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Baseline groundwater chemistry: the Corallian of the Vale of Pickering, Yorkshire

Groundwater Programme

Open Report OR/15/048

BRITISH GEOLOGICAL SURVEY

GROUNDWATER PROGRAMME

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Baseline groundwater chemistry: the Corallian of the Vale of Pickering, Yorkshire

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Keywords

Baseline, water quality, aquifer, England, trace elements, pollution.

Front cover

Cleave Dike Quarry, Hambleton Hills [SE 507 863], looking south-east. The thick-bedded unit at the base of the face is the lower leaf of the Hambleton Oolite. The overlying Birdsall Calcareous Grit forms the upper two-thirds of the face. (Photograph: G. Moore)

Bibliographical reference

BEARCOCK, J.M., SMEDLEY, P.L., AND MILNE, C.J.. 2015. Baseline groundwater chemistry: the Corallian of the Vale of Pickering, Yorkshire. *British Geological Survey Open Report*, OR/15/048. 70pp.

Keyworth, Nottingham British Geological Survey 2015

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Foreword

Although groundwater has long been seen as a relatively pure natural resource stored in subsurface aquifers, its quality is under an ever-increasing threat from human influences. Changes in chemical quality occur through direct inputs of anthropogenic substances, through groundwater abstraction and resultant change in groundwater flow regimes and through artificial recharge. Groundwater is an important resource for drinking, agricultural, industrial and domestic supply. About 35% of public water supply in England and Wales and more than 70% in south and east England is provided by groundwater resources. Groundwater flows and seepages are also vital for maintaining summer flows in rivers, streams and wetland habitats, some of which rely solely on groundwater. Monitoring, management and protection of groundwater quantity and quality are therefore important economic and environmental priorities.

Characterisation and monitoring of groundwater chemistry is a critical component of management and protection. This provides the basis for defining the suitability of groundwater for its intended purpose, identifying pollution inputs and assessing any temporal change. The main European driver for the characterisation and monitoring of groundwater quality is European Union legislation in the form of the Water Framework Directive, Groundwater Directive, EC drinking-water regulations and environmental-quality standards. A key starting point for aquifer protection is defining the natural or 'baseline' chemistry of the groundwater body concerned. This sets the framework against which anthropogenic impacts and trends can be measured.

The concept of 'baseline' in the context of groundwater quality is difficult to define in detail and opinions differ on the meaning and application of the term. The presence of purely anthropogenic substances such as pesticides or CFCs indicates a departure from the natural condition, but for many solutes which can be derived either from pollution or natural sources, for example nitrate, phosphorus or arsenic, the distinction is less clear-cut. In addition, specific chemical constituents in a given groundwater body may be identified as pollutants while other component solutes may be entirely naturally-derived. For the purposes of this study, baseline is defined as:

> "*the range in concentration (within a specified system) of an element, species or chemical substance present in solution which is derived by natural processes from natural geological, biological, or atmospheric sources*".

The baseline chemistry of groundwater varies widely as a function of the many complex geological, geochemical, hydrogeological and climatic factors. These give rise to large spatial and temporal variations in chemical quality, at a range of scales. Hence, the baseline for a given element or compound will vary significantly both between and within aquifers. It is, therefore, scale-dependent and should be considered as a range rather than a single value.

Attempting to define the natural baseline chemistry of groundwater from a number of defined aquifers or aquifer regions in England and Wales has been the objective of the project 'Baseline'. The project involves the characterisation of spatial and temporal variations in groundwater chemistry and interpretation of the dominant controlling processes within a given area, aquifer or aquifer block. For each study area, this has been achieved through collation of existing reliable groundwater, rainfall, land-use and host-aquifer mineralogical and geochemical data, as well as new strategic sampling of typically 25–30 groundwater sources for a comprehensive suite of inorganic constituents. Selected analysis of stable-isotopic compositions (e.g. O, H, C) and atmospheric tracers (CFCs, SF_6) has also been undertaken where appropriate. Statistical methods, including statistical summaries (medians, arithmetic means, percentiles), together with box plots and cumulative-probability diagrams, provide some of the most valuable analytical tools for the assessment of chemical data and have been used in the Baseline report series. The

Baseline reports provide a summary of the inorganic chemical status of groundwaters in a given study area and key pressures on water quality which should provide useful background information of value to water regulators and managers, environmental scientists and water users.

The current series of Baseline reports has been produced by the British Geological Survey with funding from the Natural Environment Research Council. This follows on from a previous series which was produced in collaboration with, and with co-funding from, the Environment Agency.

Previous published reports in the Baseline Series (British Geological Survey – Environment Agency):

1. The Triassic Sandstone of the Vale of York
2. The Permo-Triassic Sandstones of West Cheshire and the Wirral
3. The Permo-Triassic Sandstones of South Staffordshire and North Worcestershire
4. The Chalk of Dorset
5. The Chalk of the North Downs
6. The Chalk of the Colne and Lee River Catchments
7. The Great and Inferior Oolite of the Cotswolds District
8. The Permo-Triassic Sandstones of Manchester and East Cheshire
9. The Lower Greensand of southern England
10. The Chalk of Yorkshire and North Humberside
11. The Bridport Sands of Dorset and Somerset
12. The Devonian aquifer of South Wales and Herefordshire
13. The Great Ouse Chalk aquifer
14. The Corallian of Oxfordshire and Wiltshire
15. The Palaeogene of the Wessex Basin
16. The Granites of South-West England
17. The Ordovician and Silurian meta-sedimentary aquifers of central and south-west Wales
18. The Millstone Grit of Northern England
19. The Permo-Triassic Sandstones of Liverpool and Rufford
20. The Permo-Triassic Sandstone aquifer of Shropshire
21. The Chalk and Crag of North Norfolk and the Waveney Catchment
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Synthesis: The natural (baseline) quality of groundwater in England and Wales

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The Chalk aquifer of Hampshire
The Magnesian Limestone of County Durham and north Yorkshire
The Palaeogene of the Thames Basin
The Sherwood Sandstone of Devon and Somerset

Acknowledgements

We acknowledge Peter Williams for assistance with groundwater sampling, together with Debbie Allen, Sally Bourliakas, Jenny Cook, Sarah Hannay and Dan Lapworth for carrying out the chemical analysis in the BGS laboratories. George Darling and Michael Bowes are thanked for reviews of the manuscript.

We are also grateful to the numerous owners of groundwater sources that allowed access for sampling.

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Summary

This report describes the regional geochemistry of the groundwater from the Corallian aquifer in the Vale of Pickering, North Yorkshire. The study aims to assess the likely natural baseline chemistry of the groundwater. Data have been collected from strategic sampling of 24 groundwater sources, in conjunction with collation of existing groundwater, rainfall, and mineralogical data.

The Corallian aquifer comprise Upper Jurassic shallow shelf marine sediments, with a variety of facies including muds to micritic limestone and oolites, to bioclastic limestones with interbeds of silts and sands. These strata represent an important groundwater source in north-east England.

The main chemical properties of the groundwater are determined by the interaction of rainwater recharge reacting with the aquifer minerals. Within the Corallian aquifer, groundwater major ion composition is dominantly influenced by reaction with calcite, and little variation is seen within the major ion proportions.

Human impacts on the water quality are clearly evident, mainly through the presence of NO_3-N as an indicator contaminant. The widespread presence, commonly in excess of the drinking water limit and the increases over time suggest that the aquifer is heavily influenced by agricultural practices. Agricultural land dominates the area underlain by the unconfined aquifer.

With the exception of NO_3-N, the available data for groundwater within the Corallian aquifer of the Vale of Pickering indicate they are of good quality for the analytes tested, with few elevated concentrations of potentially harmful trace elements. For many analytes the 95th percentile serves as a first approximation of the upper limit of the baseline range of concentrations, as this serves to eliminate the most extreme outlier concentrations.

1 Introduction

This study concerns the Corallian aquifer of the Vale of Pickering. The aquifer crops out over the Cleveland Hills, Hambleton Hills, Howardian Hills, and North York Moors, and they underlie the superficial deposits which are found at the base of the low-lying Vale of Pickering (Allen et al., 1997).

While the River Derwent, which flows through the Vale of Pickering, is a very important source of potable water in the region, there is “no water available” for increased abstraction (Natural England, 2015). The Corallian aquifer was developed in this region after proposals to build a regulating dam in the North York Moors were rejected in 1970 (Reeves et al., 1978). As a result it is locally important to Scarborough and the surrounding areas. The upper reaches of the River Derwent provide recharge to this aquifer near to Scarborough (Natural England, 2015), and downstream the River Derwent itself is predominantly groundwater fed (Environment Agency, 2013).

The main use of water within the Derwent catchment is for aquaculture, accounting for two thirds of the water abstracted. This water is mostly non consumptive and therefore classed as throughflow. Public water supply accounts for about a quarter of the total licenced volume within the Derwent catchment (Environment Agency, 2013). Groundwater is also abstracted for spray irrigation, industrial, domestic and agricultural uses.

This report characterises the groundwater chemistry in the Corallian aquifer of the Vale of Pickering, describing available information on spatial and temporal variability.

2 Geographical setting

2.1 STUDY LOCATION

The Vale of Pickering is a low-lying flat-floored valley within the catchment of the River Derwent in North Yorkshire (Figure 2.1). The valley extends with an east-west orientation from Scarborough and Bridlington in the east, to the Howardian and Hambleton Hills in the west. The Vale is constrained to the north by the North York Moors, and to the south by the East Yorkshire Wolds. At its eastern extremity the Vale of Pickering is cut off from the North sea by a thick moraine deposit (Wilson, 1948). Jurassic Corallian strata, which form the aquifer in this region, outcrop at the periphery of the Vale of Pickering. The aquifer constitutes a major resource in the River Derwent catchment (Reeves et al., 1978; Tattersall and Wilkinson, 1974). The sample sites in this study extend over an area of approximately 1000 km^2. Figure 2.1 shows the location of the Corallian in the Vale of Pickering.

2.2 LAND USE AND PHYSICAL FEATURES

Arable farming is the dominant land use and industry in the study area (Figure 2.2). Westwards from Pickering, approximately half of the crops are cereals, the remainder include carrots, potatoes, sugar beet and oil seed rape. In the area extending eastwards from Pickering, cereals are generally not grown. Towards the north of the region, grasses, shrubs and trees prevail. These represent the higher ground and steeper slopes of the North York Moors. The grassland tends to line river valleys, the trees occupy lower slopes, and bog and shrub occupy the highest ground in the region. Scarborough, Pickering and Malton are the main urban centres.

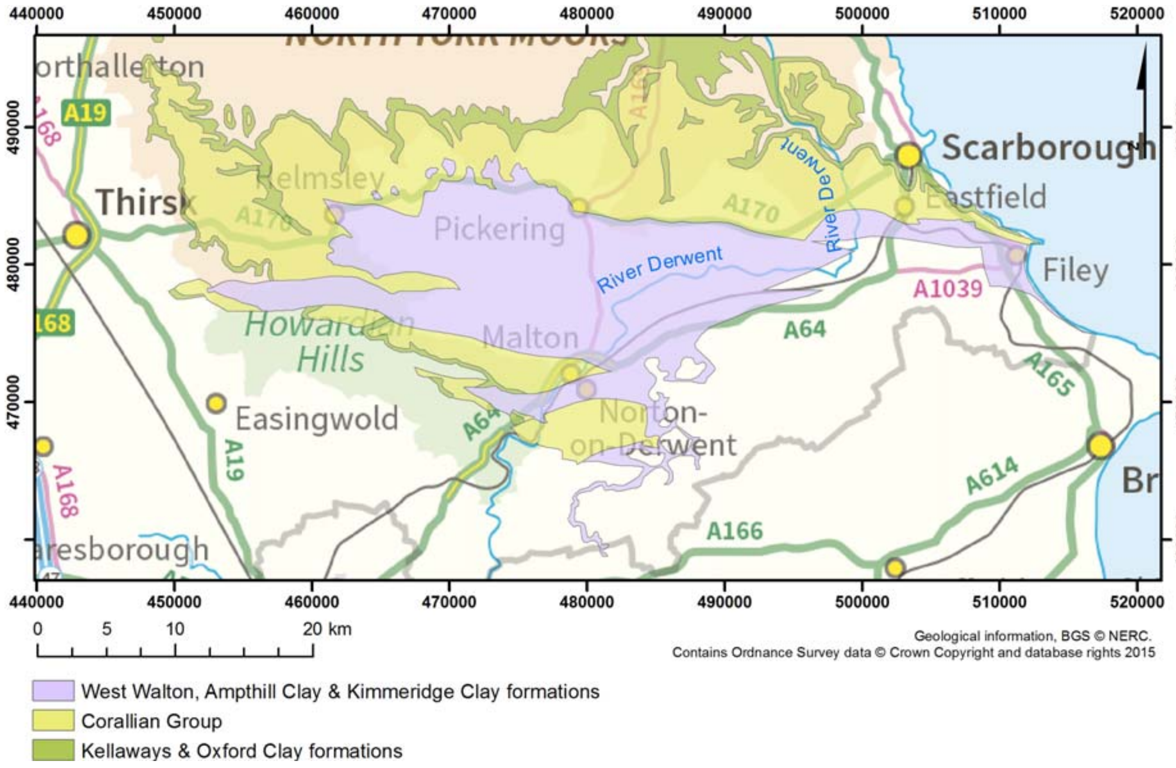

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Figure 2.1 Location of Corallian Group strata in north-east Yorkshire

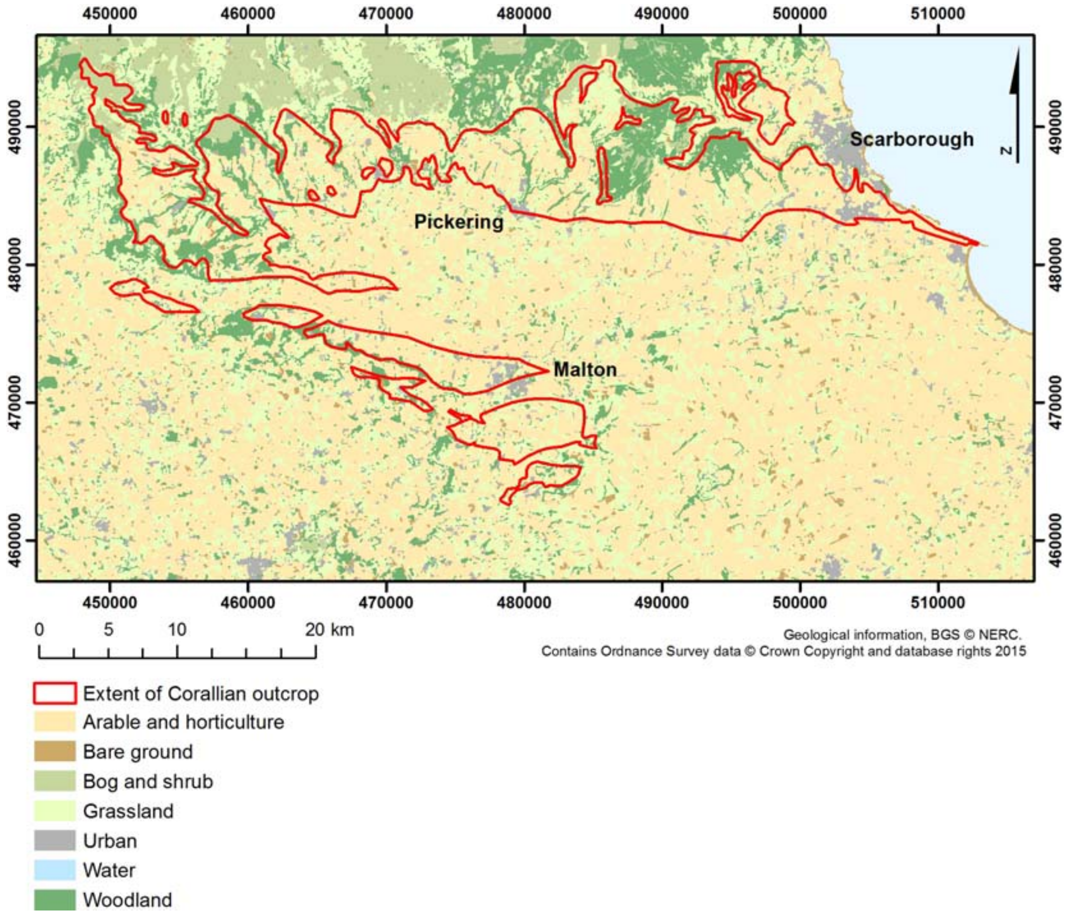

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Figure 2.2 Land use around the Vale of Pickering

The Vale of Pickering is a broad, flat, alluvial plain with an elevation less than 60 m AOD. The vale is constrained to the north by the steep dip slopes of the Jurassic Corallian strata, which form the lower slopes of the North York Moors, and to the south by the chalk escarpment of the East Yorkshire Wolds (Wilson, 1948). Besides the main outcrop that forms the northern boundary of the vale, the aquifer crops out in a narrow strip between Gilling and Malton, and it is concealed beneath the impermeable Kimmeridge Clay in the centre of the region (Tattersall and Wilkinson, 1974). The valley floor is covered by a variable thickness of alluvium (Wilson, 1948).

The Vale of Pickering is drained by the River Derwent and its many tributaries (Figure 2.3), which mainly originate in the North York Moors and flow southwards. The River Derwent itself rises in the North York Moors, approximately 17 km north-west of Scarborough. Once in the low-lying vale the Derwent is joined from the east by the canalised River Hertford, and from the west by the River Rye. The River Rye itself has numerous tributaries that originate in, and drain southwards from, the North York Moors. The Derwent flows out of the Vale of Pickering and into the Vale of York via the Kirkham Gorge, which was formed by outflow of a glacial lake, formed in the vale during the Ice Age. Summer flows of these rivers are maintained by a substantial baseflow contribution from the main Corallian and other minor aquifers. The large areas of the vale covered by impermeable strata give rise to rapid stream responses during rainfall events (Reeves et al., 1978; Wilson, 1948).

Figure 2.4 shows the major urban areas and other places named in this report for reference. Sites of groundwater samples used in this investigation are given in Figure 2.5. Samples collected in this study were supplemented by data from the Environment Agency database (discussed in section 4.1).

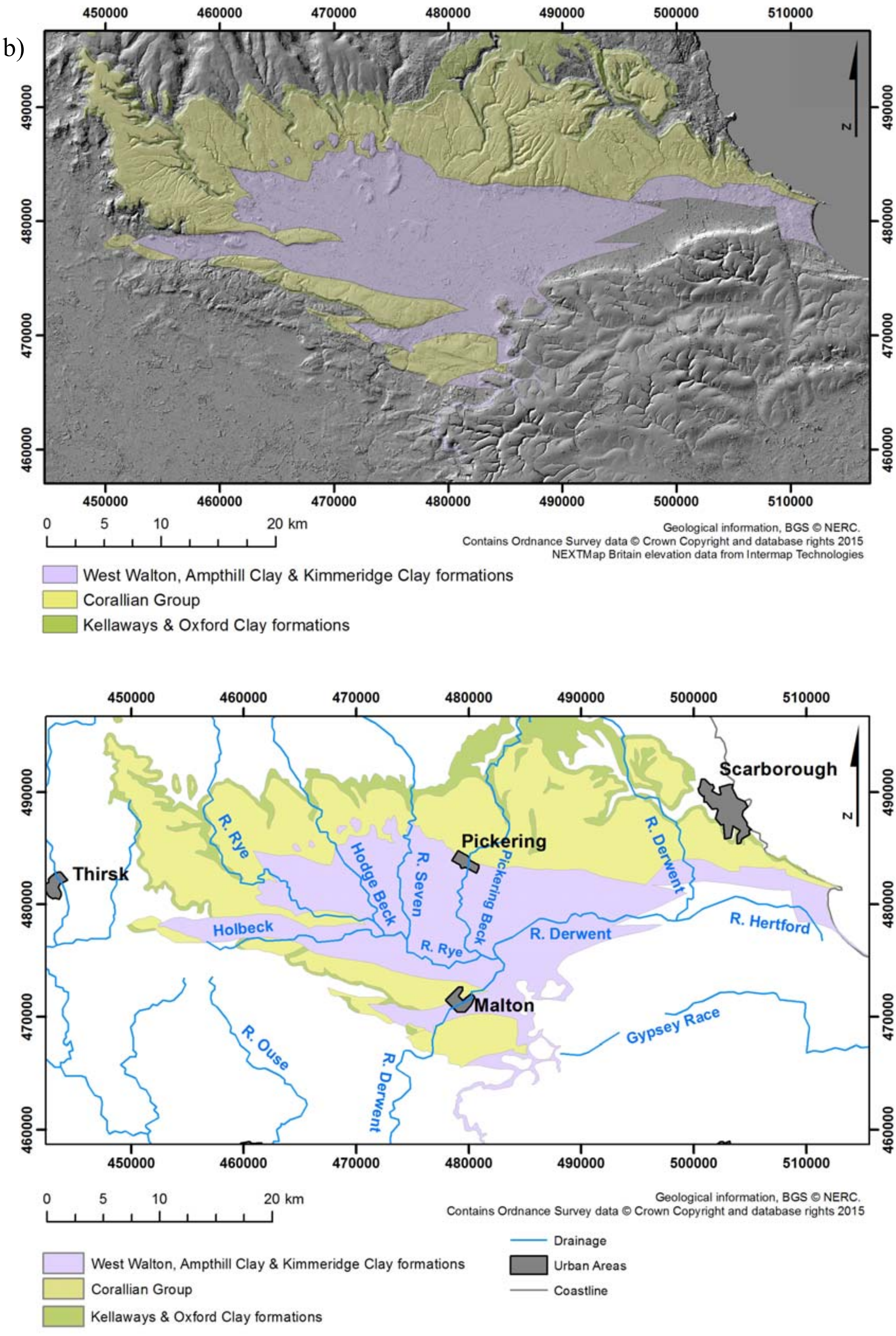

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Figure 2.3 Physical features around the Vale of Pickering.
a) Shaded geology demonstrating the nature of the valley: flat bottomed, constrained to the north by the Corallian strata forming the lower slopes of the North York Moors and to the south by the Chalk Group

b) Geology and drainage network

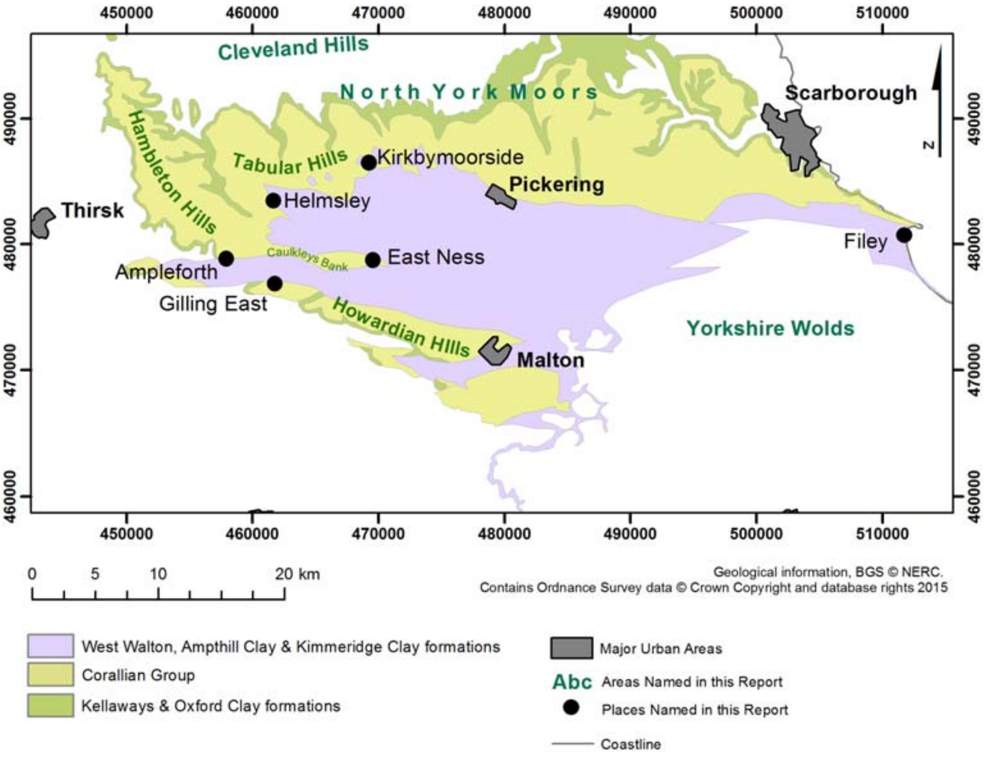

Figure 2.4 Places named in this study

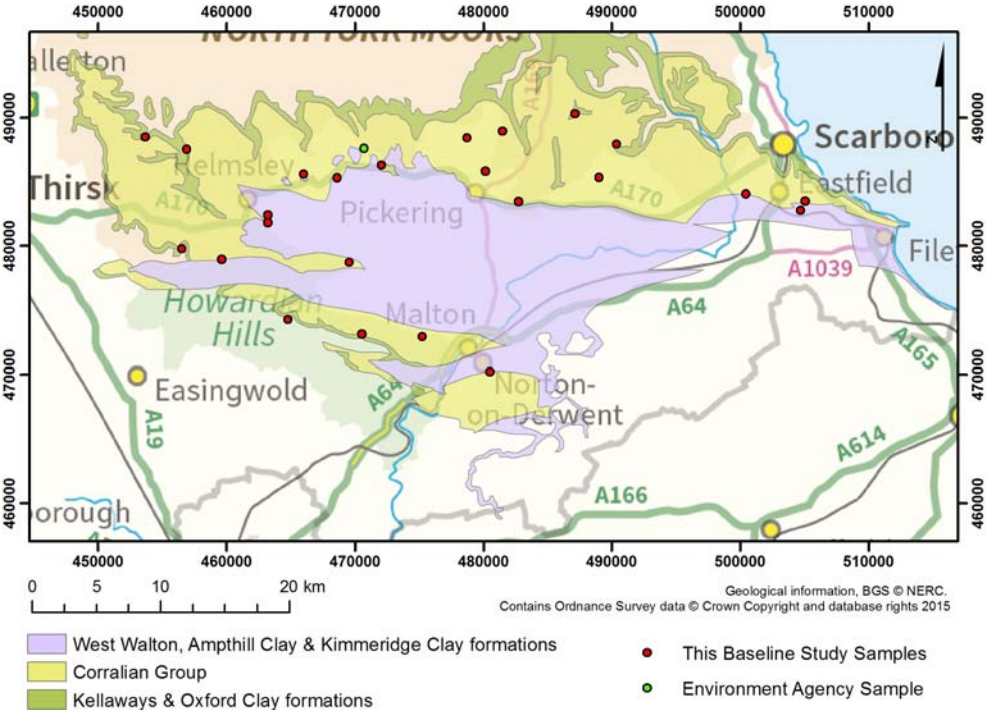

Figure 2.5 Location and data source of samples in this study

3 Regional geology and hydrogeology

3.1 REGIONAL GEOLOGY

3.1.1 Geological setting

During the Jurassic Period Britain was situated between 30 and 40º north of the equator. The warm, humid climate represented a change in climatic regime following the arid Permian and Triassic (Cope, 2006; McLeish, 1992). Throughout much of the Jurassic, Britain was covered by shallow seas; the sea rises being considered related to the creation of oceanic ridges as the supercontinent Pangaea started to break up (McLeish, 1992). Jurassic sedimentary deposition was hence affected by a series of transgressions and regressions (Allen et al., 1997).

The Jurassic Period is subdivided into three series, Lower, Middle and Upper. The Upper Jurassic series is further subdivided into Oxfordian, Kimmeridgian and Tithonian. The Jurassic rocks in the Vale of Pickering are of Oxfordian age and can be conveniently divided into three divisions based on lithological character. These divisions are the Oxford Clay Formation, the Corallian Group, and the West Walton, Ampthill and Kimmeridge Clay formations (Reeves et al., 1978). The Upper Jurassic rocks are entirely of marine origin. Marine regression had interrupted eustatic sea-level rise, causing the deposition of the Corallian Group (Powell, 2010). The subsequent re-advance of the sea resulted in the deposition of bituminous clay over the Corallian strata (McLeish, 1992). The Corallian strata form the major Jurassic aquifer. The stratigraphy of the Jurassic units is presented in Table 3.1 and Figure 3.1.

The Corallian Group is well-developed in north-east England. It mainly comprises ooidal and micritic limestone and calcareous fine-grained sandstone (Powell, 2010), but also includes a variety of facies from muds, to micritic limestone and oolites, to bioclastic limestones with interbeds of silts and sands (Cope, 2006; Reeves et al., 1978). These facies represent a shallow shelf depositional environment (Allen et al., 1997) and include a low influx of terrestrial material from the surrounding areas. The absence of debris flows and turbidites suggests that depositional slopes were very low (Hallam, 1992 cited in Allen et al., 1997). The aquifer crops out in areas including the Hambleton Hills, the Howardian Hills, the Tabular Hills and the North York Moors, forming the northern and south-western boundaries of the Vale of Pickering (Allen et al., 1997). The Corallian consists of three formations: the Lower Calcareous Grit (formally known as Passage Beds), the Coralline Oolite (formerly known as Coral Rag (Cope, 2006)) and the Upper Calcareous Grit Formation (Allen et al., 1997). The "grit" subdivisions of the Corallian are neither true sandstones, nor true limestones, but are generally fine-grained calcareous sandstones. Both the grits and the oolites vary in lithology but the most marked variations occur in the oolites where reefs are present (Wilson, 1948).

