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Radon in Chalk streams: Spatial and temporal variation of groundwater sources in the Pang and Lambourn catchments, UK

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Summary Variations in dissolved ^{222}Rn (radon) concentrations in rivers and groundwater are observed in the Cretaceous Chalk catchments of the Pang and Lambourn. Stream radon concentrations and flow data were used to model radon inputs to rivers from groundwater, with the modelled radon input concentrations (C_I) varying between 0.2 Bq l^{-1} and 3.8 Bq l^{-1}, consistent with measured groundwater values. Groundwater in both catchments was found to have higher and more variable radon concentrations (2–12 Bq l^{-1}) in the near surface, weathered horizons, compared to a consistent 1 Bq l^{-1} from the solid Chalk. The variations in C_I can be related to flow generation pathways and hydrological events. In the Lambourn, the radon budget is controlled by diffuse groundwater inputs, supporting the hypothesis that the alluvial aquifer plays a greater role during periods of high accretion. The Pang is more complex than the Lambourn having a combination of diffuse and point source inputs, with spring inputs dominating both flow and radon signatures in the lower part of the catchment. Significant temporal and spatial variations were determined for C_I in both catchments reflecting their differing geologies and flow regimes. One use of radon in hydrology is the determination of groundwater discharges to rivers, but the observed variations in C_I mean this approach may not be appropriate to all situations and that changes in source need further evaluation. Nonetheless, radon is shown to be a useful tracer of flow paths and processes within these catchments.

Introduction

River–groundwater interactions are an important part of the hydrological cycle from both ecological and water resource perspectives. The supply of water to rivers, and

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the processes by which this take place, have implications for nutrient and pollutant transport, ecological quality and the water supply for abstraction and recreational purposes. Chemical tracers are a valuable tool to aid our understanding of these processes. Here we examine the use of one such tracer, the natural radionuclide ^{222}Rn, to investigate river–groundwater interactions in the Chalk aquifer of southern England.

Radon is a radioactive noble gas that is produced by radioactive decay of radium. There are three naturally occurring isotopes ^{219}Rn, ^{220}Rn and ^{222}Rn, which are daughters of ^{223}Ra, ^{224}Ra and ^{226}Ra, respectively. In this paper we are concerned only with the ^{222}Rn isotope; the ^{219}Rn and ^{220}Rn isotopes have half-lives of less than one minute, and are therefore precluded from our analyses. From here on the term 'radon' refers solely to ^{222}Rn and 'radium' to ^{226}Ra, which are members of the ^{238}U decay series. Uranium occurs ubiquitously, albeit at a range of concentrations, in all rock types. Radium is produced by the decay of ^{238}U, but due to chemical and physical processes it may be separated from its parent and hence be enriched in some mineral phases, for example in surface coatings (Ball et al., 1991).

Radon can emanate from radium bearing minerals and, subsequently be dissolved in and transported by groundwater. The release of radon from mineral grains may occur via a number of mechanisms, including ejection from the surface during the decay process (alpha recoil) or diffusion through pores and cracks. Radon produced from the decay of surface bound radium may be more readily available to groundwater in the saturated zone, and therefore the exact geochemical distribution of radium may affect radon signatures in the groundwater. For a more detailed discussion of radon's sources and modes of entry into groundwater the reader is referred to Osmond and Cowart (1992) and Porcelli and Swarzenski (2003).

Surface waters usually contain very low concentrations of dissolved radium and, hence, similarly low concentrations of dissolved radon (Osmond and Cowart, 1992; Porcelli and Swarzenski, 2003). As a result, groundwater discharges into rivers can often be easily detected by their characteristic radon enrichment with respect to the surface water. Once discharged to a river, the radon activity rapidly decreases as a result of radioactive decay and degassing to the atmosphere, allowing successive inputs to be observed along the course of a river. As a consequence, radon has the potential to be used as a tracer of groundwater–surface water interactions.

Radon has unique characteristics that distinguish it from other natural tracers; it is a noble gas and is therefore chemically and biologically inert. Consequently, budgeting is relatively straight forward, as there are no sinks (other than radioactive decay and degassing) and no sources (other than radium decay). Nonetheless, degassing is an important process; the partition between dissolved and gaseous radon is approximately 1:4 (Clever, 1979) and so the equilibrium is in favour of loss from the river to the atmosphere. It is therefore necessary to estimate the rate of loss from a surface water body due to degassing.

Radon's short half-life ($t_{1/2}$ = 3.82 d) means that it can be used to determine the recent history of groundwater. Radon will reach radioactive equilibrium with its parent (radium) after 25 d. Therefore, the radon activity of groundwater will be indicative of the environment within an approximate travel time of 25 d from the point of sampling. This fact can be exploited to identify different sources of groundwater.

Radon has been used as a tracer in a number of studies investigating groundwater inputs to streams and rivers (e.g., Cook et al., 2003; Ellins et al., 1990; Genereux et al., 1993; Hamada, 1999), as well as to other hydrological situations such as the determination of groundwater flow rates (Hamada, 2000) and the assessment of infiltration of river water to banks (Macheleidt et al., 2002). Thus its utility as a tracer has already been demonstrated in a range of hydrological situations, providing information about flow paths and residence times.

The aims of this paper are to assess the potential for radon to be used as a hydrological tracer for river–groundwater water interactions in lowland Chalk catchments. There is currently little or no data published regarding radon in the rivers of Chalk catchments, which are of high ecological importance in the UK. Here we present data for groundwater and river water of the Pang and Lambourn catchments in West Berkshire, UK. We seek to evaluate the spatial and temporal variations in radon in these two catchments and propose mechanisms to explain these variations.

This study has been carried out as part of the wider Lowland Catchment Research (LOCAR) programme, supported by the UK Natural Environmental Research Council (NERC). LOCAR was initiated to further our understanding of lowland permeable catchments through a multi-disciplinary research programme aided by the provision of infrastructure in selected catchments.

Study area and background

The Pang and Lambourn catchments are located in West Berkshire in southern England, and are both tributaries of the River Thames. The Pang flows directly into the Thames, while the Lambourn flows into the Kennet which continues for a further 30 km before it flows into the Thames 12 km downstream of the Pang. The Pang and Lambourn have topographical catchment areas of 171 km^2 and 234 km^2, respectively (Griffiths et al., 2006).

