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Nitrogen and Carbon stocks and species in soils, sediments and groundwater of a shallow floodplain aquifer in the Trent Valley

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Nitrogen and Carbon stocks and species in soils, sediments and groundwater of a shallow floodplain aquifer in the Trent Valley

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Foreword

This report forms part of the National Capability Science Budget Research undertaken by the Sustainable Soils Program (2005-2009) at Shelford in the Trent Valley, East Midlands. The work at Shelford was comprised of a series of projects that included (i) the mapping of the near surface environment (soils, parent materials, geology) in 3D using the GSI3D modelling package, (ii) the development of a groundwater model for an extended area of the Trent Valley susceptible to flooding that utilised the 3D model and (iii) the current work that aimed to utilise the information from the 3D model and groundwater model to enhance knowledge of terrace and floodplain Nitrogen (N) and Carbon (C) dynamics. The work was carried out at Shelford, east of Nottingham and is typical of large parts of the Trent valley where Quaternary and Holocene sand and gravel terraces are underlain by Triassic mudstones. The terraces and modern day floodplain represent a shallow river aquifer extending ~1 km either side of the river. The land is used largely for arable agriculture so leaving the shallow river aquifer susceptible to the leaching of N, C and Phosphorus (P) from the topsoil. Therefore, this work reports the results of a survey to estimate the quantities and speciation of N and C throughout the soils and sediments of the aquifer and its groundwater. As the site is representative of large parts of the Trent Valley, the results can be used as an analogue to assess the potential of the levels of contamination (particularly of nitrate (NO_3^-) and Dissolved organic Nitrogen (DON) in the groundwater and its potential as a future source of potential contamination for surface waters as the aquifer interacts with the river Trent.

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Summary

This report largely concentrates on a geochemical survey of nitrogen and carbon stocks and their speciation in the different soil / sediment types and in the groundwater of a shallow river aquifer in the Trent Valley. The transect starts on a Triassic mudstone escarpment and follows the valley down onto a series of Pleistocene terraces and a modern floodplain, largely consisting of sand and gravel underlain by the Triassic mudstone, thus creating a shallow floodplain aquifer. In total 11 sites were sampled for soils / sediments down to depths ~2m. Total organic Nitrogen (N) and inorganic N were determined along with organic C concentrations. Results showed that organic Carbon (C) storage was between 5279 to 29624 g m^{-2} to depths of 120 cm. Total organic N storage was found to vary between 468 and 2199 g m^{-2} to a depth of 60cm. These figures are within the range expected for UK arable soils. Total inorganic N (NO_3-N + NH_4-N) in the alluvial sands and gravels to depths of 90 cm (water table is ~1m from the soil surface) varied from 2.00 to 5.01 g m^{-2}. In the escarpment soils, total inorganic N varied between 2.96 -7.32 g m^{-2}. Therefore the amount of inorganic N being stored in the top and sub soils equates to ~ 30 – 70 kg ha^{-1} N, roughly half of the yearly fertiliser N applications for typical arable crops.

The groundwater of the shallow aquifer was sampled 3 times over a period of a year from a series of 13 piezometers sited within the study area. Results showed that average nitrate concentrations in the groundwater were ~ 60 mg L^{-1} (Range: 9-200 mg L^{-1}). As a comparison this mean value would exceed the limits of 50 mg L^{-1} suggested within the EU Nitrates Directive. In some groundwater samples, concentrations of nitrate exceeded 150 mg L^{-1}. Dissolved Organic Nitrogen (DON) was present in the groundwaters but at concentrations generally < 2 mg L^{-1}. Thus nitrate is the major species of N that could potentially migrate from the aquifer and contaminate surface waters of the River Trent. A brief examination, using a steady-state particle tracking groundwater model constructed for the wider study area suggest that it could take >10 years for the aquifer to lose much of the nitrate. The well oxygenated aquifer waters (> 2mg L^{-1} oxygen) would suggest that denitrification potential was low. Laser fluorescence (LF) spectroscopy was used to assess the characteristics of the Dissolved Organic Matter (DOM) in the top soil and groundwater. Results suggest that the Dissolved Organic Carbon (DOC) in the groundwater is more humified and more fulvic-like in origin than that in the top soil, an indication that the carbon source in the groundwater was older and more decomposed thus not being such an effective potential source of C for denitrifying bacteria.

As the study area is representative of large parts of the Trent Valley in Nottinghamshire and Derbyshire, the results can be seen as an analogue for similar areas of the Trent Valley where intensive agriculture occurs on sand and gravel river aquifers.

1 Introduction

1.1 PROJECT BACKGROUND

Nitrogen is a major plant nutrient and its use as an agricultural fertiliser is essential in meeting the foods demands of 21st century society. However, its use as a fertiliser, the burning of fossil fuels and release through other anthropogenic activities has meant that many ecosystems have now become, or are on their way to becoming, saturated with reactive nitrogen (e.g. NO_3, NH_4, NO_x, DON) species (Emmett, 2007; Fujimaki et al., 2009). Saturation of ecosystems with reactive N can lead to (i) an early loss of plant species that are characteristic of low N environments (loss of biodiversity), (ii) suppression of microbial immobilisation of deposited NO_3^- due to increased NH_4^+ availability in the early stages of N saturation and (iii) the onset of NO_3^- leaching to surface and ground waters (Emmett, 2007). Additionally, the increased concentration of NO_3^- in ecosystems promotes denitrification which can lead to increases in the release of N_2O, a greenhouse gas (EA Science Report SC030155/SR2; Lind, 1983; Martin et al. 1999).

Intensively farmed agricultural ecosystems exist as a major potential store for reactive nitrogen because of past and current intensive use of inorganic fertilisers and organic manures. As a guideline to limit nitrate contamination of groundwater, the EU has set a limit of 11.3 mg L^{-1} N or 50 mg l^{-1} NO_3^- for groundwater (EU Nitrates Directive, 91/676/EEC). This directive is supplemented by the Water Framework Directive (2000/60/EEC) which requires all groundwater to be of a 'good status' by 2015. There has been considerable research into understanding the agricultural nitrogen cycle with the aims of improved management of fertiliser N and cost savings. One such model is NEAP-N (Anthony et al. 1996) that predicts nitrate leaching in soils and is also the model used in delineating Nitrate Vulnerable Zones (NVZ's) throughout England and Wales (DEFRA, 2008). It forms part of the ADAS MAGPIE modelling framework for the fate of agricultural fertilisers (Lord & Anthony, 2000). It is important to understand how effective these strategies have been and how large the current residual pools of reactive N are in the near surface environments of agricultural land. There is a large cost to nitrate entering groundwater (Beeson & Cook, 2004). An example of the cost of excessive nitrate entering groundwater is revealed when it is estimated that water companies in the UK currently spend £16 M yr^{-1} treating water for nitrates (Kay et al. 2009). It is therefore obvious that a need exists to understand the effects of past agricultural policy on where and how large residual reactive nitrogen stores are within the near surface environment (soils, parent materials and shallow groundwater) to enable improved agricultural stewardship in the future.

Whilst nitrate is recognised as a source of eutrophication of surface waters, the role of Dissolved Organic N (DON) has been relatively ignored in budgets of N losses to ground and surface waters. For example, Siemens and Kaupenjohann (2002) found that DON contributed 10-21% of the total flux of leached N in fallow soils and 6-21% of the total flux in highly fertilised agricultural soils at depths of 90 cm. A review by van Kessel et al. (2009) of DON losses from agricultural systems found that minimum

losses of DON were in grassland (0.3 kg DON ha^{-1} yr^{-1}) and maximum losses of 127 kg DON ha^{-1} yr^{-1} were found in grassland following the application of urine. On average DON was found to account for 26 % of the total soluble N leached.

Agriculture in Britain has undergone many changes since 1945, mostly revolving around a period of rapid intensification driven largely by the use of inorganic fertilisers, such as nitrate. In the 1990's environmental impacts of intensive agriculture were increasingly considered within agricultural practice. The intensification of agriculture has involved both arable and livestock husbandry and has been driven not only by the farmers but by politicians and economists (Addiscott, 2005). The Common Agricultural Policy (CAP), created in 1957 by the six founder members of the European Community has been one of the main drivers behind the 'nitrate problem', partly in response to the food shortages after World War II. Factors which helped increase fertiliser use after 1945 were (i) cheap fertiliser costs until 1966 (ii) the UK joining the EC in 1973 and the Common Agricultural Policy (CAP) therefore guaranteeing a price for produce and (iii) the fact that the CAP price for produce paid to farmers was sufficient to pay for the overuse of N (Addiscott, 2005). Other factors also contributed to an increase in nitrate circulation in the environment such as the ploughing up of old grassland. Not only did this increase the amount of land under arable production, and therefore fertilised, but the mineralisation of organic matter led to the release of large amounts of nitrate (Addiscott, 2005). The ploughing of temporary grassland (leys) potentially releases 100-200 kg ha^{-1} of mineral nitrogen whilst ploughing permanent grassland could release up to 4 t ha^{-1} mineral N (Addiscott, 2005). The increasing use of fertilisers and changing landuse had consequences and many aquifers and surface waters suffered from contamination or eutrophication due to the use of N and P fertilisers. Environmental legislation, in particular to protect surface and ground waters led to initiatives such as the introduction of the Environment Agency's Nitrate Vulnerable Zones (NVZ) in 1996, and re-evaluated in 2002 and 2008 (DEFRA, 2008). The designation of land under a NVZ means that is has been identified as a potential source of nitrate at concentrations possibly exceeding or being at risk of exceeding the 50 mg l^{-1} drinking water standard introduced by the EU. Under an NVZ, nitrogen inputs (inorganic fertiliser and animal waste) to land are monitored with the aim of (i) reducing the total organic N loading on the farm, (ii) extending the 'closed periods' when the spreading of farmyard manure (FYM) is not allowed, (iii) increasing the minimum storage requirements of FYM, (iv) greater planning of N use and (v) an increased depth of recording of N applications. Thus, after 15 years of NVZ designation as part of the guidelines of Good Agricultural Practice, their effectiveness and legacy is worth examining.

Baseline studies of nitrate concentrations in major UK aquifers have been undertaken. However, these have concentrated on the leaching of nitrate to the major aquifer rocks. For example, Limbrick (2003) examined the long term records of nitrate concentrations in a chalk aquifer in Dorset. Nitrate concentrations rose from 1 to 6 mg L^{-1} over a period of 100 years. Between 1928 and 1946, nitrate concentrations in the spring water had a mean value of 1.04 mg l^{-1}. By 1970 the concentration had risen to nearly 4 mg L^{-1} and by 1999 concentrations of nitrate had reached 6 mg L^{-1}. There was also evidence that river nitrate levels in the Piddle and Frome were rising at the

same time because the aquifer was providing base flow. The increases in nitrate were considered to be a result of intensified fertiliser use and increased cattle numbers. In addition the BGS have published a series of baseline hydrochemistry reports of different aquifers (For example: BGS, 2002a; 2002b).

One type of aquifer where less data exists and which are particularly susceptible to nitrate contamination are the alluvial soils and sediments of sand and gravel terraces and floodplains. These sand and gravel sediments overlay impermeable rocks thus creating shallow floodplain aquifers alongside rivers. The leaching of fertiliser nitrate into alluvial soil and sediments has been studied extensively globally (Burkart & Stoner, 2002; Costa *et al.* 2002; Onsoy *et al.* 2005). Whilst many alluvial deposits represent some of the most fertile agricultural land in many countries they are also prone to nitrate leaching because they tend to drain rapidly. However, within the UK, there appears to be a paucity of recent information relating to nitrate levels in the groundwater of shallow sand and gravel floodplain aquifers of major rivers such as the Trent. Major considerations within such aquifers are the extent of (i) biogeochemical cycling of nutrients, (ii) element speciation, (iii) sorption and precipitation reactions, (iv) the heterogeneity of the sand and gravel deposits and (v) the direction of flow-paths within the aquifer and into river courses. In addition riparian zones represent important interfaces between water bodies and the catchments' soil where an array of interacting processes contribute to the biogeochemical cycling of major nutrients (C, N, P) (Burt *et al.* 1999; Casey *et al.* 2001; Cey *et al.* 1999; Groffman *et a*l. 1996; Martin *et al.* 1999; Schilling *et al.* 2009).

1.2   STUDY AIMS

This study examines the quantities and species of nitrogen and carbon stored in the soils and groundwater along a transect of a typical landscape in the Trent Valley in the East Midlands of the U.K; an escarpment of Triassic mudstones and sandstones underlies a series of alluvial sand and gravel deposits that make up a shallow river aquifer. The link between the C and N cycles has been well established and it is important to consider both together (Cresser *et al.* 2008). For example, the denitrification process requires environments to be low in O_2, have adequate available NO_3^- but also supplies of mineralizable organic C to fuel the denitrifying bacteria (Brye *et al.* 2001).

This study utilised data obtained from a high resolution GSI3D model of the near surface environment that was made of the study area as part of the BGS Sustainable Soils Program (2004-2009). The construction of a GSI3D geological model is based on a geoscientist's ability to best interpret the geological survey, borehole data and geophysical information that they have at their disposal in one single software environment (Kessler et al. 2008; Tye *et al. In press*). Once complete the GSI3D model can be used as a predictive tool and some of the attributes of the GSI3D software enable the geological model to be interrogated to produce predictive borehole logs and cross-sections of the geology at any point. These capabilities are used within the study to develop greater understanding of the structure of the near surface environment. The GSI3D geological model was also used within a

groundwater model constructed for the region of the study area in the Trent Valley using the groundwater modelling software ZOOM (Lei *et al*., 2010).

This aims of the study were as follows: (i) drilling boreholes to depths ~2m in the different soil parent materials that make up the study area and assessing the storage of Nitrogen and Carbon species, (ii) calculating the current storage of these species in the soils and parent materials and (iii) assessing the concentration, species and properties of nitrogen and carbon in the groundwater of the shallow groundwater aquifer that interacts with the River Trent and (iv) predicting the movement of nitrate within the aquifer using the particle tracking facility of the ZOOM groundwater model developed for this part of the Trent Valley.

2 Materials and Methods

2.1 STUDY SITE AND 3D GEOLOGICAL MODEL

The study area has been predominantly used for arable agriculture for the last 60 years. It is centred round the village of Shelford, lying ~ 4 km east of the city limits of Nottingham in the valley of the River Trent, the third largest river in England. The site was selected as part of a program to develop GSI3D geological modelling methodology of soils and the near surface environment at the British Geological Survey. It consists of recent Holocene alluvial deposits and Pleistocene river terraces formed ~24000 years BP (Howard *et al. In press*). These river terraces and alluvial deposits lie over a series of Triassic mudstones and sandstones to form a shallow floodplain aquifer.

The Shelford GSI3D model covers approximately half of the entire study area and has been extensively mapped using a variety of geological, soil and geophysical surveys (Tye *et al*. In Press; Palmer, 2007). Thus it can also act as a high resolution analogue for larger parts of the Trent Valley between Nottingham and Newark. Figure 1 shows a map of the geology of the extended study area whilst Figure 2 shows the completed 3D model of the geology. The site extends south-eastwards from the River Trent, crossing alluvium and river terrace deposits at heights of 18-20m Above Ordnance Datum (AOD), then rising up an escarpment of mudstone and sandstone members of Triassic age. The highest ground in the south-east of the site is capped by glacial till at more than 50m AOD. Full details of the geological units can be found in Howard *et al*. (In press). The methodology used to create 3D geological models is fully documented in Kessler *et al*. (2008) whilst information pertaining to the geophysical mapping surveys that were used in creating the high resolution 3D geological model can be found in Tye *et al*. (In press).

Figure 1: Map of the surface geology of the Shelford study area
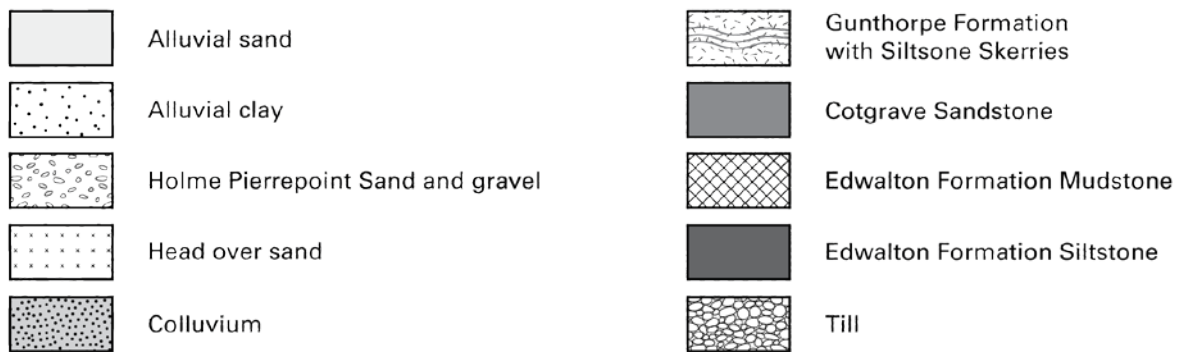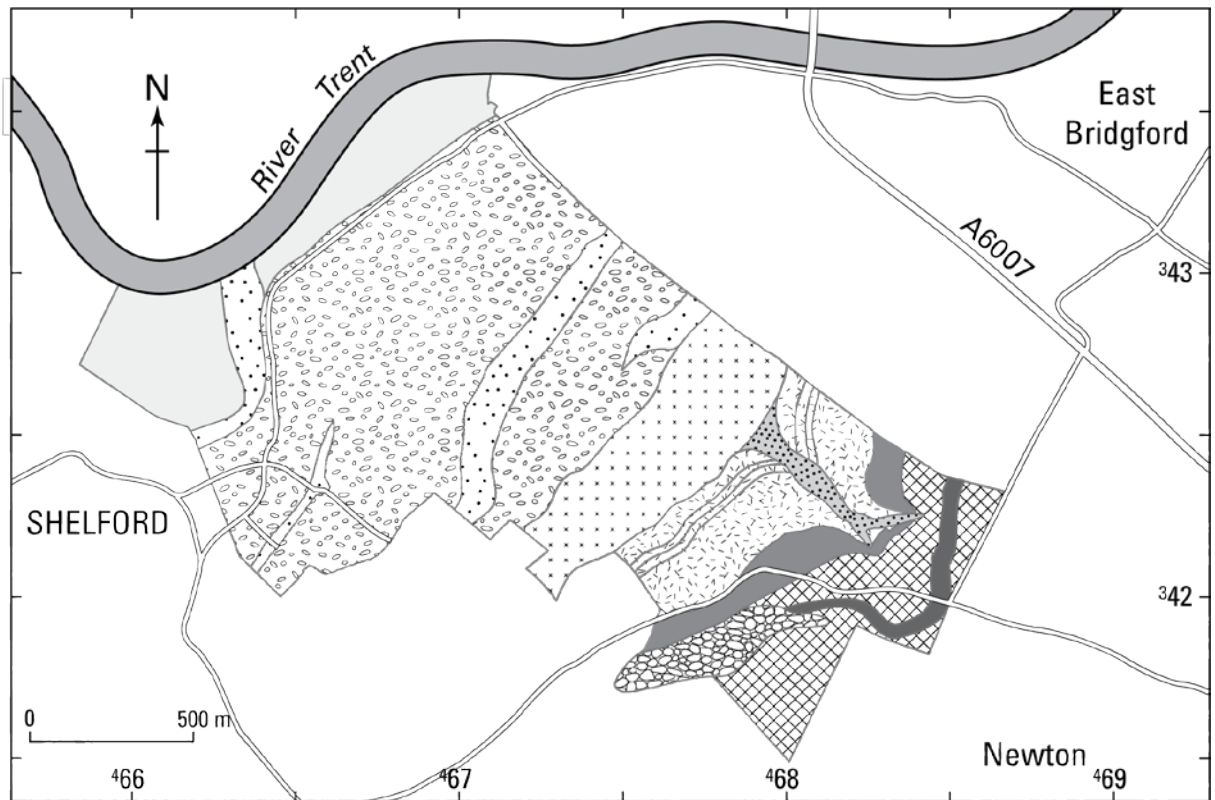
Figure 2: The GSI3D model of the near surface geology for the Shelford site
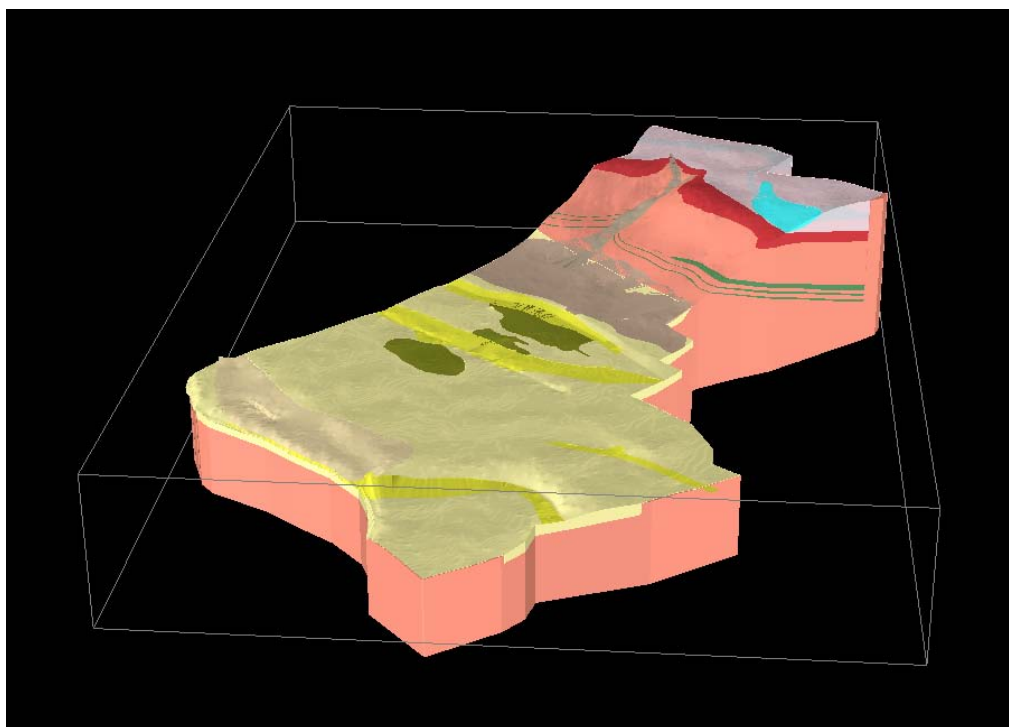
Figure 3 shows a cross section taken from the 3D geological model which demonstrates the typical characteristics of the shallow floodplain ground water aquifer. The aquifer consists of a modern floodplain as well as river terraces comprising largely of the Holme Pierrepoint sand and gravel (HPP S&G) (Figure 1). Within the HPP S&G are a series of alluvial clay and sand sediments, remnants from the changing course of the river Trent during the Pleistocene and Holocene (Tye *et al*. *In press*). Closer to the river Trent is the modern day floodplain, consisting of alluvium over sand and gravel deposits that are probably reworked from the HPP S&G. The aquifer overlies the impermeable Triassic Mercia Mudstone and has a thickness of up ~ 6m.

Figure 3: Geological cross section of the GSI3D model showing the sand and gravel deposits overlying the Gunthorpe formation Mercia Mudstone
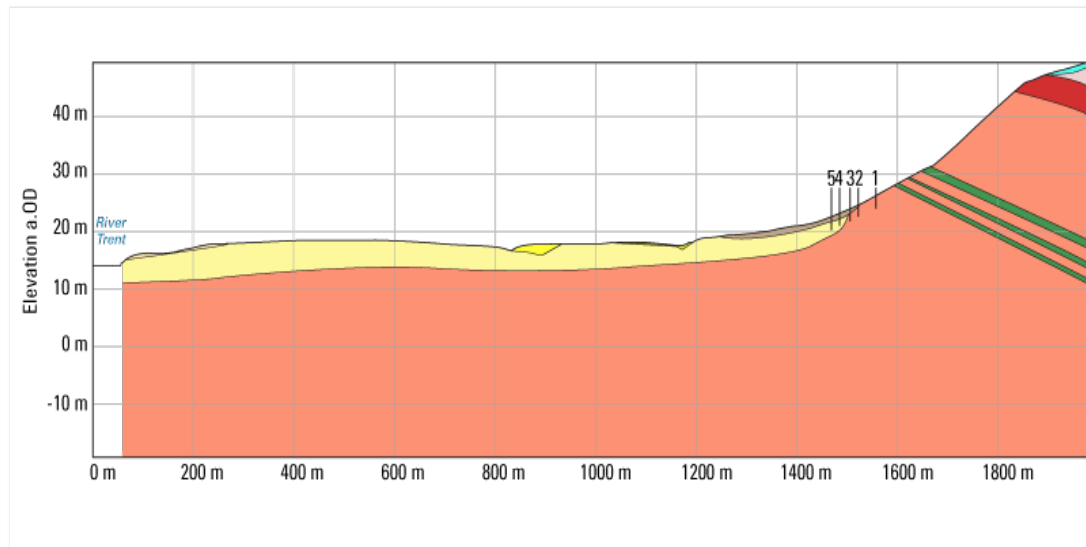
A soil survey was undertaken for the study area (Palmer, 2007) and the major description of soil types are shown on Figure 4. Full details regarding the soil survey can be found in (Palmer, 2007).

Figure 4: Map of the soil survey undertaken at Shelford. Full details can be found in Palmer (2007)
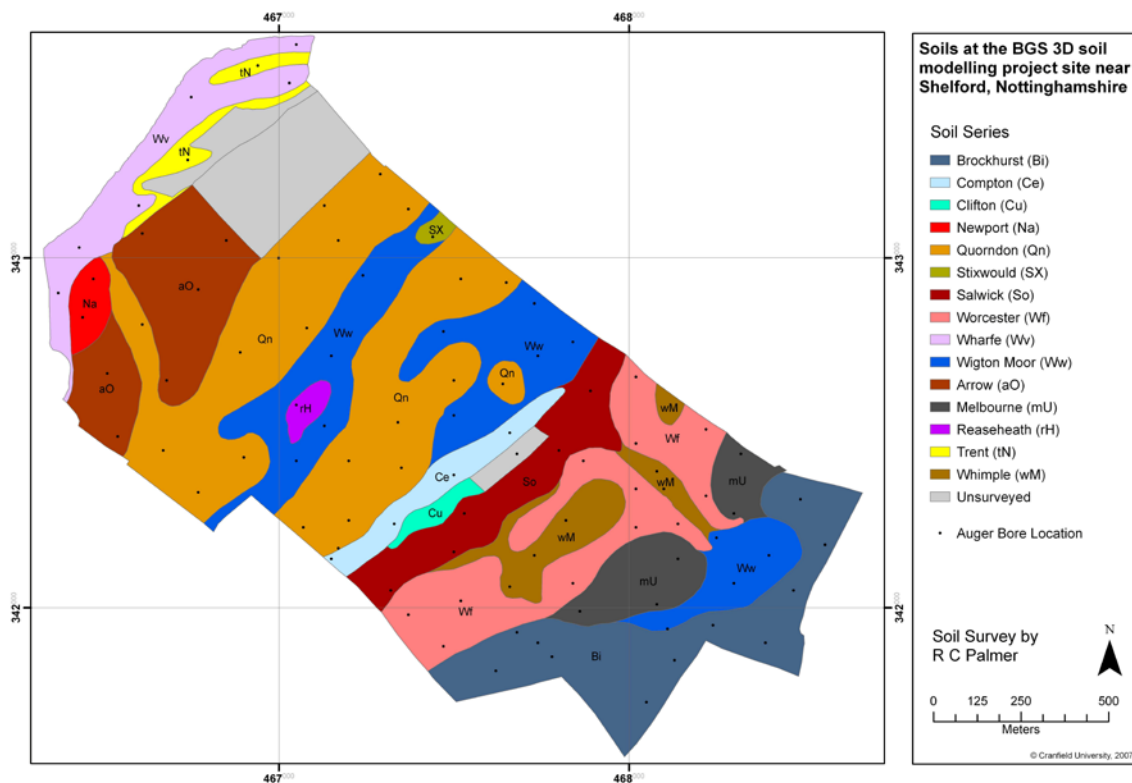
The annual precipitation (Figure 5) over the last thirty years is ~615 mm and the annual actual evaporation is ~517 mm leaving an effective precipitation of 100mm entering the soils and aquifer (Data based on Morecs square 117). After the mapping and construction of the GSI3D model, a series of 13 piezometers were installed in July 2005 to allow for the monitoring of the water table height. This continued until December 2008. Figure 6 shows the position of the piezometers. Ground water depth was monitored in the piezometers using a dipping meter on a weekly basis. Measurements from the piezometers were used to help parameterise a regional groundwater model between Nottingham and Newark, an area prone to flooding (Weng *et al*. 2010). These boreholes were also used to monitor groundwater quality.

Figure 5: The (i) annual precipitation (mm), (ii) Actual evaporation (mm) and (iii) annual effective precipitation at the Shelford site. Data from MORECS square 117 shows the (i) annual precipitation, (ii) Actual evaporation and (iii) annual effective precipitation.

(iii)
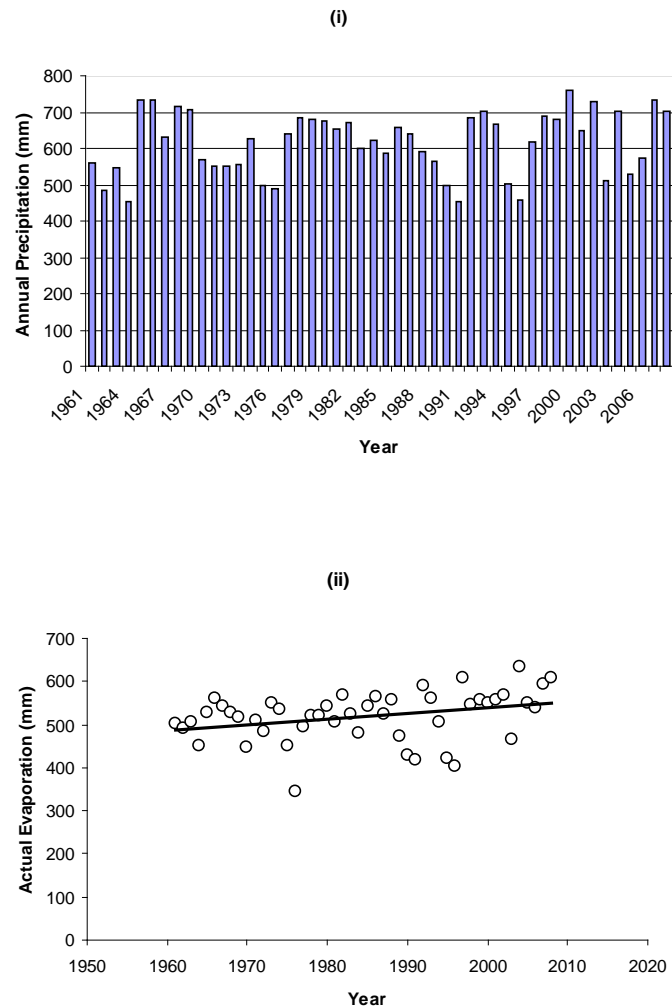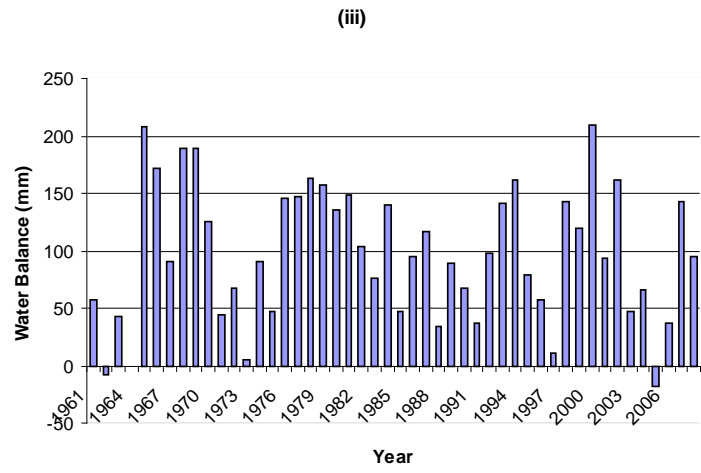
Figure 6: Position of the 13 piezometers established to monitor groundwater quality and level. The shaded area represents the extent of the GSI3D model.
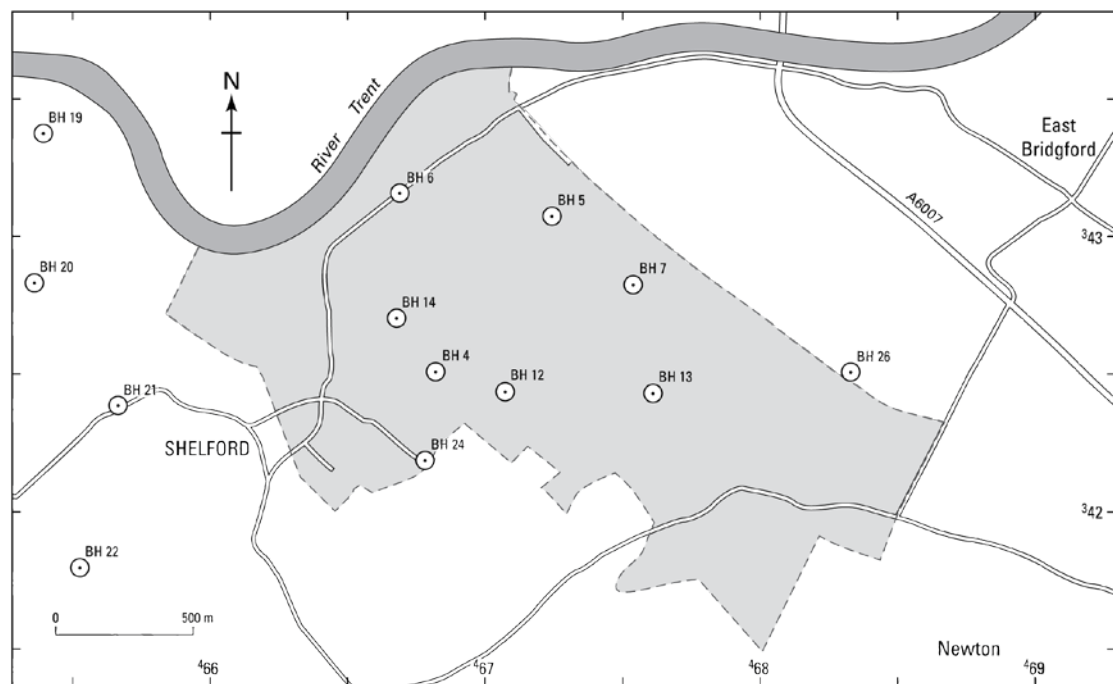
2.2 CROPS, AGRONOMICAL PRACTICE & FERTILISER APPLICATIONS

The regular crops grown at present across the study site include wheat, barley, sugar beet, potatoes and oilseed rape. Maximum N application rates for a range of crops are shown in Table 1 as defined by DEFRA (2007). Closed periods are when N is not allowed to be applied to soils in a nitrate vulnerable zone.

