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# Using chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF<sub>6</sub>) to characterise groundwater movement and residence time in a lowland Chalk catchment

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## KEYWORDS

CFCs;  
SF<sub>6</sub>;  
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Groundwater mixing;  
Surface water–groundwater interaction;  
Catchment processes;  
LOCAR;  
Chalk

**Summary** Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF<sub>6</sub>) provide a technique for dating groundwaters 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 indications of the likely groundwater flow mechanisms. Modelling shows that diffusive retardation of these age 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 interfluvial 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 m bgl. The nitrate found at the greatest depth is thought to date from the mid-1950s.

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## 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, 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 suited to 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 on average very 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 50 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 USA (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.

## Background and theoretical considerations

### 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. The aquifer matrix consists of soft microporous and

fractured calcium carbonate rock 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 pore-water 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.

### Measurement of atmospheric concentrations of CFCs and SF<sub>6</sub>

Atmospheric trace gases have been monitored at a number of sites across the globe for nearly 30 years (Prinn et al., 2000) and have been found to be generally well mixed, a factor underpinning their use in dating studies (e.g., Höhener et al., 2003). Some researchers have shown localised highs in atmospheric mixing ratios for CFCs and SF<sub>6</sub>, especially in urban areas (Oster et al., 1996; Santella et al., 2003). There is therefore an issue as to what atmospheric mixing ratio should be used in any given groundwater tracing study. CFC-12 data dating back to 1978 are available from Mace Head, Ireland (Prinn et al., 2000) which is the nearest atmospheric monitoring station to the study site. This shows average CFC-12 concentrations between 1978 and 1990 to be 6% higher than the Climate Monitoring Diagnostics Laboratory/National Oceanic and Atmospheric Administration (CMDL/NOAA) adjusted values for the Northern hemisphere. From 1990 to 1998 CFC-12 concentrations at Mace Head are just 2% greater than the averaged CMDL/NOAA values. Even closer agreement is observed for CFC-11. Air sampled near to the study site in 2001 had a CFC-12 concentration within 1% of the CMDL/NOAA data and 1.2% of the Mace Head data. A comparison of SF<sub>6</sub> sampled at Mace Head in 2001 with CMDL/NOAA data for that year shows agreement within 1%. A similar level of agreement was found for SF<sub>6</sub> sampled in air near to the study site also in 2001. It is therefore considered that the CMDL/NOAA data set, which is the longest continuous time series record for both CFCs and SF<sub>6</sub> in the Northern hemisphere, is appropriate for this study. This is consistent with the rural location of the study site.

### 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, 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.

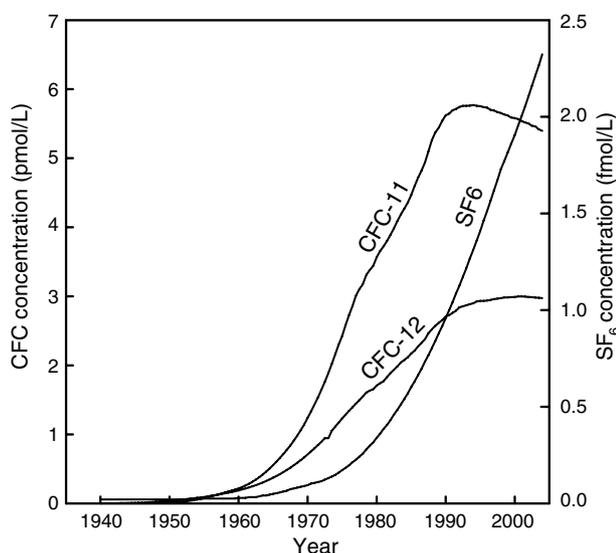
Fig. 1 shows concentrations of CFC-11, CFC-12 and SF<sub>6</sub> in pmol/L and fmol/L, respectively, expected in UK groundwater recharged between 1940 and 2000, at sea level, and in equilibrium with atmospheric air for a recharge temperature of 10 °C. This value has been selected as it is in very close agreement with the exact values obtained by Parker et al. (1992).

