



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



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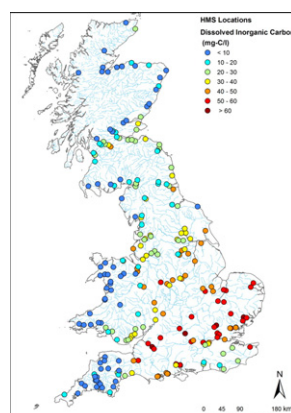
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HIGHLIGHTS

- 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, HCO_3^- ; carbonate, CO_3^{2-} ; and dissolved carbon dioxide, H_2CO_3^*) and excess partial pressures of carbon dioxide ($\text{E}p\text{CO}_2$) 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 HCO_3^- and CO_3^{2-} from weathering sources and H_2CO_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

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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⁻¹, 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 (HCO₃⁻), carbonate (CO₃²⁻) and dissolved carbon dioxide (H₂CO₃^{*}). DIC is derived from the combined effects of the weathering of carbonate rocks and soils, together with microbial breakdown of organic matter which releases CO₂. 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 HCO₃⁻, CO₃²⁻ and H₂CO₃^{*} (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 CO₂, 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 CO₂ and CaCO₃ solubility in surface- and ground-waters. Those algorithms estimate the activities of the major inorganic carbon species (H₂CO₃^{*}, HCO₃⁻, CO₃²⁻), 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 (HCO₃⁻, CO₃²⁻ and H₂CO₃^{*}). If Ca data are available, the model also calculates calcite saturation, along with concentrations of inorganic complexes with Ca (CaCO₃⁰, CaHCO₃⁺, CaOH⁺), 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 CARBon 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 CO₂ 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.

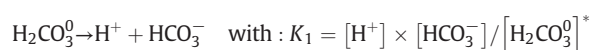
2. Methods

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, EpCO₂, 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 CO₂ concentration in the water sample and the denominator is the dissolved CO₂ concentration in pure water in equilibrium with the atmosphere at the same temperature and pressure. Values of EpCO₂ 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_{Gran}; the hydrogen ion activity (from the pH), [H⁺]; the partial pressure of CO₂ in air at STP (pCO₂); and the equilibrium constants for the speciation reactions



where

$$[\text{H}_2\text{CO}_3^0]^* = [\text{CO}_{2,\text{dissolved}}] + [\text{H}_2\text{CO}_3^0]$$

The 10^{12} term in Eq. (1) is simply a scaling factor to allow Alk_{Gran} and $[\text{H}^+]$ to be specified in units of microequivalents/liter ($\mu\text{eq/L}$). Given experimental values for Alk_{Gran} and pH and, ideally, the temperature of the water sample, since K_0 and K_1 are both temperature-dependent, EpCO_2 can then be estimated by iteratively minimising the charge balance in the model.

Neal et al. go on to refine the model with a further four successive corrections ('cases' in their language) of increasing complexity to account for: ionic strength ("case 2"); the presence of $[\text{OH}^-]$ & $[\text{CO}_3^{2-}]$ ("case 3"); the presence of $[\text{CaHCO}_3^+]$, $[\text{CaCO}_3^0]$ & $[\text{CaOH}^+]$ using an approximation linking Alk_{Gran} to the calcium concentration ("case 4"); and the presence of $[\text{CaHCO}_3^+]$, $[\text{CaCO}_3^0]$ & $[\text{CaOH}^+]$ using measured values of the calcium concentration in solution ("case 5"). CaCO_3 solubility is quantified in the model in terms of the saturation index for the mineral calcite ($\text{SI}_{\text{calcite}}$), the logarithm of the ratio of the ionic product for calcite saturation divided by the equilibrium constant for calcite: thus values of -1 , 0 and 1 , correspond to a tenth saturation, saturation and ten times saturation, respectively. An additional over-arching correction recognises that pCO_2 varies with altitude. The model does not correct for any contribution that the presence of organic acids or aluminium may have on Alk_{Gran} .

In general the model works well across the range $6 \leq \text{pH} \leq 10$, but in more acidic waters the errors in alkalinity increase as there may be significant buffers other than the inorganic CO_2 system (Neal, 1988b). In these cases, more specialised non-routine measurements are required (Neal, 2001) such as alkalimetric rather than acidimetric titrations (Neal, 1988a; Reynolds and Neal, 1987), or direct measurements based on, for example, "head space" measurements of CO_2 (Hope et al., 1995).

2.2. The THINCARB model

The original Neal et al. model, implemented in a macro-enabled Lotus™ 1-2-3 spreadsheet, was first translated into an Excel™ spreadsheet. In the process, minor corrections were made to eliminate small errors in the original formulae and altitude compensation of EpCO_2 was introduced (see Appendix B).

For any given set of water quality data, the model calculates four estimates of EpCO_2 , corresponding to "cases" 1, 2, 3 and 5 in Neal et al. The first three estimates are immediate and direct calculations, but the "case 5" estimate is determined by optimisation using the "case 3" estimate as a seed value. Within the Excel™ spreadsheet this optimisation is performed by a Visual Basic macro calling the "Goal Seek" algorithm to iteratively minimise the charge balance to a target value (typically zero). One advantage of this approach to implementation is that it permits the end user to obtain meaningful estimates of EpCO_2 even if the security settings on their computer disable embedded macros, though the optimisation procedure is obviously to be recommended. In principle, this approach also allows the THINCARB model to be implemented in other spreadsheet programs (with different intrinsic functions) should the need arise. Under optimal conditions (e.g. $\text{pH} > 6.5$, $\text{Alk}_{\text{Gran}} > 50 \mu\text{eq/L}$) the EpCO_2 estimates derived from "case 3" and "case 5" are remarkably consistent (see Appendix C). Altitude compensation is applied to the "case 5" estimate only. The output from the Excel™ implementation of THINCARB was validated against the results presented by Neal et al.

To estimate EpCO_2 and $\text{SI}_{\text{calcite}}$ the original Neal et al. model calculates the activities of the principle species present (OH^- , H_2CO_3^0 , HCO_3^- , CO_3^{2-} , Ca^{2+} , CaHCO_3^+ , CaCO_3^0 , and CaOH^+), the equilibrium constants for their formation/dissociation, and the corresponding activity coefficients. Since the molar concentration of an ion is equal to its activity

divided by the relevant activity coefficient it then follows, for example, that

$$c_{\text{HCO}_3^-} (\text{mg/L}) = 1000 \times m_{\text{HCO}_3^-} \times [\text{HCO}_3^-] / \gamma_1$$

$$c_{\text{CO}_3^{2-}} (\text{mg/L}) = 1000 \times m_{\text{CO}_3^{2-}} \times [\text{CO}_3^{2-}] / \gamma_2$$

where c_i is the mass concentration of species i , m_i is the formula weight of that species, the $[\]$ brackets denote that species activity, and γ_1 and γ_2 are the monovalent and divalent activity coefficients, respectively. For a neutral species the activity coefficient is taken to be unity.

The concentration of C, in any species containing carbon, is then simply $12/m_i$ of any concentration calculated above. The total concentration of IC, $\text{DIC}_{\text{total}}$, is then the sum of those C concentrations over all the inorganic species containing C. In the THINCARB model, in decreasing order of a species' contribution

$$\text{DIC}_{\text{total}} (\text{mg/L}) = c_{\text{C in HCO}_3^-} + c_{\text{C in H}_2\text{CO}_3^0} + c_{\text{C in CO}_3^{2-}} + \left\{ c_{\text{C in CaHCO}_3^+} + c_{\text{C in CaCO}_3^0} \right\}$$

Note that in those instances where we have calculated the species in $\{ \}$ brackets, $[\text{CaHCO}_3^+]$ is typically only $\sim 20\%$ of $[\text{CO}_3^{2-}]$, and $[\text{CaCO}_3^0]$ is several orders of magnitude lower still, so the contribution of CaHCO_3^+ and CaCO_3^0 to $\text{DIC}_{\text{total}}$ is very small (typically $< 0.5\%$). This is borne out by our validation of the DIC calculations (see Appendix D).

The calculations performed by the Excel™ spreadsheet were subsequently coded into Python programs to enable cross-platform deployment of THINCARB, and provide greater flexibility for processing large datasets. Source code for Python versions 2.7.x and 3.x.x has been provided. At present Python THINCARB is intended to be run locally, but it is worth noting that the Python language also supports cloud services, something which may interest potential future developers. Versions of Python THINCARB that process data stored in Python lists in the source code itself, or stored in an external file, are available.

In the Python programs the different parameters have been named after the column headers in the Excel™ spreadsheet implementation of THINCARB to facilitate interpretation. One difference in the Python implementation is that in place of the "Goal Seek" optimiser a simple, but tenacious, bisection algorithm has been used. This generally achieves a residual charge balance that is much closer to the target than that achieved in the spreadsheet. But when both implementations of THINCARB are forced to minimise to the same near-zero residual charge balance the results are the same within the limits of floating-point number handling.

The THINCARB model is free to use, open-source, and publically-available on GitHub at <http://smk78.github.io/thincarb/>. Instructions for use, and example input and output datasets, are also provided so that the end user may check their deployment of the model. THINCARB has been given a permissive licence to facilitate its use and community development.

2.3. Application of the THINCARB model to the Harmonised Monitoring Scheme river chemistry dataset

The Harmonised Monitoring Scheme is a major initiative to measure water quality in the major rivers draining to coastal areas in Great Britain (Fig. 1) (<https://data.gov.uk/dataset/historic-uk-water-quality-sampling-harmonised-monitoring-scheme-summary-data>). The HMS monitoring sites provide comprehensive spatial coverage of river typologies, from upland to lowland, rural and agricultural, to urban, and across a wide range of hydrogeological settings (Davies and Neal, 2007; Hurley et al., 1996; Littlewood et al., 1998; Robson and Neal, 1997). In the past, the HMS river chemistry datasets have been used to explore spatial and temporal patterns in DOC in British rivers (Worrall and Burt, 2010; Worrall et al., 2012) but, like most water

