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DYNAMICS OF WATER MOVEMENT AND TRENDS IN DISSOLVED CARBON IN A HEADWATER WETLAND IN A PERMEABLE CATCHMENT

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Abstract: We examined trends in the movement and source of water in a headwater wetland in North Shropshire, UK. Six piezometer nests along two transects were monitored over an 18 month period, and flownets were derived to estimate the rate and direction of water movement through the wetland and the interaction between precipitation and groundwater discharge. Individual water sources are identified using stable isotopes and seasonal differences in the composition of wetland soil-water are described. Variations in dissolved inorganic and organic carbon (DIC and DOC) were measured in water samples collected from discrete points in the wetland and the adjacent river and were interpreted using the hydrological data. The results suggest that end-members for DOC and DIC can be identified across the range of sampling sites: a groundwater spring (GS) had the lowest DOC and high DIC (DOC = 5.6 ± 4.5 mg/l; DIC = 36.7 ± 4.6 mg/l); a shallow well (WS) had the highest DOC and DIC (DOC = 32.5 ± 18.7 mg/l; DIC = 61.9 ± 18.9 mg/l); while surface-water (WSW) had the lowest DIC (20.6 ± 12.1 mg/l). Water fluxes between the wetland and river are estimated using the Dupuit-Forcheimer approximation to highlight the degree to which some headwater wetlands may act as a carbon source to ecosystems downstream. These wetlands are potentially a significant pool of C but are particularly sensitive to future changes in groundwater levels.

Key Words: DIC, DOC, flux estimates, $\delta^{18}O$, δD

INTRODUCTION

Dissolved organic carbon (DOC) has a fundamental role in the functioning of aquatic ecosystems, providing a source of carbon and contributing to ecosystem metabolism. DOC is largely derived from the breakdown and leaching of organic matter in terrestrial areas of the catchment. These allochthonous sources of DOC are supplemented by autochthonous DOC generated by the aquatic biota. DOC concentrations are highly variable, reflecting the extent of biotic and abiotic processing of terrestrial DOC. Most DOC, such as sugars and amino acids, has a rapid turnover time and is readily metabolized by biota, while humic substances tend to be recalcitrant. As a result, DOC has a complex and variable composition, and in many cases the processes and inter-relationships that govern the production, transport, and fate of DOC are incompletely understood. Significantly, long-term increases in DOC have been observed in northern Europe and North America, which would have implications for the biota, drinking water quality, and catchment carbon balances. Evans et al. (2005a) attributed these increases to declining acid deposition and rising temperatures, although Roulet and Moore (2006) highlighted the difficulties in identifying a single factor that may be responsible given that the observed trends reflect the integrated product of many individual processes upstream.

Generally, the quality and quantity of allochthonous DOC can be broadly related to landscape, vegetation, hydrology, and climate (Gorham et al. 1998, Inamdar and Mitchell 2006). Thus, for example, Sachse et al. (2005) successfully related four DOC fractions (recalcitrant humic substances, polysaccharides, low molecular weight acids, and low weight substances) to specific water types in the lowland catchments of the Spree and Oder rivers in Germany. However, the extent of peat and clay soils appears to be particularly significant. Dillon and Molot (1997) found a strong correlation between DOC export and peatland extent, and studies in the Canadian Shield have suggested that DOC is largely derived from the decomposition of recent peat deposits (Schiff et al. 1997). Billett et al. (2006) examined the connectivity between DOC and the soil carbon pool in a small upland catchment in Scotland and found a strong relationship between the percent peat cover and stream DOC only in the

upper catchment, due to increasing drainage from mineral soils downstream. In this respect, the clay content affects the ability of soils to act as a DOC sink through adsorption, as a result of the high surface area and the reactivity of clay minerals (Aiken and Cotsaris 1995).

Wetlands appear to be important in a number of respects in determining DOC concentrations in stream ecosystems. Generally, wetlands have high DOC concentrations as there is insufficient flow to oxygenate the water (Kaplan and Newbold 2000), and they may act as a source of DOC, particularly at times of lower water tables. However, it is difficult to generalize as pore water velocities will vary considerably with depth: lower velocities are positively related to DOC degradation over time (Bengtsson and Törneman 2004), and there are likely to be seasonal variations that cause DOC concentrations in temperate ecosystems to peak during the growing season. This has been attributed to discharge from stream channel wetlands during dry periods (Hemond 1990). At such times the magnitude of sub-surface water fluxes falls while the retention time of water within wetlands increases, although stream DOC concentrations may also display marked peaks during summer storms as a result of discharge from riparian wetlands. Differences in water flow pathways seasonally and during individual events are also likely to be important. Hinton et al. (1998) noted that relatively few studies had related stream DOC to water flow paths and found that DOC concentrations were significantly higher where groundwater had passed through a wetland, or an upper soil horizon, when flowing to a stream. In effect, two distinct pools of DOC can be identified: first, one associated with recently fixed labile DOC, derived from leaching along shallow water flow paths; and second, discharging groundwater with a low ^{14}C content, and a low concentration of labile groups (Schiff et al. 1997).

Although there appears to be a direct relationship between stream DOC concentration and the extent of wetlands in a catchment, in many cases the wetlands studied were intimately connected with the river (e.g., Kaplan and Newbold 2000). Fitzgerald et al. (2003) suggested that headwater wetlands are characterized by rapid infiltration and short flowpaths, and provide an important source of DOC. However, the contribution of floodplain wetlands and valley-side wetlands or flushes have received relatively little attention. Furthermore, with some exceptions (e.g., Elder et al. 2000), studies of DOC have generally disregarded trends in dissolved inorganic carbon (DIC). DIC is part of the carbonate system and occurs as HCO_3^-, CO_3^{2-}, H_2CO_3, or dissolved CO_2. Hope et al. (1994), in a review of carbon export, cited figures for inorganic carbon flux but mentioned that "there is little published work on the processes governing these fluxes" although mineralization of DOC may be an important source of DIC to streams (Dillon and Molot 1997).

This study addressed both research gaps by looking at the dynamics in DOC concentrations and their relationship to water source by the analysis of the stable isotopes of water and water flow pathway, through the interpretation of piezometric pressures measured along two transects across a small headwater wetland beside the River Tern in Shropshire, UK. This is a permeable catchment overlying Permo-Triassic Sandstones where groundwater provides an important contribution to total flow. Consequently, the relationship between dissolved organic and inorganic carbon should elucidate the effects of differing water flow pathways on carbon fluxes thereby helping to quantify the importance of individual wetlands to the catchment-scale carbon budget. Accordingly, the aims of the study were: 1) to determine seasonal trends in flow pathways and DOC fluxes through a headwater wetland; 2) to investigate the significance of local groundwater discharge on water movement through the wetland; and estimate water fluxes between the wetland and adjacent river; and 3) to identify the importance of valley-side/floodplain wetlands as a source of DOC in permeable catchments.

METHODS

Study Site

Dissolved carbon fluxes were determined over a 24-month period for a small headwater wetland adjacent to the River Tern in North Shropshire near the village of Norton-in-Hales (2°24′W 52°56′N) where the annual precipitation is ~770 mm. The Tern is a south flowing tributary of the River Severn, with a total catchment area of 852 km^2, overlying Permo-Triassic Sherwood Sandstone and Mercia Mudstone in the North. The catchment has a good instrumentation network: a major groundwater river augmentation scheme operates in the lower catchment, and the Tern was selected by the UK Natural Environment Research Council (NERC) as one of three catchments to study integrated catchment management under the Lowland Catchment Research Programme (Wheater and Peach 2004). As part of this programme, a new gauging station was installed on the Tern near

