

# Using Chlorofluorocarbons (CFCs) And Sulphur Hexafluoride (SF<sub>6</sub>) To Characterise Groundwater Movement And Residence Time In A Lowland Chalk Catchment

\*Daren C Gooddy, W George Darling, Corinna Abesser and Daniel J Lapworth

*British Geological Survey, Maclean Building, Wallingford, Oxon, OX10 8BB, UK*

\*Corresponding author. Tel +44-1491-692 328

Fax +44-1491-692 345

*E-mail address:* [dcg@bgs.ac.uk](mailto:dcg@bgs.ac.uk) (D.C. Gooddy)

## **Abstract**

Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF<sub>6</sub>) provide a technique for dating groundwater up to 50 years old. When used together, CFCs and SF<sub>6</sub> can help to resolve the extent to which groundwater mixing occurs, and therefore provide indicators of the likely groundwater flow mechanisms. Modelling shows that diffusive retardation of these tracers is likely to be low owing to the high moisture content of the chalk unsaturated zone. Data collected from groundwater and surface water from a lowland Chalk catchment in southern England suggest that groundwater movement can be divided into three regimes: on the interfluves of the catchment, 'piston' flow dominates with a bulk groundwater age of several decades; at the valley bottom, there is mixing between shallow groundwater and stream water; and in an intermediate zone between the top and the bottom of the valley there is approximately 3:1 mixing between new and pre-tracer groundwaters. A conceptual model of groundwater movement has been developed to describe the catchment processes. Surface water—groundwater interactions are found to take place down to depths in excess of 10 metres bgl. The nitrate found at the greatest depth are thought to originate from the mid 1950s.

## **1 Introduction**

Within the European Union, the Water Framework Directive is a major driver for change in catchment management. In the UK, the focus of a large body of experimental hydrology has been on uplands (Soulsby et al., 2002; Neal et al., 2004), whereas the majority of management pressures lie in the lowland areas. Particular problems arise for permeable lowland catchments. The scientific understanding of the major UK aquifer systems is relatively poor, and the available tools for integrated modelling of surface water-groundwater interactions are limited. In response to these issues, the Lowland Catchment Research programme (LOCAR) was conceived and initiated (Wheater and Peach, 2004).

It is necessary to have a basic understanding of the transport dynamics of the particular sub-surface environment to understand the groundwater system. Previous studies of groundwater flow in the Chalk have considered the aquifer scale (Edmunds et al., 1987) and have used geochemical and isotopic tracers effective for waters with bulk residence times up to several thousand years old. The residence time of groundwater in a lowland catchment system is likely to be much less, with mixing of recently recharged groundwater and interaction between groundwater and stream water. Consequently different tools are required to investigate this type of environment.

The concentration in groundwater of anthropogenic atmospheric trace gases such as chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF<sub>6</sub>) can provide information on groundwater residence times and mixing processes for waters up to fifty years old (Cook and Solomon, 1997; Busenberg and Plummer, 2000). Compared with some groundwater 'dating' techniques, CFCs and SF<sub>6</sub> can be rapidly determined, they require no sophisticated sampling equipment, and analysis is relatively simple. They therefore provide a cost-effective contribution to understanding groundwater in lowland catchments.

A number of studies have been undertaken using CFCs and/or SF<sub>6</sub> to understand groundwater flow in the US (e.g. Cook et al., 1995; Johnston et al., 1998; Plummer et al., 2001; Rademacher et al., 2003) and in Europe (Oster et al., 1996; Bauer et al., 2001; MacDonald et al., 2003; Bockgård et al., 2004). To date, however, only one study has been undertaken in the Chalk of southern England (Darling et al., 2005).

The objective of this paper is to show how a conceptual model for groundwater movement in part of a Chalk lowland catchment can be developed through the combined use of CFCs and SF<sub>6</sub> as groundwater tracers. In particular the paper examines the likely mixing processes that are taking place and the degree of surface water—groundwater interaction. Only by understanding flow regimes and processes will it be possible to advance the numerical tools available and so improve river basin management.

## **2 Background and Theoretical Considerations**

### *2.1 The Chalk Aquifer*

The Chalk is the major aquifer in the UK providing 15% of the water supply nationally and up to 35% regionally in the south and east. It is a soft microporous and fractured calcium carbonate aquifer with high intergranular porosity (25-45%) but low intergranular hydraulic conductivity as a result of small pore-neck size. The fracture component has low porosity (0.1-1%) but can increase the hydraulic conductivity by up to three orders of magnitude (Price et al, 1982). In the unsaturated zone of the

Chalk of Southern England, recharge has an apparent downward velocity of ~ 1 m/a (Darling and Bath, 1988), probably achieved rather discontinuously by relatively immobile porewater flooding into fractures when tensions permit (Price et al., 2000). However, faster 'preferential' flow through fractures may be important especially for transport of trace contaminants such as pesticides (Goody et al., 2001).

