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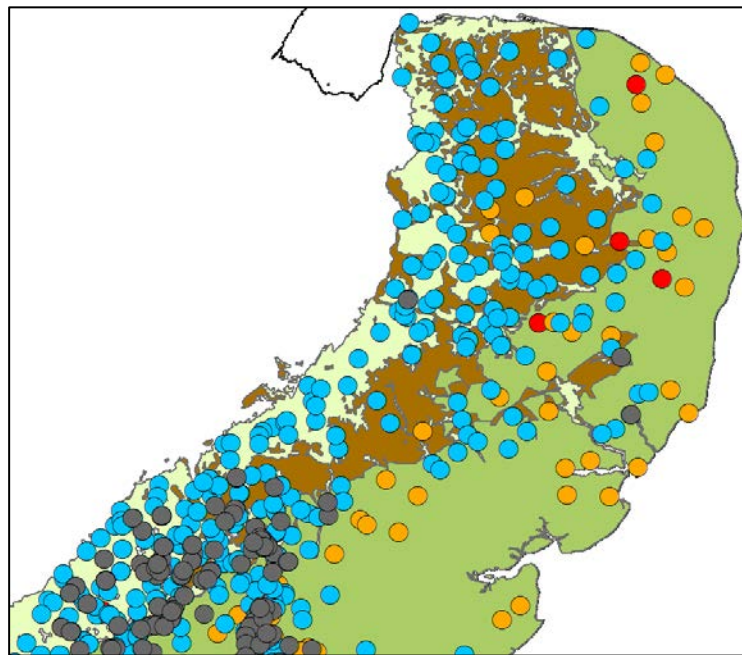


**Environment  
Agency**

# Mapping groundwater denitrification potential: Methodology report

Groundwater Programme

Open Report OR/18/009





BRITISH GEOLOGICAL SURVEY

GROUNDWATER PROGRAMME

OPEN REPORT OR/18/009

# Mapping groundwater denitrification potential: Methodology report

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## *Keywords*

Aquifer; subcrop; confined zones; low-permeability superficial deposits; indicators, nitrate; iron; manganese.

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## *Front cover*

Denitrification potential for monitoring sites on the Chalk of East Anglia. Shown are areas of outcrop chalk confined by low-permeability superficial deposits, outcrop chalk and the confined zone

## *Bibliographical reference*

STUART, M E, ASCOTT, M J, TALBOT, J C, NEWELL, A J. 2018. Mapping groundwater denitrification potential: Methodology report. *British Geological Survey Open Report*, OR/18/009. 63pp.

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## Foreword

This report is the second published product of a study by the British Geological Survey (BGS) on denitrification potential in groundwater of England, co-funded by the Environment Agency and BGS. The first was a review of denitrification potential in aquifers.

## Acknowledgements

The authors are grateful to Natalie Phillips, Alwyn Hart, Polly Wallis, Elena Armenise and Tim Besien from the Environment Agency 'who proposed the idea and sought to work collaboratively with the BGS, as well as providing the underpinning monitoring data and useful review comments.

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## Summary

An understanding of the fate of nitrate in groundwater is vital for managing risks associated with nitrate pollution, and to safeguard groundwater supplies and groundwater-dependent surface waters. One of the main mechanisms to control nitrate is the designation of nitrate vulnerable zones (NVZs). Recent review of the designation process in England has highlighted that in some locations measured groundwater nitrate concentrations are not as high as might be expected from knowledge of the surface loads of nitrate applied at the ground surface. A possible reason for this is that the nitrate is being transformed through denitrification. The aim of this work was to develop a weight of evidence approach to allow the assessment of denitrification potential across groundwater in England using literature and existing groundwater and other relevant data.

Three main lines of evidence were used:

1. Literature data on documented low redox zones indicating denitrification. These were derived from both published journal articles, BGS/Environment Agency baseline reports (Shand et al., 2007 and references therein) and Environment Agency water quality reports. These identified places where aquifers are confined by overlying low permeability bedrock or superficial deposits as potential denitrification zones. Geographical information system (GIS) shape files representing the extent of aquifer subcrop within 400 m of the surface were derived using the BGS 3D model and BGS 1:625,000-scale geological mapping for 10 aquifers chosen from importance, number of monitoring data points and availability of the top aquifer horizon in the 3D model.
2. Groundwater monitoring data, primarily Environment Agency strategic monitoring data for nitrogen and a range of other substances taken to be potential indicators of redox conditions, were used to attempt to identify zones of low redox potential. Comparison with confined zones from above provided zones where low redox conditions were present at the majority of sites within the zone. The percentage of monitoring points where data confirmed low redox and their areal coverage provided an estimate of confidence.
3. A mass balance approach comparing nitrogen inputs with measured groundwater concentrations in areas with a relatively short unsaturated zone travel time derived from the BGS NTB model and data from the 2012 NVZ designation process.

The result showed that there is widespread potential for denitrification in groundwater across England but that it is likely to be patchy within individual aquifer units. Key zones of potential denitrification highlighted by the EA monitoring data were:

- Bedrock aquifers confined by overlying bedrock strata: the Upper and Lower Greensand, Chalk, Corallian, Oolite, Permo-Triassic sandstones and the Carboniferous have denitrification potential confirmed by a good coverage of monitoring data. For the Lias, Zechstein (Magnesian Limestone) and Dinantian (Carboniferous limestone), monitoring data does not support the presence of denitrification potential, possibly an artefact of data coverage.
- Bedrock aquifers confined by overlying low permeability superficial deposits: the Crag, Chalk, Permo-Triassic sandstones and the Zechstein have denitrification potentials confirmed by a good coverage of monitoring data. Monitoring data for the Palaeogene, Upper and Lower Greensand, Corallian, Oolite, Lias and Older rocks do not confirm the presence of denitrification.

- Superficial aquifers: areas of blown sand and lacustrine superficial aquifers have denitrification potential supported by monitoring data with glacial sand and gravel and alluvium also showing some potential.

In other aquifers the presence of denitrification was not confirmed by monitoring, namely:

- Bedrock aquifers confined by overlying bedrock strata: the Lias, Zechstein (Magnesian Limestone) and Dinantian (Carboniferous limestone), possibly an artefact of data coverage.
- Bedrock aquifers confined by overlying low permeability superficial deposits: the Palaeogene, Upper and Lower Greensand, Corallian, Oolite, Lias and Older rocks.

The mass balance approach also highlighted areas of unconfined bedrock aquifers where nitrate concentrations did not appear to reflect surface inputs: areas of all important aquifers where unsaturated zones are not thick were identified particularly in East Anglia and Central Northern England.

These layers have been combined into a map package where clicking on individual areas brings up a table of the underlying information.

# 1 Introduction

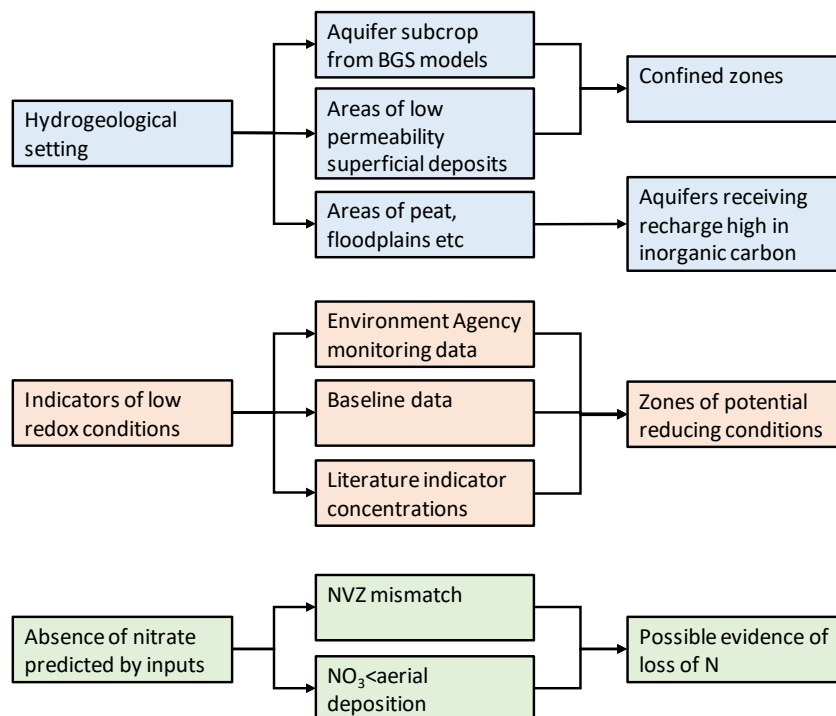
## 1.1 BACKGROUND

An understanding of the fate of nitrate in groundwater is vital for managing risks associated with nitrate pollution, and to safeguard groundwater supplies and groundwater-dependent surface waters (Rivett et al., 2008). Anthropogenic nitrate in groundwater can arise from inorganic sources such as fertiliser or from organic sources commonly comprising manure, slurry and sewage. The Environment Agency is responsible, under the Environmental Permitting Regulations (2010), for controlling sewage discharges to ground and also has a remit to control agricultural nitrogen inputs (fertilisers, slurries and manures) through the designation of Nitrate Vulnerable Zones. Denitrification is the dominant nitrate attenuation mechanism in groundwater (Rivett et al., 2008) and, under certain environmental conditions, can significantly reduce the total nitrogen in groundwater. It is therefore in the interest of the Environment Agency, Water Companies, other environmental regulators (such as Local Authorities), farmers and permit applicants to have knowledge of where in our aquifers denitrification is likely to be occurring

## 1.2 AIMS AND APPROACH

The aim of this work was to develop a weight of evidence approach to assess denitrification potential across groundwater in England using literature and existing groundwater and other relevant data. It was proposed to use three main lines of evidence:

1. Literature data on documented low redox zones indicating denitrification.
2. Groundwater monitoring data, primarily Environment Agency strategic monitoring data
3. Mass balance approaches comparing nitrogen inputs with measured groundwater concentrations.



**Figure 1.1** Lines of evidence to assess denitrification potential

Each of these lines of evidence is likely to provide a partial picture of denitrification potential. A tiered approach has been developed to combine these into a useful format together with applicability and limitations for each type of evidence. The results will be related to the geological setting for both bedrock and superficial deposits.

### **1.3 SCOPE**

The approach focusses on zones where natural environmental conditions support denitrification and exclude zones with anaerobic conditions created by pollution spills or other anthropogenic factors.

It uses geological data available at the scale of 1:625,000 that can be conveniently plotted at the national scale. For more-detailed queries it will be necessary to apply the methodology set out here to geological and monitoring datasets at a larger scale. Individual sites will always require more-detailed assessments.

This approach uses the main aquifer groupings for which key borehole information is available to construct maps of the confined zone and will not fully represent other minor aquifers or those with relatively few monitoring points.

Denitrification in soils and the unsaturated zone was outside of the scope of the mapping approach. Riparian/hyporheic zones can be important sinks of nitrate but are difficult to include in this approach using national data, as there were very few monitoring data available in the Environment Agency dataset for these zones.

Groundwater monitoring data for a series of parameters from the initial review (Stuart, 2018) were considered. In addition to N-species, iron (Fe) and manganese (Mn), dissolved oxygen (DO) and sulphate (SO<sub>4</sub>). Other parameters suggested by Environment Agency staff included nickel (Ni), pH, dissolved organic carbon (DOC) and sulphide (S).

### **1.4 STRUCTURE**

Chapter 2 sets out the results of the literature survey for low redox zones and develops a map of subcrop areas of the important aquifers. Chapter 3 evaluates Environment Agency monitoring data for evidence of zones of low redox in bedrock confined by overlying bedrock or by low-permeability superficial deposits and in superficial deposits using N species and indicator ions such as Fe and Mn. Chapter 4 covers the absence of predicted nitrate from inputs. Chapter 5 draws these lines of evidence together into the construction of a map.

## 2 Hydrological settings favouring development of low redox zones

### 2.1 REVIEW OF THE LITERATURE

Denitrification potential in groundwater of England was reviewed by Stuart (2018) as the first deliverable of the current project, and this review provides further detail on the topics outlined below. Literature data for England are predominantly for the confined zones of the three principal aquifers, the Chalk, Permo-Triassic sandstone and Lincolnshire Limestone. The distance of the redox boundary from outcrop has been established for these aquifers.

Other areas that need to be considered are areas where there are significant low permeability or high organic carbon superficial deposits and areas of floodplain deposits that may confine underlying shallow groundwater.

### 2.2 SUPERFICIAL AQUIFERS

#### 2.2.1 Sandy/outwash aquifers

There is some evidence for loss of nitrate in such aquifers (e.g. Postma et al., 1991; Puckett and Cowdery, 2002), with identification of an upper oxic zone containing oxygen and nitrate, and a lower anoxic zone characterized by iron-rich waters. It is believed that heterotrophic denitrification in groundwater relies mainly on sedimentary, organic carbon (Ghiorse and Wilson, 1988; Obermann, 1990). Concentrations of organic matter can be low in these aquifers and the rate of denitrification limited, although autotrophic processes using pyrite oxidation as an electron source to reduce nitrate may be observed.

Denitrification in these aquifers is site-specific and they have been insufficiently characterised in the literature to make predictions of behaviour at the national scale. We propose to use monitoring data in sand and gravel superficial deposits to characterise these settings.

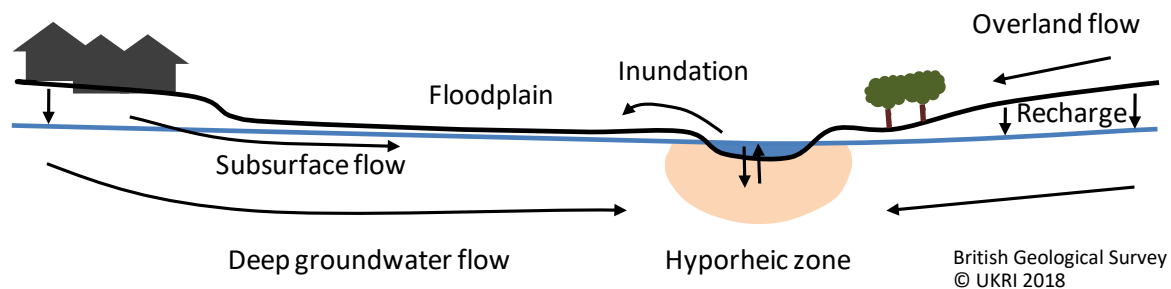
#### 2.2.2 Sources of DOC-rich recharge or low redox recharge

We find mention of increased rates of denitrification under areas where recharge is high in DOC, for example a study by Roberts and McArthur (1998) in the Lincolnshire Limestone. Denitrifiers are mostly facultative anaerobic heterotrophs, that is bacteria needing to obtain both their energy and carbon from the oxidation of organic compounds and able to change their metabolic processes, using the more efficient process of respiration in the presence of oxygen and the less efficient process of fermentation in the absence of oxygen.

Rivett et al (2008) states that the rate of denitrification is most often related to the amount of dissolved organic carbon in porewater or groundwater, or the amount of soluble organic carbon rather than the total amount of solid fraction. We propose to use any monitoring data from peat deposits to characterise these settings.

#### 2.2.3 Riparian zones, hyporheic zones and flood plains

Floodplains act as a collection point for groundwater, overland flow and river water (Burt et al., 2002) (Figure 2.1). As a result, the water table is usually close to the surface and the soil and any unsaturated zone will be close to saturation. On the landscape scale the floodplain is the reactive interface between the upland and the river (Lewandowski and Nützmann, 2010).



**Figure 2.1** Flow paths in the riparian zone (from Stuart and Lapworth (2011))

On the floodplain scale, the hyporheic zone is the reactive interface between the aquifer and surface water. The same processes that occur in the floodplain also occur in the hyporheic zone although higher concentrations in the riverbed sediments indicate more intense processes. The hyporheic zone can extend into the bedrock where superficial sediments are thin.

Dahl et al. (2007) report that an organic carbon fraction (foc) of 3% in riparian zone sediments was an effective indicator of the potential for denitrification. Smith et al. (2009) proposed a classification scheme for pollutant attenuation at the groundwater-surface water interface/mixing zone. They postulate that in the case of denitrification the organic carbon fraction of the sediments may be used as a proxy measure of denitrification potential, on the assumption that denitrifying bacteria are ubiquitous in the environment and that organic carbon fraction is a reasonable indicator of redox conditions (Rivett et al., 2008). This approach requires information on the various superficial strata present. These are not represented on geological maps that only show the surface layer.

Denitrification also occurs in other areas of superficial aquifers where anaerobic conditions associated with confined conditions exist, such as in riparian zones and floodplains. We propose to use the presence of alluvium as a top-level indicator for hyporheic zones and floodplains.

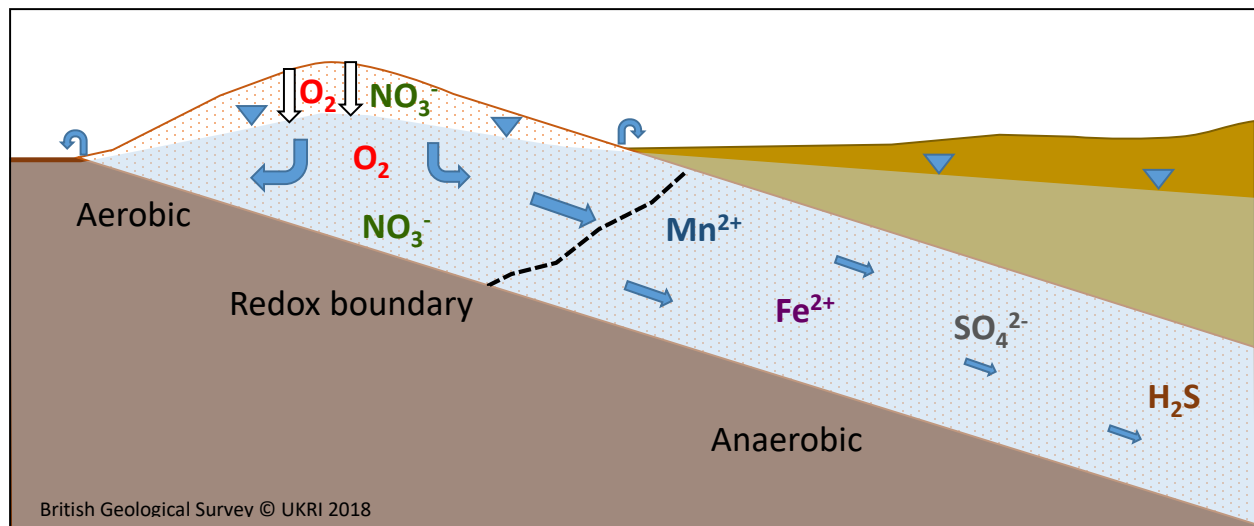
## 2.3 BEDROCK AQUIFERS

### 2.3.1 Unsaturated and unconfined zones

Studies reviewed by Rivett et al. (2007) indicate that the potential for denitrification in the unsaturated and unconfined saturated zones of major British aquifers appears to be low. None of the studies positively identified denitrification as a significant attenuation mechanism except in the soil zone. These included BGS investigations in the Chalk at Bridget's Farm and Ogbourne St George and in the Sherwood Sandstone at Gleadethorpe (Gale et al., 1994; Kinniburgh et al., 1999). However, there is some evidence for denitrification at the local scale where iron is present, for example in the Lower Greensand aquifer.

### 2.3.2 Confined zone

Evidence of denitrification in the confined (anoxic) parts of some British aquifers came from the work of Edmunds and co-workers (e.g. Edmunds et al., 1982; Edmunds et al., 1984). A sketch section is shown in Figure 2.2. This has also been confirmed by the occurrence of modern tritium-enriched groundwater with negligible  $\text{NO}_3$  (Lawrence and Foster, 1986) and from the demonstration of appropriate bacteria in core samples.



