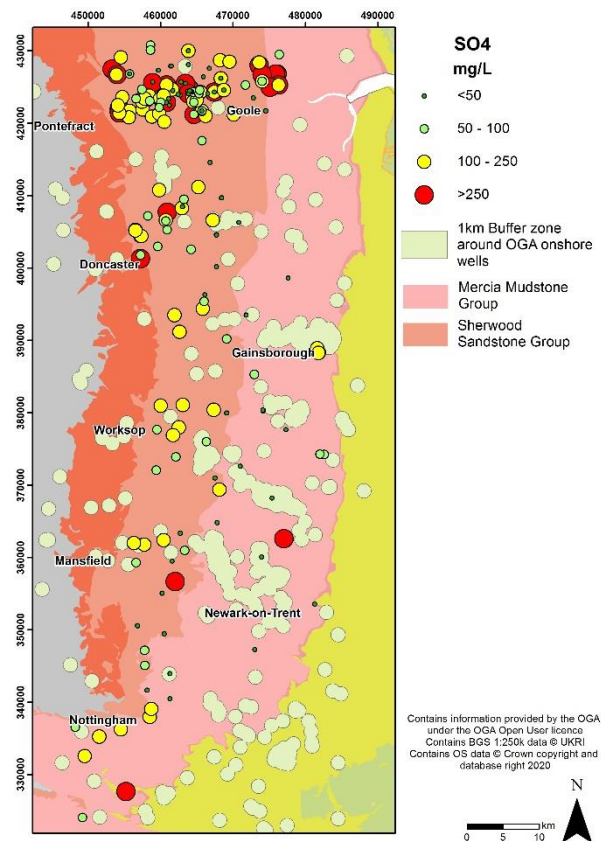




Baseline groundwater chemistry: the Sherwood Sandstone aquifer of the East Midlands and South Yorkshire

Groundwater Programme

Open Report OR/20/046



BRITISH GEOLOGICAL SURVEY

GROUNDWATER PROGRAMME

OPEN REPORT OR/20/046

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Baseline groundwater chemistry: the Sherwood Sandstone aquifer of the East Midlands and South Yorkshire

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Concentrations of SO₄ in Sherwood Sandstone groundwater in relation to geology and proximity of onshore oil and gas wells

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Foreword

This report is the product of a joint project between the British Geological Survey (BGS) and Environment Agency (EA) which aims to investigate the ranges of typical baseline chemical compositions in groundwater from aquifers in England in places where onshore oil and gas may be explored and/or exploited. The project follows on from earlier baseline groundwater studies carried out by BGS during the 1990s, 2000s and 2010s, which focussed on inorganic chemistry of groundwater in British aquifers to inform aquifer characterisation, regulation and protection. This report forms one of a number of regional summaries of groundwater chemistry (inorganic and organic) and contributes towards an overview assessment of groundwater baselines to aid in protection of groundwater in areas where oil and gas activities might take place. This work was commissioned prior to the November 2019 UK Government moratorium on high volume high pressure hydraulic fracturing.

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Summary

This report details the hydrogeochemistry of a broad suite of inorganic and organic analytes in groundwater from the Sherwood Sandstone aquifer of the East Midlands and South Yorkshire. The study aims to establish the groundwater baseline chemical compositions, particularly of those analytes that are and could be associated with onshore oil and gas (OOG) activities, in order to facilitate distinction between current compositions and any new industrial contamination from such activities. Analytes of particular interest in this context include indicators of salinity, indicators of redox conditions, dissolved gases including CO₂ and CH₄, naturally-occurring radioactive materials and organic compounds including volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs).

Groundwater from the Sherwood Sandstone aquifer of the region shows a range of chemical compositions resulting from inputs of modern atmospheric and surface pollution from varying sources, superimposed on natural water-rock interactions. Natural reactions are dominated by carbonate equilibrium, redox reactions, gypsum/anhydrite dissolution and time-dependent silicate-mineral reaction. The Sherwood Sandstone crops out in the East Midlands but further northwards into Yorkshire, the aquifer in places becomes confined or semi-confined by overlying Quaternary superficial silts and clays. The Sherwood Sandstone dips gently eastwards and becomes confined by the poorly-permeable marls and mudstones of the Mercia Mudstone Group (MMG). At outcrop, the groundwater is young and oxic with evidence of inputs of pollutants including NO₃, SO₄ and Cl and possibly of Br, Cu, Pb and Zn from urban, industrial (including mine drainage) and agricultural sources. Small quantities of PAHs, pesticides and solvents are detected occasionally in the unconfined aquifer. Further north into Yorkshire, the aquifer is oxic in parts but becomes anoxic in places with superficial cover and with increasing depth. The reducing groundwaters in this zone have low NO₃ concentrations and increased concentrations of Fe and Mn. Increased concentrations of Co, Sb and V may be associated with release of Fe and Mn into solution under mildly reducing conditions, either within the sandstone or from the superficial deposits.

As the Sherwood Sandstone becomes confined eastwards by the MMG, downgradient chemical changes are controlled by maintained equilibrium with calcite and dolomite, dissolution of gypsum or anhydrite and development of reducing conditions. These controls see progressive increases downgradient in concentrations of SO₄, and slight increases in concentrations of Fe, Mn, NH₄ and Mo. High concentrations especially of SO₄ and NH₄ in the north-east area around Goole are speculatively associated with facies changes in the sandstone further north, the groundwater possibly interacting with a greater proportion of sulphate minerals and clays. In the deep confined aquifer, conditions are insufficiently reducing for SO₄ reduction to be quantitatively important.

Under the reducing conditions in the MMG-confined aquifer and to some extent in the areas covered by superficial deposits, small quantities of dissolved CH₄ are detected (up to 120 µg/L in this study). Concentrations are low in the unconfined sections of the aquifer. Concentrations in the confined aquifer are relatively low because of a paucity of organic carbon in the aquifer for significant methanogenesis to take place. No other hydrocarbon or PAH, pesticide or solvent compounds were detected in the confined aquifer. Detection of a small quantity of chloroform at one location in the shallow confined aquifer is anomalous and difficult to explain, although the concentration observed was orders of magnitude below the drinking-water standard for this compound and not a cause for concern.

The groundwater shows a well-established downgradient increase in residence time as it passes beneath the MMG. Limited radiocarbon dating in this study supports previous conclusions that confined groundwater close to the western edge of the MMG has model ages of around 2000–10,000 years, increasing to late Pleistocene (19,000 years) along the flow path at its eastern edge. The study reiterates that within the aquifer, fresh groundwater extends to around 20 km away from the outcrop and to depths of some 400–500 m below ground. The confined aquifer may be especially vulnerable to pollution from any future deep hydrocarbon exploration activities and would require careful monitoring.

1 Introduction

1.1 PROJECT OBJECTIVES

The UK has a mature conventional OOG industry. The 2010s saw an increased interest in exploration for unconventional oil and gas resources, including shale gas, until a moratorium on high volume, high pressure hydraulic fracturing by the UK Government in November 2019. Despite this moratorium, there is still potential for further OOG development across certain regions of the UK. There is a need to obtain a better understanding of the pre-development regional water quality in a number of drinking-water aquifers with respect to naturally occurring inorganic and organic constituents. The primary way to investigate this is by undertaking a baseline survey, to determine the conditions prior to any future development. In recent years, the British Geological Survey (BGS) and BGS together with the Environment Agency (EA) have developed a number of baseline inorganic geochemistry reports for major drinking-water aquifers across the UK (e.g. BGS, 2016). These have only gone so far as to consider the dissolved organic carbon (DOC) content within the aquifer, alongside the wider inorganic geochemistry. As there is a potential risk of hydrocarbon migration to the surface via pre-existing and new pathways associated with the exploration and production of these unconventional resources, a clearer picture of the naturally occurring hydrocarbons within the aquifers needs to be ascertained, alongside their inorganic compositions.

This project supplements previous work carried out by BGS and the EA by including naturally-occurring hydrocarbons within the baseline. Using a combination of EA Water Quality Archive (WIMS) data, peer-reviewed published data and primary data collection by BGS as part of these surveys, an inorganic and organic hydrogeochemical baseline will be established for three study areas: the Sherwood Sandstone aquifer of the East Midlands and South Yorkshire, the Lower Greensand aquifer of Surrey and West Sussex, and the Pennine Coal Measures of the Midlands.

Using the data from these three study areas, alongside information about the geological setting, soil composition, hydrogeological conditions, groundwater flow paths and residence times and industrial activities, the observed characteristics of the aquifer will be extrapolated to regions where recent data collection may be lacking. The process of extrapolation will involve development of “typologies”: rules or influencing factors that may be used to categorise the given aquifers in terms of their OOG-type characteristics. These typologies will provide a broad understanding of the baseline that could be expected in analogous aquifers elsewhere. This would be important if onshore oil and gas activities expand to new areas and detailed baseline investigations were not feasible.

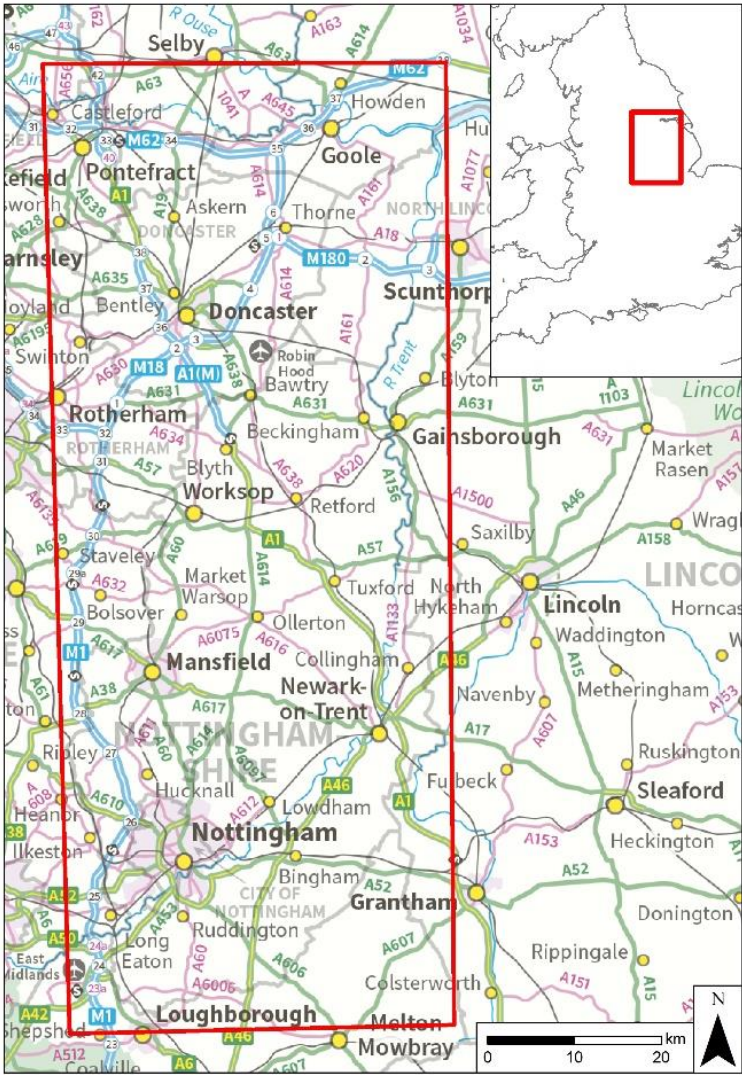
This report presents the inorganic and organic baseline of the Sherwood Sandstone aquifer of the East Midlands and South Yorkshire. The typologies development will be carried out once all three study areas have been evaluated and the final conclusions can be drawn.

1.2 STUDY AREA

The extent of the investigation for the pilot study can be seen in Figure 1.1. The Sherwood Sandstone is classed as a principal aquifer in this region, with water use consisting of public and private water supply, agricultural and industrial applications. The study area forms part of the Humber river basin district and groundwater chemical status for the Sherwood Sandstone is managed by the Environment Agency as part of the Humber River Basin Management Plan (Environment Agency, 2016).

The Sherwood Sandstone aquifer is unconfined in its south-western part where outcropping, but becomes confined moving eastwards due to overlying cover by the Mercia Mudstone Group and partially to the north-west by poorly-permeable Quaternary cover. The scope of this study will investigate both confined and unconfined hydrogeological settings. Further details on the geology and hydrogeology of the study area are given in Sections 2.2 and 2.3. The North Nottinghamshire

and South Yorkshire region are also host to a number of mature oilfields, and have also been identified as a potential region for shale-gas exploration (Andrews, 2013).



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Figure 1.1. Extent of the investigation area (defined by red boundary). OS data ©Crown copyright 2020

1.2.1 Mining legacy

The local area has a longstanding legacy of coal mining, with the Nottinghamshire, Derbyshire and South Yorkshire coal fields in operation between the early 1800s and 2015 (Northern Mine Research Society, n.d.-a, b, c). Notable collieries include Maltby, Thoresby & Annesley Bentinck. As a result of the coal-mining legacy, the wider hydrogeology and hydrogeochemistry of the Nottingham and Yorkshire region has been affected (Allen et al., 1997).

Across the Nottinghamshire coal field, long wall mining of the coal seams has resulted in the settlement of the overlying strata and an increase in localised fracturing within the sandstone aquifer, modifying the local permeability above these historic workings (Shepley et al., 2008). Whilst these may not provide connections from the worked seams to the aquifer, they modify the local hydrogeology and may make the aquifer more susceptible to pollution from the surface (Shepley et al., 2008).

Groundwater rebound following cessation of mining activities can impact on groundwater quality, as poor quality waters may be discharged into the aquifer (Younger and Adams, 1997). Within the study area, rising concentrations of chloride have been observed in groundwater, attributed to discharge from the dewatering of mine workings to local water courses (Allen et al., 1997;

Smedley et al., 2018), and leachate from spoil heaps (Klinck et al., 2004). The Coal Authority manages a number of pumped mine water-treatment schemes in the west of the Sherwood Sandstone outcrop, including the A-Winning treatment scheme, to protect the quality of groundwater in the Sherwood Sandstone aquifer (Coal Authority, 2015, 2018).

1.2.2 Urban and industrial

Urban land use can have a significant impact on water quality and resources. Both paved (impermeable) surfaces and sewerage/drainage systems can have a detrimental impact on groundwater quality by introducing pollutants via recharge and leakage (WCA Environment Ltd, 2013). Urban pollution can be both diffuse and point-source, dependent on scale, and includes:

- salt runoff from gritted roads;
- vehicular pollutants accumulating and washed from road surfaces;
- wastewater (including industrial) discharges, and leakage from sewerage;
- illegal chemical disposal.

The impacts from urban/industrial activities can be significant to groundwater quality. In response to these activities, the EA has designated a number of Source Protection Zones around major public water supply boreholes. These zones identify the magnitude of the risk for activities located within and have three designations (EA, 2019):

- Inner zone – SPZ1: a 50 day travel time of pollutant to source with a 50 m default minimum radius;
- Outer zone – SPZ2: a 400 day travel time of pollutant to source with a 250 m or 500 m minimum radius around the source, depending on volume of water abstracted;
- Total catchment – SPZ3: area around a supply source within which all the groundwater ends up at the abstraction point. This is the point from where the water is taken. This could extend some distance from the source point.

Urban land use only makes up a small percentage of the study area (Section 2.5). The major urban centres include Nottingham, Doncaster, Newark and Pontefract. Major roads include the A1(M), A1, and A46. SPZs within the study area are shown in Figure 1.2. For Zone III, this delineates the zone of the Sherwood Sandstone aquifer susceptible to recent recharge, and therefore also at risk from pollution within this setting. Where the aquifer becomes confined by the Mercia Mudstone Group towards the east (Section 2.3), this is not considered within the SPZ framework due to the protection of the confining layer.

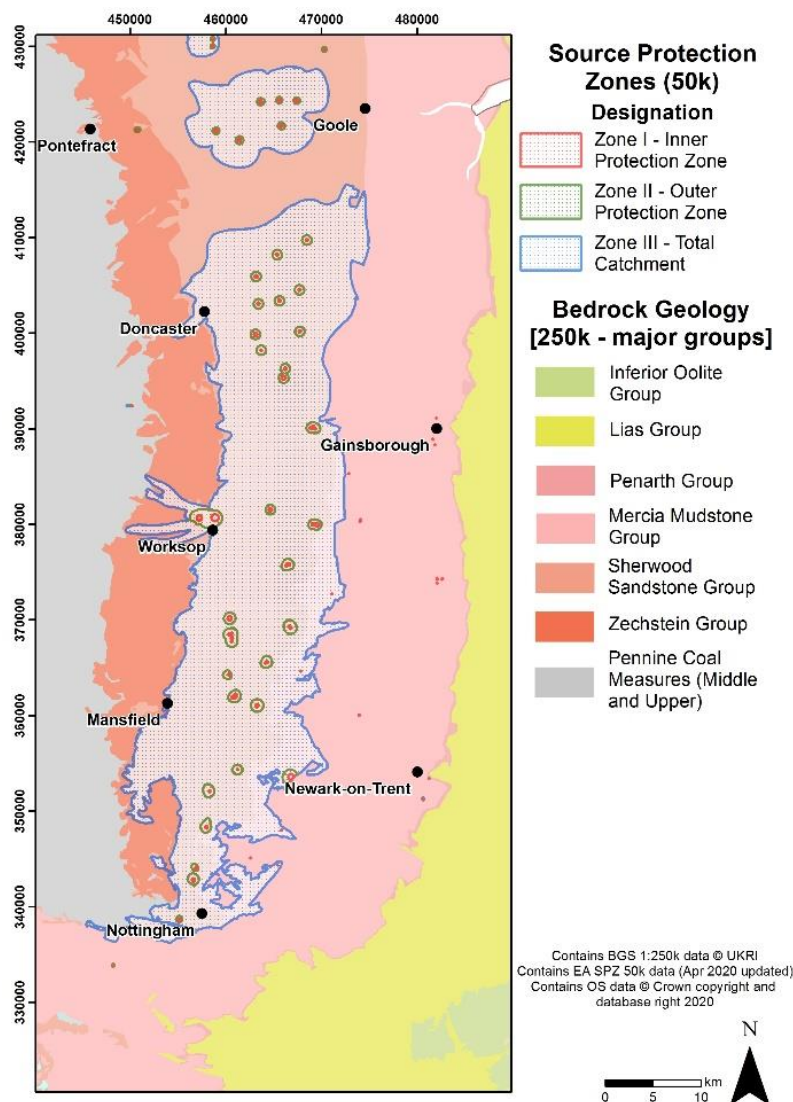


Figure 1.2. Source Protection Zones for the investigation area; data from EA (2019). BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

1.2.3 Agriculture

Much of the study area is agricultural (Section 2.5) and use of nitrogenous fertilisers, pesticides and herbicides poses a groundwater diffuse-pollution risk. Agriculture can impact both water quality and water quantity, especially from large abstractions for irrigation in the rural areas during the summer months.

Measures to counteract diffuse pollution from nitrate include the instigation of areas designated as Nitrate Vulnerable Zones (NVZs). These are areas at risk from agricultural nitrate pollution and include about 55% of land in England (DEFRA, 2018). Designations are outlined for both groundwater and surface-water bodies at risk (with special designation for surface bodies susceptible to eutrophication). In an attempt to protect groundwater quality, strict guidelines for fertiliser use are applied to agricultural land within these NVZs (DEFRA, 2018). Within the study area, much of the Sherwood Sandstone aquifer at outcrop is classified as a groundwater NVZ (Figure 1.3). Where the Sherwood Sandstone is confined by the Mercia Mudstone Group or Quaternary glacial deposits (from Doncaster northwards), the designation is only set for a risk to surface water. Additionally, restrictions arising from SPZs mentioned in Section 1.2.3 apply to agricultural businesses where in proximity to the designated zones.

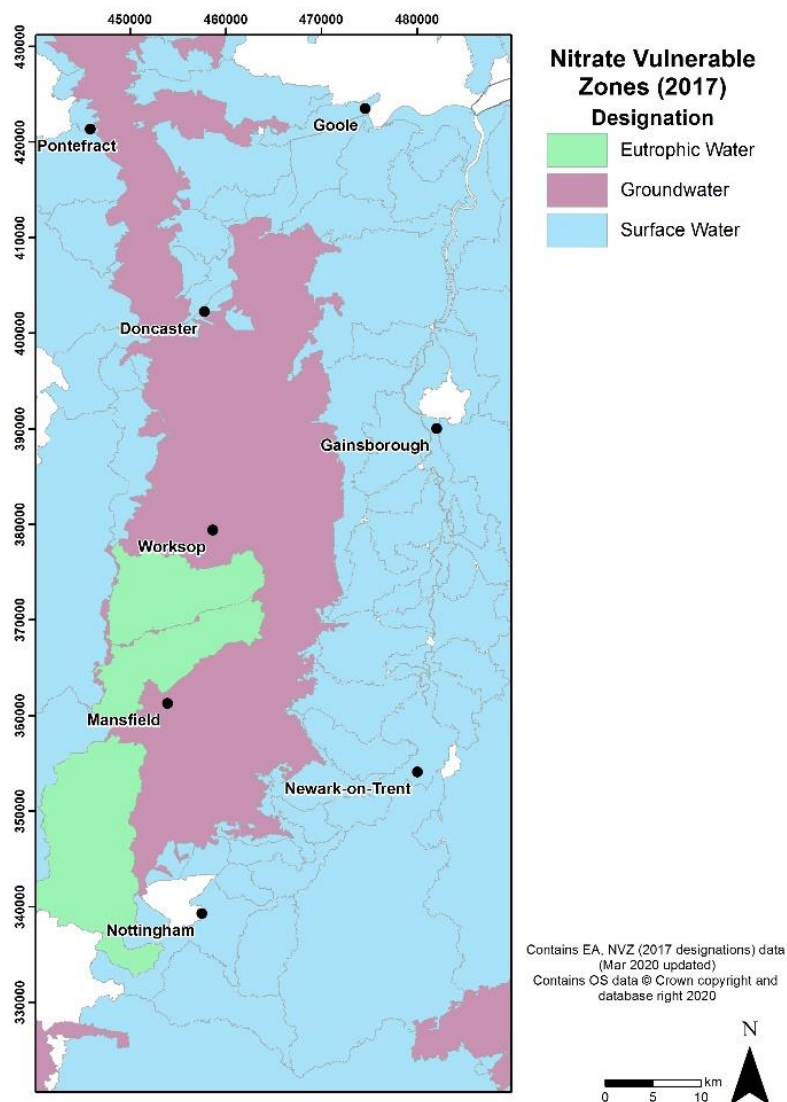


Figure 1.3. Nitrate Vulnerable Zones for the investigation area (data from DEFRA (2018))

1.2.4 Conventional hydrocarbons (oil and gas) and potential unconventional hydrocarbons

The main focus for this project is on the onshore oil and gas (OOG) sector, and building a better understanding of the compounds in groundwater that are linked to this industry and may be present in the aquifer prior to any new OOG activity. There are a number of locations with a mature and well-developed conventional OOG industry across the UK, and these and others could be developed further.

There are a number of potentially polluting activities throughout the lifetime of an onshore oil and gas well, including potential for leakage of drilling, hydraulic fracturing, flowback and production fluids via surface spills, pre-existing and induced geological pathways (faults and fractures), well casing breaches and longer-term well decommissioning failures. OOG operations are overseen and regulated by the Health and Safety Executive (HSE), Oil and Gas Authority (OGA) and the EA. Of the three, the EA is the principal regulator ensuring the operation does not damage the natural environment throughout its lifetime.

Within the study area, there are a total of 784 recorded OOG wells across a total of 55 Petroleum Exploration Development Licence (PEDL) blocks (Figure 1.4) (OGA, 2019b, 2020). These wells include conventional oil and gas (COG), coal-bed methane (CBM), mine-gas harvesting and shale gas (Table 1.1). The conventional oil and gas sector is well-established in the North Nottinghamshire and South Yorkshire region, with a number of prominent oil fields/wells still in production (Doncaster Council, 2018; Nottinghamshire County Council, 2010, 2016; OGA,

2019a, 2020). These include Beckingham, Bothamsall, Egmanton, Eakring, Gainsborough and Hatfield.

Table 1.1 OOG well types and borehole intention for the study area (OGA, 2020)

	Conventional Oil & Gas	Mine Gas	Coal Bed Methane	Shale Gas
Development	478	5	0	0
Exploration	172	19	9	2
Appraisal	98	1	0	0
	748	25	9	2

Alongside conventional sites, a number of established mine-gas recovery schemes which tap into abandoned coal workings and shafts to recover methane are located around Mansfield, Doncaster, Whitwell, Harworth and Maltby. A number of coal-bed methane exploration wells are located within the study area, but there are no active production sites to date.

Only two locations earmarked for shale-gas exploration exist in the study area: Tinker Lane, Torworth and Springs Road, Misson (Figure 1.4). The two sites, operated by iGas, were drilled in 2018 and 2019. The Tinker Lane well failed to prove the Bowland Shale and was plugged and abandoned in 2019 (iGas Energy PLC, 2019a). The site at Springs Road encountered the Bowland Shale, and is presently evaluating the retrieved core samples (iGas Energy PLC, 2019b). The moratorium on hydraulic fracturing imposed in England in late 2019 has halted much of the industrial development for the foreseeable future (BEIS et al., 2019).

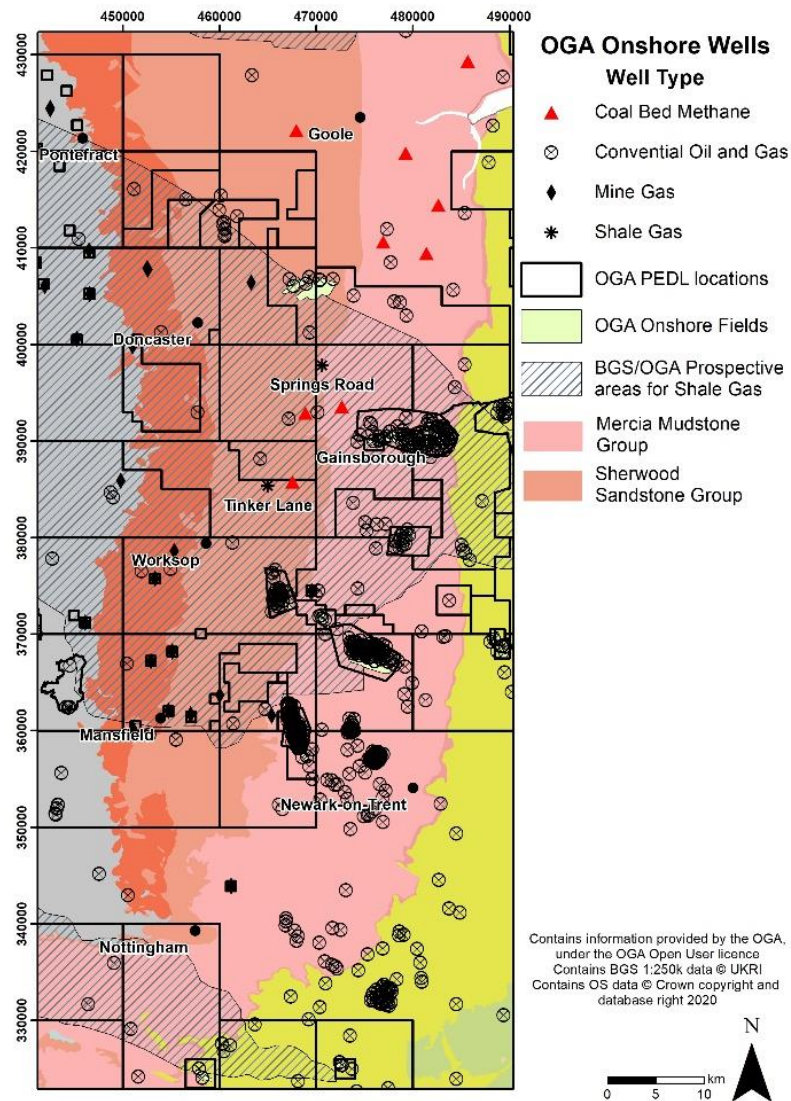


Figure 1.4. OGA data for the investigation area. Map shows onshore wells (highlighting the Springs Road and Tinker Lane shale gas sites), PEDL locations, onshore conventional fields, and the joint BGS and OGA dataset for prospective areas for shale gas (Data from BGS and OGA (2018); OGA (2019a, 2019b, 2020)). A full geological legend can be found at Figure 2.2. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

2 Regional background

2.1 GEOGRAPHICAL SETTING

The study area is approximately 100 km N-S by 30 km E-W. The area is constrained to the west by the outcrop of the Sherwood Sandstone Group, which has a boundary with the underlying Zechstein Group in the vicinity of Mansfield, Worksop, Doncaster and Knottingley. To the east, the investigation area is bounded by Newark, Gainsborough and Scunthorpe.

The topography across the region is relatively low-lying, sloping downwards towards the north and east (Figure 2.1) from the relatively elevated topography around Mansfield (c.200 m AOD). Major watercourses include the rivers Trent (Nottingham and Newark), Don (Doncaster) and Humber (Goole, Pontefract, Knottingley), including the Humber Estuary just north of the study area.

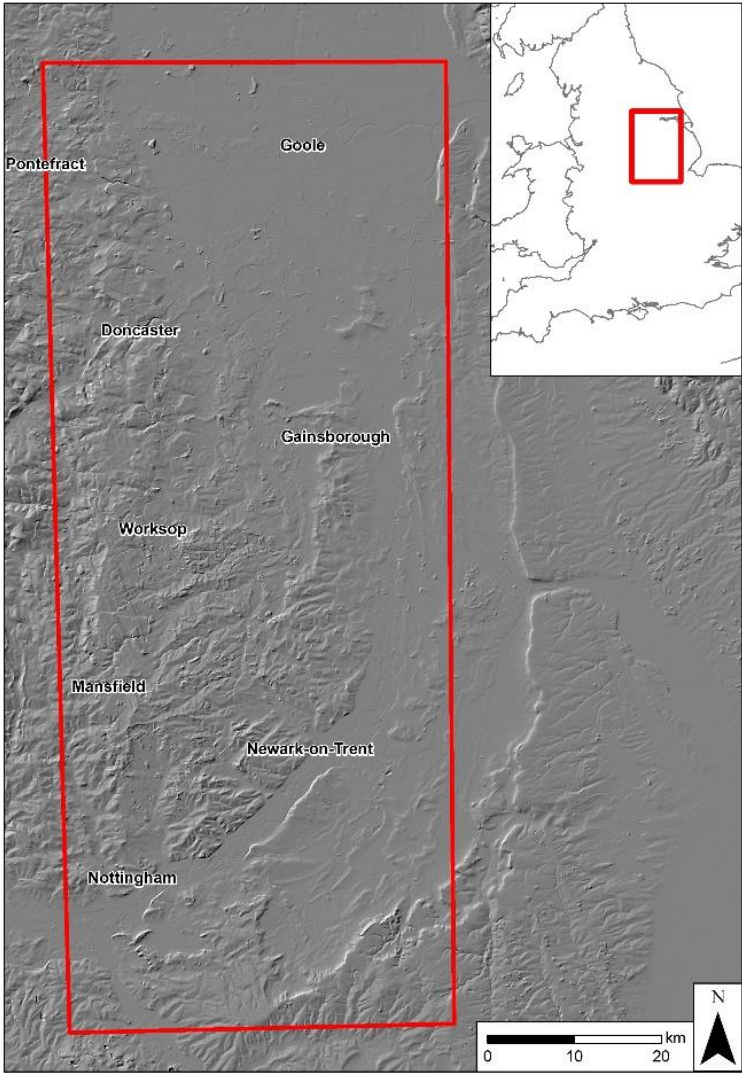


Figure 2.1. Topography for the investigation area (NEXTMap Britain elevation data from Intermap Technologies. Contains OS data © Crown copyright and database right 2020)

2.2 GEOLOGY

2.2.1 Bedrock and superficial geology

The major aquifer unit within the study area is the Sherwood Sandstone Group (SSG), a Triassic red-bed sandstone sequence of fine- to medium-grained sandstone, with interbedded mudstone, and some pebbles throughout the sequence (Figure 2.2) (Allen et al., 1997; Ambrose et al., 2014; Smedley and Brewerton, 1997). The SSG thickens progressively towards the north, from around 60 m near Nottingham, to 250 m thick around north Nottinghamshire/Worksop, and up to approximately 400 m thick in the region of the Humber Estuary in the far north. The SSG appears at outcrop, ranging from 8–20 km wide E-W in the Nottinghamshire area, becoming progressively covered by Quaternary superficial deposits towards the north, where 10% at most is visible at outcrop around Doncaster.

The SSG dips gently, around 1–4° towards the east, where it transitions into the overlying Triassic Mercia Mudstone Group (MMG). The MMG comprises a sequence of mudstone and siltstone, with some evaporitic deposits. The transition zone consists of interbedded mudstones and sandstones, with some small veins and nodules of anhydrite occurring infrequently. The MMG covers much of the east Nottinghamshire area, from south of Nottingham to the east coast at Teesside (Hobbs et al., 2002).

The SSG rests disconformably on the Permian Lenton Sandstone Formation, which in turn overlies the formations of the Zechstein Group (Ambrose et al., 2014). The Permian Zechstein Group is a mixture of dolostone, limestone, evaporites and mudstones. The Carboniferous Pennine Coal Measures (PCM) underlie the Zechstein Group and form an interbedded sequence of sandstones, mudstones and coal seams, the latter of which have been mined historically. The stratigraphy for the investigation area is summarised in Table 2.1.

The superficial cover across the study area consists primarily of glacial, periglacial and glaciolacustrine deposits, with some more recent alluvial deposits following the major river courses (the Trent, Don and Humber) (Figure 2.3). Superficial cover is thin or absent in the southern area around Nottingham, becoming progressively thicker northwards towards and beyond Doncaster (in excess of 50 m) (Price et al., 2006).

2.2.2 Organic-rich source rocks

As a focus of this study is to identify the naturally-occurring OOG-associated compounds in the groundwater, including a range of organic compounds, a brief overview of the potential sources of organic compounds within the geological sequence is outlined below.

The shallowest bedrock formation rich in organic material in the region is the Pennine Coal Measures (PCM). The shallowest coal seams of the PCM are present around of depth of ca. 25 m in the Mansfield area, becoming progressively deeper towards the east, with recorded depths greater than 500 m. At greater depths, the Bowland Shale Formation is an organic-rich sequence of shale and mudstone. The Bowland Shale was the unit considered as a potential target for unconventional shale gas exploration as well as the source rock for the Conventional oil and gas resources found at shallower depths (Andrews, 2013; DECC, 2012, 2013). Loveless et al. (2018) created a number of maps delineating the vertical separation between the shale-gas source rocks and overlying aquifers which are available online (BGS, 2018). Within the study area, the vertical separation between Bowland Shale and SSG is 400–800 m to the south of Nottingham, becoming progressively greater towards the north with a separation of some 800–1600 m (Figure 2.4).