The Cleveland Basin is an inversion structure and was a major basin of deposition during the Jurassic followed by uplift in the Cretaceous. There are a number of large faults which traverse the area including the Vale of Pickering Fault, the Weaverthorpe Fault and the Coxwold-Gilling-Linton Fault. The throw on the Pickering and Weaverthorpe faults is of the order of 200 m (Allen et al., 1997).

Table 3.1 Correlation of the formations and members within the Jurassic Corallian Series (adapted from Allen et al., 1997; Cope, 2006; Powell, 2010; Reeves et al., 1978; Wilson, 1948)

Period	**Formation**		**Members**	**Thickness (metres)**
Recent	Post Glacial Superficial Deposits			0 to 10
Pleistocene	Glacial Deposits			
Upper Jurassic	Lower Kimmeridge Clay Formation			340
	Ampthill Clay Formation			45 to 50
	Corallian Group	Upper Calcareous Grit Formation		10 to15
		Coralline Oolite Formation	Coral Rag	Up to 9
			Malton Oolite	Up to 40
			Middle Calcareous Grit	5 to 25
			Birdsall Calcareous Grit	Up to 30
			Hambleton Oolite	Up to 34
		Lower Calcareous Grit Formation		Approx 15
	Oxford Clay Formation			20 to 50

3.1.2 Oxford Clay

The base of the Oxford Clay marks the start of the Upper Jurassic period in the Vale of Pickering (Powell, 2010) (Table 3.1). This formation is found below the Corallian facies and consists of grey-green calcareous mudstone and silty mudstone (Powell, 2010), there is very little variation within these rocks (Reeves et al., 1978).

3.1.3 Lower Calcareous Grit Formation

The beginning of the Lower Calcareous Grit Formation is mostly defined by the gradual replacement of the argillaceous conditions of the Oxford Clay deposition with an influx of fine arenaceous material. The lower Calcareous Grit Formation is the same age as the Oxford Clay. The only exception to this is in the south-west part of the Hambleton Hills, where the Lower Calcaerous Grit Formation lies on Middle Jurassic beds, as the Oxford Clay is missing (Cope, 2006; Wilson, 1948; Wilson, 1949).

The formation generally comprises fine- to medium-grained calcareous sandstones which attains maximum thickness in the Tabular and Hambleton Hills, thinning southwards and eastwards towards the coast (Allen et al., 1997; Wilson, 1948). Coastal sections have shown exposed Lower Calcareous Grit Formation divided into three units. The upper unit is known as the “Ball Beds” and is 3 – 5 m thick. The “Ball Beds” comprise very ferruginous sandstone containing large, gritty, fossiliferous calcareous concretions. A hard grey siliceous sandstone 1 – 2 m thick underlies the “Ball Beds”. The lower unit is 12 – 14 m thick and comprises thickly bedded

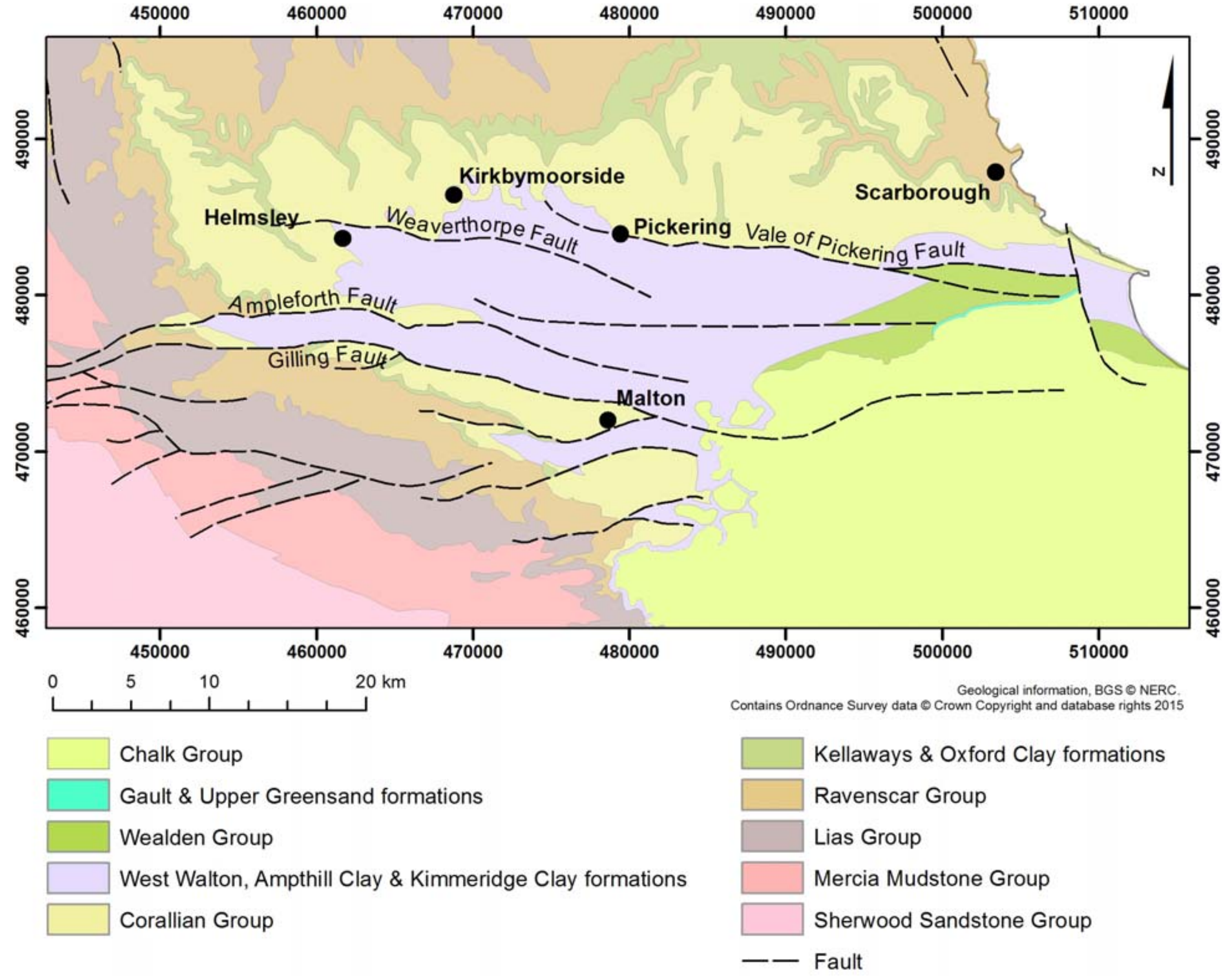

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Figure 3.1 Geology in and around the Vale of Pickering

sandstone with siliceous cement. The cement is frequently concentrated into small masses which weather out in irregular nodular bands (Wilson, 1948).

In the escarpments north of Kirkbymoorside and Helmsley the Grit becomes siliceous, because of the presence of siliceous spicules, and frequent chert bands. The grit varies from a hard siliceous spicule-bearing rock in the west to gritty limestone beds with soft sandstones in the southeast (Wilson, 1948).

3.1.4 **Coralline Oolite Formation**

The Coralline Oolite comprises the following members, in age order: Hambleton Oolite, Birdsall Calcareous Grit, Middle Calcareous Grit, Malton Oolite and Coral Rag.

The Hambleton Oolite Member is developed from the Vale of Pickering northwards. It caps the escarpment on the Hambleton Hills, and forms large dip slopes on the North York Moors. It consists mainly of oolitic limestones of considerable variation. There are also some sandstones, detrital limestones, and towards the west the member becomes siliceous. The member is lenticular, being at its thickest around Kirkbymoorside. In the southern portion of the Corallian outcrop the Hambleton Oolite Member is divided into the Upper and Lower Leaf, which are separated by the Birdsall Calcareous Grit Member. The Birdsall Calcareous Grit is a fine sandstone with ooids and chert lenses. (Allen et al., 1997; Cope, 2006; Powell, 2010; Wilson, 1948).

The Middle Calcareous Grit is absent in the Howardian Hills, but is present at thicknesses of five to 25 m in the Hambleton and Tabular Hills. The member is similar to the Birdsall Calcareous Grit, comprising sandstones with localised development of shelly layers and sandy and oolitic limestone beds. At outcrop this rock can be decalcified (Allen et al., 1997; Cope, 2006; Powell, 2010; Wilson, 1948).

The Malton Oolite Member and the Coral Rag Member were formerly known together as the Osmington Oolite. The Malton Oolite in particular is laterally persistent, extending round the fringe of the Vale of Pickering to the foot of the Chalk Wolds to the south. On average the member is approximately 18 m thick, reaching a maximum thickness of ca. 40 m inland. The Malton Oolite consists of dominantly pure, shelly oolites, but becomes more sandy, as it thins towards the west. The Malton Oolite is overlain by a variety of beds, which form the Coral Rag Member. Five kilometres south of Malton, and southwards from this point the Coral Rag and a significant portion of the Malton Oolite have been removed by erosion. The Coral Rag attains a maximum thickness of 9 m and consists of a variety of fossiliferous reef limestones, and includes impure oolite, shelly oolite, argillaceous limestone, and pure white limestone (Allen et al., 1997; Cope, 2006; Powell, 2010; Wilson, 1948).

3.1.5 Upper Calcareous Grit Formation

The uppermost formation in the Corallian Group is the Upper Calcareous Grit Formation. This comprises around 15 m of well bedded fine grained calcareous sandstone and siltstone. Abundant beds of clayey limestone occur in the middle of the unit. The Upper Calcareous Grit Formation provides an intermittent cap to some of the southern ridges of the Tabular Hills, and is continuous from Pickering into the south-east part of the Hambleton Hills. This formation is commonly leached and re-cemented with silica (Allen et al., 1997; Tattersall and Wilkinson, 1974; Wilson, 1948).

3.1.6 Kimmeridge Clay and Ampthill Clay

A thick deposit of Kimmeridge Clay and Ampthill Clay overlies the Corallian Group, covering the floor of the Vale of Pickering (Tattersall and Wilkinson, 1974; Wilson, 1948).

3.1.7 Superficial deposits

Over much of the outcrop area the only superficial deposits present are alluvium and river terrace deposits. However widespread glacial deposits exist near Scarborough. Along the southern margin of the Corallian, extensive sand and gravel deposits mask the boundary with the overlying Kimmeridge Clay. These deposits are locally underlain by 10–20 m of till (Wilson, 1948).

3.2 REGIONAL HYDROGEOLOGY

The Corallian Group forms the main aquifer in the Jurassic sequence of the Cleveland Basin (Allen et al., 1997). It was developed in response to increasing demands for water supplies in South Yorkshire after the rejection of proposals to build a regulating reservoir in the North York Moors in 1970 (Reeves et al., 1978). This aquifer is underlain by the Oxford Clay and overlain by the Kimmeridge Clay, which are both poorly permeable (Allen et al., 1997). Table 3.2 shows the hydrogeological significance of the Jurassic formations in the Vale of Pickering.

3.2.1 Aquifer properties

The aquifer is highly fractured and groundwater storage and movement takes place predominantly within the fractures. Large yields can be obtained close to such fractures or faults and springs (Allen et al., 1997).

In the unconfined part of the aquifer groundwater is likely to be in hydraulic continuity with surface water courses. Groundwater levels and stream flow both respond rapidly to rainfall due to large areas of impermeable catchment (Reeves et al., 1978). Groundwater is particularly important during summer months for maintaining stream flows with a significant baseflow component.

Groundwater discharge from the Corallian occurs mainly via a series of springs controlled by faulting. The springs usually discharge at the boundary between the Corallian and the overlying clays but may also occur along fault lines. In summer the total discharge from all of the springs exceeds the total discharge from the aquifer as all of the flow from some of the rivers disappears into swallow holes and re-emerges as springs. In these areas, solution-enhanced fractures have developed and the aquifer becomes karstic in nature. At East Ness flow rates through solution enhanced fractures range from 2 to 3500 m^3/d (Allen et al., 1997).

3.2.1.1 CORE DATA

Allen et al. (1997) presented a summary of sediment core data. There were limited data available for porosity and permeability, and only for the Corallian Oolite. Based on a total of 25 samples from 5 boreholes the mean porosity of the Corallian Oolite is 17.4 % with an interquartile range of 10.9 to 27.2%. The interquartile range for hydraulic conductivity (K) (based on plug samples) is 1.4×10^{-5} to 1.6×10^{-3} m d^{-1}, with a mean of 1.8×10^{-4} m d^{-1}. Neither the vertical K nor the horizontal K seem to be consistently greater than each other and in general, high K values correlate with higher porosities (Allen et al., 1997).

3.2.1.2 PUMPING TEST RESULTS

Allen et al. (1997) also summarised the results of pumping tests of the Corallian aquifer. Only 6 values of storage coefficient are available, which range from 4×10^{-7} to 0.023 (Allen et al., 1997). Transmissivity values have been recorded. The interquartile range of these measurements is 38 to 2249 m^2 d^{-1}, and the mean is 318 m^2/d. Transmissivities in the main outcrop area of the aquifer are generally low (<10 m^2 d^{-1}), which is a reflection of the small saturated thickness. The exception to this is the area around Malton. Transmissivity values are generally higher towards the confined aquifer and where boreholes are sited near to major springs where values can be up to 3800 m^2 d^{-1}.

3.2.2 Aquifer resources

A detailed investigation into the water resources of the aquifer was conducted between 1970 and 1974 by Reeves et al. (1978). Groundwater movement and chemistry were found to be closely

Table 3.2 Hydrological significance of Jurassic Formations in the Vale of Pickering (adapted from Allen et al., 1997; Cope, 2006; Reeves et al., 1978; Wilson, 1948)

Formation	Hydrological Significance
Lower Kimmeridge Clay	Aquitard
Ampthill Clay	
Upper Calcareous Grit	Major Aquifer - the Corallian
Coralline Oolite	
Lower Calcareous Grit	
Oxford Clay	Aquitard

related to geological structure. It was concluded that the greatest hydrogeological potential is to the north of the Coxwold-Gilling trough, which divides the relatively simple synclinal outcrop area in the north from the complex eastern extension of the Howardian Hills Fault Belt beneath the clay-covered Vale of Pickering. There is limited hydraulic connectivity between the two areas. The southernmost area is compartmentalised by a series of tensional easterly trending faults (Allen et al., 1997; Reeves et al., 1978).

Reeves et al. (1978) divided the aquifer into five hydrogeological zones, determined largely by structure and characterised by water quality (Table 3.3, mapped in Reeves et al., (1978)) They concluded that groundwater chemistry of groundwater in the Corallian aquifer was primarily determined by rate of groundwater movement (which is largely determined by structure). All the sample sites in this study were located within zones D or E.

3.3 AQUIFER MINERALOGY AND CHEMISTRY

There is sparse information available on the mineralogy of the Corallian aquifer in the Vale of Pickering owing to a scarcity of BGS memoirs in the area. The following section is paraphrased from Fox-Strangways (1880) and Powell (2010).

All formations in the Corallian aquifer are dominated by calcite, either as the main mineral or as a cement. The Lower Calcareous Grit Formation is a calcareous sandstone. It is known to contain siliceous bands and nodules. The Coralline Oolite Formation is a varied sequence of ooidal limestone, with fine grained sandstone, and various reef facies. The Upper Calcareous Grit is a fine grained calcareous sandstone. The Corallian aquifer is therefore dominated by quartz and calcite.

3.4 RAINFALL CHEMISTRY

Average annual rainfall over the Vale of Pickering and surrounding areas varies between 717-987 mm year^{-1} (based on the 1961-1990 averages), with the greatest rainfall tending to fall in the

Table 3.3 Description of hydrogeological zones in the Vale of Pickering, described by Reeves et al. (1978)

Zone	Area	Groundwater Chemistry
A	Central area of the vale. Corallian aquifer isolated from outcrop by thick clay cover. Only 1 borehole penetrates the Corallian.	Limited recharge, gives Na-HCO_3 type groundwater. Thought to be product of ion exchange.
B	Westermost area of the vale. North and South of Caulkleys Bank. Corallian aquifer in restricted hydraulic continuity with outcrop area.	Flow from recharge area is restricted, Na-HCO_3 type groundwater.
C	North and north-western part of vale, east of Caulkleys Bank. Aquifer is beneath clay, but in hydraulic continuity with the outcrop.	Aquifer is in full or almost full continuity with outcrop groundwater, gives Ca-HCO_3 type groundwater.
D	Aquifer is exposed or beneath thin clay cover around the margins of the vale. Major springs occur in this zone and transmissivity is greater than average.	Analyses from springs indicated groundwater is Ca-HO_3 type.
E	Upland outcrop area	Recharge zone where groundwater is Ca-HCO_3 type.

north-west of the region in the North York Moors (NRFA, 2008). The average annual rainfall over the outcrop is approximately 840 mm year^{-1}; evapotranspiration accounts for ~380 mm year^{-1}. The potential for infiltration therefore amounts to a maximum of 450 M L day^{-1} (Tattersall and Wilkinson, 1974). It is estimated that only 10 to 15 % of this amount occurs to the Gilling-Malton aquifer block which occurs to the south of the Gilling-Ampleforth faults (Reeves et al., 1978).

Table 3.4 shows the chemical composition of rainfall from the Moor House monitoring site [NY 757 328] located in the north Pennines, near to the source of the River Tees, 115 km north-west of Pickering.

Concentrations of Na and Cl in the Moor House analyses suggest that there are maritime influences. This site is >60 km from the coast. Concentrations are therefore likely to be higher in the Vale of Pickering rainfall than the Moor House rainfall. The Vale of Pickering is proximal to the coast, and likely to be influenced by airborne marine salts (Shand et al., 2007).

Rainwater is naturally acidic owing to the dissolution of atmospheric CO_2, which forms a weak solution of carbonic acid with an equilibrium pH of around 5.7. The Moor House rain water is pH 5.6 indicating there are few airborne pollutants present, such as oxides of sulphur (SOx) and nitrogen (NOx) which are capable of further acidification (Shand et al., 2007). Sites within the study area that are closer to industrial atmospheric inputs are likely to contain higher concentrations of SO_x and NO_x and have a lower pH. If it is assumed that all the NH_4 in rainfall oxidises to NO_3 on infiltration to groundwater, baseline concentrations of dissolved NO_3-N derived from rainfall alone are likely to be in the order of 0.73 mg L^{-1} or less. The pH of recharge may be even lower than that measured in the rainfall owing to the oxidation of NH_4^+ ions to NO_3 which results in the release of H^+ ions and concentration by evapotranspiration. This process is reflected in the pH of recharge, which is typically pH 3–5 (Shand et al., 2007; Smedley and Allen, 2004). Mineral dissolution reactions within the calcareous beds will be responsible for buffering these pH values, indeed the pH of waters in calcareous soils and aquifers rarely occurs below 6.5 (Abesser et al., 2005; Kinniburgh and Edmunds, 1986).

3.5 CURRENT ISSUES IN GROUNDWATER QUALITY

The main aim of the Environment Agency's (EA) Water Framework Directive (WFD) is for water bodies to achieve good chemical status. The EA, tasked with planning and delivering better water environments, defined the 11 river basin districts for which management plans were created to identify the current status of groundwater. The Vale of Pickering Corallian aquifer is within the Humber River Basin District. This aquifer is divided into two groundwater bodies[1], separated by the Gilling-Ampleforth faults. In both groundwater bodies the chemical status is assessed as poor; and it is predicted that the chemical status will remain poor owing to the disproportionate expense associated with achieving this target. It is anticipated, however, that good status will be achieved by 2027 (EA, 2009).

The groundwaters are monitored to assess the risks of not meeting water quality standards. The risks to the inorganic water quality are the presence of nutrients (namely nitrate and phosphate), the presence of hazardous substances or other pollutants, and saline intrusion as a result of abstraction and other artificial flow pressures. The groundwater bodies are classified as drinking-water protection areas, which mean they need to be managed for this use, and are protected by WFD legislation. In particular, action needs to be taken to prevent or limit the inputs of NO_3 to the groundwater. This will ensure that there is no future deterioration of groundwater quality, and the increasing NO_3 trends can be reversed. Actions to achieve this are by a combination of regulatory and voluntary measures. Nitrate vulnerable zones (NVZs) were first designated by the EA in 1996, and then updated in 2002 and 2008. Currently almost 70% of England is designated

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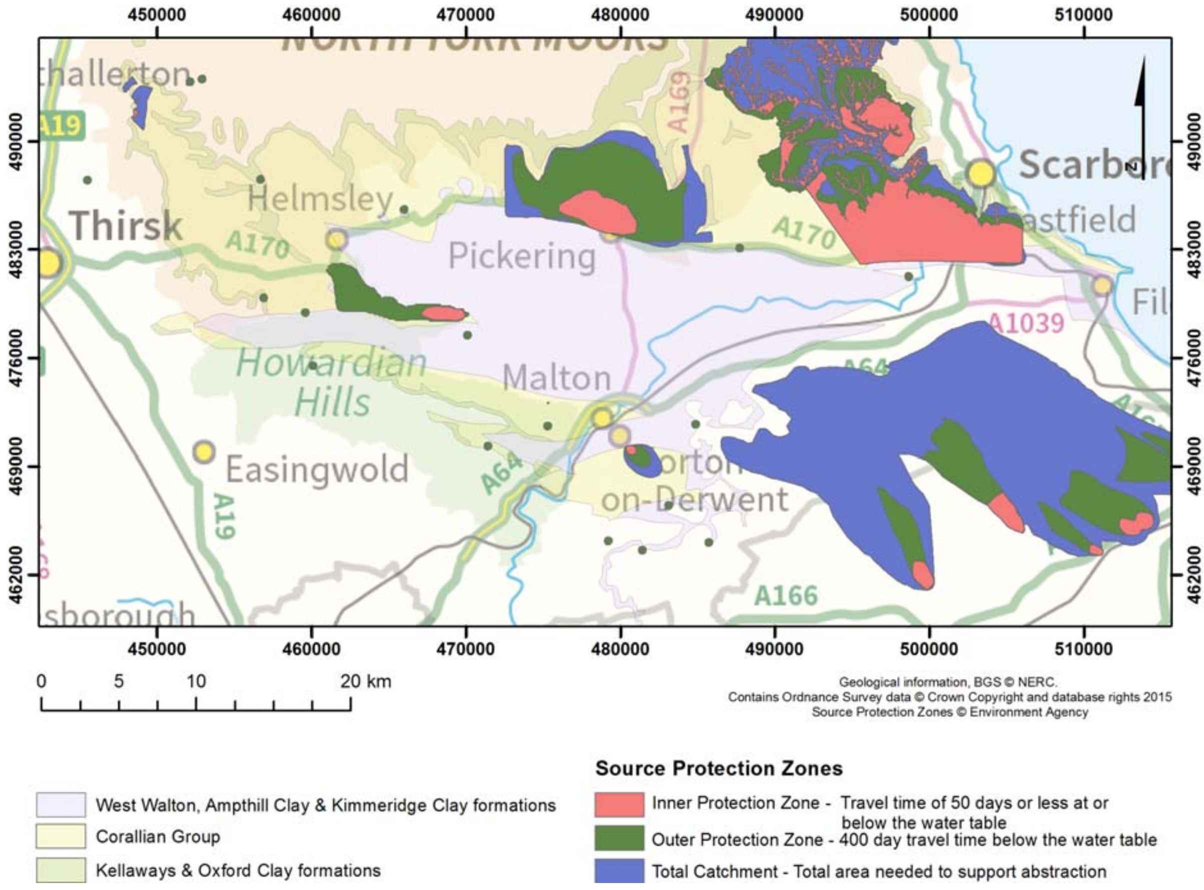
[1] Groundwater bodies are the management units defined for the purposes of the Water Framework Directive.

as an NVZ. Farms within NVZs have to comply with rules affecting their careful planning, storage and usage of NO_3 rich substances (DEFRA, 2011). Almost all of the Corallian aquifer at outcrop in this region is located within a NVZ (DEFRA, 2011; Natural England, 2015). Voluntary measures, such as catchment sensitive farming (CSF), are also encouraged in order to protect the groundwater from NO_3 contamination (DEFRA, 2011). There are significant problems of nitrate and phosphate throughout the Vale of Pickering, which is exacerbated by the high connectivity of the drainage system within the vale (Natural England, 2015).

Table 3.4 Rainfall chemistry from the Moor House monitoring site [NY 757 328]. The average rainfall composition was calculated from data provided by the Environmental Change Network (ECN) (www.ecn.ac.uk). The mean annual rainfall at this site is 2012 mm y^{-1} (1991–2007)

Parameter	Units	Average rainfall composition (2007)	Concentrated rainfall composition (enriched by evapotranspiration)
pH		5.6	
SEC	$\mu S\ cm^{-1}$	17	51
Ca	$mg\ L^{-1}$	0.19	0.57
Mg	$mg\ L^{-1}$	0.33	0.99
Na	$mg\ L^{-1}$	2.85	8.54
K	$mg\ L^{-1}$	0.10	0.31
Cl	$mg\ L^{-1}$	4.95	14.85
SO_4	$mg\ L^{-1}$	0.41	1.24
NO_3–N	$mg\ L^{-1}$	0.09	0.73*
NH_4–N	$mg\ L^{-1}$	0.15	

*Assuming all NH_4-N is oxidised to NO_3 on infiltration.



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Source Protection Zones © Environment Agency

Figure 3.2 Source Protection Zones in the study area

Source protection zones (SPZs) around boreholes have been identified by the EA (Figure 3.2). These show the risk of contamination from activities which may cause pollution. They are zoned according to the risk in terms of time for the pollution to travel to the borehole and extent of the contamination risk. Within the Corallian large SPZs are located around Pickering, Scarborough and East Ness. Local SPZs (~500m in diameter) are sparsely distributed around the periphery of valley bottom, within the Hambleton and Howardian Hills, and in the area south of Malton (EA, 2015).

4 Data availability and analytical methodology

4.1 GROUNDWATER DATA SOURCES

Groundwater chemical data were acquired for the area by collection of 24 new groundwater samples, and collation with unique sample site data from the Environment Agency (EA) database (1 additional site). The EA data include analyses of major elements, selected trace elements and field-determined parameters. These data comprise time-series analyses, generally spanning from 1995 to 2006. These time-series data are discussed separately in Section 5.5. Where there was a site monitored by the EA, but not sampled by the BGS, the most recent data were added to the 24 new groundwater samples to expand the spatial coverage and create a data set of 25 sites (see Figure 2.4). Data for 2006 were selected to be comparable to associated BGS analyses. All the groundwaters in this study were located in zones D or E as defined by Reeves et al. (1978) (See Section 3.2.2, above).

4.2 GROUNDWATER SAMPLING AND ANALYSIS

A total of 24 groundwater samples were collected by BGS during September 2006 from commercial abstraction and private boreholes exploiting the Corallian aquifer of the Vale of Pickering. These were almost exclusively from the unconfined aquifer exposed on the periphery of the Vale of Pickering. Few boreholes are available within the confined part of the Corallian aquifer below Jurassic clays. The sample locations are shown in Figure 2.4.

Samples were mostly collected from continuously pumping boreholes, although in the case of private boreholes this was not always possible. Where practical, the pumps at private sources were switched on at least 10 minutes prior to samples being taken. Efforts were made to sample the groundwater as close to the borehole as possible and with minimum transport through pipes or hoses. Sampling from storage tanks was mostly avoided. At one site this could not be avoided, although the rapid flush rate through the tank meant that a sample could be obtained that had only had a residence time in the tank of a few hours.

At each site, measurements were made of temperature, specific electrical conductance (SEC), alkalinity (by titration against H_2SO_4), pH, dissolved oxygen (DO) and redox potential (Eh). The latter three parameters were measured in a flow cell to prevent contact with the atmosphere and parameters were monitored until stable readings were obtained. In a few cases, use of a flow cell was not possible and on-site parameters were measured rapidly in a bucket. In each case a note was made of the sampling conditions.

Groundwater samples were also taken at each site for laboratory analysis. Samples for major- and trace-element analysis were collected in rinsed polyethylene bottles and filtered to <0.2 µm. Filtration was performed using either an in-line reusable filter holder attached to the outflow of the flow cell or a disposable filter and syringe. Those required for cation and trace-element analysis were acidified to 1% (v/v) HNO_3 to prevent metal precipitation and minimise sorption onto the container walls. Aliquots of the sample filtered to <0.2 µm were also collected in polyethylene bottles preloaded with potassium persulphate for the determination of total dissolved phosphorus (TDP).

Samples for dissolved organic carbon (DOC) analysis were filtered through a 0.45 µm silver-impregnated filter and collected in glass vials pre-cleaned with chromic acid. Samples for the determination of stable isotopes (^{18}O and ^{2}H in water and ^{13}C in dissolved inorganic carbon) were collected unfiltered in rinsed glass bottles.

Analysis of major cations and sulphate was carried out by inductively-coupled plasma optical emission spectrometry (ICP-OES); Cl, NO_3, Br and F were determined by ion chromatography (IC), NH_4, NO_2 and I by automated colorimetry (AC), stable isotopes by mass spectrometry and a range of trace elements by inductively-coupled plasma mass spectrometry (ICP-MS). With the exception of TDP, analyses were carried at the BGS laboratories in Wallingford and Keyworth. Total dissolved phosphorus was analysed by sample digestion followed by chromatography using the molybdenum blue method at the CEH laboratory in Wallingford.

4.3 DATA HANDLING

The data collected as a result of the sampling campaign and the archive EA data were combined into one set for the purposes of statistical handling and interpretation. For many trace elements, the concentrations were below the detection limits of the analytical techniques used. As the data reported were obtained from more than one laboratory source and by more than one method, the detection limits for any given determinand can vary, indeed detection limits can vary from day to day on a single instrument. This produces left-censored data sets that require special statistical analysis methods for calculating summary statistics.