**Figure 2.2 Schematic redox boundary in the Lincolnshire Limestone aquifer (after Griffiths et al., 2006)**

Sequential redox processes have been described in three contrasting principal UK aquifers which have confined zones, the Berkshire Chalk, the Jurassic Lincolnshire limestone and the Sherwood Sandstone (Edmunds and Walton, 1983; Edmunds et al., 1982; Edmunds et al., 1984). At the time of reporting all three aquifers had high input levels of anthropogenic  $\text{NO}_3^-$ . The occurrence of  $\text{NO}_3^-$ -free groundwater was coincident with the redox boundary and with the complete reaction of DO in all three.

Edmunds and Walton (1983) followed several indicators of agricultural pollution (Ca, K,  $\text{SO}_4$  and  $\text{NO}_3^-$ ) across the redox boundary in the Lincolnshire Limestone. The migration eastwards of Ca, K and  $\text{SO}_4$  but not  $\text{NO}_3^-$  provided circumstantial evidence of denitrification. Ammonia was found only in the  $\text{NO}_3^-$ -free zones in all three aquifers, produced by DNRA (dissimulatory nitrate reduction to ammonia) or to the accumulation of  $\text{NH}_4^+$  by incongruent reaction of clays.

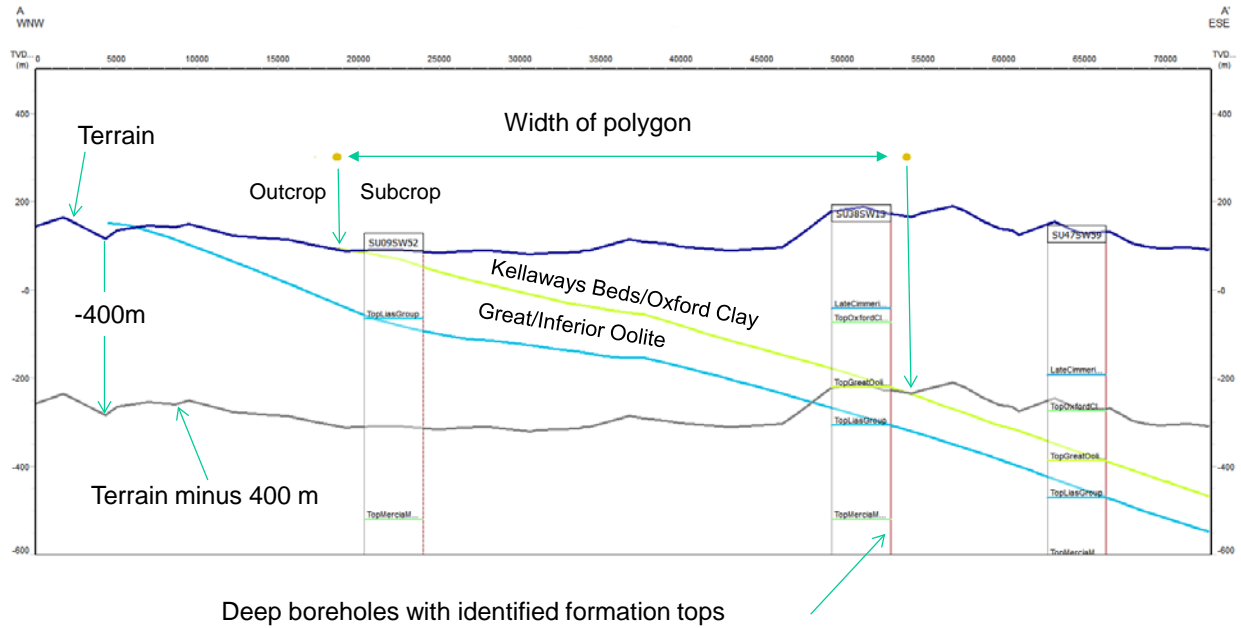
In this project, these zones were represented by the aquifer subcrop at the national scale. In more detailed studies, they may need to be refined using an indication of the redox barrier from monitoring data.

## 2.4 DERIVATION OF HYDROLOGICAL SETTINGS MAPS

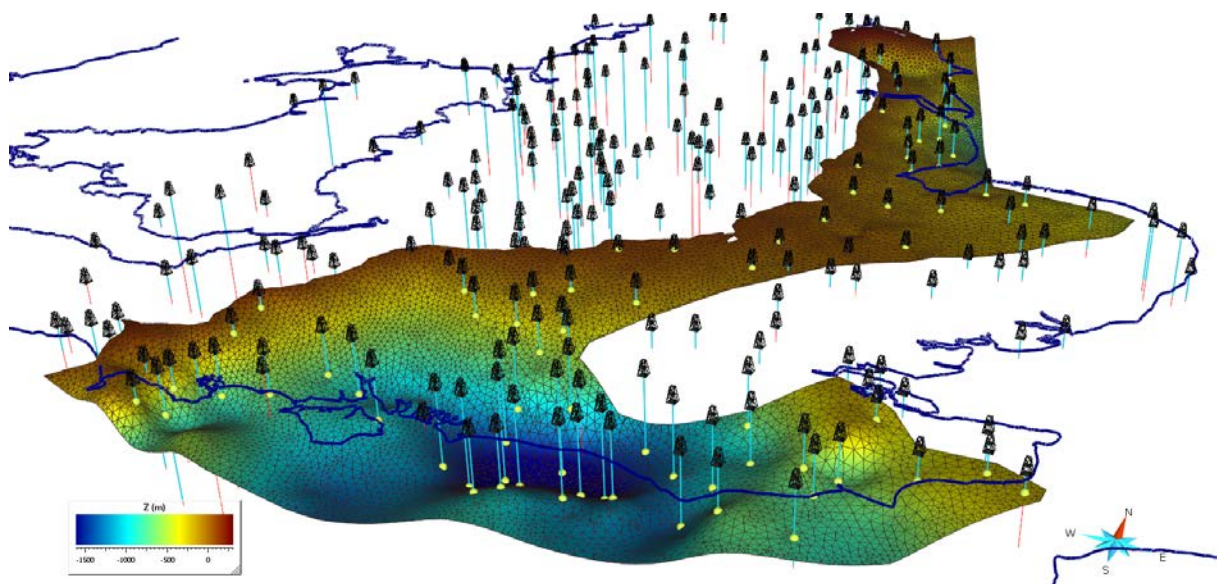
The maps were produced using BGS 1:625,000 geological mapping appropriate for national scale products. Data used to construct the base map indicating hydrogeological predisposition to denitrification are:

### 2.4.1 Aquifers confined by overlying low permeability bedrock

Confined bedrock aquifer extents were derived from the approach used to construct the BGS 3D geological model of the UK and using the same key boreholes (termed Golden Spike boreholes by BGS). Aquifers were represented by the surface projection of their subcrop (below surface extent) with a depth cut-off of 400 m below the surface defining the base of the usable aquifer. This depth is consistent with other approaches to base of aquifer definition e.g. in vulnerability to shale gas exploitation and in UKTAG guidance. Polygons were constructed from limit of subcrop (subcrop/outcrop boundary) and the point where the horizon top dips below the Terrain minus 400m surface (Figure 2.3).



**Figure 2.3 Method for construction of bedrock aquifer subcrop polygons**



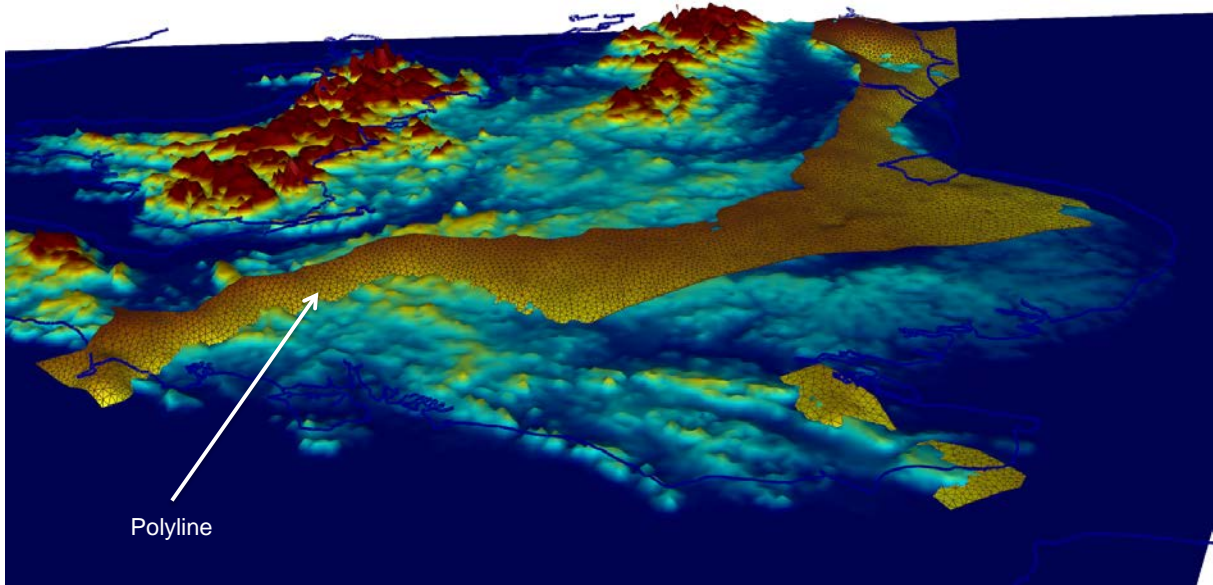
**Figure 2.4 Fitting of triangulated surface**

In the first step a triangulated surface is fitted to key borehole markers (and additional manually-drawn elevation controls where data are sparse) using discrete smooth interpolation (Figure 2.4). This derives an unfaulted surface. Figure 2.4 shows the surface representing the top of the Great Oolite Group.

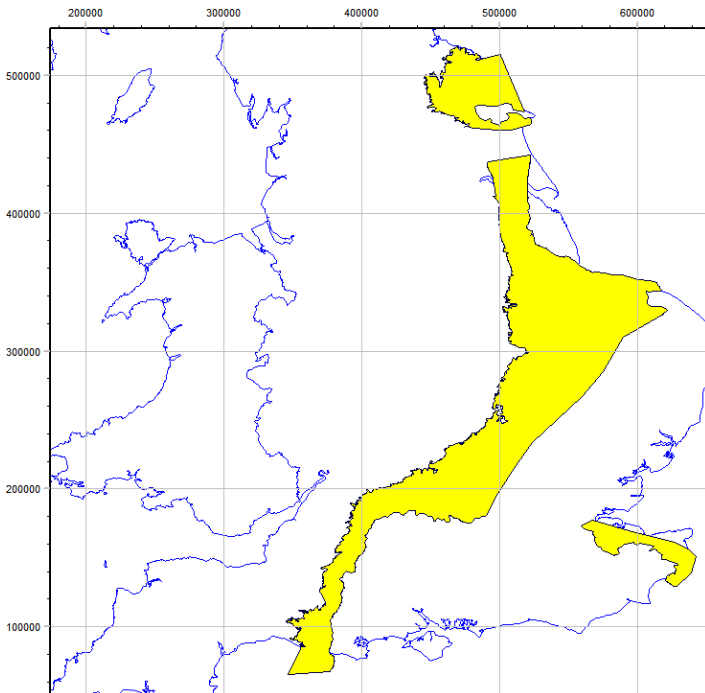
In the second step, a polyline is created at the intersection between the geological surface and the Terrain minus 400m surface (Figure 2.5).

Finally, a polygon is created between the outcrop/subcrop line and the intersection line (6). This shows the Great/Inferior Oolite Group and Middle Jurassic correlatives





**Figure 2.5 Polyline representing the base of the aquifer**



**Figure 2.6 Polygon of Middle Jurassic subcrop**

The top surfaces of some strata were already available and polygons could be readily constructed for this project. These were the tops of the Chalk, Upper Greensand Formation, Corallian Group, Great Oolite Group, Lias Group, Sherwood Sandstone Group, the Carboniferous (here Coal Measures and Millstone Grit) and the Dinantian (Lower Carboniferous) (Figures 2.7 to 2.9).

Hydrogeological considerations would suggest that the Upper Greensand would be better treated separately from the Lower Greensand, since they are not generally in hydraulic continuity and the Upper Greensand is more commonly considered with the Chalk. The Zechstein Group (Magnesian Limestone) has an established redox boundary (Stuart et al., 2007)

and the top of the strata had not been previously mapped in the BGS 3-D model. Review of the number of water quality monitoring records showed there were relatively few ascribed to the Devonian, although this can be an important aquifer and new polygons were developed in this project only for the top of the Lower Greensand Group and for the Zechstein Group (Figure 2.7 and 2.8).

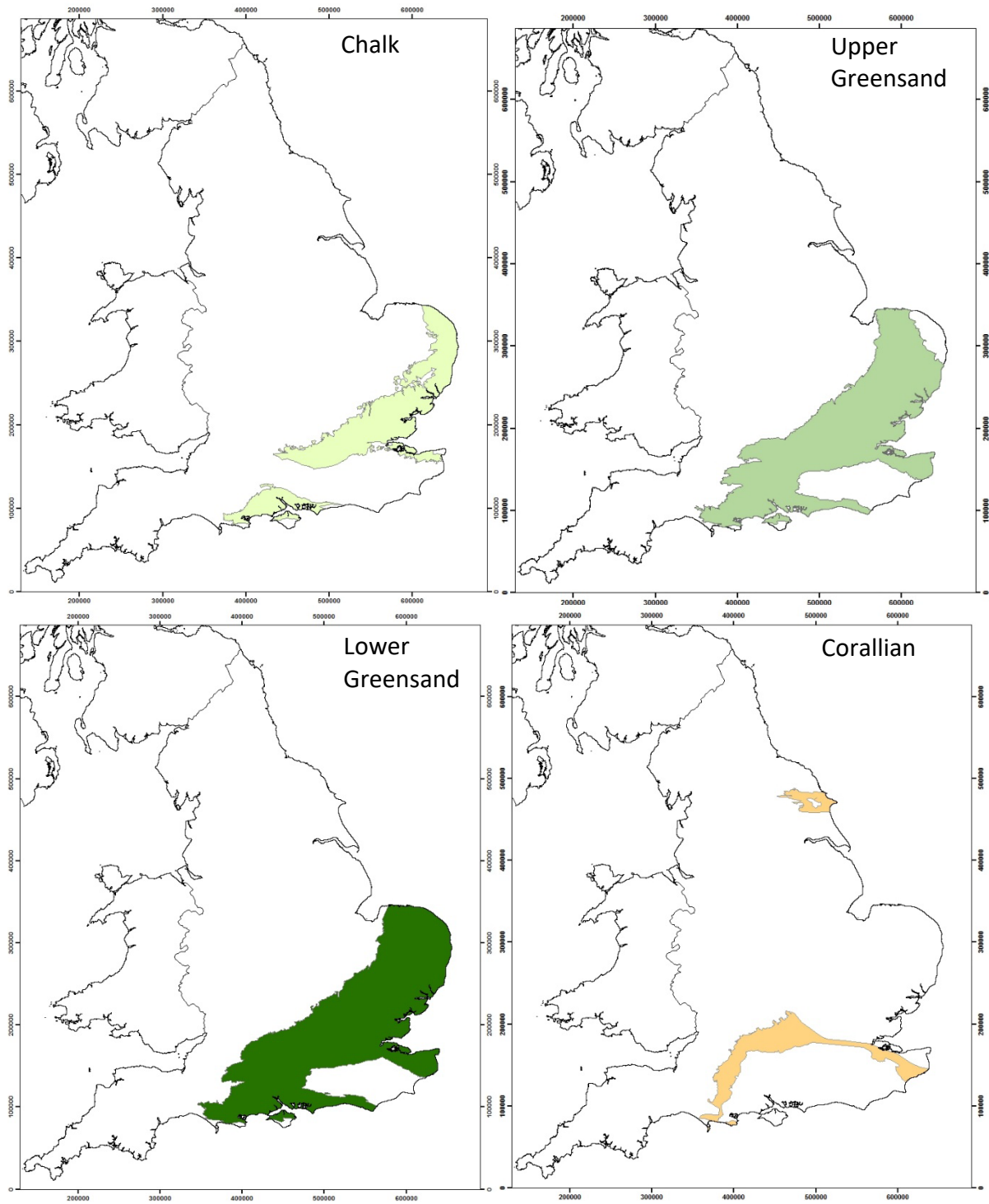
Strata were grouped for attribution to subcrop polygons (Table 2.1). Firstly, aquifer attribution in the monitoring data to be used in chapter 3 is at a number of different scales with more detailed nomenclature than used in the 1:625,000 mapping used for this assessment. These detailed names were grouped together, e.g. the Burnham Chalk Formation is part of the White Chalk Group at 50,000 scale mapping. This has been classed as Chalk in Table 2.1. Secondly, other similar strata underlying the polygons have also been included, e.g. the Inferior Oolite has been included in the polygon defined for the Oolite and the Millstone Grit in the polygon represented by the Carboniferous. This was a pragmatic decision as resources were not available to construct many new polygons.

Some compromises were made during the polygon definition process, mainly related to simplifying boundaries between the outcrop and subcrop where there were many small outliers (Table 2.2).