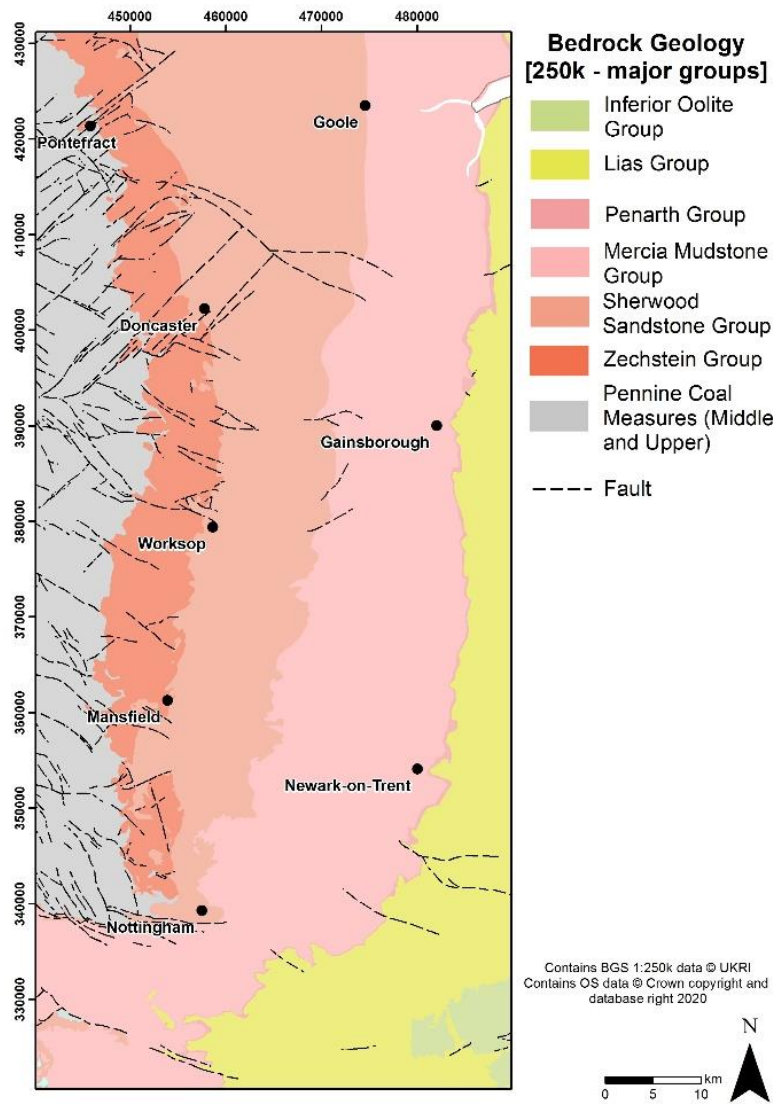


Figure 2.2. Bedrock geology for the investigation area; note the Lenton Sandstone Formation is not delineated on the BGS 1:250,000 bedrock geology map and database. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

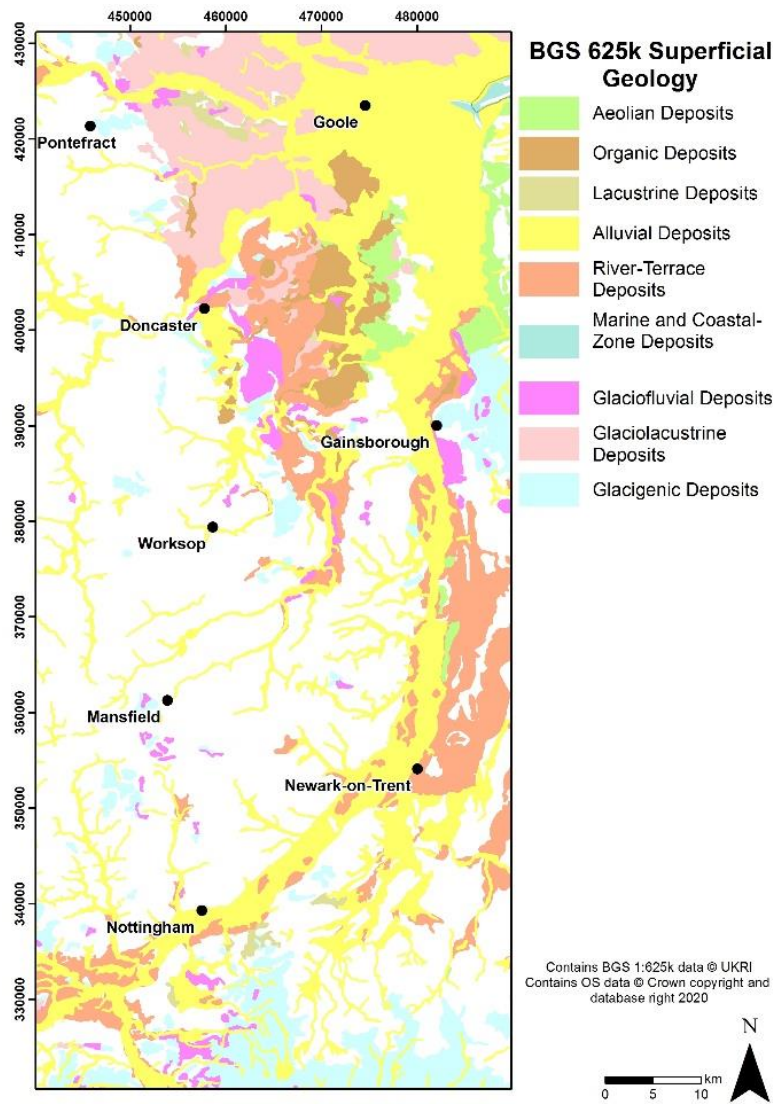


Figure 2.3 Superficial Geology for the investigation area. BGS 1:625k data ©UKRI 2020; OS data ©Crown copyright 2020

Table 2.1. Stratigraphic sequence for the groups and formations of interest within the study area. Adapted from Gaunt (1994), Allen et al. (1997), Howard et al. (2009) and (Ambrose et al., 2014)

Age	Group	Formation	Former/Obsolete Name	Dominant lithologies	Thickness (m)
Triassic	Mercia Mudstone Group	(undifferentiated)		Mudstone/siltstone	ca. 200
		Tarporley Siltstone Formation	Sneinton Formation	Siltstone/fine sandstone	40–80
	Sherwood Sandstone Group	Chester Formation	Nottingham Castle Sandstone Formation	Coarse, pebbly sandstone	60–400
Permian	Lenton Sandstone Formation		Formerly part of Sherwood Sandstone Group	Fine sandstone	10–50+
	Zechstein Group	Roxby Formation	Eskdale Group, Staintondale Group, Teesside Group, Upper Magnesian Limestone, Lower Magnesian Limestone	Mudstone, siltstone	0–23
		Brotherton Formation		Dolomitic limestone	0–5.5
		Edlington Formation		Mudstone and siltstone	0–56
		Cadeby Formation		Dolomitic limestone	0–56
Carboniferous	Pennine Coal Measures Group	Pennine Upper Coal Measures	Upper Coal Measures Formation	Coal seams, mudstone, siltstone, sandstone	0–160
		Pennine Middle Coal Measures	Middle Coal Measures Formation	Coal seams, mudstone, siltstone, sandstone	ca. 200–330
		Pennine Lower Coal Measures	Lower Coal Measures Formation	Coal seams, sandstone and mudstone, with some basalt	ca. 150–340

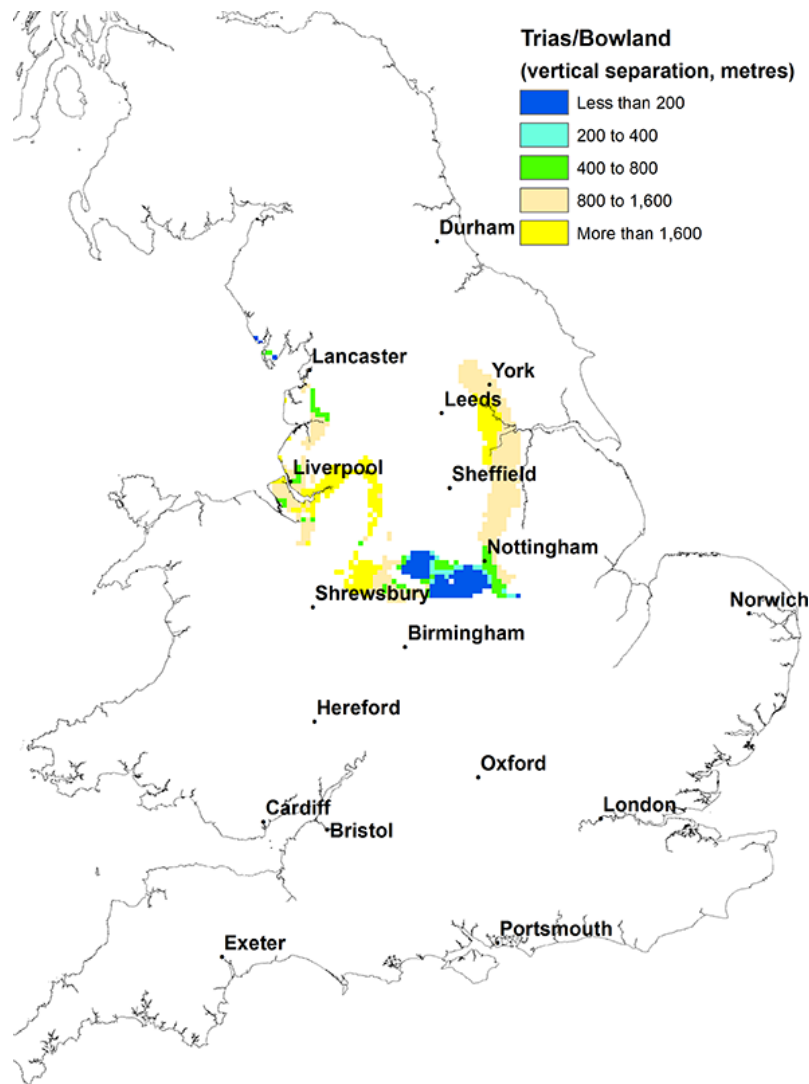


Figure 2.4. Vertical separation map of the Bowland Shale and Sherwood Sandstone Group aquifer (from BGS (2018); Loveless et al. (2018)). BGS 1:625k data ©UKRI 2020; OS data ©Crown copyright 2020

The conventional oil and gas reservoir for the East Midlands region consists primarily of the Millstone Grit and Lower and Middle Pennine Coal Measures (DECC, 2013), with the clay-rich mudstones of the PCM forming both intraformational traps and the main trap for the Millstone Grit. Historical evidence from conventional oil and gas drilling has shown that the faulting across the East Midlands region, at the target depths for conventional production, is typically sealed and impermeable, preventing oil and gas migration to higher elevations above the PCM.

Near surface, superficial peat deposits may be considered a potential source for naturally-occurring organic matter, although this cover is typically patchy and limited to the northern half of the study area. Appleton (2011) created a risk map to delineate regions in the UK where there may be a higher risk of hydrocarbon and hydrocarbon-derived gas (methane and carbon dioxide) originating from underlying or superficial geology. The risk map for the study area (Figure 2.5) shows the potential hazard from superficial peat deposits towards the northern half of the study area, but considers the SSG and MMG formations unlikely to be hydrocarbon hazards. The potential hazard from the PCM is highlighted to the west of the study area.

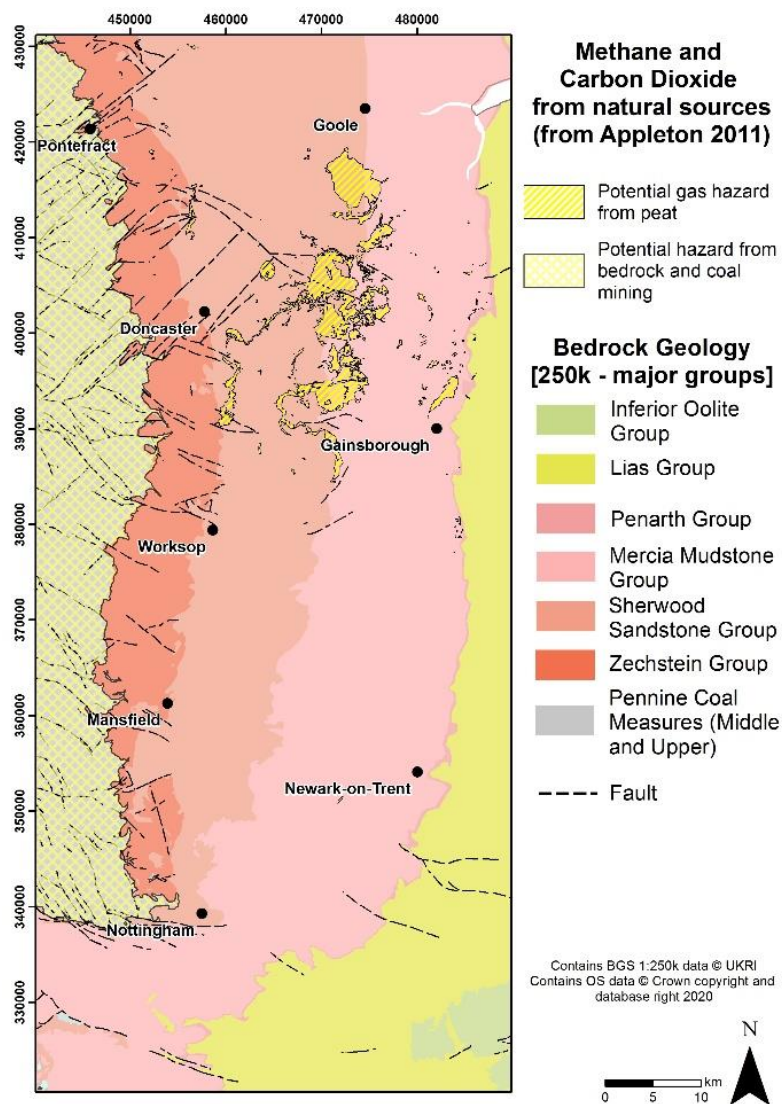


Figure 2.5. Map of methane and carbon dioxide hazard from bedrock and superficial geology; data from Appleton (2011). BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

2.3 HYDROGEOLOGY

The Sherwood Sandstone Group and the Lenton Sandstone Formation (herein considered as the Sherwood Sandstone aquifer) forms an unconfined aquifer in the west, gradually becoming confined towards the east by the MMG. In the unconfined setting, it forms a significant Principal Aquifer for the East Midlands region (Figure 2.6), with the fringe of the confined area being downgraded to a Secondary classification (EA and BGS, 2018). The Sherwood Sandstone aquifer is bounded at the base by the low-permeability Permian Cadeby Formation which forms the base of the aquifer.

Groundwater flow is dominantly intergranular and anisotropic, with horizontal conductivity around ten times greater than vertical conductivity (Allen et al., 1997). Localised fracturing results in zones of higher permeability and yield, but fracture permeability declines with both depth and confinement. Permeability ranges from 1 to 5 m/d, with core-scale permeability in the range of 0.01 to 1 m/d. Porosity has been determined to be around 24–30% (Allen et al., 1997). Transmissivity has been recorded in the range from 50–5000 m²/d, with a median of 207 m²/d. There is a general increase towards the north with increased aquifer thickness (100–1000 m²/d north of Nottingham), and a decline in transmissivity towards the south and feather-edge of the aquifer in the west, at the boundary with the Cadeby Formation (<100 m²/d), and to the east beneath the overlying Mercia Mudstone Group (Allen et al., 1997; Lovelock, 1977 in Edmunds et

al., 1982). Groundwater flow is from west to east, with a gradient of 1 in 250 (unconfined) and 1 in 900 (confined). Recharge occurs through the SSG outcrop, or where sandy superficial deposits overlie the bedrock. Recharge is hindered by the clay-rich glacial and glaciolacustrine superficial deposits towards the north (Doncaster and South Yorkshire), and the MMG to the east. Recharge to the aquifer is estimated at 150 mm/y (Edmunds et al., 1982).

The hydraulic regime through the area has been heavily modified by a number of large, long-term abstractions for public water supply and industry, along with subsidence following the historical coal mining in the region. The latter has resulted in increased fracturing. The aquifer is also susceptible to mine water rebound (see Section 1.2.1) and groundwater flows and recharge have been modified in the west by a number of mine water treatment schemes.

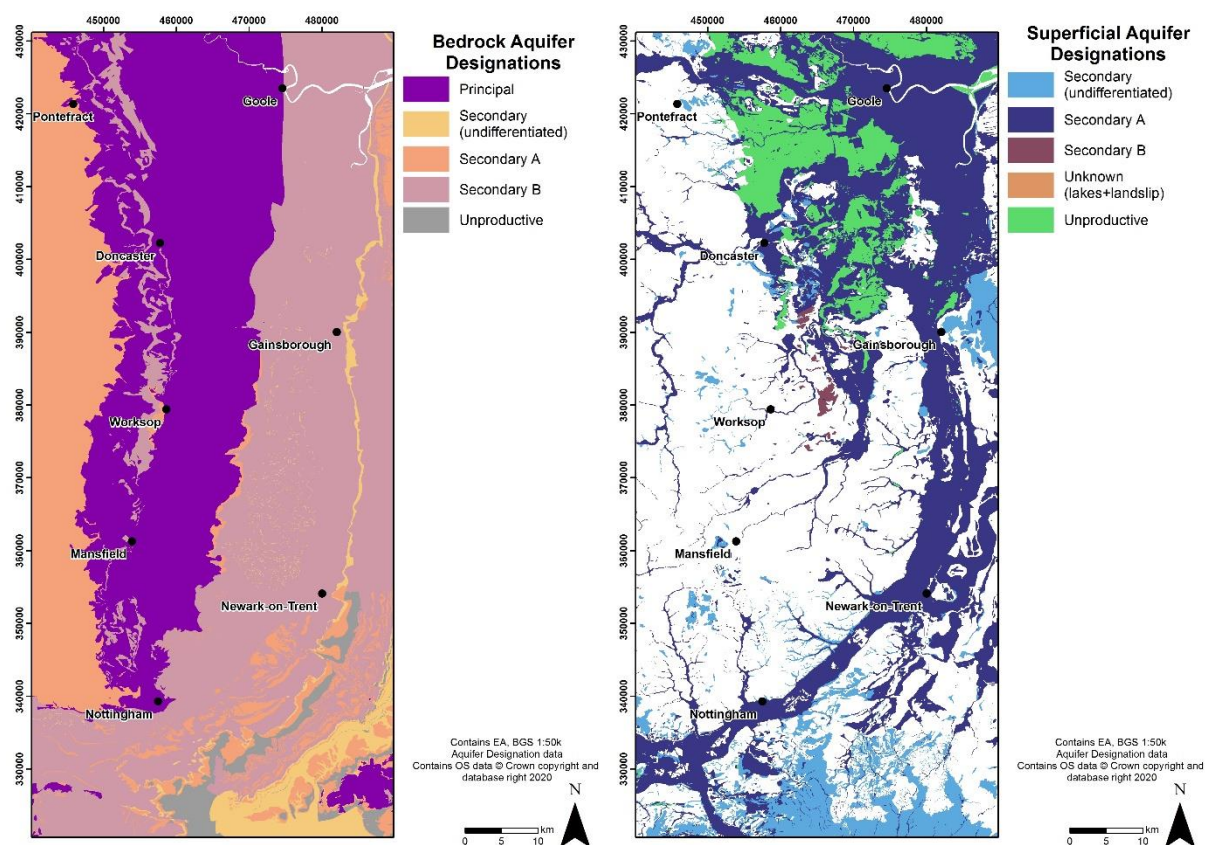


Figure 2.6. EA Aquifer designation maps for bedrock (left) and superficial (right) geology (EA and BGS, 2018). BGS/EA 1:50k data ©UKRI 2020; OS data ©Crown copyright 2020

2.4 AQUIFER MINERALOGY

The primary composition of the SSG is quartz and K-feldspar, with some plagioclase, muscovite, biotite, and lithic fragments. Alteration of K-feldspar to illite-chlorite and kaolinite is common (Bath et al., 1987). The aquifer matrix is poorly cemented by a calcareous and dolomitic cement, accounting for between 1–4 wt. % of the sandstone (Edmunds et al., 1982; Edmunds and Smedley, 2000). Dolomite constitutes greater than 50% of the carbonate content for the aquifer (Edmunds et al., 1982), with calcite existing as a partial replacement mineral/cement. Decalcification of the matrix is evident at outcrop (Edmunds and Smedley, 2000). Towards the base of the Sherwood Sandstone, there are a number of grey-green horizons, containing microcrystalline iron sulphide from incomplete oxidation of the sediments. The dominant iron oxide mineralogy present within the aquifer consists of haematite, lepidocrocite and goethite (Edmunds et al., 1982). Red-brown coatings of iron oxide on sand grains give the sandstone its characteristic colour. Gypsiferous horizons have been noted further north in Yorkshire (Shand et al., 2002).

2.5 LAND USE

Land-use data for the study area has been extracted from the CORINE land classification 2018 (CLC 2018) dataset (European Environment Agency (EEA), 2019), with a cell size of 100 m by 100 m. Figure 2.7 and Table 2.2 indicate that agricultural land makes up the principal land use/classification across the study area (over 65%), with a smaller percentage of urban land (around 19% for all urban land use types). This is concentrated around the major centres of Nottingham, Mansfield, and Doncaster.

2.6 RAINFALL CHEMISTRY

The average annual rainfall over the study area is between 612 and 651 mm/y, with a greater average towards the north around Pontefract (Climate-Data.org, 2020a, b, c). Rainfall chemistry data are somewhat limited within the study area, with the two nearest stations monitoring monthly rainfall chemistry (as part of Defra's UKEAP-Precip Net) both situated in the Peak District, some 40–50 km west of the centre of the study area (DEFRA, 2020a, b).

Statistics for 2019 rainfall from the two selected sites, Wardlow Hay Cop, and River Etherow, are shown in Table 2.3 and Table 2.4 (DEFRA, 2020a, b). Values for rainfall concentrated by three times are also computed to estimate typical values for infiltrating recharge in temperate climates following water loss by evapotranspiration (Shand et al., 2007). Both sites show a clear elevated Cl concentration (mean >2 mg/L) in the rainfall, which has long been noted within the study area (Edmunds et al., 1982). Both sites also have a corresponding relatively high mean Na concentration and a slightly acidic pH. Time series data for 2019 for each monitoring site are shown in Appendix 1 (Figure A. 1 and Figure A. 2).

The observed Cl in the rainfall suggests that there is a notable input of Cl in aquifer recharge. Edmunds et al. (1982) and Smedley et al. (2018) both indicate that a portion of the Cl in groundwater is rainfall-derived. They attribute higher concentrations of Cl in the unconfined aquifer partly to rainfall inputs from the well-established industrial activity in the west of the area. Rainfall concentrations of NO₃, NH₄, and SO₄ are relatively low for the two monitoring sites when compared to those reported by Stuart et al. (2004) for Jenny Hurn, Lincolnshire (Table 2.5), which are c. 8–9 times greater for SO₄, and 5–7 times greater for NO₃. These higher values probably originate from the relative significance of agricultural activities in this latter area.

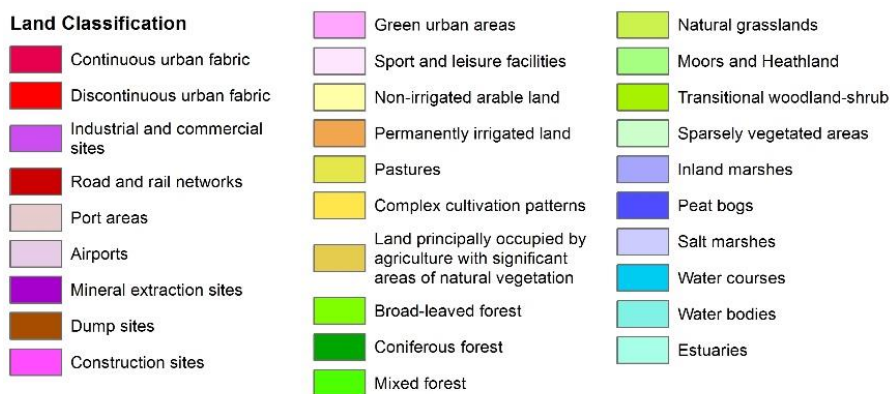
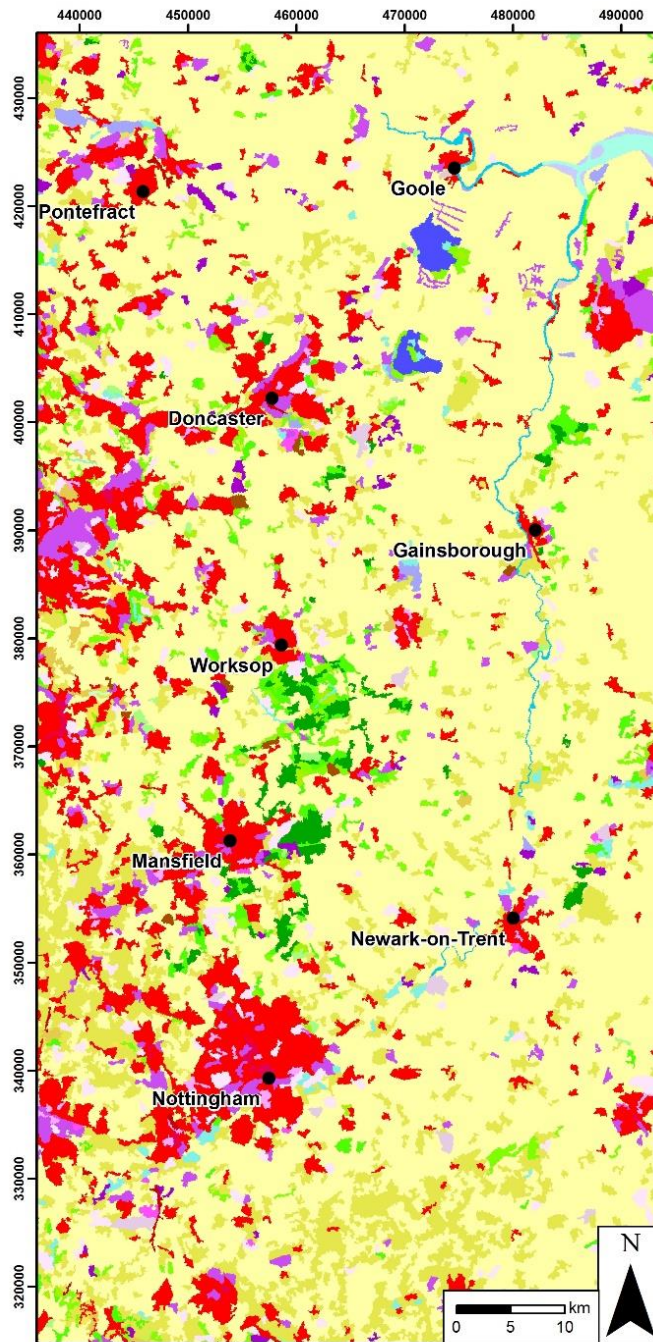


Figure 2.7. CLC 2018 land classification map for the investigation area (European Environment Agency (EEA), 2019)

Table 2.2. Land classification categories and percentage of total area for the investigation extent shown in Figure 9 (from European Environment Agency (EEA) (2019))

Land Classification (CLC 2018)	Area (km²)	Percentage total
Non-irrigated arable land	3998.09	65.4
Discontinuous urban fabric	772.64	12.6
Pastures	507.24	8.30
Industrial or commercial units	179.12	2.93
Sport and leisure facilities	126.03	2.06
Broad-leaved forest	97.30	1.59
Mixed forest	80.34	1.31
Coniferous forest	71.34	1.17
Green urban areas	33.12	0.542
Mineral extraction sites	32.21	0.527
Water bodies	31.27	0.511
Airports	25.18	0.412
Peat bogs	23.06	0.377
Water courses	18.57	0.304
Continuous urban fabric	18.07	0.296
Land principally occupied by agriculture, with significant areas of natural vegetation	15.75	0.258
Transitional woodland-shrub	14.92	0.244
Moors and heathland	10.94	0.179
Inland marshes	10.10	0.165
Complex cultivation patterns	9.99	0.163
Dump sites	8.35	0.137
Construction sites	7.55	0.123
Road and rail networks and associated land	5.73	0.094
Natural grasslands	5.29	0.087
Estuaries	5.11	0.084
Salt marshes	3.88	0.063
Port areas	2.30	0.038
Sparsely vegetated areas	0.69	0.011
Fruit trees and berry plantations	0.29	0.005
Totals	6114.47	100

Table 2.3. Summary statistics for rainfall chemistry at Wardlow Hay Cop [41773738] (2019)

Solute	Mean	Max	Min	Median	Concentrated mean (enrichment by evapotranspiration, x3)
Ca (mg/L)	0.76	4.03	0.11	0.45	2.28
Cl (mg/L)	2.57	15.00	0.01	1.12	7.71
Mg (mg/L)	0.17	0.89	0.05	0.10	0.51
K (mg/L)	0.11	0.37	0.04	0.09	0.33
Na (mg/L)	1.43	8.23	0.20	0.64	4.29
Conductivity (μ S/cm)	21.5	93.2	5.12	15.0	-
pH	6.32	7.21	5.46	6.40	-
NO ₃ -N (mg/L)	0.43	2.51	0.08	0.35	2.67* (11.8 as NO ₃)
NH ₄ -N (mg/L)	0.46	2.21	0.09	0.34	-
SO ₄ -S (mg/L)	0.36	1.66	0.07	0.27	1.08 (3.24 as SO ₄)
SO ₄ -S (non-marine, mg/L)	0.22	1.35	0.05	0.15	0.66 (1.98 as SO ₄)
Amount (mm)	43.6	128	0.00	44.8	-

*Assuming NH₄ oxidation to NO₃

Table 2.4. Summary statistics for rainfall chemistry at River Etherow [41243988] (2019)

Solute	Mean	Max	Min	Median	Concentrated mean (enrichment by evapotranspiration, x3)
Ca (mg/L)	0.48	3.17	0.08	0.24	1.44
Cl (mg/L)	2.79	7.17	0.30	2.10	8.37
Mg (mg/L)	0.19	0.51	0.05	0.13	0.57
K (mg/L)	0.11	0.46	0.03	0.07	0.33
Na (mg/L)	1.67	5.09	0.22	1.24	5.01
Conductivity (μ S/cm)	21.5	68.5	4.11	14.7	-
pH	6.46	7.37	5.56	6.38	-
NO ₃ -N (mg/L)	0.31	1.22	0.04	0.24	2.25* (9.96 as NO ₃)
NH ₄ -N (mg/L)	0.44	1.15	0.12	0.38	-
SO ₄ -S (mg/L)	0.32	1.38	0.09	0.27	0.96 (2.88 as SO ₄)
SO ₄ -S (non-marine, mg/L)	0.21	0.69	0.07	0.16	0.63 (1.89 as SO ₄)
Amount (mm)	40.8	156	3.96	29.7	-

*Assuming NH₄ oxidation to NO₃

Table 2.5. Rainfall chemistry at Jenny Hurn monitoring site, Lincolnshire [48163986] for 2001 (from Stuart et al., 2004)

SEC (μ S/cm)	SO ₄ (mg/L)	NO ₃ (mg/L)	NH ₄ (mg/L)	Na (mg/L)	Mg (mg/L)	Ca (mg/L)	Cl (mg/L)	K (mg/L)
30.3	2.8	2.3	0.98	0.90	0.15	0.41	2.1	0.08

3 Data acquisition and handling

3.1 GROUNDWATER SAMPLING AND ANALYSIS

3.1.1 Sampling procedure

A total of 19 groundwater samples were collected across the study area between January and December 2019. Sampling locations were selected from the Environment Agency’s national abstraction licence database (NALD), and covered both the unconfined and confined Sherwood Sandstone aquifer in the area (Figure 3.1). Samples were obtained at sites where pumping infrastructure was already installed, which included fourteen public-supply boreholes, and five private boreholes. Samples were collected from sample taps or discharge points prior to any water treatment.

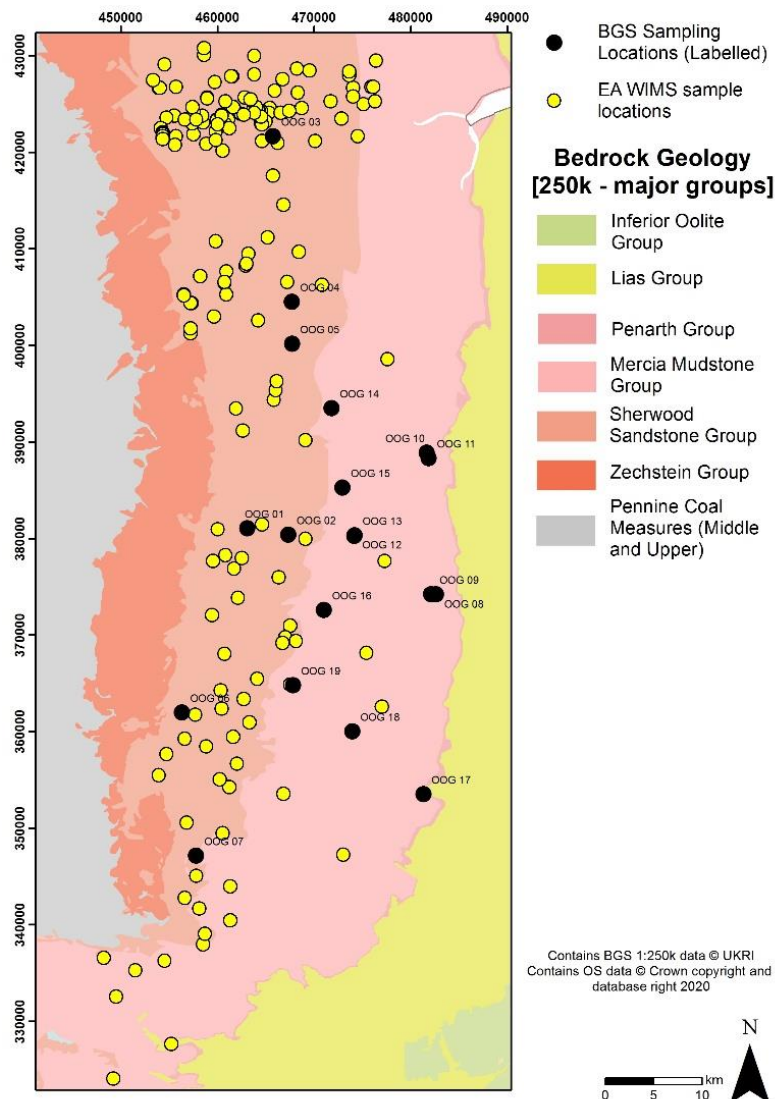


Figure 3.1. Sampling locations as part of the BGS field sampling campaign (black) across the investigation area, alongside the selected EA WIMS locations (yellow). BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

Measurements taken at each site prior to sampling included pH, redox potential (Eh), dissolved oxygen (DO), specific electrical conductance (SEC) and temperature. These were recorded from a saturated flow cell, to prevent aeration. Alkalinity was also measured on site by titration against H₂SO₄. Samples were collected once all water-quality parameters had stabilised.

Samples for major- and trace-element analysis were collected in rinsed polyethylene bottles, filtered to $<0.2\ \mu\text{m}$ using an in-line reusable filter holder. 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. A dedicated filtered aliquot was also collected unacidified for NH_4 analysis.

Samples for organic constituents were collected directly from the sample tap/point where possible, to minimise contact with additional plastic tubing and potential contamination.. Samples for non-purgeable organic carbon (NPOC) analysis were filtered through a $0.45\ \mu\text{m}$ silver-impregnated filter and collected in pre-cleaned glass vials. Additional samples were collected for volatile and semi-volatile organic carbons (VOC and SVOC), total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAH), and semi-quantitative screens for a number of modern synthetic organic compounds.

Samples for dissolved gas analysis (CH_4 and CO_2) were collected inline and under pump pressure using a double-valved steel pressure vessel. Samples for Rn analysis were collected from flowing taps in glass bottles.

Samples were also taken for analysis of the stable isotopes $\delta^{13}\text{C}$ in inorganic carbon and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in water. These were collected in rinsed HDPE bottles, with samples for $\delta^{13}\text{C}$ filtered through a $0.2\ \mu\text{m}$ filter. Five groundwater samples from the confined aquifer were also collected for analysis of ^{14}C in dissolved inorganic carbon.

3.1.2 Sample analysis

Analysis of major cations and trace elements was carried out by ICP-MS and of anions by ion chromatography. Additional methods included colorimetry for NH_4 , gas chromatography for dissolved CH_4 and CO_2 , RAD7 radon detector for radon, and mass spectrometry for the stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{13}\text{C}$). NPOC was determined by combustion using an organic carbon analyser. Radiocarbon samples were prepared by conversion to CO_2 at the RCD Lockinge Laboratory and sent to a specialist laboratory for analysis by accelerator mass spectrometry.

Samples for Total Petroleum Hydrocarbons (TPH) were solvent-extracted and hydrocarbons with carbon banding in the range C8-C40 determined by GC-FID. Gasoline Range Organics (GRO) in the carbon chain range of C4-12 were determined by headspace GC-FID. SVOCs were solvent-extracted and analysed by gas chromatography-mass spectrometry (GC-MS).

VOC determination was by direct aqueous injection purge-and-trap GC-MS, whilst PAH determination was by solvent extraction followed by GC-MS. Samples for synthetic organic compounds (e.g. pesticides/herbicides/pharmaceuticals) were analysed by a semi-quantitative target-based screening process using GC-MS and LC-MS.

Analytical charge imbalances were within 3% for all collected samples.

3.2 ENVIRONMENT AGENCY DATA

Extracts of data were taken from the Environment Agency Water Quality Archive (WIMS) for sites located either within the Sherwood Sandstone or Mercia Mudstone surface expressions. The geographical extent of the WIMS database selection is shown in Figure 1.1, with the surface expressions of the SSG and MMG shown in Figure 2.2. Extracted data comprised all groundwater samples collected between January 1990 and November 2018, with the most recent data for each sample site selected for mapping and summary statistical evaluation. Filter criteria for the WIMS dataset are shown in Appendix 2 (Table A. 1 and Table A. 2). A total of 231 sample points (including the BGS field samples) were used for the following baseline assessment and included 76 inorganic parameters, 141 organic parameters, and 3 dissolved gases.

Charge imbalances were checked to assess any obvious problems in data quality. Imbalances were typically less than 10% although balances were not calculable in cases where major-ion analyses

for individual samples were incomplete. Analyses were not omitted for samples where major-ion suites were incomplete.

3.3 STATISTICAL SUMMARY DATA

Data collected as part of the new BGS sampling campaign were combined with selected groundwater chemical data from the WIMS database for computation of statistical summaries. For many of the trace elements and most organic species, concentrations were below analytical detection limits. As the data reported were obtained from more than one laboratory and in some cases using more than one method, the detection limits for any given analyte varied. Such left-censored datasets require care with statistical handling. Statistics were calculated using the NADA package in R (Helsel, 2005). Methods used for censored data were a combination of Kaplan-Meier (K-M) and regression-on-order statistics (ROS), both of which are suitable for datasets with multiple detection limits (Helsel, 2005; Lee and Helsel, 2005b, 2007).

