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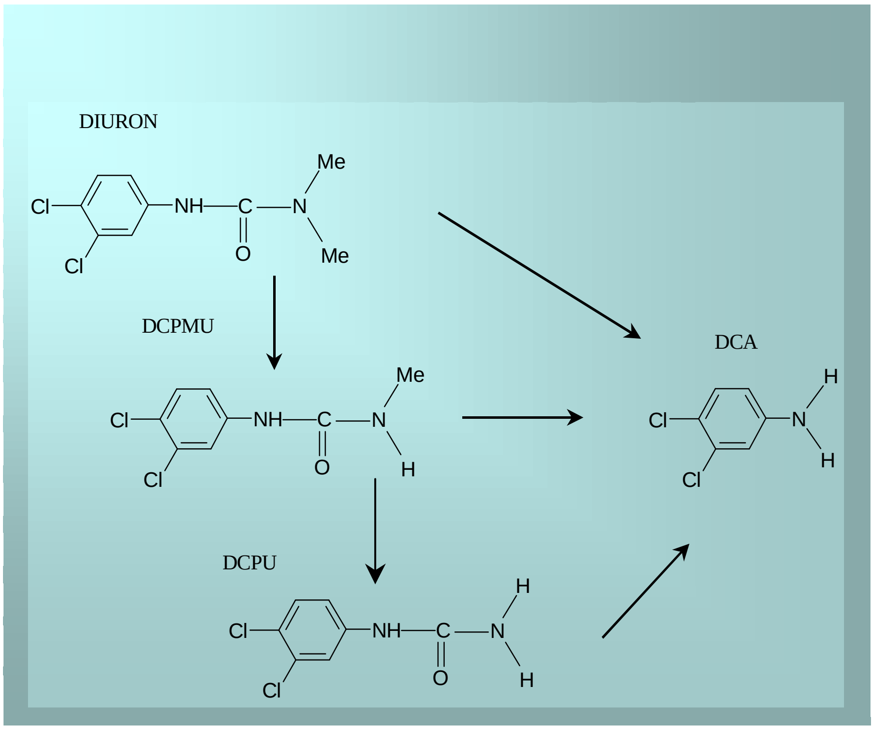
Pesticides and their metabolites in groundwater - diuron in the Isle of Thanet chalk aquifer of southeast England

Groundwater Systems and Water Quality Programme

Internal Report IR/05/049



BRITISH GEOLOGICAL SURVEY

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Summary

Pollution from diuron and its metabolites is, like nitrate pollution, a ubiquitous problem within the Isle of Thanet aquifer. The widespread diuron pollution is symptomatic of a much larger problem of historic pollution within the aquifer system. Diuron was observed in 90% of samples (0.4-214 ng/L). In 60% of these metabolites were more prevalent than diuron. Mean total diuron concentrations were above the Prescribed Concentration Vale (PCV) at nearly 30% of sites and showed a large concentration range (2.2-1161 ng/L). Maximum concentrations for diuron and its metabolites were in the following order DCA>DCPU>Diuron>DCPMU, all four compounds exceeded the PCV on at least one occasion. There is some evidence to suggest that diuron occurrence could be spatially related to areas of urban and industrial development. Results from groundwater tracers (SF_6) support the idea that high diuron concentrations were associated with the unusually high recharge observed in the winter/autumn of 2000-2001.

The Isle of Thanet Chalk aquifer has characteristically short residence times, as evidenced by the response to historic reductions in applications of other pesticides such as atrazine and simazine and recent groundwater tracer studies. This is both a benefit as well as a drawback in terms of overall groundwater quality. While the problem of diuron may be only transient, given improved application practices, the aquifer is still vulnerable in the short-term depending on the quantity of diuron stored in the unsaturated zone. Much more needs to be understood about the transport and occurrence of diuron in the unsaturated zone to determine more fully the future risk to groundwater from pesticides such as diuron.

Despite some evidence to suggest that the metabolites of diuron may be more toxic than the parent compound, there is currently no requirement to monitor metabolite concentrations in groundwater. Should this change there could be potential implications in terms of future management of the groundwater resource in the Isle Thanet aquifer, and across the UK as a whole.

1 Introduction

Recent studies have highlighted the occurrence and transport of pesticides and their metabolites from the soil to depth within different groundwater systems (Kolpin et al., 2001, 2002; Gooddy et al., 2001, 2002, and Postle et al., 2004). Reducing the impact of anthropogenic pollution on UK aquifers and ameliorating any deterioration of water quality is central to key legislative drivers such as the EU Water Framework Directive (WFD) (2000/60/EC) and the proposed daughter Directive relating to the protection of groundwater (2003/0210/COD/550).

Water quality limits for pesticide compounds are currently covered under both UK and EC legislation. The Drinking Water Regulations (HMSO, 2000) that transpose the EC Drinking Water Directive (98/83/EC) into UK law set an exceedingly low Prescribed Concentration or Value (PCV) for individual pesticides in water supplied to customers of 0.1 µg/l. As of December 2003 a limit of 30 ng/l (0.03 µg/l) has been set for certain pesticides, but this does not include diuron. Diuron is currently under review for identification as a possible ‘priority hazardous substance’ (2455/2001/EC). Recent research has suggested that some metabolites of diuron may have greater toxicity than that of the parent compound (Tixier et al., 2001) and that in groundwater the metabolites of some pesticides may be more prevalent than the parent compound (Kolpin et al., 2001). As yet there are no water quality limits for the metabolites of pesticide compounds, and therefore no legal requirement to monitor their occurrence in groundwater. However, ‘metabolites, degradation and reaction products’ are included in the proposed daughter Directive relating to the protection of groundwater.

Diuron (*N*-[3,4-dichlorophenyl]-*N*,*N*-dimethylurea) is a phenyl urea herbicide used to control broadleaf weeds. Other common phenylurea herbicides include: isoproturon, monuron, chlorotoluron, fenuron, fluometuron, metobromuron, chlorobromuron and linuron. It is used on many crops, including wheat and fruit, but is commonly used on crops as a pre-emergence herbicide (Tomlin, 1994). It is used along railway tracks (Torstensson, 2001), on hard surfaces such as pavements, airports and central reservations, and on golf courses (Swancar, 1995; Cohen et al., 1999).

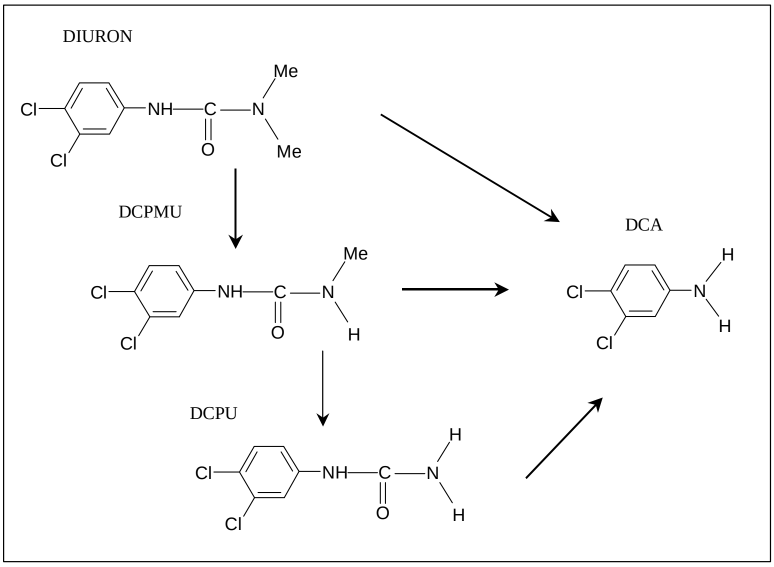


Figure 1. Aerobic degradation pathways of diuron and its metabolites

After application diuron can enter the soil where it is either absorbed to clay and organic matter, or it remains in aqueous phase and is able to be transported within the soil profile. The process of microbial degradation is able to break down diuron into its metabolites; the pathways for diuron degradation are shown in Figure 1. Plants take up diuron and its metabolites readily through their root systems where the metabolites become incorporated in the plant material. Under aerobic conditions degradation in the soil takes place by N-demethylation to two metabolites, DCPMU and DCPU (Scribner et al., 1999).

It can be seen from Figure 1 that the demethylation process is not necessarily sequential and that one or both of the intermediate compounds, DCPMU and DCPU, may be formed depending on the pathway. The final stage in the degradation process is a hydrolysis reaction resulting in the compound 3,4-dichloroanaline (DCA). The metabolites, and residual diuron, can then either remain absorbed to soil particles, or desorb where they can be transported to depth eventually reaching the groundwater table. This process may in part be facilitated by colloidal transport (de Jonge et al., 1998; Wu and Laird, 2004). Linuron (*N*-[3,4-dichlorophenyl]-*N*-methoxy-*N*-methylurea) can also lead to the formation of the same degradation products in soil as diuron through the same process of sequential N-demethylation (Sørensen et al., 2003).

