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Variability of dissolved CO_2 in the Pang and Lambourn Chalk rivers

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Abstract

This paper presents the results of a two-year field campaign to determine the spatial and temporal variability of groundwater interaction with surface waters in two Cretaceous Chalk catchments (the Pang and Lambourn) in the Upper Thames in Berkshire, UK, based on measurement of dissolved carbon dioxide (CO_2). Average stream water concentrations of dissolved CO_2 were up to 35 times the concentration at atmospheric equilibrium. Mean groundwater concentrations of 85 and 70 times the atmospheric equilibrium were determined from borehole water sampled in the Pang and Lambourn respectively. Diurnal and seasonal variation of in-stream concentration of dissolved CO_2 is not significant enough to mask the signal from groundwater inputs.

Keywords: chalk, river, groundwater, alkalinity, pH, carbon dioxide, Pang, Lambourn, LOCAR

Introduction

Analysis of stream and groundwater chemistry has been used to assess the extent of groundwater interaction with surface waters (Neal *et al.*, 1990; Hill and Neal, 1997; James *et al.*, 2000; Cook *et al.*, 2003; Malcolm *et al.*, 2004; Rodgers *et al.*, 2004). Such methods provide relatively quick and inexpensive descriptions of the spatial and temporal distribution of surface-groundwater interactions. For a naturally occurring substance to be used as an indicator of groundwater, its concentration in groundwater must be relatively consistent over both space and time, as well as significantly different from that of stream water. Initially, dissolved CO_2 is captured from the atmosphere by rainfall. Processes of organic material decomposition in the soil column further increase the CO_2 concentration of this water as it percolates through the soil. Resulting levels of dissolved CO_2 in groundwater are, therefore, higher than those found in surface waters (Neal *et al.*, 2000), making it a good candidate for use as a groundwater tracer.

When groundwater emerges at an interface with a surface-water body, dissolved CO_2 in the groundwater starts to degas

at a rate determined by the dimensional characteristics of the water-body, the amount of disturbance or turbulence in the water and external interferences such as wind-speed (Genereux and Hemond, 1992; Raymond and Cole, 2001). Once at the surface, the concentration of CO_2 in the water may be affected by photosynthetic and respirative processes of biological organisms in surface sediments and in the water column. Such processes make the interpretation of surface-water CO_2 concentrations for calculation of the rate and extent of groundwater inputs more difficult (Schurr and Ruchti, 1977; Simonsen and Harremoes, 1978). For measurements of dissolved CO_2 to be useful as reliable indicators of surface-groundwater interaction therefore, the potential magnitude of extraneous sources and sinks of CO_2 must first be quantified.

Worrall and Lancaster (2005), observed significant intra-annual variation in groundwater-dissolved CO_2, and between different aquifers. While physically-based models for simulation of conservative natural tracers may be used as a starting point in the context of CO_2 (e.g. Choi *et al.*, 1998), parameterisation of such models is difficult (Genereux and

Hemond, 1992) and extraneous processes of CO_2 production, CO_2 degassing and carbonate precipitation are still not addressed. Indeed, Finlay (2003), suggests that even the presence of canopy cover above streams can affect the temporal dynamics of dissolved CO_2 significantly.

This paper investigates the potential of using simple surface/groundwater ratios of dissolved CO_2 to describe the spatial and temporal distribution of surface–groundwater interaction in groundwater catchments. The influence of streamflow and in-stream vegetation on the seasonal and diurnal variability of in-stream dissolved CO_2 has been assessed using water sampled at nine surface water and five groundwater locations, over a three-year period in the Pang and Lambourn Chalk catchments in Berkshire, UK.

The Pang and Lambourn catchments are key sites of the Lowland Catchment Research project (LOCAR) which aims to develop a better understanding of hydrological, geo-chemical and ecological processes in permeable lowland catchments. In this research new interdisciplinary science and improved modelling tools were developed to meet the challenges of integrated catchment management as defined by the Water Framework Directive (Wheater and Peach, 2004).

Site description

Covering areas of 170.9 km² and 234.1 km² respectively, the Pang and Lambourn catchments are located on the northern side of the Thames basin (Fig. 1) and each catchment consists of predominantly Upper and Middle Cretaceous Chalk. The Upper Chalk is approximately 75 m thick and outcrops extensively on the dip slopes of both catchments. The Middle Chalk is up to 60 m thick and is slightly more argillaceous than the Upper Chalk, (Allen *et al.*, 1997; Aldiss *et al.*, 2002). Due to the highly permeable nature of Chalk aquifers, rivers in both catchments are groundwater fed. The Lambourn, for example, has an average stream gauge baseflow index (BFI) of 0.93, whilst the Pang has average BFI of 0.867 (Gustard *et al.*, 1992). In addition to groundwater springs, there are several sink holes in both catchments, the most significant one being in the lower Pang catchment (Banks *et al.*, 1995; Maurice *et al.*, 2006). Significant impermeable Tertiary (Eocene) formations are also found in the lower Pang, including Reading Beds and London Clay. Geological variation between the two catchments is reflected in contrasting landscape features and topography. The river valley of the
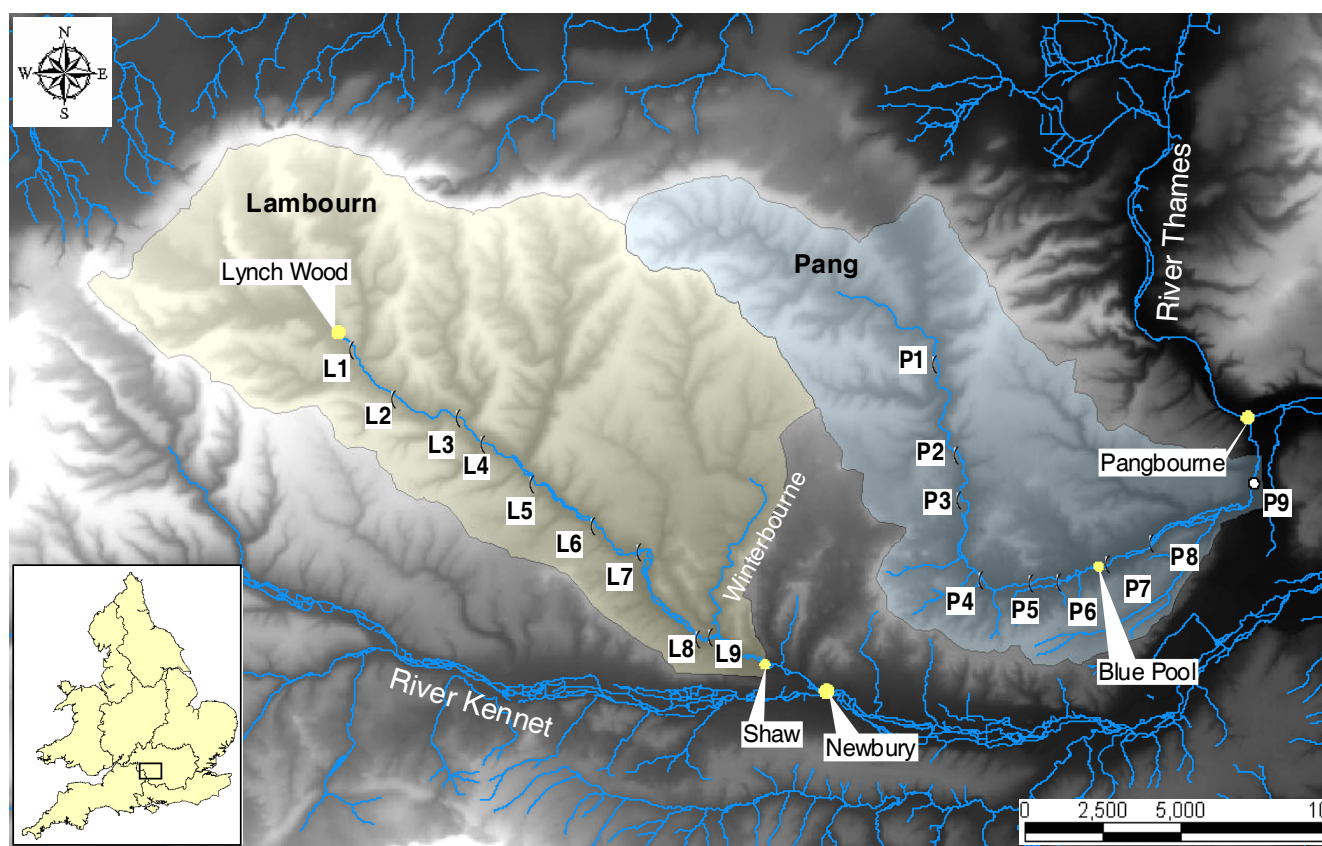