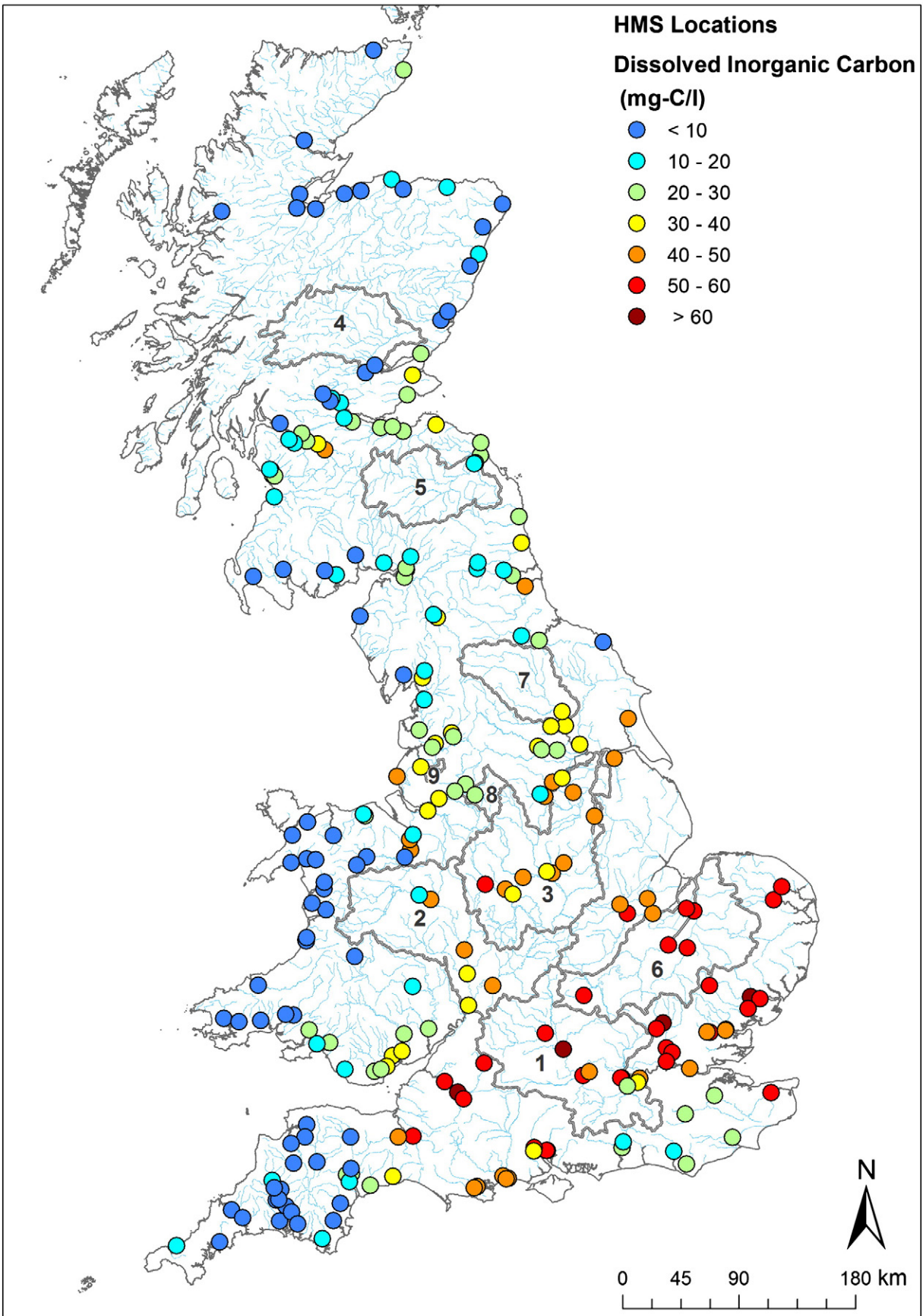


Fig. 1. Map showing the river network of Great Britain and the location of Harmonised Monitoring Scheme river chemistry sampling sites, with the catchments of the seven largest British Rivers, and the paired low-alkalinity/high-alkalinity rivers in north-west England (Mersey and Douglas) (catchments: 1 Thames; 2 Severn; 3 Trent; 4 Tay; 5 Tweed; 6 Ely Ouse; 7 Yorkshire Ouse; 8 Mersey; 9 Douglas).

quality monitoring studies, there are no corresponding DIC measurements. However, pH, alkalinity and temperature are routinely measured. To address the gap in DIC measurements, we applied the THINCARB model to the HMS dataset. More than 122,000 HMS river water samples (collected from 264 sites between 1974 and 2012), recorded simultaneous pH and alkalinity measurements, which allowed calculation of both DIC concentrations (and component species HCO_3^- , CO_3^{2-} and H_2CO_3^*) and EpCO_2 using THINCARB. A smaller number of HMS river chemistry samples (25,775) were measured for DOC. Of these, 11,073 samples had simultaneous DOC, pH and alkalinity measurements, allowing calculation of total dissolved carbon concentrations ($\text{TDC} = \text{DOC} + \text{DIC}$). For these HMS data, 99% of samples had pH measurements $6 \leq \text{pH} \leq 10$, i.e., within the optimal range for model performance.

All the HMS river chemistry sites are at, or close by, flow gauging stations. Each HMS river chemistry site was therefore matched with its corresponding gauging station, and catchment areas, hydrological data and statistics, and elevation, hydrogeology, and land cover data were extracted from the UK National River Flow Archive (NRFA) datasets (<http://nrfa.ceh.ac.uk>).

Of the 264 HMS river chemistry monitoring sites, a selection of rivers were chosen for more detailed analysis of temporal variability in DIC concentrations, speciation and fluxes in relation to DOC. Information about these rivers and their catchments are summarised in Table 1, with more detailed catchment descriptions provided in the Supplementary Material.

3. Results

3.1. Summary site statistics and correlations with catchment characteristics

A summary of the entire sample dataset for DIC, EpCO_2 , DOC, and DIC expressed as a percentage of TDC (%DIC) is shown in Fig. 2, as frequency distributions. The median DIC concentration was 27 mg-C L^{-1} , compared 4.4 mg-C L^{-1} for DOC, and DIC was the predominant fraction (accounting for >50% of TDC in 87% of the samples). Median EpCO_2 was 6 times atmospheric pressure, with 97% of samples oversaturated with respect to CO_2 (i.e., $\text{EpCO}_2 > 1$), and 23% of samples oversaturated by more than ten times atmospheric pressure of CO_2 . For each river monitoring site, summary statistics for DIC, EpCO_2 , DOC, and %DIC were calculated and are presented in the Supplementary Material (Tables SI1–4). The correlation statistics for the relationships between median values of DIC, DOC, %DIC and EpCO_2 for each river sampling site and catchment characteristics are shown in Table 2, and are outlined here, as follows:

- Median site DIC was positively correlated ($P < 0.01$) with: catchment area; baseflow index (a measure of the ratio of long-term baseflow to total stream flow, representing the contribution of groundwater to river flow); mean soil moisture deficit; the percentage of the catchment underlain by high- and moderate-permeability bedrock and high-permeability superficial deposits; the percentage of arable or horticultural land, and percentage of urban land cover. Median site DIC was negatively correlated ($P < 0.01$) with: standard annual average rainfall; the proportion of time that soils are wet; the percentage of the catchment underlain by low-permeability bedrock and low-permeability superficial deposits; altitude (level) statistics; and the percentage of woodland, grassland and mountain, heath or bog.
- Median site DIC expressed as percentage of TDC (%DIC) showed very similar correlation patterns to DIC, reflecting the transition from lower DIC in upland higher-altitude catchments (with high annual average rainfall, lower permeability geology, and wetter soils, and higher proportions of woodland, and mountain heath or bog) to higher DIC in lowland catchments (with higher baseflow index and high-permeability geology, and higher percentages of arable or horticultural and urban land cover).

Table 1 Summary of the catchment characteristics of the seven largest British rivers, and example low-alkalinity/high-alkalinity paired rivers (Rivers Mersey and Douglas, north-west England).

River	HMS river chemistry site	Grid reference	Catchment area (km ²)	% high-permeability bedrock	Minimum elevation (m)	Median elevation (m)	Maximum elevation (m)	% woodland	% arable/horticulture	% grassland	% mountain/heath/bog	% urban
Thames	Teddington Weir	TQ1702071370	9948	43	4.7	100	330	16.1	35.6	32.2	0.45	0.066
Severn	Haw Bridge	S08455027850	9895	16	10.5	110	826	12.2	29.8	47.6	1.4	0.035
Trent	Dunham	SK8192074460	8231	14	4.9	113	634	7.0	29.9	41.8	1.4	0.099
Tay	Perth (Queen's Bridge)	NO122234	4587	0	26.2	395	1210	15.9	7.2	24.7	48.1	0.002
Tweed	Northam Bridge	NT8902547280	4390	19	4.3	255	838	15.2	23.3	44.9	15.0	0.003
Ely Ouse	Denver Sluice	TF5890009000	3430	80	1.5	34	166	11.2	64.6	17.4	0.13	0.025
Yorkshire Ouse	Naburn Weir	SE5940044500	3315	34	4.6	118	714	7.0	31.4	44.0	12.4	0.015
Mersey	Flixton	SJ7421393762	679	22	10.3	216	636	10.0	1.9	42.4	18	0.149
Douglas	Wanes Blades Bridge	SD4758912612	198	6	4.4	80	456	8.9	19.0	41.4	2.9	0.134

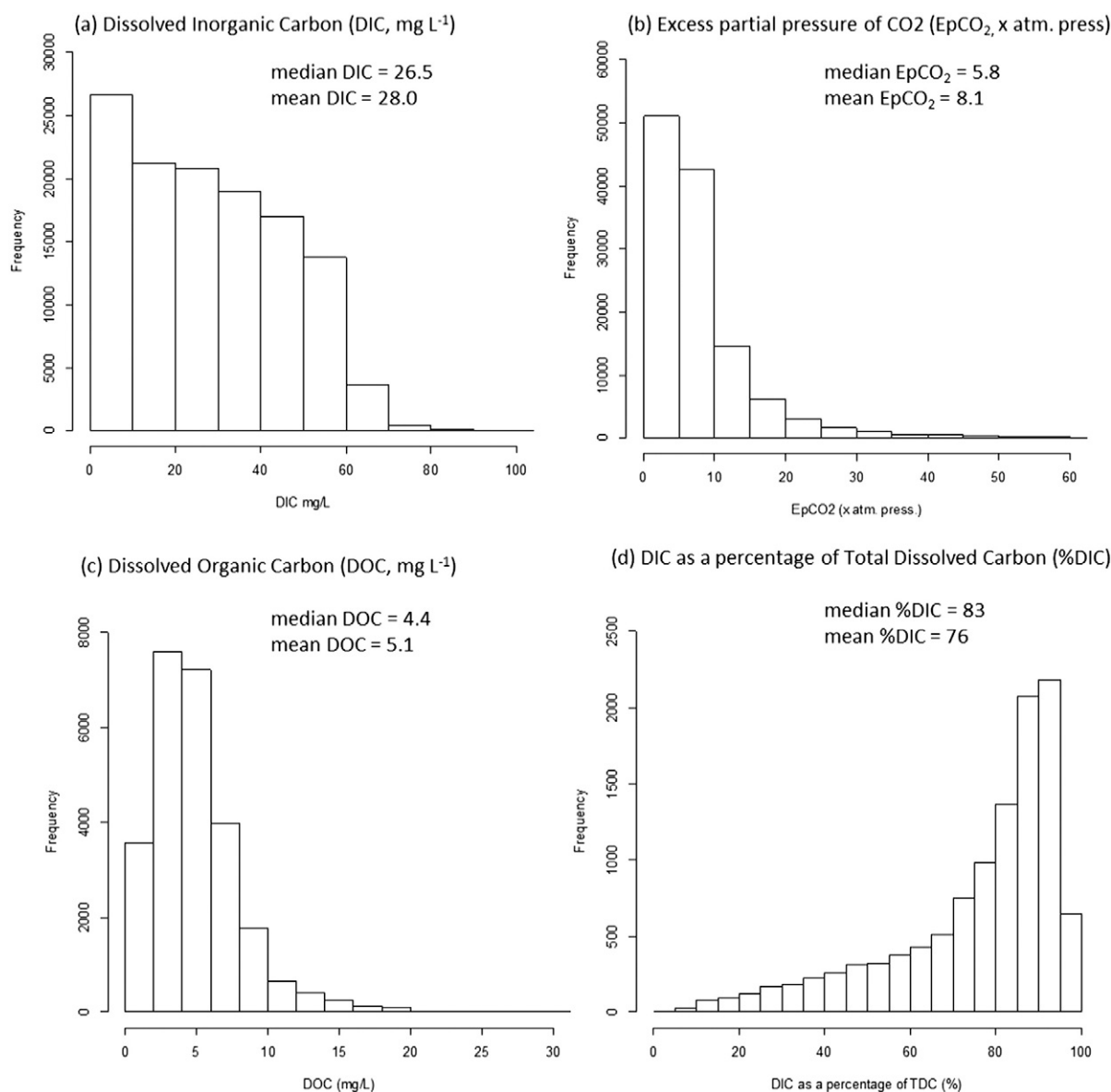


Fig. 2. Frequency distributions of (a) dissolved inorganic carbon, DIC ($n = 122,455$); (b) excess partial pressure of carbon dioxide, EpCO₂ ($n = 122,128$); (c) dissolved organic carbon, DOC ($n = 25,775$); and (d) DIC expressed as a percentage of total dissolved carbon (TDC = DIC + dissolved organic carbon, DOC) ($n = 11,073$), for Harmonised Monitoring Scheme river samples collected from 1974 to 2012, inclusive.

