

Using environmental tracers to assess the extent of river–groundwater interaction in a quarried area of the English Chalk

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Abstract The Swanscombe area of Kent, SE England represents a typical example of a heavily quarried Chalk area currently undergoing re-development. Because the Chalk is also an important aquifer, a good understanding of groundwater movement is required if environmental impacts are to be minimised and the water resource maximised. In particular, the nature of the relationship between the River Darent and groundwater in the Swanscombe Chalk Block requires better characterisation. Here, ‘environmental tracers’ in the form of ambient concentrations of stable isotopes, CFCs (chlorofluorocarbons), SF₆ (sulphur hexafluoride) and tritium (³H) are used to investigate this and other aspects of groundwater movement in the vicinity of the quarries. Stable isotopic contrasts indicate little evidence for widespread river infiltration to the regional Chalk aquifer, although stable isotope and tritium data suggest that 20–35% of the abstraction by river-valley public water supply boreholes may be derived from the river. The CFCs, while present at above-modern concentrations in almost all groundwaters, can be used as tracers, indicating basically S–N flowpaths in the area south of the quarries, though sub-karstic conduits associated with areas of Palaeogene cover add a level of uncertainty at the local scale. Simple piston flow residence times based on SF₆ range from 1 to 17 years, but the data are probably better interpreted in terms of mixing between varying amounts of modern recharge derived from the south and deeper stored groundwater. The information gained from environmental tracers can therefore contribute to effective resource management.

Keywords: *Chalk aquifer, sub-karst, river–groundwater interaction, residence time, stable isotopes, chlorofluorocarbons, sulphur hexafluoride, tritium*

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1. Introduction

The Chalk, a fine-grained and fractured coccolith limestone of Upper Cretaceous age, is an important aquifer across NW Europe (Downing et al., 1993). Although generally valued for its landscape and ecology, the Chalk has in places been intensively quarried primarily for the manufacture of cement. The resulting large-scale excavations inevitably have some effect on regional hydrogeology, but the dual-porosity nature of the Chalk aquifer (fractured but with a highly porous matrix: Price et al., 1993) means that these may be difficult to resolve or attribute. Clearly therefore, achieving a better understanding of groundwater movements in such areas is highly desirable.

An opportunity to do this has been provided by the Swanscombe area in the county of Kent, SE England. Here, quarrying has recently ceased and the resulting kilometre-scale excavations have been, or are in the process of being, redeveloped. At the same time, interception of groundwater presently draining to the quarried area is envisaged as an additional means of meeting the region's high water demand. This paper is concerned with the use of environmental tracers as an adjunct to more conventional hydrogeological techniques. Previously, non-point-source studies on the Chalk of NW Europe using environmental tracers have tended to focus on the unsaturated zone (e.g. Geake and Foster, 1989; Vachier et al., 1987), or on down-gradient flowpaths extending into confined conditions (e.g. Smith et al., 1976; Kloppman et al., 1998). The present study differs in considering a local Chalk unit, including river-groundwater interaction, in an area of anthropogenic alteration and development.

2. Background

2.1. The Swanscombe Chalk Block

The Swanscombe Chalk Block is defined for present purposes as the area lying between the River Thames and the scarp of the North Downs to the north and south respectively, and the Ebbsfleet and Darent Valleys to the east and west respectively (Fig. 1).

In the context of the proposed abstraction from the Swanscombe Block for public water supply, the hydrogeology of the area is a sensitive issue because the River Darent, an ecologically-important Chalk stream, partially dried up in the 1990s (Rippon and Wyness, 1994). In addition, the river approaches to within 3 km of the quarries and the possibility of sub-karstic leakage from the river to the quarries has been raised.

The area is dominated by two major excavations: the Western Quarry, redeveloped since 1999 as the Bluewater retail park, and the larger Eastern Quarry, now being infilled as part of the Ebbsfleet Valley redevelopment programme, the largest development site in the Thames Gateway region.

During the period of chalk extraction the base of the quarries was below sea level (down to -10 m AOD), and therefore they acted as a sump for groundwater flow in the vicinity. Latterly between 20 and 40 $10^3\text{m}^3/\text{d}$ were being pumped out of the Eastern Quarry. In general terms, while some flow against the natural pre-development gradient towards the Thames probably has occurred, it is proportionally of little significance since the median chloride concentration of quarry discharge during the study was 36 mg/l compared to the >6000 mg/l in the tidal Thames at Dartford. Most flow into the quarries is therefore presumed to be derived from the Chalk block to the south which, based on annual recharge of ~200 mm, is more than capable of supplying this volume of water. However, the existence of gentle easterly-trending anticlines and synclines south of the quarries means that direct S-N flowlines might not necessarily exist. In this possibly complex flow system, the hydrological situation of the River Darent has remained relatively unclear. Although river valleys are typically zones of groundwater discharge, Chalk streams are well known for their tendency to have gaining and losing reaches even in the absence of large-scale groundwater abstraction (e.g. Grapes et al., 2005). In the lower Darent Valley the existence of several public supply pumping stations is likely to have reinforced any pre-existing complexity.

With such questions in mind, prior to the present redevelopment, and while chalk quarrying was still being carried out by Lafarge Cement UK, the area was studied by Thames Water Utilities Ltd (TWUL) to assess the groundwater resources of the Swanscombe Chalk Block. It was clear from the amount of groundwater entering the Eastern Quarry via diffuse or sub-karstic fracture 'pipe flow' that a considerable amount of water was potentially available for development (Tyler-Whittle, 1999) but little was known about this resource in terms of

flowpaths, residence time or relationship with the River Darent. As part of the hydrogeological assessment it was decided to use ‘environmental tracers’, i.e. a range of dissolved constituents chosen to reveal different aspects of the water’s origin.

2.2. Environmental tracers

The term ‘environmental tracer’ simply means the hydrogeochemical imprinting of a groundwater due to its origin as recharge and/or its subsequent evolution. Some of this imprinting is natural (e.g. stable isotope signatures), but it may also result from anthropogenic factors (e.g. point-source pollution). It may be the result of a particular event (e.g. thermonuclear tritium), or a continuing input (e.g. chlorofluorocarbons). Tracers may be reactive (e.g. evolving inorganic water quality) or non-reactive (e.g. sulphur hexafluoride).

In the Chalk the simplest environmental tracer, inorganic chemistry, is often not especially useful because the excessively fine-grained nature of the rock matrix leads quickly to a rather uniform hydrochemical composition which tends to change only over longer timescales (Edmunds et al., 1987). At Swanscombe, most flowlines are unlikely to be long enough for this to occur to a significant extent. Therefore, three other types of tracer were chosen for the investigations: (i) O and H stable isotopes; (ii) the trace gases CFC-11, CFC-12, CFC-113 and SF₆; and (iii) ³H. Each of these types has certain unique properties, although there may be overlap in the information they provide.

2.2.1. Stable isotopes

The ratios of ¹⁸O/¹⁶O and ²H/¹H imparted to groundwaters at recharge tend to remain the same in the subsurface, at least over the relatively brief residence times of Chalk groundwaters. These ratios vary systematically across the UK owing to the balance between rainout, topography and temperature (Darling et al. 2003). For surface waters, however, isotope ratios may change with time either owing to evaporation, or seasonal rainfall inputs (Darling and Talbot, 2003). The existence of these two effects – regional variations and surface water differences – may allow areal recharge to be resolved from river leakage.