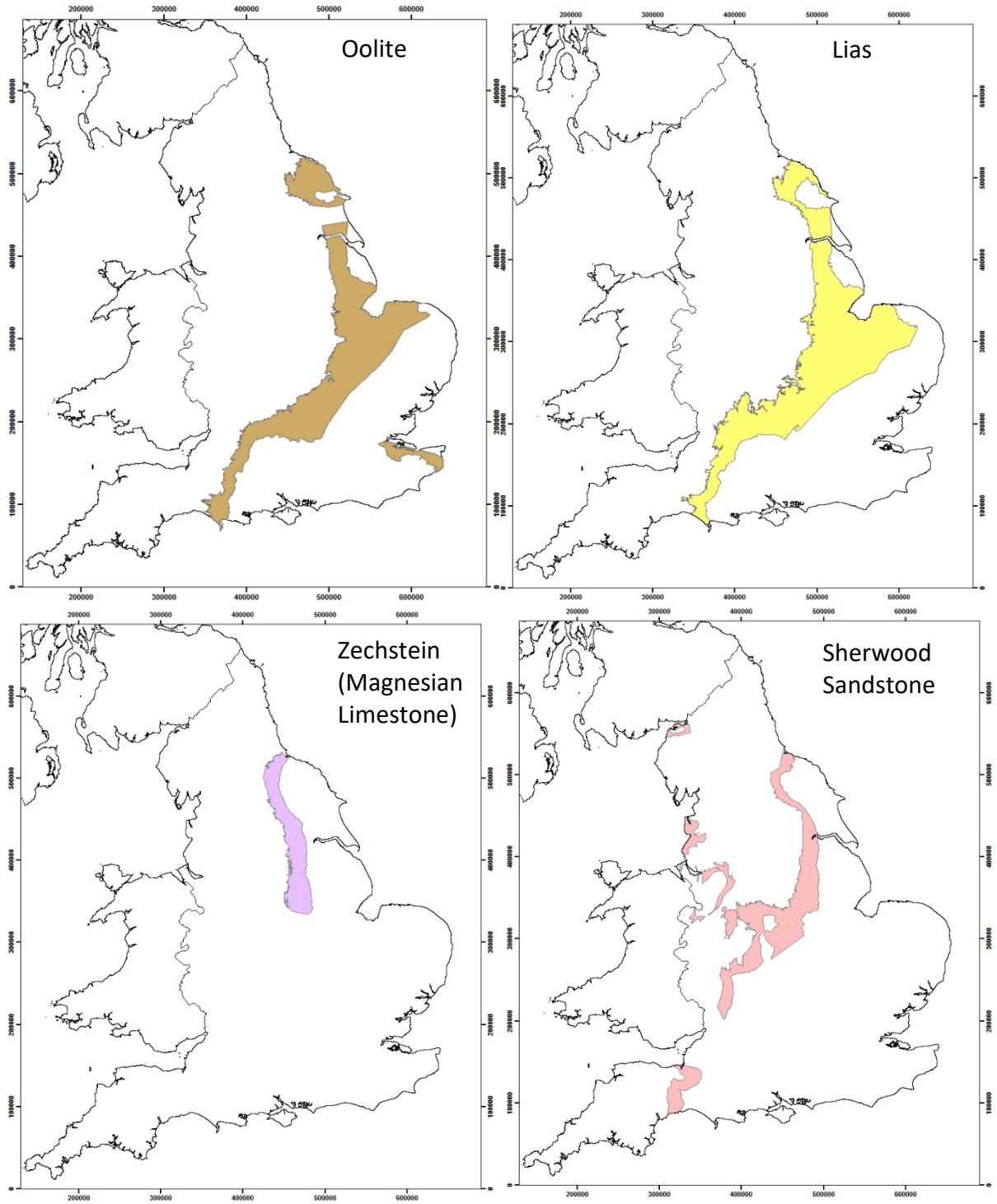
**Table 2.1 Grouping of aquifers in WIMS data for representing by polygons (bold=polygon created)**

<b>Aquifer grouping</b>	<b>Group/Period</b>	<b>Aquifer</b>
Superficial	Drift	Drift (undivided)
	Holocene	Holocene, Alluvium, River terrace deposits, Soil
	Pleistocene	Pleistocene, Glacial till, River terrace deposits, Sand and gravel
Crag	Crag	Coralline Crag Formation, Norwich Crag, Red Crag
Palaeogene	Palaeogene	Bagshot Formation, Barton Group (undivided,) Bembridge Limestone Formation, Bracklesham Group (undivided), Harwich Formation, London Clay Formation, Thanet Sand Formation, Wittering Formation, Woolwich and Reading Formation
<b>Chalk</b>	Chalk	Burnham Chalk Formation, Chalk Group (undivided), Ferriby Chalk Formation, Flamborough Chalk Formation, Holywell Nodular Chalk Member, Lewes Nodular Chalk Member, Lower Chalk Formation (undivided), Seaford Chalk Member, Tarrant Member, Upper Chalk Formation (undivided), Welton Chalk Formation, West Melbury Marly Chalk, Zig Zag Chalk Member
<b>Upper Greensand</b>	Upper Greensand	Upper Greensand Formation
	Gault	Gault Formation
<b>Lower Greensand</b>	Lower Greensand	Carstone Formation, Folkestone Formation, Hythe Formation, Lower Greensand Group (undivided), Sandgate Formation, Woburn Sand Formation
	Lower Cretaceous	Hastings ' Beds' Formation, Roach Formation, Sandringham Sand Formation, Spilsby Sandstone Formation, Tealby Formation, Weald Clay Formation, Wealden Group (undivided)
	Portland	Portland Formation
<b>Corallian</b>	Corallian	Corallian Group (undivided), Coralline Oolite Formation
<b>Oolite</b>	Great Oolite	Great Oolite, White Limestone Formation
	Inferior Oolite	Inferior Oolite Group (undivided), Lincolnshire Limestone Formation, Northampton Sand Formation
	Ravenscar	Cloughton Formation, Dogger Formation, Ravenscar Group (undivided), Saltwick Formation, Scarborough Formation
<b>Lias</b>	Lias	Beacon Limestone Formation, Blue Lias Formation, Bridport Sand Formation, Dyrham Formation, Lias Group (undivided), Marlstone Rock Formation, Redcar Mudstone Formation, Staithes Sandstone Formation
Mercia Mudstone	Mercia Mudstone	Mercia Mudstone Group (undivided)

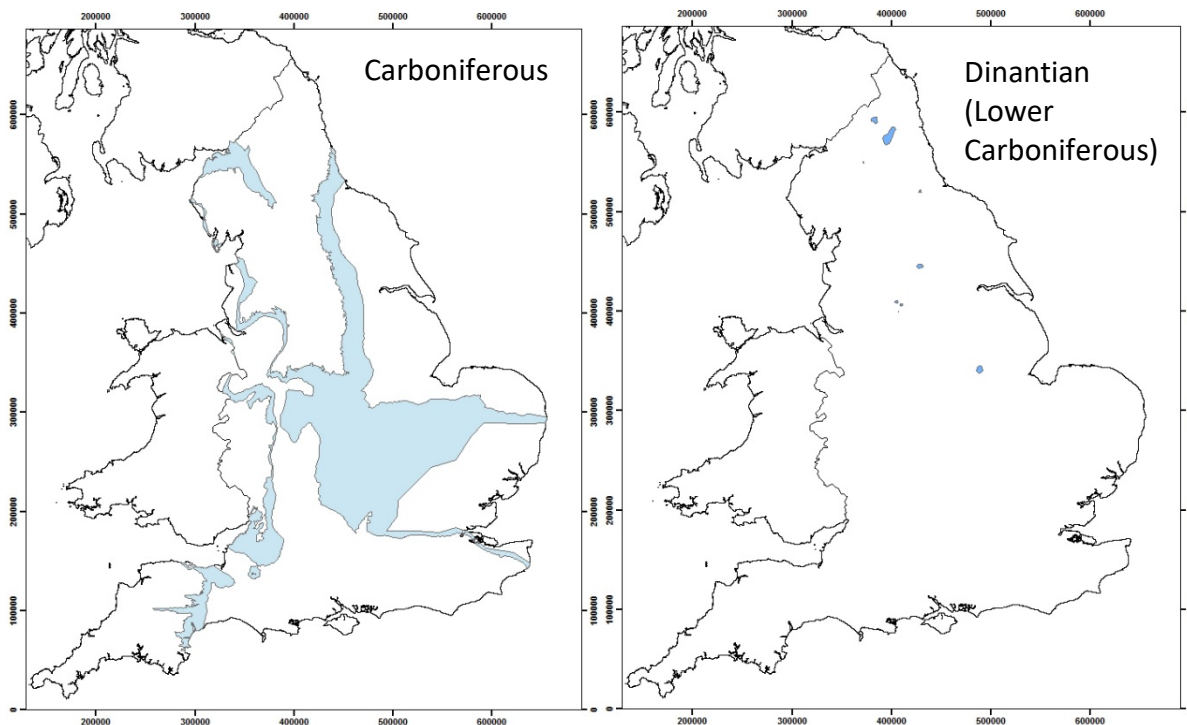
<b>Aquifer grouping</b>	<b>Group/Period</b>	<b>Aquifer</b>
<b>Sherwood Sandstone</b>	Sherwood Sandstone	Chester Pebble Beds Formation, Helsby Sandstone Formation, Kidderminster Formation, Kinnerton Sandstone Formation, Kirklington Sandstone Formation, Otter Sandstone Formation, Sherwood Sandstone Group (undivided), St Bees Sandstone Formation, Wilmslow Sandstone Formation
	Permian	Bridgnorth Sandstone Formation, Collyhurst Sandstone Formation, Manchester Marl Formation, Penrith Sandstone Formation
<b>Zechstein (Magnesian Limestone)</b>	Zechstein	Magnesian Limestone, Roxby Formation
	Basal Permian	Basal Permian Sand (and Breccia) Formation
<b>Carboniferous</b>	Coal Measures	Coal Measures Group (undivided), Lower Coal Measures 'Formation', Middle Coal Measures 'Formation', Upper Coal Measures 'Formation'
	Millstone Grit	East Carlton Grit Formation, Marchup Grit Formation, Millstone Grit Group (undivided), Shale Grit Formation, , Upper Kinderscout Grit Formation
<b>Dinantian (Lower Carboniferous)</b>	Dinantian	Alston Group (undivided), Ballagan Formation, Black Rock Limestone Formation, Bowland Shale Group (undivided), Carboniferous Limestone, Carboniferous strata (undivided), Cementstone Group, Chatburn Limestone Group (undivided), Clifton Down Group (undivided), Clifton Down Limestone Formation (Drybrook Limestone Formation), Fell Sandstone, Great Scar Limestone Group (undivided), Lower Limestone Shale Group (undivided), Stainmore Formation, Worston Shale Group (undivided)
Devonian	Old Red Sandstone	Brownstones Formation, St Maughan's Formation, Tintern Sandstone Formation, Upper Old Red Sandstone Group (undivided)
	Southwest	Meadfoot Group
Older	Silurian	Aymestry Limestone Formation, Bannisdale Formation, Coniston Group (undivided), Much Wenlock Limestone Formation, Raglan Marl, Raglan Mudstone Formation, Wenlock Rocks and Ludlow Rocks (undifferentiated), Windermere Supergroup (undivided), Yewbank Formation
	Ordovician	Borrowdale Volcanic Group, Caradoc (Undifferentiated), Skiddaw Group
	Precambrian	Malverns Complex, Stretton Group
Miscellaneous	Granite	Granite, Land's End Intrusion



**Figure 2.7** Maps showing the extent of the subcrop (confined zone) of the bedrock aquifer groupings: Chalk, Upper Greensand, Lower Greensand and Corallian



**Figure 2.8** Maps showing the extent of the subcrop (confined zone) of the bedrock aquifer groupings: Oolite, Lias, Zechstein (Magnesian Limestone) and Sherwood Sandstone



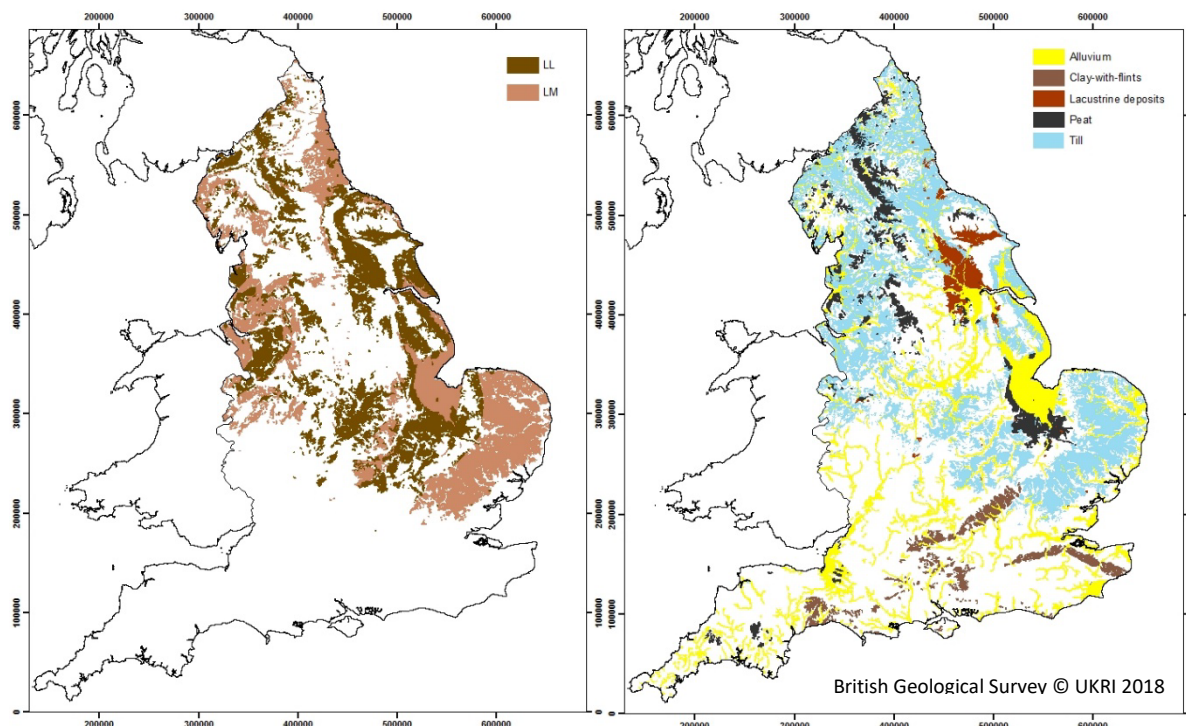
**Figure 2.9** Maps showing the extent of the subcrop (confined zone) of the bedrock aquifer groupings: Carboniferous and Dinantian

**Table 2.2** Polygon definition

Polygon	Compromises
Chalk	Numerous minor outliers omitted along outcrop/subcrop boundary
Upper Greensand	
Lower Greensand	
Corallian	Area below 400 m in the Vale of Pickering
Oolite	The Ravenscar Formation contains many low permeability horizons acting as aquitards has been included in the confined category
Lias	Numerous minor outcrop outliers omitted
Sherwood Sandstone	
Zechstein	Numerous minor outliers and inliers omitted
Carboniferous	Very complicated, the 1:625,000 geology mixes sandstones, mudstones and limestones of the same age together so a simple selection will not work.
Dinantian	

**2.4.2 Bedrock aquifers confined by low permeability superficial deposits**

Low permeability deposits were represented using the classification of Griffiths et al. (2011) which subdivides the Quaternary into a series of domains based on recharge (and attenuation potential) (MacDonald et al., 2006). The two least permeable recharge potential classes LL and LM have been used here. LM is predominantly till also with some alluvium. LL includes lacustrine deposits and peat. Periglacial deposits from the south of England have been excluded in this approach, as these are predominantly clay-with-flints covering high ground where the unsaturated zone is thick.



**Figure 2.10 Superficial deposits: a) Low permeability deposits using the classification of Griffiths et al (2011); b) Generally low permeability superficial deposits selected from the BGS 1:625,000 map**

Figure 2.10a shows the coverage of the LL and LM deposits and Figure 10b shows a simplified version of the BGS 1:625,000 scale superficial deposits map for comparison. This approach has been used by BGS to delineate areas not receiving nitrate in recharge (Ascott et al., 2017; Ascott et al., 2016; Wang et al., 2012).

**2.4.3 Superficial aquifers as potential low redox zones**

These could include sand, and sand and gravel deposits, (Section 2.2.1), organic-rich superficial deposits providing DOC-rich recharge (Section 2.2.2) and riparian, hyporheic zones and flood plains (Section 2.2.3), as well as less permeable deposits which may contain groundwater, such as lacustrine deposits, clay-with-flints and till. There are a number of sand and gravel deposits shown on the BGS 1:625,000 map, including river terrace deposits, glacial sand and gravel and blown sand. At this scale of mapping organic-rich deposits would be represented by peat. The riparian, hyporheic zones and flood plains are represented by the presence of alluvium. There are no monitoring data in the dataset used in this project for clay-with-flints, peat or brickearth.

**Table 2.3 Superficial deposit classifications**

EA classification in monitoring data	Corresponding BGS 1:625,000 superficial map class
Holocene, Alluvium	Alluvium
Holocene, River terrace deposit	River terrace deposit
Pleistocene River terrace deposit	River terrace deposit
Pleistocene Till	Till
Pleistocene sand & gravel	Glacial sand and gravel
Drift undivided*	Blown sand, Raised marine deposits, Lacustrine, Holocene sand

\*attributed using BGS 1:625,000 superficial map class and borehole records

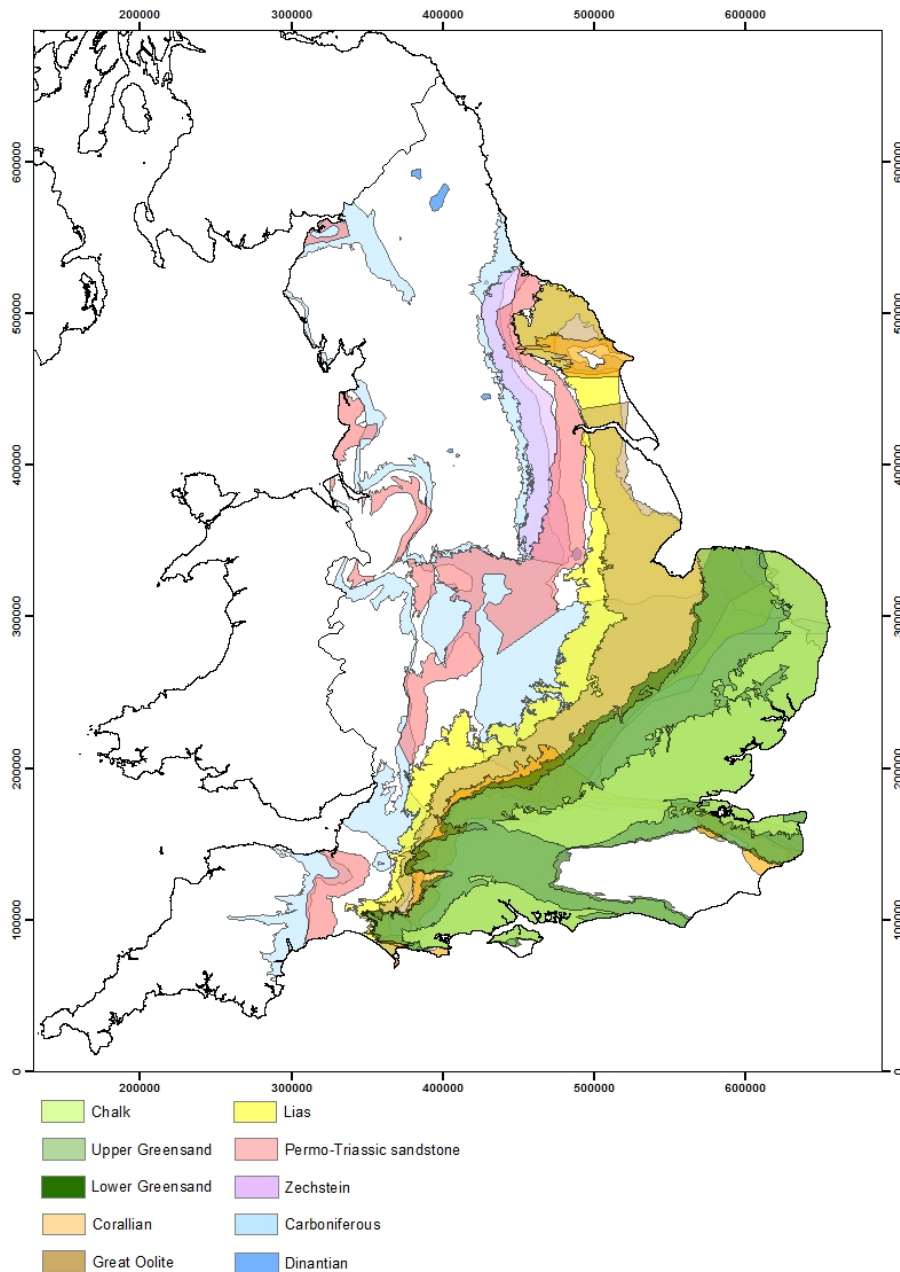


The relationship between superficial deposit classification in the Environment Agency monitoring data used in this project and the BGS 1:625,000 superficial geological map are shown in Table 2.3.

