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# Pesticides and their metabolites in groundwater - A field investigation from south east England

Groundwater Systems and Water Quality Programme

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BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/04/014

# Pesticides and their metabolites in groundwater - A field investigation from south east England

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## Summary

Contamination of groundwater by pesticides has brought increased environmental concern over the past decade although there is currently no requirement for water supply organisations to measure pesticide metabolites. Previous work on diuron has shown that metabolites are a major component of the residual compounds found in soil and groundwater following normal application. This scoping study expands on previous work carried out at the experimental plot scale to the catchment scale. Groundwater has been sampled for diuron and its metabolites from 11 sites across a catchment in south east England during the autumn of 2003. High concentrations of diuron have previously been detected in the catchment and a number of sources are possible. Diuron was found on 91% of occasions, DCPMU and DCPU on 82% of occasions, and DCA was found in more than a third of the samples. In 6 of the study sites, more than 50 % of the total diuron and degradation products was composed of the metabolites.

Concentrations of diuron and its metabolites were commonly found at significant levels throughout the catchment. From such a small ‘one-off’ sampling it is not possible to determine the likely source of the herbicide although regular analysis of the groundwater quality together with analysis of the soils and unsaturated zone, would give evidence of the likely scale of the problem.

# 1 Introduction

Contamination of groundwater by pesticides has brought increased environmental concern over the past decade (Foster et al., 1991; Soutter and Pannatier 1996; Chilton et al., 2000; Foster 2000; Gaus 2000; Gooddy et al., 2001; Johnson et al., 2001). With effect from December 2003, the European Union Drinking Water Directive (Council Directive 98/83/EC) has set limits of 0.03 µg/L for certain pesticides. Under the Directive there is currently no requirement for water supply organisations to measure pesticide metabolites (see for example SANCO/221/2000) despite evidence that they are ubiquitous (Kolpin et al., 2000) and their toxicity can be higher than the parent compound (Tixier et al., 2000; Tixier et al., 2001).

Diuron (*N*'-[3,4-dichlorophenyl]-*N,N*-dimethylurea) is a substituted urea herbicide used to control a wide variety of annual and perennial broadleaf and grassy weeds. It is used on many agricultural crops such as fruit, cotton, sugar cane, alfalfa, and wheat but is more widely applied for long-term pre-emergence weed control in non-crop areas (Tomlin, 1994) especially along railway lines (Schweinsberg et al., 1999). Microbial degradation is considered to be the primary mechanism for its dissipation from soil (Tixier et al., 2000). Under well oxygenated conditions, this is believed to occur by successive demethylation of the urea group followed by hydrolysis to produce a chlorinated aniline (Figure 1). Short term exposure to 3,4-dichloroaniline may cause effects on the blood, resulting in the formation of methaemoglobin, highlighting the toxicity of these degradation products.

The major aquifer in the UK, the Cretaceous Chalk, is a soft microporous and fractured calcium carbonate commonly overlain by thin (<1 metre) calcareous soils. It is a complex natural system and consequently is very difficult to measure or sample in a systematic manner. Once a pesticide enters the chalk rock, the potential for biodegradation is substantially reduced (Johnson et al., 2000).

This report presents the findings from a study site in the south east of England where high concentrations of diuron have been detected. The approach builds on the preliminary work on diuron and its metabolites detailed in Gooddy et al. (2002a,b and 2003) and serves as a scoping study for potentially carrying out more field work at this site.