Fig. 1. *Location of water sampling sites within the Pang and Lambourn catchments. Position of Thames, Kennet and Winterbourne Rivers also shown.*

Lambourn, for example, is relatively narrow (typically 250–500 m) with sharp gradient sides. The Pang, by comparison, is characterised by wide river valleys (up to 2 km width) with less-defined sides of lower topographic gradient. Consequently, dry-valley landscape-features that intersect the main river-valley, and which are thought to promote convergence of subsurface flow (Grapes *et al.*, 2005), are more prevalent in the Lambourn catchment. Grapes *et al.* (2006) also identified a localised alluvial gravel aquifer in the Lambourn valley which is probably associated with a number of small wetland areas in the main river valley. Larger regional-scale controls on groundwater movement in the two catchments include major hydrological sinks (the Thames and Kennet valleys), geological boundaries (Pewsey Anticline) and the stratigraphic position relative to sea level (Bradford, 2002). Hard-grounds and harder bands in the Chalk, associated with more cleanly fractured areas of deeper Chalk, may also promote the formation of preferential flow pathways (Brettal, 1971).

The River Lambourn flows in a predominantly south-easterly direction throughout its course and covers a distance of 20 km from its source at Lynch Wood to its confluence with the larger River Kennet at Newbury. The River Lambourn has a mean annual flow of 1.76 m^3 s^{-1} (1962–2003), at the Shaw gauging station, situated 2 km upstream of Newbury (NRFA, 2004a). From spring to summer, the seasonal head of the river rises from outcrops of Middle Chalk in Lynch Wood at the top of the catchment. Stream levels generally peak and begin to recede from the end of May. Summer streamflow recession is then followed by a period, usually between August and January depending on rainfall, in which the stream becomes ephemeral in its upper reaches between Lynch Wood and L4 (Fig. 1). At such times, the head of the river may occur as far as 6 km downstream of its winter location.

The Pang flows north-south for its first 10 km and then turns east for 7 km, before turning north to meet the Thames at Pangbourne 22 km downstream from its winter head (Fig. 1). The river has a mean annual flow of 0.65 m^3 s^{-1} (1962–2003) at Pangbourne (NRFA, 2004b). In late winter, the river rises from the Upper Chalk in the northern half of the catchment, flow is then supported by springs at a number of downstream locations (Maurice *et. al.*, 2006). The largest of these occurs at an area known locally as the Blue Pool (between P6 and P7). In average rainfall years, the river channel becomes ephemeral between P1 and P2 and between P3 and P6, whence perennial springs are insufficient to support flow. Such conditions may prevail from September/ November to as late as the following April.

Dissolved CO_2 in Chalk streams

In Chalk catchments, CO_2 in groundwater is the result of calcium carbonate (calcite) acid dissolution due to microbiological activity; this generates carbonic acid and nitrogen transformations. The rates of these reactions are determined by CO_2 concentrations and the degree of mineral unsaturation in the water, and the availability of individual minerals, especially those that dissolve rapidly, such as calcite and other carbonate-based minerals. Upper and middle Chalk consists of relatively pure calcium carbonate such as the mineral calcite but may still contain impurities, including Mg, Sr, Mn and Fe.

The chemistry of percolating rainwater in Chalk catchments will change gradually as it passes through different subsurface layers. Chalk soils are typically less than one metre in depth and, whilst well drained, have relatively slow infiltration times of about a metre per year. The production of CO_2 by biological activity in such soils results in the CO_2 concentration of percolating rainfall increasing from 340 ppm in the open-air to up to 6000 ppm (Edmunds *et al.*, 1992). The rate of CO_2 production through biological activity in the soil is linearly related to temperature, but the relationship is also dependent on the type of vegetation and will be greater for natural vegetation than for wheat crops, for example.

Beneath the soil layer, in the unsaturated zone of the Chalk, moisture moves in what is essentially a dual-porosity medium comprising the saturated micro-pores of the Chalk rock matrix, and a largely unsaturated fissure network that runs through the Chalk. Due to processes of CO_2 dissolution in the upper soil layers, infiltrating water is already close to equilibrium with the groundwater held in the Chalk matrix in this zone. Water is gradually displaced downwards under gravity according to the piston-flow model, allowing the liberation and transfer of bicarbonate and calcium ions from the Chalk. Variation in calcium and bicarbonate concentrations and, hence, in dissolution and precipitation rates will be related to the variation in dissolved CO_2 in percolating water.

