Dissolved and total organic and inorganic carbon in some British rivers

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Rivers transport both organic and inorganic carbon from their sources to the sea. Results of ~800 organic and inorganic analyses from various British rivers of contrasting size and land use are presented here: (1) the headwater River Tern, a rural river of 852 km^2 catchment; (2) the Ouseburn, a small urban 55 km^2 catchment; (3) the River Tyne, a larger river system of ~3000 km^2 catchment; (4) a spatial survey from 205 sample sites on ~60 rivers from SW England. We found that, with the exception of peat-rich headwaters, DIC concentration is always greater than DOC. DIC is primarily in the form HCO_3^-, with DIC concentrations highest in highly urbanised catchments, typically greater than those observed in catchments with carbonate bedrock, demonstrating a significant and previously unrecognised anthropogenic inorganic carbon input to urban rivers.

Key words: *organic carbon, inorganic carbon, rivers, land use, British Isles*

Introduction

The transfer of carbon, total and dissolved, organic and inorganic, from the land to the oceans via river systems is a key link in the global carbon cycle (Likens *et al.* 1981; Meybeck 1987; Ludwig *et al.* 1996; Amiotte-Suchet *et al.* 2003; Brunet *et al.* 2005; Richey 2005). It has been estimated that globally rivers transport on average 0.8 to 1.2 × 10^{15} g of carbon annually (Ludwig *et al.* 1996). Dissolved and total organic carbon (DOC, TOC) is produced through the mobilisation of natural and anthropogenic organic matter, derived from the solution of allochthonous, soil-derived organic matter; from autochthonous, within-stream generation of organic material; or from anthropogenic sources such as effluents and industrial discharges. Total and dissolved inorganic carbon (TIC, DIC) is produced by weathering of carbonate and silicate rocks, although may also be present as CO_2 generated by the decomposition of dissolved organic matter (Das *et al.* 2005). These processes generate the alkalinity of the river water, and also influence the pH of water, which governs the subsequent partitioning of DIC between dissolved CO_2, bicarbonate and carbonate ions. The fraction of DIC present as dissolved CO_2 is almost always at concentrations much greater than the atmosphere (Kempe 1982; Cole and Caraco 2001), which demonstrates that rivers are a source of CO_2 to the atmosphere. The only way that dissolved CO_2 can exist at supersaturated conditions in rivers is if allochthonous sources dominant, and/or the waters are net heterotrophic, fueled by carbon from land (Cole and Caraco 2001).

Carbon fluxes in river systems are a function of hydrology and river flow, land use and geology, and climate, and fluxes of both organic and inorganic forms have been the increasing focus of recent research. Many studies have focused on either the *spatial* or *seasonal patterns* in carbon flux in large, global rivers (e.g. the Congo: Negrel *et al.* 1993; Probst *et al.* 1994; the Amazon: Gaillardet *et al.* 1997; Mortatti and Probst 2003; the Rhone: Aucour *et al.* 1999). Until recently, fewer studies have investigated *long-term trends* in riverine carbon flux. Dissolved organic carbon has been demonstrated to be increasing over recent decades in many mid-latitude river systems, with many studies focusing on UK rivers

(Freeman *et al.* 2001; Worrall *et al.* 2004). The reasons for this are as yet unclear, but include a range of processes including climate change, changes in acidification, drought and land-use change. Direct loading from urban and industrial sources is less commonly addressed, but might also have an impact on riverine organic carbon (Ver *et al.* 1999; Abril *et al.* 2002). Long time series of inorganic carbon fluxes are less frequently measured, as many studies rely on calculated DIC from pH and alkalinity measurements (for example, Neal 2001; Worrall *et al.* 2005). DIC, measured via alkalinity, has recently been shown to be increasing in the Mississippi (Raymond and Cole 2003), probably due to land use change and the effect of intensive agricultural practices bringing carbonate bedrock to the soil zone. However, other rivers show a decreasing trend (Jones *et al.* 2003) in CO_2 saturation across the USA, attributed to large-scale declines in terrestrial CO_2 production and import to rivers.

Previous research demonstrates that there is a genuine need for baseline datasets of both organic, and in particular inorganic, carbon, in landscapes of changing land use. Here we present the results of organic and inorganic carbon analyses produced in our laboratory over the last 5 years, generated predominantly as a by-product of our investigations into dissolved organic matter fluorescence in British rivers (Baker 2002; Baker and Spencer 2004; Cumberland and Baker 2007). These data include a range of land uses from highly urbanised to rural, and provide in particular context to recent evidence of increasing DOC in many British rivers, and unique DIC data for some British rivers. In particular, we aim to investigate the relative importance, in terms of concentration, of inorganic vs organic carbon, as well as investigate the extent to which inorganic carbon concentrations relate to catchment land cover or geology.