### Contamination

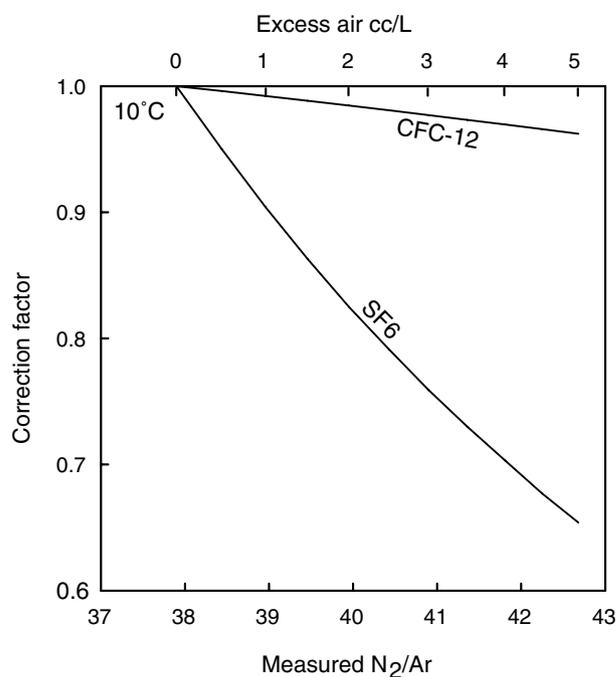
Contamination of groundwater with chlorofluorocarbons appears to be the greatest limitation on CFC dating. Groundwater samples from residential, industrial or disused landfill sites can contain concentrations of chlorofluorocarbons above modern atmospheric concentrations (Busenberg and Plummer, 1992; MacDonald et al., 2003). Morris et al. (2006) demonstrate that less than 1/10th of the amount of CFC-12 present in a single domestic refrigerator (of older design) 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.

### 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



**Figure 1** Concentrations of CFC-11, CFC-12 and SF<sub>6</sub> in water at 10 °C based on atmospheric mixing ratio data from [www.water.usgs.gov/lab/software/air\\_curve](http://www.water.usgs.gov/lab/software/air_curve).



**Figure 2** Relationship between the nitrogen argon ratio in water indicating excess air and the correction factor applied to SF<sub>6</sub> and CFC-12 data.

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 L 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. Fig. 2 shows the relationship between the N<sub>2</sub>/Ar ratio and the correction factor that must be applied for the EA. The excess air effect on CFC-11 is insignificant owing to its higher solubility.

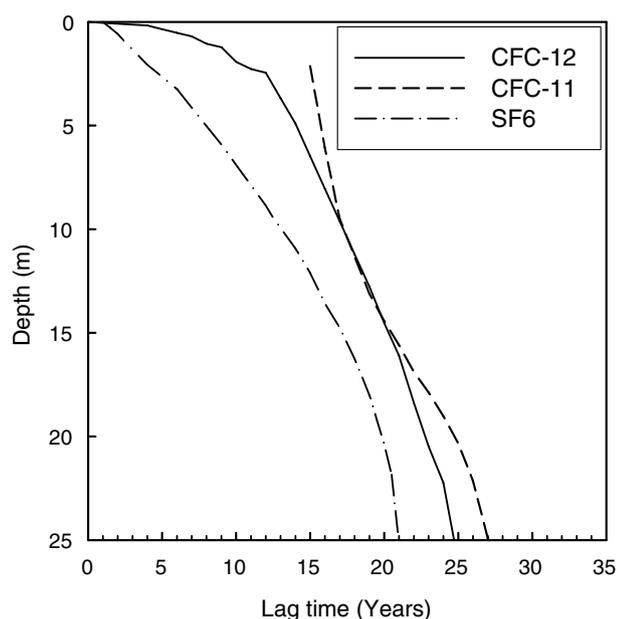
### Unsaturated zone processes

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 atmosphere (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.