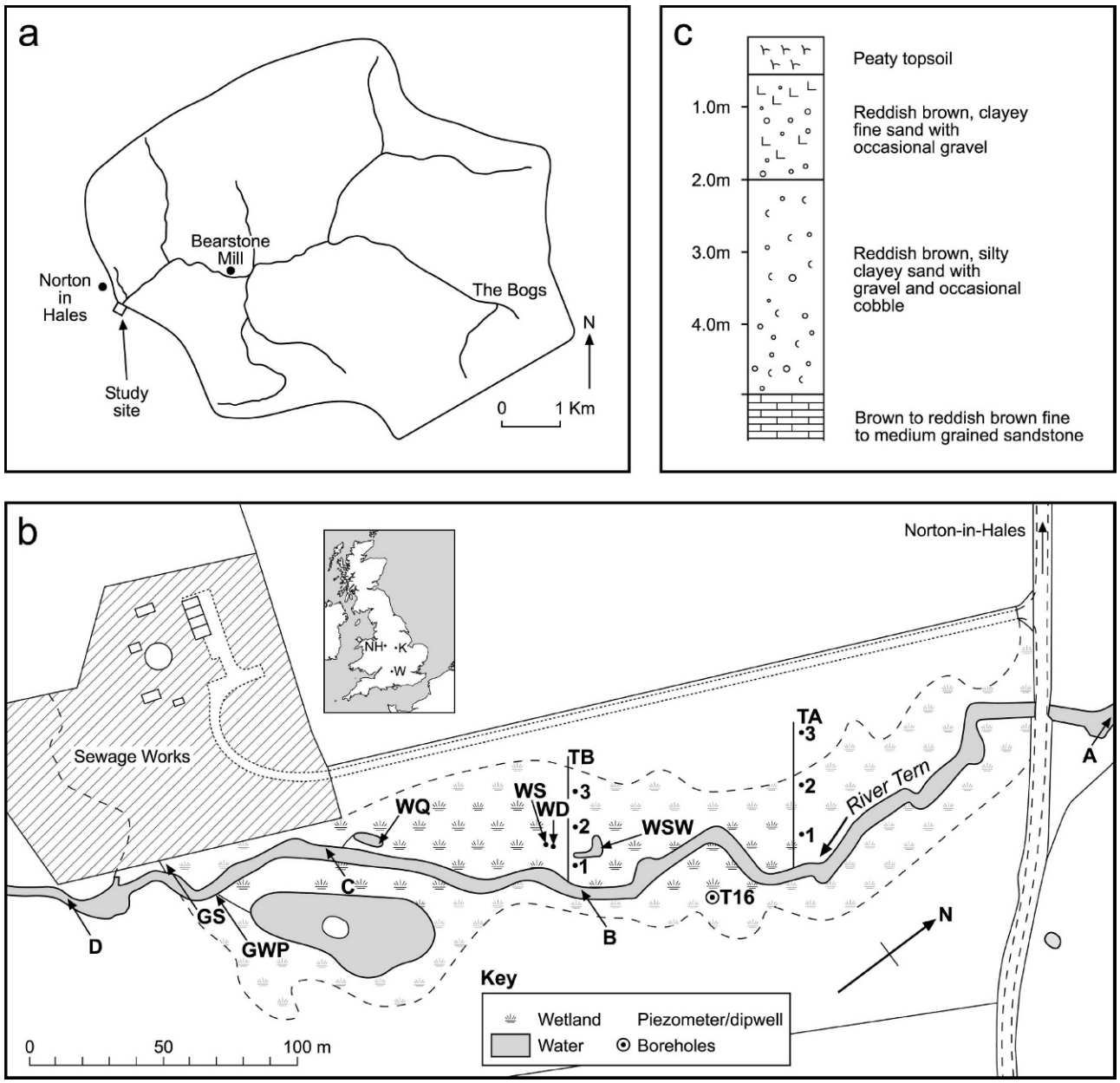

Figure 1. a) Location of the study site in the Tern catchment above Norton-in-Hales; b) distribution of sampling points; and c) local stratigraphy from boreholes at T16 (British Geological Survey Wellmaster code SJ73/64). The inset figure of the UK gives the location of the study-site (NH), Keyworth (K) and Wallingford (W).

Norton-in-Hales in 2002 with a catchment area of ~38 km^2 and surface elevations ranging from 210 to 100 m asl (Figure 1). The land use is mainly improved grassland, and small areas of woodland.

The upper catchment of the River Tern is defined to the North by an arcuate glacial moraine, variously termed the 'Wrexham' or 'Woore' Moraine (Evans et al. 2005b), which accounts for the change in the direction of flow of the River Tern near Bearstone Mill (Figure 1), and with a low sandstone ridge to the East. In the west, the catchment divide is indistinct in places: to the south west, Yates and Moseley (1967) found that a peat deposit, 3.35 m in depth, separated the catchments of the south flowing Tern from the River Duckow. Peat deposits also infill a number of glacial outwash channels incised into the eastern ridge, one of which named 'the Bogs' is the source of the Tern, and discontinuous wetlands extend along the River Tern near Norton-in-Hales. In most cases, where organic deposits are found, they overlie sand and gravel deposits of Flandrian age (Rees and Wilson 1998).

Immediately below the gauging station at Norton-in-Hales, and above a sewage treatment plant,

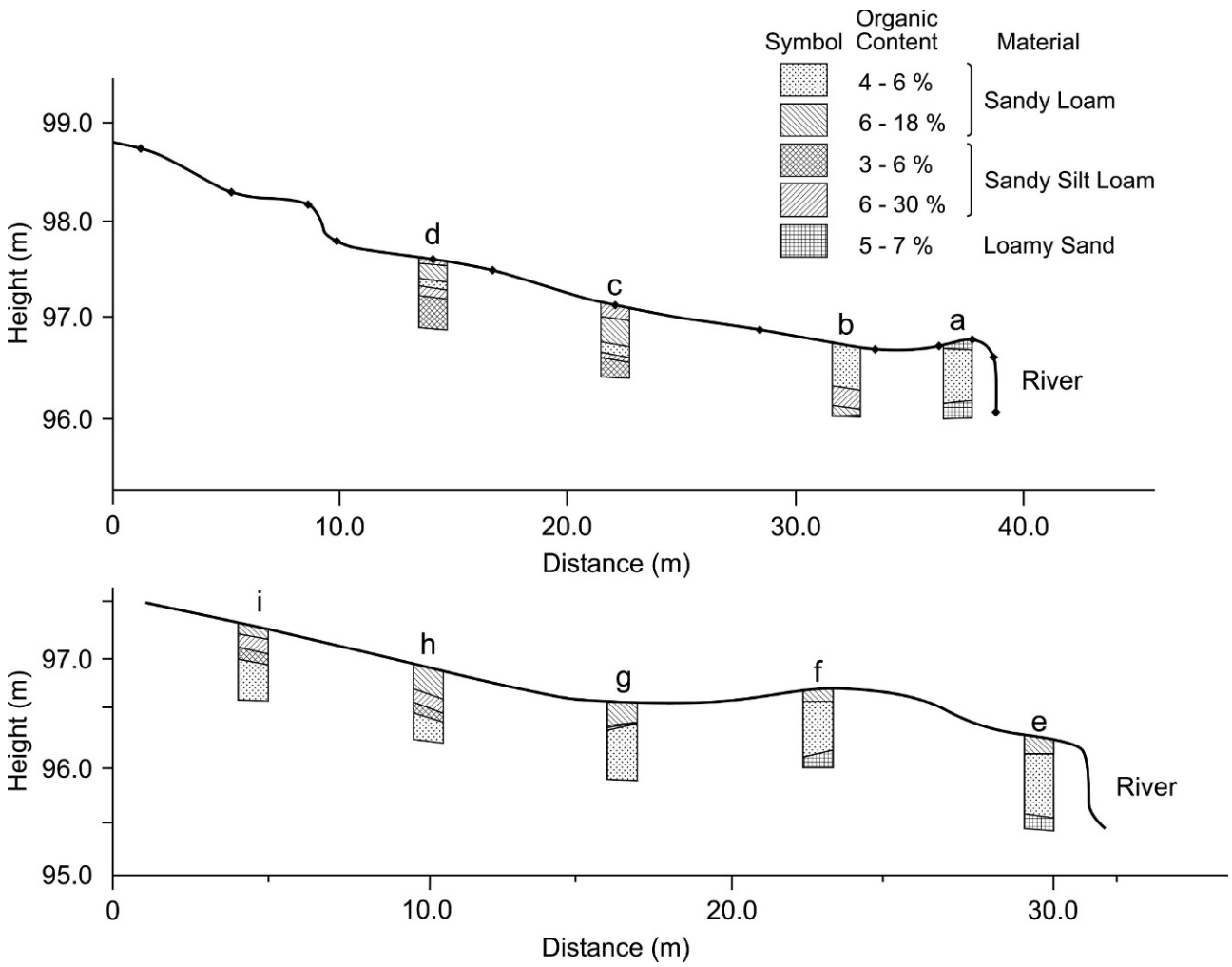

Figure 2. Variation in soil characteristics along the Transects TA and TB, identified in Figure 1 (after Clay et al. 2004).

a linear wetland extends for ~150 m along the west bank of the Tern. The wetland resembles a valley-side seep, occupying a topographic hollow at the base of the valley-side slope at a height that is only infrequently inundated by high river flows. Three boreholes drilled in the floodplain close to the wetland (Figure 1) to depths of 4 m, 10 m, and 20 m suggest that locally the stratigraphy comprises a peaty histosol overlying ~5 m of reddy brown sands and gravel that grade to a fine-grained red sandstone. A preliminary study of the wetland by Clay et al. (2004) confirmed that groundwater was the main water source for much of the year, but suggested that there were distinct spatial differences in both the water source, with precipitation being locally important, and in the extent of water storage between two transects across the wetland. This reflected the local topography and sedimentology. Analysis of nine soil cores extracted from both transects and summarized in Figure 2 indicate that both transects are predominantly sandy loam with an organic content of 4%–6%, although there are occasional sandy-silt lenses where the organic content rises to 30%.