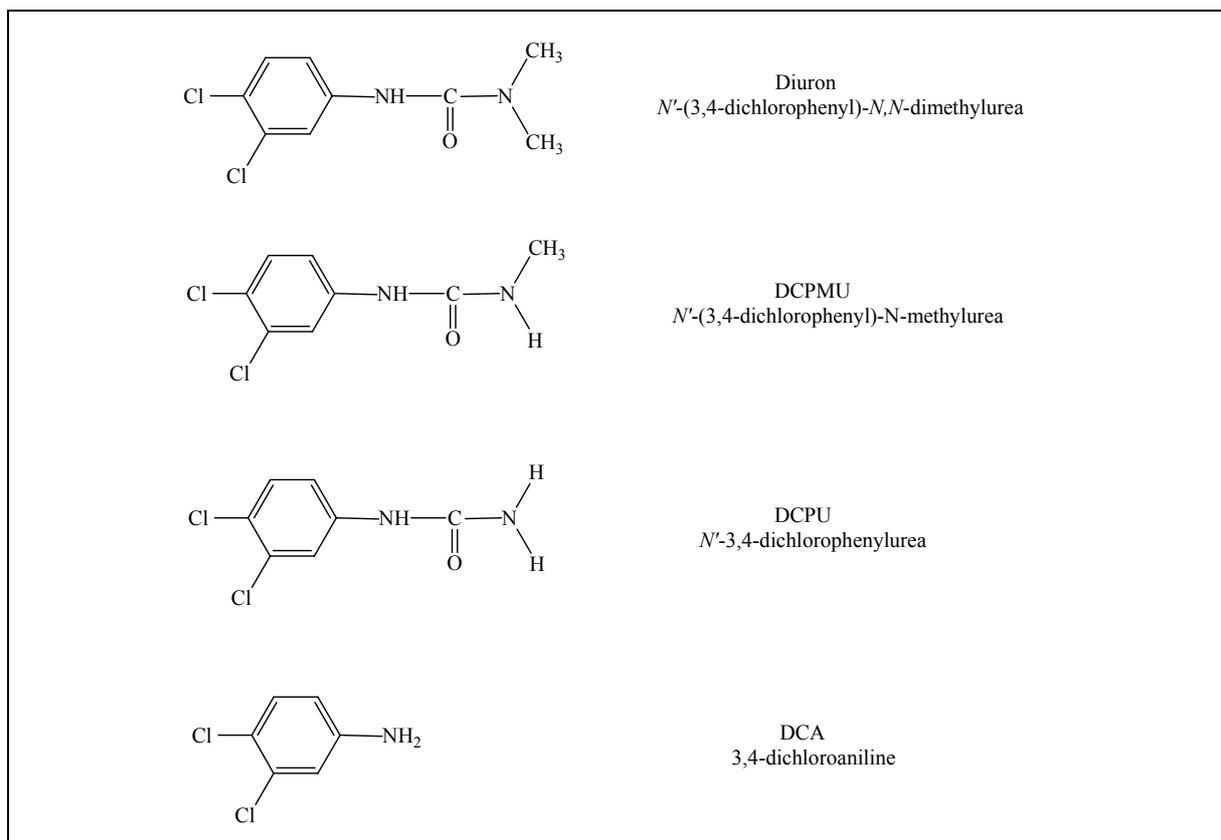


Figure 1 Chemical structure of diuron and three sequential degradation products, DCPMU, DCPU and DCA

## 2 Background

### 2.1 SOURCES OF DIURON CONTAMINATION ON THE ISLE OF THANET

The groundwater in the Isle of Thanet chalk block has been impacted historically by diuron. As the impact cannot be related to a specific incident normal Environment Agency pollution incident mechanisms, for investigation and cost recovery, cannot be used. The Environment Agency is, however, responsible for attempting to protect the quality of groundwater in the aquifers. The recognition of deteriorating trends in groundwater quality caused by diffuse pollution, such as nitrate, herbicides and pesticides, is becoming increasingly more important. The incoming Groundwater Directive and Water Framework Directive are putting a greater emphasis on investigating, understanding natural background water quality and dealing with diffuse pollution in groundwater bodies, surface water catchments and associated hydraulic links.

At present the Environment Agency has requested that known users of diuron in the high risk areas (Source Protection Zone 1) within Thanet change the product that they are using to a less mobile, less persistent herbicide or carry out manual weed control. While this acts as a temporary protection measure there is a risk that the new herbicides in use may be detected in the future in the groundwater. Similarly there is not a good understanding of the fate of the original diuron, and its breakdown products (metabolites), in the soil and aquifer which may lead to further episodes of elevated levels being detected in the Chalk groundwater. A study of the situation may provide evidence to enable control mechanisms on herbicide use to be implemented ultimately leading to preventing the groundwater quality from deteriorating.

