Environmental Modelling & Software 79 (2016) 233–255

Contents lists available at ScienceDirect

Environmental Modelling & Software

journal homepage: www.elsevier.com/locate/envsoft

Stable isotopes reduce parameter uncertainty of an estuarine carbon cycling model

Sri Adiyanti [a, *], Bradley D. Eyre [b], Damien T. Maher [b], Isaac Santos [c], Lindsay Golsby-Smith [b], Perrine Mangion [b], Matthew R. Hipsey [a]

[a] *Aquatic Ecodynamics, School of Earth & Environment, The University of Western Australia, Crawley WA 6009, Australia*
[b] *Centre for Coastal Biogeochemistry, Southern Cross University, Lismore, NSW 2480, Australia*
[c] *National Marine Science Centre, Southern Cross University, PO Box 4321, Coffs Harbour, NSW 2450, Australia*

ARTICLE INFO

Article history:
Received 21 December 2014
Received in revised form
21 January 2016
Accepted 4 February 2016
Available online 19 February 2016

Keywords:
Estuary carbon budget
Uncertainty
Equifinality
Isotope mixing model
Hydrodynamic-biogeochemical model
pCO_2

ABSTRACT

Quantifying estuarine carbon cycling is complex due to the highly-variable environmental conditions associated with the interaction between tides, riverine inflows, meteorological forcing and internal biogeochemical processes. A Markov-Chain Monte Carlo algorithm was utilized to perform unbiased calibration of parameters used by a 1-D isotope-enabled carbon model applied to stable isotope data collected in Caboolture River Estuary, Australia. The parameter posteriors were ported into a 3-D finite-volume isotope-enabled carbon model and run over a range of hydro-meteorological conditions that occurred during a 1.5-year simulation period. The model highlighted the spatio-temporal variations and uncertainties associated with carbon cycling within the estuary, including the shift from being strongly heterotrophic in the upper estuary with a higher water-atmosphere flux of CO_2, to a more balanced trophic state in the lower estuary. The approach demonstrates the usefulness of isotope data to constrain model uncertainty and advances our ability to undertake carbon budgeting in coastal environments.

1. Introduction

Estuaries are highly productive (Cloern et al., 2014) and diverse (Maher and Eyre, 2012; Mead and Weigner, 2010) ecosystems. Despite a relatively-small area, estuaries play a major role in global carbon cycling as locations where atmospheric, terrestrial, and marine carbon cycles interact (Cai, 2011). They function as a biogeochemical 'filter', processing catchment-derived inorganic and organic matter, and regulating carbon delivery to the coastal ocean (Petrone et al., 2009). Estuaries are generally considered to be net heterotrophic and return terrestrially-derived carbon to the atmosphere as CO_2 (Cai, 2011; Atkins et al., 2013). However, depending on the interaction between tides, riverine inflows, groundwater discharge, meteorological conditions and internal biogeochemical processes, carbon cycling can be highly-variable spatially and temporally (Eyre et al., 2011; Maher and Eyre, 2012; Maher et al., 2015; Macklin et al., 2014; Mead and Weigner, 2010). The natural biogeochemical function of estuaries has been further altered through over-enrichment with nitrogen and phosphorus (Smith, 2006) resulting from upstream catchment modification and sewage inputs from urban development in the coastal margin (e.g. Saeck et al., 2013).

In an effort to better define estuary function and support decision making in water quality management, coupled hydrodynamic-biogeochemical models have been increasingly used (e.g. Fontana et al., 2009; Gal et al, 2009; Robson et al., 2008), and substantial ongoing efforts continue to improve models resolution and performance (Gal et al., 2014). Models are attractive as they capture large spatiotemporal variability in water quality that would not be captured with routine monitoring programs, and can inform users to estimate spatial and temporal patterns within process pathways. By undertaking spatial and temporal integrations of model output we may further analyse the controls on carbon budgets at the system-scale and identify key factors that shape water quality evolution. Finally, models support management of catchments and waterways by providing a predictive link between management actions and ecological responses, which is necessary for finding the best possible management strategy (e.g. Skerratt et al., 2013).