The physical and chemical properties of diuron, its metabolites and two other commonly used pesticides are shown in Table 1. The relatively low Koc indicates a low tendency to sorb to organic matter in soil and sediments, while the hydrolysis half-life for diuron is quite long showing that it is persistent and therefore able to be transported down the soil profile. Howard (1991) has suggested that the metabolites are less mobile in the soil than diuron, the theoretical Koc value indicate this, however, the metabolites are much more soluble. Once transported out of the soil zone there is limited potential for microbial degradation of pesticides (Johnson et al., 2000) and their metabolites. These properties mean that there is a relatively high risk of diuron transport to groundwater.

Table 1. Physical and chemical properties of diuron and its metabolites, malathion and atrazine

Physical-chemical properties	Diuron	DCPMU	DCPU	DCA	Malathion	Atrazine
Water Solubility (mg/L 25 C)	42	486 (1)	939(1)	318(1)	140	33
Half life in aerobic soil (days)	372	-	-	-	<1	146
Hydrolysis half -life (days)	1490	-	-	Unlikely(1)	650	Stable
log Kow	2.8	-	-	2.7 (2)	2.7	2.68
logKoc	2.68	2.86(1)	2.72(1)	2.74(1)	3.08	2.17

USDA Pesticide properties database; (1) Theoretical values calculated by USEPA (personal communication) using structural information and CAS number of compound,(2) Sinclair and Boxall, 2002

This report builds on two studies: a scoping study undertaken in 2003 (Gooddy et al., 2004) in the chalk aquifer of the Isle of Thanet, southeast England, where high concentrations of diuron had previously been observed; and a field scale study on diuron, and its metabolites, in the soil and groundwater in an alluvial soil overlying a chalk aquifer in the south of England (Gooddy et al., 2002). It presents the findings from three sampling surveys in the Isle of Thanet aquifer between September 2003 and December 2004 and considers the occurrence of diuron and its metabolites in relation to the geology and landuse within the historic context of pollution in the aquifer.

2 Background

2.1 GEOLOGY AND SUPERFICIAL DEPOSITS

The Isle of Thanet is underlain by the middle sequence of the Upper Chalk Formation, Figure 2, which is part of the North Downs outcrop that extends from west of Guilford to Isle of Thanet on the east coast. The structure consists of a shallow anticline with an E-W axis. To the south the chalk dips at a steeper angle than to the north. The Thanet Beds overly the chalk and are found in two distinct zones to the south of the area, along the line of the Great Stour, and in patches to the southeast, in the locality of Minster. The Beds do not usually exceed 5m in thickness, are comprised of sandy clay, and cover only a relatively small part of the area.

A description of the soils in the area has been given in the Southern Water Authority report on nitrate (SWA, 1985). Two soil types are found on The Isle of Thanet: brown calcareous earths, of the Coombe and Andover series occupy the centre of the area, whilst to the south, and located across the area in several large patches, are argillic brown earths of the Hamble and Bursledon series. The Coombe series is a brown silty loam, found at its thickest in the dry valleys. The Andover series are thin brown calcareous soils and are located on the hill slopes. The Hamble series are brickearth deposits (wind blown silts) overlying the Chalk and Thanet Beds. They often have a deep profile and are freely draining. The Bursledon series is found to the west of Broadstairs, again on the Thanet Beds, and the soils are usually free draining.

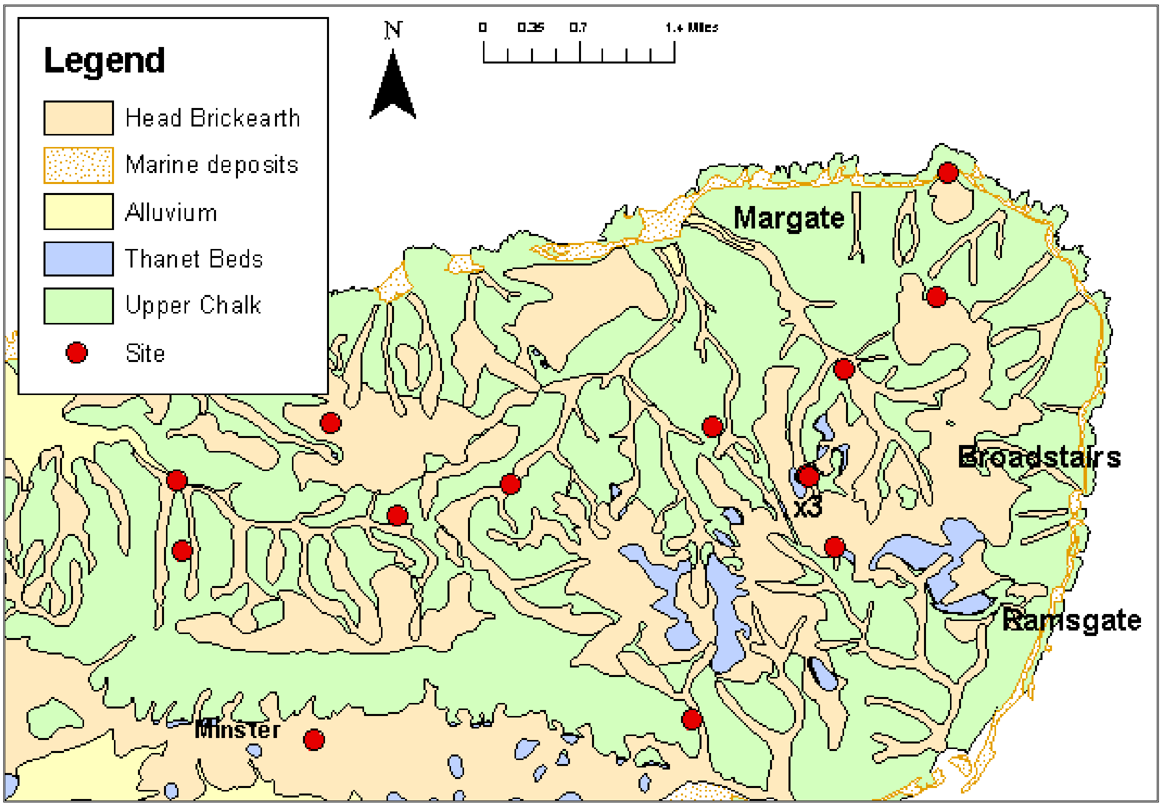


Figure 2. Solid and drift geology

2.2 HYDROGEOLOGY

Across the southern region of England as a whole 80% of public water supply is from groundwater (DETR, 1997). The Isle of Thanet Chalk aquifer has long been an important source of water for the area both for public supply and private abstraction. The aquifer is classified as over-abstracted (EA, 2002) largely due to the relatively high proportion of coastline. The groundwater contours reflect, in a subtle way, the dome-like topography of the Isle of Thanet. At the centre of the area the groundwater is around 7m AOD, which corresponds to an unsaturated zone thickness of greater than 30 m. Seasonal fluctuations in groundwater levels are small (1-2m) and dampened at low elevations (SWA, 1985).

The transmissivity of the Chalk of the North Downs show a large range, 0.14-20 m^2/a, with a geometric mean of 1.9 m^2/a (Allen et al., 1997). The most productive fractures are found within the upper sections of the aquifer, in the zone of water table fluctuation. There are a large number of dry valleys that have developed along dominant fractures (SWA, 1985) and transmissivities are usually high within these regions. Groundwater flow is likely to be affected locally by abstraction from public supply boreholes. This is especially the case for one public supply borehole, Lord of the Manor, which has a large network of adits. There is some saline intrusion to the north and east of the area. The aquifer can be considered as semi-confined across the whole area with the exception of the area to the south and two patches to the southeast where Palaeogene deposits exist.

Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) are used as residence time indicators for groundwaters (Cook and Soloman, 1995; MacDonald et al., 2003). Recent studies in the unconfined chalk of southern England (Darling et al., submitted) have used these tracers to estimate the aquifer vulnerability in the context of Cryptosporidium contamination of groundwater. These tracers will be used here to enhance the overall understanding of groundwater residence times, and may provide some insight into the occurrence of diuron and its metabolites within the Isle of Thanet aquifer, and the likely recovery of the aquifer from pesticide pollution.

2.3 LANDUSE AND SOURCES OF DIURON

Much of the Isle of Thanet to the north and east is urban, including a mixture of residential and industrial landuses. To the south of the area, near Manston, there is an airfield. There are 21 landfill sites across the area as a whole and most of them are located in the southern and eastern margins of the area. There are three areas of managed grassland in the area; the major landuse is arable farmland. There are several potential routes for pesticide contamination to reach the groundwater. These are shown in Table 2, divided into point, semi-point and diffuse sources.

Table 2. Routes of environmental contamination by pesticides

Diffuse	Point and semi-point
Spray application	Rainway tracks
Contaminated manure	Landfills sites
Sediment transport	Roads
Volatilisation and precipitation	Urban usage
Leaching from soil	Spillages and washings
	Drains, sumps and soakaways

(from Stuart, 2003). Routes to groundwater shown in blue

There are also sources specific to The Isle of Thanet, most of these were described in detail by Gooddy et al (2004), and are summarised below. Figure 4 shows the borehole locations in relation to potential source of pesticides: landfills, golf courses, roads, railway lines, Manston airfield, areas of urban development.