Table 1: Defra stated Maximum N limits for a range of crops commonly grown at the Shelford site

Crop	Maximum N application (kg ha^{-1} N)	Closed Period for application in NVZ
Winter Barley	180	1st September to 1st April
Winter Wheat	220	1st September to 1st April
Winter Oilseed Rape	250	1st September to 1st April
Sugar Beet	120	N/A
Potatoes	270	N/A
Field Beans	0	N/A

2.3 COLLECTION OF SOIL AND AQUIFER SEDIMENT SAMPLES

To measure the physical properties of the soil and sediments as well as the quantities and speciation of N and C contained therein, a series of boreholes were drilled through each of the soil / parent materials types of the study area (Table 2) in September 2007. Core material was collected by drilling with a 'Sonicbore' drilling rig where vibration is used to collect the core (Figure 7). At each sampling location, 4 cores were taken at the corners of a 20 x 20m square. The core diameter was 75mm and recovery was generally to a depth of ~ 2m. It was not possible to access sites 10 & 11 (Table 2) with the Sonic bore drilling rig. These two sites were sampled in May 2008, where a hand auger was used to obtain the samples. Figure 8 shows the locations of the sampling sites.

Figure 7: The Sonic-bore drilling rig at work at the Shelford site

Figure 8: Location where core samples were taken across the Shelford site.
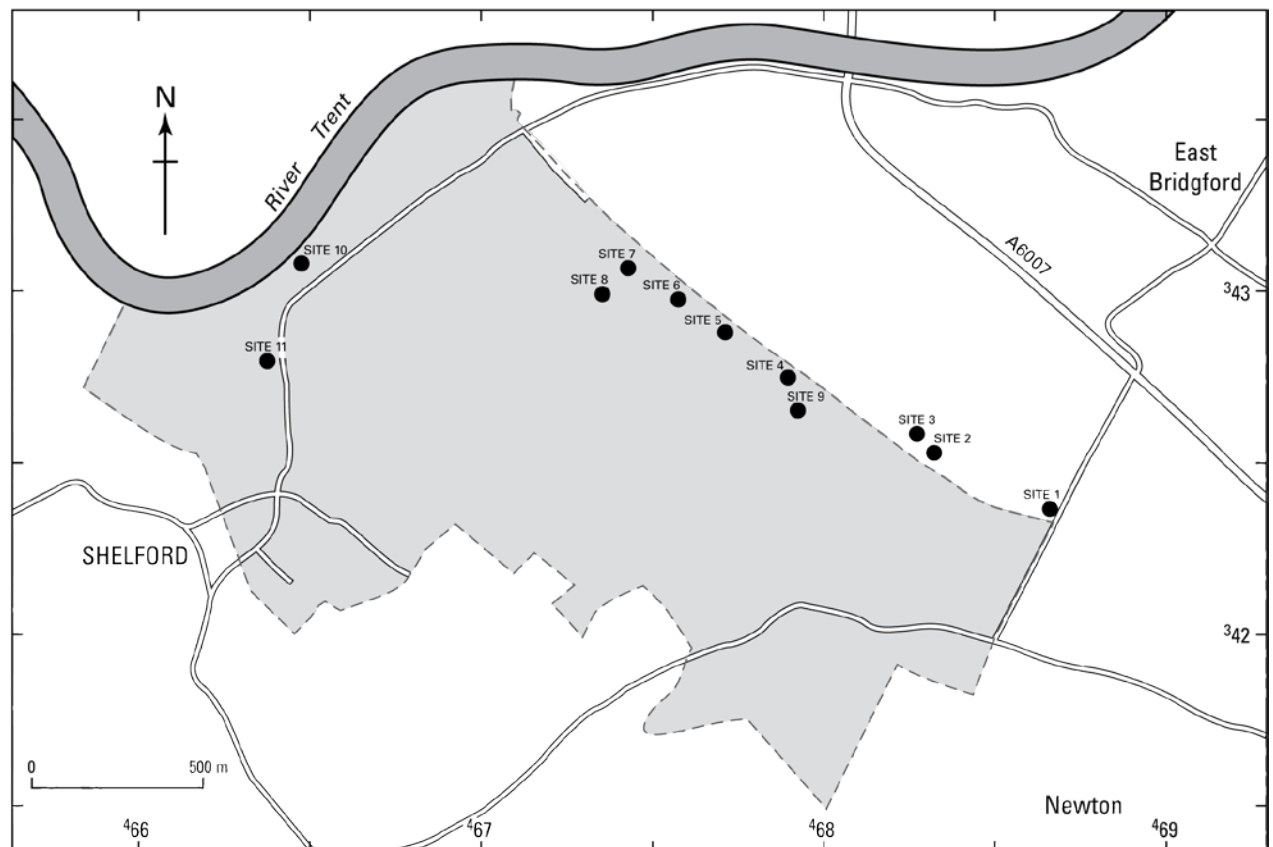
SITE 1 ● Edwalton Formation Mudstone

SITE 2 ● Cotgrave Sandstone

SITE 3 ● Gunthorpe Formation Sandstone

SITE 4 ● Head over sand

SITE 5 ● Alluvial clay, silt and sand

SITE 6 ● Holme Pierrepont Sand and Gravel

SITE 7 ● Alluvial clay, silt and sand

SITE 8 ● Alluvial clay, silt and sand

SITE 9 ● Head over sand

SITE 10 ● Alluvial sand and gravel

SITE 11 ● Alluvial sand and gravel

Table 2: Generalised descriptions of lithological units based on the 4 cores taken at each parent material site. Soil types based on the Soil Survey of England and Wales Classification and were identified by a soil survey of the site in 2006 (Palmer, 2007)

Site	Lithological unit	Soil Type	Domain Type	Description
1	Edwalton mudstone	Brockhurst (Surface water gley)	Non aquifer	Sandy loam Ap horizon 0-30cm overlying sandy clay (30-90cm) followed by mainly red clay with thin grey layers. Evidence of gleying from 30 cm.
2	Cotgrave sandstone member	Melbourne (Gleyic brown earth)	Minor aquifer	Silty clay loam Ap horizon to 30 cm. Sandy clay or clay (red/grey) from 30 - 180 cm. Evidence of gleying from 30 cm.
3	Gunthorpe mudstone	Worcester (Pelosol)	Non aquifer	Clay loam Ap horizon (0-30cm). Silty clay loam or clay from 30 – 210cm. Evidence of gleying from Ap horizon.
4	Head over sand	Salwick (Stagnogleyic argillic brown earth)	Groundwater / fluvial	Clay loam Ap horizon (0-30cm) overlying sandy clay (30-60cm), then sand down to 240cm. Sand underlain by mercia mudstone. Evidence of gleying 0-60cm.
5	Alluvial sand over mercia mudstone	Wigton Moor (Typical cambic gley soil)	Groundwater / fluvial	Sandy clay Ap horizon (0-30) over sand and gravel deposits to a depth ~2m. Then a red clay (Mercia mudstone) base is found. Evidence of gleying in more sandy gley 0-30cm.
6	Holme Pierpoint sand & gravels over Mercia Mudstone	Quorndon (Typical cambic gley soil)	Groundwater / fluvial	Sandy loam Ap horizon (0-30 cm) overlying sands and gravels. Beneath the sand and gravels is a mercia mudstone (red clay) base starting at approx 1.5 m. Evidence of gleying in occasional pockets of clay.
7	Alluvial sand & clay over Mercia Mudstone	Stixwould (Pelo-alluvial gley soil)	Groundwater / fluvial	Sandy loam Ap horizon to 0-30 cm, overlying sand and gravels to approx. 1.5m before the red Mercia Mudstone basement is reached.
8	Alluvial sand & clay over Mercia Mudstone	Wigton Moor (Typical cambic gley	Groundwater / fluvial	Sandy clay to 60 cm with Ap horizon 0-30cm overlying sand and gravels to approx 1.75m. Under this

			is the red mercia mudstone base. Signs of gleying 0-90cm.
9	Head over sand	Salwick (Stagnogleyic argillic brown earth)	Groundwater / fluvial	Clay loam Ap horizon (0-30cm) overlying sandy clay (30-60cm), then sand down to 240cm. Sand underlain by Mercia Mudstone.
10	Alluvial sand	Arrow	Groundwater/Fluvial	Deep, permeable, light loams, slight seasonal waterlogging by groundwater
11	Alluvial Sand	Arrow	Groundwater/Fluvial	Deep, permeable, light loams, slight seasonal waterlogging by groundwater

2.4 ESTIMATION OF BULK DENSITY

Accurate estimates of soil bulk density and stone content were required to enable the storage of C and N species in the different soils and parent material to be quantified. For the Edwalton mudstone, Cotgrave sandstone and Gunthorpe mudstone domains, it was possible to accurately determine soil bulk density at different core depths as it was cut into 30 cm sections. Stone (> 2mm) content and volume of each 30 cm fraction was measured. Samples were weighed moist and a moisture determination was carried out so that BD of the soil could be determined on a dry wt basis after subtraction of stone weight and volume as below:

$$Bulk\ density \left(g/cm^3\right) = \frac{Soil\ dry\ wt - Stone\ wt}{Volume\ of\ core\ section - volume\ of\ stones}$$

For the Holme Pierrepoint S&G and alluvial sand, silt & clays, the high gravel content prevented the estimation of the soil / sediment bulk density measurements using the 30 cm sections as described above. This was largely due to the incompleteness of the core in some sections. Therefore soil pits were dug to take soil bulk density samples for the 0-60 cm sections using bulk density tins. For deeper depths the cores were cut up and the dry weight of soil determined for each section. The bulk density of the soil (< 2 mm) was determined using a soil particle size and bulk density calculator based on a pedo-transfer function developed by Saxton (1986)

(http://www.pedosphere.com/resources/bulkdensity/worktable_us.cfm).

2.5   GROUNDWATER SAMPLING

Groundwater was sampled three times in July 08, October 08 and February 09 to gain an understanding of groundwater hydrochemistry and in particular N and C species. The Piezometers were purged fully 3 times with a groundwater pump before collection of the sample for analysis. Field measurements of O_2, pH temperature and mV were taken at the time of sampling using Hanna field instruments. Back in the laboratory samples were filtered using 0.45μm nylon membrane filters and the sample split for various analyses. Samples for alkalinity and pH measurements were filled to overflowing before capping the bottle. Samples for cation analysis were acidified to 1% HNO_3. Samples for anions were stored un-acidified. All bottles were Nalgene LDPE. Samples for Dissolved Organic Carbon (DOC), Dissolved Organic Nitrogen (DON) and Dissolved Organic Matter (DOM) analysis were stored in brown, Teflon capped glass bottles.

2.6   SOIL LABORATORY AND ANALYTICAL METHODS

After collection, the soil core samples were stored at $< 4°C$ until sub-sampling into 30 cm segments. Within 24 hours, each segment was extracted for inorganic N (NO_3^- and NH_4^+) using 2M KCl for 30 mins, before filtering through Whatman No.42 filters. Analysis of NO_3^- and NH_4^+ was undertaken by Eurofin Laboratories, Wolverhampton. The remainder of each borehole section was dried at $<40°C$ and the following analyses were undertaken on each sample. Total organic C and total N in the soil was determined using a Costech ECS4010 Elemental Analyser (EA) calibrated against an Acetanilide standard. Replicate analysis of well-mixed samples indicated a precision of $\pm$ <0.1 %. Sample weight for top soils were 1-2 mg whilst sub-soil samples were 10 mg. Organic C samples were analysed after leaching of the sample with 10 % HCl to remove inorganic C. Organic N was calculated as the difference between Total N – Inorganic N. Results are reported on a dry weight basis after correction for any remaining moisture. Samples for particle size analysis were oven dried. Particle size distribution was determined using a sedigraph after the removal of organic matter using H_2O_2.

2.7   GROUNDWATER ANALYSIS

Groundwater samples were analysed as follows. Water pH and alkalinity were analysed by titration using a Radiometer TIM 865 Titra-Lab analyser. Major cations were analysed using a Varian Vista ProAX ICP-AES and major anions (Cl^-, SO_4^{2-}, NO_3^-, NO_2^-) were analysed using a Dionex DX600 ion chromatograph. Ammonium was analysed by Scalar at the Eurofin Laboratiories in Wolverhampton. Analysis of DOC was carried out using a Shimadzu TOC analyser. Total N in groundwater was determined using a Thermalux TCOC/TN analyser. Organic N concentrations were estimated by subtracting inorganic N from the total N determination.

2.8 LASER FLOURESCSENCE ANALYSIS OF SOIL EXTRACTS AND GROUNDWATER

A full introduction to the work can be found in Section 3.6 and only the methods used are presented here.

2.8.1 Soil extracts

In October 2008, 4 samples were taken 0-15 cm from each of the different parent material / soil domains using a dutch auger. Nitrogen and Carbon species were extracted using 2M KCl (see Section 2.4). Jones & Willet (2007) suggested that he following analyses be undertaken on when examining nitrogen and DOC in soils so that a complete balance of N and C species can be obtained. These include inorganic N (NO_3^- and NH_4^+), DOC and DON by methods previously stated. To complete the dataset we also measured % C and % N concentrations of the <2 mm soil as well as soil particle size distribution to obtain clay contents as it is a contributing factor on how much carbon a soil can stabilize.

2.8.2 Groundwater

Samples of groundwater collected for DOC and DON analysis were analysed for DOM speciation by Laser Florescence at the October 08 and Feb 09 sampling dates.

2.8.3 Laser Flouresence methodology

Speciation of DOM in the soil extracts and groundwater was undertaken using a Varian Cary Eclipse Florescence spectrometer and the method used has been reported by Lapworth *et al*. (2008). Briefly, excitation wavelengths (Ex) examined are between 200 – 400nm with a 5nm bandwidth. Emission wavelengths were set between 250 and 500nm with 2nm bandwidth. The scan rate was 9600 nm/min and the detector voltage was 900 V. Analysis was undertaken using quartz cells with a 1 cm path length. The Raman peak of water at 348nm was used to check for instrument stability prior to analysis. Ultrapure water (ASTM type 1 reagent grade water, including a UV cracker) was used for the blank sample. Analysis of the Raman lines involved correcting for the blank and masking Raleigh-Tyndell lines for data processing purposes by multiplying the sample matrix by a matrix of '0's and '1's. Only florescence data above Ex250nm were used due to instability in the region below Ex250nm. Four components were identified from the florescence EEMs. These included two fulvic-like and two protein-like substances (tyrosine and tryptophan – like components). Tryptophan-like (TPH) intensities were reported as mean intensities from the region Ex270nm, Em330-EM350nm and fulvic-like (FA) intensities were reported as mean intensities from the region Ex330nm, 410-440nm. Total flourescence was determined by summing the intensity across the whole EEM after masking the Raman and Raleigh lines. Reported results for intensities are in relative units (RU). The ratio of the emission intensity at 450 and 500nm at an excitation wavelength of 370nm was used as a Florescence Index (FI) that can explain the source of the DOM (McKnight et al. 2001). The ratio of TPH to FA has also been used to identify different potential sources of DOM based on characteristic ratios found in different source terms (Baker,

2002). All the post processing of florescence data was carried out using the statistical package R (R Development Core Team, 2008; Lapworth and Kinniburgh, 2009).

3 Results & Discussion

3.1 PHYSICAL CHARACTERISTICS OF THE SAND AND GRAVEL AQUIFER

3.1.1 Core descriptions and Particle size distribution

One of the benefits of the GSI3D model software is that 'synthetic borehole logs' can be created at any point of the model based on the geological and sediment information data used to create the model. These are shown for each of the different parent materials from which the samples were collected (Figures 7 – 16), along with their particle size distribution with depth through the core material.

Figure 9: Synthetic borehole log obtained from the GSI3D model for the Edwalton member (Site 1). In addition Particle Size Distributions of soil and parent material with depth are given along with core photo.
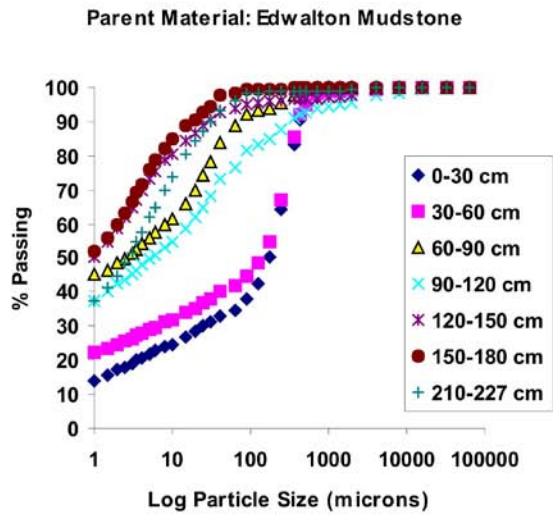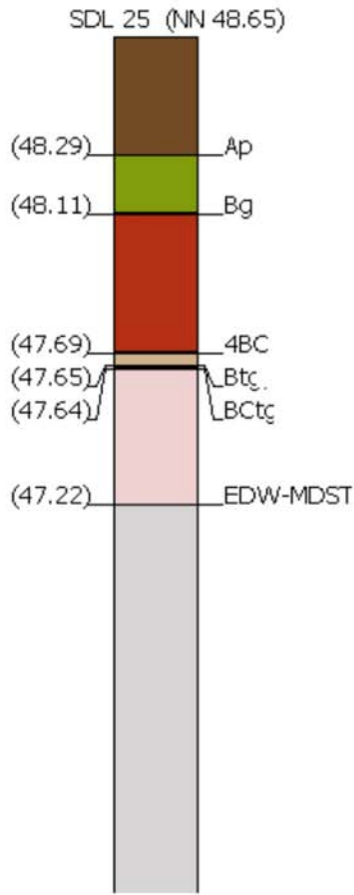
Figure 10: Synthetic borehole log obtained from the GSI3D model for the soil and parent material of the Cotgrave sandstone member (Site 2). In addition Particle Size Distributions of soil and parent material with depth is given along with core photo.
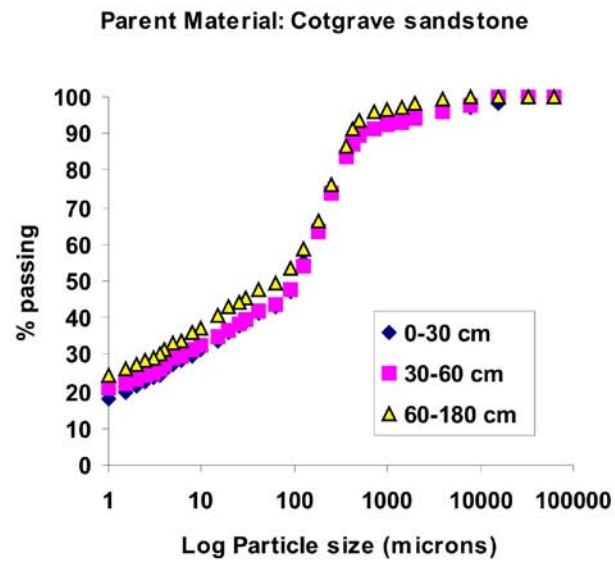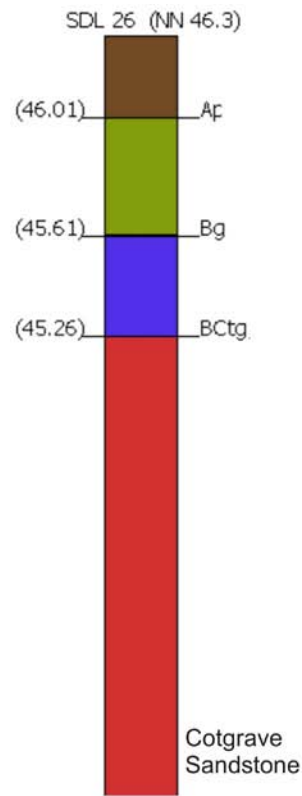
Figure 11 Synthetic borehole log obtained from the GSI3D model for the soils and parent material of the Gunthorpe mudstone member (Site 3). In addition Particle Size Distributions of soil and parent material with depth is given along with core photo.
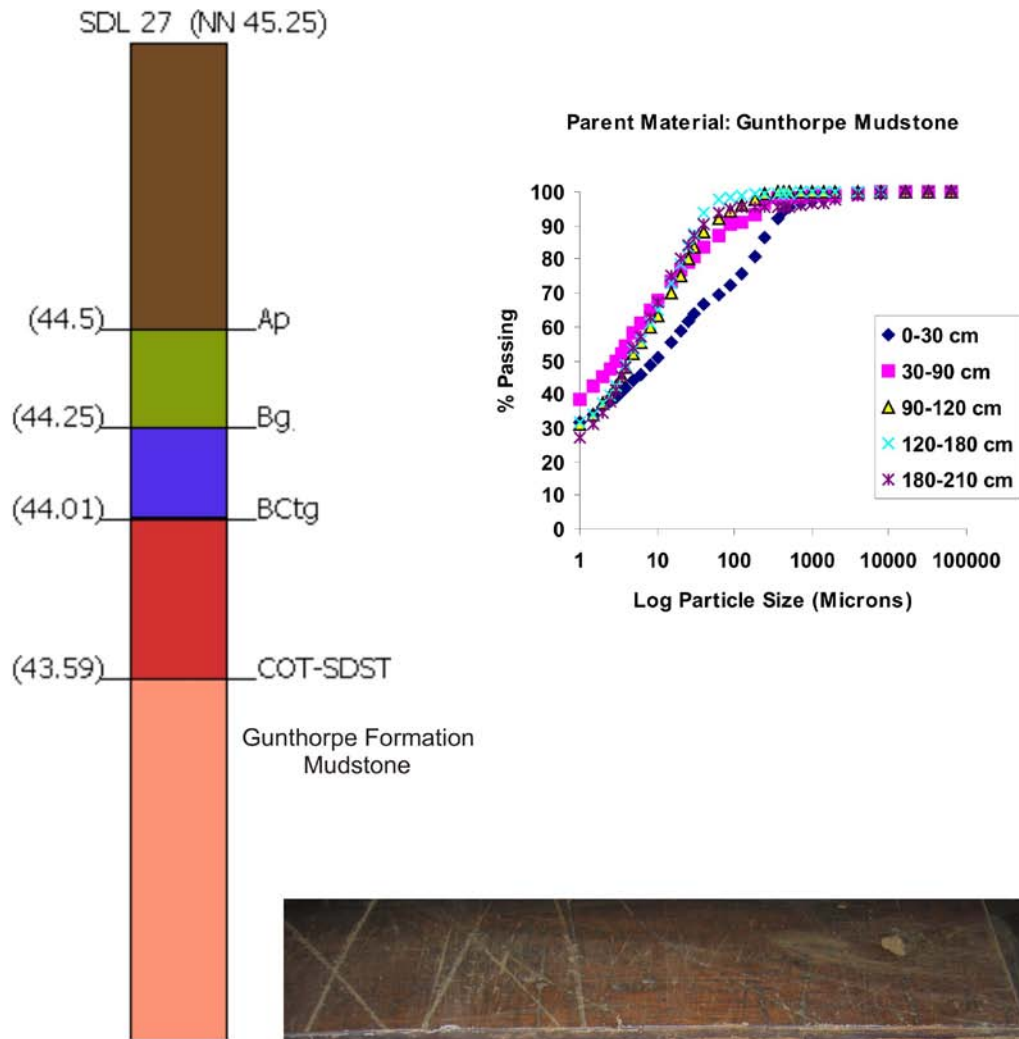
Figure 12: Synthetic borehole log obtained from the GSI3D model for soil and parent material of the Head over Sand member (Site 4). In addition Particle Size Distributions of soil and parent material with depth is given along with core photo.
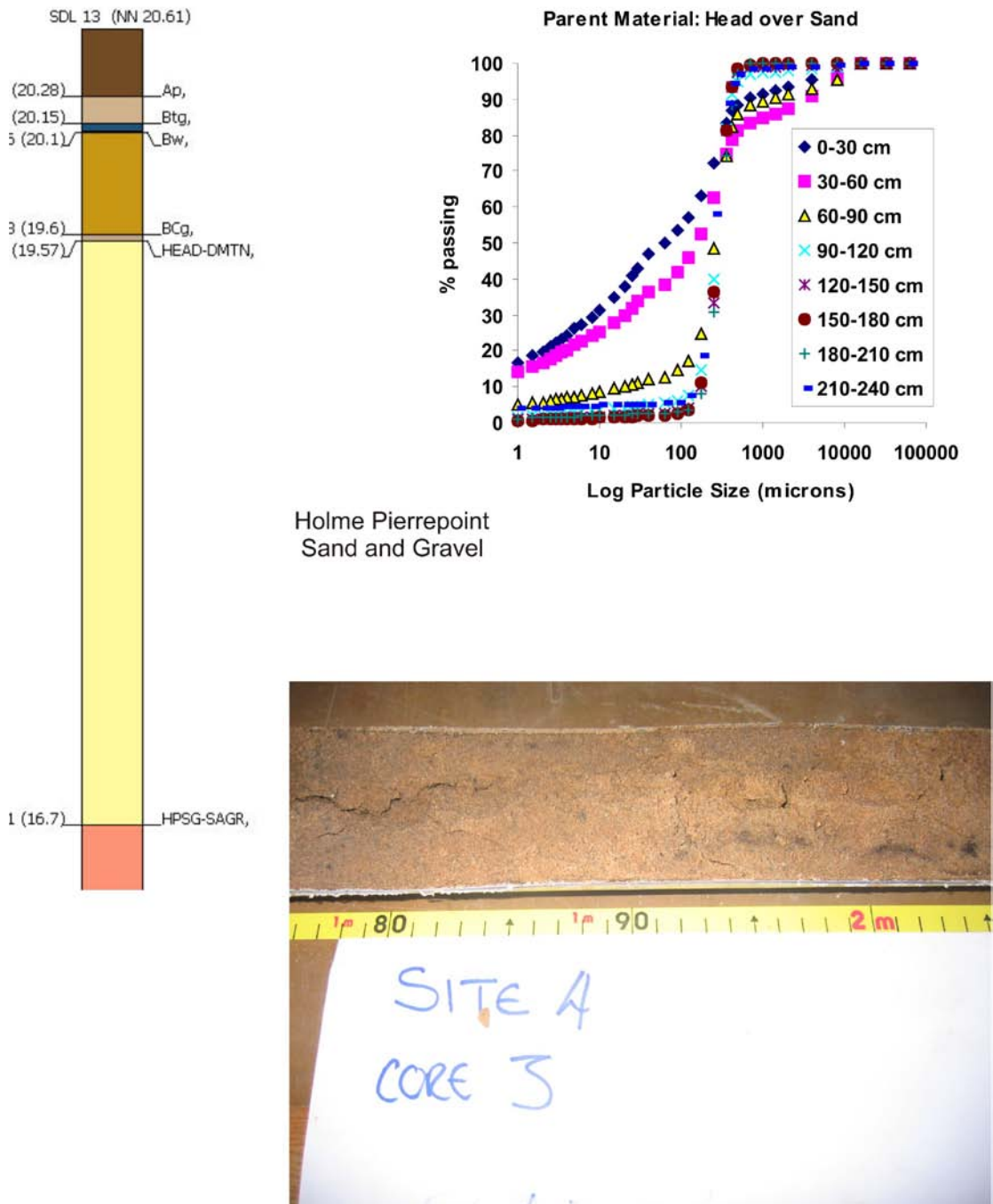
Figure 13: Synthetic borehole log obtained from the GSI3D model for the soil and parent material of the alluvial sand, silt and clay member (Site 5). In addition Particle Size Distributions of soil and parent material with depth is given along with core photo.
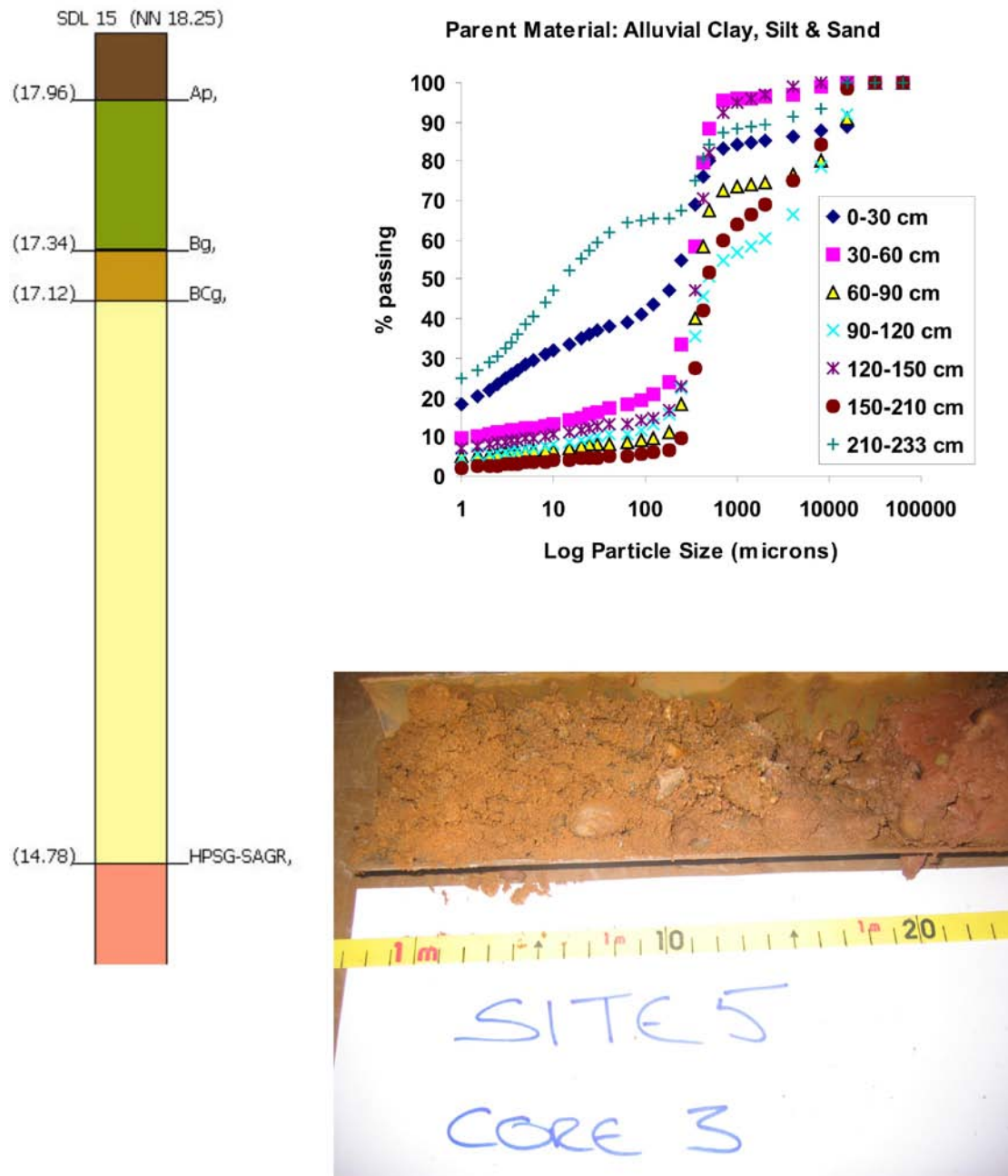
Figure 14: Synthetic borehole log obtained from the GSI3D model for the Holme Pierrepoint Sand and Gravel member (Site 6) where it is the parent material for the soil. In addition Particle Size Distributions of soil and parent material with depth is given along with core photos.
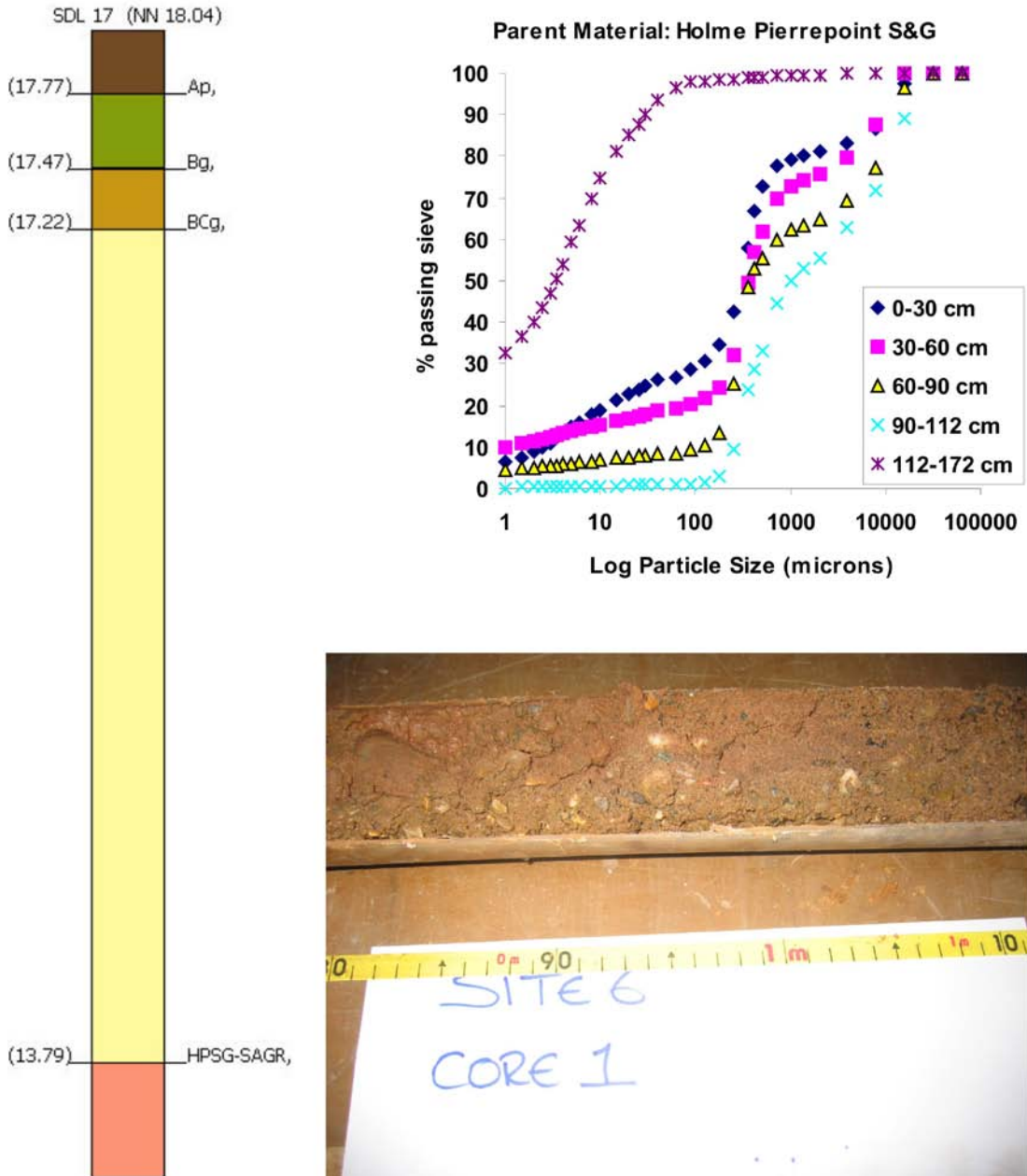
Figure 15: Synthetic borehole log obtained from the GSI3D model for the soil and parent material of the Alluvial sand, silt and clay member (Site 7). In addition Particle Size Distributions of soil and parent material with depth is given along with core photos.