The River Pang flows initially to the south (Fig. 1) to the River Barn site before turning east for 11 km; it then flows north for a final 3 km before reaching the Thames. Although the source of the river channel is at Compton village, flow is only observed from here in wetter years (Bradford, 2002), with the perennial head being found approximately 3 km north of Frilsham Meadow. The Lambourn flows in a south-easterly direction from its source in the village of Lambourn for 23 km before its confluence with the Kennet. The perennial head is found approximately 3 km upstream of East Shefford and migrates following fluctuations in the local groundwater table (Grapes et al., 2006). All river and site distances referred to in this paper are measured as distances downstream of the villages of Compton and Lambourn for the Pang and Lambourn, respectively.

Flow in both catchments is predominantly derived from groundwater, which feeds the rivers either diffusely or from point sources. The extent of point and diffuse sources differs between the two catchments. In the Lambourn accre-

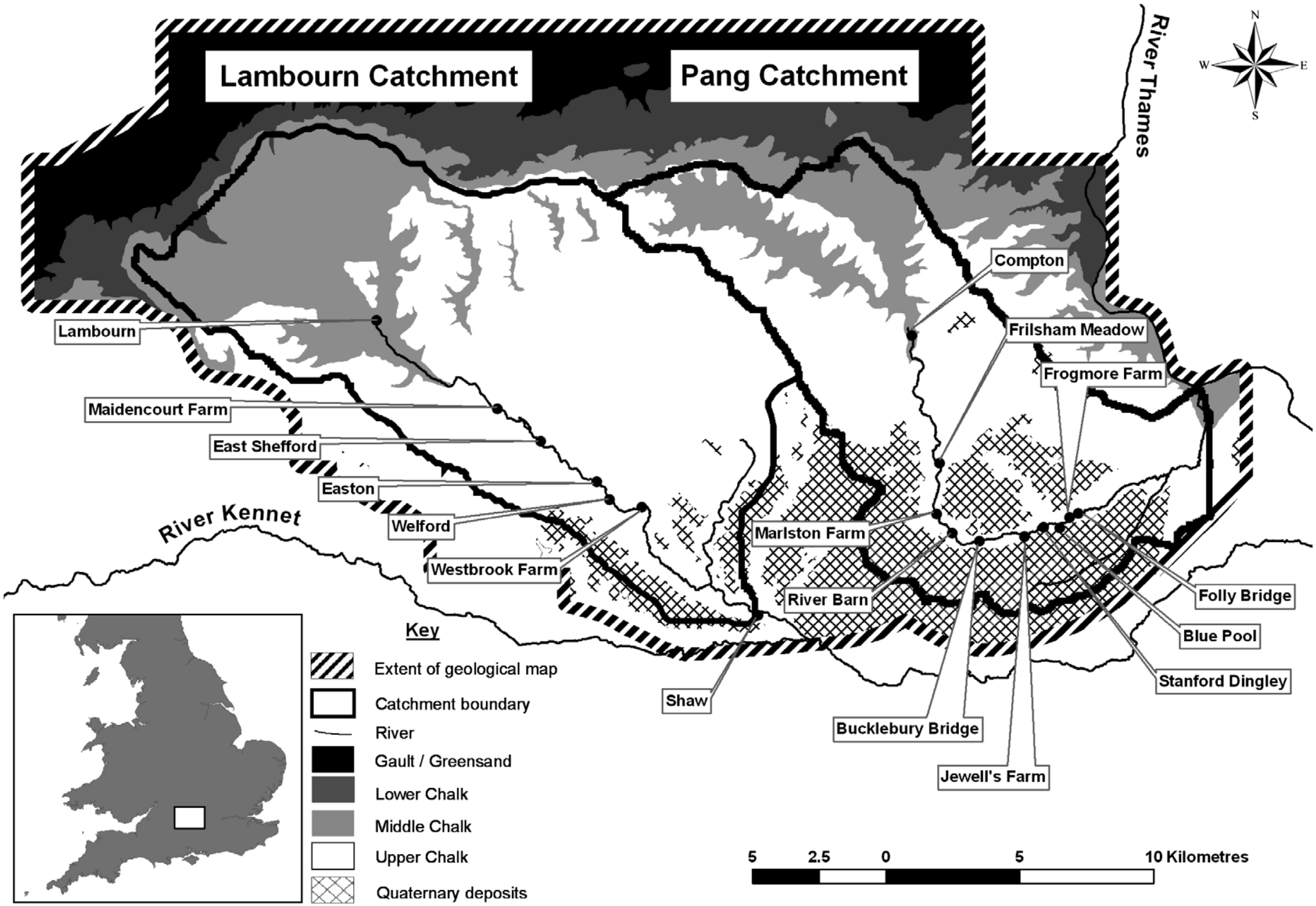

Figure 1 Map of catchment areas showing stream sample sites, borehole array locations, other measurement sites and main geological units.

tion is relatively steady throughout the catchment (Grapes et al., 2005), although several zones of higher accretion exist, which coincide with dry valley features (Griffiths et al., 2006). These observations indicate the diffuse nature of inputs to the Lambourn. In contrast, in the Pang catchment there are several spring inputs, particularly in the lower reaches, which contribute significantly to the base flow of the river (Griffiths et al., 2006).

Cretaceous Chalk (referred to hereafter as Chalk) dominates the solid geology of both the Pang and Lambourn catchments (Fig. 1). The Chalk is divided into three major formations; the Upper, Middle and Lower Chalks. The Lambourn rises in the Middle Chalk and this formation makes up most of the upper catchment. The rest of the catchment is characterised by Upper Chalk with some small areas of overlying Quaternary deposits from the Reading Beds and London Clay (Bradford, 2002). The river corridor has a bed of fluvial deposits, which increase in depth through the catchment (Grapes et al., 2005). In contrast the Middle and Upper Chalk form the upper Pang catchment, and in the lower catchment there are far more extensive Quaternary deposits overlying the Chalk.

The river water chemistry of both catchments is calcium bicarbonate type, typical of groundwater fed Chalk rivers. Associated with Ca in the Chalk rock matrix are also other members of the alkaline earth metals, namely Mg, Sr and Ba. Although, Sr and Ba are potentially useful indicators of groundwater inputs in Chalk catchments, Mg can also be associated with atmospheric and anthropogenic sources, such as sewage effluent, which can blur groundwater signatures. The groundwater is usually calcium saturated, becoming super-saturated in rivers with loss of CO_2 due to degassing and biological interactions (Neal et al., 2004).

