

# Nitrate fluctuations in groundwater: review of potential mechanisms and application to case studies

Groundwater Science Programme Open Report OR/08/046



#### BRITISH GEOLOGICAL SURVEY

GROUNDWATER SCIENCE PROGRAMME OPEN REPORT OR/08/046

# Nitrate fluctuations in groundwater: review of potential mechanisms and application to case studies

M E Stuart, P J Chilton and A S Butcher

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Conceptual model of impact on porewater concentration of winter high nitrate fissure flow

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## Foreword

This report is the published product of a study by the British Geological Survey (BGS) on the seasonal fluctuations of nitrate concentrations in groundwater. It forms the first output from the BGS project "Nitrate fluctuations in groundwater".

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## Summary

This report describes work carried out as part of the BGS research project "Nitrate fluctuations in groundwater". The aim of the project was to determine the mechanism(s) linking within-year fluctuations with groundwater level observed in many time series of nitrate concentrations in groundwater.

Four conceptual models were prepared to represent scenarios where chalk recharge is taking place by only one mechanism. These mechanisms were winter piston flow through the unsaturated zone matrix, winter bypass flow from the base of the soil bringing high nitrate water directly to the water table, water table rise from water entering elsewhere in the catchment flushing out porewater and a change in flow path giving access to a greater percentage of shallow high nitrate water. These were evaluated in a very simplified way to determine whether different relationship between water levels and nitrate concentration arriving at the water table. It was concluded that flushing by a rising water table could potentially result in a delay between the water level rising and the nitrate concentration increasing, but the other mechanisms would be all likely to result in the more or less simultaneous rising of the water level and arrival of nitrate. However the distribution of nitrate in the porewater profile was predicted to be different and this may prove to be a more-useful indicator.

Three case study sites were selected for evaluation; two previous BGS research sites at Ogbourne St George, Wiltshire and at Bircham, Norfolk where there was considerable existing data and Morestead, Twyford, Hampshire which was selected as the research site for the current project. Ogbourne St George was found to be the most informative site, primarily due to the successful deployment of a multi-level sampler which obtained saturated zone samples from small discrete intervals and also to corresponding porewater data. At this site water with a nitrate concentration higher than the porewater was observed in the zone of water table fluctuation during periods of rising water levels. Additionally increases in nitrate concentrations are inconsistent with piston flow through the matrix and correspond better with the fracture flow model or with lateral transfer of water from another part of the aquifer where nitrate concentrations are already higher.

In the Bircham area four sites were chosen; Sedgeford, Fring, Osier Carr and Great Bircham. Two of these were looked at in more detail. The boreholes at Sedgeford had a very high response to water level variation, but in dry intervals nitrate peaks had either low amplitude or were lost. At Great Bircham the pattern was different with more subdued water level rises and a more protracted impact from drier periods. This was likely to be due to differences in the physical setting of the Bircham site which was in a shallow valley where the unsaturated zone was much thinner than at Sedgeford. The porewater profiles shape and the detection of higher nitrate water as soon as the water level rose into the zone of fluctuation were consistent with the winter high nitrate peaks being derived from increased permeability in the zone of water table fluctuation allowing a greater contribution of shallow, polluted groundwater to abstracted water.

At Twyford where the porewater profile was measured after a long dry period, the distribution of nitrate in the unsaturated zone in the absence of other data did not rule out any of the mechanisms.

It was concluded that measuring the difference between the water level rise and arrival of nitrate at a borehole is unlikely to be able to distinguish the mechanism operating and other information, such as porewater concentration, may be needed.

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## 1 Introduction

### 1.1 BACKGROUND AND OBJECTIVES

Many time series of nitrate concentrations in groundwater show within-year fluctuations of various amplitudes and forms. Where suitable continuous groundwater level records are available nearby, a more or less close relationship between groundwater levels and nitrate concentrations can often be observed – higher concentrations being associated with higher groundwater levels. It is often the resulting transient winter peaks of nitrate that can be problematic for compliance by water companies, perhaps many years before the "average" concentration reaches a level requiring action.

A statistical method for trend assessment prepared by BGS for UKWIR detects the presence or absence of seasonality automatically, and is able to separate time series statistically into those with and without true seasonal fluctuations. Within the present nitrate work this approach has been applied to nearly 400 time series datasets to identify in which aquifers and which hydrogeological situations seasonality is most strongly developed (Stuart and Kinniburgh, 2005).

The aim of the project was to determine whether the mechanism linking the two and causing rising nitrate concentrations is additional rapid vertical recharge and enhanced winter leaching, flushing out of "stored" unsaturated zone nitrate by the rising groundwater levels or cutting off shallow high transmissivity flow paths during periods of low water levels.

### **1.2 APPROACH**

The proposed approach was to:

- 1. Examine a subset of existing data from locations with strong seasonal fluctuations and suitable nearby observation boreholes with continuous groundwater level measurements and make a shortlist of potential field sites.
- 2. Select field sites using other criteria such as location on aquifer outcrop, away from the influence of drift or confining layers and a thin unsaturated zone to reduce the amount of sampling through the unsaturated zone since it would be necessary to obtain unsaturated zone profiles to assist in interpretation and modelling.
- 3. Establish field measurements of nitrate and groundwater level and nitrate concentration on a continuous or frequent basis at several sites, either by instrumenting existing or new observation boreholes for continuous groundwater levels and frequent nitrate sampling by continuous probe, or floating or automatically timed sampling pump. This would determine how much nitrate is arriving at the water table.
- 4. Compare regular and frequent samples for nitrate with groundwater levels, preferably over three winters, and the relationship between the two and with local recharge events would be examined in detail. The degree of synchronicity/time displacement in the datasets, and form and amplitude of changes would be compared and interpreted in relation to mechanisms and processes.
- 5. Adapt existing models to represent the seasonal processes identified by the study and to use these to model the magnitude and duration of future peak concentrations in different scenarios.

## 1.3 LINKS

This project is linked to the Sustainable Use of Natural Resources Theme in the NERC Strategy "Next Generation Science for Planet Earth". This project was originally linked to the completed project "Nitrate mass balance in the saturated zone" in the use of common infrastructure. It follows on from co-funded work for UKWIR, commissioned work for Defra and from the nitrate component of unallocated time work.

## 1.4 CRITERIA FOR FIELD SITE SELECTION

### 1.4.1 Nitrate fluctuations in groundwater

The criteria for site selection for the field component of the project were:

- existing visual and statistical evidence of seasonal fluctuations in nitrate from analysis of long-term records (time series datasets) which are related to groundwater level fluctuations (likely to be from a public water supply);
- existing long-term time series of water level fluctuations from nearby observation borehole (needed for the statistical analysis above in any case);
- more than 1 km from any abstraction borehole to minimise the local effects of abstraction and to ensure that the cored borehole is outside the Source Protection Zone I;
- moderate, average transmissivity (T) values in aquifer, (i.e. avoiding very high T);
- the Chalk at should be at outcrop and largely drift-free;
- knowledge of vertical distribution of T (in general from existing site information and more precisely from the packer testing to be done);
- depth to water level in the range 15 25 m (at shallow water table sites low in valleys seasonal fluctuations may be damped, and a mid-slope position is preferable).

### 1.4.2 Nitrate mass balance in the saturated zone

The first site selected also needed to meet a second set of criteria to allow the use of the borehole for another nitrate project. These criteria were:

- the site should be in the catchment of a currently operating public supply borehole;
- the abstraction borehole should not be too deep (< 50m) to enable the full flow path to be penetrated by the cored borehole without excessive drilling;
- the abstraction borehole should have a good record of nitrate concentration with time (current concentrations should be moderate to high);
- T should be less than  $5000 \text{ m}^2/\text{d}$ ;
- the Chalk should be largely drift-free;
- there should be some idea of historical N leaching in the catchment based on the ADAS NEAP-N model.

## 2 Review of mechanisms/conceptual models

## 2.1 MECHANISMS

Many time series of nitrate concentrations in groundwater show within-year fluctuations of various amplitudes and forms. In a study of time-series groundwater nitrate data, Stuart and Kinniburgh, 2005: Stuart et al. 2007)) found that almost 50% of the datasets for the Chalk showed seasonal fluctuations that could be statistically recognised. The sites exhibiting the greatest fluctuations tended to be on outcrop Chalk on topographically high ground where the unsaturated zone tended to be the thickest. There was also some correlation of size of fluctuation with aquifer transmissivity.