- Median site EpCO₂ also showed a transition between the lowlands and uplands. EpCO₂ was positively correlated ($P < 0.01$) with high-permeability bedrock and high-permeability superficial deposits, mean soil moisture deficit, and the percentage of arable or horticultural land and the percentage of urban land cover. Median site EpCO₂ was negatively correlated ($P < 0.01$) with standard annual average rainfall, the proportion of time that soils are wet, low-permeability bedrock, altitude, and percentage of mountain heath, or bog).
- Median site DOC was positively correlated ($P < 0.01$ significance) with the mean soil moisture deficit, the percentage of high-permeability bedrock, high-permeability, low-permeability and mixed-permeability superficial deposits and the percentage of urban land cover. Mean site DOC was negatively correlated ($P < 0.01$) with baseflow index, standard annual average rainfall, low-permeability bedrock, altitude, and the percentage of grassland.
- All four C variables (DIC, DOC, %DIC and EpCO₂) were positively correlated ($P < 0.01$) with the proportion of urban land, suggesting that

urban areas may provide sources of *both* inorganic and organic C species.

3.2. Spatial variations in carbon concentrations and speciation along an upland-lowland land-use continuum

The transitions in DIC, DOC and %DIC with changing altitude and percent arable or horticultural land are shown in Fig. 3. Average values in C fractions with increasing altitude (<150 m, 150–300 m and >300 m), and increasing proportions of agricultural and horticultural land (<5%, 5–10%, 10–30%, and >30%) are shown in Figs. 4 and 5, respectively. Arable and horticultural land predominates in lowland catchments, as there is a direct link between the altitude of the catchment and the proportion of arable land. However, although DIC and %DIC are negatively correlated with altitude and positively correlated with arable or horticultural land ($P < 0.01$) (Table 2), the strength of these correlations is

Table 2
Summary of correlation statistics for the relationships between median dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), the percentage contribution of DIC to total dissolved carbon (TDC; DIC + DOC) (%DIC) and excess partial pressure of carbon dioxide (EpCO₂), and catchment characteristics.

Catchment characteristic	DIC		DOC		%DIC		EpCO ₂	
	r _s	P value	r _s	P value	r _s	P value	r _s	P value
Catchment area (km ²)	0.169	***	0.449	**	-0.100		-0.033	
Baseflow index	0.409	***	-0.198	***	0.472	***	0.214	**
Std annual average rainfall (1961–1990; mm)	-0.741	***	-0.652	***	-0.610	***	-0.478	***
Proportion of time that soils are wet	-0.646	***	-0.258		-0.719	***	-0.381	***
Mean soil moisture deficit (mm)	0.604	***	0.497	***	0.597	***	0.407	***
% catchment underlain by high-permeability bedrock	0.557	***	0.538	***	0.410	***	0.316	***
% catchment underlain by moderate-permeability bedrock	0.237	***	-0.041	***	-0.001		0.035	
% catchment underlain by low-permeability bedrock	-0.469	***	-0.178	***	-0.223	***	-0.252	***
% catchment underlain by high-permeability superficial deposits	0.230	***	0.573	***	-0.215	***	0.228	***
% catchment underlain by low-permeability superficial deposits	-0.293	***	0.360	***	-0.583	***	-0.146	**
% catchment underlain by mixed-permeability superficial deposits	0.141		0.484	***	-0.222	***	0.079	
Altitude: Level (m) below which 10% of the catchment lies	-0.358	***	-0.396	***	-0.063	***	-0.451	***
Altitude: Level (m) below which 50% of the catchment lies	-0.590	***	-0.396	***	-0.606	***	-0.577	***
Altitude: Level (m) below which 90% of the catchment lies	-0.594	***	-0.355	***	-0.664	***	-0.532	***
Altitude: Maximum level (m) in the catchment	-0.580	***	-0.312	**	-0.695	***	-0.467	***
% catchment where the land use is woodland	-0.390	***	-0.104	*	-0.519	***	-0.271	***
% catchment where the land use is arable or horticultural	0.708	***	0.287		0.845	***	0.377	***
% catchment where the land use is grassland	-0.478	***	-0.478	***	-0.156		-0.192	**
% catchment where the land use is mountain, heath or bog	-0.572	***	-0.063	*	-0.836	***	-0.411	***
% urban cover in the catchment	0.616	***	0.189	***	0.399	***	0.479	***

*** P value < 0.01.

** 0.01 ≤ P value < 0.05

* 0.05 ≤ P value < 0.1.

higher for arable and horticultural land than for altitude, suggesting that arable or horticultural land use may have a greater influence on DIC and %DIC than altitude per se.

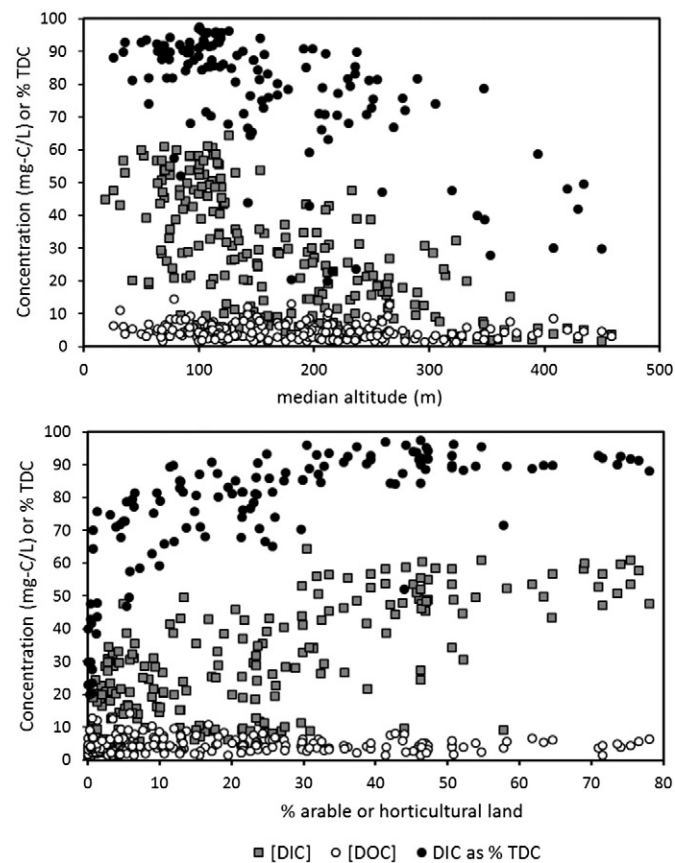


Fig. 3. Changes in median site dissolved inorganic carbon (DIC) and dissolved inorganic carbon (DOC) concentrations (mg-C L⁻¹) with median altitude (m) above sea level, and the percentage of arable or horticultural land within the catchment draining to each site.

DIC was highest in rivers draining lowland catchments, with an order of magnitude increase in DIC with decreasing altitude: median DIC concentrations increased from 4 mg-C L⁻¹ in upland catchments of >300 m to 43 mg-C L⁻¹ in the lowland catchments < 150 m (Figs. 3 and 4). EpCO₂ also increased with reductions in altitude, from 3.8 × atm. press. in the uplands to 6.4 × atm. press. in the lowlands (Fig. 4). In comparison, there was relatively little change in DOC with altitude. Median DIC expressed as a percentage of TDC increased markedly with decreasing altitude, from 45% in the uplands to 89% in the lowlands. Across the entire upland-lowland continuum, HCO₃⁻ was the dominant inorganic C fraction, accounting for 78% of DIC in the uplands, and rising to 96% of DIC in the lowlands. CO₃²⁻ accounted for a negligible proportion (typically <0.5%) of DIC in all these rivers. However, the proportion of DIC as dissolved CO₂ (H₂CO₃^{*}) decreased from 22% in the uplands to just 4% in the lowlands.

DIC increased steadily from 10 mg-C L⁻¹ in the catchments with the lowest proportions of arable or horticultural land use (<5%), to 50 mg-C L⁻¹ in catchments where >30% of the land was under arable or horticulture (Fig. 3). There was little change in concentrations of DOC with increasing arable land use, with median DOC consistently c. 4–5 mg-C L⁻¹, but there were small increases in EpCO₂, from 4.5 × atm. press in the catchments with the lowest proportions of arable/horticultural land, to 6.5 × atm. press. in the catchments with >30% arable or horticultural land (Fig. 5). Median DIC as a percentage of TDC (%DIC) increased from 43% in catchments with <5% arable/horticulture, to 91% in catchments with >30% arable or horticulture. HCO₃⁻, as a percentage of DIC, increased from 88% to 97% with increasing percentage of arable or horticulture land; correspondingly, H₂CO₃^{*}, as a percentage of DIC, decreased from 12 to 2.7% with increasing percentage of arable or horticultural land.

Median EpCO₂ also increased with the proportion of urban land, from 4.9 × atm. press. in catchments with <0.05% urban land cover, to 12.3 × atm. press. in catchments with >0.15% urban land cover (Fig. 6). DOC also increased from 4.1 mg-C L⁻¹ in catchments with the lowest proportions of urban land, to 6.3 mg-C L⁻¹ in catchments with >0.15% urban land. However, there were no consistent patterns of change in DIC, %DIC, TDC, HCO₃⁻, CO₃²⁻ or H₂CO₃^{*} with increasing extent of urban areas.