Challenges in validation of aquatic ecosystem models are well-documented, and issues related to model equifinality (Arhonditsis

---

* Corresponding author. School of Earth & Environment (M004), The University of Western Australia, 35 Stirling Hwy, Crawley WA 6009, Australia.
E-mail address: sri.adiyanti@uwa.edu.au (S. Adiyanti).

http://dx.doi.org/10.1016/j.envsoft.2016.02.011
1364-8152/© 2016 Elsevier Ltd. All rights reserved.

et al., 2008) and poor model performance assessment (Arhonditsis et al., 2006; Robson, 2014) are common. Models often suffer from being over-parameterised, making calibration difficult. Their performance depends significantly upon the accuracy of model structure (i.e. the suitability of model algorithms and theoretical context), input variables (i.e. boundary and initial conditions, meteorological forcing), and model parameters that capture all the unknowns in the model. Progress has been made on model uncertainty assessment by integrating a Bayesian Hierarchical Formulation (BHF) for simultaneously calibrating aquatic biogeochemical models at multiple sites and conditions (e.g. Zhang and Arhonditsis, 2009). BHF combines existing information (prior) with data model or current observations (likelihood) to produce a set of conditional parameters (posteriors) for projecting future ecosystem response. Hence, BHF is considered more informative than conventional model calibration practices that merely reduce the discrepancy between observed data and model output. The hierarchy also accommodates complexity by dissecting the problems into levels (Clark, 2005) required for solving spatiotemporal problems.

The amount of model uncertainties due to input variables and model parameters are intensified exponentially in higher dimensional spatially-resolved (e.g. 2 or 3-D) models, which are generally required to resolve the circulation patterns of complex estuarine morphological domains. Whilst some progress has been made on sensitivity and uncertainty assessment of spatially-resolved models for lakes (McDonald et al., 2012; Missaghi and Hondzo, 2010; Zhang and Arhonditsis, 2009), and larger oceanic domains (e.g. Mahlstein and Knutti, 2011; Ward et al., 2010), new approaches are required to improve model application and uncertainty assessment for estuarine environments.

Stable isotopes of carbon (C) can be used to reduce over-parameterisation of a biogeochemical model by adding direct constraints on the matter and energy transfers between pools, hence reducing uncertainty on predicted rates and fluxes. Isotope mixing and fractionation provide an indication of the processes and pathways. The isotope signals of δ^{13}C along the estuary continuum have been presented as evidence of the extent of conservative mixing of terrestrial and marine organic carbon (Matson and Brinson, 1990; Raymond and Bauer, 2001). Organic carbon that originates from marine phytoplankton is often isotopically heavier (i.e. enriched in ^{13}C and so less-negative δ^{13}C) and has a lower C/N ratio, distinguishing it from terrestrial organic carbon. Photosynthetic CO_2 assimilation favours the lighter isotope (^{12}C), leading to photosynthetic products being depleted in ^{13}C compared to atmospheric CO_2, and *vice versa,* respiration leaves the heavier isotope more abundant. The effect of these processes on water column δ^{13}C of dissolved inorganic carbon (δ^{13}C-DIC) values is opposite, i.e. photosynthesis leads to enriched δ^{13}C-DIC values, and respiration to depleted δ^{13}C-DIC values. As yet there has been no use of δ^{13}C data in estuarine 3-D biogeochemical model applications, despite the obvious potential of these data to constrain model parameters for processes that significantly fractionate carbon.