Where suitable continuous groundwater level records are available nearby, a close relationship between groundwater levels and nitrate concentrations can frequently be observed – higher concentrations being associated with higher groundwater levels. The question arises, therefore, as to whether the mechanism linking the two and causing rising nitrate concentrations is:

- a) recharge to the saturated zone by normal piston flow through the unsaturated zone matrix releasing nitrate stored in the unsaturated zone (Mechanism A);
- b) the establishment of rapid vertical recharge in the winter/spring period containing enhanced concentrations of leached of nitrate (Mechanism B);
- c) the flushing out of "stored" unsaturated zone nitrate by rising groundwater levels (Mechanism C);
- d) the cutting off of shallow high transmissivity flow paths during periods of low water level reducing the amount of newer water high nitrate which can move laterally to an abstraction point. (Mechanism D).

#### 2.1.1 Groundwater flow in the unsaturated zone

Groundwater in the Chalk unsaturated zone is generally considered to move mainly through the aquifer matrix with rapid, fissure flow occurring on some occasions during periods when the profile is sufficiently saturated to permit it (Mathias et al. 2005). In the Chalk the small pore size means that the matrix is always close to saturation due to capillary tension. This also has the effect that this water is not very mobile. Under natural recharge conditions most of the fissures are empty due to their larger openings. Water moves from one fissured block to the next through contact points providing hydraulic bridges and the average rate of downward migration of water is about 0.5 to 1 m/year. The chalk pore size would probably mean that a 30 m thick capillary fringe would be anticipated but in reality the fractured nature of the chalk means that 10 m may be a more realistic estimate. Ireson et al. (2006) found that measurements of matric potential and water content at a site in Berkshire were consistent with wholly matrix flow, although rapid fracture flow could not be ruled out. Further modelling work showed that unsaturated zone drainage below the zero flux plane probably occurs continuously throughout the year, albeit at different rates (Ireson et al., 2009).

Lee et al. (2006) evaluated the water table response to rainfall and found that the time lag was related to the average unsaturated zone thickness but that an element of fissure flow was required to account for the variation in times. They also concluded that the majority of rapid responses were observed during the winter/spring period and were most likely to occur when

the rainfall intensity exceeded 5 mm/day. Price et al. (2000) demonstrated that such fissure flow can be generated at any depth in the profile, not only at the surface.

Haria et al. (2003) showed that preferential fracture flow occurred at a site in Hampshire where the water table was about 4 m of the surface, whereas where the water table was deeper recharge went through the matrix. They suggested that the behaviour could be described using an intermediate storage concept with narrow contact points between chalk blocks remaining water-filled only within the capillary fringe. These serve to transmit rapid flow from the surface at shallow water table sites but also serve to attenuate flow above the capillary fringe at deeper sites as this intermediate storage needs to be filled before such flow occurs.

Ireson (2009) carried out a sensitivity analysis on their Berkshire data and concluded that a modest increase in the rainfall intensity may result in an increased depth of fracture flow initiation possibly even to the water table (32 to 44 m at this site). They also speculated that water level changes beneath interfluves are caused by the lateral propagation of pressure waves initiated where the unsaturated thickness is much less.

### 2.1.2 Nitrate concentration relationship with water level

The proposed mechanisms for fluctuations generally rely on the dual porosity aquifer model described in the previous section and commonly applied to the Chalk. Hong et al. (2007) observed low nitrate concentrations in dry periods in the summer. This was interpreted as periods of insufficient vertical movement to recharge the saturated zone. In their model of the Chalk, the fissures are not normally saturated and the aquifer matrix is divided into a series of disconnected blocks. In wet periods the water level rose intercepting higher concentrations in shallow layers and increasing concentrations in the saturated zone. This equates to Mechanism C above. Their concentration data was well related to water level and also autocorrelated (related to the previous day's level). Costa et al. (2002) and Beeson and Cook (2004) also reported low concentrations in dry periods where the water level was unusually low.

Brouyere et al. (2004) also propose Mechanism C. They found that iodide tracer introduced into the unsaturated zone using a piezometer was detected in a nearby pumping borehole. The experiment was monitored over 2 annual recharge cycles. The concentration rose at a monotonic rate with increasing water level and then fluctuated as water levels stabilised. Mechanism D was clearly excluded by the use of a point source of contaminant.

### 2.2 HYDROGEOLOGICAL SETTING OF MODEL

The following series of conceptual models are designed to represent scenarios where only one individual mechanism is operating. It is accepted that this is unrealistic and that in reality more than one mechanism will normally occur at a particular site.

The underlying model setting is a schematic chalk site with:

- a relatively thick unsaturated zone;
- very simplified vertical fissuring connecting the soil zone and the water table;
- a zone of enhanced permeability corresponding to the zone of water table fluctuation.

A schematic porewater profile is shown at the left on the figures representing the starting and final conditions and a combined hydrograph and plot of saturated zone concentrations below. This also assumes that nitrate leaching from agricultural practices remains similar to recent decades and has not been affected by control measures, such as Nitrate Vulnerable Zones.

#### 2.3 INITIAL CONDITIONS – SUMMER

The scenario for initial summer conditions is shown in Figure 2.1. This represents the starting conditions for the various recharge scenarios:

- no recharge occurring;
- high nitrogen concentrations in the soil;
- relatively high concentrations of nitrate in the porewater above the winter peak water level;
- water levels are at the minimum for normal years;
- porewater concentrations between the peak water level and the normal minimum are lower than the permanently unsaturated zone but higher than the shallow saturated zone;
- the deeper saturated zone has low nitrate.



Figure 2.1 Conceptual model during summer conditions

### 2.4 MECHANISM A – PISTON FLOW IN THE UNSATURATED ZONE

#### 2.4.1 Mechanism

The mechanism for the piston flow scenario is shown in Figure 2.2:

- nitrate from the base of the soil is transferred to the top of the unsaturated zone;
- water moves slowly through the matrix as a result of recharge at the surface;
- the base of the unsaturated zone becomes saturated with recharge from above.

#### WINTER WATER TABLE RISE

#### (a) Mechanism



Figure 2.2 Piston flow in the unsaturated zone – mechanism



#### WATER TABLE RISE

Figure 2.3 Piston flow in the unsaturated zone – results

### 2.4.2 Result

The results of the piston flow scenario are shown in Figure 2.3:

- the uppermost layer of the saturated zone has similar concentrations to the porewater in the base of the unsaturated zone;
- the increase in water levels should be accompanied by a simultaneous increase in nitrate concentration.

#### Dry years

Recharge will be limited during dry years but will have concentrations of nitrate similar to other periods.

#### 2.5 MECHANISM B – WINTER BYPASS FLOW FROM THE BASE OF THE SOIL

#### 2.5.1 Mechanism

The mechanism for the winter bypass flow scenario is shown in Figure 2.4:

- recharge occurs as a result of a heavy rainfall event;
- high concentrations of nitrate are leached from the base of the soil zone;
- water moves slowly through the aquifer matrix and there is diffusive exchange of nitrate with the porewater;
- hydrogeological conditions are suitable for bypass flow to occur and water containing high concentrations of nitrate moves rapidly to the water table;
- the water table rises as recharge arrives. The majority of the nitrate comes from rapid flow;
- high nitrate concentrations at the water table diffuse into the porewater and mix within the saturated zone.



Figure 2.4 Winter bypass flow from the base of the soil – mechanism

### 2.5.2 Result

The results of the winter bypass flow scenario are shown in Figure 2.5:

- the uppermost layer of the saturated zone has a very high concentration of nitrate;
- this has resulted in high porewater concentrations which could theoretically in extreme cases be greater than those in the porewaters higher in the unsaturated zone;
- the increase in water levels should be accompanied by a simultaneous increase in nitrate concentration:
- the results can be distinguished from Mechanism A by the different porewater profile.

#### Dry years

Whilst it may be less likely that conditions permitting bypass flow will occur during drier years, should this happen then it could still be possible for a pulse of high nitrate water to reach the water table. The results would be similar to a normal year.

#### WINTER BYPASS FLOW FROM BASE OF SOIL



Figure 2.5 Winter bypass flow from the base of the soil – result

### 2.6 MECHANISM C – WINTER WATER TABLE RISE

#### 2.6.1 Mechanism

The mechanism for the winter water level rise is shown in Figure 2.6:

- the water table rises as a result of recharge elsewhere in the catchment or from bypass flow which also bypasses the soil zone;
- this water is assumed to have a nitrate concentration similar to the summer concentration;
- nitrate in the newly saturated zone diffuses into the shallow saturated zone.