1. *The Isle of Thanet District Council*

The council reported an over-spray incident in 2001. Neat diuron was used by a contractor which resulted in widespread contamination of flowerbeds, parks, and paths etc. Applications are likely to have been within the SPZ of public water supplies. The thin soils in the area result in a higher risk of transport to the groundwater.

2. *Connex Depot, Ramsgate*

Diuron was used regularly on-site up until 2003. The site is within the SPZ 1 of the Lord of the Manor public supply borehole. There was a possibility of by-pass flow by way of soakaways within the depot. Only a patchy layer of ash and made ground covered the site rendering the aquifer vulnerable to pollution.

3. *Landfill sites and golf cources*

Of the 20 landfill sites on Thanet, 10 are within the catchment of the SPZ of three public supply boreholes, Lord of the Manor, Minster B and Sparrow Castle. There is a golf course located north of Broadstairs.

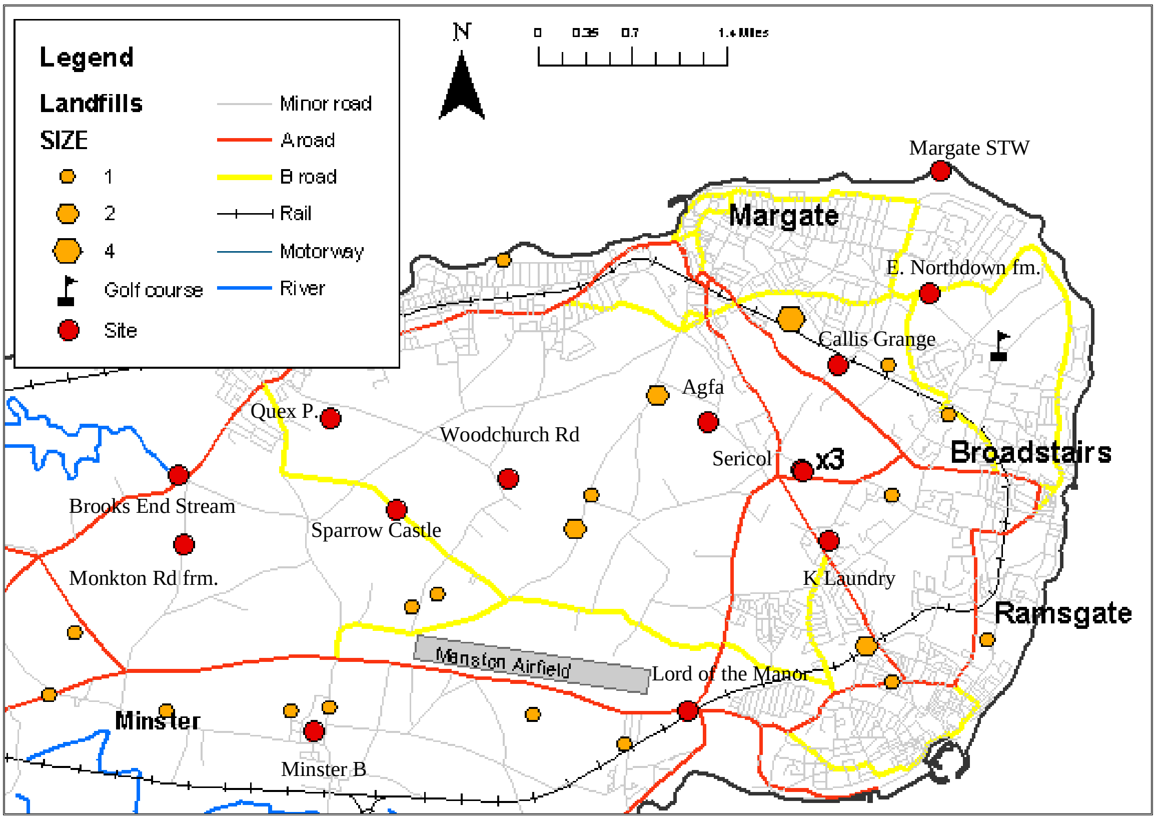


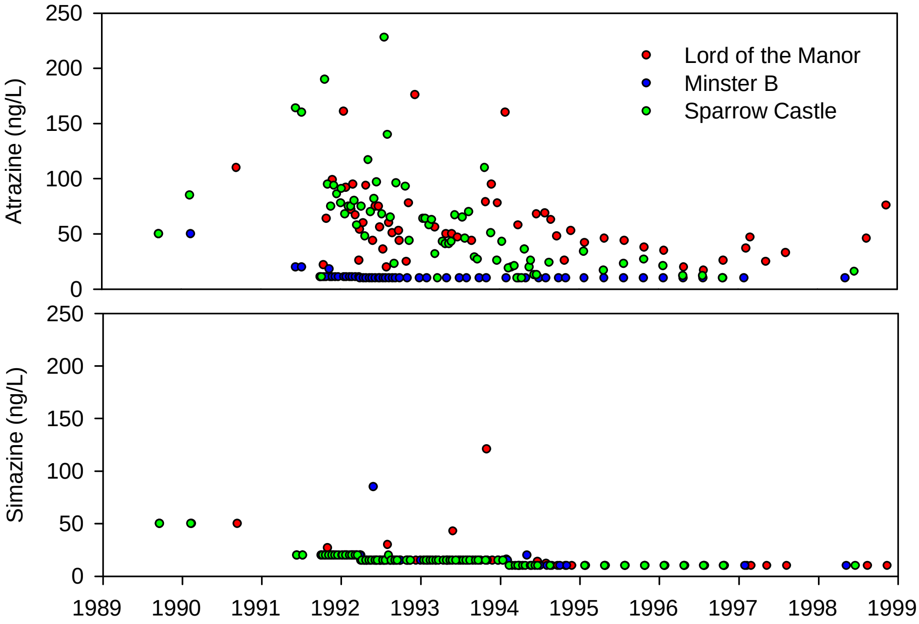
Figure 3. Land use and potential pesticide sources in the study area

Table 3. Landfill sites within the SPZ for three public supply boreholes

Site	SPZ 1	SPZ 2	SPZ 3
Sparrow Castle	-	1	2
Minster B	2	-	1
Lord of the Manor		3	1

2.4 HISTORIC POLLUTION OF THE ISLE OF THANET AQUIFER

The Isle of Thanet aquifer has historically been impacted by pollution from several sources, both diffuse and point. In December 2000 Southern Water Services reported elevated concentrations of diuron in their raw water samples at the Lord of the Manor public supply borehole. They took the abstraction out of supply for several weeks to prevent diuron entering the supply system and then installed a temporary Granular Activate Carbon treatment scheme. The incident co-incided with heavy rainfall and high groundwater levels and resulted in a peak diuron concentration of 1200 ng/l. This peak may have been the result of a one-off point source incident, such as an accidental spillage of diuron next to a soakaway allowing quick bypass of the soil and unsaturated zone, or may be the result of a more general diffuse type of pollution caused by the groundwater levels rising and picking up diuron from the unsaturated zone over a large area.



(Adapted from Smedley et al., 2003)

Figure 4. Changes in atrazine and simazine concentrations 1989-1999.

Other triazine pesticides, including atrazine and simazine, have also been detectable in the Isle of Thanet aquifer. Figure 4 shows the changes in atrazine concentrations between 1989 and

1999 for the three public supply boreholes Lord of the Manor, Minster B and Sparrow Castle. There has been an observed drop in concentrations since the early 1990s and this is thought to be the direct result of wide restrictions imposed since the 1993 on the use of the two compounds (Smedley et al., 2003). By 1995 triazine herbicides were no longer present in the market in any significant volume, having been replaced by the less persistent compounds glyphosate and diuron (DoE, 1996).

There have been incidents of aquifer contamination from leaky fuel tanks resulting in high levels of MTBEs and cyclohexanone near the Sericol boreholes. Three of the monitoring boreholes for this incident, Sericol BHs1-3, were sampled as part of this pesticide survey.

Lord of the Manor and Sparrow Castle show comparable concentrations of pesticide pollution and signal noise. This is in contrast to Minster B with much lower concentrations and a relatively constant signal. This could be the result of the differences in borehole depth, Minster is >60 mbgl while the others are less deep at ~30 mbgl and thus the water quality could be a reflection of the relative groundwater ages. Likewise, the degree of protection that the overlying Thanet Beds and brickearth deposits provide to the catchment of Minster B could be reflected in the groundwater quality from this borehole. Similar trends are also observed for simazine, although the resolution is worse due to the poorer detection limits.

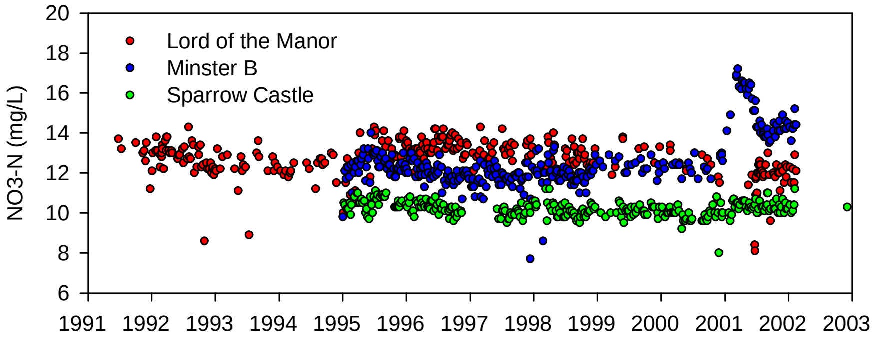
If this apparent recovery of the water quality is due to the change in application practices then this would imply, amongst others three important points.

