

# Modeling the seasonal autochthonous sources of dissolved organic carbon and nitrogen in the upper Chesapeake Bay

David P. Keller\*, Raleigh R. Hood

Horn Point Laboratory, University of Maryland Center for Environmental Science, P.O. Box 775, Cambridge, MD 21613, USA

## ARTICLE INFO

### Article history:

Received 27 August 2010

Received in revised form

10 December 2010

Accepted 16 December 2010

Available online 15 January 2011

### Keywords:

Dissolved organic matter (DOM) cycling  
Dissolved organic nitrogen (DON) cycling  
Dissolved organic carbon (DOC) cycling  
Marine biogeochemical ecosystem model

## ABSTRACT

In this paper we investigate the seasonal autochthonous sources of dissolved organic carbon (DOC) and nitrogen (DON) in the euphotic zone at a station in the upper Chesapeake Bay using a new mass-based ecosystem model. Important features of the model are: (1) carbon and nitrogen are incorporated by means of a set of fixed and varying C:N ratios; (2) dissolved organic matter (DOM) is separated into labile, semi-labile, and refractory pools for both C and N; (3) the production and consumption of DOM is treated in detail; and (4) seasonal observations of light, temperature, nutrients, and surface layer circulation are used to physically force the model. The model reasonably reproduces the mean observed seasonal concentrations of nutrients, DOM, plankton biomass, and chlorophyll *a*. The results suggest that estuarine DOM production is intricately tied to the biomass concentration, ratio, and productivity of phytoplankton, zooplankton, viruses, and bacteria. During peak spring productivity phytoplankton exudation and zooplankton sloppy feeding are the most important autochthonous sources of DOM. In the summer when productivity peaks again, autochthonous sources of DOM are more diverse and, in addition to phytoplankton exudation, important ones include viral lysis and the decay of detritus. The potential importance of viral decay as a source of bioavailable DOM from within the bulk DOM pool is also discussed. The results also highlight the importance of some poorly constrained processes and parameters. Some potential improvements and remedies are suggested. Sensitivity studies on selected parameters are also reported and discussed.

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## 1. Introduction

In many mid-Atlantic estuaries, the biochemical composition and isotopic signature of DOM changes across the salinity gradient with biomarkers and carbon isotopes indicating that a significant amount of DOM production and modification occurs within the estuary (Loh et al., 2006; Mannino and Harvey, 2000; Raymond and Bauer, 2001). In the largest of these estuaries, Chesapeake Bay, DOC exhibits a non-conservative distribution at certain times of the year, suggesting that seasonal autochthonous DOM production can be significant (Fisher et al., 1998; Rochelle-Newall and Fisher, 2002). Fisher et al. (1998) estimated that this DOC accumulation was greater than atmospheric or terrestrial organic carbon inputs and was equivalent to ~10% of estuarine primary production. Dissolved organic nitrogen (DON) has also been suggested to accumulate seasonally in estuaries (Bronk, 2002; Bronk et al., 1998; Lomas et al., 2002). Radiocarbon measurements of

estuarine, continental shelf, and slope DOM indicate that the large pool of >10 kDa DOM is relatively young and has a residence time of 1–30 days, whereas the smaller pool of 1–10 kDa DOM is between 380 and 4500 years old (Santschi et al., 1995). These observations suggest that autochthonous estuarine DOM production plays an important role in estuarine biogeochemistry. An understanding of these sources and their effect on the DOM cycle is critical for constraining local carbon and nitrogen budgets and for evaluating the role of estuaries in the global carbon cycle.