Fig. 3 simulates the time lag for SF<sub>6</sub>, CFC-11 and CFC-12 passing through a 25-m unsaturated zone with a water velocity of 1 m/a typical of the Chalk, 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). The top few meters of the CFC-11 curve have been omitted as the current atmospheric concentrations for this gas are beyond their maximum.

Fig. 3 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



**Figure 3** Lag times for water recharged through tracer-diffusion profiles in unsaturated zone air with different depths to the water table based on the model of Cook and Solomon (1995). Parameters used for Chalk are given in text.

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.

### Groundwater mixing models

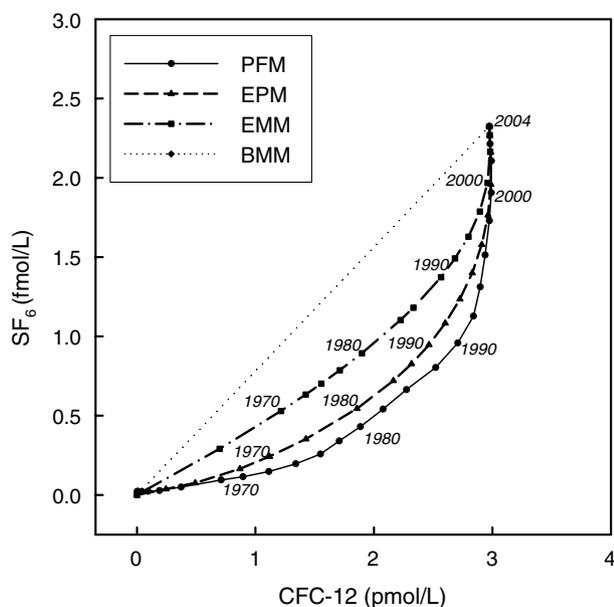
Water extracted from a borehole or flowing from a spring is generally considered to be a mixture of waters from all the flow lines reaching the discharge point. The age frequency distribution and mean age of the mixture affect the interpretation of the groundwater dating methods as well as the interpretation 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, 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. Fig. 4 shows an example of the four different mixing models for a cross-plot of sulphur hexafluoride with CFC-12. The model parameters are taken from the equations given in Cook and Böhlke (2000) and calculated using the spreadsheet model of Böhlke (2006).

### Study area

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



**Figure 4** Mixing model ideal curves based on CFC-12 and SF<sub>6</sub> concentration in groundwater. Dates labelled are the groundwater age at that point on the curve.

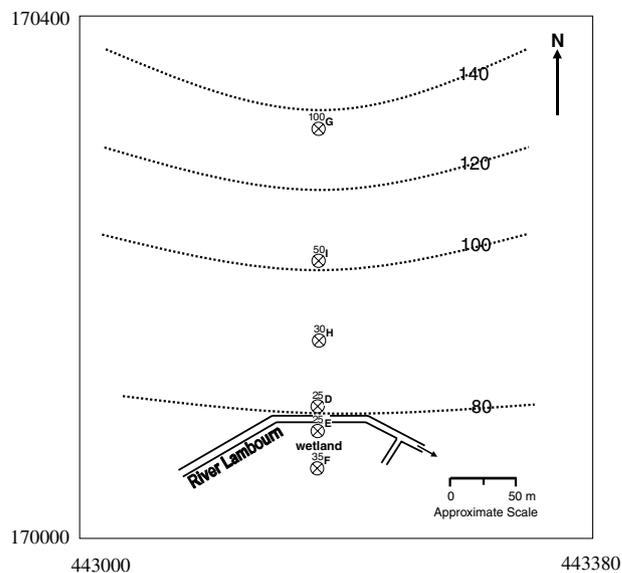
Within the catchment the Chalk matrix porosity generally decreases linearly with depth from about 45% near ground surface, to less than 25% at 100 m bgl. This is consistent with previously reported depth trends in Chalk matrix porosity (Bloomfield et al., 1995) and reflects the diagenetic grade and maximum 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 to 0.001 for the unconfined Chalk. The maximum thickness of the Chalk in the catchment is about 200 m.