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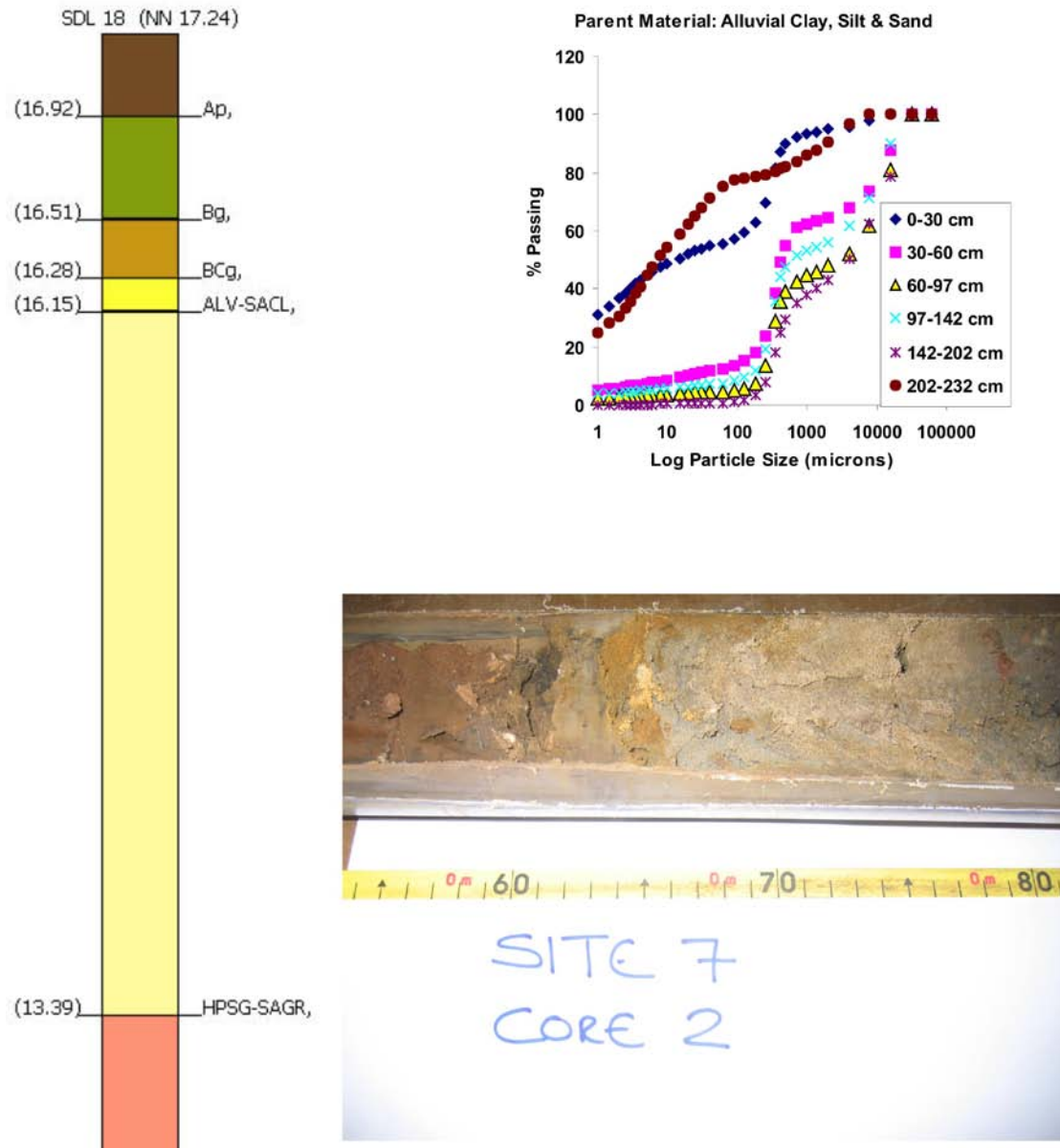
Figure 16: Synthetic borehole log obtained from the GSI3D model for the soils and parent material of the Alluvial sand, silt and clay member (Site 8). In addition Particle Size Distributions of soil and parent material with depth is given along with core photos.
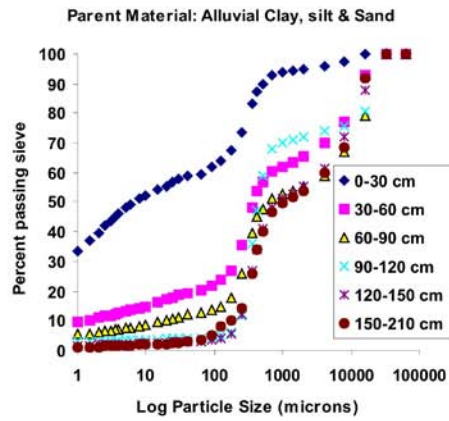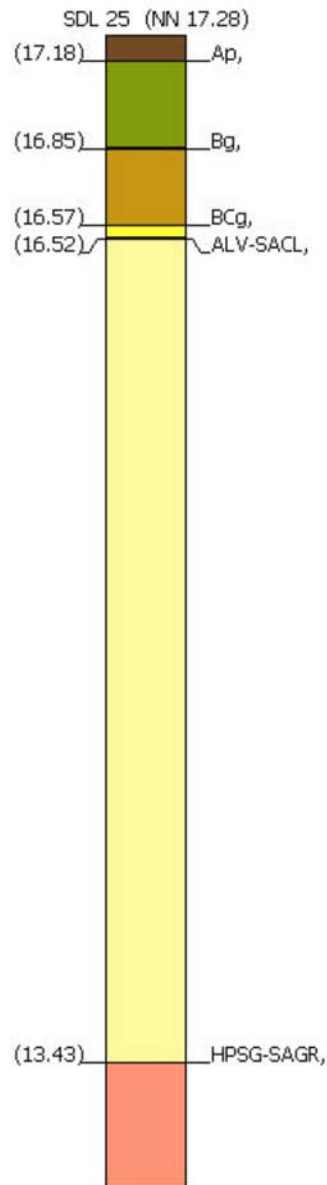
Figure 17: Synthetic borehole log obtained from the GSI3D model for soils and parent material of the Head over Sand member (Site 9). In addition Particle Size Distributions of soil and parent material with depth is given along with core photos.
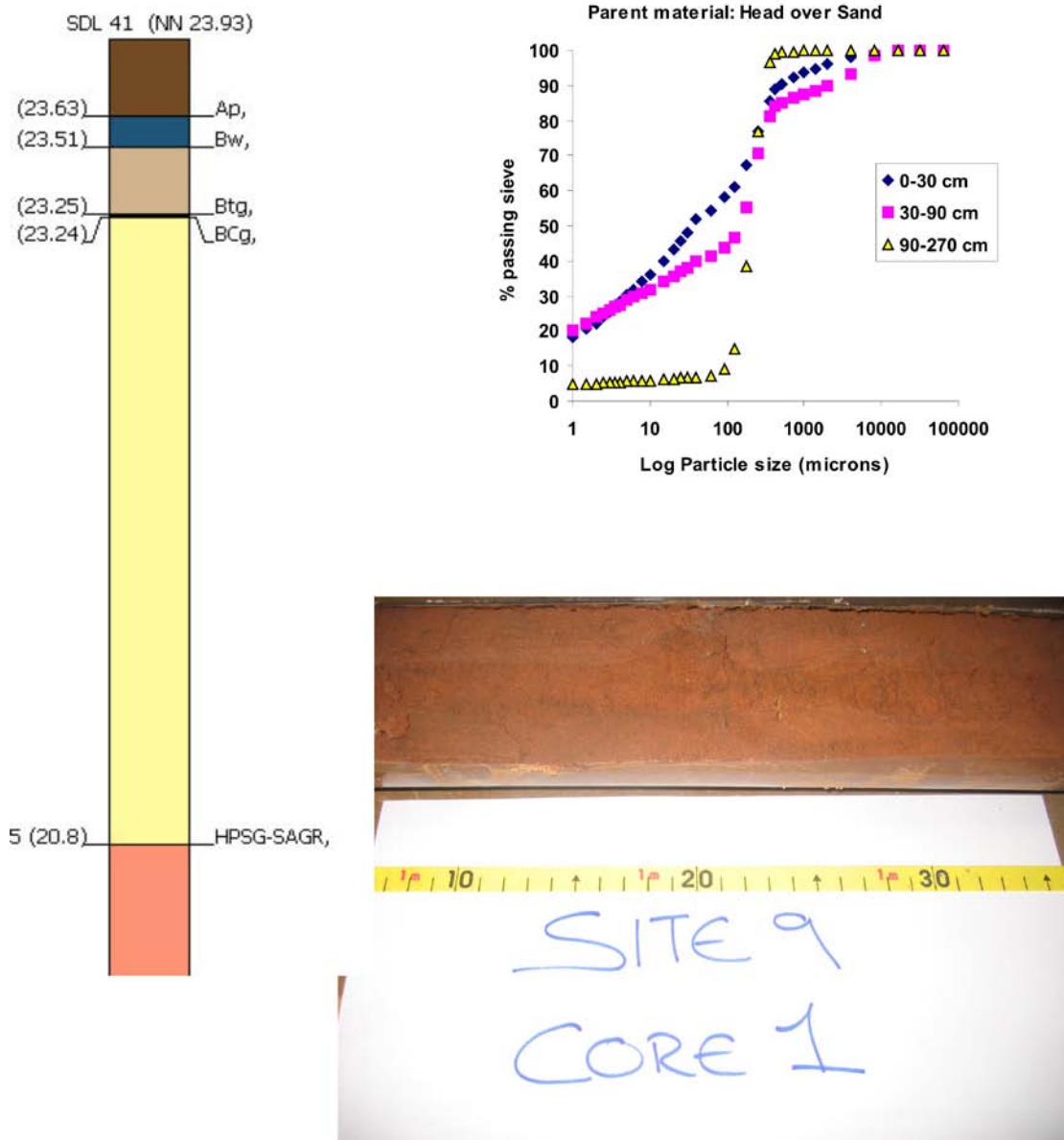
Figure 18: Synthetic borehole log obtained from the GSI3D model for the soils and parent material of the Alluvial sand and gravel member (Site 10). In addition Particle Size Distributions of soil and parent material with depth are given.
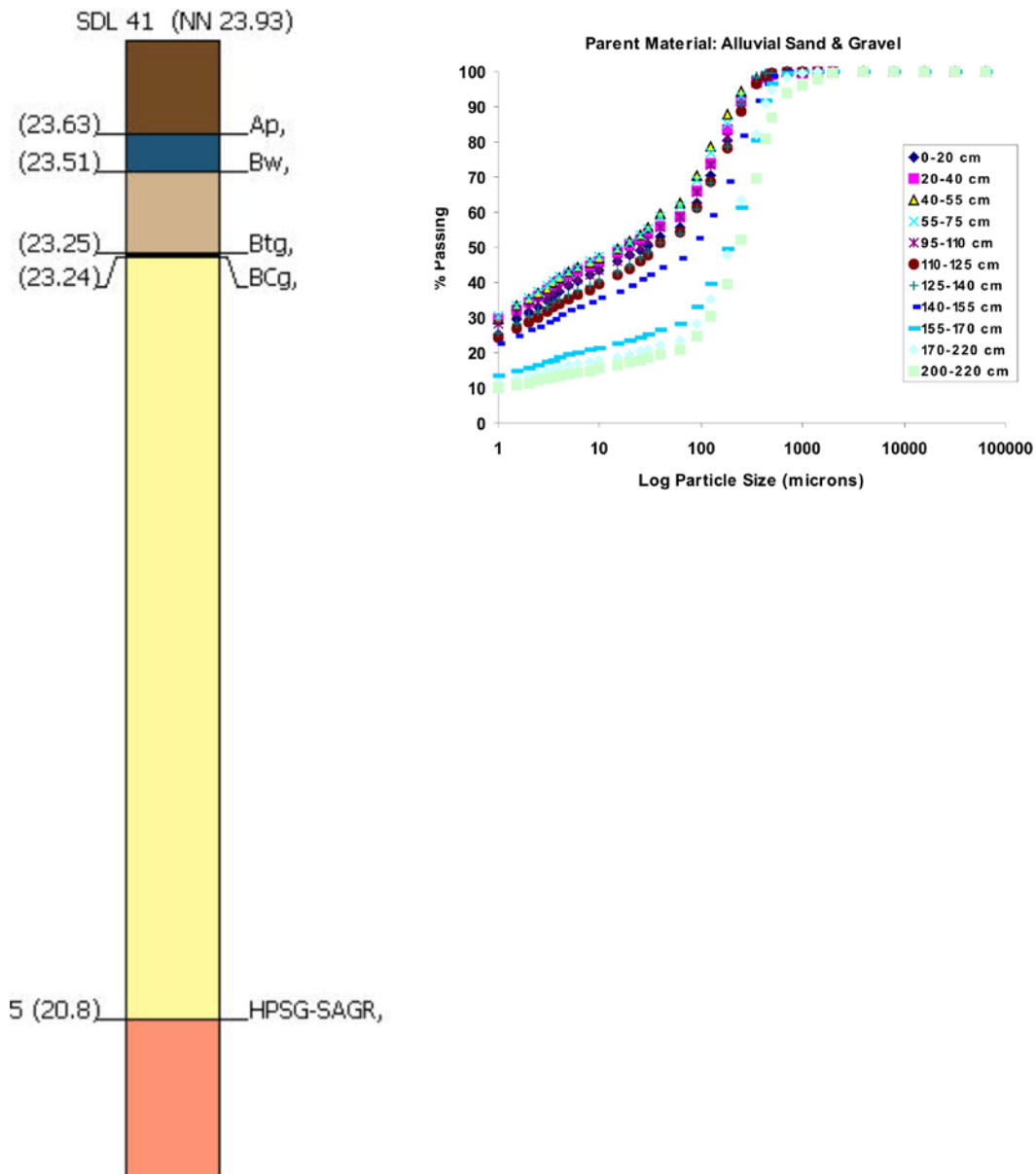
Figure 19: Synthetic borehole log obtained from the GSI3D model for the soils and parent material of the Alluvial sand and gravel member (Site 10). In addition Particle Size Distributions of soil and parent material with depth are given.
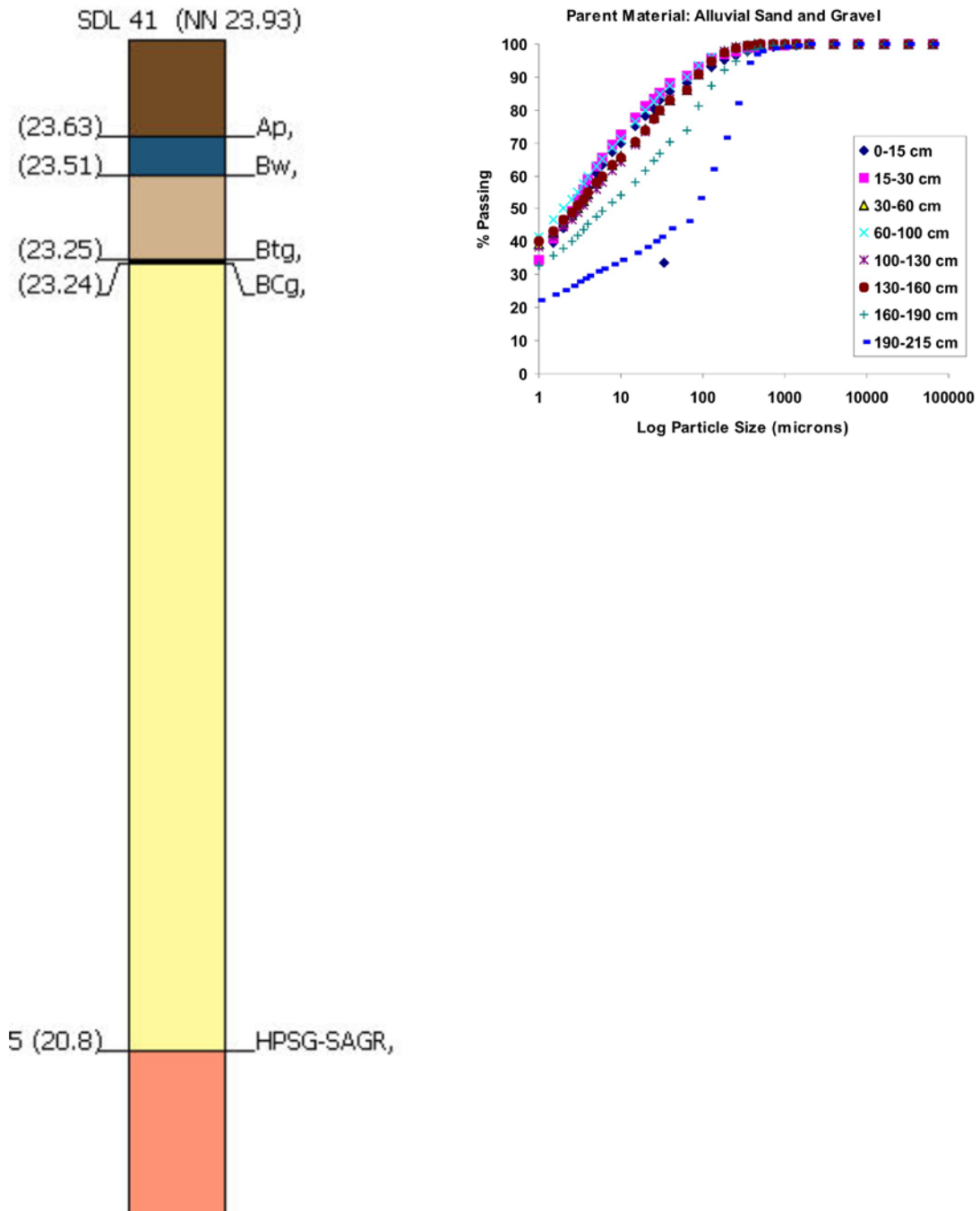
The particle size distribution of soils / sediments is one of the major controlling factors on water and solute movement within the soil and aquifer. Particle size distribution was found to reflect the origins of the parent material of the different domains sampled (Figure 8-17). Particle size through the Edwalton mudstone was more variable than the Gunthorpe mudstone, although both show a coarsening of particle size in the top 30cm compared to the subsoil. This coarsening of the top soil has been noted previously (Lobe *et al*. 2001; Jolivet *et al*. 2003), and has been linked to fine soil particles being lost during and after cultivation when the soils are bare. There is little variation in particle size through the soils formed on the narrow band of Cotgrave sandstone, although there appears to be a very slight coarsening of texture in the top 30cm. The Head over Sand deposits have a ~60 cm thick clay and silt layer above the sand. The 'head' was probably deposited through peri-glacial gelifluction processes during the late Quaternary and comprises material of the Gunthorpe Formation. Modern colluvial wash from the soils formed from the Gunthorpe Formation is probably also present. However, the head fraction contains less clay than the top soil formed over the Gunthorpe Formation, possibly reflecting some mixing with the sand.

Greater variability of particle size is found through the soils and sediments of the old river terraces comprising the HPS&G and the alluvial sand silts and clays (Figs 11-17). Results show the finer particle size of the underlying Gunthorpe Formation Mudstone at the bottom of each profile. There is a general fining of material towards the surface where clay and silt contents increase. This coarsening of sediments towards the surface may reflect the deposition environment of the sediments which is believed to be through aggradation in a glacial meltwater charged, braided river system (Tye *et al*., In press). Two boreholes are shown from the alluvial sands of the present floodplain. These show that the modern day flood plain sediments are considerably finer in texture than the ancient river terraces of the HPS&G and associated sediments. Both these cores show a show a similar pattern of coarsening with depth. This coarsening with depth is likely to be a result of modern day clay rich Holocene alluvial sediments being deposited on the reworked HPS&G. The coarser sediment at depths (>160cm) may constitute a primary flow path that connects the aquifer to the River Trent as the clay rich surface sediments will have a lower hydraulic conductivity.

3.1.2 Bulk density of soil and sediments

Measured and estimated bulk density values (g cm^{-3}) are shown in Table 3. These values are required to estimate (i) storage of C and N in the soils and sediments and (ii) to estimate hydraulic conductivity of the aquifer sediments. The table differentiates between those BD values measured and estimated values determined using the BD calculator (Section 2.4).

Table 3: Bulk density values for soil and sediment profiles to be used in calculations of N and C storage. Figures in shaded area were calculated using a soil bulk density pedotransfer function after Saxton (1986).

	Edwalton mudstone	Cotgrave sandstone	Gunthorpe mudstone	Head over sand	Alluvial clay, silt and sand	Holme Pierrepoint S & G	Alluvial sand	Alluvial sand	Head over sand	Modern Floodplain 1	Modern Floodplain 2
0-30cm	1.38	1.21	1.15	1.38	1.40	1.55	1.31	1.29	1.39	1.34	1.24
30-60cm	1.70	1.76	1.50	1.69	1.57	1.52	1.60	1.49	1.39	1.32	1.24
60-90cm	1.62	1.79	1.65	1.57	1.65	1.64	1.69	1.49	1.39	1.33	1.21
90-120cm	1.53	1.71	1.31	1.57	1.6	1.64	1.64	1.56	1.64	1.36	1.25
120-150cm	1.31	1.49	1.55	1.57	1.62	1.42	1.64	1.64	1.64	1.45	1.24
150-180cm	1.42	1.61	1.63	1.57	1.62	1.42	1.64	1.64	1.64	1.57	1.23
180-210cm	1.42	1.75	1.69	1.57	1.62		1.29	1.64	1.64	1.56	1.29
210-240cm				1.57	1.31				1.64	1.56	1.40

3.1.3 Hydraulic conductivity (k_s) of aquifer soils and sediments

Information from our drilled cores and data previously obtained from boreholes drilled by the Crown Estates (Brett, 2005) were used to calculate values of k_s across the area where the piezometers were situated. Data for particle size and bulk density were used in the Hydrous 2D model (Rassam *et al.* 2003) to predict the saturated conductivity (K_s) of soils and parent materials using the Rosetta database. For the sand and gravel sediments, where the gravel content was high, the Hazen equation (Head, 1982) was used to estimate K_s. In Fig 18, K_s is plotted with depth for boreholes 1-11. Whilst K_s values for the alluvial clay deposits within the HPP S&G are below 10 cm d^{-1}, values for sand and gravel exceed 5000 cm d^{-1}. Fig 19 shows the cumulative frequency that includes K_s values obtained from the Crown Estates boreholes using the Hazen equation. The median K_s value was 1500 cm d^{-1} and is close to the figure of 2000 cm d^{-1} used to parameterise the groundwater model for the sand and gravel aquifer (Weng *et al.* 2010).

Figure 20: Summary of potential saturated hydraulic conductivity (k_s) measurements determined using either the Hazen equation for sands and gravels and Hydrus 1 for soils for the different parent material domains sampled.
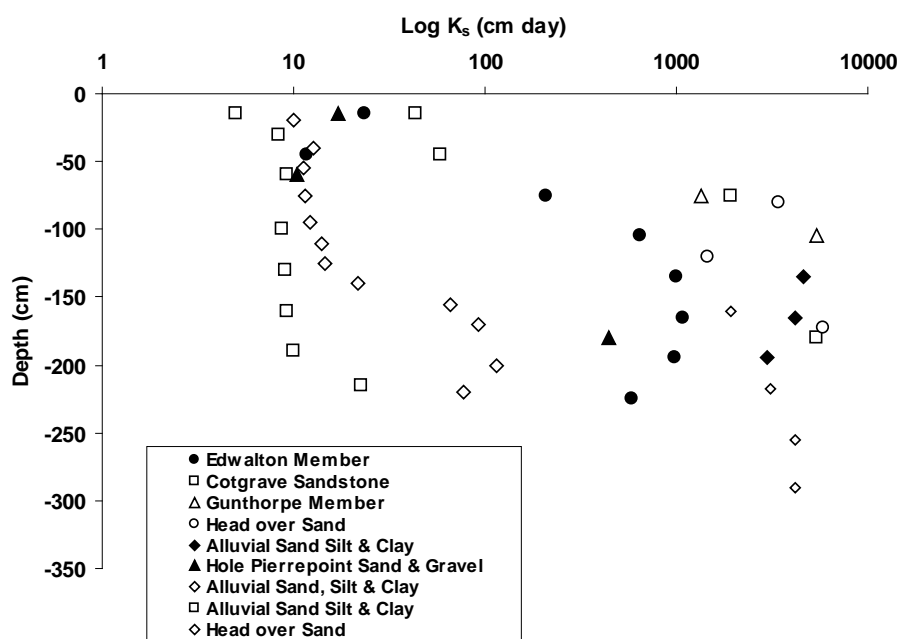
Figure 21: Cumulative frequency of estimated Log K_s values across the soils and sediments of the shallow floodplain aquifer.
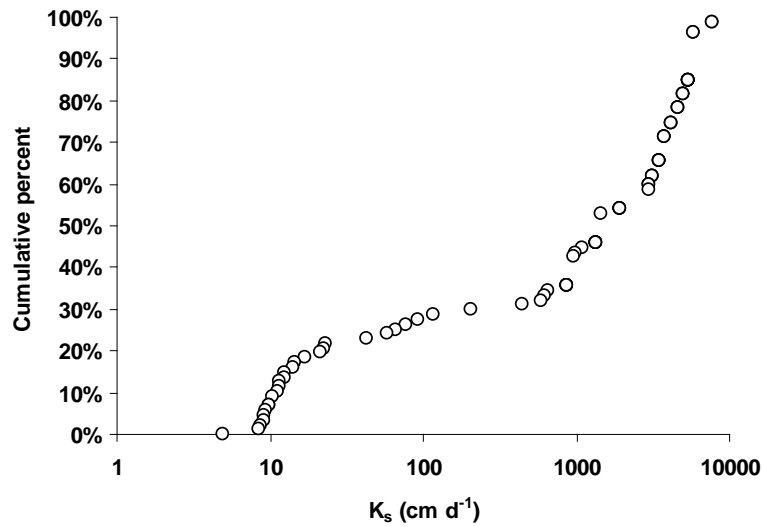
3.1.4 Groundwater levels across the aquifer at Shelford

Groundwater levels (GWL) were determined by dipping each of the 14 piezometers on a weekly basis. Figure 20 shows the GWL at several of the boreholes over nearly 2 years. Generally groundwater levels were approximately 1 to 2.5m below the surface of the soil. Variation within the dataset is likely a function of the aquifer sediment type and the time it takes to respond to precipitation events and river stage.

Figure 22: Variation of groundwater levels along two transects of boreholes. In (a) the transect runs along the eastern side of the study area from river Trent to the southern edge of the sands and gravel terraces, and in (b) a similar transect runs along the western extent of the study area (see Figure 6 for borehole positions). Data was collected between April 07 and Dec 08.

