Pamunkey River in Virginia, USA (Neubauer et al., 2000, 2002; Neubauer and Anderson, 2003; Figure 1). The budget was developed from a variety of measurements, including repeated measurements of whole-system CO<sub>2</sub> and CH<sub>4</sub> exchange. This approach avoids several problems with estimating C input from biomass harvests, such as accounting for biomass turnover and translocation (see discussion in Neubauer et al., 2000), and is especially useful for understanding ecosystem-level C cycling. We present the Sweet Hall C budget as a case study to illustrate the processes that distribute C among pools and fluxes in a typical TFW, and review studies of other TFW sites that focused on one or more components of the C cycle.

[FIGURE 19.1 HERE]

### 2.1 Carbon inputs

Gross primary production is the photosynthetic assimilation of CO<sub>2</sub> by macrophytes and microalgae, and the dominant source of metabolic energy driving biogeochemical cycles in tidal

wetlands. GPP contributes two-thirds of annual C inputs to Sweet Hall marsh (Figure 1), with the balance from allochthonous sources associated with sediment deposition. About 37% of macrophyte GPP is consumed for plant growth and maintenance respiration, and thus quickly returned to the atmosphere as CO<sub>2</sub>. The remainder is net primary production (NPP; 625 g C/m<sup>2</sup>/year), some of which may be allocated to root exudates or mycorrhizae. NPP is supported both by photosynthates produced in a given year, and by C from previous years that is translocated from storage organs such as rhizomes. Accounting for both photosynthesis and translocation, macrophyte NPP was 557-736 g C/m<sup>2</sup>/year (1,150-1,500 g biomass/m<sup>2</sup>/year), which is about double the peak aboveground biomass at Sweet Hall marsh (Neubauer et al., 2000). It is difficult to generalize about the relative importance of below- and aboveground NPP because belowground production is difficult to measure, and estimates vary widely from NPP ratios <<1 to >>1 (Whigham and Simpson, 1978; Schubauer and Hopkinson, 1984; Bellis and Gaither, 1985). TFWs dominated by annual species are expected to have lower above:below NPP ratios than tidal saline marshes because annuals lack permanent storage organs such as rhizomes (Whigham, 2009).

Weston et al. (2014) applied similar techniques to three sites arranged along a salinity gradient in Delaware Bay, USA, and concluded that TFW marsh productivity is equivalent to more saline marshes on average, but that TFW marshes exhibit far more interannual variation. Salinity explained 50-60% of the interannual variation in oligohaline and mesohaline marshes, but not in the TFW marsh where factors such as spring inundation may regulate production indirectly through the recruitment success of annual plants (Weston et al., 2014). In general, the aboveground productivity of TFWs is higher (> 1,000 g/m<sup>2</sup>/year) on sites dominated by annual than perennial species, and this appears to hold for tidal freshwater wetland forests (Whigham, 2009).

Sediment deposition is an important vehicle for importing allochthonous particulate organic C into TFW soils, and it enhances organic C preservation and nutrient removal through burial. TFWs that can maintain vertical accretion and areal extent with sea level rise are net C sinks as organic matter is buried in accreting sediments (Stevenson et al., 1988). The amount of C added via sediment deposition at Sweet Hall marsh (517 g C/m<sup>2</sup>/year; Neubauer et al., 2002), is one-third of all organic C inputs to the site (Figure 1). This rate may not be typical because it exceeds estimates from other TFWs (Craft, 2007; Neubauer, 2008; Weston et al., 2014; Noe et al., 2016). Sediment carbon fluxes vary dramatically with extreme events such as hurricanes (Noe et al., 2016), and with geomorphic setting (Pasternack, 2009). Of particular importance is the location of the site in relation to the estuarine turbidity maximum, a feature that forms at the freshwater-saltwater interface of tidal rivers, and has a profound effect on C deposition rates (Darke and Magonigal, 2003; Morse et al., 2004; Loomis and Craft, 2010; Ensign et al., 2014a,b). Sediment deposition and associated C deposition are generally faster in TFW marshes than TFW forests in the short-term (Ensign et al., 2014a and references therein), but this relationship is less prognostic in areas where sea level rise is changing the factors that control local deposition, such as the position of the estuarine turbidity maximum, plant biomass, shallow subsidence rates, or soil elevation (Noe et al., 2016).

The sources of allochthonous C compounds imported with TFW sediment deposits are

not well characterized, but can include upland soils, dissolved organic carbon (DOC) sorbed to mineral particles, and plankton. The age and chemical composition of these sources varies, affecting the extent to which they are ultimately preserved as soil organic matter or exported. A meta-analysis of >300 samples from salt marshes, mangroves, and seagrass beds suggested that the organic matter preserved in coastal sediments is dominated by allochthonous sources at sites with  $\leq 10\%$  organic soil C (Boullion and Boschker, 2006). At Sweet Hall marsh, allochthonous C is  $\sim 33\%$  of C inputs, but only  $\sim 10\%$  of microbial soil respiration ( $54\text{--}71\text{ g C/m}^2/\text{year}$ ; Neubauer et al., 2002), suggesting that allochthonous C sources are better protected against microbial decomposition than autochthonous C (mainly fresh plant) sources. Sequestered organic matter is a sink for N, P, and other elements in organic tissues (see Sections 4 and 5).

## 2.2 Carbon outputs

The collective respiration of plants, microbes, and animals at Sweet Hall marsh is supported by total organic C inputs (GPP + sediment-associated C) of  $1,579\text{ g C/m}^2/\text{year}$  (Figure 1). One-third of GPP is consumed by plant respiration that releases  $\text{CO}_2$  directly to the atmosphere, soil atmosphere, or soil solution. Most of the remaining GPP takes the form of plant biomass that supports the heterotrophic respiration of bacteria, fungi, insects, grazing snails, and a variety of other organisms (Hines et al., 2006). An uncertain fraction of GPP is lost from plants as root exudates.

Organic C inputs from plants and sediments are eventually subjected to decomposition and microbial degradation, producing soil organic matter, dissolved inorganic carbon (DIC), DOC, and  $\text{CH}_4$ . At Sweet Hall marsh,  $15\%$  of organic C inputs ( $229\text{ g C/m}^2/\text{year}$ ) are buried by accreting soil and enter a very slowly decomposing soil organic matter pool. The remaining  $85\%$  is cycled in timeframes of hours to months via plant, animal, and microbial respiration, and other microbial degradation processes such as fermentation. Rates of organic C burial in TFWs along the Atlantic and Gulf coasts of North America, and on the Scheldt River of Europe, ranged from  $10$  to  $930\text{ g C/m}^2/\text{year}$  (Table 1; Neubauer, 2008 and references therein). In addition to sequestering organic C, sediment accumulation adds elevation to wetland soils at a rate that is regulated by relative sea level rise (Morris et al., 2002).

[TABLE 19.1 HERE]

### 2.2.1. Exports of $\text{CO}_2$ , DIC, DOC, and POC

C compounds exported from tidal wetlands influence the chemical composition of adjacent estuaries and the atmosphere. The plant and microbial respiration that takes place in saturated or flooded soils generates DIC, which partitions into  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  according to pH. At Sweet Hall marsh,  $12\%$  of all organic C added to the marsh is exported as DIC. A portion of the DIC pool is emitted directly to the atmosphere as  $\text{CO}_2$ , while the remainder is exported to the York River (Figure 1; Neubauer and Anderson, 2003).

Evidence is mounting that tidal wetlands are a significant source of DIC and alkalinity to estuaries and coastal shelves (Cai, 2011; Bauer et al., 2013; Wang et al., 2016). Extrapolating

seasonal estimates of DIC export from Sweet Hall marsh (197 g C/m<sup>2</sup>/year) to all tidal marshes of the York River estuary suggested that 47% of excess water column DIC (DIC unexplained by conservative mixing of fresh and marine end-members) is imported from wetlands (Neubauer and Anderson, 2003). High temporal resolution measurements in a polyhaline tidal marsh show that DIC exports can be larger than previously estimated, and comparable to major fluxes such as riverine DOC and DIC fluxes to continental shelves (Wang et al., 2016). It is presently unclear whether there are meaningful differences between TFWs and more saline tidal wetlands in the total or area-based rate of DIC export. However, several studies suggest that freshwater and low-salinity tidal wetlands are significant DIC sources to estuaries and coastal oceans (Smith and Hollibaugh, 1993; Frankignoulle et al., 1996; Frankignoulle et al., 1998; Nietch, 2000).

Far less DOC is exported from tidal wetlands to estuaries compared to DIC, yet DOC is arguably the most important form of C exported from these systems. Saline tidal marshes generally export DOC to estuaries (Nixon, 1980 and references therein; Tobias and Neubauer, this volume; Tzortziou et al. 2011), where it influences estuarine microbial metabolism, nutrient cycling, and ultraviolet (UV) light penetration of the water column (Epp et al., 2007). Although there is no evidence of DOC export from Sweet Hall marsh (Neubauer, 2000), DOC is exported from TFWs on the Patuxent River, USA (Figure 2), the Hudson River, USA (Findlay et al., 1998), and the Dovey River, Wales, UK (Dausse et al., 2012). Raymond and Bauer (2001) proposed that TFWs are 30% of DOC sources to the comparatively pristine York River, USA.

[FIGURE 19.2 HERE]

The chemical composition of DOC influences the biogeochemical effects it will have on receiving estuaries. Features such as the aromatic ring content affect UV radiation adsorption (Tzortziou et al., 2007), and perhaps the ability of DOC to support microbial respiration. Chromophoric dissolved organic matter (CDOM) is the light adsorbing component of DOC and a dominant fraction of the DOC pool in estuaries. The spectral slope ( $S_{CDOM}$ ) of CDOM exported from a TFW on the Patuxent River, USA, indicated that the marsh is a source of relatively complex, high molecular weight, and aromatic-rich DOC (Figure 2). Presumably the  $S_{CDOM}$  of this TFW marsh reflects the relatively high lignin content and complexity of organic C compounds in emergent wetland plants compared to phytoplankton (Enriquez et al., 1993; Tzortziou et al., 2008).