§ A relatively short residence time for groundwater within the semi/unconfined part of the aquifer

§ The source term for the pollution has an important diffuse component, and is likely to be the result of agricultural applications, although this may not be the case for diuron

§ There may be potential for the recovery of any pollution due to diuron and its metabolites within a relatively short timescale if there is a significant reduction in diuron application within the area.

For many years there has been a problem of nitrate pollution in the aquifer. Leaky urban sewage systems and fertilizer from arable agricultural practices have both been important sources of nitrogen (SWA, 1985). Approximately 70% of the Isle of Thanet is considered a Nitrate Vulnerable Zone. At present public supply is kept below the PCV for NO_3-N of 11.3 mg/L by blending with water from outside the area and by treatment. Raw water time series data for nitrate from three public supply boreholes are shown in Figure 5. All show consistent



(Adapted from Smedley et al., 2003)

Figure 5. Changes in nitrate concentrations 1991-2003.

concentrations above the PCV since the early 1990s. Minster B has shown an upturn in nitrate concentrations since 2000. The converse is true for Lord of the Manor. This could be the result of rising groundwater levels following the unusually wet autumn and winter of 2000-2001. The different responses are likely to be the result of different hydraulic and geological settings. Lord of the Manor has an extensive series of adits complicating any interpretation of trends from this borehole. No seasonal trends are obvious from any of the series and there is no correlation between pesticide and nitrates.

3 Methods

3.1 SAMPLING SITES AND SAMPLING METHODOLOGY

Three surveys were conducted over a period of 16 months, the first in September 2003, the second in April 2004 and the third in December 2004. Fifteen sites were sampled across the semi-confined Isle of Thanet aquifer, including one stream site. Table 4 shows the sites, organised from north to south across the aquifer and details landuse and the purpose of the borehole. The spatial distribution of sites across the area can also be seen in Figure 4. It can be seen that there are three main landuse types: arable agriculture/nurseries, industrial and urban. Three sites are Southern Water abstraction boreholes, Margate is a borehole in a sewage treatment works (STW) very close to the coast, the three sites at Sericol are monitoring boreholes and the remaining sites are a mixture of private abstraction boreholes for use in irrigation and other purposes.

Table 4. Site locations, landuse, and purpose of the borehole

Sample site	Easting	Northing	Landuse	Purpose/usage
Margate STW	638368	171581	Urban	Sewage treatment works
East Northdown Farm	638239	170115	Nursery	Irrigation
Callis Grange	637150	169253	Nursery/Arable	Irrigation
Quex Park BHA	631050	168610	Industrial	
Agfa	635592	168580	Industrial	
Sericol BH1	636709	167990	Industrial	Monitoring boreholes
Sericol BH2	636717	167980	Industrial	Monitoring boreholes
Sericol BH3	636717	167980	Industrial	Monitoring boreholes
Brooks End Stream	629236	167935	Arable	
Woodchurch Road	633188	167891	Arable	Irrigation
Sparrow Castle	631849	167522	Arable	Abstraction
K Laundry	637028	167142	Urban	Abstraction
Monkton Road Farm	629297	167101	Arable	Irrigation
Lord of the Manor	635347	165100	Arable	Abstraction
Minster B	630858	164860	Arable/suburban	Abstraction

Samples were taken with a submersible pump, or using the pump installed in the borehole. The borehole was purged prior to taking a sample. Pesticide samples were taken in 2.5L amber bottles with PTFE-lined caps. These were taken to BGS Keyworth where 5g of sodium azide was added (0.2%) for preservation prior to refrigeration.

In December 2004 samples were also taken for analysis of major and trace inorganic chemisty, total organic carbon (TOC), dichlorodifluoromethane (CFC-12), trichlorofluoromethane (CFC-11) and sulfur hexafluoride (SF_6). Field measurements of groundwater temperature, dissolved oxygen, redox potential, conductivity and pH were also made where possible.

Inorganic chemistry samples were passed through a 0.45μm cellulose filter, and an aliquot acidified (1%v/v) with HNO_4. The acidified samples were analysed for major and trace cations and the unfiltered samples analysed for anions. CFC and SF_6 samples were taken using the displacement method described by Oster et al (1996). These parameters were analysed at BGS Wallingford.

Table 5 shows the geology, drift cover, completion depths and raw water levels (RWL), where known. A drift cover index was compiled from the drift cover data as an indication of the aquifer vulnerability in the immediate (500m) vicinity of the borehole. Most sites comprise Upper Chalk with head brickearth deposits, at five sites Thanet Bed deposits overlie the Chalk, and at three sites the Chalk is completely exposed.

Table 5. Drift geology, vulnerability index, and field observations

Site	Drift Geology	Index	Depth (m)	RWL (mbgl)
Margate WTW	Brickearth	2		
East Northdown Farm	None	1		42.7
Callis Grange	None	1	37.2	24.1
Quex Park BHA	None	1		
Agfa	-			
Sericol BH1	TB, Brickearth	3		27.8
Sericol BH2	TB, Brickearth	3		
Sericol BH3	TB, Brickearth	3		
Brooks End Stream	Brickearth	2		
Woodchurch Road	Brickearth	2		19.1
Sparrow Castle	Brickearth	2	34	
K Laundry	TB, Brickearth	3	137	
Monkton Road Farm	Brickearth	2		
Lord of the Manor	Brickearth	2	36	
Minster B	TB, Brickearth	3	61	

TB= Paleogene Thanet Bed deposits, RWL= rest water level (mbgl) on 01-Dec-04.

Index (indication of aquifer vulnerability): 1= no drift cover, 3= extensive Thanet Bed cover

3.2 PESTICIDE AND INORGANIC ANALYSIS

Pesticide sample pre-concentration was performed by SPE using Waters OASIS HLB (200 mg sorbent) cartridges. Two litres of preserved sample was passed through two of these cartridges in series. However, it became apparent that no significant quantities of compounds of interest were eluting from the second cartridge and so only a single cartridge was used subsequently.

A cartridge was pre-conditioned by the passage of 2 x 6ml of Romil UpS acetone followed by 2 x 6 ml of MilliQ water (18 MΩ). Then the two litres of sample were passed through at a flowrate of *ca.* 5 - 7 ml/min. The cartridge was washed with 2ml of MilliQ water. The sorbent bed was not dried but left in a water-wetted state (holding approx. 1 ml water) and eluted with Romil UpS acetone into a 15 ml graduated glass centrifuge tube (with a tapered base). The acetone was evaporated under a gentle stream of oxygen-free nitrogen until 1 ml of liquid remained (predominantly water). This was then made to 2 ml with MilliQ water.

The 2 ml of 1000 x pre-concentrated sample was used to rinse and charge an HPLC syringe. The syringe contents were then used to completely fill a 1 ml injection loop. The HPLC pumped a mobile phase consisting of 35% v/v aqueous acetonitrile (1 ml/min) through a Supelco LC18-DB column (150 mm x 4.6 mm i.d.), protected by a Supelguard LC18-DB guard column. Both the guard and the main column contained 5 μm particles of stationary phase. The detection wavelength was 252 nm and peak area integration was undertaken by a Perkin-Elmer Turbochrom chromatographic data handling system.

Acidified samples were analysed for major and trace cations (Na, K, Ca, Mg, SO4, Si, Al, B, Ba, Be, Cd, Co, Cr, Cu, Fe_{total}, La, Li, Mn, Ni, Mo, Pb, P_{total}, Sc, Sr, V, Y, Zn, Zr, As) using a Perkin-Elmer DV3300 ICP-OES. Anions (Cl, NO_3, NO_2, NH_4) were analysed using a Skalar flow colorimeter, and Br and F were analysed using a Dionex HPLC. TOC was analysed using a Thermalox TC analyser, CFCs and SF_6 were analysed by gas chromatography after pre-concentration using a purge-and-trap technique (Oster et al., 1996).

4 Results

4.1 INORGANIC CHEMISTRY, DOC AND RESIDENCE TIME INDICATORS

A summary table for a range of chemical parameters is shown in Table 6. A full table of results is in the appendix, including median and mean values. Where median values are less than the detection limit the detection limit values have been substituted. The waters have typically Ca-HCO3-dominant compositions. Chloride concentrations vary (48-5620 mg/L), with all but one site being below 200mg/L. These concentrations are significantly higher than mainland chalk due to wind-blown marine deposition. Margate is on the coast and the high Na, Cl and SO_4 concentrations are due to saline intrusion. The two Sericol sites have a history of contamination and this explains their high Cl and SEC.