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).

### Site description

The study site (PL26) is in a rural area approximately 25 km south east of the nearest large urban centre (Swindon, population 160,000) and contains a series of boreholes located on either sides of the River Lambourn at Boxford (NGR 442900 172200). Fig. 5 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.



**Figure 5** Borehole and piezometer locations for the samples taken from Boxford for this study. The drilled depth are given by the number above the borehole. Dotted lines show topographic contours in meters above ordinance datum.

## Methodology

### 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 and 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.

### Groundwater analysis

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). The error on duplicate N<sub>2</sub>/Ar measurements is typically within ±0.2. N<sub>2</sub>O

was measured by gas chromatography with electron capture detection as detailed in Gooddy 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 was 0.01 pmol/L, whereas SF<sub>6</sub> was 0.1 fmol/L.

## Results and discussion

Selected field-measured parameters together with nitrogen species data are shown in Table 1. 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 samples from 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 1 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 (Fig. 2). These are within the expected range based on previous studies (Busenberg and Plummer, 2000). The error on the N<sub>2</sub>/Ar measurement corresponds to a difference in the correction factor of roughly 0.03 or typically <4% of the SF<sub>6</sub> concentration.

Table 1 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>. 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 small anthropogenic addition of CFC-11. This occurs in the piezometers on the south side of the river (E2 and F). The deepest sample (G) also shows some unexpectedly high CFC-11 values (90% modern fraction) when compared with the other tracers (60% modern fraction from CFC-12 and 14% from SF<sub>6</sub>) suggesting some CFC-11 contamination of this sample.

Both CFC-12 and CFC-11 in the river have 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. Even allowing for temperature effects (CFC

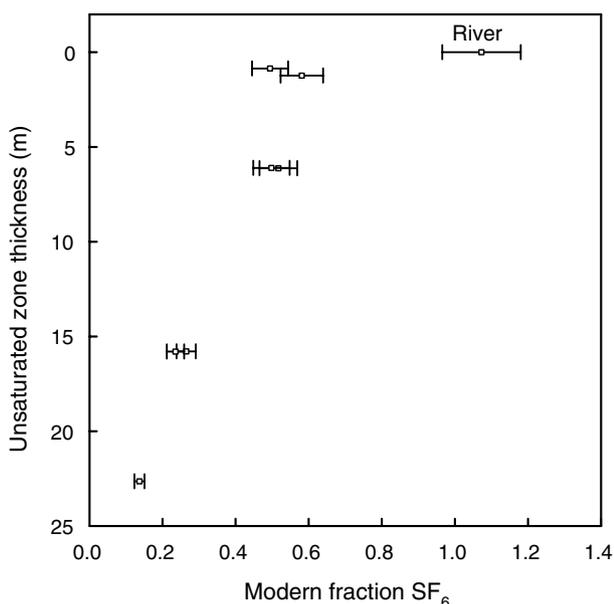
**Table 1** Borehole construction details, depth to the water table and chemical parameters measured in 10 piezometers and the Lambourn at Boxford in August 2004

Piezometer	Open section range		Water level (m)	Temperature (°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	CFC-12 (pmol/L)	CFC-11 (pmol/L)	SF <sub>6</sub> (fmol/L)	±
	Top (m)	Bottom (m)											
River													
PL26D-1	10.7	25.35	0.86	13.6	10.7	568	6.8		40.3	3.81	9.10	2.49	0.46
PL26D-2	0	3.8	1.23	10.9	7.2	620	6.4	6	39.4	2.32	4.80	1.15	0.24
PL26H-1	25.03	30	6.12	10.8	8.3	621	6.8	5	40.4	2.48	4.61	1.35	0.23
PL26H-2	20	24	6.11	10.5	7.2	630	5.8	<2	40.4	2.33	3.92	1.20	0.20
PL26I-1	39.4	52.3	15.79	11.3	7.2	619	6.4	<2	41.1	2.25	4.60	1.16	0.23
PL26I-2	30	35	15.8	10.5	7.2	660	5.4	<2	41.4	2.06	3.48	0.61	0.17
PL26G	50.5	100	22.65	10.9	7.0	663	5.9	<2	40.8	2.05	3.38	0.55	0.17
PL26E-1	11.15	25.2	1.04	10.6	6.8	659	4.8	<2	38.9	1.79	4.86	0.32	0.24
PL26E-2	0	4.7	1.04	10.3	6.3	633	6.2	9	40.5	1.80	5.05	1.54	0.25
PL26F	10.6	34	1.00	10.2	7.6	629	6.3	6	41.8	2.00	5.45	1.44	0.27
					7.6	608	6.9	<2		1.86	5.51	0.82	0.28