Under normal diffuse recharge conditions in the saturated zone, calcite saturation is rapidly established near bedrock outcrops (Edmunds *et al*., 1992). As a marine limestone however, Chalk will continue to undergo diagenetic changes, especially where younger influent water comes into contact with older water stored in the Chalk matrix. Groundwater chemistry may thus be modified slowly as it flows through the Chalk, resulting in increases in Mg/Ca and Sr/Ca ratios (Elliot *et al*., 1999). These ratios are useful in determining water to rock contact times, but because of the heterogeneity of groundwater movement and mixing in the subsurface

(Younger and Elliot, 1995), may be difficult to use in estimating groundwater residence times. Deeper groundwater in the Chalk may undergo mineral dissolution, precipitation and cation exchange at a slower rate than groundwater nearer the surface. The salinity of deep groundwater may also be higher, depending on the extent of system flushing with freshwater that has occurred since formation. Both of the above factors will produce a distinct geochemical zonation of groundwater with depth. In general, groundwaters are approximately calcite saturated in the Chalk, at least in the present study area (Neal *et al.*, 2002b).

Elevated concentrations of dissolved CO_2 in groundwater entering surface-water drainage systems will result in accelerated rates of CO_2 degassing which can significantly affect stream water-chemistry (Jacobson and Usdowski, 1975). Degassing of CO_2 will take place at a rate determined by stream dimensions, turbulence and wind-speed, but will invariably be susceptible to modification through biogeochemical processes (Wilcock *et al.*, 1999). For example, processes of photosynthesis and respiration by benthic algae, phytoplankton and macrophytes, will generate or remove CO_2 from the water column depending on temperature and daylight available. Biological photosynthesis and respiration processes described by Neal *et al.* (1998a, 2002a) in long-term studies in the Kennet Valley, suggest a diurnal variation in dissolved CO_2 of up to 150% in summer but just 50% in winter (maximum CO_2 occurs at night). The breakdown of dissolved or particulate organic carbon will occur in the surface and near-subsurface environment and will, thus, also promote increased levels of dissolved CO_2 in the aquifer in summer.

Methods and analysis

The variability of pH and dissolved CO_2 have often been used as an indicator of groundwater interaction with surface waters to characterise water quality in lowland rivers (Neal *et al.*, 1998a,b,c, 2000). Similarly, variation of in-stream alkalinity and silica have been used as groundwater tracers in upland rivers (Neal *et al.*, 1990; Rodgers *et al.*, 2004). In the present study, pH and Gran alkalinity were used to calculate dissolved CO_2 from water samples of 200 ml from up to ten locations in each catchment (Fig. 1 and Table 1), at weekly intervals from Dec 2002 to June 2005. Unfiltered samples were retrieved in sealed glass bottles for measurement of pH and of Gran alkalinity determined using a method derived from Neal (1988, 2001a).

The partial pressure of dissolved CO_2 (EpCO$_2$) was determined from Gran alkalinity and pH using a method described by Neal *et al.* (1998b). The method assumes that the effect of other ions on Gran alkalinity will be negligible

Table 1. Sample sites location and downstream distances in the Lambourn and Pang catchments.

Location	Site Name	National Grid ref.	Distance (km)
Riverside Cottage	L1	SU 328 792	0.1
Eastbury	L2	SU 343 775	2.75
East Garston	L3	SU 366 768	4.95
Maidencourt Farm	L4	SU 373 759	6.45
East Shefford House	L5	SU 389 747	7.8
Welford Park	L6	SU 410 732	10.45
Westbrook Farm	L7	SU 426 722	12.75
Woodspeen	L8	SU 446 693	16.2
Bagnor	L9	SU 451 693	17
Compton	P1	SU 528 787	0
St Abb's	P2	SU 534 756	4
Frilsham Meadow	P3	SU 536 740	6.45
River Barn	P4	SU 543 713	8.9
Bucklebury	P5	SU 560 711	10.8
Jewell's Farm	P6	SU 570 711	11.8
Frogmore Farm	P7	SU 587 719	13.68
Bradfield	P8	SU 602 725	15.43
Tidmarsh	P9	SU636 747	21.13

and that EpCO$_2$ does not vary under different meteorological conditions. EpCO$_2$ represents the number of times that the sampled water is oversaturated with CO_2, with respect to a similar sample that has reached equilibrium with the atmosphere. Thus, for example, the CO_2 concentration of a sample with an EpCO$_2$ equal to ten, will be ten times that of a sample that has been given time to equilibrate with atmospheric conditions.

River water chemistry of the Pang and Lambourn is characteristic of most Chalk streams in the UK; it is both calcium-rich and of high alkalinity (Neal *et al.*, 2000, 2002b, 2004a). As precipitation of carbonate material in the river is minimal (Neal, 2002), CO_2 gas exchange to the atmosphere will cause an increase in pH, but a negligible change in alkalinity. Variation in pH therefore, can also be used as a surrogate measure of changes in dissolved CO_2 when linked to average alkalinity values (Neal *et al.*, 2002a). Previous studies illustrate a strong inverse relationship between pH and EpCO$_2$ (Neal *et al*., 1998b,c; Howland *et al.*, 2000). To assess the degree of diurnal variation in dissolved CO_2, in-stream EpCO$_2$ was also calculated from pH data sampled at 15 minute intervals from October 2002 to June 2004. Measurements of pH were obtained at sites P3, P5, P7 and P9 in the Pang catchment and at site L5 and the streamflow gauge at Shaw in the Lambourn catchment. The method of calculation used (Neal *et al.,* 1998b), also required alkalinity/Gran alkalinity and, preferably,

temperature data. For this purpose, in-stream alkalinity was assumed to be constant and calculated for each site from samples analysed previously. Daily temperature data were obtained from the LOCAR weather station at site P3 in the Pang.

Results and discussion

VARIATION IN STREAM EPCO$_2$

Figure 2 illustrates long-term variation of calculated EpCO$_2$ for site P9 in the lower Pang. Data between July 1997 and October 2002, taken from Neal *et al.* (2000), have been added to measurements from the present study for October 2002 to June 2004. In addition to a marked diurnal variation identified by Neal *et al.* (2004b), levels of dissolved CO$_2$ dip in the summer months and peak in the winter months. Significant inter-month variation also occurs, perhaps because under wetter conditions the less permeable geology of the site in the lower reaches of the Pang catchment promotes rainfall runoff. If the long term variation in dissolved CO$_2$ at this site is representative of the variation in the catchments studied, then the period of study was one of increased variability. Catchment averaged EpCO$_2$ over the studied period was 19.8 in the Pang, compared to 16.8 in the Lambourn.