The differences in physical characteristics between the Pang and Lambourn catchments give rise to differing flow characteristics and chemical responses. Both rivers show seasonal minimum and maximum flows, which usually occur in October—November and March—April, respectively. Griffiths et al. (2006) observed that the Lambourn catchment has a greater total discharge than the Pang, even when normalised to catchment area (Lambourn = 0.0074 $m^3\,s^{-1}\,km^{-2}$; Pang = 0.0035 $m^3\,s^{-1}\,km^{-2}$). Assuming equivalent rainfall, this analysis indicates that the Pang has a proportionally smaller groundwater catchment than the Lambourn.

Neal et al. (2004) noted that the Pang demonstrates a much greater and more rapid response to rainfall events, which can be seen in its sharply spiked hydrograph. Fig. 2 shows discharge data during the study period for (a) the Lambourn at Shaw and (b) the Pang at Bucklebury, combined with effective precipitation based on values from the UK Meteorological Office Rainfall and Evapotranspiration Calculation System (MORECS) (Hough and Jones, 1997) estimates. The smoother response of the Lambourn can be seen in comparison to the relatively sharp spikes in the Pang hydrograph, which coincide with precipitation events. This difference in behaviour demonstrates the effect of the relatively impermeable Quaternary deposits in the Pang, which give rise to shorter residence times of rainwater through runoff and preferential flow paths. The contrastingly small response to rainfall in the Lambourn may either be the result of a dampening effect by the permeable Chalk slowing transit times of rainfall to the river, or as a result of a greater proportion of rainfall infiltrating and recharging the aquifer.

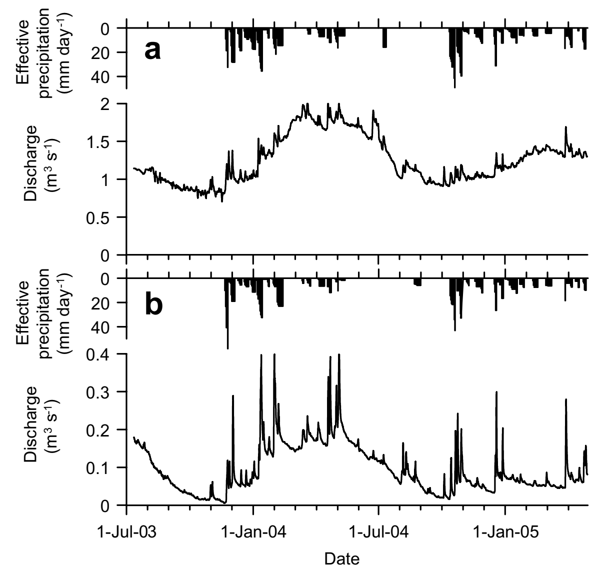

Figure 2 Daily discharge measurements from LOCAR gauging stations in the two catchments. (a) River Lambourn at Shaw — effective precipitation based on MORECS estimates using data from Lambourn. (b) River Pang at Bucklebury — effective precipitation based on MORECS estimates using data from Compton.

Methods

Field sampling

Sampling was conducted quarterly in the Pang and Lambourn catchments over the period May 2003—February 2005. On each occasion, discharge was measured at the river sites and water samples were collected for the analysis of dissolved radon. In addition, groundwater was sampled from a number of riparian zone borehole arrays.

River sites were located at convenient sampling locations and distributed along the course of the rivers between 1 and 3 km apart (Fig. 1). To ensure contemporaneous data all sites were located downstream of the perennial heads of the rivers. Flow at river sites was measured using a handheld acoustic Doppler flow meter (SonTek FlowTracker). Surveys were carried out following the guidance of the relevant British Standard (ISO748:2000,) and Environment Agency R&D Technical Report W4 (Ramsbottom et al., 1997) to provide discharge data that is accurate to ±10%.

For the analysis of radon, individual water samples were taken directly from river sites and the Blue Pool spring by immersing a pre-weighed standard 600 ml screw cap glass bottle carefully avoiding any aeration, and then sealing the full bottle under the water surface to exclude all air.

To ensure that there was no stratification of radon in the river; samples were taken by filling bottles from the surface as described above and also by pumping 5-l samples, with a submersible pump, from the surface, mid-depth and the bottom of the water column. Triplicate samples were taken for radon analysis of river water during these tests to ensure consistency in river sampling and analysis. No stratification was observed in the river samples and replicate samples were in good agreement.

Groundwater sampling sites were selected to be in the vicinity of the riparian zone to allow sampling of water that was within the shortest possible travel time of the river. In the Lambourn samples were taken from three borehole array sites at Westbrook Farm, Maidencourt Farm and East Shefford. Sampled piezometers ranged in depth from 1.5 to 12 metres below ground level (mbgl). In the Pang samples were taken from two sites at Frilsham Meadow and Frogmore Farm where piezometers ranged in depth from 3.5 to 20 mbgl.

Groundwater samples were taken from piezometers using a submersible pump fitted with a suitable length of hose and located in middle of the screened section. First the piezometer was purged of three times the volume of the screened section to remove any stagnant water. Then 5 l water were carefully pumped in to a bucket from which the standard 600 ml bottle was filled. Samples were taken in triplicate to ensure that the radon concentrations measured were representative and had stabilised after purging, with a further three screen volumes being removed between each sample. The radon stratification test carried out on river samples (outlined above) was also used to confirm that no radon losses were occurring as a result of the pumping process.

Analytical methods

Dissolved radon activities were determined by toluene extraction and liquid scintillation spectrometry (LSS) as described in Pates and Mullinger (2007). Errors for individual river water samples are based upon counting statistics (Friedlander et al., 1981). Errors for borehole samples are standard deviations of triplicate sample results.

In order to confirm the absence of dissolved ^{226}Ra in water samples a number of river and borehole samples were kept sealed for 30 d and then re-extracted. This procedure allows all excess radon present to decay and any remaining activity is due to the ingrowth of radon from radium present in the water. No detectable dissolved radium was found in any of the river or borehole water samples.