Summary statistics were calculated in the R statistical computer environment using the NADA package. This package is used to perform statistical analysis on censored data and uses the methods described in Helsel (2005). The methods used to summarise the combined BGS-EA dataset were the Kaplan-Meier (K-M) method the “regression on order statistics” (ROS) method. These methods can both be used to summarise multiply-censored data sets (Lee and Helsel, 2005b, 2007). The ROS method is particularly useful for small data sets (n<30) where other methods may become inaccurate. It is also particularly useful where the non-detects comprise up to 80% of the data set.

As noted by Lee and Helsel (2005a, b), where the data set has greater than 80% non-detects, the estimated summary statistics are very tenuous. They suggest that in such cases the data can only be summarised by presenting minimum and maximum concentrations (Lee and Helsel, 2005a). The summary statistics in this report were calculated using each of the above methods. The most appropriate method for each analyte was taken following the recommendations of Helsel (2005), as given below:

<50% non-detects	K-M method
50% and 80% non-detects	ROS method
>80% non-detects	ranges only quoted.

The summary statistics reported are therefore derived from a range of methods and do not all present the same parameters.

In the Baseline report series the 95th percentile of a data distribution has typically been used as an upper cut-off for outlier compositions. The choice of percentile is somewhat arbitrary and other percentiles have been used within the literature. The 90–95th percentile was used by Lee and Helsel (2005a) and the 97.7th percentile was used by Langmuir (1997). While using percentiles as an upper limit provides a simple definition of outliers, the method clearly has its limitations. For example, many UK groundwaters are contaminated by nitrate derived from long-term use of nitrogenous fertilisers in agriculture. Nitrate concentrations are therefore variable and the 95% threshold in unconfined aquifers rarely represents a cut-off between natural and anthropogenically-influenced compositions. Likewise, for some elements data presented above a given threshold are presented as anomalous, when they can in fact represent baseline concentrations. However, the 95th percentile represents a simplification to exclude the upper 5% of the data distribution and has been used in the Baseline report series as one measure for estimating likely upper limits to baseline concentrations. Concentrations above this threshold are unlikely to be exceeded in future samples unless conditions within the aquifer have changed. It should be emphasised that this is not the only factor used when attempting to characterise the baseline groundwater compositions. A combination of understanding of the hydrogeological and geochemical processes, rainfall compositions, land use and residence times, together with temporal variability observed through time-series data are also taken into consideration.

In addition to the statistical analysis, saturation indices were calculated for the newly collected groundwater samples using PHREEQCi and the `wateq4f.dat` database. Saturation indices will be discussed where appropriate in Section 5. It should be remembered that minerals which are predicted to dissolve or precipitate may not actually do so because of kinetic constraints or indeed absence of the mineral in the case of dissolution (Zhu and Anderson, 2002).

5 Regional hydrogeochemistry

Corallian strata are dominated by calcite, and it is likely that groundwater chemical compositions will be dominated by interactions with this mineral. The data set obtained from the study of the Corallian aquifer of the Vale of Pickering is discussed below in terms of data distribution (i.e. summary statistics) as well as spatial distribution.

5.1 MAJOR CONSTITUENTS

Statistical data for major ions, field-determined parameters and stable isotopes are summarised below (Table 5.1, Figure 5.1 to Figure 5.3). In addition spatial variations are presented in this section. It should be noted that where an element was not analysed in the EA sample, only the 24 new BGS analyses are presented. The summary statistics reported are derived from a range of methods, depending on the proportion of non-detects (see Section 4.3). To produce the box plots in this report (Figure 5.2), ROS statistics have been applied using functions available in the NADA package in R.

The main mineral in the Corallian aquifer is calcite (Table 5.1, Figure 5.1).Calcium and HCO_3 dominate the aqueous chemistry in all samples (Figure 5.1). There is little variation between sites, which demonstrates the homogeneity of the groundwaters from the Corallian aquifer, despite the variable proportions of calcite and quartz in different formations. When calcium carbonate minerals are present in rocks or soils at levels of 1% or more they tend to dominate the aqueous geochemistry, as demonstrated here.

Table 5.1 Statistical summary of field-determined parameters, major ions, and stable isotope compositions

	units	**n**	**n(c)**	**min**	**mean**	**max**	**P5**	**P25**	**P50**	**P75**	**P90**	**P95**
Temp	ºC	24	0	8.70	11.1	15.6	8.90	9.70	10.7	12.1	13.3	15.2
pH		25	0	6.96	7.36	7.95	7.02	7.20	7.30	7.48	7.76	7.87
Eh	mV	23	0	203	379	469	243	350	395	434	444	451
DO	mg L^{-1}	24	1	<0.1	6.56	12.7	0.56	5.14	6.33	9.24	9.81	11.5
SEC	µs/cm	24	0	341	622	1020	361	485	616	754	780	781
δ^2H	‰	23	0	-57.6	-53.8	-47.0	-57.1	-56.3	-54.0	-52.0	-51.0	-49.5
δ^{18}O	‰	23	0	-8.61	-8.11	-7.28	-8.57	-8.39	-8.24	-7.93	-7.62	-7.42
δ^{13}C	‰	23	0	-18.0	-15.0	-12.1	-16.6	-15.8	-15.2	-14.0	-13.8	-13.0
Ca	mg L^{-1}	25	0	48.8	101	161	52.7	82.3	108	124	134	137
Mg	mg L^{-1}	25	0	2.12	7.72	19.4	2.53	4.58	6.91	8.80	14.3	17.1
Na	mg L^{-1}	25	0	8.71	13.6	29.7	8.77	10.4	11.4	15.9	19.8	21.5
K	mg L^{-1}	25	0	0.660	2.18	15.5	0.720	1.31	1.60	2.01	2.73	3.07
Cl	mg L^{-1}	25	0	13.2	33.4	63.8	15.9	23.0	29.5	41.0	56.3	56.5
SO_4	mg L^{-1}	25	0	25.3	51.0	102	25.9	37.2	47.2	57.7	77.0	78.9
HCO_3	mg L^{-1}	25	0	114	220	324	136	177	221	260	291	305
NO_3-N	mg L^{-1}	25	0	0.0860	7.75	24.4	1.50	3.85	5.70	10.6	16.0	22.6
Si	mg L^{-1}	25	0	2.91	4.10	7.50	3.43	3.58	3.95	4.26	4.65	5.29

DO: dissolved oxygen; SEC: specific electrical conductance; DOC: dissolved organic carbon; P: percentile; n(c): number censored; min and max are observed values

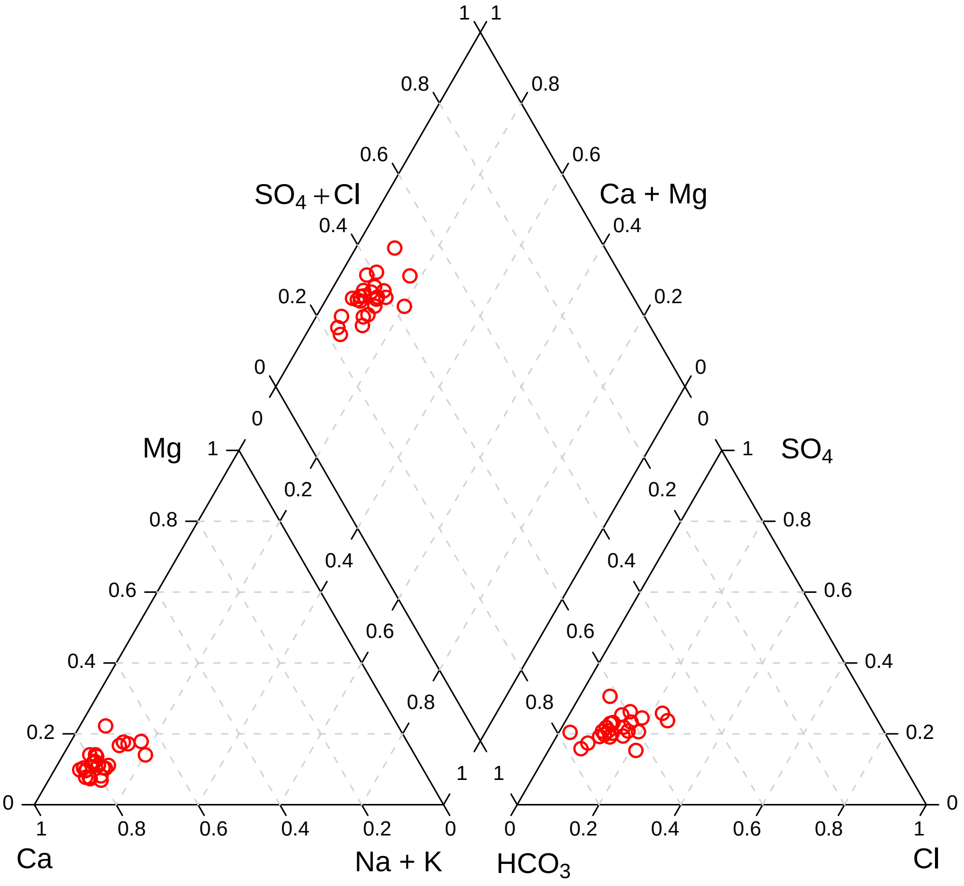

Figure 5.1 Piper digram of Corallian groundwaters in the Vale of Pickering

The temperatures of the groundwaters range from 8.7 to 15.6ºC, with a 5th to 95th percentile range of 8.9 to 15.2 ºC and a median of 10.7 ºC (Table 5.1). This is fairly typical of modern recharge in UK aquifers. Temperature can be a good indicator of depth, and therefore to some extent indicates residence time. There are no depth data to verify this, however. The temperature tends to be higher around the margins of the confined aquifer (Figure 5.4), which suggests that the groundwaters in these areas are deeper, and therefore older.

The pH of the groundwaters has a range of 6.96 to 7.95, a 5th to 95th percentile range of 7.02 to 7.87 and a median of 7.3 (Table 5.1). This range is similar to other limestone aquifers in the UK, including the Chalk, which typically has a narrow range and median values between 7.1 and 7.3 (Shand et al., 2007). Such a small range is typical of unconfined groundwaters that are dominated by carbonate equilibrium reactions, again suggesting that $CaCO_3$ is the mineral with the most influence over the aqueous geochemistry of the Corallian aquifer. The lowest pH values are found in the areas around Pickering and Malton, while the higher values are found near Scarborough and to the west of Pickering (Figure 5.5). There is no clear reason for this distribution; however there is little variation between the maximum and minimum values. It is very likely therefore that the entire range of pH values represents the range of baseline compositions.

The measured dissolved oxygen (DO) has a range of <1 to 12.7 mg L^{-1}, a 5th to 95th percentile range of 0.56 to 11.1 mg L^{-1} and a median of 6.33 mg L^{-1} (Table 5.1). This represents a large range up to DO saturated conditions . The Eh values range from 203 to 469 mV, with a 5th to 95th percentile range of 243 – 451 mV, and a median of 395 mV(Table 5.1). This represents a relatively narrow range, dominated by oxidised water. This is typical of unconfined groundwaters. The DO content of the waters is generally lowest in the east of the area (Figure 5.6), and around the edge of the zone confined by Jurassic Clays. The higher values are found in the west. The spatial distribution of Eh is similar with the lowest concentrations generally found in the east and around the periphery of the confining Jurassic Clay (Figure 5.7). The highest values are found in the north-west portion of the Corallian aquifer. The most north-westerly

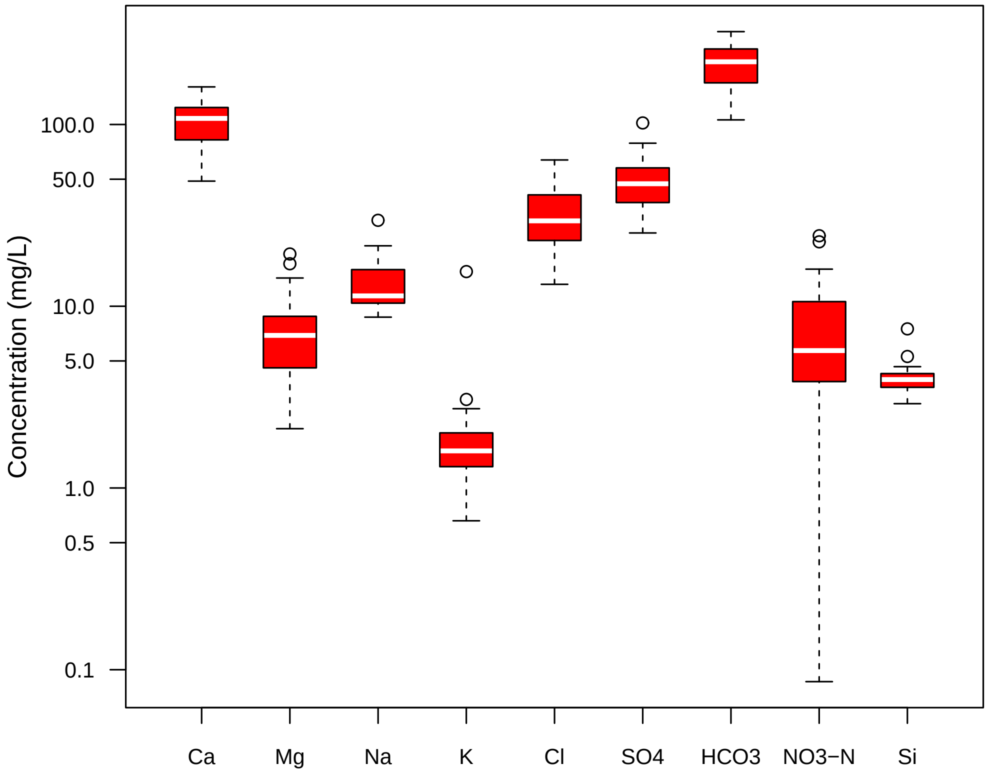

Figure 5.2 Box plot of major ions in the Corallian aquifer.

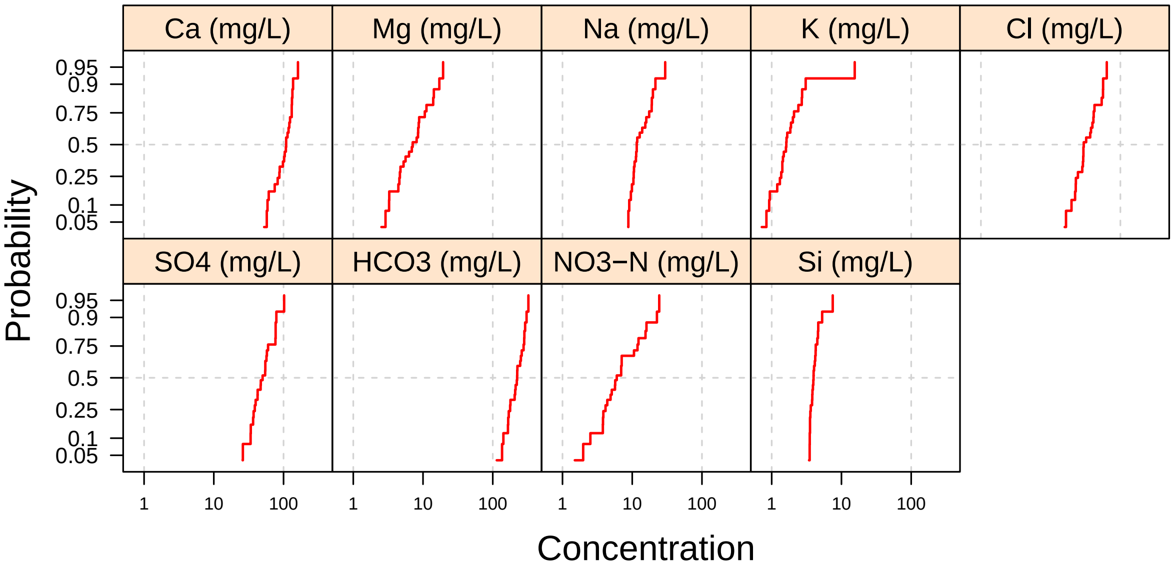

Figure 5.3 Cumulative-probability plots of major ions in the Corallian aquifer

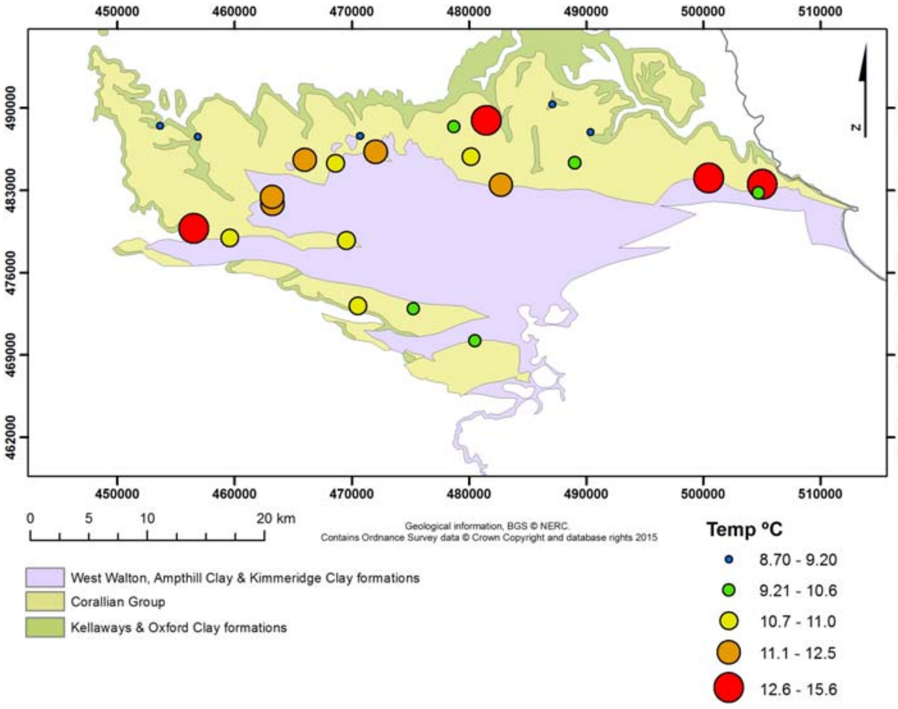

Figure 5.4 Regional variation of temperature within the Corallian aquifer

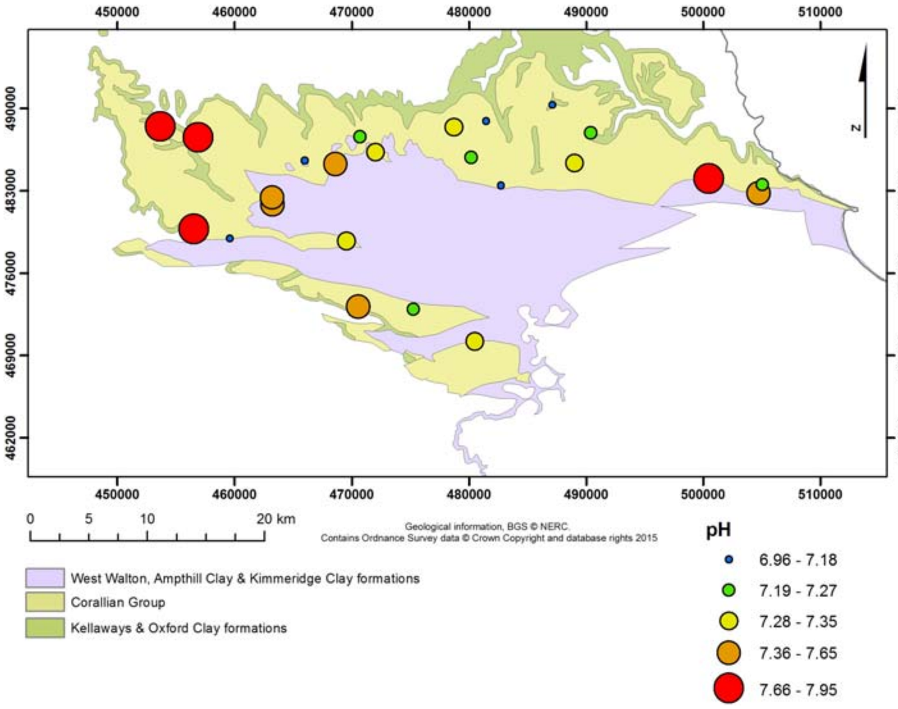

Figure 5.5 Regional variation of pH within the Corallian aquifer

samples also have the highest pH values. The interdependence of Eh and pH are the important factors which determine the solubility of minerals and speciation of chemical constituents (Levinson, 1974).

The specific electrical conductance (SEC) has a range of 341 to 1020 µS cm^{-1}, a 5th to 95th percentile range of 361 to 781 µS cm^{-1} and a median of 616 µS cm^{-1} (Table 5.1). This range is similar to other limestone aquifers in the UK (Shand et al., 2007). There is a cluster of lower SEC values in the north-west of the area, which corresponds to the highest DO and EH values. The highest SEC values are found in the south (Figure 5.8). There is no obvious reason why this distribution exists.

The major-ion data are presented as box plots in Figure 5.2 and cumulative probability

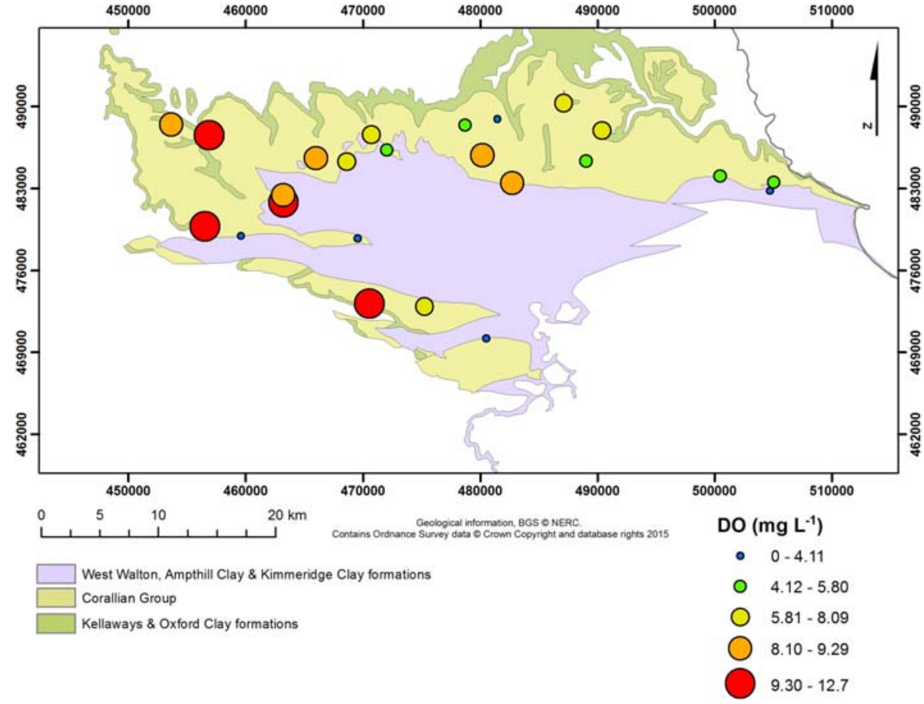

Figure 5.6 Regional variation of dissolved oxygen in the Corallian aquifer

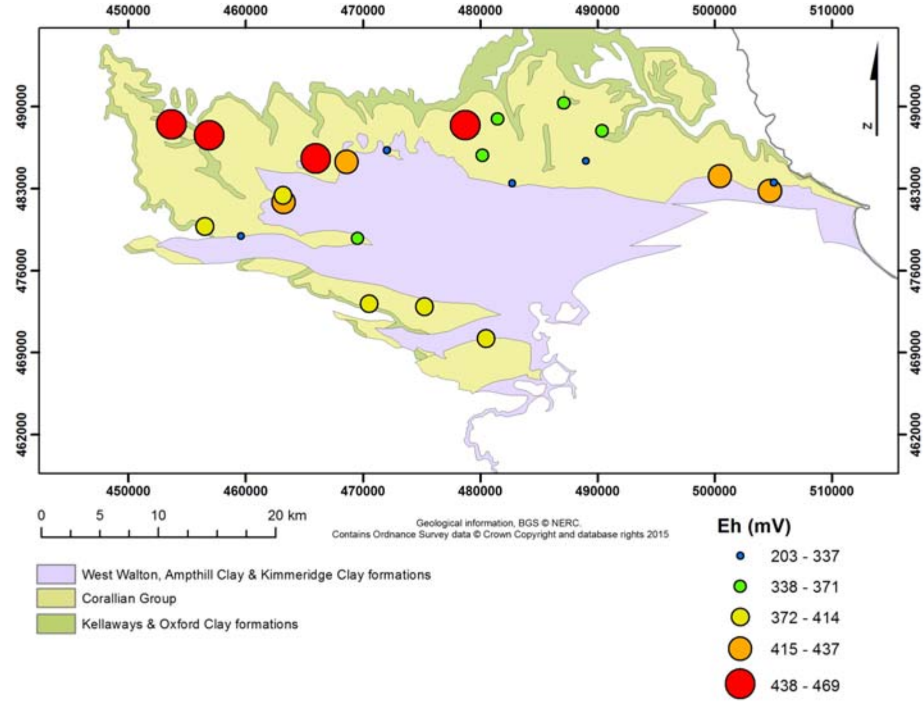

Figure 5.7 Regional variation of Eh in the Corallian aquifer

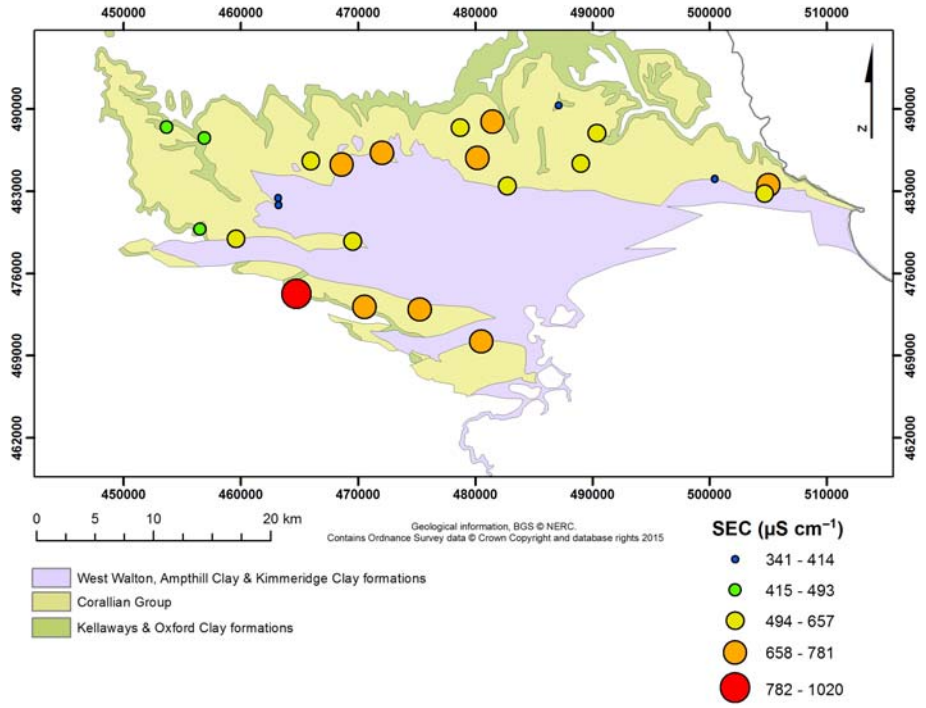

Figure 5.8 Regional variation of specific electrical conductance (SEC) in the Corallian aquifer

distribution plots in Figure 5.3. Both these graphical methods are useful for summarising and characterising geochemical data distributions (Shand et al., 2007).

Box plots are effective at showing data ranges within a population, and for identifying outliers. This means that they can be used to identify concentrations that could be outside a typical baseline range. Cumulative-probability plots are also an efficient way to identify distinct populations and to define anomalies. In Figure 5.3 the x axis (concentration) is logarithmic, meaning that a log normal distribution will plot as a straight line. A bimodal, or multimodal distribution would plot as a curve (Shand et al., 2007), and may be used to differentiate baseline concentrations from anomalous populations. However, natural reactions, including redox reactions, sorption, and denitrification can introduce anomalies, which are of entirely natural origin (Shand et al., 2007).

Figure 5.2 and Figure 5.3 present the ranges and outliers for the major ions. The range of concentrations for each element generally spans less than one order of magnitude. The exception to this is NO_3-N, (around 2 orders of magnitude). This is a relatively narrow range of NO_3-N. As NO_3-N is redox sensitive it is common for concentrations to range over five orders of magnitude (Shand et al., 2007). In such situations many data are left-censored as denitrification has taken place in reducing environments. The data presented here do not contain any censored data, although the lowest value is just 0.086 mg L^{-1}. Most of the groundwaters sampled have nitrate concentrations consistent with oxidising conditions, although the lowest suggest that conditions are reducing in some. The box plot of K shows there is an upper outlier (1.2 mg L^{-1}), which is shown by the cumulative-probability plot to be separate to the main population. This sample would warrant further investigation as it is unlikely to be representative of a baseline range. For the remaining major ions the cumulative-probability plots display steep curves, and the box plots have few outliers, indicating a near log-normal distribution. It is likely that these represent natural baseline ranges. Each element will be discussed individually, below.