The Chalk aquifer is a highly complex natural system (Foster and Milton, 1974; Price et al 1993) and consequently is very difficult to measure or sample in a systematic manner in either the saturated or unsaturated zones. Recharge is probably localized due to the highly inhomogeneous nature of the shallow weathered Chalk (Lloyd et al., 1981). Although this may not have particularly significant resource implications, it is an important consideration when attempting to model or predict the movement of water and contaminants through the Chalk.

### 2.2 *Dating Groundwaters Using CFCs and SF<sub>6</sub>*

Groundwater dating with CFCs and SF<sub>6</sub> is based on historical data for the atmospheric mixing ratios of these compounds over the past 50 years (Figure 1), their Henry's Law solubilities in water, and measurement of CFC and SF<sub>6</sub> concentration in water samples. The apparent age of a groundwater is then dependent on the Henry's Law constant calculated at the recharge temperature, which is generally taken to be equivalent to the annual average air temperature. Figure 2 shows concentrations of CFC-11, CFC-12 and SF<sub>6</sub> in pmol/L and fmol/L respectively, expected in groundwater recharged between 1940 and 2000, at sea level, and in equilibrium with atmospheric air for a recharge temperature of 10°C.

### 2.3 *Contamination*

Contamination of groundwater with chlorofluorocarbons appears to be the greatest limitation to CFC dating. Groundwater samples from residential, industrial or disused landfill sites can contain concentrations of chlorofluorocarbons above modern atmospheric concentrations (Busenberg and Plummer, 1992; MacDonald et al., 2003). Morris et al. (2005) demonstrate that less than 1/10<sup>th</sup> of the amount of CFC-12 present in a single domestic refrigerator could contaminate a moderately sized aquifer to more than 10 times current atmospheric levels. Fortunately SF<sub>6</sub> appears to be less susceptible to anthropogenic contamination, although Busenberg and Plummer (2000) have identified possible natural causes of elevated concentrations.

### 2.4 *Excess Air*

Groundwaters usually contain excess air (EA) in addition to air dissolved by simple equilibration between rainfall and the atmosphere. The reason for this EA is the forcible solution of air bubbles trapped in soil or rock as water infiltrates (Heaton and Vogel, 1981). This process supplements the

equilibrium gas content with the direct, non-equilibrium addition of air, causing dissolved gas contents to rise in inverse proportion to their solubility. Accordingly, this has most effect on sparingly soluble gases: for example, each addition of 0.5 cc of air to 1 litre of equilibrated water raises the SF<sub>6</sub> concentration by 5.3 %, while CFC-11 and CFC-12 are only raised by 0.1 and 0.4 % respectively. Most groundwaters contain a few cc/L of excess air and therefore SF<sub>6</sub> concentrations can rise significantly, requiring correction to arrive at the 'datable' component. For the present study this has been based on measuring N<sub>2</sub>/Ar ratios, because N<sub>2</sub> is only about half as soluble as Ar and therefore the ratio rises as excess air increases. Provided no denitrification is occurring, the rise in N<sub>2</sub>/Ar above its 10°C equilibrium value of 37.9 can be used to calculate the SF<sub>6</sub> excess due to EA. Figure 3 shows the relationship between the N<sub>2</sub>/Ar ratio and the correction factor that must be applied for SF<sub>6</sub> and CFC-12 respectively to compensate for the EA. The excess air effect on CFC-11 is insignificant.

### 2.5 *Unsaturated Zone Processes*

The movement of atmospheric trace gases through the unsaturated zone may occur both in the liquid and gas phases (Cook and Solomon, 1995). When the unsaturated zone is relatively thin, the unsaturated zone composition tracks that of the troposphere (Cook and Solomon, 1995; Engesgaard et al., 2004). In deeper unsaturated zones of simple porous aquifers, there is a lag time for the diffusive transport of both CFCs and SF<sub>6</sub> through the unsaturated zone. The time lag is a function of the tracer diffusion coefficients, tracer solubility in water, and soil water content (Weeks et al., 1982; Cook and Solomon, 1995). In a deep unsaturated zone the apparent tracer age will be older than the true age of recharge.