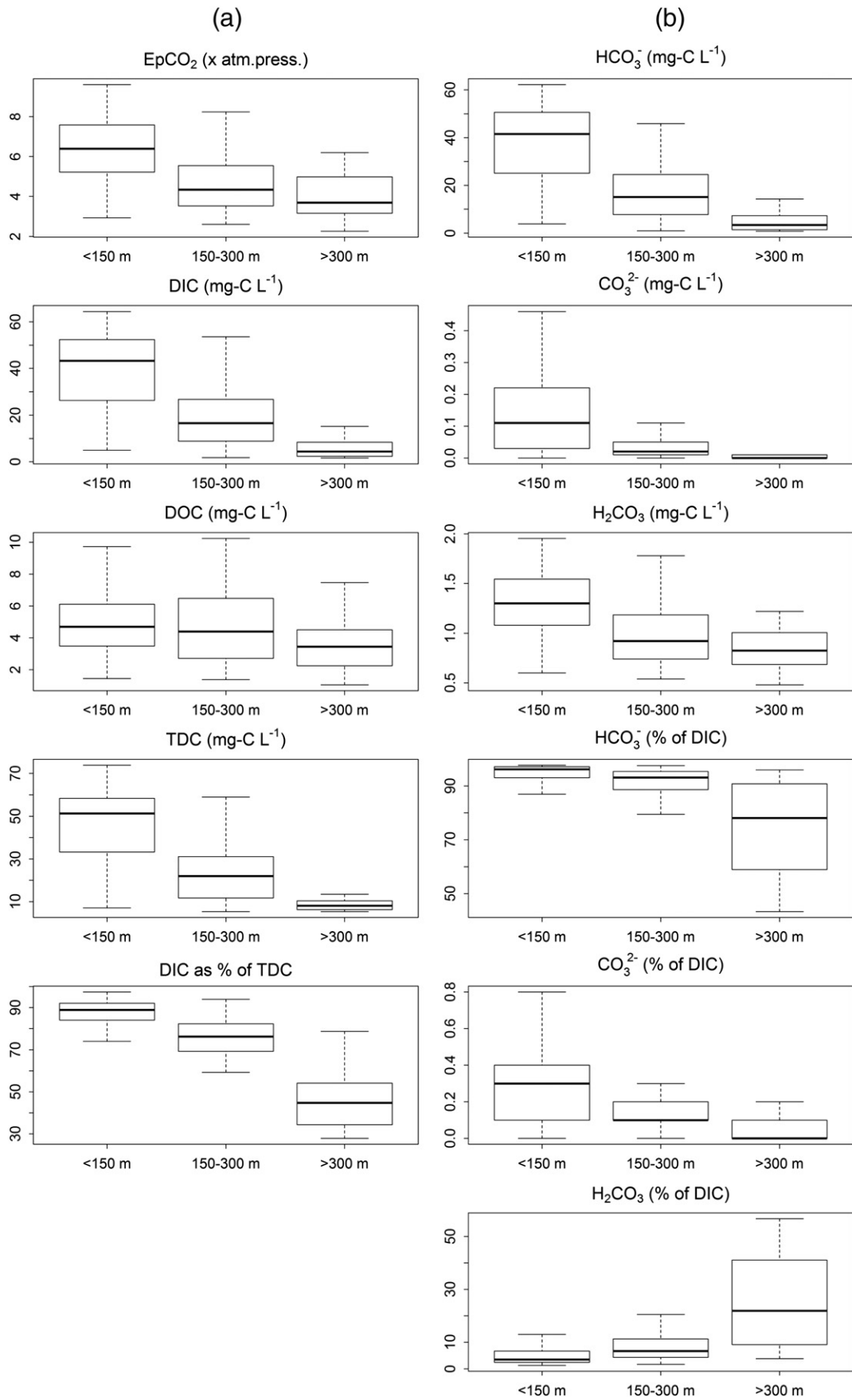


Fig. 4. Boxplots showing changes with increasing median catchment altitude of (a) excess partial pressure of CO₂ (EpCO₂), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), total dissolved carbon (TDC), and DIC expressed as a percentage of TDC; and (b) concentrations of DIC species: bicarbonate (HCO₃⁻), carbonate (CO₃²⁻), and carbonic acid (H₂CO₃), and their percentage contributions to DIC concentrations.

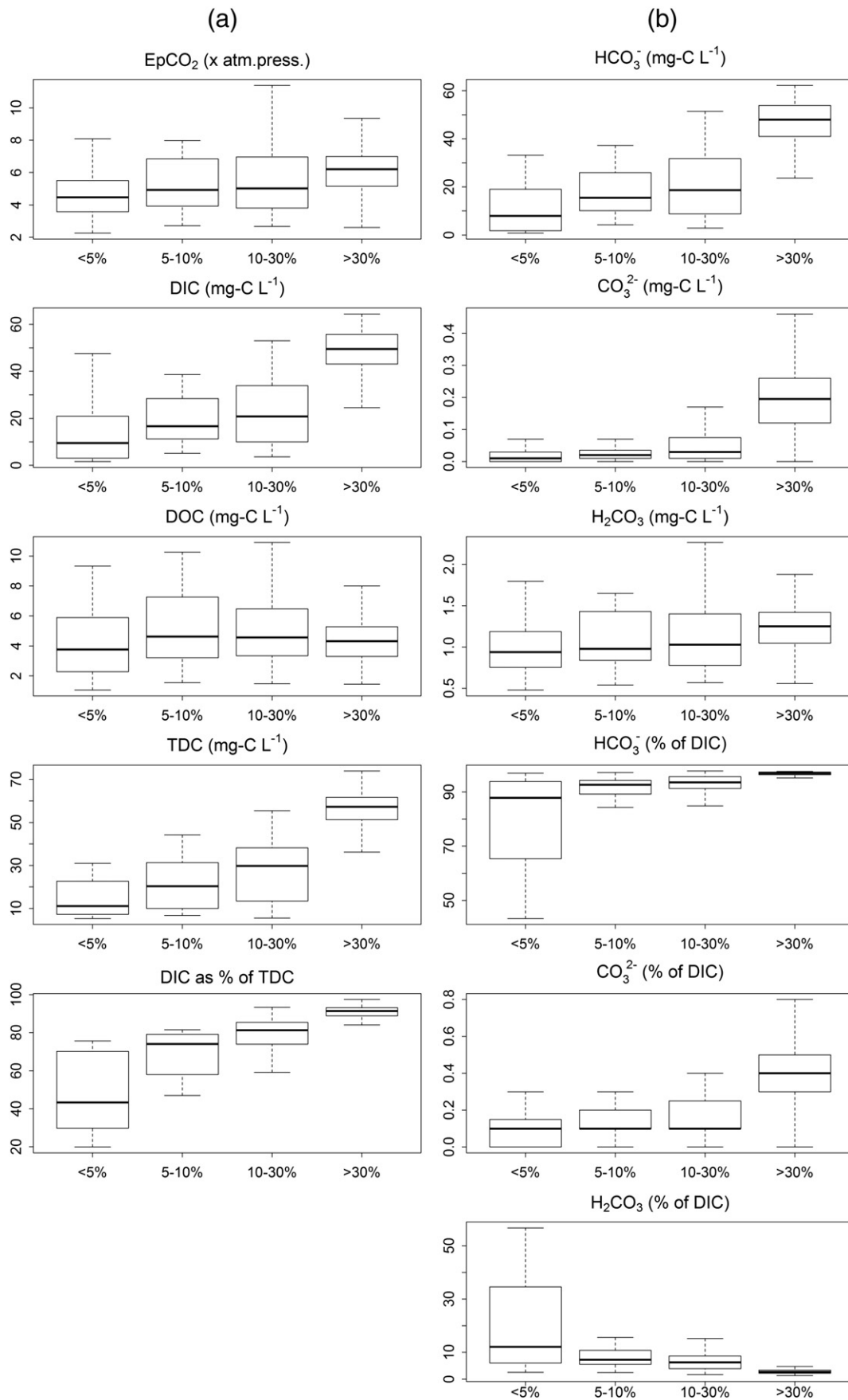


Fig. 5. Boxplots showing changes with increasing percentages of arable/horticultural land of (a) excess partial pressure of CO₂ (EpCO₂), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), total dissolved carbon (TDC), and DIC expressed as a percentage of TDC; and (b) concentrations of DIC species: bicarbonate (HCO₃⁻), carbonate (CO₃²⁻), and carbonic acid (H₂CO₃), and their percentage contributions to DIC concentrations.

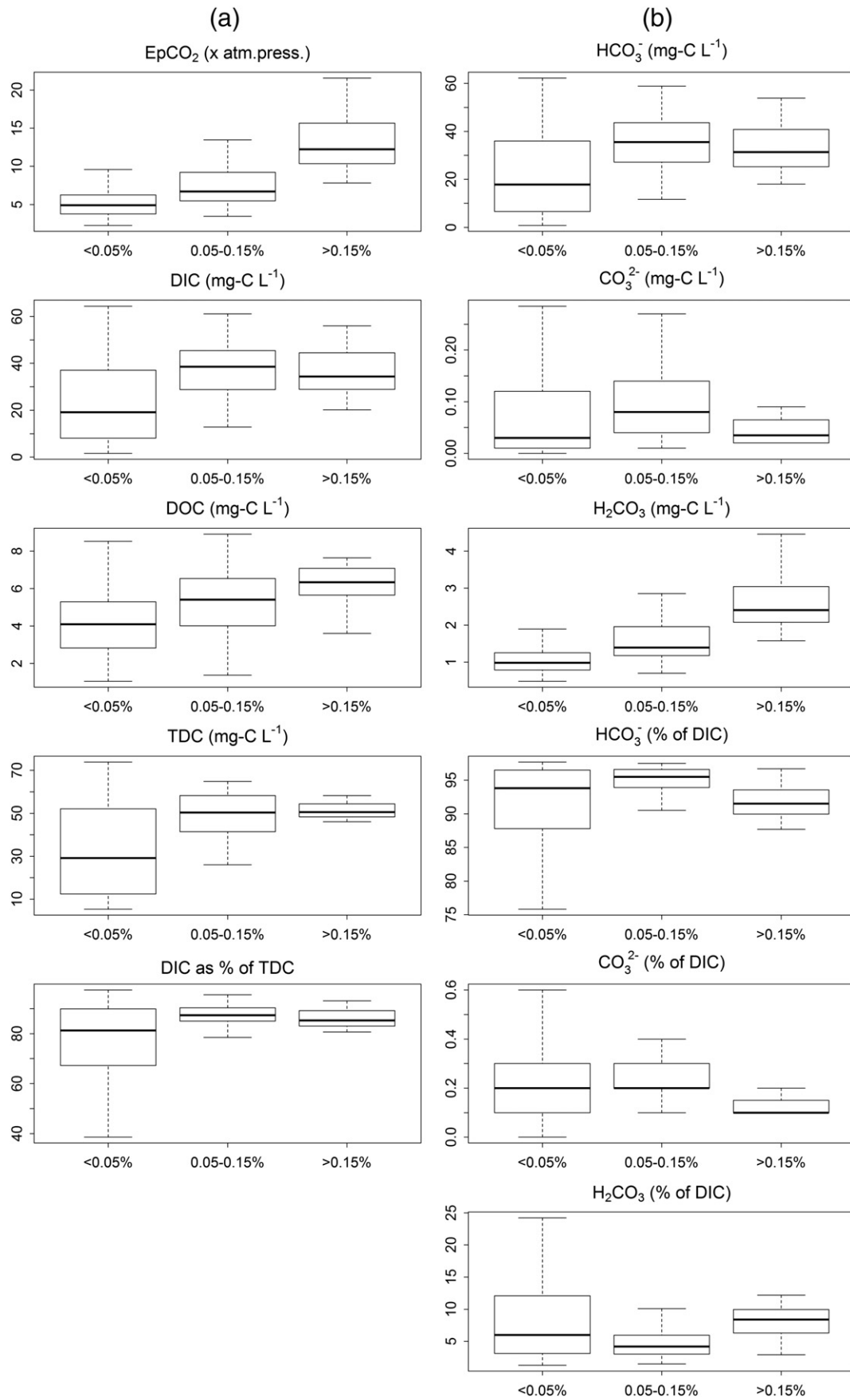


Fig. 6. Boxplots showing changes with increasing percentages of urban land, of (a) excess partial pressure of CO₂ (EpCO₂), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), total dissolved carbon (TDC), and DIC expressed as a percentage of TDC; and (b) concentrations of DIC species: bicarbonate (HCO₃⁻), carbonate (CO₃²⁻), and carbonic acid (H₂CO₃), and their percentage contributions to DIC concentrations.

Table 3

Summary statistics for the example paired low-alkalinity and higher-alkalinity rivers, the Mersey and Douglas, in north-west England: regression relationships between dissolved inorganic carbon (DIC) and excess partial pressure of CO₂ (EpCO₂); and mean and median alkalinity, DIC concentrations, EpCO₂, and H₂CO₃^{*} expressed as a percentage of DIC.

	Mersey	Douglas
DIC vs EpCO ₂ ; r ² (P value)	0.529 (<0.01)	0.195 (<0.01)
Average alkalinity (µeq/L): mean (median)	1699 (1680)	2961 (2980)
Average DIC (mg/L): mean (median)	24 (23)	39 (39)
Average EpCO ₂ (× atm. press.): mean (median)	17 (13)	16 (13)
Average H ₂ CO ₃ [*] as % of DIC: mean (median)	13 (11)	9 (7)

Microbial respiration, which releases CO₂, can assume greater importance as a source of DIC in lower-alkalinity rivers, draining catchments with higher proportions of upland or moorland, compared with high-alkalinity lowland rivers draining agricultural land and carbonate-rich permeable sedimentary bedrock. This is exemplified by the paired lower-alkalinity and higher-alkalinity river types in north-west England, the urban Rivers Mersey and Douglas (Table 3). There was a stronger positive correlation between DIC and EpCO₂ for the lower-alkalinity River Mersey (r² = 0.529) which drains a higher altitude catchment with higher proportions of mountain heath, or bog, compared with the higher-alkalinity River Douglas (r² = 0.195) which drains a lowland catchment with a higher proportion of arable land. In the lowland catchments, both DIC concentrations and EpCO₂ were higher, but with a smaller percentage of DIC composed of H₂CO₃^{*}. In the rivers draining the lower alkalinity higher-elevation catchments, although EpCO₂ and DIC were lower, H₂CO₃^{*} accounted for a larger percentage of DIC concentrations.