Diuron use to control weed growth in the Isle of Thanet has been quite widespread. Enquiries over the last couple of years by the Environment Agency have led to three main sources being discovered, although it is acknowledged that there may be more. The key ones identified include:

1. *The Airport at Manston*

Diuron was used regularly by the contractor providing weed control at the airport. The diuron was used following manufacturers guidelines but the fact that the airport runway and infrastructure was sited on the Chalk and over the western adit and Source Protection Zone 1 for Lord of the Manor public supply borehole had not been identified. The runway discharged to a pipeline out of the area, but spraying may have occurred inside the catchment area, and taxiway drainage discharged over the edge of the concrete to the ground. As soon as the contractor was made aware he stopped using diuron and has started using less persistent herbicides. This change was in Spring 2000 and was agreed after discussion with the Environment Agency's BASIS trained officer.

2. *Thanet District Council*

In Summer 2001 Thanet District Council reported an irregularity in diuron use in Thanet. The Tree Officers within the Council had launched an investigation to determine why healthy plants in the new flowerbeds were dying as soon as they were planted. They discovered that the contractor that they had employed had been applying the herbicide in neat form rather than diluting it prior to use. Soil samples in the affected areas were found to be heavily contaminated. The use of diuron had been widespread – including parks, gardens, footpaths, cemeteries etc throughout Thanet. The person responsible at the contractors had left, without trace, so very few details have been determined since. The contractors were advised of the risk to groundwater by the Council and have amended their application of herbicides although it is not clear if they have changed from the use of diuron. The applications are likely to have been within all Source Protection Zones for Thanet public water supplies and the Chalk is likely to be covered by variable thickness of soils, ranging from a couple of centimetres to a reasonable depth.

3. *Connex Depot, Newington Road, Ramsgate*

An unrelated incident at the Connex goods yard led the Environment Agency to carry out a thorough site inspection. The geology beneath the goods yard and buildings comprises Chalk which is covered, in places, by a layer of ash / made ground. The eastern arm of the adit to Lord of the Manor public water supply, and the associated Source Protection Zone 1, passes beneath the goods yard. Diuron has been used regularly on the site by the contractor who was unaware of the groundwater vulnerability. The hardstandings were sprayed up to four times per year. It is quite possible that spraying occurred around soakaways allowing by-pass of any layers with the potential to protect the underlying Chalk and associated groundwater. As soon as the contractor was made aware he stopped using diuron and has changed to less persistent herbicides. This change was in made March 2003 and was agreed after discussion with the Environment Agency's BASIS trained officer.

There are likely to be several other potential sources but these are the main ones identified. The Highways Agency were approached at the time of the initial incident but reported that they did not use diuron. This may need to be checked as the Council and the Railway operators also reported "no use" but have subsequently found to be using diuron.

## **2.2 IMPACT ON GROUNDWATER IN THE ISLE OF THANET**

In December 2000 Southern Water Services reported extremely elevated levels of diuron in their raw water samples at Lord of the Manor abstraction from the Chalk aquifer. 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 was to be reported to the Drinking Water Inspectorate. The incident co-occurred with heavy rainfall and high groundwater levels and resulted in a peak diuron reading of 1200 ng/l.

At the time the Environment Agency had no particular knowledge of anyone using diuron in Thanet but as users have become apparent they have been asked to change methods or herbicides to prevent the more mobile, persistent herbicides being used. Several large companies and organisations were contacted to see if the use could be pin pointed but nothing was discovered. Due to the nature of the use and lack of evidence it was not possible to register this as an incident and to recover costs from any particular user. On discovering the first major user this stance was evaluated and, the Environment Agency could not be certain that they were the sole users, the only action taken was to ask them to review their spraying regime and diuron use. This situation has now been repeated as more users have come to light.

While the diuron user(s) responsible for the incident is unlikely to be traced there is a need to gain understanding of this situation. The widespread use of diuron on Thanet in high concentrations may give rise to an impact in years to come. Diuron and its metabolites may be percolating through the soil and the unsaturated zone towards groundwater. The groundwater provides water for public water supply, irrigation of agricultural land and potentially forms part of the base flow for wetland systems and streams. The peak shown in late 2000 may have been the result of a point source one-off incident, such as 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.

## **3 Methods**

### **3.1 FIELD SITE AND SAMPLING**

Sampling of ground (and one) surface waters was carried out in September 2003. At this time of year groundwater levels are likely to be at their lowest. Similarly, pesticide concentrations will also be at their lowest so this sampling exercise gave a 'best case' scenario for the degree of diuron contamination on the Isle of Thanet.