Field Techniques

Our work was developed further by the installation in March 2005 of six piezometer nests; each of two piezometers, along two transects (TA and TB) perpendicular to the river (Figure 1). The piezometers were constructed of 3-cm diameter plastic pipe, slotted over the bottom 10 cm, which were installed to varying depths below the surface (Table 1). The piezometer nests were located: 1) adjacent to the river (1D and 1S); 2) in a topographic hollow (2D and 2S); and 3) above a break-in-slope at the valley-side (3D and 3S). The heights of individual piezometers were determined by Leica Total Station and related to Ordnance Datum (height above sea level) at the upstream river gauging station.

Table 1. Summary characteristics of piezometers in Transects TA and TB.

Piezometer No.	Surface Elevation m. asl.	Depth below Surface (m)
Transect TA		
1D	96.930	0.870
1S		0.384
2D	97.653	0.675
2S		0.379
3D	98.603	1.465
3S		0.616
Transect TB		
1D	96.926	0.994
1S		0.454
2D	96.800	0.759
2S		0.411
3D	97.204	0.793
3S		0.455

The site was visited at ~14-day intervals from March 2005 to April 2006 at which time water level depths in the piezometer network were determined using an electric dipper. The timing of these individual field visits over the period and their relationship to river stage were recorded continuously at the upstream gauging site and are shown in Figure 3. River flows fluctuated in a characteristic manner above a consistent base flow with flow peaks associated with high precipitation (e.g., 31 mm in the 24 hrs before March 31, 32 mm before October 25, and 36 mm before November 9). The majority of sample points coincide with background base-flow or minor flow events throughout the period; however, two points correspond with peak flow events on March 31 and October 25, 2005.

Water samples were collected during each visit from a range of sites within the area, as shown in Figure 1. In-stream water samples were collected at four sites (A, B, C, and D) following a downstream transect from a point immediately above the wetland (A) to below the sewage treatment outflow pipe (D). Between these points water samples were also taken from a groundwater-fed pond (GWP), a wetland discharge site (WQ) (which was only infrequently connected to the main river), and a culverted groundwater spring (GS). Three further samples were taken from the wetland: surface water (WSW); 0–45 cm depth (WS); and 50–100 cm depth (WD). Depth samples were collected from two wells that were installed to depths of 50 cm and 100 cm between piezometer nests 1 and 2 of Transect TB. Both wells were constructed of 15 cm diameter plastic pipes with pre-drilled 5 mm holes to enable water movement into the sampling well over a given depth (the 100 cm deep well was only perforated from 50–100 cm). Pipes were sealed at both ends to reduce oxidation and contamination from other external sources. Water samples were obtained by dipping a sample bottle in the well, after which the wells were emptied completely before resealing. Water in the pipes was thus not allowed to stagnate as the perforations enabled water flow and the water samples should therefore be representative of recent

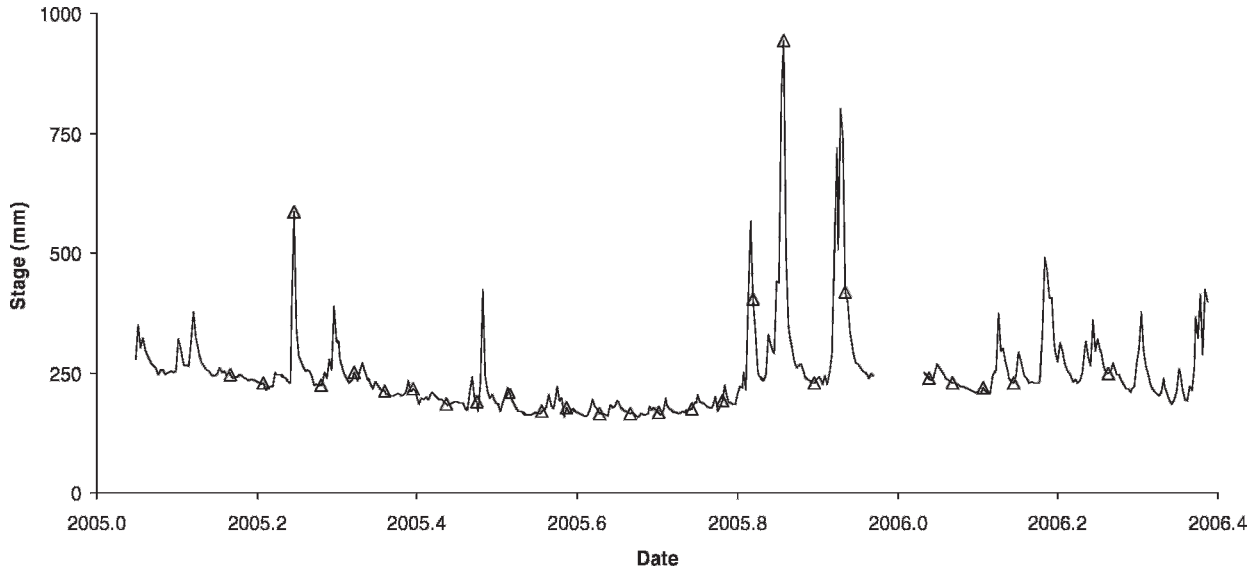

Figure 3. Distribution of sampling days during the study period and their relationship to river stage recorded near point A (see Figure 1).

aliquots of water flowing through the wetland substrate at that particular depth.

Laboratory Analyses

The water samples collected from individual points were analysed in the Mass Spectrometry and Environmental Luminescence Laboratory at the University of Birmingham. Samples were first filtered through pre-rinsed Whatman GF/C filter papers under vacuum, and a 30 ml sub-sample was transferred to HDPE bottles and refrigerated for subsequent isotope analysis. Samples were refrigerated overnight from 4–6°C and were analyzed for TOC the next day. DOC analysis was completed within 36 hrs of sample collection (24 hrs later on two occasions). DOC was determined using a Shamadzu 5050 carbon analyser. Glass vials were washed in a 2% Decon solution and rinsed with 10% HCl and millipore water. Total carbon was measured directly, and DOC was estimated by measuring dissolved inorganic carbon (DIC). Samples were analyzed in duplicate to a coefficient of variation (CV) of 2%. Reagacon standards from a 1000 mg/l stock solution TOIC and TOC were machined diluted to 20, 25, 33, 40, and 50 mg/l C.

Water stable isotopes were determined using a GV Instruments Isoprime isotope ratio mass spectrometer connected to a Eurovector Environmental Analyser. Stable isotope values are expressed using the δ convention, where $\delta^{18}O = (^{18}O/^{16}O_{sample}) / (^{18}O/^{16}O_{standard}) - 1$, and similarly for hydrogen isotopes (δD) expressed as ‰. The standard was Vienna Standard Mean Ocean Water (V-SMOW). For hydrogen isotope analysis, approximately 0.3 µl of water was injected from sample vials on an autosampler into a column where reduction to hydrogen took place at 1050°C over a chromium metal catalyst. For oxygen isotope analysis, approximately 0.3 µl of water was injected from sample vials on an autosampler into a column where reaction of water at 1250°C with carbon dioxide, provided by nickel plated carbon over glassy carbon, yielded carbon monoxide for oxygen isotope analysis. For both isotopes at least two successive analyses were made by repeat injections from the same vial. In order to eliminate sample hangover effects for oxygen analysis, samples were first analyzed for δD, before arranging samples in order of decreasing δD for determination of $\delta^{18}O$. Internal (within-run) precision is 0.4 per mil for δD and 0.08 per mil for $\delta^{18}O$, and overall (external) precision estimated at 1 per mil for δD and 0.15 per mil for $\delta^{18}O$.