DO, nitrate and Eh values are consistent with semi/unconfined Chalk groundwater. Where the groundwaters are aerobic the nitrate concentrations were close to or above the PCV of 11.3 mg/L. The obvious exceptions are the Sericol sites where the environment is likely to be anaerobic, with relatively high Fe and reduced nitrate concentrations. The large NO_2 concentrations at the sericol sites indicate that there could be denitrification taking place. These concentrations are in excess of the PCV for NO_2-N of 0.03 mg/L.

Margate and the two Sericol sites show higher TOC concentrations. This is likely to be due to localised contamination. The former site is a Sewage Treatment Works, and the latter has a history of organic contamination.

Zn and Ni are variable across the aquifer and elevated in some locations indicating potential contamination from landfill sites. High Zn concentrations could be derived from sulphide minerals in the Chalk, notably pyrite.

Table 6. Summary table of chemical determinands from December survey

	Concentration mg/L												Fraction of modern			
	Ca	Mg	Na	K	Cl	SO_4	HCO_3	NO_3-N	NO_2-N	TOC	Zn	Ni	CFC-11	CFC-12	SF_6	*Bulk age
Callis Grange	157	6.21	45.9	5.81	72.5	62.3	267	16.1	0.004	1.2	0.090	0.0057	3.47	1.23	0.59	1995
E. Northdown Farm	108	6.53	40.7	1.63	59.8	39	266	10.7	< 0.0003	1.52	0.035	0.0082	0.22	0.23	0.84	2000
Sericol BH1	187	8.73	85.2	19.4	126	50.9	460	4.57	0.696	158	0.034	0.0111				
Sericol BH2	180	8.56	75	11	114	42	464	0.685	0.405	2.94	0.029	0.0081				
Woodchurch Road	114	4.11	28.3	2.14	48.1	17.9	269	12	0.0032	1.01	0.085	< 0.005				
K Laundry	136	6.34	48.5	3.41	74.2	28.8	332	12.7	0.004	1.04	0.067	0.0088				
Minster AB	113	6.86	38.6	2.94	68	26.6	280	13.5	0.0025	0.8	0.041	0.0051	1.56	0.45	0.35	1988
Sparrow Castle	114	5.19	31.4	2.36	54.2	15.2	310	9.91	< 0.0003	0.87	0.027	< 0.005	2.80	351	0.46	1991
Margate STW	217	350	2990	112	5620	746	271	15	0.0043	2.36	0.089	0.0114	2.22	2.04	0.79	1999
Mean	147	45	376	17.9	693	114	324	10.6	0.1	1.5	0.055	0.0				
Median	136	6.53	45.9	3.41	72.5	39	280	12	0.0038	1.12	0.041	0.0081				

* Based on SF_6 data

Five sites were sampled for the three residence time indicators, CFC-11, CFC-12 and SF_6. Overall there is a poor agreement between results obtained for the two CFC gases, with only the results at East Northdown Farm and Margate showing any agreement. CFC-12 fractions are consistently lower than CFC-11. This is not usually the case as CFC-11 is more prone to microbial degradation. However, the aquifer is aerobic and so microbial degradation might be inhibited (Plummer and Busenberg, 1999). The excess CFC with respect to modern water implies that the aquifer is highly contaminated with CFCs. This is clearly the case at Sparrow Castle. The contamination is likely to be from several sources including urban developments, landfill sites and from the illegal disposal of refrigerators (several were seen dumped on the roadside within the catchment during sampling).

SF_6 is a more reliable tracer, being less prone to contamination (MacDonald et al., 2003), and with atmospheric concentrations still increasing. The SF_6 results show a range of modern fraction results, 0.35-0.84, from which 'bulk dates' were estimated. These bulk ages seem reasonable given the overall semi/unconfined nature of the aquifer. The results fit well with the concept of a short residence time implied by the rapid recovery of the aquifer from atrazine contamination. The bulk ages also highlight the more confined nature of the aquifer and/or the relatively older source of groundwater at Minster B.

4.2 DIURON AND ITS METABOLITES

The diuron and metabolite results for the three sampling surveys are summarised in Table 7 (the full data set is in the Appendix). Diuron or one of the metabolites was detected in all but one sample. Diuron was detected in 90% of the samples, DCPMU and DCPU in around 60% and DCA in 43%. Mean concentrations (calculated excluding below detection limit results), were below the PCV for all compounds except DCA (183 ng/L). Maximum total concentrations for each compound exceeded the PCV. The mean total pesticide concentration was twice the PCV. Median values are lower than the mean values and this is due to a small number of outliers within the dataset. This is also reflected in the large % coefficient of variation for each compound. All four compounds were detected over a large concentration range.

Table 7. Summary statistics for diuron and metabolites

	Concentration ng/L				
	Total	Diuron	DCPMU	DCPU	DCA
Detections (%)	97	90	67	63	43
Mean	213	26.6	18.8	27.8	183
Median	24	11.4	0.9	1.85	38.2
Max	1161	214	162	356	902
Min	2.2	0.42	0.16	0.23	0.89
CV%	176	55.4	42.6	34.1	62.2
*Detection limit (ng/L)		0.1	0.1	0.1	0.7

*Optimal detection limit shown (n=30)

Table 8. Mean diuron and metabolite concentrations

Site	Total	Diuron	DCPMU	DCPU	DCA	%Metabolites
Margate STW	22	11.7	0.4	7.0	2.6	56
East Northdown Farm	86	5.5	2.0	1.7	77	71
Callis Grange	3.4	0.4	<0.1	<0.1	2.9	87
Agfa	466	34	0.5	<0.1	431	93
Quex Park BHA	2.2	1.7	0.2	0.2	<3.8	20
Sericol BH1	920	140	162	356	263	85
Sericol BH3	52.8	44.3	<0.1	1.3	7.2	16
Sericol BH2	1161	74	109	76	902	94
Brooks End Stream	208	123	41.6	17.6	26.2	42
Woodchurch Road	<0.1	<0.1	<0.1	<0.1	<3.8	0
Sparrow Castle	7.7	6.3	0.6	0.9	<3.8	18
K Laundry	26	7.9	2.9	0.5	15	61
Monkton Barn Farm	4.6	2.2	0.6	1.8	<3.8	55
Lord of the Manor	15.1	14.6	0.5	0.1	<3.8	3
Minster B	9.9	1.1	0.1	8.7	<3.8	77

Concentrations in ng/L

Table 8 shows the relative variation in diuron and its metabolites across the survey area. The sites are ordered from north to south. All four diuron compounds were found at six sites, three compounds were found at seven sites and two compounds at only one site. Two of the 15 sites had mean diuron concentration over the PCV. Mean total pesticide concentrations had a large variation (2.2-1161 ng/L) and at four sites the mean total concentrations were over the PCV. At nine sites (60%) metabolites were more prevalent than diuron.

Figures 6 and 7 show the spatial distribution of mean total diuron concentrations and the proportion of metabolites. It can be seen that there is no correlation with landfill site location and no clear relationship with geology. However, there is a zone in the centre of the Isle of Thanet, relatively free from roads and development, which does seem to have lower concentrations and fewer metabolites compared to the developed areas around the edge. This does suggest that roads and areas of urban development could be a major source of diuron and agrees with the specific sources of diuron identified on the Isle of Thanet, Section 2.3. The four locations with the highest diuron concentrations all had a high percentage of metabolites. Sites located in the centre of the aquifer all had relatively low total diuron concentrations and few detectable metabolites.

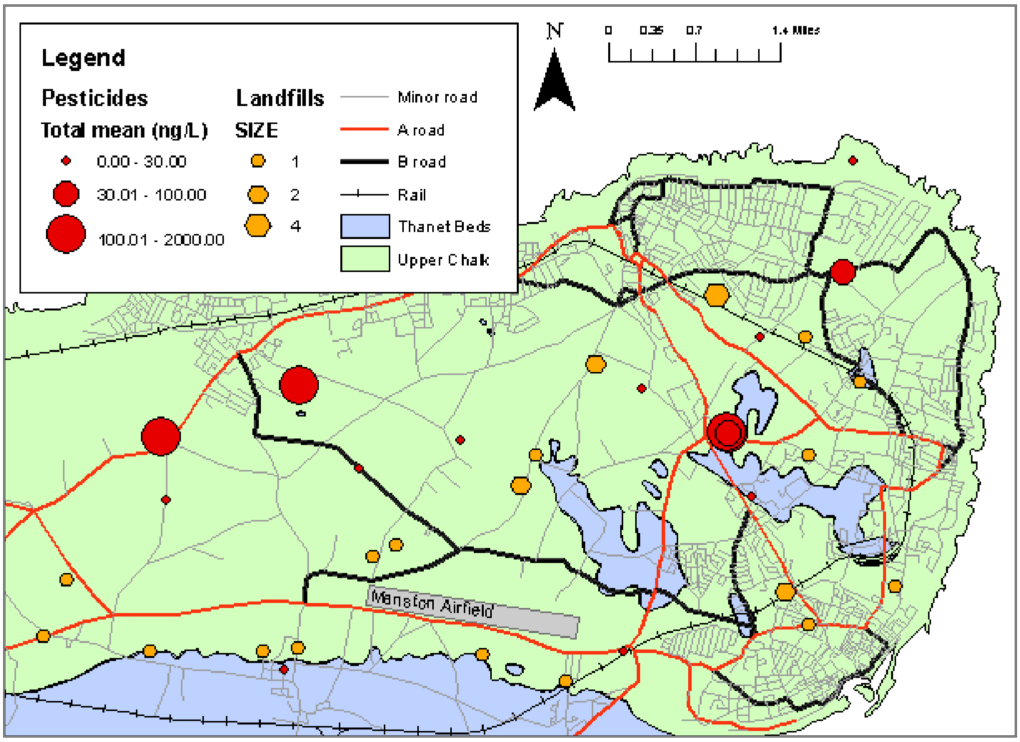


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Figure 6. Spatial variations in mean concentrations for total diuron