Variation of catchment-averaged monthly EpCO$_2$ for the Pang and Lambourn is shown in Figs. 3 and 4. These figures represent the mean dissolved CO$_2$ in samples collected at all sites in a catchment, in a given month. The standard deviation boundaries represent both in-month variability (temporal) and variability between sites (spatial). The higher standard deviation observed for the Pang catchment represents greater spatial variability (mean monthly s.d. between sites = 10.3), as opposed to temporal variability
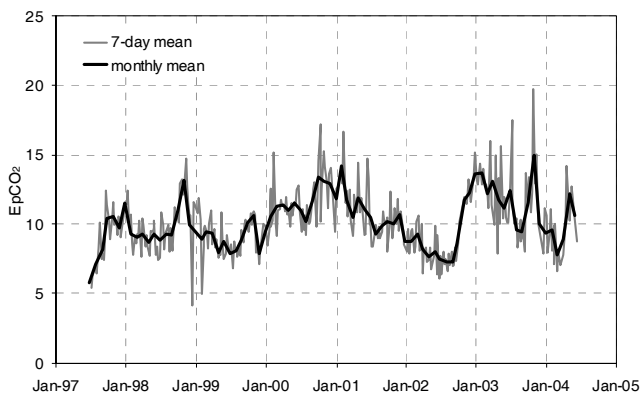

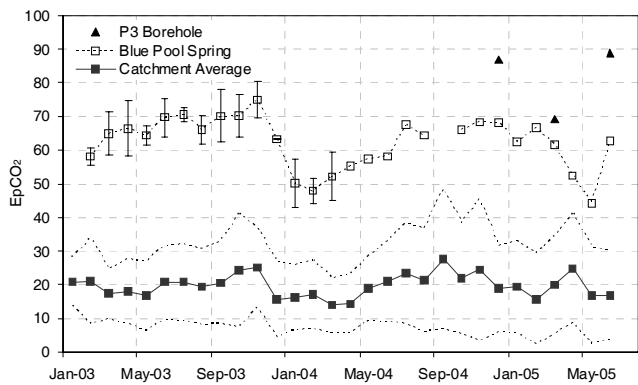Fig. 2. *Monthly and 7-day mean EpCO$_2$ at site P9 in the Pang catchment.*

Fig. 3. *Variation in averaged stream-water dissolved CO$_2$ (s.d. boundaries indicated), compared to dissolved CO$_2$ in spring and borehole sampled waters in the Pang catchment.*
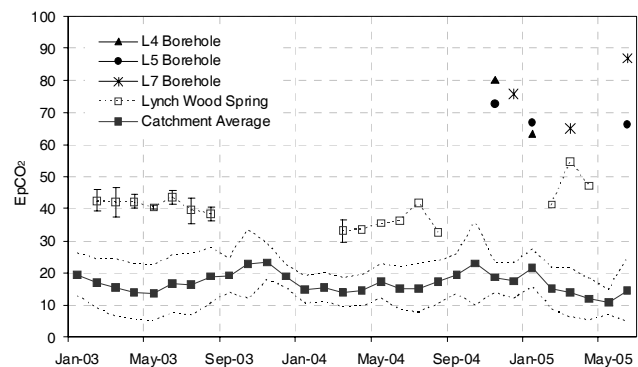

Fig. 4. *Variation in averaged stream-water dissolved CO$_2$ (s.d. boundaries indicated), compared to dissolved CO$_2$ in spring and borehole sampled waters in the Lambourn catchment.*

(mean monthly s.d. of all sites = 3.4). Both temporal and spatial variability is lower in the Lambourn catchment: variability between sites (mean monthly s.d. = 6.9) is still greater than variability in sites (mean monthly s.d. = 2.7), but to a lesser degree than samples taken from the Pang. EpCO$_2$ data for bore-hole and spring water sampled in each catchment are also shown in Figs. 3 and 4. The EpCO$_2$ calculated for spring-water samples was at least twice that calculated for river water samples (mean EpCO$_2$ of 62.2 at the Blue Pool spring in the Pang, and 40.3 at Lynch Wood springs in the Lambourn). Groundwater samples retrieved from boreholes at P3 and L7 exhibited mean EpCO$_2$ values of 81.8 and 76.2, respectively.

For both rivers, catchment averaged in-stream EpCO$_2$ was minimal in May of 2003, 2004 and 2005, when streamflow in the rivers was near its maximum. Conversely, catchment averaged in-stream EpCO$_2$ was at a maximum between September and November in 2003 and 2004, when streamflow in both rivers was low. This seasonal variability

may also be amplified by increased plant, macrophyte and algal activity in the river-bed in summer months (Neal *et al.*, 2002a), which promotes the breakdown of dissolved or particulate organic carbon (Neal *et al.*, 1998a). This seasonal variation is also observed in water samples taken from springs in each catchment, indicating that water being delivered to rivers via springs is also influenced by microbial activity that is more intense in summer.

The temporal variation in $EpCO_2$ at selected sites in the Lambourn and Pang catchments (Figs. 5 and 6) confirms that the trend of increasing stream $EpCO_2$ through the summer occurs at most sampled sites. This is particularly obvious for the sites in the Lambourn catchment (Fig. 5) which exhibit a relatively small range of variation between sites throughout the period of study. However, the relative ranking of $EpCO_2$ at sampling sites in each catchment may change with time relative to the location of the nearest active source of groundwater input. For example, low flow conditions in the upper Lambourn between September 2004
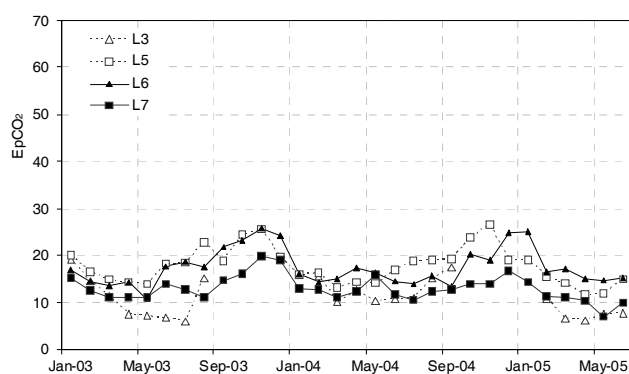
and January 2005 (as indicated by the cessation of flow at L3), led to increased $EpCO_2$ at L5 and L6, as springs in that area became the dominant source of streamflow. When streamflow in the upper catchment recommenced, $EpCO_2$ at these sites fell again as a higher proportion of streamflow consisted of groundwater from the upper catchment that was closer to atmospheric equilibrium.