RESULTS

Hydrological Dynamics

Variations in hydraulic head observed in the six piezometer nests on field visits during the study and their relationship to weekly precipitation at Oakley Folly (3 km to the SE and 160 m asl) are shown in Figure 4. Results indicated considerable differences in the response of piezometers at various depths (Table 1) to individual rain events and seasonal trends in precipitation and evapotranspiration. In some cases there was little variation in hydraulic head through the year (e.g., 1D and 1S adjacent to the River in Transect TA), while in other areas there were relatively rapid changes in hydraulic head following precipitation, and with a clear seasonal trend (e.g., 1D and 1S adjacent to the River in Transect TB). Results suggest that there were considerable differences in the connectivity between individual piezometer nests that probably reflect local differences in permeability and water flow pathways.

Although it was very difficult to relate variations in hydraulic head to general trends in water movement through each transect, the approximate direction of water movement could be seen in a selection of simple flow-nets (Figure 5). These were produced by interpolating hydraulic heads from individual piezometers along both transects. This simple flow analysis assumed that the direction of subsurface flow was predominantly perpendicular to the river, and the effects of hydraulic conductivity variation on flow direction were minimal. The isolines connect points of equal hydraulic head and indicate the direction of water movement that occurs perpendicular to each isoline in the direction of falling head at a rate proportional to isoline density and hydraulic conductivity. The flownets illustrated considerable differences between the two transects. In Transect TA, the isolines suggest that water movement tended to follow the surface slope, but with distinct changes in the hydraulic gradient occurring over time (evident in the higher isoline density on August 2 and September 14). In Transect TB the direction of water movement was more variable, probably as a result of hydrologic interaction with the surface water pool on the wetland at site WSW. The flow direction was initially parallel to the surface with a vertical downwards component near the river (May 24), while on 2 August the isolines were distorted by the high hydraulic heads in a valley-side piezometer (3S) following precipitation. The dense packing of isolines in the middle of Transect TB suggests that hydraulic conductivity was low in the vicinity. On September 14, the

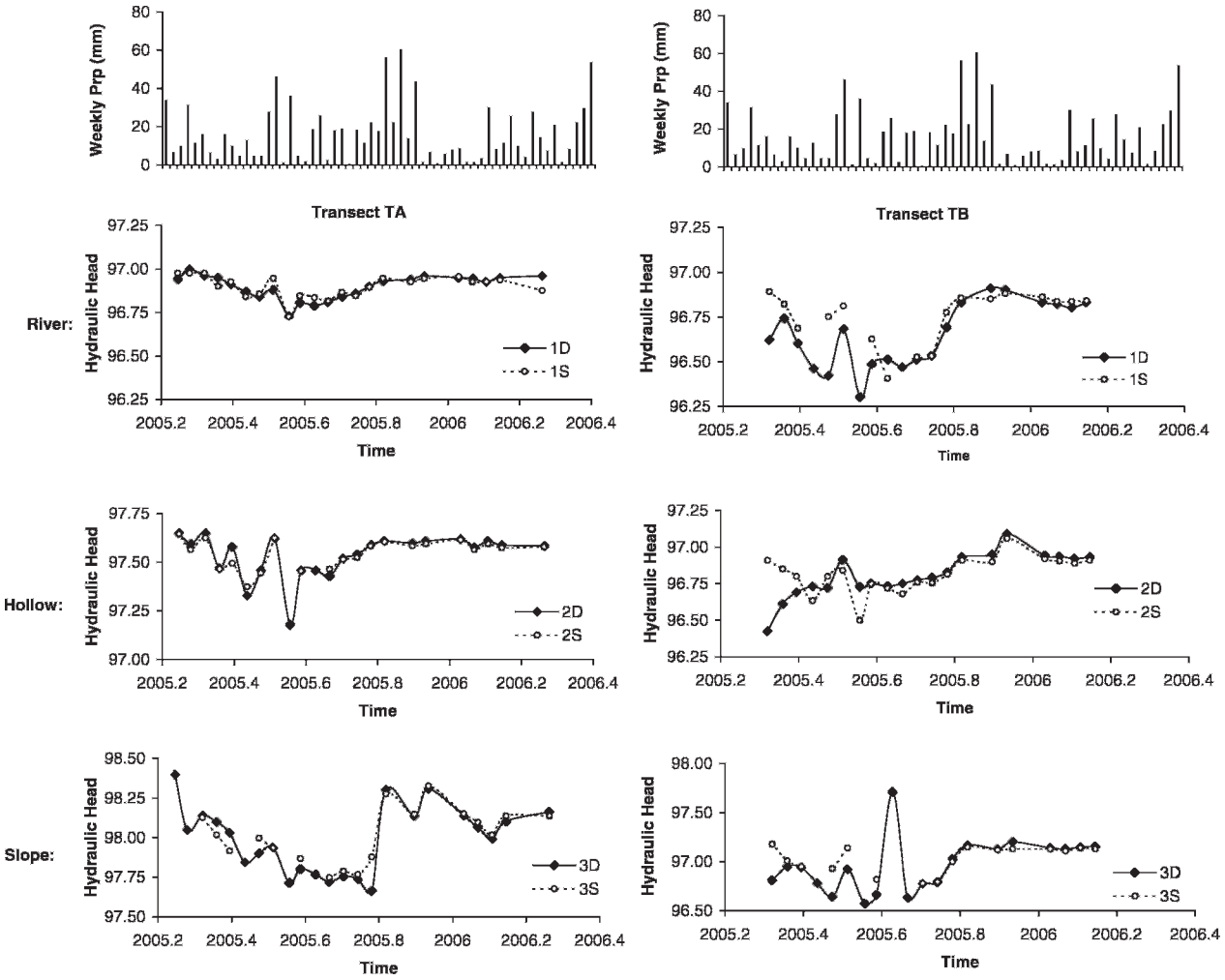

Figure 4. Variations in hydraulic head across Transects TA and TB and weekly precipitation. Occasional gaps in the data series occurred when water levels fell below the base of shallow piezometers.

isolines suggest that water was moving laterally through the wetland, with some upward movement near the river. The latter, which becomes more pronounced on November 24, suggests that upwelling groundwater could be locally significant in the valley bottom.

Variations in the isotopic composition of the samples are shown in Figure 6 and summarized in Table 2. Figure 6 shows $\delta^{18}O$ plotted against D/H for all samples sites, together with regional meteoric water lines derived from precipitation data from Keyworth (1985–1996; July $\delta^{18}O = -5.2$ per mil; January $\delta^{18}O = -9.1$ per mil; annual weighted mean $\delta^{18}O = -7.7$ per mil) $\sim$ 95 km to the East, and Wallingford (1982 to 2001), $\sim$ 230 km to the SE (Darling and Talbot 2003). All samples lie close to the local meteoric line, with a small evaporation trend in ^{18}O for the pond (site GWP) samples that were collected in summer and would have been affected by evaporation. It is clear in Figure 6 that river (A, B, C, and D) and groundwater (GS) samples plot close to the weighted mean isotopic composition of modern precipitation at Keyworth (-7.7 per mil). River water samples therefore had very similar isotopic composition to groundwater, which in turn reflected the isotopic composition of the annual weighted mean of precipitation. In contrast, wetland surface water (WSW) had an isotopic composition that varied between that of the groundwater (in winter) and the isotopic composition of precipitation (in summer). Site WSW did not reflect the isotopic composition of winter rainfall ($\delta^{18}O < 7.7$ per mil), demonstrating a winter groundwater input to the wetland surface. Shallow (WS) and deep (WD) wetland waters followed a similar trend, but with a more muted variation in the amplitude of isotopic variations. Using a simple mixing model we can apportion the sources of water in the wetland samples between summer precipitation and groundwater. Assuming the sum-