The radon present at the time of sampling was calculated as a decay-corrected mean. Radon in water is measured by its specific activity in Becquerels per litre (Bq l^{-1}). Specific activity is directly related to the concentration of a particular radionuclide and for simplicity is referred to hereafter as concentration.

Modelling approach

To analyse the results of the river radon data, a simple mass balance model was used, similar to those of Cook et al. (2003) and Genereux and Hemond (1990). When calculating a mass balance for radon, as opposed to a conservative tracer, two additional factors must be considered, i.e., the rate of loss of radon due to radioactive decay and the rate of loss from the river's surface to the atmosphere (degassing).

The mass balance of radon along the stream length is given by

$$\frac{\partial QC}{\partial x} = IC_I + kdwC - \lambda dwC, \tag{1}$$

where Q is the stream discharge (m^3 s^{-1}), C is the stream radon activity (Bq l^{-1}), x is the distance downstream (m), I is the groundwater inflow rate (m^{3}m^{-1} s^{-1}), C_I is the input water radon concentration (Bq l^{-1}), k is the gas transfer coefficient (s^{-1}), w is the stream width (m), d is the stream depth (m) and λ is the radioactive decay constant (1.8245×10^{-6} s^{-1}).

The change in flow with distance is given by

$$\frac{\partial Q}{\partial x} = I - Ew, \tag{2}$$

where E is the evaporation rate (m s^{-1}). This equation assumes no additional surface water inputs such as tributaries, which is valid in the case of these permeable lowland catchments and all inputs estimated from flow surveys are assumed to be of groundwater origin. Estimates of evaporation made from MORECS potential evaporation data (UK Met Office) and the physical dimensions of the Pang and Lambourn rivers show that evaporation accounts for loss of less than 0.0005% of flow accretion over the considered reaches and can therefore be ignored.

Previous workers have used a variety of groundwater measurements to estimate a single value for the radon concentration of input water (Cook et al., 2003; Ellins et al., 1990). This single value has then been used to calculate the rate of groundwater accretion along selected river sections, with flow observations being used to verify the modelling results. Here we seek to examine how the input concentration of radon (C_I) varies spatially and temporally within and between catchments. Therefore, we do not assume a groundwater activity, but use flow observations to calculate C_I.

Eq. (1) is solved to determine the input concentration (C_I) that minimises the least squares misfit between model results and stream radon observations for a given survey. If we assume a uniform input concentration along the reach then the optimisation process seeks a single value of C_I that is consistent with the observed spatial variation in river radon concentrations. Alternatively, sub-reaches may be assigned, each with different input concentration. Increasing the degrees of freedom in this way may lead to a marginally better fit between data and model, but results in more uncertainty in the final result due to non-uniqueness of the solution. We have therefore approached the problem by selecting the simplest model that is consistent with the data.

In the Lambourn catchment a model which allows a single value of C_I was considered most suitable. There are no distinct geological boundaries that are seen to cause any major changes in the way the river system behaves as it runs through the catchment.

In the Pang catchment, there are significant Quaternary deposits overlying the Chalk in the lower catchment (Fig. 1). When modelling radon in the Pang, this geological distinction led to the river being divided into two reaches: an upstream section from Frilsham Meadow at 6.5 km to Jewell's Farm at 11.8 km and a downstream section from Jewell's Farm to Folly Bridge at 14.1 km (Fig. 1). This boundary was chosen on the basis of observed flow and CO_2 profiles in the Pang (Griffiths et al., 2006, 2007), which indicate a distinct change in behaviour near Jewell's Farm, associated with the spring systems found downstream of this point (Bradford, 2002). This two reach model allows each to have an independent value of C_l.

One of the greatest difficulties in using radon, and other dissolved gases, for budgeting and tracer work in river systems is accounting for the impact of atmospheric transfer (in either direction). The rate of loss from the river surface or dissolution of atmospheric gases into stream water is dependant upon the gas transfer coefficient (k) with units of time^{-1}. The final equilibrium water concentration depends on atmospheric concentrations of the gas in question. In the case of radon, atmospheric concentrations are considered to be negligible due to its short half-life. There are several different approaches that can be taken to estimate degassing from streams, and it is important to carefully consider the choice of method.

Methods for estimating k include:

- the use of a range of empirical models are available that describe k as a function of physical characteristics of the river, many of which are described in Genereux and Hemond (1992);
- estimating degassing on a particular river or reach where it is assumed no groundwater interacts with the river system; the loss of radon from the reach is then attributed only to degassing (e.g., Genereux and Hemond, 1992);
- direct measurement using an artificially introduced gaseous tracer such as propane or SF_6 (e.g., Wanninkhof et al., 1990), used in conjunction with a conservative tracer, such as salt, to account for dilutions effects, however, this type experiment is complex and costly to set up;
- deriving a degassing coefficient from modelling exercises by fitting to observed data (e.g., Cook et al., 2003).

Here we have chosen a combination of approaches, evaluating several empirical models against a set of observations made upon a 1-km reach of the River Pang at Frilsham Meadow (Fig. 1). This reach differs from the majority of other reaches in the Pang and Lambourn as it is relatively hydrologically isolated from the aquifer system. Flow observations made over the sampling period indicate that there is often negligible accretion or loss along its length. During one such period of negligible accretion (10 February 2005) river water samples were collected at eight sites along the reach and analysed for radon. The results show a steady decrease in radon concentration with distance and, therefore, these data were used to evaluate the empirical models reviewed by Genereux and Hemond (1992) for use in the Pang and Lambourn rivers. From this exercise two gas transfer models (Negulescu and Rojanski, 1969; O'Connor and Dobbins, 1958) were selected as they bracket the stream radon observations. The equations for the gas transfer coefficients of these models are

$$k = 3.1642 \times 10^{-5} u^{0.5}/d^{1.5}, \tag{3}$$

and

$$k = 8.8472 \times 10^{-5} (u/d)^{0.85} \tag{4}$$

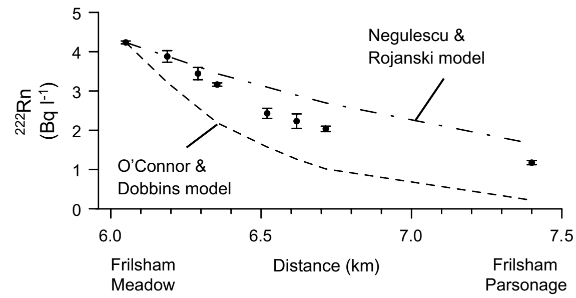

Figure 3 Comparison of degassing models for Frilsham (Pang) sub-reach radon survey. Symbol indicates observed stream radon concentration. Error bars show ± one standard deviation based on three replicates.

for the O'Connor and Dobbins and Negulescu and Rojanski models, respectively, where u is the mean stream velocity (m s^{-1}) and d is the mean stream depth (m). Note that in Eqs. (3) and (4) the multiplier 0.7 is introduced to account for physico-chemical differences between oxygen (for which the models were derived) and radon (Genereux and Hemond, 1992).