Sites and methods

Site 1: River Tern at Norton in Hales
Norton in Hales (UK National Grid Reference SJ 706 384), N Shropshire, UK, is situated along the River Tern, a tributary of the River Severn, 16 km from its source. The River Tern is a lowland catchment, primarily groundwater-fed from red sandstone overlying the Permo-Triassic Sherwood sandstone. Its catchment boundary thus is not defined by its topography (described by Clay *et al.* 2004). This amounts to a very stable base flow in

the River Tern, showing minimal response to normal rainfall events. Soil cover comprises peaty histosols and sandy loams developed on fluvial and glacial sands and gravels. Local land use is generally under semi-intense mixed cereal/dairy/beef farming; land cover at Ternhill (~10 km downstream, upstream catchment area 92.6 km²) comprises 52.9 per cent grassland, 29.9 per cent arable and horticulture, 11.7 per cent woodland and 5.2 per cent built-up (2000 UK Land Cover Map). Figure 1 illustrates the diversity of the sample sites within a small area. In-stream water samples were collected (river sites A, C, E and H) as a transect down the river starting above the wetland (A) and finishing below the sewage treatment outflow pipes (H). Between these points samples were also taken from the sewage treatment works outlet itself (STW (G)), a groundwater-fed pond overflow (POND (B)), a wetland discharge site (D) (not always connected to the main river) and a groundwater spring diverted through a small concrete conduit (F). Additionally, samples were taken from the wetland surface water (I). Environment Agency samples from the river classify its chemical water quality over the period 2002–2004 as being 'Fairly Good', with 'Very Good' levels of ammonia and dissolved oxygen but only 'Fairly Good' biochemical oxygen demand.

Water samples were collected fortnightly from Norton-in-Hales from March 2005 to February 2006 in 500 ml pre-acid washed (10% HCl, distilled water rinsed) plastic bottles. Bottles were also pre-rinsed with sample before filling. On return to the lab (same day) the samples were then filtered through pre-rinsed Whatman GF/C filter papers under vacuum to obtain dissolved and colloidal fractions, and a split of both filtered and unfiltered sample kept in the fridge in 50 ml pre-acid washed (10% HCl, distilled water rinsed) plastic bottles. Both were then analysed for DOC/DIC and TOC/TIC within (usually) 48 hours.

Site 2: Ouseburn, Newcastle-upon-Tyne
The Ouseburn, NE England, is 55 km² in area. Figure 1 shows the catchment together with water sampling locations for water samples which were collected in 2001. Sample locations and numbering follow that of Turnball and Bevan (1994) and incorporate the UK Environment Agency chemical water quality sample sites on the river. The lower catchment (downstream of site 3) is urbanised as it flows through the city of Newcastle-upon-Tyne; land cover in 2000 comprised 16.3 per cent grassland,

Figure 1 Locations of study sites used in this paper

33 per cent arable and horticulture, 5.7 per cent woodland and 42.1 per cent built-up. The upper catchment (upstream of site 3) is dominated by farmland (67% arable and horticulture) and the city international airport (runoff draining into sites 6 and 8), with only 11.5 per cent built-up. The underlying geology is Carboniferous coal measures. The catchment has a long history of research; integrated water-quality monitoring on the river found it adversely affected by combined sewer overflows, cross connected sewers and airport de-icer (Turnball and Bevan 1994). Environment Agency data classify the chemical water-quality of the river as Fair to Fairly Good over the period of sample collection.

Water samples were collected in 50 ml polypropylene bottles which had been pre-cleaned in 10 per cent HCl and then rinsed with distilled water. The samples were filtered (Whatman GF/C glass microfibre filter papers) upon return from the field to obtain colloidal and dissolved fractions, and refrigerated until analysis, which occurred within 48 hours.