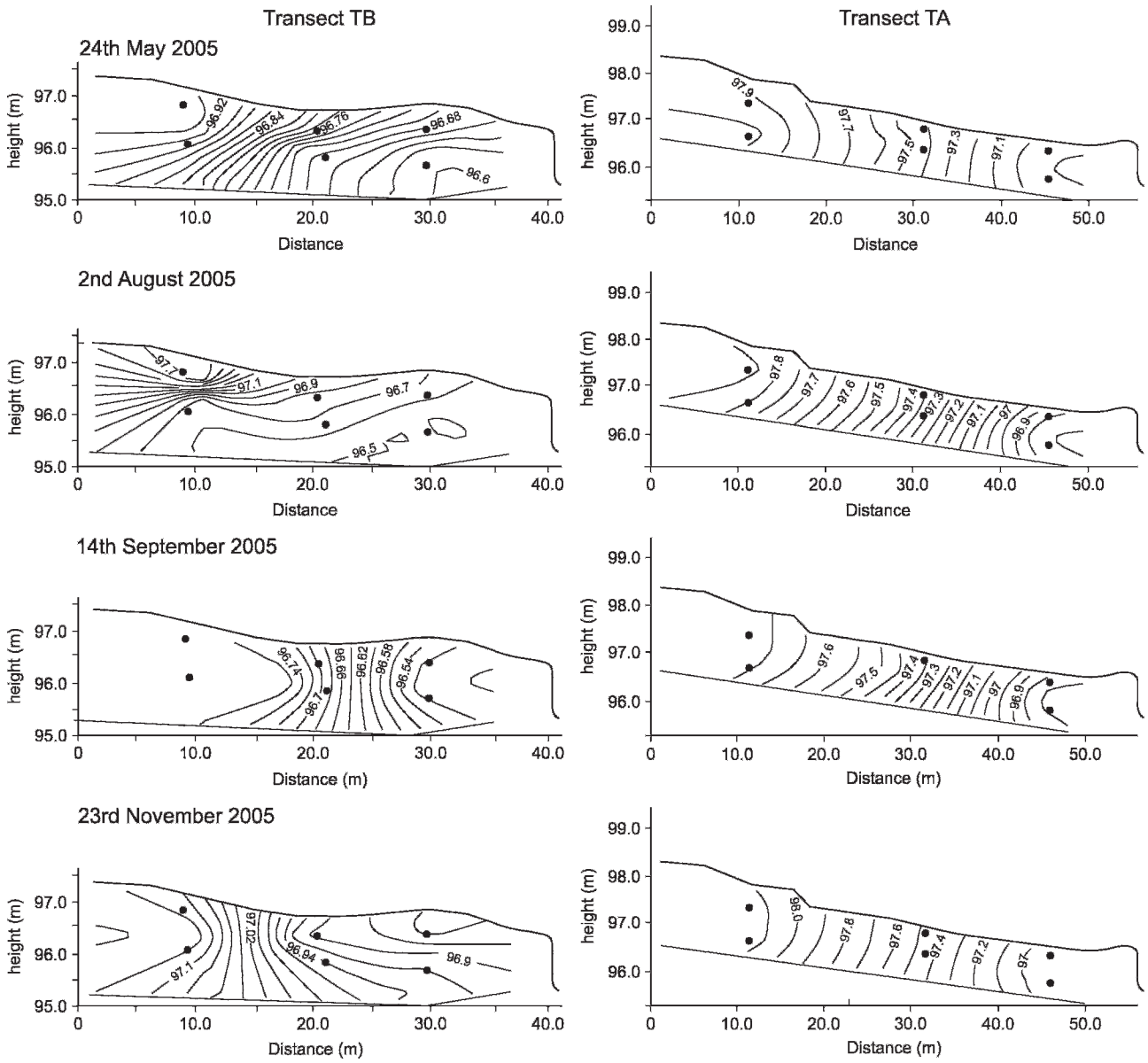

Figure 5. Flownets derived from interpolating hydraulic head data from piezometers along Transects TA and TB on: May 24; August 2; September 14; and November 23, 2005. Locations of individual piezometers are indicated by the filled circles (•) in each flownet.

mer maximum isotopic composition of rainfall as one end-member ($\delta^{18}O = -5.2$ per mil) and the mean isotopic composition of groundwater site GS ($\delta^{18}O = -8.1$), then the surface wetland water (WSW) varied in composition from 100% precipitation in September to 93% groundwater in winter, the shallow wetland (WS) from 28% groundwater in summer to 81% groundwater in winter, and the deep wetland (WD) from 69% groundwater in summer to 100% groundwater in winter.

This indicates both a general seasonality of water isotopic composition in the wetland related to the balance between groundwater and surface water inputs, as well as the potential for subtle changes in the rate and direction of water movement through valley-side/riparian wetlands. Surface topography and variations in permeability are likely to be important in determining the nature of individual water fluxes that can vary significantly over comparatively small distances. The possible implications for carbon fluxes are considered below.

Dissolved Carbon Concentrations

Variations in Total Carbon, DIC, and DOC of wetland and river-water samples are given in

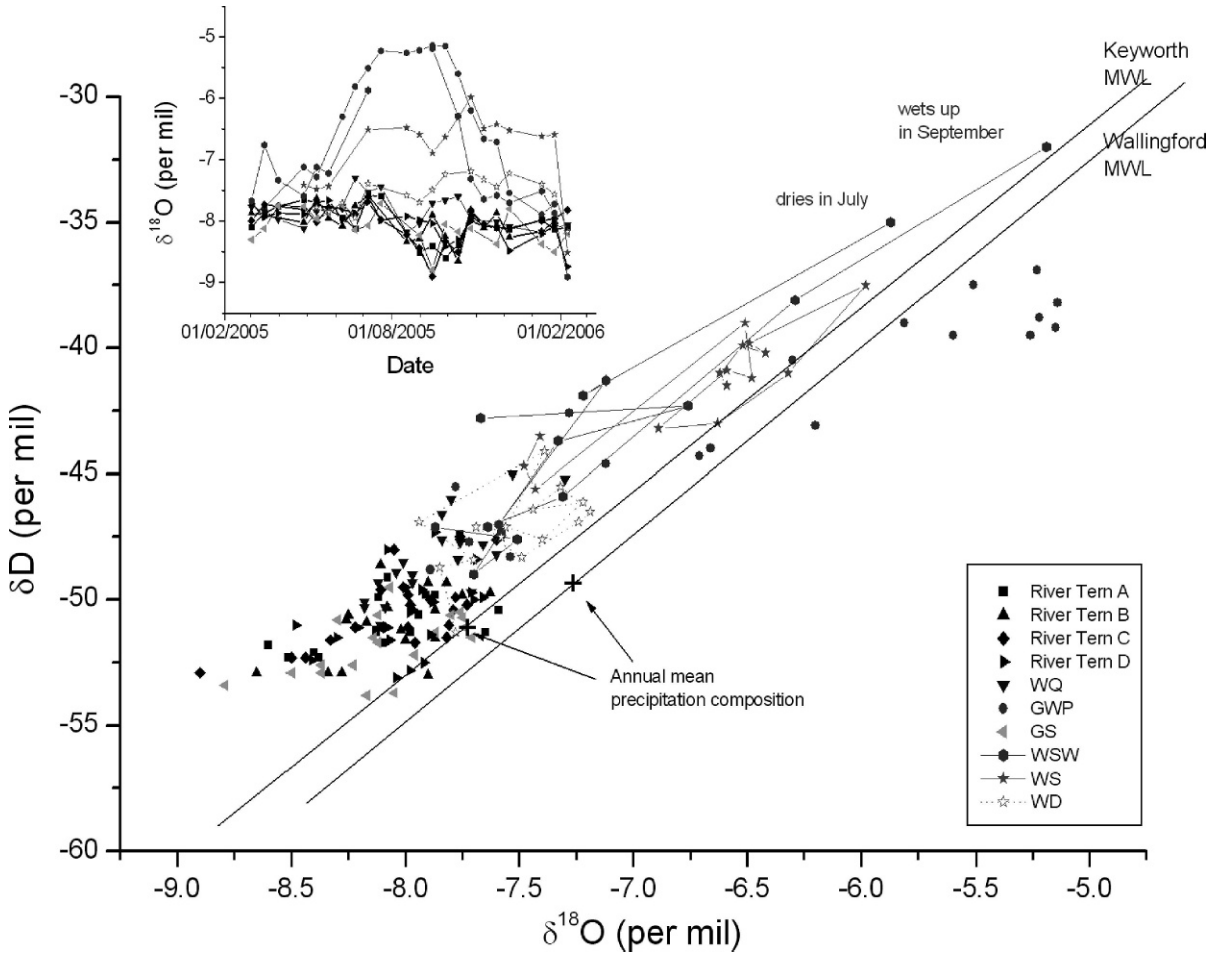

Figure 6. Variations in the isotopic composition of water samples collected at Norton-in-Hales with the annual trend presented in the inset figure.

Figure 7, with summary statistics in Table 2. Dipwells WS and WD have consistently high concentrations of DIC and DOC. The near-surface samples (WS) tended to have higher DIC concentrations than the deep samples (WD) in the summer. This may reflect some biological production of DIC, supplementing DIC from upwelling groundwater. However, concentrations of DIC will also be affected by controls on the solubility of DIC (reflecting changes in pH and temperature). Field measurements of pH on 6 occasions over the period of study averaged 6.67 ± 0.06 for WD, 6.73 ± 0.17 for WS, and 6.83 ± 0.55 for WSW, suggesting that for these sites, abiotic changes in the solubility of DIC was probably not a factor, although it might be important at other points.