The K-M method calculates the rank of the dataset, placing each non-detect at its detection limit before the ranking. The summary statistics are estimated using the empirical cumulative distribution function of the ranked data. The method may produce a small positive bias in the mean but is considered suitable for datasets where fewer than 50% of the data are censored (Bearcock and Smedley, 2012; Helsel, 2005).

The ROS method (Helsel and Cohn, 1988; Lee and Helsel, 2005b) is a robust semi-parametric method which has been evaluated as one of the most reliable for producing summary statistics of multiply-censored data (Shumway et al., 2002). The method is particularly useful for small datasets ($n < 30$) where other methods may become unreliable. It is also particularly useful where the non-detects comprise up to 80% of the data. ROS is a probability-plotting and regression approach that models censored distributions using a linear regression of observed concentrations against their normal quantiles (“order statistics”) (Lee and Helsel, 2005a). The method firstly computes Weibull-type probability distributions including both censored and non-censored data. The formula is designed to account for multiply-censored data. The plotting positions of the uncensored observations and their normal quantiles define a linear regression. This regression model can then be used to estimate the concentrations of the censored observations as a function of their normal quantiles (Lee and Helsel, 2005a). The last stage in the algorithm is to combine the observed uncensored values with the modelled censored values to produce estimations of the summary statistics. This combination of observed and modelled censored values creates a method that is more resistant to non-normality of errors and reduces any transform biases (Lee and Helsel, 2005a).

Lee and Helsel (2005a, 2005b) noted that where the dataset contains >80% non-detects, estimated summary statistics are tenuous and data evaluation should be limited.

The summary statistics in this report were computed following the recommendations of (Helsel, 2005): where non-detects represented <50% of analyte data, the K-M method was used; where non-detects represented between 50% and 80% of analyte data, ROS was used; where non-detects were >80%, only ranges were quoted.

In the BGS Baseline report series (BGS, 2016), the 95th percentile of a data distribution was used as an upper cut-off for outlier compositions for most analytes. As discussed in the baseline report series documents, this choice of percentile is somewhat arbitrary and other percentiles have been used elsewhere in the literature. The 90–95th percentile was used by Lee and Helsel (2005a) and the 97.7th percentile by Langmuir (1997). While using percentiles as an upper limit provides a simple definition of outliers, the method clearly has limitations. For some analytes, data presented above a given threshold may present as anomalous, when they can in fact represent natural baseline concentrations. The 95th percentile merely represents a simplification to exclude the upper 5% of the data distribution and has been used 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. The 95th percentile value has also been determined in this report as a useful estimate of upper baseline concentrations. The summary statistics are used in combination with developing a conceptual understanding of the regional and temporal variations in groundwater chemistry and the processes controlling them. These are discussed in Sections 4 and 5.

4 Regional groundwater chemistry

The following section presents the statistical and analytical results from the combined WIMS data and the recent field sampling conducted by the BGS. It summarises the results for both the confined and unconfined aquifer sections. The statistical summary data are presented in Table 4.1.

4.1 FIELD-DETERMINED PARAMETERS

Temperatures for the aquifer range between 4.1 °C to 17.7 °C, with a median of 11.3 °C. The 5th to 95th percentile range is 9.0 °C to 16.9 °C (Figure 4.1a). Temperatures are typically greater in the confined setting to the easternmost extremities of the study area (Figure 4.2a); slightly higher temperature can also be seen in parts of the north-west where the aquifer is partially confined by Quaternary deposits.

Groundwater pH ranges between 6.9 and 8.7, with a median of 7.6. The 5th to 95th percentile range is 7.1 to 8.2 (Figure 4.1b). There is no clear distinction of pH between the MMG-confined and unconfined settings of the Sherwood Sandstone (Figure 4.2b). The pH is marginally lower to the north of the study area, around the Doncaster area. From Mansfield through to Worksop there is a band of higher (>8.0 pH) values.

Dissolved oxygen (DO) results for the aquifer are recorded between 0.03 mg/L to 14.3 mg/L, with a median of 6.9 mg/L. The 5th to 95th percentile range is 0.2 mg/L to 11.3 mg/L (Figure 4.1c). Redox potential (Eh) has a range of 36.7–478 mV with a median of 100 mV. The 5th to 95th percentile range is 54.6–431 mV. There is a clear grouping of values in both the low Eh (<100 mV), and high Eh (>250 mV), with an absence of values between (Figure 4.1d). Both DO and Eh highlight differences between redox conditions in MMG-confined and unconfined settings, showing a large range in values. Both DO and Eh are low in the confined portion of the aquifer, indicating prevalence of reducing conditions (Figure 4.2c and d), and become more oxic in the unconfined section.

Specific electrical conductance (SEC) ranges between 216 µS/cm and 3270 µS/cm, with a median of 781 µS/cm. The 5th to 95th percentile range is 314 µS/cm to 2590 µS/cm (Figure 4.1e). SEC is typically greatest in the north of the study area, parts of the unconfined aquifer and on the eastern part of the confined aquifer (Figure 4.2e). The data show a number of locations in the MMG-confined aquifer where the SEC is <500 µS/cm.

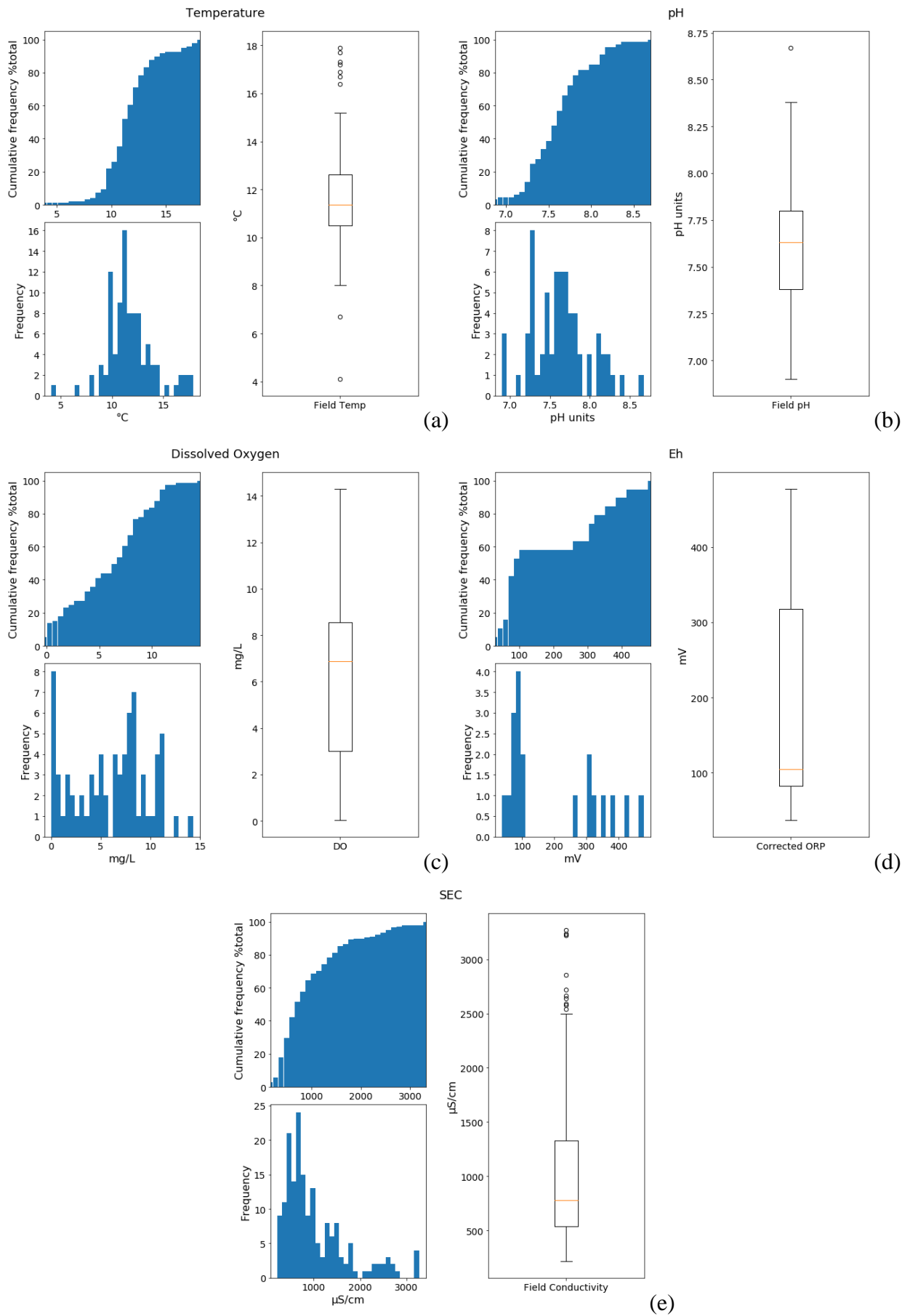
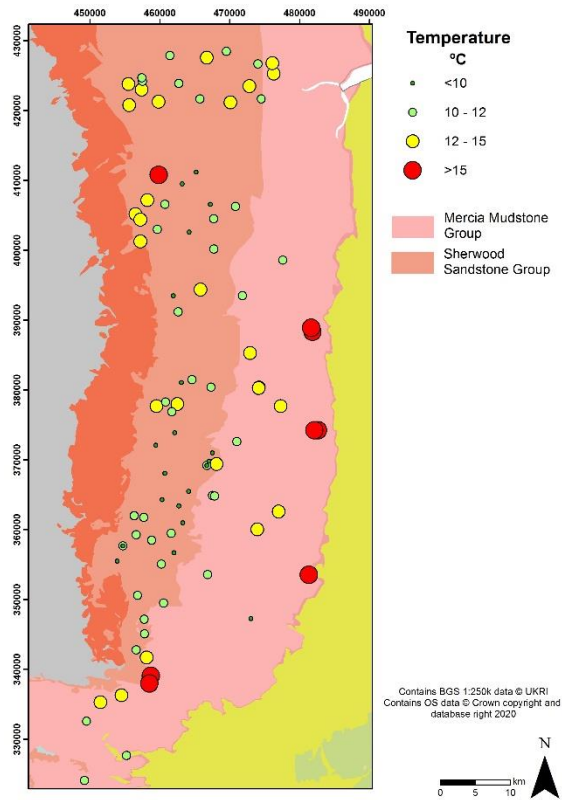
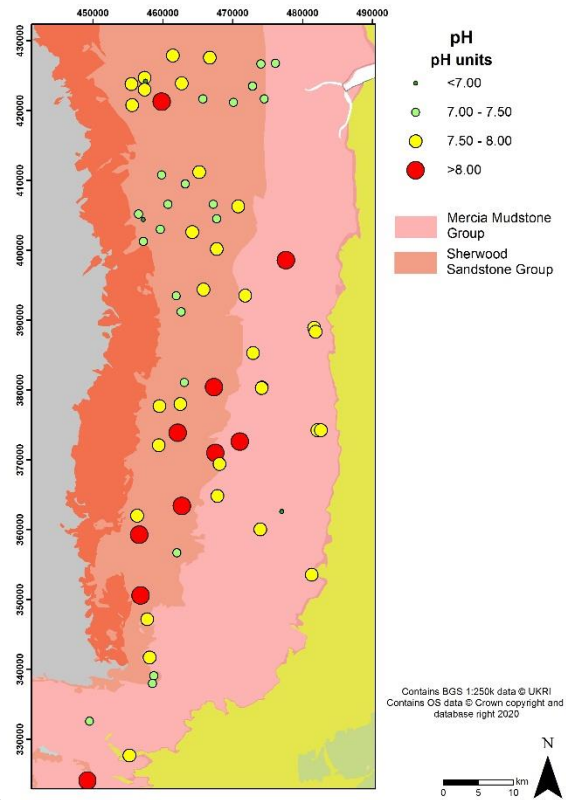


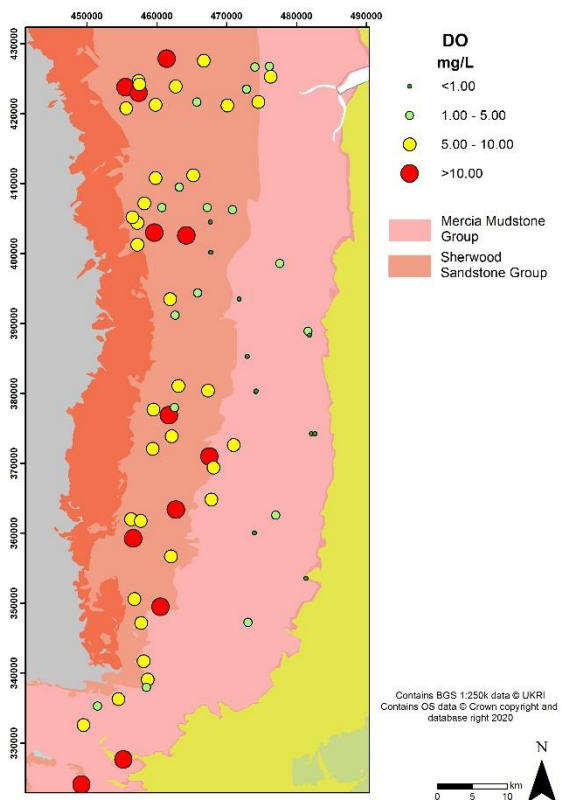
Figure 4.1. Statistical summary for field parameters; (a) temperature, (b) pH, (c) dissolved oxygen, (d) Eh and (e) specific electrical conductance (SEC)



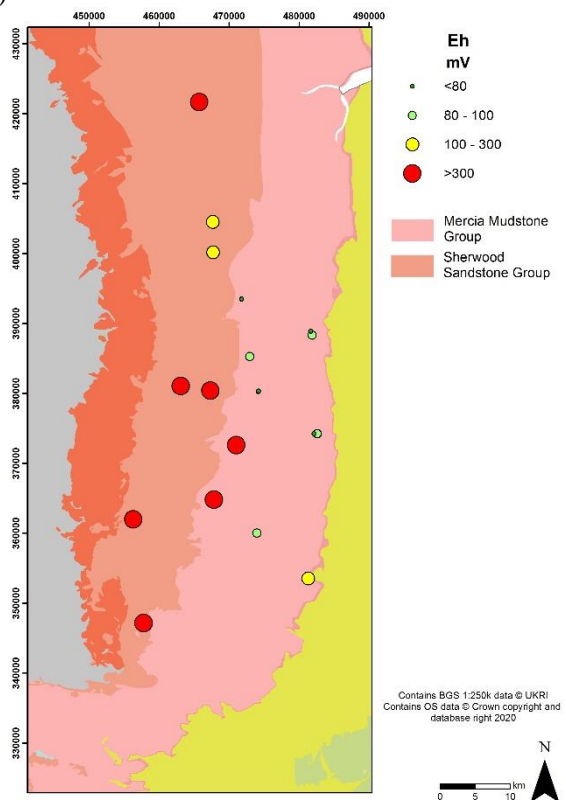
(a)



(b)



(c)



(d)

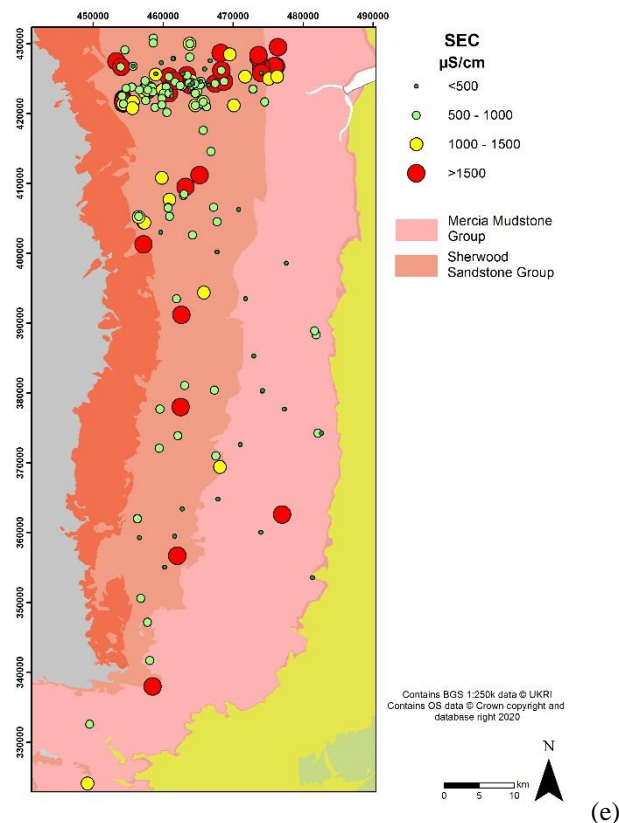


Figure 4.2. Geological maps showing groundwater temperature (a), pH (b), dissolved oxygen (DO) (c), Eh (d), specific electrical conductance (e). A full geological legend be seen in Figure 2.2. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

4.2 MAJOR IONS

The calcium concentration ranges from 13.3 mg/L to 579 mg/L, with a median of 69.7 mg/L. The 5th to 95th percentile range is 23.6 mg/L to 248 mg/L (Figure 4.3a). Calcium concentrations are typically greater in the northern half of the unconfined setting, with typically low (<50 mg/L, 50–100 mg/L) concentrations in the confined setting (Figure 4.3a).

Magnesium concentrations range from 4.51 mg/L to 161 mg/L, with a median of 31.5 mg/L. The 15th to 95th percentile range is 13.4 mg/L to 70.6 mg/L. Magnesium concentrations are generally more variable in the unconfined setting but with often high values (>45 mg/L). The confined setting has predominantly low concentrations of Mg albeit with a few exceptions greater than 45 mg/L (Figure 4.3b).

Sodium concentrations range from 2.76 mg/L to a maximum at 391 mg/L, with a median of 14.7 mg/L. The 5th to 95th percentile range is 4.66 mg/L to 164 mg/L. Sodium occurs at greater concentrations in some parts of the northern unconfined aquifer, but typically shows a relatively low concentration across the larger part of the aquifer. A few isolated high concentrations occur around the Nottingham and Doncaster areas (Figure 4.3c).

The median potassium concentration is 3.91 mg/L, with a range of 0.948 to 100 mg/L. The 5th to 95th percentile range is 1.59 mg/L to 13.3 mg/L. Potassium is consistently in the 3–9 mg/L range within the confined setting, with a notable group in the centre of the study area in this range. Concentrations in the unconfined setting vary, predominantly in the <3 mg/L to 15 mg/L range, with two sites >15 mg/L (Figure 4.3d).

Chloride concentrations range from 4 mg/L to 471 mg/L, with a median of 46 mg/L. The 5th to 95th percentile range is 10 mg/L and 296 mg/L. Chloride concentrations are greater in the unconfined portion of the aquifer, and are highest in the western edge and around the Humber estuary in the north. Concentrations are predominantly in the 50–200 mg/L range with a few sites greater than 200 mg/L. The concentration in the confined setting is <50 mg/L (Figure 4.3e).

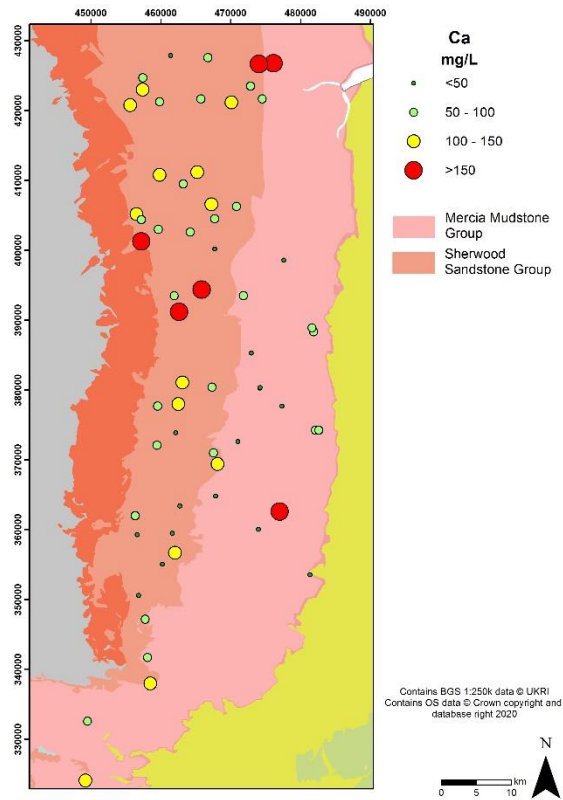
Alkalinity as HCO_3 (bicarbonate) concentrations have a median of 217 mg/L, with a range of <6 mg/L to 798 mg/L. The 5th to 95th percentile range is 84.1 mg/L to 524 mg/L. Alkalinities are elevated at the fringe of the MMG-confined aquifer and within the confined setting, in the 150–500 mg/L range. Concentrations are in the 250–500 mg/L range in the northern half of the unconfined aquifer (Figure 4.3f).

Median sulphate (SO_4) concentrations are 93.2 mg/L, with a total range between <2 mg/L and 1810 mg/L. The 5th to 95th percentile range is 2.8 mg/L to 963 mg/L. Sulphate concentrations are elevated in the unconfined aquifer, but can also be relatively high in a few areas downgradient in the confined aquifer, especially towards the easternmost extent of the study area (Figure 4.3g).

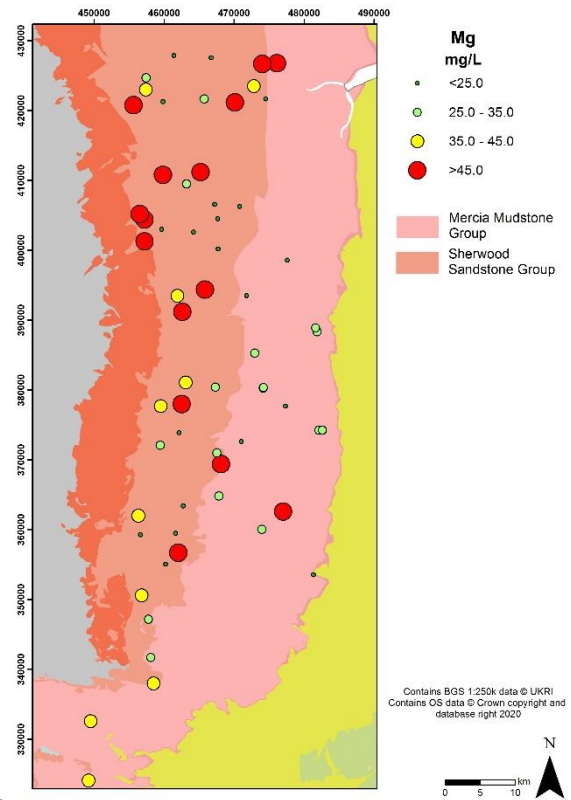
Nitrate concentrations have a median value of 20.1 mg/L with a range of <0.06 mg/L to 240 mg/L. The 25th to 95th percentile range is 0.864 mg/L to 155 mg/L. Nitrate concentrations are considerably higher in the unconfined aquifer, being greater than 25 mg/L as NO_3 , and often greater than 50 mg/L. Groundwater in the Nottingham and Mansfield areas has some of the highest concentrations. Sites in the confined aquifer have concentrations <0.9 mg/L (Figure 4.3h). The skewed distribution of the data are also illustrated in the cumulative-probability plot in Figure 4.13. The different populations reflect different concentrations between the confined and unconfined aquifers.

Major-ion concentrations are summarised in a Piper Plot in Figure 4.4. The water type of the Sherwood Sandstone is primarily Ca-Mg- HCO_3 , with a few of Mg- HCO_3 hydrochemical type points. Some samples also trend towards Na+K, SO_4 or Cl enrichments. Major-ion distributions are also plotted on cumulative probability plots in Figure 4.5.

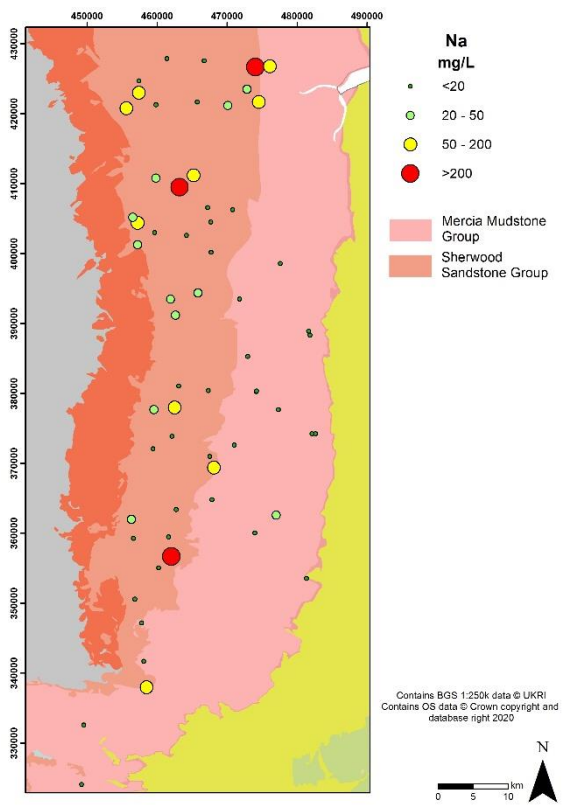
For silica (SiO_2), the median concentration is 8.71 mg/L, with a range of 5.37–17.9 mg/L. The 5th to 95th percentile range is 6.5 mg/L to 15.4 mg/L. The northern half of the study area has more sites with a value in the range of 10–13 mg/L, or even >13 mg/L. South of Doncaster, most sites show silica concentrations in the range of 7–10 mg/L. Values appear consistent across both confined and unconfined parts (Figure 4.3i). The range of concentrations for silica is small and the cumulative-probability distribution (Figure 4.13) is log-linear. This suggests a mineral solubility control, likely to be quartz.



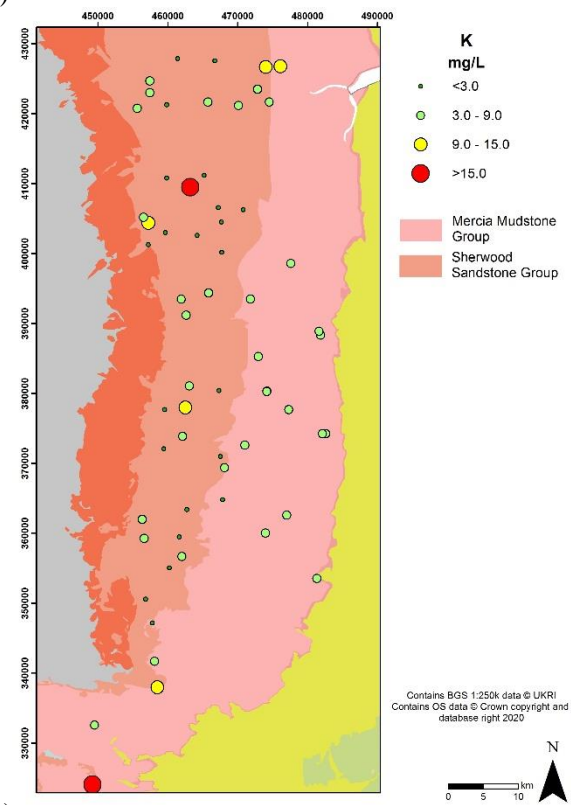
(a)



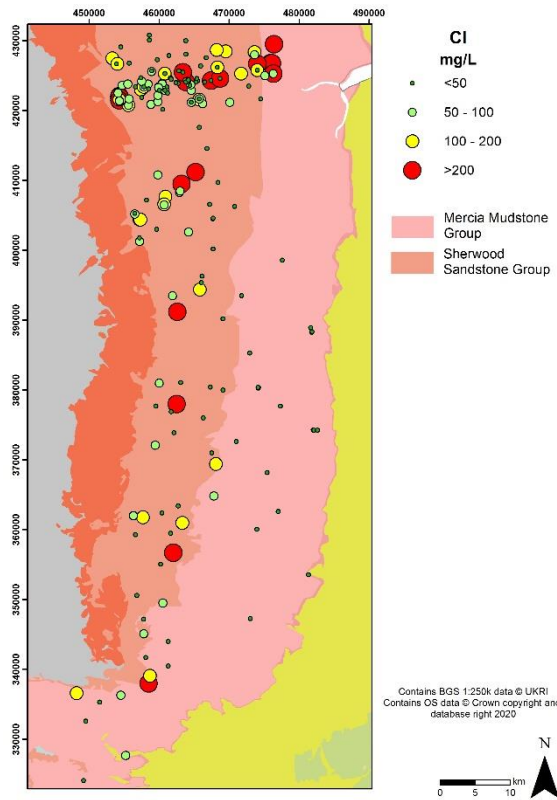
(b)



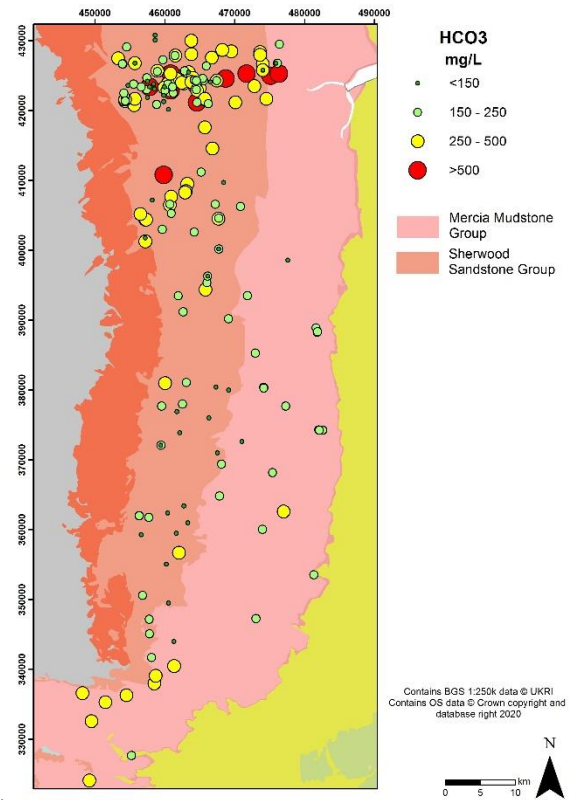
(c)



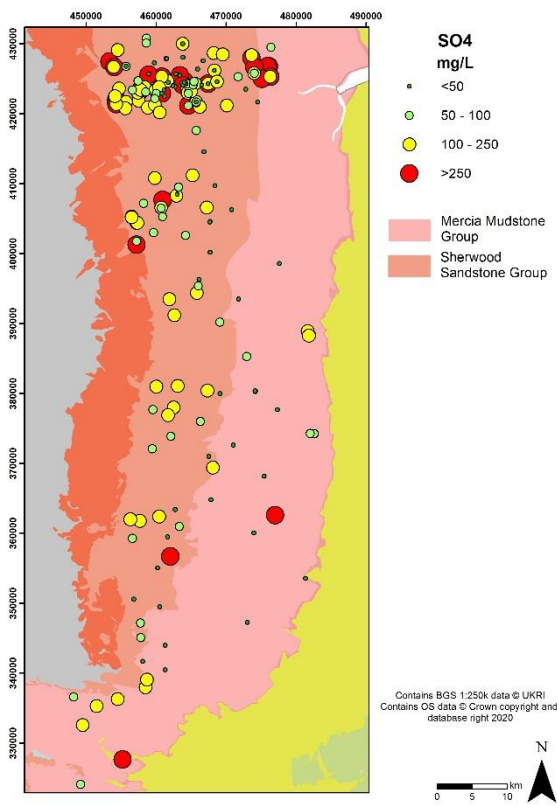
(d)



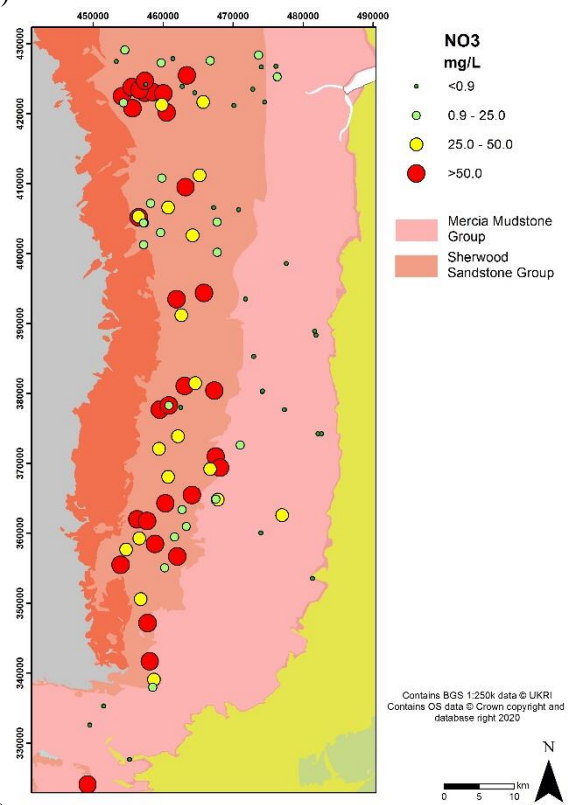
(e)



(f)



(g)



(h)

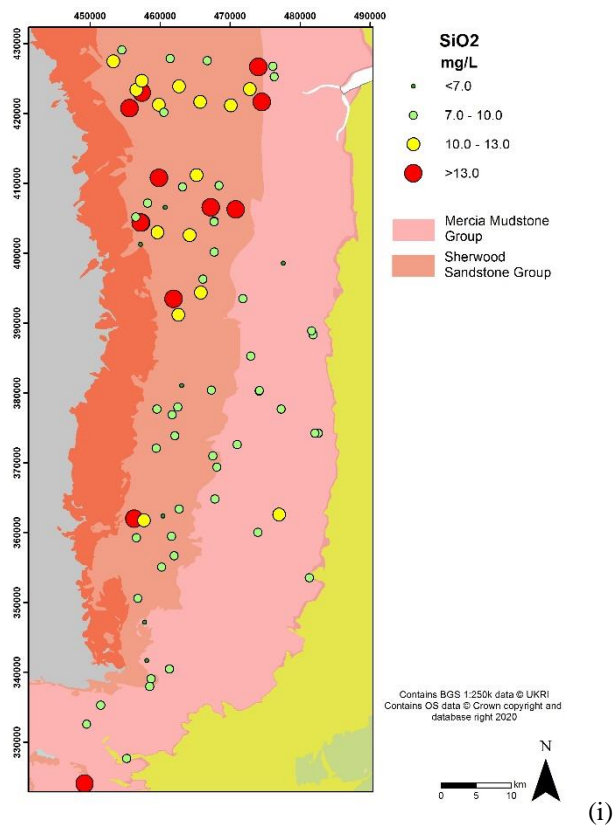


Figure 4.3. Geological maps showing the distributions of the major ions (a) calcium, (b) magnesium, (c) sodium, (d) potassium, (e) chloride, (f) alkalinity as bicarbonate, (g) sulphate, (h) nitrate, and (i) silica. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

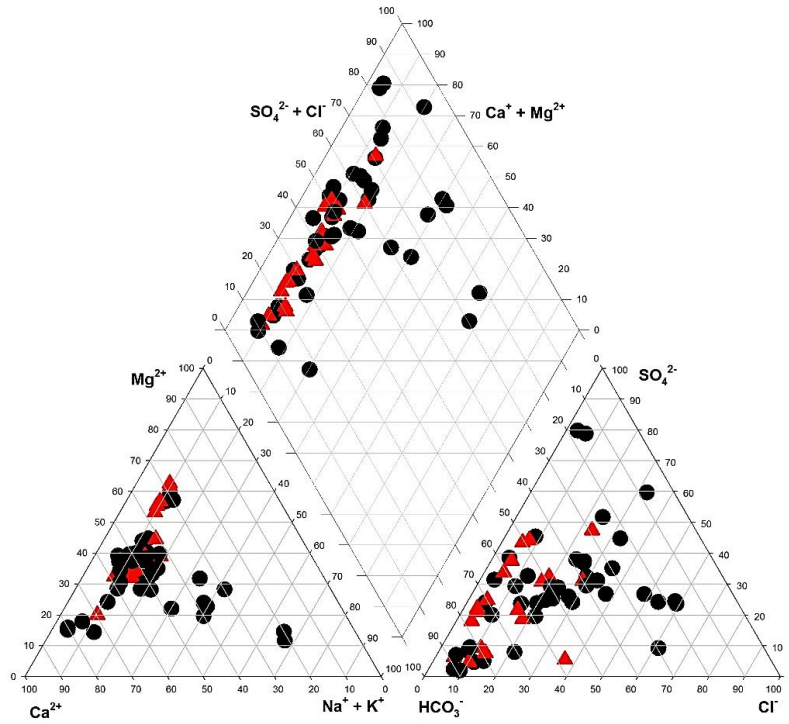


Figure 4.4. Piper plot of EA-WIMS (black) and BGS (red) groundwater samples from the Sherwood Sandstone Group (for full analytical suites only)

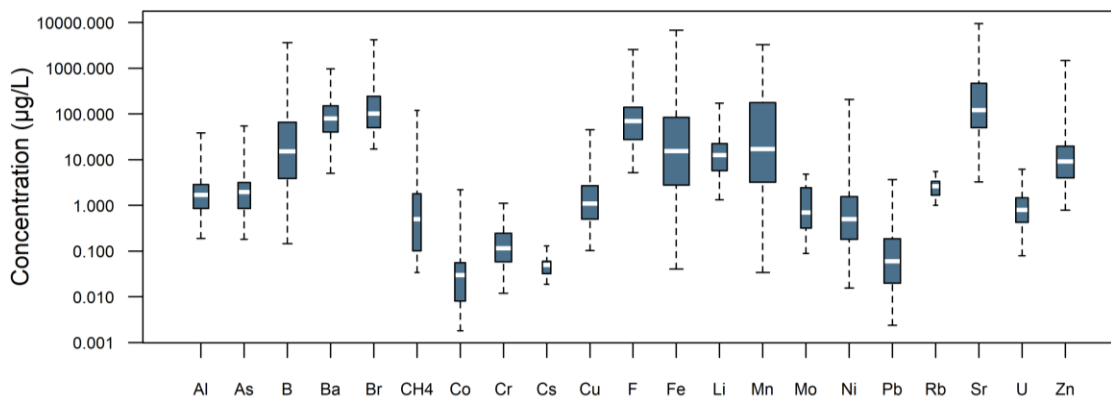
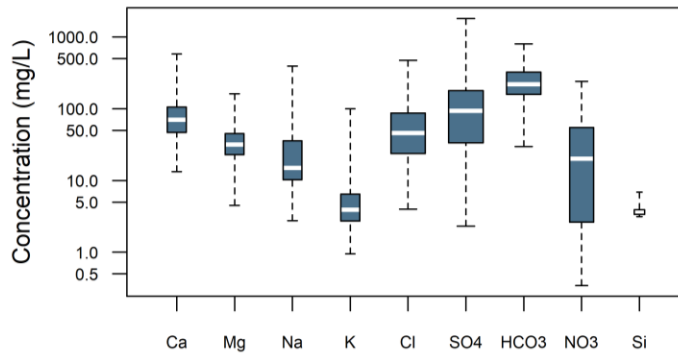


Figure 4.5. Summary box plots for the major, selected minor and trace elements and dissolved methane in groundwater from the Sherwood Sandstone, includes WIMS and BGS data. Whiskers depict the total range, hinges the interquartile range, central white line the median; box widths are proportional to the square root of the number of analyses

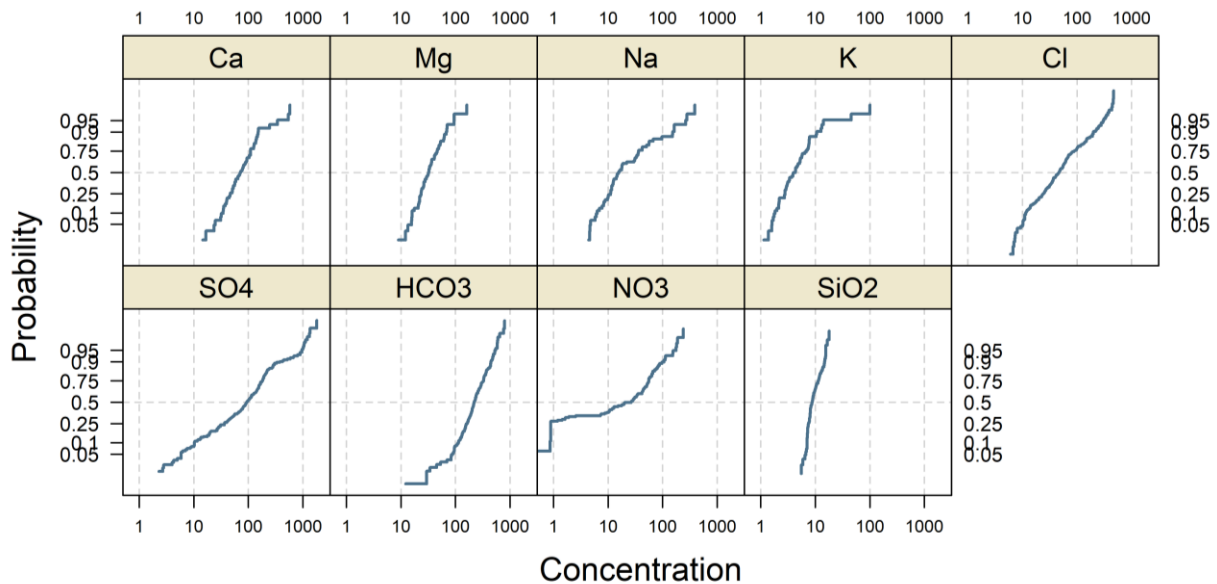


Figure 4.6. Cumulative-probability plots for major ions and silica (mg/L) in groundwater from the Sherwood Sandstone aquifer

4.3 MINOR AND TRACE ELEMENTS

4.3.1 Phosphorus

Phosphorus (reactive)/orthophosphate (as P) has a median concentration of 0.009 mg/L, with a range of <0.01 mg/L to 1.3 mg/L. The 5th to 95th percentile range is 0.00073 mg/L to 0.112 mg/L. Concentrations above 0.05 mg/L occur in the unconfined setting, but values are clearly low across the aquifer (Figure 4.7a). Results for total phosphorus (as P) are presented separately. These are from BGS data, which are from different sites, for fewer samples, and using a different analytical method (ICP-MS). Concentrations of total dissolved P have a median of 0.006 mg/L, with a range of <0.006–0.05 mg/L (Figure 4.7b). The highest frequency of results are in the 0.006–0.014 mg/L range. As with orthophosphate, the higher concentrations appear in groundwater predominantly from the unconfined section of the aquifer.