Figure 4 simulates the time lag for SF<sub>6</sub>, CFC-11 and CFC-12 passing through a 25-metre unsaturated zone with a velocity of 1 m/a typical of the Chalk (Darling and Bath, 1988), calculated with a one-dimensional flow equation with gas- and liquid-filled porosities of 0.05 and 0.3 respectively using the model of Cook and Solomon (1995). Gas diffusion coefficients of 260, 285 and 192 m<sup>2</sup>/a were used for CFC-11, CFC-12 and SF<sub>6</sub> respectively, with the latter calculated from data given in Vulava et al. (2002). Air-water partition coefficients have been taken to be 0.51, 0.13 and 0.0095 for CFC-11, CFC-12 and SF<sub>6</sub> respectively (Cook and Solomon, 1995).

Figure 4 demonstrates that with the high moisture content and relatively high liquid phase velocity common in the Chalk, advection in the liquid phase is much greater than diffusion in the gas phase and as such, time lags are all approximately equal to the water residence times. Thus, the timescales for CFC and SF<sub>6</sub> movement through the unsaturated zone would be the same as they would be for tritium or any other tracer in the liquid phase. However, this analysis neglects the complexity of Chalk unsaturated zone flow processes (Price et al., 2000). The discontinuous flow of porewater into fractures may provide several, or even many, opportunities for the tracer 'clock' to be reset. Darling et

al. (1998) showed that modern CFC and SF<sub>6</sub> concentrations were present in Chalk unsaturated zone air even at 25 m bgl. Therefore diffusion effects could be considered minimal, with the local lithology and antecedent conditions determining the degree of interaction between tropospheric air and unsaturated zone porewaters. A better understanding of unsaturated zone processes is clearly required to resolve this issue and the degree to which retardation occurs.

### 2.6 *Groundwater Mixing Models*

Water extracted from a borehole or flowing from a spring is generally considered to be a mixture of waters from all the flow lines reaching the discharge point. The age frequency distribution and mean age of the mixture affect the interpretation of the groundwater dating methods as well as the interpretation of other groundwater solute fluxes (Böhlke, 2002). There are four hypothetical mixing models that can be typically used to describe some of the variation seen in groundwater mixtures: piston flow (PFM), exponential piston flow (EPM), exponential mixing (EMM) and binary mixing (BMM) (Cook and Böhlke, 2000; Zuber, 1986). In some cases, water reaching the open interval of a borehole or discharging from a spring is nearly uniform and can be approximated with a piston-flow model, analogous to water flowing through a pipe from the point of recharge to the point of discharge without mixing during transit. The exponential-piston model corresponds to a situation in which an aquifer receives distributed recharge in an up-gradient unconfined area, then continues beneath a down-gradient confined area. Exponential mixing can be used to describe discharge from an unconfined aquifer receiving uniform areal recharge (Maloszewski and Zuber, 1982). Binary mixing of young water with old (pre-tracer) water is one of the simplest models to consider and is perhaps the most important in many fractured-rock environments (Bockgård et al., 2004) although not all (Rademacher et al., 2003). In binary mixing, simple dilution occurs because the old fraction is assumed to be free of the tracer and, consequently, the age of the young fraction can be calculated from the ratio of the two tracers.

Comparison of multiple environmental tracer data can indicate if simple models like these are applicable. As the three atmospheric environmental tracers considered here have differing temporal patterns to their input functions (Figure 1), plots of one tracer against another can be useful in distinguishing the hypothetical groundwater mixing processes that may affect the samples, in addition to identifying anthropogenic contamination. Figure 5 show an example of the four different mixing models for a cross plot of sulphur hexafluoride with CFC-12.

## 3 **Study Area**

### 3.1 *Regional Geology and Hydrogeology*

A detailed account of the geology of the Pang-Lambourn catchment is given by Aldiss and Royse (2002). Briefly, the catchment comprises Chalk (Upper Cretaceous) underlain by a thin layer of

Upper Greensand (Lower Cretaceous) in hydraulic continuity, and sealed beneath by mudrocks of Jurassic age. The Chalk is overlain by Palaeogene deposits and superficial drift from the Quaternary.

In the catchment the Chalk matrix porosity generally decreases linearly with depth from about 45% near ground surface, to less than 25% at 100 m bgl. This is consistent with previously reported depth trends in Chalk matrix porosity (Bloomfield et al. 1995) and reflects the diagenetic grade and maximum burial depth of the Chalk. Variations from this overall trend reflect primary lithological variations such as the presence of marls and hardgrounds.