#### WINTER WATER TABLE RISE

(a) Mechanism



Figure 2.6 Winter water table rise – mechanism

#### 2.6.2 Result

The results of the winter water level rise scenario are shown in Figure 2.7:

- the uppermost layer of the saturated zone has a higher concentration of nitrate than the bulk;
- saturated porewater concentrations are likely to be lower than those in the porewaters in the unsaturated zone;
- The increase in water levels may be followed by an increase in nitrate concentration.

#### Dry years

The results would be lower than for a normal year.

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Figure 2.7 Winter water table rise – result

### 2.7 MECHANISM D – CHANGE IN FLOW PATHS

#### 2.7.1 Mechanism

The flow paths operating during the winter period of high water levels are shown in Figure 2.8:

- more recent water with a high concentration of nitrate moves laterally at higher velocity in the most permeable part of the aquifer matrix forming the uppermost layer of the aquifer;
- older water moves more slowly at greater depths;
- as water levels fall the high permeability layer of the aquifer is no longer saturated;
- newer high nitrate water is held in the unsaturated zone so forms a smaller fraction of the water arriving at the point of abstraction and travels more slowly.

The flow paths operating during the summer period of lower water levels are shown in Figure 2.9.

#### WINTER PATHWAYS



Figure 2.8 Winter flowpaths

#### 2.7.2 Result

- the porewater profile remains similar throughout the year;
- the fall in nitrate concentration and water level are simultaneous.

#### Dry years

In dry years the water level falls further, cutting off a greater number of high nitrate pathways and the concentration at the point of abstraction falls still further.

#### 2.8 SUMMARY OF RESULTS

The outcomes of the four individual mechanisms are summarised in Table 2.1. These show that in all cases other than Mechanism C nitrate and water level would be anticipated to rise more or less simultaneously and measurements would not distinguish between them. The distribution of porewater concentration may therefore be a more useful indicator of which mechanism is operating.

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Figure 2.9 Summer flowpaths

#### Table 2.1 Results of different possible mechanisms for nitrate fluctuations

Mechanism	Description	Nitrate arrival	Porewater nitrate
А	Unsaturated zone piston flow	Simultaneous	Similar in base of unsaturated zone and top of saturated zone
В	Bypass flow	Simultaneous	Saturated zone may exceed unsaturated zone
C	Flushing by rising water table	Possibly after increase in water level	Saturated zone may be lower than unsaturated zone
D	Changes in flowpath	Simultaneous	Remains similar throughout year

## 3 Case study – Ogbourne St George

The public supply borehole site at Ogbourne St George has been the subject of a considerable amount of BGS work related to bacterial denitrification in aquifers. This project was reported in Gale (1994). Cored boreholes were drilled to obtain porewater profiles and the completed borehole were use to monitor water quality at the water table during recharge and changes in water quality in the zone of fluctuation.

It also fulfils the project criteria:

- public supply boreholes with strongly seasonal behaviour;
- on aquifer outcrop;
- away from the influence of drift or confining layers;
- thin unsaturated zone.

This site was therefore selected as a case study. The objectives were to:

- re-examine data from porewater profiles and borehole multilevel samplers;
- attempt to relate these to possible fluctuation mechanisms.

### 3.1 SETTING

#### 3.1.1 Location and catchment



Figure 3.1 Location of public supply, investigation boreholes and water level monitoring sites at Ogbourne St George

The pumping station at Ogbourne St George is located about 8 km south of Swindon, Wiltshire [SU 1916 7623]. The site is located on the dip slope of the Berkshire Downs (Figure 3.1). The pumping station is at an elevation of about 150 m and the ground rises steeply to the southwest and south to a maximum of 268 m at Barbury Castle. The catchment of the pumping station is indicated by the Source Protection Zone and occupies the lower lying ground at the foot of the Downs to the northwest to Draycot Foliat and west to Hackpen Farm. The site was previously an NSA and there are several observation wells which are used to monitor water quality and groundwater levels. The locations of some of these are also shown in Figure 3.1.

#### 3.1.2 Geology

The site is underlain by the West Melbury and Zig Zag Chalk Formations (the former Lower Chalk) which extends about 4 km to the north (Figure 3.2). This overlies the Upper Greensand aquifer, with which it is in hydraulic continuity. The base of the Lower Chalk dips to the SSE whereas the water table has a hydraulic gradient to the ESE swinging to a more southerly direction close to the pumping station, controlled by the underlying Gault Clay. Groundwater discharges to the north along a spring line. The aquifer is about 45 m thick at the pumping station. The Chalk is moderate to highly transmissive in this area. Table 3.1 show the values for abstraction boreholes to the east of the study site.



Figure 3.2 Geological setting of Ogbourne St George Pumping Station

Borehole	Grid Reference	T ( $m^2/day$ )	Depth (m)
No. 2	SU 2013 7536	1800	72
No. 3	SU 2016 7517	2400	73
No. 4	SU 1968 7561	3200	50
No. 5	SU 1934 7550	2200	50

Table 3.1Chalk transmissivity values at Ogbourne New PS (from Allen et al. 1997)

### 3.1.3 Landuse

Landuse in 1990 and 2000 is shown in Figure 3.3 and Figure 3.4. For both of these datasets the classifications have been aggregated (see Table 3.2) to give simpler and hopefully comparable types. The 1990 data is on a 25-m<sup>2</sup> raster and was originally developed to distinguish between various types of grass. The later 2000 polygon data is much better at distinguishing arable crops. The area is predominantly arable with a proportion of improved grassland. The larger areas of suburban land identified in 1990 are probably ground which was bare at the time of the survey. Otherwise the pattern of landuse appears very similar in both surveys.



Figure 3.3 Aggregated landuse in 1990 for Ogbourne catchment from CEH Landcover Map



Figure 3.4 Aggregated landuse in 2000 for Ogbourne catchment from CEH Landcover Map

199	0 Land Cover	2000 Land Cover		
Aggregated class	Classes present	Aggregated class	Classes present	
Woodland	Deciduous	Woodland	Broad-leaved/mixed	
woodialid	Coniferous	woodialid	Coniferous	
		Cereals	Cereals	
Tilled land	Tilled land	Horticulture	Horticulture	
		Hornculture	Non annual crop	
Meadow/verge	Meadow/verge/semi-natural	Improved greesland	Improved greesland	
Mown/grazed turf	Mown/grazed turf	Improved grassiand	mproved grassiand	
Grass heath	Grass heath	Calcareous grass	Calcareous grass	
		Setaside grass	Setaside grass	
	Moorland grass			
Soruh/brookon	Bracken			
SCIUD/DIACKCII	Scrub/orchard			
	Open shrub heath			
Inland have ground	Inland bare ground	Inland have ground	Inland have ground	
iniana bare ground	Felled forest	finalia bare ground	initialità bare ground	
Pural davalonment	Suburban/rural develop	Pural davalopment	Suburban/rural develop.	
Kurai developillelli	Urban	Kurai development	Urban	

#### **3.1.4** Pumping station details

There are five wells at the pumping station. Two of these penetrate the Zig Zag and West Melbury Chalk Formations, the Upper Greensand Formation and into the Gault Clay Formation. The other three are completed in the Chalk. All are connected by a series of adits which follow zones of enhanced permeability to increase yield. Currently only one of the wells at the pumping station is used for production. The licensed abstraction from the site is 13,638 m<sup>3</sup>/day, but the average daily abstraction was only 8100 m<sup>3</sup>/day at the time of the study.