2.2.2. Trace gases

The use of the chlorofluorocarbons CFC-11 (CCl₃F), CFC-12 (CCl₂F₂) and CFC-113 (C₂Cl₃F₃) and sulphur hexafluoride (SF₆) as age tracers is based on the known rise of their

concentrations in the atmosphere over the past half-century, the observation that they are well-mixed in the atmosphere, and the assumption that they dissolve in water according to their Henry's Law solubilities at the recharge temperature (Plummer and Busenberg 1999). In the case of the Swanscombe area recharge temperature is taken as being 10°C, based on the regional mean annual air temperature (Tout, 1976). Figure 2 shows the concentrations of CFC-11, CFC-12, CFC-113 and SF₆ to be expected in groundwater recharged between the years 1950 and 2005 at a temperature of 10°C. Providing there is no subsurface addition, groundwater concentrations can then be directly related to the year of recharge. However, the CFCs in particular are prone to augmentation under certain circumstances (Höhener et al., 2003). In such an event they may still be useable as flowpath tracers.

2.2.3. Tritium

The aerial thermonuclear weapons testing of the mid-1960s injected a large amount of tritium (³H) into the atmosphere, providing a marker for the presence of groundwater recharged in the past ~50 years. By the end of the 20th Century, the ³H activity of rainfall had declined to near-background levels as a result of rainout and the relatively short half-life of ³H (12.3 yrs). A further complication is that some landfills may be sources of elevated ³H (Robinson and Gronow, 1996). Despite these potential limitations, ³H can still play a useful role in groundwater investigations by providing a crosscheck on information obtained from the trace-gas indicators.

3. Sample collection and analysis

In the Darent Valley, a number of locations from Westerham downstream were chosen to characterise the river water, in four cases being sited as near as feasible to public water supply groundwater pumping stations (Fig. 3).

About a dozen private and TWUL test boreholes were available for sampling in a 3 km-wide zone to the south of the quarries. Two instances of pipe flow from the southern face of the Eastern Quarry were also sampled (Fig. 3).

Sampling for stable isotopes and tritium was carried out by collecting unfiltered samples of river or groundwater in glass bottles of 28 ml and 1 litre respectively. Samples for CFC and SF₆ analysis were collected in ground-glass-stoppered bottles immersed within metal cans containing the same water to prevent atmospheric contamination (based on the method of Oster, 1994).

Borehole samples were considered to be representative of groundwater in the vicinity, with the possible exception of CFCs and SF₆ in the Test BHs 3 and 7, in which cascading in the wellbore could be heard and from which ‘gassy’ water was obtained, indicating the possibility of gaseous exchange, which would presumably tend towards re-equilibration with the atmosphere. BH 3 appeared to be affected more than BH 7. Samples collected from the pipe flows in the Eastern Quarry may have been similarly affected.

Analysis for stable isotopes was carried out by dual-inlet mass spectrometry at the Wallingford laboratories of the British Geological Survey (BGS) after preparation by standard techniques. Isotope ratios are expressed as permil (‰) relative to VSMOW (Vienna Standard Mean Ocean Water):

$$\delta = [(R_{\text{sample}}/R_{\text{std}})-1] \times 10^3$$

Tritium was analysed by RCD Lockinge (Wantage, England) by radioactive counting following electrolytic pre-concentration. Activities are expressed as TU (Tritium Units, where 1 TU = 1 tritium in 10¹⁸ hydrogen atoms). CFCs and SF₆ were analysed by gas chromatography after cryogenic pre-concentration, either by Spurenstofflabor (Wachenheim, Germany) or by BGS Wallingford (CFC-11 and CFC-12 from 2002 to 2003). Analyses are reported as pmol/L (CFCs) and fmol/L (SF₆). Measurements of SF₆ have been corrected to compensate for incorporation of ‘excess air’ during recharge. This is based on the average excess air component of 2.5 ccSTP/L found for Chalk groundwaters by Goody et al. (2006). Such a component could lead to an underestimate of groundwater age of up to 5 years, somewhat exceeding the effect of measurement precision and therefore considered to be worth applying.

Measurement precisions are within $\pm 0.1\%$ for $\delta^{18}\text{O}$ and $\pm 1\%$ for $\delta^2\text{H}$, and $\pm 10\%$ for the CFCs and SF_6 , with detection limits of 0.01 pmol/L (CFC-12, CFC-113), 0.05 pmol/L (CFC-11) and 0.1 fmol/L (SF_6). Precision of tritium measurements is $\pm 5\%$ for activities in excess of 7 TU, ± 0.4 TU for activities from 7 to 2.5 TU, and ± 0.3 TU for activities below this down to the detection limit of 1 TU.

4. Results

4.1. Sites in the Darent Valley

Results for these sites are presented in two tables: Table 1, periodic monitoring of the stable isotopic composition of the river at the downstream sampling site SW7 between autumn 2001 and spring 2003; Table 2, low-flow and high-flow sampling of the river and valley boreholes for stable isotopes, tritium and CFCs in October 2001, October 2002 and February 2003.

Figure 4 shows a plot of the river-monitoring $\delta^{18}\text{O}$ data from Table 1. Also shown is the daily flow of the river at SW7 (Hawley gauging station), and the date of the detailed low-flow and high-flow sampling, i.e. the Oct-02 and Feb-03 samples of Table 2. The plot shows that the river varies in its isotopic composition well beyond measurement error, reaching its most depleted (negative) composition in the high-flow period of early 2003. Typically winter rainfall in the UK is isotopically depleted compared to the whole-year weighted mean (Darling and Talbot 2003), so the more negative winter river values may simply reflect this.

Figure 5 shows a $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plot based on sampling in the river valley in October 2001, October 2002 and February 2003 (data from Table 2). In both autumns, the river water is isotopically enriched (i.e. less negative). Overall the river data give a regression with a slope of 5.2, typical of evaporation from surface waters. This may be attributable to a degree of evaporative enrichment occurring in the river, most likely largely due to exposure in gravel pit lakes. The most notable of these (approximately 1×0.5 km in size) occurs above the Chalk block on the Gault Clay in the vicinity of Sevenoaks, so sampling points SW2 and SW3 were added above and below the lake for the low-flow/high-flow sampling campaigns, plus an extra point above the lake (SW1, Fig. 3) for the final sampling. The October 2002 results (Table 2) confirm that in the autumn the composition of river water below the lake is

enriched following the higher temperatures and longer lake turnover of summer. Above the lake, river values appear to be constant, and in better agreement with the expected composition of a river largely derived from groundwater in this area (Darling et al., 2003).

The river valley public supply pumping stations (PSs) on the other hand show little evidence of seasonal change. Nevertheless they are on average slightly isotopically enriched compared to the mean for boreholes away from the river (-7.3‰ in $\delta^{18}\text{O}$, see next section), which could be explained by a river water contribution of about one-fifth assuming an average river composition between SW4 and SW7 of -6.7‰ $\delta^{18}\text{O}$ (Table 2). Comparisons between the pumping stations and the river composition at different seasons are probably inappropriate, partly because the isotopic variations in the river depicted in Fig. 4 seem likely to be smoothed out in the hyporheic zone, but also because of a lack of the detailed piezometric data necessary to establish head gradients.

Tritium was analysed for two river–borehole pairs in the lower part of the valley (SW6 / Horton Kirby PS, SW7 / Darenth PS). The results (Table 2) show that the river had a significant tritium content (up to 15 TU) at the low-flow sampling, with a decline to about 70% of this at the high-flow sampling. Although there are no published monitoring data for tritium in UK rainfall in recent years, study of records from NW Europe shows that the activity of tritium in winter rainfall is typically around 50% of that in the summer (see the IAEA-WMO Global Network of Isotopes in Precipitation or GNIP, <http://nds121.iaea.org/wiser/index.php>). Allowing for a degree of damping due to bank storage, the Darent results are consistent with this. The Darent average activity during the study period of approximately 11 TU may reflect mean rainfall composition in the area; but would be almost twice the value ($\sim 6\text{ TU}$) indicated by the UK composite input function used in connection with groundwater dating in the next section. This raises the possibility that upstream inputs of groundwater with a remanent thermonuclear ^3H content are contributing, but no information on the tritium activities of the Chalk and Lower Greensand groundwater feeding the upper reaches of the river is available to test this.