Transmissivity values for the catchment range from 1 to 3200 m<sup>2</sup>/day with a mean of 913 m<sup>2</sup>/day and a median of 600 m<sup>2</sup>/day; 25% are less than 258 m<sup>2</sup>/day and 75% are less than 1333 m<sup>2</sup>/day (Allen et al., 1997). Storativity ranges from 0.02-0.001 for the unconfined Chalk. The maximum thickness of the Chalk in the catchment is about 200 metres.

The Chalk aquifer in the study area feeds the river Lambourn which exhibits the characteristics of a Chalk groundwater dominated river system, with a slow, damped response to rainfall and 'bourne' (ephemeral) behaviour of headwater reaches (Grapes et al., 2005).

### 3.2 Site Description

The study site (PL26) consists of a series of boreholes located on either sides of the River Lambourn at Boxford (NGR 442500 172300). Figure 6 shows the location of the boreholes relative to each other and to the River Lambourn. Boreholes D, E and F are drilled in the flood plain of the river while G, H and I are located on the Chalk outcrop which rises northwards from the valley. Most of the boreholes contain two piezometers set at different depths. The boreholes used in this study all lie in an approximate north-south line.

## 4 Methodology

### 4.1 Groundwater Sampling

Groundwater samples were collected from 10 piezometers and the River Lambourn at an adjacent point in August 2004. Samples were collected using a submersible pump, with each borehole purged for roughly 3-5 well volumes prior to the sample being taken. On-site parameters (temperature, dissolved oxygen and specific electrical conductivity) were monitored in flow cells until stable readings were obtained prior to sample collection. Samples for inorganic analysis were filtered through a 0.45 µm cellulose nitrate membrane.

Samples for nitrous oxide and nitrogen/argon ratio analysis were collected by pumping groundwater through plastic tube containing a T-piece connected to a nominally 350 mL evacuated glass bulb. Once

the tube and T-piece were purged of air, the tube was opened and allowed to half fill the glass bulb. The valve was then closed and the dissolved gases allowed to partition into the headspace.

CFC and SF<sub>6</sub> samples were collected unfiltered without atmospheric contact in glass bottles contained within metal cans by the displacement method of Oster et al. (1996). This method ensures that the sample is protected from possible atmospheric contamination by a jacket of the same water.

#### 4.2 Groundwater Analysis

All analyses were carried out at BGS Wallingford. Nitrogen species were determined using automated colorimetry. N<sub>2</sub>/Ar ratios were determined by mass spectrometry based on the method of Martin et al. (1995). N<sub>2</sub>O was measured by gas chromatography with electron capture detection as detailed in Goody et al. (2002). This method has a detection limit of 2 µg/L. CFCs and SF<sub>6</sub> were measured by gas chromatography with an electron capture detector after pre-concentration by cryogenic methods, based on the methods of Oster et al. (1996) and Busenberg and Plummer (2000) respectively. The detection limit of CFC-11 and CFC-12 concentrations in water can be determined to 0.01 pmol/L, whereas SF<sub>6</sub> can be determined to 0.1 fmol/L.

## 5 Results

Selected field-measured parameters together with nitrogen species data are shown in Table 2. Temperature and dissolved oxygen both show a generally decreasing trend with depth. In both cases the highest value is recorded for the river water. Similarly the lowest specific electrical conductivity is recorded in the river and higher values are commonly found at greatest depths. Nitrate-nitrogen varies from 4.8 mg/L in the deepest sample to nearly 6.8 mg/L in the shallower samples. The mean nitrate-N concentration found in all the boreholes over this part of the catchment is 6.1 mg/L (standard deviation of 0.6 mg/L). Concentrations of N<sub>2</sub>O are typically very low (<10 µg/L) with concentrations in the deepest boreholes below the detection limit.

The presence of high concentrations of oxygen and moderate concentrations of nitrate, together with very low concentrations of nitrous oxide suggest an oxidising environment where negligible denitrification is taking place. Consequently it is feasible to use the N<sub>2</sub>/Ar ratio to compensate for excess air during recharge. Table 2 shows nitrogen/argon ratios vary from 38.9 to 41.8 (mean of 40.4 and standard deviation 0.9) which corresponds to excess air contributions of 1-4 cc/L (Figure 3). These are within the expected range based on previous studies (Busenberg and Plummer, 2000).