Samples were taken by using a submersible pump or from pumps already present in the boreholes. Figure 2 shows the location of the different sites across the Isle of Thanet. Eleven samples in 2.5 litre amber bottle with PTFE-lined screw-caps were collected and taken to BGS Keyworth. To each 5g of sodium azide was added (i.e. 0.2% w/v) for preservation purposes before storing in the dark at 4°C prior to analysis.

### **3.2 DIURON AND METABOLITE ANALYSIS**

Sample pre-concentration was performed by SPE using Waters OASIS HLB (200 mg sorbent) cartridges. Two litres of preserved sample were passed through two of these cartridges in series initially. 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.

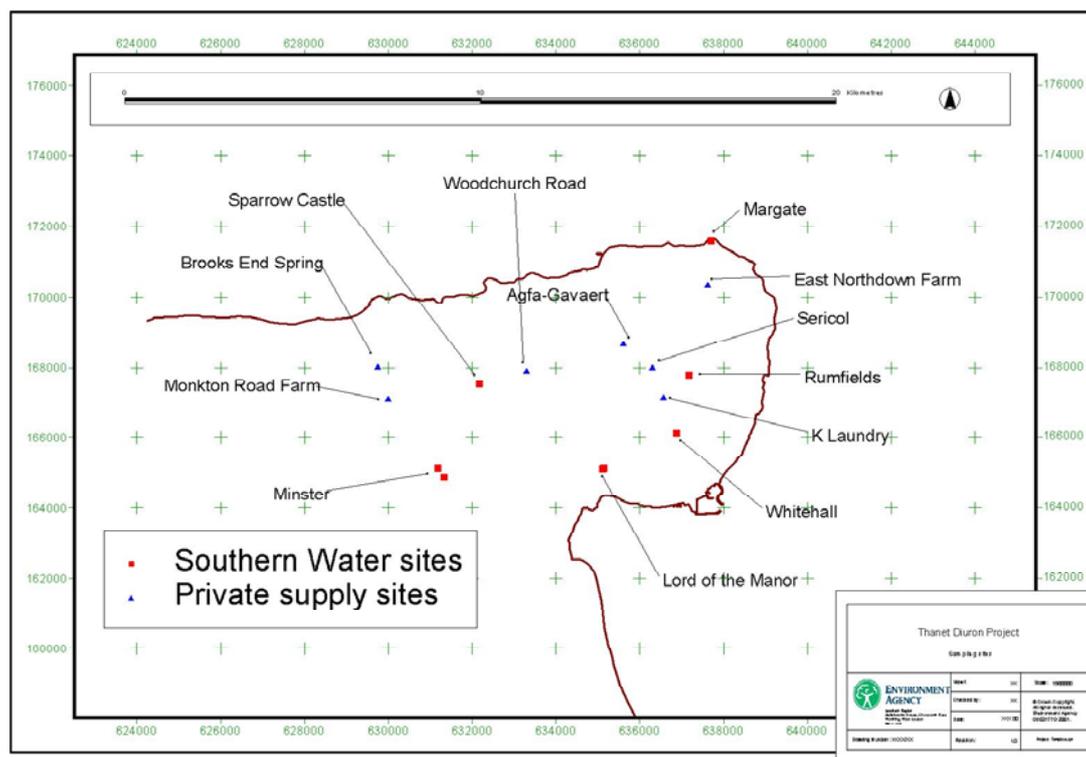


Figure 2 Location of sites used during sampling exercise carried out in September 2003.

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 M $\Omega$ ). 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, on the analytical HPLC system. The HPLC analytical system pumped a mobile phase consisting of 35% v/v aqueous acetonitrile at 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, with both containing 5  $\mu$ m particles of stationary phase. Detection was conducted at 252 nm with data being captured, and peak area integration undertaken, by a Perkin-Elmer Turbochrom chromatographic data handling system.

## 4 Results

Results of the sampling exercise are statistically summarised in Table 1. Diuron is found on 91% of occasions, DCPMU and DCPU on 82% of occasions, and DCA is found in more than a third of the samples. The data show some surprisingly high mean concentrations of diuron and all metabolites. Indeed, the maximum concentrations of metabolites analysed are even greater than those found by Goody et al. (2003) from soil porewaters. Mean (excluding value below detection) and median concentrations show some significant differences, with mean values being the greater, reflecting a few very high concentrations of the parent and each of the metabolites. However, in each case, where the compound was detected, it is above the EU MAC.