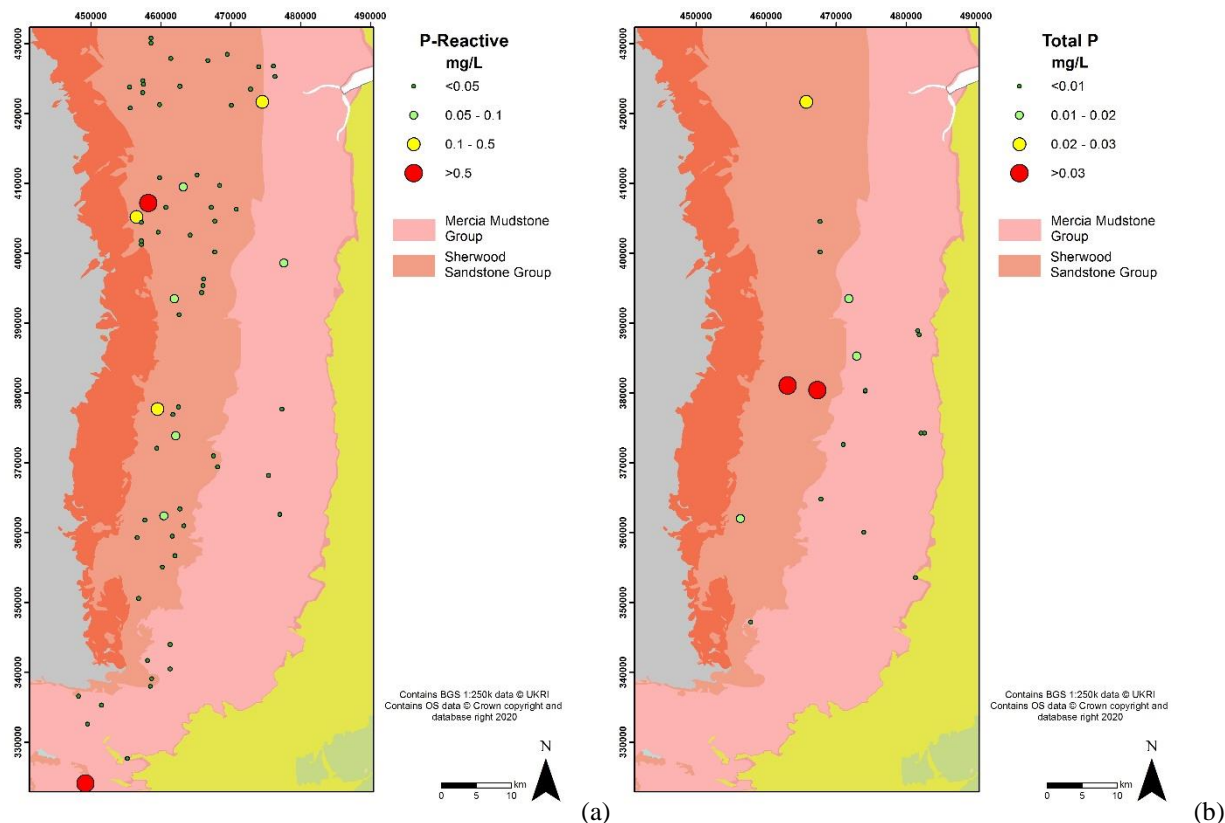


Figure 4.7. Geological map showing distribution of (a) reactive phosphorus (from WIMS only) and (b) total phosphorus as P (from BGS sampling) in groundwater

4.3.2 Halogens

Bromide has a median concentration in the groundwater of 0.102 mg/L, with a range of <math><0.05</math>–4.2 mg/L. The 5th to 95th percentile range is 0.022 mg/L to 2.7 mg/L. Bromide concentrations are notably higher in the unconfined setting (0.10–0.30 mg/L), with a number of sites >0.30 mg/L. There is an area of low groundwater bromide concentration (<math><0.05</math> mg/L) around Workshop and Gainsborough within the confined aquifer. High concentrations (>0.30 mg/L) occur around Mansfield and Nottingham, and extend into the fringe of the confined section (Figure 4.8a).

Fluoride has a median concentration of 0.07 mg/L, with a range of <math><0.02</math>–2.55 mg/L. The 5th to 95th percentile range is 0.023–0.55 mg/L. Fluoride concentrations are between 0.05 mg/L and 0.50 mg/L from Doncaster towards the north, with a drop in concentrations towards Nottingham (<math><0.05</math> mg/L), before a rise back to 0.05–0.50 mg/L south of Nottingham. Low concentrations are observed in both confined and unconfined sections of the aquifer (<math><0.50</math> $\mu\text{g/L}$; Figure 4.8b).

Iodine has a median concentration of 2.4 $\mu\text{g/L}$, with a range of <math><3</math>–29 $\mu\text{g/L}$. The 5th to 95th percentile range is 1.3–14.2 $\mu\text{g/L}$. A number of sites in the unconfined aquifer have concentrations >6 $\mu\text{g/L}$; such concentrations are not observed in the confined section. A number of sites in the confined aquifer have concentrations of 3.0–4.5 $\mu\text{g/L}$. Results <math><3.0</math> $\mu\text{g/L}$ occur across much of the aquifer in both confined and unconfined settings (Figure 4.8c).

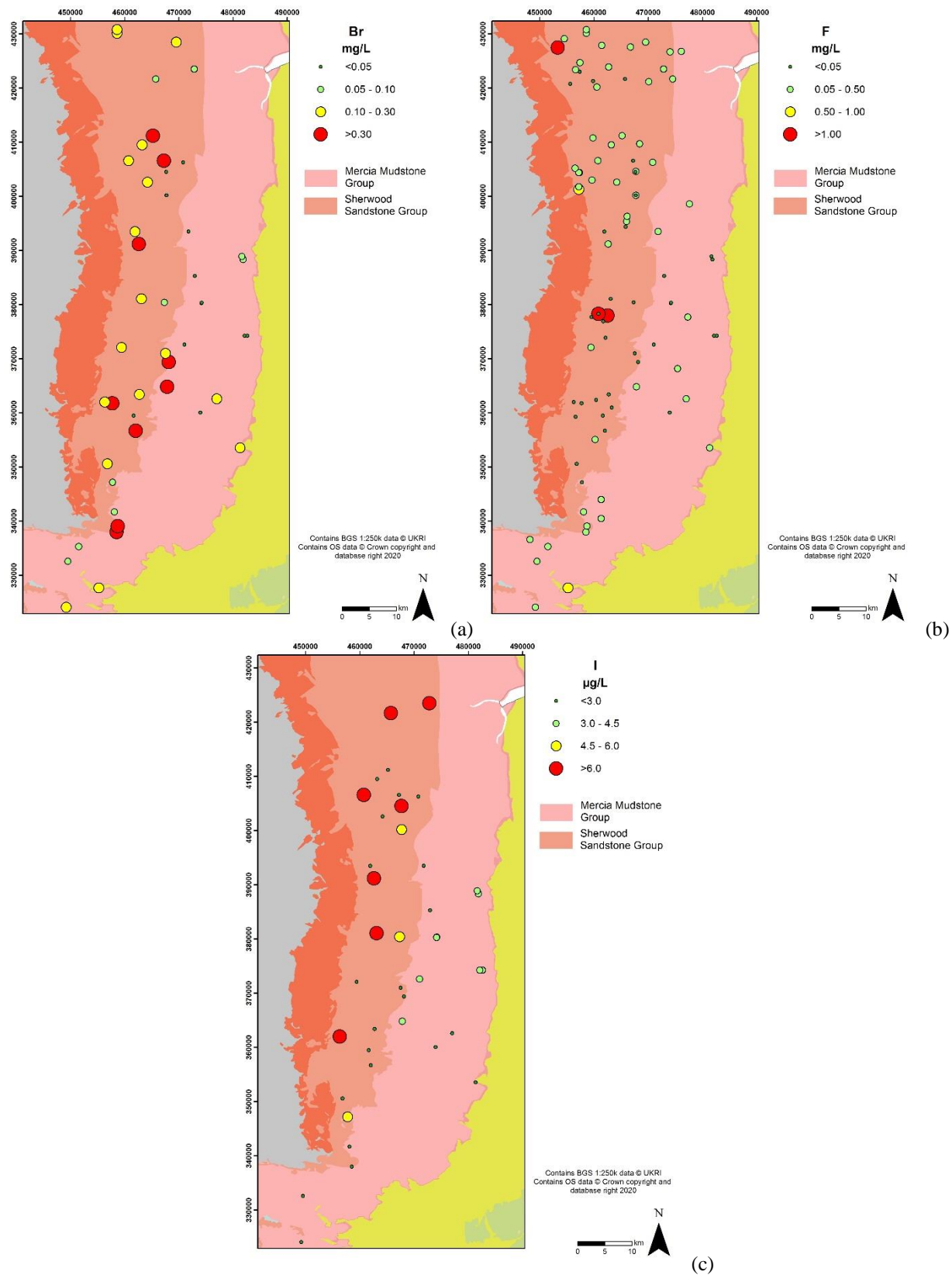


Figure 4.8. Geological maps showing distributions of bromide (a), fluoride (b) and iodine (c) in groundwater. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

4.3.3 Alkaline-earth metals

Barium has a median concentration of 78.9 µg/L, and a range of <10–960 µg/L. The 5th to 95th percentile range is 13.8 µg/L to 455 µg/L. A cluster of high barium concentrations (>150 µg/L) can be observed running south from Worksop towards Nottingham, straddling both the confined and unconfined aquifer. A band north of Worksop towards Gainsborough shows lower concentrations (typically <100 µg/L) until a rise in concentrations around Doncaster in the unconfined setting. South of Nottingham, concentrations are also <100 µg/L. Samples within the confined setting are constrained to much of the central portion of the study area, with notable gaps to the east of Nottingham and south of the Humber Estuary (Figure 4.9a).

Few data are available for caesium in the groundwater. Of those available, the median concentration is 0.05 µg/L, with a range of <0.04 µg/L to 0.13 µg/L. The 50th to 95th percentile range is 0.05 µg/L to 0.088 µg/L. Caesium concentrations are greater in the confined setting, with concentrations of between 0.04 µg/L and 0.08 µg/L or higher in the central part of the study area. From Worksop south towards Nottingham, concentrations are typically less the 0.04 µg/L. The data in the north are especially limited (Figure 4.9b).

Strontium has a median concentration of 119 µg/L, and a range of <20 µg/L to 9470 µg/L. The 5th to 95th percentile range is 24.4–3710 µg/L. Strontium concentrations are typically <50 µg/L in the southern half of the unconfined setting, but rise to >150 µg/L in the northern half. Values in the confined setting are dominantly in the range of 150–450 µg/L, or even >450 µg/L. There are a cluster of sites with concentrations >450 µg/L to the north of the study area in proximity to the Humber River. Concentrations are typically lower north of Nottingham/around Mansfield, gradually increasing towards the north within the unconfined aquifer (Figure 4.9c).

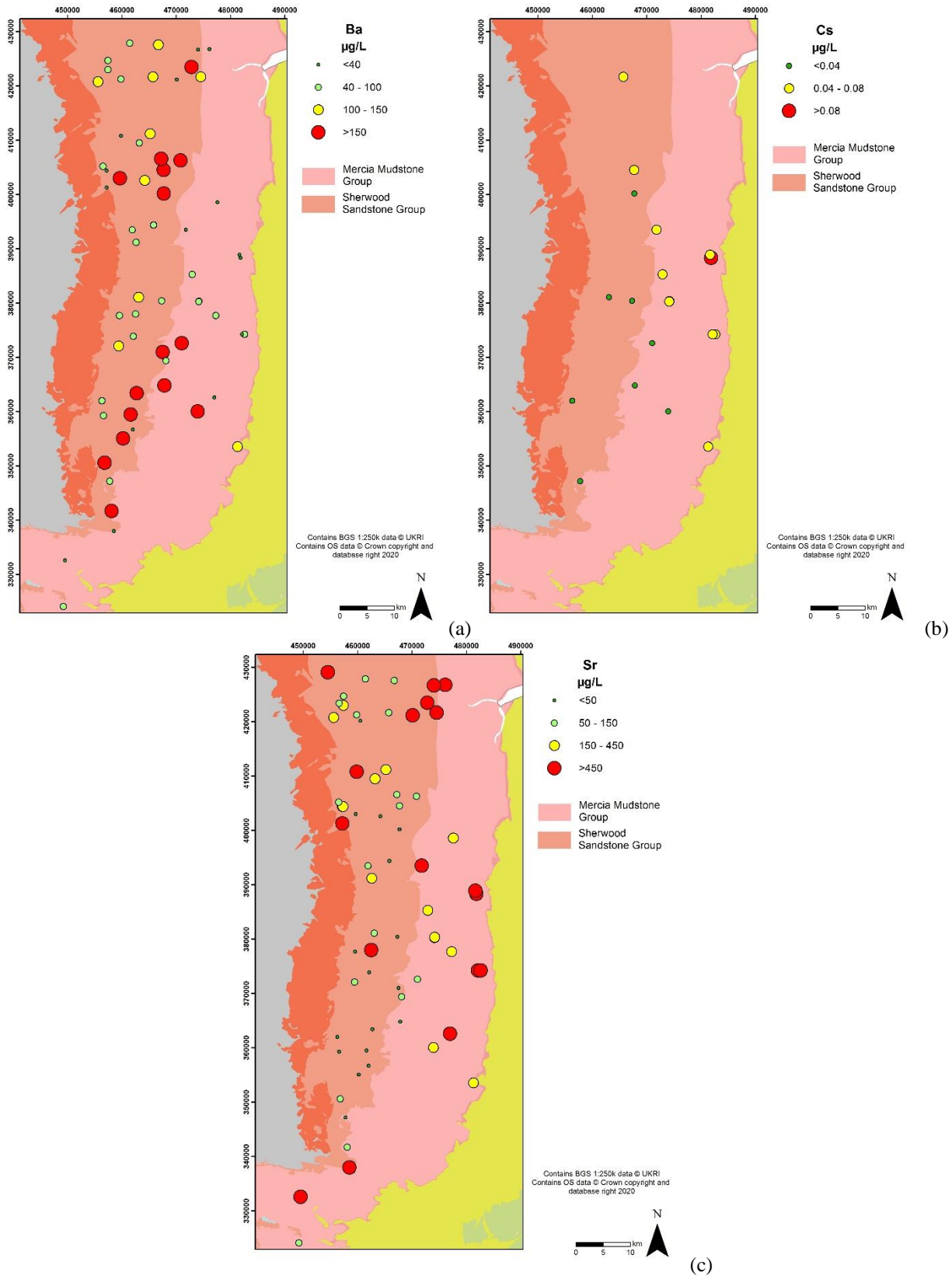


Figure 4.9. Geological map showing distributions of barium (a), caesium (b) and strontium (c) in groundwater. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

4.3.4 Alkali metals

Lithium has a median concentration of 12.6 µg/L, with a range of <7 µg/L (below detection limit) to 171 µg/L. The 5th to 9th percentile range is 2.35–59.1 µg/L. Lithium concentrations appear to be within the 30–50 µg/L range across much of the aquifer, with only three locations showing values above 50 µg/L. Within the centre of the study area, there are more sites with values in the 7.0–30 µg/L range, with a few locations of greater concentrations (Figure 4.10a).

Rubidium has a median concentration of 2.63 µg/L, with a range of 1.0 µg/L to 5.53 µg/L. The 5th to 90th percentile range is 1.01 µg/L to 5.52 µg/L. Rubidium shows a clear distinction of higher concentrations in the confined setting, with results above 3 µg/L, but there are a limited number of data points. Values in the unconfined setting are below 3 µg/L. The sample points are predominantly focussed around the central part of the study area, and comprised only BGS recent samples (Figure 4.10b).

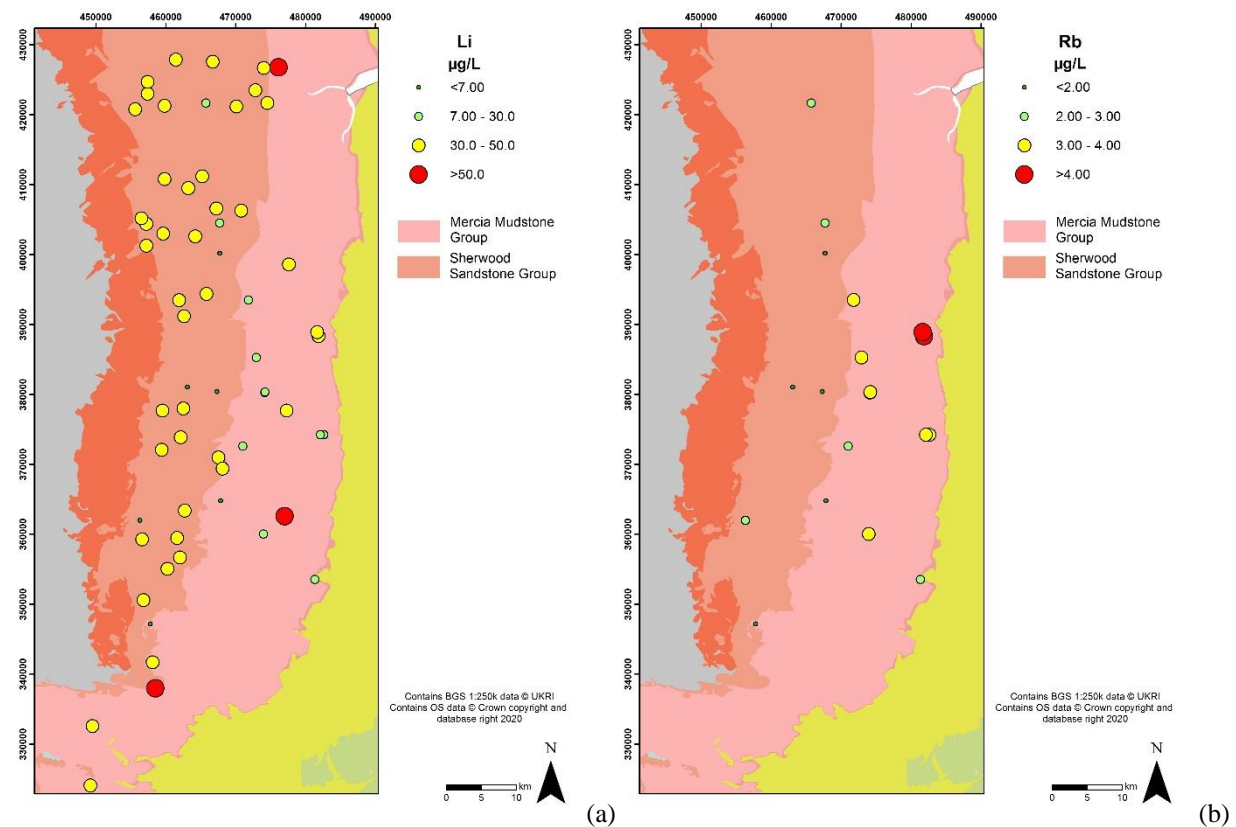


Figure 4.10. Geological map showing distributions of lithium (a) and rubidium (b). BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

4.3.5 Iron and manganese

Iron has a median concentration of 15.3 µg/L, with a range of <10 µg/L to 6750 µg/L. The 5th to 95th percentile range is 0.303 µg/L to 1570 µg/L. Iron concentrations in the central confined area are within the 100–200 µg/L range, whilst the unconfined setting shows a greater degree of variation. The north of the study area shows a notable mix of concentrations around the Humber Estuary, with further hotspots near Doncaster and to the south of Nottingham, in the fringe of the confined aquifer (Figure 4.11a). Between Nottingham and Worksop, concentrations are low, <40 µg/L. Concentrations across the aquifer are predominantly <40 µg/L, with a total number of 119 results.

Manganese has a median concentration of 17.9 µg/L, with a range of <0.04 µg/L to 3270 µg/L. The 10th to 95th percentile range is 0.2 µg/L to 1160 µg/L. Manganese concentrations increase towards the north (>200 µg/L), from Doncaster up to the Humber Estuary, but are <50 µg/L in much of the confined setting, and the southern portion of the unconfined aquifer (Figure 4.11b).

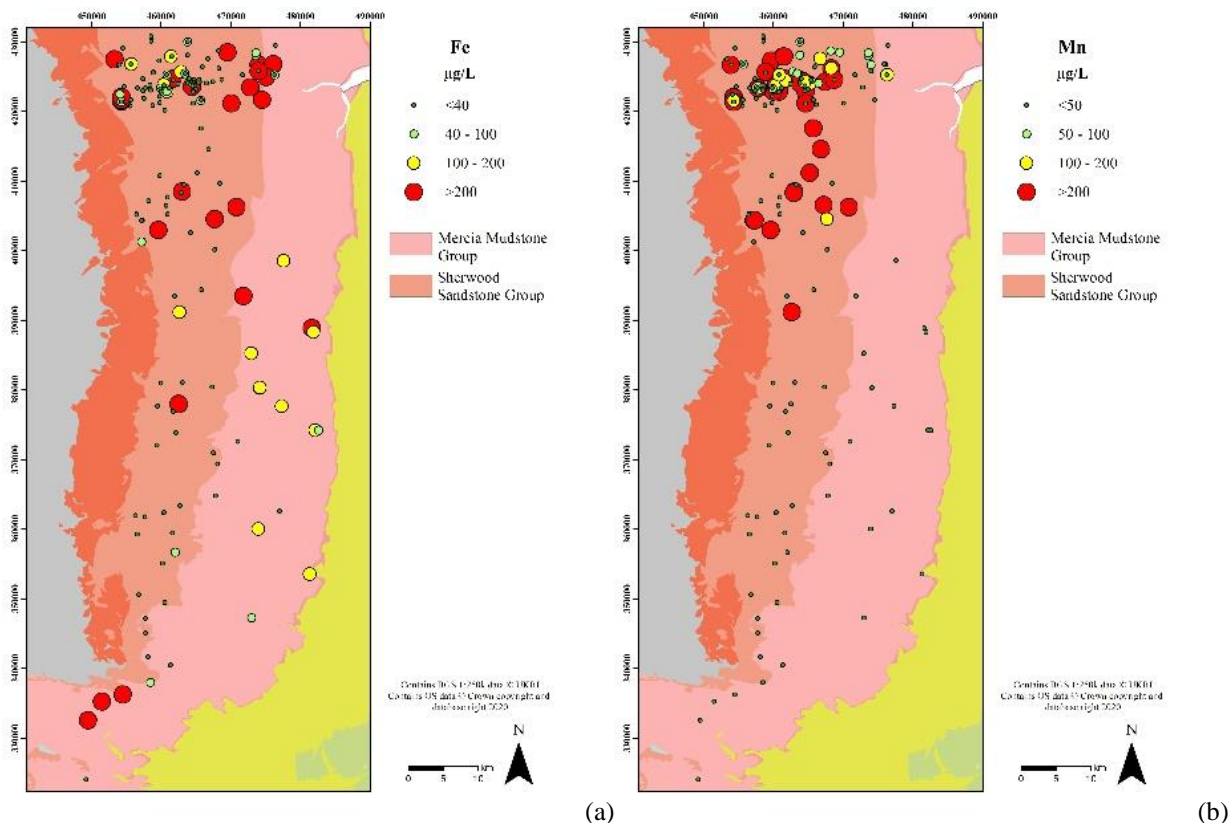


Figure 4.11. Geological map showing distributions for iron (a) and manganese (b) in groundwater. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

4.3.6 Other trace elements

Aluminium has a median concentration of 1.69 µg/L, and a range of <0.6 µg/L to 38.7 µg/L. The 5th to 95th percentile is 0.33–10.5 µg/L. Much of the aquifer appears to have results in the 3.0–5.0 µg/L range, with a cluster of lower values (<3.0 µg/L) in the central portion of the confined aquifer. There is a minor divide in concentrations across the confined and unconfined setting, with the confined portion having marginally lower concentration, but the sampling density does not match that of the unconfined portion (Figure 4.12a).

Ammonium as NH₄ has a median concentration of 0.042 mg/L, and a large range of <0.01–6.55 mg/L. The 5th to 95th percentile range is 0.0018 mg/L to 1.26 mg/L. Concentrations are 0.01–0.15 mg/L for much of the aquifer, apart from Doncaster and further north, where a number of concentrations are above 0.5 mg/L. Some high values are found in unconfined settings but most high values are in the MMG-confined aquifer (Figure 4.12b).

Antimony has a median concentration of 0.05 µg/L, and a range of <0.04 µg/L to 1.82 µg/L. The 5th to 95th percentile range is 0.0101–0.157 µg/L. Concentrations are greatest to the west and north of Doncaster, especially around Goole and Pontefract (>0.15 µg/L). In the central portion of the aquifer, concentrations are marginally greater than the unconfined setting (<0.04 µg/L versus 0.04–0.10 µg/L) (Figure 4.12c).

Arsenic has a median concentration of 1.9 µg/L, with a range of <1–54.4 µg/L. The 5th to 95th percentile range is 0.25–39.4 µg/L. Arsenic concentrations are in the range 2–10 µg/L from Worksop heading northwards towards Goole and the northern extent of the study area, with the greatest number of concentrations >10 µg/L occurring around the Humber Estuary. Concentrations around Nottingham and Mansfield are typically <1 µg/L, sometimes 1–2 µg/L. A group of concentrations in the 2–10 µg/L range are visible around the Doncaster area. There are few data points in the dataset within the confined setting; it is therefore hard to distinguish any pattern aside from some relatively high values in the centre of the study area (Figure 4.12d).

Boron has a median concentration of 15.2 µg/L, with a range of <0.6–3600 µg/L. The 5th to 95th percentile range is 0.615 µg/L to 645 µg/L. Concentrations across much of the aquifer are less than 100 µg/L, with no clear trend in the spatial distribution or differences between the confined or unconfined setting (Figure 4.12e).

Cadmium has a median concentration 0.004 µg/L, with a range of <0.005–4.07 µg/L. The 5th to 95th percentile range is 0.000064 to 0.308 µg/L. Concentrations in the northern half of the aquifer are greater than those in the southern half, with some concentrations around Doncaster and northwards greater than 0.05 µg/L. There is no clear distinction in concentrations between the confined and unconfined aquifer (Figure 4.12f).

Chromium has a median concentration of 0.115 µg/L, with a range of <0.04–1.11 µg/L. The 5th to 95th percentile range is 0.0249–0.783 µg/L. Concentrations in the unconfined aquifer are greater than those observed in the central confined setting, with slightly higher concentrations (0.25–0.75 µg/L or higher) observable to the east of Mansfield and northwards from Doncaster. A few sites within the confined setting (south and north-east of Nottingham) show concentrations in the 0.08–0.25 µg/L range, with one site having a concentration greater than 0.75 µg/L (Figure 4.12g).

Cobalt has a median concentration of 0.03 µg/L, with a range of <0.006–2.19 µg/L. The 5th to 95th percentile range is 0.00295–0.13 µg/L. Concentrations are greatest from Doncaster towards the north-west, with a significant cluster of sites >1.0 µg/L. There is a group with lower concentrations around Blyth/Worksop in the confined setting, with values <0.05 µg/L. Concentrations in the eastern confined area range from 0.006 µg/L to 0.10 µg/L (Figure 4.12h).

Copper has a median concentration of 1.1 µg/L, and a range of <0.2–45 µg/L. The 5th to 95th percentile range is 0.13–9.3 µg/L. Concentrations in the unconfined setting are typically greater than those in the confined setting, with only two sites greater than 3 µg/L in the confined aquifer (close to and south of Nottingham). There are a number of high concentrations (>3 µg/L) in the vicinity of Doncaster, with concentrations between 1.0 and 3.0 µg/L prevalent between Doncaster and Nottingham. Confined concentrations are more notably in the 0.2–1.0 µg/L range (Figure 4.12i).

Lead has a median concentration of 0.059 µg/L, with a range from <0.02 µg/L to 3.67 µg/L. The 5th to 95th percentile range is 0.00584–0.952 µg/L, indicating 3.67 is a significant outlier. Lead distribution is variable but concentrations are typically greatest in the unconfined aquifer. The greatest cluster of high concentrations (>0.10 µg/L) occurs around Doncaster and towards the north. Some locations with a lead concentration >0.50 µg/L can be observed in the confined setting south of Nottingham, and one location to the east of Doncaster. Typically, lead concentrations are <0.05 µg/L in the confined setting, with marginally higher values (0.10–0.50 µg/L) at the fringe of the confined section (Figure 4.12j).

Molybdenum has a median concentration of 0.7 µg/L, with a range of <0.2–4.83 µg/L. The 25th to 95th percentile range is 0.2–4.6 µg/L. Molybdenum concentrations are greater in the confined setting compared to the unconfined setting. There are a number of locations close to Goole with concentrations greater than 3 µg/L, and a notable group of concentrations in the 0.2–1.5 µg/L range from Doncaster towards the north-west. Concentrations are below detection limits around Worksop and to the north of Nottingham (Figure 4.12k).

Selenium has a median concentration of 0.073 µg/L, with a range of <0.07–1.45 µg/L. The 5th to 95th percentile range is 0.00872 µg/L to 0.749 µg/L. Selenium concentrations are greater in the unconfined aquifer than the confined setting. Concentrations are in the 0.15–0.50 µg/L range around Pontefract and Goole, with fewer but similar results towards the south. The central confined region shows results <0.07 µg/L, aside from two sites at the fringe of the confined aquifer to the east of Worksop (Figure 4.12l).

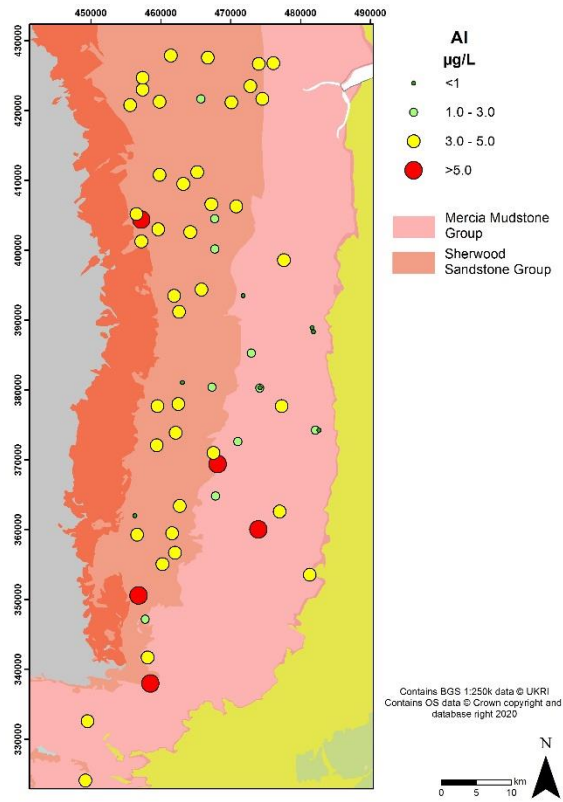
Uranium has a median concentration of 0.8 µg/L, with a range of <0.5–6.2 µg/L. The 5th to 95th percentile range is 0.085 µg/L to 5.6 µg/L. Concentrations of U across the aquifer are typically below 1.50 µg/L, with a few sites with greater concentrations. The greater concentrations are

within the southern half of the study region, with three sites having concentrations above 3 µg/L (Figure 4.12m).