In the Pang catchment, larger differences in $EpCO_2$ between sample sites are due to a greater number of groundwater springs contributing to streamflow. Where springs join the stream under low flow conditions, in-stream dissolved CO_2 is more significantly affected. For example, the mean monthly $EpCO_2$ calculated for P3 is ten times the atmospheric equilibrium than that of P7 (Fig. 6), even though a greater volume of groundwater actually enters the river channel just upstream of P7 (at Blue Pool). In-stream $EpCO_2$ at each site will, therefore, be a function of the distance of the site from the nearest upstream input of groundwater; the volume and CO_2 concentration of groundwater entering the stream; the volume and CO_2 concentration of water already in the stream; and the rate at which CO_2 will degas from the stream into the atmosphere.

A summary of downstream variation in mean $EpCO_2$ for the period studied is shown for the Pang and Lambourn in Figs. 7 and 8, respectively. Also shown is the mean flow accretion ($m^3 s^{-1} km^{-1}$) between the sites in each catchment. $EpCO_2$ was generally high at upstream sites in both rivers (P2 and P3 in the Pang and L1 in the Lambourn). Increases in stream $EpCO_2$ between each site correlate well with streamflow accretion. The increase in $EpCO_2$ between sites P6 and P7, representing the input from the Blue Pool springs, for example, corresponds to a streamflow accretion of approximately 0.15 $m^3 s^{-1} km^{-1}$. Similarly, Fig. 8 shows an increase in $EpCO_2$ between L3 and L4 in the Lambourn. This level of dissolved CO_2 is conserved through sites L5 and L6, representing a more diffused input of groundwater to the river, which is characteristic of this catchment. This is reflected by mean flow accretion of between 0.07 and 0.18 $m^3 s^{-1} km^{-1}$, between L3 and L7 These findings are consistent with previous studies in this area (Bradford, 2002; Grapes *et al.*, 2005; Grapes *et al.*, 2006; Griffiths *et al.*, 2006).

For both rivers, $EpCO_2$ reaches its maximum in November and its minimum in May. The summer rise in $EpCO_2$ coincides with the fall in streamflow, which reduces the dilution of the CO_2-rich groundwater as it enters the stream. This result is similar to that of Pinol and Avila (1992) who found an inverse relationship between dissolved CO_2 and discharge in Mediterranean catchments, though lowest flows tended to exhibit greater variation in $EpCO_2$ and degassing of $EpCO_2$ tended to precipitate calcite. They also found, as

Fig. 5. *Monthly average measured $EpCO_2$ for the sites at East Garston (L3), East Shefford House (L5), Welford Park (L6), and Westbrook Farm (L7) in the Lambourn catchment.*
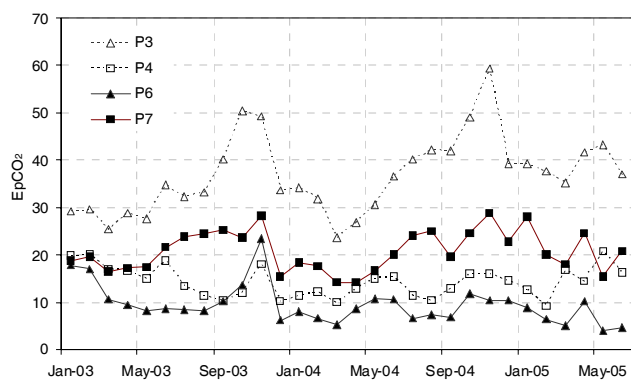

Fig. 6. *Monthly average measured $EpCO_2$ for the in-stream sites at Frilsham Meadow (P3), River Barn (P4), Jewell's Farm (P6) and Frogmore Farm (P7) in the Pang catchment.*
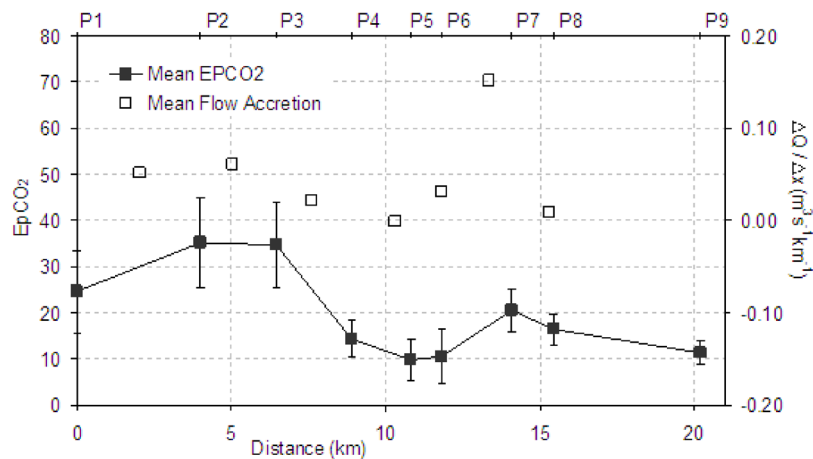
Fig. 7. *Average calculated EpCO$_2$ and mean flow accretion between sample points on the River Pang in the period Jan 2003 to Feb 2005.*
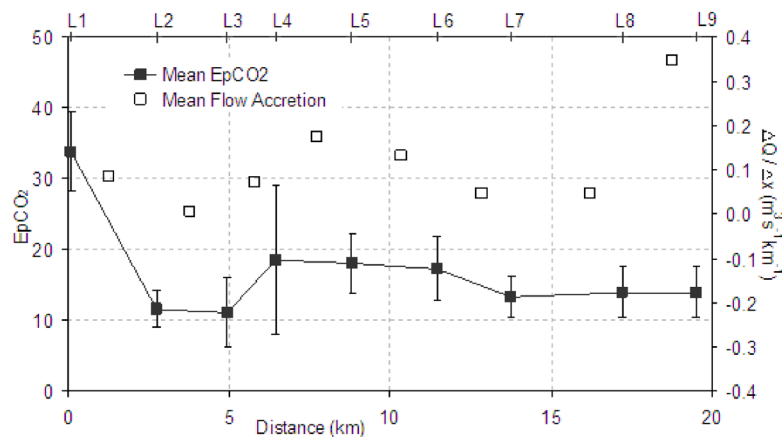

Fig. 8. *Average calculated EpCO$_2$ and mean flow accretion between sample points on the River Lambourn in the period Jan 2003 to Feb 2005.*

in this study, that this pattern is disrupted during large storm events when EpCO$_2$ increased with the storm hydrograph, in response to greater shallow groundwater delivery to the main channel system.