Table 3 shows the concentrations of CFCs and SF<sub>6</sub> found in each of the piezometers and the river water. The analyses are within a precision of ± 5% for the two CFCs and ± 10% for SF<sub>6</sub>. The data in this table have been corrected for excess air based on the measured N<sub>2</sub>/Ar ratios. Modern air saturated

water (ASW) at 10°C is calculated to have a concentration of 2.97 pmol/L for CFC-12, 5.40 pmol/L for CFC-11 and 2.3 fmol/L for SF<sub>6</sub> (based on atmospheric data from [www.water.usgs.gov/lab/cfc/background/air\\_curve.html](http://www.water.usgs.gov/lab/cfc/background/air_curve.html)). All groundwater samples have a CFC-12 and SF<sub>6</sub> concentration below modern atmospheric concentrations whereas some of the CFC-11 concentrations are above or close to modern, suggesting some anthropogenic addition of CFC-11. Both CFC-12 and CFC-11 have river concentrations greater than modern (roughly 1.5 times modern for CFC-12 and twice modern for CFC-11 based on the measured river temperature of 13°C). River concentrations for SF<sub>6</sub> are close to atmospheric equilibrium within the error of the measurement. Figure 7 shows the relationship between unsaturated zone thickness and groundwater SF<sub>6</sub> concentration expressed as a fraction of modern groundwater (measured concentration divided by ASW at 10°C). This figure suggests the fraction of modern water decreases with increasing depth to groundwater.

## 6 Discussion

Figure 8 shows a cross plot of the concentrations for CFC-12 and SF<sub>6</sub>, super-imposed on the mixing models described in Figure 5. Figure 8 demonstrates that the deep samples (G, I1, I2) all fall on, or close to, the piston flow mixing model. The samples mid-way down the catchment fall on and slightly above the exponential mixing model curve, and the samples close to the river in the flood plain lie on the binary mixing model curve or between the EMM and BMM curves. The modern fraction of these samples close to the river is between 0.7 and 0.8 (based on CFC-12 data), which would be equivalent to approximately 3 parts modern water to 1 part pre-tracer water if a binary mixing model only were considered. The water in the deepest borehole, G, has a piston flow age of 23 years (1981) when determined by either CFC-12 or SF<sub>6</sub>. The groundwater in the two piezometers at borehole I has piston flow ages between 16 years (1988) based on the SF<sub>6</sub> measurement and 20 years (1984) based on CFC-12. (see Figure 2).

A conceptual model to describe groundwater flow in this part of the catchment has been devised and is presented in Figure 9. Three principal flow regimes have been identified: Regime 1 on the interfluvium, where the unsaturated zone is very deep and flow appears to follow a piston flow model; Regime 2 where the unsaturated zone is much thinner and there is mixing between the old groundwater from up gradient and modern water from recent recharge; and Regime 3 where there is interaction between groundwater and surface water in the river.

The lateral extent to which groundwater—surface water interaction occurs is not altogether clear from this data. However, groundwater from E1 and E2 which are sited adjacent to the river and near to the wetland, shows signs of interaction with the surface water. This is significant as this borehole is cased, suggesting that surface water-groundwater interaction can occur at depths below 10 metres. This

would support the views of Grapes et al. (2005) that the Boxford reach of the Lambourn varies between 'gaining' and 'losing'. Indeed, the situation at this particular reach could be of groundwater flowing in with the topographic gradient on the northern bank and the river discharging to groundwater from the southern bank.

Previous studies have made comparisons between groundwater age and nitrate concentrations (Johnston et al., 1998; MacDonald et al., 2003) and found reasonable linear correlations. Figure 10 shows a cross plot of nitrate-nitrogen against the date of application, that is, the date has been corrected for transit through the unsaturated zone based on the model of Cook and Solomon (1995) (see Figure 4), although as previously stated this transit time is roughly the same as for any conservative solute transport through the unsaturated zone. This data shows that the oldest NO<sub>3</sub>-N arise from recharge in the mid 1950s and rise fairly linearly at slightly less than 0.1 mg/L/a over a thirty year period.

## **7 Summary and Conclusions**

Groundwater in the catchment is found to have concentrations of CFC-11 sometimes greater than modern concentrations in air equilibrated water, making it ineffective as a groundwater dating tool. Concentrations of CFC-11 and CFC-12 were also present at greater than modern concentrations in air equilibrated water for samples taken from the river. Concentrations of SF<sub>6</sub> taken from the river were found to be in equilibrium with the atmosphere.

The combined use of CFC and SF<sub>6</sub> data has facilitated the development of a conceptual model for groundwater movement in this part of the catchment, based on a series of theoretical mixing models. Three distinct regimes can be identified. In the deepest samplers, groundwaters are found to date from the early to mid 1980s at depths of 50 metres below ground level. The nitrate found in these boreholes is thought to arise from recharge in the mid 1950s. In shallower samples, groundwater is found to be a mixture of modern and 'old' water in a ratio of approximately 3:1 assuming binary mixing of CFC free and water in equilibrium with the current atmosphere. Adjacent to the stream, groundwater—surface water interaction is believed to take place to depths in excess of 10 metres. The necessary time series data required to investigate this further are the subject of on-going work.