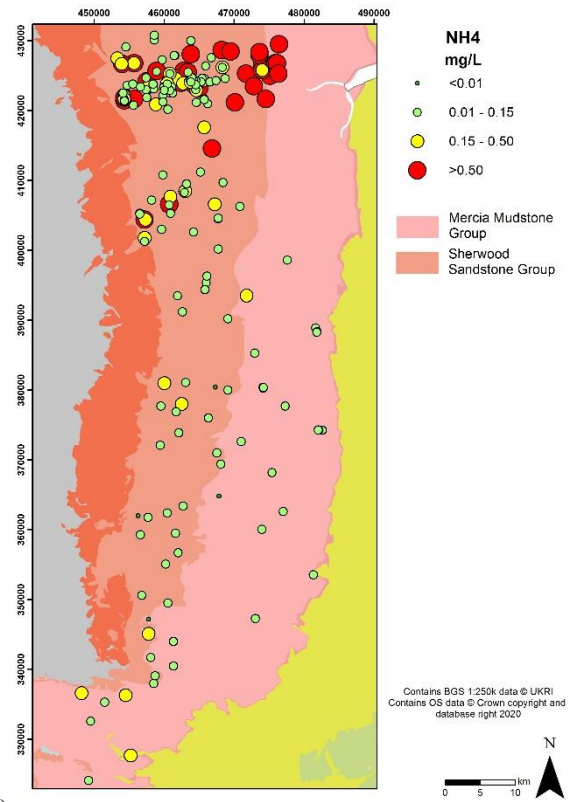
Vanadium has a median concentration of 0.08 µg/L, and a range of <0.05–7.04 µg/L. The 5th to 95th percentile range is 0.00562 µg/L to 1.46 µg/L. The spatial distribution of vanadium in the aquifer shows a clear group of values in the 0.50–1.50 µg/L range from Doncaster towards Goole/the Humber. Concentrations south of Doncaster are typically lower, aside from two sites with concentrations >1.0 µg/L. Six sites have concentrations <0.06 µg/L, clustered in the central confined portion of the aquifer (Figure 4.12n).

Zinc has a median concentration of 9.15 µg/L, and a range of <5–1470 µg/L. The 5th to 95th percentile range is 1.5–191 µg/L. The data have a right skew, with 70 results less than 50 µg/L. Across the aquifer, the concentrations of zinc are typically greater in the unconfined setting, with a number of sites around Doncaster and towards the north with results greater than 10 µg/L. The central region of the confined setting shows a typically low concentration (<5.0 µg/L), although with a few sites of higher concentration (Figure 4.12o).

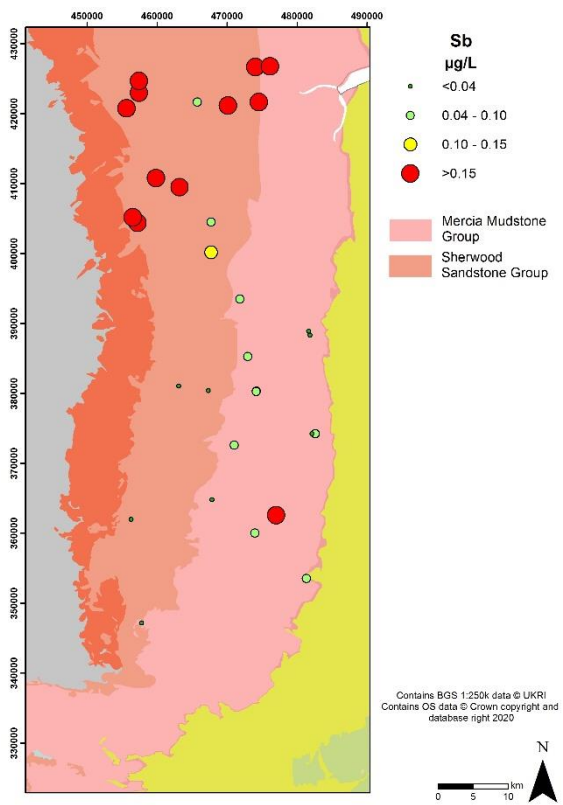
Distributions of minor and trace elements are plotted in summary box plots in Figure 4.5. Cumulative-probability plots are also shown for selected minor and trace elements in Figure 4.13.



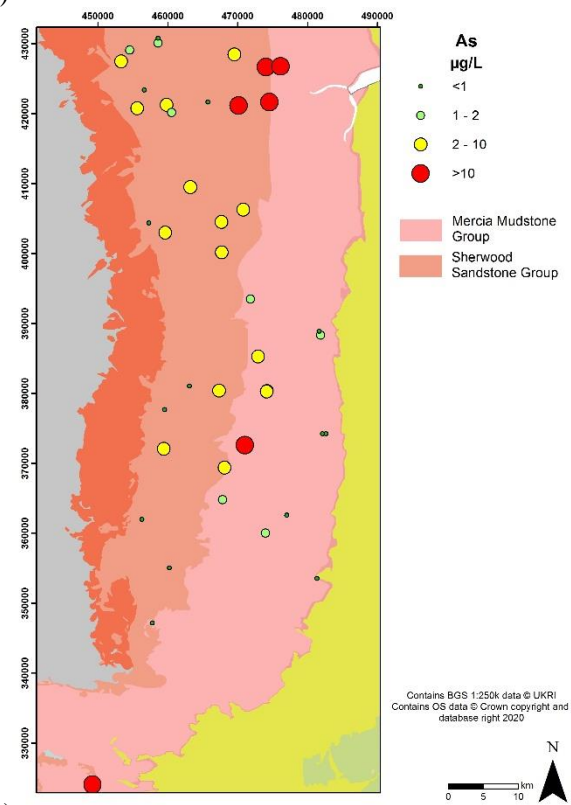
(a)



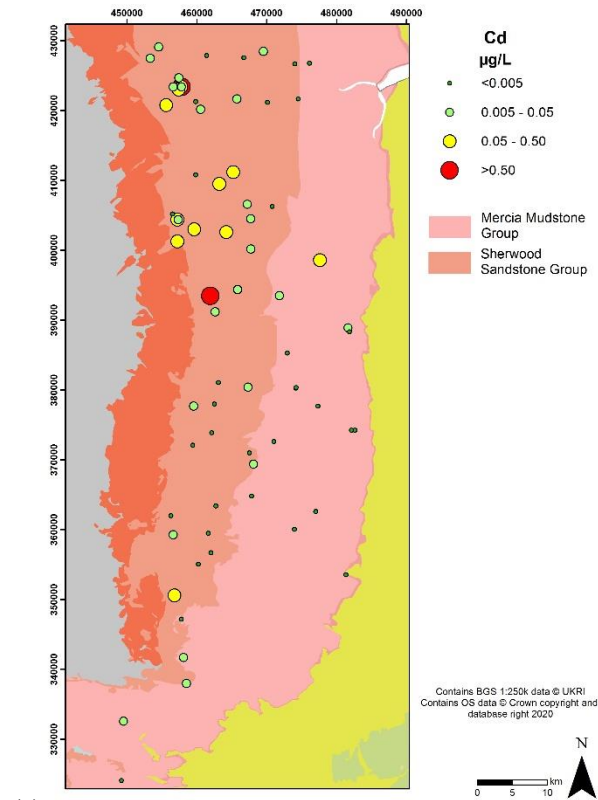
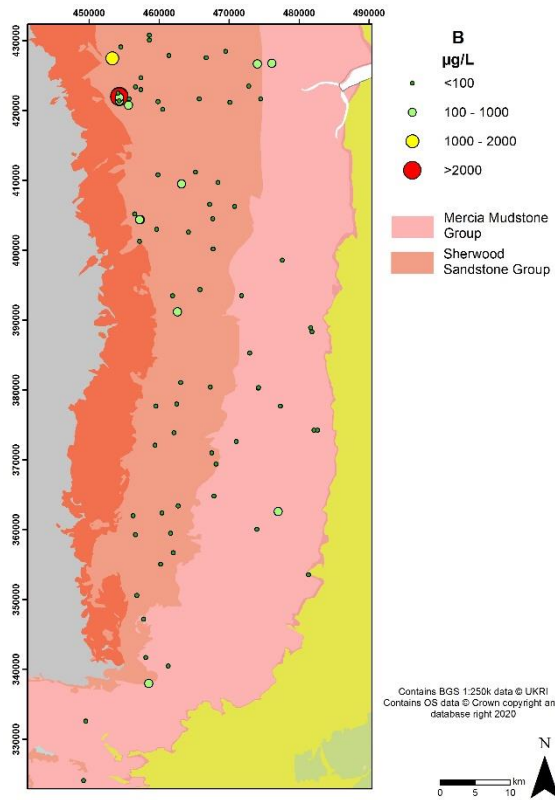
(b)



(c)

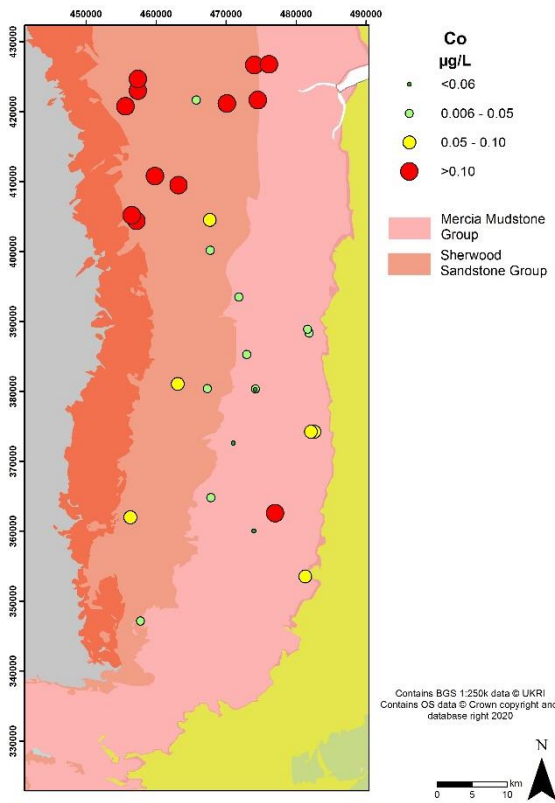


(d)

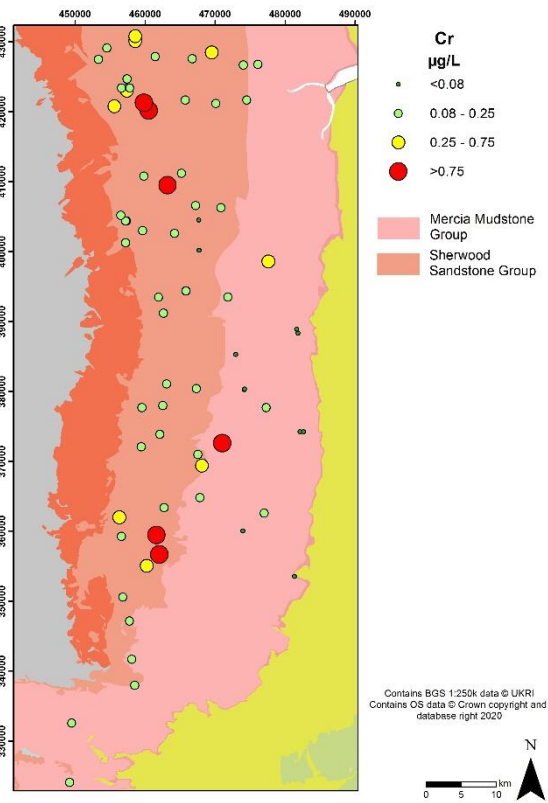


(e)

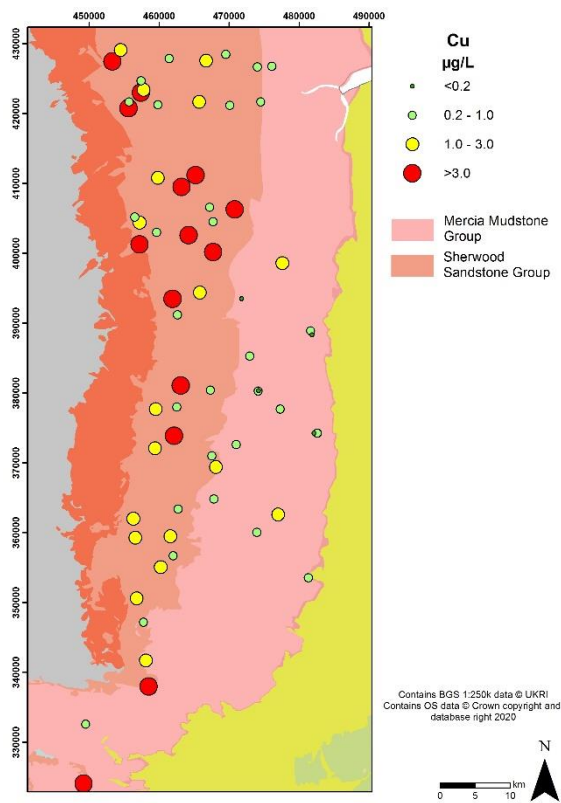
(f)



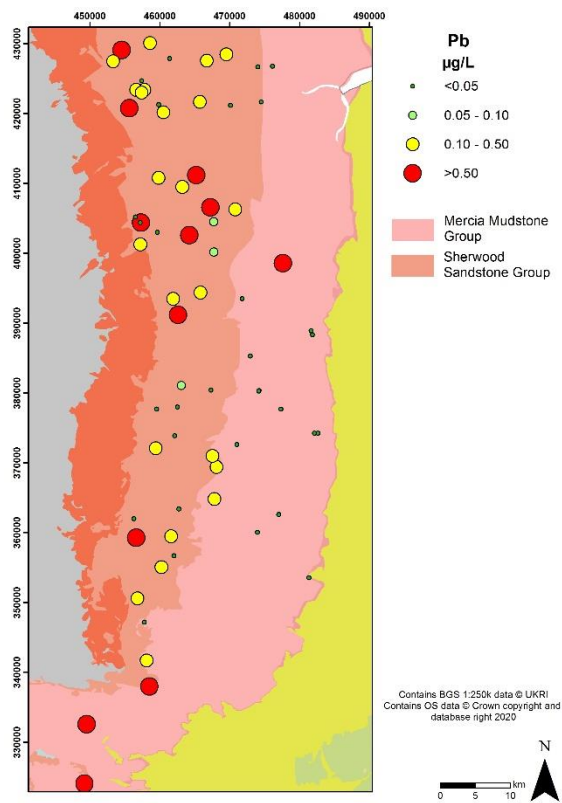
(g)



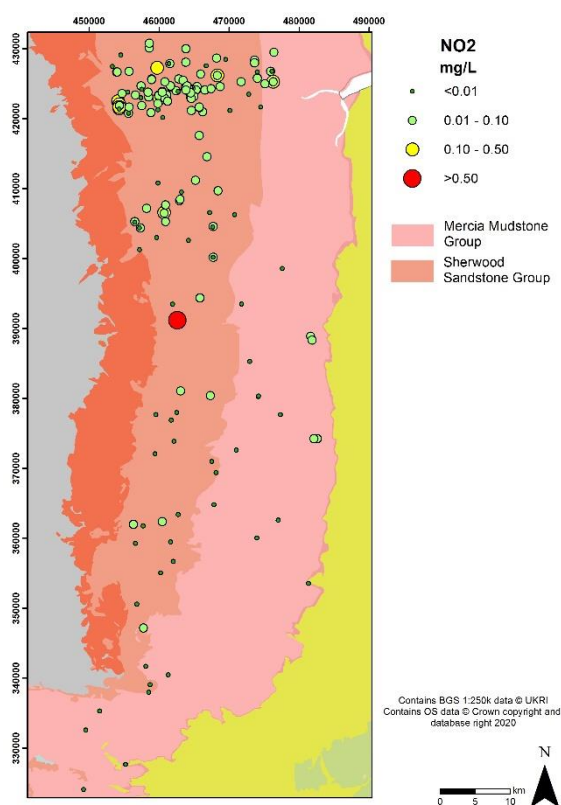
(h)



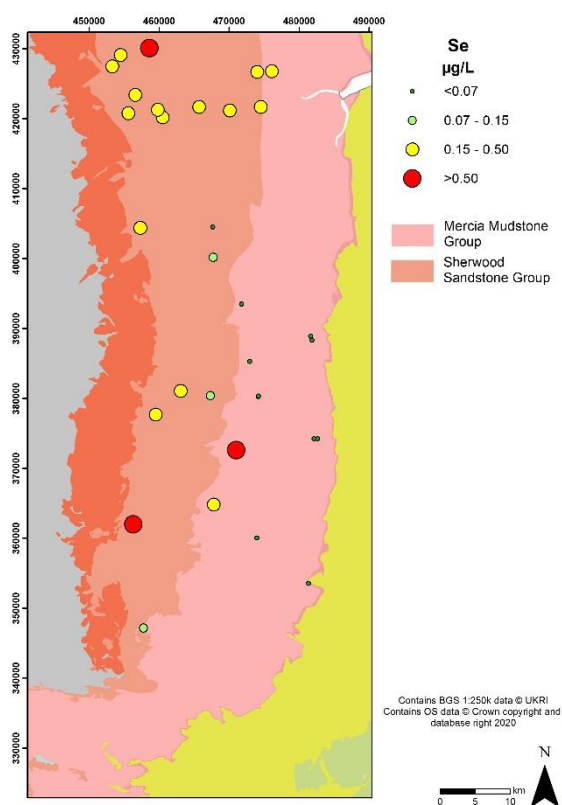
(i)



(j)



(k)



(l)

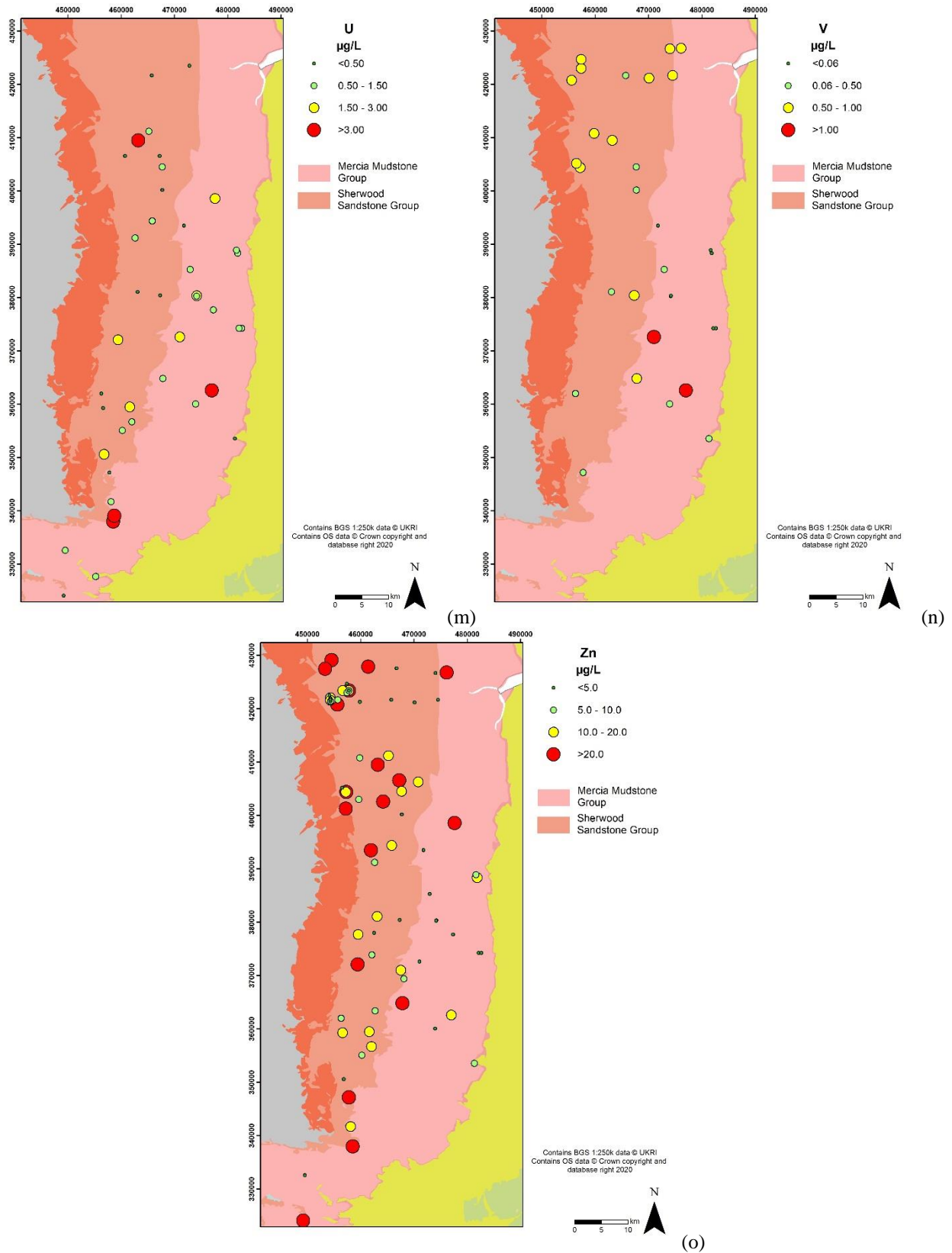


Figure 4.12. Geological maps showing distributions of minor ions: aluminium (a), ammonium (b), antimony (c), arsenic (d), boron (e), cadmium (f), cobalt (g), chromium (h), copper (i), lead (j), NO_2 (k), selenium (l), uranium (m), vanadium (n) and zinc (o) in the groundwater. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

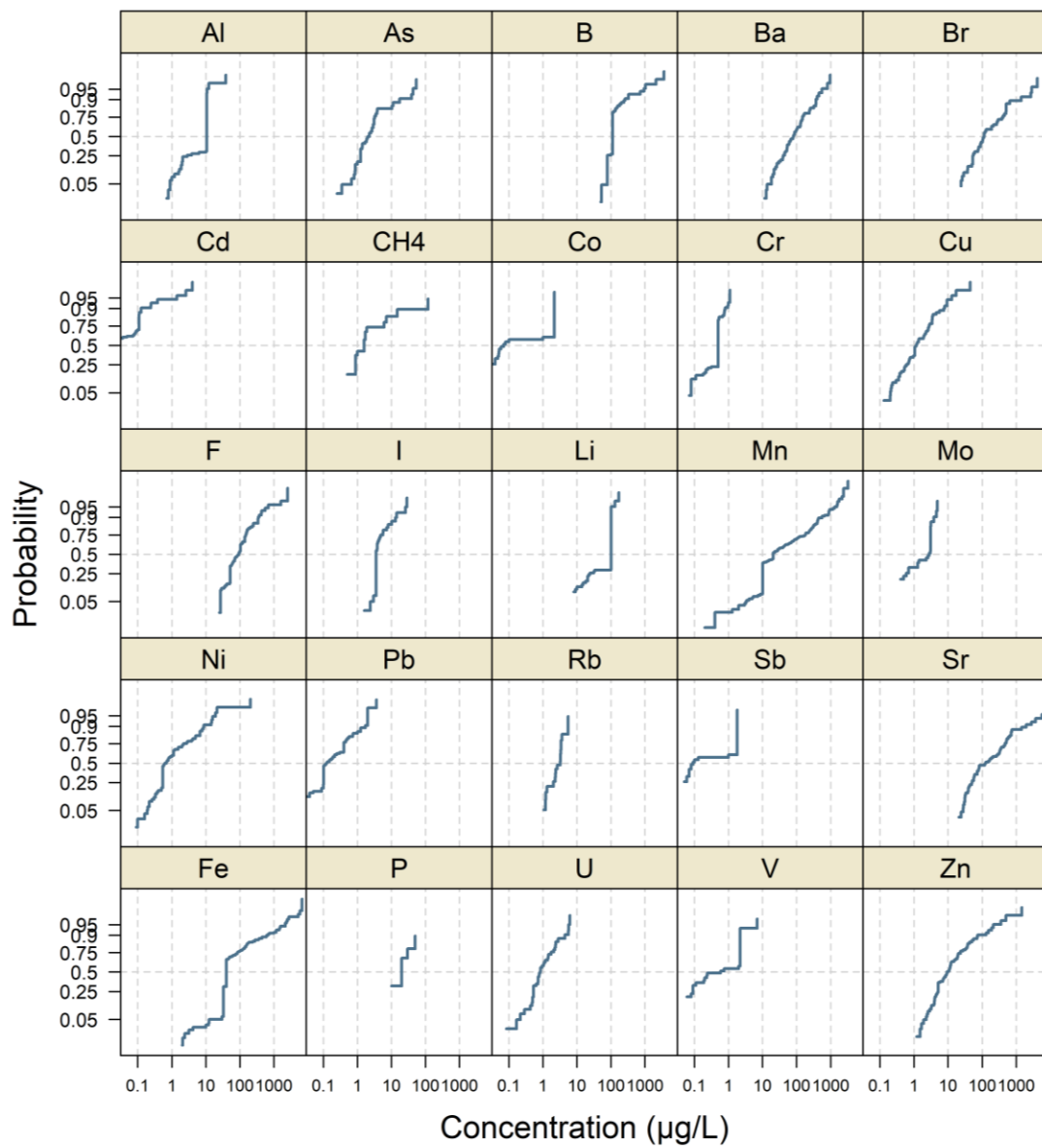


Figure 4.13. Cumulative-probability plots for selected minor and trace elements from the Sherwood Sandstone groundwater

Table 4.1. Statistical summary data including percentiles (5th–95th) for groundwater from the Sherwood Sandstone aquifer from the EA WIMS database and new samples collected and analysed by BGS

Parameter	unit	n	no. cens	min	mean	max	5 th	10 th	25 th	50 th	75 th	90 th	95 th
Ag	µg/L	31	31	<0.04		<1							
Al	µg/L	62	43	<0.6	2.98	38.7	0.327	0.45	0.869	1.69	2.83	5.92	10.5
As	µg/L	42	6	<1	5.7	54.4	0.25	0.35	0.85	1.9	3.14	11.3	39.4
B	µg/L	85	65	<50	141	3600	0.615	1.17	3.89	15.2	65.7	224	645
Ba	µg/L	62	1	<10	142	961	13.8	20.3	40.2	78.9	150	376	455
Be	µg/L	31	31	<0.08		<1							
Bi	µg/L	13	13	<0.08		<0.08							
Br	mg/L	47	5	<0.05	0.367	4.16	0.022	0.024	0.05	0.102	0.269	0.649	2.72
Ca	mg/L	62	0	13.3	96.4	579	23.6	32	46.6	69.7	105	148	248
Cd	µg/L	72	45	<0.005	0.142	4.07	0.000064	0.000142	0.000648	0.00457	0.0308	0.124	0.308
Ce	µg/L	19	17	<0.004		0.005							
Cl	mg/L	206	0	4	78.5	471	10	11.1	23.8	46	86.9	200	296
Co	µg/L	31	16	<0.006	0.107	2.19	0.00295	0.00469	0.00803	0.03	0.0555	0.0929	0.13
Cr	µg/L	74	57	<0.04	0.219	1.11	0.0249	0.0358	0.0595	0.115	0.246	0.632	0.783
Cs	µg/L	19	7	<0.04	0.0553	0.13				0.05	0.06	0.08	0.088
Cu	µg/L	71	6	<0.2	2.78	45	0.13	0.213	0.5	1.1	2.74	5.6	9.3
DO	mg/L	73	0	0.03	6.08	14.3	0.2	0.45	3.02	6.87	8.56	10.7	11.3
Dy	µg/L	19	19	<0.003		<0.003							
Eh	mV	18	0	36.7	202	478	54.6	65.4	80.7	100	323	398	431
Er	µg/L	19	19	<0.003		<0.003							
Eu	µg/L	19	19	<0.003		<0.003							
F	mg/L	93	31	<0.025	0.165	2.55	0.023	0.023	0.023	0.07	0.141	0.341	0.55
Fe	µg/L	180	108	<10	299	6750	0.303	0.734	2.8	15.3	83.4	598	1570
Ga	µg/L	19	18	<0.04		0.1							
Gd	µg/L	19	19	<0.005		<0.005							
HCO ₃	mg/L	225	3	<6.095	246	798	84.1	114	158	217	299	442	524
Hf	µg/L	19	19	<0.006		<0.006							
Hg	µg/L	9	9	<0.01		<0.01							
Ho	µg/L	19	19	<0.003		<0.003							

Parameter	unit	n	no. cens	min	mean	max	5 th	10 th	25 th	50 th	75 th	90 th	95 th
I	µg/L	40	18	<3	4.89	28.7	1.3	1.3	1.6	2.4	4.5	10.3	14.2
K	mg/L	62	0	0.948	6.86	100	1.59	1.76	2.74	3.91	6.43	10.4	13.3
La	µg/L	19	17	<0.003		0.006							
Li	µg/L	62	46	<7	21	171	2.35	3.21	5.77	12.6	22.4	38.4	59.1
Lu	µg/L	19	19	<0.003		<0.003							
Mg	mg/L	62	0	4.51	36.8	161	13.4	16	23	31.5	45	62.9	70.6
Mn	µg/L	182	69	<0.04	201	3270	n/a	0.2	3.2	17.9	176	440	1160
Mo	µg/L	31	13	<0.2	1.44	4.83	n/a	n/a	0.2	0.7	2.6	3.12	4.6
Na	mg/L	62	0	2.76	43.5	391	4.66	6.1	10.2	14.7	35.7	152	164
Nb	µg/L	19	19	<0.01		<0.01							
Nd	µg/L	19	18	<0.005		0.007							
NH ₄	mg/L	211	114	<0.01	0.303	6.55	0.00182	0.00369	0.0124	0.042	0.25	0.785	1.26
Ni	µg/L	76	30	<0.2	4.92	206	0.09	0.1	0.22	0.49	1.56	8.44	15.8
NO ₂	mg/L	183	154	<0.01		2.6							
NO ₃	mg/L	99	26	<0.06	37.5	240			0.864	20.1	55.3	97	155
Pb	µg/L	73	39	<0.02	0.233	3.67	0.00544	0.0083	0.02	0.0599	0.185	0.502	0.952
pH		65	0	6.9	7.63	8.67	7.12	7.25	7.38	7.63	7.8	8.15	8.2
Pr	µg/L	19	18	<0.003		0.005							
P-react	mg/L	71	43	<0.01	0.051	1.3	0.00073	0.0012	0.0030	0.009	0.032	0.069	0.112
Rb	µg/L	19	0	1.01	2.75	5.53	1.01	1.07	1.32	2.63	3.41	5.52	
Sb	µg/L	31	16	<0.04	0.113	1.82	0.0101	0.0133	0.0251	0.05	0.076	0.125	0.157
Se	µg/L	32	23	<0.07	0.203	1.45	0.00872	0.0139	0.0289	0.0736	0.244	0.521	0.749
SEC	µS/cm	175	0	216	1020	3270	314	407	535	781	1330	2070	2590
SiO ₂	mg/L	84	0	5.37	9.59	17.9	6.5	7.06	7.42	8.71	10.6	14.7	15.4
Sm	µg/L	19	19	<0.005		<0.006							
Sn	µg/L	31	31	<0.08		<2							
SO ₄	mg/L	211	11	<2	178	1810	2.8	9	31	93.2	180	330	963
Sr	µg/L	66	2	<20	682	9470	24.4	30.1	49.8	119	465	1430	3710
Ta	µg/L	19	19	<0.006		<0.006							
Tb	µg/L	19	19	<0.004		<0.004							
TDS	mg/L	19	0	124	327	654	124	126	201	319	445	537	

Parameter	unit	n	no. cens	min	mean	max	5 th	10 th	25 th	50 th	75 th	90 th	95 th
Temp	°C	96	0	4.1	11.7	17.9	9	9.8	10.5	11.3	12.6	14.4	16.9
Th	µg/L	19	19	<0.03		<0.03							
Ti	µg/L	31	26	<0.06		10.8							
Tl	µg/L	19	19	<0.02		<0.02							
Tm	µg/L	19	19	<0.003		<0.003							
Tot P	mg/L	19	10	<0.006	0.013	0.05	0.00182	0.00204	0.00356	0.00601	0.015	0.034	0.05
U	µg/L	41	5	<0.5	1.37	6.2	0.085	0.169	0.485	0.797	1.46	2.79	5.63
V	µg/L	31	18	<0.05	0.439	7.04	0.00562	0.0106	0.0203	0.08	0.227	0.649	1.46
W	µg/L	19	19	<0.06		<0.06							
Y	µg/L	19	14	<0.006	0.00527	0.008	0.00354	0.00376	0.00428	0.00503	0.006	0.007	0.00735
Yb	µg/L	19	19	<0.004		<0.004							
Zn	µg/L	81	9	<5	49.5	1470	1.5	2.3	4	9.15	19.6	70.7	191
Zr	µg/L	19	17	<0.009		0.014							

no. cens: number of censored analyses

Table 4.2. Statistical summary data including percentiles (5th–95th) for dissolved gases in groundwater from the Sherwood Sandstone aquifer (BGS and WIMS data)

Parameter	unit	n	no. cens	min	mean	max	5%	10%	25%	50%	75%	90%	95%
CH ₄	µg/L	37	12	<0.5	5.28	120	0.1	0.1	0.1	0.5	1.7	7.1	14.9
CO ₂	mg/L	19	0	1.7	7.6	13.1	1.88	3.02	4.55	7.4	10.4	12.0	12.5
Rn	Bq/L	6	0	8	12.4	20	8.49	8.99	9.98	11.4	13.4	16.8	18.4

no. cens: number of censored analyses

4.4 DISSOLVED GASES

Although few analyses are available for dissolved methane, the median concentration is 0.5 µg/L, with a range of <0.5–120 µg/L (Table 4.2). The 5th to 95th percentile range is 0.1–14.9 µg/L although majority have concentrations <5 µg/L. The cumulative-probability distribution can be seen in Figure 4.13. Dissolved CH₄ concentrations are overall higher in the confined aquifer (Figure 4.14a). There are a number of sites with concentrations greater than 1 µg/L in the central portion of the aquifer, but concentrations are typically less than 0.5 µg/L southwards towards Nottingham.

The few analyses of dissolved CO₂ concentrations reported in the dataset lie in the range 1.7–13.1 mg/L with a median of 7.4 µg/L (Figure 4.14b). Distributions show no clear relationship with those of dissolved CH₄ but as expected have a positive correlation with alkalinity and an inverse one with pH.

Dissolved radon activities lie in the range 8–20 Bq/L for the few measurements made in the BGS sampling. No obvious spatial trend is apparent. Radon activities are comparable to those reported in groundwater from the same region of the Sherwood Sandstone by Smedley et al. (2018).

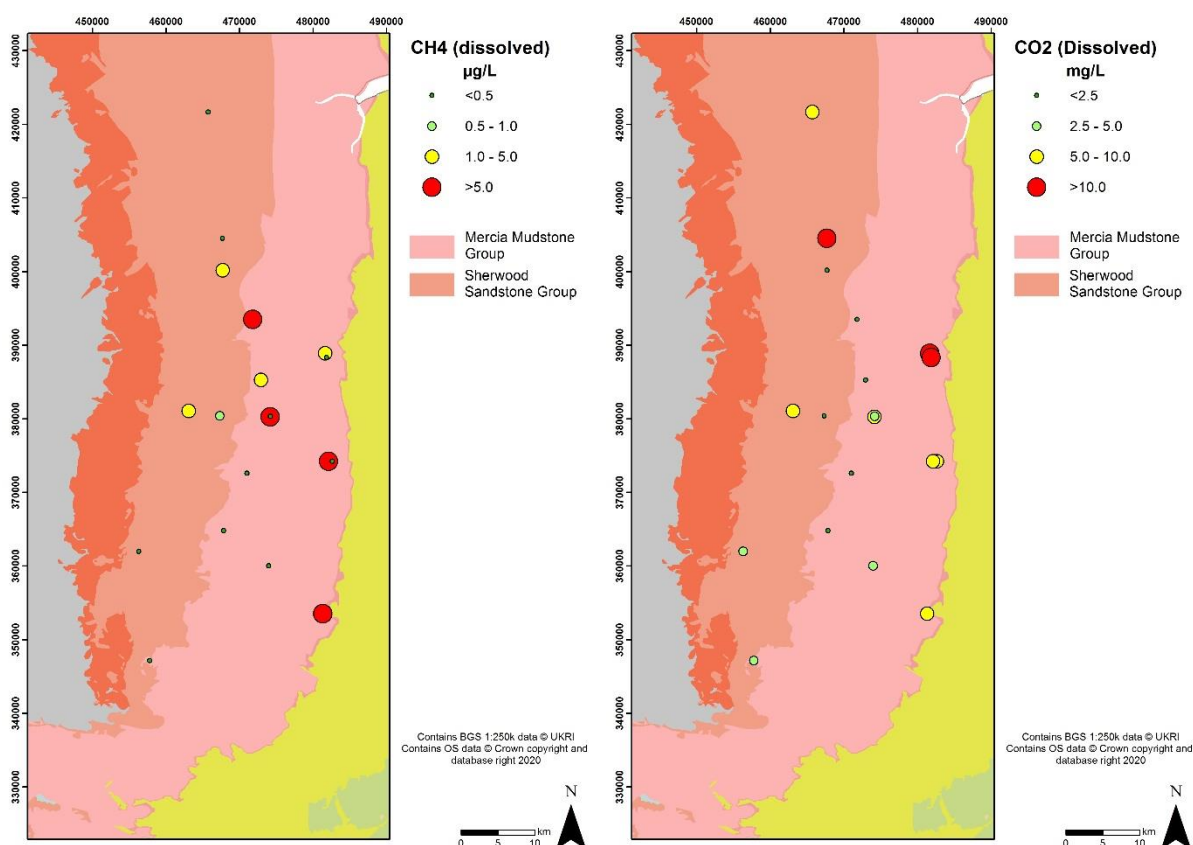


Figure 4.14. Geological maps showing distributions of dissolved methane (CH₄) and CO₂. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

4.5 ORGANIC COMPOUNDS

4.5.1 TPH, volatile/semi-volatile organic carbon and PAHs

Table 4.3 shows the summary statistics for results of a number of organic compounds from both the WIMS database and the BGS sampling campaign. Very few analyses have concentrations above the respective detection limit, and few in sufficient numbers to determine descriptive statistics.