Name	Grid ref	Depth (m)	Aquifer	Adits
Ogbourne PS				
No. 1 Engine House	SU 1916 7624	77.3	UGS	
No. 2	SU 1917 7622	32	Chalk	To No. 1 at 32 mbgl
No.3 Hargreaves Well	SU 1921 7621	36.2	Chalk	To No. 2 & NE & ENE
No.4 Marlins Well	SU 1912 7606	33.8	Chalk	To No.2 at 29 mbgl & SW
No.5 Engine House	SU 1915 7623	61.0	UGS	To No. 1 at 32 mbgl
Herdswick Farm OBH	SU 177 755	103	UGS	
Hackpen Cottages OBH	SU 161 779	20.1	Chalk	
Burderop Down OBH	SU 166 767	86	UGS	

Table 3.3Summary of pumping station and observation boreholes

#### 3.2 WATER QUALITY FLUCTUATIONS AND WATER LEVELS

Nitrate monitoring data for Ogbourne PS are summarised in Table 3.4. The site is well characterised and exhibits marked seasonal fluctuations. Figure 3.5 shows the time series from 1985 to 2003 together with water levels from two nearby observation boreholes. This shows that whilst nitrate concentrations and water levels are related, the pumping station shows a number of step changes, in 1993 for example. The water levels in the two observation boreholes are more consistent. During periods of high water levels and the greatest nitrate peaks, the nitrate concentration does not return to the baseline concentration (about 7 mg  $L^{-1}$ ). A visual inspection suggests that the peaks in nitrate at the pumping station are detected later than the peaks in water level in the observation borehole further up the catchment.

Table 3.4Summary of analysis of the results from nitrate monitoring at Ogbourne St George PS<br/>(from Stuart and Kinniburgh 2005)

Site	Period	n	Frequency (samples year <sup>-1</sup> )	Regul -arity	Median trend (mg N L <sup>-1</sup> year <sup>-1</sup> )	AIC	Probability non- seasonal	Concentration @ 1/1/2000 (mg N L <sup>-1</sup> )
Ogbourne St George	17	1310	77	0.73	0.3	-252	0	11.6



Figure 3.5 Nitrate concentrations in Ogbourne PS and water levels in the Environment Agency observation boreholes at Burderop Down and Hackpen Cottages

In the Herdswick Farm observation borehole, nitrate and water level are measured at the same point. During the period 1990 to 2003, nitrate concentration showed a wide seasonal variation from about 3.2 mg  $L^{-1}$  in the summer of 1990 to 21.6 mg  $L^{-1}$  in the winter of 1995 (Figure 3.6). Concentrations are very well related to the water level measured at the same with good correspondence to both low and high water levels. A visual inspection of the data suggests that in this observation borehole the high nitrate concentrations appear ahead of the water level rise.



Figure 3.6 Seasonal fluctuations in nitrate and water levels Environment Agency observation borehole at Herdswick Farm

#### 3.3 DATA FROM BGS 1991 INVESTIGATION BOREHOLES

#### 3.3.1 Porewater profiles

Two cored boreholes (A and B) were drilled in April 1991 when the water table was at the top of its seasonal fluctuation and a third (C) was drilled at the site in November 1991 to obtain a profile when the water table was near the base of the seasonal recession. The porewater profiles from April and November 1991 are shown in Figure 3.7. These show that maximum concentrations (20-40 mg L<sup>-1</sup>) occurred above the level of the water table. Concentrations declined within the zone of water level fluctuation to low concentrations (c 2 mg L<sup>-1</sup>) within the permanently saturated zone.



Figure 3.7 Nitrate porewater profiles from 1991 and multilevel sampler results from 1992 from BGS investigation

Gale et al. (1994) interpreted that data as showing that the high nitrate concentrations in the top 5 m of the profile represent a 'store' or 'source' of nitrate for leaching to the water table. Nitrate and recharge could migrate by:

- 1. Matrix flow with piston flow displacement-nitrate concentrations in recharge arriving at the water table should be equal to nitrate concentrations in the matrix at the water table;
- 2. Fracture flow which bypasses the matrix nitrate concentrations in recharge arriving at the water table could be significantly higher than porewater concentrations at the water table.

#### **3.3.2** Multilevel sampling

Groundwater samples were collected by multilevel samplers in piezometers A and C during spring 1992. In piezometer A the seals in the sampler were directly against the borehole wall (Figure 3.8. In B the seals were against the screen. It is possible that samples from the piezometer A represent more reliable water samples from the specific aquifer horizon as in piezometer C some vertical water movement may have occurred within the sandpack. In A water samples were collected both during the rise in water table and in the subsequent recession.



Figure 3.8 Schematic diagram of multi-level sampler emplacement in piezometers A and C at BGS investigation borehole, Ogbourne St George

The first result from each of the deployments of the multilevel samplers is shown together with the porewaters in Figure 3.7). The results from piezometer C are broadly similar to the porewater nitrate concentrations at the equivalent depth. This is consistent with matrix flow, but not necessarily with rapid recharge via fractures.

The results from piezometer A show that nitrate concentrations in groundwater are similar to the porewaters in autumn (depth to water 23-24 m but diverge as the water table rises so that groundwater concentrations are consistently higher. When water levels decline, the nitrate concentrations decline more rapidly with time than they rose and are closer to the porewater concentrations.

The higher nitrate concentrations observed in groundwater than in the corresponding porewater suggests either:

• Nitrate is derived from higher up within the profile, where nitrate porewater concentrations are higher, and that rapid downward recharge through fractures occurs (Option 1, Figure 3.9).



Figure 3.9 Option 1, rapid recharge through fractures



Figure 3.10 Option 2, rapid transfer of water in the zone of fluctuation

• High nitrate recharge is arriving at the water table, possibly by matrix flow in adjacent areas, and being transferred laterally to the piezometers by fracture flow within the saturated zone (Option 2, Figure 3.10).

These mechanisms would both be anticipated to give a simultaneous rise in water level and nitrate concentration.

### 3.4 CONCLUSIONS

Mobile groundwater with a nitrate concentration higher than the porewater has been observed to be present in the zone of water table fluctuation during periods of rising water levels and possibly high nitrate concentrations are detected ahead of water level rises. This is inconsistent with piston flow through the matrix (Mechanism A).

It is not possible to say from the results described which of the other mechanisms occur or their relative importance, as several may operate together, particularly to give Option 2 above. It would be useful to estimate the matrix hydraulic conductivity, to assess whether the matrix is able to transmit a significant component of the recharge.

There is some evidence to suggest that the rapid decline in groundwater nitrate concentrations as the water table declines (as compared to the rising hydrograph) may indicate that fracture flow to the water table (Mechanism B) occurs during the rising limb of the hydrograph and that matrix flow dominates the recession (Mechanism A). Some recharge will continue to occur even though the water table declines.

## 4 Case Study – Bircham

## 4.1 SETTING

#### 4.1.1 Location

There are three public supply sites in the study area, Great Bircham, Fring and Sedgeford. All three are situated at about 30 m aOD on the scarp of the West Norfolk Chalk of East Anglia. In this area the chalk outcrop does not form a prominent scarp slope. The topographic high to the east is formed by drift deposits. Surface drainage is westwards with the major rivers following the courses of buried channels. Great Bircham and Fring are situated in a dry valley above the head of the Heacham river (Figure 4.1) Sedgeford is some 5 km to the northwest.

### 4.1.2 Landuse

Catchment landuse in 1990 and 2000 is shown in Figure 4.2 and Figure 4.3. The earlier data were collected with an ecological emphasis and have difficulty in distinguishing bare ground and urban development. Taking this into account it is clear that landuse over the three catchments is broadly similar being predominantly arable with some improved grassland. The later survey shows that this is a mixture of cereals and other crops.

### 4.1.3 Geology

The West Norfolk Chalk outcrop is about 20 km wide, mostly unconfined or covered by thin till and sand and gravel deposits. The Lower Chalk (Zig Zag and West Melbury Chalk Formations in Figure 4.4) outcrops in a thin band 1-2 km wide, overlain by Middle (Holywell Formation), then Upper Chalk (Lewes Nodular Chalk Formation). Beneath are a thin bed of the Lower Cretaceous Red Chalk and the ferruginous sandstones of the Carstone. The Chalk dips gently to the northeast at about 4°.

All five of the boreholes penetrate the Middle and Lower Chalk through a thin Drift cover. The top of the Middle Chalk is often rubbly or broken, with the remainder being hard with a few fractures. The Lower Chalk is clayey and contains more marly and soft bands.

The Protection Zone 1 for Sedgeford and Fring is wholly on the Middle Chalk whereas for Great Bircham it extends onto the Upper Chalk. At Great Bircham parts of Zone 1 and Zone 2 are under a thin cover of till. At Sedgeford there is a small area of till around the borehole but it seems likely that this is broken Chalk or very chalky till since it is not identified in the drilling logs. Part of Zone 2 has a thin cover of glaciolacustrine clay and silt deposits. There are also alluvial deposits in the dry valley at Great Bircham and Sedgeford.