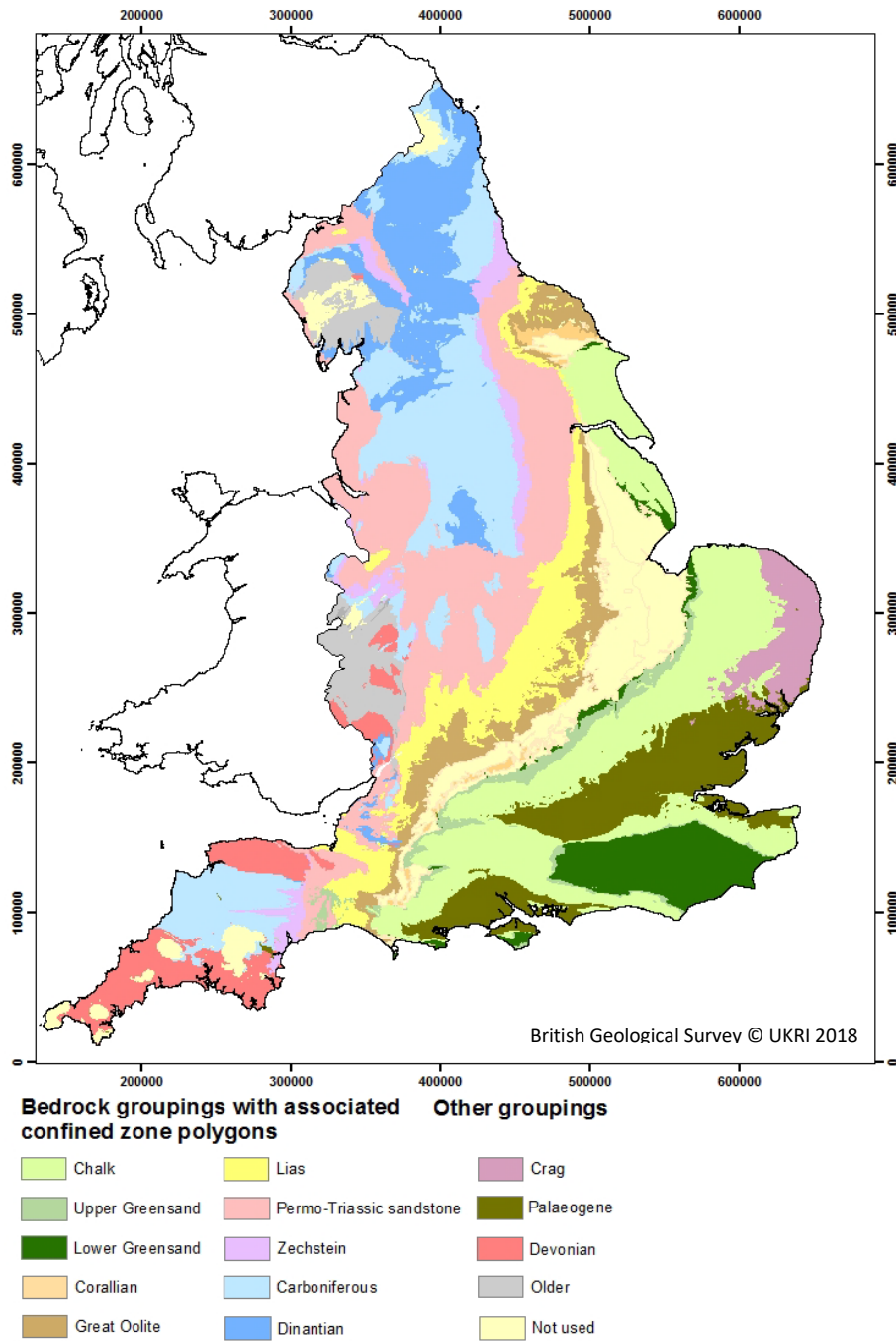
## 2.5 HYDROGEOLOGICAL SETTING MAPS

Maps representing the hydrological settings for confined bedrock aquifers, outcrop bedrock aquifers, superficial aquifers and low-permeability superficial deposits are shown in Figures 2.11 to 2.14.

Figure 2.11 shows the sequence of confined bedrock aquifers from youngest (Chalk) to oldest (Dinantian). There is considerable overlap but in reality, there are likely to be few instances where borehole penetrate a confined aquifer to access another.

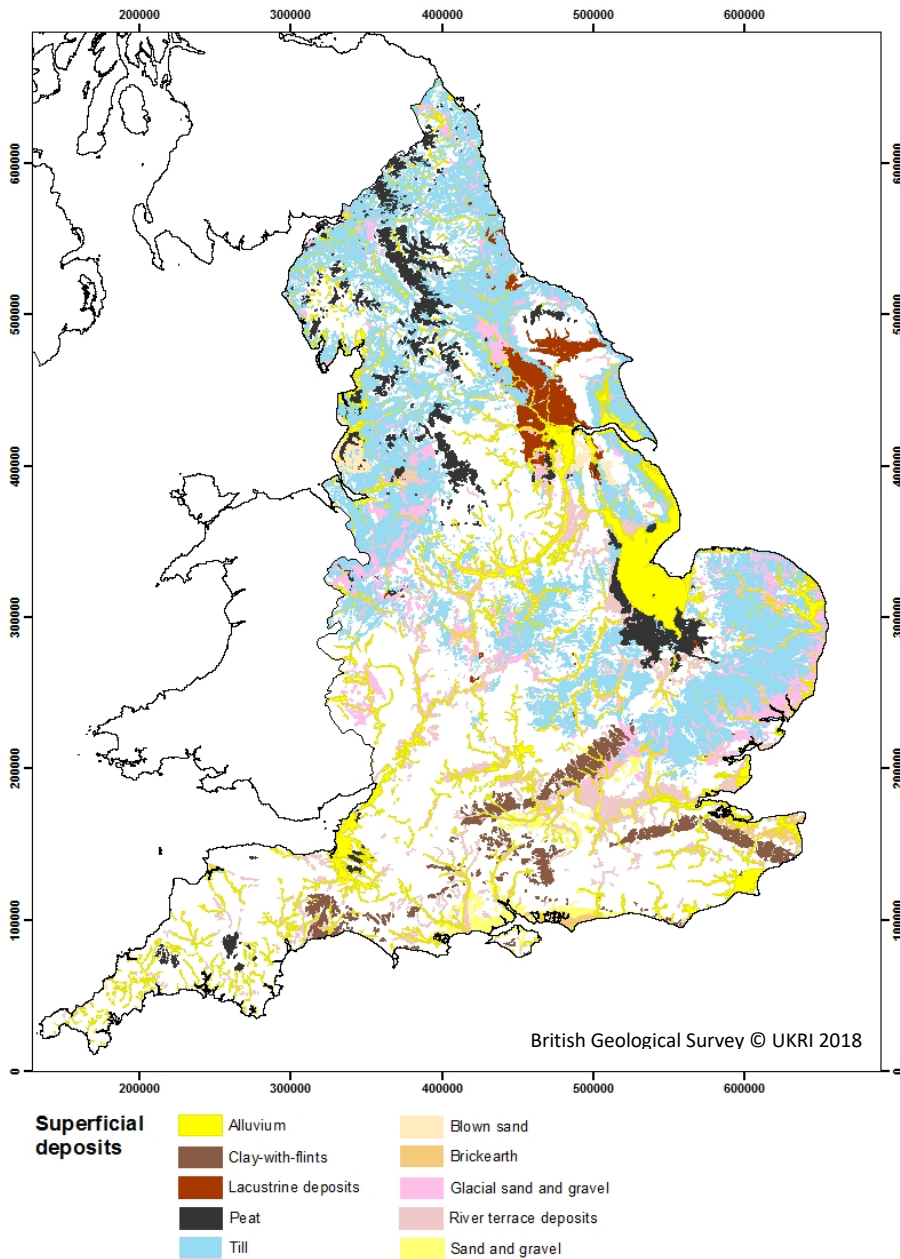


**Figure 2.11** Sequence of bedrock aquifers confined by low permeability bedrock deposits



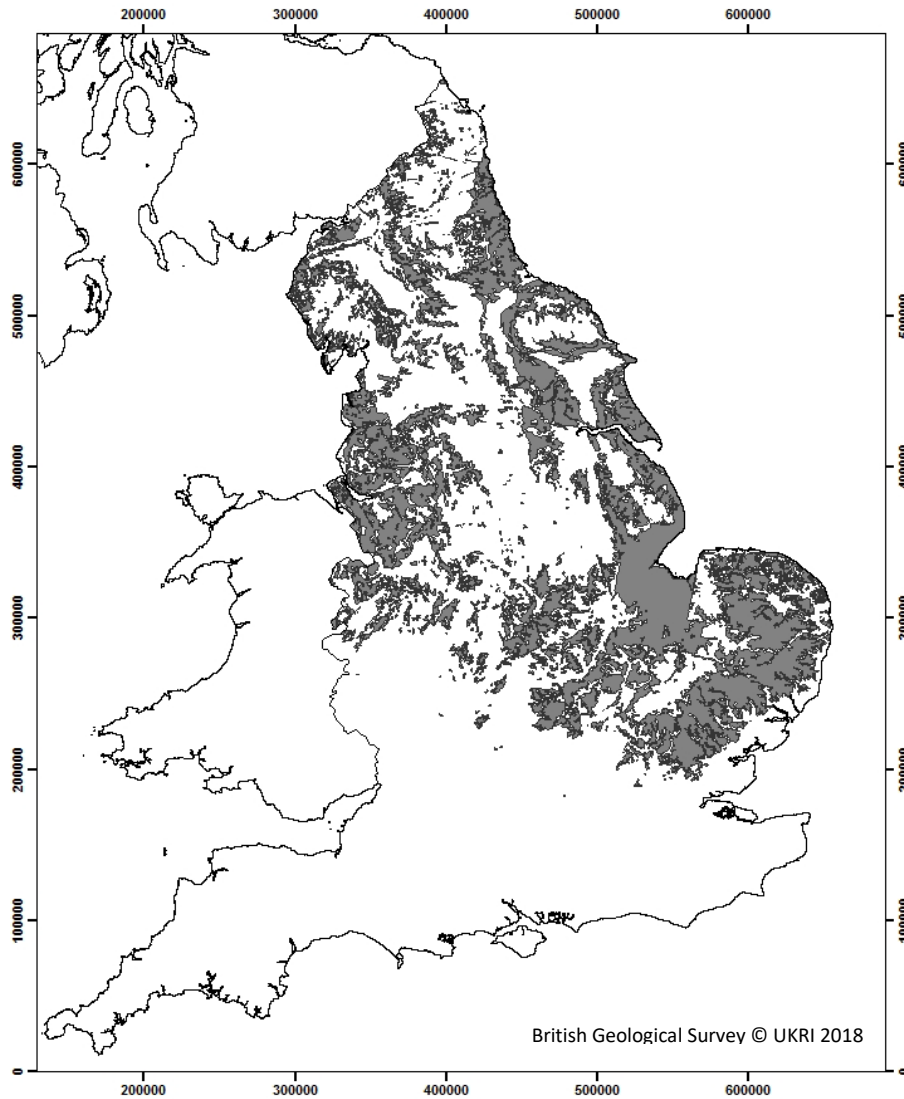
**Figure 2.12** Simplified 1:625,000 scale bedrock geological map coloured to correspond to polygons in Figure 2.11

Figure 2.12 shows a simplified representation of outcrop geology based on the 1:625,000 scale map. The aquifers groupings used correspond to those in Table 2.1 and have been coloured to correspond to Figure 2.11. Aquifers for which confined bedrock polygons were not created are also shown (Crag, Palaeogene, Devonian, and Older). Low permeability strata such as the Oxford Clay and unnamed igneous and extrusive rocks are shown as “not used”.



**Figure 2.13** Simplified 1:625,000 scale superficial deposits geological map

Figure 2.13 is a version of the superficial deposits map showing generally low permeability strata on the left of the legend and potential aquifers on the right. There are no monitoring data in the dataset used in this project for clay-with-flints, peat or brickearth and these are shown for completeness.



**Figure 2.14** Areas overlain by low permeability superficial deposits (after Griffiths et al 2012)

Figure 2.14 shows the areas potentially confined by low permeability superficial deposits, here the combined LL and LM classes. Overlaying Figure 2.14 on Figure 2.12 shows areas of aquifer groups confined by low permeability superficial deposits.

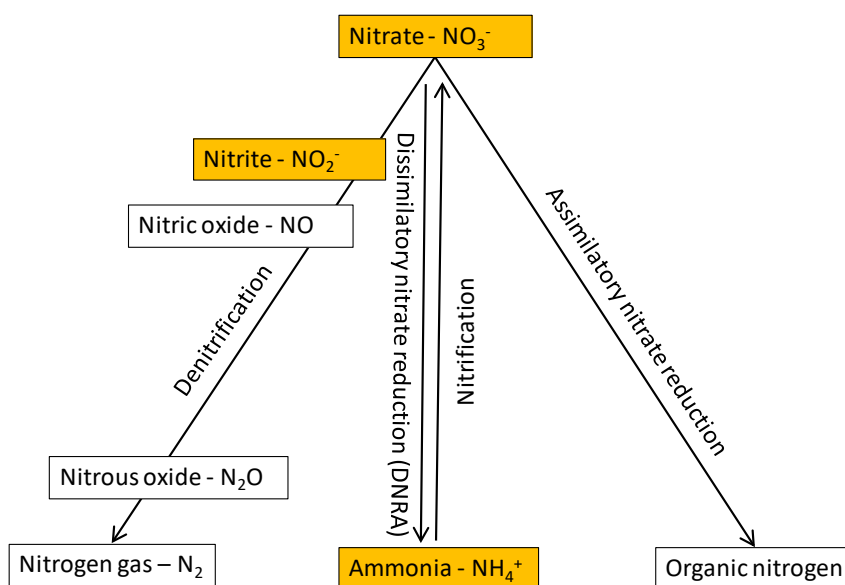
## 3 Groundwater monitoring data indicating potential denitrification

### 3.1 INDICATORS OF POTENTIAL DENITRIFICATION

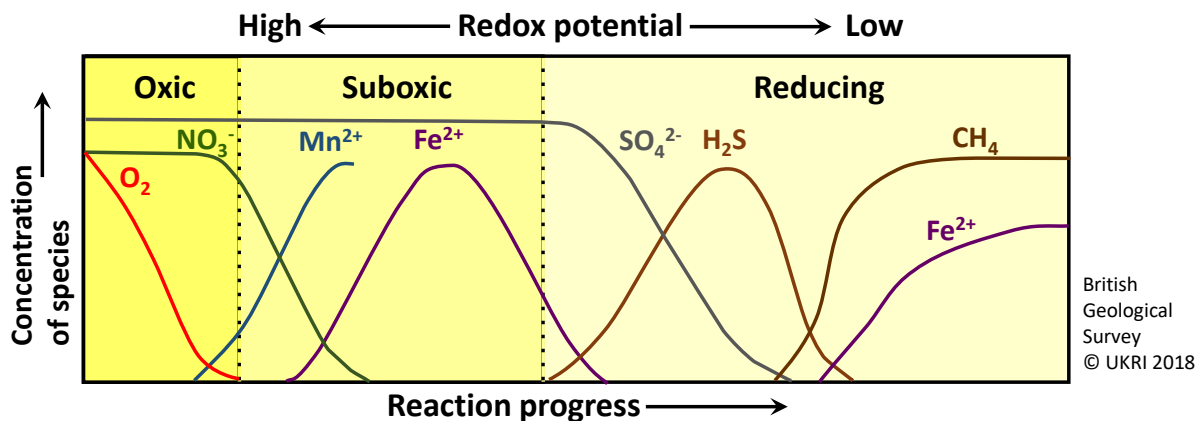
In groundwater, denitrification is the dominant nitrate ( $\text{NO}_3^-$ ) attenuation process and becomes active where oxygen is depleted. Denitrification is the reduction of  $\text{NO}_3^-$  and is normally carried out by anaerobic bacteria to form N species that are ultimately lost to the atmosphere. In aerobic heterotrophic respiration, organic carbon is oxidized preferentially using dissolved oxygen (DO) (Rivett et al, 2008). With an excess of organic carbon, these bacteria consume DO until it is depleted whereupon reduction of other electron acceptors becomes energetically favourable. Once DO is consumed, facultative anaerobes use  $\text{NO}_3^-$  as an electron acceptor for anaerobic respiration, the denitrification process.

This process produces a series of intermediates, including the nitrite ion ( $\text{NO}_2^-$ ), nitric oxide (NO) and nitrous oxide ( $\text{N}_2\text{O}$ ), with the final step being the production of gaseous nitrogen ( $\text{N}_2$ ) (Figure 3.1). Denitrification is thus a dissimilatory  $\text{NO}_3^-$  reduction process with N being lost from the groundwater system. The presence of these N intermediaries has been used to demonstrate denitrification (Anderson et al., 2014; Bragan et al., 1997; Duff and Triska, 1990; Groffman et al., 1998; Li et al., 2013; Mühlherr and Hiscock, 1997, 1998), but these are not parameters commonly measured in strategic groundwater monitoring.

Rivett et al. (2008) concluded that the critical limiting factors are oxygen and electron donor concentration and availability. Other factors such as  $\text{NO}_3^-$  concentration, nutrient availability, pH, temperature, presence of toxins and microbial acclimation appear to be less important. Korom (1992) included both denitrification and dissimilatory reduction to ammonia (DNRA) in their review of saturated zone processes. They concluded that natural denitrification occurs in modern waters but that it was difficult to predict the rate. The partitioning of  $\text{NO}_3^-$  between denitrification and DNRA is believed to be controlled by the availability of organic matter: DNRA is the favoured process when  $\text{NO}_3^-$  (electron acceptor) supplies are limiting and denitrification is favoured when carbon (electron donor) supplies are limiting (Korom, 1992).



**Figure 3.1** Part of the N cycle showing processes relating to nitrate concentration in water (parameters usually measured in strategic groundwater monitoring shown in yellow)



**Figure 3.2** The sequence of reaction zones developing as groundwater moves along flow pathways from recharge to confined conditions (after Appelo and Postma, 2005) in Shand et al. (2007)

After consumption of  $\text{NO}_3^-$  a further sequence of ions can be used as electron acceptors with decreasing energetic yields (Figure 3.2). These include reduction of  $\text{Mn}^{4+}$  then  $\text{Fe}^{3+}$  to soluble oxidation states ( $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  species) with increase in observed concentrations, reduction of sulphate ( $\text{SO}_4^{2-}$ ) to S species, and finally the reduction of carbon dioxide to methane. The presence or absence of these parameters can be used as indicators of low redox and therefore of denitrification potential (McMahon and Chapelle, 2008). This reaction sequence is seen along groundwater flow lines (Edmunds et al., 1982; Edmunds et al., 1984) typically as aquifers become confined.

There is also evidence for autotrophic denitrification coupled to sulphide or Fe oxidation. Autotrophic organisms are able to synthesise organic compounds from inorganic substances. Nitrate reduction by oxidation of pyrite should lead to increased concentrations of  $\text{SO}_4$ . Jahangir et al. (2013) found a positive correlation between groundwater  $\text{SO}_4$  concentration and denitrification rate and suggest that, due to low DOC in most groundwater environments, denitrification may well be autotrophic. A similar correlation with  $\text{NH}_4$  was attributed to possible DRNA.

Table 3.1 summarises the range of values measures for key parameters in redox zones of the three main UK aquifers. These demonstrate a consistent pattern with the anaerobic zone characterised by  $\text{DO} < 0.4 \text{ mg/L}$ ,  $\text{NO}_3$  generally  $< 1$ ,  $\text{Fe} > 100 \text{ } \mu\text{g/L}$   $\text{Mn} > 4 \text{ } \mu\text{g/L}$ .

Zones of low redox in groundwater were assessed using a similar approach to that of McMahon and Chapelle (2008) for evaluating redox conditions in 15 principal aquifers across the USA. They used a series of indicators including the electron acceptors  $\text{DO}$ ,  $\text{NO}_3$  and  $\text{SO}_4$ , and the solid phase acceptors  $\text{Mn}^4$  and  $\text{Fe}^3$ , indicated by the presence of dissolved  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  (Table 3.2). Indicator concentrations are shown as shaded cells in Table 3.2. Thresholds for nitrate in the suboxic and nitrate reduction zones have been amended (replacing  $<$  by  $>$ ) since these appear to be erroneous in the original.

Concentration thresholds are variable and dependent on multiple factors and McMahon and Chapelle (2008) recognised this limitation in their methodology. Concentration thresholds for aquifers in England were developed using monitoring data in section 3.3.2.