The conjunctive use of CFCs and SF<sub>6</sub> has been shown to be both diagnostic, for determining groundwater movement, and quantitative, as residence time indicators. The work has demonstrated the efficacy of using CFCs and SF<sub>6</sub> for determining groundwater movement and residence times and have been successfully employed in a lowland Chalk catchment. This now provides a framework for modelling based studies to underpin catchment management decisions.

## Acknowledgements

The authors gratefully acknowledge the assistance of Peter Cook of CSIRO Adelaide for helpful advice with gas movement in the unsaturated zone. David Kinniburgh, Paul Shand and John Bloomfield of BGS Wallingford also proved fruitful in discussion. This paper is published with the permission of the Executive Director, British Geological Survey (NERC).

## References

- Aldiss, D.T. and Royse, K.R., 2002. The geology of the Pang-Lambourn catchment, Berkshire. British Geological Survey, CR/20/298N.
- Allen, D.J., Brewerton, L.J., Coleby, L.M., Gibbs, B.R., Lewis, M.A., Wagstaff, S.J. & Williams, A.T. 1997. The Physical Properties of Major Aquifers in England and Wales. British Geological Survey Report WD/97/34.
- Bauer, S., Fulda, C. and Schäfer, W., 2001. A multi-tracer study in a shallow aquifer using age dating tracers <sup>3</sup>H, <sup>85</sup>Kr, CFC-113 and SF<sub>6</sub> – indication for retarded transport of CFC-113. J. Hydrol., 248: 14-34.
- Bloomfield, J. P., Brewerton, L.J. and Allen, D.J., 1995. Regional trends in matrix porosity and dry density of the Chalk of England. Q. J. Eng. Geol., 28: S131-S142.
- Bockgård, N., Rodhe, A. and Olsson, K.A., 2004. Accuracy of CFC groundwater dating in a crystalline bedrock aquifer: Data from a site in southern Sweden. Hydrogeol. J., 12: 171-183.
- Böhlke, J-K., 2002. Groundwater recharge and agricultural contamination. Hydrogeol. J., 10: 153-179.
- Busenberg, E. and Plummer, L.N., 1992. The use of chlorofluorocarbons (CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub>) as hydrologic tracers and age-dating tools: the alluvium and terrace system of Central Oklahoma. Water Resour. Res., 28: 2257-2283.
- Busenberg, E. and Plummer, L.N., 2000. Dating young groundwater with sulphur hexafluoride: Natural and anthropogenic sources of sulfur hexafluoride. Water Resour. Res., 36: 3011-3030.
- Cook, P.G., and Böhlke, J-K., 2000. Determining timescales for groundwater flow and solute transport. In Cook, P. and Herczeg, A. eds. Environmental Tracers in subsurface hydrology. Kluwer Academic Publishers, Boston, Mass., pp 1-30.