Particulate organic carbon (POC) in rivers is derived from aquatic (e.g. phytoplankton) and terrestrial (e.g. emergent plant) sources. Although the fraction of POC from terrestrial sources increases toward freshwater end of tidal rivers (Hoffman and Bronk, 2006), studies of particulate organic carbon (POC) dynamics in TFWs indicate that they can vary from net sinks to net sources (Findlay et al., 1990; Neubauer et al., 2002; Hunsinger et al., 2010, 2012). Perhaps the most detailed study of TFW export of POC to date reported that river POC concentrations were positively correlated with wetland area in tidal freshwater reaches of the Hudson River, USA (Hunsinger et al., 2012). Based on temporal and spatial variation in lignin phenols and stable isotopes, Hudson River TFWs are sources of aromatic-rich compounds derived from emergent and submerged vascular plants (Hunsinger et al., 2010, 2012). Generalizations about

POC dynamics require long-term studies that quantify the influence of seasonal and episodic events such as storms on POC fluxes.

### 2.2.2 Methane emissions and export

A portion of organic matter decomposition in saturated soils yields methane (CH<sub>4</sub>) rather than CO<sub>2</sub>. Emissions from 13 TFW sites average  $32 \pm 37$  g CH<sub>4</sub>/m<sup>2</sup>/year (Table 2), which is similar to  $36 \pm 47$  g CH<sub>4</sub>/m<sup>2</sup>/year from all freshwater wetlands in the conterminous United States (mean  $\pm$  sd) (Bridgham et al., 2006). However, it is noteworthy that the lowest CH<sub>4</sub> emissions in this compilation are from six sites located along a 2.5 km reach of a single tidal freshwater river (Kelley et al., 1995; Megonigal and Schlesinger, 2002). The average of the remainder of the sites is  $58 \pm 36$  g CH<sub>4</sub>/m<sup>2</sup>/year, which is perhaps a more representative sample of TFW sites across the Atlantic and Gulf coasts of the USA. This insight suggests that increasing the sample size will effectively reduce the high variation in current estimates of TFW CH<sub>4</sub> emissions, and that there are specific sites where new studies can be focused to understand the mechanisms that cause low emissions.

[TABLE 19.2 HERE]

Salinity is currently the most useful predictor of spatial variation in CH<sub>4</sub> emissions across tidal wetlands (Bartlett et al., 1987; Poffenbarger et al., 2011; Figure 3). Salinity is a proxy for SO<sub>4</sub><sup>-2</sup> supply, which regulates CH<sub>4</sub> production indirectly through the activity of SO<sub>4</sub><sup>-2</sup>-reducing bacteria that compete with methanogens for electron donor compounds (see Section 3.4). However, salinity is also an imperfect proxy because it fails to explain a great deal of spatial and temporal variation in emissions. Across tidal salinity gradients, both rates and variation in CH<sub>4</sub> emissions peak in oligohaline wetlands (salinity 0.5-5) compared to wetlands in either fresher or saltier estuaries (Poffenbarger et al., 2011). This pattern has been reported across transects within single estuaries, including Delaware Bay, USA, where CH<sub>4</sub> emissions were nearly an order of magnitude higher in an oligohaline marsh than a tidal freshwater marsh (Weston et al., 2014). However, the pattern was absent in Mobile Bay, USA, where emissions were similar across sites ranging from oligohaline to polyhaline (Wilson et al., 2015). Plant community composition may explain some of the oligohaline site variation. For example, two oligohaline marshes in the Scheldt Estuary, EU, that differed by an order of magnitude were dominated by species with distinct morphology and physiology, both of which influence CH<sub>4</sub> emissions (van der Nat and Middelburg, 2000). In particular, emissions from a *Phragmites australis* marsh were higher than from a *Scirpus lacustris* marsh due to a combination of higher carbon additions and lower rhizosphere CH<sub>4</sub> oxidation (van der Nat and Middelburg, 2000). Flooding frequency is another important variable that influences CH<sub>4</sub> emissions (van der Nat and Middelburg, 2000; Megonigal and Schlesinger, 2002). However, it is clear that part of the variability arises from biogeochemical interactions that do not conform to our current understanding of anaerobic metabolism (Section 3.3.4).

[FIGURE 19.3 HERE]

Rates of CH<sub>4</sub> emission underestimate the contribution of methanogens to overall microbial respiration because they do not account for export of dissolved CH<sub>4</sub> in groundwater, microbial CH<sub>4</sub> oxidation to CO<sub>2</sub>, or ebullition (bubble export). Lateral export of dissolved CH<sub>4</sub> from a TFW swamp on the White Oak River, USA, amounted to 30% of CH<sub>4</sub> production (Kelley et al., 1995). At two nearby TFW swamps (i.e. forested wetlands) on the same river, CH<sub>4</sub> oxidation reduced CH<sub>4</sub> emissions 50-80% (Meronigal and Schlesinger, 2002). Methane export by ebullition is rarely measured, but it is expected to be a relatively minor pathway in emergent wetlands where plants effectively vent CH<sub>4</sub> through aerenchyma tissue (van der Nat and Middelburg, 1998a, 2000). Ebullition is an important pathway of CH<sub>4</sub> export in the absence of emergent vegetation, occurring episodically in response to changes in hydrostatic pressure or temperature (Chanton et al., 1989). Ebullition accounted for 44% of CH<sub>4</sub> efflux from tidal freshwater river sediment (Chanton et al., 1989), and 90% of emissions from a plant-free TFW soil (van der Nat and Middelburg, 1998a). Ebullition can increase in importance during seasonal transitions in plant biomass, such as plant emergence or senescence (van der Nat and Middelburg, 1998a).

### 3. Organic Carbon Preservation and Metabolism

A small fraction of the organic carbon produced by plants is ultimately preserved in soils. The fate of organic matter in wetland ecosystems is regulated by complex interactions between plant processes that affect electron donor and electron acceptor availability, and microbial processes that degrade and modify organic matter (Meronigal et al., 2004). Here we review the TFW literature on C cycling processes, focusing on pathways of microbial respiration that are ultimately responsible for key wetland functions such as carbon sequestration and greenhouse gas emissions.

#### 3.1 Carbon quality

A major initial constraint on carbon metabolism in wetlands is the chemical composition of plant material. Mass loss from freshly senescent litter follows an exponential decay curve, with an initial period of rapid loss as the litter is physically fractured and subjected to leaching (Day, 1983), and progressively slower mass loss as organisms depolymerize macromolecules to relatively simple monomers, or as molecules are transformed by microbial and chemical reactions into new, decay resistant compounds (Arndt et al., 2013). Proteins, carbohydrates, and lipids tend to be more susceptible to degradation than lignin, alkyl-C or S-rich compounds (Baldock et al., 2004; Arndt et al., 2013). Mechanistic explanations for differences in the degradation rate of organic compounds have been proposed, but a cohesive conceptual model that integrates organic transformations with microbial and environmental agents remains elusive (Arndt et al., 2013).

A fundamental constraint on organic matter mineralization rates is the amount of energy produced to support microbial respiration and growth, a characteristic that can be quantified by the free energy yield of coupled reduction-oxidation reactions. Differences in free energy yield are commonly invoked to explain the outcome of competition for organic carbon

among microorganisms using different terminal electron acceptors, such as the suppression of methanogenesis by sulfate reduction. Of equal importance is the thermodynamic yield of the electron donor (i.e. organic carbon), a characteristic that varies with the elemental stoichiometry of the compound, and is conveniently expressed as the nominal oxidation state of carbon (NOSC; LaRowe and Van Cappellan, 2011). NOSC is inversely related to thermodynamic yield, and appears promising for understanding the influence of carbon quality on anaerobic carbon degradation rates (Boye et al., 2017). This quantity may prove particularly useful in tidal wetlands where organic matter comes from disparate sources such as herbaceous plants, woody plants, algae, phytoplankton, and eroded terrestrial soil organic matter.

Because TFW plant communities are species-rich compared to tidal saline wetlands (Odum, 1988), organic matter quality may be particularly sensitive to shifts in plant species (Kögel-Knabner, 2002). Plant community composition indirectly controlled root and rhizome decomposition rates across modest salinity gradients (salinity range 0-5) in two tidal freshwater rivers (Stagg et al., 2017). In this case, the dominant plants changed from TFW tree species with high-lignin content, to oligohaline herbaceous species with low-lignin content. Because salt marshes generally lack genera with very low-lignin content such as *Nuphar*, *Peltandra*, and *Pontederia*, it can be hypothesized that litter decomposition rates should be slower in salt marshes than TFWs. For example, Williams and Rosenheim (2015) concluded that soil organic matter stability in three tidal marshes ranging from oligohaline to saline was explained by the lignin content of the dominant plant species. However, Craft (2007) and Stagg et al. (2017) reported higher rates of root decomposition in relatively high salinity sites across five USA estuaries, suggesting that factors other than tissue quality also regulate TFW decomposition rates.

Sulfate availability is one of the most commonly cited factors affecting decomposition along salinity gradients (Craft, 2007). Sutton-Grier et al. (2011) investigated the interaction of carbon quality and sulfate availability by performing a reciprocal transplant of soils between a brackish (mean salinity 14) and a TFW marsh over a 24-31 month period. They found that soil organic matter from the tidal freshwater marsh decomposed faster than the brackish marsh regardless of salinity regime. However, soil organic matter from both sites decomposed more rapidly at the brackish site, and  $\text{SO}_4^{2-}$  additions tended to increase mineralization rates. Thus, the chemical nature of electron donors (organic matter) interacts with the availability of electron acceptors ( $\text{SO}_4^{2-}$ ) to regulate decomposition rates in TFWs.