Site 3: The River Tyne, N England

The River Tyne has a catchment area of 2935 km^2 and comprises two main tributaries, the North and South Tyne that meet near Hexham (Figure 1). The North Tyne rises in the Cheviot Hills near the Scottish Border, the South Tyne in the Cumbrian Pennines. The two rivers join to form the River Tyne, which flows in an easterly direction to Wylam, where it becomes tidal for the last ~33 km of its course. Another major tributary of the Tyne is the River Derwent, which enters the Tyne in its tidal section, as do the lesser tributaries of the Team, Don and Ouseburn. The Tyne catchment generally consists of rolling hills, rising to 500 m in the north and 800 m in the south, with the Tyne valley reaching a downstream width of several kilometres. The geology of the catchment is largely Carboniferous limestones. Rainfall in the catchment varies from <700 mm in the eastern lowlands to 1500 mm in the uplands, with precipitation falling as snow in the uplands in winter. Soils in the catchment are dominated by large areas of peat in the uplands, which provide a substantial store of organic carbon and a source of coloured water, and by stagnogleys in the majority of the remaining areas. In general the soils are slow draining, and are underlain by shallow or low permeability aquifers, leading to the hydrology of many sub-catchments being dominated by surface runoff with rapid response to rainfall as a result of saturation excess. However, both the North

Tyne and Derwent contain reservoirs, and downstream flow is highly regulated. The largest reservoir is that at Kielder, which impounds water from 240 km^2 of the North Tyne. Upstream of site 33, the catchment is predominantly rural (53.8% grassland; 20.9% woodland; 17.9% upland heath and bog; 1% built-up). Below site 33, and along the River Derwent, an urban population of approximately 750 000 influences the water quality of the river, with 214 consented discharges from sewage treatment works, 126 consented industrial discharges and 492 storm sewage discharges. River lengths of poor water quality are predominantly in lowland urbanised parts of the catchment (including the lower reaches of the River Derwent), with many sewage inputs and without substantial upland clean water supplies to dilute them (Baker and Inverarity 2004).

River samples were taken from 55 sites along the Tyne, Derwent, Don and Ouseburn rivers every two months between May 2002 and May 2003. The sites are main river locations, frequently downstream samples of major sub-catchments and mid-catchment samples at points of changing land use or anthropogenic impact. Figure 1 shows the location of the sample sites, which are grouped into the North Tyne (sites 4–23), South Tyne (sites 52–63), River Tyne (sites 24–33), River Derwent (sites 40–51) and urban (Rivers Don, Team and Ouseburn; sites 1–3; 34–39). Measurements of river water at the sample sites were taken under a range of flow regimes (measured at site 33: 58 ± 89 m^3 s^{-1}) from summer base flow (August 2002) through to winter storm flow (November 2002) and during winter low flows during extensive snow cover (January 2003). Water samples were collected in 50 ml polypropylene bottles which had been pre-cleaned in 10 per cent HCl and distilled water. Samples were filtered upon return from the field (Whatman GF/C microfibre filter papers) to obtain dissolved and colloidal fractions, refrigerated, and analysed within 48 hours.

Site 4: SW England

Two hundred and five samples from SW England were analysed over a 12 month period in 2005–2006, with 20–30 samples taken every 1 or 2 months as split samples from water samples collected by the Environment Agency as part of their routine chemical water-quality analyses. Samples were collected by field officers between Friday and Monday and shipped to the Environment Agency laboratory, where they were kept cool. A 50 ml split sample was taken on the following day, and couriered cool

and in the dark to the University, where samples were analysed unfiltered (typically 3 days after sampling). Split samples were randomly selected from the ~200 freshwater samples that are analysed daily at the Environment Agency laboratories; over the annual sampling period very few samples were replicated, producing a random spatial dataset as shown in Figure 1. Within the data presented, the 205 TOC/TIC values are from 196 sites. Nine sites have replicate data.

SW England is predominantly rural in character: 48.3 per cent of land cover is grassland, 28.1 per cent arable and horticulture, 12.4 per cent woodland and 6.8 per cent built-up in the South West Environment Agency Region according to the 2000 Land Cover Map.

TIC/TOC analysis
Analyses up to and including 2003 were determined using a Shimadzu 5000 TOC analyser. Analyses subsequent to 2004 were measured by means of a Shimadzu TOC-Vcpn analyser. In both cases identical methodology was used. DOC and DIC were obtained from the filtered samples, and TOC and TIC from the unfiltered samples, although tubing width within the TIC analyser effectively defines the TOC and TIC fraction to be <2 mm. In all instances, total carbon was determined by high temperature combustion incorporating a platinised alumina catalyst. Inorganic carbon was determined by phosphoric acid digestion. Organic carbon was determined by the difference. The mean of three to five injections of 100 µl was used to determine total and inorganic carbon for every sample and precision, described as a coefficient of variance (CV), was <2 per cent for the replicate injections. Sample replicates, when analysed, agree within ±1 mg l^{-1}. The instruments were calibrated using total and inorganic carbon standards. Glass vials used for analysis were washed in 4 per cent Decon 90© and 10 per cent HCl and pre-rinsed with ultrapure water and sample.