The list of compounds where detections were observed comprises:

- 2-chlorotoluene
- acenaphthene
- benzene
- benzo(a)pyrene
- benzo(b)fluoranthene
- benzo(b.k)fluoranthene
- benzo(e)pyrene
- benzo(g,h,i)perylene
- benzo(k)fluoranthene
- chloroform
- dimethylbenzene: sum of isomers (1,3- 1,4-) : (m+p xylene)
- ethylbenzene
- fluoranthene
- fluorene
- naphthalene
- NPOC/TOC
- phenanthrene
- tetrachloroethylene (perchloroethylene)
- toluene (methylbenzene)
- trichloroethylene (trichloroethene)

Only two compounds were detected at sufficient sites to obtain summary statistics: chloroform and the PAH fluoranthene. The median concentration of chloroform is 0.037 $\mu\text{g/L}$, with a range of <0.1–0.39 $\mu\text{g/L}$. The 5th to 95th percentile range is 0.0077–0.273 $\mu\text{g/L}$. Only four sites show evidence of chloroform concentrations above 0.1 $\mu\text{g/L}$, with two sites >0.2 $\mu\text{g/L}$ (Figure 4.15a). For indicative comparisons, the values are much below the national drinking-water limit of 100 $\mu\text{g/L}$ for trihalomethanes (including chloroform).

Fluoranthene has a median concentration of 0.0047 $\mu\text{g/L}$, with a range of <0.005–0.054 $\mu\text{g/L}$. The 5th to 95th percentile range is 0.0015–0.015 $\mu\text{g/L}$. Only ten samples have concentrations greater than the detection limit, with 40 samples below the maximum <0.5 detection limit. The spatial distribution of fluoranthene across the aquifer shows that the sites with detections above 0.01 $\mu\text{g/L}$ occurred in the unconfined aquifer, in both the north and in the vicinity of Mansfield (Figure 4.15b).

Aside from targeted analyses, both NPOC (non-purgeable organic carbon) and TOC (total organic carbon) data were represented in the dataset, the former from the BGS analyses and the latter from WIMS. The median concentration for NPOC was 0.94 mg/L, with a range of <0.2–8.24 mg/L. The 10th to 95th percentile range is 0.23–4.32 mg/L. The TOC median concentration was 1.83 mg/L, with a range from <0.5–10.4 mg/L. The 10th to 95th percentile range for TOC was 0.81–6.9 mg/L. Included TOC data were from limited locations across the aquifer, with most located sites along the western edge of the Sherwood Sandstone outcrop; higher concentrations were present in the north-west of the study area. As the analytical methods to determine NPOC and TOC may and do not correspond exactly, TOC values have been plotted along with the NPOC data in Figure 4.15c. NPOC concentrations in the confined aquifer are typically <0.5 mg/L, with the higher concentrations being found in the unconfined setting and at the edge of confinement. NPOC concentrations in the 0.5–5.0 mg/L range can be observed through much of the unconfined aquifer, especially around Goole and both around and to the south of Doncaster (Figure 4.15c). A few sites with concentrations greater than 5.0 mg/L can be observed to the south of Nottingham, near Doncaster, and at the edge of the confined aquifer to the north in the Humber Estuary/Goole area.

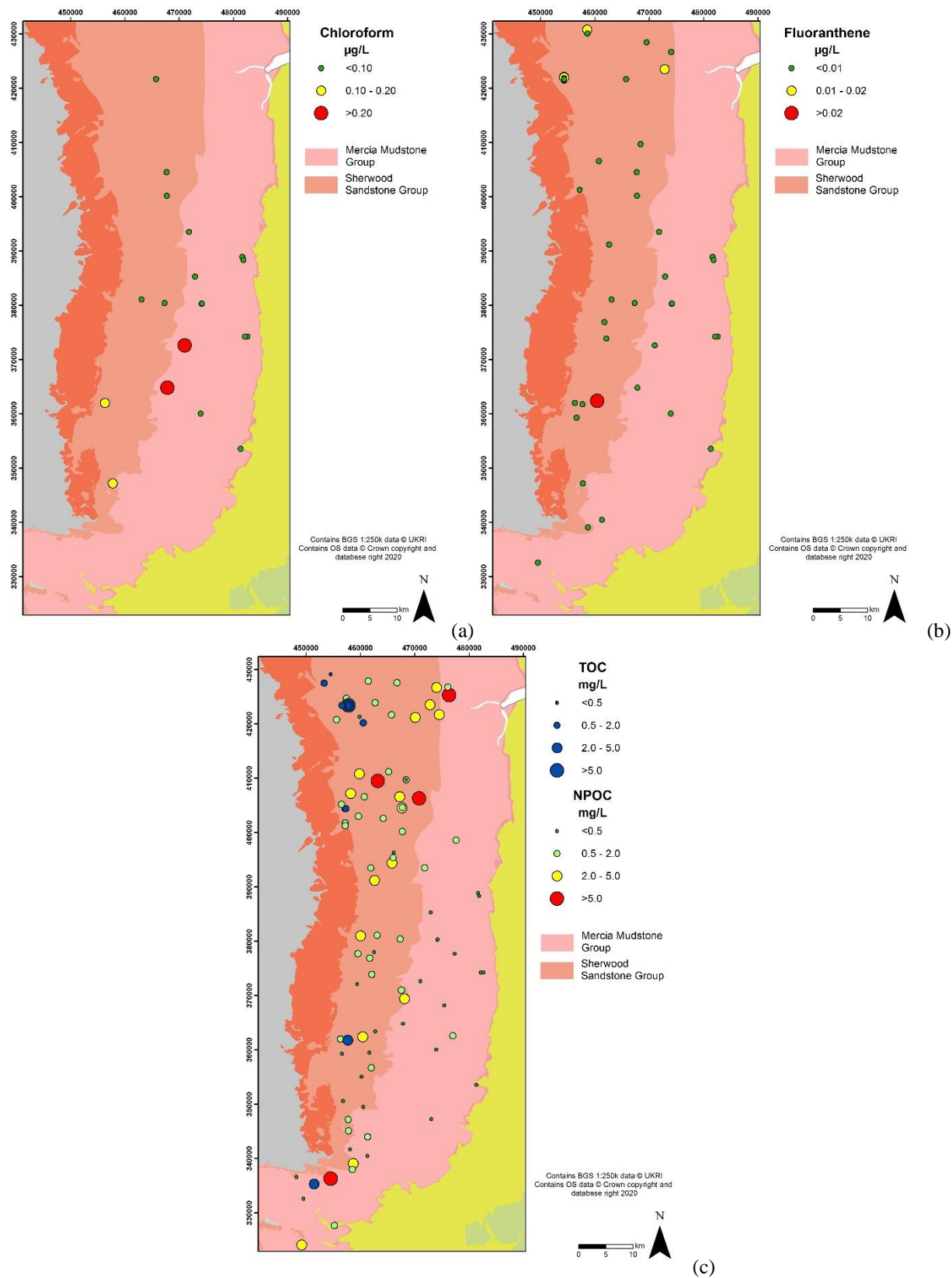


Figure 4.15. Geological maps showing distributions of chloroform (a), fluoranthene (b), NPOC/TOC (c). BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

Table 4.3. Statistical summary data including percentiles for organic compounds in groundwater from the Sherwood Sandstone aquifer from the EA WIMS database and sampling by BGS (summary statistics are not computed where non-detects exceed 80% of analyses)

Parameter	unit	n	no. cens	min	mean	max	5%	10%	25%	50%	75%	90%	95%
>C10-C12	µg/L	15	15	<5		<5							
>C12-C16	µg/L	15	15	<10		<10							
>C16-C21	µg/L	15	15	<10		<10							
>C21-C35	µg/L	15	15	<10		<10							
>C5-C6	µg/L	15	15	<10		<10							
>C5-EC7	µg/L	15	15	<10		<10							
>C6-C8	µg/L	15	15	<10		<10							
>C8-C10	µg/L	15	15	<10		<10							
>EC10-EC12	µg/L	15	15	<5		<5							
>EC12-EC16	µg/L	15	15	<10		<10							
>EC16-EC21	µg/L	15	15	<10		<10							
>EC21-EC35	µg/L	15	15	<10		<10							
>EC7-EC8	µg/L	15	15	<10		<10							
>EC8-EC10	µg/L	15	15	<10		<10							
1-Dichloroethane	µg/L	19	19	<0.1		<0.5							
1-Dichloroethene	µg/L	19	19	<0.1		<0.1							
1-Dichloropropene	µg/L	19	19	<0.1		<0.1							
1-Trichloroethane	µg/L	19	19	<0.1		<0.1							
2-Tetrachloroethane	µg/L	19	19	<0.1		<0.1							
2-Trichloroethane	µg/L	19	19	<0.1		<0.1							
2-Tetrachloroethane	µg/L	19	19	<0.1		<0.1							
2-Dibromo-3-chloropropane	µg/L	19	19	<0.1		<0.1							
2-Dibromoethane	µg/L	19	19	<0.1		<0.1							
2-Dichlorobenzene	µg/L	20	20	<0.1		<1							
2-Dichloroethane	µg/L	19	19	<0.1		<0.1							
2-Dichloropropane	µg/L	19	19	<0.1		<0.1							
2-Dimethylbenzene (o-xylene)	µg/L	20	20	<0.1		<5							
3-Trichlorobenzene	µg/L	19	19	<0.1		<0.1							
3-Trichloropropane	µg/L	19	19	<0.1		<0.5							

Parameter	unit	n	no. cens	min	mean	max	5%	10%	25%	50%	75%	90%	95%
3-Trimethylbenzene	µg/L	19	19	<0.1		<0.1							
4-Trichlorobenzene	µg/L	20	20	<0.1		<1							
4-Trimethylbenzene	µg/L	19	19	<0.1		<0.1							
3-Dichlorobenzene	µg/L	20	20	<0.1		<1							
3-Dichloropropane	µg/L	19	19	<0.1		<0.1							
5-Trichlorobenzene	µg/L	19	19	<0.1		<0.1							
5-Trimethylbenzene (mesitylene)	µg/L	19	19	<0.1		<0.1							
4-Dichlorobenzene	µg/L	20	20	<0.1		<1							
2-Chloronaphthalene	µg/L	15	15	<1		<2							
2-Chlorophenol	µg/L	15	15	<1		<2							
2-Chlorotoluene (1-chloro-2-methylbenzene)	µg/L	19	18	<0.1		0.24							
2-Methylnaphthalene	µg/L	15	15	<1		<2							
2-Methylphenol	µg/L	15	15	<0.5		<1							
2-Nitroaniline	µg/L	15	15	<1		<2							
2-Nitrophenol	µg/L	15	15	<0.5		<1							
2-Dichloropropane	µg/L	19	19	<0.1		<0.1							
4-Dichlorophenol	µg/L	15	15	<0.5		<1							
4-Dimethylphenol	µg/L	15	15	<1		<2							
4-Dinitrotoluene	µg/L	15	15	<0.5		<1							
5-Trichlorophenol	µg/L	15	15	<0.5		<1							
6-Trichlorophenol	µg/L	15	15	<1		<2							
6-Dinitrotoluene	µg/L	15	15	<1		<2							
3-Chlorotoluene (1-chloro-3-methylbenzene)	µg/L	19	19	<0.1		<0.1							
3-Nitroaniline	µg/L	15	15	<1		<2							
4-Bromophenylphenylether	µg/L	15	15	<1		<2							
4-Chloro-3-methylphenol	µg/L	15	15	<0.5		<1							
4-Chloroaniline	µg/L	15	15	<1		<2							
4-Chlorophenylphenylether	µg/L	15	15	<1		<2							
4-Chlorotoluene (1-chloro-4-methylbenzene)	µg/L	19	19	<0.1		<0.1							
4-Isopropyltoluene (4-methyl-isopropylbenzene)	µg/L	19	19	<0.1		<0.1							
4-Methylphenol	µg/L	15	15	<1		<2							
4-Nitroaniline	µg/L	15	15	<0.5		<1							

Parameter	unit	n	no. cens	min	mean	max	5%	10%	25%	50%	75%	90%	95%
4-Nitrophenol	µg/L	15	15	<10		<20							
Acenaphthene	µg/L	34	32	<0.005		0.0636							
Acenaphthylene	µg/L	29	29	<0.01		<0.5							
Anthracene	µg/L	20	20	<0.01		<0.5							
Azobenzene	µg/L	15	15	<0.5		<1							
Benzene	µg/L	65	64	<0.1		3570							
Benzo(a)anthracene	µg/L	20	20	<0.01		<0.5							
Benzo(a)pyrene	µg/L	46	40	<0.005		0.0495							
Benzo(b)fluoranthene	µg/L	45	41	<0.005		0.0465							
Benzo(b,k)fluoranthene	µg/L	15	15	<1		<2							
Benzo(e)pyrene	µg/L	27	26	<0.005		0.028							
Benzo(g,h,i)perylene	µg/L	46	43	<0.005		0.0221							
Benzo(k)fluoranthene	µg/L	39	34	<0.001		0.0379							
Bis(2-chloroethoxy)methane	µg/L	15	15	<0.5		<1							
Bis(2-chloroethyl)ether	µg/L	15	15	<1		<2							
Bis(2-ethylhexyl)phthalate	µg/L	15	15	<5		<10							
Bromobenzene	µg/L	19	19	<0.1		<0.1							
Bromochloromethane	µg/L	19	19	<0.1		<0.1							
Bromodichloromethane	µg/L	19	19	<0.1		<0.1							
Bromoform (tribromomethane)	µg/L	19	19	<0.1		<0.1							
Butylbenzyl phthalate	µg/L	15	15	<1		<2							
Carbazole	µg/L	15	15	<0.5		<1							
Carbon disulphide	µg/L	19	19	<0.1		<0.1							
Carbon tetrachloride (tetrachloromethane)	µg/L	19	19	<0.1		<0.5							
Chlorobenzene	µg/L	19	19	<0.1		<0.1							
Chlorodibromomethane	µg/L	19	19	<0.1		<0.5							
Chloroform (trichloromethane)	µg/L	19	15	<0.1	0.0715	0.39	0.00773	0.00876	0.0163	0.0372	0.0777	0.148	0.273
Chloromethane (methyl chloride)	µg/L	19	19	<0.1		<0.5							
Chrysene	µg/L	20	20	<0.01		<0.5							
cis-1,2-Dichloroethylene (cis-1,2-dichloroethene)	µg/L	19	19	<0.1		<0.1							
cis-1,3-Dichloropropylene (cis-1,3-dichloropropene)	µg/L	19	19	<0.1		<0.1							

Parameter	unit	n	no. cens	min	mean	max	5%	10%	25%	50%	75%	90%	95%
Di-n-butyl phthalate	µg/L	15	15	<1.5		<3							
Di-n-octyl phthalate	µg/L	15	15	<1		<2							
Dibenzo(a,h)anthracene	µg/L	30	30	<0.01		<0.5							
Dibenzofuran	µg/L	15	15	<0.5		<1							
Dibromomethane	µg/L	19	19	<0.1		<0.1							
Dichloromethane (methylene dichloride)	µg/L	19	19	<0.1		<0.5							
Diethyl phthalate	µg/L	15	15	<1		<2							
Dimethyl phthalate	µg/L	15	15	<1		<2							
Dimethylbenzene: sum of isomers (1,3-1,4-) (m+p xylene)	µg/L	64	61	<0.1		2.56							
Ethyl tert-butyl ether (ETBE)	µg/L	19	19	<0.1		<0.1							
Ethylbenzene	µg/L	65	63	<0.1		1.89							
Fluoranthene	µg/L	46	36	<0.005	0.00698	0.054	0.00151	0.00197	0.00307	0.00471	0.00758	0.0118	0.0149
Fluorene	µg/L	31	29	<0.005		0.0282							
Hexachlorobenzene	µg/L	34	34	<0.001		<2							
Hexachlorobutadiene	µg/L	20	20	<0.1		<1							
Hexachlorocyclopentadiene	µg/L	15	15	<1		<2							
Hexachloroethane	µg/L	20	20	<0.1		<1							
Indeno(123-cd)pyrene	µg/L	19	19	<0.01		<0.01							
Isophorone	µg/L	15	15	<0.5		<1							
Isopropylbenzene	µg/L	19	19	<0.1		<0.1							
m/p-Xylene	µg/L	15	15	<5		<5							
MTBE (Methyl tert-butyl ether)	µg/L	60	59	<0.1		0.588							
n-ButylBenzene (1-phenylbutane)	µg/L	23	23	<0.1		<0.2							
N-nitrosodi-n-propylamine	µg/L	15	15	<0.5		<1							
n-Propylbenzene (1-phenylpropane)	µg/L	24	24	<0.1		<0.1							
Naphthalene	µg/L	42	40	<0.01		0.0472							
Nitrobenzene	µg/L	15	15	<1		<2							
NPOC	mg/L	87	17	<0.2	1.48	8.24		0.23	0.37	0.94	1.82	3.69	4.32
Pentachlorophenol	µg/L	15	15	<1		<2							
Perylene	µg/L	22	22	<0.01		<0.1							
Phenanthrene	µg/L	34	31	<0.01		0.093							

Parameter	unit	n	no. cens	min	mean	max	5%	10%	25%	50%	75%	90%	95%
Phenol	µg/L	15	15	<1		<2							
Pyrene	µg/L	34	32	<0.005		0.035							
sec-Butylbenzene (1-methylpropylbenzene)	µg/L	19	19	<0.1		<0.5							
Styrene (vinylbenzene)	µg/L	19	19	<0.1		<0.1							
tert-Amyl methyl ether (TAME)	µg/L	19	19	<0.1		<0.1							
tert-Butylbenzene (1-dimethylethyl)benzene)	µg/L	19	19	<0.1		<0.1							
Tetrachloroethylene (perchloroethylene)	µg/L	19	16	<0.1		1.7							
TOC	mg/L	12	1	<0.5	2.57	10.4	0.81	1.03	1.83	2.57	4.03	6.90	
Toluene (methylbenzene)	µg/L	65	63	<0.1		0.45							
Total aliphatics and aromatics (C5-35)	µg/L	15	15	<10		<10							
Total aliphatics C5-35	µg/L	15	15	<10		<10							
Total aromatics C5-35	µg/L	15	15	<10		<10							
trans-1,2-Dichloroethylene (trans-1,2-Dichloroethene)	µg/L	19	19	<0.1		<0.1							
trans-1,3-Dichloropropylene (trans-1,3-dichloropropene)	µg/L	19	19	<0.5		<0.5							
Trichloroethylene (trichloroethene)	µg/L	19	18	<0.1		0.14							
Trichlorofluoromethane	µg/L	19	19	<0.1		<0.1							
Vinyl chloride (chloroethylene)	µg/L	19	19	<0.1		<0.1							

no. cens: number of censored data

4.5.2 Organic compounds from LCMS/GCMS semi-quantitative screening

The semi-quantitative LCMS and GCMS screens detected a number of synthetic organic compounds. Although not naturally-occurring, many may still be relevant to appreciate the nature of organic compounds present and the likely implications for groundwater flow. From eight samples collected for analysis, there were a total of 111 detections, of a total of 59 unique compounds. The compounds and their uses are presented in Table 4.4. Many compounds present are agricultural chemicals (pesticides/herbicides/fungicides), but there is evidence of a few pharmaceutical and industrial compounds, as well as some other contaminants.

The two sites with the most LCMS and GCMS detections were OOG4 and OOG7 (Table 4.5). These are both from the unconfined section of the aquifer (Figure 3.1). Both groundwaters were oxic with relatively high concentrations of NO₃ (>30 mg/L). Most of the compounds detected in these two samples were pesticides.

Samples OOG8 and OOG10 are from the confined setting and show the lowest number of detections of synthetic compounds. Sample OOG1 also showed a low number of detections, despite being located within the unconfined setting, being oxic and with a high NO₃ concentration (112 mg/L). The unconfined samples clearly show a greater number of detections compared to the confined groundwater.

Table 4.4. Compounds detected from LCMS/GCMS analysis (with usage provided by laboratory catalogue)

Compound detected	CAS#	Usage/Description
1,2,4,5-tetrachlorobenzene	95-94-3	Volatile solvent
2,3,5,6-tetrachloroaniline	3481-20-7	Intermediate
2,6-dichlorobenzamide	2008-58-4	Pesticide/dichlobenil metabolite
4,4'-methylenebis (phenyl isocyanate)	101-68-8	Adhesive/intermediate
Acesulfame (acesulfame-K)	33665-90-6	Sweetener
Atrazine	1912-24-9	Herbicide/pesticide/veterinary drug
Atrazine-desethyl (desethylatrazine)	6190-65-4	Pesticide breakdown product [atrazine]
Atrazine-desisopropyl (deisopropylatrazine)	1007-28-9	Pesticide breakdown product [atrazine]
Bentazone	25057-89-0	Herbicide/pesticide/veterinary drug
Benzenesulfonamide, N-butyl	3622-84-2	Neurotoxic plasticiser
bis(2-ethylhexyl)phthalate (DEHP)	117-81-7	Plasticiser
Boscalid (nicobifen)	188425-85-6	Herbicide/pesticide/veterinary drug
Bromacil	314-40-9	Herbicide/pesticide/veterinary drug
Carbamazepine	298-46-4	Equine drug/anticonvulsant
Chloridazon (PAC)	1698-60-8	Pesticide/herbicide
Chloridazon-desphenyl	6339-19-1	Pesticide
Chloridazon-desphenyl-methyl	17254-80-7	Pesticide/herbicide
Chlorothiazide	58-94-6	Equine drug/diuretic
Chlortoluron (chlorotoluron)	15545-48-9	Pesticide/herbicide
Clopidol	2971-90-6	Veterinary drug/coccidiostatic
Cyproconazole	15545-48-9	Pesticide/fungicide/veterinary drug
Dibenzofuran	132-64-9	Pesticide/insecticide
Dimethomorph	110488-70-5	Pesticide/fungicide
Diuron	330-54-1	Pesticide/herbicide
Epoxiconazole (BAS 480F)	135319-73-2	Pesticide/fungicide/veterinary drug
Ethofumesate	26225-79-6	Herbicide/pesticide/veterinary drug
Fenuron (N,N-dimethyl-N-phenylurea)	101-42-8	Pesticide/herbicide
Fluoranthene	206-44-0	Polyaromatic hydrocarbon

Compound detected	CAS#	Usage/Description
Fluorene	86-73-7	Polyaromatic hydrocarbon
Flurtamone	96525-23-4	Herbicide/pesticide/veterinary drug
Indane	496-11-7	Petrochemical compound
Isoproturon	34123-59-6	Herbicide/pesticide/veterinary drug
Lenacil	2164-08-1	Herbicide/pesticide/veterinary drug
MCPP/Mecoprop	7085-19-0	Pesticide/herbicide
Metalaxyl	57837-19-1	Pesticide/fungicide/veterinary drug
Metazachlor	67129-08-2	Herbicide/pesticide/veterinary drug
Methabenzthiazuron	18691-97-9	Pesticide/herbicide
Metribuzin	21087-64-9	Herbicide/pesticide/veterinary drug
Metribuzin-desamino	35045-02-4	Pesticide
Metribuzin-diketo	56507-37-0	Pesticide
Monuron	150-68-5	Pesticide/herbicide
N,N-diethyl-m-toluamide	134-62-3	DEET/insect repellent
Oxadixyl	77732-09-3	Pesticide/fungicide/veterinary drug
Pentobarbital	76-74-4	Equine drug/anaesthetic/hypnotic
Perfluorobutane sulfonate	375-73-5	Surfactant
Perfluorohexane sulfonate	108427-53-8	Surfactant
Piroxicam	36322-90-4	Veterinary drug/equine drug/antiphlogistic
Pyrene	129-00-0	Polyaromatic hydrocarbon
Saccharin	81-07-2	Pharmaceutical aid/sweetener
Simazine	122-34-9	Herbicide/pesticide/veterinary drug
Sucralose	56038-13-2	Sweetener
Sulfamethoxazole	723-46-6	Veterinary drug/antibiotic
Sulfanilamide	63-74-1	Veterinary drug/antibiotic/chemotherapeutic
Tebuconazole (Terbuconazole)	107534-96-3	Pesticide/fungicide
Tebufenozide	112410-23-8	Pesticide/insecticide
Terbumeton or Prometon	33693-04-8	Herbicide/pesticide/veterinary drug
Terbuthylazine	5915-41-3	Herbicide/pesticide/veterinary drug
Triphenyl phosphate	115-86-6	Flame retardant/plasticizer

Table 4.5. LCMS/GCMS compound detections in BGS samples. Sites with two detections of the same compound are from the separate LCMS and GCMS laboratory analyses

LCMS/GCMS analysed compounds	Sample number								Total
	01	02	03	04	05	07	08	10	
1,2,4,5-tetrachlorobenzene						1			1
2,3,5,6-Tetrachloroaniline						1			1
2,6-Dichlorobenzamide	1		1			2			4
4,4'-Methylenebis (phenyl isocyanate)						1			1
Acesulfame (Acesulfame-K)				1		1			2
Atrazine			1		1	2			4
Atrazine-desethyl (Desethylatrazine)			1	1	1	1			4
Atrazine-desisopropyl (Deisopropylatrazine)		1	1	1	1	1			5
Bentazone			1	1	1	1			4
Benzenesulfonamide, N-butyl		1				1			2
bis(2-ethylhexyl)phthalate (DEHP)	1					1			2
Boscalid (Nicobifen)				1		1			2

LCMS/GCMS analysed compounds	Sample number								Total
	01	02	03	04	05	07	08	10	
Bromacil					1				1
Carbamazepine						1			1
Chloridazon (PAC)		1	1	1		1			4
Chloridazon-desphenyl		1	1	1		1			4
Chloridazon-desphenyl-methyl		1	1	1	1	1			5
Chlorothiazide					1				1
Chlortoluron (Chlorotoluron)			1						1
Clopidol			1	1	1	1			4
Cyproconazole				1					1
Dibenzofuran						1		1	2
Dimethomorph						1			1
Diuron						1			1
Epoxiconazole (BAS 480F)				1					1
Ethofumesate				1					1
Fenuron (N,N-Dimethyl-N-phenylurea)					1	1			2
Fluoranthene		1				1			2
Fluorene						1		1	2
Flurtamone						1			1
Indane								1	1
Isoproturon		1		1		1			3
Lenacil				1					1
MCCP / Mecoprop				1					1
Metalaxyl		1				1			2
Metazachlor				1					1
Methabenzthiazuron				1					1
Metribuzin		1							1
Metribuzin-desamino		1		1					2
Metribuzin-diketo		1							1
Monuron					1				1
N,N-diethyl-m-toluamide		1							1
Oxadixyl		2				2			4
Pentobarbital					1				1
Perfluorobutane sulfonate					1				1
Perfluorohexane sulfonate				1	1	1			3
Piroxicam	1								1
Pyrene		1							1
Saccharin				1					1
Simazine			1	1	1	2			5
Sucralose				1	1				2
Sulfamethoxazole						1			1
Sulfanilamide						1			1
Sulphur (S8)							1	1	2
Tebuconazole (Terbuconazole)				1					1
Tebufenozide						1			1
Terbumeton or Prometon						1			1
Terbuthylazine				1					1
Triphenyl phosphate	1								1
Total	4	15	11	24	15	37	1	4	111

5 Geochemical controls

5.1 EVOLUTION OF GROUNDWATER CHEMISTRY

The groundwater chemistry of the East Midlands and South Yorkshire Sherwood Sandstone aquifer has been the subject of numerous investigations over the last 40 years (Andrews et al., 1994; Andrews and Lee, 1979; Bath et al., 1979; Bath et al., 1987; Edmunds et al., 1982; Edmunds and Smedley, 2000; Smedley and Edmunds, 2002; Smedley et al., 2018). As a result, a detailed interpretation of the key hydrogeochemical processes, groundwater flow paths and residence times has developed. The groundwater compositional range is influenced variously by atmospheric inputs to recharging rainfall, mineral dissolution and precipitation reactions and redox reactions in the aquifer, and inputs from surface pollution. This section summarises the main likely controls on inorganic and organic compositions of the groundwater and their changes down the groundwater flow gradient.

5.1.1 Recharge inputs and downgradient change

Rainfall and inferred modern recharge compositions were discussed in Section 2.6. Recharge introduces small quantities of the major ions, especially Na and Cl into the shallow groundwater system. Estimated concentrations of nitrogen in recharge of the order of 12 mg/L as NO₃ (Table 2.5) suggest the scale of modern inputs of NO₃ and NH₄ from industrial and agricultural atmospheric emissions in the region. Inputs of trace halogens (I and F) in the groundwater are likely also derived substantially from atmospheric inputs since concentrations appear not to increase across the aquifer.

Relatively high concentrations of Cl, SO₄ and NO₃ in groundwater from the unconfined aquifer were highlighted by Edmunds et al. (1982), Edmunds and Smedley (2000) and Smedley and Edmunds (2002). These were concluded to derive from surface contaminants such as urban and agricultural effluents as well as industrial atmospheric emissions and mine drainage from former coal-mined areas. The risks to the aquifer from coal-mine drainage have been well-documented (Holloway et al., 2005; Yang et al., 1999). Increased concentrations of solutes in groundwater from coal-mine spoil have also been reported for the Sherwood Sandstone to the east of Thoresby colliery (Klinck et al., 2004).

Contamination of groundwater from coal-mine drainage is a likely origin of relatively high concentrations of dissolved Br. Concentrations were noted to be highest in the unconfined section of the aquifer, with particular highs around Nottingham and Mansfield (Figure 4.8a). Relatively high concentrations of Cu, Pb and Zn are also a feature of the unconfined aquifer and may originate from surface urban or industrial contamination. Concentrations in the MMG-confined aquifer are lower. It is possible that some of the increased concentrations of Co, V, Sb and Mn in the north-west, derive from recharge via the Quaternary superficial deposits under oxic or mildly reducing conditions, depending on lithology of the superficial strata.

Studies of downgradient changes in groundwater chemistry from the East Midlands Sherwood Sandstone aquifer (Edmunds et al., 1982; Edmunds and Smedley, 2000; Smedley and Edmunds, 2002) have highlighted the notable variations in major-ion concentrations (Figure 5.1) with relatively high concentrations of Cl, SO₄ and NO₃ in the unconfined aquifer at outcrop in the west, giving way downgradient to lower concentrations of each as the groundwater passes beneath the MMG into the confined part of the aquifer. In the section just into the confined aquifer, Cl concentrations in particular were noted to be very low (<20 mg/L). Radiocarbon dating of the groundwaters in this section showed them to be of likely Holocene age and the low Cl concentrations were attributed to recharge of low-Cl rainfall unaffected by modern atmospheric pollutants (Edmunds and Smedley, 2000). Concentrations of Cl were noted to be much higher (ca. 5000 mg/L) in groundwater from the deep confined aquifer at its easterly extent. This was taken to be old brackish formation water, likely of Pleistocene age (Figure 5.1). The groundwater

samples included in the dataset for the current study did not extend as far east into Lincolnshire as the studies identifying brackish groundwater at depth and so the salinity range of samples in this study is less extreme.

The trend of changing concentrations of Cl, SO₄ and NO₃ with increasing groundwater residence time identified laterally across the aquifer has also been observed vertically with depth in some boreholes from the unconfined aquifer. The change is also related to increasing residence time with depth and the changing chemistry of recharge since the Holocene (Figure 5.2). Some of the loss of NO₃ with depth can be attributed to denitrification under mildly reducing conditions (Smedley et al., 2018), although the paucity of electron donors in the red-bed Sherwood Sandstone sequence likely limits the capacity for this reaction.

Edmunds et al. (1982) and other workers subsequently have used groundwater temperature as a proxy for groundwater residence time/depth in the East Midlands Sherwood Sandstone aquifer. This highlighted some clear chemical trends downgradient over lateral distances of some 40 km, where the aquifer outcrops in the west and dips gently eastwards beneath the MMG. The lateral association between temperature and groundwater chemistry is much less clear in the South Yorkshire section. Here, groundwater chemistry is more variable in the north-west section. Though not covered by MMG, the aquifer is covered partially by Quaternary superficial deposits whose thickness and lithology can also lead to confined or semi-confined conditions and produces more varied recharge rates, flow paths and redox conditions. The South Yorkshire aquifer section also has a paucity of sampling points in the MMG-confined part.

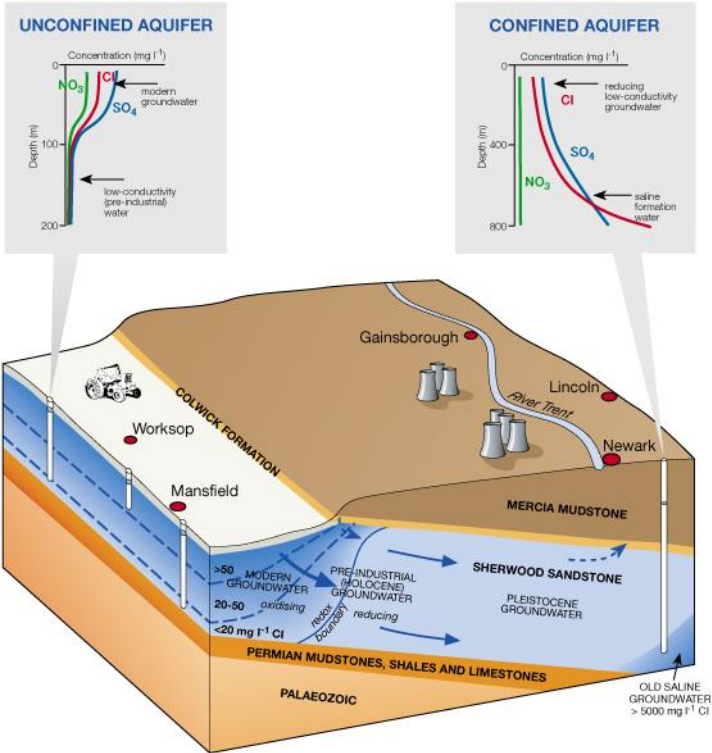


Figure 5.1. Block diagram depicting the Sherwood Sandstone aquifer of the East Midlands (after Edmunds and Smedley, 2000; Smedley and Edmunds, 2002), Colwick Formation now known as the Tarporley Siltstone Formation)

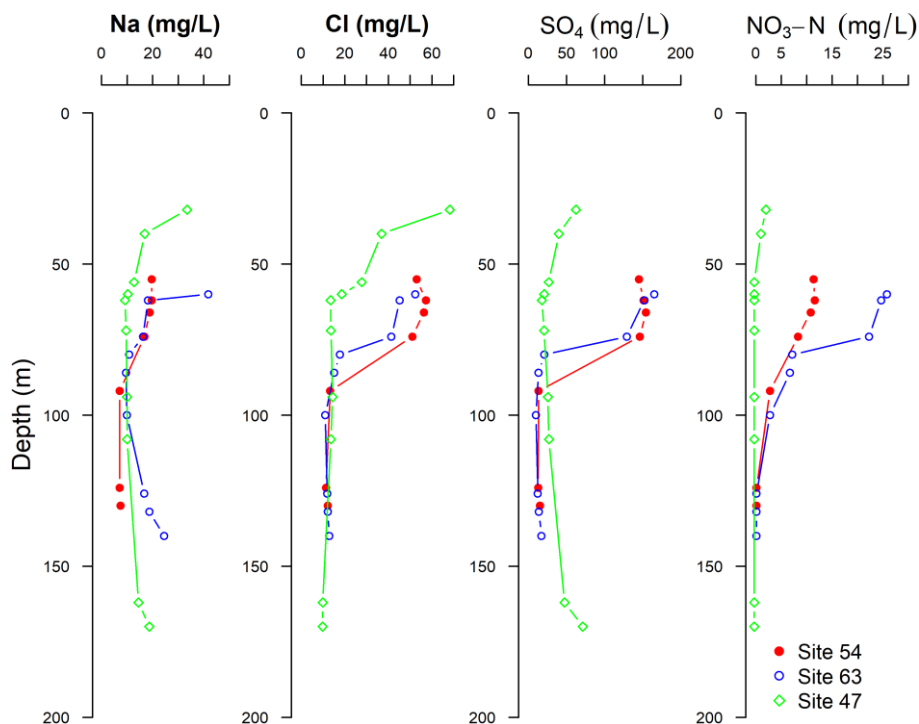


Figure 5.2. Profiles of major-ion chemistry in groundwater from three boreholes from the unconfined aquifer in South Yorkshire (from Smedley et al., 2018)

Some relatively high concentrations of Cl and SO₄ and high SEC values are also apparent in the area around Goole and Pontefract, towards the Humber Estuary. There has been little information documented on the variations in this area but similar processes are likely to apply, with oxic, modern NO₃-bearing groundwaters in the western part, giving way to anoxic groundwater downgradient in sections confined by superficial deposits, and then MMG deposits. High concentrations of Ca, Mg, and SO₄ in the north-east suggest dedolomitisation with gypsum/anhydrite dissolution has been an important control. Redox processes control distributions of redox-sensitive solutes, including higher concentrations of Fe and Mn in the confined aquifer and among the highest concentrations of NH₄ observed. This is likely of natural origin. It is possible that the higher SEC, Ca, SO₄ and NH₄ concentrations in this part of the aquifer relate to facies variations in the Sherwood Sandstone.