These two empirical models allowed a reasonable degree of uncertainty in the gas transfer coefficient to be estimated (Fig. 3). Given the two extreme models for degassing, Eq. (1) was solved using a finite difference approximation (see, for example, Cook et al., 2003). A spatial discretisation of 25 m was adopted for this solution. Stream depth, width and mean velocity measured at each site along the reach were interpolated (assuming linear variation) to assign properties in Eqs. (1), (3) and (4) at each node of the finite difference grid. Then, the radon concentration of the lateral input (C_l) was determined by optimising the model given the observed stream radon concentration for a particular survey.

The loss and gain of water from the river is interpreted as a net linear function constrained by flow observations at each gauging site. C_l is only influenced by net water inputs to the river where it must be altered to provide the best fit to balance observed stream radon concentrations between sites. When water is lost from the river this does not affect the river radon concentration and, therefore, there is no impact upon the value of C_l.

Results and discussion

Groundwater radon

The results of groundwater radon observations in the Lambourn catchment (Fig. 4a) show a distinct vertical profile across all sites. Higher and more variable radon concentrations occur in the near surface and a general decrease in concentration is observed with increasing depth. From the borehole geological logs it can be seen that groundwater radon concentrations reflect the degree of weathering as it changes with depth. Near the surface, from 0 to 7 mbgl, there is much more weathered material overlying and mixed with weathered Chalk. This overlying material comprises a mixture of clay, sand and flint gravels and is typically heterogeneous in composition. It not only has a greater surface

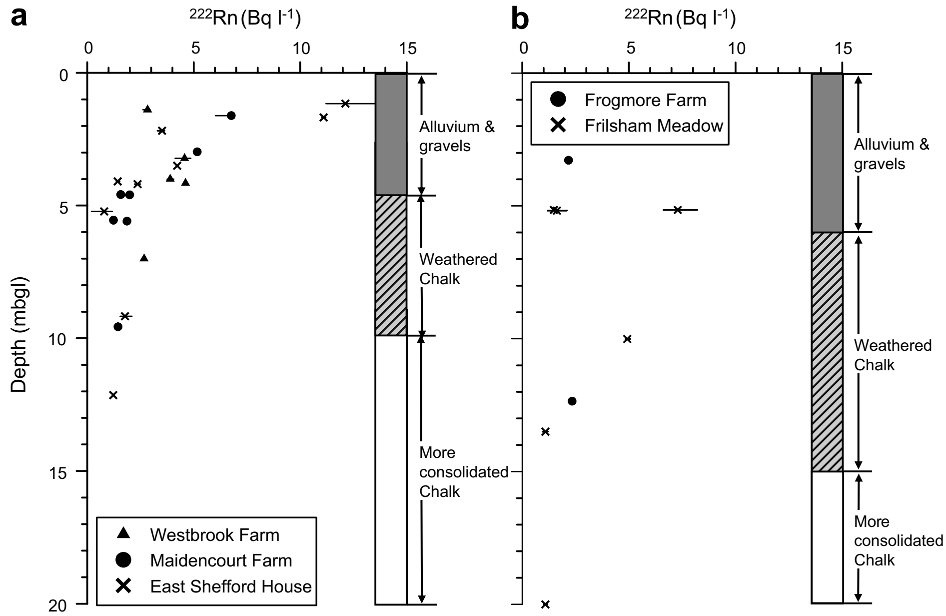

Figure 4 (a) Lambourn catchment borehole water radon concentrations. (b) Pang catchment borehole water radon concentrations. Samples collected 02 December 2004 (Westbrook Farm and Pang boreholes) and 08 January 2005 (Maidencourt Farm and East Shefford House). Symbols show average of three replicate samples. Horizontal bar for each symbol shows range of three measurements.

area for the release of radon, but is likely to contain higher radium concentrations than the Chalk, which is predominantly composed of calcium carbonate, thus leading to the higher activities of 3–12 Bq l^{-1} that are observed in the near surface. From 7 to 10 mbgl is predominantly weathered Chalk where groundwater radon concentrations tend to be below 3 Bq l^{-1}. As the more consolidated Chalk is reached, between 10 and 15 mbgl, the groundwater activity is found to be lower and more consistent, reaching a highly stable value of 1 Bq l^{-1} in the deepest samples.

Groundwater in the sampled Pang boreholes (Fig. 4b) follows a similar vertical profile to that of the Lambourn boreholes. Radon concentrations tend to be slightly higher at greater depths than at the Lambourn borehole sites, but still reach a very stable 1 Bq l^{-1} at approximately 14 mbgl. Stable radon concentrations of 1 Bq l^{-1} are seen across both catchments in piezometers screened at 15 mbgl and deeper. Some values are observed between 5 and 10 m that are slightly higher than in seen in the Lambourn, which is related to the increased weathering of the Chalk and depth of alluvial materials at the Frilsham Meadow borehole site.

