



## Carbon dynamics and export from flooded wetlands: A modeling approach



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### ABSTRACT

Described in this article is development and validation of a process based model for carbon cycling in flooded wetlands, called WetQual-C. The model considers various biogeochemical interactions affecting C cycling, greenhouse gas emissions, organic carbon export and retention. WetQual-C couples carbon cycling with other interrelated geochemical cycles in wetlands, i.e. nitrogen and oxygen; and fully reflects the dynamics of the thin oxidized zone at the soil-water interface. Using field collected data from a small wetland receiving runoff from an agricultural watershed on the eastern shore of Chesapeake Bay, we assessed model performance and carried out a thorough sensitivity and uncertainty analysis to evaluate the credibility of the model. Overall, model performed well in capturing TOC export fluctuations and dynamics from the study wetland. Model results revealed that over a period of 2 years, the wetland removed or retained equivalent to  $47 \pm 12\%$  of the OC carbon intake, mostly via OC decomposition and DOC diffusion to sediment. The study wetland appeared as a carbon sink rather than source and proved its purpose as a relatively effective and low cost mean for improving water quality.

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### 1. Introduction

Wetlands are environments characterized with waterlogged soils and biota adapted to saturated soil conditions. They are found in almost every climate and continent (with exception of Antarctica) and recognized for their unique role in regulating global biogeochemical cycles (Reddy and DeLaune, 2008).

In the context of global biogeochemical budgets, it is the carbon (C) cycle that wetlands influence the most. Because of high productivity and slow decomposition rates, wetlands have the highest carbon density among all terrestrial ecosystems (Kayranli et al., 2010). Despite covering less than 8% of the terrestrial land surface (Aselmann and Crutzen, 1989; Mitsch and Gosselink, 2007), wetlands are the greatest individual source of methane emission to the atmosphere (Walter and Heimann, 2000). Wetland methane

emissions have been estimated about 100–231 Tg CH<sub>4</sub> yr<sup>-1</sup> which accounts for 17–40% of the global (anthropogenic + natural) methane emissions annually (Denman et al., 2007). Influence of wetlands on global carbon balance is not limited to sequestering atmospheric carbon and emitting greenhouse gasses. When hydrologically connected to surface flow, wetlands export carbon in form of dissolved and particulate organic material (DOM and POM) to receiving waters (Reddy and DeLaune, 2008), acting as primary source of humic substances to freshwater aquatic systems (Stern et al., 2007; Ziegler and Fogel, 2003). Much of the organic material exported from wetlands eventually end up in oceans and it is estimated that 15% of the terrestrial organic matter flux to the oceans originate from wetlands (Hedges et al., 1997; Tranvik and Jansson, 2002).

Wetlands are widely referred to as “the kidneys of the catchment” due to their effectiveness in trapping sediment and nutrient loadings from surface waters (Mitchell, 1994; Mitsch and Gosselink, 2007). But the fact that wetlands can be net exporters of organic carbon (OC) potentially offsets their purifying benefits. Discharge of

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carbon from wetlands will result in water quality degradation with the release of dissolved organic carbon (DOC), also known as water color (Worrall et al., 2003). At high concentrations, DOC reacts with chlorine during drinking water treatment to form carcinogenic disinfection byproducts (Chow et al., 2003). Also because of its hydrophobic nature, DOC is shown to be a medium of transport for other pollutants such as nutrients and heavy metals (Canário et al., 2008; Steinberg, 2003).

Because of the great influence of wetlands on global C cycling, and specifically considering the significant impact of wetlands greenhouse gas (GHG) emissions on global warming, considerable scientific efforts have been invested in quantifying wetland C storage, turnover, hydrologic exports and carbon interchanges between wetland soils and atmosphere. Wetland models have provided powerful tools for quantifying these budgets where field studies were not practical or projections for future budgets were called for. Various C cycling models have been developed for wetlands over the past three decades (Mitsch et al., 1988). Although these models varied in scale of application (temporally and spatially), complexity and approach (empirical vs. physically based) they all roughly targeted similar objectives. These objectives were to (1) synthesize our knowledge of complex interactions between wetland soil, hydrology and vegetation; and (2) assess, quantify and predict impacts of climate change or management alternatives on C dynamics, storage and export from wetlands (Cui et al., 2005; Zhang et al., 2002). Existing wetland C models can generally be classified into various categories based on the final specific product of the C cycle that they are geared to simulate. These categories can be confined to long term-peat accumulation related models, greenhouse gas (CH<sub>4</sub> and CO<sub>2</sub>) emission models and wetland OC turnover and export models. Models falling into the last category are more or less specific to treatment wetlands (e.g. King et al., 2003; Penha-Lopes et al., 2012 and Stern et al., 2007). Wetland GHG emission models have received the most attention among all categories in recent years. Among the latest and most comprehensive models in this category is the work of Tang et al. (2010) where they revised a previously developed geochemistry model (TEM model, Zhuang et al., 2004) into a multi substance model to simulate methane production, oxidation and transport with different model complexities. The model uses a probabilistic algorithm to account for the effects of hydrostacy on ebullition. At the most complex, the model considers four substances (O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>) and accounts for the inhibitory effect of O<sub>2</sub> on CH<sub>4</sub> production and the stimulatory effect of O<sub>2</sub> on CH<sub>4</sub> oxidation. At the simplest, the model was reduced to a one substance system (CH<sub>4</sub> only) by ignoring the role of O<sub>2</sub>. The authors concluded that the four substance model predicted the effects of atmospheric pressure and water table dynamics on methane effluxes more accurately than simpler tested models. Another recent methane model development, designed for large-scale simulation of CH<sub>4</sub> emissions from northern peatlands, is described by Wania et al. (2010). The methane model takes into account the interactions between hydrology, soil temperature and vegetation leading to methane production and emission. The model was integrated into a dynamic global vegetation model and applied to various peatland sites. Despite the fact that the model setup does not require site-specific input data, it performs reasonably well in predicting methane production and emission from northern peatlands.