Detailed analysis of the accuracy of TOC analyses with this instrument can be found in Aiken *et al.* (2002). Of particular relevance to this study is the storage conditions of our water samples between sampling and analysis, as supersaturated waters are likely to continuously degas as long as there is a headspace with lower p^{CO_2} above the water sample. As we report later, the high DIC concentrations in many of our samples are indicative of supersaturated river waters. Water samples were collected in 50 ml containers as detailed above and with no headspace, but up to ~10 ml of both filtered and unfiltered samples were initially removed for spectrophotometric
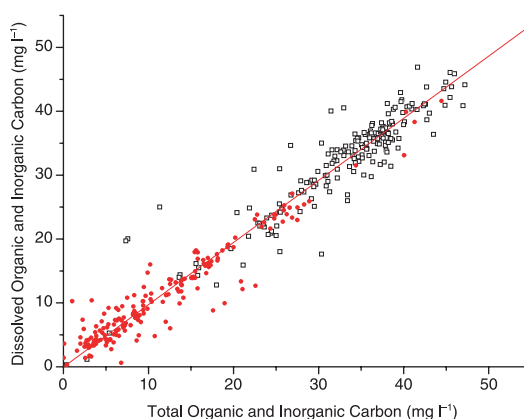

Figure 2   Comparison of dissolved and total organic and inorganic carbon. Circles: organic carbon. Squares: inorganic carbon. Data from sites A–I on the River Tern. r = 0.93, gradient = 0.97 (n = 192)

analyses and the samples were refrigerated with this headspace for up to 48 hours before TOC and TIC analysis. Some degassing may have occurred during this time period, as well as during TOC analysis from unsealed vials; however, evidence to suggest that degassing may not be a significant issue is the lack of difference between filtered and unfiltered samples after vacuum filtration (Figure 2). Figure 2 shows a strong correlation between dissolved and total carbon analyses (r = 0.93, n = 192) for a range of samples that include ground waters, surface waters, river water and a final treated effluent. The gradient (0.97) is close to unity, demonstrating that most of the carbon is in colloidal or dissolved (less than 1.2 micron) form, matching results presented elsewhere (Dawson *et al.* 2002; Aucour *et al.* 1999), and that degassing losses due to vacuum filtration are minimal. In the rest of this paper, we present both total and dissolved carbon analyses, but will presume that the dissolved fraction dominates. Additionally, given the potential for DIC loss between sampling and analysis, all measured values should be considered minimum values, with the in situ DIC being higher.

Electrical conductivity and pH of the water samples were also measured either in the field (sites 1 and 4), or immediately on return to the laboratory (sites 2 and 3).

Results

Both dissolved and total organic and inorganic carbon data, as well as pH and electrical conductivity

Table 1   Summary organic and inorganic carbon data. Data from the River Tern has been published in part in Cumberland and Baker (2007), that from the Ouseburn in part in Baker (2002), and from the Tyne in Baker and Inverarity (2004)