3.3. Temporal variability in DIC concentrations

The relative contributions of H₂CO₃^{*} (from microbial respiration) and HCO₃⁻ (from weathering) can have important implications for the long-term (39-year) trends in river DIC concentrations, related to changes in organic matter availability for microbial respiration. For example, there were large-scale reductions in EpCO₂ in the Rivers Mersey and Douglas, from the mid-1970s to the mid-1980s, as a result of improvements in sewage treatment, which reduced gross organic pollution and rates of microbial respiration in these rivers (Fig. 7).

In the River Douglas, the mean EpCO₂ decreased from 42 × atm. press. in 1975, to 10 × atm. press. in 1985 (Fig. 7). The corresponding decrease in mean EpCO₂ in the Mersey was very similar: from 43 × atm. press. in 1975 to 10 × atm. press. in 1985. However, in the lower alkalinity River Mersey, where H₂CO₃^{*} comprised a larger percentage of DIC, the reductions in CO₂ production, resulting from improved wastewater treatment, were linked with a larger a reduction in mean DIC concentrations than in the River Douglas. In the River Mersey, mean DIC declined by a third, from 36 mg-C L⁻¹ in 1975 (when H₂CO₃^{*} accounted for 23% of DIC) to 24 mg-C L⁻¹ (when H₂CO₃^{*} accounted for 9% of DIC). In the higher-alkalinity River Douglas, the impacts of reduced microbial CO₂ production on DIC concentrations were smaller: mean DIC in the Douglas reduced from 44 mg-C L⁻¹ in 1975 to 39 mg-C L⁻¹ in 1985, as a result of H₂CO₃^{*} contributing a smaller proportion of the DIC (13% in 1975 and 5% in 1985). The HMS DOC data has large gaps in the temporal record, with the greatest availability of DOC data available after 2005; therefore the long-term time series in DOC were not considered here. However, other data resources, such as the UK Environmental Change Network, have shown increases in DOC in upland acid-sensitive catchments, related to air-quality improvements and reversal of acidification (Evans et al., 2005; Monteith et al., 2007).

3.4. DIC contributions to total dissolved carbon fluxes from the seven largest British rivers

Using daily flows measured at the nearest gauging station to the HMS monitoring sites, annual riverine loads of DOC, DIC (and the three component DIC species, (HCO₃⁻, CO₃²⁻ and H₂CO₃^{*}) were calculated for the seven largest rivers in Great Britain (Fig. 1), using “Method 5”, the favoured OSPARCOM method for estimating determinand loads from periodic concentration and flow data (Littlewood et al., 1998). Annual loads are presented for 2007 (Tables 1 and 4), a year with simultaneous measurements of DOC, pH, and alkalinity across all seven rivers, allowing a full characterisation of river dissolved carbon fluxes.

Annual Total Dissolved Carbon fluxes in 2007 ranged from 112 kg-C ha⁻¹ year⁻¹ in the Tweed to 205 kg-C ha⁻¹ year⁻¹ in the Yorkshire Ouse. DIC loads ranged from 68 kg-C ha⁻¹ year⁻¹ in the Tay to 177 kg-C ha⁻¹ year⁻¹ in the Yorkshire Ouse and Trent. DIC provided the dominant contribution to annual TDC loads in all of the seven largest British rivers. DIC accounted for 91% of the TDC load in the Thames, >80% of the TDC load in the Severn, Trent and Ely Ouse, and >70% of the TDC load in the Tweed and Yorkshire Ouse. In all of the rivers, HCO₃⁻ was the dominant fraction of the DIC load, ranging from 86% of DIC in the Tay to 97% in the Thames and Ely Ouse. The highest contributions of H₂CO₃^{*} to DIC (14%) were found in the River Tay. In the Rivers Tay and Tweed, which drain upland catchments with smaller proportions of arable land, DIC loads contributed a lower percentage of TDC loads (57 and 74%, respectively). The Tay had the highest DOC load of 50 kg-C ha⁻¹ year⁻¹, followed by the Yorkshire Ouse with 43 kg-C ha⁻¹ year⁻¹. Lowest DOC loads were found in the rivers draining lowland arable catchments: the Ely Ouse and Thames (12 and 14 kg-C ha⁻¹ year⁻¹, respectively). The DOC and DIC loads presented here for 2007 are closely consistent with an earlier study (Eatherall et al., 1998) which calculated DIC and DOC fluxes from the Humber Rivers (including the Yorkshire Ouse and Trent). The total riverine flux of DOC in 2007 from these seven largest British rivers amounted to 120 kt, compared with 575 kt of DIC. Therefore, expressed as a percentage of TDC, DOC accounted for only 17% of the total annual flux of dissolved carbon in 2007.

The HMS datasets, from which the annual DOC and DIC fluxes were calculated, are based on monthly water quality data. This type of sampling regime may be biased towards lowflow conditions (Littlewood et al., 1998; Robson and Neal, 1997), which may underestimate DOC fluxes, given the importance of high flows for riverine DOC transport (Eatherall et al., 1998; Tipping et al., 1997). Therefore to evaluate the impacts of high and low flows on the contributions of DIC and DOC to TDC fluxes, we used the entire 39-year record to quantify mean baseflow and stormflow DIC, DOC and TDC fluxes (Table 5). A mean daily baseflow flux was calculated for each river from samples collected at flows below the 10th flow percentile. A mean daily stormflow flux was calculated from samples collected at flows above the 90th flow percentile. At baseflow, DOC contributes <20% of the mean daily TDC flux in six of the seven rivers; with DOC accounting for 38% of the mean baseflow TDC flux in the upland River Tay. DOC contributions to daily stormflow TDC fluxes were greater, but still only accounted for <25% of TDC fluxes in 5 of the seven rivers. DOC accounted for 35% of the mean daily stormflow fluxes in the Tweed and 49.5% of the mean daily TDC flux in the Tay. Therefore, even under the highest 10% of flows sampled over 39 years, stormflow DIC fluxes exceeded stormflow DOC fluxes in all seven of the largest British Rivers, even those with a large proportion of upland peat-dominated catchment areas. The mean daily baseflow TDC load from all seven largest British rivers was 0.361 kt-C day⁻¹, of which only 14% was DOC; and the mean daily stormflow TDC load from all seven rivers was 5.80 kt-C day⁻¹, of which only 21% was DOC.

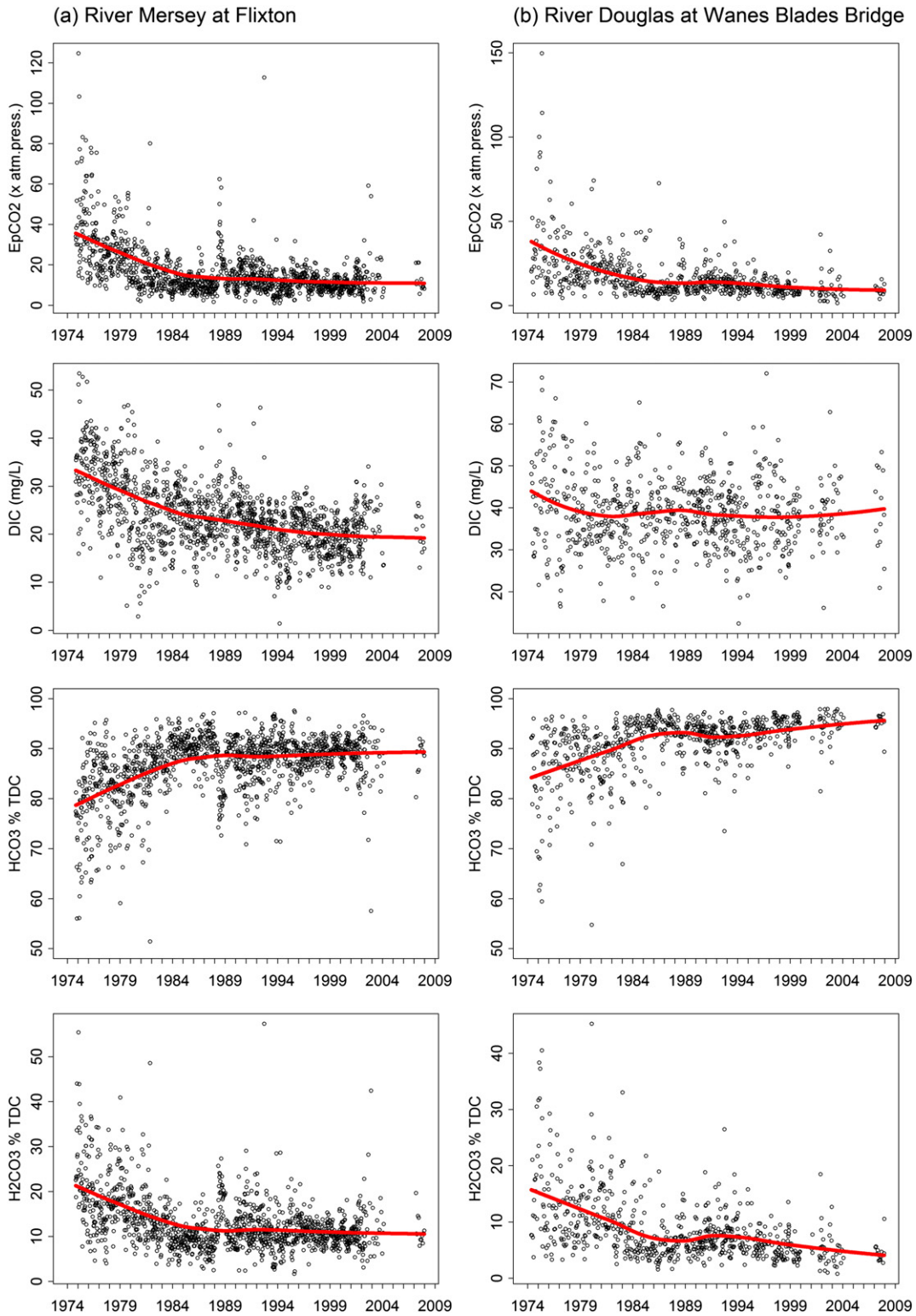


Fig. 7. Time series of excess partial pressure of CO₂ (EpCO₂) and dissolved inorganic carbon (DIC) for the River Mersey and River Douglas, with a Loess smoothing line shown in red.

4. Discussion

DIC was the dominant fraction of the dissolved carbon loads and concentration across all the major rivers in Great Britain draining into the coastal zone. The overwhelmingly dominant source of DIC in these rivers was HCO₃⁻. The dominance of HCO₃⁻ from weathering sources

for DIC concentrations in lowland rivers is directly linked to the greater contributions of groundwater discharge from permeable carbonate-rich sedimentary bedrock in the lowlands, and enhanced rates of weathering associated with tillage of lowland arable land. This leads to a strong upland-lowland gradation in DIC concentrations, with: (a) strong positive correlations between DIC concentrations and variables

Table 4
Annual loads of total dissolved carbon (TDC), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), the percentage contributions of DIC and DOC to TDC loads, and the percentage contributions of bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and carbonic acid (H_2CO_3^*) to the DIC loads, for the seven largest British rivers (by catchment area) in 2007.