Calcium has a concentration range of 48.8 to 161 mg L^{-1}, a 5th to 95th percentile range of 52.7 to 137 mg L^{-1} and a median of 108 mg L^{-1} (Table 5.1). The cations in the groundwaters are dominated by Ca (Figure 5.1). The shape of the cumulative-probability plot is similar to those produced for groundwaters in Chalk (Shand et al., 2007). By contrast the Cotswold Oolite and the Corallian of Oxfordshire and Wiltshire, which are more geologically similar to the Corallian of the Vale of Pickering, show a strong negative skew. This is due to the presence of deeper groundwaters which have exchanged Ca for Na in ion-exchange reactions. The lack of such a skew indicates that the groundwaters sampled as part of this study are all fresh shallow groundwaters. The Ca is derived from dissolution reactions with the carbonate minerals.

Most samples were at equilibrium, or supersaturated, with respect to calcite, which is why the distribution of these Ca data is similar to that of the Chalk aquifers. In addition, there are no clear trends in the spatial distribution of Ca (Figure 5.9).

Magnesium has a concentration range of 2.12 to 19.4 mg L^{-1}, a 5th to 95th percentile range of 2.53 to 17.1 mg L^{-1} and a median of 6.91 mg L^{-1} (Table 5.1). This range is similar to that found in the Cotswold Oolite and the Corallian of Oxfordshire and Wiltshire, as well as the Chalk aquifers. The cumulative-probablity plot shows that the distribution of Mg concentrations is log normal. The lowest concentrations of Mg are all found in the north-west corner of the study area (Figure 5.10); the highest concentrations are in the northern portion. There is scant information regarding the mineralogy of the Vale of Pickering in the available memoirs, but it is most likely that the source of Mg is within calcite or clays. It is unlikely, however, that the source is dolomite, as all the waters analysed in this study are undersaturated with respect to it.

Sodium has a concentration range of 8.71 to 29.7 mg L^{-1}, a 5th to 95th percentile range of 8.77 to 21.5 mg L^{-1} and a median of 11.4 mg L^{-1}. This range is relatively narrow as Na in many UK groundwaters ranges over two orders of magnitude (Shand et al., 2007). The data presented here lack the positive skew seen in data from comparable groundwaters of the Cotswold Oolite and Corallian of Oxfordshire and Wiltshire. While the highest concentration is found close to the coast, there is no trend of Na decreasing away from the sea, which suggests that the influence of marine aerosols or saline intrusion is limited (Figure 5.11). It is likely that many of the lower concentrations represent evapotranspired rainwater. The remaining Na is probably sourced from percolation through overlying soils, and minor proportions of feldspars or clays that may be present in the gritty layers of the Corallian aquifer.

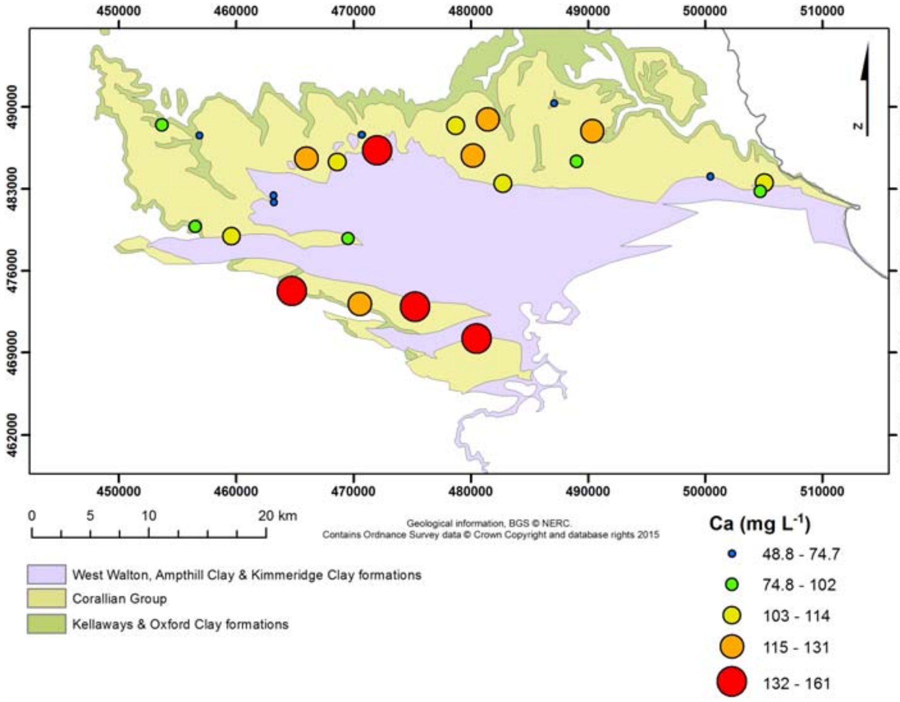

Figure 5.9 Regional Variation of Ca in the Corallian aquifer

Potassium has a concentration range of 0.660 to 15.5 mg L^{-1}, a 5th to 95th percentile range of 0.720 to 3.07 mg L^{-1} and a median of 1.60 mg L^{-1}. This range is comparable to those found in the groundwaters of Cotswold Oolite and Corallian of Oxfordshire and Wiltshire (Shand et al., 2007). There is no obvious spatial trend (Figure 5.12), but there are very low K concentrations in the groundwaters in the area to the north-east of Pickering, which may represent concentrated rainfall. This is a wooded area of high ground (Figure 2.2), whereas the rest of the study area is

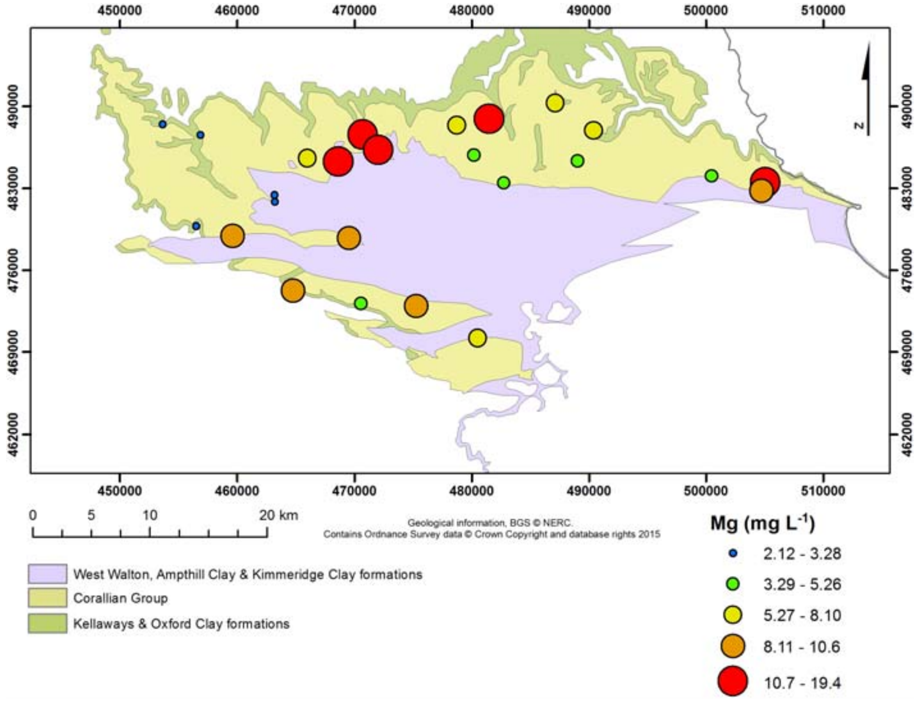

Figure 5.10 Regional variation of Mg in the Corallian aquifer

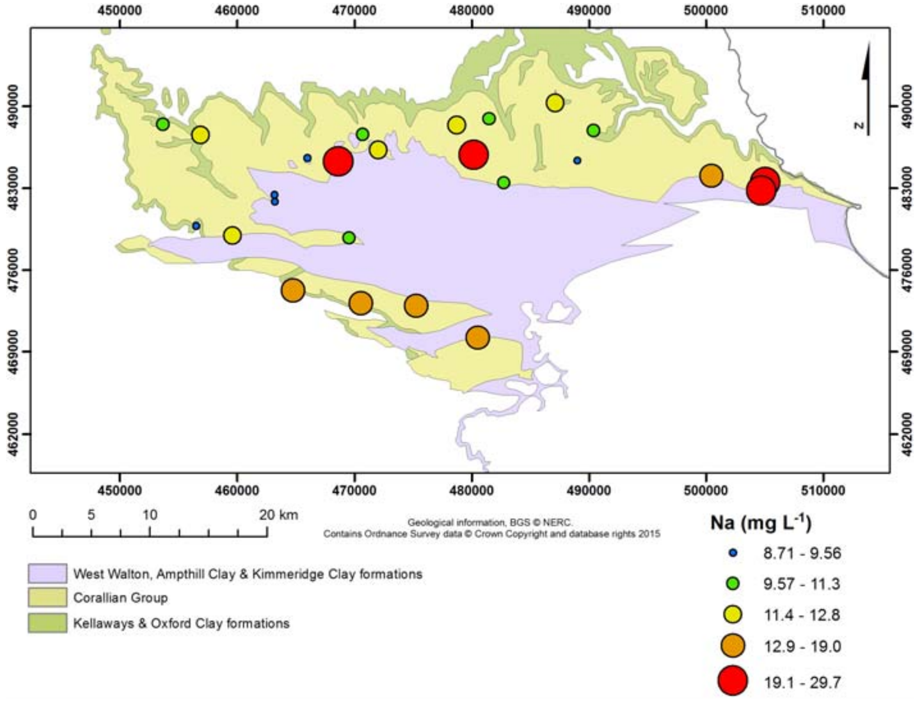

Figure 5.11 Regional variation of Na in the Corallian aquifer

predominantly arable and horticulture, and may receive K inputs from fertilisers and soil enhancement. The highest concentration is an outlier and is found at a farm site in the Howardian Hills (Figure 5.3). This is likely caused by agricultural contamination. The relatively high concentrations found in groundwaters around Scarborough may be derived from marine aerosols, but this is not a dominant source of K.

Chloride has a concentration range of 13.2 to 63.8 mg L^{-1}, a 5th to 95th percentile range of 15.9 to 56.5 mg L^{-1} and a median of 29.5 mg L^{-1}. This is also a narrow range although the cumulative probability plot is very similar to that of the Corallian of Oxfordshire and Wiltshire (Shand et al., 2007). The lower end of the range is consistent with rainfall impacted by evapotranspiration. Higher values could be derived from fertilizers, although the higher values are not extreme and contamination appears to be minor. There is a good correlation between Na and Cl ($r^2 = 0.64$). There is no simple clear spatial trend (Figure 5.13) and no clear relationships with the proximity to the sea suggesting that marine aerosols are not a significant influence. The lowest values are found around the Howardian Hills and the North York Moors. The highest values are found in groundwaters near Scarborough, and commonly also from sites along the foot of the slopes which surround the Vale of Pickering.

Sulphate has a concentration range of 25.3 to 102 mg L^{-1}, a 5th to 95th percentile range of 25.9 to 78.9 mg L^{-1} and a median of 47.2 mg L^{-1}. The cumulative probability plot is similar to that of the groundwaters of the Corallian of Oxfordshire and Wiltshire (Shand et al., 2007). The highest concentrations of SO_4 are generally found near Scarborough, in the Howardian Hills, and around the foot slopes of the North York Moors (Figure 5.14). Lower concentrations of SO_4 are found in the higher ground of the North York Moors, and the west of the region. The groundwaters mostly saturated or supersaturated with respect to barite.

Alkalinity as HCO_3 has a concentration range of 114 to 324 mg L^{-1}, a 5th to 95th percentile range of 136 to 305 mg L^{-1} and a median of 221 mg L^{-1}. This is a very narrow range and the cumulative probability plot is very similar to those of the Cotswold Oolite and the Corallian of Oxfordshire and Wiltshire (Shand et al., 2007). The aquifer mineralogy is dominated by $CaCO_3$; hence the anion chemistry is dominated by HCO_3, as shown on the Piper Plot (Figure 5.1). There

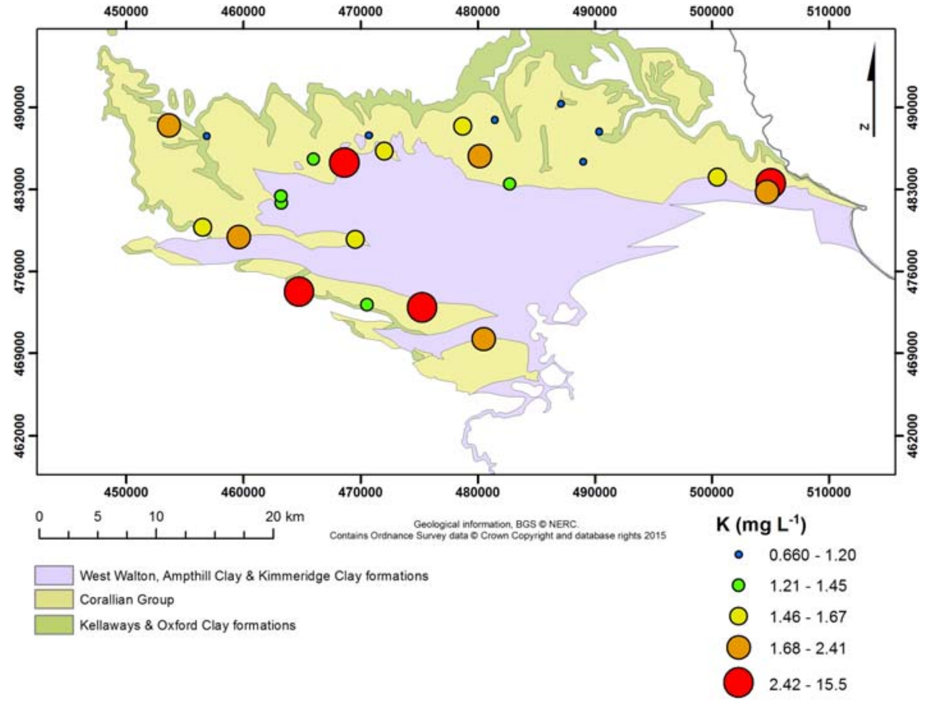

Figure 5.12 Regional variation of K in the Corallian aquifer

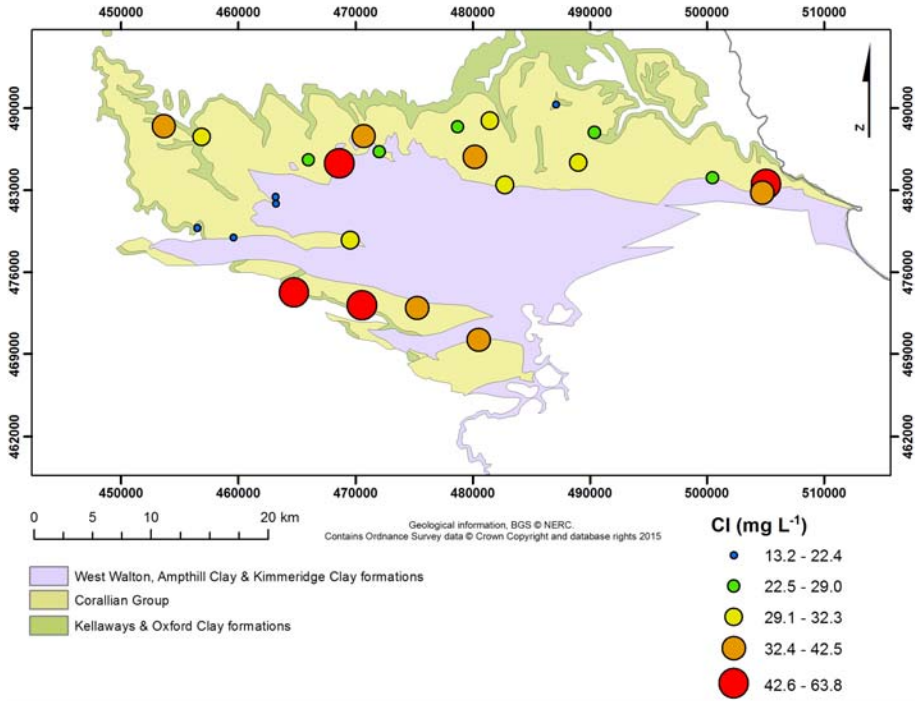

Figure 5.13 Regional variation of Cl in the Corallian aquifer

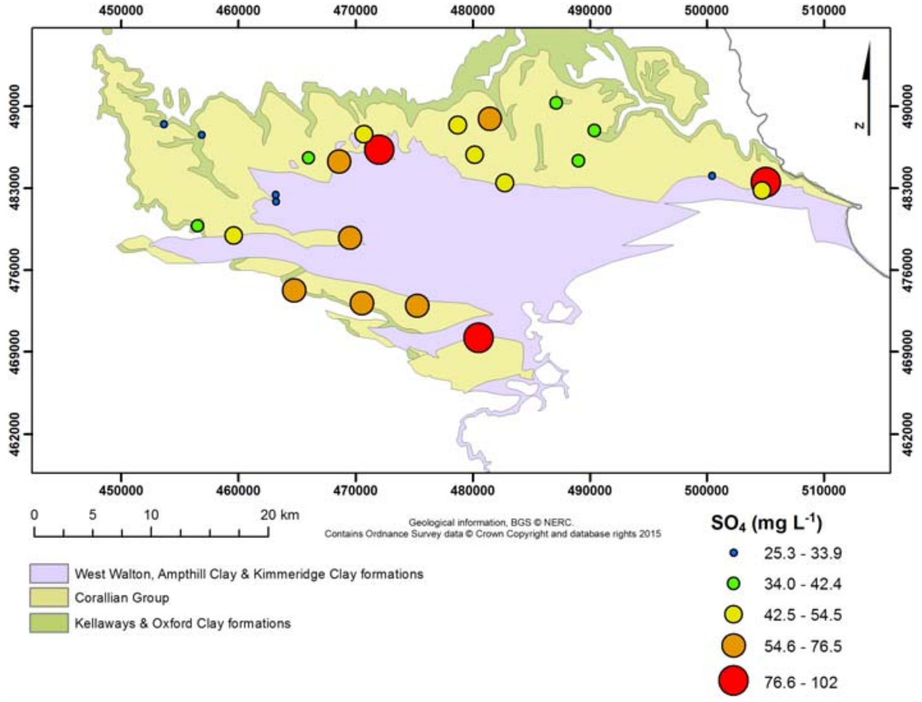

Figure 5.14 Regional variation of SO_4 in the Corallian aquifer

is a strong correlation between HCO_3 and Ca ($r^2 = 0.74$). While there are no clear spatial trends of HCO_3 (Figure 5.15) the distribution is similar to that of Ca (Figure 5.9).

Nitrate as N has a concentration range of 0.086 to 24.4 mg L^{-1}, a 5th to 95th percentile range of 1.5 to 22.6 mg L^{-1} and a median of 5.7 mg L^{-1}. The cumulative probability curve is relatively shallow as a result of a large concentration range, probably caused by varying human inputs. The drinking water limit of NO_3-N is 11.3 mg L^{-1}, and one fifth of the analyses exceed this value, suggesting significant human inputs. There are no distinct spatial trends (Figure 5.16), but all the concentrations > 7mg L^{-1} are found in groundwaters sampled within 500m of farm land. The

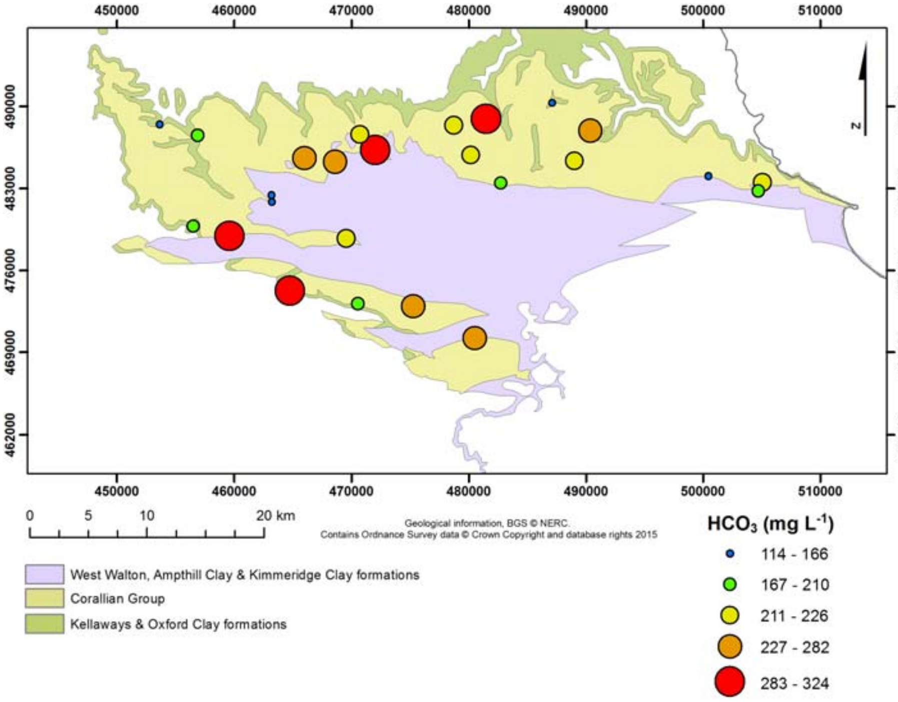

Figure 5.15 Regional variation of HCO_3 in the Corallian aquifer

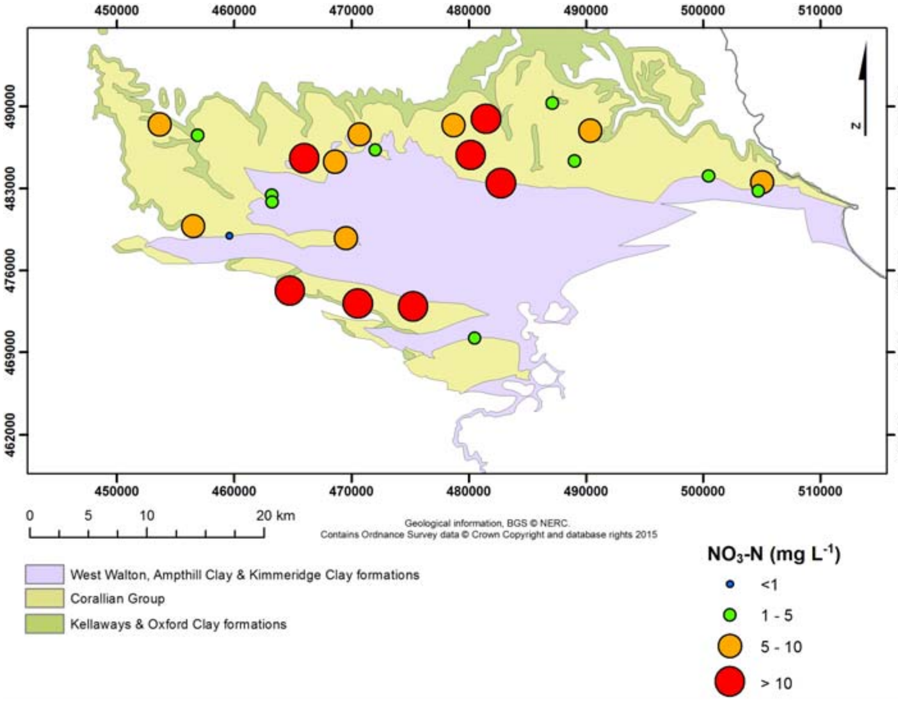

Figure 5.16 Regional variation of NO_3-N in the Corallian aquifer

concentration of NO_3-N in groundwaters is dependent on the redox conditions as well as availability of NO_3 in the environment. Figure 5.17 demonstrates how larger NO_3-N concentrations occur in oxic conditions (higher Eh values)

Silicon has a concentration range of 2.91 to 7.5 mg L^{-1}, a 5th to 95th percentile range of 3.43 to 5.29 mg L^{-1} and a median of 3.95 mg L^{-1}. The near-vertical line presented on the cumulative probability curve indicates that Si rapidly attains saturation. Despite the abundance of Si in the Earth's crust (it is the second most abundant element) the concentrations of Si are relatively low, owing to low solubility of silicate minerals (Hem, 1992). The most soluble of the SiO_2 polymorphs is amorphous SiO_2 and the least soluble is quartz. From modelled saturation indices,

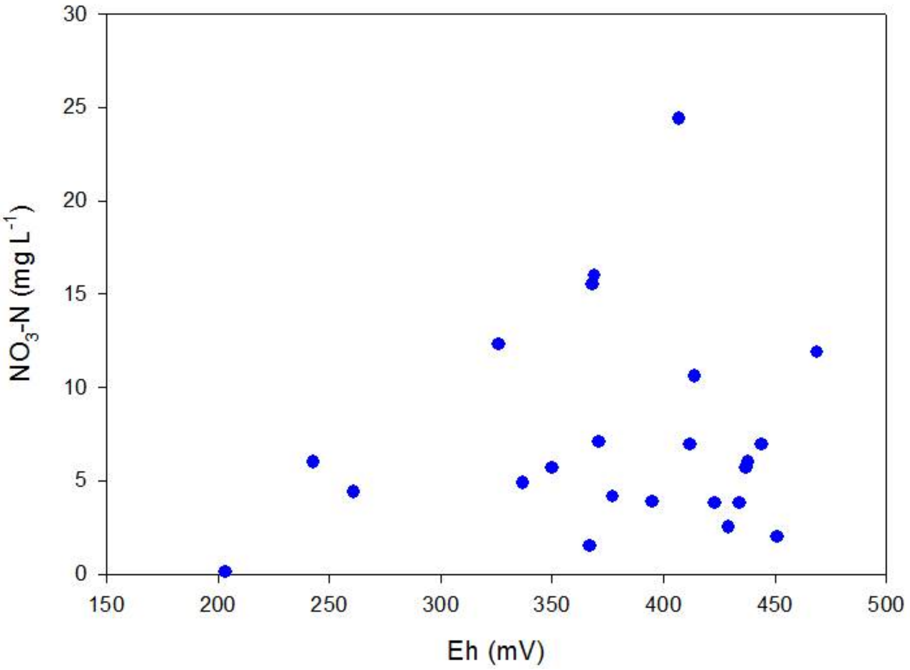

Figure 5.17 Relationship of NO$_3$-N and Eh

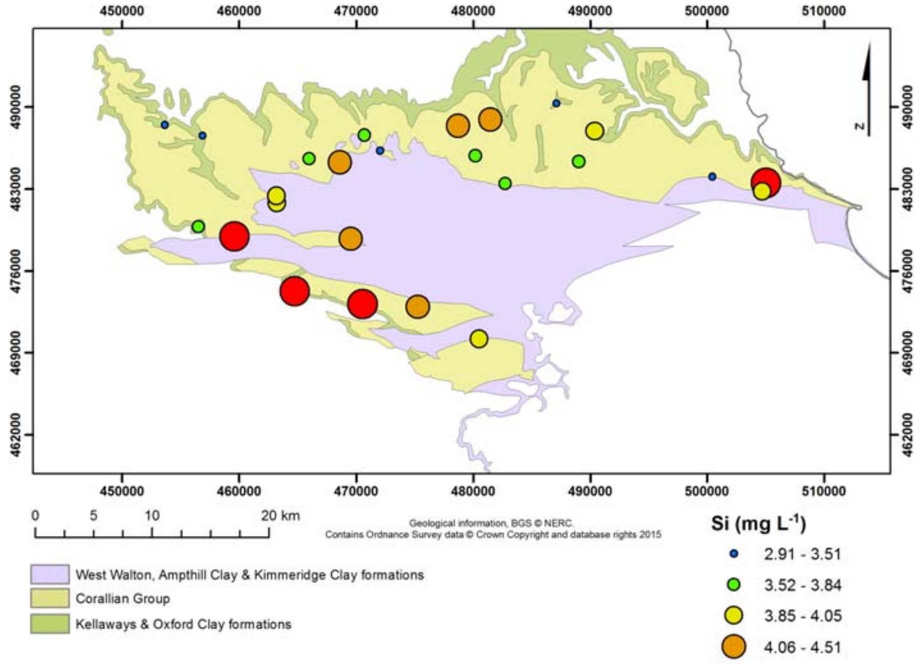

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Figure 5.18 Regional variation of Si in the Corallian aquifer

quartz is generally close to equilibrium, with one site being supersaturated. In contrast, all sites were undersaturated with respect to amorphous SiO_2. There is no particular spatial trend (Figure 5.18), which probably indicates there are variable concentrations of Si present in the aquifer.

5.2 MINOR AND TRACE CONSTITUENTS

Summary statistical data (Table 5.2, Figure 5.19 and Figure 5.20) and spatial variations (Figure 5.21 to Figure 5.43) for minor and trace constituents are presented in this section. Where all the determinations are below the detection limit, the element is not discussed here (see Table 5.2).

5.2.1 Phosphorus

Phosphorus has a concentration range of <0.02 to 0.043 mg L^{-1}, and 17 of the 24 analyses are below the detection limit (Table 5.2). The concentrations of P are generally lower than those found in the groundwaters of the Cotswold Oolite and the Corallian of Oxfordshire and Wiltshire, which ranged from <0.02 to 0.12 mg L^{-1} (Cobbing et al., 2004; Neumann et al., 2003). There are no spatial trends evident in the Vale of Pickering (Figure 5.21), which is probably a function of the large number of censored data.