| Catchment/region and year	Sample ID/ subcatchment	pH mean	pH sd	EC µS cm⁻¹ mean	EC µS cm⁻¹ sd	OC (mg l⁻¹) mean	OC (mg l⁻¹) sd	IC (mg l⁻¹) mean	IC (mg l⁻¹) sd	%TC as IC mean	Number of samples	Dissolved or total?
River Tern 2005–2006	a	7.65	0.04	nd		10.8	7.8	32.4	7.3	75.0	23	D
	b	7.87	0.19	nd		8.6	4.3	33.5	4.7	79.6	21	D
	c	7.59	0.21	nd		11.2	8.9	32.0	7.4	74.0	23	D
	d	7.30	0.26	nd		9.3	5.5	38.9	4.8	80.7	22	D
	e	7.63	0.23	nd		10.3	7.5	32.8	6.1	76.1	22	D
	f	7.19	0.33	nd		6.3	6.1	35.8	6.3	85.1	23	D
	g	7.31	0.21	nd		13.0	4.6	26.3	5.1	66.9	23	D
	h	7.47	0.35	nd		10.7	8.8	33.0	6.7	75.5	22	D
	i	6.94	0.56	nd		21.9	6.5	20.9	11.6	48.9	17	D
Ouseburn 2001	3	7.87	0.46	956	301	5.7	1.3	46.5	6.1	89.1	11	D
	4	7.69	0.50	1169	709	8.3	4.9	40.0	9.3	82.8	10	D
	6	7.82	0.49	1534	896	9.7	3.3	49.0	8.1	83.5	11	D
	8	7.73	0.61	1035	395	81.2	179.0	63.8	81.8	44.0	9	D
	10	7.93	0.67	1133	774	11.9	14.2	47.6	5.8	80.0	9	D
	11	7.79	0.56	1009	672	8.2	3.0	44.2	13.0	84.4	9	D
	13	7.9	0.36	1094	761	8.7	4.5	47.0	6.3	84.4	11	D
	16	7.81	0.40	1095	764	8.3	4.4	45.3	6.3	84.5	10	D
	17	7.79	0.37	611	76	4.2	1.6	31.1	11.7	88.1	12	D
	21	8.06	0.28	900	139	9.3	2.2	52.3	7.8	84.9	9	D
	22	7.93	0.37	991	493	5.7	1.6	43.1	8.3	88.3	11	D
	23	7.97	0.31	924	260	8.1	3.2	52.4	20.2	86.6	11	D
Tyne 2002–2003	Don, Team & Ouseburn	7.58	0.32	1040	625	5.7	6.3	46.4	18.5	89.1	30	D
	Downstream Tyne	7.76	0.34	364	266	8.4	5.8	21.5	11.2	71.9	99	D
	N Tyne	7.97	0.28	218	138	9.8	6.4	14.5	5.6	59.7	45	D
	S Tyne	7.87	0.27	250	101	5.3	4.5	20.4	7.0	79.4	56	D
	Derwent	7.95	0.30	306	146	4.2	2.6	15.9	10.4	79.1	59	D
SW England 2005–2006		7.73	0.55	nd	nd	4.2	3.6	32.6	24.3	88.6	205	T
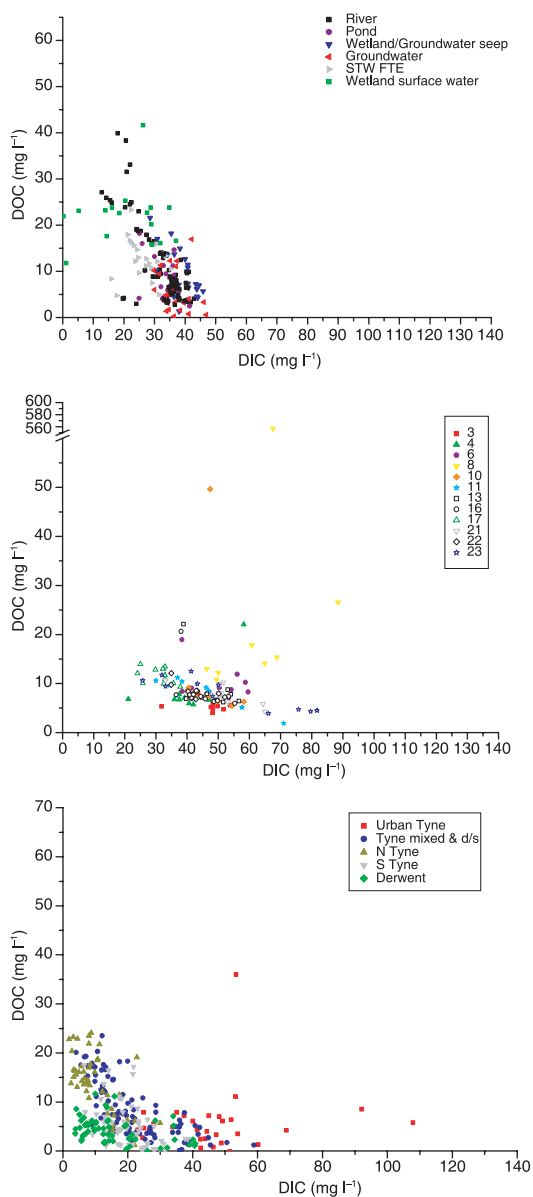
Figure 3 **DOC vs DIC for (a) the River Tern, (b) the Ouseburn and (c) the Tyne catchment**