(a)
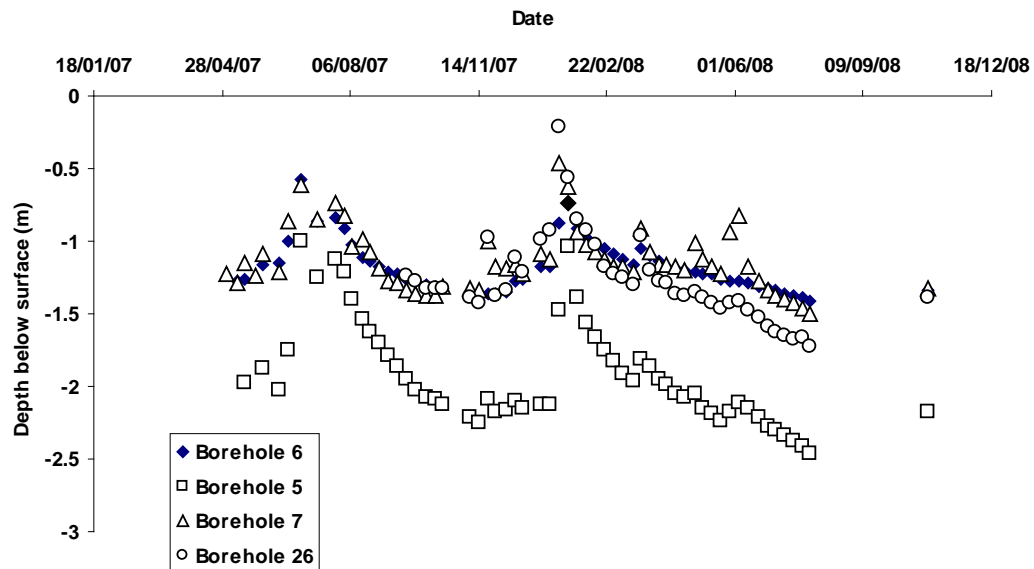
(b)
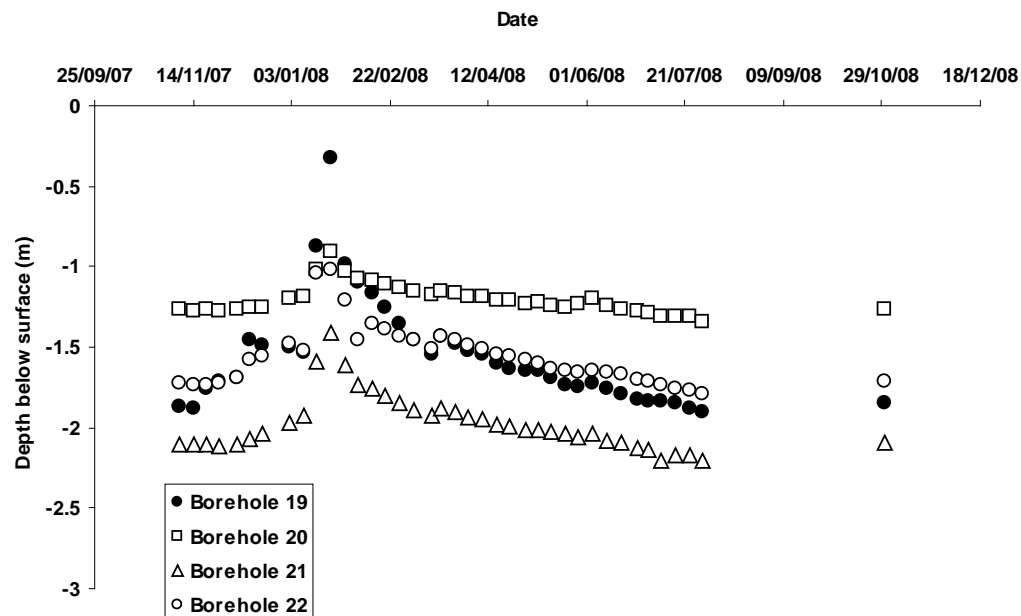
3.2   CARBON AND NITROGEN STOCKS IN SOILS AND SEDIMENTS

3.2.1   Organic C and N distributions with depth in the soil and parent materials

Concentration profiles for organic C and N through the soils and sediments of the study area provide an indication of the long term storage and transport through the soil profile. The concentration of N and C within the soil and sediments are a function of land use, the physical properties of the soils/sediments as well as the depositional history of the parent material. Figures 23 and 24 show the concentration profiles of organic C and N in each of the borehole locations. Typically exponential decreases in organic C and N values are found with increasing depth as has been demonstrated by Schilling *et al*. (2009) in riparian soils. In cores taken from the Shelford site, concentrations of organic C are generally < 0.2 % at depths greater than 60cm with the exception of those samples on the modern floodplain (0.67 – 1.3%). Concentrations of organic N range from 0.04 – 0.35% in the top 30 cm whilst at greater depths concentrations are generally <0.1 % on the old river terraces. On the modern day floodplain % N values at depth in the sediment are generally slightly greater and are ~0.1%.

Figure 23: Organic C (%) profiles on the different parent materials and aquifer sediments sampled.

Site 7: Alluvial clay & sand
Organic C (%)

Site 8: Alluvial sand & gravel
Organic C (%)

Site 9: Head over sand
Organic C (%)

Site 10: Alluvial Sand
Organic C (%)

Site 11: Alluvial Sand
Organic C (%)
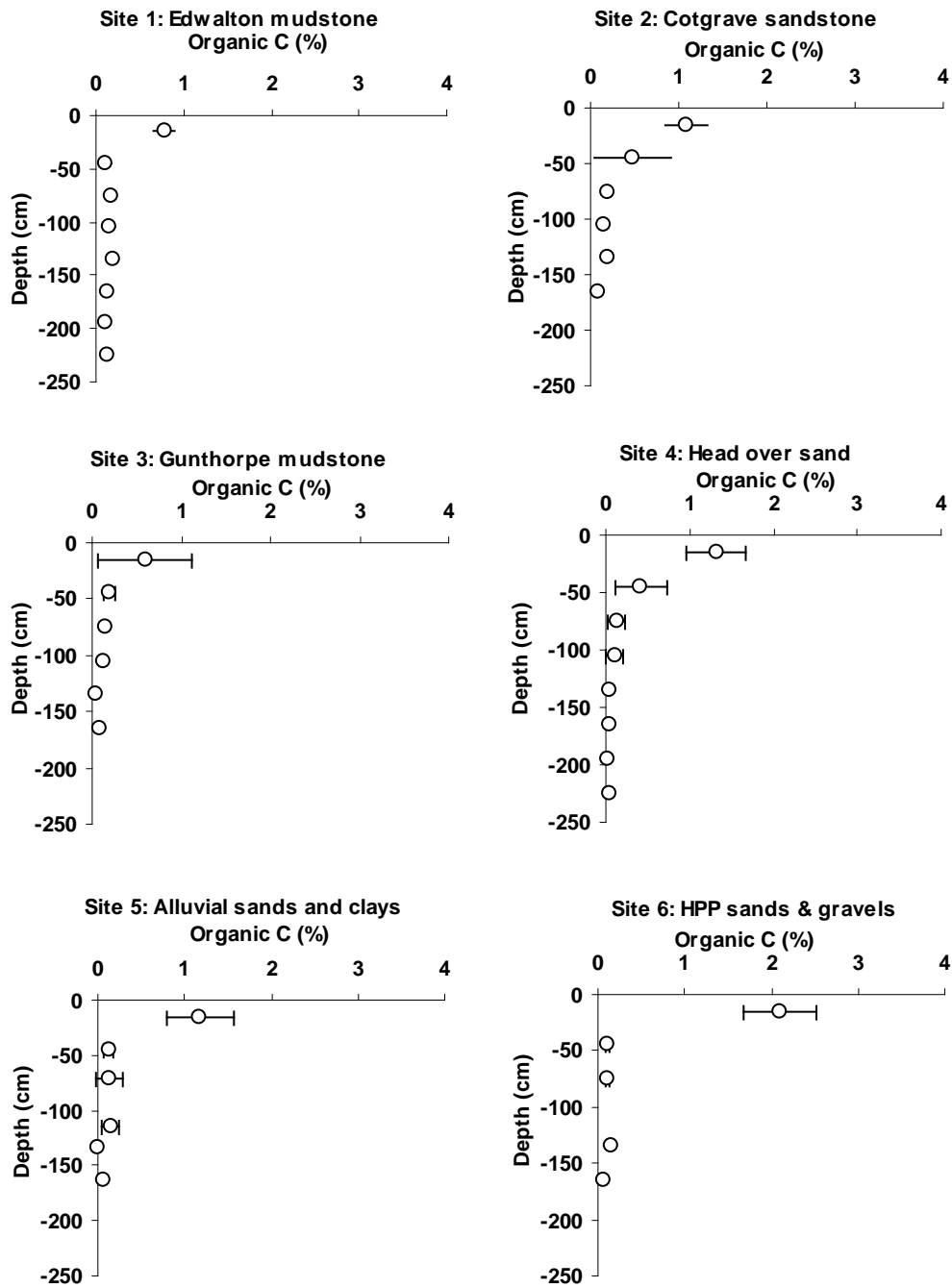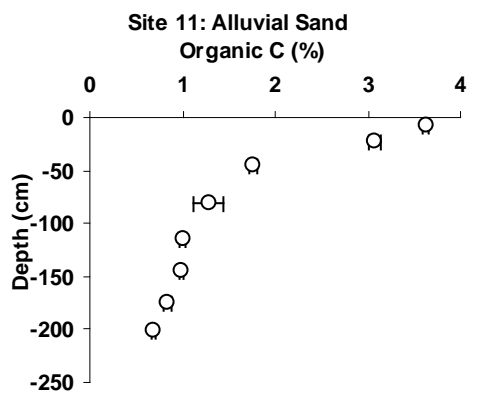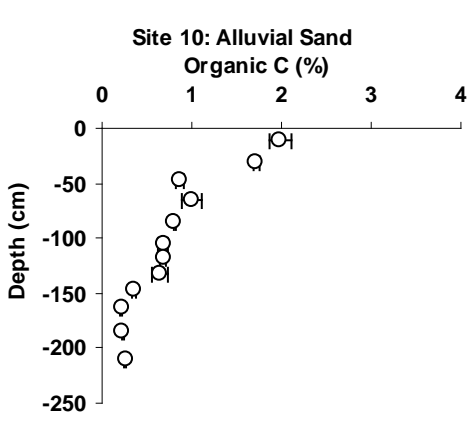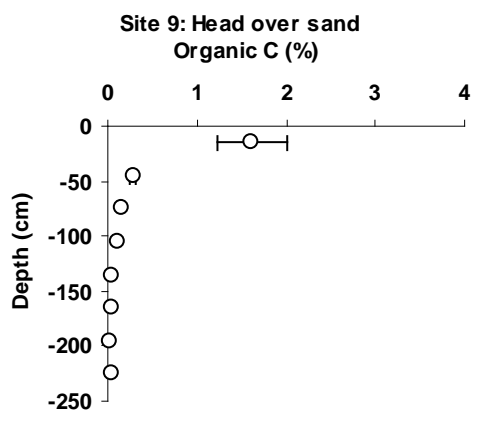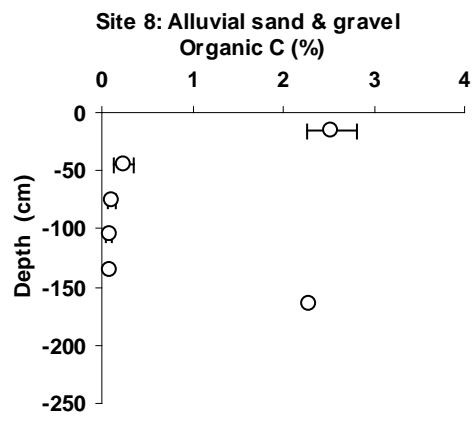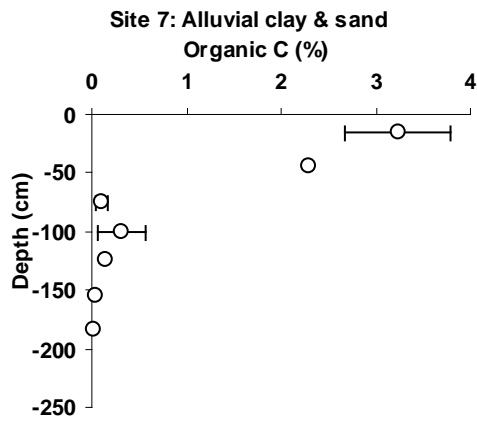
Figure 24: Organic N (%) profiles on the different parent materials and aquifer sediments sampled

Site 1: Edwalton mudstone
Total N (%)

Site 2: Cotgrave sandstone
Total N (%)

Site 3: Gunthorpe mudstone
Total N (%)

Site 4: Head over sand
Total N (%)

Site 5: Alluvial sands and clays
Total N (%)

Site 6: Holme Pierpoint s & g
Total N (%)

Site 7: Alluvial clay & sand

Site 8: Alluvial sand & gravel

Site 9: Head over sand

Site 10: Alluvial Sand

Site 11: Alluvial Sand
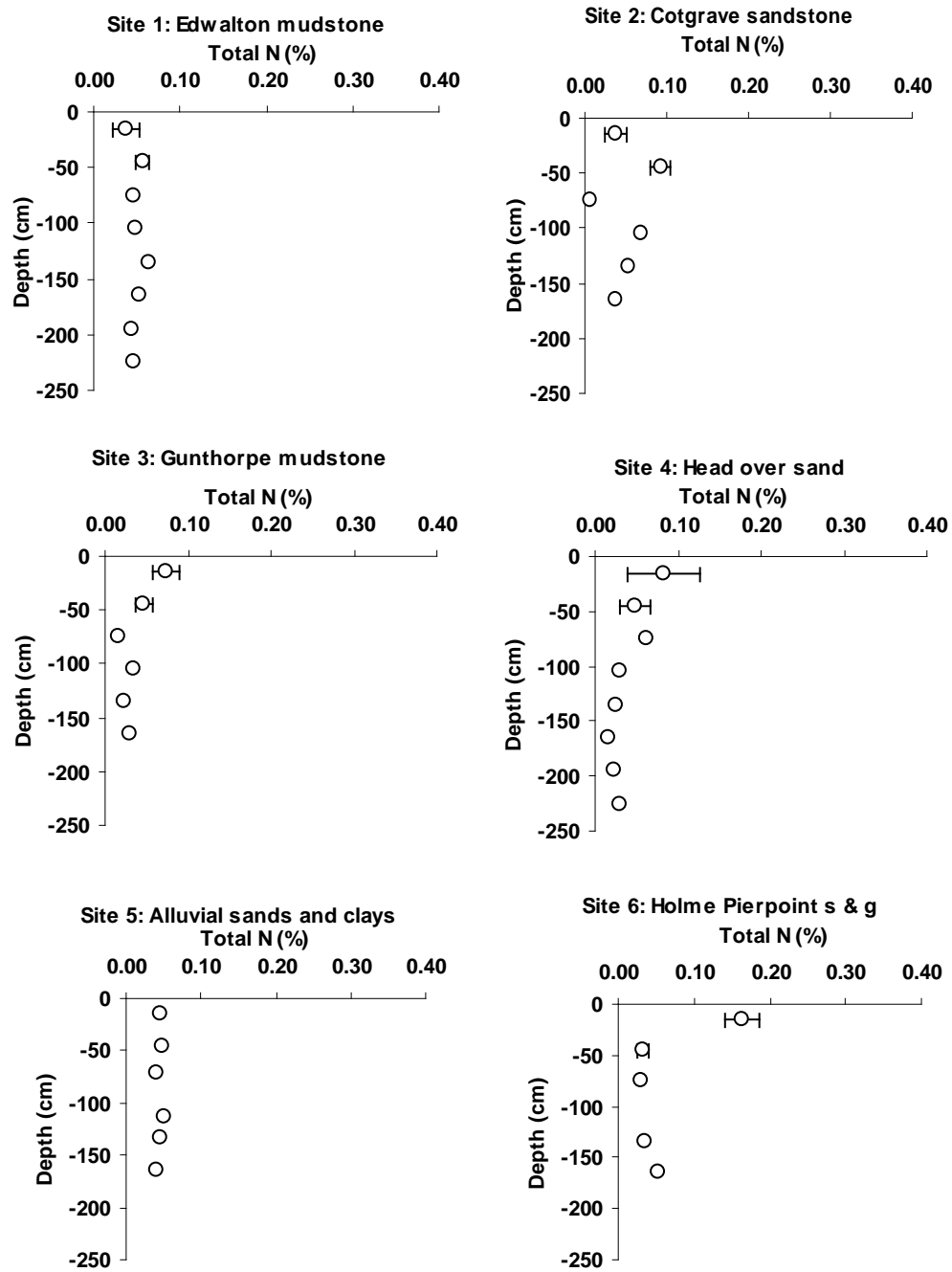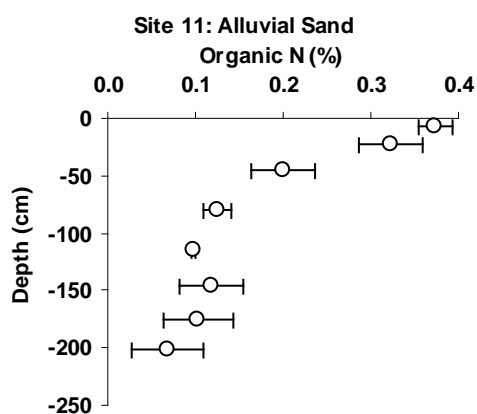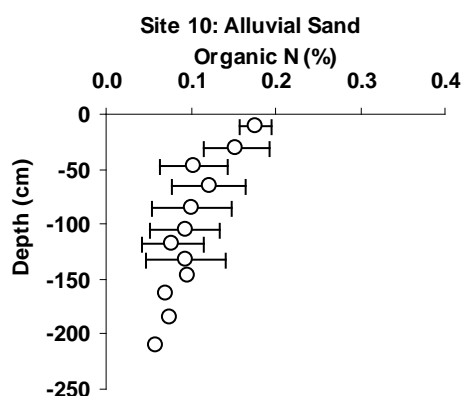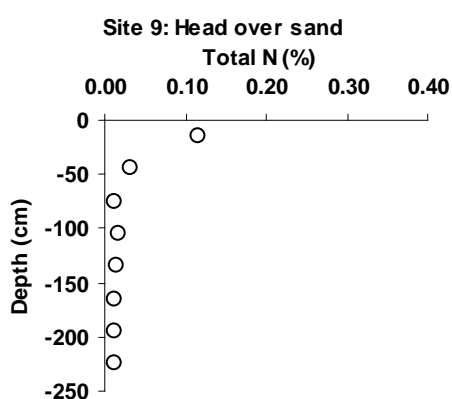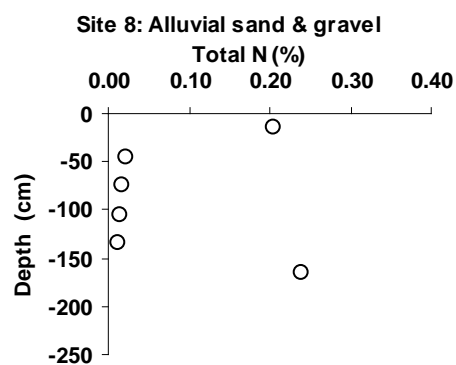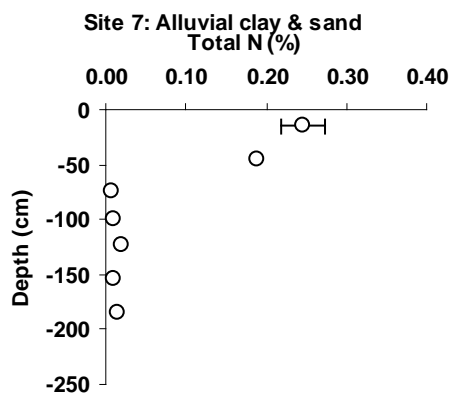
Tables 4 and 5 report the statistical analysis of how organic C & N concentrations change with depth. One way analysis of variance was followed by calculation of Least Significant Difference (LSD) to show where significant differences for depth intervals between the different soil parent materials (Table 4) and within sediment profiles (Table 5) occur. The Least Significance Difference (LSD) statistical test is used to test significant differences between samples using information from the output of the One Way Analysis tests. It is defined as

$$LSD =_t \sqrt{\left(\left[\frac{1}{n_L} + \frac{1}{n_S}\right] x (within - sample \, \mathrm{var} iance\right)}$$

Where

t = the value of t at P=0.05 for the within-sample degrees of freedom

n_L and n_S are the number of data values for the largest and smallest samples

The differences between the means of planned comparisons should now be compared with the LSD. If the differences are greater than the LSD then they are significantly different.

For organic carbon, statistical analysis was carried out for samples down to 120 cm depth as beyond this depth only a single core was analysed. For organic nitrogen statistical analysis was undertaken on the 0-30cm and 30-60cm samples. Below this depth only a single core was analysed. For both organic N & C the greatest concentrations were generally found in the top 30 cm. Within the top 30 cm organic C concentrations varied between 0.78 – 3.34 %. These are typically in the range of organic C concentrations for arable soils in England (Verheijen *et al.* 2005; King *et al.*, 2005; Webb *et al.*, 2003). Organic N in the top 30 cm varied between 0.04 – 0.35 % for the different soil types. Significant differences were found between domains and soil types and a major influence on the storage of organic C and N in the top 30 cm of the soils was found to be the % clay content.

The relationship between clay and mean organic C and mean organic N from the top 30 cm of the profiles is shown in Figure 25. Positive Pearsons's correlations of r = 0.79 and r = 0.69 were found between % clay and organic C and organic N respectively. Guggenberger & Kaiser (2003) suggest three mechanisms through which stable organic matter is formed in soils. These are (i) the 'selective enrichment' of organic compounds where there is an inherent recalcitrance of specific organic molecules against degradation by micro-organisms and enzymes, (ii) 'chemical stabilization' refers to all intermolecular interactions between organic and inorganic substances leading to a decrease in availability of the organic substrate due to surface condensation and changes in conformation (e.g. sorption to minerals and precipitation) and (iii) 'physical stabilization' whereby there is a decrease in the accessibility of the organic substrates to micro-organisms caused by occlusion within aggregates. Thus clay minerals and their oxy-hydroxide coatings play an important role in the amount of organic matter soils can retain. Verheijen *et al.* (2005) found a strong positive correlation between clay and organic C in arable soils of England and Wales. They also confirmed the presence of a minimum % SOC for arable soils that rises with increasing clay content and which other authors have found (Korschens *et al.* 1998; Ruhlmann, 1999). Skjemstad *et al.* (1998) and Eusterhues *et al.* (2003) also considered that SOC may sorb to clay surfaces, become occluded between the layers of clay particles and form stable aggregates that offer protection to the SOC from microbial decomposition. Sorption of organic C has been found to be associated with metal oxyhydrides as well as smectite suggesting that mineralogy plays an important role in the sorption of organic carbon (Ransom *et al.*, 1997; Kaiser & Guggenberger, 2000). There are few examples where the relationship between organic N and clay have been cited in the literature. One example is that of Hassink (1997) who estimated the maximum amounts of C and N that could be preserved in soils by their clay and

silt concentrations. However as organic N forms part of the organic molecules that are sorbed by clays and oxyhydroxides then it is logical to assume that increasing clay concentrations will result in greater sorption capacity for organic N.

Table 4: Comparison of mean values (n=4) and LSD (*P* < 0.05) for Total C (%), Total N (%) and C:N ratios with depth between the different soils and sediments sampled

	Total C 0 - 30 cm	Total C 30 – 60 cm	Total C 60- 90 cm	Total C 90-120cm	Total N 0 - 30 cm	Total N 30 – 60 cm	C:N 0 - 30 cm	C:N 30 – 60 cm
Edwalton Mudstone	0.78[a]	0.11[a]	0.17[a]	0.16[a]	0.04[a]	0.06[ab]	22.2[c]	2.0[a]
Cotgrave Sandstone	1.09[bc]	0.47[ab]	0.19[a]	0.16[a]	0.06[a]	0.09[ab]	22.0[c]	4.8[abc]
Gunthorpe Mudstone	1.00[ab]	0.19[a]	0.15[a]	0.13[a]	0.09[a]	0.05[ab]	11.4[b]	4.3[ab]
Head over sand	1.31[bc]	0.42[ab]	0.13[a]	0.11[a]	0.08[a]	0.05[ab]	17.5[bc]	10.9[bc]
Alluvial sand, silt & Clay	1.24[bc]	0.12[a]	0.13[a]	0.15[a]	0.07[a]	0.05[ab]	18.6b[c]	2.6[a]
Holme Pierpoint Sand & gravel	2.09[cde]	0.11[a]	0.10[a]		0.16[bc]	0.03[a]	13.1[ab]	3.2[a]
Alluvial sand, silt & Clay	3.23[f]	1.18[c]	0.12[a]	0.32[b]	0.24[d]	0.10[b]	13.1[ab]	11.1[bc]
Alluvial sand, silt & Clay	2.53[de]	0.24[ab]	0.11[a]	0.08[a]	0.21[cd]	0.02[a]	12.4[ab]	11.6[c]
Head over sand	1.61[cd]	0.28[ab]	0.16[a]	0.11[a]	0.11[b]	0.03[a]	14.3[ab]	9.03[abc]
Modern Floodplain 1	3.34[f]	1.76[d]	1.29[c]	1[d]	0.35[e]	0.20[c]	9.64[a]	8.67[abc]
Modern Floodplain 2	1.86[d]	0.83[bc]	0.9[b]	0.66[c]	0.17[c]	0.10[b]	11.48[ab]	9.16[abc]
LSD (*P*<0.05)	0.52	0.65	0.14	0.19	0.05	0.05	7.51	7.23

Differences in superscript letters signify significant differences between samples as calculated using Least Significant Differences (*P* < 0.05)

Table 5: Mean (n=4) and LSD ($P < 0.05$) values of total C (%), total N (%) and C:N ratios with depth for the different soils and sediments sampled

Depth (cm)	Edwalton mudstone	Cotgrave sandstone	Gunthorpe mudstone	Head over sand	Alluvial sand	Holme Pierpoint sand & gravel	Alluvial sand & clay	Alluvial sand & clay	Head over sand	Modern floodplain 1	Modern floodplain 2
Total C											
0-30	0.78[a]	1.09[a]	1.00[a]	1.31[a]	1.24[a]	2.09[a]	3.23[a]	2.53[a]	1.61[a]	3.34[a]	1.86[a]
30-60	0.11[b]	0.48[b]	0.2[b]	0.41[b]	0.13[b]	0.32[b]	1.18[b]	0.24[b]	0.28[b]	1.76[b]	0.83[b]
60-90	0.17[b]	0.19[b]	0.15[b]	0.13[b]	0.13[b]	0.10[b]	0.12[b]	0.11[b]	0.16[b]	1.28[c]	0.9[c]
90-120	0.16[b]	0.16[b]	0.13[b]	0.1[b]	0.15[b]	N/a	0.33[b]	0.08[b]	0.11[b]	1.0[d]	0.67[d]
LSD ($P<0.05$)	0.13	0.48	0.24	0.47	0.30	0.45	1.27	0.28	0.37	0.08	0.09
Total N											
0-30	0.04[a]	0.06[a]	0.09[a]	0.08[a]	0.07[a]	0.16[a]	0.25[a]	0.21[a]	0.12[a]	0.35[a]	0.16[a]
30-60	0.06[a]	0.09[a]	0.05[a]	0.05[a]	0.05[a]	0.03[b]	0.10[a]	0.02[b]	0.03[b]	0.20[b]	0.10[b]
LSD ($P<0.05$)	0.02	0.07	0.05	0.07	0.02	0.04	0.23	0.03	0.03	0.07	0.04
C:N											
0-30	22.27[a]	22.0[a]	11.4[a]	17.5[a]	18.6[a]	13.1[a]	13.1[a]	12.4[a]	14.3[a]	9.64[a]	11.42[a]
30-60	2.03[b]	4.8[b]	4.3[b]	10.9[a]	2.64[b]	3.2[b]	11.1[a]	11.7[a]	9.0[b]	8.97[a]	8.33[b]
LSD ($P<0.05$)	9.92	16.35	2.95	20.61	9.59	5.92	3.42	7.77	3.56	2.31	2.62

Differences in superscript letters signify significant differences between samples as calculated using Least Significant Differences ($P < 0.05$)

Figure 25: Plots showing the relationships between (i) % C, (ii) % N and (iii) C:N ratios and % clay demonstrating the importance of clay in storage of organic matter in the top 30 cm soil.
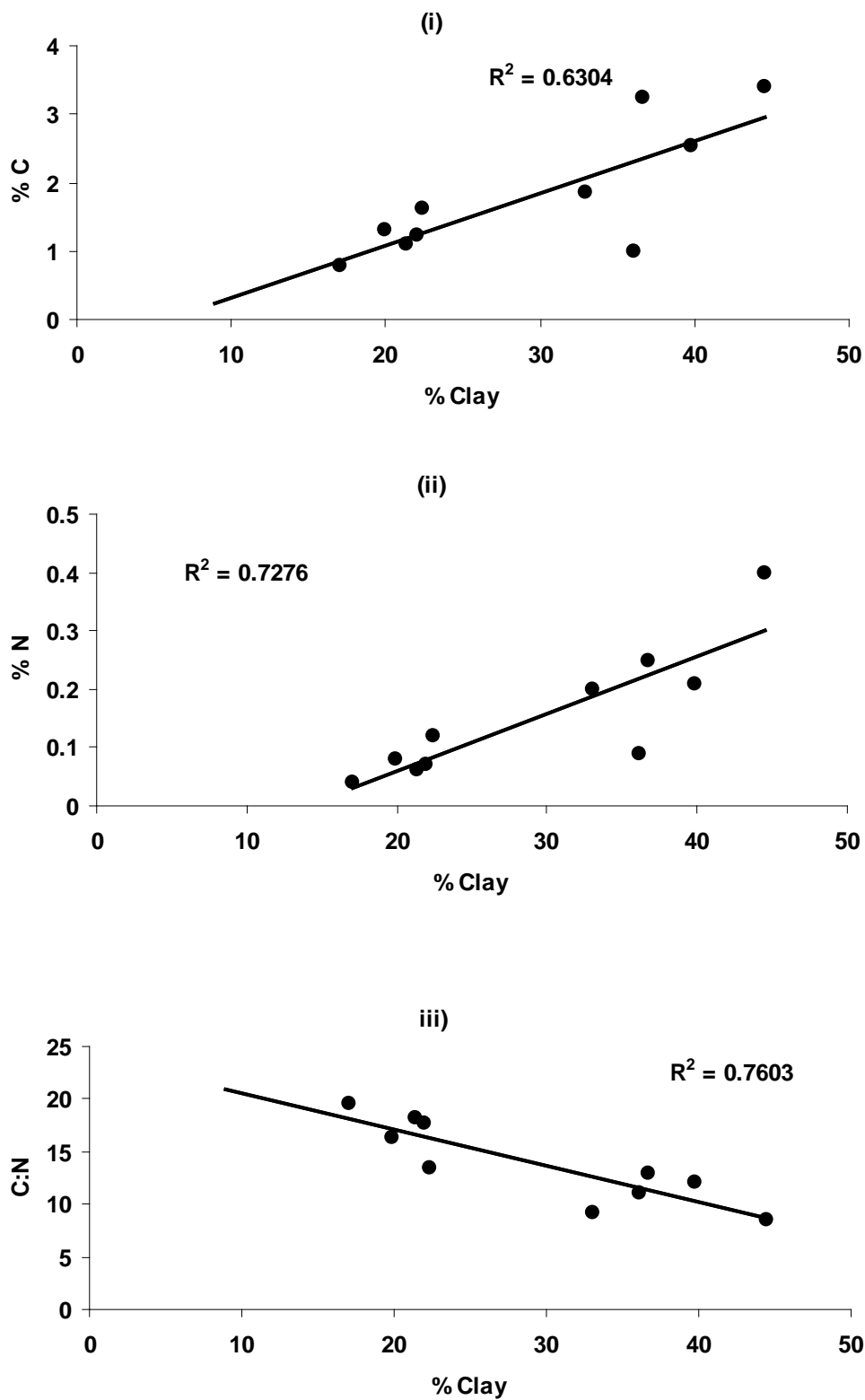
At depths of 30-60 cm some significant differences (P < 0.05) in organic C and organic N were found between different soil types. The depositional history of the parent material, texture and clay properties appear to be important in determining the extent of transport of organic C and N. For example, the very sandy sediments such as the Head over sand and HPP S&G have the lowest concentrations, possibly because of their low clay content. This effectively means that these sediments, despite encouraging greater infiltration and transport of DOM may have a lower particle surface area, particularly of clays on which DOC and DON may be sorbed. The modern (Holocene) floodplain sediments have significantly greater (P < 0.05) concentrations of SOC and SON with depth than the sediments of the Pleistocene Holme Pierrepoint S&G terraces. On the HPS&G terraces the quantities of C & N at depths > 30cm are generally low, possibly reflecting their depositional origins. These were formed ~24000 yrs ago in periglacial braided stream environments when there was little plant growth within the environment. Therefore very small amounts of organic matter would have been deposited with the sediments by the floodwaters. However the Holocene deposited on modern day terraces have much greater organic C and N concentrations to depths of >2 m. Holocene alluvial sediment deposition would be accompanied by greater deposits of organic matter as the modern day floodplain was created.