Periods of high DOC concentration at WS coincide with consistently high water levels in piezometer nests 1 and 2 of Transect TB adjacent to the well (Figure 4), indicating the importance of local water levels in determining DOC production. There was a comparatively small range in TC of the remaining 'wetland' samples. Of these, the wetland discharge (WQ) and floodplain pond (GWP) had similar TC, DIC, and DOC contents, but with more variability in GWP (which is matched by a greater isotopic variability) on the opposite river bank, where the floodplain was largely pasture and no wetland was present. The wetland surface-water (WSW) displayed more variation through the year, with DIC falling to zero on two occasions, suggesting that water at this point mainly consisted of recent precipitation.

The trend in total, inorganic, and dissolved carbon in river-water samples (A, B, C, and D) and the groundwater spring (GS) in Figure 7 show relatively little variation between samples. Peak DOC concentrations were observed on March 31, 2005, following heavy rainfall (precipitation totalled 34 mm from March 25–31), while DIC concentrations were relatively low. The lowest DOC concentrations were consistently found in samples collected

Table 2. Summary carbon and stable isotope data from water samples collected at Norton-in-Hales. Units are mg l^{-1} for TC, DIC and DOC; per mil for δD and $\delta^{18}O$.

		TC	DIC	DOC	$\delta^{18}O$	δD
Wetland Samples:						
Shallow Well (WS)	Mean	94.5	61.9	32.5	−6.7	−41.5
	St. Dev.	30.6	18.9	18.7	0.5	2.2
Deep Well (WD)	Mean	84.8	63.1	21.8	−7.5	−47.2
	St. Dev.	17.4	12.8	10.1	0.2	1.6
Surface-water (WSW)	Mean	42.0	20.6	21.4	−7.3	−43.2
	St. Dev.	14.2	12.1	6.8	0.7	5.0
Groundwater-fed Pond (GWP)	Mean	41.5	33.2	8.3	−6.4	−42.1
	St. Dev.	5.0	5.7	3.8	1.0	3.8
Wetland Discharge (WQ)	Mean	48.3	39.1	9.3	−7.9	−48.4
	St. Dev.	4.0	4.7	5.0	0.3	1.7
River Samples:						
'PE16' (A)	Mean	42.9	32.2	10.8	−8.0	−50.5
	St. Dev.	6.2	8.2	7.7	0.3	1.5
River-water (B)	Mean	42.8	31.8	11.0	−8.0	−50.7
	St. Dev.	6.6	8.2	8.5	0.3	1.6
River-water (C)	Mean	42.5	31.9	10.6	−8.1	−50.4
	St. Dev.	5.9	7.8	7.6	1.48	0.3
River-water (D)	Mean	43.1	32.9	10.3	−8.0	−50.6
	St. Dev.	5.3	7.6	8.6	0.27	1.54
Groundwater Spring:						
Discharge (GS)	Mean	42.5	36.9	5.6	−8.1	−51.8
	St. Dev.	5.7	4.6	4.5	1.23	1.23

from the culverted spring (GS) suggesting that water from this source failed to come into contact with surficial sources of DOC.

Certain end-members could be identified across the range of sampling sites (Table 2). The groundwater spring (GS) had the lowest DOC, and high DIC (DOC = 5.6 ± 4.5 mg/l; DIC = 36.7 ± 4.6 mg/l). The shallow well (WS) had the highest DOC and the highest DIC (DOC = 32.5 ± 18.7 mg/l; DIC = 61.9 ± 18.9 mg/l). The wetland surface-water (WSW), adjacent to wells WS and WD, had the lowest DIC (20.6 ± 12.1 mg/l). River samples lie between these end-members with DOC rich waters during winter and autumn high flow (DOC > 30 mg/l; DOC > DIC), and DOC poor waters during groundwater-dominated summer low flows (DOC < 10 mg/l; DIC > DOC).

Water and Carbon Fluxes

The significance of the results described above depends to a large extent upon the connectivity between individual landscape units and potential sources of DOC and DIC across the wetland and the adjacent river. Most carbon flux studies have considered wetlands that have a clear and well-defined connection with a river, which may be most comparable to the GWP and WQ samples. In the upper Tern catchment most wetlands were only infrequently connected by flowing surface water to the river and thus the degree to which they were a source of DOC and DIC to the river depended largely upon the extent of sub-surface seepage. The magnitude of sub-surface flows can be estimated using the Dupuit equation:

$$q = \frac{1}{2}K\left(\frac{h_1^2 - h_2^2}{L}\right)$$

where q is the flow per unit width (m^2/day), h_1 and h_2 are hydraulic heads at points 1 and 2, L is the horizontal distance between the two points (m), and K is the hydraulic conductivity (m/day). The equation assumes that in any vertical section, flow is horizontal and uniform over the depth of flow, with flow velocities that are proportional to the water-table shape and saturated depth. Although in many cases, a small vertical component to flow was inevitable, the flownets indicated that flow direction was predominantly horizontal, particularly for Transect TA.

Accordingly, water fluxes were estimated separately for Transects TA and TB, taking h_1 to be the hydraulic head of Piezometer Nest 1 (mean of 1S and 1D), while river stage for each transect (h_2) was estimated separately from the gauged flows at point A and the river cross-sectional area adjacent to each transect. Hydraulic conductivities (K) were not

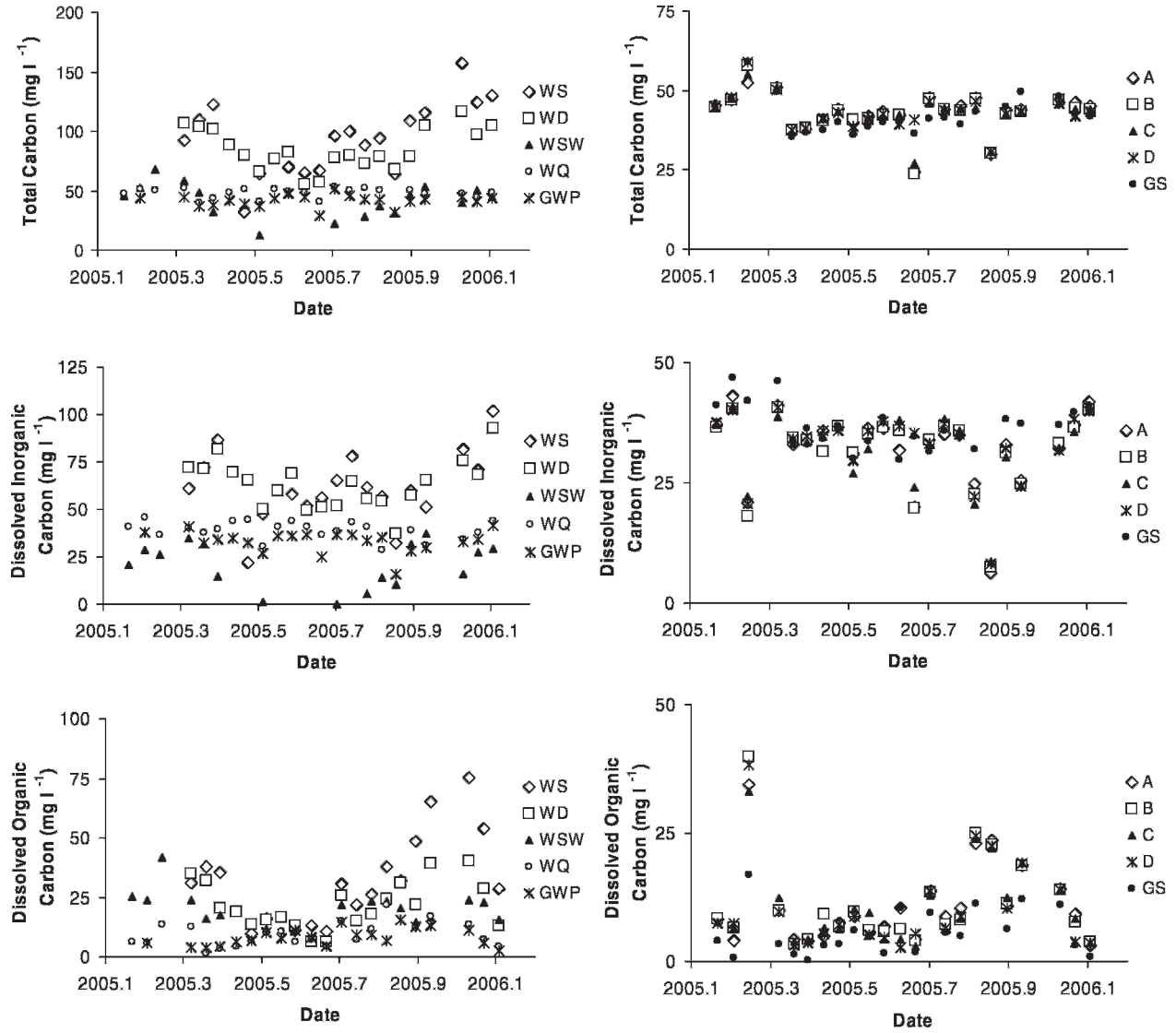

Figure 7. TC, DIC, and DOC concentrations of water samples collected from the river (A, B, C, D), wetland (WSW, WS, WD), groundwater spring (GS), and groundwater-fed pond (GWP).