Table 1 Statistical summary of diuron and metabolites collected from 11 sites on the Isle of Thanet. Mean concentration has only been calculated on the basis of samples above the detection limit.

	Diuron	DCPMU	DCPU	DCA
<b>Mean</b>	32.1	9.29	7.22	107
<b>s.d.</b>	65.3	25.4	11.6	103
<b>Median</b>	10.1	0.43	1.85	95.4
<b>Max</b>	214	77.0	31.0	230
<b>Min</b>	0.67	0.16	0.23	7.23
<b>n</b>	10	9	9	4
<b>Detection Limit</b>	<0.1	<0.1	<0.1	<3.8

Figure 3a shows the relative concentration of each of the compounds at each site, with the relative sample composition of diuron and metabolites shown in Figure 3b. At just one site is diuron and all three metabolites found. In 5 of the 11 sites diuron, DCPMU and DCPU are found but no DCA. However, DCA is found at one site where there is no DCPMU, at another site where there is no DCPU and at a third site where there is neither DCPMU or DCPU present (Figure 3a). Some sites with very high DCA and little or no diuron suggest that there is another source of DCA within the catchment. In 6 of the study sites, more than 50 % of the total diuron and degradation products is composed of the metabolites (Figure 3b). The site with the highest concentration of diuron is the only site where all three metabolites are also found.

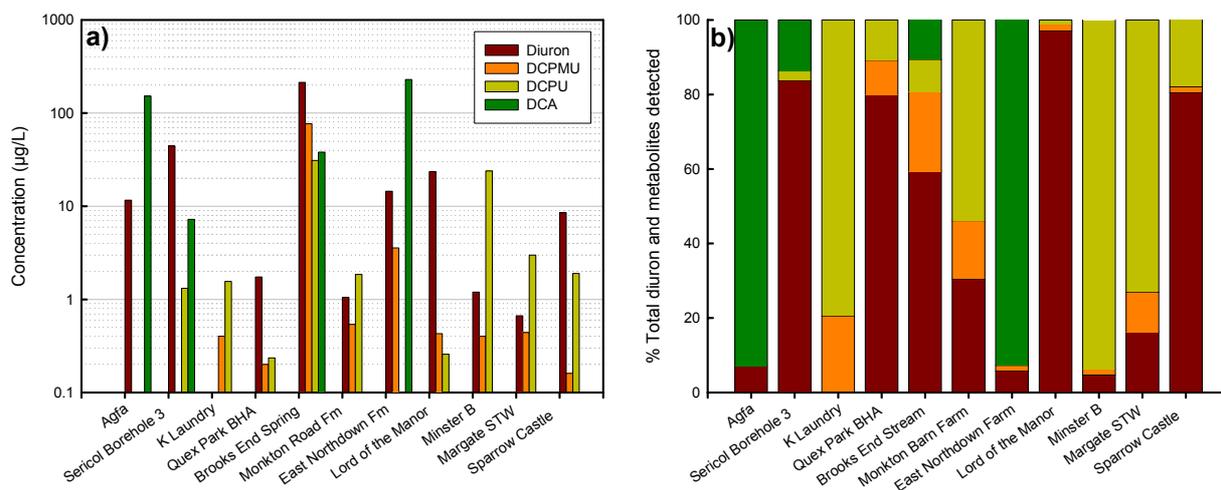


Figure 3 Diuron and metabolites from sampling in September 2003 expressed as a) concentration over a log scale and b) percentage of total diuron and metabolites detected.

## 5 Conclusions

Although this scoping study was carried out at a time of year when herbicide concentrations are likely to be at their lowest, concentrations of diuron and its metabolites were commonly found at significant levels throughout the catchment. From such a small ‘one-off’ sampling it is not possible to determine the likely source of the herbicide. Regular analysis of the groundwater quality together with analysis of the soils and unsaturated zone in areas of known diuron use, would give evidence of the scale of the problem in years to come. In addition, further monitoring and an investigation of the unsaturated zone should provide a valuable insight of into the fate and transport of diuron and its metabolites in the Chalk aquifer at the catchment scale.

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