In the non-aquifer sediments, slightly greater transport of organic N and C were found through the soil profile in the soils derived from the Cotgrave Sandstone than those with the Gunthorpe and Edwalton formation mudstones as a parent material. However, there were no significant differences between the concentrations of organic C and N found in the Triassic mudstones (Edwalton & Gunthorpe Formations). It is not known whether the organic C and N found in the mudstones and sandstone is 'ancient geological' or modern (i.e. from recent decomposition of plant or microbial matter). For example, in the Gunthorpe formation of the Mercia Mudstone, the environment of deposition was desert playa. The red colour of the bulk of the Gunthorpe Formation is indicative of iron (III) oxide. It is characteristic of a hot, arid environment. However, in places bacterial decomposition of organic matter after deposition may have reduced the ferric iron to ferrous iron. If there was sufficient organic matter present to reduce all the ferric oxide the resulting rock became green/grey (Hobbs *et al*. 2008). Therefore, as you go deeper within these sediments some of the carbon and nitrogen may be as a result of geological deposition rather than all resulting from modern day inputs.

As organic carbon and nitrogen is stored within the profile, one of the major factors that may determine its residence time is its lability. A common measure of the extent that organic matter has been decomposed is the C:N ratio. During decomposition C is respired whilst N is assimilated by the microbial population. It is common to find C:N ratios of between 9:1 and 12:1 in agricultural top soils of temperate climates (Rowell, 1994; Batjes et al. 1996). As C:N ratio's increase it is indicative that greater microbial decomposition has taken place. Results from the survey at Shelford (Figure 24) show mean C:N values in the top 30 cm to be between 8 and 20 with highest C:N values being found in the soils and parent materials of the Edwalton mudstone and Cotgrave sandstone parent materials, where C:N ratios are greater than generally expected for agricultural soils in the top 30 cm. Significant differences (P<0.05) were found within

the soils of the different domains (Table 4). The major difference would appear to be associated with the soil texture. Figure 23 shows the relationship between % Clay and C:N ratio in the top 30 cm where a Pearson correlation of R = -0.87 was found. These results show that with increasing clay concentrations, lower C:N ratios are found, suggesting that increasing clay concentration acts to protect organic matter from microbial decomposition to a greater extent than in sandy soils in the top soils.

Figure 26: C:N ratio profiles for the different soils and sediments sampled

Site 7: Alluvial clay & sand

Site 8: Alluvial sand & gravel

Site 9: Head over sand

Site 10: Alluvial Sand

Site 11: Alluvial Sand
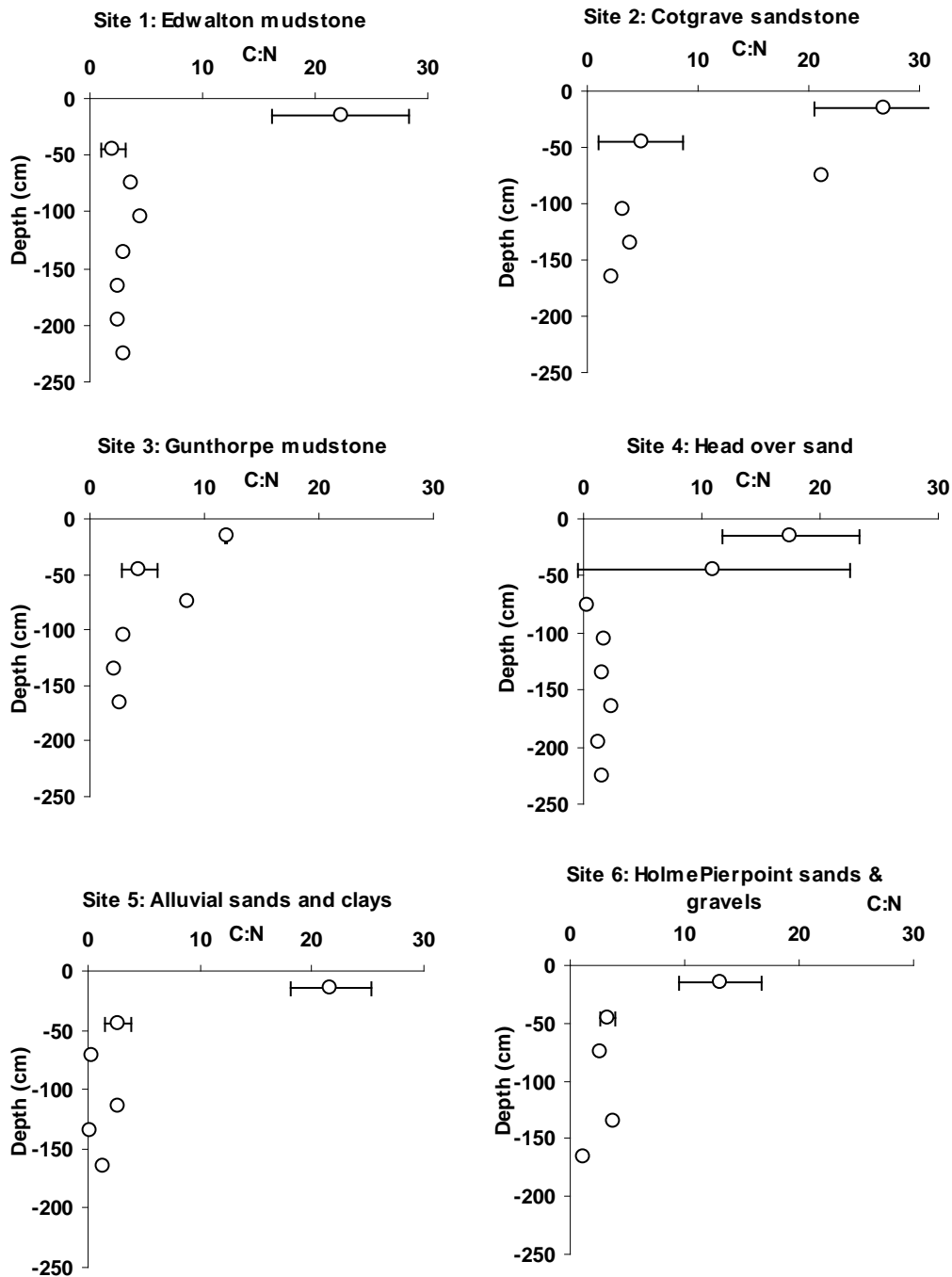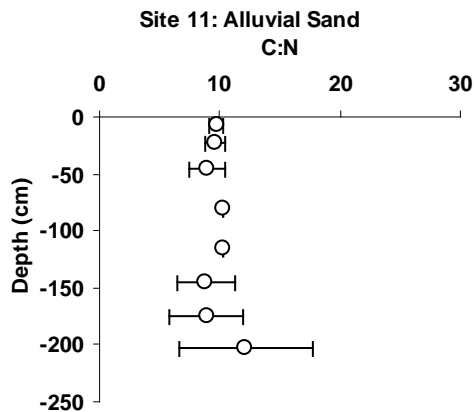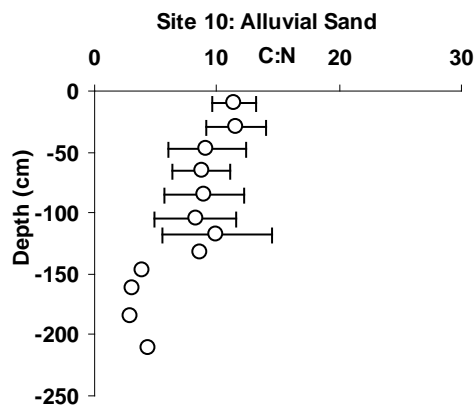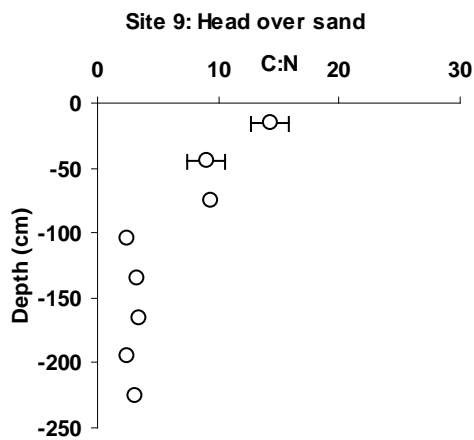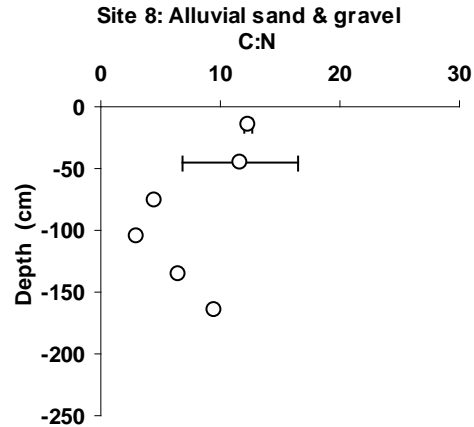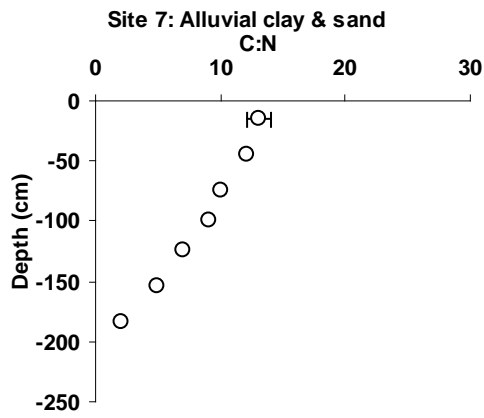
Statistical analysis within individual domains show that there are generally significant decreases in the C:N ratio between the 0-30 cm and 30-60 cm depth (Table 5). The lower C:N ratios found in the 30-60 cm fraction may be a result of soluble organic matter being leached below the level where large microbial populations exist that may decompose the organic matter further.

3.3   INORGANIC NITROGEN PROFILES

Nitrate is the most mobile species of N found in soil, and is the species that most work has been undertaken on because of its potential for leaching into ground and surface waters. Figure 27 shows nitrate profiles found through the soil and parent materials. Greatest concentrations are generally found in the top soil (0-30cm), where the major pool of organic matter accessible to the microbial biomass is situated for mineralisation and where fertiliser N is applied. Mean concentrations varied between 2 and 8 mg kg^{-1} NO_3-N. Decreases in NO_3-N concentration were generally found between 30 and 90 cm in all the parent materials. The decrease between 30 and 90 cm is probably a combination of (i) uptake of NO_3^- by the roots of the crop which can typically extend to depths of ~1m or more or (ii) where denitrification may eventually convert NO_3^- to N_2. For the non-aquifer soils, below ~1m there appears to be slight increase in concentration of NO_3^- and thus accumulation. This nitrate is most likely lost to the plant system as it is deeper than rooting depth. Whilst a small number of studies have suggested that denitrification can take place at fast rates in deep vadose zones (Holden & Fierer (2005), it is generally accepted that denitrification rates decrease sharply with depth below the surface. For example Luo *et al*. (1998) found rates decreasing between 10-100 fold for a depth interval 0-10 cm to 30 cm whilst Paramasivam *et al*. (1999) found that denitrification decreased between 50 and 100 % between the surface and 90 cm. Low rates of denitrification at depths can be attributed to low numbers of denitrifying bacteria, low NO_3^- concentrations and low availability of suitable organic C substrates (Holden & Fierer, 2005). Thus the accumulation being found in these profiles would suggest that the long term leaching of nitrate to these depths exceeds denitrification. In the aquifer soils and sediments concentrations of leached nitrate at depths below 1m will be discussed within the groundwater section. There was one exception to the general trend of decreasing NO_3-N concentrations with depth and this was for the Head over Sand domain. In both areas examined there was an increase of NO_3-N. We believe that this was caused because the domain was at the break of slope. Therefore nitrate may get washed into this area by overland flow where it then accumulates with depth. This was further backed up by results from another study where pore water NO_3^- concentrations sampled in this domain were found to exceed 300 mg l^{-1} (A. Tye *pers. comm*).

Figure 27: NO₃-N profiles for the different soils and sediments sampled

Site 7: Alluvial clay & gravels

Site 8: Alluvial clay & gravels

Site 9: Head over sand
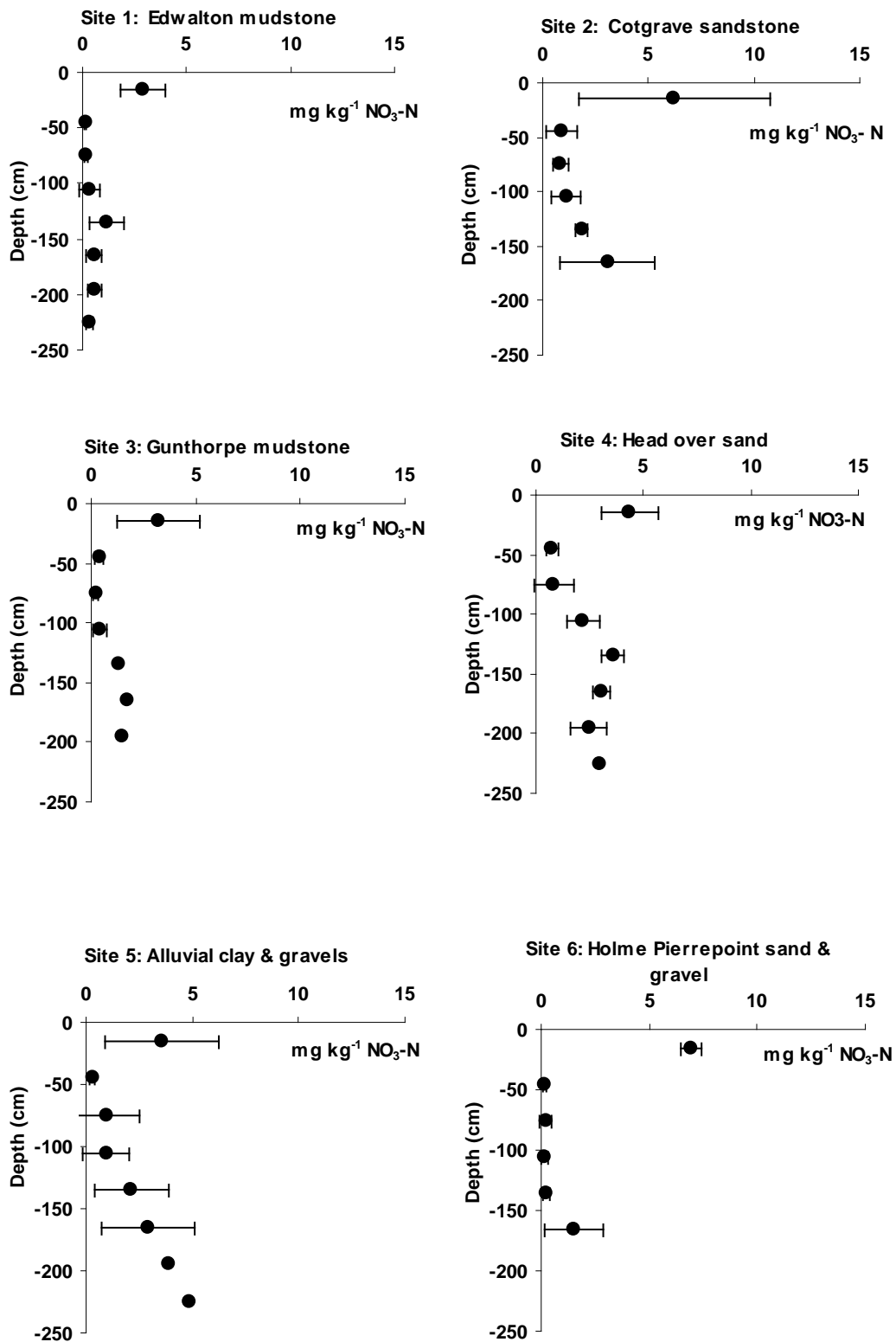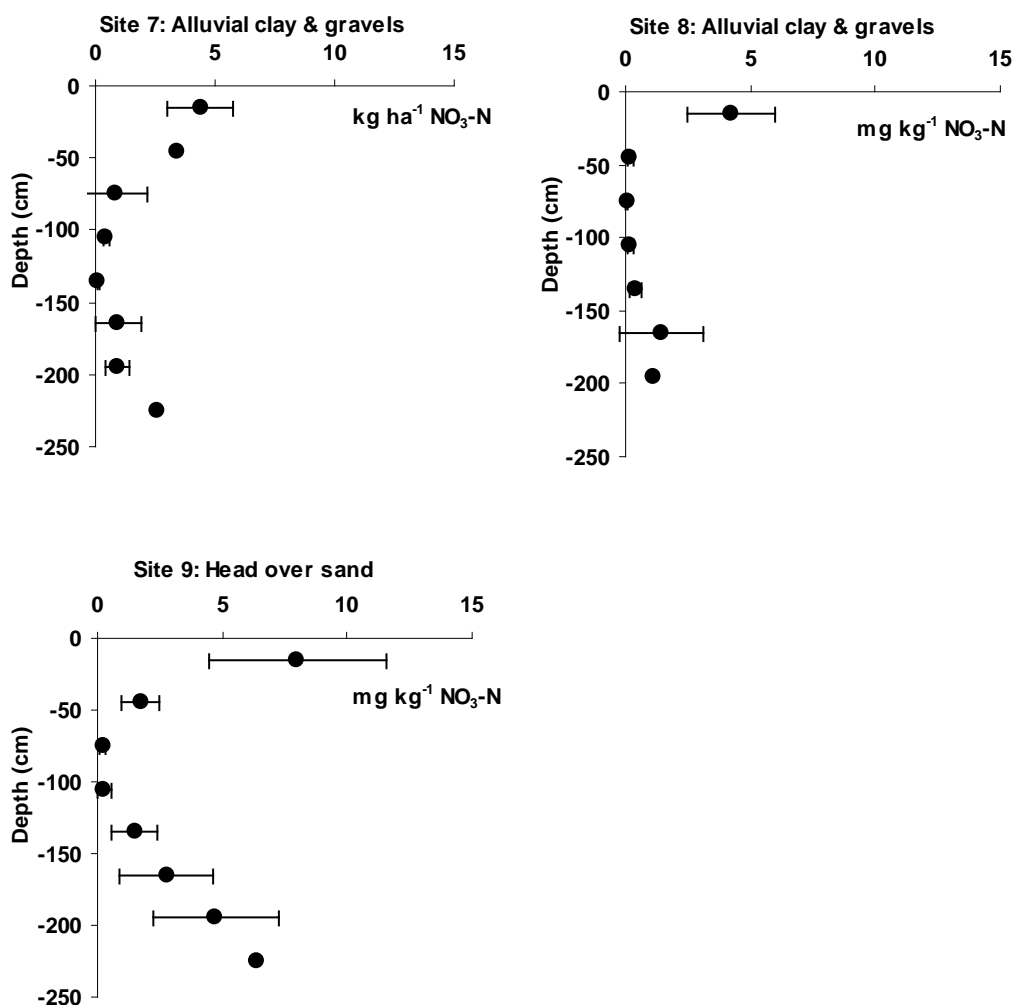
Ammonium is typically far less mobile than nitrate, being held on the soils cation exchange complex and within clays where it can enter into the interlayer space of Illite/Smectite minerals. This can act as a storage mechanism. Figure 28 shows the variation in NH_4-N with depth. Typically for all soils and parent materials concentrations of NH_4-N were below 1 mg kg^{-1}. There was generally considerable variation and this may reflect the variation in clay content, the degree of cracking a soil may undergo to allow transport of NH_4^+ ions or clay infiltration. In deeper soils a potential further source of NH_4-N may have come from that already sorbed to the clay minerals as the mudstones and sandstones were formed. Thus some NH_4-N may be of geological origin.

Figure 28: Concentration profiles for NH₄-N in the different soils and sediments sampled

Site 7: Alluvial Sand, Silt & Clay

Site 8: Alluvial Sand, Silt & Clay

Site 9: Head over Sand
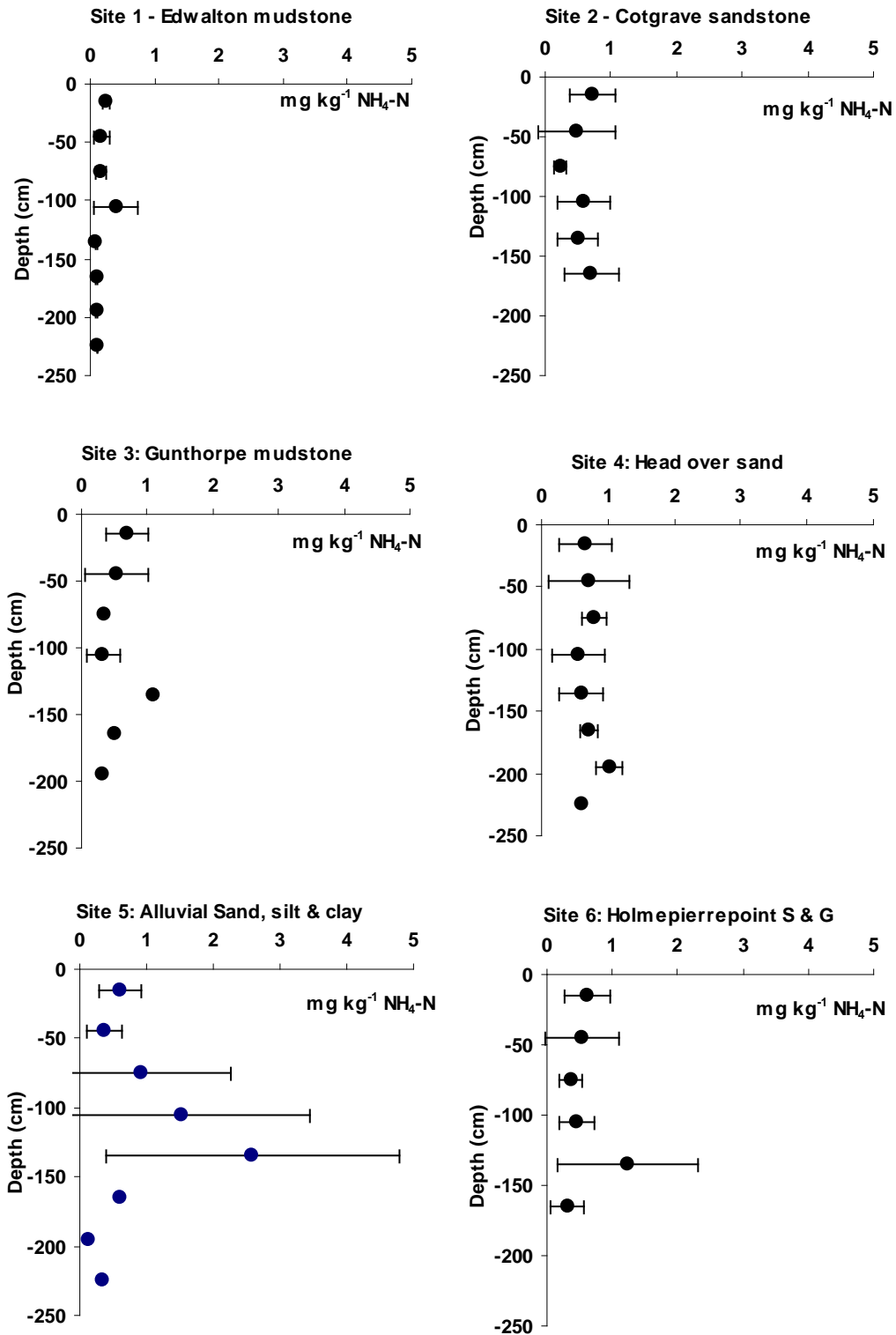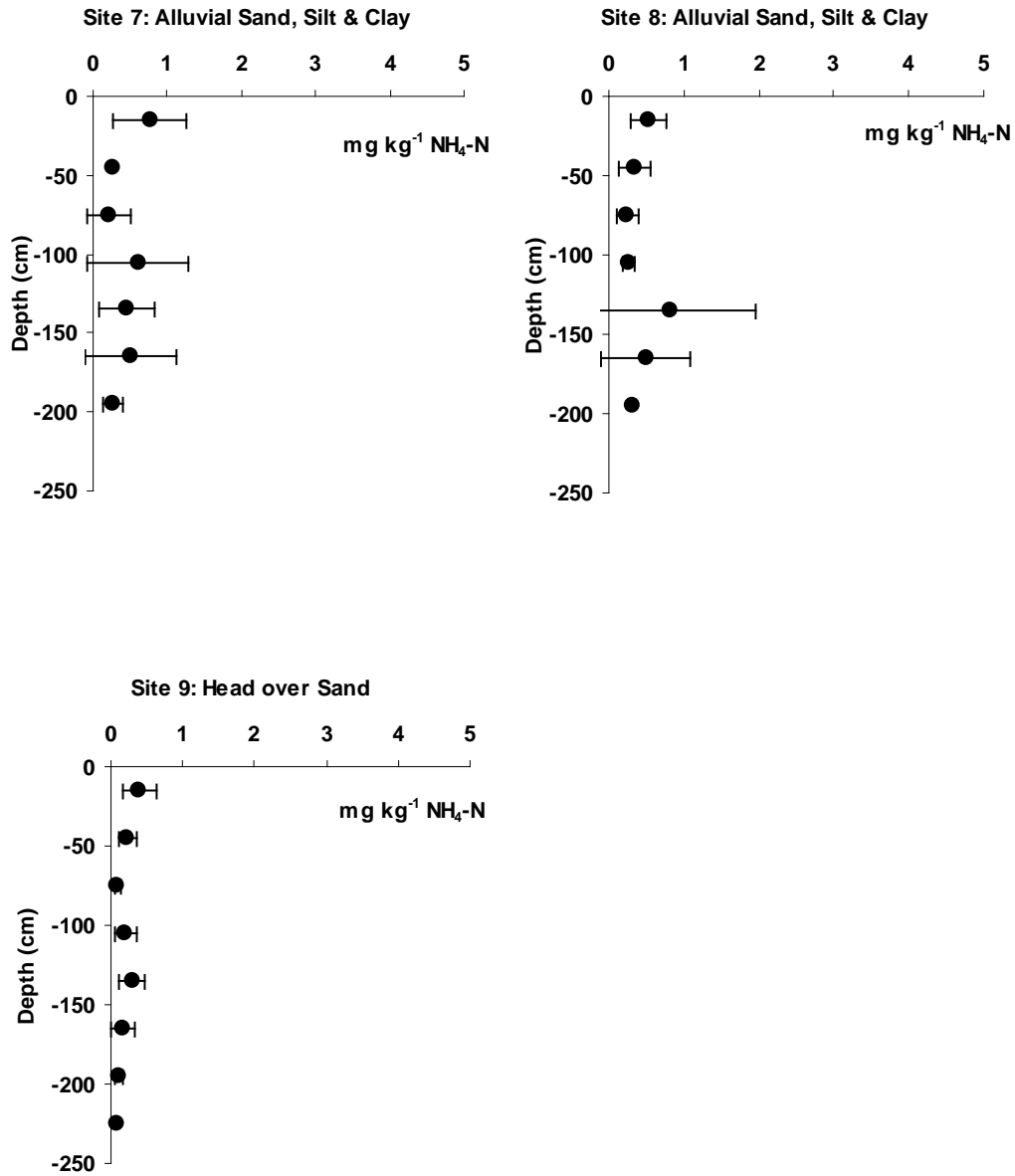
Tables 6 and 7 report the mean nitrate concentrations with statistical analysis by domain and depth whereas Tables 8 and 9 report ammonium values by domain and depth. In all cases one way analysis of variance followed by Least square differences (LSD, $P<0.05$) were undertaken to demonstrate where statistical differences occur.

Table 6: Mean NO$_3$-N concentration with depth and LSD (P<0.05) values for the different soils and sediments sampled

|	Edwalton mudstone	Cotgrave sandstone	Gunthorpe mudstone	Head over sand	Alluvial Sand	Holme Pierpoint sand & gravel	Alluvial sand & clay	Alluvial sand & clay	Head over sand
Depth (cm)									
0-30	2.93^c	5.50^b	2.46^a	4.37^c	3.58^b	6.91^c	4.39^a	4.23^b	8.01^b
30-60	0.13^a	1.01^a	0.31^a	0.73^a	0.31^a	0.15^a	2.31^a	0.19^a	1.72^a
60-90	0.16^a	0.91^a	0.29^a	0.83^a	0.22^a	0.05^a	0.93^a	0.04^a	0.21^a
90-120	0.35^a	1.48^a	0.49^a	2.21^b	1.12^a	0.28^a	0.21^a	0.16^a	0.27^a
120-150	1.14^a	1.82^a	1.34^a	3.57^b	1.34^a	0.22^a	0.32^a	0.39^a	1.49^a
150-180	0.54^a	3.13^a	1.72^a	3.05^b	1.62^a	1.51^b	1.27^a	1.43^a	2.76^a
180-210	0.58^a		1.46^a	2.46^b	3.67^b		2.54^a	1.10^a	4.72^b
210-240	1.42^b			2.96^b	5.14^b				6.37^b
									5.69^b
LSD (p<0.05)	1.07	3.73	3.33	1.47	2.49	1.00	4.06	1.81	4.16

Differences in superscript letters signify significant differences between samples as calculated using Least Significant Differences ($P < 0.05$)

Table 7: Comparison of NO$_3$-N (mg kg^{-1}) concentrations with depth between the different soils and sediments sampled.

	0 - 30 cm	30 – 60 cm	60 – 90 cm	90 – 120 cm	120 – 150 cm	150 – 180 cm	180 – 210 cm
Edwalton mudstone	2.93^a	0.13^a	0.15^a	0.35^a	1.14^{ab}	0.54^a	0.59^a
Cotgrave Sandstone	5.25^{ab}	1.01^{ab}	0.91^a	1.49^b	1.82^c	3.14^b	N/A
Gunthorpe mudstone	2.46^a	0.31^a	0.29^a	0.49^{ab}	1.34^{ab}	1.72^{ab}	1.46^{ab}
Head over sand	4.39^a	0.73^{ab}	0.84^a	2.20^b	3.57^d	3.05^{ab}	2.46^{abc}
Alluvial sand	3.58^a	0.32^a	0.23^a	1.12^{ab}	1.34^{ab}	1.62^{ab}	3.67^{bc}
Holme Pierpoint Sand & gravel	6.91^{ab}	0.15^a	0.06^a	0.28^a	0.22^a	1.50^{ab}	N/A
Alluvial sand & clay	4.39^{ab}	2.31^b	0.93^a	0.21^a	0.32^{ab}	1.28^{ab}	2.54^{abc}
Alluvial sand & clay	4.23^{ab}	0.19^a	0.05^a	0.18^a	0.39^{ab}	1.43^{ab}	1.10^{ab}
Head over sand	8.01^b	1.72^{ab}	0.21^a	0.27^a	1.49^b	2.75^{ab}	4.72^c
LSD (p<0.05)	3.91	1.74	1.06	1.05	1.21	2.57	2.95

Differences in superscript letters signify significant differences between samples as calculated using Least Significant Differences (*P* < 0.05)

Table 8: Comparison of NH_4-N (mg kg^{-1}) concentrations with depth in the different soils and sediments sampled.