The relatively high tritium activities in the river are to an extent reflected in the river valley PS outputs at Horton Kirby and Darenth, which have activities exceeding any measured in boreholes away from the vicinity of the river (see next section). This suggests that up to one-third of the pumped water could ultimately be derived from the river, though the uncertainties

associated with such a limited dataset are large and require consideration along with more direct hydrological and hydrogeological flow and hydraulic head data. As with the stable isotopes, there is little seasonal change in ^3H activity, supporting the concept that any water abstracted from the river is already well mixed in the hyporheic zone or adjacent Chalk.

The CFC-12 compositions reported in Table 2 are shown in map form (Fig. 6) in terms of ‘modern fraction’, i.e. the fraction of modern air-equilibrated water in the sample assuming mixing between present-day recharge and pre-CFC (>50 yrs) groundwater. This is based on the Northern Hemisphere atmospheric mixing ratio curves (http://water.usgs.gov/lab/software/air_curve/), and the conclusion of Darling and Goody (2007) that these are likely to be applicable to southern England. Although the measured river water concentrations change significantly between October and February (Table 2), once they are corrected for temperature-related solubility effects most of the river waters give a modern fraction value of ~1, implying they are in equilibrium with the atmosphere. By contrast, the borehole waters vary much less seasonally and show a change from below-modern values in the south to considerably greater than modern in the north. The latter indicates a degree of CFC addition, most likely in the subsurface. Horton Kirby PS is about 4 times modern, and Darenth PS about 9 times modern. Each shows a slight decline for the high-flow sampling, but these could be the same within measurement error. CFC-11 is elevated to a similar extent as CFC-12 at both sites, indicating the source of enhancement is not biased towards a particular CFC species. There are landfilled areas in the vicinity of each PS, and these or light industrial activity are likely to be the cause of the CFC enhancement.

From the river water analyses at Horton Kirby and Darenth there is little overt evidence of any outflow of CFC-enhanced groundwater to the river. Gauge data suggest minor loss from the river at the low-flow sampling, but a minor gain from groundwater at the high-flow sampling, so higher CFC concentrations might have been expected in the river at this time. Decay of CFCs during infiltration has been observed for some rivers (Höhener et al., 2003), but Chalk stream hyporheic zones, where so far measured, do not achieve the low-oxygen status necessary for CFC reduction (Pretty et al., 2006; Allen et al., in press). Alternatively, it is possible that the relatively shallow depth of the river promotes rapid atmospheric equilibration and attenuation of any CFC signal, even if the discharging groundwater is at ~10 times the modern background. Further research on river–atmosphere gas exchange rates would be required to confirm or disprove this.

4.2. Sites in the Eastern Quarry and adjacent area

These include PS and private boreholes, Test boreholes, the Western Quarry borehole BW6, and two instances of significant pipe flow into the Eastern Quarry at Washmills and Cherry Orchard (Fig. 3). The pipe flows were among the first sites of the present study to be sampled (March 2001), when special sampling facilities were temporarily installed because of the otherwise difficult access to the normally copious flows (Tyler-Whittle, 1999). A borehole sampling campaign was undertaken during the approximately two-month-long group pump testing of the Test boreholes in November 2002 (details of the testing are provided in Mansour et al., *subm.*). While the testing caused the Cherry Orchard flow effectively to cease, by April 2003 it had recovered sufficiently for a final sampling (though only for isotopes, since access difficulties precluded the collection of the air-free samples necessary for trace gas analysis).

The O and H stable isotope data (Table 2) are reasonably well correlated, so $\delta^{18}\text{O}$ will be used to illustrate processes, as with the river data above. The data (Table 2) show that there is no significant difference between the boreholes sampled in 2001 and 2002; this is as expected particularly since the boreholes (except for BW6) were sampled in the same season (autumn). However, the Washmills pipe flow was sampled in March 2001 and November 2002, but again no significant change was noted.

Tritium results (Table 2) show that Court Lodge Farm, Hook Place Farm and Southfleet PS, which are believed to represent groundwater recharged areally by rainfall, have values of approximately 1–3 TU. Apart from the river valley boreholes (Darenth PS and Horton Kirby PS), most other sites are within (or within measurement error of) this range. The exceptions are BH 7 (slightly higher) and the Washmills inflow (significantly higher). In the context of a likely rainfall mean ^3H activity of 6–7 TU over the sampling period, groundwater values in the range 1–3 TU imply waters either a decade or two in age or, more likely in the Chalk, mixtures of recent recharge with ‘dead’ pre-thermonuclear tritium water (i.e. >50 yrs). The higher values from BH 7 and the Washmills inflow (4.6 and 8.4 TU respectively) suggest a greater proportion of modern water and/or a possible landfill contribution.

Maps of CFC distribution are shown in Fig. 7. As with the Darent valley results discussed above, the analytical results (Table 2) have been converted into ‘modern fraction’ format to make comparisons between the species more straightforward. It is apparent that the widespread enhancement, characterised by modern fractions >1 , is seen in all boreholes (with the exception of CFC-11 and -113 at Betsham).

The Football Field lower borehole, the only one to be depth-sampled for CFCs, revealed evidence of layering. While the sample from 17 m below water table was similar in composition to the pumped discharge for both CFC-11 and CFC-12, the sample from 9 m was approximately one-third lower in both CFCs (Table 2). This layering presumably reflects ingress of waters derived from different flowpaths. Chalk boreholes are not normally lined/screened and localised fracture-related inflow horizons are typical (Tate et al., 1970), therefore all the other boreholes in this study are likely to be producing a mixture of waters from different flow horizons. However, information on the depth and magnitude of inflows is seldom known or recorded.

Figure 8 shows that SF_6 does not reach the levels of enhancement recorded for the CFCs. By far the highest value is seen in the Darent Well sample. Otherwise, only slightly above-modern values are found in boreholes near landfilled areas (e.g. Pinden Quarry), the Test Borehole BH9 (also high in CFCs) and in the pipe flows at Washmills and Cherry Orchard, though it is possible (see section 3) that the latter contain a degree of entrained air which may have elevated the measured values. While the below-modern borehole waters can be assigned ‘piston flow’ age values, which range from 1 to 17 years (Fig 8), these are ages that take no account of mixing. Since this is likely in unconfined Chalk aquifers particularly where karstified (e.g. Darling et al., 2005), it may be safer to assume that the borehole waters are mixtures between modern and pre- SF_6 deeper waters, and that the modern fraction values of Fig. 8 are the most appropriate way to interpret the data.

It should be emphasised that the enhanced CFC and SF_6 concentrations observed for some sites are still well below the drinking water limit for dissolved organics (currently $1 \mu\text{g/L}$). For example, a CFC-11 concentration of 300 pmol/L , equivalent to a modern fraction value of ~ 50 , would be equivalent to only $0.04 \mu\text{g/L}$ on a weight-per-volume basis.

5. Discussion

5.1. Isotopic variations in the River Darent

Rivers rising and flowing wholly on the Chalk depend almost entirely on groundwater inputs and therefore vary little beyond measurement precision in their stable isotopic composition (e.g. Lawler 1987). The Darent cannot be regarded as a typical ‘chalk stream’ as the upper 30% of its course lies mostly on the Gault Clay that stratigraphically underlies the Chalk. This part of the course is likely to be the main contributor to the variation in composition observed in the river at the various downstream sampling points (Figs 4 and 5). The enrichment in isotopic composition observed during the autumn low-flow periods of 2001 and 2002 argues against major flow accretion where the river passes over the Chalk outcrop, since the groundwater in the Chalk Block away from the river valley is comparatively depleted in isotopic terms (Table 2).