In the euphotic zone of the Chesapeake Bay estuary, the site of this study, several sources and processes control DOM cycling. The major allochthonous source of DOM is the Susquehanna river (Fisher et al., 1998). Smaller rivers (sub-estuaries), atmospheric deposition (Seitzinger and Sanders, 1999), wetland discharge (Tzortziou et al., 2008), and terrestrial runoff and leaching (Berman and Bronk, 2003) also add significant amounts of DOM to the estuary. Internal sources of DOM include benthic fluxes (Burdige and Zheng, 1998), extracellular release by phytoplankton, grazer-mediated release and excretion, release via cell lysis (both viral and bacterial), solubilization of particles, and bacterial transformation and release (Carlson, 2002). Free-living heterotrophic bacterioplankton are the dominant consumers of DOM (Nagata,

\* Corresponding author. Present address: IFM-GEOMAR, Leibniz-Institut für Meereswissenschaften, Düsternbrooker Weg 20, 24105 Kiel, Germany. Tel.: +49 0431 600 4513.

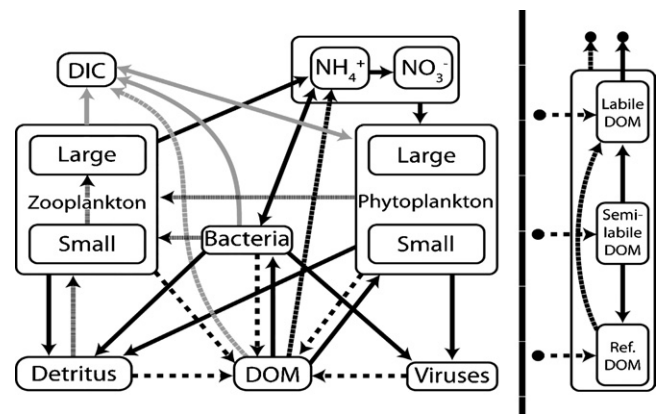
E-mail address: [dkeller@ifm-geomar.de](mailto:dkeller@ifm-geomar.de) (D.P. Keller).

2000). Some phytoplankton also have the ability to take up DOM to supplement their metabolic needs (Mulholland et al., 2003). Photochemical processes, through UV excitation, directly and indirectly remove and transform DOM (Mopper and Kieber, 2002). DOM can also potentially form gels that may aggregate to form particulate organic matter (POC) (Verdugo et al., 2004) which may sink out of surface waters. As in other temperate systems, the rate and magnitude of these sources and sinks varies on a seasonal basis as changes in light, temperature, and freshwater flow affect the environment (Apple et al., 2006; Bronk et al., 1998; Jonas and Tuttle, 1990; Lomas et al., 2002; Malone et al., 1991; Mulholland et al., 2003; Shiah and Ducklow, 1994b; Wommack et al., 1992).

Quantifying the role of these sources and sinks in Chesapeake Bay DOM cycling has proven difficult. Most of the research has focused on characterizing the composition of DOM and understanding the individual role of different functional groups (i.e., primary producers, secondary consumers, predators, etc.) and species in DOM cycling. Few studies have quantified the amounts of C or N that flux into, and out, of the DOM pool relative to the other major C and N pools. Those that have provide an incomplete picture of DOM cycling as they often cannot distinguish between the individual sources and sinks of DOM (Bronk et al., 1994, 1998). Additionally, as far as we are aware, there are no long-term time series measurements of the C and N flux through the DOM pool that adequately describe the annual DOM cycle.

Models can be a powerful tool for integrating data and running long term simulations. They are also valuable for determining the magnitude and importance of processes that are difficult to measure and observe in the field. Many recent coastal and open ocean biogeochemical ecosystem models have included DOM (Anderson and Pondaven, 2003; Anderson et al., 2007; Anderson and Williams, 1998, 1999; Aumont et al., 2003; Baklouti et al., 2006a,b; Druon et al., 2010; Faure et al., 2006; Grégoire and Soetaert, 2010; Llebot et al., 2010; Luo et al., 2010; Nakata and Doi, 2006; Pahlow and Vézina, 2003; Pahlow et al., 2008; Polimene et al., 2006, 2007; Ruardij et al., 2005; Salihoglu et al., 2008; Schmittner et al., 2005; Vichi et al., 2007) in order to better simulate and understand biogeochemical cycles. Carbon and nitrogen are typically accounted for in these models, although a few include phosphorus as well. Most of these models are quite complex and typically have state variables that describe the lability of DOM and multiple size classes or functional types of phytoplankton and zooplankton. Bacteria are also often, but not always, included as state variables. Sources and sinks of DOM such as phytoplankton exudation, zooplankton grazing processes, the breakdown of detritus, and uptake by bacteria are almost always accounted for in these models. However, other processes that play a role in DOM cycling, like viral lysis and photochemical reactions, are often implicitly accounted for, if at all. Despite the recognized importance of DOM cycling in these and many other studies, few estuarine biogeochemical models have included DOM cycling.