#### 4.1.4 Hydrogeological setting

There are three boreholes at Great Bircham abstracting from the Chalk and a new hole reported as penetrating the Sandringham Sands. Boreholes 1 and 2 are inside the pumping station and 3 situated 250 m to the southwest. Only two pumps can run at one time. Borehole 1 was historically the lead pump with the longer operating periods. There is also a borehole at Osier Carr which is sometimes referred to as Great Bircham 4

There are two operating boreholes very close together at Fring, a third has collapsed, possibly due to ingress of water behind the casing. Only borehole 2 has enough monitoring data to evaluate trend and seasonality. The two pumps operate alternately as duty and standby. There are two operating boreholes at Sedgeford, 175 m apart. These alternate as duty and standby except in the summer when both pumps run.



Figure 4.1 Location of public supply source, source protection zones and water level monitoring boreholes in the Bircham area





Aggregated landuse in 1990 from CEH landcover for the Great Bircham area





Aggregated landuse in 2000 from CEH landcover for the Great Bircham area





Solid geology for the Great Bircham area

OR/08/046



Figure 4.5 Drift geology for the Great Bircham area

	Licen	sed	Actual 1989	Average	
	Annual (m <sup>3</sup> /year)	Daily (m <sup>3</sup> /day)	(m³/year)	(m³/year)	
Great Bircham	1,246,000	5,682	1,378,000	1,016,000	
Fring	547,500	2,415	353,000	377,000	
Sedgeford	1,246,000	5,682	1,378,000	1,016,000	

Table 4.1	Summary of	f abstraction	data for	boreholes	in the	Bircham a	area
		1 40004 4001011		001010100			

The catchments of the three sites are shown in Figure 4.1. All three sites have a composite Zone 3 which also includes boreholes to the south. Great Bircham and Fring also have the same Zone 2. The Fring SPZ is very small. Abstractions from the three sites as of 1989 are shown in Table 4.1.

#### 4.1.5 Borehole details

The boreholes at the three sites were constructed over a period of 70 years with the oldest at Fring 2 and the newest at Osier Carr (Table 4.2). All sites are at a similar elevation and the boreholes have similar depths. The boreholes at Sedgeford have deeper plain casing.

Aquifer property summary data sheets state that the major flows in this area are in and above the Melbourn Rock. This occurs at similar depth at all three sites (Table 4.2). Inflows to the boreholes measured during geophysical logging appear to be different at each of the sites. In Great Bircham 1 the main inflow occurs between 12 and 17 m aOD with fissures noted at 3.4 to 4.5 m. Main inflows are deeper in Great Bircham 3, corresponding to the Melbourn Rock and also water flowing from behind the casing. At Osier Carr there are inflows from a large diagonal fissure at 24.1 m and a major fissure at 31m. There is little flow below 39 m. At Fring, the base of the main flow zone is at 3 maOD but minor inflows occur below this level. Two thirds originate above 8 maOD. Details are for a now collapsed hole not the present borehole 2.

The four newer boreholes have estimates of transmissivity from pumping tests. Values are lower for the Great Bircham boreholes than at Sedgeford. Transmissivity for the nearby Bircham Newton in the APM is estimated to be  $1100 \text{ m}^2/\text{day}$ . Allen et al. (1997) state that the Great Bircham area has high transmissivity relative to other areas of the Norfolk Chalk. This has been ascribed to the better fracture development in the Lower and Middle Chalk of west Norfolk compared to the Upper Chalk of east Norfolk. Regional transmissivity values average 500 m<sup>2</sup>/day.

Site	Date of drilling	Acidised	Elevation (maOD)	Casing depth (mbgl)	Borehole depth (mbgl)	Melbourn Rock (maOD)	Large inflows (maOD)	Minor inflows (maOD)
Great Bircham 1	1947	No	36.36	9.14	51	-0.50–3	13–17	12, 5, 4, -12
Great Bircham 3	1989	Yes	~36	11.5	50	-0.50–2	0, 2	6
Osier Carr	1991	Yes	~35	6.5	45		31 m	24.1 m
Fring 2	1935	No	29.6	10.6	42	-0.3–4.7	8–13	2-6, -4-7
Sedgeford 1	1969	Yes	31.72	22.4	47	-1.5–3	Flow three	oughout total
Sedgeford 2	1976	Yes	29.78	22	46	-1.5–3	(	lepth

 Table 4.2
 Summary of borehole and flow regime for boreholes in the Bircham area

Site	T from	Pumping test results						
	AP Manual (m²/day)	T(m <sup>2</sup> /day) K (m/d)		Sy	S			
Great Bircham 1				0.03				
Great Bircham 3	250	Obs well: 220	4.4 (open section 40 m)	0.03	$1.5e^{-3}$			
		Pumped well: 125	2.5 (open section 40 m)					
Osier Carr	2100							
Fring 2		200-4500, centred at 1900	76 (open section 25 m)					
Sedgeford 1	4000	3700-12200	160 (open section (25 m)					
Sedgeford 2	4000	2100-15000		0.005				

Table 4.3Summary of aquifer properties (from Allen et al. 1997)

#### 4.2 WATER QUALITY FLUCTUATIONS AND WATER LEVELS

#### 4.2.1 Analysis of nitrate monitoring data

All three sites have a similar monitoring period averaging 18 years, with Great Bircham 3 being the shortest (Table 4.4). The monitoring frequency at Great Bircham is about half that at the other two sites but monitoring is more regular. The largest differences between the sources are for seasonality. Great Bircham 1 appears to be 'not seasonal' and Great Bircham 3 is slightly seasonal, whereas the others show clear seasonality. This could be due to the lower sampling frequency at Great Bircham or there could be other factors involved. The nitrate time-series data are plotted in Figure 4.6.

Site	Period	n	Frequency (samples year <sup>-1</sup> )	Regul -arity	Median trend (mg N L <sup>-1</sup> year <sup>-1</sup> )	AIC	Probability non- seasonal	Concentration @ 1/1/2000 (mgN L <sup>-1</sup> )
Bircham 1	19	124	6.5	0.38	0.19	16.7	0.932	17.1
Bircham 3	13	67	5.2	0.51	0.07	-0.16	0.0562	17.4
Fring 2	19	212	11.2	0.29	0.08	-6.24	0.00444	15.5
Sedgeford 1	16	181	11.3	0.24	0.25	-29.8	5.31E-7	14.8
Sedgeford 2	21	320	15.2	0.22	0.18	-61	$1.05e^{-12}$	15.4

Table 4.4Summary of analysis of the results from nitrate monitoring in the Great Bircham area<br/>(from Stuart and Kinniburgh, 2005)



Figure 4.6 Nitrate concentrations from Great Bircham, Fring and Sedgeford

#### 4.2.2 Seasonal fluctuations and water levels

Time-series water levels were available for six points in the area, three in the catchments and three in adjacent catchments. Three of these series are shown in Figure 4.7 and indicate that the unsaturated zone is shallow at these points. The most regular series is seen at Old Barn near Shernborne, TF73/001 (Figure 4.7). Water levels rise in all years measured, generally by about 10 m but varying from as little as 2 m up to 12.5 m.



Figure 4.7 Water levels in the Environment Agency observation boreholes at Bircham, Sedgeford and Shernborne showing range of fluctuation in 'normal' years

At Bircham there is a similar pattern, although TF73/007 is in the adjacent catchment. There are seasonal rises in water level in most years of some 2 to 6 m but these are overlaid by large longer-term water level declines in the early 1970s, 1989-94 and 1996-98. At Sedgeford the two series are also similar to each other with annual peaks in water levels of between 3 and 7 m. In the periods 1989 to 1993 and 1996 to 1998 minimum levels are depressed but peaks are still seen.

Figure 4.8 shows nitrate concentrations from Figure 4.6 superimposed on water levels. The shaded areas are periods where water levels fell below the long-term average minimum. Levels did not return to this value immediately following the wet winter of 2001.

The minimum water level occurs in November or December and is normally followed by a steep rise in January. This is closely matched by nitrate with little apparent lag. At Sedgeford the relative size of the nitrate peak matches the size of the water level peak quite closely in 'normal' years. The source has a very high response to water level variation for Chalk sources (about 5 mg nitrate  $L^{-1}$  per metre rise) with annual water level fluctuations of about 5-6 m giving a nitrate peak above the baseline of 25 mg  $L^{-1}$ . In the dry intervals (1989-1992 and 1996-1998) nitrate peaks have either low amplitude or are lost.