Standard deviation of EpCO$_2$ was higher at sites of significant but intermittent surface-groundwater interactions. This occurred, for example, at L4 in the Lambourn catchment and at P2 and P3 in the Pang catchment, where the groundwater to surface water ratio varies throughout the year in response to seasonal groundwater recharge of streams. In addition to annual variation, Fig. 9 illustrates the monthly standard deviation (n=4) of calculated EpCO$_2$ at each site for 2003 to 2004. The higher variability when streamflow is at its annual minimum and stream EpCO$_2$ is at its annual maximum, indicates that stream water-chemistry is extremely sensitive to even small increases in groundwater delivery (the variation is certainly above that expected in relation to

analytical chemistry errors). The standard deviation at the sampling site just downstream of the Blue Pool springs (P7) is small, underlining the consistency of its contribution to streamflow of the Pang as identified by Neal *et al.* (2000).

DIURNAL VARIATION

Average Gran alkalinity values determined for the Pang and Lambourn (4986 and 4532 µEq l^{-1}, respectively), were used with 15-minute resolution pH data collected from L5 and Shaw in the Lambourn catchment, and at P3, P5, P7 and P9 in the Pang catchment, to examine diurnal variation in EpCO$_2$. The method used follows one akin to that described by Neal *et al.* (2002a). At all of the sites, diurnal variation in EpCO$_2$ was a maximum between 03:00 and 10:00, and a minimum between 14:00 and 15:00. Though both catchments had the same annual average pH (6.7), temporal variability in pH (and thus EpCO$_2$) tended to differ between
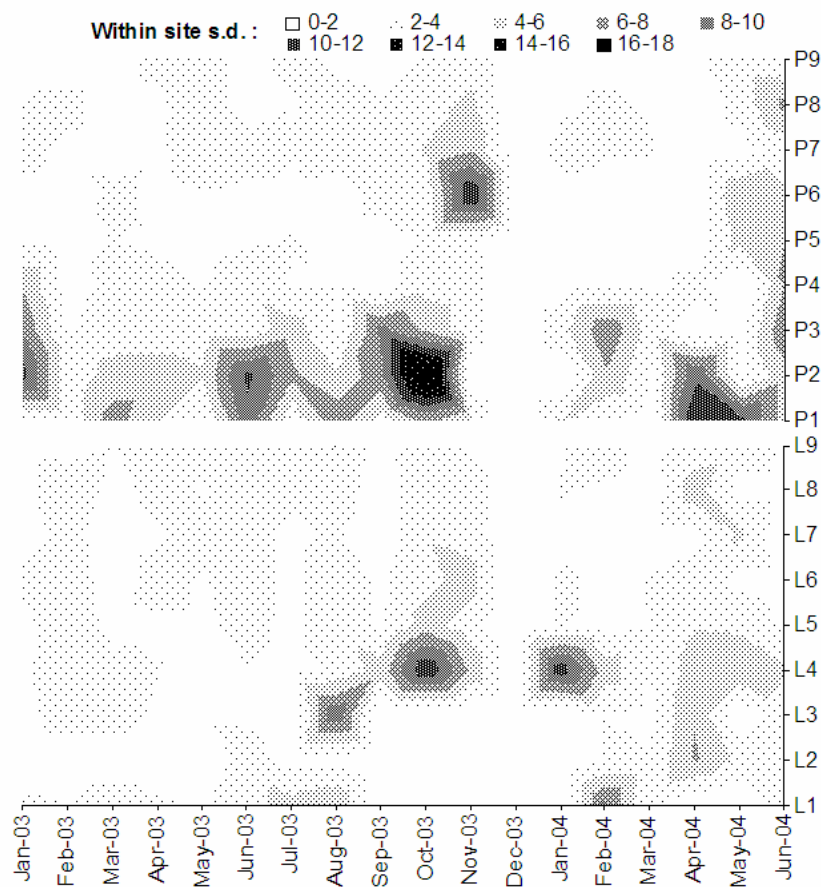
Fig. 9. *Spatial variation in standard deviation of monthly calculated EpCO$_2$ at sampling sites within the Pang and Lambourn catchment (2003–2004).*

the catchments. For example, the maximum amplitude of diurnal variation occurred in the summer at sites in the Lambourn, but in spring at sites in the Pang. Catchment-averaged changes in stream $EpCO_2$ are shown in Fig. 10 and Fig. 11. The flatter shape of the profile between evening and morning represents the duration of lower light levels and thus lower photosynthetic activity. Whilst the size of the diurnal variation is related to the amount of biological activity in the stream channel, the maximum percentage change in $EpCO_2$ (relative to the catchment average) was lower in the Lambourn, reflecting not only lower concentrations of groundwater $EpCO_2$ at many sites, but also higher volumes and velocity of streamflow, which tended to keep sites more free of vegetation.

In addition to the effect of increased biological activity, variations in stream $EpCO_2$ may be related to river flow. Seasonal trends in streamflow were similar in both catchments. In the Lambourn, high flows (>3 m^3 s^{-1}) occurred in January 2003, then decreased throughout the year to an autumn minimum of 0.38 m^3 s^{-1}. Flow then increased into the spring of 2004. In the Pang, flows