data, are presented Table 1, and dissolved organic carbon plotted against dissolved inorganic carbon in Figure 3. For all sites, mean pH is in the range 6.9–8.1, indicating that dissolved inorganic carbon will primarily be in the form HCO_3^-. For the rural River Tern (Figure 3a), sample sites have a wide range of organic and inorganic carbon concentrations. Taken as a whole, there is a negative relationship between DIC and DOC ($r = -0.72$), reflecting sites dominated by either groundwater (with higher DIC) or soil water (with higher DOC). The sample site with the highest DIC and lowest DOC is the groundwater spring (DIC = 36.7 ± 4.6 mg l^{-1}; DOC = 5.8 ± 4.7 mg l^{-1}), and the site with the highest DOC and lowest DIC is the riparian wetland surface water (summer mean DIC = 8.9 ± 7.7 mg l^{-1}, summer mean DOC = 20.0 ± 4.5 mg l^{-1}). The latter site exhibits seasonality in DIC, with higher values in winter after flooding by river water. River samples fall between these end members, with wetland-derived, DOC-rich waters at times of winter and autumn high flow (DOC > 30 mg l^{-1}, DOC>DIC), and DOC-poor, groundwater-dominated summer low flows (DOC < 10 mg l^{-1}, DIC > DOC). Discharge data, available from the river site A, confirms this relationship with river flow. A strong positive correlation exists between the logarithm of river flow and DOC ($r = 0.89$), a negative correlation between log Q and DIC ($r = -0.63$) and a weak positive correlation between log Q and total C ($r = 0.40$, significant at a 90% confidence level).

DIC and DOC data for the urban Ouseburn (Figure 3b) exhibit greater scatter than the River Tern, with some samples with elevated DOC (between 20 and 600 mg l^{-1}), almost all relating to one point-source pollution event with a release of deicer into the river from the airport situated within the catchment of tributary 8 (Baker *et al.* 2003). It is also notable that no sites have a DIC < 20 mg l^{-1}. Site 17, a relatively rural sub-catchment with some forest and agricultural land cover, has relatively high DOC and low DIC (DOC = 11.7 ± 1.6 mg l^{-1}; DIC = 31.2 ± 4.2 mg l^{-1}). The highest DIC site is best expressed by summer data from site 23 (DOC = 4.4 ± 0.4 mg l^{-1}; DIC = 75.8 ± 6.9 mg l^{-1}); this tributary is predominantly culverted and in summer base-flow conditions is predominantly fed by groundwater. Several tributaries exhibit a strong negative correlation between DOC and DIC. This is clearest for site 11 (correlation between DIC and DOC, $r = -0.91$), site 23 ($r = -0.89$) and site 21 ($r = -0.81$). Site 11 is a rural tributary with agricultural land use and seasonal (winter) groundwater inputs, site 23 is a partly culverted tributary within Newcastle city but one that predominantly drains the Town Moor, a large expanse of grazed grassland, and site 21 is also a partly culverted urban fringe tributary with mixed land uses. For some sites, however, this inverse relationship between DIC and DOC does not occur and,

for two tributaries, sites 4 and 8, it is replaced by a positive (but statistically weak) correlation between DIC and DOC (r = 0.67 and 0.60, respectively). The cause for this is unclear, but both sub-catchments have substantial transport land cover, with site 8 dominated by an international airport and site 4 to a lesser extent by a major highway (the A69). Discharge data are available for site 22, the most downstream sample site that integrates the whole catchment. For this site, the correlation between DOC and DIC is r = −0.74, with highest DIC in winter and spring and highest DOC in summer. For the Ouseburn catchment, there are no statistically significant correlations between DIC, DOC or total dissolved C and the logarithm of discharge (−0.17, 0.34 and −0.09). This reflects the complexity of processes affecting carbon fluxes in this urbanised catchment, namely sources from soil, ground-water and anthropogenic diffuse and point sources.

DIC and DOC data are presented for the River Tyne in Figure 3c. The sample sites are grouped according to their sub-catchment, and it is apparent that different sub-catchments have different concentrations of DIC and DOC. Sites on the North Tyne are characterised by higher DOC than DIC (DOC = 14.5 ± 5.6 mg l^{-1}; DIC = 9.8 ± 6.4 mg l^{-1}), indicative of the catchment soil cover which is dominated by upland peat that reaches accumulations of ~10 m thickness in places. In contrast, the South Tyne and Allen catchments generally have a higher DIC than DOC (DIC = 20.4 ± 7.0 mg l^{-1}; DOC = 5.3 ± 4.5 mg l^{-1}). Again, this generally reflects that catchment soil cover, which has a greater proportion of brown earth and rendzina soils overlying limestone bedrock. Samples from the downstream River Tyne fall between these tributary characteristics. Samples from the River Derwent have lower DOC than the Tyne (DOC = 4.2 ± 2.6 mg l^{-1}). However, samples from the urbanised sub-catchments, the Ouseburn, River Team and River Don, stand out from all other Tyne sample sites, with significantly higher mean DIC concentrations (46.4 ± 18.5 mg l^{-1}). Geologically, these sites are similar to downstream River Tyne and Derwent sample sites, suggesting that the elevated DIC concentrations are due to the urban land cover that distinguishes these sub-catchments. The relatively high DIC concentration end member is also in agreement with the results of the detailed Ouseburn study (see previous section), where DIC > 20 mg l^{-1}.