	Edwalton mudstone	Cotgrave sandstone	Gunthorpe mudstone	Head over sand	Alluvial sand	Holme Pierpoint sand & gravel	Alluvial sand & clay	Alluvial sand & clay	Head over sand
Depth (cm)									
0-30	0.25^a	0.85^a	0.42^a	0.66^a	0.60^{ab}	0.62^a	0.76^a	0.54^a	0.40^a
30-60	0.14^a	0.26^a	0.41^a	0.72^a	0.37^{ab}	0.54^a	0.15^a	0.34^a	0.26^a
60-90	0.11^a	0.41^a	0.65^a	0.78^a	0.90^{ab}	0.42^a	0.21^a	0.23^a	0.04^a
90-120	0.39^a	0.38^a	0.18^a	0.56^a	2.31^b	0.39^a	0.86^a	0.27^a	0.16^a
120-150		0.80^a	1.10^a	0.59^a	1.09^{ab}	1.25^a	0.44^a	0.81^a	0.27^a
150-180		0.66^a	0.48^a	0.72^a	0.77^{ab}	0.29^a	0.27^a	0.49^a	0.10^a
180-210			0.32^a	1.02^a	0.09^a		0.17^a	0.30^a	0.06^a
210-240	0.22^a			0.60^a	0.33^{ab}				
LSD (p<0.05)	0.26	0.59	0.97	0.64	2.20	0.89	0.99	0.94	0.40

Differences in superscript letters signify significant differences between samples as calculated using Least Significant Differeces ($P < 0.05$)

Table 9: Comparison of NH$_4$-N (mg kg^{-1}) concentrations with depth between the different soils and sediments sampled.

	0 - 30 cm	30 – 60 cm	60 – 90 cm	90 – 120 cm	120 – 150 cm
Edwalton mudstone	0.25^a	0.14^a	0.11^a	0.38^a	B/D
Cotgrave Sandstone	0.85^a	1.03^a	0.40^a	0.38^a	0.80^a
Gunthorpe mudstone	0.41^a	1.65^{cd}	0.65^a	0.18^a	1.10^a
Head over sand	0.66^a	2.89^e	0.78^a	0.56^{ab}	0.59^a
Alluvial sand	0.60^a	1.46^c	0.90^a	2.31^b	1.08^a
Holme Pierpoint Sand & gravel	0.62^a	2.16^d	0.42^a	0.38^a	1.24^a
Alluvial sand & clay	0.76^a	0.45^a	0.21^a	0.85^{ab}	0.44^a
Alluvial sand & clay	0.54^a	1.36^{bc}	0.22^a	0.26^a	0.81^a
Head over sand	0.40^a	0.86^{ab}	0.04^a	0.16^a	0.27^a
LSD (p<0.05)	0.51	0.59	0.86	1.32	1.33

Differences in superscript letters signify significant differences between samples as calculated using Least Significant Differeces ($P < 0.05$)

3.4 STOCKS OF NITROGEN AND CARBON STORED IN SOILS AND PARENT MATERIALS

The quantities of organic C and N stored within each profile are summarised in Tables 10 and 11 and for inorganic N in Tables 12, 13 and 14. These values have been corrected for soil bulk density and stone content to derive values of $g\ m^{-2}$. Weights of organic C in the top 30 cm are comparable to published values (Table 10). For example, in the Broadbalk wheat experiment at Rothamsted, organic C values of 26t ha^{-1} (0-23 cm) have been found in unmanured plots (Rowell, 1994). In our study, quantities of organic N varied between 164 – 1407 $g\ m^{-2}$ in the top 30 cm, 468 -2199g m^{-2} in the 0-60 cm fraction and for the whole profiles ranged from 997 – 4087 $g\ m^{-2}$.

For inorganic N, totals were calculated for the whole of the soil parent material to drill depth for the Edwalton mudstone, Cotgrave sandstone and Gunthorpe Mudstone and to 90cm for the aquifer sediments. This was because of the interaction of the water table. Values for NO_3-N, NH_4-N and total inorganic N (NO_3-N + NH_4-N) can be found in Tables 12, 13 and 14. Within the mudstone and sandstone soils, calculated quantities of inorganic N to depths ~2m were between 30-70 $kg\ ha^{-1}$. At the top end of the scale for the Cotgrave sandstone, this represents about half of an average N application for a typical crop (e.g. wheat ~130 $kg\ N\ ha^{-1}$). Inorganic N generally makes up < 1 % of the total N in the soil.

Table 10: Total organic C storage g m^{-2} for different soils and sediments sampled. Figures are given for 0-120 cm (where C measurements are n=3) whilst rest of core is determined on C measurements (n=1).

	Edwalton mudstone	Cotgrave sandstone	Gunthorpe mudstone	Head over sand	Alluvial Sand	Holme Pierpoint sand & gravel	Alluvial sand & clay	Alluvial sand & clay	Head over sand	Modern Floodplain 1	Modern Floodplain 2
Depth (cm)											
0-30	3194	3739	3395	5060	4437	7881	12034	9311	6445	13427	6919
30-60	558	2338	846	1819	589	1106	3642	704	2104	6970	3087
60-90	825	1002	734	559	480	320	358	321	1202	5147	3267
90-120	702	806	510	509	436	201	1330	207	509	4080	2475
120-150	723	904	246	196	18.9	561	207	276	215	1957	3720
150-180	570	398	381	173	194	268	63	6225	197	942	2952
180-210	708			136					151	936	2709
210-240				214					186		
Total 0-120 cm	**5279**	**7885**	**5485**	**7947**	**5942**	**9508**	**17364**	**10543**	**10260**	**29624**	**15748**
Total Whole Profile	**7281**	**9187**	**6113**	**8454**	**6155**	**10337**	**17634**	**17046**	**10823**	**33459**	**25130**

Table 11: Total organic N storage g m^{-2} for different soils and sediments sampled. Figures are given for 0-60 cm (where N measurements are n=3) whilst rest of core is determined on N measurements (n=1).

	Edwalton mudstone	Cotgrave sandstone	Gunthorpe mudstone	Head over sand	Alluvial Sand	Holme Pierpoint sand & gravel	Alluvial sand & clay	Alluvial sand & clay	Head over sand	Modern Floodplain 1	Modern Floodplain 2
Depth (cm)											
0-30	164	206	306	309	250	603	931	772	480	1407	632
30-60	304	448	224	222	227	104	309	59	225	792	372
60-90	228	37	78	271	148	99	24	52	90	439	454
90-120	211	348	137	134	151	62	46	36	83	351	375
120-150	246	237	112	121	217	149	85	42	65	413	439
150-180	226	175	142	75	141	221	21	654	56	334	380
180-210	291			104			30		61	351	449
210-240				140					61		
Total (0-60cm)	**468**	**653**	**528**	**530**	**477**	**707**	**1240**	**832**	**706**	**2199**	**1004**
Total Whole Profile	**1670**	**1451**	**997**	**1376**	**1134**	**1238**	**1445**	**1617**	**1123**	**4087**	**3101**

Table 12: Estimates of quantities of NO$_3$-N stored in different parts of the profiles of the different soils and sediments sampled (g m^{-2})

	Edwalton mudstone	Cotgrave sandstone	Gunthorpe mudstone	Head over sand	Alluvial sand	Holme Pierpoint sand & gravel	Alluvial sand & clay	Alluvial sand & clay	Head over sand
Depth (cm)									
0-30	1.20	1.80	0.84	1.69	1.28	2.61	1.64	1.56	3.21
30-60	0.07	0.50	0.14	0.32	0.14	0.05	0.71	0.06	1.29
60-90	0.08	0.48	0.14	0.36	0.08	0.02	0.28	0.01	0.16
90-120	0.15	0.75	0.19						
120-150	0.44	0.80	0.62			Within limits of water table			
150-180	0.23	1.49	0.84						
180-210	0.39		0.72						
210-240									

Table 13: Estimates of quantities of NH$_4$-N stored in different parts of the profiles of the different soils and sediments sampled (g m^{-2})

	Edwalton mudstone	Cotgrave sandstone	Gunthorpe mudstone	Head over sand	Alluvial sand	Holme Pierpoint sand & gravel	Alluvial sand & clay	Alluvial sand & clay	Head over sand
Depth (cm)									
0-30	0.10	0.29	0.14	0.25	0.21	0.24	0.28	0.20	0.16
30-60	0.07	0.13	0.18	0.32	0.17	0.19	0.05	0.10	0.16
60-90	0.06	0.21	0.32	0.34	0.33	0.14	0.06	0.07	0.16
90-120	0.17	0.19	0.07	Within limits of water table					
120-150	0	0.35	0.51						
150-180	0	0.31	0.23						
180-210	0	0	0.16						
210-240	0	0	0						

Table 14: Estimated quantities of Total inorganic N (NO$_3$-N + NH$_4$-N) stored in profiles of different domains (g m^{-2}). The depths to which the estimations are made are stated.

	Edwalton mudstone	Cotgrave sandstone	Gunthorpe mudstone	Head over sand	Alluvial sand	Holme Pierpoint sand & gravel	Alluvial sand & clay	Alluvial sand & clay	Head over sand
To depth	210cm	180cm	210 cm	90cm	90cm	90cm	90cm	90cm	90cm
Total Inorganic N	2.96	7.32	5.12	3.28	2.22	3.24	3.03	2.00	5.01

3.5 NITROGEN AND CARBON HYDROCHEMISTRY IN GROUNDWATERS

Groundwater from the shallow floodplain aquifer was sampled three times from each of the 14 piezometers (Jul 08, Oct 08 and Feb 09). Full results of the hydrochemistry are presented in Tables 15-17. Overall the groundwater hydrochemistry was reasonably consistent at the three sampling dates suggesting that the analyses present a representative picture of groundwater quality within the aquifer.

Two of the most important chemical parameters for the speciation of N present in the groundwater are pH and O_2. Measurements showed that the waters generally had pH values between 7 and 8 and that the water was generally well oxygenated. This means that (i) anaerobic conditions necessary for denitrification within the aquifer are not present and (ii) the pH is within the range where the conversion of ammonium to ammonia gas may take place. The well oxygenated conditions were confirmed by the low Fe concentrations found in the groundwater (generally <50 ug l^{-1}), suggesting that no reduction of FeO was taking place and these concentrations would normally be expected to be complexed with DOC, and leached from the top soil. However, it is likely that small pockets of different redox potential may exist within the sediments. For example, BH24 in March 09 showed a higher than expected Fe value (0.1 mg l^{-1}) suggesting that reducing conditions may occur within the more clay rich sediments of the aquifer. These pockets of anaerobic conditions are probably very localized.

For the nitrogen species measured, ammonium was measured in July 08 only and was found to have concentrations below the detection limits (< 0.1 mg l^{-1}). These results confirmed a small series of analyses taken the previous summer (July 07) where ammonium was again found to be below the detection limits. This low level of ammonium in the groundwater probably reflects the difference in behaviour compared to nitrate; ammonium being far less mobile than nitrate as it sorbs to clay minerals and will therefore exist as an exchangeable cation as demonstrated by the results in Section 3.3. Alternatively, small concentrations of ammonium present in the waters could potentially volatilise as ammonia due to the alkaline pH of the water.

Nitrate concentrations in the ground waters were found to range between 16.2 – 186 mg l^{-1} in July 08, between 15.9 – 185 mg l^{-1} in October 08 and between 9 – 165 mg l^{-1} in February 09. Concentrations of nitrate of this magnitude have been found in riparian zones by Banaszuk *et al*. (2005) in Poland. For comparative purposes, many of these aquifer groundwater samples would exceed the 50 mg l^{-1} drinking water standard (EU Nitrates Directive, 91/676/EEC). Average concentrations across the study area were 60, 62 and 68 mg l^{-1} at July 08, October 08 and February 09 respectively. As the study area is largely arable agriculture, with relatively similar inputs of fertiliser N (Table 1), the variability of the nitrate concentrations in the water is probably a function of crop uptake, transport speed through the aquifer materials and the extent of denitrification rather than due to a land management effect. Results also demonstrated that the groundwater in the floodplain had concentrations of NO_3^- that greatly exceeded the concentration of nitrate in the River Trent (18 and 36 mg l^{-1}). Generally concentrations of nitrite were found to be below the level of detection (<0.01 mg l^{-1}). However, occasional nitrite concentrations of between 0.03 to 0.74 mg l^{-1} were found as NO_2-N. Typically in UK aquifers nitrite concentrations are rarely greater than 1 mg L^{-1} (BGS, 2007). In addition, some of these nitrite values are considerably higher than those found in groundwater extracted from a Moorland catchment in mid-Wales (Lapworth et al. 2008) but are common for more intensively farmed areas with values > 0.1 mg L^{-1} often indicating nitrogen contamination (Guo *et al*., 2006). The presence of nitrite could result from either the nitrification of ammonium or via the denitrification pathway and both processes may be possible within the aquifer. Burns *et al*.

(1996), using ^{15}N as a tracer suggested that the presence of nitrite could result from simultaneous nitrification or denitrification. Nitrite could be produced through the denitrification of nitrate. However, concentrations of dissolved oxygen within the aquifer water were generally > 1mg l^{-1}. Tiedje, (1988) suggested that denitrification needs concentrations of dissolved oxygen <1mg l^{-1}. Thus, the nitrite present could be from the nitrification of NH_4^+.

Table 15: Major anions and cations found in groundwater of the shallow sand and gravel aquifer taken in Jul 08.

Borehole	Sediment	Conductivity	O_2	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	Tot Fe	Mn	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	NO_2^-	HPO_4^{2-}	NPOC
		$\mu s\ cm^{-1}$	$mg\ l^{-1}$									$mg\ L^{-1}$						
BH4	HP S&G	600	8.4	7.9	70.1	29.3	12.7	2.1	<0.3	0.04	0.11	19.8	148	96.4	76.6	0.27	<0.5	4.94
BH5	HP S&G	566	5.9	7.4	71.6	14.1	24.9	6.3	<0.3	0.02	0.10	32.6	167	67.8	66.3	0.05	<0.1	5.17
BH6	HP S&G	725	9.8	7.8	92.6	21.4	17.3	1.8	<0.3	0.02	<0.002	52.7	230	62.1	98.9	<0.01	0.221	2.02
BH7	All Clay	490	5.4	7.7	69.2	15.2	13.2	4.5	<0.3	0.03	0.09	15.1	250	28.0	27.3	0.18	<0.1	4.28
BH12	All Clay	493	N/A	7.7	72.8	17.1	11.9	2.7	<0.3	0.03	0.25	12.2	251	57.1	7.05	0.041	<0.1	6.36
BH13	HS&G	808	6.8	7.8	97.7	38.5	6.96	1.6	<0.3	0.03	0.05	30.9	324	127	69.6	<0.01	<0.1	1.09
BH14	HP S&G	789	N/A	7.7	96.4	16.0	32.7	11.5	<0.3	0.02	0.04	121	68.8	37.3	186	0.58	<0.1	0.51
BH19	All S&G	818	1.9	7.7	128	23.2	32.2	3.1	<0.3	0.03	0.06	47.5	359	121	16.1	0.24	<0.1	2.63
BH20	All S&G	897	6.8	7.3	135	29.5	19.6	1.8	<0.3	0.02	0.04	93.3	135	218	66.9	<0.01	<0.1	1.03
BH21	HP S&G	675	20.3	7.4	81.8	22.0	10.2	1.4	<0.3	0.08	1.06	49.8	128	108	108	<0.01	<0.1	1.52
BH22	All S&G	917	9.4	7.3	124	36.0	22.4	6.2	<0.3	0.05	0.58	46.7	336	198	27.5	0.09	<0.1	2.86
BH24	HP S&G	1090	13.1	7.7	169	54.1	13.5	27.6	<0.3	0.04	0.15	13.7	336	419	16.2	0.05	<0.1	4.48
BH26	HS&G	790	7.2	7.8	113	35.2	10.8	2.7	<0.3	0.04	0.01	48.0	352	34.0	51.5	0.11	<0.1	6.35
River Trent		836	N/A	8.2	81.2	20.1	57.0	10.3	<0.3	0.03	0.26	81.3	213	148	35.5	0.11	2.10	5.28

Table 16: **Major anions and cations found in groundwater of the shallow sand and gravel aquifer taken in October 08.**

	Sediment	Conductivity	*O_2	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	Tot Fe	Mn	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	NO_2^-	HPO_4^{2-}	NPOC	Org N	Org C:N
		µs cm^{-1}	mg l^{-1}											mg L^{-1}						
BH4	HP S&G	690	2.6	7.7	93.7	32.9	15.4	3.85	<0.3	0.04	0.63	39.5	231	115	49.4	0.74	<0.1	7.57	1.54	7.47
BH5	HP S&G	514	1.7	7.2	63.4	12.9	24.3	6.12	<0.3	0.02	0.05	30.8	168	62.2	48.0	<0.01	<0.1	4.69	0.56	8.80
BH6	HP S&G	750	3.2	7.7	105	25.0	19.4	1.90	<0.3	0.03	<0.002	52.1	250	66.9	103	<0.01	0.28	1.87	0.10	61.98
BH7	All S&C	527		7.8	76.5	18.1	18.6	3.78	<0.3	0.03	0.12	16.3	288	41.7	17.1	0.13	<0.1	5.27	0.24	60.33
BH12	All S&C	427		7.8	67.1	14.5	13.2	1.73	<0.3	0.03	0.07	10.7	228	46.4	3.56	<0.01	<0.1	5.91	0.21	71.44
BH13	HS&G	832		7.8	115	47.4	9.01	1.64	<0.3	0.04	0.004	33.7	336	139	66.8	<0.01	<0.1	1.53	0.51	16.68
BH14	HP S&G	910		7.6	114	18.0	35.3	6.45	<0.3	0.02	0.08	150	75.4	39.5	185	<0.01	<0.1	3.06	BD	-
BH19	All S&G	856	2.8	7.6	133	28.7	28.7	2.77	<0.3	0.04	0.06	40.7	329	170	32.8	0.05	<0.1	2.86	0.13	32.99
BH20	All S&G	908	3.1	7.5	133	30.8	18.8	1.22	<0.3	0.04	0.04	88.0	129	229	60.4	0.07	<0.1	1.48	0.06	37.94
BH21	HP S&G	689	2.8	7.4	91.3	24.6	12.3	1.56	<0.3	0.03	0.01	53.4	134	116	101	<0.01	<0.1	1.73	BD	-
BH22	All S&G	987		7.4	136	42.2	21.0	8.61	<0.3	0.05	0.74	52.0	329	210	47.9	0.10	0.14	2.28	0.48	18.99
BH24	HP S&G	1354	3.8	7.6	206	75.2	14.5	29.8	<0.3	0.06	0.44	20.4	394	566	15.9	<0.01	<0.1	5.36	0.49	22.95
BH26	HS&G	520		7.7	71.6	13.4	18.4	1.88	<0.3	0.03	0.05	50.9	159	21.2	75.6	0.011	<0.1	11.5	1.42	9.71
River Trent		424		8.0	54.6	10.8	19.7	5.70	<0.3	0.13	0.01	29.6	135	63.1	18.4	0.20	0.85	8.23	0.76	15.07

*Where O2 values missing is because of a faulty probe.

Table 17: Major anions and cations found in groundwater of the shallow sand and gravel aquifer taken in Feburary 09.

	Sediment	Conductivity	O_2	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	Cl^-	Tot Fe	Mn	HCO_3^-	SO_4^{2-}	NO_3^-	NO_2^-	HPO_4^{2-}	NPOC	Org N	Org C:N
		$\mu s\ cm^{-1}$	$mg\ l^{-1}$												$mg\ L^{-1}$					
BH4	HP S&G	663	8.9	7.3	81	27	10	2.2	<0.3	66	0.04	0.011	66	56	153	<0.02	<0.1	11.0	1.24	8.8
BH5	HP S&G	506	1.1	7.1	63	10	26	7.6	<0.3	31	0.03	0.019	130	68	56	<0.02	<0.1	5.0	0.8	6.3
BH6	HP S&G	566	8.3	7.6	92	10	20	1.4	<0.3	34	0.02	<0.002	197	29	80	<0.02	0.42	3.6	0.65	5.2
BH7	All S&C	449	2.9	7.5	70	16	11	2.1	<0.3	20	0.02	0.03	223	28	9	0.03	<0.1	3.0	0.07	42.3
BH12	All S&C	978		7.8	162	40	14	1.9	<0.3	41	0.05	0.23	312	233	41	0.08	<0.1	3.6	0.13	28.0
BH13	HS&G	836		7.8	120	47	10	1.8	<0.3	33	0.05	<0.002	309	133	66	<0.02	0.18	6.6	0.16	42.2
BH14	HP S&G	834		7.3	103	17	33	12.5	<0.3	118	0.03	0.01	68	61	165	<0.02	0.14	5.4	BD	-
BH19	All S&G	913		7.6	145	34	19	2.8	<0.3	27	0.04	<0.002	392	162	24	<0.02	<0.1	2.9	BD	-
BH20	All S&G	901		7.5	135	30	19	1.2	<0.3	81	0.04	0.02	129	216	58	<0.02	<0.1	1.2	0.66	1.7
BH21	HP S&G	715		7.5	103	25	12	1.9	<0.3	54	0.03	<0.002	123	115	120	<0.02	0.11	1.6	BD	-
BH22	All S&G	762		7.8	124	29	15	2.1	<0.3	36	0.04	0.36	317	136	10	0.05	<0.1	6.8	0.12	57.7
BH24	HP S&G	1484		7.8	240	95	19	28	<0.3	31	0.129	0.55	422	601	19	0.05	<0.1	4.8	BD	-
BH26	HS&G	500	11.6	7.8	79	13	13	1.7	<0.3	29	0.03	<0.002	157	22	90	<0.02	0.23	8.6	0.55	15.6
River Trent		655		8.1	85	17	34	5.7	<0.3	60	0.07	0.02	195	94	26	0.11	0.56	5.8	0.43	13.4

DON concentrations were generally less than 1 mg l^{-1} and were often only just above the limits of detection, especially in Mar 09. The DON values found in the aquifer were of a similar magnitude to those reported by Lapworth *et al.* (2008) in shallow groundwater in a moorland catchment in Wales. However, in comparison to the results of Lapworth *et al.* (2008) who found that DON was the largest component of N in groundwater of the largely natural moorland catchment, in our agriculturally dominated area, nitrate concentrations are many times greater. In natural ecosystems it is expected that DON can make up a significant component of nitrogen lost from watersheds (Perakis & Hedin, 2002).

Inorganic C concentrations were generally between 60 and 350 mg l^{-1} C as HCO_3, whereas DOC concentrations ranged between 0.5 and 11.5 mg l^{-1} at the three sampling dates. There were generally poor relationships found between DOC and DON, although a slightly better relationship was found for October 08 than Feb 09 (Figure 29). Pearson correlation co-efficients for these relationships were r = 0.51 for October 08 and r = 0.39 for February 09. Figure 30 shows the relationship between DOC concentrations and C:N values. In October 08, for the sand and gravel soils there was negative correlation whereby higher C:N ratios were found with lower concentrations of organic C. However two outliers existed and both of these came from the alluvial clay, silt and sand soils and sediments. This suggests that there may have been a parent material effect on the cycling of C. In Feb 09 no relationship between DOC and C:N was found. There were negative correlations between DON and the C:N ratio (Figure 31). In October 08, the correlation (Pearson correlation) was r = -0.72 and in Feb 09 r = -0.78 suggesting that greater organic N concentrations are present when the C:N ratio is generally lower. Low organic C:N ratios in the waters would suggest that the DOM has been released from recently decomposed plant or microbial material. Overall relationships between organic C and N are stronger at the October sampling suggesting that a component of easily leached DOM may have been leached into the groundwater after the harvest (i.e reincorporated straw).

Figure 29: Relationship between DOC and DON in groundwater at Shelford at (i) October 08 and (ii) Feb 09.
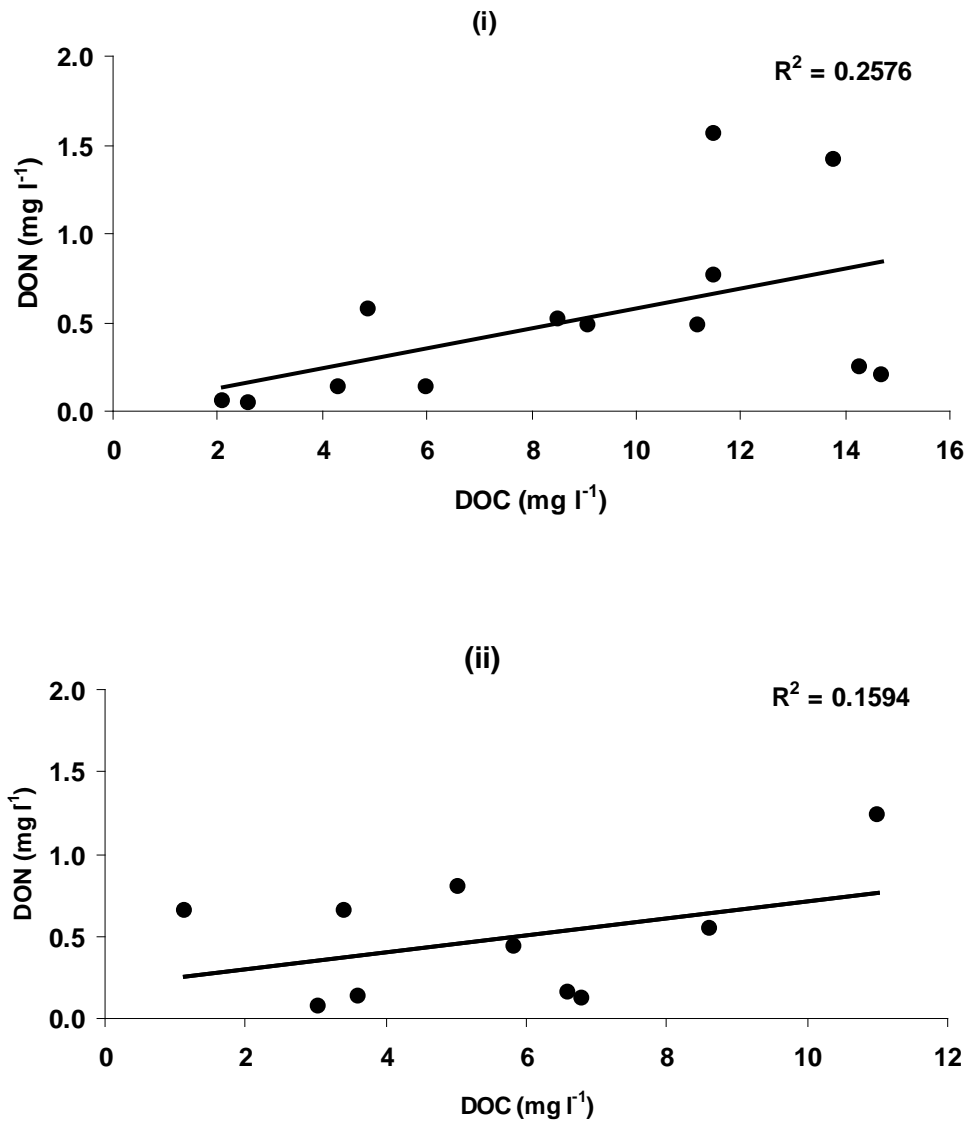
Figure 30: Relationship between Org C and C:N in groundwater in (i) Oct 08 and (ii) Feb 09.
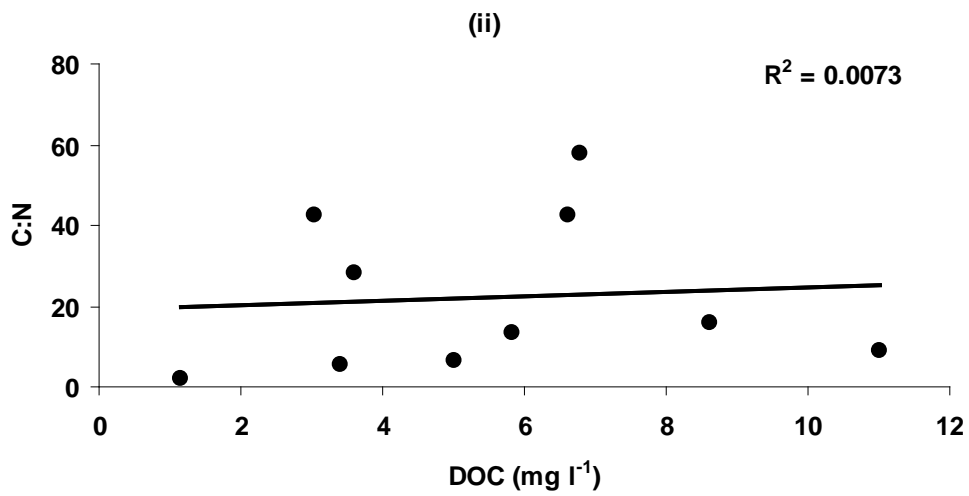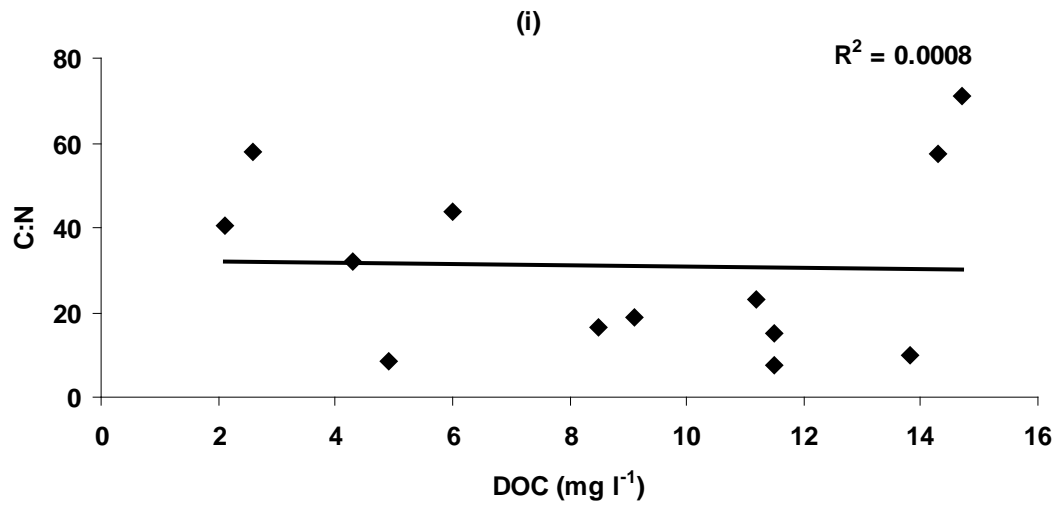
Figure 31: Relationship between Organic N and C:N in groundwater at Shelford in (i) October 08 and (ii) February 09.