>1.21 m^3 s^{-1} in January decreased to a minimum of 0.06 m^3 s^{-1} in October and, following this minima, flows began to increase into spring of 2004. These trends of low flows in the spring/summer due to decreased precipitation, coincide with values of high $EpCO_2$. This suggests that high summer in-stream $EpCO_2$ is due both to increased biological activity and lower flows. The lower volume of 'degassed' water in the channel results in higher values of in-stream $EpCO_2$ if inputs from local groundwater sources remain constant throughout the year (such as at Blue Pool). Under such conditions, biological activity will result in higher diurnal variation than is seen at sites with lower mean in-stream concentrations of $EpCO_2$. Tables 2 and 3 show the mean, minimum and maximum seasonal (monthly) values for streamflow, pH, $EpCO_2$ and water temperature values for the Lambourn and Pang catchments during 2003. Whilst streamflow, $EpCO_2$ and pH reach their seasonal maximum and minimum turning points around May and November, maximum water temperatures (representative of photosynthetic and respirative activity) occur mid-way between these months, in August. Seasonal variability in
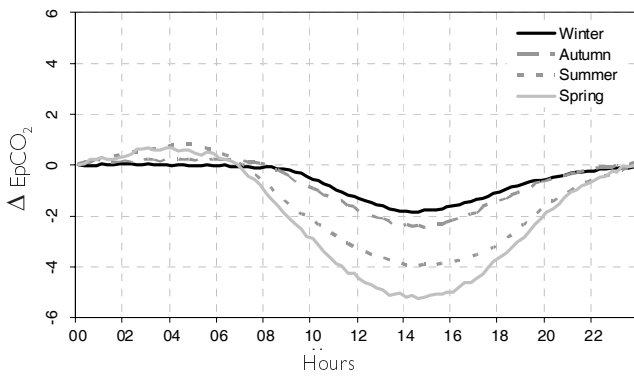
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Fig 10. *Seasonally averaged diurnal change in EpCO$_2$ as calculated from 15 minute resolution pH data measured at P3, P5, P7 and P9 in the Pang.*
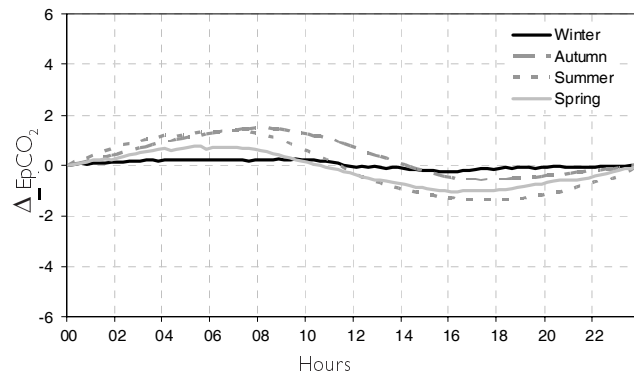

Fig. 11. *Seasonally averaged diurnal change in EpCO$_2$ as calculated from 15 minute resolution pH data measured at L5 and Shaw gauging station in the Lambourn.*

the standard deviation of the monthly averaged pH (and thus EpCO$_2$) are greater in the Lambourn than in the Pang, with the standard deviation increasing during low flow spring/summer conditions.

GROUNDWATER EPCO$_2$

Values of the EpCO$_2$ of groundwater, sampled from boreholes adjacent to the rivers studied, are similar in both catchments, ranging between 65 and 90 times the concentration at atmospheric equilibrium (Figs. 3 and 4). In contrast, a mean magnitude of EpCO$_2$ in water sampled from the Lynch Wood spring in the upper Lambourn (*c.* 100 m upstream of L1) of 40.3 (s.d.= 5.7), suggests that these springs are derived from a groundwater environment different from that of the groundwater sampled from boreholes. Mean EpCO$_2$ of Blue Pool spring water in the lower Pang (*c.* 100 m upstream of P7) was 62.6 (s.d.= 7.6).

A more detailed description of the variability of shallow groundwater was obtained by sampling groundwater from a set of boreholes at L4 and at L5 (Fig. 12). Variability in EpCO$_2$ decreased with depth at both sites and the highest levels of EpCO$_2$ occurred at depths between 2 and 6 m below ground level in surveys conducted in November. This result agrees with the pattern seen in the streams and suggests that there may be some connectivity between the surface water and shallow groundwater at this site.

Catchment-averaged increases of in-stream EpCO$_2$ correspond with increases in shallow groundwater EpCO$_2$, as indicated by samples obtained from spring water and

Table 2. The monthly physio-chemical variables for the Lambourn catchment (January-December 2003)

Variable	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
DISCHARGE (m^3 s^{-1})												
Minimum	0.21	0.17	0.33	0.20	0.14	0.12	0.02	0.00	0.00	0.13	0.00	0.12
Maximum	5.53	3.49	3.11	1.86	1.78	1.22	0.94	1.02	0.86	0.55	0.73	0.97
Mean	3.08	2.03	1.78	1.15	0.83	0.62	0.41	0.39	0.41	0.40	0.38	0.55
pH												
Minimum	7.31	7.20	7.20	7.23	7.22	7.22	7.24	7.24	7.42	7.23	7.36	7.45
Maximum	7.83	7.91	8.05	8.27	8.10	8.15	8.19	8.27	7.89	7.77	7.72	7.68
Mean	7.63	7.66	7.71	7.77	7.76	7.68	7.70	7.64	7.63	7.60	7.56	7.61
EPCO$_2$												
Minimum	12.2	8.2	7.3	5.8	6.1	5.2	5.6	4.5	13.7	9.1	15.4	15.1
Maximum	39.2	45.7	49.0	45.2	41.5	45.9	47.6	42.2	33.3	55.3	39.9	25.1
Mean	19.2	19.0	17.7	16.5	16.1	19.5	18.8	20.2	20.6	23.9	24.6	20.5
WATER TEMPERATURE (°C)												
Minimum		8.3	9.8	9.0	9.6	10.1	10.7	12.2	8.7	6.7	6.2	9.1
Maximum		10.1	11.6	11.8	13.4	13.4	15.3	22.5	15.7	12.4	13.5	9.8
Mean		9.6	10.6	10.7	11.5	12.0	13.2	15.6	10.8	9.2	9.6	9.3

Table 3. The monthly physio-chemical variables for the Pang catchment (January-December 2003)