5.1.2 Carbonate and sulphate mineral reactions

Although a sandstone aquifer, the small quantity of carbonate minerals (calcite, dolomite) within the Sherwood Sandstone matrix has an important impact on groundwater chemistry. The concentrations of HCO₃ (alkalinity), Ca and Mg as well as pH are strongly influenced by carbonate mineral reactions. The groundwater pH is buffered between 6.9 and 8.7 (Table 4.1), the higher values suggesting equilibrium reactions in a closed system where CO₂ is not replenished from the atmosphere or soil zone. A few areas of sandstone at outcrop are reported to have been decalcified (Section 2.4) but where carbonate minerals are present, the groundwater reaches equilibrium with calcite and dolomite and dolomite dissolves congruently. Further downgradient into the confined aquifer of the East Midlands, Edmunds et al. (1982) concluded that dolomite dissolution continued but became incongruent, and further into the deeper confined aquifer, dissolution of gypsum or anhydrite promoted dolomite dissolution with associated calcite precipitation. The groundwater samples collected in the BGS campaign support this inference, with all being close to or at saturation with respect to calcite (saturation index calcite 0 ± 0.1) and close to or at saturation with dolomite (-0.6 to 0.2). Molar Mg/Ca ratios across the aquifer range between 0.19 and 2.2 (n=62, BGS and WIMS data). Values just below unity (ca. 0.8) would suggest equilibrium with respect to pure dolomite (CaMg(CO₃)₂) and calcite (CaCO₃) but values distant from this may relate to carbonate impurities (Appelo and Postma, 2007; Edmunds et al., 1982). Gypsum dissolution has

also been inferred to explain increases in SO_4 concentrations in Sherwood Sandstone groundwater around Birmingham (Jackson and Lloyd, 1983) and north-west England (Kimblin, 1995). Dissolution of gypsum/anhydrite are the most likely cause of increasing concentrations of SO_4 downgradient in the confined aquifer of the East Midlands (Edmunds et al., 1982).

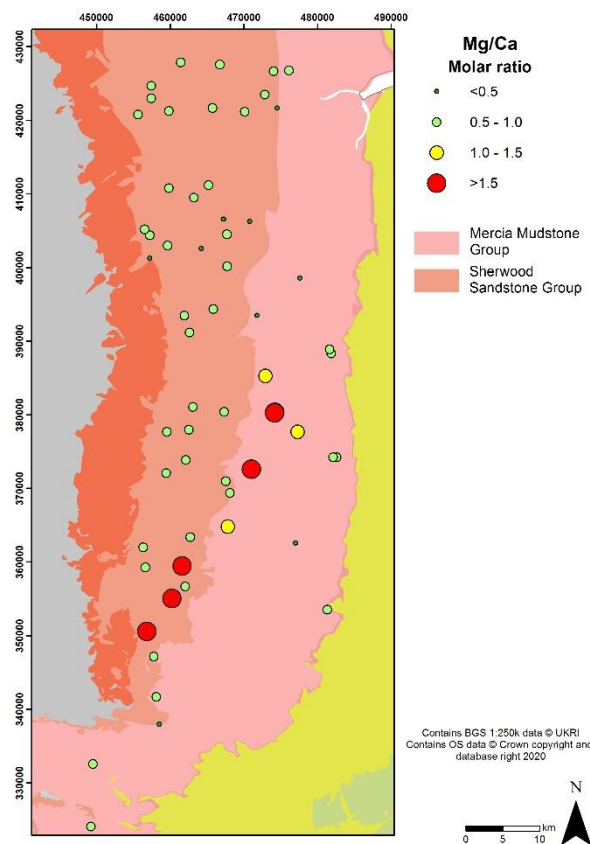


Figure 5.3. Molar Mg/Ca ratio for groundwater samples from the BGS campaign and WIMS data. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

Barium in the groundwater is probably also derived from dissolution of carbonate minerals but concentrations are ultimately determined by the solubility control of barite: all samples in the BGS campaign were saturated or near-saturated with barite, as is expected given the relative abundance of SO_4 in many of the groundwaters. Barite solubility control is also supported by the near linear trend in the cumulative-probability distribution (Figure 4.13).

Distributions of strontium are most likely also related to dissolution of carbonate minerals and gypsum/anhydrite. Concentrations are typically higher into the MMG-confined aquifer (Figure 4.9), suggesting build-up of the element in solution with increasing residence time.

5.1.3 Silicate reactions

Concentrations of SiO_2 show a relatively limited range (5.37–17.9 mg/L; Si, 3.1 to 6.9 mg/L) and the cumulative-probability plot showed a linear trend (Figure 4.6). This is considered due to equilibration with respect to quartz: the groundwaters are saturated or close to saturation with respect to quartz but undersaturated with respect to chalcedony and amorphous silica.

Downgradient increases in the concentrations of K, Li, Cs and Rb in the groundwater probably relate to the dissolution of silicate minerals (alkali feldspar, clays) with increasing residence time. These trace elements were used as proxy residence-time indicators in the East Midlands aquifer by Edmunds and Smedley (2000).

5.1.4 Redox reactions

Redox reactions have a strong influence on the spatial distributions of many solutes in the groundwater as the aquifer has varying redox conditions between the outcrop in the East Midlands section, the Quaternary-confined aquifer in the South Yorkshire section and the MMG-confined aquifer in both. Groundwater evolves downgradient from oxic conditions at outcrop (DO >5 mg/L and Eh >300 mV), to sub-oxic or anoxic (DO <1 mg/L; Eh <300 mV) in the confined and semi-confined sections. Concentrations of NO₃ are high in the unconfined aquifer, commonly in excess of the national standard for drinking water. Under anoxic conditions, concentrations of NO₃ diminish to very low values or are not detected. This is likely a combination of older pre-contamination recharge in the confined aquifer and denitrification, albeit the limited supply of reducing agents for the reaction is noted. Concentrations of Fe, Mn, Mo and NH₄ increase slightly in response to the onset of reducing conditions in the confined aquifer. Relatively high concentrations of NH₄ are observed in northern part of the area, around the Ouse/Humber area, under conditions which appear to be largely oxic (north-west) or anoxic (north-east). The reasons are unclear but contamination from anthropogenic pollutants might be a factor in the oxic conditions, while reduction of nitrate by degradation of organic matter may be the cause under more strongly reducing conditions. Release of adsorbed NH₄⁺ from clays in the superficial deposits is also a possibility.

Onset of reducing conditions with confinement also leads to diminishing concentrations of Cr as its mobility decreases, probably due to a change of oxidation state and sorption onto Fe oxides (Smedley and Edmunds, 2002).

Confined and semi-confined parts of the aquifer are associated with mildly reducing conditions and increased concentrations of Fe and Mn, derived by reductive dissolution of Fe and Mn oxides. Increased concentrations of both are a particular feature of the Quaternary-confined section in South Yorkshire (Figure 4.11). Mapping shows that relatively high concentrations of Sb, Co and V also occur in the Quaternary-confined conditions in South Yorkshire. Concentrations of Mo also increase in the confined sections, also likely related to release from Fe oxides under reducing conditions.

Increased concentrations of As, U and Sb tend to be highest on the marginal area of the MMG-confined aquifer and have been attributed to increases in pH under oxic or mildly reducing conditions, affecting the sorption affinity for surfaces of Fe oxides.

In the deep part of the MMG-confined further east than the current study area, conditions are inferred to be more strongly reducing, with evidence from S isotopic compositions for sulphate reduction at a minority of sites (Smedley and Edmunds, 2002). There is little evidence for this reaction within the bounds of the confined aquifer considered in this study however: SO₄ concentrations in the confined aquifer are typically high and evidence for the presence of H₂S is lacking.

5.1.5 Dissolved gases

Distributions of dissolved CO₂ are associated with carbonate reactions and pH. Distributions of dissolved methane are clearly redox-controlled with low concentrations in unconfined conditions and higher concentrations under reducing conditions in the MMG-confined aquifer and to some extent in the Quaternary-confined aquifer in the north-west (Bell et al., 2016; Bell et al., 2017) (Figure 5.4). Concentrations up to 120 µg/L (95th percentile 15 µg/L) in groundwater from the BGS campaign suggest a limited capacity for methanogenesis in the relatively oxic red-bed sandstone aquifer.

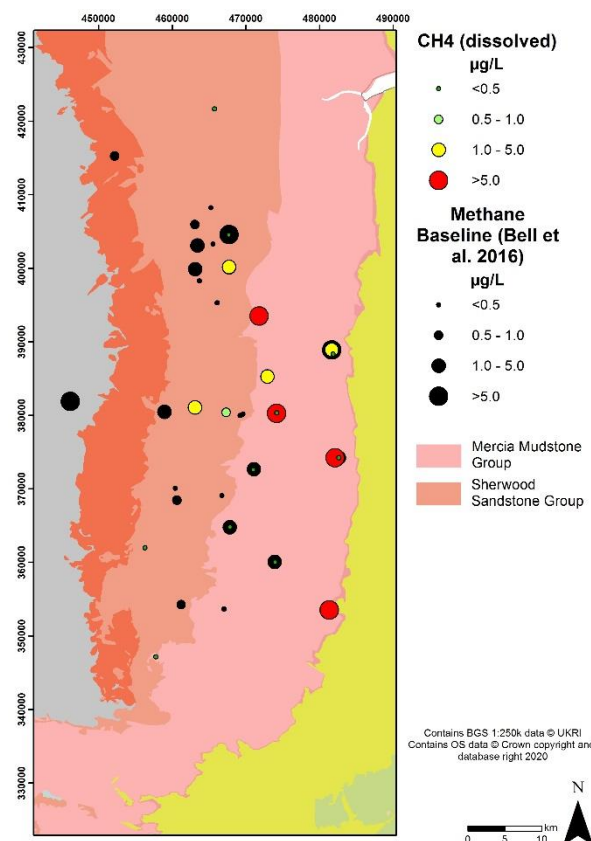


Figure 5.4. Geological map showing distributions of dissolved methane; includes data from the Bell et al. (2016) study. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

Activities of dissolved Rn up to 20 Bq/L are comparable with the values reported for groundwater in the Smedley and Edmunds (2002) study (11–12 Bq/L) and with activities of Rn reported elsewhere in British Permo-Triassic red-bed sandstones (Young, 2015). The origin of the Rn is taken to be alpha decay of U within Fe oxides in the sandstone matrix.

5.2 ORGANIC COMPOUNDS

Concentrations of NPOC/TOC are typically highest in groundwater from the unconfined aquifer, diminishing downgradient into the confined section. The higher concentrations in the unconfined aquifer are likely linked to additional inputs from modern surface and atmospheric pollution (Raymond, 2005), albeit concentrations are only up to a 95th percentile value of around 6 mg/L. Naturally-occurring, soil- and aquifer-derived organic carbon in the groundwater will also likely to have diminished downgradient into the confined aquifer as it becomes consumed in the sequence of redox reactions described above (Section 5.1.4).

Investigation of data from the WIMS database revealed few detections of organic compounds in the VOC, SVOC, PAH and TPH groups: in all, 19 compounds were detected. Only two (chloroform and fluoranthene) were detected at sufficient sites to warrant a statistical evaluation. Chloroform (CHCl₃) occurs in groundwater as a disinfection by-product (Ivahnenko and Zogorski, 2006) and is therefore an anthropogenic input. Its occurrence in groundwater samples in the marginal part of the MMG-confined aquifer (Figure 4.15a) is therefore surprising and unexplained. Contamination by local treated drinking water is a possibility but better knowledge of the site characteristics would be needed to evaluate the cause more thoroughly.

Detections of fluoranthene were in the unconfined aquifer, in the northern part and around Mansfield (Figure 4.15b). Occurrence of this PAH could originate from atmospheric or local industrial contamination, including coal-mine drainage.

Analyses for a range of synthetic organic compounds by GCMS and LCMS revealed a number of detections, mainly of pesticides, and those detected were mainly from the unconfined aquifer. This is consistent with inputs of modern diffuse pollutants into the younger, oxic groundwaters of the unconfined aquifer.

5.2.1 Proximity to onshore oil and gas locations

The relationship between the proximity of samples to onshore oil and gas wells and the reported values has been explored, considering that these may be a potential pathway for organic constituents and deeper saline groundwater. The analytes in Table 5.1 were plotted against a 1 km buffer around the OGA Onshore well dataset (OGA, 2020), and measurements within the buffer zone were extracted. The number of measurements, and the range of data extracted, are shown in Table 5.1. The number of intersecting measurements were limited, with 15 locations for both Chlorine and Sulphate (Table 5.1 and Figure 5.5). Methane, Fluoranthene and Chloroform only had 7 or less locations.

The data in Table 5.1 identify that there are an insufficient number of intersecting locations to draw any statistically robust evaluation of a relationship between proximity to onshore oil and gas wells and the reported hydrochemistry. The geochemical controls highlighted in sections 5.1 and 5.2 have a much greater impact on the observed distribution of data than a proximity to oil and gas developments.

Table 5.1. Selected intersecting analytes within 1 km of the OGA (2020) onshore wells dataset

Analyte	Number of intersects (n)	Range of extracted data
Na	9	4.4 – 34.2
Cl	15	7.5 – 135 mg/L
SO ₄	15	2.3 – 205 mg/L
CH ₄	6	<0.5 – 6.1 µg/L
Fluoranthene	7	<0.01 µg/L
Chloroform	6	<0.1 – 0.39 µg/L

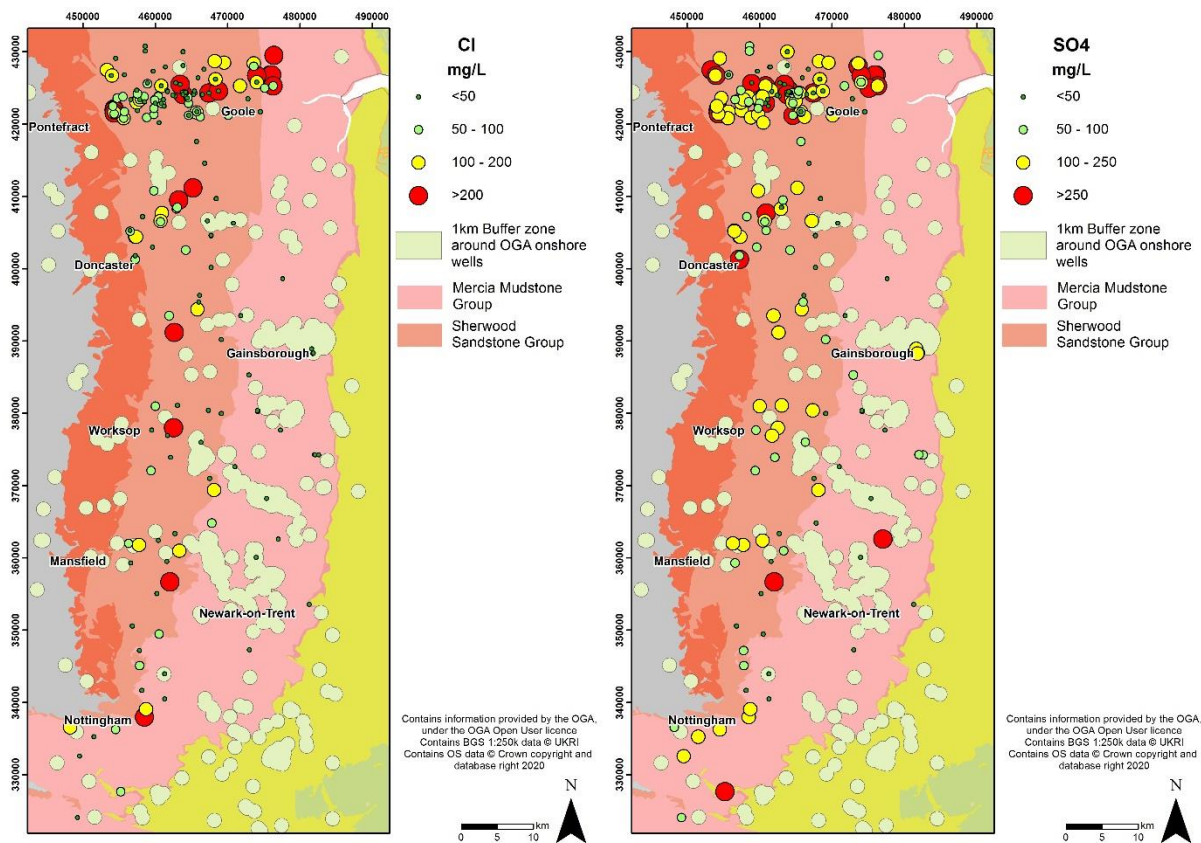


Figure 5.5. Plots of (a) chloride and (b) sulphate, and their intersection with a 1 km buffer around OGA (2020) onshore wells. BGS 1:250k data ©UKRI 2020; OS data ©Crown copyright 2020

5.3 TEMPORAL VARIATION

Temporal variability in chemistry of groundwater from the Sherwood Sandstone aquifer is apparent from up to 30 years' worth of data for sites contained in the WIMS database. Variations are greatest in the concentrations of inorganic constituents and in the unconfined aquifer. Concentrations of organic constituents are, as for the spatial evaluation, overwhelmingly below detection limits and temporal trends not apparent (non-detects are distinguished from detects in the figures). Time-series plots for dissolved inorganic constituents in groundwater are given as examples for three sites in the unconfined aquifer in Figure 5.6, Figure 5.7 and Figure 5.8, and for two sites in the MMG-confined aquifer in Figure 5.9 and Figure 5.10. Sites in the unconfined aquifer show variability with time in concentrations of a number of major and minor ions, and with variable increasing or decreasing trends. Increasing or decreasing concentrations of inorganic constituents (e.g. NO_3 , Cl and SO_4) presumably relate to variations over time in land-use, agricultural management and inputs of urban pollutants and mine drainage.

Far fewer trends are seen in the groundwater from the confined aquifer, although some variability is still apparent in the absolute concentrations of solutes.

The temporal variations have implications for assessments of baseline concentrations of individual parameters in the groundwaters, particularly in the unconfined parts of the aquifer. The baseline assessment has been made on the basis of latest available site data. Evaluation of data for individual sites and causes of temporal variations in chemistry would need a more thorough investigation of factors such as pumping rates, pump and water levels and local land-use.

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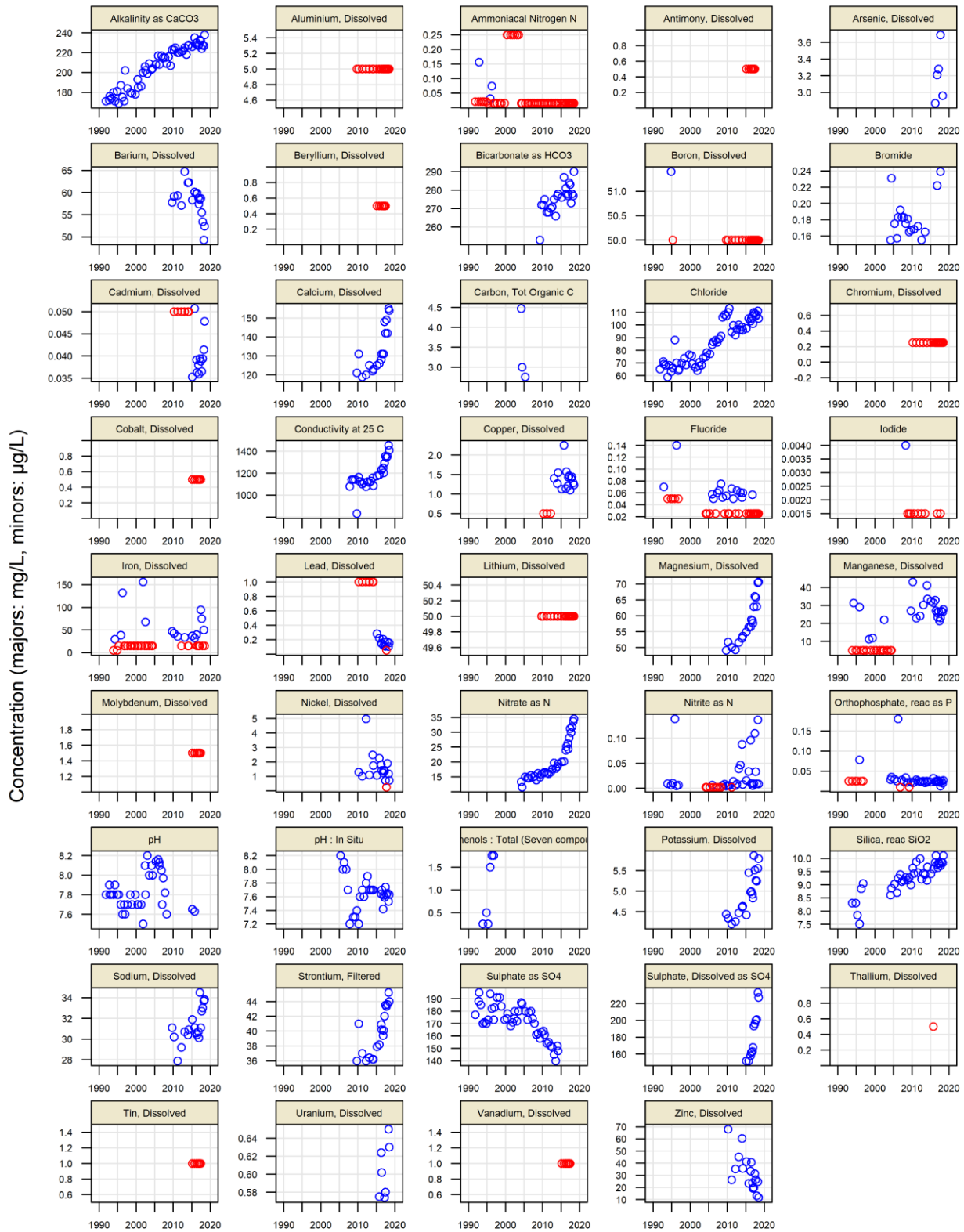


Figure 5.6. Temporal variation in groundwater compositions from a site in the unconfined aquifer (WIMS data)

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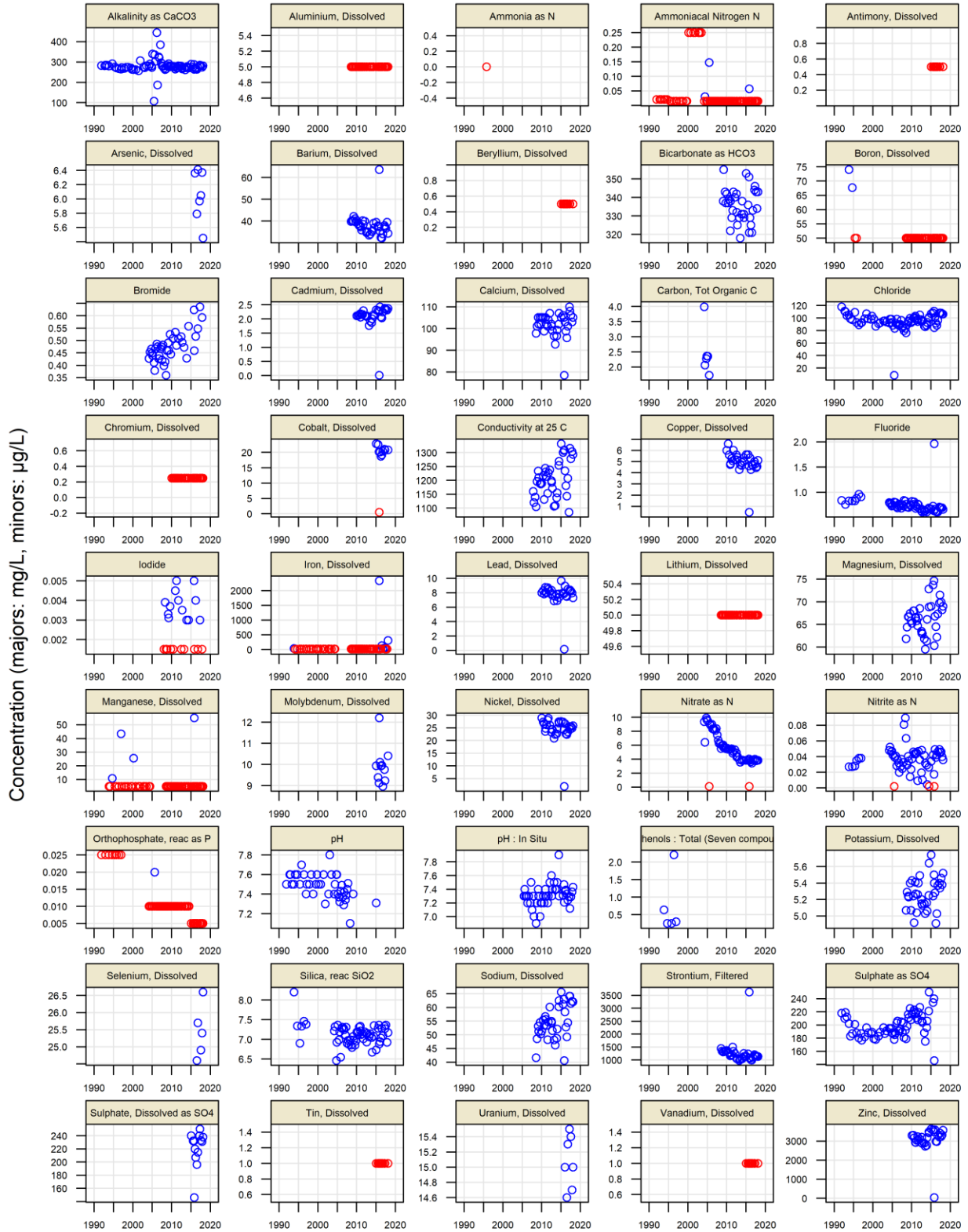


Figure 5.7. Temporal variation in groundwater compositions from a site in the unconfined aquifer (WIMS data)

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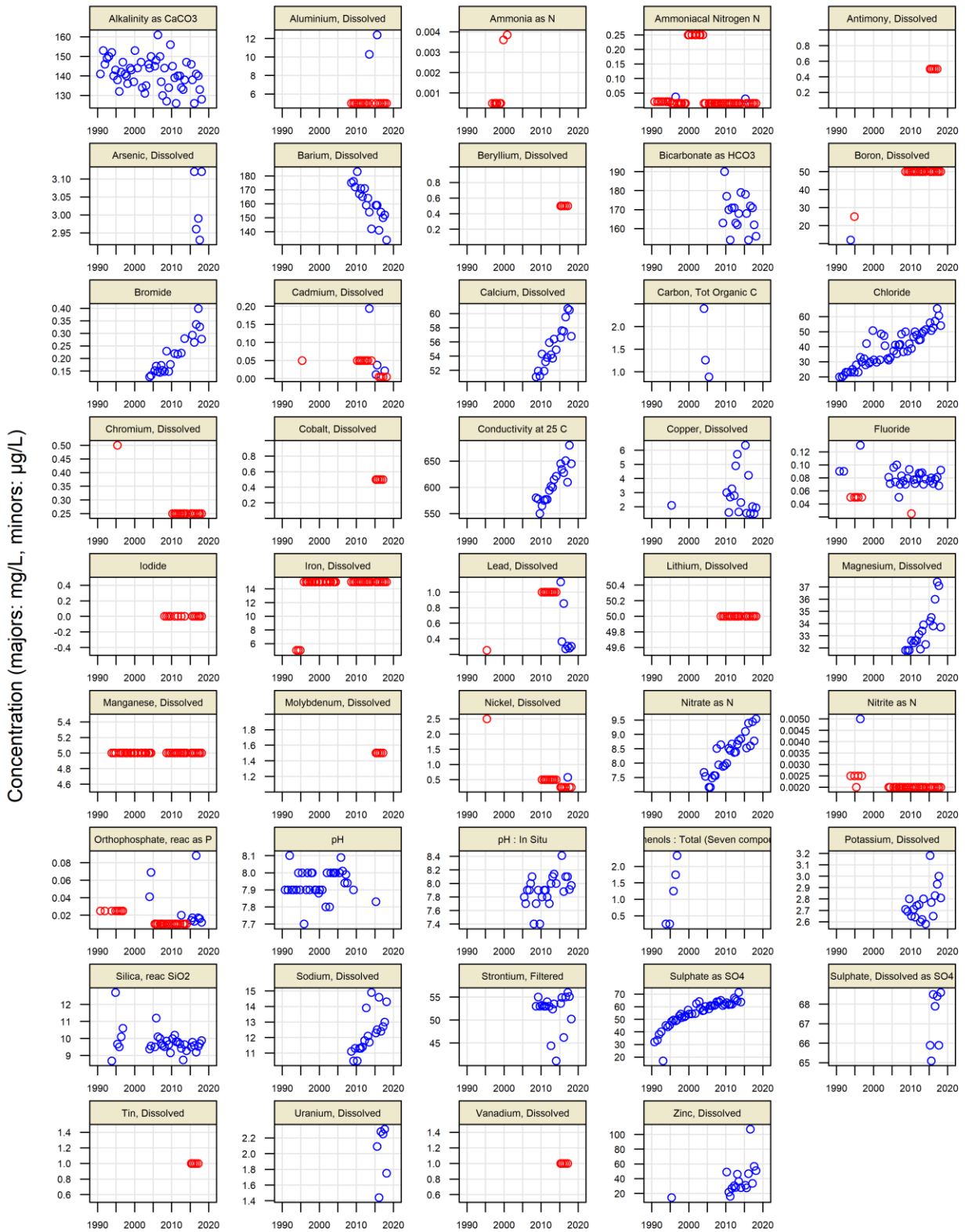


Figure 5.8. Temporal variation in groundwater compositions from a site in the unconfined aquifer (WIMS data)

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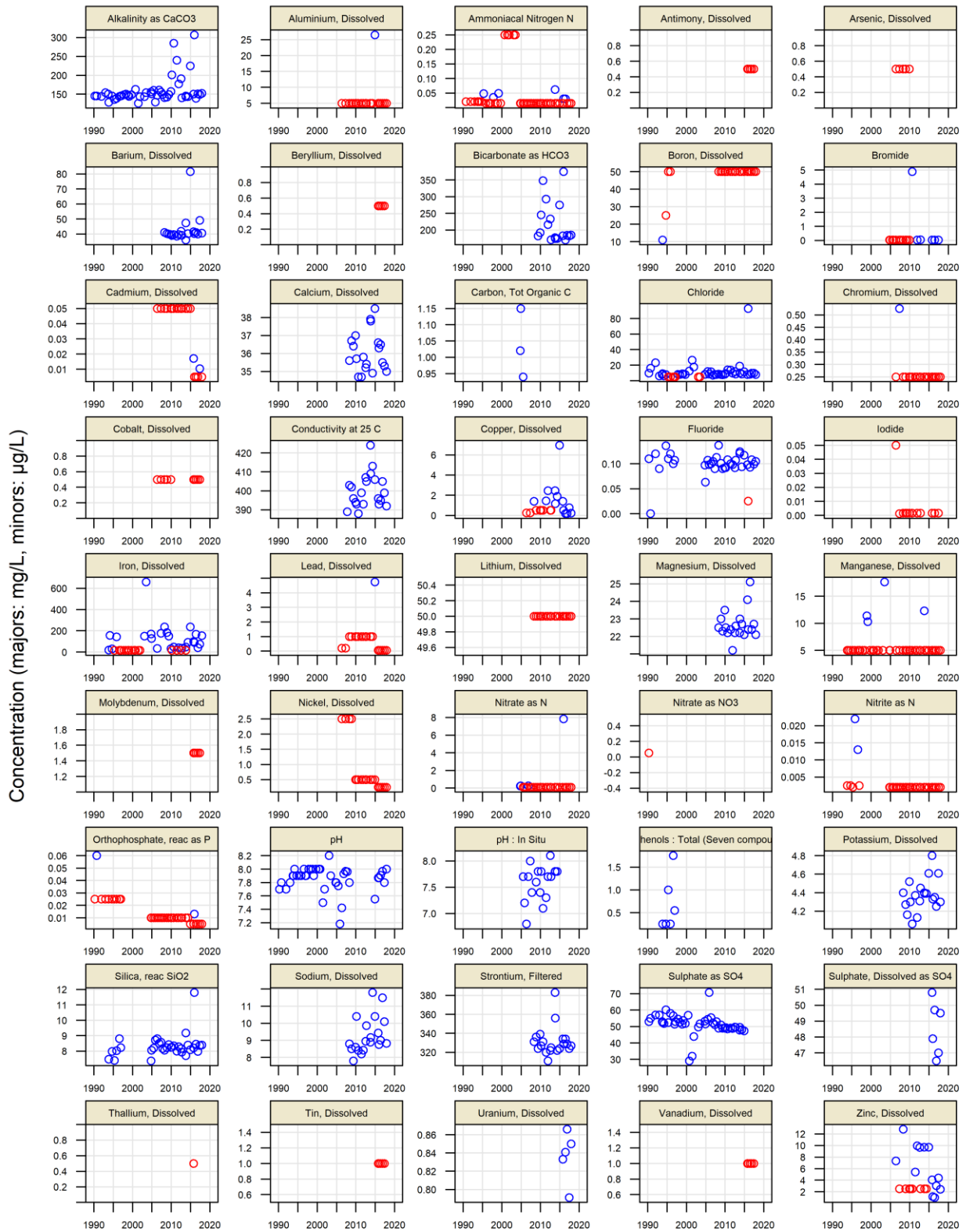


Figure 5.9. Temporal variation in groundwater compositions from a site in the MMG-confined aquifer (WIMS data)

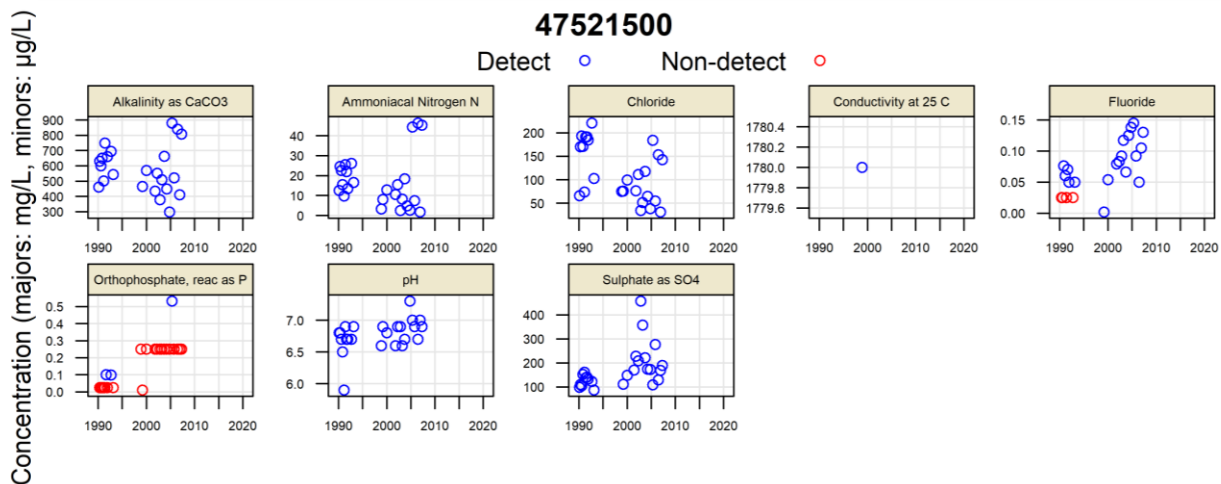


Figure 5.10. Temporal variation in groundwater compositions from a site in the MMG-confined aquifer (WIMS data)

5.4 ISOTOPIC EVIDENCE FOR GROUNDWATER FLOW AND RESIDENCE TIME

5.4.1 Stable-isotopic compositions

Results for stable isotopes of water ($\delta^{18}\text{O}/\delta^2\text{H}$) in selected samples have been plotted in Table 5.2 and Figure 5.11. The global meteoric water line (GMWL) and the meteoric water line for Keyworth, Nottingham (KW MWL) (Darling and Talbot, 2003), which define the trends for compositions of modern rainfall, are also plotted for comparison. Groundwater samples OOG15, OOG16 and OOG19 are from the edge of the MMG-confined aquifer and have broadly similar compositions ($\delta^{18}\text{O}$ ca. -8.2 ‰). Sample OOG18 is from the deeper MMG-confined aquifer (Figure 3.1) but with a relatively enriched stable-isotopic signature ($\delta^{18}\text{O}$ -7.4 ‰). A comparable stable-isotopic signature for groundwater from the same site was reported by Edmunds and Smedley (2000) and supports the validity of the data. From the combination of locations along the groundwater flow path and stable-isotopic compositions, these four groundwaters are considered likely of pre-industrial but post-glacial age, i.e. Holocene.