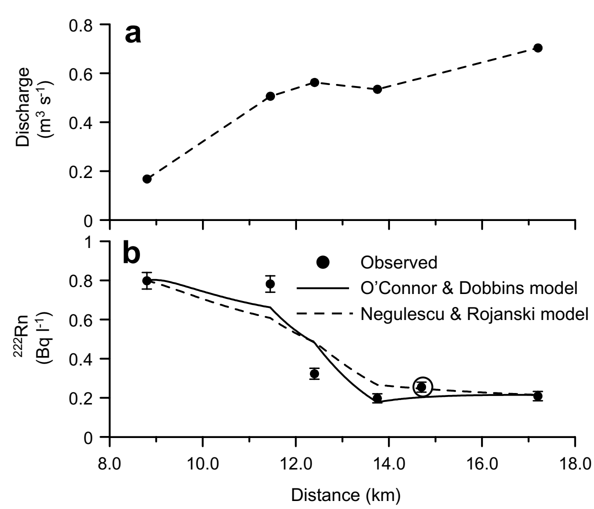

Figure 5 (a) Example stream discharge profile for the River Lambourn (data collected 17 December 2004). (b) Example stream radon profile for the River Lambourn and modelled response using the two degassing models (data collected 17 December 2004). Error bars are based on counting statistics. The circled symbol at 14.7 km shows a value that was not used to constrain the model as flow data were not available.

Lambourn

A relationship is observed between the radon concentration and discharge profiles in the Lambourn catchment (Fig. 5). The higher stream radon concentrations of 0.8 Bq l^{-1} are due to the initial inputs of radon rich groundwater to the river channel, which make up a large proportion of the total flow at this point. The continued high radon coincides with the region of higher accretion between East Shefford (8.8 km) and Welford (11.5 km). Between Welford and Westbrook Farm at (13.8 km) accretion is reduced and radon also decreases, to 0.2 Bq l^{-1}. As accretion increases again further downstream the radon concentration stabilises at 0.2 Bq l^{-1}, with groundwater inputs balancing losses due to degassing.

The ranges of stream parameters for the degassing models in the Lambourn were d 0.13–0.53 m and u 0.09–0.51 m s^{-1}. These values resulted in degassing constants of

2.95–33.79 d^{-1} for the O'Connor and Dobbins model and 2.20–16.49 d^{-1} for the Negulescu and Rojanski model.

The results of the Lambourn model (Fig. 5b) display a broad agreement with the river radon concentrations. The higher radon concentrations are maintained in the high accretion zone then decrease further downstream, where accretion is low and losses due to decay and degassing dominate. The lower reaches are in equilibrium with radon inputs being equal to losses. Here the two degassing models are in close agreement with each other and also with the circled data point, which has been included in the radon plot, but was not used to constrain the model due to the absence of flow data.

The results of the two degassing models (Fig. 6a) display good agreement on all sampling occasions, typically to within 0.5 Bq l^{-1}, except in December 2004 where they differ by 1 Bq l^{-1}. A significant variation in the radon concentration of incoming groundwater is observed over the sampling period, given that the degassing models used provide a ranged estimate of radon loss. Although the sampling resolution for radon is lower than that of the flow data, there is a noticeable similarity between changes in calculated input concentrations and flow accretion for the studied section of the river (Fig. 6b). When accretion is lower, radon input concentrations tend to be low and as accretion peaks radon inputs are also at their highest. It follows that these changes in river radon concentrations are due to changes in the net groundwater input radon concentrations to the Lambourn.

Relating the observed groundwater radon profiles to the changes in calculated groundwater input radon concentrations seen in the River Lambourn suggests that at times of higher flow accretion more inflow to the river travels through the near surface alluvial gravel deposits. Inputs during higher accretion periods are higher in radon, which indicates either a greater proportion of flow passing through the near surface alluvium or a greater residence time in this part of the aquifer. During lower flows the input concentrations return to the levels observed in the deeper piezometer water samples (1 Bq l^{-1}) and may indicate a more direct connection between the river and the consolidated Chalk during lower flows. Thus, radon may provide a useful tool in elucidating the flow paths of groundwater–surface water interactions in Chalk catchments, which can be problematic to evaluate due to anthropogenic impacts upon or the uniformity of other chemical tracers, particularly in the Lambourn.

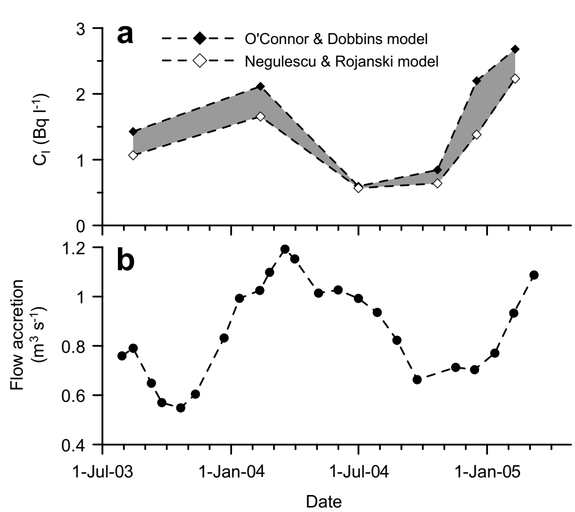

Figure 6 (a) Lambourn radon input concentrations for the two degassing models. (b) Flow accretion along radon sampled reach.

Pang

Taking firstly the river observations for the Pang (Fig. 7) it can be seen that the river behaves differently in the upstream reach between Frilsham Meadow (6.5 km) and Jewell's Farm (11.8 km) compared to the downstream reach between Jewell's Farm and Folly Bridge (14.1 km). There is little accretion along the upstream reach, with a series of marginally losing and gaining sections, which contrasts with the downstream reach where there is consistent input of 0.2–0.4 m^3 s^{-1} (Fig. 8a) due to spring sources. The upstream reach exhibits seasonality in the flow, with accretion occurring during higher flow periods and net flow loss during lower flow periods. Accretion occurs for only a short period in the second half of the study period due to poor winter recharge. The lower reach in contrast has a steady accretion, which is not seen to vary seasonally. Both reaches show two rainfall response peaks in January and May 2004.

The variations in flow through the catchment are reflected in the radon profile (Fig. 7b). Relatively high river radon concentrations of 1.7 Bq l^{-1} are observed at the point of initial groundwater input to the river channel. This concentration falls sharply by 8 km as the river loses flow and degassing and decay processes dominate. The radon concentrations remain at 0.1–0.2 Bq l^{-1} as the river marginally gains and loses water until Jewell's Farm. There is then an increase in radon concentration below 11.8 km associated with the spring inputs occurring in this area.