### 3.2 Aerobic respiration and carbon preservation

Organic matter preservation in saturated soils and sediments is governed by interactions between the chemical composition of tissues and environmental factors (Day, 1982; Benner et al. 1985). Factors that regulate  $\text{O}_2$  supply are particularly important because aerobic respiration yields far more free energy than anaerobic respiration, and does not require a full consortia of microorganisms to complete (Magonigal et al., 2004). In addition,  $\text{O}_2$  supply can indirectly affect extracellular enzyme activity by regulating phenol oxidase, and therefore concentrations of enzyme-inhibiting phenolic compounds (Freeman et al., 2001). Belowground plant biomass is

presumably preserved more efficiently than aboveground biomass in tidal wetlands because it is deposited directly into hypoxic or anaerobic environments. Similarly, organic matter deposited at the soil surface is preserved better in sites with faster rates of burial, due in part to the decrease in O<sub>2</sub> supply (Hedges and Keil, 1995). For example, long term (<sup>210</sup>Pb-determined) C accumulation rates increased with sediment accretion rates in tidal freshwater and oligohaline wetlands (Noe et al., 2016; Table 3). Despite the importance of aerobic respiration for carbon preservation, there are virtually no estimates of aerobic respiration in wetlands (Howes et al., 1984), and no methods for measuring in situ O<sub>2</sub> flux that account for root O<sub>2</sub> loss.

[TABLE 19.3 HERE]

Extracellular enzyme activity is an important control of organic matter degradation rates. Morrissey et al. (2014) found that small differences in salinity (salinity range 0-2) had a direct positive effect on the activity of key carbon-degrading extracellular enzymes across eight tidal freshwater and oligohaline marshes. They attribute this pattern to salinity-induced increases in enzyme activity, organic matter bioavailability, microbial community structure. If confirmed by other studies, stimulation of hydrolytic enzyme activity by salinity may contribute to the widespread observation that soil organic matter content is lower in tidal saline than tidal freshwater wetlands (Craft, 2007). However, other studies on extracellular enzyme responses to salinity show positive, negative and null responses (Morrissey et al., 2014 and citations therein). Organic compounds are protected from extracellular enzymes through interactions with mineral surfaces or sequestration in mineral microaggregates (Blair and Aller, 2012), which are mediated by reactive Fe compounds in TFWs (Shields et al., 2016).

### 3.3 Pathways of anaerobic respiration

Microorganisms derive energy by transferring electrons from an external electron donor to an external electron acceptor. Most respiration in wetland soils depends directly or indirectly (in the case of H<sub>2</sub>) on organic C as the electron donor, and carbon supply tends to limit microbial respiration. This is true of even organic soils where carbon accumulates because it is protected from microbial activity by a variety of factors that ultimately relate to anaerobiosis (Keiluweit et al., 2016). Competition for electron donors favors the respiration pathway that yields the most free energy in the order: aerobic respiration > denitrification > manganese reduction > iron reduction > sulfate reduction > methanogenesis (Meronigal et al., 2004). Humic substances act as electron acceptors under circumstances that are poorly understood, and appear to yield more free energy than methanogenesis (Meronigal et al., 2004).

Many TFWs occur in urbanized watersheds and are exposed to high NO<sub>3</sub><sup>-</sup> concentrations in floodwater, but the contribution of the denitrification pathway to organic C mineralization has not been quantified in TFW soils to our knowledge. In tidal freshwater river sediments from the Altamaha River, USA, denitrification supported 10% of anaerobic C mineralization (Weston et al., 2006). The NO<sub>3</sub><sup>-</sup> concentrations in this study were 20 μM, which is similar to NO<sub>3</sub><sup>-</sup> concentrations in the Hudson River and many other TFW systems. However, Krauss et al. (2016) observed net N<sub>2</sub>O uptake in a TFW, suggesting very low rates of denitrification. Although it

seems unlikely that denitrification is ever a dominant pathway of microbial respiration in TFW soils, it can be an important  $\text{NO}_3^-$  sink in TFW-dominated estuaries (see Section 4.2).

Iron oxide minerals can be the dominant electron acceptor in TFW mineral soils (Roden and Wetzel, 1996; Megonigal et al., 2004), and TFWs have been used extensively for studies of Fe(III) reduction. Tidal freshwater river sediments were used in the first studies to conclusively establish that Fe(III) reduction supports microbial growth (Lovley and Phillips, 1986, 1987). A decade later, van der Nat and Middelburg (1998a) concluded that Fe(III) reduction explained up to 80% of anaerobic respiration in TFW mesocosms, and that the contribution was higher in mesocosms planted with *S. lacustris* than *P. australis*, suggesting that species-specific plant characteristics influence Fe(III) reduction rates. A field study in a *Peltandra virginica*-dominated TFW showed that Fe(III) reduction mediated 20–98% of anaerobic C metabolism (Neubauer et al., 2005b). The importance of Fe(III) reduction declined during the growing season in parallel to plant activity, again suggesting that plants indirectly regulate this microbial process (Figure 4). However, this seasonal pattern can also be explained by direct temperature effects on microbial processes. Bullock et al. (2012) subjected TFW sediments to a range of temperatures and found that rates of Fe(III) reduction were 50% more sensitive to temperature than Fe(II) oxidation. The result was that Fe(III) oxide pools declined with warming temperatures when the two processes are coupled, similar to patterns observed in the field (Neubauer et al., 2005b; Keller et al., 2013).

[FIGURE 19.4 HERE]

Manganese-respiration has received very little attention because concentrations of Mn(III, IV) are usually far lower than Fe(III) in soils (Neubauer et al., 2005b). In theory, this limitation could be overcome by differences in Fe and Mn chemistry, such as the fact that Mn(III,IV)-reduction is favored thermodynamically over Fe(III) reduction. Indeed, solid-state Au/Hg voltammetric microelectrode profiles in a TFW suggested that Mn(III, IV) reduction is more important than Fe(III) reduction in some locations (Ma et al., 2008).

Humic substances are the most recent class of terminal electron acceptor identified in anaerobic substrates (Nevin and Lovley, 2000), and the process remains virtually unstudied in any ecosystem. Keller et al. (2009) amended TFW soil with humic substances extracted from TFW plant species (*Nuphar advena*, *P. australis*, *Salix nigra*, and *Typha latifolia*). The extract amendments inhibited  $\text{CH}_4$  production, supporting the notion that microbial reduction of humic substances yields more free energy than methanogenesis, and that humic substance reduction can suppress  $\text{CH}_4$  production. Indeed, humic substance respiration contributed 33-61% of anaerobic respiration in bog soils (Keller and Takagi, 2013). Humic substance respiration may explain why the amount of  $\text{CO}_2$  and  $\text{CH}_4$  produced in root-free, anaerobic soil incubations often far exceeds the summed contributions of denitrification, metal reduction, and sulfate reduction (Neubauer et al. 2005b; Keller and Bridgham, 2007).

Sulfate reduction is often assumed to be unimportant in TFWs because of limitation by  $\text{SO}_4^{2-}$  at concentrations  $<1$  mM (Weston et al., 2006), but the sparse literature on the process in TFWs suggests there is a need for more research. For example,  $\text{SO}_4^{2-}$ -reduction rates were an

order of magnitude higher in a tidal freshwater marsh than a polyhaline marsh (7 vs 144 mmol m<sup>-2</sup> d<sup>-1</sup>, respectively), despite lower SO<sub>4</sub><sup>2-</sup> concentrations at the TFW site (Segarra et al., 2013). A possible explanation for this unexpected pattern is that SO<sub>4</sub><sup>2-</sup>-reducing bacteria have a greater affinity for SO<sub>4</sub><sup>2-</sup> in the TFW wetland (Ingvorsen and Jørgensen, 1984). Similarly, Weston et al. (2014) reported that SO<sub>4</sub><sup>2-</sup> reduction mineralized 60% as much organic C as methanogenesis. By contrast, Neubauer et al. (2005b) reported that SO<sub>4</sub><sup>2-</sup> reduction in a TFW was <2% of anaerobic C metabolism, while methanogenesis was 40-70% (Fe reduction was the remainder). It would be profitable to resolve the causes of spatial and temporal variation in TFW SO<sub>4</sub><sup>2-</sup> reduction, in part because of implications for CH<sub>4</sub> emissions.

### 3.4 Methane regulation by other anaerobic and aerobic microbial processes

Plants enhance CH<sub>4</sub> emissions as the primary source of organic C that supports methanogenesis, and simultaneously depresses CH<sub>4</sub> emissions as a source of O<sub>2</sub> that either inhibits CH<sub>4</sub> production or enhances CH<sub>4</sub> oxidation. Several lines of evidence suggest that methanogenesis is tightly coupled to photosynthesis and NPP (Megonigal et al., 2004). In TFWs, the evidence includes plant removal experiments (van der Nat and Middelburg, 1998a), a <sup>14</sup>CO<sub>2</sub> tracing experiment (Megonigal et al., 1999), and relationships between CH<sub>4</sub> emissions and photosynthetic rates (Vann and Megonigal, 2003). Plants reduce potential CH<sub>4</sub> emissions by releasing O<sub>2</sub> into the rhizosphere that generates competing terminal electron acceptors such as Fe(III) and supports microbial CH<sub>4</sub> oxidation. The combined effects of plants on CH<sub>4</sub> production, oxidation, and transport generally favor higher net CH<sub>4</sub> emissions. Evidence of this includes higher CH<sub>4</sub> emissions from TFW systems exposed to elevated versus ambient CO<sub>2</sub> (Megonigal and Schlesinger, 1997; Vann and Megonigal, 2003), and higher emissions in the presence versus absence of plants (Kelley et al., 1995; van der Nat and Middelburg, 2000). However, when Keller et al. (2013) tested this hypothesis by removing plants in a TFW field experiment, there was no difference in potential CH<sub>4</sub> production between treatments. One explanation for this result is that plant effects on CH<sub>4</sub> production and oxidation approximately balanced in this case.