5.2. The relationship between the River Darent and groundwater in the quarried area

Sub-karstic features as exemplified in visible form by the Washmills and Cherry Orchard fracture pipes are typically developed in the Chalk where acidic waters have penetrated from present or now-eroded Palaeogene cover rocks (Maurice et al, 2006). Yields from the Test boreholes, all drilled through Palaeogene cover, were highly variable (Mansour et al., *subm.*) suggesting that sub-karst is extensively developed in the vicinity. While the extent of this sub-karst beyond the present Palaeogene cover is impossible to ascertain directly, environmental tracers provide some indirect evidence.

In stable isotopic terms, the Test boreholes (Table 2) are compositionally distinct from the river waters, even when these are at their most depleted (Table 1, Fig. 4), and this therefore appears to limit the proportional amount of river leakage (if any) that might be flowing towards the Eastern Quarry. Taking values from boreholes which are highly unlikely to have any component of river water (Beslee, Betsham, Court Lodge Farm, Hook Place Farm, Pinden Quarry and Southfleet PS), an average areally-recharged groundwater composition of -7.3 ± 0.25 ‰ $\delta^{18}\text{O}$ is implied. The simple mean composition of river water at sampling point SW7 is -6.7 ‰ $\delta^{18}\text{O}$, i.e. significantly different from the groundwater average. Since all

the Test boreholes and the quarry inflows are more negative than the observed river water range, it appears that they cannot contain significant amounts of river water. While there is some uncertainty about the long-term range of variation in the river and consequently of any leakage, the river would have to have a sizeable flow more isotopically negative than that measured during the study just to reach the average groundwater composition. It seems unlikely that the approximately monthly sampling over what was a wetter-than-average winter could have missed such a flow. Only if it is assumed that the scale of river variation has been underestimated by 50%, and the true range of values is (say) from -6 to -7.5‰ , and only the most negative river water invades the Chalk Block (which is unlikely because groundwater levels are normally high in the winter months, which would preclude riverbed infiltration), could there be a sizeable proportion of river water in the Test boreholes, BW6 and the Eastern Quarry pipe flows. In addition, the lower Football Field observation borehole lies between the Test boreholes and the river (Fig. 3), but also shows no evidence of a significant river water component.

Although the Washmills inflow sample of November 2002 had a higher ^3H activity than local borehole waters, the stable isotopic evidence above makes any direct connection with the Darent appear unlikely, leaving the explanation that infiltration of relatively unmixed modern local recharge was responsible for the inflow. The group test pumping (Mansour et al., *subm.*) may well have affected the balance between recent recharge and older groundwater in the vicinity of the quarry; there was certainly a profound reduction in the rate of discharge from the main fracture pipes during the test (see section 4.2). Support for this interpretation comes from the April 2003 sampling, by which time the pipe flows were recovering from the effects of the test pumping. At Washmills the tritium activity was reducing, while at Cherry Orchard it was similar to the groundwater background.

The lack of above-modern SF_6 values from the Test boreholes when compared to the high excess at Darent Well is some further evidence for the lack of a significant hydraulic connection between the river valley and the Eastern Quarry. In particular the relatively high residence time for BH 3, which may in reality be even higher if the sample was affected by cascading (see section 3), indicates an element of storage in the Chalk south of the quarried area.

The environmental tracer evidence therefore indicates that karstic development is not widespread enough to promote significant flow between the river and the quarries. It may be noted that the Test boreholes were sited with the aim of intercepting groundwater flowpaths heading towards the quarries while avoiding the drawing of water away from the river valley, so the above evidence is consistent with this aim having been achieved.

5.3. Groundwater flow in the area south of the Eastern Quarry

The general similarity in stable isotopic compositions of the groundwaters south of the quarry offers little detailed information on flowpaths. However, the CFCs have greater potential for this. As mentioned earlier, inflow to the quarried area must basically be coming from the south. The southernmost boreholes such as Pinden Quarry and Hook Place Farm have different CFC fingerprints, likely due at least in part to the presence of nearby landfills (Fig. 7). Since there are three CFCs, relationships between different sites can conveniently be interpreted via a trilinear plot (Fig. 9). Such plots are commonly used in the interpretation of inorganic hydrochemical data as a way of detecting patterns of groundwater mixing or evolution (e.g. Hem, 1992), though they require a certain amount of care in interpretation since they depict ratios rather than absolute concentrations.. Trilinear plots do not appear to have been previously applied to the interpretation of CFC data. As with all such plots, concentrations of the three CFCs need to be converted to percentages. It is most convenient to do this using modern fraction values (Fig. 7), which are themselves directly proportional to the measured concentrations. Modern air-equilibrated water sits in the centre of the plot. To assist in the interpretation of Fig. 9, the total CFC load in pmol/l is also shown.

It is apparent from Fig. 9 that there are three main dilution/mixing trends based on the dominance of a particular species: a CFC-11 trend (source probably to the south of BH 9) could account for BH 5 and the quarry pipe flows; a CFC-12 trend probably sourced at Pinden landfill and directed north through Betsham; and a CFC-113 trend linking Hook Place Farm with Court Lodge Farm and Southfleet PS. In each case the CFC load drops with progress along the assumed flowpath. While BH 7 has an intermediate composition perhaps indicating mixing between the Pinden and BH 9 flowpaths, there are two sites which do not fit readily into this scheme: Green Street Green PS has an extremely elevated CFC-113 content which is not reflected in any neighbouring boreholes; BH 3 may be derived from a different, more westerly flowpath. Nevertheless there is sufficient evidence for the existence

of S–N flowpaths despite the E–W structures in the area alluded to earlier, such as the Bean Anticline.

Both tritium and SF₆ are relatively consistent in the boreholes south of the Eastern Quarry (Table 2, Fig. 8). While tritium on its own can be interpreted only semi-quantitatively, a plot against SF₆ brings out more detail (Fig. 10). This shows results in the context of an SF₆–³H piston flow curve (see figure caption for more information). Boreholes with a modern fraction <1 are arrayed close to and sub-parallel with the mixing line extending from ‘modern’ (in this case 2001) water to pre-SF₆, tritium-dead water. This tends to confirm that the SF₆ ages are best interpreted in terms of binary mixing. Southfleet PS has the lowest modern fraction, perhaps because as a public supply PS its yield is significantly greater than those of the other boreholes, with the result that there is likely to be greater upconing of older water. The position on the plot of the two over-modern boreholes (BH9 observation and Green Street Green) suggests that these too are basically mixed waters, but with some SF₆ enhancement presumably from local landfill sources.

6. Conclusions

A range of environmental tracers has been used to investigate the hydrogeology an area of major quarrying in the Chalk adjacent to a river valley at Swanscombe in north Kent. To achieve this, samples were collected from surface waters, regional groundwater, and pipe flows from the southern face of the Eastern Quarry.

The mean O and H stable isotopic composition of the nearby River Darent differs from the composition of typical groundwaters in the Chalk Block, probably as a consequence of summer evaporation effects. This contrast indicates that major sub-karstic river leakage into the Swanscombe quarried area is not occurring. However, stable isotope and tritium data from the river and public supply boreholes suggest that between one-fifth and one-third of abstracted water is derived from the river in the lower part of the valley. While there are uncertainties over the exact figure, it would be consistent with the view based on regional modelling that below Lullingstone the river is frequently perched above the groundwater table (Rippon & Wyness, 1994), with consequent potential for some river loss.

Enhanced chlorofluorocarbon (CFC) concentrations in Chalk groundwaters to the south of the quarries are likely to be the product of leakage and dilution of landfill effluents with differing characteristics. Flowpaths from south to north are clearly demonstrated in the eastern half of the area, but less so in the west where there is more landfill activity to complicate the issue. The above-modern concentrations rule out interpretation in terms of residence time, but in no case do they exceed water quality guidelines.