In this study we report a framework that has been developed for application to estuaries that: (a) aims to reduce model equifinality through application of an “isotope-enabled” hydrodynamic-biogeochemical model, and (b) simultaneously introduce an approach to estimate uncertainty on the biogeochemical parameters by using a 1-D isotope-enabled carbon mixing model within a Markov-chain Monte Carlo (MCMC) state-space algorithm. We use this framework to capture the carbon budget of the sub-tropical Caboolture River Estuary in south east Queensland, Australia. A simple steady-state 1-D carbon isotope mixing model is first utilised to reproduce the general horizontal trends of dissolved inorganic and organic carbon concentrations, and their δ^{13}C signatures. This was done for five individual “snap-shots” between December 2011 to May 2012, and for each the mean (μ), $\mu\pm\sigma$ (σ = standard deviation), minimum, maximum, and median values of the posterior estimates of each biogeochemical model parameter resulting from the MCMC self-calibration were summarised. These parameter sets were then ported into a compatible 3-D isotope-enabled carbon model to simulate a detailed carbon budget that captures the wide range of hydro-meteorological conditions experienced by the estuary over a 1.5-year simulation period. The net result is a partial assessment of the uncertainty in the carbon budget predictions from the 3-D model, which would otherwise have simply used a single set of parameters, and also an assessment of uncertainty on process pathways within the final carbon budget estimates.

2. Experimental methods

2.1. Study site

The Caboolture River Estuary is a sub-tropical estuary situated in south east of Queensland, Australia, approximately 40 km north of Brisbane (Fig. 1) and at the mouth of a 383 km^2 catchment. The estuary discharges into Deception Bay, a small embayment within the larger Moreton Bay. Moreton Bay is a semi-enclosed embayment bay located adjacent to Brisbane. The major freshwater input to the estuary is from the upper Caboolture River, 5 km northwest of the estuary. Other contributions are from smaller three tributaries (Sheep Station, Goong, King John Creeks), two sewage treatment plans, stormwater discharges (Fig. 1), and groundwater discharge (Makings et al., 2014).

2.2. Measurement, water quality sampling and analysis

Seven CTD-divers (Schlumberger Water Services, Germany) were placed in the lower half of the estuary (Fig. 1) and deployed at the surface (0.5 m) and bottom (1.0 m from the sediment) 15–19 February 2012 to gain a high frequency data set of tidal propagation, temperature and salinity. The discharge of the two tributaries (Sheepstation and Goong Creeks) was measured using an acoustic Doppler current profiler (Sontek Argonaut XR) on different days during the experiment. This data was supplemented by temperature, salinity, and pH data collected monthly by the Southeast Queensland Ecosystem Health Monitoring Program (SEQ-EHMP) since 2000 (Healthy Waterways, 2014).

High spatial resolution water quality samples were collected at 25 locations (~1 km apart) along the estuary (Fig. 1) for five sampling campaigns: 15 December 2011 (CR_1; CR stands for Caboolture River), 20 January 2012 (CR_2), 16 February 2012 (CR_3), 30 April 2012 (CR_4) and 31 May 2012 (CR_5). Samples were analysed for concentrations of dissolved oxygen (DO), chlorophyll-*a* (chl-*a*), dissolved inorganic and organic carbon (DIC and DOC) including δ^{13}C values of each, and pCO_2. Water samples collected during CR_2 were also analysed for particulate organic carbon (POC) and δ^{13}C-POC.

Samples for DIC and DOC, and δ^{13}C of each were filtered through Whatman GF/F into acid rinsed pre-combusted (450°C for 4 hours) 40 ml borosilicate vials and capped with a Teflon lined septum, leaving no headspace or air bubbles. Samples were preserved with 100 μL of saturated $HgCl_2$ solution and stored at 4°C until analysis. DIC and DOC concentrations and δ^{13}C values of each were analysed using the wet oxidation method (St-Jean, 2003) using an OI Aurora 1030W analyser coupled to a thermo Delta V + Isotope Ratio Mass Spectrometer (IRMS) (Oakes et al, 2010; Maher and Eyre, 2011). Briefly, the sample was placed into the reaction chamber and acidified, and the CO_2 was purged from the system using helium as a carrier gas to the IRMS to measure DIC concentration and δ^{13}C