The purpose of this paper was to develop a physically based model for carbon cycling and methane production in flooded wetlands. As stated earlier, many of the existing wetland water quality models focus on a single end product of the carbon cycle, i.e. methane production, OC export or OC deposition. In this study, we aim to advance the current state of wetland modeling by introducing a computationally simple – yet comprehensive – mechanistic wetland carbon cycling model. The proposed model in this study

reflects various biogeochemical interactions affecting C cycling in wetlands, and is capable of simulating the dynamics of OC retention, OC export and GHG emissions. What makes this model special is the fact that it is coupled with other interrelated geochemical cycles (i.e. nitrogen and oxygen) and fully reflects the dynamics of sediment–water interactions in flooded wetlands. Another unique aspect of the developed model is its approach towards modeling the formation of the thin oxidized zone at wetlands soil–water interface and the oxidation–reduction reactions taking place within that zone (Mitsch and Gosselink, 2007; Reddy and DeLaune, 2008). We perform a thorough sensitivity and uncertainty analysis on model components to validate its credibility using field collected data from a small wetland that receives runoff from an agricultural land. In the following sections of the paper, we describe the structure of the model and the methodology on model assessment. Finally the results are presented and discussed.

## 2. Model description

### 2.1. WetQual-C model

WetQual-C model is an extension to WetQual model, a previously developed wetland nutrient cycling model (Hantush et al., 2012). WetQual is a process based model for nitrogen and phosphorus retention, cycling, and removal in flooded wetlands. The model simulates oxygen dynamics and impact of oxidizing and reducing conditions on nitrogen transformation and removal as well as phosphorus retention and release. WetQual explicitly accounts for nitrogen loss pathways of volatilization and denitrification. The model separates free floating plant biomass (e.g., phytoplankton) from rooted aquatic plants and uses a simple model for productivity in which daily growth rate is related to daily solar radiation and annual growth rate of plants. In developing WetQual-C, we followed the same compartmental structure as WetQual, where a wetland is partitioned into two basic compartments; the water column (free-water) and wetland soil layer. The soil layer is further partitioned into a generalized model of aerobic and anaerobic zones where the boundary between the two zones fluctuates up or down based on competing oxygen supply and removal rates. To reflect the complex cycling of organic matter and methane production in flooded wetlands, it was necessary to posit several organic and inorganic carbon pools within WetQual-C model. As can be viewed in Fig. 1, two pools for particulate organic carbon (POC) are considered in the model, one representing fast reacting, easily degradable organic material (e.g. non-humic substances, carbohydrates) and the other describing recalcitrant, slow reacting solids (e.g. phenolic and humic substances). The former pool is called labile particulate organic carbon (LPOC) and the latter pool is referred to as refractory particulate organic carbon (RPOC). A third organic pool represents dissolved organic carbon (DOC). Model allows for allochthonous sources (hydrologic loads) and autochthonous sources to contribute to all three organic pools. If wetland is hydrologically connected to surface flow, or is intended as means for treating water, a significant amount of external organic C can be transferred into the system via incoming flow, originating from point sources (e.g. sewage pipes) or diffuse source upland areas (e.g. agricultural fields). An internal source for DOC and POC includes plant matter from emergent macrophytes, algal mats and litter fall from trees in forested wetlands.

A stepwise conversion process is considered in the model to portray all stages of plant turnover and OM decomposition. When plants senesce, part of their biomass leaches out physically in form of water soluble–highly labile–organic compounds (Reddy and DeLaune, 2008). Within each compartment in the model (water and sediment), this portion of the biomass is directly added to the

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