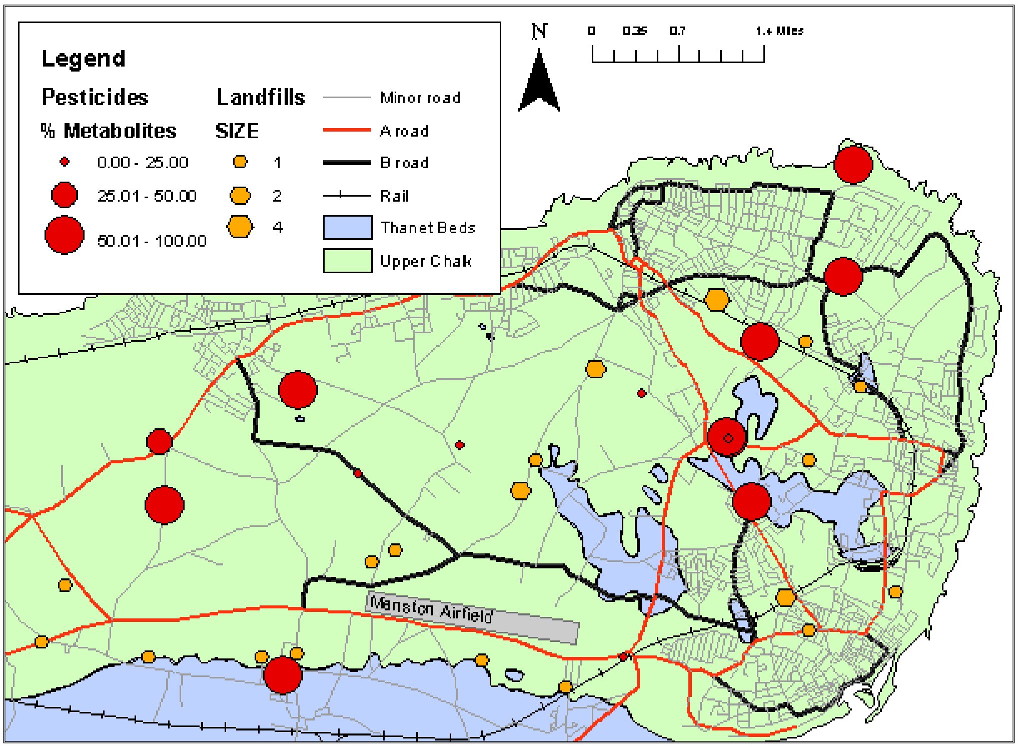

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Figure 7. Spatial variations in proportion of metabolites

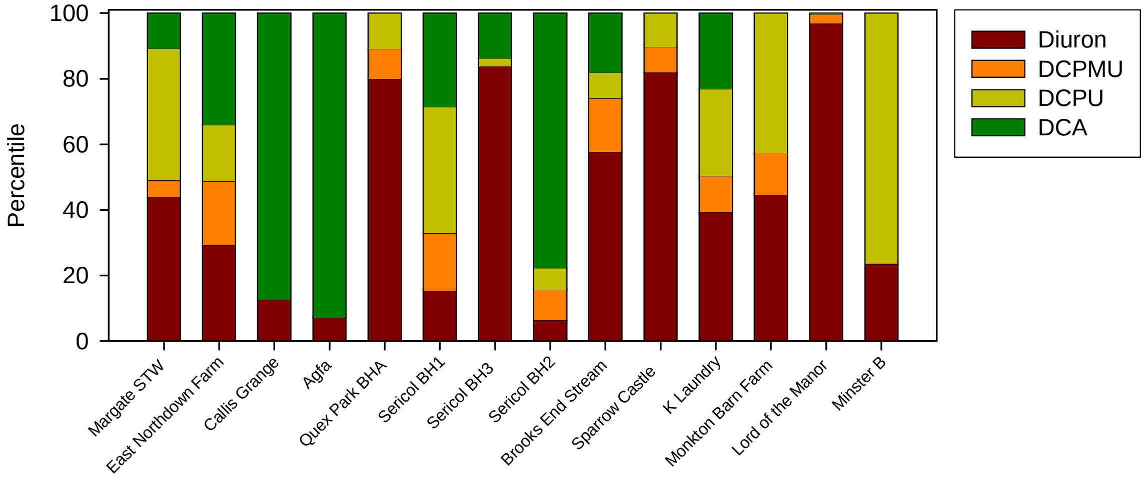


Figure 8. Mean relative abundance of diuron and its metabolites at each sampling site

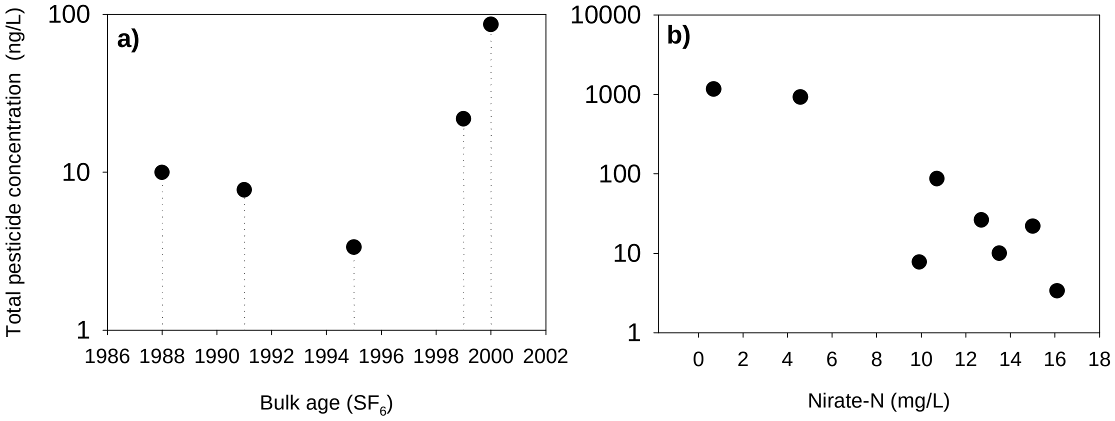


Figure 9. Plot of (a) total pesticide concentration and bulk SF_6 age, and (b) total pesticide concentration and nitrate (note log scale for pesticide concentration)

Mean relative abundances are shown in Figure 8. It can be seen that there is a large variation in pesticide composition across the survey area as a whole. Diuron is the major component at 8 sites, DCA at 4 sites and DCPU at 2 sites. DCPMU is a minor component at all sites. Overall diuron and metabolite occurrence is in the following order: diuron>DCA>DCPU>DCPMU. A variety of location-specific soil characteristics: depth of profile, moisture content, hydraulic conductivity, clay/organic content, and the historic usage of diuron are likely to be significant in controlling pesticide compositions at the different sites.

Figure 9 (a) shows a plot of total pesticide concentration and bulk SF_6 'age'. It can be seen that there is an increase in pesticide concentration for the two waters with ages of 1999 and 2000. These correspond with the peaks in diuron concentrations observed at Southern Water public supply boreholes following the wet autumn/winter of 2000-2001. There is no positive correlation with nitrate (see Figure 9 (b)) and the two sites with the highest pesticide concentrations were both anaerobic. This was also found to be the case in the Triassic sandstone of south Yorkshire (Gooddy et al., 2005).