	TDC load kg-C ha^{-1}	DIC load kg-C ha^{-1}	DOC load kg-C ha^{-1}	DIC % TDC load	DOC % TDC load	HCO_3^- % DIC load	CO_3^{2-} % DIC load	H_2CO_3^* % DIC load
Thames at Teddington Weir	147	134	14	91	9	97.3	0.49	2.3
Severn at Haw Bridge	173	140	33	81	19	96.2	0.57	3.2
Trent at Dunham	201	177	24	88	12	95.8	0.56	3.6
Tay at Perth (Queen's bridge)	118	68	50	57	43	86.3	0.06	13.6
Tweed at Norham Bridge	112	83	29	74	26	95.8	0.37	3.8
Ely Ouse at Denver Sluice	118	106	12	90	10	96.9	0.39	2.7
Yorkshire Ouse at Naburn Weir	205	162	43	79	21	93.7	0.18	6.1

characteristic of lowland catchments, including baseflow index and percentage of high-permeability bedrock, percentages of arable or horticulture and urban land, and soil moisture deficit; and (b) negative correlations with variables which are characteristic of the uplands, including altitude, rainfall, catchment wetness, low-permeability bedrock and upland land use types, including woodland and mountain heath or bog.

Despite upland peaty soils being an important source of DOC, there were no clear-cut upland-lowland transitions in DOC concentrations. DOC, EpCO_2 and DIC all showed positive correlations with the percentage of urban land, suggesting that urban areas provide a key lowland source of DOC and DIC. However, CO_2 production by microbial respiration assumes greater significance for DIC in the uplands than in the lowlands. The changes in inorganic C speciation, from lowland rivers, where DIC is overwhelmingly dominated by HCO_3^- to upland catchments, which have higher proportions of H_2CO_3^* , reflect an important transition in the relative importance of the two major sources of DIC to rivers: (i) weathering of soils and carbonate rocks which generates HCO_3^- , and (ii) microbial respiration, which releases CO_2 to produce H_2CO_3^* . Although both HCO_3^- and H_2CO_3^* increase in lowland agricultural catchments, the rates of increase in HCO_3^- are generally greater than for H_2CO_3^* , owing to the large increase in rates of carbonate weathering in lowlands. Higher rates of weathering in the lowlands arise from (a) higher contributions of groundwater, often from carbonate-rich permeable lithologies; and, (b) soil tillage in arable land, which increases the rates of and depth of weathering in the soil profile, increasing HCO_3^- concentrations in drainage waters.

Low-alkalinity rivers draining upland catchments tend to have greater proportions of DIC as H_2CO_3^* , and lower proportions of HCO_3^- , owing to lower weathering rates. In low-alkalinity rivers, especially those draining upland catchments, this has key significance for long-term trends in DIC. EpCO_2 and thus H_2CO_3^* are highly sensitive to changes in wastewater management: improvements to sewage treatment in the 1970s and 1980s reduced gross organic pollution of rivers, and thus reduced rates of microbial respiration and CO_2 production. In the lower-alkalinity rivers, improved wastewater treatment has reduced DIC concentrations; for example, there was decrease in DIC

concentrations of c.33% in the River Mersey between 1975 and 1985. In contrast, in the lowland higher alkalinity rivers, the effects of improved wastewater treatment and reduced CO_2 production on DIC concentrations and fluxes are masked by the dominance of DIC by HCO_3^- .

DIC fluxes exceeded DOC fluxes even under the highest flow conditions sampled over a 39-year period, and even for rivers such as the Tay and Tweed which drain upland peaty catchments. These results clearly demonstrate the importance of accounting for DIC concentrations and fluxes for quantifying dissolved carbon transfers from land via rivers to the coastal zone. Currently, only DOC is routinely measured in most water-quality studies. Our results show that, even in major rivers draining upland catchments, such as the River Tay, by only measuring DOC, we are failing to account >50% of the dissolved carbon flux. In the lowlands such as the Thames, Severn, Trent, Ely Ouse and Yorkshire Ouse, by only measuring DOC, we fail to account for 80% or more of the annual dissolved carbon flux.

Particulate organic carbon (POC) was not routinely measured as part of the HMS monitoring programme; however, earlier UK river flux studies have shown that POC fluxes are consistently smaller than DOC fluxes (Eatherall et al., 1998; Tipping et al., 1997), with POC contributing 29–40% of the Total Organic Carbon flux. Applying this POC-DOC fractionation to the annual C fluxes from the seven largest British rivers would produce an estimated POC flux of between 49 and 79 kt-C year^{-1} . This means that POC would contribute between 7% and 11% of a total annual C flux (DIC + DOC + POC), compared with 15–16% from DOC, and 74–77% from DIC. Thus even when POC contributions are taken into consideration, DIC remains the overwhelmingly dominant C flux to the British coastal zone. By quantifying freshwater DIC contributions to TDC fluxes, the THINCARB model addresses strategic requirements to identify and characterise the components of carbon budgets along the river continuum from headwaters, through rivers, discharging to estuaries. This is a fundamental requirement for understanding the connectivity of carbon sources and pathways, and carbon cycling in freshwaters, including the sources and sinks of CO_2 linked to heterotrophy, autotrophy, and precipitation of CaCO_3 , under varying climate and hydrological settings.

Table 5
Baseflow and stormflow loads of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) and the percentage contributions of DOC to baseflow and stormflow total dissolved carbon (TDC) loads, for the seven largest British rivers.

	Baseflow (<10th percentile flow)		Stormflow (>90th percentile flow)		Baseflow DOC expressed as % TDC load	Stormflow DOC expressed as % TDC load
	DIC load kg-C ha^{-1} day^{-1}	DOC load kg-C ha^{-1} day^{-1}	DIC load kg-C ha^{-1} day^{-1}	DOC load kg-C ha^{-1} day^{-1}		
Thames at Teddington Weir	0.016	0.002	0.830	0.142	12.7	14.6
Severn at Haw Bridge	0.056	0.008	0.753	0.195	12.6	20.6
Trent at Dunham	0.122	0.016	0.999	0.235	11.8	19
Tay at Perth (Queen's bridge)	0.054	0.032	0.451	0.443	37.5	49.5
Tweed at Norham Bridge	0.055	0.011	0.724	0.394	16.5	35.3
Ely Ouse at Denver Sluice	0.187	0.017	3.828	0.520	8.2	12
Yorkshire Ouse at Naburn Weir	0.072	0.009	1.113	0.337	11.4	23.2

5. Conclusions

River water-quality monitoring studies rarely measure DIC concentrations, but routinely-measured alkalinity, pH and temperature can be used to determine DIC concentrations using established thermodynamic calculations. Here, we provide the *THINCARB* model as tool for calculating this vital and missing inorganic component of the freshwater carbon flux. *THINCARB* calculates DIC concentrations, speciation (HCO_3^- , CO_3^{2-} and H_2CO_3^*) and EpCO_2 from routine measurements of pH, alkalinity and temperature. If measurements of Ca are available, the *THINCARB* model also calculates calcite saturation. The application of the *THINCARB* model to the 39-year UK Harmonised Monitoring Scheme dataset provides new insight into the national-scale spatial and temporal variability in DIC in British rivers, the contributions of DIC relative to DOC, and the importance of the two major sources of DIC to rivers: HCO_3^- from weathering of carbonate-rich rocks, and CO_2 production by respiration of aquatic organisms.

Despite an overwhelming focus on measuring DOC in rivers, our research shows that DOC represents a minor component of the dissolved carbon fluxes entering the coastal zone from British rivers. In the seven largest British rivers, DIC accounted for an average of 80% of the TDC (ranging from 57% in the upland River Tay, to 91% in the lowland River Thames). Moreover, given that POC fluxes from UK rivers are consistently lower than DOC fluxes (Eatherall et al., 1998; Tipping et al., 1997), DIC fluxes are therefore most likely also the major source of total carbon fluxes to the coastal zone. The current paucity of information on DIC transfers from the terrestrial environment, via rivers to the coastal zone, highlights a major gap in our understanding of carbon cycling along the land–water continuum. Recent work on macronutrient (C:N:P) stoichiometry and cycling in British rivers, lakes and groundwaters (e.g., Stewart and Lapworth, 2016; Tipping et al., 2016) relies solely on DOC measurements, with no consideration of DIC. However, understanding the coupling of nutrient cycles, and their impacts on the macronutrient status of water bodies, requires quantification of both inorganic and organic concentrations and fluxes of C, N and P. This national-scale study of carbon concentrations and fluxes for British rivers, using the Harmonised Monitoring Scheme data reveals, for the first time, the widespread dominance of inorganic C to dissolved carbon fluxes in British rivers. The *THINCARB* model addresses a fundamental, pressing and strategic need to quantify the contributions of DIC to freshwater carbon fluxes. Quantification of freshwater DIC concentrations and fluxes is required for understanding current carbon cycling and processing along the land–water continuum, the implications for aquatic ecosystem primary productivity, and the role of freshwaters as sources and sinks of CO_2 within the global carbon cycle, and for predicting the long-term evolution of C fluxes between terrestrial and marine environments.

Acknowledgements

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Appendix A. Estimating Gran alkalinity from bicarbonate alkalinity

Alkalinity is the acid neutralizing capacity of solutes in a water sample, but it can be reported in different ways. In many studies it is often assessed in terms of bicarbonate or a total carbonate alkalinity. This assumes that the only buffers in solution are carbonate and bicarbonate and the alkalinity is then determined by a fixed-endpoint acidimetric titration to a given pH (often 4.5) or to a colour change using indicators such as methyl orange. The problem with this is that during the titration, not only are the carbonate and bicarbonate titrated together with any other buffers in solution, but some acid is used to acidify the

solution to the endpoint pH and, in the case of a colourimetric endpoint, an additional amount of acid is required to change the colour of indicator (Neal, 2001; Reynolds and Neal, 1987).

The most precise measure of alkalinity follows the acidimetric titration method developed by Gran (Gran, 1950; Gran, 1952; https://en.wikipedia.org/wiki/Gran_plot) and, in particular, ‘is recommended for water in which the alkalinity ... is expected to be less than about 0.4 milliequivalents per liter (meq/L) (20 milligrams per liter (mg/L) as CaCO_3), or in which conductivity is less than 100 microsiemens per centimeter ($\mu\text{S}/\text{cm}$), or if there are appreciable noncarbonate contributors or measurable concentrations of organic acids’ (Rounds, 2006) This Gran alkalinity, Alk_{Gran} , is approximately the difference between the concentrations of the bicarbonate and carbonate buffers in solution minus the hydrogen ion concentration, that is

$$\text{Alk}_{\text{Gran}} \approx [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}] - [\text{H}^+]$$

where the [] brackets here denote concentrations in micromoles per liter ($\mu\text{M}/\text{L}$) and the factor two converts the carbonate term to microequivalents per liter ($\mu\text{eq}/\text{L}$) (N.B. for monovalent ions, $\mu\text{M}/\text{L}$ and $\mu\text{eq}/\text{L}$ are the same). This equation is approximate because other buffers in solution such as organic matter may also contribute to Alk_{Gran} (Neal, 2001). Under acidic conditions, where $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ are small but $[\text{H}^+]$ is high, Alk_{Gran} becomes a negative number approximately equal to minus the hydrogen ion concentration.

As indicated above, alkalinity can be expressed as a concentration of either CaCO_3 or HCO_3^- . Such values must be converted to equivalents (as $\mu\text{eq}/\text{L}$) before use in *THINCARB*, as shown in Table A1.

Table A1

Concentration to equivalent charge conversion factors.