Variable	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03	Jul-03	Aug-03	Sep-03	Oct-03	Nov-03	Dec-03
DISCHARGE ($m^3 s^{-1}$)												
Minimum	0.19	0.50	0.11	0.05	0.08	0.10	0.06	0.03	0.01	0.00	0.00	0.01
Maximum	1.82	1.88	1.26	0.99	0.81	0.58	0.47	0.32	0.33	0.20	0.21	0.58
Mean	1.21	1.19	0.73	0.56	0.44	0.29	0.21	0.13	0.09	0.06	0.07	0.18
pH												
Minimum	7.37	7.11	7.10	7.10	7.10	7.10	7.10	7.10	7.06	7.00	7.04	7.21
Maximum	7.84	7.85	8.12	8.08	8.35	8.12	8.24	8.16	8.15	8.22	7.98	8.12
Mean	7.62	7.60	7.71	7.72	7.77	7.67	7.67	7.70	7.66	7.60	7.51	7.73
$EpCO_2$												
Minimum	11.3	12.9	7.5	6.3	2.3	7.2	6.3	6.9	7.2	6.4	8.7	5.5
Maximum	40.2	60.7	74.5	78.8	67.9	75.6	72.8	71.2	78.3	81.0	81.7	63.3
Mean	20.8	24.2	21.6	22.3	20.5	24.2	25.2	23.7	25.7	29.8	31.1	20.2
WATER TEMPERATURE (°C)												
Minimum	6.1	7.4	9.5	10.5	10.2	10.5	10.5	8.1	5.2	6.9	4.2	
Maximum	9.6	10.7	13.4	16.9	18.8	18.9	23.6	19.2	13.4	12.1	10.6	
Mean	8.2	9.1	10.4	12.6	13.6	13.8	15.0	11.9	9.8	9.7	7.1	
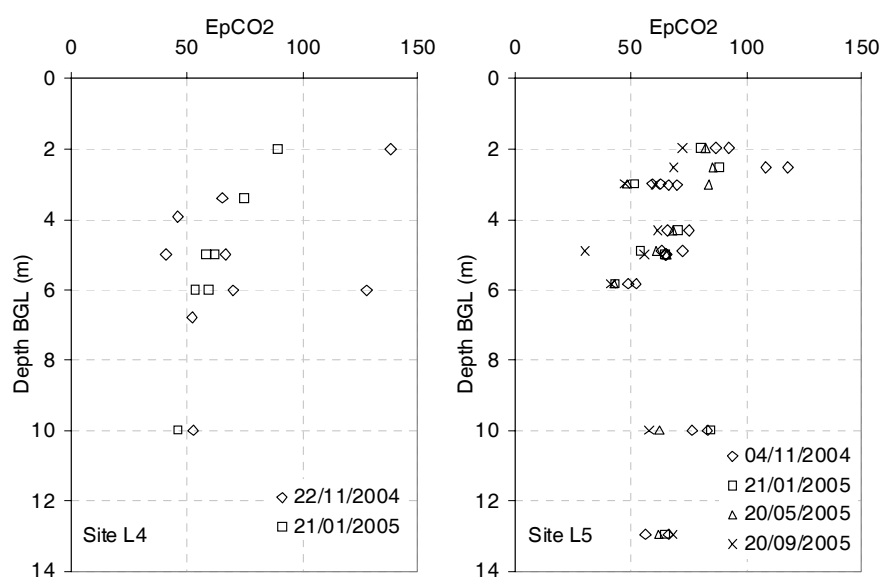
Fig. 12. *EpCO$_2$ sampled from borehole at site L4 and L5 in the Lambourn between winter 2004 and autumn 2005.*

shallow boreholes in both catchments. The Blue Pool spring, for example, shows an increase in $EpCO_2$ of approximately ten times the atmospheric equilibrium between May and September in 2004, a period in which mean river $EpCO_2$ saw a comparable increase. This pattern is repeated in the Lambourn, where stream $EpCO_2$ between L1 and L5 shows good correlation with $EpCO_2$ at Lynch Wood spring. This effect may be due to mixing of surface and groundwater, and microbial activity within the hyporheic zone. The groundwater samples obtained from shallow boreholes at sites L4 and L5 in November 2004 (Fig. 10), indicate greater variability at depths of between 2 and 6 m at this time of year.

Conclusion

A better understanding of surface-groundwater interactions is crucial for the effective management of groundwater-fed rivers. To date, the description of such interactions has been limited by a lack of readily available data regarding the extent and nature of such interactions. In this study, it is suggested that a simple sampling strategy, together with a laboratory analysis method for calculation of $EpCO_2$, could improve understanding of surface-groundwater interaction in riparian areas of permeable lowland catchments.

Using measurements of river flow, pH, and average Gran alkalinity, semi-quantitative analysis to characterise the extent of surface-groundwater interaction in a catchment was achieved. The spatial variation in surface-water $EpCO_2$ was related predominantly to flow accretion due to the inflow of CO_2 rich groundwater. CO_2 production and consumption due to biological photosynthetic activity was not significant enough to mask the net difference in dissolved CO_2 between most sites (max. diurnal variation in $EpCO_2$ = –5.25). Changes in $EpCO_2$ between sample sites could therefore be related directly to the delivery of groundwater from diffuse or point-source locations in both the Lambourn and the Pang. The results indicate that the source of groundwater in these two catchments is of different origin. The Pang for example, exhibits higher levels of $EpCO_2$ in groundwater, spring water and stream water.

Seasonal variation of in-stream $EpCO_2$ due to biotic photosynthetic activity was greater in the Pang, but followed groundwater $EpCO_2$ closely in both the Lambourn and Pang — again confirming a high level of surface–groundwater interaction in these catchments. The assessment of the diurnal $EpCO_2$ variation using high-resolution pH data showed an early morning maximum and a mid-afternoon minimum. This is consistent with maximum respiration (release of CO_2 into the water column) during darkness, and photosynthesis (removal of CO_2 from the water column) during the daytime. Diurnal variation is at its highest in the spring/summer; which is consistent with the study by Neal *et al.* (2002a) which shows that large diurnal patterns of change in dissolved CO_2 were maximal during the summer months.

This paper assesses the dynamics of surface–groundwater interactions, and thus, the extent of processes related to changes in dissolved CO_2 in the Pang and Lambourn. This new information on the spatial and temporal variability of $EpCO_2$ in the Pang and Lambourn catchments at a number of different scales may help in assessing the variability in calcite saturation of the rivers studied, which in turn may be used to describe the potential for phosphorous co-precipitation and the so-called 'self-cleansing' potential of

Chalk rivers (Neal, 2001b, 2002). Similarly, as CO_2 degassing affects the pH of water bodies, the estimates of dissolved CO_2 may be a measure of the propensity of a stream to carry metal contaminants relative to processes of dissolution and precipitation (Runkel *et al.*, 1996).

This paper confirms the appropriateness of using a simple water sampling strategy to identify areas of increased surface-groundwater interaction in Chalk catchments. Such a method may well be a simple but effective tool in improving scientific understanding of catchment-scale processes of major aquifers in the UK, a need identified in the main objectives of the LOCAR project. This is particularly relevant for the study and management of water resources in lowland permeable catchments where competition in socio-economic demands can lead to increased stress on water-dependent ecology.

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