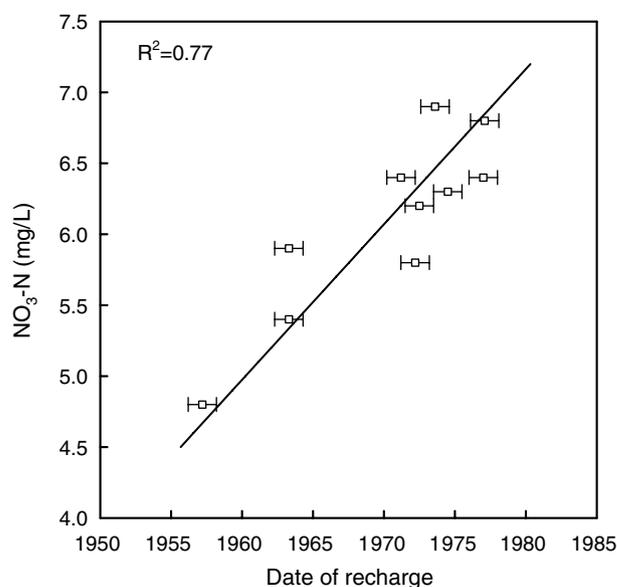
and SF<sub>6</sub> solubility increases inversely with temperature) and assuming that all the stream water originates from groundwater at 10 °C, CFC-12 and CFC-11 would still exceed modern ASW by 1.3 and 1.7 times, respectively. Since the groundwater concentrations are all much lower than this it appears that the origin of the high CFC concentrations in the river occurs further upstream, possibly from former landfill sites. In addition, this implies that the rate of CFC input exceeds the rate of atmospheric exchange from the river.

Fig. 6 shows the relationship between unsaturated zone thickness (depth to the top of the water table) and groundwater SF<sub>6</sub> concentration expressed as a fraction of modern groundwater (measured concentration divided by air-equilibrated water at 10 °C). This assumes that the water is well mixed within the piezometer during sampling and the groundwater obtained is from across the full length of the screen interval (a similar relationship also exists between SF<sub>6</sub> and the open screen range). This figure suggests the fraction of modern water decreases with increasing depth to groundwater, which also corresponds with increasing distance from the river.

Previous studies have made comparisons between groundwater age and nitrate concentrations (Johnston et al., 1998; MacDonald et al., 2003) and found reasonably linear correlations. Fig. 7 shows a cross-plot of nitrate-nitrogen against the date of application. Date of application has been calculated by taking the piston flow age for CFC-12 (Fig. 1) and subtracting the unsaturated zone transit time based on the depth to water table (Fig. 3). Johnston et al. (1998) used a similar approach within a glacial aquifer beneath a thick unsaturated zone using CFC-11 and <sup>3</sup>H/<sup>3</sup>He groundwater ages and estimated unsaturated zone travel times based on tritium. The data from the present study shows that the oldest NO<sub>3</sub>-N arises from recharge in the