measured directly, and a K of 0.6 m/day was assumed for both transects, on the basis of the local sedimentology (Figure 2) and correlating the silt-clay concentration of local samples with published studies of hydraulic conductivity (Rawls et al. 1982). The estimates of seepage (m^3/day) on each field visit are shown for both transects in Figure 8a and suggest relatively low but consistent rates of water movement through both transects to the river. Fluxes from Transect TB were in some cases 50% higher than Transect TA, but are affected by the variability in hydraulic head of the piezometer nest close to the river which appeared sensitive to recent precipitation and evapotranspiration (Figure 4).

There are considerable difficulties in determining subsurface water fluxes accurately but our results were only intended to be used for indicative purposes. Although analysis of soil cores indicated the relative consistency in soil units, actual water fluxes will depend on local variations in sedimentology, the potential for macro-pore flow, and the nature and extent of any land drainage. Conceivably therefore, the effective hydraulic conductivity could vary by several orders of magnitude. However, the implications of smaller variations in K are indicated in Figure 8a by calculating water fluxes separately for hydraulic conductivities of $\pm$ 25% of the original value selected (i.e., K of 4.8 m/day and 7.5 m/day). The results given in the figure by small (3 pt) markers for both transects indicate the possible range in water fluxes from the wetland reach (per meter along the river) with a mean water flux across the period of measurement of 0.01745 $\pm$ 0.004 m^3/day for Transect TA and 0.0245 $\pm$ 0.005 m^3/day for Transect TB.

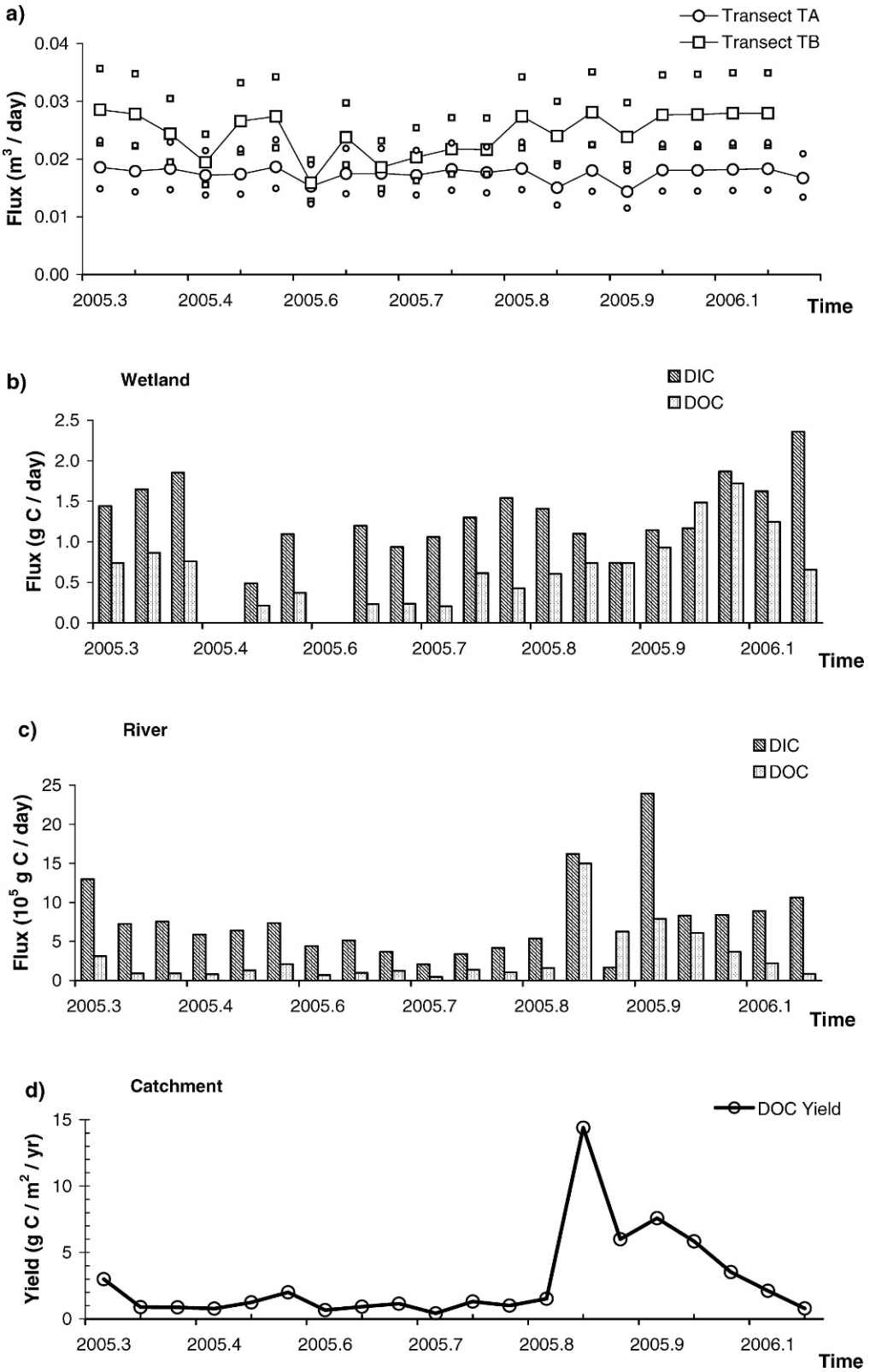

Figure 8. a) Estimated water flux (per m) between Transects TA and TB and the river, with the effects of varying K by ± 25% shown using small (3 pt) markers; b) DOC and DIC fluxes from the wetland; c) DOC and DIC fluxes from the river; and d) catchment DOC yield.

Wetland carbon fluxes estimated from the product of DIC and DOC concentrations observed at shallow well WS and the mean seepage of Transects TA and TB are given in Figure 8b (as carbon flux per meter along the river bank). Calculations assumed conservative transport of DOC and DIC which is likely for sub-surface flow, particularly given the predominantly mineral substrate. The results indicated considerable variation in both DIC and DOC. However, DIC fluxes consistently exceed DOC, and the latter increased considerably through the late summer and autumn of 2005, probably reflecting the decomposition of seasonal vegetation. For comparison, DIC and DOC fluxes in the river are given in Figure 8c (calculated using local discharge and data from in-stream samples), while variations in the equivalent annual yield of DOC are shown in Figure 8d (estimated using the surface-water catchment area). Given the difficulty in accounting for changes in the solubility of inorganic carbon, DIC yields were not estimated. However, peak DOC yield was 14.4 g C m^{-2} yr^{-1}, but < 2 g C m^{-2} yr^{-1} for much of the time.

From these data the proportional contribution of small valley-side wetlands to the total carbon budget could be estimated. To do this the river carbon flux data in Figure 8c were converted to show the proportional increase in river carbon flux per km of upstream river channel. An upstream channel length of 25 km was assumed to comprise 8 km of the main stem of the river, and a further 17 km of tributary channels based upon a combination of field survey and examination of topographic maps (Figure 1). Similarly, the approximate carbon flux from wetland to river was also converted to give carbon flux per km by multiplying the per m carbon flux data in Figure 8b by 2000 (recognizing the potential for water to move to the river from both sides of the valley). Dividing the river carbon flux (per km) by the wetland carbon flux (per km) yields the ratio shown in Figure 9b. This summarizes the potential contribution of headwater wetlands to the total carbon budget. Although the results are only indicative of broad trends, and fail to take into account potentially significant variations in water flux rates, land drainage, and agricultural activities, the data suggest that headwater wetlands might contribute significantly to the total carbon budget, albeit with marked seasonal fluctuations. The proportional carbon contribution from wetland seepage reflected a combination of local production of DOC and the movement of water through valley-side wetlands to the river, and approached 50% in winter.