Alkalinity in mg/L CaCO_3	Alkalinity in mg/L HCO_3^-
Formula weight of $\text{CaCO}_3 = 100.09$	Formula weight of $\text{HCO}_3^- = 61.01$
Charge on ion: 2 (Ca^{2+} & CO_3^{2-})	Charge on ion: 1 (HCO_3^-)
Equivalent weight of $\text{CaCO}_3 = 50.045$	Equivalent weight of $\text{HCO}_3^- = 61.01$
1 mg/L $\text{CaCO}_3 = 1/50.045 = 0.01998$	1 mg/L $\text{HCO}_3^- = 1/61.01 = 0.01639$
meq/L = 19.98 $\mu\text{eq}/\text{L}$	meq/L = 16.39 $\mu\text{eq}/\text{L}$

One may then write

$$\text{Alk}_{\text{Gran}} (\mu\text{eq}/\text{L}) \approx 19.98 \times \text{Alk}_{\text{CaCO}_3} (\text{mg}/\text{L}) \left\{ -\text{Alk}_{\text{H}^+ \text{ endpoint}} (\mu\text{eq}/\text{L}) \right\}$$

or

$$\text{Alk}_{\text{Gran}} (\mu\text{eq}/\text{L}) \approx 16.39 \times \text{Alk}_{\text{HCO}_3^-} (\text{mg}/\text{L}) \left\{ -\text{Alk}_{\text{H}^+ \text{ endpoint}} (\mu\text{eq}/\text{L}) \right\}$$

where

$$\text{Alk}_{\text{H}^+ \text{ endpoint}} \approx 10^{(6 - \text{endpoint pH})}$$

The $\text{Alk}_{\text{H}^+ \text{ endpoint}}$ correction term in {} brackets is approximate (due to pH being a measure of chemical activity rather than concentration) but small (typically less than 10%) and may be ignored for samples with strongly positive alkalinities. As an example, for a titration endpoint of pH 4.5 the correction term is approximately 32 $\mu\text{eq}/\text{L}$, but for a methyl orange endpoint the correction term can be three times higher.

Appendix B. Corrections to the Neal et al. (1998) model

After publication of the Neal et al. (1998). model it became apparent that trivial errors had crept into some formulae. In developing *THINCARB* the opportunity has been taken to correct these errors. Table B1 below details these corrections and should be read alongside Table 1a in Neal et al. (1998). Note, however, that in the *THINCARB* Excel™ spreadsheet the actual cell references shown in Table B1 are different.

Table B1

Details of the original and corrected formulae.

Parameter	Neal et al. 1998 original formulae	Equivalent corrected formulae
EpCO ₂ rough (case 1)	$(B17 + (10^{6-A17}) * (10^{6-A17})) / 5.25$	$(B17 + (10^{6-A17})) * (10^{6-A17}) / 5.25$
EPCO ₂ less rough (case 2)	$((0.95 * B17) + (10^{6-A17}) * (10^{6-A17})) / (6.46 - (0.0636 * C17))$	$((0.95 * B17) + (10^{6-A17})) * (10^{6-A17}) / (6.46 - (0.0636 * C17))$
EpCO ₂ less rough inc CO ₃ (case 3)	$((0.95 * B17) + ((10^{6-A17}) / 0.95) + ((10^{A17+6+LOG10(R17)})) / 0.95)) * (10^{6-A17}) / ((6.46 - (0.0636 * C17)) * (1 + (2 * (0.95 / 0.8) * 10^{A17+LOG10(N17)})))$	$((0.95 * B17) + ((10^{6-A17}) / 0.95) + ((10^{A17+6+LOG10(R17)})) / 0.95)) * (10^{6-A17}) / ((6.46 - (0.0636 * C17)) * (1 + (2 * (0.95 / 0.8) * 10^{A17+LOG10(N17)})))$
Ca tot	$IF(D17 <= 0, B17 / 2000000, D17 / 40000)$	$(D17 / 40000)$
Kwater (K6 H ₂ O)	$10^{-(6.0846 + (4471.33 / (273 + C17)) + (0.017053 * (273 + C17)))}$	$10^{-(6.0846 + (4471.33 / (273 + C17)) + (0.017053 * (273 + C17)))}$
K7 (K7 CaCO ₃)	$10^{-(13.543 + (3000 / (273 + C17)) + 0.0401 * (273 + C17))}$	$10^{-(13.543 + (3000 / (273 + C17)) + 0.0401 * (273 + C17))}$

When tested on the randomly selected set of experimental data shown in Table B2, the impact of the corrections in Table B1 across any of the 36 parameters calculated by the THINCARB model range from a change of -0.07% to a change of +2.4%, with a mean change of +0.18% (for the same residual charge balance of $\sim 10^{-5}$ e; assuming sea level). The effect of the corrections is generally to fractionally reduce the value of EpCO₂, though in some instances it is unaffected, reflecting the complex interplay between pH, alkalinity and temperature. There is a similar effect on the calculated total DIC concentration, DIC_{total}, from the THINCARB model if the corrected formulae are not applied (values in *italics*).

Table B2

Illustration of the impact of the corrections to the original Neal et al. (1998) formulae.

pH	Alk _{gran} (µeq/L)	Temp (°C)	[Ca] (mg/L)	EpCO ₂ (original formulae)	EpCO ₂ (corrected formulae)	DIC _{total} (original formulae)	DIC _{total} (corrected formulae)
7.86	4558	10.0	128.3	10.3380	10.0880	57.20	55.80
8.01	4915	7.2	140.0	7.5379	7.5344	60.33	60.31
8.05	5393	9.3	142.9	7.7188	7.7188	69.59	69.59
7.94	5637	6.8	139.1	10.1163	10.1163	66.12	66.12

Finally, there was also an error in the altitude compensation correction, Eq. (A1-c) in Neal et al. (1998).

$$EpCO_{2,compensated} = EpCO_{2,calculated} \times P_s/P_0$$

which should have read

$$EpCO_{2,compensated} = EpCO_{2,calculated} \times P_0/P_s$$

where P_0 is the atmospheric pressure at sea level, P_s is the atmospheric pressure at an altitude of s metres, and the ratio P_0/P_s is given by the empirical relationship in Eq. (A1-a). Although this altitude compensation was never actually included in the original Lotus™ 1-2-3 spreadsheet implementation of the Neal et al. model, it is implemented in THINCARB.

Appendix C. Comparison of “case 3” vs “case 5” calculations

EpCO₂ and SI_{calcite} values for a wide range of UK surface waters, based on the extensive compilation provided by Neal et al. (2012) ($n = 7828$), were calculated using the THINCARB model both with and without optimisation. These two sets of calculations correspond to the “case 5” and “case 3” calculations in Neal et al. (1998), respectively. The pairs of values were then compared by linear regression of “case 5” (Y) against “case 3” (X). As shown in Table C1 below, the two pairs of relationships are virtually 1:1 whether or not a constant is included in the regression analysis.

Table C1

Linear regression analysis comparing “case 5” (Y) calculations against “case 3” (X).

Parameter	Gradient	Constant	r ²
EpCO ₂	1.0078 ± 0.0003	0.0351 ± 0.2356	0.9999
EpCO ₂	1.0096 ± 0.0002	0.0000 ± 0.2402	0.9999
SI _{calcite}	0.9939 ± 0.0001	0.0094 ± 0.0072	1.0000
SI _{calcite}	1.0004 ± 0.0002	0.0000 ± 0.0170	0.9998

Appendix D. Validation of the THINCARB model DIC calculations

The DIC concentrations calculated by THINCARB have been validated by comparison with experimental data from the literature, of which it must be said there is not a significant body. This no doubt reflects the difficulties associated with the robust experimental determination of DIC in water samples and in turn highlights the usefulness of a model like THINCARB. Example comparisons, using water sample data sourced from three continents, are shown in Tables D1 and D2 below. Estimated altitudes were derived from internet sources. Where the temperature of a sample was not provided a default value of 20 °C has been used in the calculations.

In the first set of comparisons (Table D1) the agreement between experiment and model calculation is seen to be extremely good ($r^2 = 0.999$).

Table D1

Comparison of total DIC measured experimentally and calculated by the THINCARB model.

Data source (Polesello et al., 2006; Davies et al., 2003)	Alt. (m)	pH	Alkalinity (µeq/L)	Temp. (°C)	Quoted DIC (mg/L)	THINCARB DIC _{total} (mg/L)
Polesello_Table2_Bottle_Water	0	7.45	460	20	5.8	5.9
Polesello_Table2_River_Cannobino	192	7.16	190	20	2.5	2.7
Polesello_Table2_River_Ticino_emis	192	7.97	840	20	9.5	10.3
Polesello_Table2_River_Ticino_trib	192	7.7	760	20	8.5	9.6
Davies_Table1_Lake_227	370	6.5	94	20	1.1	2.0
Davies_Table1_Lake_240	370	7.2	134	20	1.6	1.9
Davies_Table1_Lake_Malawi	500	8.5	2450	20	28.8	29.2

In the second set of comparisons (Table D2), whilst THINCARB generally mirrors the changes in the experimental values, there is rather greater variability between the experimental and calculated values of the DIC concentration. However, there is likely a very good reason for

this variability. Whitfield et al. (2009) studied boreal lakes in northern Canada, an area in which peatlands are a dominant landscape component. The lakes have low alkalinity and high DOC: conditions under which the thermodynamics underlying the THINCARB model become less reliable because of the impact of organic acids in the DOC on the alkalinity titration (see Appendix A). It may also be the case that, at low alkalinities, the contributions of dissolved CO₂ to the DIC are proportionally greater, meaning measurements are more sensitive to CO₂ degassing. For low alkalinity waters in general, the alkalinity estimates of EpCO₂ become less reliable as linked to a number of issues (Neal, 2001), pH measurements using conventional electrode systems can become more problematical (Neal and Thomas, 1985) and the value of alkalimetric rather than acidimetric titrations becomes clear (Neal, 1988). Lastly, to convert the alkalinity data provided by Whitfield et al. (2009) to equivalent units it was necessary for us to make an assumption about the speciation of the data: CaCO₃ has been assumed.

Table D2

Comparison of total DIC measured experimentally and calculated by the THINCARB model.

Data source (Whitfield et al., 2009)	Alt. (m)	pH	Alkalinity (µeq/L)	Temp. (°C)	Quoted DIC (mg/L)	THINCARB DIC _{total} (mg/L)
Whitfield_Table1_BM_08	370	6.7	192	16.3	1.0	3.5
Whitfield_Table1_BM_09	370	6.8	214	16.5	2.6	3.6
Whitfield_Table1_NE_04	370	6.9	72	20.5	2.0	1.1
Whitfield_Table1_NE_05	370	7.6	262	17.7	3.8	3.4
Whitfield_Table1_NE_09	370	8.4	1414	20.9	15.7	16.9
Whitfield_Table1_NE_10	370	8.6	1176	21.3	15.3	13.9
Whitfield_Table1_SM_02	370	7.2	158	22.6	1.3	2.2
Whitfield_Table1_SM_07	370	7.5	204	22.1	1.3	2.6
Whitfield_Table1_WF_02	370	7.2	62	18.9	3.9	0.9
Whitfield_Table1_WF_08	370	7.7	702	19.8	6.8	8.7

Supplementary Material

This includes catchment descriptions; and Tables S11–4: Summary statistics (mean median, max and min, and sample numbers) for dissolved inorganic carbon (DIC), excess partial pressure of carbon dioxide (EpCO₂), dissolved organic carbon (DOC), and dissolved inorganic carbon expressed as a percentage of total dissolved carbon (%DIC), for the UK Harmonised River Scheme river monitoring sites. Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.scitotenv.2016.08.201>.