5.2.2 Halogen elements

Fluoride has a concentration range of <0.25 to 0.311 mg L^{-1}, a 5th to 95th percentile range of 0.024 to 0.252 mg L^{-1}, and a median of 0.06 mg L^{-1} (Table 5.2). All these values are well within the drinking water limit of 1.5 mg L^{-1} (The Water Supply Regulations, 2010). One of the samples contained F below the detection limit of 0.25 mg L^{-1}. However this detection limit is higher than some of the measured values, of which the minimum is 0.033 mg L^{-1}. The F range in the Corallian of the Vale of Pickering is much smaller than those of the comparable groundwaters found in the Cotswold Oolite and the Corallian of Oxfordshire and Wiltshire, which are between <0.05 to 4.8 mg L^{-1}, and 0.05 to 1.98 mg L^{-1} respectively (Cobbing et al., 2004; Neumann et al., 2003). In these the higher concentrations were the result of ion exchange.

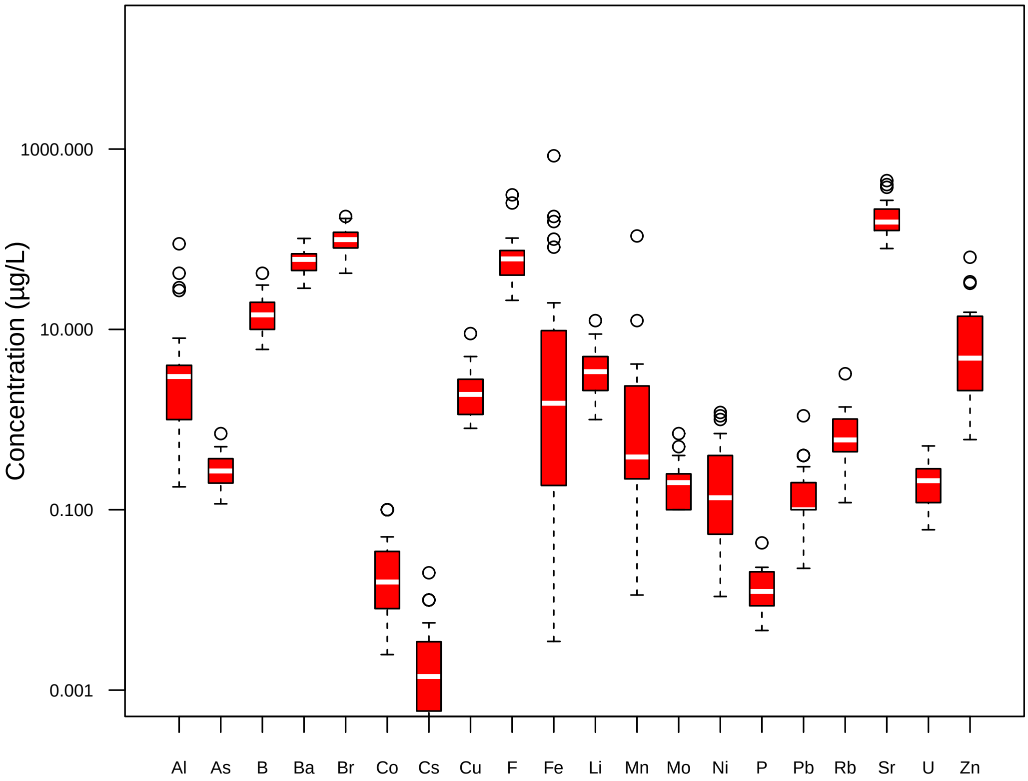

Figure 5.19 Box plot for the minor and trace elements in the Vale of Pickering Corallian

Table 5.2 Statistical summary of data for minor and trace elements

(P= percentile; n(c) = number censored; min and max are observed values**)**

	units	n	n(c)	min	mean	max	P5	P25	P50	P75	P90	P95
Ag	µg L^{-1}	25	25	<0.05		<0.05						
Al	µg L^{-1}	25	1	<1	9.52	89	1	1	3	4	29	42
As	µg L^{-1}	24	20	<0.5		0.7						
Au	µg L^{-1}	24	24	<0.05		<0.05						
B	µg L^{-1}	25	1	<100	16	42	7	10	14	19	26	31
Ba	µg L^{-1}	25	0	28.6	60.4	102	35.5	45	59.7	68.9	89.4	89.8
Be	µg L^{-1}	25	25	<0.05		<0.05						
Bi	µg L^{-1}	24	24	<0.05		<0.05						
Br	mg L^{-1}	25	0	0.042	0.0998	0.179	0.042	0.081	0.096	0.117	0.15	0.17
Cd	µg L^{-1}	25	25	<0.05		<0.05						
Ce	µg L^{-1}	24	14	<0.01		0.11						
Co	µg L^{-1}	25	19	<0.02		0.1						
Cr	µg L^{-1}	25	25	<0.5		<0.5						
Cs	µg L^{-1}	24	21	<0.01		0.02						
Cu	µg L^{-1}	24	0	0.8	2.39	9	0.8	1	1.9	2.8	3.6	5
Dy	µg L^{-1}	24	17	<0.01		0.03						
Er	µg L^{-1}	24	22	<0.01		0.02						
Eu	µg L^{-1}	24	23	<0.01		0.01						
F	mg L^{-1}	25	1	<0.25	0.0756	0.311	0.024	0.04	0.06	0.073	0.103	0.252
Fe	µg L^{-1}	24	14	<5		842						
Ga	µg L^{-1}	24	24	<0.05		<0.05						
Gd	µg L^{-1}	24	18	<0.01		0.05						
Ge	µg L^{-1}	24	23	<0.05		0.07						
Hf	µg L^{-1}	24	24	<0.02		<0.02						
Hg	µg L^{-1}	24	20	<0.1		0.1						
Ho	µg L^{-1}	24	23	<0.01		0.01						
In	µg L^{-1}	24	23	<0.01		0.01						
Ir	µg L^{-1}	24	24	<0.05		<0.05						
La	µg L^{-1}	24	2	<0.01	0.0146	0.07		0.01	0.01	0.01	0.02	0.02
Li	µg L^{-1}	24	0	1	3.75	12.5	1.3	1.7	2.9	4.85	6.2	8.1
Lu	µg L^{-1}	24	24	<0.01		<0.01						
Mn	µg L^{-1}	25	4	<0.05	5.71	109		0.18	0.38	2.18	4.13	12.5
Mo	µg L^{-1}	24	0	0.1	0.221	0.7	0.1	0.1	0.2	0.2	0.4	0.5
Nb	µg L^{-1}	24	23	<0.01		0.01						
Nd	µg L^{-1}	24	2	<0.01	0.02	0.14		0.01	0.01	0.01	0.05	0.05
Ni	µg L^{-1}	25	15	<0.2		1.2						
Os	µg L^{-1}	24	24	<0.05		<0.05						
P	mg L^{-1}	24	17	<0.02		0.043						
Pb	µg L^{-1}	25	4	<0.1	0.206	1.1		0.1	0.1	0.2	0.4	0.4
Pd	µg L^{-1}	24	24	<0.2		<0.2						
Pr	µg L^{-1}	24	20	<0.01		0.02						
Pt	µg L^{-1}	24	24	<0.01		<0.01						
Rb	µg L^{-1}	24	0	0.12	0.779	3.22	0.3	0.42	0.59	1.01	1.16	1.38
Re	µg L^{-1}	24	5	<0.01	0.016	0.07		0.01	0.01	0.01	0.03	0.035
Rh	µg L^{-1}	24	7	<0.01	0.0608	0.16			0.05	0.1	0.15	0.15
Ru	µg L^{-1}	24	20	<0.05		0.08						
Sb	µg L^{-1}	25	22	<0.05		0.14						
Sc	µg L^{-1}	24	0	1	1.04	2	1	1	1	1	1	1
Se	µg L^{-1}	24	3	<0.5	0.754	1.2		0.6	0.8	0.9	1.1	1.1
Sm	µg L^{-1}	24	23	<0.02		0.03						
Sn	µg L^{-1}	24	18	<0.05		0.12						
Sr	µg L^{-1}	24	0	78.9	191	447	106	125	155	216	377	403
Ta	µg L^{-1}	24	24	<0.02		<0.02						
Tb	µg L^{-1}	24	23	<0.01		0.01						
Te	µg L^{-1}	24	24	<0.05		<0.05						
Th	µg L^{-1}	24	24	<0.05		<0.05						

Table 5.2 (continued) Statistical summary of data for minor and trace elements

	units	n	n(c)	min	mean	max	P5	P25	P50	P75	P90	P95
Ti	µg L^{-1}	24	24	<10		<10						
Tl	µg L^{-1}	24	10	<0.01	0.0112	0.03			0.01	0.01	0.01	0.02
Tm	µg L^{-1}	24	24	<0.01		<0.01						
U	µg L^{-1}	24	0	0.06	0.225	0.51	0.08	0.12	0.21	0.25	0.4	0.41
V	µg L^{-1}	25	5	<0.2	0.283	0.5		0.2	0.3	0.3	0.4	0.5
W	µg L^{-1}	24	24	<0.02		<0.02						
Y	µg L^{-1}	24	0	0.01	0.0367	0.19	0.01	0.02	0.03	0.04	0.06	0.07
Yb	µg L^{-1}	24	22	<0.01		0.01						
Zn	µg L^{-1}	25	1	<5	10.2	63.2	0.7	1.8	4.8	14	32.4	33.8
Zr	µg L^{-1}	24	23	<0.02		0.06						

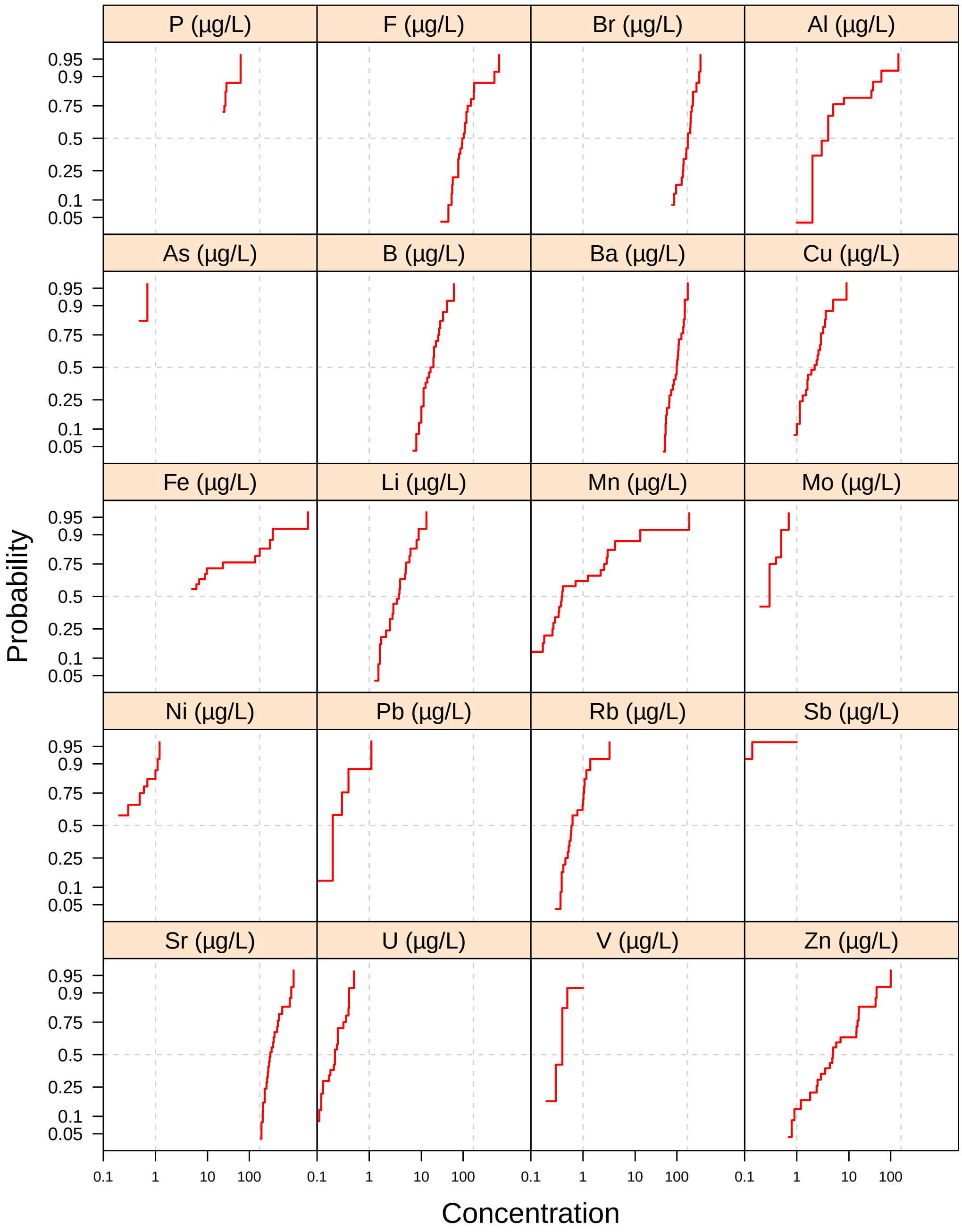

Figure 5.20 Cumulative probability plots for selected trace elements in the groundwater from the Vale of Pickering Corallian aquifer

In general, the highest F concentrations are found in the areas around the periphery of the valley floor (Figure 5.22) and the lowest concentrations are found in groundwaters sampled higher up the valley sides, towards the north and west of the region. Fluoride concentrations in rainfall are generally low, so the dominant source of F tends to be mineralogical. Unfortunately the lack of mineralogical information makes it difficult to draw firm conclusions, although CaF_2, the most common F-rich mineral, is the most likely source.

Bromide has a concentration range of 0.042 to 0.179 mg L^{-1}, a 5th to 95th percentile range of

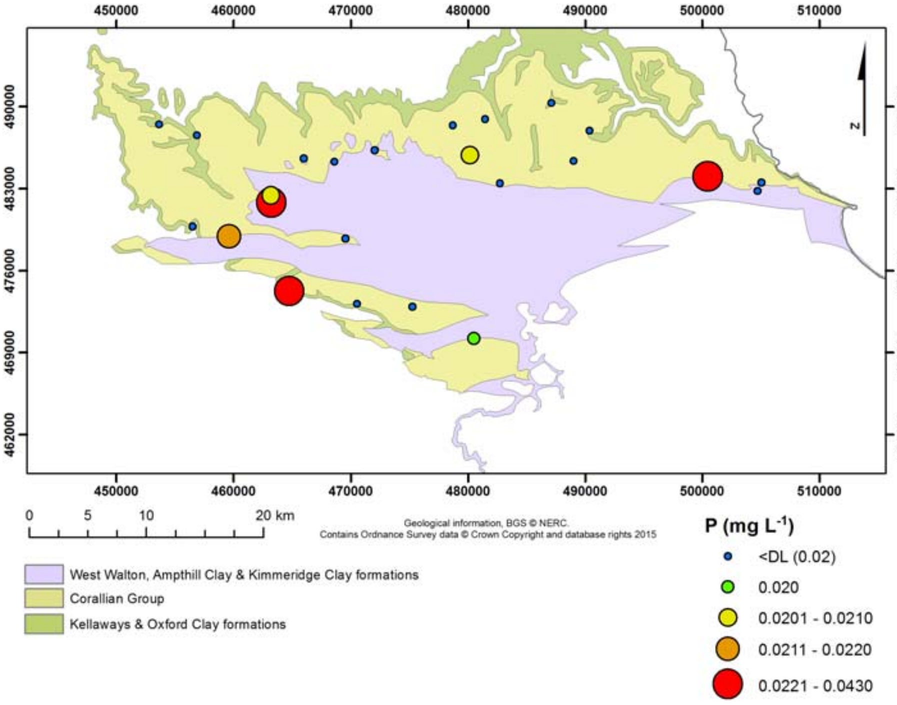

Figure 5.21 Regional variation of P in the Corallian aquifer

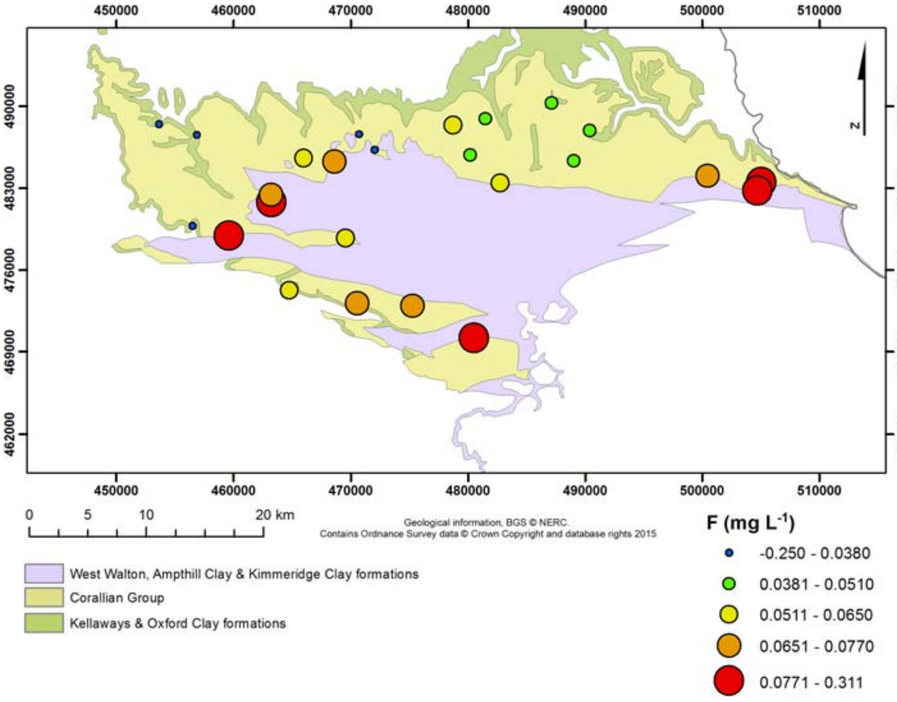

Figure 5.22 Regional variation of F in the Corallian aquifer

0.042 to 0.17 mg L^{-1}, and a median of 0.096 mg L^{-1} (Table 5.2). This is a smaller range than that of either the Cotswold Oolite and the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004; Neumann et al., 2003), for which Br concentrations are up to an order of magnitude greater. Bromide behaves in a similar way to Cl, and the two elements have a moderate-strong correlation ($r^2 = 0.59$) and a similar spatial distribution (Figure 5.23). High concentrations of Cl and Br are found around Scarborough, and to the north-west of Malton, while the lowest concentrations are found north of the Howardian Hills.

Edmunds et al. (1989) noted that because of the similar geochemical behaviour of Cl and Br the ratio Cl/Br is usually very similar to that of sea water (Cl/Br = 288). They suggested that deviation from this ratio would have diagnostic value in interpreting the origin of Br. The Cl/Br ratios of 25 samples in this study range from 207 to 604. Most calculated ratios (n=18) are greater than the seawater value of 288, which indicates Br depletion or Cl enrichment. If Cl/Br values far exceed 288, it is likely that there has been a dilution effect from a halite source, either a natural geological source or from agriculture or industry (Edmunds et al., 1989). The most enriched sites are generally surrounded by farmland or are industrial, suggesting that there is some NaCl contamination. Where the Cl/Br values are moderately higher than that of seawater, the deviation from a seawater average is most likely caused naturally on infiltration (Edmunds, 1996).

5.2.3 Alkaline earth elements

Barium has a concentration range of 28.6 to 102 µg L^{-1}, a 5th to 95th percentile range of 35.5 to 89.8 µg L^{-1}, and a median of 59.7 µg L^{-1} (Table 5.2). These concentrations are much higher than those found in the geologically similar aquifers of the Cotswold Oolite and the Corallian of Oxfordshire and Wiltshire, which have ranges of 3.46 to 14.0 µg L^{-1}, and 3.23 to 50.19 µg L^{-1}, respectively. There are however few diffuse anthropogenic sources of Ba, and the higher concentrations found here likely reflect natural regional variations in Ba.. The groundwaters in the study area are mostly saturated or supersaturated with respect to barite, which is the limiting control on Ba. Where the SO_4 concentration is low (<40 mg L^{-1}), Ba ranges between 38 and

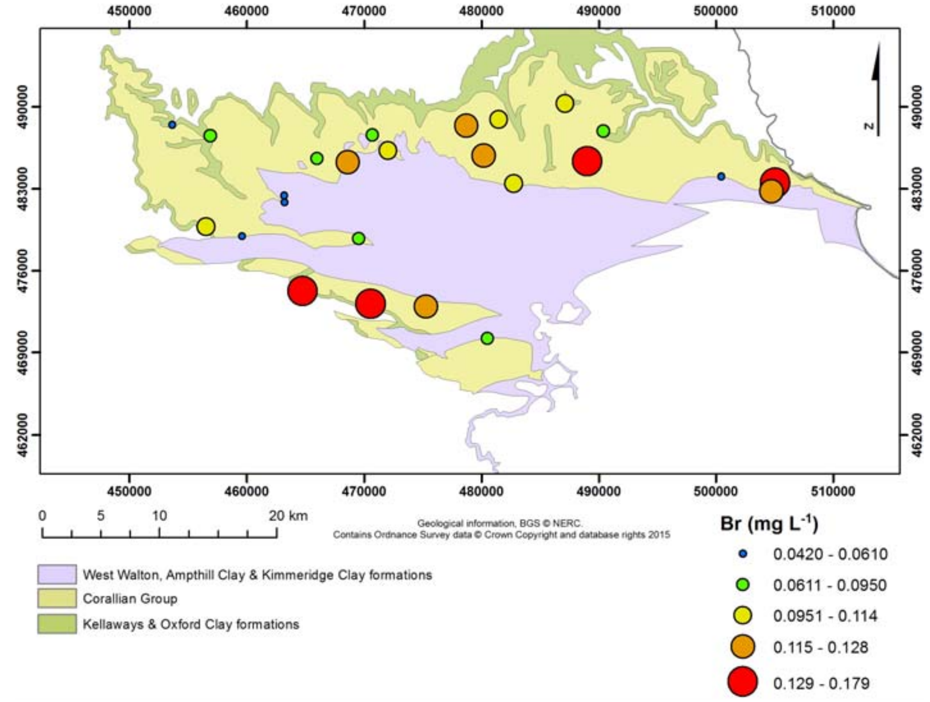

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Figure 5.23 Regional variation of Br in the Corallian aquifer

102 µg L^{-1}. There is no distinct spatial distribution of Ba (Figure 5.24), which likely represents natural variability as well as barite solubility.

Strontium has a concentration range of 78.9 to 447 µg L^{-1}, a 5th to 95th percentile range of 106 to 403 µg L^{-1}, and a median of 155 µg L^{-1} (Table 5.2). This range is about half that of the geologically similar Corallian of Oxfordshire and Wiltshire, which ranges from 88.6 to 1860 µg L^{-1} (Cobbing et al., 2004). Strontium is geochemically similar to Ca, and can be present at high concentrations in Ca-bearing minerals owing to the similarities in the ionic radius of Ca and Sr. In fresh groundwater there are generally no solubility controls on Sr, and it typically increases with residence time. Increases in the Sr/Ca ratio likewise reflect increasing residence time (Shand et al., 2007). The Sr/Ca ratio of the data presented here has a moderate-strong relationship with the Sr concentrations ($r^2 = 0.64$). The spatial distribution of Sr in the Vale of Pickering is similar to that of Ca (Figure 5.25), and there is a moderate relationship between the two elements ($r^2 = 0.38$). These values indicate that, while there is no information available on the aquifer mineralogy and chemistry, is it most likely that the Sr concentrations presented here, represent baseline concentrations.

5.2.4 Alkali metals

The cumulative-probability distributions (Figure 5.20) for the alkali metals show a small range of concentrations. The distributions of Li and Rb are very similar (Figure 5.26 and Figure 5.27).

Lithium has a concentration range of 1 to 12.5 µg L^{-1}, a 5th to 95th percentile range of 1.3 to 8.1 µg L^{-1}, and a median of 2.9 µg L^{-1} (Table 5.2). This range is narrower than either of those observed in the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004) and the Cotswold Oolite (Neumann et al., 2003), which range up to 78.3 and 48 µg L^{-1} respectively. The concentration of Li in groundwaters is a combination of availability and residence time, so it would be expected that the baseline vary greatly between groundwater systems. Lithium-rich minerals such as clays are likely to be rare in the Corallian limestone aquifer, as reflected by the low concentrations. The highest concentrations are found in the south of the area, and near to the boundary of the Corallian outcrop and the valley bottom clays (Figure 5.26). This may indicate

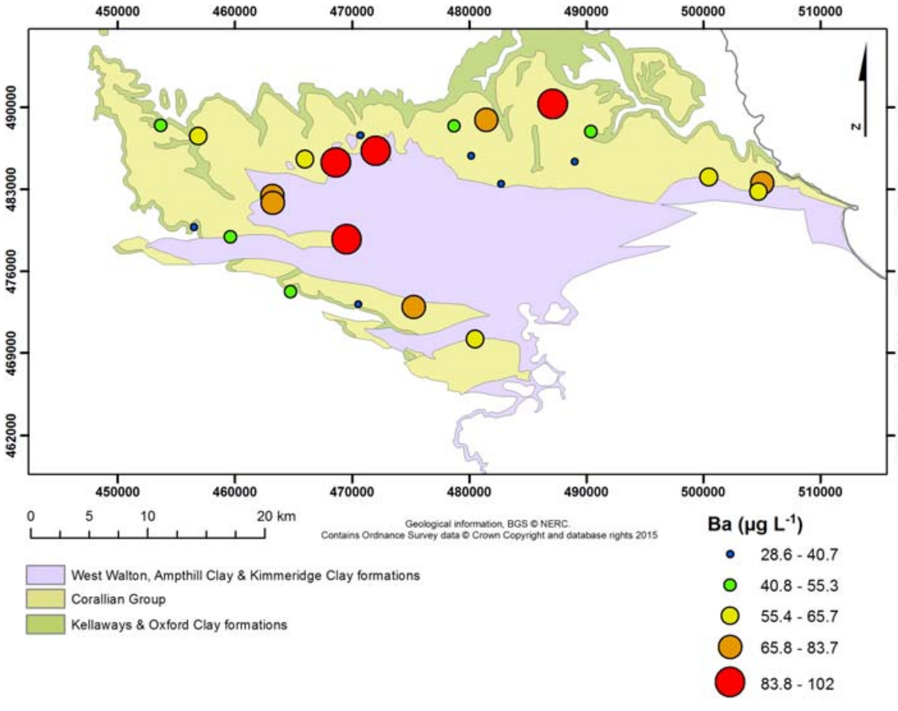

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Figure 5.24 Regional variation of Ba in the Corallian aquifer

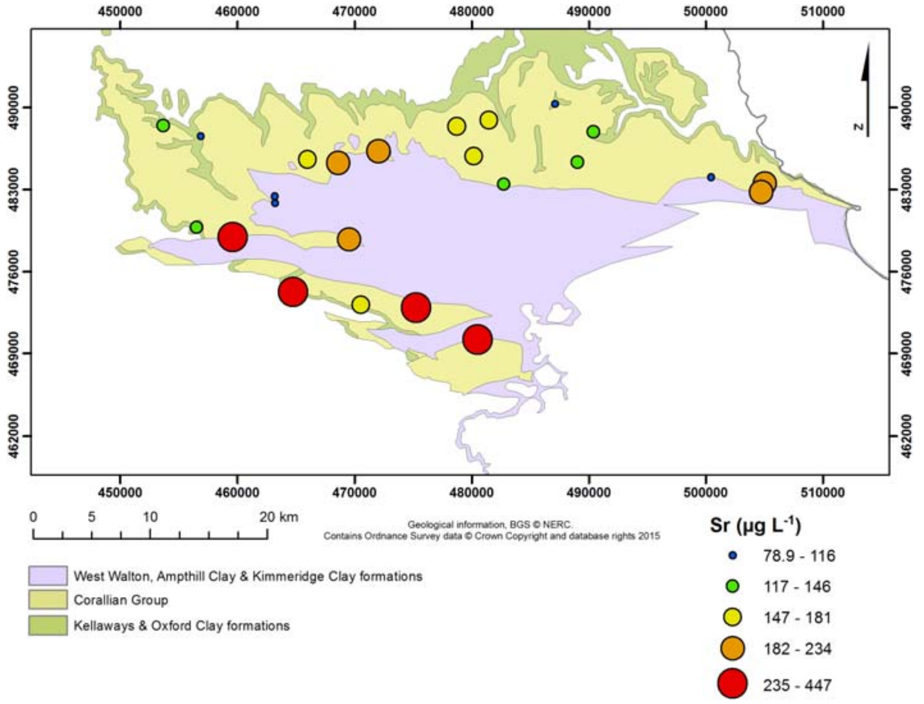

Figure 5.25 Regional variation of Sr in the Corallian aquifer

interaction with the clays, but could also be related to residence times, as the lower concentrations are generally found in groundwaters sampled from higher up on valley slopes.

Rubidium has a concentration range of 0.12 to 3.22 µg L^{-1}, a 5th to 95th percentile range of 0.3 to 1.38 µg L^{-1}, and a median of 0.59 µg L^{-1} (Table 5.2). This range is much smaller than that found in the Corallian of Oxfordshire and Wiltshire, which has a minimum of 0.22 and a maximum of 23.4 µg L^{-1}. Rubidium displays similar geochemical behaviour to K, and the two elements are strongly correlated (r^2 = 0.79), the processes controlling K likely also affect Rb. The spatial variation of Rb is similar to that of K, with the highest concentrations found in the Howardian Hills, and lower concentrations to the west of Scarborough (Figure 5.27). The observed maxima for both Rb and K occur in the same sample. The sample was taken from a farm, and may therefore represent contamination derived from fertilizer or other soil enhancement materials. It is likely that concentrations up to the 95th percentile represent baseline.