At Great Bircham the pattern is different. Firstly, the water level rises are much more subdued. This is likely to be due to the physical setting of the site in a shallow valley rather than an interfluve. Average water level rises are only about 3-4 m. At the water level monitoring borehole at the Cottages the long-term minimum water level is about 44 maOD. This is above the elevation of the Bircham borehole and the corresponding level must be less at the site. The impact of the drier periods on water levels is more protracted, and combined with the wet winter of 2000-2001 there have been no periods of regular water level fluctuations since 1989.





Figure 4.8 Nitrate concentrations and nearby water levels for Bircham and Sedgeford. The dashed lines indicate the approximate 'normal' minimum water level at the monitoring site.

Nitrate concentrations at Great Bircham 1 do show fluctuations although these are not regular enough for the data to be recognised as seasonal. Unlike Sedgeford clear peaks are seen in the first dry interval (1989-1993). At the end of this period the data are very variable and a pattern cannot be detected. From 1995 onwards the data are much less variable but have intervals where there are few data. It does not appear that higher nitrate concentrations are related to a water level rise above a particular level.

The greater the sensitivity to water level fluctuations, the greater the likely contribution of shallow groundwater to the source and/or the greater the degree of pollution of the shallowest groundwater. This is undoubtedly due to greater near-surface pollution but may also include a contribution from permeability of shallow horizons. At Sedgeford, it appears that water levels need to rise to the equivalent of 7 or 8 maOD at the monitoring point before high nitrate water is accessed. Sedgeford is at about 30 m so there is at least 22 m of unsaturated zone. At Bircham the unsaturated zone is thinner close to the borehole.

### 4.3 HISTORICAL POREWATER PROFILES

There is some information on historical groundwater quality stratification in the aquifer from a series of porewater profiles from sites within the Bircham catchment. In 1976-77, porewater profiles in the unsaturated zone had concentrations of up to 40 mg N L<sup>-1</sup> down to about 7 m below the surface, up to 30 mg N L<sup>-1</sup> to 14 m and up to 10 mg N L<sup>-1</sup> to 25 m (Foster et al, 1986). By 1990, profiles were still similar but showed peaks at 3 m below the surface of 40-80 mg N L<sup>-1</sup>, ascribed at one of the sites to high applications of nitrate to sugar beet and lower than average effective rainfall. Below this, concentrations peaked at up to 35 mg L<sup>-1</sup> to 20 m below the surface (Parker et al, 1991).

These porewater data are corroborated by monitoring of piezometers which were completed in the zone of fluctuation. These indicated that from 1976-1981 recharge in the winter and spring had concentrations of nitrate in the range 20-30 mg N L<sup>-1</sup>. The piezometers were dry in the summer and autumn.



Figure 4.9 Composite porewater profiles from close to Great Bircham Pumping Station in 1976 with zone of seasonal water table fluctuation as shown in Foster (1986).

In 1976, in the zone of fluctuation, aquifer porewaters had concentrations of nitrate in the range 10-15 mg N L<sup>-1</sup> and in the shallow saturated zone (0-30 maOD) had concentrations of nitrate in the range 7-15 mg NO<sub>3</sub> L<sup>-1</sup>(Figure 4.9). The two profiles extending into the unsaturated zone were collected in February 1976 when water levels were about 15-16 m below the surface (32-33 maOD). The bottom of the zone of fluctuation at these sites is consistent with the minimum water level in Observation Borehole 3-142 in Figure 4.7. It is not clear now whether the zone of fluctuation was located in Figure 4.9 from physical or visual evidence or whether the upper boundary was chosen to match the change in slope of the profile. At the time the profiles were measured the water level would have needed to rise to 40 maOD to access high nitrate water.



Figure 4.10 Expanded section of water level record from Cottages, Bircham-007 with pumped nitrate concentrations from Foster (1986)

Figure 4.10 shows that water levels were at their maximum in 1975 in June 1975 and continued to fall until October 1976. At the time of profiling, February 1976, water levels at 007 had fallen some 4 m from their maximum and were at the normal long-term minimum level of about 44 maOD shown in Figure 4.7. This is about 12 m higher than at the profile site but it is assumed that relative water level changes will be similar.

It is difficult to see how the shapes of the profiles could have developed from flushing of the unsaturated zone by rising water levels. The long-term maximum water level at 007 is about 51 m aOD, that is a rise of 7 m above the minimum. This would correspond to about 38 maOD at the profile site and is broadly consistent with the zone of fluctuation shown in Figure 4.9. However, the antecedent water levels in 1975 were only at about 48 maOD at 007, assumed to correspond to 35 m aOD at the profile site. Additionally the nitrate concentration record in the supply boreholes starts in September 1976 and suggests that higher nitrate water is accessed as soon as water levels in 007 rise above 44 m aOD, that is into the zone of fluctuation.

Instead, these profiles are consistent with the winter high nitrate peaks being derived from increased permeability in the zone of water table fluctuation allowing a greater contribution of shallow, polluted groundwater to abstracted water.

### 4.4 CONCLUSIONS

The borehole at Sedgeford has a very high response to water level variation (about 5 mg nitrate  $L^{-1}$  per metre rise) with annual water level fluctuations of about 5-6 m giving a nitrate peak above the baseline of 25 mg  $L^{-1}$ . In dry intervals nitrate peaks have either low amplitude or are lost. At nearby Great Bircham the pattern is different with more subdued water level rises. This is likely to be due to the physical setting of the site in a shallow valley rather than an interfluve. The impact of the drier periods on water levels is more protracted.

The porewater profile shapes and the detection of higher nitrate water as soon as the water level rises into the zone of fluctuation are consistent with the winter high nitrate peaks being derived from increased permeability in the zone of water table fluctuation allowing a greater contribution of shallow, polluted groundwater to abstracted water (Mechanism D).

## 5 Case Study – Twyford

The site at Twyford met many of the criteria set out in Section 1.4 and was selected as the first field site. These criteria were:

- located on outcrop Chalk;
- moderate to high transmissivity;
- autumn minimum water level about 20-25 m below the surface;
- in flowpath to public supply borehole with pronounced seasonal fluctuations;
- nitrate concentrations in the public supply not high enough to be sensitive;
- convenient for frequent visits from Wallingford.

## 5.1 SETTING

### 5.1.1 Physical setting

The site was about 1.5 km east of the public supply borehole at Twyford, Hampshire on the Chalk of the South Downs (Figure 5.1). The site [SU 5073 2528] was at an elevation of about 55 metres above Ordnance Datum (maOD) on the southeastern slopes of a dry valley running southwestwards down towards the pumping station which is at about 38 m aOD. The area is drained by the River Itchen which is about 2.7 km to the west at an elevation of about 25 maOD. The Downs rise to a highpoint at Cheesefoot Head [SU 531 277] about 3.4 km to the northeast of the site.

The landowner's agent stated that the lowest point of the field, the northwestern corner, was liable to become very water logged during wet winters. On average the area receives about 850 mm of rainfall.



Figure 5.1 Site location and autumn rest water levels from Hydrogeological map of Hampshire

## 5.1.2 Geology

The area immediately around the pumping station is largely free from superficial deposits, with the Seaford chalk being covered only by a thin, flinty soil. To the west of the borehole, the River Itchen flows across a cover of alluvium and river terrace gravels. To the south and the north of Morestead, hilltops have caps of Clay-with-flints. Clayey, flinty solifluction deposits (Head) occur in valley bottoms (Figure 5.2).

The site is on the southern flank of the Winchester Anticline, one of several major west-east trending fold structures that formed in response to compression during Miocene inversion of the Wessex Basin (Figure 5.3). The Winchester Anticline is an asymmetrical structure with strata dipping at approximately 4-5 degrees on the southern limb in the area of the pumping station and up to 10 degrees on the northern limb (Figure 5.3). The central core of the Winchester Anticline is deeply eroded providing an elongate west-east trending window in the Lower Chalk. Steep scarps developed around the eroded core of the anticline expose the overlying Middle and Upper Chalk up to the level of the Seaford Chalk. The remainder of the Chalk succession and the overlying Palaeogene succession of the Hampshire Basin are exposed to the south of the anticline. The River Itchen cuts through the core of the Winchester Anticline and flows southward toward the Palaeogene crop.