The potential importance of carbon fluxes from valley-side wetlands can be demonstrated in a different manner by calculating the proportional increase in riverine dissolved carbon arising as a result of seepage from adjacent wetlands. Accordingly, the increase in riverine DOC and DIC concentrations (mg/l) arising from the transport of dissolved carbon from a linear wetland extending for 1 km along one bank of the River Tern is shown in Figure 9b, using the water flux estimates described above. While some of the seasonal trends, particularly in DIC in summer, were an artefact of fluctuations in discharge, the increase in DOC was 0.03 ± 0.2 mg/l, with local peaks reflecting the combination of differences in DOC production and rates of sub-surface seepage, as well as seasonal changes in river discharge.

DISCUSSION

Our results are significant in that they highlight a number of conditions under which headwater wetlands may represent a significant source of dissolved carbon to downstream aquatic ecosystems. Data from a variety of sources were analyzed to investigate the relationship between water movement, concentrations of dissolved carbon, and estimated flux rates. Hydrological data suggest significant variation in water source, in the rate and direction of water movement, and in the wetland water-table, across relatively small areas in a headwater wetland. Differences in water source were particularly marked with depth: stable isotopes indicated that water at the wetland surface (WSW) varied from 100% precipitation in September to 93% groundwater in winter; while at a depth of 50–100 cm the composition of the water was 69% groundwater in summer and 100% groundwater in winter. Like many wetlands, the hydrology and biogeochemistry of the headwater wetlands of the River Tern were influenced to a large extent by the dynamics of regional groundwater flow (Winter et al. 2003, Vidon and Hill 2004). However, local topography and sedimentology were also important.

These variations in hydrological processes have considerable implications when considered in conjunction with the dissolved carbon data. Previously, most studies have focused on either DIC or more frequently DOC. Our results suggest this may lead to a significant underestimate in the catchment carbon flux. Samples from the groundwater spring suggest that local groundwater is characterized by the low DOC and high DIC (Table 2), while water samples collected from the wetland surface had

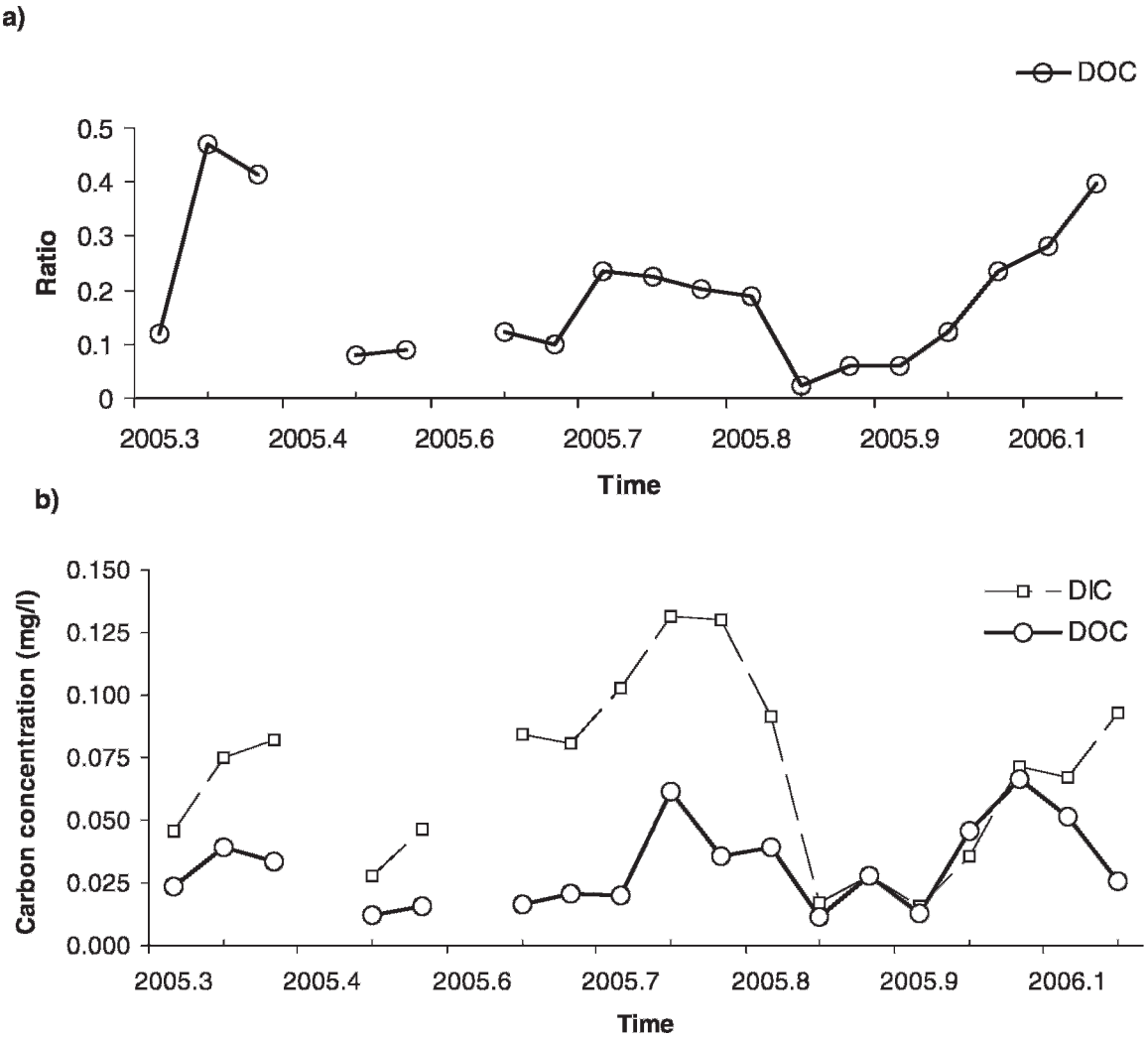

Figure 9. Estimates of the significance of carbon fluxes from riparian wetlands to the river: a) the ratio between the riverine DOC per km of channel and calculated carbon flux from valley-side wetlands to the river; and b) the increase in riverine DOC and DIC reflecting dissolved carbon flux from a linear wetland extending for 1 km along one river bank.

medium to low DOC and low DIC. Peak DOC and DIC concentrations were found in water samples extracted from a depth of 0–50 cm, indicating the importance of recently fixed carbon near the surface and suggesting that biological production of DIC may be more significant than previously thought.

Ultimately, however, the significance of these results depends on the degree to which the flow of water through the wetland enables dissolved carbon to be flushed through the system and thereby avoid subsequent decomposition and sorption on soil surfaces. While some wetlands display considerable variations in hydrological processes on a seasonal or event-basis (Hinton et al. 1998), our estimates of water flux from the headwater wetland at Norton-in-Hales suggest that seepage rates were relatively low and relatively constant, particularly for Transect TA (Figure 8a). At this site, dissolved carbon concentrations were presumably high because flow was insufficient to oxygenate the water. Connectivity between wetland and river thus provided an important constraint on the volumetric contribution that such wetlands made towards to the total catchment carbon budget. However, their contribution could become significant if the full upstream river channel length is taken into account. Moreover, our results indicated that river DOC exhibited large variations, with the highest DOC at high discharge. However, the isotopic signature of the river samples remained similar to those of local groundwater, suggesting that headwater sources of DOC were important, and the interaction among groundwater flow-paths, sources of carbon, and the subsequent movement of water to the river channel were critical in explaining the results from Norton-in-Hales.

Our results further emphasize the need for further research on the hydrological connectivity of riparian wetlands and on understanding the dynamic hydrological, physical-chemical, and biological interactions of water in the various environments that characterize the riparian corridor. Of particular significance were the considerable variations in the direction of water flow over small areas (see water flownets of Figure 5), which reflected the interaction between local groundwater levels and precipitation. The implication is that headwater wetlands, such as those at Norton-in-Hales, are vulnerable to changes in groundwater levels and may potentially represent a significant source of riverine carbon if groundwater levels fall. This is of particular significance in the UK, given the long-term groundwater drought in SE England, and the general increase in carbon concentrations have been observed – albeit largely based upon work on upland rivers and blanket peatlands (Freeman et al. 2001, Worrall et al. 2005). These trends reflect factors such as changes in land use (particularly drainage) and the frequency of summer drought that might affect lowland catchments in a similar fashion.

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