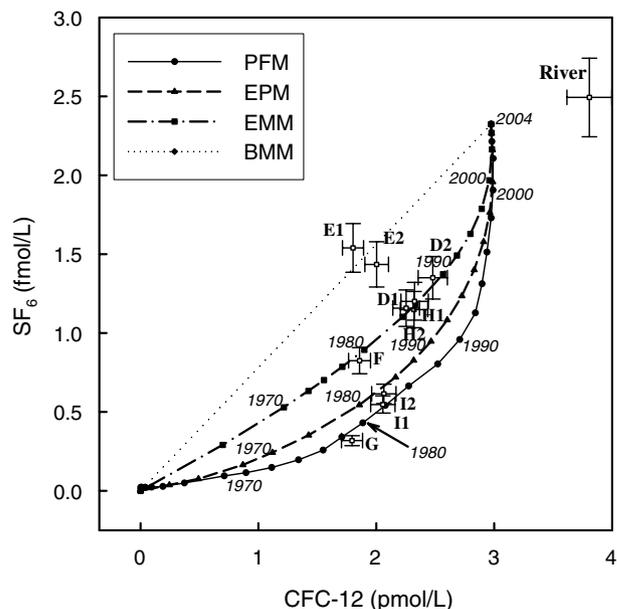
**Figure 6** Cross-plot showing the relationship between sulphur hexafluoride and the depth of the unsaturated zone. Sulphur hexafluoride is expressed in terms of the modern fraction (2.3 fmol/L for waters recharged in 2004).



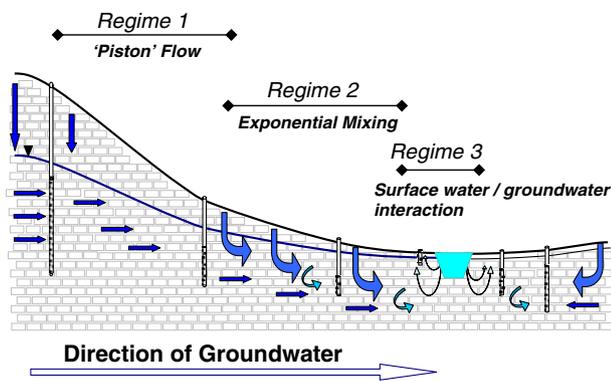
**Figure 7** Cross-plot of nitrate-nitrogen concentration against calculated date of recharge based on CFC-12 groundwater age and modelled gas diffusion transit time through the unsaturated zone.

mid-1950s and concentrations rise fairly linearly at slightly less than 0.1 mg/L/a over a 30-year period. This is likely to be associated with post-war land-use change and increasing fertiliser application rates.

Fig. 8 shows a cross-plot of the concentrations for CFC-12 and SF<sub>6</sub>, super imposed on the mixing models described in Fig. 4. Fig. 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



**Figure 8** CFC-12 and SF<sub>6</sub> groundwater data overlaid on the ideal mixing model curves. Selected sites have been labelled.



**Figure 9** Conceptual model showing the three groundwater flow regimes moving down gradient through the catchment.

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 Fig. 1).

A conceptual model to describe groundwater flow in this part of the catchment has been devised and is presented in Fig. 9. Three principal flow regimes have been identified: Regime 1 on the interfluvium, where the unsaturated zone is very deep and piston flow predominates; 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 river water.

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 because this borehole is cased, suggesting that surface water–groundwater interaction can occur at depths below 10 m. 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. This is consistent with the slightly above-modern ASW concentrations of CFC-11 found in piezometers F and E2 and by inference suggests that the CFC-12 concentrations in these piezometers are slightly elevated (although still below modern modern air-equilibrated water) due to the ingress of a fraction of river water.

## Summary and conclusions

Groundwater at Boxford in the Lambourn catchment is found to have concentrations of CFC-11 sometimes greater

than in modern 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 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 m 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. Adjacent to the stream, groundwater–surface water interaction is believed to take place to depths in excess of 10 m.

This study has demonstrated the efficacy of using CFCs and SF<sub>6</sub> for determining groundwater movement and residence times in a lowland Chalk catchment, thereby providing a framework for modelling-based studies to underpin catchment management decisions.

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