## 5.1.3 Hydrogeology

The water level contours on the Hydrogeological Map (for October 1973) indicate that groundwater flow is to the southwest at the site, generally towards the River Itchen. The autumn water level at the site would be predicted to be 20-25 m below the surface. The local direction of groundwater flow will be influenced by abstraction from the pumping station. The groundwater level cuts across the relatively steeply dipping strata of the Winchester Anticline (Figure 5.4).



Figure 5.2 Superficial deposits in the area to the northeast of Twyford



Figure 5.3 3-D model of the Winchester Anticline showing the location of the Morestead Anticline



Figure 5.4 December 1990 groundwater level cross-cutting the Winchester Anticline

## 5.1.4 Pumping Station

The Twyford pumping station comprises the original complex 3-well site with adits and 3 newer deep boreholes further to the west. The three wells were constructed in 1897, 1905 and 1933 and are situated beneath the same engine house, which is at about 38 m aOD [SU 490 248]. The first two were originally about 2.4 m in diameter and 50 m deep and the third was 1.1 m in diameter and 41 m deep. They are interconnected by a heading some 39 m below the surface. There are two adits: one at 30 m below the surface running 128 m to the northeast and the second at 38 m below the surface running 174 m to the south.

The three boreholes were drilled in 1962. The first borehole (No. 1) [SU 4895 2509] was 450 mm in diameter and 152 m deep. Water was struck at 40 m, 61 m and 119 m below the surface. At this time the water level was 18.5 m below the surface (about 20 m aOD). After acidisation the borehole provided a yield of 76 l/s for a water level drawdown of 35 m during a 14-day pumping test No. 2 [SU 4880 2471] was similar but was 137 m deep and struck was at 21 m and 122 m below the surface. The yield was 60 l/s for a water level drawdown of 8 m. No. 3 [SU 4907 2454] was also 137 m deep and struck water at 20 m and 51 m below the surface, and yielding 34 l/s for a water level depression of 49 m.

There are also a number of domestic or farm boreholes in the area. These indicate that the Chalk may be low yielding in the area to the east of the site, but most of the records are old and incomplete. The nearest site with aquifer properties data is the public water supply at Easton. Borehole 1 [SU 5013 3229] had a transmissivity of 4700 m<sup>2</sup>/day, whilst Borehole 2 [SU 5030 3200] was lower at 2400 m<sup>2</sup>/day (Allen et al. 1997).

### 5.1.5 Variation of aquifer properties with depth

Several studies have investigated the variability of aquifer properties with depth in this area. In the Candover catchment to the north a study of artesian boreholes at watercress farms at Alresford found that a narrow zone at the top of the boreholes was contributing the majority of the flow, with the rest of the aquifer providing upwards leakage to this high transmissivity layer (Headworth, 1978). A detailed investigation of the River Itchen augmentation scheme showed a decrease in storage with water level. During the prolonged drought period in 1976 an analysis of drawdowns from a group pumping test indicted that the aquifer was multi-layered. The 6-m thick top layer, just below the water table, had high transmissivity and storage. Beneath this was a lower transmissivity and storage layer constituting the remainder of the Upper Chalk. Detailed tests in 3 different boreholes in dry valleys: Abbotstone [SU 558 349], Itchen Down Farm [SU 546 334] and Totford [SU 569 380] in the Candover catchment, included core permeability testing, geophysical logging and packer injection testing (Price et al. 1977). This study showed that:

- throughout the borehole, the permeabilities measured were one or two orders of magnitude greater than the core permeability;
- zones that had very high permeability corresponded to fracture locations;
- most of the saturated thickness of the Chalk had very low permeability only a few fractures were required to give the total transmissivity;
- the most important flow horizons were near the top of the borehole with very little flow below 40 or 50 m;
- there appeared to be little correlation between the high transmissivity layers and the Upper Chalk stratigraphy.

#### 5.1.6 Landuse

The Chalk downland in the Twyford catchment is typical of the area with the wetter valley bottoms used for cattle grazing and the higher slopes used for a mixture of arable and unimproved grass. Figures 5.5 and 5.6 show a summary of land cover from satellite imagery in 1990 and 2000. The 2000 Land Cover boundaries correspond well with mapped field boundaries on the 1:10, 000 topographic map which underlies the data in Figure 5.6.

The wooded dry valley and the wide headland strip on which the borehole is sited can be seen on both these maps and is clearer in 2000. These maps indicate that the borehole field was under grass in both 1990 and 2000.

Details of cropping and fertiliser applications which were provided by the landowner for the field are shown in Table 5.1. These data shows that the field has been predominantly used for cereals since 1992 with a period of setaside in 2000 and 2001. Fertiliser applications to spring barley have been at a relatively consistent level averaging 160 kg N/ha. Heavier applications were made to oil seed rape in 2004 and winter wheat in 2005.



Figure 5.5 Aggregated landuse in 1990 for the Twyford area from CEH Landcover Map



Figure 5.6 Aggregated landuse in 2000 for the Twyford area from CEH Landcover Map

Period	Crop	Yield (t/ha fresh)	Planting date	Inorganic fertiliser (kg N /ha)		Other factors affecting N balance
				Aug-Dec	Jan-July	
1992	Winter barley					Straw removed
1993	Winter oil seed rape					Straw incorporated
1994	Winter wheat					Straw removed
1995	Spring barley					Straw removed
1996	Spring barley					Straw removed
1997	Spring barley					Straw removed
1998	Winter wheat					Straw removed
1999	Spring barley	6.1	2/3/99		175	Straw removed
2000						
2001	Set aside					Cut once/sprayed once
2002	Spring barley	5.2	15/2/02		159	Straw removed
2003	Spring barley	6.3	22/2/03		169	Straw removed
2004	Winter oil seed rape	2.5	3/9/03	38	160	Straw incorporated
2005	Winter wheat	8.5	8/9/04		245	Straw incorporated
2006	Spring barley	6.9	5/2/06		162	Straw incorporated

Table 5.1Cropping record for the Morestead borehole site

#### 5.2 WATER QUALITY FLUCTUATIONS AND WATER LEVELS

Nitrate concentrations at the Pumping Station up to the beginning of 2007 were provided by Southern Water (Figure 5.7). These show:

- the three time series are essentially similar with little difference between the well and the deeper boreholes;
- all three showed very high concentrations during the wet winter of 2000-2001;
- the winter peak concentrations were very subdued over the years 2004-2005 and 2005-2006 as a result of the sustained period of dry weather;
- the leading edge of the 2006-2007 peak can be seen by the end of December 2006;
- the minimum nitrate concentrations are in the range  $6-7 \text{ mg N L}^{-1}$  in all three series;
- the borehole series both indicate an increasing trend. This is probably an underestimate since the 2004 and 2005 peaks are relatively repressed.

Figure 5.7 also shows that nitrate concentrations correspond very well to water levels recorded in the area at Hazeley Down Farm and Twyford Reservoir. Two of the series are shown on the same plot in Figure 5.8. The nitrate and water levels are very similar in both normal and dry periods. Nitrate arrives at the pumping station some time after the water level in the observation boreholes rises.



Figure 5.7 Nitrate concentrations at Twyford Pumping Station compared with water levels at Hazeley Down Farm and Twyford Reservoir

#### OR/08/046



Figure 5.8 Nitrate concentrations at Twyford Pumping Station Borehole 1 and Hazeley Down Farm

# 5.3 INSTALLATION OF BOREHOLE FOR MONITORING NITRATE CONCENTRATIONS AND WATER LEVELS

Drilling at the site was started on 10<sup>th</sup> May 2006 using 150 mm rotary cored drilling with airflush. After a few metres the tool became stuck and water from the bowser had to be added. The method was then changed to 140 mm wireline Geobore S. This required a water mist to allow the barrel to rotate. Drilling was continued to 50 m below the water table and the hole was completed at 75 m on 17<sup>th</sup> May 2006.

The borehole was caliper logged prior to testing to check that the hole was of adequate diameter (160 mm) to accept the packer string and to contribute to the identification of suitable intervals to be tested. Some intervals in the lower part of the hole were of insufficient diameter and the borehole was reamed out to 160 mm and developed. The caliper log was run again and the diameter was satisfactory.

The borehole was completed after sampling as two 50 mm diameter piezometers, both with 6 m screened sections (Figure 5.9). The shallow piezometer was about 30 m deep and was designed to sample the water in the permeable zone close to the water table. The deeper piezometer reached close to the base of the borehole.