Figure 10. Temporal changes in pesticide concentrations at six sites

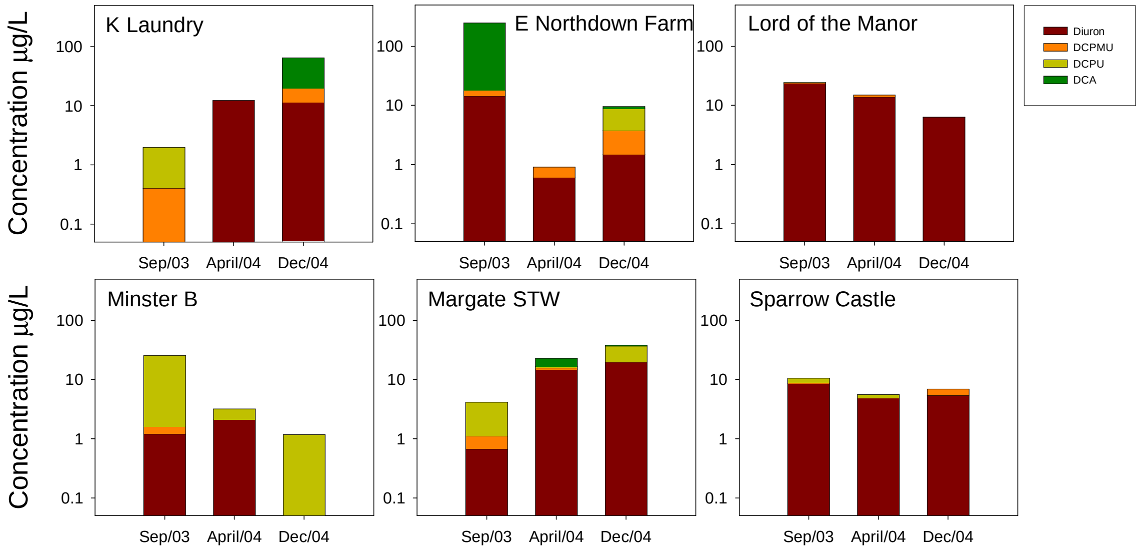
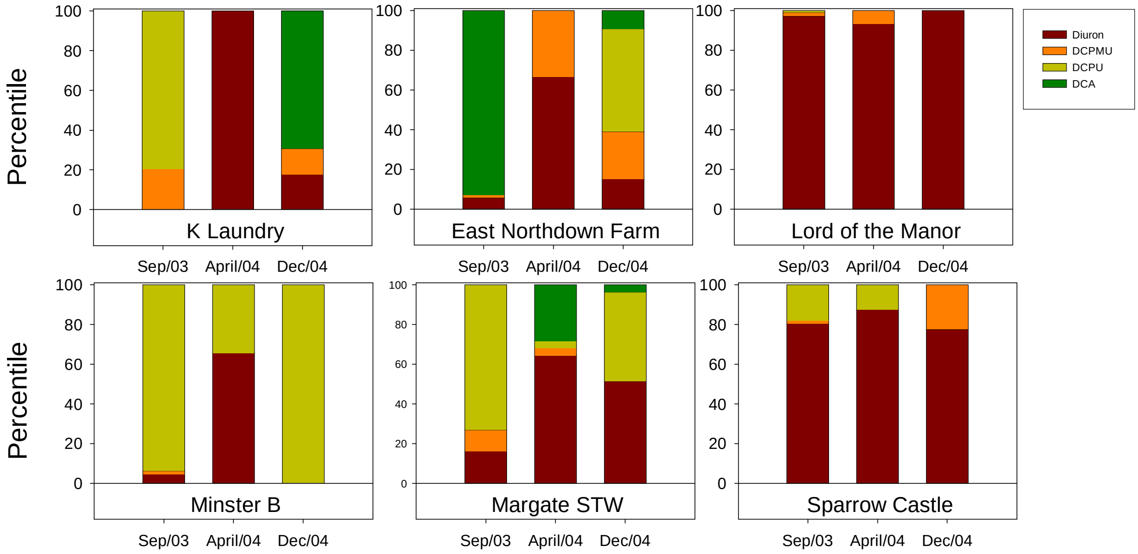


Figure 11. Temporal changes in groundwater composition expressed as percentiles at six sites



Figures 10 and 11 show the changes in groundwater composition expressed as mean concentration and percentiles for six sites. It can be seen that the composition of the groundwater with respect to diuron and its metabolites is variable both in terms of overall concentration and in terms of relative concentrations.

At K Laundry and Margate STW there was an increase in pesticide concentrations with time, while Minster B, East Northdown Farm and Lord of the Manor showed an overall decrease, and at Sparrow Castle concentrations remained constant. At Lord of the Manor and Sparrow Castle the pesticide composition remained relatively unchanged, while at the other four sites it varied considerably. At these four sites the proportion of diuron was highest in the April sampling round. This may be due to the higher water tables/recharge during this period compared to the other sampling rounds. Colloidal transport from the soil zone may be bypassing any natural attenuation process within the unsaturated zone.

The number of positive pesticide detections per sample (PPS) are given as the number of positive detections on a given date divided by the number of sites. Figure 12 (a) shows the changes PPS between sample rounds. Figure 12 (b) shows the changes in PPS that are greater than the PCV.

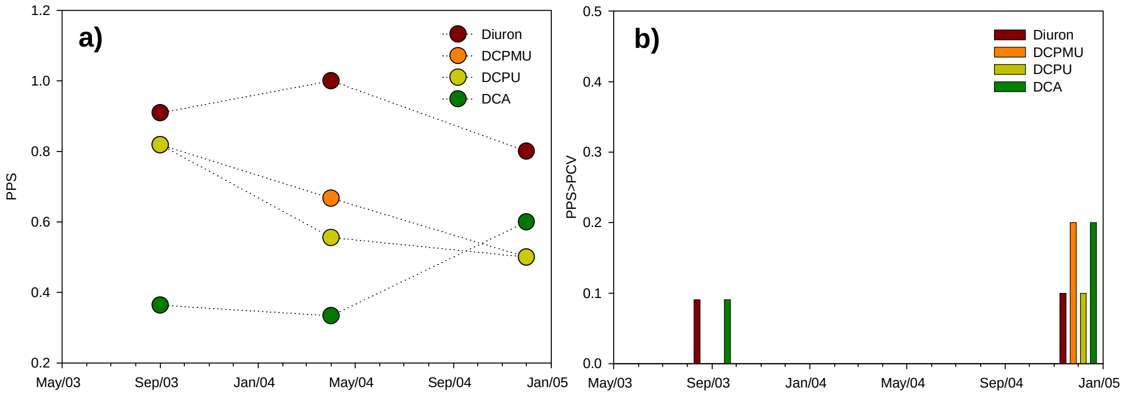


Figure 12. (a) Changes in positive pesticide detections per sample, (b) Changes in positive pesticide detection per sample greater than the prescribed concentration value

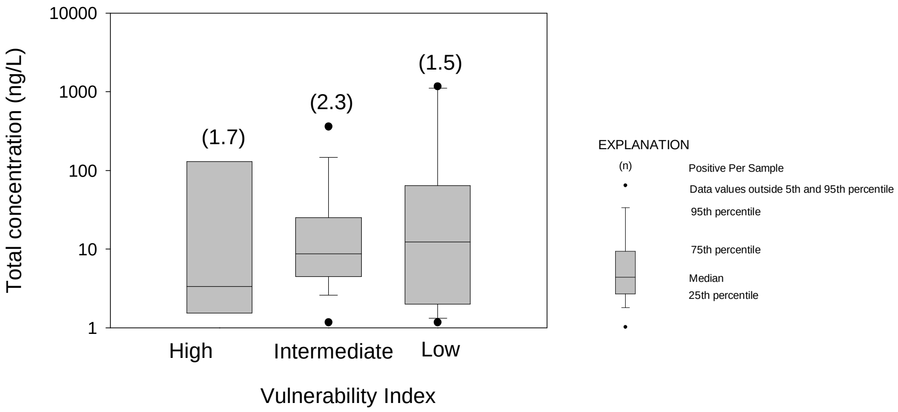


Figure 13. Total concentration of diuron metabolites classified by vulnerability index

The PPS for diuron did not change significantly between sampling rounds, remaining relatively high throughout. The PPS for DCPMU and DCPU both decreased during sampling from 0.8 to 0.5. The PPS for DCA increased in December. There were no pesticide detections exceeding the PCV in April, Figure 12 (b). This is in contrast with the results in December 2004 in which at least 10% of samples exceeded the PCV for all four compounds.

Figure 13 shows a box plot of total diuron concentration for the three vulnerability classes. It can be seen that there is no significant difference in pesticide concentrations as a function of vulnerability (derived from the drift geology). This was also the case in the shallow Triassic sandstone aquifer of south Yorkshire (Lapworth et al., 2005). In fact median concentrations were highest in the low vulnerability sites, and lowest in high vulnerability sites. The relative frequency of detections was greatest in the intermediate vulnerability sites, and was comparable for the other two classes. It is possible that this could be a function of historic diuron pollution in the Thanet aquifer and recent changes in pesticide application practices. These results highlight the ubiquitous nature of pesticide pollution in this aquifer irrespective of aquifer vulnerability. It also demonstrates the difficulty in predicting, from readily available data, the extent of pollution of a particular source.

Figure 14 shows a box plot of the total concentration of diuron for different landuse types: arable/nursery, industrial and urban. Highest median concentrations were found at industrial sites, although these had the lowest relative frequency of detection, highlighting the importance of a relatively small number of high concentration detections. Urban sites showed the greatest frequency of detections, although relatively few sites with this landuse were sampled. Median total diuron concentrations were in the following order: industrial/nursery>urban>arable. Median concentrations for sites with industrial landuse were above the PCV.