In this paper we describe a modeling study of the DOM cycle in the surface waters of Chesapeake Bay. Our objective is to elucidate the seasonal autochthonous sources of DOC and DON in the upper bay. We specifically focus on the roles that phytoplankton extra-cellular release, non-grazing mortality, bacterial and phytoplankton viral lysis, and grazer-mediated sloppy feeding, egestion, and excretion play in the production of DOM. In addition, we explore how seasonal variability affects the physical, chemical, and biological processes that drive DOM cycling. Observations are used to evaluate the model performance. Through comparisons with observations we show that the model is capable of reproducing the seasonal patterns in plankton biomass and productivity. This then allows us to examine how biologically mediated DOM production, transformation, and consumption change in response to seasonal forcing. These comparisons also highlight the importance of some



**Fig. 1.** A schematic diagram of the ecosystem model. Grey lines indicate the flow of carbon only. Segmented lines indicate photochemical reactions. Dashed lines indicate sources of DOM. Hatched lines indicate zooplankton grazing. Processes within the DOM pool are shown on the right.

poorly constrained processes that require additional research or more complex numerical approaches.

## 2. Model description

The model of Anderson and Williams (1998) provided the basic structure for our biogeochemical model. However, we modified their model in several significant ways to explicitly account for specific sources of DOM and photochemical reactions that effect DOM. Important modifications include: (1) dividing DOM into labile, semi-labile, and refractory pools, (2) dividing zooplankton and phytoplankton into two size classes, (3) removing sedimentation, (4) including phytoplankton and bacterial viruses as state variables, and (5) including dissolved inorganic carbon (DIC) as a state variable. A complete list of the model equations can be found in the Appendix (Section A.2). Tables 1 and 2 give lists of parameters and variables used in the model. Fig. 1 is a schematic diagram that shows the flow of nitrogen, and in some instances carbon, between the model compartments.

The model includes 18 state variables that span the herbivorous and microbial food webs, with compartments for large phytoplankton ( $P_L$ ), small phytoplankton ( $P_S$ ), large zooplankton ( $Z_L$ ), small zooplankton ( $Z_S$ ), bacteria ( $B$ ), phytoplankton viruses ( $V_P$ ), bacteriophages ( $V_B$ ), ammonium ( $A$ ), nitrate ( $N_n$ ), detritus ( $D_N$  and  $D_C$ ), dissolved inorganic carbon (DIC), and labile ( $L_C$  and  $L_N$ ), semi-labile ( $S_C$  and  $S_N$ ), and refractory ( $R_C$  and  $R_N$ ) DOC and DON. Nitrogen is the basic unit for simulation and mass balance. However, carbon has been accounted for by allowing the state variables to have fixed or varying C:N ratios. Close attention has been paid to the formulation of the interactions between these two elements. Thus, both the carbon and nitrogen cycles have been constrained. Phosphorus was not included in the model.

### 2.1. Station description and data availability

The model was formulated to simulate the mean seasonal cycling of dissolved organic matter in the surface layer at the Chesapeake Bay Program's (CBP) station CB3.3C (38.9960°N, 76.3597°W) which is located in the main channel of the upper Chesapeake Bay near the bay bridge (Fig. 2). The mean water depth at this station from 1997 to 2007 was 25 m with a mixed layer depth that ranged seasonally between 3.25 and 7.37 m. Due to physical circulation and the influence of Susquehanna River flow the mixed layer was deeper during the summer than at other times of year. Mean surface salinities at this station ranged between 5.05 and 11.86 with the highest salinities occurring in the summer. The mean seasonal

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