- Cook, P.G. and Solomon, D.K., 1995. Transport of trace gases to the water table: Implications for groundwater dating with chlorofluorocarbons and krypton 85. *Water Resour. Res.*, 31: 263-270.
- Cook, P.G., Solomon, D.K., Plummer, L.N., Busenberg, E. and Schiff, S.L., 1995. Chlorofluorocarbons as tracers of groundwater transport processes in a shallow, silty sand aquifer. *Water Resour. Res.*, 31: 425-434.
- Cook, P.G. and Solomon, D.K., 1997. Recent advances in dating young groundwater: Chlorofluorocarbons, <sup>3</sup>H/<sup>3</sup>He and <sup>85</sup>Kr. *J. Hydrol.*, 191: 245-265.
- Darling, W.G. and Bath, A.H. 1988. A stable isotope study of recharge processes in the English Chalk. *J. Hydrol.*, 101: 31-46.
- Darling, W.G., Kinniburgh, D.G. and Gooddy, D.C., 1998. Gas compositions and processes in the unsaturated zone of Chalk and Triassic sandstone aquifers, England. In *Isotope Techniques in the Study of Environmental Change*, International Atomic Energy Agency, Vienna, 265-274.
- Darling, W. G., Morris, B.L., Stuart, M. E. and Gooddy, D. C., 2005. Groundwater age indicators from public supplies tapping the Chalk aquifer of southern England. *J. Chart. Inst. Water E.* 19: 30-40.
- Edmunds, W.M., Cook, J.M., Darling, W.G., Kinniburgh, D.G., Miles, D.L., Ball, A.H., Morgan-Jones, M. and Andrews, J.N., 1987. Baseline geochemical conditions in the Chalk aquifer, Berkshire UK: a basis for groundwater quality management. *Appl. Geochem.*, 2: 251-274.
- Engesgaard, P., Højberg, A.L., Hinsby, K., Jensen, K.H., Laier, T., Larsen, F., Busenberg, E. Plummer, L.N., 2004. Transport and time lag of chlorofluorocarbon gases in the unsaturated zone, Rabis Creek, Denmark. *Vadose Zone J.*, 3: 1249-1261.
- Foster, S.S.D., and Milton, V.A., 1974. The permeability and storage of an unconfined Chalk aquifer. *Hydrol. Sci. B.*, 19: 485-500.
- Gooddy, D.C., Bloomfield, J. P., Chilton, P. J., Johnson, A. C. and Williams, R. J., 2001. Assessing herbicide concentrations in the saturated and unsaturated zone of a Chalk aquifer in Southern England. *Ground Water*, 39: 262-271.
- Gooddy, D. C., Clay, J. W. and Bottrell, S. H., 2002. Redox-driven changes in pore-water chemistry of the Chalk unsaturated zone beneath unlined cattle slurry lagoons. *Appl. Geochem.*, 17: 903-921.

- Grapes, T.R., Bradley, D. and Petts, G.E., 2005. Dynamics of river—aquifer interactions along a chalk stream: the River Lambourn, UK. *Hydrol. Process.* 19: in press.
- Heaton, T.H.E. and Vogel, J.C., 1981. “Excess air” in groundwater. *J. Hydrol.*, 62: 201-216.
- Johnston, C.T., Cook, P.G., Frappe, S.K., Plummer, L.N., Busenburg, E. and Blackport, R.J., 1998. Ground water age and nitrate distribution within a glacial aquifer beneath a thick unsaturated zone. *Ground Water*, 36:171-180.
- Lloyd, J. W., Harker, D. and Baxendale, R.A., 1981. Recharge mechanisms and groundwater flow in the Chalk and drift deposits of southern East Anglia. *Q. J. Eng. Geol.*, 14: 87-96.
- MacDonald, A.M., Darling, W.G., Ball, D.F. and Oster, H., 2003. Identifying trends in groundwater quality using residence time indicators: an example from the Permian aquifer of Dumfries, Scotland. *Hydrogeol. J.*, 11: 504-517.
- Maloszewski, P. and Zuber, A., 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers – 1. Models and their applicability. *J. Hydrol.*, 57: 207-231.
- Martin, G.E., Snow, D.D., Kim, E. and Spalding, R.,F., 1995. Simultaneous determination of argon and nitrogen. *Ground Water*, 33: 781-785.
- Morris, B. L., Darling, W. G., Goody, D. C., Litvak, R. G., Neumann, I., Nemaltseva, E. J. and Podubnaia, I., 2005 Assessing the extent of induced leakage to an urban aquifer using environmental tracers: an example from Kyrgyzstan, Central Asia. *Hydrogeol. J.* (in press).
- Neal, C., 2004. The water quality functioning of the upper River Severn, Plynlimon, mid-Wales: issues of monitoring, process understanding and forestry. *Hydrol. Earth Syst. Sc.*, 8: 521-532.
- Oster, H., Sonntag, C. and Münnich, K.O., 1996. Groundwater age dating with chlorofluorocarbons. *Water Resour. Res.*, 32: 2989-3001.
- Plummer, L.N., Busenberg, E., Böhlke, J-K., Nelms, D.L., Michel, R.L. and Schlosser, P., 2001. Groundwater residence times in Shenandoah National Park, Blue Ridge Mountains, Virginia, USA: a multi-tracer approach. *Chem. Geol.*, 179: 93-111.
- Price, M., Morris, B.L. and Robertson, A.S., 1982. A study of intergranular and fissure permeability in Chalk and Permian aquifers, using double-packer injection testing. *J. Hydrol.*, 54: 401-423.