(i)

$y = 12.422x^{-0.5658}$

$R^2 = 0.6873$

(ii)
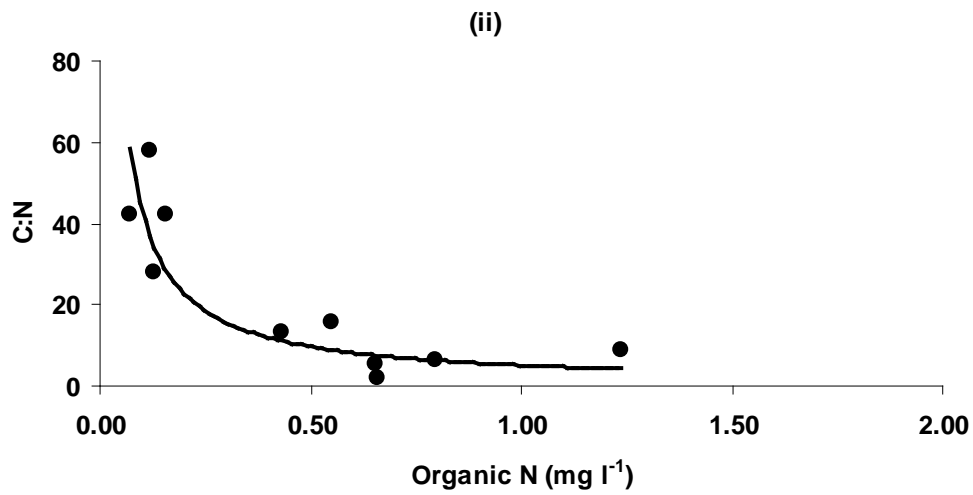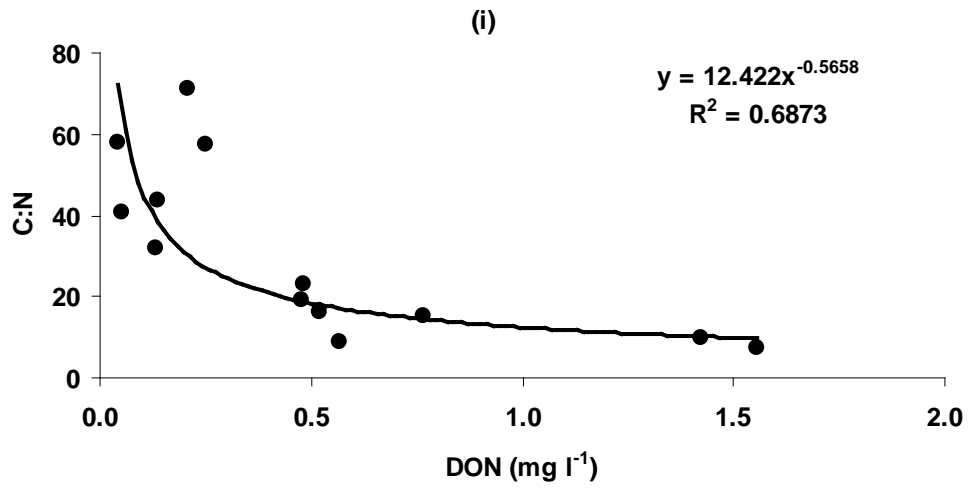
3.6 SPECIATION OF DISSOLVED ORGANIC MATTER (DOM) IN TOPSOILS AND GROUNDWATERS

3.6.1 Introduction

Dissolved Organic Matter (DOM) is largely composed of humic acids, fulvic acids, carbohydrates and proteins from the breakdown of plant and other biota such as bacteria. It is largely composed of Carbon, Nitrogen, Sulphur and Hydrogen and exists in molecules of different size. The elemental ratios of the elements are an indication as to the degree of decomposition the DOM has undergone. The characteristics of DOM in soils and that entering water courses from terrestrial ecosystems is important as its composition will determine the degree of further microbial processing it may undergo within the water body, including processes such as microbial uptake, retention and degassing (CO_2).

Results from the initial survey of different top-soils in this study, indicates that both organic C and N concentrations (0-30 cm) are strongly related to the amount of clay in the soil. This agrees with previous work that suggests that OC is protected by clays through aggregation of particles (Guggenberger & Kaiser, 2003). In this part of the study we are interested in whether the (i) composition of the soluble and exchangeable DOM that can be extracted from soils differs between soil types and whether physical properties that protect organic matter in soils such as % clay have an influence and (ii) whether there was a difference in DOM characteristics between soils, groundwater and the river water of the river Trent.

The technique that we used to assess the quality and composition of DOM was that of Laser Fluorescence spectroscopy (LF). The LF method has been used to understand the source and composition of DOM in marine, surface ground and terrestrial waters. Recently, it has also been used to discriminate between different sources of DOM within different water flow pathways in aquifers (Lapworth *et al.* 2008). It works by producing high resolution matrices of excitation-emission wavelengths that represent the 3D fluorescence landscape of a particular sample. For example, Lapworth *et al* (2008) used LF to examine pollution in two locations of the Sherwood Sandstone aquifer in England. They showed decreasing fulvic-like intensities of DOM with depth in the aquifer. Measurement of tryptophan-like fluorescence centres were used to examine the possible rapid routing of waters that provided evidence of slurry application. A second example is that of Wilson & Xenopoulous (2009) who showed that the nature of DOM in 34 watersheds was related to agricultural land use, nitrogen loading and wetland loss. They found that the degree of structural complexity of DOM decreased as the ratio of continuous cropland to wetland increased. Concomitantly, the amount of bacterially produced DOM increased with agricultural landuse.

Four different indices of general DOM structure were applied in our study:-

- *Fulvic-like intensities* – Fulvic-like intensities are reported as mean intensities from the following region Ex330 nm, Em410-440 nm.

- *Fluorescence Index (FI)* - The FI is used to differentiate between microbial and terrestrial sources of DOM. It shows strong correlation, particularly with per cent aromaticity and degree of structural conjugation. As FI decreases it suggests a more fulvic-acid and less microbial input (Lapworth *et al*. 2008).

- *Humification Index* - The humification index is associated with the condensing of fluorescing molecules and lower H/C ratios in the DOM. Increasing Humification Index values indicate increasing humicity.

- **β/α -** The ratio of two fluorescing components (β/α). This ratio is an indicator of autochthonous inputs and provides an indication of the relative contribution of recently produced DOM. (β represents more recently derived DOM and α represents highly decomposed DOM). Therefore the ratio increases with increasing autochthonous carbon production.

3.6.2 Materials and methods

Please see Section 2.8.3

3.6.3 Results

3.6.3.1 DOM CHARACTERISTICS OF THE SOIL

Table 18 shows the mean (n = 4) results for each of the measured components. Significant differences were found between the different soil types for % Clay, % C, % N and C:N ratios as determined by one way analysis of variance followed by a Least Significant Difference test to determine where significant differences existed ($P<0.05$).

After extraction with 2M KCl, significant differences were found in NO_3-N between soil types with the Head over sand soils showing the highest concentration of NO_3-N. The nitrate concentrations in the other soils were not significantly different. The Head over sand also had significantly higher concentrations of NH_4-N. The likely explanation for this is that the soils of this domain, being sited at the break of a slope, are subject to runoff from the slope leading to increased NO_3^- concentrations. The increased ammonium concentrations could have been due to greater microbial populations existing because of the greater NO_3-N availability leading to greater mineralization of organic forms of N back to ammonium, although this wasn't measured. Total Dissolved Nitrogen showed that the Head over sand values were significantly ($P < 0.05$) higher than the other soils which showed no significant differences.

Concentrations of DOC in the 2M KCl extracts varied between 6.9 to 14.2 mg l^{-1} whilst DON values ranged from 0.69 to 1.86 mg l^{-1}. The DON pools were found to represent a sizeable concentration of the total N pool in the soils. The results obtained here between the different soils show that the DOC and DON pools are highly variable and are probably a function of historic plant additions and microbial populations. There were some significant differences between soil types found. Jones & Willett (2006) also found highly variable DOC and DON contents between soils without any one factor being the obvious cause.

Two protein like molecules (Tryptophan and Tyrosine) and 4 DOM indices were assessed from the laser fluorescence analysis. There were significant differences in the characteristics determined using laser fluorescence between the soil types and these are shown in Table 18. For most of the LF variables there were only small differences in RU, but significant differences between soil types existed, demonstrating the complexity of DOM pools in soils. There were several results that showed a greater difference between soil types. For example, the Cotgrave Sandstone and HPP S&G had greater RU of Tryptophan and Fulvic like (RU) than the other soils. The HPP S&G also had a much greater HI index, suggesting greater humicity of the DOM extracted.

A correlation matrix (not shown) between all the measured variables in the experimental dataset was constructed (n=36). The following were the major correlations found (Figure 32). As in the original study of the soils in the catena (Section 3.2), a positive correlation between both organic C and N and clay content was found. Values of the Pearsons correlation co-efficient (r) between % Clay and organic C and organic N were 0.72 and 0.74 respectively. Soil C and soil organic N were correlated with a positive correlation value of r = 0.97. Soil C:N ratio was positively correlated with % clay (r = 0.61) suggesting that with increasing clay content more organic C is being held within the soil. This may be due to an increase in lignin type substances being present in the soils. However, there appeared to be no relationship between soil physical properties e.g. % clay content and the amount of soluble or exchangeable DOC and DON extracted. There was also no relationship between % clay or the indices measured using the laser fluorescence methodology.

Within the soluble and exchangeable pool of DOM extracted using the 2M KCl extracted there were several strong correlations. Figure 33 shows a strong correlation between DOC and Fulvic-like intensity (r=0.64). This is not surprising as many molecules within the DOM will fluoresce and was also found by Lapworth *et al*. (2008). As DOC increased it was found that the Tryptophan-like component increased (Figure 33). A correlation of r = 0.55 was found and a likely cause is because C molecules will be found in Trytophan. Additionally higher DOC concentrations could suggest a greater food source for bacteria, increasing the populations found within the soils. However this was not examined in this work. Figure 33 shows the very strong correlation between the fulvic-like component and the tryptophan-like component (r = 0.95), a result of fulvic-like molecules making up a large proportion of the DOM and C molecules also being found in the Trytophan-like component. A possible reason why an improved correlation may exist between the Fulvic-like component and Tryoptophan is that the DOC measurement may include other carbon sources including sugars and root exudates such as oxalate. Thus a link may exist between the products of microbial degradation (Fulvics) and a protein largely originating from bacteria. It may also be possible that any protein, containing DON, released from plant material will be rapidly assimilated by soil bacteria.

When considering the extracted DOM quality through the various indices described previously (Section 3.6.1) it was found that DOC was negatively correlated with the β/α ratio (r = -0.52) (Figure 33). This suggests that there is an increase in highly decomposed carbon molecules in the DOM as DOC increases. This is confirmed by the HI index that was found to increase as the fulvic-like component increases (r = 0.58). As previously shown there was an increase in the fulvic-like component with increasing DOC. Thus when examining the quality of the DOM extracted in the 2M KCl extract the two major findings were that there was an (i) increase in the tryptophan protein compounds as the DOC increased suggesting a link between the amount of carbon and a food source for bacteria and (ii) that as DOC concentrations increased a greater fulvic-like component, possessing greater humified properties was found.

Table 18: Mean values and significant differences between DOM properties of soils sampled on different parent material domains. Statistical analysis was performed by one way analysis of variance followed by LSD. Significant differences are at P<0.05.

Soil parent material	Soil Type	Clay	C	N	C:N	DOC	TDN	NO_3-N	NH_4-N	DON	Tryptophan	Tyrosine	Fulvic-Like	FI	β/α	HI
		%	%	%		mg l⁻¹	mg l⁻¹	mg l⁻¹	Mg l⁻¹	mg l⁻¹	(RU)	(RU)	(RU)			
Edwalton		6.6[a]	1.23[a]	0.16[a]	7.6[a]	9.3[ab]	3.0[a]	0.4[a]	0.78[a]	1.86[c]	0.64[a]	0.35[a]	1.59[b]	1.34[a]	0.47[ab]	8.49[ab]
Cotgrave		8.6[ab]	1.85[bc]	0.18[abc]	10.1[bc]	11.3[b]	4.0[a]	1.44[a]	1.03[abc]	1.74[b]	1.20[b]	0.35[a]	2.79[c]	1.36[a]	0.52[ab]	9.74[ab]
Gunthorpe	Worcester	14.1[c]	2.01[cd]	0.20[a]	9.9[bc]	9.1[ab]	3.4[a]	1.66[a]	0.80[a]	0.86[a]	0.44[a]	0.30[a]	1.05[ab]	1.40[ab]	0.54[abcd]	9.38[ab]
Head over sand		9.5[b]	1.67[b]	0.17[ab]	9.6[c]	10.2[ab]	9.3[c]	7.55[c]	1.15[bc]	1.68[bc]	0.62[a]	0.31[a]	1.60[bc]	1.51[c]	0.59[cd]	9.95[b]
Alluvial Sand, silt & clay		14.4[c]	2.11[c]	0.21[b]	9.9[bc]	10.7[b]	4.05[a]	2.38[a]	0.89[ab]	0.69[a]	0.70[a]	0.31[a]	1.71c	1.43[ab]	0.52[abc]	9.27[ab]
Holmepierrepoint S&G		8.7[b]	2.38[d]	0.22[c]	10.7[cd]	14.2[c]	4[a]	0.84[a]	1.07[abc]	1.96[c]	1.04[b]	0.33[a]	2.73[c]	1.32[a]	0.46[a]	12.41[c]
Alluvial Sand, silt & clay		14.3[c]	3.18[e]	0.28[d]	11.4[d]	7.3[a]	2.75[a]	0.21[a]	0.83[ab]	1.73[bc]	0.54[a]	0.31[a]	1.21[abc]	1.38[a]	0.55[bcd]	7.57[ab]
Alluvial Sand, silt & clay		17.5[d]	3.04[e]	0.29[d]	10.6[cd]	6.9[a]	2.8[a]	0.21[a]	0.85[ab]	1.68[bc]	0.46[a]	0.37[a]	0.99[a]	1.50[bc]	0.61[d]	7.29[a]
Head over sand		9.14[b]	1.54[ab]	0.17[a]	8.9[b]	8.5[ab]	6.8[b]	5.00[b]	1.26[c]	0.84[ab]	0.58[a]	0.28[a]	1.33[abc]	1.53[c]	0.56[bcd]	7.37[a]
LSD (P<0.05)		**2.00**	**0.43**	**0.04**	**1.16**	**3.33**	**2.31**	**2.26**	**0.33**	**0.98**	**0.26**	**0.10**	**0.55**	**0.10**	**0.08**	**2.40**

Differences in superscript letters signify significant differences between samples as calculated using Least Significant Differeces (*P* < 0.05)

Figure 32 Relation ship between (i) %C and % Clay, (ii) % N & % clay, (iii) soil C v soil N, (iv) Soil organic C and C:N and (v) soil organic N and C:N.
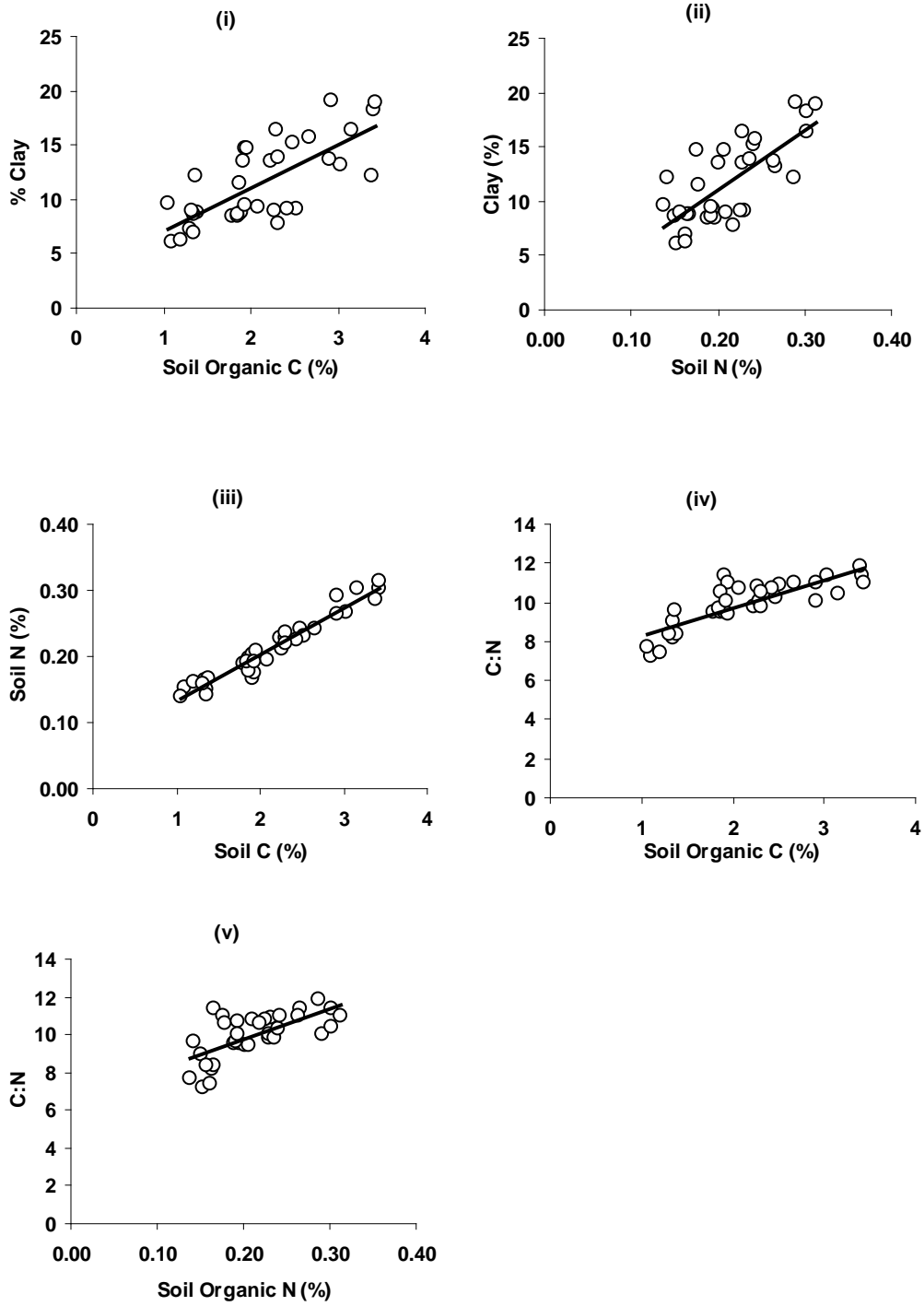
Figure 33: Graphs showing relationships between DOM properties in soil extracts
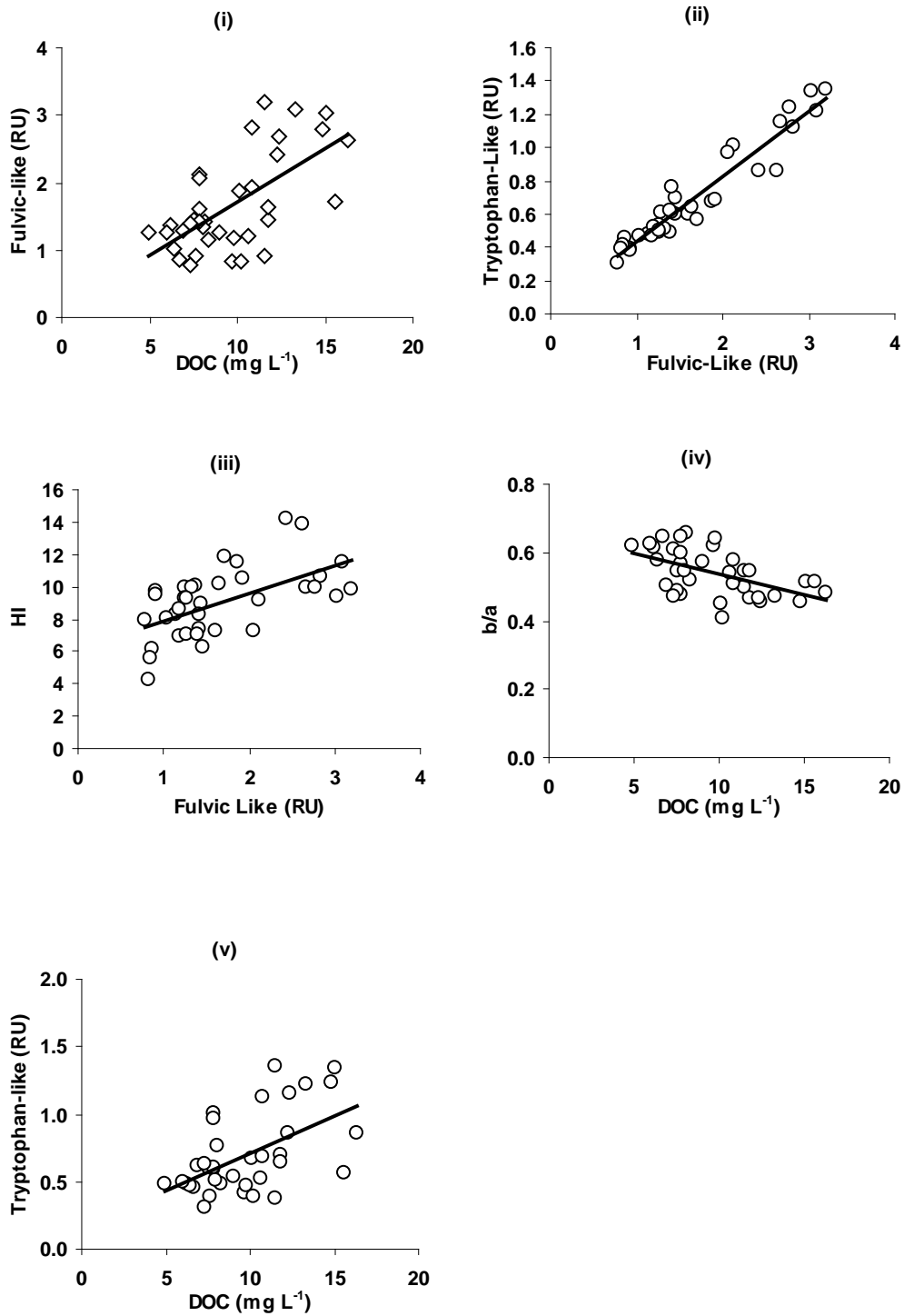
3.6.3.2 DOM PROPERTIES IN GROUNDWATER

DOM properties were measured by laser fluorescence on the October 08 and February 09 groundwater and River Trent samples. Results are shown in Tables 19 and 20 and Pearson correlation coefficients are reported in Table 21.

Table 19 Results of laser fluorescence analysis on groundwater and River Tent samples taken in October 08

	DOC mg l^{-1}	TDN mg l^{-1}	DON mg l^{-1}	Fulvic-like RU	Tryptophan-like RU	Tyrosine-like RU	FI	b/a	HI
BH4	11.5	12.7	1.55	3.76	1.09	0.10	1.63	0.66	18.65
BH5	4.9	11.4	0.56	2.38	0.63	0.05	1.73	0.69	18.69
BH6	6.0	23.4	0.13	0.92	0.30	0.04	1.59	0.65	14.94
BH7	14.3	4.1	0.25	2.76	0.76	0.10	1.58	0.54	20.35
BH12	14.7	1.01	0.21	2.62	0.64	0.29	1.50	0.56	16.73
BH13	8.5	15.6	0.51	0.58	0.25	0.18	1.68	0.72	6.72
BH14	7.2	41.1		1.29	0.47	0.27	1.66	0.70	9.47
BH19	4.3	7.5	0.13	1.14	0.40	0.19	1.49	0.66	11.70
BH20	2.1	13.7	0.04	0.44	0.15	0.20	1.41	0.61	6.56
BH21	2.6	22.75	0.03	0.65	0.21	0.19	1.65	0.69	8.60
BH22	9.1	11.3	0.47	1.18	0.35	0.06	1.66	0.64	16.83
BH24	11.2	4.08	0.48	2.36	0.63	0.17	1.59	0.64	19.01
BH26	13.8	1.4	1.41	4.74	0.97	0.18	1.47	0.55	24.65
River Trent	11.5	0.8	0.77	2.70	0.84	0.19	1.35	0.55	14.04

Table 20 Results of laser fluorescence analysis on groundwater and River Tent samples taken in February 09

	DOC mg l^{-1}	TDN mg l^{-1}	DON mg l^{-1}	Fulvic-like RU	Tryptophan-like RU	Tyrosine-like RU	FI	b/a	HI
BH4	11.0	35.83	1.24	4.06	1.00	0.05	1.67	0.65	22.8
BH5	5.02	13.4	0.81	2.16	0.53	0.05	1.73	0.67	20.57
BH6	3.41	18.8	0.65	1.24	0.33	0.04	1.59	0.70	21.45
BH7	3.04	2.02	0.07	1.32	0.31	0.05	1.31	0.57	22.67
BH12	3.61	9.41	0.13	1.18	0.37	0.08	1.58	0.61	19.49
BH13	6.61	15.0	0.16	0.61	0.18	0.05	1.72	0.63	20.41
BH14	5.39	37.28		2.01	0.64	0.40	1.65	0.65	12.23
BH19	2.91	5.2		0.99	0.31	0.05	1.69	0.72	17.01
BH20	1.15	13.7	0.66	0.35	0.13	0.06	1.42	0.69	13.14
BH21	1.59	25.08		0.57	0.17	0.06	1.60	0.74	18.4
BH22	6.79	2.28	0.12	1.09	0.36	0.07	1.49	0.71	17.61
BH24	4.82	4.28		1.82	0.49	0.06	1.50	0.66	23.02
BH26	8.63	20.88	0.55	3.31	0.76	0.06	1.34	0.53	29.57
River Trent	5.82	6.34	0.43	1.88	0.64	0.13	1.46	0.55	14.26

Table 21: Summary of Pearson correlation coefficients for DOM components in Shelford groundwater samples taken in October 08 and February 09.

	October 08	February 09
DOC v Fulvic-like	0.75	0.82
DOC v Tryptophan	0.74	0.82
Fulvic like v Tryptophan	0.96	0.99
DON v Fulvic like	0.72	0.67
DON v Tryptophan	0.70	0.66
DOC v b/a	-0.65	-0.39
DOC v HI	0.71	0.49
Fulvic like v HI	0.87	0.56
Trytophan v HI	0.82	0.65
FI v B/a	0.65	0.51

Correlation matrices were undertaken on the groundwater samples and Table 21 summarises the major correlations. There were strong linear correlations between DOC and Fulvic-like RU of 0.75 and 0.82 in October 08 and February 09 respectively (Figure 34). Similarly there were

correlations between DOC and Tryptophan-like RU of 0.74 and 0.82 in October 08 and February 09 respectively (Figure 34). However, there was a greater correlation between Fulvic-like substances and Tryptophan of 0.96 and 0.97 in October 08 and February 09 respectively. This would suggest that by discounting some of the sources of DOC (e.g. carbohydrates), an improved relationship is found between fulvic-like material and Trypotophan. Tryptophan (an amino acid) is produced by micro-organisms and plants and therefore it may be expected to increase with DOC, as DOC is used as a potential food source by micro-organisms. The greater correlation with fulvic-like RU suggests that this tryptophan may come from a bacterial source linked with the production of fulvic-like substances.

Figure 34: Graphs showing correlations between (i) DOC and Fulvic-Like RU, (ii) DOC and Tryptophan and (iii) Fulvic-like RU and Tryptophan in groundwater sampled at Shelford in October 08 and February 09.
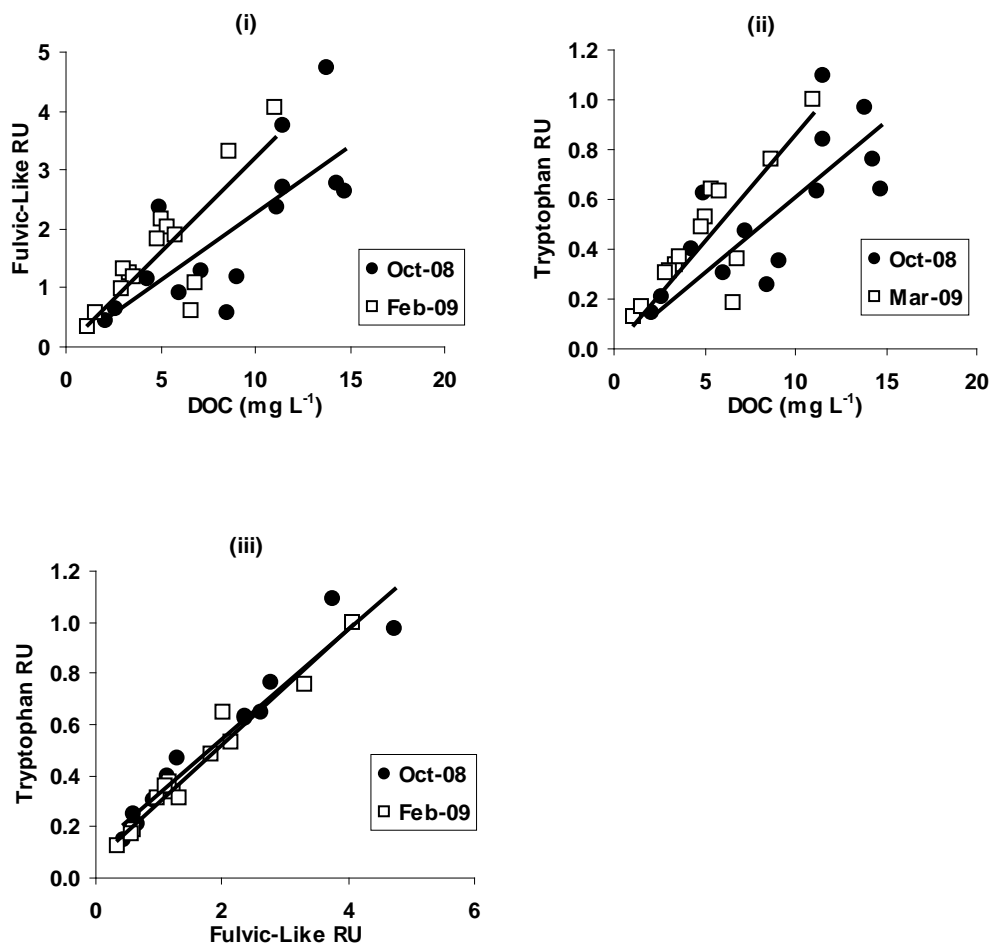
DON was found to show some correlations with DOM properties identified by laser fluorescence (Figure 35). The increase in DON as fulvic like intensity increases may reflect the correlation between tryptophan and Fulvic-like substances as the DON present may make up a large part of the Tryptophan (amino acids) with microbial activity being a source.

Figure 35: Graphs showing relationships between (i) DON and Fulvic-Like RU and (ii) DON and Tryptophan-Like RU.
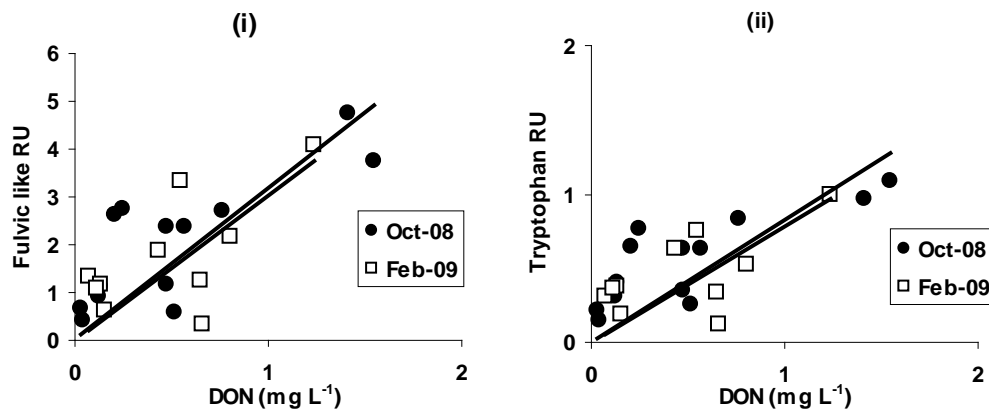
There appeared to be a difference in DOM properties that were correlated with DOC between the October 08 and February 09 samplings. In Oct 08 there were improved correlations between (i) DOC v β/α , (ii) DOC v HI, (iii) Fulvic like v HI and (iv) Tryptophan v HI (Table 21 & Figure 36). These results suggest that in October 08, the groundwater may be less heterogenous than in February 09. This may reflect the time lag for new DOM inputs to reach the groundwater after the return of harvest residues, the previous summer, and the mixture of substances contained therein.