Sample OOG14 is also from the edge of the MMG-confined aquifer but is much more isotopically depleted. Sample OOG17 from much further downgradient is also depleted. Each have $\delta^{18}\text{O}$ signatures <-9 ‰ and $\delta^2\text{H}$ <60 ‰, suggesting recharge under colder than modern climatic conditions. This supports a tentative pre-Holocene age, i.e. likely Pleistocene.

Table 5.2. Stable-isotopic compositions ($\delta^{18}\text{O}/\delta^2\text{H}$) of groundwater samples from the BGS sampling campaign

Sample number	$\delta^{18}\text{O}$ VSMOW2 (‰)	$\delta^2\text{H}$ VSMOW2 (‰)
OOG14	-9.65	-66.6
OOG15	-8.28	-52.0
OOG16	-8.21	-52.7
OOG17	-9.27	-60.4
OOG18	-7.37	-53.5
OOG19	-8.24	-54.5

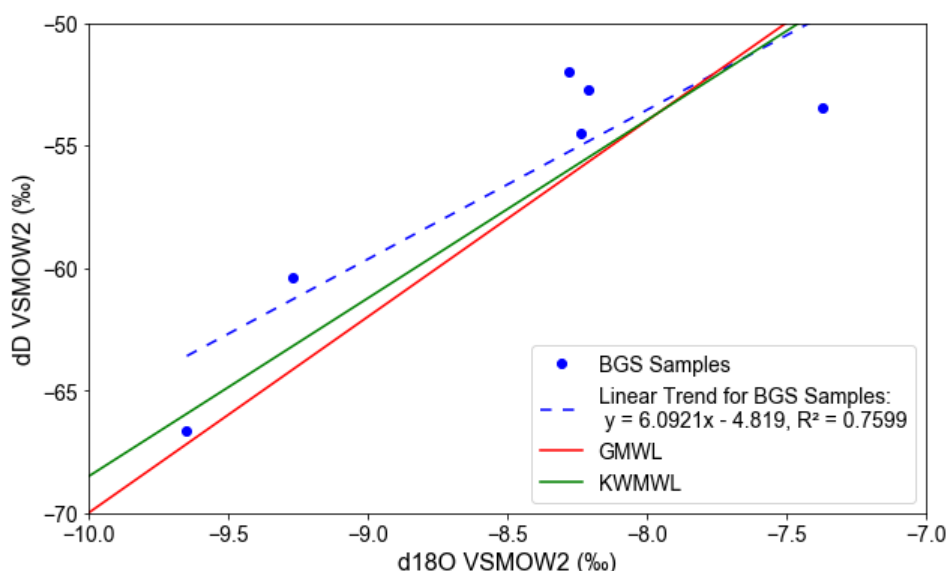


Figure 5.11. Stable-isotopic compositions ($\delta^{18}\text{O}$ versus $\delta^2\text{H}$) of collected groundwater samples relative to the global and local Keyworth meteoric water line (GMWL, KMWL) (KMWL from Darling and Talbot, 2003)

The $\delta^{13}\text{C}$ isotopic compositions of DIC in groundwater from the BGS sampling campaign are shown in Table 5.3. Compositions range from -16.1 ‰ to -9.7 ‰ and are more enriched in groundwater from the confined aquifer (samples OOG8, OOG10, OOG13–18). Compositions of $\delta^{13}\text{C}$ around -13 ‰ are consistent with the closed-system congruent dissolution of dolomite, the stoichiometry of which involves equal proportions of soil-zone CO_2 ($\delta^{13}\text{C}$ ca. -26 ‰) and dolomite (ca. 0 ‰). Subsequent incongruent dissolution of dolomite with precipitation of calcite can result in the DIC $\delta^{13}\text{C}$ composition becoming more enriched as it evolves towards the composition of the dissolving carbonate. More enriched compositions are therefore typically indicative of longer groundwater residence times in the aquifer (Clark and Fritz, 1997). Compositions around -10 ‰ are a feature of groundwater samples from the MMG-confined aquifer (Table 5.3).

Table 5.3. Stable-isotopic compositions of dissolved inorganic carbon ($\delta^{13}\text{C}$ ‰ VPDB) in groundwater samples from the BGS campaign

Sample number	$\delta^{13}\text{C}$ (‰ VPDB)
OOG01	-16.0
OOG02	-16.1
OOG03	-12.7
OOG04	-13.6
OOG05	-13.2
OOG06	-13.2
OOG07	-13.6
OOG08	-10.4
OOG10	-9.7
OOG13	-12.1
OOG14	-10.4
OOG15	-12.7
OOG16	-11.6
OOG17	-10.0
OOG18	-12.1

5.4.2 Radiocarbon dating

Model age estimates from the four groundwater samples analysed for ^{14}C were computed by correcting for initial ^{14}C (A_0) using a revision of the (Fontes and Garnier, 1979) model following (Han and Plummer, 2013). ^{14}C activities of the samples were low (3.8–31.5 pmc) and estimated model ages span the range 2,800 and 19,000 years (Table 5.4). This places the likely age of recharge of three of the analysed samples as Holocene (<10,000 years), but with the least

radiogenic sample, 3.77 pmc, being of likely late Pleistocene age. This older groundwater sample is from the Newark area, and one of the furthest down the groundwater flow gradient, almost to the easterly outcrop extent of the overlying MMG (Figure 3.1).

The age profiles of the water samples are consistent with earlier indications of increasing groundwater age downgradient in the confined aquifer (Edmunds et al., 1982; Edmunds and Smedley, 2000), with Holocene ages inferred for confined groundwater near the edge of the zone of confinement, but increasing eastwards. A gap in model ages for groundwaters was noted between 10,000 and 18,000 years, considered due to lack of recharge during the glacial maximum (Edmunds and Smedley, 2000). The model ages confirm the palaeowater status of the confined groundwater. Palaeowaters up to 35,000 years were identified in the East Midlands aquifer at its extreme easterly extent, some 30 km downgradient of the confined margin, but these were in deep brackish groundwater. The oldest age estimate from this study, 19,000 years, was from a groundwater of drinking-water quality (Na 11.7 mg/L, Cl 17.9 mg/L, SO₄ 19.6 mg/L), abstracted from a borehole some 400 m deep and located in the Newark area, around 20 km from outcrop. This complements previous evidence for fresh palaeowater existing in a borehole some 500 m deep in the Gainsborough area, at around 10 km from outcrop (Smedley et al., 2018).

Table 5.4. Radiocarbon activity (% modern carbon, pmc) for groundwater samples from the BGS campaign and estimated model ages

Sample	¹⁴C activity (pmc)	± error	Model age (y)
OOG15	19.7	0.2	7,500
OOG16	31.5	0.3	2,800
OOG17	3.77	0.1	19,000
OOG18	24.4	0.2	5,200

6 Baseline characteristics of the Sherwood Sandstone groundwater

6.1 INORGANIC CHEMICAL COMPOSITIONS

Groundwater chemical composition across the Sherwood Sandstone aquifer shows clear spatial and temporal variations related to varying atmospheric inputs, surface pollutants, natural water-rock interactions and groundwater flow paths and residence times. The understanding of what constitutes a baseline composition is context-dependent. A pristine pre-industrial baseline would reflect groundwater devoid of modern and historical inputs from atmospheric emissions or pollution from legacy mineral exploitation or historical impacts from changes of land-use. On the other hand, a baseline in the context of fulfilling the environmental objectives of the European Water Framework Directive might be more reasonably directed at evaluating and mitigating modern anthropogenic contaminants and activities and reversing modern trends. By contrast again, a baseline in the context of future exploration for, and exploitation of, onshore oil and gas resources would be more appropriately defined as the current, pre-exploration condition. This would include the impacts from modern industrial and agricultural activities, and legacy impacts, including from conventional oil and gas. An adequate understanding of the spatial and temporal variations in chemistry and their likely controls can serve all three purposes, but evaluation of the conditions prior to any new onshore oil and gas activity is the simplest approach as a summary of the current position with respect to chemical spatial and temporal variability could suffice.

Evaluation of the data from the BGS groundwater sampling campaign and the WIMS data has revealed that the chemical characteristics, controls and variability are very different between the sections of unconfined and confined aquifer. Unconfined groundwater has been recharged more recently, is typically oxic and contains relatively high concentrations of solutes from anthropogenic atmospheric emissions and surface pollutants (e.g. Na, Cl, SO₄, NO₃). Concentrations of dissolved Cu, Pb and Zn may also be enhanced by anthropogenic inputs. Concentrations of Br appear to be relatively high in the unconfined groundwater, possibly due to inputs from organic-rich sources, including coal-mine drainage. Concentrations of NO₃ in the unconfined groundwater commonly exceed the drinking-water standard of 50 mg/L, most likely as a result of modern agricultural inputs. The anthropogenic signatures superimpose on impacts from natural water-rock interactions, especially carbonate reactions, which control compositions of many solutes, notably Ca and Mg as well as alkalinity and pH. The time-series graphs presented indicate that concentrations of NO₃ have varied substantially with time in groundwater from a number of sites in the unconfined aquifer. These temporal variations need to be taken account of when evaluating the chemical baseline ranges in the context of future OOG-type industrial activities.

In the confined aquifer, modern anthropogenic pollutants are absent or at least less prevalent and the chemistry of the groundwater is controlled dominantly by natural mineral dissolution and precipitation reactions and redox reactions, each in turn controlled by downgradient flow and residence times. Carbonate mineral reactions continue to be important controls and have a dominant influence on Ca, Mg, Sr, alkalinity and pH. Redox reactions involve a loss of DO and associated slightly increased concentrations of Fe and Mn, NH₄ and Mo in the confined groundwater. In the northern part of the study area, Sherwood Sandstone is confined or semi-confined by Quaternary superficial deposits which also promotes redox changes, both laterally and with depth. Slight increases in concentrations of trace elements such as Co, V, Sb and Mn are apparent in the north-west, which could be released from minerals in the sandstone under mildly reducing conditions, or from the superficial deposits.

Concentrations of SO₄ are relatively low (<50 mg/L) in the shallow confined aquifer near the edge of the MMG-confined zone, but increase further downgradient as a result of dissolution of gypsum or anhydrite. This increase continues further, beyond the easterly extent of the study area

(Edmunds and Smedley, 2000). Barite solubility controls concentrations of Ba. Reactions of silicate and aluminosilicate minerals control concentrations of dissolved K, SiO₂, Li, Rb and Cs. This involves limitation of SiO₂ concentrations by solubility of quartz, but progressive increase in concentrations of the alkali metals downgradient. For some solutes, e.g. F, concentrations appear to be little changed over the extent of the aquifer, e.g. F, and reflect recharge inputs with little or no further mineral reaction.

For the study area, downgradient flow into the MMG-confined aquifer involves some 20 km of lateral distance away from the recharge zone and evidence from the current and previous studies suggests that this involves residence times of several thousand years down the flow path. Confined groundwater just into the MMG-confined aquifer is inferred to be largely of Holocene age (<10,000 years), but increasing to late Pleistocene age further downgradient towards the eastern limit of the study area.

For many purposes, consideration of the 95th percentile of inorganic solute concentrations (Table 4.1) would appear to be a reasonable estimate of the upper end of the baseline range where obvious outliers exist in the data distribution. This is a somewhat arbitrary cut-off but use of such thresholds has been a common approach for baseline evaluations (Lee and Helsel, 2005b; Shand et al., 2007). By definition, this represents the concentration exceeded by only 5% of samples and defines the concentration unlikely to be exceeded in samples analysed subsequently unless conditions change. Clearly for NO₃ (95th percentile 155 mg/L as NO₃; Table 4.1) this would not be an appropriate approach if trying to estimate the upper baseline concentration without modern agricultural inputs, and it is likely that baseline conditions for NO₃ do not exist in the unconfined aquifer in this study area. For evaluation of conditions ahead of any future oil and gas exploration, consideration of the full compositional range might be a more appropriate approach as outliers are also a component of the baseline in that context and need to be identifiable and distinguishable from any new sources of contamination.

6.2 DISSOLVED GAS COMPOSITIONS

Rather less analysis is typically performed of dissolved gases in groundwaters, principally because of the difficulties of sampling and preserving sample integrity. Some key measurements determined in this and other specialist gas studies in the region have helped to define baseline conditions in the context of potential new risks from hydrocarbon exploration. The concentrations of dissolved CH₄ in the Sherwood Sandstone aquifer are shown to be low overall (Bell et al., 2016; Bell et al., 2017; Gooddy and Darling, 2005), being up to 120 µg/L in this study and up to 465 µg/L in the Gooddy and Darling (2005) study. Concentrations are higher in the confined aquifer than under unconfined conditions. The higher concentrations are found under the most reducing conditions represented and even there, the limited concentration range is consistent with paucity of organic carbon in the sandstone and groundwater for a methanogenesis reaction to yield significant quantities of dissolved methane.

Although the presence of dissolved CO₂ can be an indication of oxidation of CH₄ in CH₄-rich systems, the dominant control in the carbonate-bearing Sherwood Sandstone aquifer is carbonate mineral reactions. Few data are available for dissolved CO₂ measured in groundwater specifically but those from the BGS sampling campaign had range of 1.7–13.1 mg/L, the lower values being associated with high pH and low alkalinity.

The range of activity of dissolved Rn observed (up to 20 Bq/L) is comparable with previous, albeit limited, studies of groundwater in the aquifer. The Rn derives from production by radioactive decay of ²²⁶Ra and ultimately ²³⁸U. Uranium is present in small quantities (0.5–5 mg/kg in the Sherwood Sandstone) (Andrews and Lee, 1979; Smedley et al., 2006), principally adsorbed to iron-oxide coatings and disseminated grains.

6.3 ORGANIC CHEMICAL COMPOSITIONS

Analyses of NPOC/TOC indicate that concentrations tend to be higher in groundwater from the unconfined than from the confined aquifer, the cause potentially being a combination of anthropogenic increases in the former and redox reactions leading to consumption in the latter. The PAH fluoranthene was detected in the unconfined aquifer and number of other PAHs and hydrocarbon compounds (e.g. benzene) have been detected at a small number of sites and in small quantities, all likely due to inputs of modern pollutants. For all the other organic compounds detected in the groundwater in this study (disinfection by-products, pesticides and solvents), their presence is unequivocally anthropogenic. In terms of environmental protection, detection of these compounds signals a departure from baseline conditions. In terms of assessment for any future subsurface activities, their detection under the current conditions needs to be noted.

7 Conclusions

The Sherwood Sandstone aquifer of the East Midlands and South Yorkshire is an important aquifer for regional water supply, including for drinking water. The aquifer is a red-bed sandstone with small quantities of accessory carbonate minerals (calcite, dolomite), as well as feldspar, clays and iron oxides, and a paucity of organic matter. Its groundwater has chemical compositions dominated by controls from natural carbonate-mineral and redox reactions, superimposed in the unconfined section of the aquifer by inputs of modern anthropogenic pollutants.

This study has highlighted a portion of the aquifer including unconfined outcropping sandstone, or sandstone partially confined by Quaternary superficial deposits, passing eastwards into confined conditions imposed by the overlying Mercia Mudstone Group. Groundwater residence time increases downgradient as it passes from the unconfined to deeper confined conditions. Throughout the region studied, the groundwater continues to be relatively fresh (95th percentiles for Cl; 296 mg/L; Na: 164 mg/L) to some 20 km away from the confined/unconfined interface and to depths of some 400–500 m.

The area has a number of subsurface mineral resources including coal, oil and gas that either have been exploited, or could be in the future. Despite this, few organic compounds have been detected in the Sherwood Sandstone groundwaters that would highlight a significant pre-existing impact of these occurrences on baseline chemical conditions. Of the few organic compounds that were detected, most were in younger groundwater from the unconfined aquifer and link to modern surface pollution from, for example, agricultural and urban activities. Small PAH detections in some unconfined groundwaters could be linked to coal-mining legacy contaminants, again likely to be from surface or shallow subsurface origins. Baseline concentrations of dissolved methane in the groundwaters are generally low, up to a maximum observation of 120 µg/L in the MMG-confined aquifer (95th percentile value of 15 µg/L).

The MMG-confined groundwater in the deepest part of the aquifer is pristine in the sense of absence of pollution from modern surface sources, yet amongst the most vulnerable to inputs from any new contamination from such deep hydrocarbon exploration targets. This report has characterised the baseline compositions of the groundwater in the Sherwood Sandstone in order to provide context for assessing the risks to groundwater quality from human activity in the form of both surface-derived and deep subsurface sources. The investigation summarises a large body of inorganic chemical data that serves to provide a robust characterisation of the baseline conditions across the aquifer. Data for organic compounds and dissolved gases are more sparse but nonetheless also contribute to the baseline characterisation and can be of value for assessing any future compositional changes.

Appendix 1 Time series plots for PRECIP-NET stations

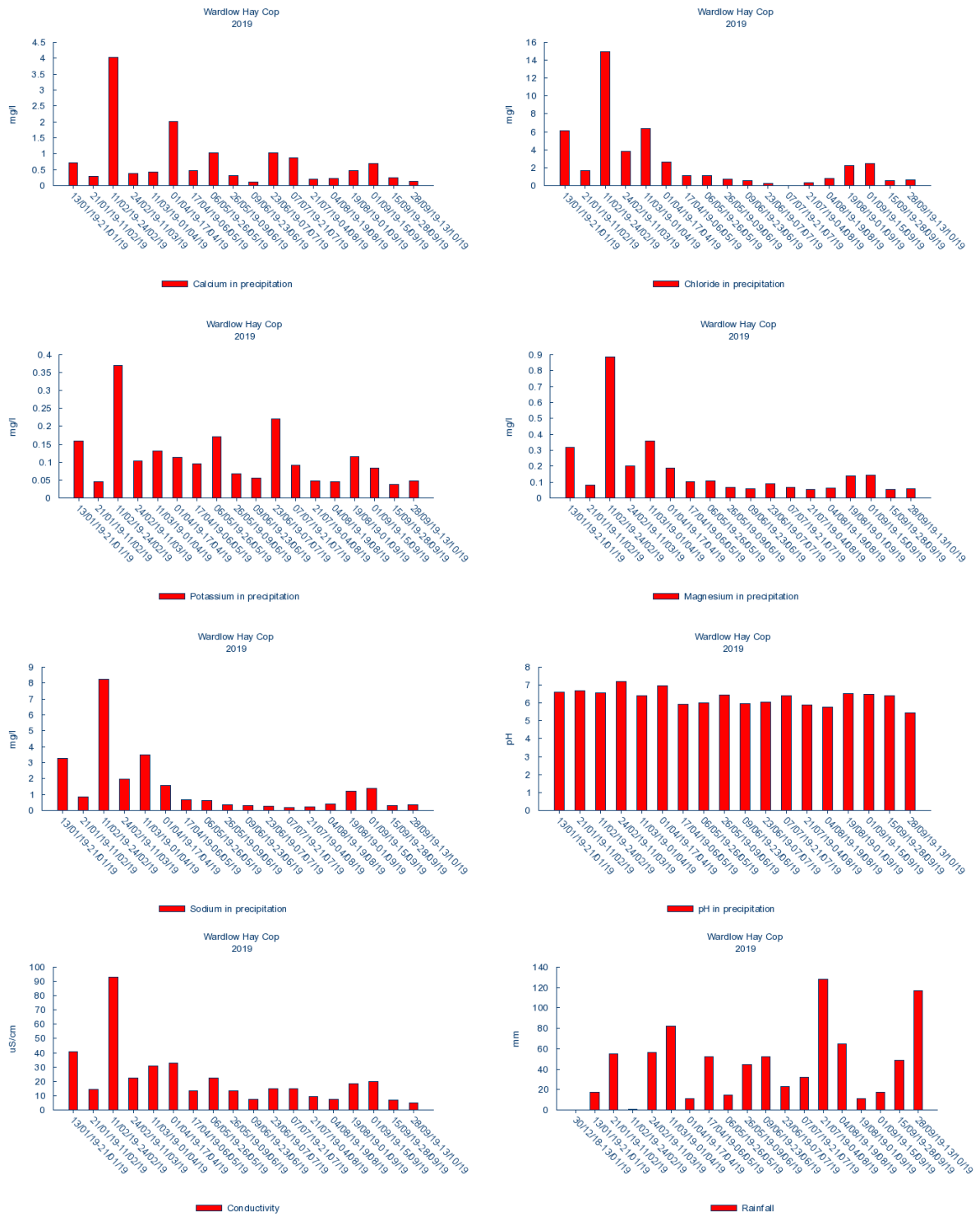


Figure A. 1. Time-series plots for Wardlow Hay Cop (2019) (DEFRA, 2020b).

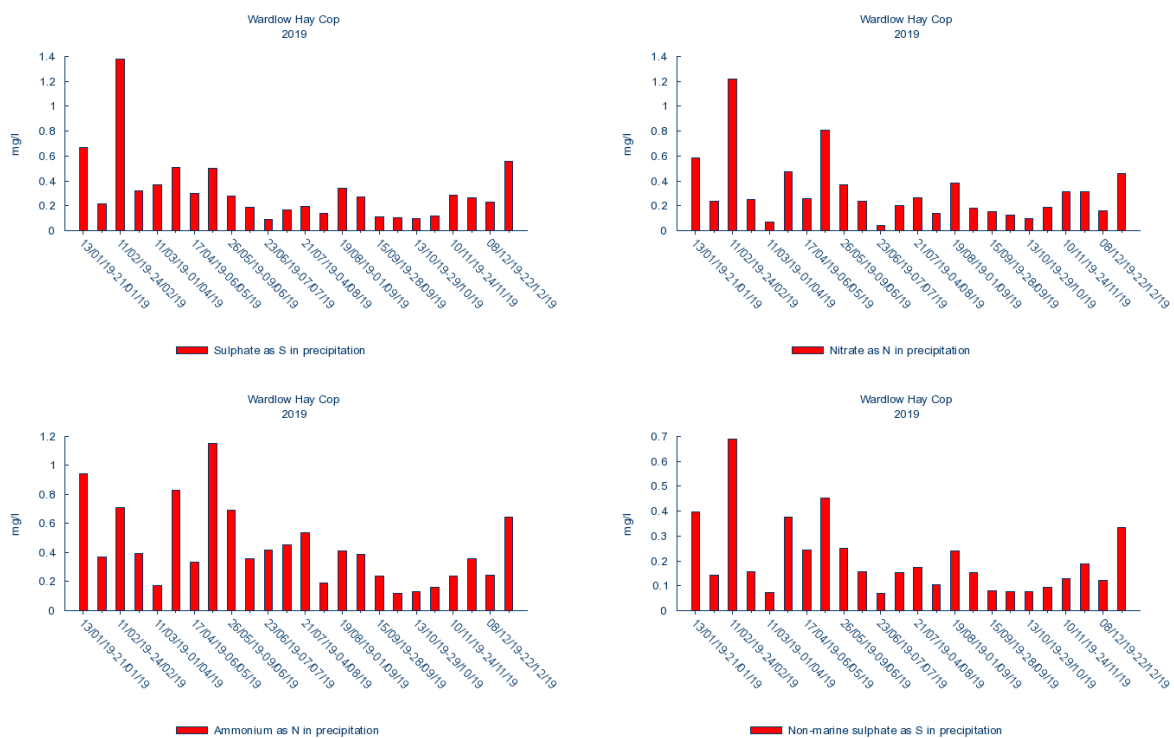


Figure A. 1 (cont). Time-series plots for Wardlow Hay Cop (2019) (DEFRA, 2020b).

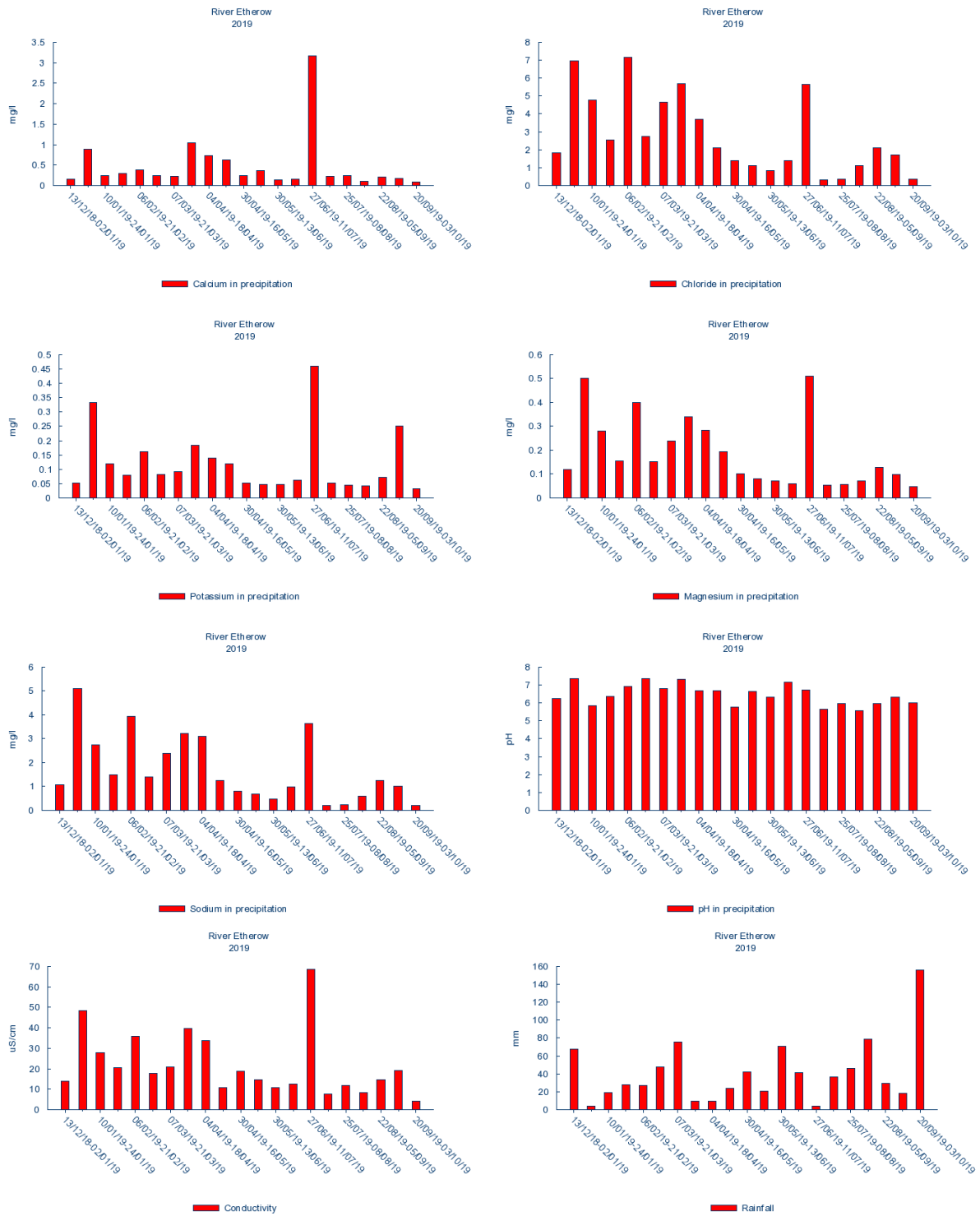


Figure A. 2 Time-series plots for River Etherow (2019) (DEFRA, 2020a).

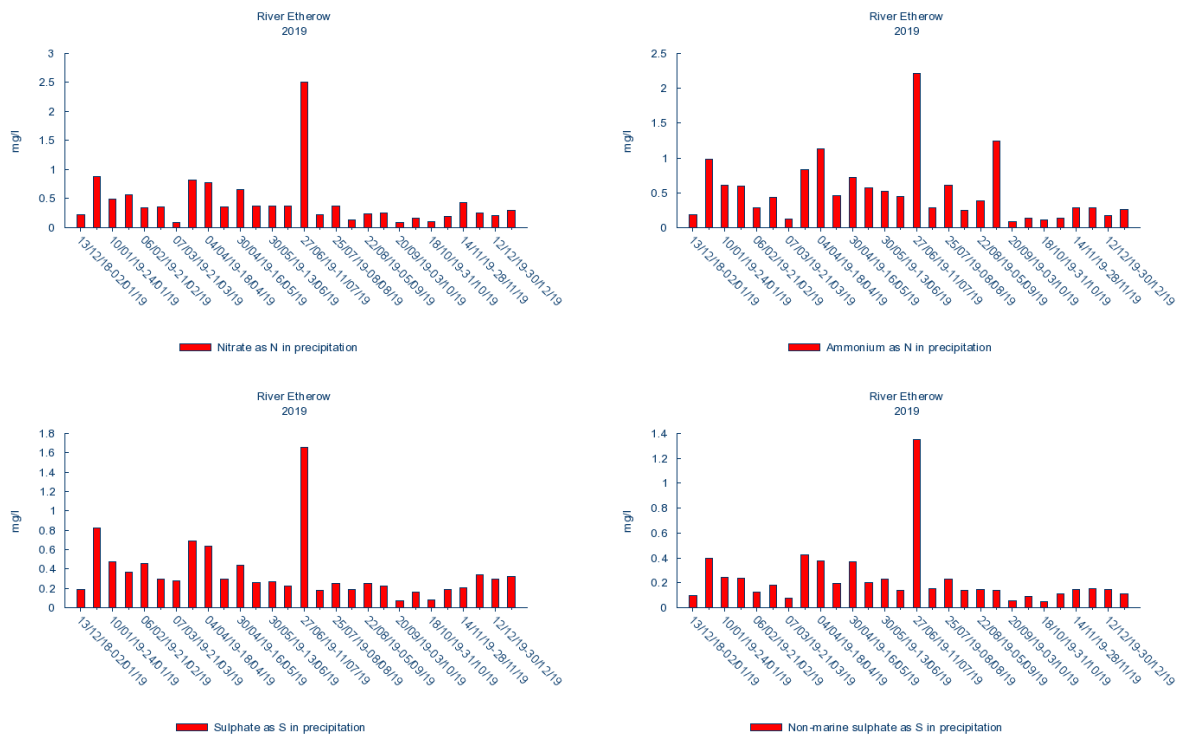


Figure A. 2. (cont.). Time-series plots for River Etherow (2019) (DEFRA, 2020a).

Appendix 2 WIMS database filter criteria

Table A. 1. WIMS Database filter criteria

Site location	Purpose description	Date criteria
Sherwood Sandstone 1:250k Geology Shapefile	Environmental monitoring (GQA & RE only)	Most complete suite of analyse for each location
Mercia Mudstone 1:250k Geology Shapefile	Environmental monitoring statutory (EU directives) Monitoring (national agency policy) Monitoring (UK Govt policy - not GQA or RE) Planned formal non-statutory (permit/env mon) Planned investigation (local monitoring)	

Table A. 2. Determinands filtered from combined WIMS and BGS field samples dataset

Organic determinands	Inorganic determinands
>C10-C12	Al
>C12-C16	As
>C16-C21	B
>C21-C35	Ba
>C5-C6	Be
>C5-EC7	Bi
>C6-C8	Br
>C8-C10	Ca
>EC10-EC12	Cd
>EC12-EC16	Ce
>EC16-EC21	Cl
>EC21-EC35	Co
>EC7-EC8	Cr
>EC8-EC10	Cs
1,1,1,2-Tetrachloroethane	Cu
1,1,1-Trichloroethane	DO
1,1,2,2-Tetrachloroethane	Dy
1,1,2-Trichloroethane	Eh
1,1-Dichloroethane	Er
1,1-Dichloroethylene :- (1,1-Dichloroethene)	Eu
1,1-Dichloropropylene :- (1,1-Dichloropropene)	F
1,2,3-Trichlorobenzene	Field Conductivity
1,2,3-Trichloropropane	Field HCO ₃
1,2,3-Trimethylbenzene	Field pH
1,2,4-Trichlorobenzene	Field Temp
1,2,4-Trimethylbenzene	Ga
1,2-Dibromo-3-chloropropane	Gd
1,2-Dibromoethane	HCO ₃
1,2-Dichlorobenzene	Hf
1,2-Dichloroethane	Hg
1,2-Dichloropropane	Ho
1,2-Dimethylbenzene :- (o-Xylene)	HPO ₄
1,3,5-Trichlorobenzene	I
1,3,5-Trimethylbenzene :- (Mesitylene)	K
1,3-Dichlorobenzene	La
1,3-Dichloropropane	Li
1,4-Dichlorobenzene	Lu
2,2-Dichloropropane	Mg
2,4,5-Trichlorophenol	Mn
2,4,6-Trichlorophenol	Mo
2,4-Dichlorophenol	Na
2,4-Dimethylphenol	Nd
2,4-Dinitrotoluene	NH ₄
2,6-Dinitrotoluene	Ni
2-Chloronaphthalene	NO ₂
2-Chlorophenol	NO ₃
2-Chlorotoluene :- (1-Chloro-2-methylbenzene)	Pb

Organic determinands	Inorganic determinands
2-Methylnaphthalene	pH
2-Methylphenol	Pr
2-Nitroaniline	Phosphorus - Reactive
2-Nitrophenol	Rb
3-Chlorotoluene :- (1-Chloro-3-methylbenzene)	S
3-Nitroaniline	Sb
4-Bromophenylphenylether	Se
4-Chloro-3-methylphenol	Si
4-Chloroaniline	SiO ₂
4-Chlorophenylphenylether	Sm
4-Chlorotoluene :- (1-Chloro-4-methylbenzene)	Sn
4-Isopropyltoluene :- (4-methyl-Isopropylbenzene)	SO ₄
4-Methylphenol	Sr
4-Nitroaniline	Tb
4-Nitrophenol	TDS
Acenaphthene	Th
Acenaphthylene	Ti
Anthracene	Tl
Azobenzene	Tm
Benzene	Fe
Benzo(a)anthracene	P
Benzo(a)pyrene	U
Benzo(b)fluoranthene	V
Benzo(b.k)fluoranthene	W
Benzo(e)pyrene	Y
Benzo(g,h,i)perylene	Yb
Benzo(k)fluoranthene	Zn
Bis(2-chloroethoxy)methane	Zr
Bis(2-chloroethyl)ether	
Bis(2-ethylhexyl) phthalate	
Bromobenzene	
Bromochloromethane	
Bromodichloromethane	
Bromoform :- (Tribromomethane)	
Butylbenzyl phthalate	
Carbazole	
Carbon Disulphide	
Carbon tetrachloride :- (Tetrachloromethane)	
CH ₄	
Chlorobenzene	
Chlorodibromomethane	
Chloroform :- (Trichloromethane)	
Chloromethane :- (Methyl Chloride)	
Chrysene	
cis-1,2-Dichloroethylene :- (cis-1,2-Dichloroethene)	

Organic determinands	Inorganic determinands
<p>cis-1,3-Dichloropropylene :- (cis-1,3-Dichloropropene)</p> <p>Dibenzo(a,h)anthracene</p> <p>Dibenzofuran</p> <p>Dibromomethane</p> <p>Dichloromethane :- (Methylene Dichloride)</p> <p>Diethyl phthalate</p> <p>Dimethyl phthalate</p> <p>Dimethylbenzene : Sum of isomers (1,3- 1,4-) : (m+p xylene)</p> <p>Di-n-butyl phthalate</p> <p>Di-n-Octyl phthalate</p> <p>Ethyl tert-butyl ether :- (ETBE)</p> <p>Ethylbenzene</p> <p>Fluoranthene</p> <p>Fluorene</p> <p>Hexachlorobenzene</p> <p>Hexachlorobutadiene</p> <p>Hexachlorocyclopentadiene</p> <p>Hexachloroethane</p> <p>Indeno(1,2,3-cd)pyrene</p> <p>Isophorone</p> <p>Isopropylbenzene</p> <p>m/p-Xylene</p> <p>MTBE :- (Methyl tert-butyl ether)</p> <p>Naphthalene</p> <p>Nb</p> <p>n-ButylBenzene :- (1-Phenylbutane)</p> <p>Nitrobenzene</p> <p>N-nitrosodi-n-propylamine</p> <p>NPOC</p> <p>n-Propylbenzene :- (1-phenylpropane)</p> <p>Pentachlorophenol</p> <p>Perylene</p> <p>Phenanthrene</p> <p>Phenol</p> <p>Pyrene</p> <p>sec-Butylbenzene :- (1-Methylpropylbenzene)</p> <p>Styrene :- (Vinylbenzene)</p> <p>tert-Amyl methyl ether :- (TAME)</p> <p>tert-Butylbenzene :- ((1,1-Dimethylethyl)benzene)</p> <p>Tetrachloroethylene :- (Perchloroethylene)</p> <p>TOC</p> <p>Toluene :- (Methylbenzene)</p> <p>Total aliphatics and aromatics(C5-35)</p> <p>Total aliphatics C5-35</p> <p>Total aromatics C5-35</p>	

Organic determinands	Inorganic determinands
trans-1,2-Dichloroethylene :- (trans-1,2-Dichloroethene) trans-1,3-Dichloropropylene :- (trans-1,3-Dichloropropene) Trichloroethylene :- (Trichloroethene) Trichlorofluoromethane Vinyl Chloride :- (Chloroethylene)	

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