- Price, M., Downing, R.A. and Edmunds, W.M., 1993. The Chalk as an aquifer. In Downing, R.A., Price, M. and Jones G.P. eds. *The Hydrogeology of the Chalk of North-West Europe*. Clarendon Press, Oxford, pp35-58.
- Price, M., Low, R.G. and McCann, C., 2000. Mechanisms of water storage and flow in the unsaturated zone of the Chalk aquifer. *J. Hydrol.*, 233: 54-71.
- Rademacher, L.K., Clark, J.F. and Boles, J.R., 2003. Groundwater residence times and flow paths in fractured rock determined using environmental tracers in the Mission Tunnel; Santa Barbara County, California, USA. *Environ. Geol.*, 43: 557-567.
- Soulsby, C., Gibbins, C., Wade, A.J., Smart, R. and Helliwell, R., 2002. Water quality in the Scottish uplands: a hydrological perspective on catchment hydrochemistry. *Sci. Tot. Env.*, 294: 73-94.
- Vulava, V.M., Perry, E.B., Romanek, C.S. and Seaman, J.C., 2002. Dissolved gases as partitioning tracers for determination of hydrogeological parameters. *Environ. Sci. Technol.*, 36: 254-262.
- Weeks, E.P., Earp, D.E. and Thompson, G.M., 1982. Use of atmospheric fluorocarbons F-11 and F-12 to determine the diffusion parameters of the unsaturated zone in the southern high plains of Texas. *Water Resour. Res.*, 18: 1365-1378.
- Wheater, H.S. and Peach, D., 2004. Developing interdisciplinary science for integrated catchment management: The UK LOwland CAtchment Research (LOCAR) programme. *Int. J. Water Resour. D.*, 20: 369-385.
- Zuber, A., 1986. Mathematical models for the interpretation of environmental radioisotopes in groundwater systems. In Fritz, P. and Fontes, J-C., eds. *Handbook of Environmental Isotope Geochemistry*, Vol. 2, pp1-59, Elsevier, Amsterdam.

Table 1. Borehole Construction Details and the depth to the water table measured in August 2004.

Piezometer	Open Section Range		Water Level (m)
	Top (m)	Bottom (m)	
PL26D-1	10.7	25.35	0.86
PL26D-2	0	3.8	1.23
PL26H-1	25.03	30	6.12
PL26H-2	20	24	6.11
PL26I-1	39.4	52.3	15.79
PL26I-2	30	35	15.8
PL26G	50.5	100	22.65
PL26E-1	11.15	25.2	1.04
PL26E-2	0	4.7	1.04
PL26F	10.6	34	1.00

Table 2. Temperature, dissolved oxygen, specific electrical conductivity, nitrate-nitrogen, nitrous oxide and the nitrogen/argon ratio for the Lambourn at Boxford and the 10 piezometers sampled in August 2004.

Site/piezomter	Temp °C	DO mg/L	SEC µS/cm	NO <sub>3</sub> -N mg/L	N <sub>2</sub> O µg/L	N <sub>2</sub> /Ar
River	13.6	10.7	568	6.8		
PL26D-1	10.9	7.2	620	6.4	6	40.3
PL26D-2	10.8	8.3	621	6.8	5	39.4
PL26H-1	10.5	7.2	630	5.8	<2	40.4
PL26H-2	11.3	7.2	619	6.4	<2	40.0
PL26I-1	10.5	7.2	660	5.4	<2	41.1
PL26I-2	10.5	7.0	663	5.9	<2	41.4
PL26G	10.9	6.8	659	4.8	<2	40.8
PL26E-1	10.6	6.3	633	6.2	9	38.9
PL26E-2	10.3	7.6	629	6.3	6	40.5
PL26F	10.2	7.6	608	6.9	<2	41.8

Table 3. CFC-12, CFC-11 and SF<sub>6</sub> concentrations measured in August 2004 from the Lambourn at Boxford and in the 10 piezometers.

Site/Piezometer	CFC-12		CFC-11		SF <sub>6</sub>	
	pmol/l	±	pmol/l	±	fmol/l	±
River	3.81	0.19	9.10	0.46	2.49	0.25
PL26D-1	2.14	0.11	4.80	0.24	1.15	0.11
PL26D-2	2.23	0.11	4.61	0.23	1.35	0.14
PL26H-1	2.33	0.12	3.92	0.20	1.20	0.12
PL26H-2	2.25	0.11	4.60	0.23	1.16	0.12
PL26I-1	2.06	0.10	3.48	0.17	0.61	0.06
PL26I-2	2.05	0.10	3.38	0.17	0.55	0.05
PL26G	1.79	0.09	4.86	0.24	0.32	0.03
PL26E-1	1.80	0.09	5.05	0.25	1.54	0.15
PL26E-2	2.00	0.10	5.45	0.27	1.44	0.14
PL26F	1.86	0.09	5.51	0.28	0.82	0.08