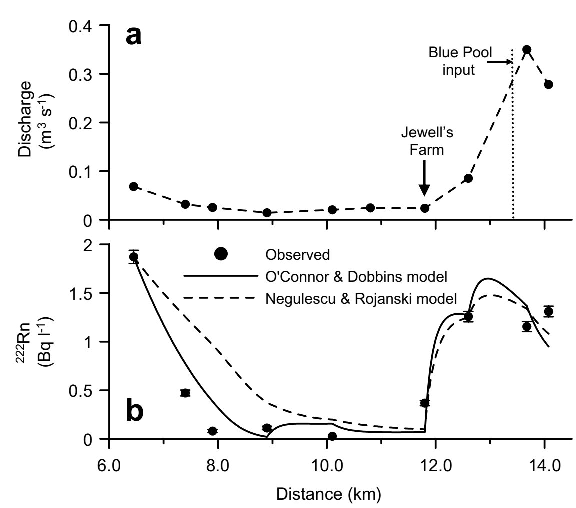

Figure 7 (a) Example stream discharge profile for the River Pang (data collected 22 October 2004). (b) Example stream radon profile for the River Pang and modelled response using the two degassing model (data collected 22 October 2004). Error bars are ± one standard deviation based on counting statistics.

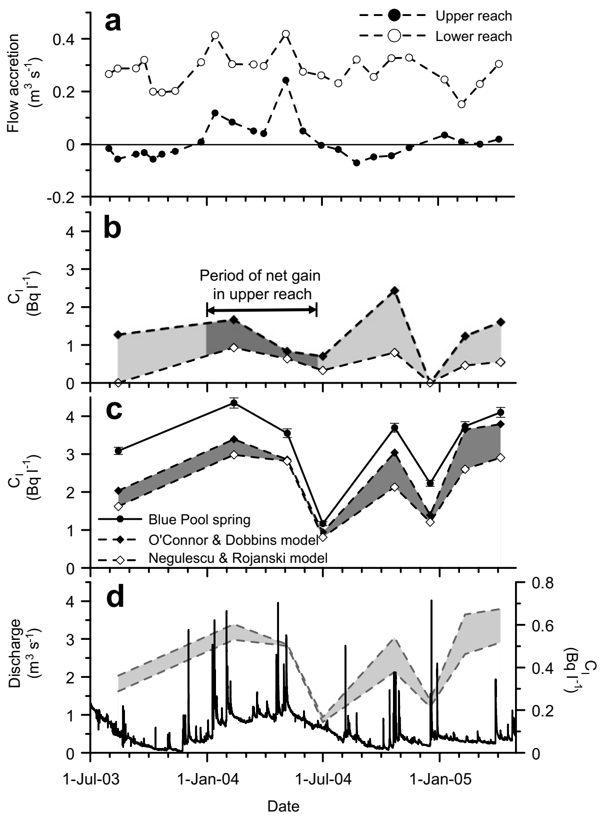

Figure 8 (a) Pang accretion in the two designated reaches over the study period. (b) Upstream reach radon input concentration. (c) Downstream reach radon input concentration, compared with the Blue Pool (spring) concentration. Error bars are ± one standard deviation based on counting statistics. (d) Comparison of model radon groundwater input in the downstream reach of the River Pang and observed daily flows at Bucklebury.

The ranges of stream parameters for the degassing models in the Pang were d 0.08–0.52 m and u 0.04–0.48 m s^{-1}. These resulted in degassing coefficients of 0.76–59.94 d^{-1}, for the O'Connor and Dobbins model, and 0.87–24.78 d^{-1}, for the Negulescu and Rojanski model.

The Pang model results closely match the river radon concentrations (Fig. 7b) at all points for both degassing models. There is a rapid decay in the first 2 km where degassing and decay dominate. There are then low but stable radon concentrations from 9 to 11.8 km, after which there is a sharp increase as groundwater with an enhanced radon concentration enters the river. The model of Negulescu and Rojanski (1969) slightly underestimates degassing in the first 2 km, but then aligns closely with that of O'Connor and Dobbins (1958). The upstream reach input concentrations are generally low and poorly constrained by the two degassing models (Fig. 8b). In the upstream reach there is generally closer agreement between the degassing models at times of higher flow when the upstream reach has a net accretion. In the lower catchment input concentrations are higher and the degassing models are in closer agreement (Fig. 8c). Radon inputs in the downstream reach are higher than those of the upstream reach demonstrating that radon input concentrations vary spatially in the Pang.

The calculated inputs for the downstream reach reflect observations made at the Blue Pool spring (Fig. 8c). The downstream modelled radon input concentrations closely correlate with the changes in spring concentrations, but are slightly lower. Thus, it can be concluded that the majority of water entering the river in this area is of spring origin and analogous to that of the Blue Pool in radon concentration. The reason that calculated input concentrations are slightly lower than the observed spring water is likely to be due to degassing that occurs before the water enters the main river (the Blue Pool feeds a cress bed pool complex so that discharge is not directly to the river). Fig. 8d indicates that a number of sampling occasions coincide with significant rainfall events, which produce large spikes in the Pang hydrograph. The events do not appear to influence the spring radon concentrations in a consistent manner with high and low radon corresponding with peak and base flow conditions. It is also notable that the temporal variation in radon occurs despite apparently constant accretion in the downstream reach.

The temporal variation in spring radon concentration and the corresponding changes in river radon will be due to the flow path of water issuing from these springs. The interactions of theoretically high radon pore water (Low, 1996a) along with lower activity water similar to that observed in the boreholes, and at times newer catchment water from rainfall runoff, create a mixture from which the components are difficult to separate and is beyond the scope of this work. However, it is clear that there are significant temporal changes in spring water radon concentrations and that they may be influenced in the short term by rainfall events, but in an inconsistent manner, based on our current understanding.

Comparing the Pang and Lambourn catchments

Groundwater radon is comparable between the two catchments with the Pang showing slightly higher concentrations at depth (Fig. 4). This corresponds to the increased depth of weathering at the Pang sampling sites.

The results from the two catchments show that despite their close proximity the radon signatures are very different and are impacted by variations in geology. In the Lambourn a relatively homogeneous system is observed, with lower river radon through the catchment. It may be that the alluvial gravels in the Lambourn valley are influencing this homogeneity; spring systems that exist in the Lambourn will not be as directly connected to the river and the radon signal from them will be attenuated by interaction with the alluvial gravels.