Sub-karstic conduits certainly exist in parts of the Chalk, as demonstrated by the instances of pipe flow into the Eastern Quarry. However, while such conduits are probably responsible for at least some of the heterogeneity observed, particularly among the Test Borehole grouping immediately south of the Eastern Quarry, they do not seem to have sufficient lateral persistence to provide preferential flowpaths on the kilometre scale.

This combined use of isotopic and trace gas indicators has provided new insights into the hydrogeology of an area where development pressures mean a balance must be struck between environmental amenity and water supply. The information gained can be used to inform appropriate management strategies.

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References

Allen, D.J., Darling, W.G., Goody, D.C., Lapworth, D.J., Newell, A.J., Williams, A.T., Allen, D. and Abesser, C. (2010). Interaction between groundwater, the hyporheic zone and a Chalk stream: a case study from the River Lambourn, UK. *Hydrogeology Journal*, DOI: 10.1007/s10040-010-0592-2.

Darling, W.G. and Goody, D.C. 2007. Assessing the applicability of global CFC and SF₆ input functions to groundwater dating in the UK. *Science of the Total Environment*, 387, 353–362.

Darling, W.G. and Talbot, J.C. 2003. The O & H stable isotopic composition of fresh waters in the British Isles. 1. Rainfall. *Hydrology & Earth System Sciences*, 7, 163–181.

Darling, W.G., Bath, A.H. and Talbot, J.C. 2003. The O & H stable isotopic composition of fresh waters in the British Isles. 2. Surface waters and groundwater. *Hydrology & Earth System Sciences*, 7, 183–195.

Darling, W.G., Morris, B.L., Stuart, M.E. and Goody, D.C. 2005. Groundwater age indicators from public supplies tapping the Chalk aquifer of Southern England. *Water and Environment Journal* 19, 30–40.

Downing, R.A., Price, M. and Jones, G.P. 1993. *The Hydrogeology of the Chalk of North-West Europe*, Clarendon Press, Oxford.

Edmunds, W.M., Cook, J.M., Darling, W.G., Kinniburgh, D.G., Miles, D.L., Bath, 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. *Applied Geochemistry*, 2, 251–274.

Geake, A.K. and Foster, S.S.D. 1989. Sequential isotope and solute profiling in the unsaturated zone of British Chalk, *Hydrological Sciences Journal* 34, 79–95.

Goody, D.C., Darling, W.G., Abesser, C. and Lapworth, D.J. 2006. Using chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF₆) to characterise groundwater movement and residence time in a lowland Chalk catchment. *Journal of Hydrology*, 330, 44–52.

Grapes, T.R., Bradley, C. and Petts, G.E. 2005. Dynamics of river–groundwater interactions along a chalk stream: the River Lambourn, UK. *Hydrological Processes* 19, 2035–2053.

Hem, J.D. 1992. Study and interpretation of the chemical characteristics of natural water. United States Geological Survey Water-Supply Paper 2254, 3rd edn, 263 pp.

Höhener, P., Werner, D., Balsiger, C. and Pasteris, G. 2003. Worldwide occurrence and fate of chlorofluorocarbons in groundwater. *Critical Reviews in Environmental Science and Technology* 33, 1–29.

Kloppmann, W., Dever, L. and Edmunds, W.M. 1998. Residence time of Chalk groundwaters in the Paris Basin and the North German Basin: a geochemical approach. *Applied Geochemistry* 13, 593–606.

Lawler, H.A. 1987. Sampling for isotopic responses in surface waters. *Earth Surface Processes and Landforms* 12, 551–559.

Mansour, M.M., Hughes, A.G., Spink, A.E.F and Riches, J. (subm.). Pumping test analysis using a layered-R-q numerical model in a complex, heterogeneous Chalk aquifer. *Journal of Hydrology*.

Maurice, L.D., Atkinson, T.C., Barker, J.A., Bloomfield, J.P., Farrant, A.R., Williams, A.T. 2006. Karstic behaviour of groundwater in the English Chalk. *Journal of Hydrology* 330, 63–70.

Plummer, L.N. and Busenberg, E. 1999. Chlorofluorocarbons. In: P G Cook and A L Herczeg (eds), *Environmental Tracers in Subsurface Hydrology*, Kluwer, Dordrecht, 441–478.

Oster, H. 1994. Datierung von Grundwasser mittels FCKW: Voraussetzungen, Möglichkeiten und Grenzen. Dissertation, Universität Heidelberg.

Pretty, J.L., Hildrew, A.G. and Trimmer, M. 2006. Nutrient dynamics in relation to surface–subsurface hydrological exchange in a groundwater fed chalk stream. *Journal of Hydrology*, 330, 84–100.

Price, M., Downing, R.A. and Edmunds, W.M. 1993. The Chalk as an aquifer. In: Downing R.A., Price, M., Jones, G.P. (Eds), *The Hydrogeology of the Chalk of North-West Europe*, Clarendon Press, Oxford, 35–58.

Rippon, P.W. and Wyness, A.J. 1994. Integrated Catchment Modelling as a Water Resources Management Tool. *Journal of the Institution of Water & Environmental Management* 8, 671–679.

Robinson, H.D. and Gronow, J.R. 1996. Tritium levels in leachates and condensates from domestic wastes in landfill sites. *Journal of the Institution of Water & Environmental Management* 10, 391–398.

Tate, T.K., Robertson, A.S. and Gray, D.A. 1970. The hydrogeological investigation of fissure flow by borehole logging techniques. *Quarterly Journal of Engineering Geology* 2, 195–215.

Tout, D. 1976. Chapter 5: Temperature. In: Chandler, T.J. and Gregory, S. (Eds), *The Climate of the British Isles*, Longman, London, 96–128.

Tyler-Whittle, R. 1999. The hydrogeology and hydrochemistry of the Swanscombe Chalk Block, Kent. MSc dissertation, University of Reading.

Smith, D.B., Downing, R.A., Monkhouse, R.A., Otlet, R.L. and Pearson, F.J. 1976. The age of groundwater in the Chalk of the London Basin. *Water Resources Research* 12, 392–404.

Vachier, P., Dever, L. and Fontes, J.C. 1987. Mouvements de l'eau dans la zone non saturée et alimentation de la nappe de la craie de Champagne, France. In: *Isotope Techniques in Water Resources Development*, International Atomic Energy Agency, Vienna, pp 367–379.

Table 1. Stable isotope results for the River Darent at site SW7 (Hawley). Results expressed in ‰ VSMOW.

Site	Date	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰
SW7	15-Oct-01	-6.73	-42.9
SW7	30-Apr-02	-6.39	-42.9
SW7	31-Jul-02	-6.20	-38.9
SW7	11-Sep-02	-6.52	-44.7
SW7	11-Oct-02	-6.44	-41.5
SW7	29-Nov-02	-6.46	-40.3
SW7	03-Dec-02	-6.57	-40.6
SW7	15-Jan-03	-7.02	-45.1
SW7	24-Feb-03	-7.11	-44.0
SW7	30-Apr-03	-6.72	-43.6

Table 2. Stable isotope, tritium, CFC and SF₆ data from river and groundwater sampling sites in the Darent Valley and Swanscombe Quarry areas.