**Table 3.1 Ranges of literature values of chemical characteristics of redox zones identified in UK aquifers (all in mg/L except Fe and Mn ( $\mu\text{g/L}$ ) and Eh (mV))**

Lithology	Area	Zone 1 (Aerobic)	Zone 2 (Intermediate)	Zone 3 (Anaerobic)	Reference
Chalk	Berkshire	DO = 4–10 NO <sub>3</sub> = 20–30 Eh = +350–00 NH <sub>4</sub> = <0.01 Fe = <0.3 Mn = <0.03		DO = <LOD NO <sub>3</sub> = <LOD Eh = 0–+50 NH <sub>4</sub> = 0.05–0.85 Fe = 7–170 Mn = 4–57	Edmunds et al. (1984)
	Lincolnshire	NO <sub>3</sub> = 26–77 Eh = >+300		NO <sub>3</sub> = <4 Eh = -50–+100	Howard (1985)
	London Basin	NO <sub>3</sub> = 2.5–51	NO <sub>3</sub> = 2.5	NO <sub>3</sub> = 0.04	Elliot et al. (1999)
Sherwood Sandstone	East Midlands	DO = 2.5–10 NO <sub>3</sub> = 6.8–54 Eh = +127–336 Fe = <4–236 Mn = <0.5–21	DO = <0.5–8.7 NO <sub>3</sub> = 0.02–6.7 Eh = -7–+406 Fe = 6–372 Mn = 1.5–6	DO = <0.1 NO <sub>3</sub> = 0.04–1.15 Eh = -5–0–+78 Fe = 115–1970 Mn = 5.5–37	Edmunds et al. (1982)
		DO = 2–10 NO <sub>3</sub> = 3–54 Eh = +250–400 Fe = <15 $\mu\text{g/L}$		DO = <LOD NO <sub>3</sub> = <LOD Eh = 0–+100 Fe = 130–2000	Edmunds et al. (1984)
		DO = 0.5–10.1 NO <sub>3</sub> = <0.04–67 Eh = +116–485		DO = <0.4 NO <sub>3</sub> = <0.4–2.1 Eh = -99–+183	Smedley and Edmunds (2002)
Lincolnshire limestone	Lincolnshire 1969	DO = 1.5–7 NO <sub>3</sub> = 6–40 Eh = +400 Fe = <LOD		DO = <LOD NO <sub>3</sub> = <LOD Eh = 0–+100 Fe = 100–1800	Reported in Edmunds et al. (1984)
	Lincolnshire 1983	DO = 0.5–7 NO <sub>3</sub> = 10–62 Eh = +400 Fe = <LOD		DO = <LOD NO <sub>3</sub> = <LOD Eh = 0–+100 Fe = 30–2800	Edmunds et al. (1984); Edmunds and Walton (1983)
	Lincolnshire	NO <sub>3</sub> = 25		NO <sub>3</sub> = <5	Lawrence and Foster (1986)

**Table 3.2 Threshold concentrations for identifying redox processes in regional aquifer systems (after McMahon and Chapelle, 2008)**

Status	Redox process	Water quality criteria (mg/L)					Reference for criteria
		DO	NO <sup>3-</sup>	Mn <sup>2+</sup>	Fe <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	
Oxic	O <sub>2</sub> reduction	≥0.5	-	<0.05	<0.1		Seitzinger et al. (2006); Tiedje (1988)
Suboxic		<0.5	≥0.5	<0.05	<0.1		Further definition not possible
Anoxic	NO <sup>3-</sup> reduction	<0.5	≤0.5	<0.05	<0.1		
	Mn <sup>4+</sup> reduction	<0.5	<0.5	≥0.05	<0.1		Chapelle and McMahon (1991); Chapelle et al. (1995); Christensen et al. (2000); Elliot et al. (1999); Murphy and Schramke. (1998); Plummer et al. (1990)
	Fe <sup>3+</sup> /SO <sub>4</sub> <sup>2-</sup> reduction	<0.5	<0.5	-	≥0.1	≤0.5	Chapelle et al. (2002)
	Methano-genesis	<0.5	<0.5	-	≥0.1	<0.5	
Mixed		-	-	-			Criteria for more than one process are met

## 3.2 MONITORING DATA

### 3.2.1 Distributions of concentration in groundwater

Groundwater monitoring data from the Environment Agency monitoring network were used to evaluate groundwater concentrations. This information was provided to BGS as an extract from the WIMs database and included boreholes, wells and springs, as well as surface water sites. Monitoring points for surface water and for groundwater sites for monitoring waste disposal were excluded. Information on aquifer, confinement and depth was provided separately in the Boreholes, Wells and Springs (BWS) database. These were related using the BWSID and site name from BWS, and WIMS code and site name from WIMs. An additional spreadsheet containing BWSID-WIMS code relationships was also used. This provided a subset of 4291 predominantly strategic monitoring boreholes with suitable water quality data and attributed to an aquifer. Of these, some reported confinement and borehole depth.

A wide range of numbers of values for each parameter were available for each site covering different time intervals. Average values were calculated for each parameter at each borehole site with aquifer information. Because detection limits (DL) were not consistent within each dataset a pragmatic decision was taken to set all < values to zero, rather than 0.5 DL. This potentially makes the average value for individual sites slightly lower than if 0.5 DL had been used.

Table 3.3 summarises the final dataset. Oxidised nitrogen species were reported as TON, NO<sub>3</sub>-N or NO<sub>3</sub>, and may include replicate data which has been interconverted. Parameters generally were reported for between 3000 and 12,000 monitoring points with laboratory pH (pH\_lab) and total SO<sub>4</sub>, Fe and Mn having the most and NO<sub>3</sub>, dissolved S and dissolved SO<sub>4</sub> (SO<sub>4</sub>\_dis) the least. Data reported for NO<sub>3</sub> were not considered further as there were relatively few of these and other reported N-species had over 3600 values.



**Table 3.3 Summary of selected groundwater monitoring data**

Group	Parameter	No of sites	Detection Limit (range)	Range of average values		
				Min	Median	Max
N-species	TON (mg/L)	3707	0.1 (0.05-0.5)	0	4.41	53.1
	NO <sub>3</sub> _N (mg/L)	3631	0.1	0	4.16	54.2
	NO <sub>3</sub> (mg/L)	310	0.1	0	27	71.2
	NO <sub>2</sub> _N	3697	0.002 (0.0007-0.005)	0	0.0004	17.6
	NH <sub>4</sub> _N (mg/L)	3999	0.015 (0.0005-0.25)	0	0.0051	175
Trace metals	Fe_total (µg/l)	3327	6.5-7.5(0.005-50)	0	72.7	264,211
	Fe_dis (µg/l)	3327	15 (0.05-25)	0	7.00	205,735
	Mn_total (µg/l)	3930	2.5-5 (0.5-5)	0	3.24	6844
	Mn_dis (µg/l)	3282	2.5-5 (0.75-5)	0	1.05	6835
	Ni_total (µg/l)	3630	2.5 (0.5-25)	0	0.47	1687
	Ni_dis (µg/l)	2773	2.5 (0.5-5)	0	0.26	338
O and S species	DO (mg/L)	3053	0.25 (0-5)	0.045	6.91	108
	DO (%)	3116	0.25	0.466	62.3	140
	SO <sub>4</sub> _total (mg/L)	4158	2.5-5	0	35.9	2,877
	SO <sub>4</sub> _dis (mg/L)	1809	2.5-5	0	35.32	2,675
	S (mg/L)	1588	0.005	0	0	31
DOC and pH	DOC (mg/L)	3016	0.1 (0.05-5)	0	0.831	38
	pH_lab	4183		4.56	7.32	65
	pH_insitu	3013		4.43	7.32	71

\_tot = total (unfiltered sample), \_dis = dissolved (filtered sample), \_lab = measured in the laboratory, \_insitu = measured on site during sample collection

Most of the parameters contained a few extremely high values. Since this project is using data at the low end of the frequency distribution this was not considered to be important and was disregarded. Median average values are sometimes lower than the DL, this is an artefact of setting values below the DL to zero. The criteria for indicating denitrification potential were higher than the largest detection limit in all cases.

### 3.2.2 Selection of criteria

For a first pass the criteria of McMahon and Chapelle (2008) were applied. The data were plotted out to determine visually which threshold values would provide sufficient discrimination of potential redox conditions within the data. Selected plots are presented in Appendix 1. The threshold values selected are shown in Table 3.4. Analyses resulted in unfiltered samples generally being allocated a higher threshold value than those in the dissolved phase to reflect their higher concentrations.

In comparison to the threshold criteria all of the analysed parameters had detection limits below these. Parameters which have a few extreme or erroneous high average values recorded in the database were used since the project team had no ready means of filtering these values out. The maximum average values are shown in Table 3.3. The impact on the assessment was considered to be slight.

**Table 3.4 Low-redox criteria used for analysis of groundwater monitoring data for both bedrock and superficial aquifers**

Group	Indicator parameter	Criterion	McMahon and Chapelle, 2008
N-species	TON (mg/L)	$\leq 1$	$\leq 0.5$
	NO <sub>3</sub> -N(mg/L)	$\leq 1$	$\leq 0.5$
	NO <sub>2</sub> -N (mg/L)	$\geq 0.1$	
	NH <sub>4</sub> -N (mg/L)	$\geq 0.3$	
Trace metals	Fe total ( $\mu\text{g/L}$ )	$\geq 500$	
	Fe dissolved ( $\mu\text{g/L}$ )	$\geq 100$	$\geq 100$
	Mn total ( $\mu\text{g/L}$ )	$\geq 500$	
	Mn dissolved ( $\mu\text{g/L}$ )	$\geq 100$	$\geq 50$
	Ni total ( $\mu\text{g/L}$ )	$\geq 10$	
	Ni dissolved ( $\mu\text{g/L}$ )	$\geq 10$	
O and S species	DO (mg/L)	$\leq 1$	
	DO (%)	$\leq 10$	
	SO <sub>4</sub> total (mg/L)	$\leq 1$	
	SO <sub>4</sub> dissolved (mg/L)	$\leq 0.5$	$\leq 0.5$
	S (mg/L)	$\geq 0.02$	
Doc and pH	pH insitu	NA	
	pH lab	NA	
	DOC (mg/L)	$\geq 3$	

### 3.2.3 Evaluation of monitoring data

Monitoring data did not include a complete classification for confined/unconfined so for each parameter all data were allocated to an aquifer group and plotted out on:

- Subcrop polygons for Chalk, Upper Greensand, Lower Greensand, Corallian, Oolite, Lias, Sherwood Sandstone, Zechstein (Magnesian Limestone), Carboniferous and Dinantian (Lower Carboniferous)
- Outcrop geology at the 1:625,000 scale overlain by low-permeability superficial deposits. Data were aggregated into the same groups as the polygons plus the Crag, Palaeogene and Neogene, Devonian and pre-Devonian groups that do not have subcrop polygons.

The total number of records in each aquifer grouping including both outcrop and subcrop are shown in Table 3.5. Plots of individual parameters on subcrop polygons and on outcrop overlain by low-permeability superficial deposits for each aquifer grouping are shown in Appendix 2. From these maps an idea of the usefulness of individual parameters can be gained.

This process highlighted that concentrations of trace metals and SO<sub>4</sub> are related to natural occurrence in the aquifer matrix as well as potentially to redox conditions. Aquifer lithology mainly controls pH, with sandstones being more acid than limestones, and within an individual group by residence time, with pH increasing with time due to ion exchange of Na for Ca. No criteria could be set for pH in this project. For more detailed studies it could potentially be possible to derive aquifer specific redox criteria.

**Table 3.5 Monitoring point coverage per aquifer group**

<b>Aquifer groupings</b>	<b>Associated subcrop polygon</b>	<b>Number of monitoring points</b>
Superficial		172
Crag Group		36
Palaeogene		40
Chalk	TopChalk	1617
Upper Greensand Formation	TopUpperGreensand	89
Lower Greensand Group	TopLowerGreensand	221
Lower Cretaceous		110
Corallian Group	TopCorallian	51
Oolite and other Middle Jurassic	TopGreatOolite	309
Lias Group	TopLias	50
Mercia Mudstone Group		37
Permo-Triassic Sandstone	TopSherwoodSandstone	846
Zechstein Group (Magnesian Limestone)	TopZechstein	142
Carboniferous (Coal Measures and Millstone Grit)	TopCarboniferous	327
Carboniferous (Dinantian)	TopDinantian	152
Devonian		34
Older (Ordovician, Silurian and Precambrian)		55
Miscellaneous (SW England volcanics)		3
<b>Total points with aquifer ascribed</b>		<b>4291</b>

Evaluating the role of the superficial deposits is more challenging. Plots of monitoring parameters on the 1:625,000 superficial geology are also shown in Appendix 2. These deposits are complex even using these simplified classifications.

### 3.2.4 Evaluation of parameters

An evaluation of the evidence supporting denitrification potential in bedrock confined zones is shown in Tables 3.6 and 3.8 below low-permeability superficial deposits in Tables 3.7 and 3.9. The patterns of concentrations for each individual parameter was evaluated visually from the maps presented in Appendix 2 and classed in Table 3.6 for bedrock confined zones and Table 3.8 for bedrock zones confined by low-permeability superficial deposits as:

- Clear relationship = Yes
- Possible relationship =P
- No relationship = N
- None or only very few monitoring points in the confined or low-permeability superficial covered zone = S

These classifications were given a simple score in Table 3.7 derived from Table 3.6 and Table 3.9 derived from Table 3.8 to allow the tabulated data to be sorted, where Y=1, P=0.5 and N or S=0.

**Table 3.6 Parameters indicating low redox in bedrock confined zone polygons**

Aquifer Group	N-species				Trace metals						DO and S-species					DOC and pH		
	TON	NO <sub>3</sub> -N	NO <sub>2</sub> -N	NH <sub>4</sub> -N	Fe total	Fe dis	Mn total	Mn dis	Ni total	Ni dis	DO (mg/l)	DO (%)	SO <sub>4</sub> total	SO <sub>4</sub> dis	S	DOC	pH insitu	pH lab
Chalk	Y	Y	P	Y	Y	Y	N	N	N	P	N	N	N	N	N	N	P	P
Upper Greensand	Y	Y	N	N	P	Y	N	N	N	N	N	N	N	N	N	N	N	N
Lower Greensand	Y	Y	N	P	Y	Y	N	P	N	N	N	N	N	N	N	N	P	P
Corallian	Y	Y	N	Y	Y	Y	N	N	N	N	N	N	N	N	N	P	N	N
Oolite	Y	Y	N	Y	N	Y	N	N	N	N	P	P	N	P	P	P	P	P
Lias	N	N	N	N	N	N	N	N	S	N	S	S	S	S	S	N	N	N
Sherwood Sandstone	Y	Y	P	N	P	Y	N	N	P	N	N	N	N	N	N	N	N	N
Zechstein (Mag Lmst)	P	P	N	N	P	P	N	N	N	N	N	N	N	P	S	N	P	P
Carboniferous	P	P	N	P	P	P	P	P	N	P	N	N	N	N	N	N	N	N
Dinantian	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S

Y=Yes, N=No, P=Possibly, S=Very few or no monitoring points in confined zone polygon,

**Table 3.7 Parameters indicating low redox in bedrock aquifer confined zones scored from Table 3.6 and sorted**

	TON	NO <sub>3</sub> -N	Fe dis	Fe total	NH <sub>4</sub> -N	pH insitu	pH lab	NO <sub>2</sub> -N	Mn dis	Ni dis	SO <sub>4</sub> dis	DOC	Mn total	Ni total	DO (mg/l)	DO (%)	S	SO <sub>4</sub> total	Score
Oolite	1	1	1	0	1	0.5	0.5	0	0	0	0.5	0.5	0	0	0.5	0.5	0.5	0	7.5
Chalk	1	1	1	1	1	0.5	0.5	0.5	0	0.5	0	0	0	0	0	0	0	0	7
Upper Greensand	1	1	1	0.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7
Lower Greensand	1	1	1	1	0.5	0.5	0.5	0	0.5	0	0	0	0	0	0	0	0	0	6
Corallian	1	1	1	1	1	0	0	0	0	0	0	0.5	0	0	0	0	0	0	5.5
Sherwood Sandstone	1	1	1	0.5	0	0	0	0.5	0	0	0	0	0	0.5	0	0	0	0	4.5
Carboniferous	0.5	0.5	0.5	0.5	0.5	0	0	0	0.5	0.5	0	0	0.5	0	0	0	0	0	4
Zechstein (Mag Lmst)	0.5	0.5	0.5	0.5	0	0.5	0.5	0	0	0	0.5	0	0	0	0	0	0	0	3.5
Lias	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Dinantian	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<b>Score</b>	7	7	7	5	4	2	2	1	1	1	1	1	0.5	0.5	0.5	0.5	0.5	0	

Y=1, N=0, S=0, P=0.5

Cells coloured orange represent parameters and those coloured grey represent aquifer groupings with the highest scores. Where these overlap, cells are coloured pink

**Table 3.8 Parameters indicating low redox in bedrock aquifer zones confined by low-permeability superficial deposits**

Aquifer Group	N-species				Trace metals						DO and S-species					DOC and pH		
	TON	NO <sub>3</sub> -N	NO <sub>2</sub> -N	NH <sub>4</sub> -N	Fe total	Fe dis	Mn total	Mn dis	Ni total	Ni dis	DO (mg/l)	DO (%)	SO <sub>4</sub> total	SO <sub>4</sub> dis	S	DOC	pH insitu	pH lab
Crag	Y	Y	N	N	Y	Y	N	Y	N	N	P	S	N	N	S	N	N	N
Palaeogene	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Chalk	Y	Y	N	P	P	Y	N	Y	N	P	Y	N	N	N	N	N	N	N
Upper Greensand	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Lower Greensand	N	N	N	N	N	P	N	P	N	P	N	N	N	N	N	P	N	N
Corallian	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Oolite	N	N	N	N	N	N	N	N	N	N	N	N	N	N	S	N	N	N
Lias	P	P	N	N	N	N	N	N	N	N	N	N	N	N	S	N	N	N
Mercia Mudstone	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Sherwood Sandstone	P	Y	N	Y	Y	Y	N	Y	N	N	N	N	N	N	N	P	P	P
Zechstein (Mag Lmst)	P	P	P	P	P	P	N	Y	N	N	Y	P	P	N	P	N	N	N
Carboniferous	P	Y	N	P	Y	Y	P	Y	N	N	N	N	N	P	N	P	P	P
Dinantian	Y	Y	N	N	N	P	N	N	N	N	N	N	N	P	S	Y	P	P
Older	P	P	P	N	P	P	N	N	N	N	N	N	N	P	S	N	N	N

Lower Greensand includes Lower Cretaceous in plot

Devonian no overlap

**Table 3.9 Parameters indicating low redox in bedrock aquifer zones confined by low-permeability superficial deposits scored from Table 3.7 and sorted**

	NO <sub>3</sub> -N	Fe dis	TON	Mn dis	Fe total	NH <sub>4</sub> -N	DO (mg/l)	DO C	SO <sub>4</sub> dis	pH insitu	pH lab	NO <sub>2</sub> -N	Ni dis	Mn total	DO (%)	SO <sub>4</sub> total	S	Ni total	Score
Carboniferous	1	1	0.5	1	1	0.5	0	0.5	0.5	0.5	0.5	0	0	0.5	0	0	0	0	7.5
Sherwood Sandstone	1	1	0.5	1	1	1	0	0.5	0	0.5	0.5	0	0	0	0	0	0	0	7
Chalk	1	1	1	1	0.5	0.5	1	0	0	0	0	0	0.5	0	0	0	0	0	6.5
Zechstein (Mag. Lmst)	0.5	0.5	0.5	1	0.5	0.5	1	0	0	0	0	0.5	0	0	0.5	0.5	0.5	0	6.5
Crag	1	1	1	1	1	0	0.5	0	0	0	0	0	0	0	0	0	0	0	5.5
Dinantian	1	0.5	1	0	0	0	0	1	0.5	0.5	0.5	0	0	0	0	0	0	0	5
Older	0.5	0.5	0.5	0	0.5	0	0	0	0.5	0	0	0.5	0	0	0	0	0	0	3
Lower Greensand	0	0.5	0	0.5	0	0	0	0.5	0	0	0	0	0.5	0	0	0	0	0	2
Lias	0.5	0	0.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
Palaeogene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Upper Greensand	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Corallian	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oolite	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mercia Mudstone	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Score	6.5	6	5.5	5.5	4.5	2.5	2.5	2.5	1.5	1.5	1.5	1	1	0.5	0.5	0.5	0.5	0	

Y=1, N=0, S=0, P=0.5

Cells coloured orange represent parameters and those coloured grey represent aquifer groupings with the highest scores. Where these overlap, cells are coloured pink.