Methanogenesis is suppressed when there is an adequate supply of competing electron acceptors. In mineral-rich TFW soils, the dominant competing electron acceptor is Fe(III), which plants regenerate as poorly crystalline Fe(III) oxides in the rhizosphere (Weiss et al., 2004). Suppression of methanogenesis by Fe(III) can range from complete to negligible depending on several factors, including plant activity (van der Nat and Middelburg, 1998a; Neubauer et al., 2005b; Keller et al., 2013). Two studies at the same tidal freshwater marsh arrived at opposite conclusions about the importance of plants as sources of Fe(III) oxides for Fe-reducing bacteria. Neubauer et al. (2005b) found that Fe(III) reduction was strongly related to plant activity, while Keller et al. (2013) reported Fe(III) reduction rates that were 75% lower, and largely unaffected by plants. The two study sites were separated by 440 m, but differed in soil mineral content and plant species (Keller et al., 2013), factors that influence ROL and Fe(III) oxide availability.

Species-specific plant traits can indirectly regulate CH<sub>4</sub> production via rhizosphere Fe cycling. Sutton-Grier and Megonigal (2011) planted mesocosms with the TFW species *Peltandra virginica*, *T. latifolia*, *Juncus effusus*, and *P. australis*, and found that plant traits such as biomass are related to root O<sub>2</sub> loss, rhizosphere-generation of Fe (III) oxides, and CH<sub>4</sub> emission rates.

TFW sites and plant species have been used to elucidate the mechanisms that create rhizosphere hot spots of Fe-cycling compared to non-rhizosphere soil. Fe plaque deposits on wetland plant roots are enriched in poorly crystalline Fe(III) oxide minerals and Fe-reducing bacteria, and therefore support relatively high rates of Fe(III) reduction under anaerobic conditions (Weiss et al., 2003, 2004, 2005). Under aerobic rhizosphere conditions, Fe(II)-oxidizing bacteria accelerate Fe(II) oxidation by 18-83% (Neubauer et al., 2007, 2008).

Sulfate reduction inhibits methanogenesis, but the two processes nevertheless coexist even in highly saline soils because of spatial and temporal variation in the supply of electron donors and acceptors (Megonigal et al., 2004). Sulfate concentrations typically decrease with depth in TFW soils (Segarra et al., 2013), but this does not necessarily translate into lower  $\text{SO}_4^{2-}$  reduction rates. Sulfate reduction in TFWs sometimes maintains high rates at depth, and appears to occur simultaneously with  $\text{CH}_4$  production (Segarra et al., 2013; Weston et al., 2011). One mechanism that can explain the coexistence of these processes is that the two groups of microorganisms use different electron donors, and therefore are not competing (Oremland et al., 1982; Segarra et al., 2014).

Aerobic  $\text{CH}_4$ -oxidizing bacteria are abundant in microaerobic zones of TFW rhizospheres, and have the potential to respond to variations in plant physiology and morphology that influence root  $\text{O}_2$  loss. In TFW mesocosms planted with *P. australis* and *S. lacustris*, both absolute  $\text{CH}_4$  oxidation rate and  $\text{CH}_4$  oxidation efficiency (i.e. as a percentage of  $\text{CH}_4$  production) were significantly greater when the plants were actively growing than after they matured (van der Nat and Middelburg, 1998a).  $\text{CH}_4$  oxidation apparently became  $\text{O}_2$ -limited as ROL declined. Because the capacity to transport  $\text{O}_2$  was similar in growing versus mature plants, an increase in  $\text{O}_2$  demand by roots or aerobic rhizosphere bacteria was the most likely cause of seasonality in  $\text{CH}_4$  oxidation (van der Nat and Middelburg, 1998b).

Aerobic  $\text{CH}_4$  oxidation in wetland soils can be  $\text{O}_2$ -limited or  $\text{CH}_4$ -limited (Lombardi et al., 1997; Bosse and Frenzel, 1998).  $\text{CH}_4$  oxidation in a TFW forest was linearly related to  $\text{CH}_4$  production (Figure 5), indicating that the process was  $\text{CH}_4$ -limited (Megonigal and Schlesinger, 2002). By contrast,  $\text{CH}_4$  oxidation was  $\text{O}_2$ -limited in TFW marsh mesocosms (van der Nat and Middelburg, 1998b). These different conclusions may be explained by the observation that  $\text{CH}_4$  transport in the continuously flooded marsh mesocosms occurred across the thin, oxidized zone around roots, whereas transport in the TFW swamp site also occurred across a relatively thick (5 cm) oxidized zone at the soil surface. The high efficiency of  $\text{CH}_4$  oxidation at the soil surface may have made the process less dependent on  $\text{O}_2$  availability at the swamp site.

[FIGURE 19.5 HERE]

Anaerobic  $\text{CH}_4$  oxidation rates were quantified in great detail at a TFW marsh site on the Altamaha River, USA. Rates of anaerobic  $\text{CH}_4$  oxidation were comparable at a TFW marsh and a polyhaline marsh (Figure 5; Segarra et al., 2013). Rates of anaerobic  $\text{CH}_4$  oxidation at the TFW exceeded rates of methanogenesis, suggesting that the process has the capacity to significantly suppress TFW  $\text{CH}_4$  emissions. The electron acceptor coupled to anaerobic  $\text{CH}_4$  oxidation is

uncertain, but includes sulfate, nitrate, nitrite, Fe and Mn oxides, and humic substances. A strong correlation between sulfate reduction and anaerobic CH<sub>4</sub> oxidation rates (Segarra et al., 2014) suggest that anaerobic CH<sub>4</sub> oxidation is a process that allows methanogenesis and SO<sub>4</sub><sup>2-</sup> reduction to coexist.

#### 4. Nitrogen Biogeochemistry

The biogeochemistry of N, like that of C, is strongly influenced by the supply and availability of electron acceptors and electron donors, as well as the degree of soil oxidation, leading to considerable variability in the importance of individual processes across the marsh surface and over time. For example, sediment deposition and long-term burial of N are often higher close to creek banks than in the marsh interior (Merrill, 1999; Neubauer et al., 2005a). Porewater concentrations of NH<sub>4</sub><sup>+</sup> can be higher in topographically low hollows versus elevated hummock areas (Courtwright and Findlay, 2011), a pattern that may be driven by higher rates of nitrification of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup> in hummocks (Noe et al., 2013). Daily rates of denitrification depend on multiple factors including the duration of inundation (Ensign et al., 2013), which will vary between high marsh and low marsh zones and between hummocks and hollows. Determining the existence and persistence of “hot spots and hot moments” (McClain et al., 2003) and “control points” (Bernhardt et al., 2017) within TFWs remains an enduring challenge for determining ecosystem rates of N cycling.

Tidal freshwater marsh nutrient studies have historically focused on understanding marsh effects on estuarine water quality, and were designed to quantify exchanges of dissolved inorganic nitrogen (DIN) between marshes and tidal waters (i.e. “flux studies”) (Grant and Patrick, 1970; Heinle and Flemer, 1976; Simpson et al., 1978; Bowden, 1986; Chambers, 1992; Campana, 1998; Ziegler et al., 1999). This approach provides valuable information and can average across small-scale spatial variability within an individual basin, but is limited by high variability between marsh basins and across time, and difficulties in obtaining accurate hydrologic budgets to scale up the measurements. Flux studies do not provide detailed information on internal transformations that are occurring within marsh soils and sediments. Numerical simulation models allow process rates to be calculated from measurements of soil organic and inorganic nutrients (Morris and Bowden, 1986), and if robustly designed, can be used to explore how the system might respond to future environmental changes (e.g., level of watershed nutrient loading). Recently, isotope tracers have been used to determine both the fate of water column N, and the processes by which the N is transformed or removed from the water column (Gribsholt et al., 2005, 2006, 2007). This approach provides an elegant means of quantifying N transformations that eliminates many of the issues associated with flux studies and process rate measurements. Isotope tracer studies can be used to quantify fluxes and transformations in the water column (Tobias et al., 2003; Gribsholt et al., 2005, 2006, 2007), and processes occurring in the root zone across a range of temporal scales (White and Howes, 1994; Tobias et al., 2001b).