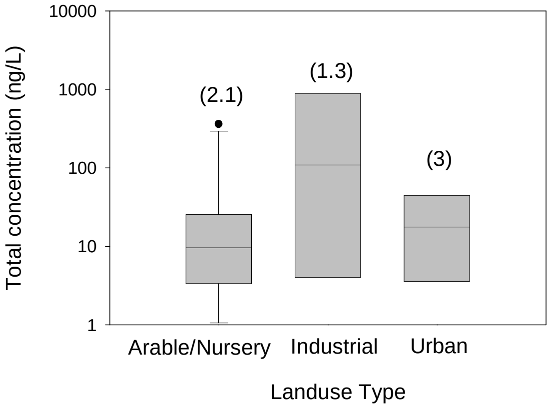


Figure 14. Total concentration of diuron metabolites by landuse type

5 Conclusions

- Diuron and its metabolites were detected throughout the Isle of Thanet aquifer. Diuron was detected in 90% of samples (0.4-214 ng/L). At 60% of sites, diuron metabolites were more prevalent than the parent compound. Mean total diuron concentrations were above the PCV at four of the 15 sites (~30 %). The diuron pollution in this area, like nitrate, is a regional problem and is not limited to a few individual cases. The widespread nature of diuron pollution in the aquifer is symptomatic of the historic application practices in the area and of the overall short residence times in the shallow aquifer system.
- No systematic temporal trends were observed throughout the survey. Groundwater pesticide composition was shown to vary greatly both between and within sample sites, highlighting the complex nature of pesticide transport and degradation within the soil and aquifer. Significantly higher diuron concentrations were observed in spring when groundwater levels are at their highest, although this was not the case for total diuron concentrations (diuron plus metabolites). April had the lowest frequency of detections for diuron and its metabolites.
- Aquifer vulnerability could not explain the occurrence of diuron in groundwater. This highlights, perhaps, the relative importance that specific source terms, localised soil characteristics and soil microbial processes play in the occurrence, transport and degradation of diuron.
- While all landuse types showed the potential for high concentrations of diuron, highest median concentrations were observed at industrial sites and were significantly greater than at urban and arable/nursery sites. The spatial variation in total diuron also suggests that areas of urban development might show higher concentrations of diuron compared with rural locations.
- No correlation was observed between nitrate and pesticides. Where groundwater was aerobic, concentrations of nitrate were close to, or exceeded, the PCV on all occasions highlighting the underlying historic pollution of this aquifer from diffuse nitrate sources. Groundwater contamination from CFCs was found to be widespread and this shows the limited usefulness of CFCs for groundwater dating in highly contaminated semi-confined aquifers of this type. Likely sources of contamination include landfills and discarded refrigerators.
- There is some evidence from groundwater tracers (SF_6) to support the idea that high diuron concentrations were associated with the high groundwater levels in the winter/autumn of 2000-2001. Future periods of high groundwater levels could cause an increase in pesticide concentrations in groundwater. Much more needs to be understood about the transport and occurrence of diuron in the unsaturated zone to more fully quantify the future risk to groundwater.
- Despite some evidence to suggest that the metabolites of diuron may be more toxic than the parent compound, there is currently no requirement to monitor metabolite concentrations in groundwater. Should this change there could be potential implications in terms of future management of the groundwater resource in the Isle Thanet aquifer, and across the UK as a whole.

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Appendix

Full chemistry data from December survey

	Units	Callis Grange	E. Northdown Farm	Sericol BH1	Sericol BH2	Woodchurch Road	K Laundry	Minster B	Sparrow Castle	Margate STW	**Mean**	**Median**
T	^{o}C	11.6	11.5	-	-	11.6	-	11	10.6	12.1	11.4	11.55
pH		6.83	7.09	-	-	7.22	7.12	6.77	7.00	6.98	7.0	7.00
Eh	mV	453	464	-	-	327	-	403	386	369	400	395
DO2	mg/L	8.7	7.6	-	-	7.7	-	8.3	7.1	6.3	7.6	7.64
SEC	μScm^{-1}	973	769	1199	1129	688	888	790	732	1662	981	888
Ca	mg/L	157	108	187	180	114	136	113	114	217	147	136
Mg	mg/L	6.21	6.53	8.73	8.56	4.11	6.34	6.86	5.19	350	45	6.53
Na	mg/L	45.9	40.7	85.2	75	28.3	48.5	38.6	31.4	2990	376	45.9
K	mg/L	5.81	1.63	19.4	11	2.14	3.41	2.94	2.36	112	17.9	3.41
Cl	mg/L	72.5	59.8	126	114	48.1	74.2	68	54.2	5620	693	72.5
SO4	mg/L	62.3	39	50.9	42	17.9	28.8	26.6	15.2	746	114	39
HCO3	mg/L	266.9	265.7	460.2	464.4	269.4	332.2	279.8	309.6	271.2	324	279.8
NO3-N	mg/L	16.1	10.7	4.57	0.685	12	12.7	13.5	9.91	15	10.6	12
NO2-N	mg/L	0.004	< 0.0003	0.696	0.405	0.0032	0.004	0.0025	< 0.0003	0.0043	0.1	0.0038
NH4-N	mg/L	< 0.004	< 0.004	0.0291	0.136	< 0.006	< 0.006	< 0.006	< 0.006	0.0228	0.023	< 0.006
P	mg/L	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
TOC	mg/L	1.2	1.52	158	2.94	1.01	1.04	0.8	0.87	2.36	1.5	1.12
F	mg/L	0.17	0.37	0.21	0.21	0.18	0.18	0.24	0.17	0.25	0.22	0.21
Br	mg/L	0.33	0.58	0.71	0.75	0.32	0.55	0.24	0.25	18.90	2.52	0.55
Si	mg/L	4.99	8.96	6.53	6.99	4.7	5.53	7.07	5.6	8.03	6.5	6.53
Al	mg/L	< 0.01	< 0.01	0.017	0.015	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.0074	< 0.01
As	mg/L	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
B	mg/L	0.19	0.15	0.12	0.11	< 0.1	< 0.1	< 0.1	< 0.1	1.38	0.2	0.11
Ba	mg/L	0.051	0.075	0.094	0.092	0.054	0.076	0.110	0.066	0.065	0.076	0.075
Be	mg/L	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Cd	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.0014	0.0006	< 0.001
Co	mg/L	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
Cr	mg/L	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Cu	mg/L	0.0083	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	0.0112	< 0.008	0.0202	0.007	< 0.008
Fe	mg/L	0.014	0.005	0.371	0.195	0.106	0.007	< 0.005	0.006	0.058	0.085	0.014
La	mg/L	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.0024	< 0.002	< 0.002
Li	mg/L	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	0.0381	0.0060	< 0.004
Mn	mg/L	0.0053	< 0.002	0.0211	0.0115	0.0096	< 0.002	< 0.002	< 0.002	0.0044	0.0062	< 0.002
Mo	mg/L	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
Ni	mg/L	0.0057	0.0082	0.0111	0.0081	< 0.005	0.0088	0.0051	< 0.005	0.0114	0.007	0.0081
Pb	mg/L	0.02	0.019	0.018	0.017	0.022	0.022	0.02	0.021	0.031	0.021	0.02
Sc	mg/L	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0004
Sr	mg/L	0.40	0.59	0.46	0.47	0.35	0.44	0.50	0.39	2.47	0.68	0.46
V	mg/L	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.0068	0.0008	< 0.002
Y	mg/L	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003
Zn	mg/L	0.090	0.035	0.034	0.029	0.085	0.067	0.041	0.027	0.089	0.055	0.041
Fraction of Modern Water												
CFC-11		3.47	0.22					1.56	2.80	2.22		
CFC-12		1.23	0.23					0.45	351.11	2.04		
SF6		0.59	0.84					0.35	0.46	0.79		
*Bulk age		1995	2000					1988	1991	1999		

* based on SF$_6$ data

Pesticide Data

	Sampled			**Diuron** **ng/L**			**DCPMU** **ng/L**			**DCPU** **ng/L**			**DCA** **ng/L**			**Total** **ng/L**		
	Sep	April	Dec	Sep	April	Dec	Sep	April	Dec	Sep	April	Dec	Sep	April	Dec	Sep	April	Dec
Agfa	I	I		12	56			0.9					153	710		164	767	
Sericol BH3	I			44						1.3			7.2			53		
K Laundry	I	I	I		12	11	0.4		8.3	1.6					44.3	2.0	12.3	64
Quex Park BHA	I			1.7			0.2			0.2						2.2		
Brooks End Stream	I	I		214	31		77	6.2		31.0	4.2		38.2	14.2		360	56	
Monkton Barn Farm	I	I		1.0	3.4		0.5	0.6		1.9	1.8					3.4	5.8	
East Northdown Farm	I	I	I	14	0.6	1.5	3.6	0.3	2.3			5.0	230.0		0.9	248	0.9	9.6
Lord of the Manor	I	I	I	24	14	6.4	0.4	1.0		0.3						24	14.9	6.4
Minster B	I	I	I	1.2	2.1		0.4			24	1.1	1.2				25	3.2	1.2
Margate STW	I	I	I	0.7	14.8	20	0.4	0.9		3.0	0.8	17.1		6.5	1.4	4.1	23	38
Sparrow Castle	I	I	I	8.5	4.9	5.4	0.2		1.5	1.9	0.7					11	5.6	6.9
Callis Grange			I			0.4									2.9			3.4
Sericol BH1			I			140.4			162			356			263			920
Sericol BH2			I			73.8			109			76			902			1161
Woodchurch road			I			<0.1			<0.1			<0.1			<0.1			<0.5