Caesium has a concentration range of <0.01 to 0.02 µg L^{-1}, of 24 analyses 21 are censored reflecting its scarcity in natural groundwaters (Table 5.2). These values most likely represent baseline concentrations.

5.2.5 Iron and manganese

Iron and Mn are both redox- and pH-sensitive. Iron is mobilised as dissolved Fe(II) under moderately reducing and acidic conditions. Under oxidising conditions, Fe(III) prevails. This forms insoluble Fe oxyhydroxides at circum-neutral pH (Drever, 1997). Fe and Mn display a similar cumulative probability curve, which is relatively shallow, but skewed at the upper end (Figure 5.20).

Iron has a concentration range of <5 to 842 µg L^{-1}, (Table 5.2) of 24 analyses, 14 are censored. This is a similar range to the Cotswold Oolite (Neumann et al., 2003), but the Corallian of Oxfordshire and Wiltshire ranges from <5 to 1770 µg L^{-1} (Cobbing et al., 2004). The highest Fe concentration (842 µg L^{-1}) is found in the groundwater with the lowest Eh value (203 mV). This is the only sample which exceeds the drinking water standard for Fe of 200 µg L^{-1} (The Water Supply Regulations, 2010), and would require treatment if used for potable supply. This sample probably represents contamination as the Fe concentration is five times higher than the next most

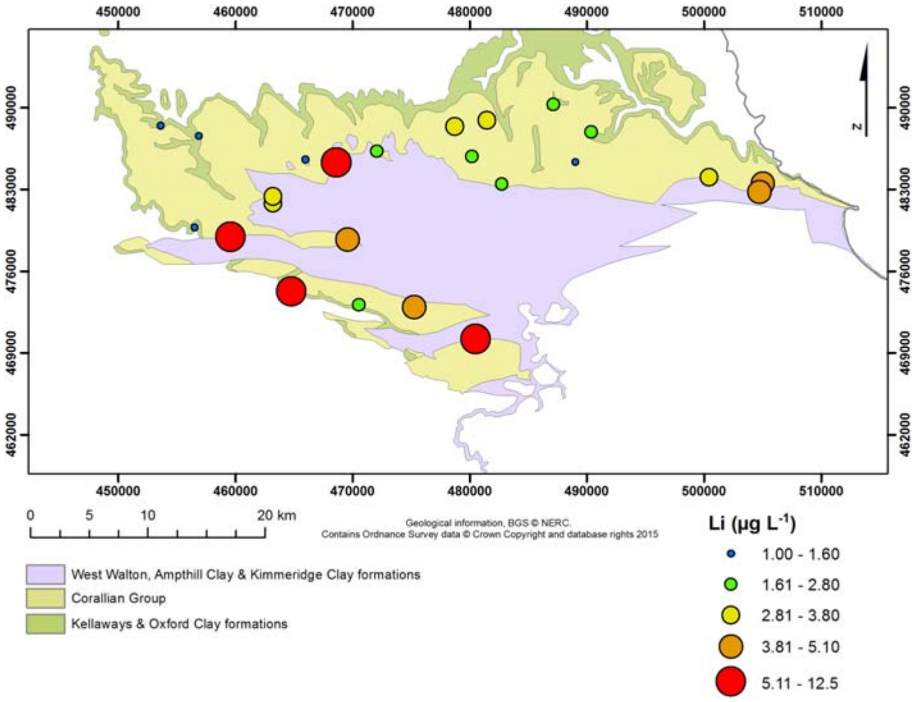

Figure 5.26 Regional Variation of Li in the Corallian aquifer

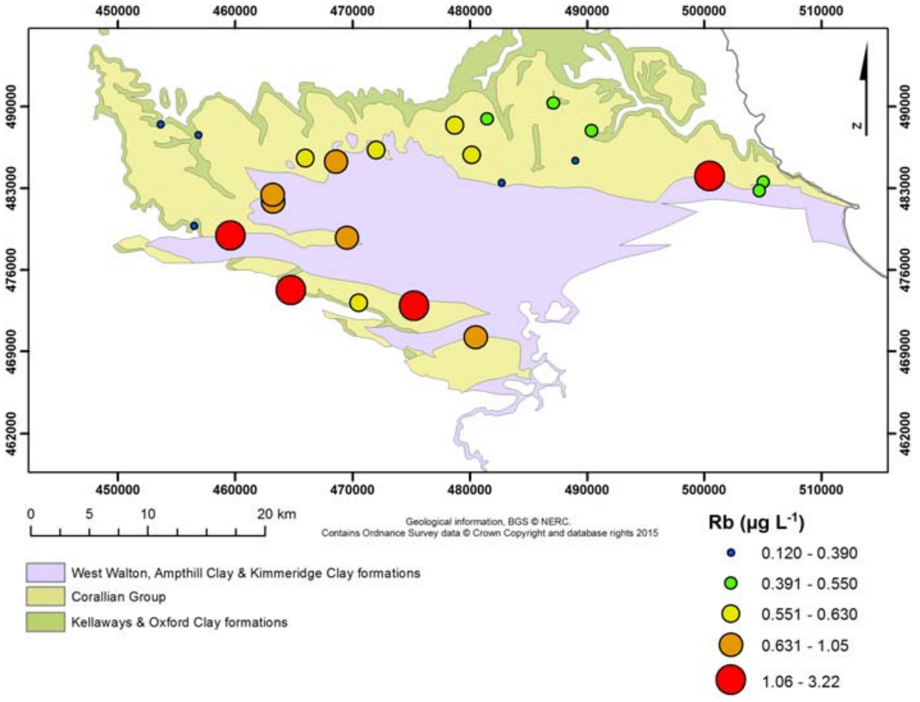

Figure 5.27 Regional Variation of Rb in the Corallian aquifer

concentrated sample. The Eh is weakly correlated with Fe ($r^2 = 0.26$), and indicates that the distribution of dissolved Fe is controlled by the oxidation state. The spatial variation is indistinct (Figure 5.28), although there are some spatial relationships with the Eh. The most oxidised waters are found to the north-west of the region, where the Fe concentrations are below detection limits.

Manganese has a concentration range of <0.05 to 109 µg L^{-1}, a 95th percentile of 12.5 µg L^{-1}, and a median of 0.38 µg L^{-1} (Table 5.2). Of 25 analyses, four are censored. This is a larger range of concentrations than is found in the Cotswold Oolite (Neumann et al., 2003), where the Mn ranges from <2 to 18 µg L^{-1}, but a much smaller range than that of the groundwaters of the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004), where the Mn ranges from <2 to 466 µg L^{-1}. Most of the concentrations of Mn are very low (out of 25 analyses 23 are <4.2 µg L^{-1}), while the sample containing the highest Mn concentration also has the highest Fe concentration. This sample could represent contamination, and the 95th percentile is a good approximation for a baseline range. This sample exceeds the drinking water limit of 50 µg L^{-1} for Mn and would require treatment for drinking (The Water Supply Regulations, 2010) .The spatial trends are indistinct (Figure 5.29), and are dissimilar to both Fe (Figure 5.28) and Eh (Figure 5.7).

5.2.6 Rare earth elements

The rare earth elements (REE) are here, as commonly, considered as a group together with yttrium due to their similar behaviour in the environment (Cornell, 1993). The REEs are most commonly below detection limits in groundwaters in the UK (Shand et al., 2007). Yttrium, La and Nd are found in this study to be detectable in most groundwaters analysed. The remaining REEs are detectable in up to 40% of the samples collected. Where detectable the concentrations are generally low; the maximum REE concentration is 0.14 µg L^{-1} (Nd) and Y has a concentration of 0.19 µg L^{-1} (Table 5.2). As the REEs behave geochemically so similarly the spatial variation is very similar for each element and the highest concentration of each element is found at the same site. Figure 5.30 presents an example of the spatial distribution of the REEs. This presents Ce, which is below detection limits in 14 of the 24 samples, and shows a typical distribution. There are no clear spatial trends and it is likely that these data represent baseline concentrations.

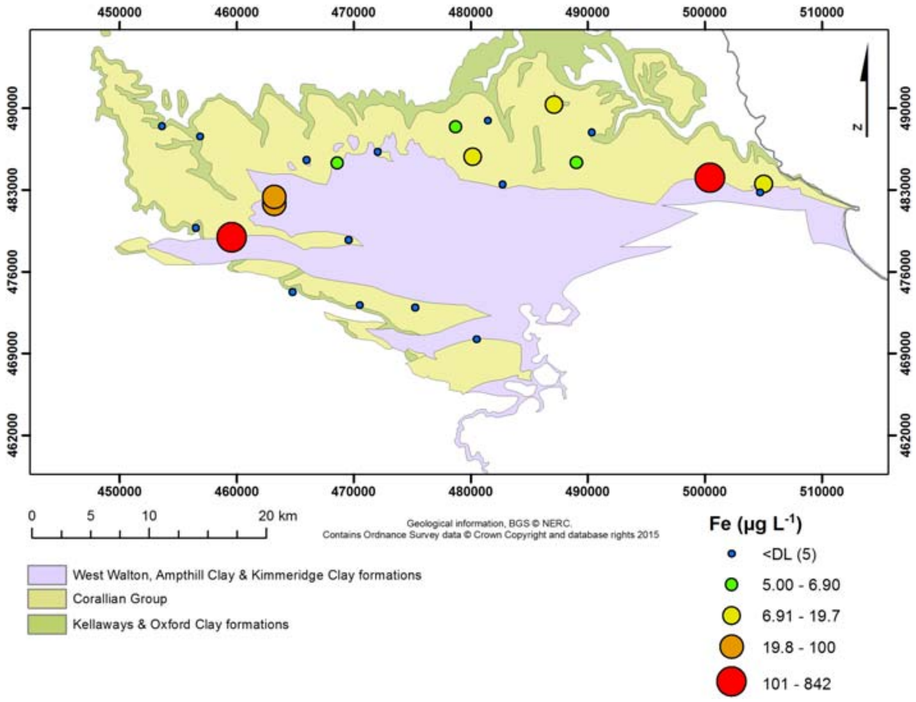

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Figure 5.28 Regional variation of Fe in the Corallian aquifer

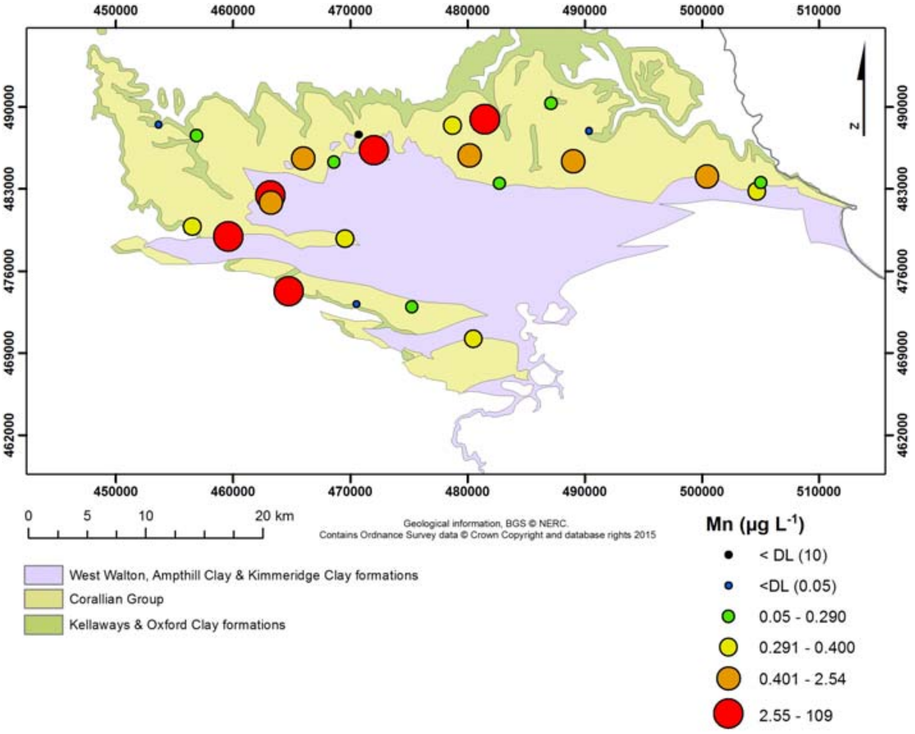

Figure 5.29 Regional variation of Mn in the Corallian aquifer

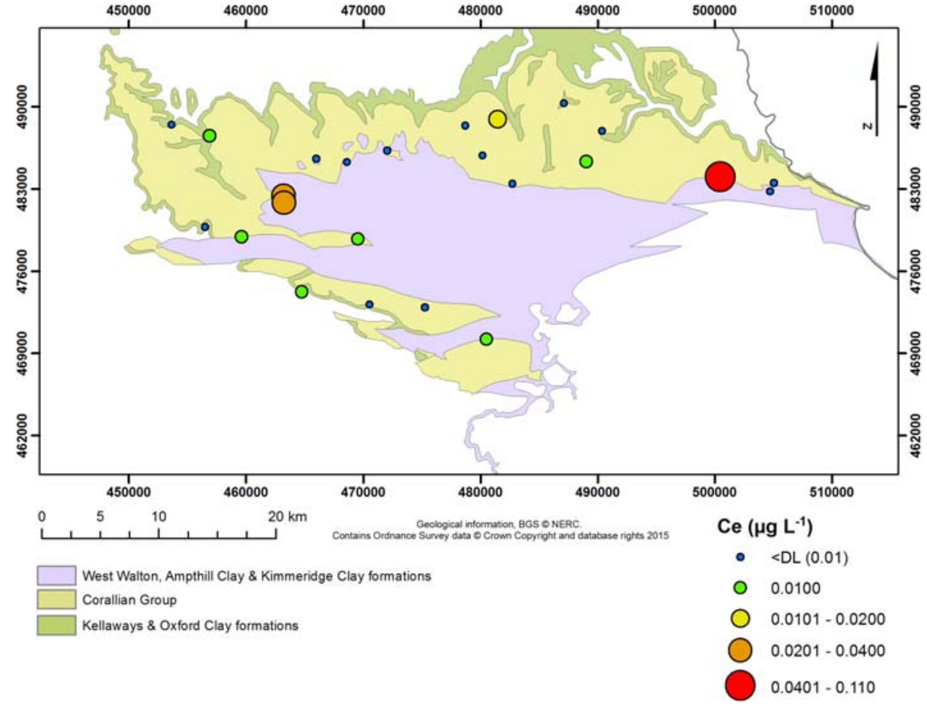

Figure 5.30 Regional variation of Ce in the Corallian aquifer

5.2.7 Other trace elements

Aluminium has a concentration range of <1 to 89 µg L^{-1}, a 5th to 95th percentile range of 7 to 31 µg L^{-1}, and a median of 14 µg L^{-1} (Table 5.2). This range is very similar to that of the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004). While Al is one of the most abundant elements on Earth, with an average crustal and soil abundance of 6 to 7 wt%, it is classed as a trace element in natural waters because the solubility of Al minerals is limited at

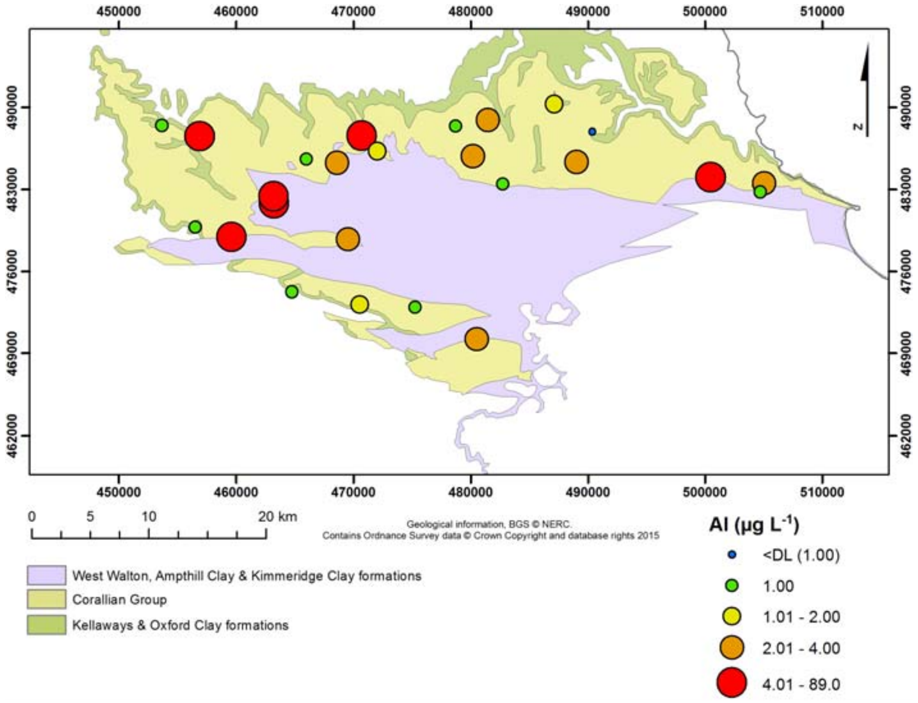

Figure 5.31 Regional Variation of Al in the Corallian aquifer

circum-neutral pH values (pH 6–8). All the groundwaters in the Corallian of the Vale of Pickering fell into this pH range; hence Al concentrations are low. There is no distinct spatial distribution of Al (Figure 5.31), and as there is no evidence that the Al concentrations in the groundwaters are of anthropogenic origin, the 5th to 95th percentile range is taken to represent baseline compositions.

Arsenic has a concentration range of <0.5 to 0.7 μg L^{-1}, of the 24 analyses 20 were below detection limits (Table 5.2). The measurable concentrations were found close to Scarborough, and in the Howardian Hills. This concentration range is slightly smaller than that found in the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004) and Cotswold Oolite (Neumann et al., 2003), and it is likely it represents baseline concentrations.

Boron has a concentration range of <100 to 42 μg L^{-1}, a 5th to 95th percentile range of 7 to 31 μg L^{-1}, and a median of 14 μg L^{-1} (Table 5.2). These are very low concentrations when compared to those found in aquifers hosted within geologically similar rocks (Cobbing et al., 2004; Neumann et al., 2003). One sample has a high detection limit, which is greater than the maximum measured concentration. It is likely that this value falls within the range of the rest of the samples. There are no clear spatial patterns, however the lowest concentrations are generally found higher up the valley sides (Figure 5.32).

Cobalt has a concentration range of <0.02 to 0.1 μg L^{-1}. Of the 25 analyses 19 were below detection limits (Table 5.2). This range is similar to that found in the Cotswold Oolite (Neumann et al., 2003), while the concentrations found in the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004) is an order of magnitude larger, ranging from <0.02 to 1.96 μg L^{-1}. Cobalt mobility is strongly limited at neutral pH values, and the concentrations represented here most likely represent baseline concentrations. Most of the detectable Co is found in groundwaters sampled from the west of the study area, with one sample containing detectable Co near Scarborough (Figure 5.33)

Copper has a concentration range of 0.8 to 9 μg L^{-1}, a 5th to 95th percentile range of 0.8 to 5 μg L^{-1}, and a median of 1.9 μg L^{-1} (Table 5.2). This range is smaller than those observed in the

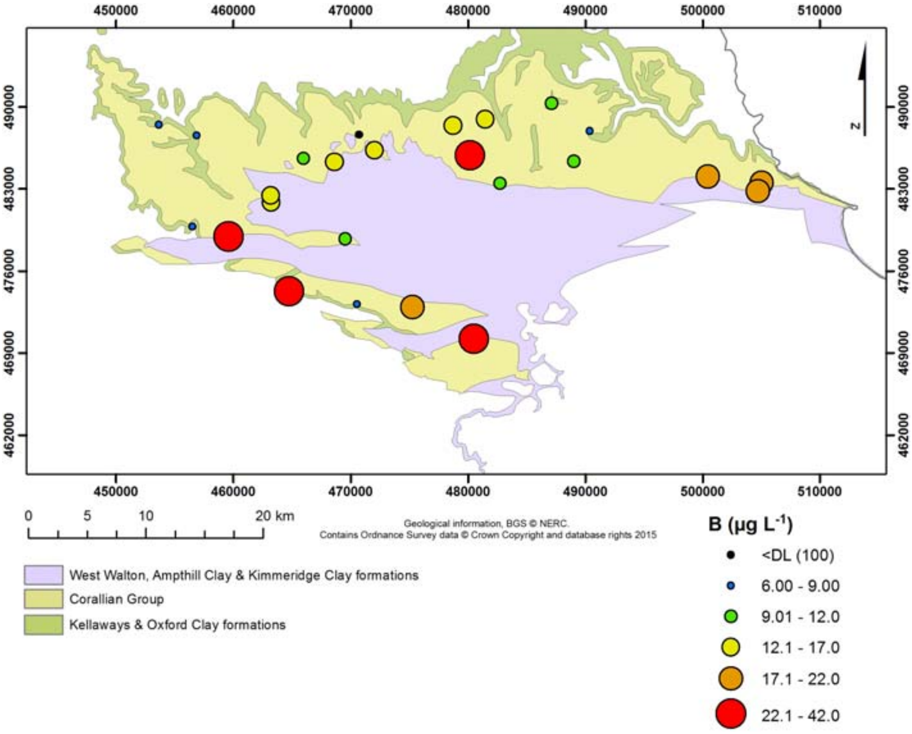

Figure 5.32 Regional Variation of B in the Corallian aquifer

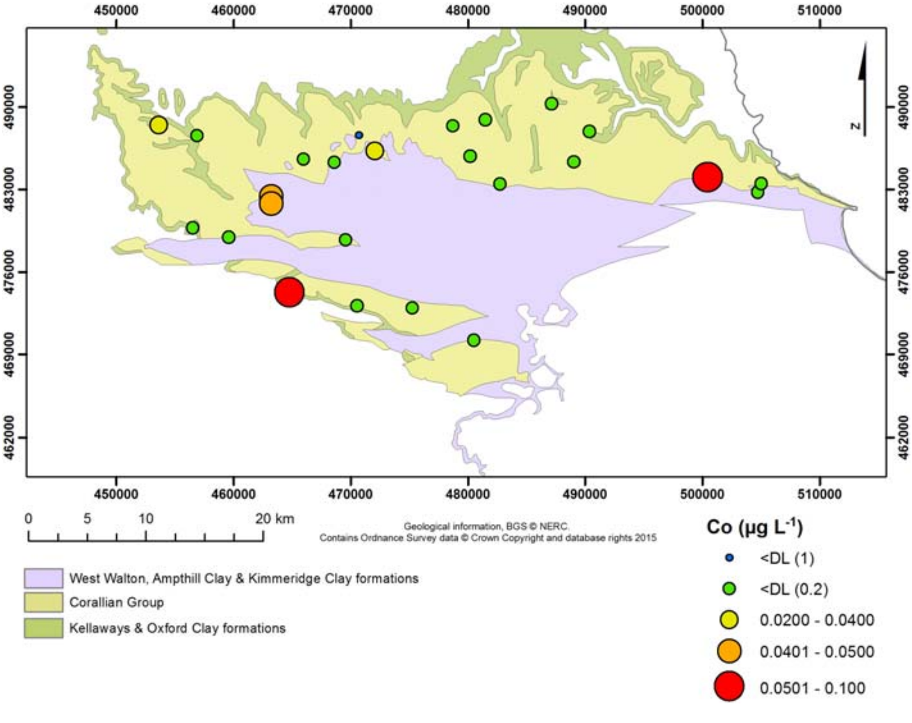

Figure 5.33 Regional Variation of Co in the Corallian aquifer

Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004) and Cotswold Oolite (Neumann et al., 2003), which range from 0.5 to 304 µg L^{-1} and 0.1 to 115 µg L^{-1} respectively. Copper occurs naturally as native metal, or in sulphide ore deposits, but is also a very commonly used metal in industrialised countries, and in pipework in water supply infrastructure. Anthropogenic inputs are to be expected in young groundwaters (Shand et al., 2007). Where the groundwater is oxidising, Cu is most soluble under acidic conditions. As the pH increases, Cu can adsorb to organic matter or Fe and Mn oxyhydroxides (Shand et al., 2007). There is a poor correlation

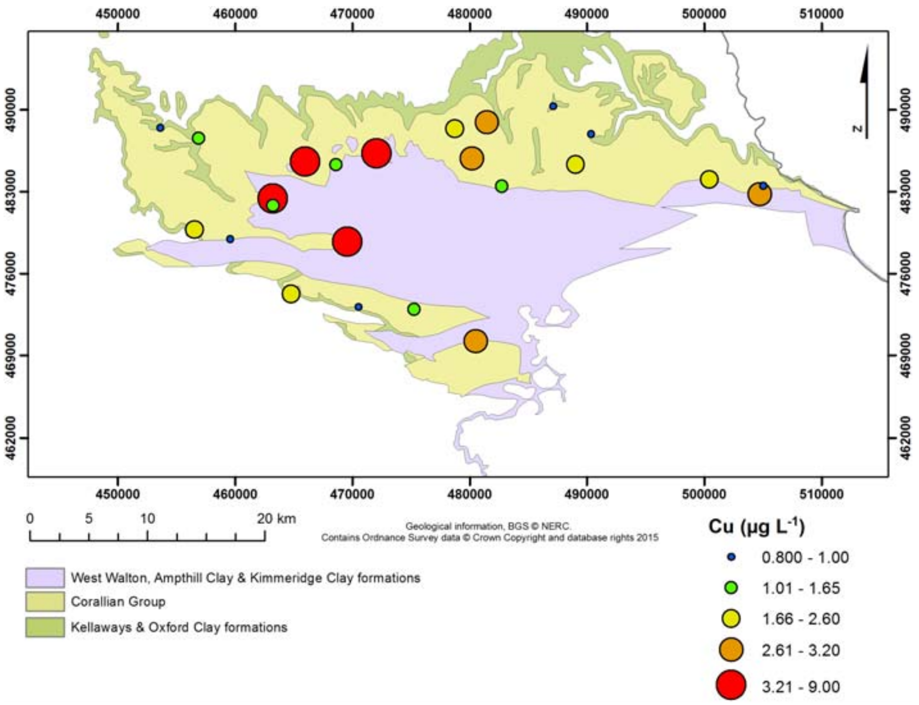

Figure 5.34 Regional Variation of Cu in the Corallian aquifer

between pH and Cu (r^2=0.02), and there is no clear spatial distribution (Figure 5.34). The distribution of Cu could be influenced by anthropogenic activities.

Molybdenum has a concentration range of 0.1 to 0.7 µg L^{-1}, a 5th to 95th percentile range of 0.1 to 0.5 µg L^{-1}, and a median of 0.2 µg L^{-1} (Table 5.2). In comparison the Mo is at or below detection limits (<0.1) in the majority of grounwaters from the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004) and Cotswold Oolite (Neumann et al., 2003). The concentration range is much narrower than that observed in the groundwaters in these similar aquifers, which have maximum Mo concentrations of 5.2 and 1.8 µg L^{-1}, respectively. It is likely that the Mo concentrations measured in the Vale of Pickering Corallian represent baseline concentrations. The highest Mo concentrations are found in groundwaters in the south of the area, around the Howardian Hills (Figure 5.35). Lower concentrations are observed in the groundwaters from the hillslopes in the north of the region.

Nickel has a concentration range of <0.2 to 1.2 µg L^{-1}, of the 25 samples 15 were below the detection limit (Table 5.2). There is no clear spatial trend of Ni in the Vale of Pickering, as groundwaters with measurable Ni are in close proximity to those where Ni is not detectable. It is therefore possible that the highest concentrations are associated with anthropogenic influences. Nickel behaves in a similar way to Co, and Ni is commonly detectable in groundwaters where Co is also present, hence the spatial variation (Figure 5.36) is similar to that of Co (Figure 5.33).