We only know of two comprehensive N models for tidal freshwater marshes that consider exchanges of N between the marsh, estuary, and atmosphere, as well as internal N transformations in soils (Figure 6a,b; Bowden et al., 1991; Neubauer et al. 2005a). Both models

were built with seasonal data from different locations. Although neither is seasonally or spatially explicit, both integrate measurements made at multiple times and in multiple locations within a wetland. The model by Bowden and colleagues (Figure 6a) describes N cycling at a North River, Massachusetts, USA marsh that had organic-rich soils (40-63% organic matter) and a well-developed, persistent plant litter layer. Neubauer and collaborators (Figure 6b) studied Sweet Hall marsh on the Pamunkey River, USA, which had relatively little plant litter and more mineral soils (16-21% organic). Average nutrient concentrations ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) in the North River were ~4 times greater than those in the Pamunkey River (Neubauer et al., 2005a). Despite the limitations of mass balance modeling and differences between these marshes in plant community, soil type, marsh elevation, nutrient loading, and climate, several features of the N cycle were similar and may be common to TFWs generally:

- 1) Exchanges of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  between the TFW and tidal waters were small compared to rates of internal N cycling and transformations in soils. Nitrogen in sediments deposited on the soil surface can be a significant source of new N to marshes, although the importance of this N source varies with flooding frequency and a suite of factors that influence sediment deposition rates (Darke and Megonigal, 2003).
- 2) Marsh-estuary exchanges of  $\text{NO}_3^-$  are generally directed into the marsh (i.e. net uptake by the marsh), and are similar in magnitude to rates of denitrification, suggesting the two processes are coupled.
- 3) TFWs are efficient at recycling and retaining nutrients within the soil profile. The efficiency of nutrient recycling may be greater in older wetlands with deep soils than in younger wetlands (Morris and Bowden, 1986).
- 4) The generation of inorganic N via organic matter mineralization can provide more than enough N to support primary production. This suggests that plant production may be largely uncoupled from nutrient loading in the adjacent tidal waters over relatively short periods of time (ca. one to several years). Over longer periods of time, the progressive assimilation and accumulation of water column N by the TFW offsets N losses to denitrification and helps build the soil N pool, which can then be mineralized to support plant demands.

[FIGURE 19.6 HERE]

#### 4.1 Nitrogen exchanges

Exchanges of  $\text{NH}_4^+$  between TFWs and floodwaters are controlled by the diffusive gradient between soil pore waters and tidal waters, which is influenced strongly by microbial  $\text{NH}_4^+$  assimilation. TFWs with an extensive litter layer often show net  $\text{NH}_4^+$  uptake from the water column (Heinle and Flemer, 1976; Bowden, 1986) despite high porewater concentrations

because the litter layer is acting as a sink for both porewater and water column  $\text{NH}_4^+$ . Other wetlands are sources of  $\text{NH}_4^+$  to tidal waters (Campana, 1998; Ziegler et al., 1999; Neubauer et al., 2005a). Although wetland-estuary exchanges of  $\text{NH}_4^+$  (and other N forms) may be significant on a whole-estuary basis, the magnitude of these fluxes is generally small relative to internal N transformations occurring in soils (e.g., Figure 6a,b). In a pair of elegant  $^{15}\text{NH}_4^+$  labeling experiments conducted in May (early growing season with active plant growth) and September (late growing season with senescent, flowering plants), the fate of water column  $\text{NH}_4^+$  was tracked over about 15 days in a N-rich tidal freshwater marsh in Belgium, EU (Gribsholt et al., 2005, 2006, 2007). Despite the temporal separation between the experiments, the fates of  $\text{NH}_4^+$  were remarkably similar between the months. In each experiment, the majority of the water column  $\text{NH}_4^+$  was exported from the system without being transformed by the marsh (Figure 7). Approximately 4% of the  $\text{NH}_4^+$  was sequestered in plant biomass, litter, or soil (either via physical sorption or microbial assimilation). Overall, microbial pathways of N uptake were more important than the direct assimilation of tidal water  $\text{NH}_4^+$  by plants (Gribsholt et al., 2006). However, plants are likely to play indirect roles in modifying water column N loads by providing both  $\text{O}_2$  and labile organic C to soil microbes. The  $^{15}\text{N}$  label was also found in other N pools within the water column, indicating that active N transformations were occurring within the water column and/or in flooded marsh soils. Of these N transformations, nitrification accounted for the largest fraction of the added  $\text{NH}_4^+$ , with smaller amounts in the suspended particulate N,  $\text{N}_2$ , and  $\text{N}_2\text{O}$  pools. The marsh soils appeared to be a significant site for nitrification in May (Gribsholt et al., 2005), whereas soil denitrification rates were highest in September (Gribsholt et al., 2006).

In contrast to the high variability in the direction and rate of  $\text{NH}_4^+$  exchanges between TFW soils and tidal waters, TFWs are generally strong sinks for water column  $\text{NO}_3^-$  (Arrigoni et al., 2008; Bowden et al., 1991; Findlay and Fischer, 2013; McKellar et al., 2007; Neubauer et al., 2005a; Van Damme et al., 2009). This  $\text{NO}_3^-$  is often used to support denitrification in TFW soils (see section 4.2, below). Although there is generally a consistent trend of  $\text{NO}_3^-$  uptake by TFW soils, it has proven difficult to develop predictive relationships to quantify the amount of  $\text{NO}_3^-$  uptake. Findlay and Fischer (2013) reported that 40% of the variation in the amount of  $\text{NO}_3^-$  decline between flood and ebb tide could be explained by the coverage of graminoid-dominated high-intertidal vegetation within a wetland basin. However, Arrigoni et al. (2008), who worked with a smaller subset of TFWs in the same Hudson River (NY, USA) region studied by Findlay and Fischer (2013), reported no ability to predict  $\text{NO}_3^-$  fluxes on the basis of vegetation type or geomorphic factors. Flux studies in TFWs on the Patuxent River, USA, have shown that the amount of  $\text{NO}_3^-$  removal is strongly correlated with the incoming load of  $\text{NO}_3^-$ , but only weakly with the concentration of incoming  $\text{NO}_3^-$  (Seldomridge and Prestegard, 2014), suggesting that nitrate removal is limited by the hydrological delivery of  $\text{NO}_3^-$  to TFWs, and not to kinetic factors that control rates of denitrification (Seldomridge and Prestegard, 2011). Structural equation modeling pointed toward tidal exchange volume, ambient  $\text{NO}_x$  concentrations (which determine the  $\text{NO}_3^-$  load), and ecosystem respiration as the primary controls on  $\text{NO}_3^-$  removal in a recently restored TFW in Virginia, USA (Bukaveckas and Wood, 2014). Despite lower fluvial  $\text{NO}_3^-$  loading, total  $\text{NO}_3^-$  removal in tidal freshwater rivers is

greatest in warmer months because denitrification is a biological process that increases with temperature (Bukaveckas et al., 2017). Denitrification is often the ultimate sink for water column  $\text{NO}_3^-$ , converting it to  $\text{N}_2$  gas.

TFWs are often significant sinks for water column particulate N deposited on the soil during tidal flooding. The N content of accumulated sediments ranged from 4 to 16 mg N/g sediment in several tidal freshwater marshes in Virginia (Morse et al., 2004; Neubauer et al., 2005a) and is significantly correlated with the soil N content (Morse et al., 2004). The sediment-associated N is presumably a combination of detrital material, microbial biomass, and  $\text{NH}_4^+$  sorbed to mineral surfaces. On an annual basis, inputs of allochthonous particulate N can be large with respect to the marsh N budget, contributing up to 20 g N/m<sup>2</sup>/year (Bowden et al., 1991; Morse et al., 2004; Neubauer et al., 2005a). There is significant spatial variation in deposition rates driven by marsh elevation and flooding frequency (Morse et al., 2004). Over decadal scales, the burial of N sequesters significant amounts of N in tidal freshwater marsh soils, on the order of 10–30 g N/m<sup>2</sup> /year (Table 1 and references therein). Deposition and burial rates are much higher in Sweet Hall marsh than the North River marsh (Figure 6a,b), a difference reflected in the lower organic content of Sweet Hall marsh soils. Indeed, regional patterns of sedimentation may explain why soil accretion rates in TFWs of the Northeast United States are correlated only with organic accumulation, while those in the Southeastern United States are correlated with both mineral and organic accumulation (Neubauer, 2008).

Over each tidal cycle, a large volume of water floods and ebbs from the surface of TFWs. Because of the high rate of surface-water exchange, wetland uptake of DIN from floodwaters is inefficient (Hopkinson, 1992) and can meet only a small fraction of plant N demand. This leads to the “requirement” that existing nutrients are retained within the wetland. Indeed, only ~1% of the total N supplied to the  $\text{NH}_4^+$  pool from external and internal sources is lost; the remainder is recycled to other N reservoirs in the marsh (Figure 6a,b). It is likely that the slow turnover of marsh porewater (67 to >800 days in the upper 30 cm at Sweet Hall marsh) drives this efficient N retention. Microbial immobilization of  $\text{NH}_4^+$  into particulate matter is a primary mechanism by which N is retained in the marsh; this mechanism can retain > 50% of mineralized N in tidal freshwater (Bowden et al., 1991; Neubauer et al., 2005a) and salt marshes (Anderson et al., 1997). In contrast to the porewater  $\text{NH}_4^+$  pool, plant biomass N in TFWs is directly exposed to the tides and less efficiently retained, with ~50% exported as dissolved or particulate organic matter (Hopkinson, 1992; Neubauer et al., 2005a). In support of the link between water turnover and system closure, there was little evidence of N export from a “periodically flooded” high marsh (Bowden et al., 1991).

#### 4.2. Nitrogen transformations

Tidal freshwater marshes permanently remove DIN from riverine and estuarine waters via burial and denitrification (Section 4.1), the reduction of  $\text{NO}_3^-$  to gaseous  $\text{N}_2$ . Sources of  $\text{NO}_3^-$  include nitrification within the marsh and the uptake of external (water column)  $\text{NO}_3^-$ . Mass balance calculations indicate high rates of N removal in upper estuaries (Howarth et al., 1996), and many characteristics of TFWs appear to favor denitrification, such as high active surface area, shallow depth to anaerobic zone, high organic matter availability. High denitrification

rates have been confirmed in multiple TFW studies (Groszkowski, 1995; Merrill, 1999; Merrill and Cornwell, 2000; Elsey-Quirk et al., 2013; Ensign et al., 2008, 2013; Von Korff et al., 2014). Greene (2005) reported that median denitrification rates for a tidal freshwater marsh ( $\sim 120 \mu\text{mol N/m}^2/\text{h}$ ) were slightly larger than the median rate for a wide range of intertidal and aquatic systems ( $\sim 75 \mu\text{mol N/m}^2/\text{h}$ ). However, there is considerable spatial variability between and within TFWs (Merrill, 1999; Greene, 2005).