From this simple classification in Tables 3.7 and 3.9 the best evidence for low redox conditions is provided by TON, NO<sub>3</sub>-N, Fe species and NH<sub>4</sub>-N for bedrock aquifer confined zones and by TON, NO<sub>3</sub>-N, Fe species and Mn-dissolved for bedrock aquifers confined by superficial cover.

Lower Confidence is given to the confined zones of the Lias, Zechstein (Magnesian Limestone and the Dinantian (Lower Carboniferous) by this method, primarily due to the sparsity of records in the monitoring data for these zones (Table 3.9). Similarly the Palaeogene, Upper Greensand, Lower Greensand, the Jurassic strata of the Corallian, Oolite and the Lias and the Older (pre-Devonian) rocks have limited cover by low-permeability deposits. The Devonian has no overlap.

This methodology has limitations in representing strata which are themselves multi-layered but are shown as a single unit. Here these include the Palaeogene, Lower Greensand, Lower Cretaceous, oolites of the Middle Jurassic and the Millstone Grit and Coal Measures of the Carboniferous. A subcrop polygon was not available for the rocks of the Lower Cretaceous. Data for these strata have been plotted on the outcrop map for the Lower Greensand. These data do show some evidence of low redox.

The relationship observed for some confined zones with pH probably reflects a longer residence time in confined zones.

### 3.2.5 Evaluation of monitoring point coverage for confined zones

#### BEDROCK AQUIFER CONFINED ZONES

Table 3.10 shows the areas of the confined zones together with an estimate of the area containing monitoring points used in this project. These were estimated by manually sketching a GIS polygon around the monitoring points within the confined zone, giving a very approximate area. This assessment shows that only the confined Chalk has a reasonable coverage of monitoring points, with the Oolite and the Sherwood Sandstone also being 20% or more. This may mean that the deeper confined zones are not usable or at any rate not used, rather than not monitored. As above, this methodology has limitations in representing strata that are themselves multi-layered but are shown as a single unit.

**Table 3.10 Monitoring point coverage for the bedrock aquifer confined zones**

Confined zone	Total area (km <sup>2</sup> )	Approximate area with monitoring points		Confidence from coverage
		(km <sup>2</sup> )	(%)	
Chalk	11857	5177	44	Medium
Upper Greensand	28639	1658	5.8	Low
Lower Greensand	31472	1854	5.9	Low
Corallian	7289	538	7.4	Low
Oolite	20631	4188	21	Medium
Lias	23580	302	1.3	Low
Sherwood Sandstone	13490	2649	20	Medium
Zechstein (Mag Lmst)	3812	333	8.7	Low
Carboniferous	31278	197	0.63	Low
Dinantian	196	0	0	Low

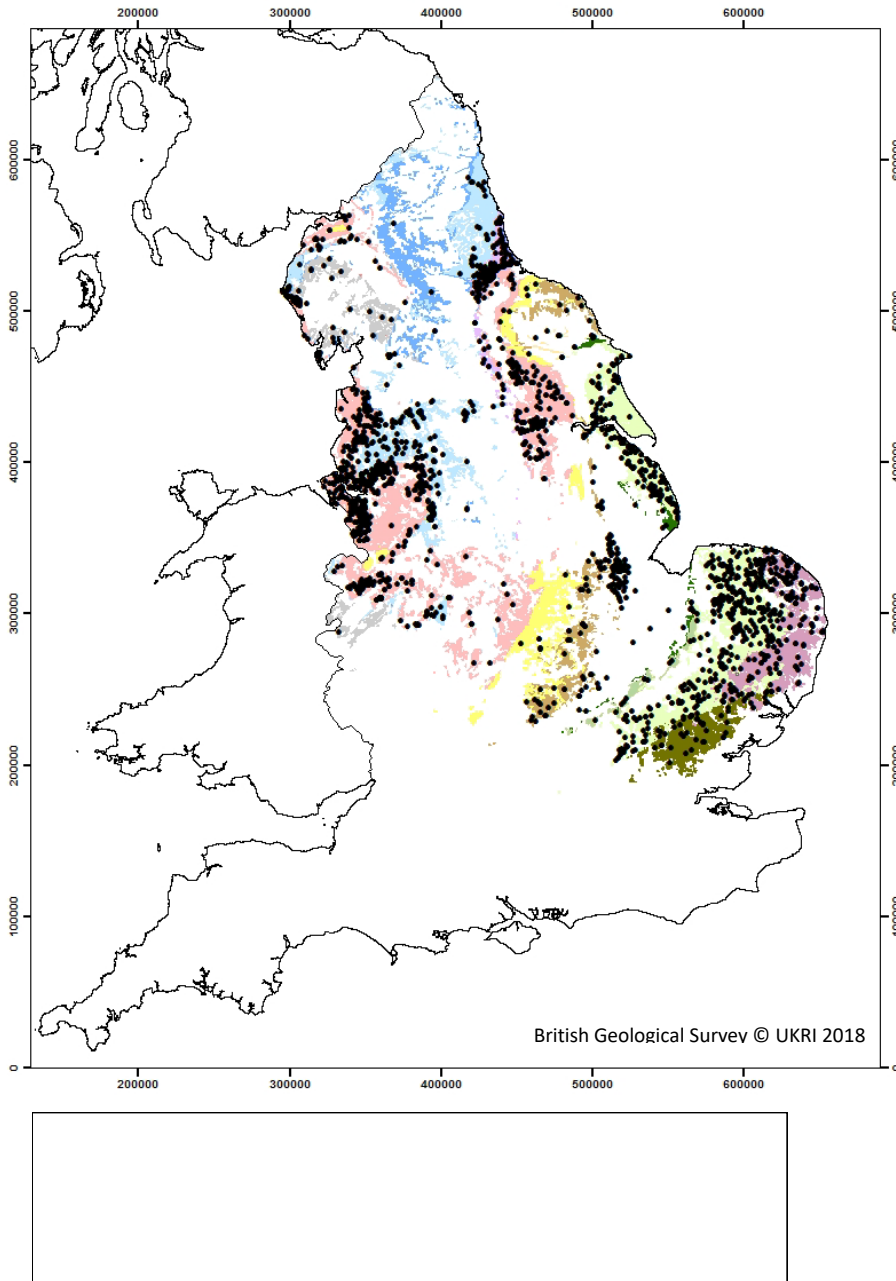
Ranges Low = <20%, Medium = 20-50%, High = >50%



BEDROCK AQUIFERS CONFINED BY SUPERFICIAL DEPOSITS

Figure 3.2 shows the distribution of monitoring points in bedrock aquifers in areas where these are confined by low-permeability superficial deposits. It was not possible to apply a simple method to estimate aquifer coverage because the superficials are complex and result in many small areas of bedrock. A visual estimate of coverage was used instead (High, Medium or Low).

All aquifer groupings apart from the Dinantian have a good distribution of points. However, a low coverage score was given where the area was less than 100 km<sup>2</sup>. Areas of the Lias, Yorkshire Chalk and the Carboniferous of the northeast have fewer points. These are summarised in Table 3.11.



**Figure 3.3** Distribution of monitoring points in bedrock aquifers overlain by low-permeability superficial deposits

**Table 3.11 Monitoring point coverage in bedrock aquifers overlain by low-permeability superficial deposits**

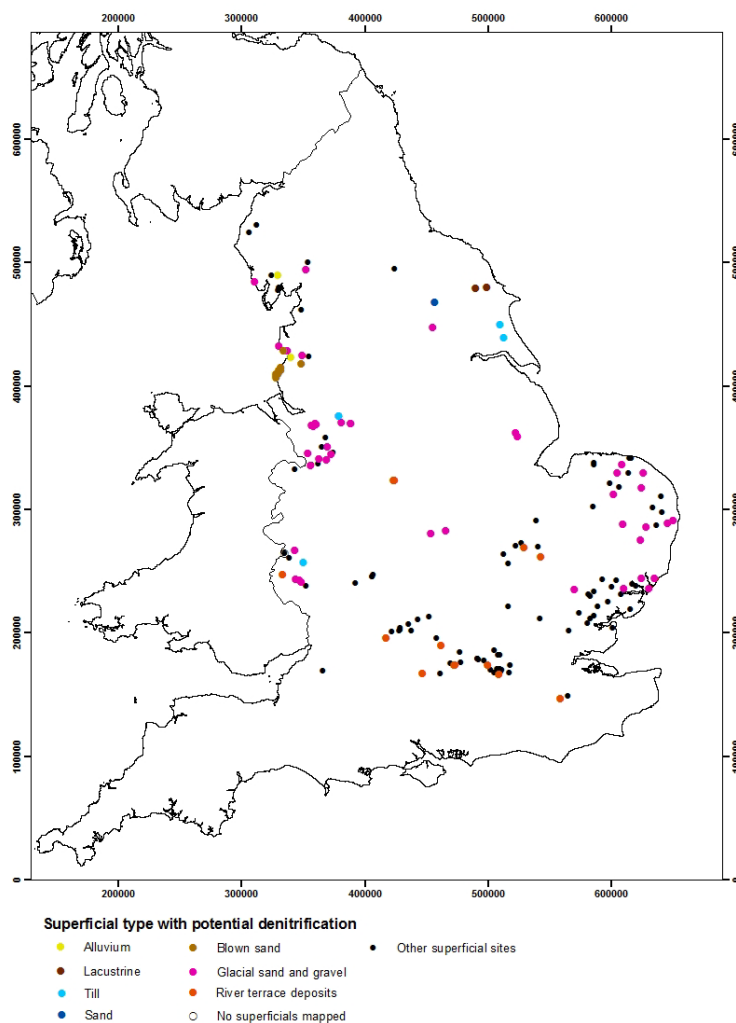
Bedrock aquifer	Total area (km <sup>2</sup> )	Confidence from coverage
Crag	2131	High
Palaeogene	1245	Medium
Chalk	5258	High
Upper Greensand	261	Medium
Lower Greensand	202	Medium
Lower Cretaceous	-	None
Corallian	27	Low
Oolite	1225	Medium
Lias	1594	Low
Permo-Trias including Mercia Mudstone	6431	High
Zechstein (Magnesian Limestone)	675	High
Carboniferous	3581	Medium
Dinantian	1206	Low
Devonian	1	None
Older	803	Medium
<b>Total</b>	<b>24043.3</b>	

### 3.2.6 Superficial aquifers

Of the 171 monitoring points classed as being in the superficial deposits 78 had concentrations of at least one out of N-species, Fe or Mn suggesting that there was potential for denitrification (Table 3.12).

**Table 3.12 Monitoring points in superficial aquifers with at least one indicator of low redox**

Class	No of sites with low redox indicator	Total no of sites	Area with possible potential	Characteristics
Glacial sand and gravel	45	94	Hereford, Cheshire-Macclesfield, East Anglia	No clear pattern
River terrace deposits	13	37	Thames	
Till	4	15	Hull, Knutsford	High Fe and Mn, Low NO <sub>3</sub>
Blown sand	11	11	Lancashire coast	High NH <sub>4</sub> Fe and Mn, Low NO <sub>3</sub>
Alluvium	2	5		No clear pattern
No mapped drift	1	3		High NH <sub>4</sub> Fe and Mn, Low NO <sub>3</sub>
Raised marine deposits	-	3		
Lacustrine deposits	2	2	Vale of Pickering	High NH <sub>4</sub> Fe and Mn, Low NO <sub>3</sub>
Holocene sand	1	1	York	High NH <sub>4</sub>



**Figure 3.4 Map of monitoring points in superficial aquifers with points showing denitrification potential classified by superficial type**

Of these 27 were classed as being in Drift (undivided) in the BWS database. Since this was a small number these sites were classified here into broad categories using BGS borehole records and the 1:625,000 superficial geological map. These only represent a fraction of the sites except for the blown sands of the Lancashire coast. The majority of sites in the superficial deposits with denitrification potential are in glacial sand and gravel and areas of river terrace deposits (Figure 3.4).

### 3.3 AQUIFER MAP LAYERS

Three layers are taken to the final map from this evaluation. The final potential score is a combination of the support from low redox from monitoring data and confidence from site coverage. Table 3.13 shows the method for derivation of the final score. Table 3.14 shows these for denitrification within superficial deposits. Table 3.15 shows these for zones confined by bedrock or low permeability superficial deposits.

**Table 3.13 Derivation of final denitrification potential score in aquifers**

<b>Low redox in confined zone supported by monitoring data</b>	<b>Confidence from coverage</b>	<b>Potential</b>
Yes	High	High
Yes	Medium	High
Limited or None	High	Low
Limited or None	Medium	Low
Yes	Low	Not classified (NC)
Limited or None	Low	Not classified (NC)

**Table 3.14 Summary of evidence for low redox conditions in superficial deposits**

<b>Superficial class</b>	<b>Low redox supported by monitoring data</b>	<b>Confidence from coverage</b>	<b>Potential</b>
Glacial sand and gravel	Yes	Medium	High
River terrace deposits	No	Low	NC
Till	No	Medium	Low
Blown sand	Yes	High	High
Alluvium	Yes	Medium	High
Raised marine deposits	No	Low	NC
Lacustrine deposits	Yes	High	High

**Table 3.15 Summary of evidence for low redox conditions in bedrock aquifers**

Aquifer group	Denitrification potential in subcrop bedrock				Denitrification potential in outcrop overlain by low permeability superficial deposits			
	Subcrop polygon defined	Low redox in confined zone supported by monitoring data	Confidence from coverage	Potential	Outcrop with low permeability superficial deposits	Low redox below superfcials supported by monitoring data	Confidence from coverage	Potential
Crag	No	NA	Low	NC	Yes	Yes	High	High
Palaeogene	No	Yes	Medium	High	Yes	No	Medium	Low
Chalk	Yes	Yes	High	High	Yes	Yes	High	High
Upper Greensand	Yes	Yes	High	High	Yes	No	Medium	Low
Lower Greensand	Yes	Yes	High	High	Yes	No	Medium	Low
Lower Cretaceous	No	Yes	Medium	High	No	NA	None	NC
Corallian	Yes	Yes	High	High	Yes	No	Low	NC
Oolite	Yes	Yes	High	High	Yes	No	Medium	Low
Lias	Yes	No	Low	NC	Yes	No	Low	NC
Permo-Triassic	Yes	Yes	High	High	Yes	Yes	High	High
Zechstein (Mag Lmst)	Yes	No	Medium	Low	Yes	Yes	High	High
Carboniferous	Yes	Yes	High	High	Yes	Yes	Medium	High
Dinantian (Lower Carb)	Yes	No	Low	NC	Yes	Yes	Low	NC
Devonian	No	NA	Low	NC	No	NA	None	NC
Older	No	NA	Low	NC	Yes	No	Medium	Low

### 3.4 SITE LAYER

A suite of 4 selected indicators was used to assess denitrification potential for individual site data (Table 3.16). The criteria were taken from Table 3.2. There were TON <1 mg/L, NH<sub>4</sub>>0.3 mg/L, Fe\_dis >100 µg/L and Mn\_dis >100 µg/L.

To allow for missing data the number of indicator measurements at each site was included in the assessment. Only sites with measurements for all four indicators meeting the criteria were assessed as having High potential. Sites with 3 indicators meeting the criteria were classed as Medium. All sites with 2 or fewer measurements were classed as NC.

**Table 3.16 Criteria for assessing individual site denitrification potential**

No of indicators with measurement	Number of measurements meeting criteria	Confidence
4	4	High
4	3	Medium
3	3	Medium
4	2 or fewer	Low
3	2 or fewer	Low
2 or fewer	-	Not classified (NC)

## 4 Mass balance approaches

### 4.1 OVERVIEW

In this approach, denitrification is considered to be the primary mechanism for nitrate losses in the subsurface below the base of the soil. Consequently, where unsaturated zone lags (UZL) are minimal, areas with high N inputs at the surface but low groundwater concentrations may be indicative of denitrification. The NVZ risk-scoring model provides 1 km gridded datasets of both surface nitrate loading and observed nitrate concentrations in groundwater. It is beyond the scope of this report to review the model inputs and risk scoring methodology, and the reader is referred to previous work by DEFRA (2016) for detailed information. In brief, N loadings to groundwater are calculated from models for agricultural and aerial deposition (NEAP-N, Lord and Anthony (2000)) and urban N sources (Environment Agency, 2013; Lerner, 2003). Observed groundwater nitrate concentration datasets are interpolated using kriging to derive gridded current and future predicted concentrations. Based on the N loading and observed concentration data, a risk-scoring model is then used to identify areas of high, medium and low risk of nitrate concentrations exceeding 11.3 mg N/L. In the rest of this section, we detail how the NVZ model data could be used as a potential indicator for denitrification.

### 4.2 APPROACH USING NVZ RISK SCORING MODEL

The loading and observed nitrate concentration data in the NVZ risk-scoring model have been used to develop an initial assessment of where denitrification may be occurring. To account for unsaturated zone lags, we assigned each 1 km grid cell a lag time based on the travel times derived by Wang et al. (2012). This approach only considers vertical transport from the base of the soil zone to groundwater. In areas underlain by low permeability superficial deposits and non-aquifers, nitrate leaching from the base of the soil zone is unlikely to reach groundwater. Consequently, we also assigned each cell with the underlying superficial deposit permeability class derived from SNIFFER (Griffiths et al., 2011) and bedrock hydrogeological classification derived from 1:625,000 hydrogeological maps. We then used the following rules to identify areas where there is a mismatch between N loading and observed concentrations:

- High nitrate loading. Total N loading (agriculture + urban) concentrations > 11.3 mg N/L
- Low groundwater nitrate concentrations (low “final observed score” < 4)
- Short USZ lag time (less than 10 years)
- Underlain by moderate and highly productive aquifers only, with no low permeability superficial deposit cover (LM and LL).

The resulting areas are shown in Figure 4.1. These areas include the edge of the Chalk and the Middle Jurassic oolites, and some areas of the Crag and Permo-Triassic sandstones. In these areas, high nitrate loadings are likely to reach groundwater (due to presence of significant aquifers and no low permeability cover), but unsaturated zone lags are small and observed nitrate concentrations are low. This mismatch between loading and concentration may be attributable to denitrification.

Areas identified in this approach could include strata where there is internal confinement and ferruginous aquifers.

**Figure 4.1** Areas on moderate and highly productive aquifers without low permeability superficial cover which have high nitrate loadings, short unsaturated zone lags but low groundwater nitrate concentrations.

### 4.3 LIMITATIONS

It must be noted that the areas derived in Figure 4.1 are subject to a number of limitations. The analysis of the NVZ risk model data only considers a mismatch between nitrate loadings and kriged groundwater concentrations. The kriging process used to derive interpolated nitrate concentrations does not take into account aquifer boundaries (DEFRA, 2016), and consequently the “final observed score” in the NVZ lines of evidence spreadsheet may not necessarily reflect observed concentrations at a given location.

Moreover, whilst denitrification may be a factor in controlling this mismatch, it must be noted that no detailed process-based explanation for this difference is being made in this study. The dominant setting for groundwater denitrification is confined aquifers (Rivett et al., 2008). In these settings, the source of nitrate is from laterally up hydraulic gradient in unconfined areas, rather than vertically from the soil zone. Previous studies have considered that denitrification in the unsaturated zone is likely to be negligible, with only 1-2% of the influent N load removed.