Figure 4 maps the TIC and TOC data for SW England, and results are summarised in Table 1. TOC ranges from 0 to 23 mg l^{-1}, with an average of 4.2 ± 3.6 mg l^{-1}. TIC range from 0.2 to 126 mg l^{-1},
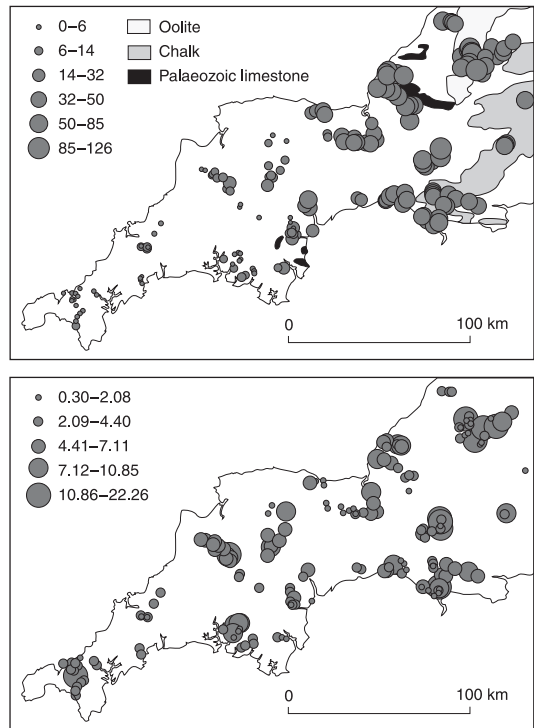

Figure 4   (top) TIC concentrations (mg l^{-1}) in SW England river samples and (base) TOC concentrations (mg l^{-1})

with an average of 32.6.0 ± 24.3 mg l^{-1}; data fall into to two clusters with concentrations 0–20 and 35–55 mg l^{-1} respectively, as well as two outlying data points >100 mg l^{-1} from tufa-precipitating headwaters. Figure 4 shows that the two main TIC concentration clusters relate closely to geology and the presence of carbonate bedrock (Cretaceous chalk, Jurassic oolites and Carboniferous limestone). Rivers with high TOC concentration, in contrast, occur in regions of upland peat cover. Our TIC concentration data from ~60 rivers in SW England, and from a wide range of geologies but urban land cover in the range 3.4–7.9 per cent, show that even in the carbonate-dominated catchments, TIC is lower than that observed in the urbanised Tyne sub-catchments, confirming the significance of our observations of elevated DIC in urban catchments.

Discussion

Analyses of inorganic and organic carbon have shown that inorganic carbon concentrations are greater

than organic carbon for the majority of our samples sites, excepting headwater streams with thick soil cover. Our DIC values are in agreement with those reported for the Humber rivers (Jarvie *et al.* 1997). In most previous studies, riverine DIC has been attributed to geological (e.g. HCO_3^- from dissolved carbonate material) or biological (e.g. CO_2 from biological respiration) sources in non-urbanised catchments (for example, Dawson *et al.* 2001 2004; Kawasaki *et al.* 2005). Here, we observe elevated river DIC concentrations in urbanised catchments, an observation not previously well studied. Our sampling campaigns took place throughout the hydrological year and at a wide range of discharge, including both base flow and storm flow conditions, suggesting that the elevated DIC–urban land cover relationship persists cross a wide range of discharge rates. Within urban areas, it suggests that the elevated DIC cannot be related simply to a single source, with either one of a low flow source, e.g. groundwater or storm sewer cross-connections, or high flow source, e.g. impervious surface runoff, combined sewer overflow, being possible.