Appendix references

- Davies, J.M., Hesslein, R.H., Kelly, C.A., Hecky, R.E., 2003. PCO₂ method for measuring photosynthesis and respiration in freshwater lakes. *Journal of Plankton Research* 25, 385–395.
- Gran, G., 1950. Determination of the equivalence point in potentiometric titrations. *Acta Chemica Scandinavica* 4, 559–577.
- Gran, G., 1952. Determination of the equivalence point in potentiometric titrations. *Analyst* 77, 661–671.
- Neal, C., 1988. pCO₂ variations in streamwaters draining an acidic and acid sensitive spruce forested catchment in Mid Wales. *Science of the Total Environment* 76, 279–283.
- Neal, C., 2001. Alkalinity measurements within natural waters: towards a standardised approach. *Science of the Total Environment* 265, 99–113.
- Neal, C., Bowes, M., Jarvie, H.P., Scholefield, P., Leeks, G., Neal, M., et al., 2012. Lowland river water quality: a new UK data resource for process and environmental management analysis. *Hydrological Processes* 26, 949–960.
- Neal, C., House WA, Down, K., 1998. An assessment of excess carbon dioxide partial pressures in natural waters based on pH and alkalinity measurements. *Science of the Total Environment* 210, 173–185.
- Neal, C., Thomas, A.G., 1985. Field and laboratory measurement of pH in low conductivity natural waters. *Journal of Hydrology* 79, 319–322.
- Polesello, S., Tartari, G., Giacomotti, P., Mosello, R., Cavalli, S., 2006. Determination of total dissolved inorganic carbon in freshwaters by reagent-free ion chromatography. *Journal of Chromatography A* 1118, 56–61.
- Rounds, S.A., 2006. Alkalinity and acid neutralizing capacity (ver. 3.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, sec. 6.6, July 2006. accessed 17-July-2016, from <http://pubs.water.usgs.gov/twri9A6/>.

- Reynolds, B., Neal, C., 1987. A comment on the use of acidimetric titrations for the estimation of the alkalinity and bicarbonate content of acid upland surface waters. *Science of the Total Environment* 65, 155–161.
- Whitfield, C., Ahern, J., Watmough, S., 2009. Predicting the Partial Pressure of Carbon Dioxide in Boreal Lakes. *Canadian Water Resources Journal* 34, 415–425.

References

- Baker, A., Cumberland, S., Hudson, N., 2008. Dissolved and total organic and inorganic carbon in some British rivers. *Area* 40, 117–127.
- Billett, M.F., Harvey, F.H., 2013. Measurements of CO₂ and CH₄ evasion from UK peatland headwater streams. *Biogeochemistry* 114, 165–181.
- Billett, M.F., Palmer, S.M., Hope, D., Deacon, C., Storeton-West, R., Hargreaves, K.J., et al., 2004. Linking land-atmosphere-stream carbon fluxes in a lowland peatland system. *Glob. Biogeochem. Cycles* 18.
- Davies, H., Neal, C., 2007. Estimating nutrient concentrations from catchment characteristics across the UK. *Hydrol. Earth Syst. Sci.* 11, 550–558.
- Dawson, J.J.C., Bakewell, C., Billett, M.F., 2001a. Is in-stream processing an important control on spatial changes in carbon fluxes in headwater catchments? *Sci. Total Environ.* 265, 153–167.
- Dawson, J.J.C., Billett, M.F., Hope, D., 2001b. Diurnal variations in the carbon chemistry of two acidic peatland streams in north-east Scotland. *Freshw. Biol.* 46, 1309–1322.
- Dawson, J.J.C., Billett, M.F., Hope, D., Palmer, S.M., Deacon, C.M., 2004. Sources and sinks of aquatic carbon in a peatland stream continuum. *Biogeochemistry* 70, 71–92.
- Dawson, J.J.C., Soulsby, C., Hrachowitz, M., Speed, M., Tetzlaff, D., 2009. Seasonality of epCO₂ at different scales along an integrated river continuum within the Dee Basin, NE Scotland. *Hydrol. Process.* 23, 2929–2942.
- Eatherall, A., Naden, P.S., Cooper, D.M., 1998. Simulating carbon flux to the estuary: the first step. *Sci. Total Environ.* 210, 519–533.
- Eatherall, A., Warwick, M.S., Tolchard, S., 2000. Identifying sources of dissolved organic carbon on the River Swale, Yorkshire. *Sci. Total Environ.* 251, 173–190.
- Evans, C.D., Monteith, D.T., Cooper, D.M., 2005. Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. *Environ. Pollut.* 137, 55–71.
- Griffiths, J., Nutter, J., Binley, A., Crook, N., Young, A., Pates, J., 2007. Variability of dissolved CO₂ in the Pang and Lambourn Chalk rivers. *Hydrol. Earth Syst. Sci.* 11, 328–339.
- Hope, D., Billett, M.F., Cresser, M.S., 1994. A review of the export of carbon in river water - fluxes and processes. *Environ. Pollut.* 84, 301–324.
- Hope, D., Dawson, J.J.C., Cresser, M.S., Billett, M.F., 1995. A method for measuring free CO₂ in upland streamwater using headspace analysis. *J. Hydrol.* 166, 1–14.
- Huang, W.J., Cai, W.J., Powell, R.T., Lohrenz, S.E., Wang, Y., Jiang, L.Q., et al., 2012. The stoichiometry of inorganic carbon and nutrient removal in the Mississippi River plume and adjacent continental shelf. *Biogeochemistry* 9, 2781–2792.
- Hurley, M.A., Currie, J.E., Gough, J., Butterwick, C., 1996. A framework for the analysis of Harmonised Monitoring Scheme data for England and Wales. *Environmetrics* 7, 379–390.
- Jarvie, H.P., Neal, C., Leach, D.V., Ryland, G.P., House WA, Robson, A.J., 1997. Major ion concentrations and the inorganic carbon chemistry of the Humber rivers. *Sci. Total Environ.* 194, 285–302.
- Jarvie, H.P., Neal, C., Withers, P.J.A., Wescott, C., Acornley, R.A., 2005. Nutrient hydrochemistry for a groundwater-dominated catchment: the Hampshire Avon, UK. *Sci. Total Environ.* 344, 143–158.
- Jones, J.L., Young, J.O., Eaton, J.W., Moss, B., 2002. The influence of nutrient loading, dissolved inorganic carbon and higher trophic levels on the interaction between submerged plants and periphyton. *J. Ecol.* 90, 12–24.
- Keeley, J.E., Sandquist, D.R., 1992. Carbon - freshwater plants. *Plant Cell Environ.* 15, 1021–1035.
- Littlewood, I.G., Watts, C.D., Custance, J.M., 1998. Systematic application of United Kingdom river flow and quality databases for estimating annual river mass loads (1975–1994). *Sci. Total Environ.* 210, 21–40.
- Maberly, S.C., 1996. Diel, episodic and seasonal changes in pH and concentrations of inorganic carbon in a productive lake. *Freshw. Biol.* 35, 579–598.
- Maberly, S.C., Madsen, T.V., 2002. Use of bicarbonate ions as a source of carbon in photosynthesis by *Callitriche hermaphrodita*. *Aquat. Bot.* 73, 1–7.
- Maberly, S.C., Spence, D.H.N., 1983. Photosynthetic inorganic carbon use by freshwater plants. *J. Ecol.* 71, 705–724.
- Maberly, S.C., Berthelot, S.A., Stott, A.W., Gontero, B., 2015. Adaptation by macrophytes to inorganic carbon down a river with naturally variable concentrations of CO₂. *J. Plant Physiol.* 172, 120–127.
- Meybeck, M., 1993. Riverine transport of atmospheric carbon - sources, global typology and budget. *Water Air Soil Pollut.* 70, 443–463.
- Monteith, D.T., Stoddard, J.L., Evans, C.D., de Wit, H.A., Forsius, M., Hogasen, T., et al., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450, 537–U9.
- Neal, C., 1988a. Bicarbonate estimation from alkalinity determinations for neutral to acidic low-alkalinity natural waters - theoretical considerations. *Hydrological Sciences Journal-Journal Des Sciences Hydrologiques* 33, 619–623.
- Neal, C., 1988b. pCO₂ variations in streamwaters draining an acidic and acid-sensitive spruce forested catchment in mid-wales. *Sci. Total Environ.* 76, 279–283.
- Neal, C., 2001. Alkalinity measurements within natural waters: towards a standardised approach. *Sci. Total Environ.* 265, 99–113.
- Neal, C., Harrow, M., Williams, R.J., 1998a. Dissolved carbon dioxide and oxygen in the River Thames: spring-summer 1997. *Sci. Total Environ.* 210, 205–217.
- Neal, C., House WA, Down, K., 1998b. An assessment of excess carbon dioxide partial pressures in natural waters based on pH and alkalinity measurements. *Sci. Total Environ.* 210, 173–185.

- Neal, C., House WA, Jarvie, H.P., Eatherall, A., 1998c. The significance of dissolved carbon dioxide in major lowland rivers entering the North Sea. *Sci. Total Environ.* 210, 187–203.
- Neal, C., Watts, C., Williams, R.J., Neal, M., Hill, L., Wickham, H., 2002. Diurnal and longer term patterns in carbon dioxide and calcite saturation for the River Kennet, south-eastern England. *Sci. Total Environ.* 282, 205–231.
- Palmer, S.M., Hope, D., Billett, M.F., Dawson, J.J.C., Bryant, C.L., 2001. Sources of organic and inorganic carbon in a headwater stream: evidence from carbon isotope studies. *Biogeochemistry* 52, 321–338.
- Räike, A., Kortelainen, P., Mattsson, T., Thomas, D.N., 2015. Long-term trends (1975–2014) in the concentrations and export of carbon from Finnish rivers to the Baltic Sea: organic and inorganic components compared. *Aquat. Sci.* 1–19.
- Reynolds, B., Neal, C., 1987. A comment on the use of acidimetric titrations for the estimation of the alkalinity and bicarbonate content of acid upland surface waters. *Sci. Total Environ.* 65, 155–161.
- Robson, A.J., Neal, C., 1997. A summary of regional water quality for Eastern UK rivers. *Sci. Total Environ.* 194, 15–37.
- Sandjensen, K., Pedersen, M.F., Nielsen, S.L., 1992. Photosynthetic use of inorganic carbon among primary and secondary water plants in streams. *Freshw. Biol.* 27, 283–293.
- Stewart, M.E., Lapworth, D.J., 2016. Macronutrient status of UK groundwater: nitrogen, phosphorus and organic carbon. *Sci. Total Environ.* 572, 1543–1560.
- Tipping, E., Marker, A.F.H., Butterwick, C., Collett, G.D., Cranwell, P.A., Ingram, J.K.G., et al., 1997. Organic carbon in the Humber rivers. *Sci. Total Environ.* 194, 345–355.
- Tipping, E., Boyle, J.F., Schillereff, D.N., Spears, B.M., Phillips, G., 2016. Macronutrient processing by temperate lakes: a dynamic model for long-term, large-scale application. *Sci. Total Environ.* 572, 1573–1585.
- Wang, Z.A., Bienvenu, D.J., Mann, P.J., Hoering, K.A., Poulsen, J.R., Spencer, R.G.M., et al., 2013. Inorganic carbon speciation and fluxes in the Congo River. *Geophys. Res. Lett.* 40, 511–516.
- de Wit, H.A., Austnes, K., Høyen, G., Dalsgaard, L., 2015. A carbon balance of Norway: terrestrial and aquatic carbon fluxes. *Biogeochemistry* 123, 147–173.
- Worrall, F., Burt, T.P., 2010. Has the composition of fluvial DOC changed? Spatiotemporal patterns in the DOC-color relationship. *Glob. Biogeochem. Cycles* 24.
- Worrall, F., Davies, H., Bhogal, A., Lilly, A., Evans, M., Turner, K., et al., 2012. The flux of DOC from the UK - predicting the role of soils, land use and net watershed losses. *J. Hydrol.* 448, 149–160.