Denitrification in unconfined groundwater at the broad scale has also been considered as insignificant (Rivett et al. 2008). However, there will clearly be areas of localised/microscale



denitrification due to appropriate geochemical conditions, for example low oxygen or high iron concentrations. Given the uncertainties in both kriged groundwater nitrate concentrations and the limited evidence for denitrification in unconfined aquifers and the unsaturated zone, further work is required to refine the areas in Figure 4.1 before they can be used in denitrification potential maps. Comparing areas of high nitrate loading with raw (i.e. not interpolated) groundwater nitrate monitoring data would remove the impact of kriging on the results. Further work to attribute Environment Agency monitoring data to aquifers would be required prior to this.

There is also some subjectivity involved in developing filtering criteria for N loading, observed nitrate concentrations and unsaturated zone lag times. Comparison between the areas derived using different filtering criteria against key denitrification indicators (e.g. DOC, iron, DO) could be used to validate this approach. Given these limitations, the mass balance work is not considered further in the map of denitrification potential in Chapter 5.

## 5 Map of denitrification potential

### 5.1 MAP STRUCTURE

This section brings the three lines of evidence together (Figure 5.1). These are described in the following sections covering the subcrop of the main aquifers, areas of bedrock aquifers confined by low-permeability superficial deposits and superficial aquifers.

These are constructed as shape files that contain the outline of the strata together with the denitrification potential and confidence. Individual layers can be switched on depending on the context.

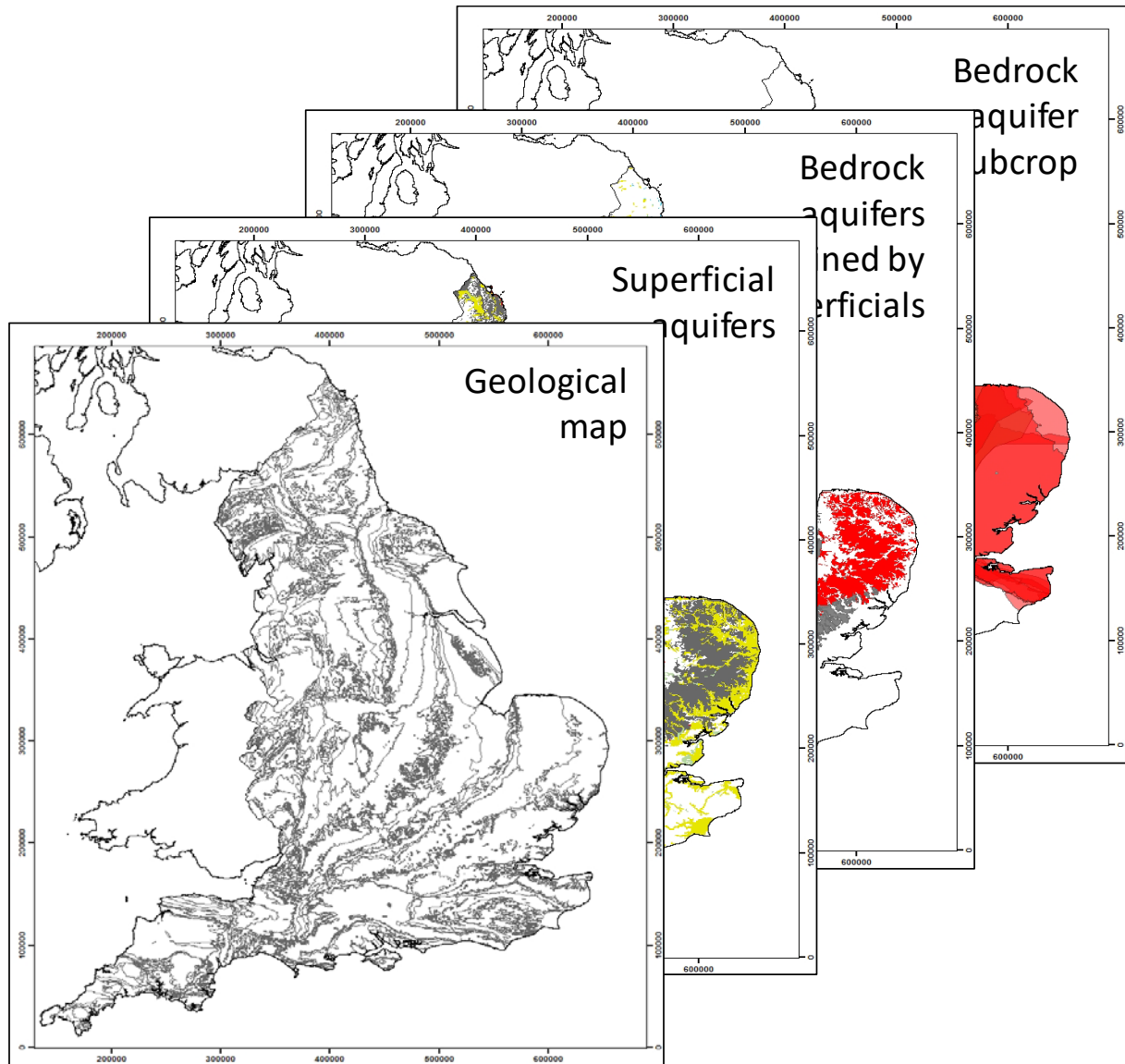
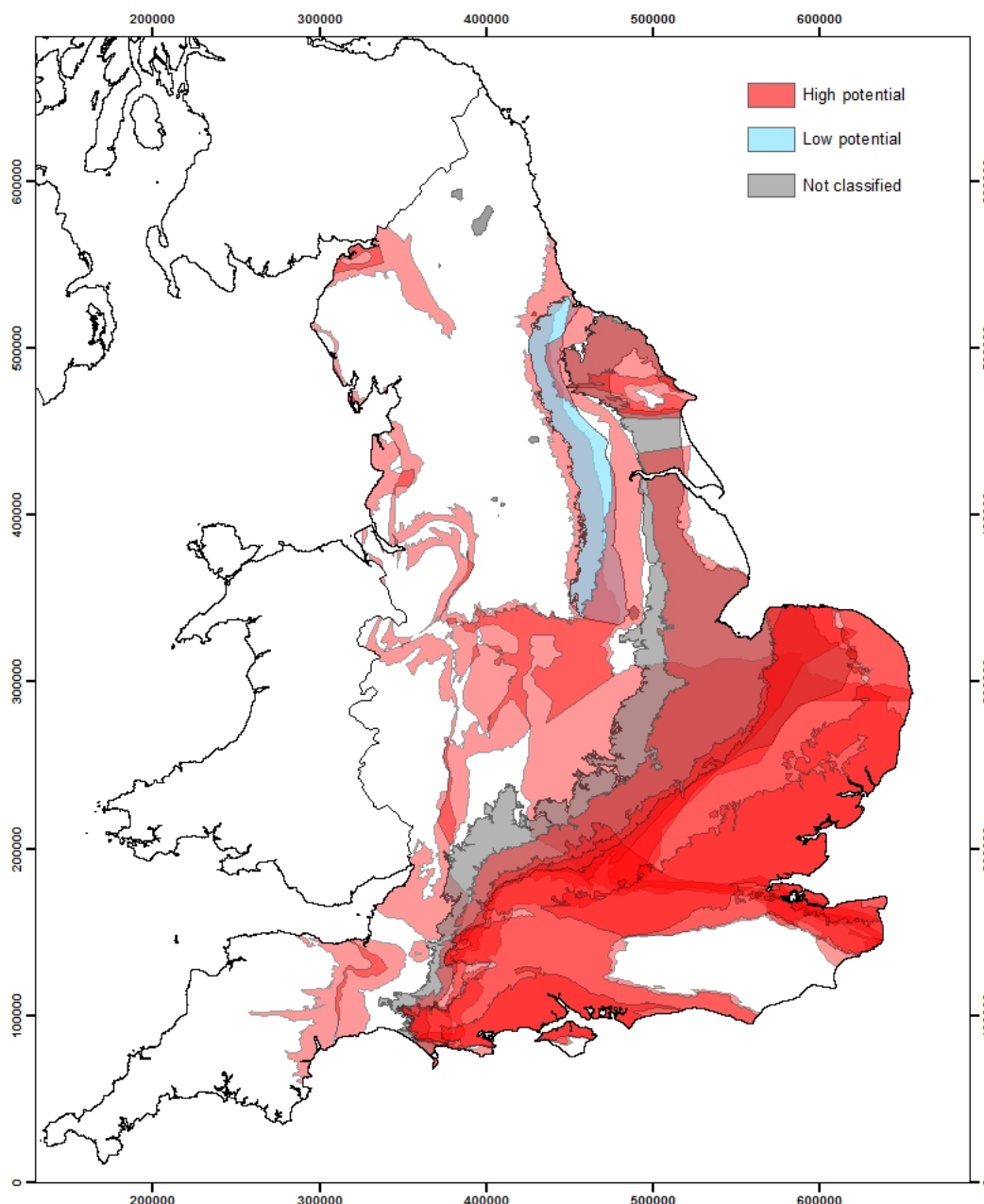


Figure 5.1 Map layers

## 5.2 BEDROCK AQUIFER CONFINED ZONES

As shown in Table 3.13, the confined zones of the Upper and Lower Greensand, Chalk, Corallian, Oolite, Permo-Triassic sandstones and the Carboniferous have denitrification potential with confidence provided by a good coverage of monitoring data (Figure 5.2). For the remaining bedrock aquifers with defined confined zones, Lias, Zechstein and Dinantian, monitoring data does not support the presence of broad scale denitrification potential. Particularly for the Zechstein, this may be an artefact of data coverage, so confidence is low and this has not been classified.

Other aquifer groups with monitoring data which suggests denitrification potential but do not have confined zones defined in this project – Crag, Palaeogene, Lower Cretaceous, Mercia Mudstone have not been included.

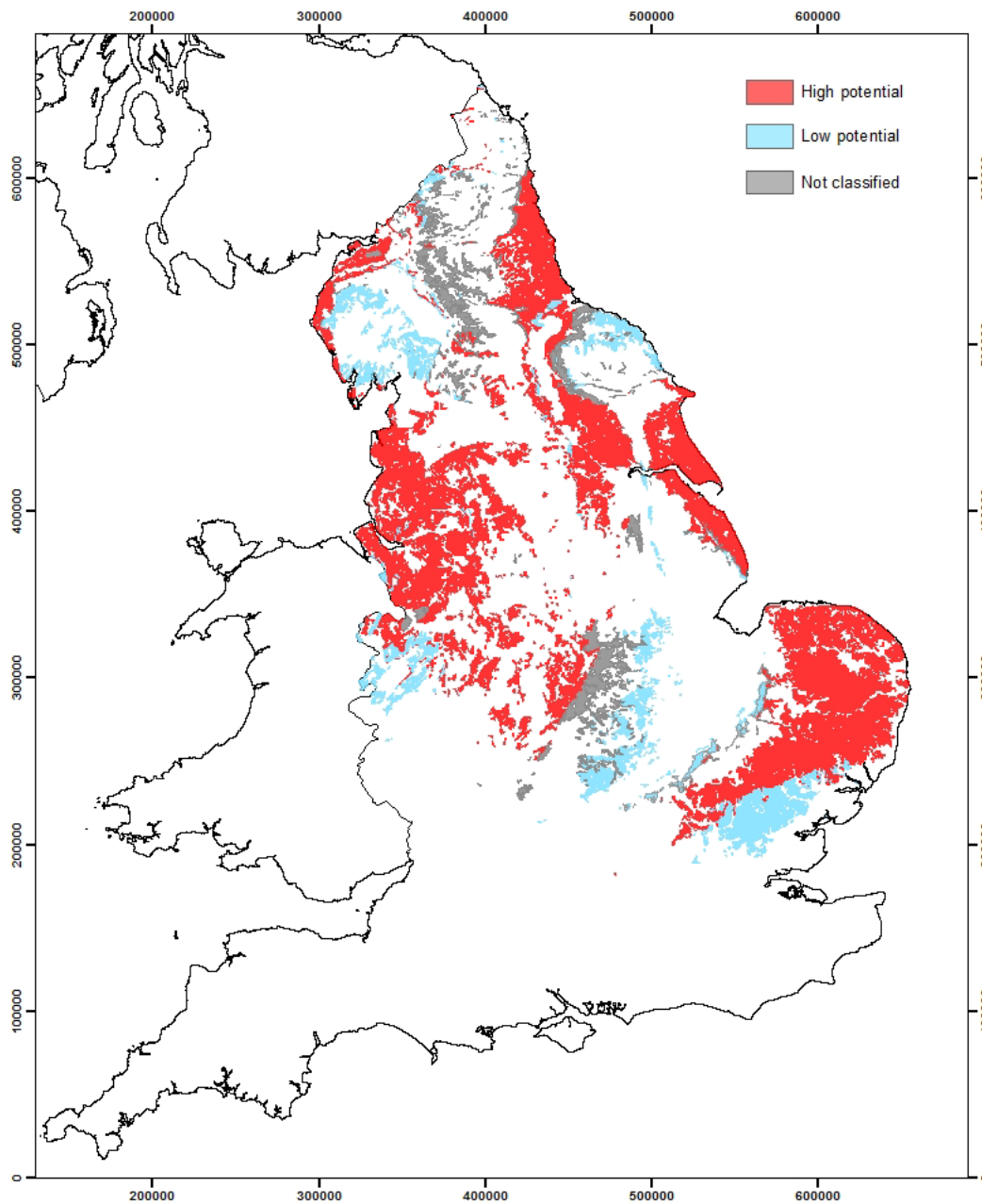


**Figure 5.2** Map of bedrock aquifer confined zones ranked by denitrification potential and confidence

### 5.3 AQUIFERS CONFINED BY LOW PERMEABILITY SUPERFICIAL DEPOSITS

#### 5.3.1 Bedrock

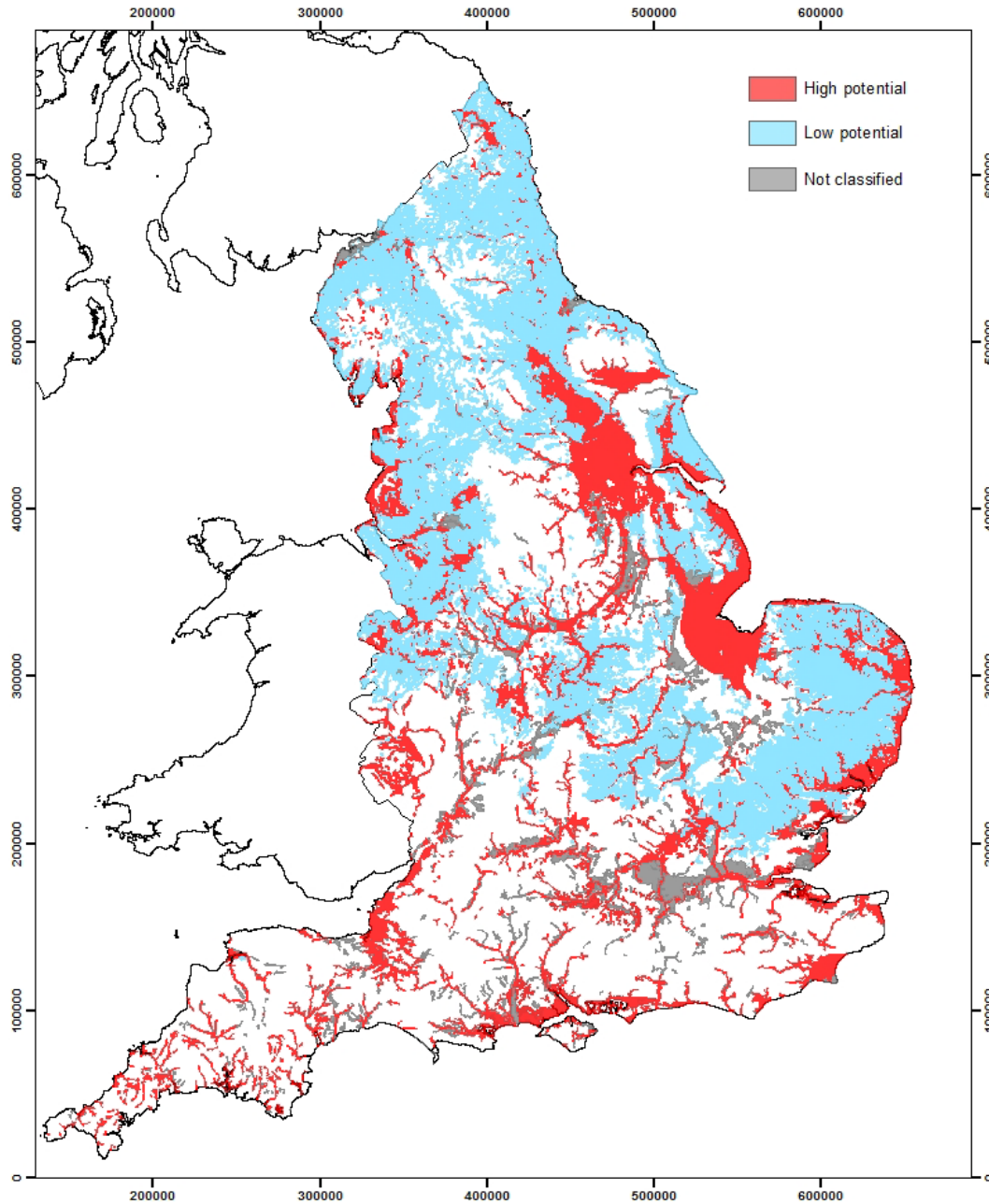
As shown in Table 3.13, aquifers in areas of Crag, Chalk, Permo-Triassic sandstones and the Zechstein confined by low permeability superficial deposits have denitrification potentials confirmed by a good coverage of monitoring data (Figure 5.3). These are shown in red on Figure 5.2. Aquifers with medium confidence of denitrification potential are also shown in red. Monitoring data for the Palaeogene, Upper and Lower Greensand, Oolite and Older rocks do not confirm the presence of denitrification at the broad scale. Areas with low confidence in the assessment are shown in grey, the Corallian, Lias and Dinantian.



**Figure 5.3** Map of bedrock aquifers confined by low-permeability superficial deposits ranked by denitrification potential and confidence

### 5.3.2 Superficial aquifers

Figure 5.4 is based on data in Table 3.14. Areas of blown sand and lacustrine superficial aquifers have denitrification potential supported by monitoring data with glacial sand and gravel and alluvium also showing some potential.