Figure 36: Graphs showing relationships between (i) DOC and β/α, (ii) DOC and HI, (iii) Fulvic-Like RU and HI, and (vi) Trytophan-Like RU and HI
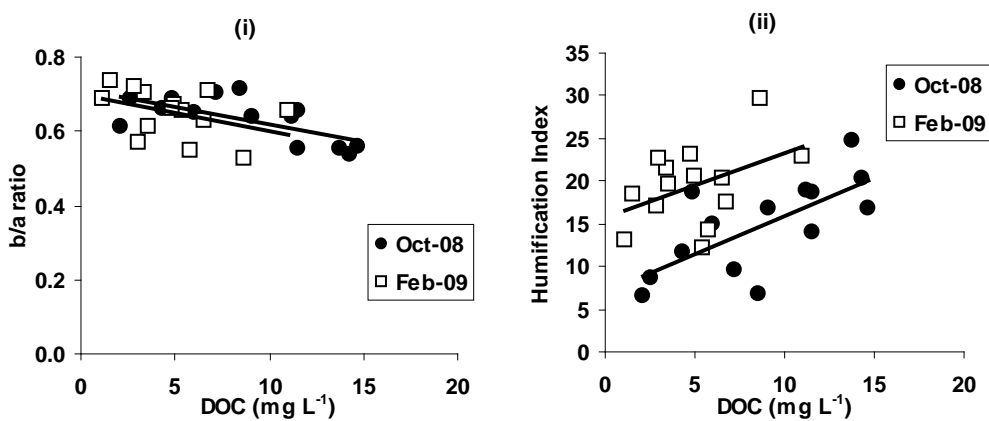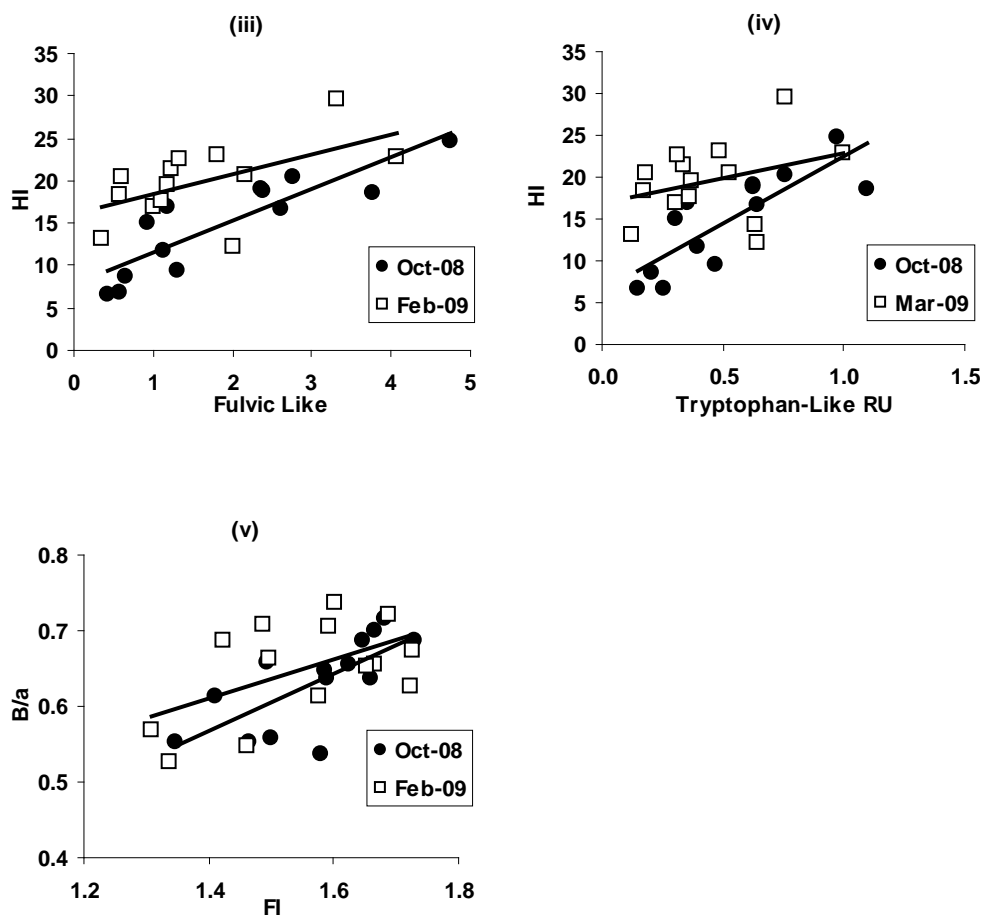
3.6.3.3 COMPARISON OF DOM PROPERTIES OF SOILS AND GROUNDWATER

Table 22 shows the mean and SD of the DOM in the soil and groundwater samples along with the River Trent samples. The SD of the mean values in the groundwater were generally quite high, especially for the HI, reflecting the range of different sources of DOM as well as the speed of infiltration into the different sediments that make up the shallow aquifer. Previous results (Section 3.1.3) have demonstrated the large range of K_{sat} values found in the aquifer sediments. The transport rate of DOM from soil to groundwater is likely to have a major effect on the degree of microbial processing that the DOM may have undergone. For example, in those areas with greater gravel contents the infiltration rate will be much greater, thus the transfer of DOM to the groundwater would be quicker and subsequently may not be as decomposed as DOM that has a slower passage through the top-soil. Figure 37 shows the complete dataset of soil, groundwater and river DOM properties determined using LF plotted against DOC concentration.

Figure 37(i) shows that the Fulvic-like component of the DOM in the groundwater has a greater range of values than it does in the soil, suggesting a greater range of input products (a result of different transport rates of DOM) from the soils as well as there being a possibility of further decomposition of the DOM once in the groundwater system. Soil DOM will have a large component of fresh plant material (root exudates, harvest residues) probably dominating the measurement. Figure 37(ii) shows that the humification index (HI) which is associated with the condensing of fluorescing molecules as a result of a lower H/C ratio was generally found to be higher in the groundwater. This was particularly evident for the measurements taken in Feb 09. It is likely that the groundwater samples taken in Oct 09 included greater amounts of fresh DOM as

a result of harvest residues being transported to the groundwater. However, the greater HI of the DOM in the groundwater confirms the generally higher fulvic-like (RU) component of DOC found in the groundwater, particularly those taken in Feb 09.

Figure 37(iii) shows that there was generally a slightly higher FI in the groundwater DOM than in the soil. The FI is used to differentiate microbial and terrestrial sources of DOM as the FI increases with greater autochonthonous carbon production. Hence, in groundwater there would appear to be a slightly greater proportion of DOM derived from microbial sources. Figure 37(iv) shows the β/α ratio and provides an indication of inputs of microbial produced DOM with the ß component being inputs from autochonthonous bacteria and the α component being terrestrial DOM. Results follow that found for the FI index, suggesting that proportionally there is a greater input of microbial DOM in the groundwater.

To assess whether there were significant differences in the properties of the DOM between the soil and groundwater two tailed T-Tests assuming unequal variances were undertaken (Table 23). There were significant differences ($P<0.05$) in FI, HI and β/α between the DOM properties of the soil and groundwater. The inference from the LF results are that the DOM in the groundwater contains a greater proportion of microbial DOM, but the older DOM in the groundwater is more decomposed, thus having a higher fulvic-like RU, FI and HI, than the soils. The FI and β/α indexes do not consider how decomposed the non-bacterial DOM is, therefore the argument is coherent for the results found from the β/α index.

The LF analysis also assesses two protein-like molecules, Tryotophan and Tyrosine, both of which were found to be higher in the soil than the groundwater. This is likely a result of greater microbial populations in the soil than the groundwater. However, the tyrosine results showed the least difference between soil and groundwater of all the properties measured. A further interesting feature of the results is that those samples taken from the River Trent generally had more soil like DOM properties than groundwater properties. This suggests that a major contribution to the river DOM was via the soil. Two processes are likely, these being through land drainage and from soil erosion, which may include river bank erosion.

Table 22: Comparison of DOM properties in soil extracts, groundwater and the River Trent

Sample		Fulvic like (RU)	Tryptophan like (RU)	Tyrosine-like (RU)	FI	β/α	HI
Soil	Mean	1.09	0.69	0.33	1.42	0.54	9.06
(n=36)	SD	0.67	0.26	0.03	0.08	0.05	1.63
Groundwater Oct 08	Mean	1.91	0.5	0.2	1.6	0.60	14.80
(n=14)	SD	1.29	0.29	0.08	0.09	0.06	5.72
Groundwater Feb 09	Mean	1.59	0.43	0.08	1.56	0.66	19.87
(n=14)	SD	1.05	0.25	0.09	0.14	0.07	4.58
Trent Oct 08		2.7	0.84	0.19	1.35	0.55	14.00
(n=1)							
Trent Feb 09		1.87	0.63	0.12	1.46	0.54	14.25
(n=1)							

Table 23: Results of two-sample T tests assuming unequal variances to identify significant differences (P<0.05) between DOM characteristics found in soil and against those properties in groundwater sampled at October 08 and February 09.

Variable	October 08			February 09		
	T-value	*P*-value	DF	T-value	*P*-value	DF
Fulvic-Like RU	-0.62	0.547	14	0.24	0.814	15
Florescence Index RU	-5.32	0.000	21	-3.26	0.005	16
B/a	-4.97	0.000	24	-5.75	0.000	23
Humification Index	-3.56	0.004	13	-8.34	0.000	13
Trypotophan RU	1.76	0.093	21	3.11	0.005	24
Tyrosine RU	6.82	0.000	18	8.54	0.000	16

Figure 37: Comparison of (i) DOC v Fulvic-like, (ii) DOC v HI, (iii) DOC v FI and (iv) DOC v β/α

(iv)

Legend:
- Groundwater Oct 08
- Groundwater Feb 09
- Soils
- Trent Oct 08
- Trent Feb 09

b/a vs DOC (mg L^{-1})
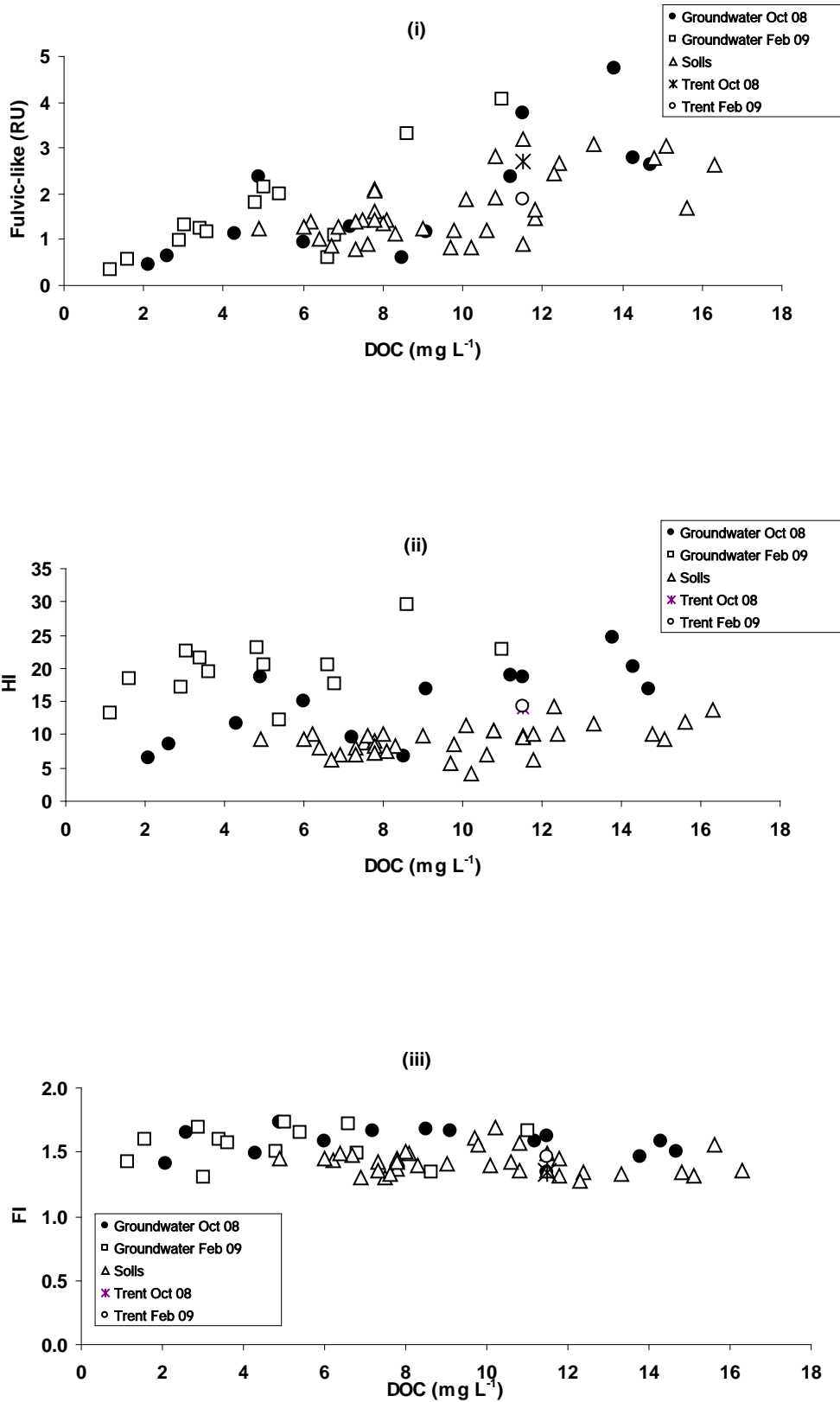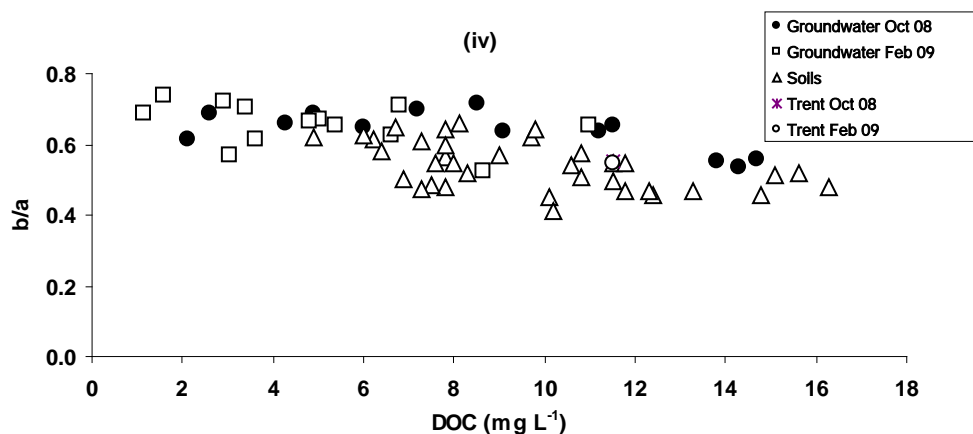
3.6.4 Laser Fluorescence Conclusions

The use of laser fluorescence analysis has demonstrated that there are differences in the DOM characteristics in the soil-groundwater-river system of the study site. The similarities in the soil and Trent DOM characteristics would suggest that there may be a common source either through the erosion of soil or the leaching of DOM to the rivers via surface waters. The leaching of groundwaters may be through drain systems. Whilst there may be proportionally a greater input of bacterial DOM in the groundwater, the old DOM would appear to be of a greater fulvic nature suggesting that it has undergone greater humification.

4 Discussion

The results described provide a snapshot of the quantities and speciation of residual N & C found in the soils, parent materials and groundwater of a largely arable landscape after long-term nitrogen use. The results, for nitrate in particular, represent the legacy of different political and socio-economic policies of the last 60 years outlined in the introduction. In this discussion we assess the likely future fate of nitrogen stored in the soils, sediment and groundwater of the study area.

4.1 THE FATE OF N AND C IN THE NON-AQUIFER SOILS AND SEDIMENTS

Long term management of soil in respect to fertiliser applications eventually leads to pseudo-equilibriums being reached between microbial interactions, crop uptake and leaching (Addiscott, 2005), with excess N being lost from the system largely as NO_3^- or as DON. Therefore it is expected that continued agricultural management under similar conditions will result in organic C and N concentrations that stay broadly at similar concentrations in the top soil, largely due to the soils capacity to hold organic C & N. The major mobile species of N is nitrate, and evidence suggests that this could be very slowly increasing in concentration at depths below the rooting zone; an indication of N saturation. One of the major pathways will be through preferential flow, especially in the soils of the Gunthorpe member which are prone to shrink-swell due to the high smectite content. Therefore, the long term question is whether the nitrate will stay below the rooting zone and continue increasing in concentration or undergo denitrification. For soils with high clay content, such as those formed from the Edwalton and Gunthorpe Triassic mudstone formations, conditions of poor drainage leading to water saturated and anaerobic conditions required for denitrification are common. This is revealed in the soil survey of the area where indications of gleying are common (Palmer, 2007). For denitrification, saturated conditions are

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required as this reduces O_2 diffusion through the soils. Wilson and Bouwer (1997) suggest that denitrifiers require extremely low concentrations of dissolved O_2, (<0.4 mg l^{-1}). In the non-aquifer soils and sediments of this study there appears to be a slight build up of NO_3^- at depths >120cm suggesting that factors other than saturated soil may influence the degree of denitrification. One factor that is likely to be controlling the denitrification process is the presence of a suitable carbon substrate in the subsoil (Byre et al. 2001). The decrease of NO_3^- in the 30-120 cm root zone found in the Gunthorpe, Edwalton and Cotgrave formations suggest that conditions may be suitable for denitrification in this depth range as the organic molecules exuded from the roots will provide a suitable carbon supply for the denitrifiers. The roots also consume O_2 which is also critical for inducing the anaerobic conditions required for denitrification. Below this rooting zone, the increases in NO_3^- found suggest that a long, slow accumulation and subsequent storage is occurring as a result of the low carbon concentrations and the exponentially decreasing populations of denitrifying bacteria found as depth increases (Luo *et al.*, 1998; Paramasivam *et al.*, 1999). In these non-aquifer soils and parent materials approximately 25 - 50 kg^{-1} ha^{-1} of NO_3-N exists within the profile to depths of ~2m. This figure is between approx 35-50% of the fertiliser N typically applied to arable crops (Table 1) within the UK at present. If we assume for the Edwalton, Cotgrave and Gunthorpe formations that at depths below ~120 cm little denitrification occurs, then Figure 36 shows that approximately 50 % of the NO_3-N stored in the soil profiles may only slowly be de-nitrified as all the conditions required (Bacteria population size, NO_3^-, C and anaerobic conditions) are unavailable.

Figure 38: Percentages of NO$_3$-N potentially available for de-nitrification in non aquifer soils at Shelford.
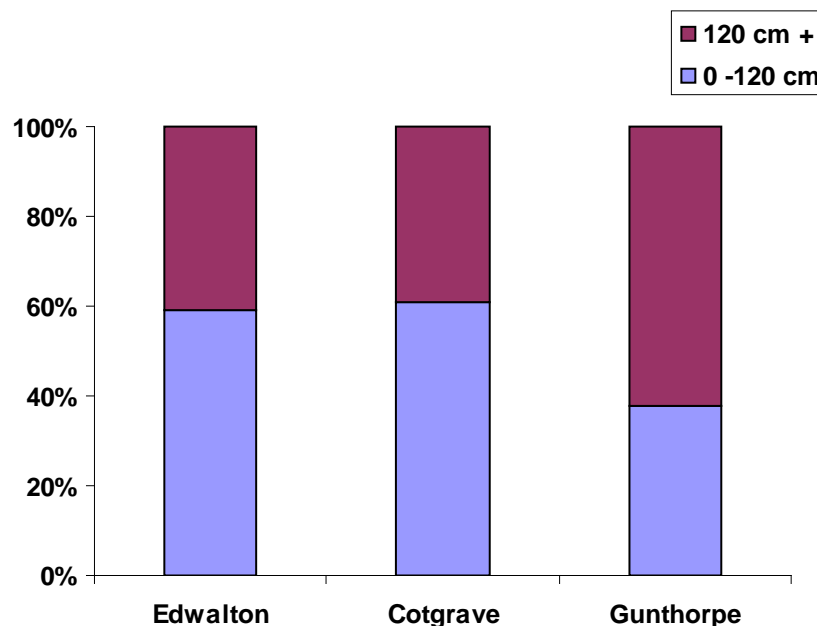
Therefore, it is likely that the NO_3^- stored at depth in the Edwalton, Cotgrave and Gunthorpe parent materials will probably remain resident for the long term due to the low denitrifier populations and the generally fairly impermeable nature of the soil/parent material matrix. In addition, with continued fertiliser application the concentrations may increase slowly.

4.2   THE FATE OF C AND N IN AQUIFER SOILS AND SEDIMENTS

The store of nitrate in the soils and sediments that make up the aquifer represents the greatest area of potential concern with respect to nitrate leakage to ground and surface waters. The fate of the nitrate in the aquifer will be determined by (i) de-nitrification within the aquifer or (ii) effluent flow into the River Trent, because the aquifer is effectively sealed by the underlying Gunthorpe mudstone. Denitrification rates in alluvial soils of woodland within the Trent catchment are considered to be some of the highest in Europe (Piany *et al*., 2007). The maximum rate of denitrification generally occurs at 0-30 cm. It was suggested that this was a function of the high availability of NO_3^- combined with the maritime conditions of the UK that regularly creates waterlogged soils.

Results from our study suggest that the rates of denitrification may be low within the groundwater of the shallow aquifer. With respect to carbon sources our aquifer could be split into two; (i) the old terrace deposits comprising of the HPS&G which has low % C concentrations in the sediments and (ii) the modern floodplain which has much higher concentrations throughout its depth. This difference in % C concentrations, being a historical depositional feature, is one that could potentially protect the river system from NO_3^- leakage because of its position as a buffer zone where denitrification could take place. In previous studies, nitrate concentrations in groundwater have been related to the bioavailablity of DOC used by organoheterotrophic bacteria (Chapelle *et al*. 2009); the source of which being soils and sediments. In deep aquifers, organotrophic denitrification in groundwater may rely on sedimentary, 'autochthonous' carbon (Ghiorse & Wilson, 1988). Siemens *et al*. (2003) suggested that DOM leached from the soil may not contribute significantly to the attenuation of nitrate in an aquifer because the zones within the aquifer where DOM and NO_3^- concentrations decreased were separated spatially and the bioavailability of the DOM was low. However, in the shallow sand and gravel terrace aquifers such as the one in our study, the DOM required is likely to be derived from the soil and its quality or bioavailability will be important. Our study has shown that concentrations of DOC in the aquifer waters are generally low (< 10 mg l^{-1}), and the laser fluorescence analysis suggests that there is a difference in quality of DOM between the groundwater and that found in the soil and river; the groundwater DOM seemingly having a higher humification index (HI) and being more fulvic-like in composition. This suggests that the groundwater DOM is becoming more recalcitrant and a less reliable food source for denitrifying bacteria. This is either a function of greater decomposition as the DOM is transferred from the soil to the groundwater or that further decomposition of DOM is occurring in the groundwater. Sourcing of DOM using laser fluorescence analysis also suggests that a large source of DOM in the river is probably from either erosion or overland flow, and not the aquifer. Therefore a question remains as to the relationship between water flow between the aquifer and river and how long it would take nitrate to enter the river, in the absence of denitrification.

However, ultimately, denitrification could be low throughout the aquifer because the shallow depth of the aquifer appears to keep the water well oxygenated, leading to conditions unsuitable for denitrifying bacteria. This may be the principal reason for the reasonably stable concentrations of nitrate in the aquifer waters found in our study. The problem of oxygenation of shallow aquifers being a constraint on denitrification has been found in the USA. A survey of four shallow aquifers by Green *et al*. (2008) where stable isotope analysis (Ar/N) and excess N_2 analysis revealed that in two of the aquifers minimal denitrification was found as a result of oxic conditions, whereas partial denitrification was found in one of the other aquifers tested. These results therefore suggest that where denitrification is limited the residence time of NO_3^- in the aquifers will be in the order of decades.

As part of the Shelford 3D modelling project a groundwater model was produced for the wider study area (Wang *et al*. 2010). The groundwater model was produced using the ZOOM suite of groundwater flow and transport models and incorporated geological information from the 3D model. The ZOOM suite consists of a groundwater flow model (ZOOMQ3D), recharge model (ZOODRM) and a particle tracking model (ZOOPT). The latter enables estimates of the potential route and residence time of a conservative mass of solute in the aquifer to be made. Thus we can use this to examine the possible time and passage that nitrate, DON or DOC may take to leave the aquifer. Time periods of 2 and 10 years for the particle tacking were carried out in this study. Figure 37 reveals the paths and distances that the particles are likely to take based on an average aquifer saturated conductivity of 2000 cm day^{-1} which is roughly the median value of hydraulic conductivity (see section 3.1.3). The results suggest that residence time within the aquifer depends on the distance away from the Trent, but could be in excess of 10 yrs for those areas furthest away from the river. These results give an indication of the length of time the aquifer could remain with levels of NO_3^- exceeding the current water directive guidelines.

Although this particle tracking approach produces likely estimates it is overly simplistic and many other factors need to be considered. Firstly, the model results are produced under steady state conditions (i.e. steady inputs of water entering and leaving the aquifer). Thus important temporal interactions between the river and aquifer are not considered fully. For example, the steady state model does not account for the likely interactions between the floodplain aquifer and river stage. For example, Alden and Munster (1997) found linear relationships between effluent groundwater flow and river stage on a floodplain aquifer. One question that needs to be asked is how do the interactions between aquifer and river change during the year when high groundwater levels may not coincide with high river stage and vice versa. This could be exacerbated in climatic extremes e.g. periods of drought and high precipitation. In times of drought the aquifer would be expected to contribute more groundwater to the river to maintain base-flow. Therefore, it may be that in periods of low river baseflow, greater nitrate is supplied to the river system. During wetter than average periods the river may flood or supply water to the aquifer through influent flow and this may have a diluting effect.

Secondly, the particle tracking output may be oversimplified because it assumes movement through a uniform material. However, it is likely that much of the transport of solutes will be along flowpaths. Peiffer *et al*. (2006) used a combination of groundwater modelling and hydrochemistry to determine flowpaths. They found that oxbow lakes within their floodplain caused upwards flow and that ridge and swale micro-topography helped control recharge patterns and generate local flow systems. The current understanding, as can be seen in (Figure 1), is that there is very little geological complexity in the terraces and floodplain of the Shelford study area with the exception of the Holocene alluvial sand, silt and clay deposits. However, these are mostly composed of sandy material through much of their sections.

Figure 39: Examples of steady state particle tracking from the shallow groundwater aquifer around the Trent at Shelford, assuming steady state conditions for 2 and 10 yr periods. The area of the 3D model is outlined in red.
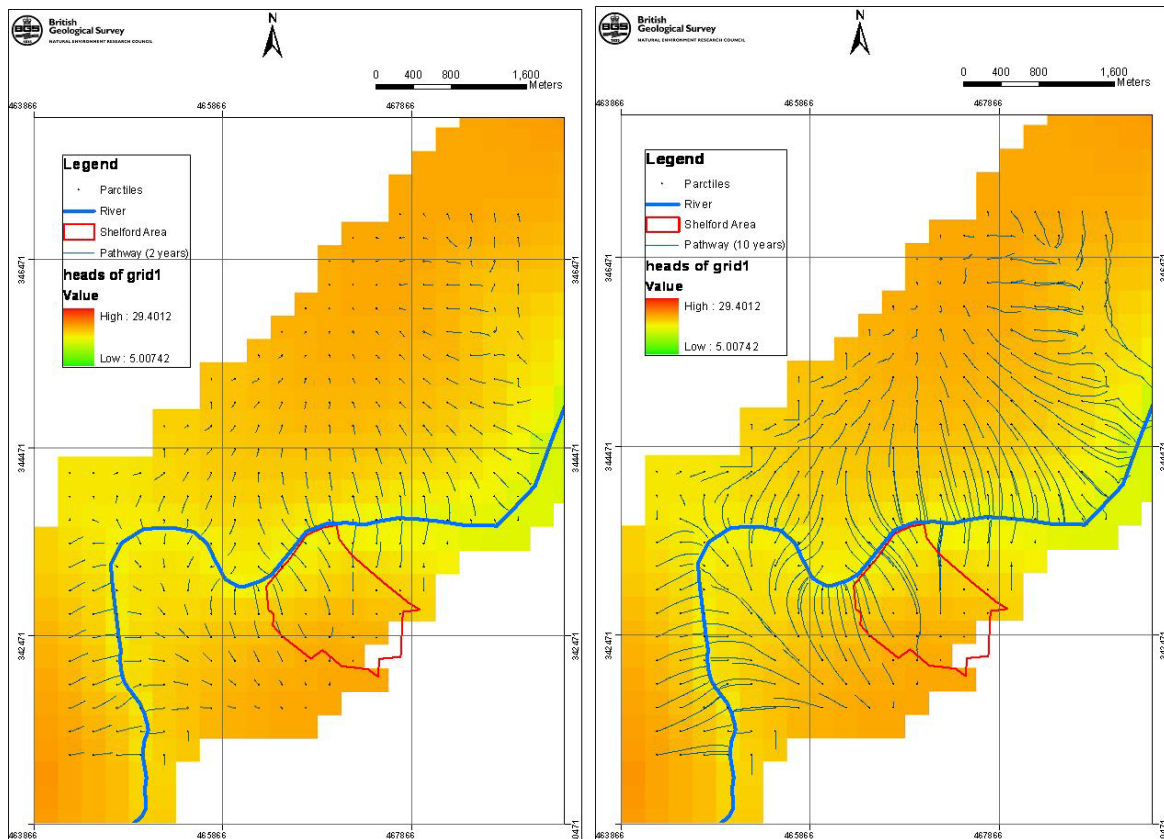
4.3   WIDER IMPLICATION OF THE WORK

The use of the GSI3D model and the understanding our study has developed with regard to the shallow floodplain aquifers of the River Trent allow it to be used as an analogue for similar landscapes within the Trent Valley. In recent years the River Trent has undergone considerable water quality improvements, largely as a result of investment of sewerage and sewage treatment in line with pollution control legislation (Martin, 1994), particularly to decrease the amount of PO_4^- in the river. However, this work suggests that the sand and gravel aquifers of the terraces and floodplains, exist as a future source of nitrate input into the River Trent. With respect to remediation of such aquifer groundwater, one method that could be used to protect water courses is the introduction of vegetated buffer zones. For example, Yamada et al. (2007) showed that a buffer zone consisting of walnut and cottonwood trees, alfalfa and grasses could yield improved water quality within years. The vegetation buffers work by extracting nitrate from waters and increasing denitrification through the input of C via the plant roots. This would lead to increased microbial activity that could lead to decreases in dissolved O_2 concentrations and create anaerobic conditions suitable for denitrification.

4.4   FURTHER WORK

There are a number of areas of work that could be undertaken to further the survey reported in this work.

- Continued and increased temporal monitoring to assess the quality of the hydrochemistry of the shallow floodplain aquifer. Although results suggest that a relatively steady hydrochemistry was found, seasonal trends in DOM, DON and DOC could change, especially in post harvest times when harvest residue is returned to the soil.

- A wider investigation of nitrate concentrations across the sand and gravel terraces of the River Trent would reveal the extent of the nitrate problem that may increase the time required to improve the water quality of the River Trent.

- A study to assess the extent of denitrification occurring within the soils, sediments and groundwater of the aquifer. This could be carried out using ^{15}N techniques within the soil and subsoil or through Ar/N and excess N_2 ratios in the groundwater.

- Although only an initial examination of the technique, the laser fluorescence methodology appears to be a useful tool in examining temporal changes in soil and groundwater DOM quality. It would also be useful to look at the DOM in the sub-soils.

- The major knowledge gap that would require further work is to examine the interactions between the River Trent and the aquifer. Increased understanding of the aquifer with river stage along with denitrification would allow an improved estimation of residence times of nitrate within the aquifer.

- Further work is required to supplement the conceptual understanding of groundwater flow in the alluvial aquifer.

- The steady-state groundwater model could be developed to investigate the variant behaviour of the system. Particularly, the relationship between groundwater head in the alluvial deposits and river stage.

5 Conclusions

The major conclusions from this work are

- The build up of nitrate, after many years of intensive agriculture, in the non aquifer soil / parent materials is between 50-70 kg ha^{-1}, approximately 30-50 % of annual N applications. This suggests that despite many years of intensive arable agriculture there has not been a huge build up of nitrate at depth. Denitrification appears to extend to the rooting depth of ~120 cm and beyond this is a slight build up of NO_3^-, probably as there is not a suitable C source for denitrifying bacteria.

- In the ground water of the shallow river floodplain aquifer there has been considerable leaching of nitrate through the sand and gravels. This has led to nitrate concentrations in the groundwater exceeding EU limits of 50 mg l^{-1}.

- The groundwater appears to be well oxygenated and with low DOC concentrations. Laser fluorescence analysis suggests that this DOM has high fulvic-like components and with a higher humification index than the soils suggesting that conditions are not ideal for denitrifiying bacteria. The presence of low nitrite concentrations and very low Fe concentrations in the groundwaters suggest that at best anaerobic conditions may be localised as a result of small changes in sediment types (e.g. Holocene silts and clays) in the floodplain.

- Particle tracking using the Zoom groundwater model suggests that it would take in excess of 10 years to lose the nitrate under steady state conditions. However, interactions between the river and aquifer need to be considered further.

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