We can directly compare DIC concentrations with the percentage urban land cover for 12 sample sites on the River Tyne, where samples sites are close to river flow monitoring sites where catchment land use has been determined using the UK Land Cover Map 2000 as recorded in the National River Flow Archive. Sites are nested within each sub-catchment; two sites within the Derwent (sample sites 48 and 40 in Figure 1), two within the S Tyne (sites 60 and 25), five within the North Tyne (head water sites 10, 14, 16; downstream sites 20 and 23) and two within the Ouseburn (sites 1 and 3); one site on the River Team. Figure 5 shows that, despite catchment-wide variations in geology, the highest DIC values are observed in the urbanised catchments, with good replication between different sampling years for two Ouseburn sample sites, with higher DIC than observed in the carbonate headwaters with <1 per cent urban land cover. Empirically, an urban land cover of greater than ~5 per cent seems to be critical for land cover to affect DIC: a similar percentage urban land cover has been previously demonstrated to be important for other water-quality variables (Baker 2003; Donahue *et al.* 2006) Several processes may provide the source of this high DIC. These include unweathered carbonate bedrock material brought to the surface by urban development. Raymond and Cole (2003) suggest that increased alkalinity in the Mississippi was caused by agricultural soil disturbance;
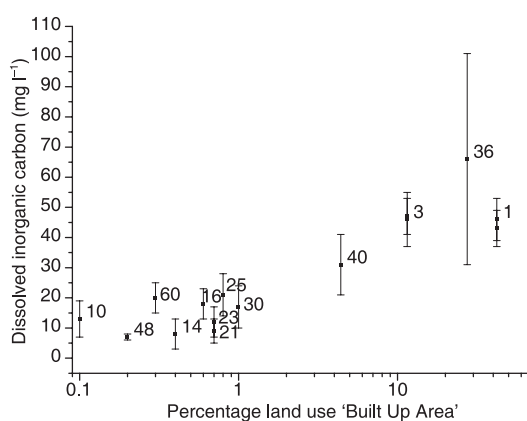

Figure 5   Relationship between land use and DIC in the Tyne catchment. Sample site identifiers refer to Figure 1

urban soil disturbance can also be invoked as a similar mechanism, bringing bedrock material to the surface or soil zone where it is available for weathering. The chemical weathering of inorganic carbon-rich urban structures may also be a source of DIC. For example, the dissolution of concrete such as that used in bridges, culverts, engineered river banks and the drainage infrastructure in urban areas by natural organic acids and chloride in road salts has been widely documented (Lea 1970; Kayyali *et al.* 1986). Lime (CaO) reacts with excess CO_2 in river water to precipitate $CaCO_3$, which may subsequently be redissolved to increase riverine DIC. Alternatively, $CaCO_3$ present within concrete may be directly dissolved by acidic river or waste waters. Finally, diffuse or point pollution may provide DIC-rich inputs (Daniel *et al.* 2002). For example, the highest DIC values are observed on the River Team, which is known to be impacted from diffuse landfill leachate pollution (Baker 2005) and for which raw leachate DIC values can reach in excess of 300 mg l^{-1}. Further research to source DIC inputs in urban catchments is needed, potentially utilising carbon isotopes (Palmer *et al.* 2001) as a sourcing tool.

Conclusions

In the rural River Tern, riverine DOC and DIC are shown to relate to the relative importance of DIC-rich ground waters and DOC-rich riparian wetlands for all sample sites. In the urbanised Ouseburn catchment, some tributaries follow a pollutant trend of simultaneous increases in both DOC and DIC. The Ouseburn is part of the larger Tyne catchment:

this larger catchment follows the contrasting sources of groundwater-dominated high-DIC water vs soil water high-DOC water, with the exception of the urban catchments which exhibit an elevated DIC compared to rural sites. Urbanisation is demonstrated to increase DIC compared to equivalent rural catchments; this DIC has potential sources including diffuse source inputs from the dissolution of concrete, point sources such as trade effluents and landfill leachates, and bedrock-derived carbonates relocated to the soil dissolution zone by urban development. DIC in rural SW England demonstrates that spatial variability in DIC can be attributed to variations in geology, but that DIC concentrations in the SW England rivers dataset are typically lower than the urbanised Tyne catchments despite the presence of carbonate bedrock in many of the sample catchments in the SW England dataset.

Recent investigations into carbon fluxes in British rivers have focused on long-term increases in DOC in rural and predominantly upland catchments (Freeman *et al.* 2001; Worrall *et al.* 2004). Our results suggest that research is needed into understanding long-term variations in inorganic carbon concentration, as well as total (organic and inorganic) carbon fluxes from British rivers, to obtain total carbon loads. In particular, we provide evidence that DIC concentrations may be greater in urbanised catchments compared to equivalent non-urban catchments, with the implication that increasing urbanisation in the future will see increases in riverine DIC and a decrease in the strength of any DOC–DIC anti-correlation. Further studies of urban catchment DIC sources, within-stream processing, long-term trends and potential ecological impacts are required.

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