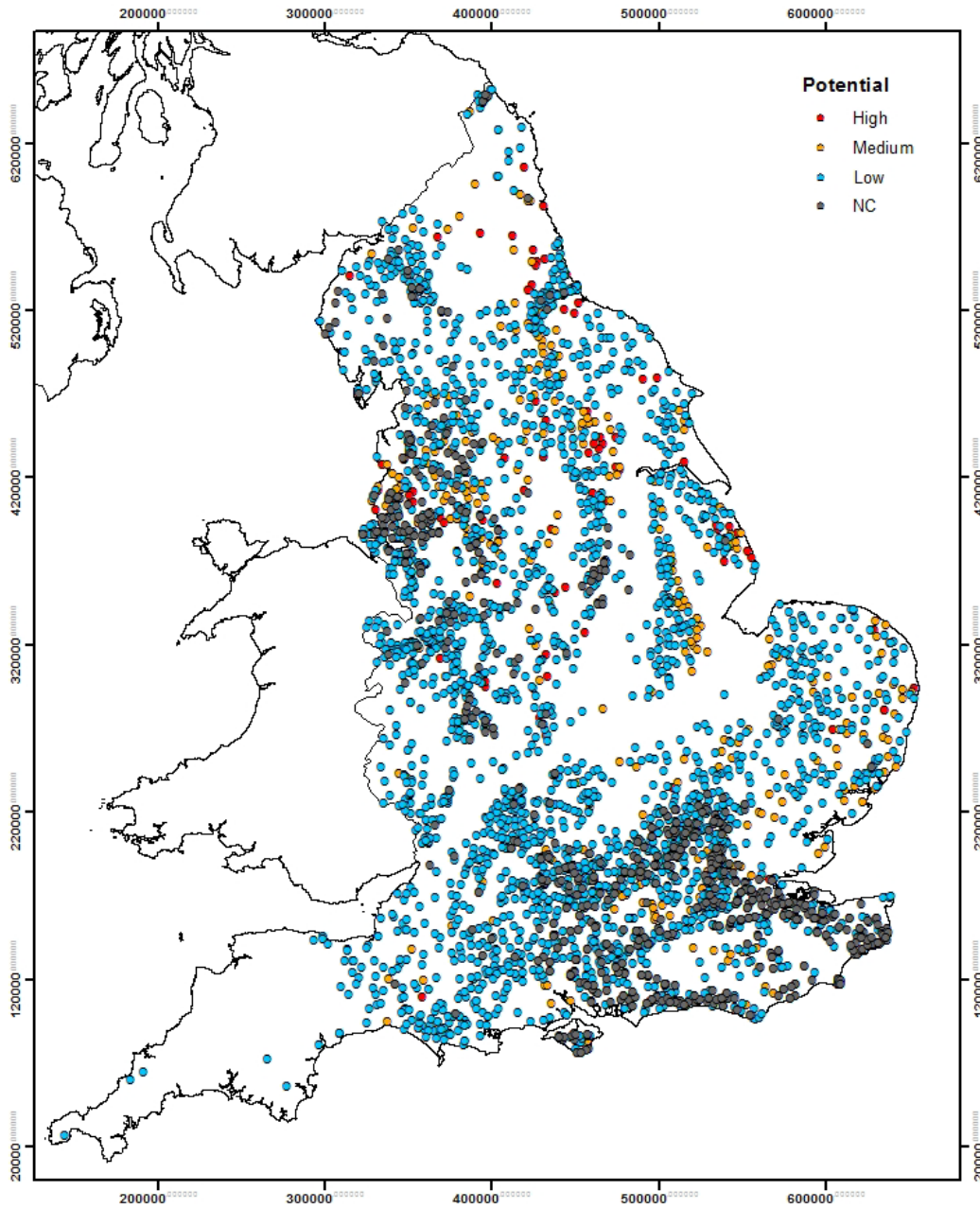
**Figure 5.4** Map of superficial aquifers ranked by denitrification potential and confidence

### 5.3.3 Individual sites

Points have been classified using the method shown in Table 3.15. Four indicators were selected from the ranking in Tables 3.6 and 3.8, selecting one oxidised nitrogen species (TON), one reduced nitrogen species (NH<sub>4</sub>) and dissolved Fe (Fe\_dis) and dissolved Mn (Mn\_dis). Data are listed in the “Site scoring method” spreadsheet which forms part of the final tool.

The next columns in the spreadsheet (suffixed M) check that there is a measurement present and records this as 1. The next column sums the number of measurements for each sample for

these indicators as shown in column 2 of Table 5.1. The next columns in the spreadsheet assess whether the criterion for each indicator is met for each sample. This provides column 3 in Table 5.1. The resulting denitrification potentials are shown on the plot in Figure 5.5. The majority of sites are shown to have low potential with about 11% having High or Medium potential.



**Figure 5.5** Map of monitoring points classed by denitrification potential

**Table 5.1 Summary of site denitrification potential**

No of sites	No of indicators measured at the site	No of indicators meeting the criteria	Denitrification potential
97	4	4	High
366	4	3	Medium
2711	4	<3	Low
2	3	3	Medium
110	3	<3	Low
1005	<3		Not classified
<b>4291</b>			

#### 5.4 FINAL PRODUCT

This has been provided in an ARCGIS 9.3 format. The outcrop confined by low-permeability superficial deposits and the confined subcrop for each of the assessed aquifers are presented in a separate GIS layer. Figure 5.6 shows the map for the Chalk as an example. The point with high and medium potential map well to the areas of subcrop and low-permeability superficial deposits.

Clicking on each area brings up the attribute table, which contains a summary of denitrification potential taken from Table 3.13. The outcrop area is also included but has not been classified. The monitoring sites in the Chalk are over plotted and have been coloured according to the assessed denitrification potential.

Monitoring sites for individual geologies can be selected using a simple definition query. This is in the layer properties box for the monitoring sites. To build a query SELECT 'Polygon' from the first list then SELECT = then SELECT 'Get Unique Values' and SELECT the geology required.

Zooming in on the East Anglia Chalk (Figure 5.7) confirms that the points shown having High or Medium denitrification potential tend to be in the confined zones. However, there are some points in outcrop chalk which also exhibit potential indicating local low-redox conditions.

The Identify box provides Lithology = Chalk, Aquifer designation = Principal, Formation Type = Confined, Low redox conditions = Yes, Potential of low redox =High, Confidence = High.

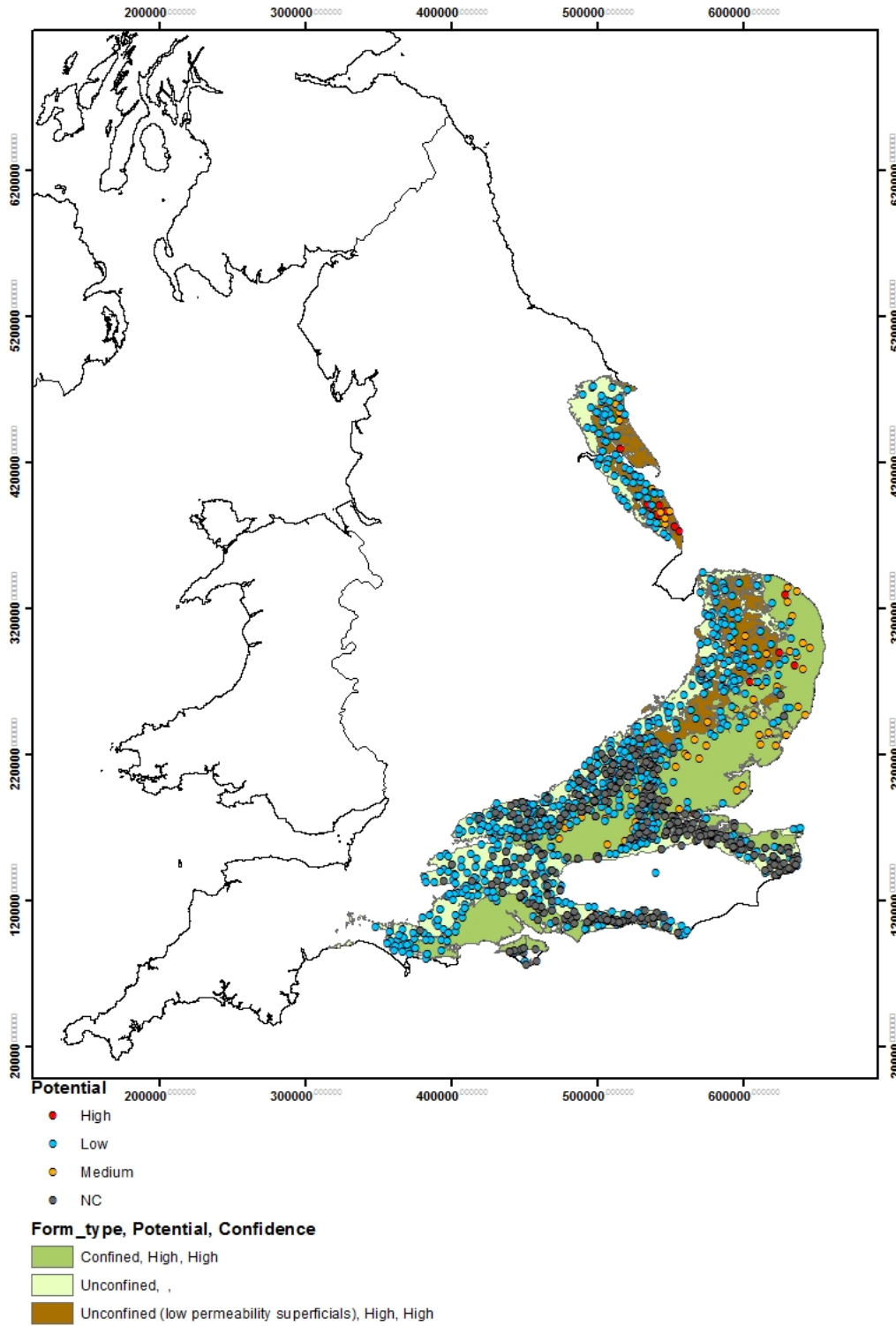
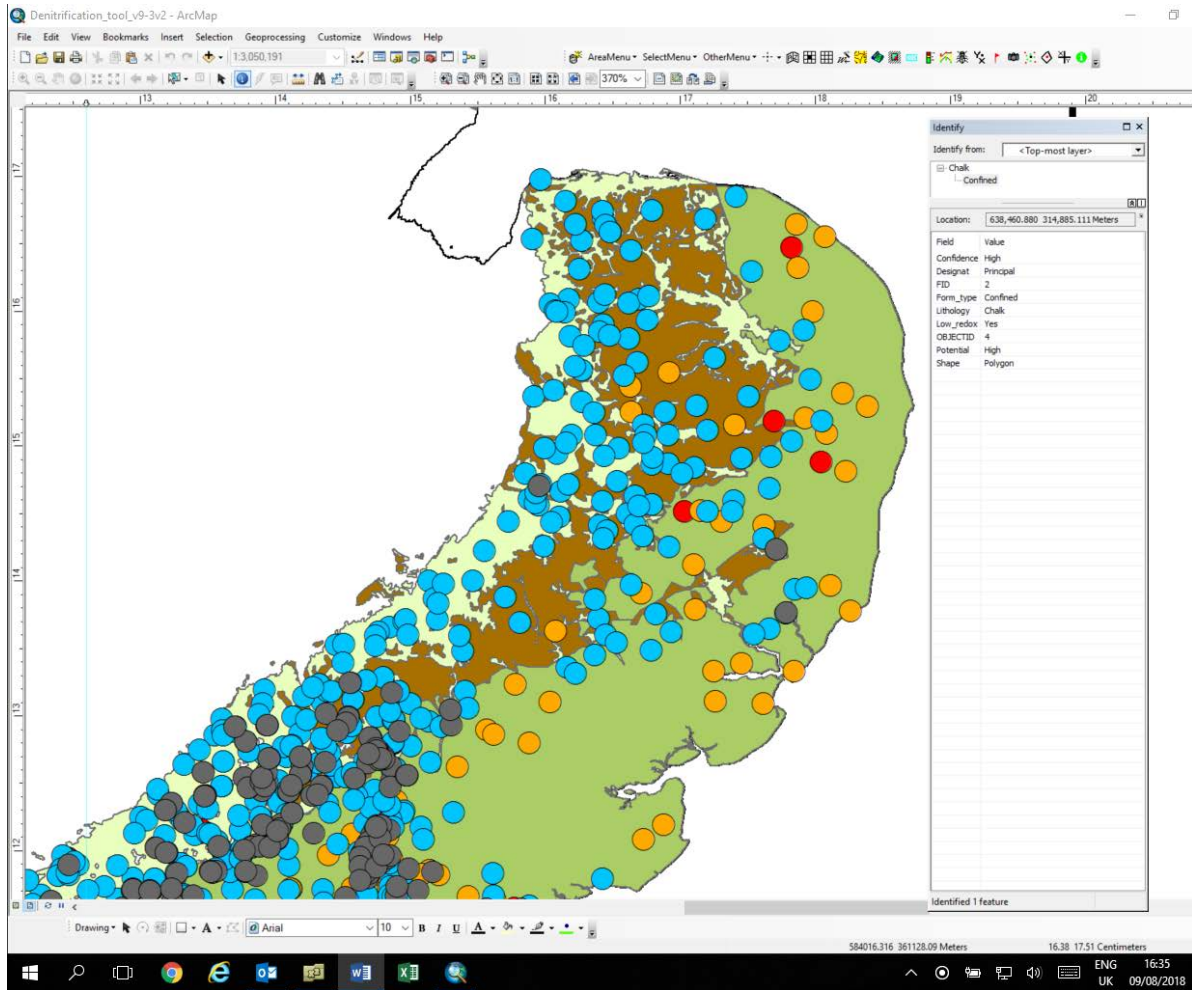


Figure 5.6 Example from final tool for the Chalk





**Figure 5.7** Screen shot of the GIS showing the East Anglian Chalk with monitoring points and information from clicking identify ① on the confined chalk area

## 6 Conclusions

### 6.1 APPROACH AND MAIN FINDINGS

This project has developed an initial approach to assessing the potential for denitrification in groundwater. It has assessed three aquifer settings where denitrification would be predicted from the literature to be most likely to occur. These are areas of aquifer subcrop where bedrock is confined by overlying low permeability bedrock strata, areas of bedrock aquifers overlain by low-permeability superficial deposits and superficial aquifers where groundwater has high DOC.

Since this project was carried out at the national scale, BGS geological mapping at a scale of 1:625,000 was used. Aquifer outcrop was defined to define the edge of the subcrop and key borehole information to define the area of aquifer down to 400 m below the surface. Low permeability superficial deposits were classified using the method of Griffiths et al. (2011). Denitrification potential in these settings was assessed using a range of indicator determinands in the Environment Agency strategic groundwater quality monitoring data. Nitrate species, Fe and Mn species and  $\text{NH}_4$  appeared to be best related to areas of potential low redox and were also used to assess individual sites. Other parameters such as DO, DOC and  $\text{SO}_4$  were less useful, DO probably because its measurement is unreliable at low concentrations, DOC because it is a parameter containing many different species not all of which will be actively degradable and  $\text{SO}_4$  because it is present in the aqueous environment at a wide range of concentrations and is only reduced at low redox potentials. The percentage of monitoring points where data confirmed low redox and their areal coverage provided an estimate of confidence.

A mass balance approach was also applied which compared nitrogen inputs with measured groundwater concentrations in areas with a relatively short unsaturated zone travel time derived from the BGS NTB model and data from the 2012 NVZ designation process.

The results showed that there is widespread potential for denitrification in groundwater across England but that it is likely to be patchy within individual aquifer units. Key zones of potential denitrification were:

- Bedrock aquifers confined by overlying low permeability bedrock strata: the Upper and Lower Greensand, Chalk, Corallian, Oolite, Permo-Triassic sandstones and the Carboniferous have denitrification potential confirmed by a good coverage of monitoring data. For the Lias, Zechstein (Magnesian Limestone) and Dinantian (Carboniferous limestone), monitoring data does not support the presence of widespread denitrification potential.
- Bedrock aquifers confined by overlying low permeability superficial deposits: the Crag, Chalk, Permo-Triassic sandstones and the Zechstein have denitrification potentials confirmed by a good coverage of monitoring data. Monitoring data for the Palaeogene, Upper and Lower Greensand, Corallian, Oolite, Lias and Older rocks do not confirm the presence of denitrification.
- Superficial aquifers: areas of blown sand and lacustrine superficial aquifers have denitrification potential supported by monitoring data with glacial sand and gravel and alluvium also showing some potential.

The mass balance approach highlighted areas of unconfined bedrock aquifers where nitrate concentrations did not appear to reflect surface inputs: areas of important aquifers where unsaturated zones are not thick were identified particularly in East Anglia and Central Northern England.

This work has set out a framework for using available data to assess the potential for denitrification.

## **6.2 FURTHER WORK TO ADDRESS LIMITATIONS**

### **6.2.1 Scale**

The mapping generated by this product was based on BGS geological mapping at a scale of 1:625,000, which was further aggregated into a series of units to facilitate the construction of subcrop polygons. This approach has a number of limitations:

- Geological detail provided by larger mapping scales is lost and linework may differ slightly
- Many of these aggregated aquifers are themselves multi-layered at various scale, for example, the Great and Inferior Oolite Groups are treated together and the formations comprising the Lower Greensand Group, Coal Measures Group and Millstone Grit Group are also each treated together by this approach.
- This means that the final product will not be appropriate for use at the local or site-scale. It does however set out an approach to assessment of denitrification where local datasets can be applied.

The principles of this approach can be applied at a larger scale using appropriate mapping and treating aquifer units separately. Further work could also include the evaluation of local geochemical conditions within aquifer units to provide an understanding of local-scale controls on denitrification potential. This could include evaluating other possible losses of nitrate or the development of aquifer specific criteria.

### **6.2.2 Coverage**

#### **BEDROCK AQUIFERS**

Limitation of project resources has meant that only 10 polygons for aggregated principal aquifers were constructed. Bedrock confined zones for other aquifers, such as the Palaeogene, Mercia Mudstone, the Devonian and all older rocks were not mapped. This could be addressed by the construction of further subcrop polygons for other aquifers and also within the aggregated groupings used in this initial approach, perhaps drawing on more detailed geological mapping. Borehole data could also be used to further differentiate denitrification potential within existing aquifer settings.

Only a subset of the Environment Agency groundwater quality monitoring data, which had aquifer attributed was used. This will have limited the coverage and density of monitoring data and reduced the confidence level of some aquifers in the final product. The final product is an illustration of how data can be used and does not reflect the overall quality and quantity of monitoring data collected by the Environment Agency. Attribution of aquifer and confined status to other groundwater monitoring data to allow this data to be used in this approach.

#### **SUPERFICIAL AQUIFERS**

- The approach to superficial aquifers was limited by the relatively small amount of monitoring data available (4% of the total) and the consequent restricted areal coverage.

- Some data were just reported for Drift (undivided) rather than for type of superficial deposit.
- Superficial deposits are more heterogeneous than many bedrock aquifers.

These points could be addressed by increasing data coverage and by improving the characterisation of the geological setting for existing data, for example by allocating superficial deposit type or by recording if groundwater in a till deposit comes from a sand and gravel lens or basal layer.

### **6.2.3 Other processes affecting nitrate concentrations**

Although generally the most important, heterotrophic denitrification is not the only process which may be operating to reduce nitrate concentrations in groundwater. Other processes could include autotrophic denitrification possibly linked to pyrite oxidation and dissimilatory reduction to ammonia (DNRA). Autotrophic denitrification can be important in settings where dissolved organic carbon is low and another electron donor is available, e.g.  $\text{Fe}^{2+}$  in pyrite or ferruginous sandstones. The partitioning between denitrification and DNRA is also believed to be controlled by the availability of organic matter: DNRA is the favoured process when nitrate (electron acceptor) supplies are limiting, such as very organic-rich shallow groundwater. These would not necessarily produce the same end products and/or pattern of indicators. Pyrite oxidation leads to an increase in sulphate and DNRA to increased ammonia.

### **6.2.4 Mass balance**

This approach is empirical and depends solely on a discrepancy between nitrate loading at the surface and observed concentrations. Limitations of this approach reside around the use of scores derived from processed nitrogen load and monitoring data and developed for the purpose of NVZ designation rather than identification of denitrification potential. This could be improved by using actual nitrogen loading figures modelled from agricultural census data in locations with monitoring data attributed to geological formation. Although the coverage would be less the data would be more reliable.

Application of the mass balance approach using nitrogen loading and monitored concentration data rather than scores attributed for the NVZ method. In addition use of raw, as opposed to kriged, monitoring data for nitrate concentration to avoid concerns with kriging data across geological boundaries.

### **6.2.5 Rate**

None of these lines of evidence give any information on denitrification rate or the mass of nitrate which is transformed. Determining the rate would require a combination of measurements in groundwater and process-based modelling.

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