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## Inorganic carbon dominates total dissolved carbon concentrations and fluxes in British rivers: Application of the *THINCARB* model – Thermodynamic modelling of inorganic carbon in freshwaters

Helen P. Jarvie <sup>a,\*</sup>, Stephen M. King <sup>b,1</sup>, Colin Neal <sup>a</sup>

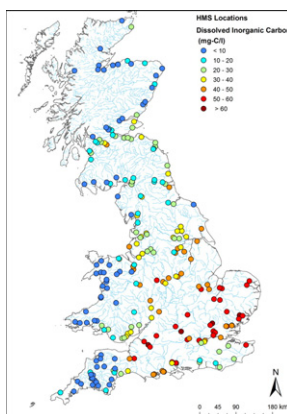
<sup>a</sup> NERC Centre for Ecology & Hydrology, Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB, UK

<sup>b</sup> STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot, Oxfordshire OX11 0QX, UK

### HIGHLIGHTS

- Dissolved inorganic carbon (DIC) is rarely measured in water-quality monitoring.
- *THINCARB* models DIC using routine alkalinity, temperature and pH measurements.
- *THINCARB* was applied to a large UK river quality dataset (> 250 sites over 39 years).
- DIC accounted for av. 80% of total dissolved carbon concentrations in UK rivers.
- Highlights importance of DIC in carbon fluxes from land, via rivers, to the coast

### GRAPHICAL ABSTRACT



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### ABSTRACT

River water-quality studies rarely measure dissolved inorganic carbon (DIC) routinely, and there is a gap in our knowledge of the contributions of DIC to aquatic carbon fluxes and cycling processes. Here, we present the *THINCARB* model (THERmodynamic modelling of INorganic CARBon), which uses widely-measured determinands (pH, alkalinity and temperature) to calculate DIC concentrations, speciation (bicarbonate,  $\text{HCO}_3^-$ ; carbonate,  $\text{CO}_3^{2-}$ ; and dissolved carbon dioxide,  $\text{H}_2\text{CO}_3^*$ ) and excess partial pressures of carbon dioxide ( $\text{EpCO}_2$ ) in freshwaters. If calcium concentration measurements are available, *THINCARB* also calculates calcite saturation. *THINCARB* was applied to the 39-year Harmonised Monitoring Scheme (HMS) dataset, encompassing all the major British rivers discharging to the coastal zone. Model outputs were combined with the HMS dissolved organic carbon (DOC) datasets, and with spatial land use, geology, digital elevation and hydrological datasets. We provide a first national-scale evaluation of: the spatial and temporal variability in DIC concentrations and fluxes in British rivers; the contributions of DIC and DOC to total dissolved carbon (TDC); and the contributions to DIC from  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  from weathering sources and  $\text{H}_2\text{CO}_3^*$  from microbial respiration. DIC accounted for >50% of TDC concentrations in 87% of the HMS samples. In the seven largest British rivers, DIC accounted for an average of 80% of the TDC flux (ranging from 57% in the upland River Tay, to 91% in the lowland River Thames). DIC fluxes exceeded DOC

\* Corresponding author.

E-mail address: [hpij@ceh.ac.uk](mailto:hpij@ceh.ac.uk) (H.P. Jarvie).

<sup>1</sup> Joint first authors.

fluxes, even under high-flow conditions, including in the Rivers Tay and Tweed, draining upland peaty catchments. Given that particulate organic carbon fluxes from UK rivers are consistently lower than DOC fluxes, DIC fluxes are therefore also the major source of total carbon fluxes to the coastal zone. These results demonstrate the importance of accounting for DIC concentrations and fluxes for quantifying carbon transfers from land, via rivers, to the coastal zone.

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## 1. Introduction

River systems provide a vital link in the global carbon (C) cycle, by transferring, storing, and processing organic carbon (OC) and inorganic C (IC) between terrestrial and marine environments. The total global carbon flux between the continents and oceans is estimated (Meybeck, 1993) to be around 1 Gt-C year<sup>-1</sup>, and is composed of approximately equal proportions of OC and IC (Hope et al., 1994). However, there is large geographical variability in the forms of C, with dissolved OC (DOC) dominating C fluxes in boreal rivers draining peat catchments (de Wit et al., 2015; Raike et al., 2015) and in tropical catchments (Wang et al., 2013). Dissolved IC (DIC) in river water is composed of three main species: bicarbonate (HCO<sub>3</sub><sup>-</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>) and dissolved carbon dioxide (H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>). DIC is derived from the combined effects of the weathering of carbonate rocks and soils, together with microbial breakdown of organic matter which releases CO<sub>2</sub>. The latter not only provides an additional source of IC to rivers, but also influences river-water pH which, in turn, governs the partitioning of DIC between HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> (Jarvie et al., 1997; Maberly, 1996).