The environmental controls on denitrification have been extensively reviewed (Seitzinger, 1988; Cornwell et al., 1999; Wallenstein et al., 2006) and will not be covered in great detail here. In tidal freshwater marshes, denitrification rates are correlated with benthic sediment  $\text{O}_2$  demand in a New York marsh, but not in a TFW in Maryland, USA (Merrill, 1999). Based on laboratory manipulations, denitrification rates increase with increases in water column  $\text{NO}_3^-$  (Merrill, 1999; Greene, 2005). Similarly, the N models of Bowden et al. (1991) and Neubauer et al. (2005a) suggest that denitrification is supported primarily by water column  $\text{NO}_3^-$ . Because ROL and diffusion of  $\text{O}_2$  across the soil surface can support oxidation in tidal freshwater marsh soils (Neubauer et al., 2005b), denitrification is likely to be coupled to both in situ nitrification and water column  $\text{NO}_3^-$  uptake. Gribsholt et al. (2005, 2006, 2007) presented evidence for coupled nitrification-denitrification in TFWs; following the addition of a  $^{15}\text{NH}_4^+$  to tidal flood waters, some of the  $^{15}\text{N}$  label appeared in the dissolved  $\text{N}_2$  and  $\text{N}_2\text{O}$  pools (Figure 7). Much of this nitrification takes place in marsh soils – possibly associated with plant roots – rather than in the water column (Gribsholt et al., 2005). The importance of the soil as a site for nitrification can vary seasonally (Neubauer et al., 2005a; Gribsholt et al., 2006) and spatially, with higher-elevation hummocks having roughly three-times higher rates of nitrification than lower-elevation hollows (Noe et al., 2013). Most laboratory measurements of denitrification give potential rates, in that incubations are done under anaerobic conditions. Scaling these measurements across space and time requires considering the duration that a particular location in a TFW is sufficiently reduced (that is, has a low-enough redox potential) to support denitrification, which itself is a function of soil characteristics and marsh topography (Elsey-Quirk et al., 2013; Ensign et al., 2008, 2013; Von Korff et al., 2014).

[FIGURE 19.7 HERE]

When integrated over the entire network of TFWs within an estuary, nutrient removal may be substantial because the small contributions of individual marshes can have a large cumulative impact on water quality. This is especially true in systems with large areas of tidal marsh relative to open water. For example, in the Patuxent and Choptank Rivers, USA, slightly more than 30% of the total N input at the fall line is permanently removed by low-salinity tidal marshes via burial and denitrification (Merrill, 1999; Malone et al., 2003). In contrast, N removal by tidal freshwater marshes in larger systems such as the Hudson and Delaware Rivers, USA, is less efficient, with only  $\sim 2\text{-}5\%$  of the N sequestered or denitrified (Academy, 1998; Merrill, 1999; Elsey-Quirk et al. 2013).

Dissimilatory  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$  (DNRA) is a mechanism by which  $\text{NO}_3^-$  can be retained in the marsh, rather than lost to the atmosphere as  $\text{N}_2$  as in denitrification. There is

very little evidence from TFWs on the relative importance of DNRA and denitrification as alternative fates for soil  $\text{NO}_3^-$ . Bowden (1986) determined that DNRA rates were 5% of  $\text{NO}_3^-$  supply (i.e., nitrification) rates. In contrast, Neubauer et al. (2005a) calculated that DNRA was about 40% of nitrification. Based on work in other systems, the availability of labile C relative to  $\text{NO}_3^-$  (i.e., electron donor: electron acceptor ratio) is important in determining the fate of  $\text{NO}_3^-$ , with high organic C availability favoring DNRA (Fazzolari et al., 1998; Christensen et al., 2000; Giblin et al., 2013), and denitrification increasing in importance at higher  $\text{NO}_3^-$  concentrations (Nijburg et al., 1997; Tobias et al., 2001a,b). Thus, relatively low  $\text{NO}_3^-$  in the Pamunkey River (Neubauer et al., 2005a) may explain the higher importance of DNRA in that system. Across the estuarine gradient, DNRA is generally more important (relative to denitrification) in estuarine and marine systems, whereas denitrification is more important in freshwater systems (Tobias et al., 2001b). This pattern that may be related to sulfide inhibition of denitrification (Brunet and Garcia-Gil, 1996; An and Gardner, 2002).

#### 4.3 Nutrient regulation of plant production

It has proven difficult to unambiguously determine the nature (or existence) of nutrient limitations in TFWs (Chambers and Fourqurean, 1991). Inconsistent responses to allochthonous nutrient inputs suggest that rates of plant production in tidal freshwater marshes are largely uncoupled from allochthonous nutrient inputs. Indeed, rates of N mineralization in TFWs are considerably greater than plant N demand and rates of diffusive DIN uptake from tidal waters (Figure 6a,b; Bowden et al., 1991; Neubauer et al., 2005a). In these studies, gross N mineralization provided almost 3 times more  $\text{NH}_4^+$  than was needed to support annual plant N requirements. Further, there are multiple examples in which direct fertilization of TFWs with N, P, or N+P did not increase either aboveground biomass or biomass nutrient content (Whigham and Simpson, 1978; Walker, 1981; Booth, 1989; Chambers and Fourqurean, 1991; Morse et al., 2004).

There are some examples in which fertilization increased plant growth (Booth, 1989; DeLaune et al., 1986; Frost et al., 2009). Instances when TFW plant productivity responds to fertilization may reflect differences in plant species composition (e.g., annuals vs. perennials, or graminoid vs. broadleaf vs. woody) and/or the level of applied fertilizer. A gradient fertilization study of a Virginia, USA, TFW applied N and P fertilizers in four annual doses ranging from 18-73 g  $\text{N}/\text{m}^2$  and 0.5-1.7 g  $\text{P}/\text{m}^2$  (for comparison, annual tidal nutrient inputs to the site were roughly 60 g  $\text{N}/\text{m}^2$  and 2.9 g  $\text{P}/\text{m}^2$ ). Compared to control plots, there were few significant plant responses to fertilization at lower fertilization levels, but several (not all) species responded with higher growth at the highest levels of fertilization (Burton and Neubauer, in prep.).

There is a generalization that aquatic primary production is limited by phosphorus (P) availability in freshwaters, and by N in brackish and saline waters, but this does not appear to hold in tidal wetlands, where primary production is often limited by N in both TFWs and salt marshes. This is illustrated by a factorial nutrient addition study in a *Zizaniopsis miliacea*-dominated TFW in Georgia, USA. Aboveground plant productivity significantly increased following N additions, but did not change (relative to controls) with P fertilization. Further, plant production was no higher in experimental plots that received both N and P, compared to

N-only plots (Gautam, 2015). Similarly, P additions did not affect primary productivity in TFWs in Virginia and Georgia, USA (Morse et al., 2004; Frost et al., 2009), although Baldwin (2013) observed that N and P had contrasting effects on annuals vs. perennials.

## 5. Phosphorus Biogeochemistry

Because TFWs are located in upper estuaries where watershed-derived inputs of P are concentrated, these intertidal systems may be key sites in landscapes for P sequestration and transformation. In a pair of tidal freshwater marshes, sediments deposited on the soil surface contained 0.3–1.7 mg P /g sediment and contributed inputs of 0.6–2.3 g P/m<sup>2</sup>/year (Morse et al., 2004). Uptake of inorganic P by organisms results in a relative enrichment of organic P in surface soils (Morse et al., 2004). In a South Carolina TFW, much of the soil organic P was bound to humic acids whereas the inorganic P was primarily associated with Fe or Al (Paludan and Morris, 1999).

Phosphatase is an enzyme that liberates organic-bound P, and is secreted by plants, algae, and bacteria under conditions of PO<sub>4</sub><sup>3-</sup> limitation. Phosphatase activity is expected to be greatest where the biological demand for inorganic P is high, most soil P is in organic forms, and soil sorption limits porewater PO<sub>4</sub><sup>3-</sup> concentrations. The activities of three phosphatase enzymes were highly, positively correlated with aboveground plant biomass and soil organic content in a successional sequence of TFWs (Huang and Morris, 2003). Similar correlations between phosphatase activity, soil organic matter, and soil organic P were observed along a salinity gradient, with the highest activity in TFWs (Huang and Morris, 2005). By comparison, Morrissey et al. (2014) reported lower phosphatase activity in TFW than oligohaline wetlands (Figure 4).

Organic P made up a greater fraction of total P in the late (intertidal marsh) versus early (open water) successional stages. The interactions between P availability and demand may lead to a positive feedback that drives ecosystem succession, whereby high demand for inorganic P reduces available PO<sub>4</sub><sup>3-</sup> concentrations, leading to an increase in phosphatase activity and increased organic P mineralization, further increasing plant growth (Huang and Morris, 2003). Over years to decades, P mineralization results in a significant decrease in organic P concentrations with increasing soil depth (Paludan and Morris, 1999). Despite high phosphatase enzyme activities in TFW soils, concentrations of dissolved PO<sub>4</sub><sup>3-</sup> are often low due to the combined effects of biological demand and chemical sorption processes that remove free PO<sub>4</sub><sup>3-</sup> from marsh porewaters. Sundareshwar and Morris (1999) showed that P sorption rates were lower in systems where sediments had lower surface areas and lower Fe/Al mineral contents. The lack of significant accumulation of inorganic P in deeper soils (Paludan and Morris, 1999) implies that organic P is not simply mineralized to inorganic P, but is instead removed from the soil via plant uptake or hydrological export. The amount of extractable total P and extractable inorganic P is related to soil type, where soils that were higher in clay content and bulk density had greater P concentrations, compared to soils that were higher in organic matter and sand content (Noe et al., 2013). Higher total P content was associated with higher rates of P mineralization and a greater P turnover rate (Noe et al., 2013).