In order to monitor nitrate and water levels continuously a Troll 9500 sonde was purchased. This had an external diameter of 48 mm and was designed to be suitable for deployment in nominal 50 mm piezometers. The sonde had a pressure transducer to enable water levels to be measured and also barometric pressure and temperature as standard features. A nitrate ion-selective electrode sensor was added to the array. The limitations on depth for the liquid junction in the probe imposed a limit of deployment of 15 m below the water table. This limit meant that the deployment of a second probe in the deeper piezometer was abandoned.

In the event there were two separate problems with the sensor installation:

- the diameter of the piezometers was slightly reduced in places by installation out of the vertical and the probe could not be installed;
- laboratory testing of the probe indicated that whilst the pressure transducer appeared to be stable the nitrate readings drifted considerably over a few hours.



Figure 5.9 Borehole completion as 50-mm piezometers

### 5.4 POREWATER PROFILE

The porewater profile was collected at the period of minimum water level after a dry period where there had been limited recharge in the previous winter (Figure 5.10). The nitrate concentrations in the unsaturated zone below 5 m are higher than those at the top of the saturated zone. This means that it would be difficult to distinguish between the various possible mechanisms as nitrate is available to be leached immediately above the water table.

In the following winter period water levels rose to within 10 m of the surface and it is likely that nitrate from the peak in the unsaturated zone was flushed out.



Figure 5.10 Upper part of the porewater profile from the Morestead borehole

#### 5.5 CONCLUSIONS

From the available data it is difficult to draw any firm conclusions from this site. Unlike the other examples piston flow from the overlying unsaturated zone cannot be ruled out. The good correspondence between nitrate and water levels throughout the time series presented does not suggest that the rising of the water table to a particular level triggers an increase of nitrate into the borehole.

## 6 Conclusions

Four conceptual models were prepared to represent chalk recharge mechanisms, namely winter piston flow through the unsaturated zone matrix, winter bypass flow from the base of the soil bringing high nitrate water directly to the water table, water table rise from water entering elsewhere in the catchment flushing out porewater and a change in flow path giving access to a greater percentage of shallow high nitrate water. These four mechanisms were evaluated in a very simple way to determine the relationship between nitrate concentration at the water table and water level. It was concluded that all mechanisms except flushing by a rising water table would be likely to result in the more or less simultaneous rising of the water level and arrival of nitrate and the distribution of nitrate in the porewater profile may be a more-useful indicator.

Three potential sites were selected for evaluation as case studies using existing data:

- 1. At Ogbourne St George water with a nitrate concentration higher than the porewater was observed to be present in the zone of water table fluctuation during periods of rising water levels and increases in nitrate were detected ahead of water level rises in a local observation borehole. This would be inconsistent with piston flow through the matrix and corresponded perhaps with fracture flow or lateral transfer of water.
- 2. In the Bircham area, the boreholes at Sedgeford had a very high response to water level variation but in dry intervals nitrate peaks had either low amplitude or were lost. At Great Bircham the pattern was different with more subdued water level rises and a more protracted impact from drier periods. This is likely to be due differences in the physical setting of the site in a shallow valley rather than an interfluve. This response is not consistent with piston flow through the matrix. The porewater profiles shape and the detection of higher nitrate water as soon as the water level rises into the zone of fluctuation are consistent with the winter high nitrate peaks being derived from increased permeability in the zone of water table fluctuation allowing a greater contribution of shallow, polluted groundwater to abstracted water.
- 3. At Twyford where the porewater profile was measured after a long dry period, the distribution of nitrate in the unsaturated zone did not rule out the piston flow mechanism but there was insufficient information to draw other conclusions.

It was concluded that measuring the difference between the water level rise and arrival of nitrate at a borehole may not be able to distinguish the mechanism operating and other information, such as. porewater concentration, may be needed.

## References

Most of the references listed below are held in the Library of the British Geological Survey at Keyworth, Nottingham. Copies of the references may be purchased from the Library subject to the current copyright legislation.

ALLEN, D. J., BREWERTON, L.B., COLEBY L.M., GIBBS, B.R., LEWIS, M.A., MACDONALD, A.M., WAGSTAFF, S. J. and WILLIAMS, A. T. 1997 The physical properties of major aquifers in England and Wales, British Geological Survey Technical Report WD/97/34 and Environment Agency R&D Publication 8.

BEESON, S. and COOK, M. 2004. Nitrate in groundwater: a water company perspective *Quarterly Journal of Engineering Geology & Hydrogeology*, Vol. 37, 4, 261-270.

BROUYERE, S., DASSARGUES, A. and HALLET, V. 2004. Migration of contaminants through the unsaturated zone overlying the Hesbaye chalky aquifer in Belgium: a field investigation. *Journal of Contaminant Hydrology*, Vol. 72, 1-4, 135-164.

COSTA, J. L., MASSONE, H., MARTINEZ, D., SUERO, E. E., VIDAL, C. M. and BEDMAR, F. 2002. Nitrate contamination of a rural aquifer and accumulation in the unsaturated zone. *Agricultural Water Management*, Vol. 57, 1, 33-47.

FOSTER, S.S.D, BRIDGE, L.R., GEAKE, A.K., LAWRENCE, A.R. and PARKER, J.M. 1986. The groundwater nitrate problem: a summary of research on the impact of agricultural land-use practices on groundwater quality between 1976 and 1985. British Geological Survey Hydrogeological Report 86/2.

GALE, I. N., MARKS, R.J., DARLING, W.G. and WEST, J.M. 1994. Bacterial denitrification in aquifers. Evidence from the unsaturated zone and the unconfined Chalk and Sherwood Sandstone aquifers. *National Rivers Authority R&D Project Record*, 306/11/ST. (Bristol: National Rivers Authority.)

IRESON A.M., WHEATER, H.S., BUTLER, A.P MATHIAS, S.A., FINCH, J. and Cooper, J.D. 2006. Hydrological processes in the Chalk unsaturated zone – Insights from an intensive field monitoring programme. *Journal of Hydrology*, 330, 29-43.

IRESON A.M., MATHIAS, S.A., WHEATER, H.S., BUTLER, A.P. and FINCH, J. 2009. A model for flow in the chalk unsaturated zone incorporating progressive weathering. *Journal of Hydrology*, 365, 244-260.

HARIA, A.H., HODNETT, M.G. and JOHNSON, A.C. 2003. Mechanisms of groundwater recharge and pesticide penetration to a chalk aquifer in southern England. *Journal of Hydrology*, 275, 122-137.

HEADWORTH, H.G. 1978. Hydrogeological characteristics of artesian boreholes in the Chalk of Hampshire. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol 11, 139-144.

HONG, N., WHITE, J. G., WEISZ, R., GUMPERTZ, M. L., DUFFERA, M. G. and CASSEL, D. K. 2007. Groundwater nitrate spatial and temporal patterns and correlations: Influence of natural controls and nitrogen management. *Vadose Zone Journal*, Vol. 6, 1, 53-66.

LEE, L.D.J., LAWRENCE, D.S.L. and PRICE, M. 2006. Analysis of water-level response to rainfall and implications for recharge pathways in the Chalk aquifer, SE England. *Journal of Hydrology*, Vol. 330., 604-620.

MATHIAS, S.A., BUTLER, A.P., MCINTYRE, N. and WHEATER, H.S. 2005. The significance of flow in the matrix of the Chalk unsaturated zone. *Journal of Hydrology*, Vol. 310, 62-77.

PARKER, J M, CHILTON, P.J. and BRIDGE, L.R. 1991. Pore-water profiles in the Chalk unsaturated zone: results of 1990 redrilling. British Geological Survey Technical Report WD/91/13C

PRICE, M; ROBERTSON, A.S AND FOSTER, S.S.D., 1977. Chalk permeability - study of vertical variation using water injection tests and borehole logging. *Water Services*, Vol.81, 980, 603.

PRICE, M. LOW, R.G. and MCCANN, C. 2000. Mechanisms of water storage and flow in the unsaturated zone of the Chalk aquifer. *Journal of Hydrology*, Vol. 233, 54-71.

STUART, M.E. and KINNIBURGH, D.G. 2005. Nitrate trends in groundwater. British Geological Survey Internal Report, IR/05/137R.

STUART, M.E., CHILTON, P.J., KINNIBURGH, D.G. and COOPER, D.M. 2007. Screening for long-term trends in groundwater nitrate monitoring data. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 40, 361-376.