In contrast, the Pang is more complex and can be divided into two discrete reaches that have different hydrological controls under the range of conditions observed. Each of these reaches must be treated differently to accurately model the radon behaviour of the whole catchment. The upper Pang has little or no accretion under low flows and gradual accretion during higher flow periods, with generally lower radon input concentrations similar to those observed in the Lambourn. The upper part of the Pang is still influenced mainly by the Chalk in a similar manner to the Lambourn, whereas the lower Pang has more point source inputs from springs. These spring inputs contribute a consistently high volume to the total catchment discharge and have higher radon concentrations. This spring influence is most apparent in the Jewell's Farm to Blue Pool section where the course of the river brings it into very close proximity with the Quaternary deposits. These deposits bound the river to the south and it is at this boundary that the springs occur as water escapes from beneath the confining layers.

In the Lambourn it was found that the radon inputs varied over the sampling period and this temporal variability precludes deriving a single input radon concentration for the catchment from previous observations. The Pang is controlled in very different ways in the two reaches and this is readily observed in the radon signal in the main river and the calculated values of C_I. The influence of Quaternary deposits in the lower Pang is not only reflected in its differences from the Lambourn hydrograph, but also in the radon signature in the river. The radon concentrations in the spring discharge are more analogous to those of shallow groundwaters than of the deeper Chalk.

The systems controlling flow generation and radon in the Pang catchment are complex. Influences of diffuse groundwater transfers between the aquifer and river combine with the point source inputs from springs, which are subject to very different controls. Diffuse inputs will be more closely related to changes in the local water table as seen in the Lambourn (Grapes et al., 2006). Point source inputs may be controlled by changes in the aquifer, but are also seen to have a rapid response to catchment inputs and the springs reflect a combination of these.

There is no clear seasonal variation in the input radon concentrations observed in the Pang data. When calculated input concentrations are compared to the river hydrograph over the sampling period (Fig. 8d) it can be seen that a number of the sampling occasions coincide with large spikes in the river discharge. The data resolution is not adequate to be able to evaluate exactly how river radon responds to hydrological events. It may be that the rainfall response of the Pang in this data set is masking any seasonality that exists, where as the dampened rainfall response of the Lambourn allows these to be observed at lower temporal resolution. Here the recharge capacity of the Chalk helps to prevent rapid inputs of water to the river during and immediately after rainfall events. This buffering means that river sampling in the Lambourn is less impacted by rainfall events than in the Pang.

Implications for previous radon studies and future research

We have shown that the different flow conditions and inputs must be considered when deciding how to constrain catchment models. The more diffuse nature of the Lambourn compared to the point source discharges to the Pang create different flow regimes and must be modelled accordingly. The differences between and within the study catchments illustrates that spatial variation occurs in radon inputs as well as accretion. Most previous studies, with the exception of Genereux et al. (1993) who discriminate between vadose and saturated zone water, have made use of single values for radon input concentrations. While it may be possible to generalise at the scale of catchments described by Ellins et al. (1990) and Cook et al. (2003), this is not always the best approach, as seen in the River Pang.

We have seen significant spatial variation in near surface groundwater radon concentrations while deeper Chalk groundwater is highly consistent. Ellins et al. (1990) observed large variation in radon concentrations in a karst aquifer, while Low (1996b) and Younger and Elliot (1995) observe higher and more variable radon concentrations for deeper groundwater samples from the Chalk in other areas.

Temporal variability in radon input concentrations is observed to both catchments, which is important given that we wish to understand the controls on flow generation in the Pang and Lambourn and how they change in space and time. Part of the key to understanding how radon reflects these changes, particularly in the Lambourn, lies in our observations of the groundwater of the alluvial aquifer. Here high, variable groundwater radon concentrations exist and are therefore a potential source of variation in river radon concentrations. The apparent relationship between accretion and river radon concentrations in the Lambourn supports this hypothesis.

The variation in C_I during the study period would have a significant impact upon estimates of discharge made from radon observations. Simulating groundwater inputs to the Lambourn by varying C_I within the range calculated by the model in this study found that significant over- and underestimation of groundwater inputs was made. From a calculated groundwater C_I of $1.5\,\mathrm{Bq\,l^{-1}}$ in the Lambourn, underestimation of C_I to $0.8\,\mathrm{Bq\,l^{-1}}$ would produce a 100% overestimation of flow. Underestimation of groundwater radon concentration is a possible error to make based on our observations of the deeper Chalk groundwater, where concentrations are consistently low ($\sim 1\,\mathrm{Bq\,l^{-1}}$). Care must therefore be taken when making assumptions about the stability of radon concentrations in groundwater entering river systems of this type.

Spring inputs to these rivers differ significantly in radon from the more diffuse seepage inputs. Springs, which are more directly connected to the rivers (e.g., in the Pang), show strong radon signals in the stream water, whereas diffuse inputs, such as seen in the Lambourn, provide a more uniform radon profile. In the Lambourn this uniformity may be due to general seepage from the Chalk through the alluvium or to attenuation of springs that do exist, but whose water has a significant flow path through the alluvial aquifer before discharging to the river. Temporal variation of major spring inputs has a significant impact on river radon concentrations in the Pang. The responses of these springs to events is complex due to multiple flow paths and sources, i.e., fracture flow, runoff and the dual porosity of the Chalk feeding them.

Radon therefore has useful applications in observing input processes from the Chalk and alluvial aquifers of these catchments. It may be possible to determine the duration of short (up to 25 d) residence times of water in the alluvial gravels (c.f. Macheleidt et al., 2002). With additional chemical data radon may also be applied to determining the degree of mixing of alluvial aquifer water with Chalk aquifer groundwater (c.f. Genereux et al., 1993).

Conclusions

Temporal and spatial variations in radon inputs to rivers are observed in the Pang and Lambourn catchment. These variations reflect seasonal changes in flow accretion in the Lambourn and changes in spring radon concentrations in the Pang. Spatial variation in radon in these catchments reflects the geological controls on flow generation and the different types of inputs that occur (diffuse and spring). These results show that caution must be used when applying radon to flow estimation, but that useful information about flow paths and flow generation can be gained from river radon observations. There is still much to understand about temporal changes in river and groundwater radon, particularly in the complex spring systems of the Pang, but we have shown that the alluvial aquifer of the Lambourn may have an important role in influencing stream radon concentrations and flow generation.

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