Site	Date	Temp °C	δ ¹⁸ O ‰	δ ² H ‰	³ H TU	CFC-12 pmol/L	CFC-11 pmol/L	CFC-113 pmol/L	SF ₆ fmol/l
River waters									
SW7	Oct-01	15.4	-6.73	-42.9		2.9	6.0		
	Oct-02	12.4	-6.44	-41.5	14.9	2.9	5.2		
	Feb-03	6.2	-7.11	-44.0	9.8	4.8	8.4		
SW6	Oct-01	15.3	-6.81	-43.8		2.5	4.9		
	Oct-02	12.5	-6.40	-41.5	12.2	2.5	5.3		
	Feb-03	6.4	-7.21	-45.7	9.1	4.5	8.5		
SW5	Oct-01	15.0	-6.62	-44.3		2.5	5.2		
	Oct-02	12.3	-6.15	-41.9		2.6	5.2		
	Feb-03	6.4	-6.96	-45.5		4.3	7.7		
SW4	Oct-01	15.2	-6.65	-44.4		2.4	6.0		
	Oct-02	12.5	-6.56	-41.2		2.7	5.5		
	Feb-03	6.5	-7.04	-46.4		4.6	7.7		
SW3	Oct-02		-5.96	-39.8					
	Feb-03		-7.22	-46.9					
SW2	Oct-02		-7.01	-46.3					
	Feb-03		-7.14	-45.3					
SW1	Feb-03		-7.09	-45.4					
River valley pumping stations									
Darenth PS	Oct-02	11.5	-7.30	-47.0	6.4	27	57		
	Feb-03	11.5	-7.32	-46.8	5.0	24	60		
Horton Kirby No 1	Feb-03	11.4	-7.07	-45.5	5.8	11	35		
Horton Kirby No 2	Oct-02	11.3	-7.21	-45.7	5.4	13	24		
Eynsford PS	Oct-02	10.8	-7.24	-47.7		2.6	5.3		
	Feb-03		-7.12	-46.0		3.1	6.6		
Lullingstone No 1	Oct-02	11.1	-7.36	-47.4		1.9	13		
Lullingstone No 2	Feb-03	10.7	-7.31	-46.4		2.3	16		
Boreholes									
Beslee Discharge	Oct-01		-6.95	-47.5					
Betsham	Oct-01	12.4	-7.09	-48.3		5.5	4.6	0.47	1.2
Bluewater BW6	Mar-01		-7.28	-49.9					
Court Lodge Fm	Nov-02	11.7	-7.64	-47.4	2.7	6.7	12	2.8	1.3
Darenth Well	Oct-01		-6.98	-47.3		37	91	3.4	32
Football Field Lr bulk	Aug-03	12.1	-7.49	-46.8		5.3	14.4		
Football Field Lr 9 m	Aug-03					3.8	9.0		
Football Field Lr 17 m	Aug-03					5.4	14.8		
Green St Green PS No 2	Oct-01	12.0	-6.79	-47.5		5.8	26	190	3.6
	Nov-02	10.9	-7.20	-47.5	1.9	5.4	16		
Hook Place Fm	Oct-01	11.8	-7.36	-48.2		6.0	16	8	1.2
	Nov-02	10.8	-7.51	-47.4	1.4	7.8	12.1		
Pinden Quarry	Oct-01	12.7	-7.30	-47.9		360	52	3.5	2.8
Southfleet PS	Oct-01	12.0	-7.32	-47.6		7.5	6.6	1.9	0.6
	Nov-02		-7.27	-47.3	2.0	5.9	10.6		
Test Boreholes									
BH 3 (W Bean Farm)	Nov-02	11.6	-7.29	-49.1	2.2	14	75	2.1	(1.4)
BH 5 (E Beacon Wood)	Nov-02	11.6	-7.31	-46.8	3.3	43	81	7.0	1.6
BH 7 (Mid Drudgeon Fm)	Nov-02	11.7	-7.41	-46.7	4.6	75	88	5.0	(2.1)
BH 9 (W Beacon Wood)	Nov-02	11.6	-7.68	-48.1	2.5	76	310	11	1.8
BH 9 observation	Nov-02	11.4	-7.51	-48.1	2.5	97	273	16	4.2
Eastern Quarry pipe flow									
Cherry Orchard	Mar-01	10	-7.41	-47.2		51	110	5.5	2.5
	Apr-03				3.1				
Washmills	Mar-01	10	-7.49	-47.3		55	130	6.2	2.4
	Nov-02		-7.65	-47.3	8.4				
	Apr-03				6.6				

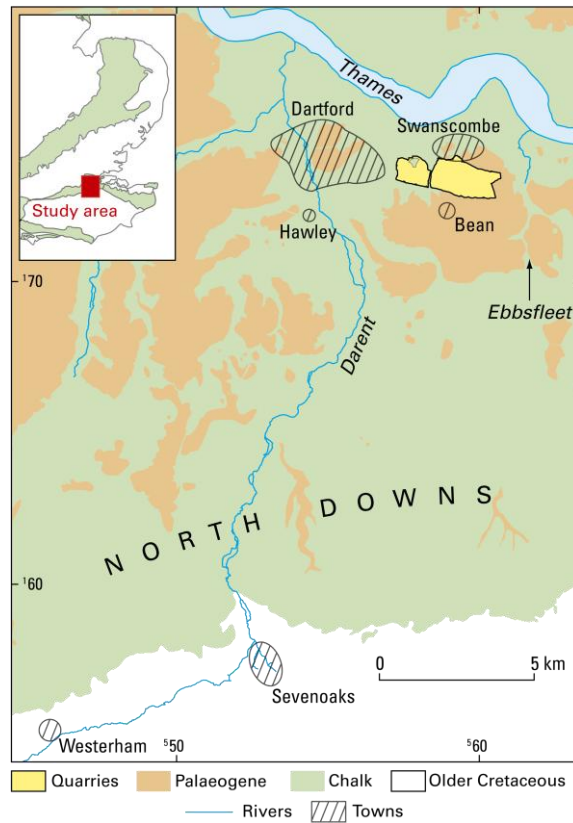


Figure 1 Map showing the basic geology of the River Darent corridor and the Swanscombe Chalk block between the Darent and Ebbsfleet valleys. Also shown are the locations of the Eastern and Western quarries, and urban areas mentioned in the text. Inset: the location of the area in the context of the Chalk outcrop in SE England.

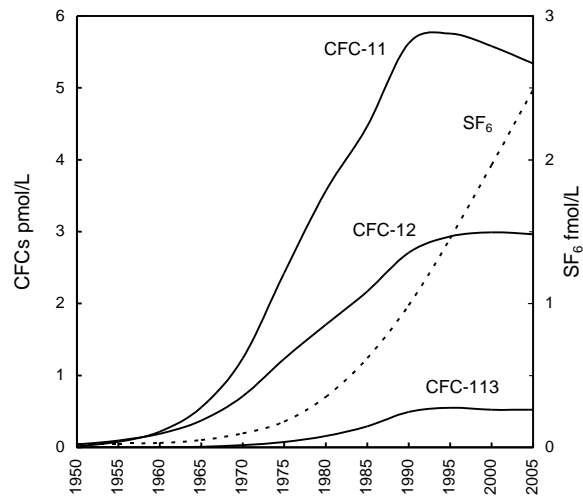


Figure 2 Variation over time of the concentrations in groundwater of the CFCs and SF₆ assuming equilibrium with the Northern Hemisphere atmospheric mixing ratios at a recharge temperature of 10°C. Based on data from http://water.usgs.gov/lab/software/air_curve/.