DIC plays a critical role in primary productivity, where it provides a bioavailable C source for aquatic plant photosynthesis (Keeley and Sandquist, 1992; Maberly and Madsen, 2002; Maberly and Spence, 1983; Sandjensen et al., 1992), and DIC concentrations influence aquatic plant community structure (Jones et al., 2002; Maberly et al., 2015). But, while DOC is a routinely-measured water quality parameter, DIC is measured infrequently in routine water quality monitoring (Baker et al., 2008) or often without due regard for degassing of CO<sub>2</sub>, with the exception of more detailed process-based studies (e.g., Billett and Harvey, 2013; Billett et al., 2004; Dawson et al., 2001a; Dawson et al., 2001b; Dawson et al., 2004; Palmer et al., 2001). This means there is a strategic gap in information on the spatial variability and long-term temporal trends in riverine DIC. This is critical for understanding the sources, sinks and processing of C in catchments, and the wider coupling of C with other macronutrient (nitrogen and phosphorus) cycles along the land-water continuum (Huang et al., 2012).

However, routinely-measured alkalinity, pH and water temperature measurements can be used to calculate DIC concentrations and speciation, using established thermodynamic equations. In this contribution, we extend existing algorithms from the proven thermodynamic model developed by Neal et al. (1998b) to evaluate CO<sub>2</sub> and CaCO<sub>3</sub> solubility in surface- and ground-waters. Those algorithms estimate the activities of the major inorganic carbon species (H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>), and were validated against field data and other thermodynamic models. While the Neal et al. model has proved invaluable to the authors, and has been widely applied in a range of freshwater settings (Dawson et al., 2009; Eatherall et al., 1998; Eatherall et al., 2000; Griffiths et al., 2007; Jarvie et al., 2005; Neal et al., 1998a; Neal et al., 1998c; Neal et al., 2002), its application has become increasingly limited through time, for two reasons. Firstly, the spreadsheet package in which it was originally deployed (Lotus™ 1-2-3) has been discontinued. Secondly, the increasing availability of national-scale water-quality datasets, improvements in instrumentation, and a realisation of the added scientific value of high-frequency sampling, have resulted in much larger datasets (so-called “Big Data”) which are beyond the sensible data processing capabilities of spreadsheets.

For this contribution, the Neal et al. model was extended to calculate the dissolved inorganic carbon (DIC) concentrations in rivers and groundwaters by the major species (HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>). If Ca data are available, the model also calculates calcite saturation, along with concentrations of inorganic complexes with Ca (CaCO<sub>3</sub><sup>0</sup>, CaHCO<sub>3</sub><sup>+</sup>, CaOH<sup>+</sup>), although these Ca complexes have a negligible contribution to the DIC concentration (<0.5% of DIC). We call this updated model THINCARB (Thermodynamic modelling of INorganic CARB on in freshwaters), and to facilitate its use and adoption we have made both Excel™ and Python versions publically-available and open-source.

In this paper we document the THINCARB model, and use it to demonstrate the importance of quantifying DIC concentrations, by applying it to an extensive national water quality dataset: the UK Harmonised River Monitoring Scheme (HMS) water-quality dataset (c. 250 river sites, sampled typically on a monthly basis, over 39 years, 1974–2012). The HMS river alkalinity, pH and temperature measurements were used to quantify, for the first time, DIC concentrations and speciation, and their contributions to total dissolved carbon (TDC) across all the major British rivers discharging to the coastal zone. By then combining the THINCARB model outputs with the HMS DOC datasets, and with spatial land use, geology, digital elevation and hydrological datasets, we: (a) provide a first national-scale evaluation of spatial and temporal patterns in DIC concentrations; (b) explore the significance of bicarbonate weathering sources and CO<sub>2</sub> production from microbial respiration for DIC concentrations and trends across different river typologies; and (c) examine the relative magnitude of DIC and DOC contributions to dissolved carbon fluxes from British rivers to the coastal zone.

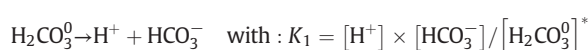
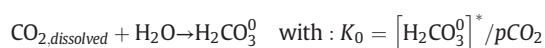
## 2. Methods

### 2.1. Overview of the original Neal et al. (1998b) model

The basis of the Neal et al. model is an equation for the excess partial pressure of carbon dioxide in a water sample, EpCO<sub>2</sub>, of the form

$$\text{EpCO}_2 = (\text{Alk}_{\text{Gran}} + [\text{H}^+]) \times [\text{H}^+] / (p\text{CO}_2 \times K_0 \times K_1 \times 10^{12}) \quad (1)$$

where the numerator is the dissolved CO<sub>2</sub> concentration in the water sample and the denominator is the dissolved CO<sub>2</sub> concentration in pure water in equilibrium with the atmosphere at the same temperature and pressure. Values of EpCO<sub>2</sub> of 0.1, 1 and 10 correspond to a tenth saturation, saturation and ten times saturation, respectively. The constituent variables of Eq. (1) are: the Gran alkalinity (see Appendix A), Alk<sub>Gran</sub>; the hydrogen ion activity (from the pH), [H<sup>+</sup>]; the partial pressure of CO<sub>2</sub> in air at STP (pCO<sub>2</sub>); and the equilibrium constants for the speciation reactions



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