Lead has a concentration range of <0.1 to 1.1 µg L^{-1}, a 5th to 95th percentile range of <0.1 to 0.4 µg L^{-1}, and a median of 0.1 µg L^{-1} (Table 5.2). Four of the 25 analyses were below the detection limit. This range is slightly smaller than other geologically similar aquifers where the maximum Pb values are 5.4 µg L^{-1} (Cotswold Oolite (Neumann et al., 2003)) and 3.9 µg L^{-1} (Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004)). Lead can be found in the natural environment in sulphide minerals and metal oxides, and as a trace constituent in K feldspars (Shand et al., 2007). However the baseline of Pb is likely to be anthropogenically influenced in built up areas. The relatively low Pb concentrations may reflect the mainly rural surroundings and the range presented here most likely represents baseline concentrations. In general the

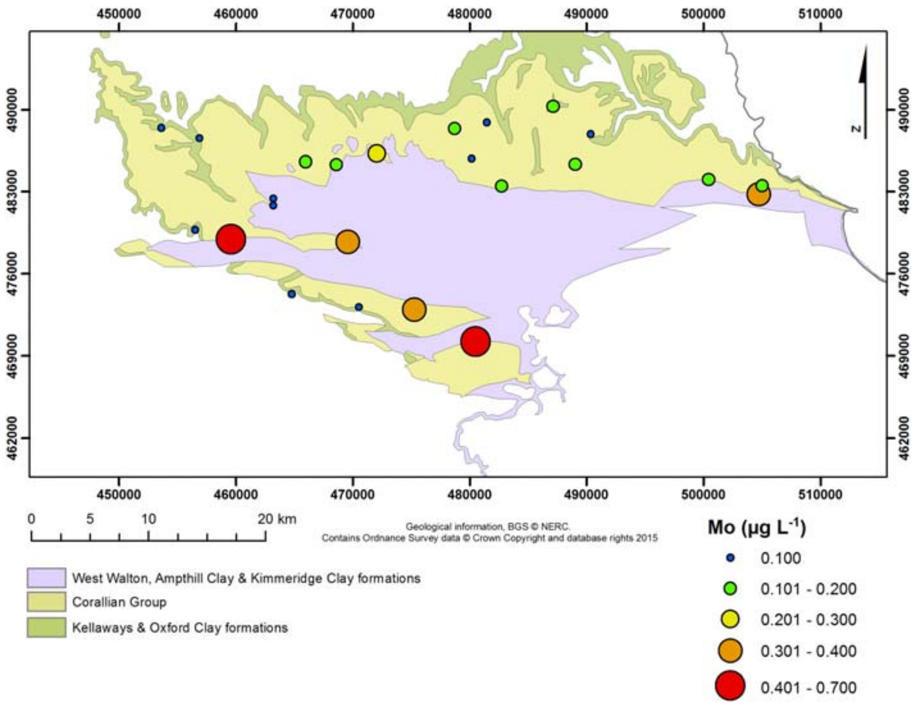

Figure 5.35 Regional variation of Mo in the Corallian aquifer

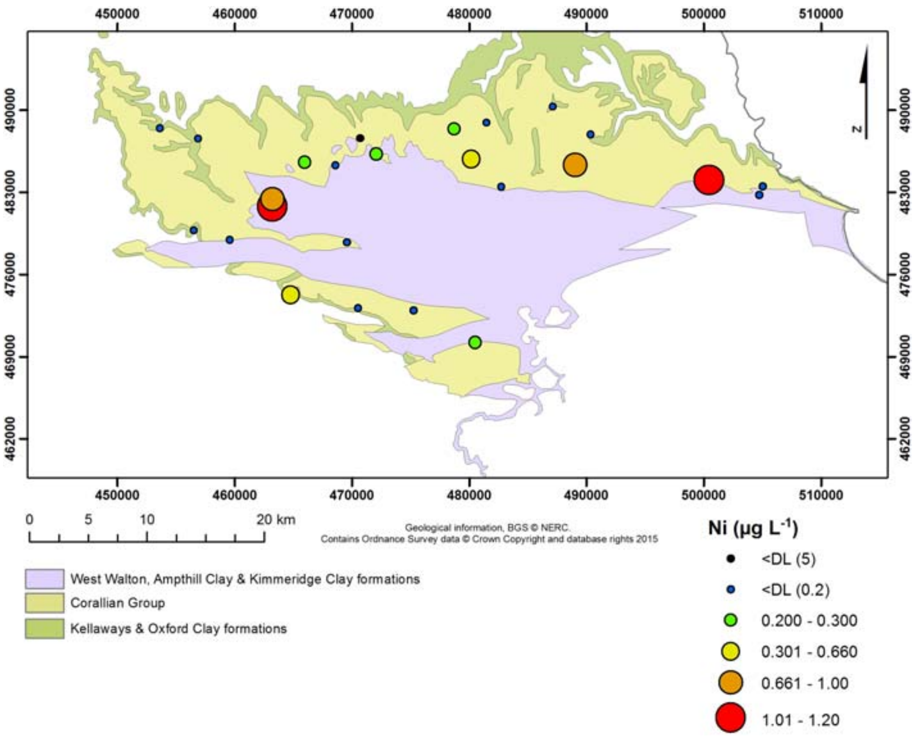

Figure 5.36 Regional variation of Ni in the Corallian aquifer

highest concentrations are found in groundwaters in the east of the area (Figure 5.37), with two outliers evident towards the south of the outcrop in the Howardian Hills.

Rhenium has a concentration range of <0.01 to 0.07 µg L^{-1}, a 5th to 95th percentile range of <0.01 to 0.035 µg L^{-1}, and a median of 0.01 µg L^{-1} (Table 5.2). Five of the 24 analyses were below the detection limit. These values are slightly high when compared to other similar UK aquifers: groundwaters in the Cotswold Oolite (Neumann et al., 2003) contain no detectable Re, while there was a maximum concentration of 0.02 µg L^{-1} in groundwaters in the Corallian aquifer of Oxfordshire and Wiltshire (Cobbing et al., 2004). In general the highest concentrations in the Vale of Pickering are found in groundwaters around the periphery of the flat valley floor, with lower concentrations found in groundwater samples taken higher up the valley slopes, especially in the north and west of the region (Figure 5.38). The generally low Re concentrations reflect the limited use and rarity of this element.

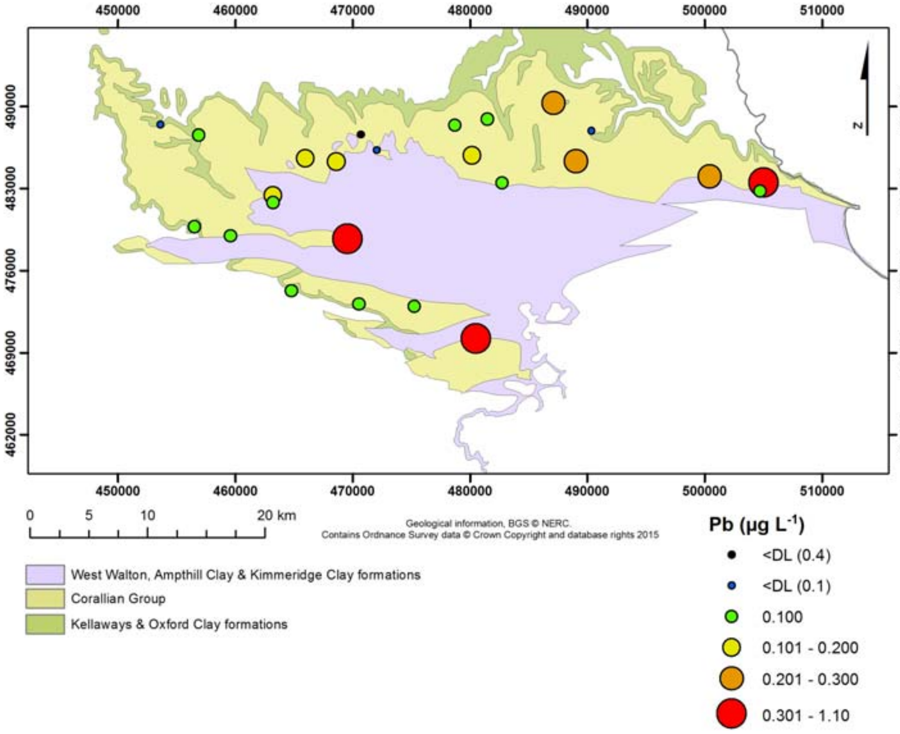

Figure 5.37 Regional variation of Pb in the Corallian aquifer

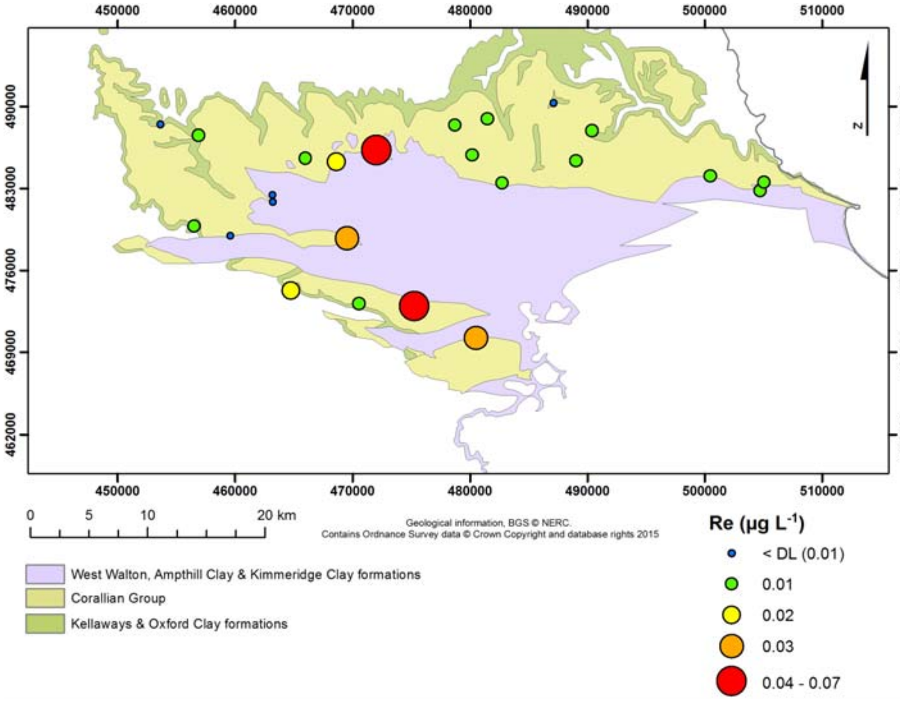

Figure 5.38 Regional variation of Re in the Corallian aquifer

Rhodium has a concentration range of <0.01 to 0.16 µg L^{-1}, a 5th to 95th percentile range of <0.01 to 0.015 µg L^{-1}, and a median of 0.05 µg L^{-1} (Table 5.2). Seven of the 24 analyses were below the detection limit. These values are higher than those recorded in other similar UK aquifers. Rhodium in the groundwaters of Cotswold Oolite (Neumann et al., 2003) and the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004) did not exceed 0.02 µg L^{-1}. The highest Rh concentrations in the Vale of Pickering are found in groundwaters in the north-west of the region, while the lowest concentrations are found in the south (Figure 5.39).

Ruthenium has a concentration range of <0.05 to 0.08 µg L^{-1}, of the 24 analyses 20 were below detection limits (Table 5.2). The measurable concentrations were found in close proximity to each other in the north-west of the region (Figure 5.40). There was no measurable Ru (<0.05 µg L^{-1}) in the groundwaters of the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004) and the Cotswold Oolite (Neumann et al., 2003). It is therefore possible that the measured concentrations found in the Vale of Pickering represent values outside baseline groundwater concentrations.

Antimony has a concentration range of <0.05 to 0.14 µg L^{-1}, of the 24 analyses 22 were below detection limits (Table 5.2).

Scandium has a concentration range of 1 to 2 µg L^{-1}: one value was 2 µg L^{-1}, while the remaining 23 analyses were 1 µg L^{-1} (Table 5.2). There is insufficient variation within these data to comment on any spatial trends, although for comparison Sc concentrations in the Cotswold Oolite (Neumann et al., 2003) groundwaters range up to 5.94 µg L^{-1}.

Selenium has a concentration range of <0.5 to 1.2 µg L^{-1}, a 5th to 95th percentile range of <0.5 to 1.1 µg L^{-1}, and a median of 0.8 µg L^{-1} (Table 5.2). The range of values is typical for UK aquifers (Shand et al., 2007), Se concentrations tend to be low in natural waters, rarely exceeding 1 µg L^{-1}(Hem, 1992). Selenium is a relatively rare element, mobilised in oxidising waters, but immobile under reducing conditions (Hem, 1992). The spatial variation is indistinct (Figure 5.41), although there are some spatial relationships with the Fe concentrations. The highest concentrations of Se are found in groundwaters where the Fe is low (Figure 5.28), indicating the

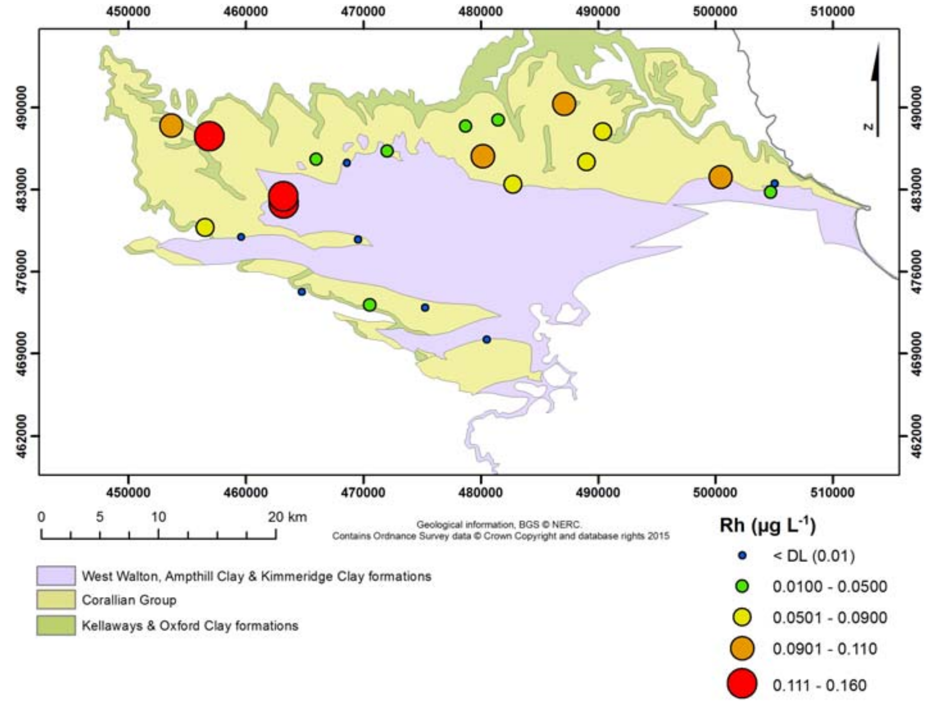

Figure 5.39 Regional variation of Rh in the Corallian aquifer

redox control on this element. The dominance of agriculture in this area may provide a source of Se to groundwaters.

Tin has a concentration range of <0.05 to 0.12 µg L^{-1}, of the 24 analyses 18 are below the detection limit (Table 5.2). The use of Sn as a coating for corrosion prevention and on steel containers for food storage means that Sn can be widespread in the urban environment, especially around landfill sites. However it is generally low in groundwaters (Shand et al., 2007).

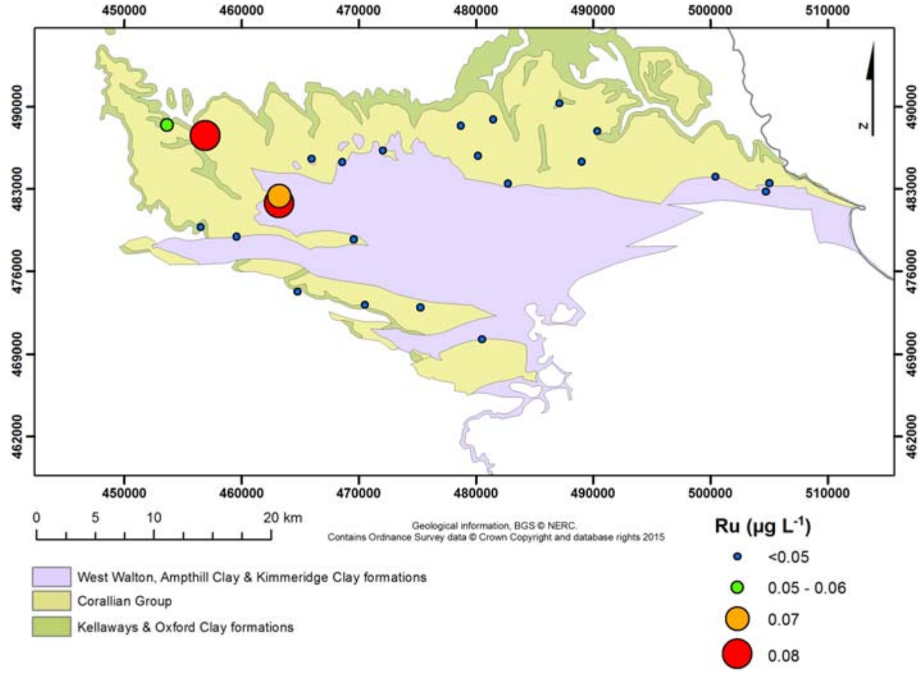

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Figure 5.40 Regional variation of Ru in the Corallian aquifer

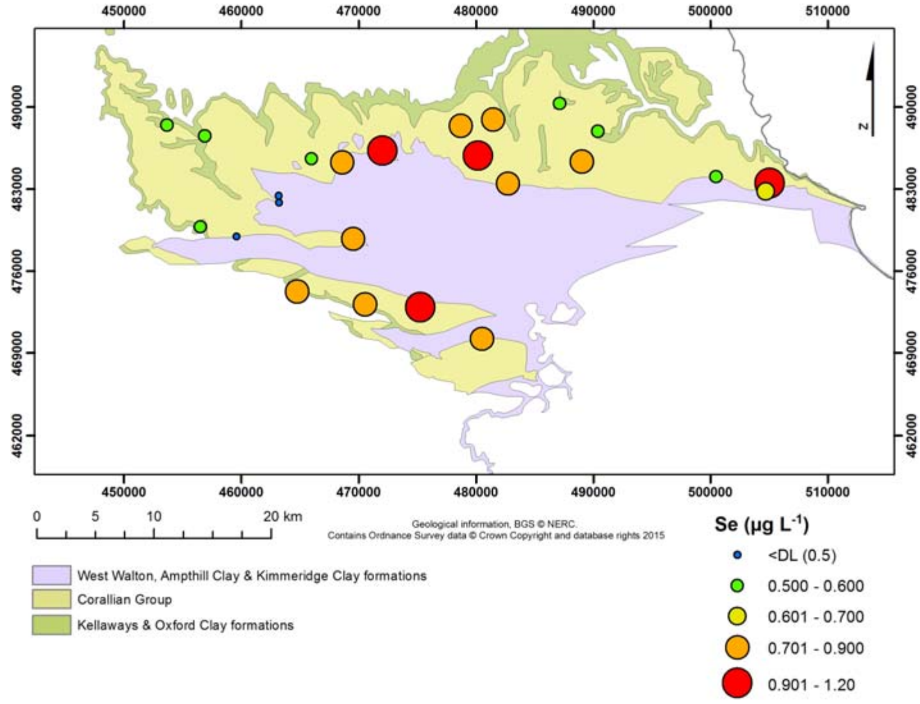

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Figure 5.41 Regional variation of Se in the Corallian aquifer

There is no clear spatial distribution, and the low concentrations are typical of the largely arable environment.

Thallium has a concentration range of <0.01 to 0.03 µg L^{-1}, a 5th to 95th percentile range of <0.001 to 0.02 µg L^{-1}, and a median of 0.01 µg L^{-1} (Table 5.2). Of the 24 analyses, 10 were below the detection limit. There are no distinct spatial trends, in part owing to the small range of values. This distribution is similar to that found in the groundwaters from the similar aquifers of Cotswold Oolite (Neumann et al., 2003) and the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004).

Uranium has a concentration range of 0.06 to 0.51 µg L^{-1}, a 5th to 95th percentile range of 0.08 to 0.41 µg L^{-1}, and a median of 0.21 µg L^{-1} (Table 5.2). This range is relatively small, as groundwaters from the similar aquifers of Cotswold Oolite and the Corallian of Oxfordshire and Wiltshire have maximum concentrations that are over three times the maximum value reported here. There are no clear spatial distributions, although there is a cluster of lower concentrations around the north-west of the region. The higher concentrations tend to be close to the edge of the flat valley floor with the maximum concentrations in the south of the region (Figure 5.42). Uranium mobilisation is strongly controlled by its redox state. It is usually only the oxidised form (U(VI)) that occurs significantly in solution (Smedley et al., 2006). Where there are reducing conditions, the concentration of U is generally low. There is some spatial correlation of U to Eh, as the lowest U concentrations occur where the Eh is the highest (Figure 5.7). Uranium occurs naturally in soils and rock-forming minerals, and it is likely that the source of U in these waters is predominantly natural, although fertilizers are a known possible additional source. All of the determinations are well within the WHO provisional drinking water guideline value of 30 µg L^{-1}.

Zinc has a concentration range of <5 to 63.2 µg L^{-1}, a 5th to 95th percentile range of 0.7 to 33.8 µg L^{-1}, and a median of 4.8 µg L^{-1} (Table 5.2). There is one value below the detection limit, however, this detection limit is higher than most measured values within this data set (Figure 5.43). This is a relatively small range when compared to the groundwaters from the similar aquifers of the Cotswold Oolite (Neumann et al., 2003) and the Corallian of Oxfordshire and Wiltshire (Cobbing et al., 2004) which have maximum concentrations of 133 and 289 µg L^{-1}

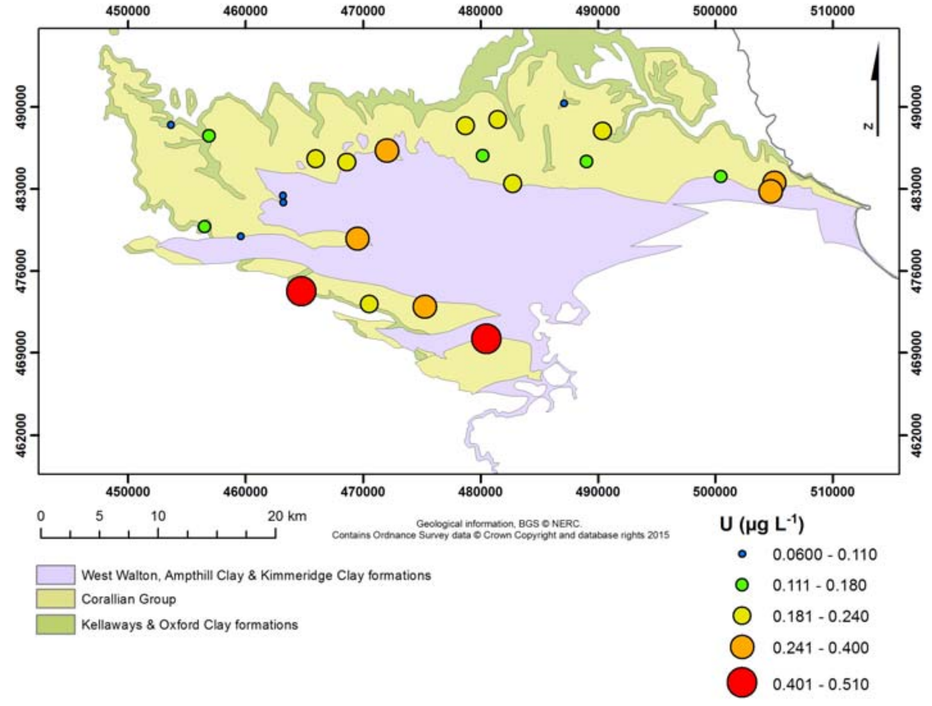

Figure 5.42 Regional variation of U in the Corallian aquifer

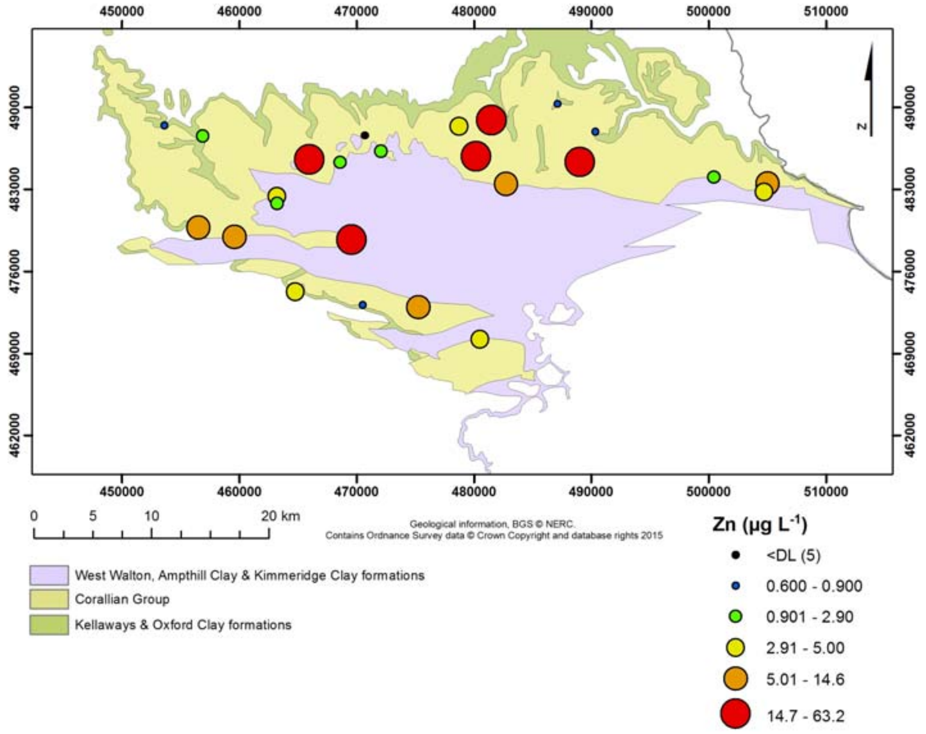

Figure 5.43 Regional variation of Zn in the Corallian aquifer

respectively. The solubilities of some Zn minerals are high, meaning that Zn can be widespread in groundwaters, and present in higher concentrations than many other transition metals. In addition, Zn in groundwaters can be derived from anthropogenic sources such as road dust, landfill leachate, and urban industry. There is no clear spatial trend (Figure 5.43), and this coupled with the low concentration range suggests that the values presented here represent baseline concentrations.

5.3 ISOTOPIC COMPOSITIONS AND TRACERS

Stable oxygen and hydrogen isotope ratios are extremely useful as tracers of physical processes in groundwater and can help to define recharge condition (Darling and Talbot, 2003). The rainfall in north-east England is depleted in the heavier isotopes of O and H relative to western parts of the country in response to the Rayleigh fractionation effect: the rain which falls first, over the west of the country, is relatively enriched isotopically (Darling and Talbot, 2003). Measured compositions of $\delta^{18}O$ lie in the range -8.61 to -7.28 ‰ with an average of -8.11 ‰ (Table 5.2). The $\delta^{2}H$ has a range of -57.6 to -47 ‰, with an average of -53.8 ‰. These values are consistent with compositions of recently recharged (Holocene) groundwaters analysed from north-east England (Darling et al., 2003). The relationship between $\delta^{18}O$ and $\delta^{2}H$ (Figure 5.44) shows a general correspondence with the world meteoric water line, indicating that the groundwaters represent recharged regional modern rainfall. There are no clear spatial trends (Figure 5.45 and Figure 5.46), which would be expected if the waters were being affected by local factors such as evaporation or mixing.

Values of $\delta^{13}C$ are an index of the evolution of the dissolved inorganic carbon system (DIC) (Clark and Fritz, 1997; Darling et al., 2005). Groundwater in calcareous sedimentary terrain acquires DIC through reaction with soil CO_2 and reaction with carbonate minerals in the soil and aquifer. The $\delta^{13}C$ composition of DIC is fundamentally governed by interaction between soil CO_2 ($\delta^{13}C \sim -26$ ‰) and carbonate minerals ($\delta^{13}C \sim 0$ ‰), resulting in a $\delta^{13}C$-DIC value of around ~ -13 ‰, but further modified depending on the nature of the carbonate system. If open

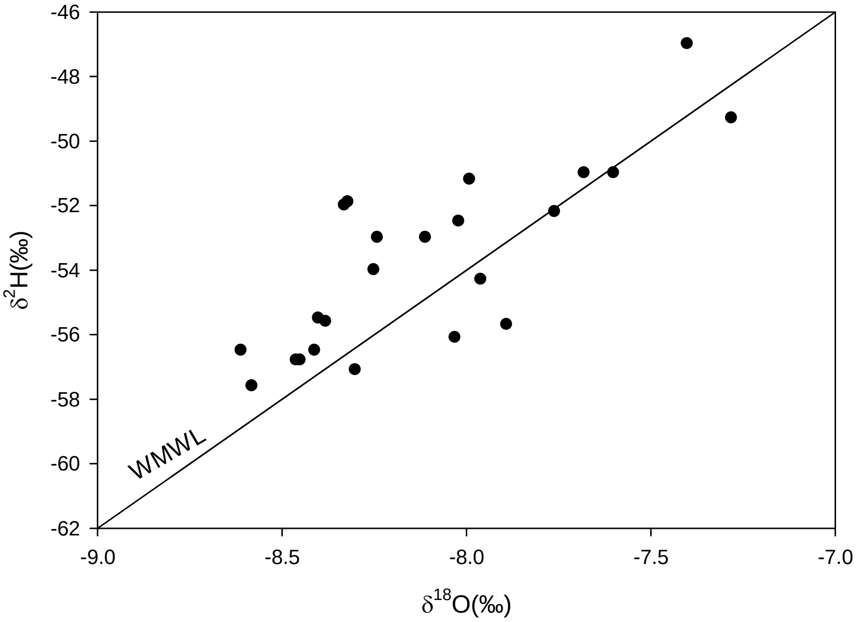

Figure 5.44 O and H stable isotopic composition of the Corallian aquifer. WMWL = world meteroric water line (Craig, 1961).

(typical of unconfined aquifer conditions), further exchange with soil-derived CO_2 will result in $\delta^{13}C$-DIC values <-13 ‰. If closed (typical of confined conditions), $\delta^{13}C$-DIC will start to evolve towards the rock composition, resulting in $\delta^{13}C$-DIC values rising progressively above -13 ‰.The compositions in the Corallian groundwaters range between -18.0 and -12.0 ‰ with an average of -15 ‰. Most of the sites are therefore relatively depleted in $\delta^{13}C$, which suggests a relatively immature DIC system of generally limited residence time. This conclusion supports the $\delta^{18}O$ and δ^2H results insofar as they suggest no significant modification (i.e. mixing with old groundwater) since recharge. However the most $\delta^{13}C$ enriched sites tend to be close to the valley floor and probably signify slightly older waters. (Figure 5.47)

5.4 CHEMICAL VARIATIONS WITH DEPTH

At the time of writing, no data could be found on groundwater chemical variations with depth.