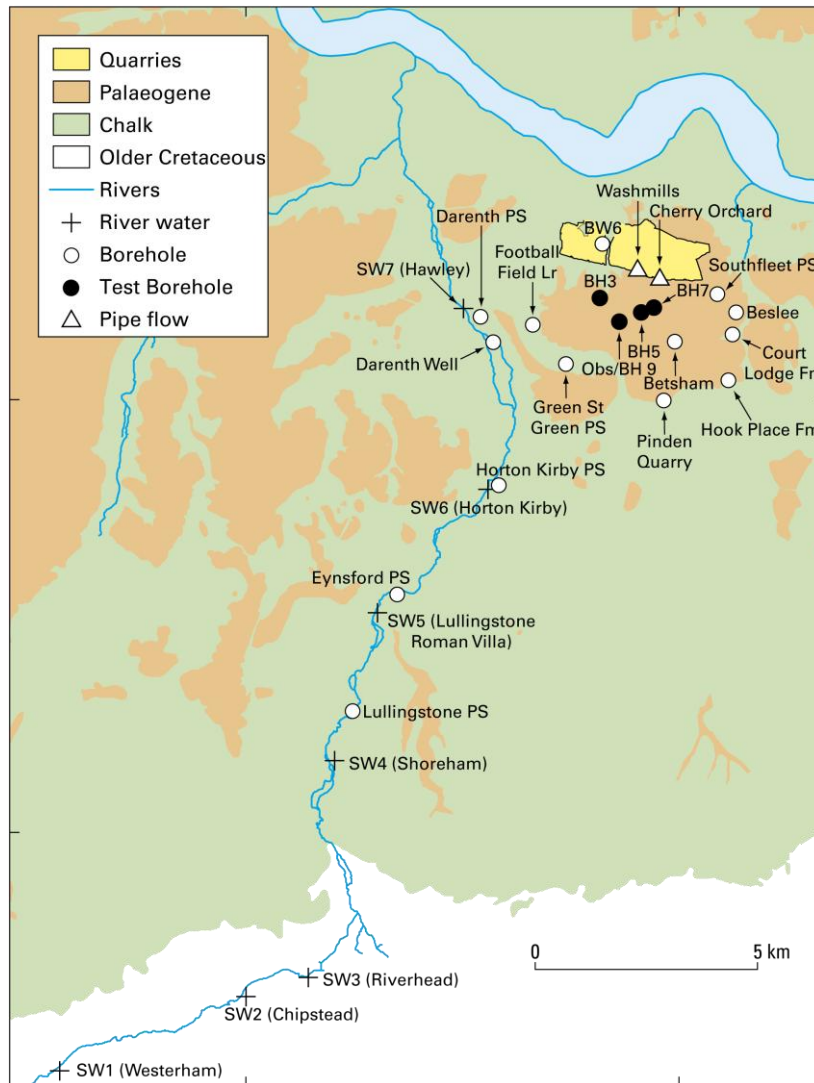


Figure 3 Map showing the location of river and borehole sampling sites in the Darent Valley and the Eastern Quarry area. PS – pumping station.

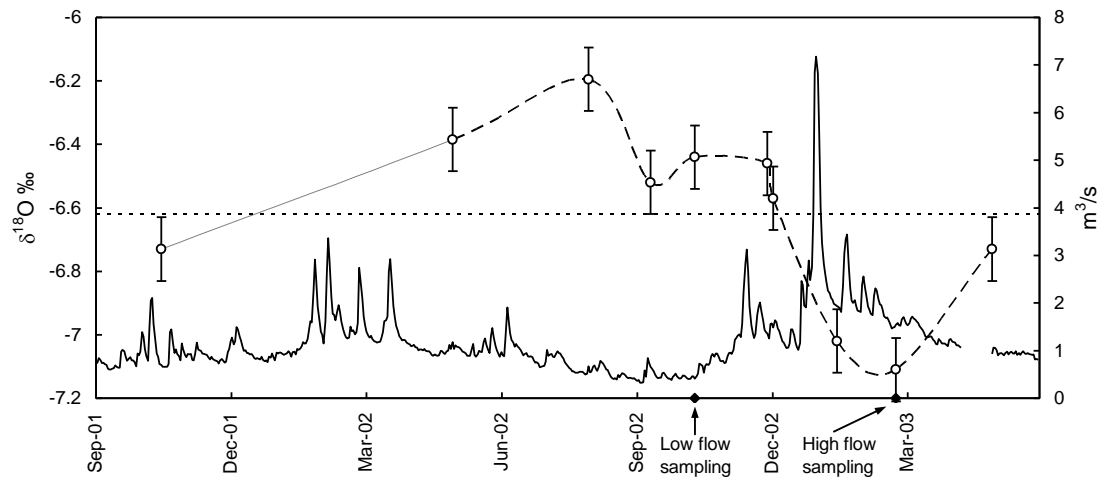


Figure 4 Plot of $\delta^{18}\text{O}$ vs time for spot samples collected from the River Darent at site SW7 (Hawley). The dotted line represents the simple mean for the period. Also shown is the daily average flow of the river at Hawley expressed as m^3/s . The dates of the low- and high-flow samplings (see text) are also indicated.

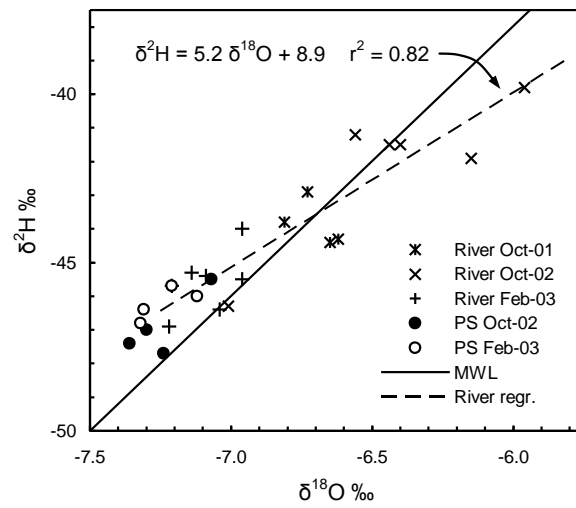


Figure 5 Plot of $\delta^{18}\text{O}$ vs $\delta^2\text{H}$ for samples from the River Darent and associated valley pumping stations (PS), showing the seasonal change in river water but not PS samples. Also shown are the meteoric water line (MWL) and the regression line through the river water data.

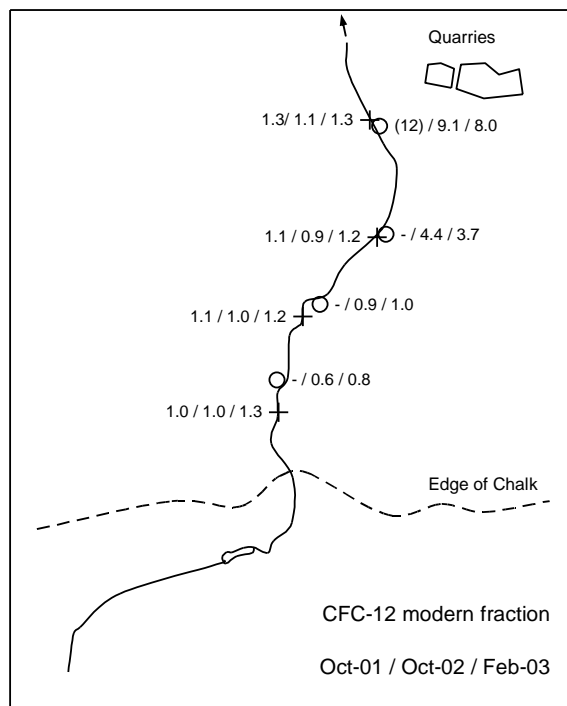


Figure 6 Map showing the distribution of CFC-12 as 'modern fraction' values (see text) in the River Darent and adjacent valley boreholes during the samplings of October 2001, October 2002 and February 2003. Value in brackets from Darenth Well rather than Darenth PS. Site symbols as in Fig. 3.