Although TFWs are sinks for sediment-associated particulate P, PO<sub>4</sub><sup>3-</sup> fluxes are highly

variable and there can be net  $\text{PO}_4^{3-}$  uptake (Simpson et al., 1978; Gilbert, 1990), seasonal variability (Simpson et al., 1983; Campana, 1998), or negligible  $\text{PO}_4^{3-}$  fluxes (Anderson et al., 1998) between TFWs and tidal waters. One factor that may affect spatial and temporal variations in marsh-estuary tidal fluxes of  $\text{PO}_4^{3-}$  is the interplay between P, Fe, and  $\text{O}_2$  dynamics. In soils that are regularly exposed to  $\text{O}_2$  during low tides (e.g., the marsh surface and creek bank edges), Fe(II) can oxidize to Fe(III) and lead to the formation of an “iron curtain” of iron oxyhydroxide minerals that efficiently sorb  $\text{PO}_4^{3-}$ , causing P retention in the marsh (Chambers and Odum, 1990). In combination with diagenetic effects, this mechanism may contribute to decreases in total soil P content with increasing depth, which has been observed in some TFWs (Bowden, 1984; Chambers and Odum, 1990; Merrill, 1999; Paludan and Morris, 1999), though not in all (Simpson et al., 1983; Greiner and Hershner, 1998). The mineral content of the soils is likely to play a role in the efficiency of such an iron curtain because minerals are rich in Fe. The ecological implications of the iron curtain on ecosystem P dynamics are unclear because it retains a potentially limiting nutrient within the marsh, but not necessarily in a bioavailable form. That said, P mineralization rates in tidal wetlands along an alluvial river were positively correlated with total soil Fe, suggesting that reduction of Fe-P minerals was contributing to P release (Noe et al., 2013). Another implication is that high marshes, which are flooded less frequently and therefore exposed to air for longer periods of time, may have an extensive iron curtain that allows for more efficient P retention and recycling than low marshes, leading to increased P accumulation in high versus low marsh habitats (Khan and Brush, 1994).

The storage (burial) of P in marsh soils is an important mechanism by which P can be removed and sequestered from estuarine waters. Over time scales ranging from decades to centuries, TFWs sequester significant amounts of P, with burial rates ranging from  $< 0.5$  to  $> 4$  g  $\text{P}/\text{m}^2/\text{year}$  (Table 1 and references therein). These burial rates are roughly comparable to rates of sediment-associated P deposition onto the marsh surface (Morse et al., 2004). There is often significant variability in P burial rates within an individual marsh. This is correlated with plant community composition, which is a function of marsh elevation and proximity to creek banks, and differs strongly between watersheds (Merrill, 1999; Merrill and Cornwell, 2000). For example, in the Patuxent River, USA, total P burial rates were significantly higher in the *Nuphar luteum* (spatterdock)-dominated low marsh (12 g  $\text{P}/\text{m}^2/\text{year}$ ) relative to high marsh areas dominated by *Hibiscus moscheutos* (marsh hibiscus), *Typha* spp., or *Zizania aquatica* (northern wild rice) (1.2-2.5 g  $\text{P}/\text{m}^2/\text{year}$ ) (Merrill, 1999). Extrapolating marsh P burial rates to a landscape scale shows that low-salinity tidal marshes can sequester a significant fraction ( $>60\%$ ) of watershed-derived P in relatively small, marsh-dominated estuarine systems (Merrill, 1999; Malone et al., 2003). In contrast, about 12% of the combined sewage and riverine-derived P to the upper Hudson River, USA, is buried in freshwater tidal and nontidal marshes (Limburg et al., 1986; Phillips and Hanchar, 1996; Merrill, 1999). Based on average literature values for marsh P burial, only  $\sim 7\%$  of the P entering the upper Delaware River estuary, USA, is permanently buried in tidal marshes (Academy, 1998). Thus, TFWs can be long-term sinks for significant amounts of watershed-derived P, but the extent of wetlands within the estuary (relative to the size of the estuary or watershed) appears to be important in determining how efficiently TFWs perform this function.

## 6. Silicon Biogeochemistry

The weathering of terrestrial silicate (Si) minerals ultimately leads to inputs of dissolved silica (DSi) to estuaries and the coastal ocean where diatom production can be limited by low DSi availability. Evidence suggests that silica transformations in TFWs play a key role in transforming silica from biogenic (BSi) to DSi forms. For example, under low discharge conditions (summer) in the Scheldt estuary, EU, the input of DSi from fluvial sources was as low as 10,000 kg/month, an amount that can be exported from the 450 ha of TFWs in the system in six tidal cycles (Struyf et al., 2006). Because rates of DSi export increased with decreasing concentrations of DSi in estuarine waters, marsh-mediated recycling of Si may be especially important when low, ambient DSi concentrations otherwise limit aquatic primary productivity (Struyf et al., 2006). Indeed, marsh DSi export has the greatest effect on estuarine N:DSi ratios during summer when the concentrations of both DSi and inorganic N are lowest (van Damme et al., 2009). Understanding the factors that regulate DSi export from TFWs requires additional research on biogeochemical transformations in TFW soils (Struyf et al. 2005a, 2005b, 2007).

## 7. Responses and Contributions to Global Change

In their landscape position between uplands and estuaries, TFWs are subject to changes in the terrestrial landscape (freshwater, nutrient, and sediment delivery), the estuarine/oceanic seascape (sea level rise, saltwater intrusion), and the atmosphere (global warming, rising CO<sub>2</sub>) (Neubauer and Craft, 2009). In this section, we briefly discuss the effects of saltwater intrusion on TFW biogeochemistry, both because saltwater intrusion changes a defining characteristics of TFWs -- the existence of freshwater vs. brackish conditions -- and because saltwater intrusion has impacts on the biogeochemical cycling of multiple elements including C, N, P, Fe, and S. We also consider TFWs as sinks for CO<sub>2</sub> and sources for CH<sub>4</sub>, and the potential for TFWs to influence global radiative forcing.

### 7.1 Biogeochemical effects of saltwater intrusion

Saltwater intrusion is the upstream movement of brackish or saline water that causes concentrations of salt and other seawater-derived ions to increase above natural background levels (Herbert et al., 2015). The increase in global sea level has the potential to affect TFWs by modifying their hydroperiod, and by pushing the salt front up-estuary so that these systems are exposed to more saline waters. Similarly, decreases in river discharge that are caused by changes in watershed precipitation and/or anthropogenic activities (e.g., construction of dams) that reduce river flow can lead to increased salinity in the tidal freshwater zone. Future changes in salinity in a given TFW will depend on the wetland's position on the current salinity gradient, rates of sea level rise, and changes in river discharge. Both sea level rise and river discharge are influenced by global warming (Burkett et al. 2001). We briefly discuss the impacts of saltwater intrusion on the biogeochemical cycling of C, N, P, Fe, and S in TFWs, but this global change stressor affects TFWs from physiological to ecosystem to landscape scales (Figure 8).

[FIGURE 19.8 HERE]

Changes in salinity can affect a number of nutrient cycling processes including N and P sorption, denitrification, and nitrification (Howarth et al., 1988; Caraco et al., 1989; Rysgaard et al., 1999). The intrusion of saltwater and associated  $\text{SO}_4^{2-}$  can lead to the breakdown of the “iron curtain” described by Chambers and Odum (1990). For example, Meiggs and Taillefert (2011) showed enhanced Fe(III) reduction rates following saltwater intrusion. Along estuarine gradients, more sediment P is bound to Fe(III) oxides in freshwater, whereas the abundances of organic P and free  $\text{PO}_4^{3-}$  are greater in brackish water (Jordan et al. 2008). As Fe oxides are reduced either biologically (by Fe(III)-reducing bacteria) or chemically (via  $\text{H}_2\text{S}$ ), sediment-bound P is released and the Fe(II) can be sequestered in Fe-S compounds (e.g., pyrite) (Caraco et al., 1989; Lamers et al. 2001). The release of soil P and increases in soil sulfides can lead to internal eutrophication (Smolders et al., 2010), reductions in plant productivity and diversity (Lamers et al., 2013; Sutter et al., 2014), and alterations to soil N cycling.

Production of the greenhouse gas  $\text{N}_2\text{O}$  can increase if high  $\text{H}_2\text{S}$  concentrations inhibit nitrification and denitrification, as has been shown for unvegetated sediments (Joye and Hollibaugh, 1995; Brunet and Garcia-Gil, 1996; An and Gardner, 2002). However, these effects may be minimized in TFWs with large quantities of soil Fe because Fe(III) can scavenge sulfides that are produced by  $\text{SO}_4^{2-}$  reduction during saltwater intrusion episodes (Schoepfer et al., 2014). Elevated salinity can also lead to decreased sorption of  $\text{NH}_4^+$  to soil particles as  $\text{NH}_4^+$  is displaced by positively charged cations such as  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . Increased  $\text{NH}_4^+$  concentrations may suppress  $\text{N}_2$  fixation because nitrogenase is inhibited by free  $\text{NH}_4^+$  (Howarth et al., 1988). The physiological effects of salinity on nitrifying and denitrifying microbes reduce the activity of these organisms (MacFarlane and Hebert, 1984; Furumai et al., 1988; Stehr et al., 1995, Rysgaard et al., 1999) and can lead to changes in denitrification rates (Craft et al., 2009; Marton et al., 2012). If increased  $\text{SO}_4^{2-}$  concentrations accelerate soil organic matter decomposition (see Section 3.1), rates of nutrient mineralization would also increase.