5.5 TEMPORAL VARIATIONS

Data are available from the EA database for eleven sites for a period of five to 10 years. These span from 1995 to 2006 to coincide with the new BGS samples presented here. Generally sites have been sampled twice a year, although in most cases there are only sufficient data for the major ions, temperature and pH. There are generally variations in temperature and pH, but these follow no distinct trend. This is unsurprising given the dynamic nature of these parameters.

In many cases the major ions follow similar trends over the period they were measured. For example at one site about 2km south-east of Helmsley [SE 63 82], Ca, Cl, and Mg all increase gradually, but steadily, over a period of 10 years (Figure 5.48). At the same site this is mirrored by a general decrease in the HCO_3 concentration (Figure 5.49) over the same time period. There is no obvious reason for these changes.

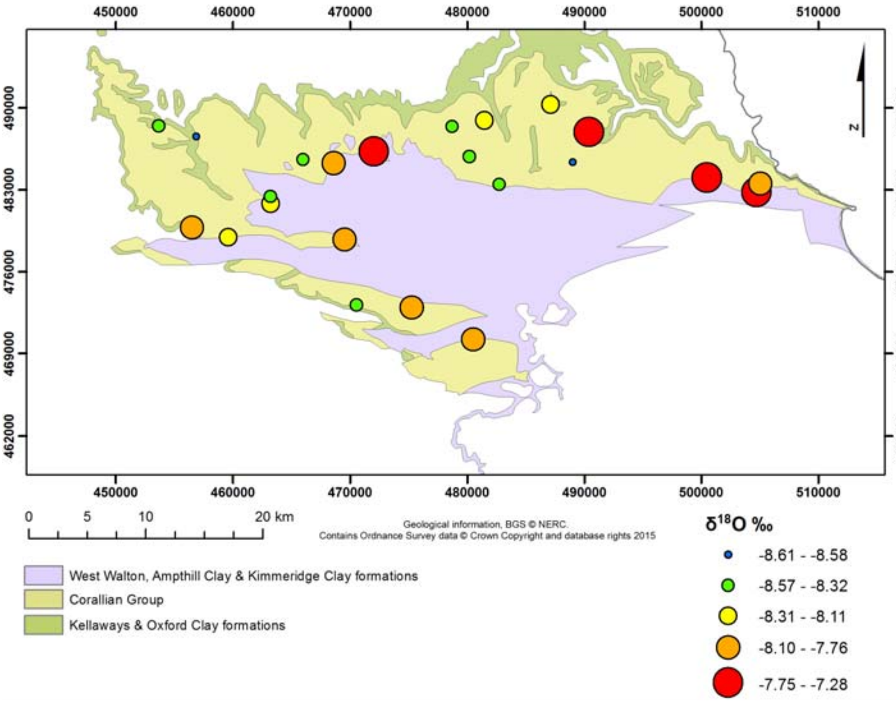

Figure 5.45 Regional variation of $\delta^{18}O$ in the Corallian aquifer

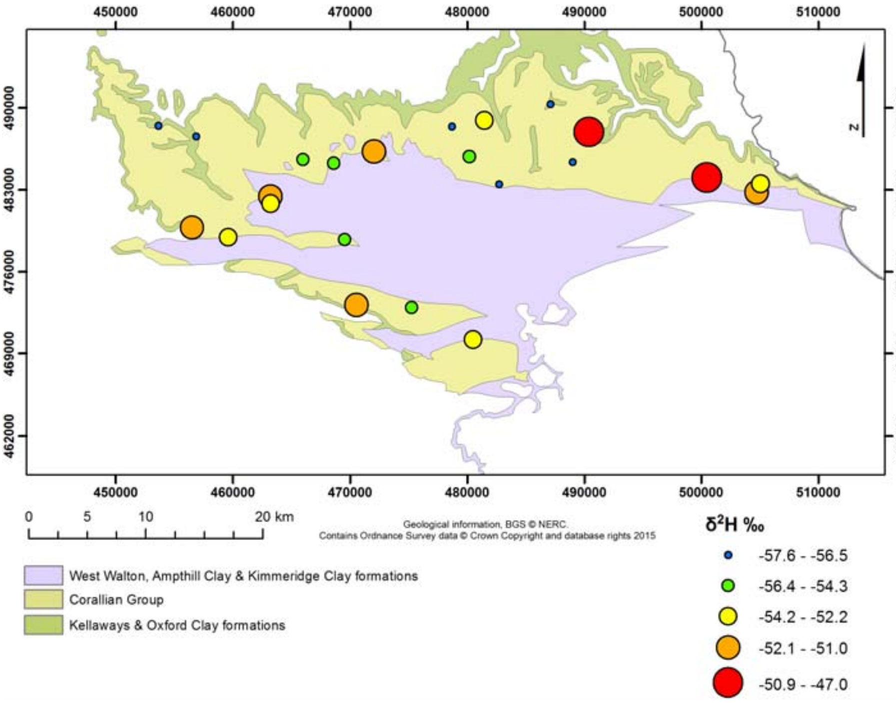

Figure 5.46 Regional variation of $\delta^{2}H$ in the Corallian aquifer

At the same site near Helmsley there is an increase in NO_3-N over a period of six years. This is not an unusual trend in areas dominated by agriculture, as NO_3-N is a common diffuse pollutant derived from agricultural practices. At this site the concentration increases from values around the drinking water limit (11.3 mg L^{-1} NO_3-N)at an average of 1.7 mg L^{-1} each year, to twice the drinking water limit over a period of seven years (Figure 5.50).

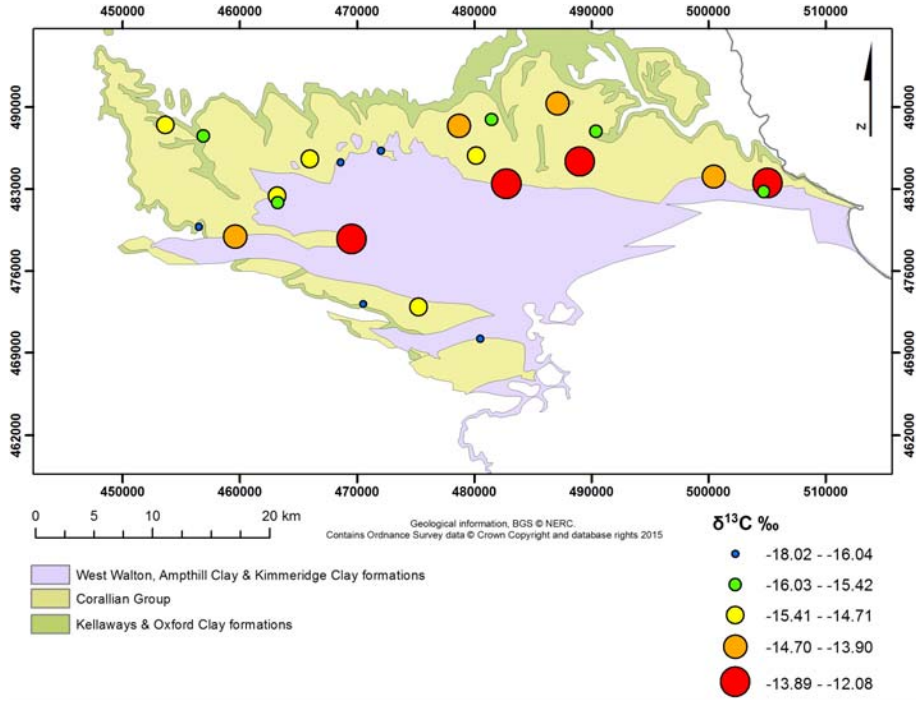

Figure 5.47 Regional variation of $\delta^{13}C$ in the Corallian aquifer

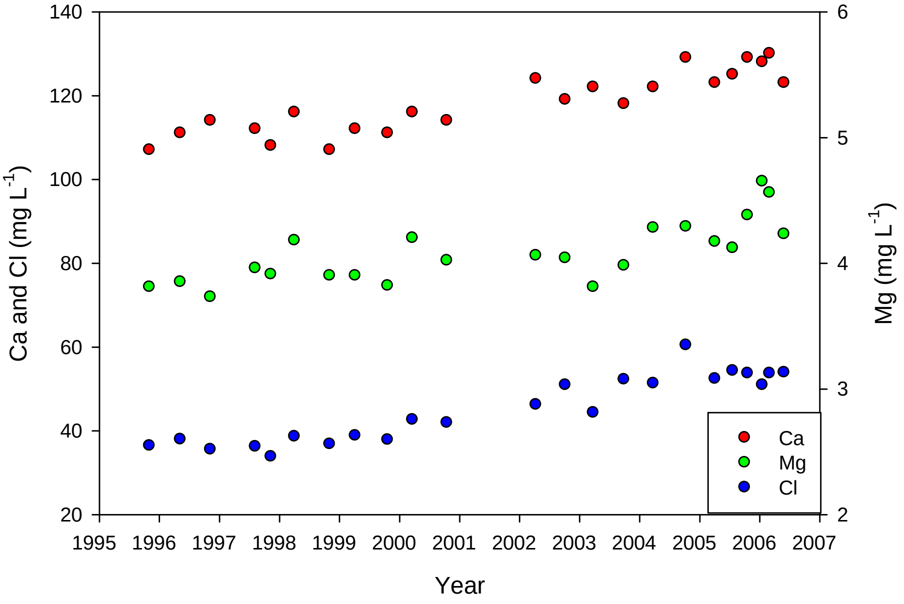

Figure 5.48 Temporal changes in Ca, Mg, and Cl at a site near Helmsley

Another four of the EA's monitoring sites show similar NO_3-N trends, and are distributed throughout the Vale of Pickering. This finding is consistent with previous reports which document the high concentrations of NO_3-N and PO_4^{3-} in the region (EA, 2009; Natural England, 2015).

A more unusual temporal variation was observed in groundwaters at a site near Kirbymoorside [SE 70 87]. Concentrations of the major elements were relatively constant between 1995 and 1998, most elements increased until 1999, where they stayed relatively constant, with the exception of three lower values recorded on 9/11/99, 17/10/03 and 20/10/05. The exceptions to this are Na and K, which mirror this trend (Figure 5.51 and Figure 5.52). There is no clear reason for this trend.

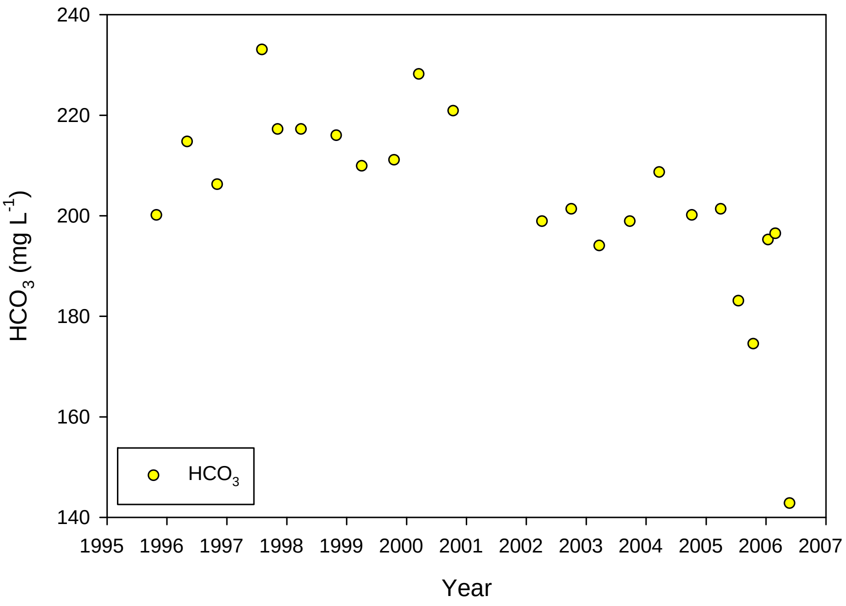

Figure 5.49. Temporal changes in HCO_3 at a site near Helmsley

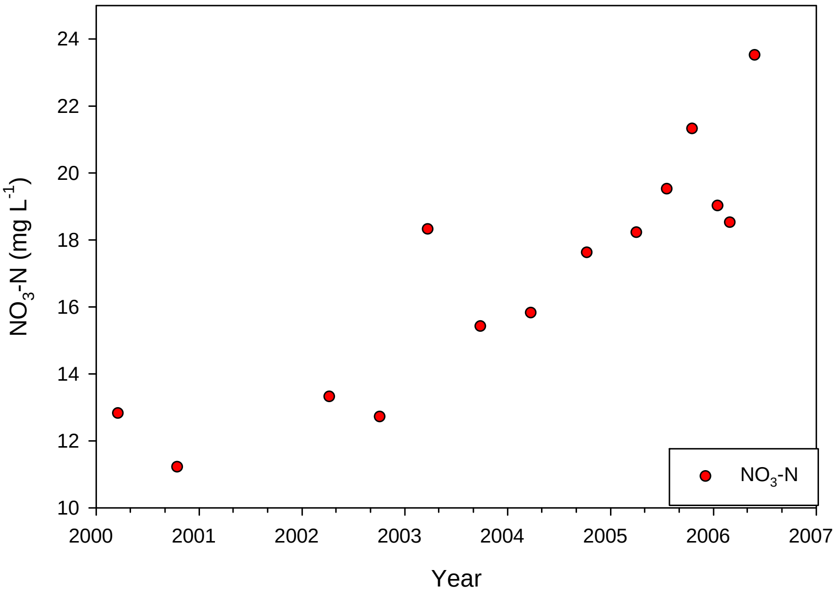

Figure 5.50. Temporal changes in NO_3–N at a site near Helmsley

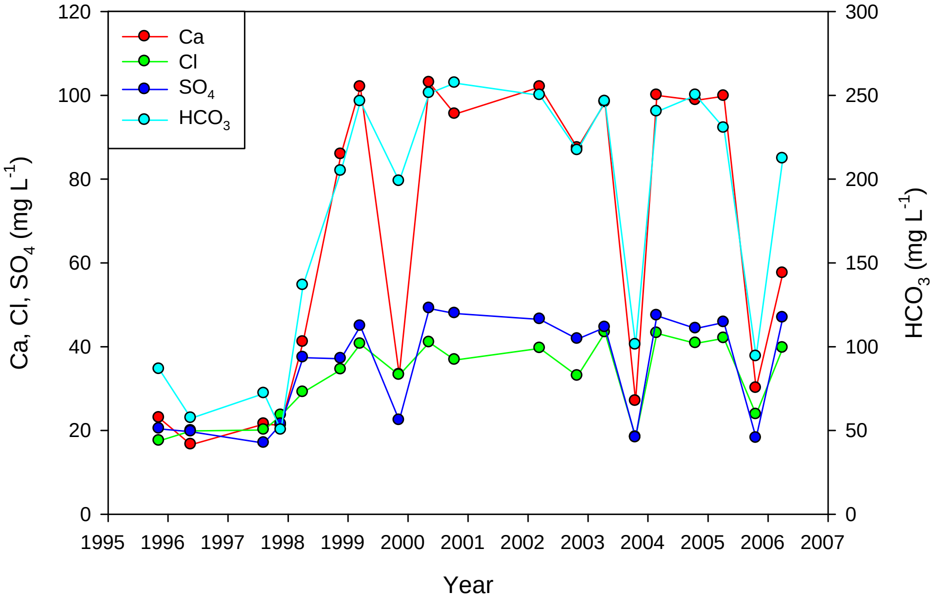

Figure 5.51. Temporal changes in Ca, Cl, SO_4, HCO_3 at a site near Kirkbymoorside

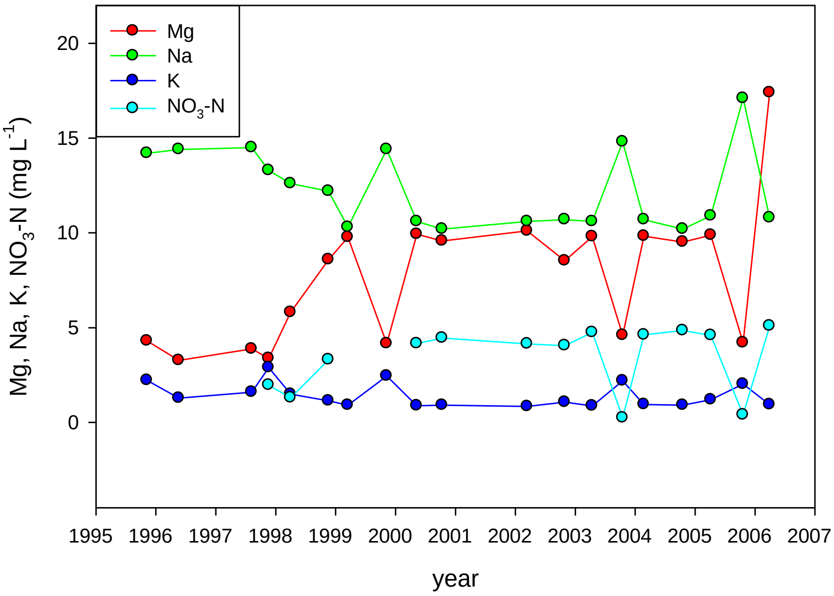

Figure 5.52. Temporal changes in Mg, Na, K and NO_3–N at a site near Kirkbymoorside

6 Baseline groundwater chemistry

6.1 REGIONAL BASELINE CHARACTERISTICS

The baseline chemistry of an aquifer is determined by a wide range of physical and chemical processes. The major source of most groundwaters is rainfall. The Corallian aquifer of the Vale of Pickering is recharged by rainfall on the slopes of the North York Moors, and by the river Derwent (Natural England, 2015). The aquifer discharges water to springs and the River Derwent and its tributaries (Environment Agency, 2013). A series of chemical reactions takes place during recharge; the most important of which are mineral dissolution and precipitation along with mixing, redox reactions, ion exchange and sorption/ desorption reactions.

The waters in this study are all Ca-HCO_3 type. This is a reflection of the dominance of calcite in mineral reactions. The waters are at equilibrium, or supersaturated with respect to calcite. Concentrations of solutes in groundwaters can span many orders of magnitude. However all the major elements (with the exception of NO_3-N), have concentration ranges which span less than one order of magnitude. These are all indicative of a fresh, shallow, oxidised aquifer.

For most determinands the 95th percentile can be taken to indicate the upper limit of the baseline concentrations. This removes obvious outliers for most elements. In the case of the Vale of Pickering groundwaters, there are elements without obvious outliers, which can mean the entire range is likely to be representative of baseline concentrations. A notable exception to this is NO_3-N, for which the 95th percentile is 22.6 mg L^{-1}, and 20% of the analyses are above the drinking water limit of 11.3 mg L^{-1}. This is highly unlikely to be naturally derived, as supported by the fact that the concentrations at a number of sites are increasing. The most likely source is from farming, which is extensive across the Vale of Pickering, and the predominance of this widespread diffuse source, coupled with the mainly oxidised nature of the Corallian aquifer means that NO_3-N remains the major concern to groundwater quality in the Vale of Pickering. Additional potential sources of NO_3-N include domestic pollution.

Trace elements in groundwaters can be derived naturally from minor minerals within aquifer strata. Their distribution is dependent on natural abundance as well as speciation and local aquifer conditions. The baseline can be elevated by anthropogenic influences, which are usually evident as outliers in the data set. The cumulative probability diagrams show that such outliers are limited in the Vale of Pickering groundwater data, which is a reflection of the predominantly rural setting.

6.2 EXTENT OF ANTHROPOGENIC INFLUENCES

Superimposed on natural baseline concentration ranges are anthropogenic influences. Such influences can directly affect groundwater chemistry via point source or diffuse pollution.

As discussed above, the major anthropogenic influence is via farming practices. Nitrate is a useful indicator of human impacts from farming. Nitrate pollution is one of the largest problems facing unconfined groundwaters in the UK (Rivett et al., 2007). The main cause of these high concentrations is the development of intensive agriculture, which uses NO_3-rich fertilisers. Nitrate is extremely mobile and there are a number of sites within the study with high, and increasing, NO_3-N concentrations which present a real concern to the groundwater quality in the region. In addition to the NO3-N, there is an outlier of K and high Na and Cl concentrations which can also be attributed to farming practices.

There is no evidence for widespread contamination by trace elements; there are only a few isolated exceedances of drinking water limits. The lack of urbanisation in the region means there are more limited sources of such solutes.

7 Conclusions

The Corallian aquifer in the Vale of Pickering comprises three formations, although the formation cannot be distinguished from the groundwater chemistry, as its natural character is relatively unvaried. The chemical compositions have been characterised by investigation of the statistical distributions, mapping the spatial variability, assessment of temporal changes and interpretation of the most likely geochemical processes. For many analytes the 95th percentile can be taken to be a first approximation of the upper limit of baseline concentrations, for others it is likely the entire range represents baseline concentrations, but for NO_3-N the upper limit of the natural range is more uncertain.

The main properties of groundwater are determined by rainwater recharge reacting with aquifer minerals. Of these minerals calcite is the dominant influence on the water chemistry, resulting in waters of Ca-HCO_3 type. There is little variation in the major ion proportion in the Corallian groundwaters of the Vale of Pickering, suggesting these data represent groundwater in equilibrium with the minerals which give it its character. Most of the groundwaters are oxic reflecting the dominance of samples from the unconfined aquifer. Mildly reducing conditions are apparent only on the periphery of the confined aquifer.

The most obvious anthropogenic influences on the groundwater chemistry are seen in the spatial and temporal variations in NO_3-N, which is likely to be dominated by modern intensive farming practices. One fifth of the spatial data exceed the current drinking water limit of 11.3 mg/L, and half of the EA's monitoring data show a trend of increasing concentrations, some to more than twice the drinking water limit. This is a reflection of the prevalence of farming in the region, and probably reflects the intensification of farming methods over the last few decades.

Of the elements tested there was no evidence for widespread contamination by potentially harmful trace elements, any outlier concentrations tend to be localised and probably represent natural anomalies, a small point source pollution source, or contamination derived from the borehole head workings.

The groundwaters in this region were generally of good inorganic quality, with the exception of the prevalence of high concentrations of nitrate.

References

ABESSER, C, SHAND, P, and INGRAM, J. 2005. The Millstone Grit of Northern England. *British Geological Survey and Environment Agency*, BGS Report CR/05/015N; Environment Agency Report NC/99/74/22 (Keyworth and Solihull).

ALLEN, D J, BREWERTON, L M, COLEBY, L M, GIBBS, B R, LEWIS, M A, MACDONALD, A M, WAGSTAFF, S, and WILLIAMS, A T. 1997. The physical properties of major aquifers in England and Wales. *British Geological Survey*, WD/97/34 (Keyworth).

CLARK, I, and FRITZ, P. 1997. *Environmental Isotopes in Hydrogeology*. (Boca Raton, USA: Lewise Publishers.)

COBBING, J, MOREAU, M, SHAND, P, and LANCASTER, A. 2004. The Corallian of Oxfordshire and Wiltshire. *British Geological Survey and Environment Agency*, BGS Report CR/04/262N; Environment Agency Report NC/99/74/14 (Keyworth and Solihull).

COPE, J C W. 2006. Jurassic: The Returning Seas. 559 in *The Geology of England and Wales*. BRENCHLEY, P J, and RAWSON, P F (editors). (London: The geological Society.)

CORNELL, D H. 1993. Rare-earths from supernova to superconductor. *Pure and Applied Chemistry*, Vol. 65, 2453-2464.

CRAIG, H. 1961. Isotopic variations in natural waters. *Science*, Vol. 133, 1702-1703.

DARLING, W G, BATH, A H, and TALBOT, J C. 2003. The O & H stable isotope composition of fresh waters in the British Isles. 2. Surface waters and groundwater. *Hydrology and Earth System Sciences*, Vol. 7, 183-195.

DARLING, W G, MORRIS, B L, STUART, M E, and GOODDY, D C. 2005. Groundwater age indicators from public supplies tapping the Chalk aquifer of southern England. *Water and Environment Journal*, Vol. 19, 30-40.

DARLING, W G, and TALBOT, J C. 2003. The O & H stable isotope composition of fresh waters in the British Isles. 1. Rainfall. *Hydrology and Earth System Sciences*, Vol. 7, 163-181.

DEFRA. 2011. Department for Environment Food and Rural Affairs. http://www.defra.gov.uk/food-farm/land-manage/nitrates-watercourses/nitrates/Accessed 7/9/11. [cited 11/1/11]. http://ww2.defra.gov.uk/food-farm/land-manage/nitrates/

DREVER, J I. 1997. *The Geochemistry of Natural Waters: Surface and Groundwater Environments, 3rd Edition*. (Upper Saddle River: Prentice-Hall, Inc.)

EA. 2009. River Basin Management Plan Humber River Basin District, Environment Agency.

EA. 2015. What's in your backyard? Interactive maps http://www.environment-agency.gov.uk/homeandleisure/37793.aspx Accessed 10/7/15. [cited 10/7/15].

EDMUNDS, W M. 1996. Bromine geochemistry of British groundwaters. *Mineralogical Magazine*, Vol. 60, 275-284.

EDMUNDS, W M, COOK, J M, KINNIBURGH, D G, MILES, D L, and TRAFFORD, J M. 1989. Trace element occurrence in British groundwaters. *British Geological Survey*, Research Report SD/89/3 (Keyworth, Nottingham).

ENVIRONMENT AGENCY. 2013. Derwent Abstraction Licencing Strategy. LIT 7863.

FOX-STRANGWAYS, C. 1880. *The Oolitic and Cretaceous Rocks South of Scarborough*. (London: HMSO.)

HELSEL, D. 2005. *Nondetects and Data Analysis: Statistics for Censored Environmental Data*. (New York: Wiley & Sons.)

HEM, J D. 1992. *Study and Interpretation of the Chemical Characteristics of Natural Water* (Third Edition edition). US Geological Survey Water-Supply Paper 2254. (Washington: United StatesGovernment Printing Office.)

KINNIBURGH, D G, and EDMUNDS, W M. 1986. The susceptibility of UK groundwaters to acid deposition. Hydrogeological Report, British Geological Survey No. 86/3.

LANGMUIR, D. 1997. *Aqueous Environmental Geochemistry*. (New Jersey: Prentice-Hall.)

LEE, L, and HELSEL, D. 2005a. Baseline models of trace elements in major aquifers of the United States. *Applied Geochemistry*, Vol. 20, 1560-1570.

LEE, L, and HELSEL, D. 2005b. Statistical analysis of water-quality data containing multiple detection limits: S-language software for regression on order statistics. *Computers & Geosciences*, Vol. 31, 1241-1248.

LEE, L, and HELSEL, D. 2007. Statistical analysis of water-quality data containing multiple detection limits II: S-language software for nonparametric distribution modeling and hypothesis testing. *Computers & Geosciences*, Vol. 33, 696-704.

LEVINSON, A A. 1974. *Introduction to Exploration Geochemistry*. (Calgary: Applied Publishing Ltd.)

MCLEISH, A. 1992. *Geological Science*. (Cheltenham: Nelson Thornes Ltd.)

NATURAL ENGLAND. 2015. National Character Area Profile: 26. Vale of Pickering www.gov.uk/natural-england.

NEUMANN, I, BROWN, S, SMEDLEY, P L, and BESIEN, T. 2003. The Great and Inferior Oolite of the Cotswolds District. *British Geological Survey and Environment Agency*, BGS Report CR/03/202N; Environment Agency Report NC/99/74/7 (Keyworth and Solihull).

NRFA. 2008. http://www.nwl.ac.uk/ih/nrfa/station_summaries/op/EA-NorthEast_map.html. [cited 30/10/08].

POWELL, J H. 2010. Jurassic sedimentation in the Cleveland Basin: a review. *Proceedings of the Yorkshire Geological Society*, Vol. 58, 21-72.

REEVES, M J, PARRY, E L, and RICHARDSON, G. 1978. Preliminary investigation of the groundwater resources of the western part of the Vale of Pickering. *Quarterly Journal of Engineering Geology*, Vol. 11, 253-262.

RIVETT, M O, SMITH, J W N, BUSS, S R, and MORGAN, P. 2007. Nitrate occurence and attenuation in the major aquifers of England and Wales. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 40, 335-352.

SHAND, P, EDMUNDS, W M, LAWRENCE, A R, SMEDLEY, P L, and BURKE, S. 2007. The natural (baseline) quality of groundwater in England and Wales. *British Geological Survey & Environment Agency*, RR/07/06 & NC/99/74/24 (Keyworth and Solihull).

SMEDLEY, P L, and ALLEN, D. 2004. The Granites of south-west England. *British Geological Survey and Environment Agency*, BGS Report CR/04/255; Environment Agency Report NC/99/74/16 (Keyworth and Solihull).

SMEDLEY, P L, SMITH, B, ABESSER, C, and LAPWORTH, D J. 2006. Uranium occurence and behaviour in British groundwater. *British Geological Survey*, BGS Report CR/06/050N.

TATTERSALL, K H, and WILKINSON, W B. 1974. Groundwater Investigation in the Vale of Pickering: Final report on preliminary investigation. *Yorkshire River Authority and Water Resources Board*.

THE WATER SUPPLY REGULATIONS. 2010. Statutory Instrument 2010 No. 991.

WILSON, V. 1948. *East Yorkshire and Lincolnshire*. British Regional Geology. (London: HMSO.)

WILSON, V. 1949. The Lower Corallian Rocks of the Yorkshire Coast and Hackness Hills. *Proceedings of the Geologists' Association*, Vol. 60, 235-271.

ZHU, C, and ANDERSON, G. 2002. *Environmental Applications of Geochemical Modeling*. (Cambridge: Cambridge University Press.)