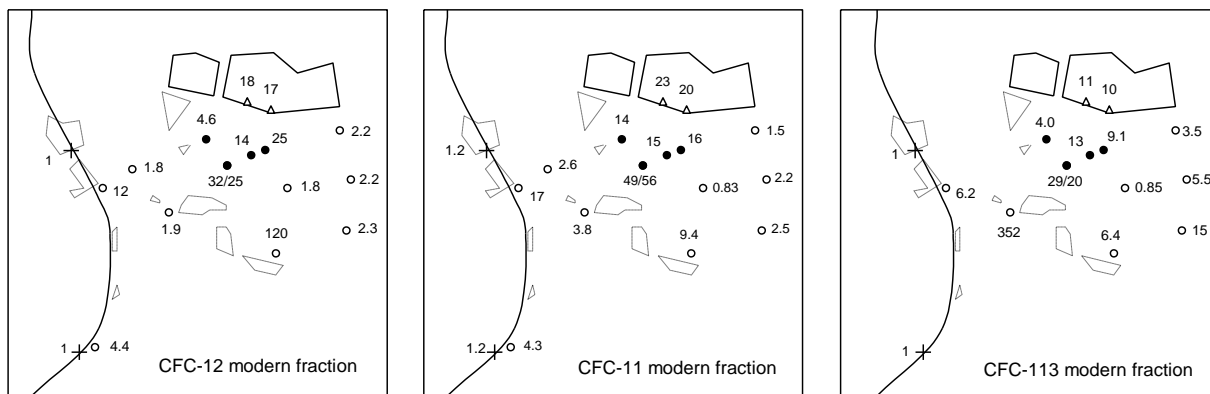


Figure 7 Maps showing the distribution of CFCs in terms of modern fraction for sampling sites in the vicinity of the Eastern Quarry. Adjacent river valley sites included. Outlines of known landfills indicated. For the Test BH 9 pair the result for the shallower observation borehole is shown first, e.g. '32/25'. Where sites have two sequential analyses (see Table 2), these have been averaged to provide a single modern fraction value. Site symbols as in Fig. 3.

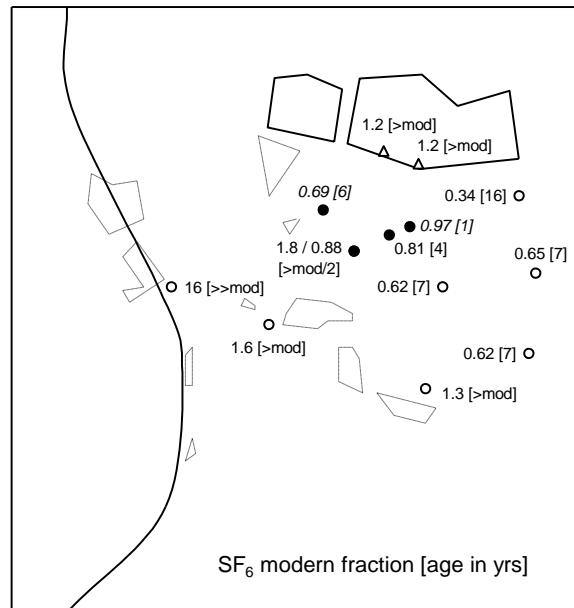


Figure 8 Maps showing the distribution of SF₆ in terms of modern fraction and piston flow residence time in years (in square brackets) for sampling sites in the vicinity of the Eastern Quarry. Adjacent river valley sites included. Outlines of known landfills indicated. For the Test BH 9 pair the result for the shallower observation borehole is shown first, e.g. '1.9/0.85'. Values for Test BHs 3 and 7 are italicised to indicate the possibility of air entrainment. Site symbols as in Fig. 3.

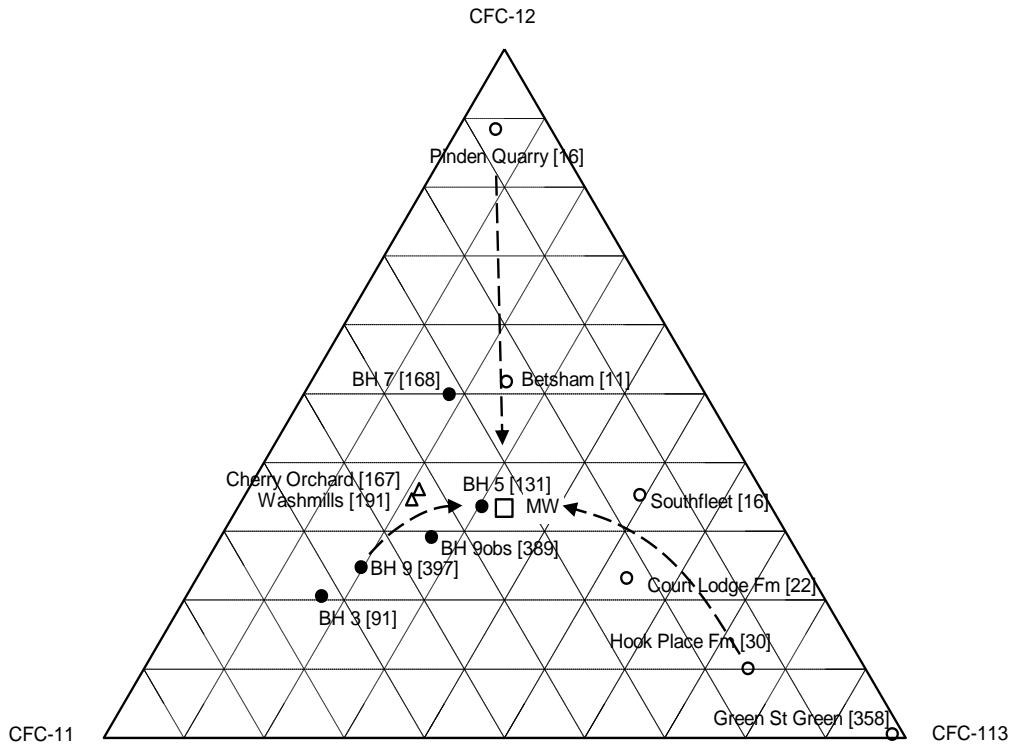


Figure 9 Trilinear plot (see text) of the three CFC species in terms of modern fraction for sampling sites in the vicinity of the Eastern Quarry. MW represents modern air-equilibrated water. Probable flow/dilution lines are indicated.

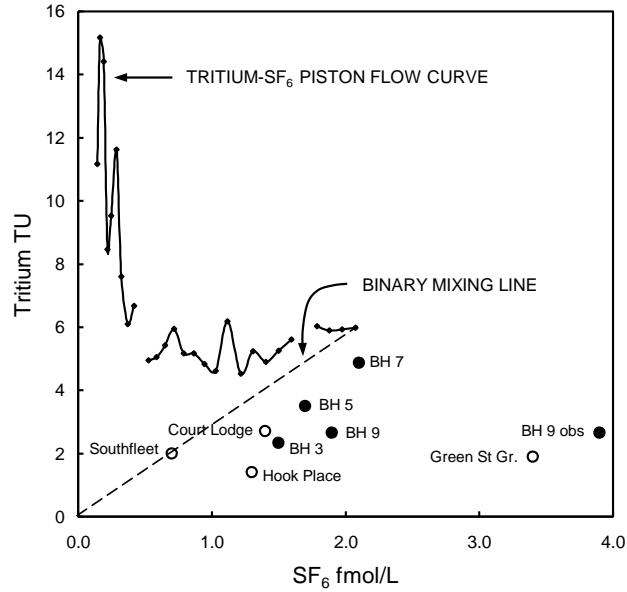


Figure 10 Plot of SF₆ versus tritium for borehole sampling sites in the vicinity of the Eastern Quarry. Also shown is the piston flow curve for the period 1972–2001 based on SF₆ data from http://water.usgs.gov/lab/software/air_curve/ and precipitation tritium data from the IAEA-WMO Global Network for Isotopes in Precipitation (<http://nds121.iaea.org/wiser/index.php>). In the absence of recent ³H data for the UK, the average of data for Valentia (Ireland) and Groningen (Netherlands) has been used. The binary mixing line between modern and pre-thermonuclear recharge is also shown. All ³H data (including the curve) have been corrected for decay to 2001 values. The pipe flow samples from Washmills and Cherry Orchard are not shown as the two determinands were measured more than two years apart.