Over short time periods (months to years), saltwater intrusion acts as a stressor to TFW plants and consequently reduces ecosystem-scale primary productivity. Over periods of several days (Chambers et al., 2011; Neubauer et al., 2013) to a year (Weston et al., 2011), saltwater intrusion also tends to increase soil carbon mineralization rates. Overall, salinity tends to lower marsh-atmosphere  $\text{CO}_2$  emissions in the field due to a combination of lower plant respiration, and lower inputs of labile organic matter to soils (Neubauer, 2013b; Lee et al., 2016; Neubauer et al., 2013).

Thermodynamics dictate that microbial  $\text{SO}_4^{2-}$  reducers will outcompete methanogens for substrates such as organic C. The contribution of  $\text{SO}_4^{2-}$  reduction to C mineralization is expected to increase with TFW proximity to the saltwater boundary, which makes TFWs and oligohaline wetlands susceptible to incursions of  $\text{SO}_4^{2-}$  due to drought, storm surge, and sea level rise. Saltwater intrusion favors the  $\text{SO}_4^{2-}$  reducers that compete against methanogens, leading to lower emissions of the greenhouse gas  $\text{CH}_4$  (Meronigal et al., 2004; Neubauer and Craft, 2009). Measurements consistent with this prediction have been reported in multiple laboratory (Chambers et al., 2011; Neubauer et al., 2013) and field studies (Neubauer, 2013b; Lee et al., 2016; Herbert et al., in review), although a smaller number of studies have reported

unexpected increases in CH<sub>4</sub> production and/or emission following saltwater intrusion (Weston et al., 2011, 2014). Further, there is evidence that increased SO<sub>4</sub><sup>2-</sup> reduction rates will stimulate organic matter mineralization (Portnoy and Giblin, 1997; Weston et al., 2006; Craft, 2007; Neubauer et al., 2013). However, other studies reported no differences in rates of anaerobic organic matter mineralization in comparisons of brackish versus tidal freshwater marsh soils (Neubauer et al., 2005b, Figure 4) and sediments (Kelley et al., 1990). Over days to months, saltwater intrusion may increase mineralization as existing C pools are degraded more rapidly due to increased rates of SO<sub>4</sub><sup>2-</sup> reduction (Sutton-Grier and Megonigal, 2011), but longer-term (multi-year) saltwater intrusion can reduce pools of soil organic matter and lead to lower overall rates of mineralization (Neubauer et al., 2013). This is an important question to understand with respect to climate change because of the implications for soil C pools and nutrient turnover in former TFWs (Neubauer and Craft, 2009). In TFWs, an average of 62% of vertical accretion is due to the accumulation of organic matter (Neubauer, 2008). If saltwater intrusion reduces rates of organic matter accumulation by reducing rates of primary production and/or by increasing rates of decomposition, TFWs will be less able to accrete vertically and keep pace with ever-increasing rates of sea level rise.

Thus far, there are no consistent trends in the impact of saltwater intrusion on net ecosystem productivity (NEP). NEP is the balance between gross primary production and ecosystem respiration, and is used as a proxy for ecosystem carbon storage or loss. In a multiyear in situ salinity manipulation in a South Carolina, USA, tidal freshwater marsh, saltwater intrusion decreased annual NEP by 55–63% during two years, but had no effect in a third year (Neubauer, 2013b; Neubauer unpubl.). Similarly, experimental in situ saltwater intrusion led to lower NEP in a Georgia, USA, TFW (Herbert et al., in review), but had no effect on NEP in a Virginia, USA, marsh (Neubauer and Lee, in prep.). Over longer time periods, salt-sensitive plants, animals, and microbes will likely be replaced by salt-tolerant species (Magalhães et al., 2005). There is relatively little known from direct manipulations of salinity about the direction of these longer-term effects, or how they will affect ecosystem fluxes and carbon storage.

## 7.2 Radiative forcing

High rates of primary production and low rates of decomposition are features that are common to most wetlands that typically lead to high rates of C sequestration in TFWs (Neubauer, 2013a; Table 1). However, TFWs are also sources of CH<sub>4</sub> to the atmosphere (see Section 2.2.2) and may be either sources or sinks of N<sub>2</sub>O (e.g., Krauss and Whitbeck, 2012; Krauss et al., 2016). Because TFWs are both sources and sinks of greenhouse gases, there is interest in determining the overall climatic effect of these ecosystems; that is, to ask whether they have a net warming or cooling effect. Neubauer and Megonigal (2015) developed the sustained-flux global warming potential (SGWP) as a straightforward metric of the radiative balance in ecosystems that emit and remove multiple greenhouse gases from the atmosphere. The SGWP avoids some inherent limitations of the global warming potential (GWP) when applied to ecosystems, especially the GWP assumption that greenhouse gas exchanges occur a single discrete pulse rather than as a continuously flux. Over the commonly used 100-year time frame, TFWs consistently have a net

warming effect on the climate (Table 3), meaning that the warming due to the emission of CH<sub>4</sub> exceeds the cooling due to the uptake of CO<sub>2</sub> (annual N<sub>2</sub>O fluxes have rarely been measured in TFWs, but typical wetland N<sub>2</sub>O exchange rates would have only a small effect on the radiative balance)(Neubauer, 2014). This is true whether one uses net ecosystem production as a proxy for the rate of ecosystem C storage (Chapin et al., 2006) or uses <sup>137</sup>Cs- or <sup>210</sup>Pb-based estimates of C sequestration (Bridgham et al., 2014; Table 3). However, a warming effect on climate does not mean that TFWs contribute to anthropogenic climate change; such an effect (i.e., radiative forcing) only occurs if the radiative balance of TFWs has changed since the pre-Industrial era baseline (pre-1750). This would occur if either the C sequestration or CH<sub>4</sub> emission rate has changed, such as in response to saltwater intrusion, human modifications, or another global change, or if the wetland itself had formed since 1750.

As an ecosystem develops, there is a time when the cumulative lifetime warming due to CH<sub>4</sub> emissions is exceeded by the cumulative lifetime cooling due to CO<sub>2</sub> sequestration (Frolking et al. 2006; Neubauer, 2014). This point is known as the radiative forcing switchover time. Using the atmospheric perturbation model of Neubauer and Megonigal (2015), we calculate that the radiative forcing switchover time of TFWs is on the order of 400-1000 years (Table 3), although there are some TFWs that emit both CO<sub>2</sub> and CH<sub>4</sub> and therefore may not ever have a lifetime cooling effect. There are few TFWs where CH<sub>4</sub> emissions, C sequestration rates, and wetland ages have been determined; Sweet Hall marsh, Virginia, USA (Figure 1) is one such example. Because the switchover time for Sweet Hall (756 years; Table 3) is less than the age of the site (3640 years BP; Neubauer et al., 2002), this TFW has had a lifetime net cooling effect on the climate, even though it has a positive radiative balance over a 100-year period. This suggests that TFWs created today will contribute to climate change for several centuries; however, the global area of TFWs is insignificant in the context of anthropogenic climate change, while it is highly significant for the many non-climate ecosystem services that TFW provide.

## 8. Concluding Comments

It is perhaps appropriate that TFW biogeochemistry has not been well studied given the fact TFWs occupy less area than many other wetland ecosystems. However, TFWs are grossly underrepresented even in the tidal wetland literature. A Web of Science search (1980-2017) shows that <6% of all tidal wetland literature concerns TFWs, whereas TFWs can represent ~20% of the total tidal wetland area in a region (Stevenson et al., 1988; Dahl, 1999). Tidal wetlands deserve increased attention for many reasons. They are species-rich ecosystems that support waterfowl, fish, and terrestrial wildlife. They influence the chemistry of adjacent estuarine waters through exchange and transformation of organic C and nutrients. Because of their location at the head of estuaries, TFWs are important sites for the deposition of nutrient-laden sediments, and they can rapidly sequester C, N, and P through burial. In short, TFWs are important features of the landscapes in which they occur.

TFWs are sentinel ecosystems for monitoring the influence of global climate change on coastal ecosystems. Poised at the interface of nontidal rivers and saline estuarine waters, they are influenced by river discharge and sea level rise. River discharge is sensitive to precipitation

and evapotranspiration, which are in turn sensitive to global warming (Palmer et al., 2008). Increasingly frequent incursions of saline water into TFW ecosystems can be expected as sea levels rise and droughts become more common (Herbert et al., 2015). It is uncertain what the long-term effects of such episodic events will have on element cycling and plant community composition in TFWs, but based on current distributions of plant species, even small increases in salinity will elicit dramatic changes in plant and microbial community composition, and fundamentally alter the characteristics of TFW biogeochemical cycles (Neubauer and Craft, 2009). At present, there are many hypotheses about the response of TFWs to these perturbations. For example, we could expect TFWs to be less sensitive to sea level rise than tidal saline wetlands because they are located at the head of estuaries near riverine sediment sources. However, their steep slopes and human infrastructure present barriers for TFW transgression inland. We do not understand TFWs well enough to fully predict how they will respond to climate and land use change.

Tidal freshwater wetlands have not received the level of biogeochemical scrutiny that has been directed toward nontidal freshwater and tidal saline wetlands. In the absence of more complete knowledge, it is often assumed that TFW processes adhere to generalizations drawn from better-studied ecosystems. This approach has proved fruitful, but limited. For example, there is now doubt about the assumption that TFW plants decompose more rapidly than saline tidal wetland plants (Craft, 2007). Based on hydrology, it seems reasonable to assume that TFWs have relatively open nutrient cycles, but that was not the case in two TFW systems that have been fully studied (Section 4.3). Clearly, understanding biogeochemical processes in TFWs will require more direct observations of TFWs in relation to their tidal saline and nontidal analogues.