



British
Geological
Survey

Baseline groundwater chemistry: the Pennine Coal Measures of the East Midlands and South Yorkshire

Environmental Change and Resilience Programme

Open Report OR/21/023

BRITISH GEOLOGICAL SURVEY

ENVIRONMENTAL CHANGE AND RESILIENCE PROGRAMME

OPEN REPORT OR/21/023

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groundwater in relation to
geology and proximity of
onshore oil and gas wells

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Baseline groundwater chemistry: the Pennine Coal Measures of the East Midlands and South Yorkshire

D Mallin Martin, P L Smedley

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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 areas where onshore oil and gas may be explored and/or exploited. The following assessment has been conducted using water quality data derived from the EA Water Quality Archive (WIMS) database. 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 suite of inorganic and organic analytes in groundwater for the Pennine Coal Measures aquifer of the East Midlands and South Yorkshire region. 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 special interest in this context include indicators of salinity, redox conditions, dissolved gases including carbon dioxide (CO₂) and methane (CH₄), and organic compounds including volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). The following assessment has been derived solely from Environment Agency Water Quality Archive (WIMS) data.

The Pennine Coal Measures aquifer is a complex, multi-layered secondary aquifer, comprising sandstones interbedded with low-permeability mudstones and coal seams. Groundwater flow is influenced regionally both by natural structural features and a lasting legacy of coal-mining activities. Groundwater quality in the aquifer is characterised by a large range of pH values (4.9–9.3) and commonly high dissolved-solids contents (SEC up to 6030 µS/cm). Conditions in the aquifer appear reducing to strongly reducing, with typically elevated Fe and NH₄, and in places high Mn, alongside low concentrations of NO₃, U and V. Both dissolved Fe and SO₄ are found in high concentrations in groundwater in a number of locations and are considered to be derived from the now-flooded mine workings and the dissolution of oxidised pyrite.

Organic-carbon content in the groundwater has an upper baseline concentration of 5.22 mg/L for dissolved organic carbon (DOC), and 6.45 mg/L for total organic carbon (TOC). Sources for organic carbon within the aquifer may be partly anthropogenic (industry, urban, agricultural) in origin, but are in large part derived from the abundant coal seams present within the aquifer. No dissolved gas (CH₄, CO₂) analyses were available from the EA WIMS data, but previous studies have identified up to 9 mg/L of dissolved methane in groundwater from the area. Only a small number of PAH and VOC compounds were detected within the EA WIMS dataset, typically each of low concentrations (<1 µg/L), but with some evidence of localised pollution from anthropogenic sources.

1 Introduction

1.1 PROJECT OBJECTIVES

The UK has a mature conventional onshore oil and gas (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 in England was imposed by the UK Government in November 2019. Despite this moratorium, potential for further OOG development theoretically remains across some regions of the UK at some point in the future. There is a need to obtain a better understanding of the pre-development regional groundwater quality in a number of drinking-water aquifers with respect to both 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 (Loveless et al., 2018), 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 (Mallin Martin and Smedley, 2020), the Lower Greensand aquifer of Surrey and West Sussex (Mallin Martin and Smedley, 2021), and the Pennine Coal Measures of the Midlands (this report).

Using the data from these three study areas, alongside information about the geological setting, soil composition, hydrogeological conditions, groundwater flow paths, 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. Understanding the groundwater baseline would also be of value in investigations relating to impacts from any other proposed subsurface activities or developments. The methodology for typologies development and assessment will be presented separately (Bell et al., 2021).

The study area of the Pennine Coal Measures of the East Midlands has been assessed entirely with data provided by the EA WIMS water quality archive. This is in response to the movement restrictions across England caused by the COVID-19 pandemic and the inability to carry out new groundwater sampling. The study provides an opportunity to explore the suitability of the WIMS dataset alone as a source of data to assess baseline aquifer typologies.

1.2 STUDY AREA

The study area centres on the Pennine Coal Measures outcrop of the North Derbyshire and South Yorkshire region, extending from just north of Derby in the south, to Leeds and Bradford in the north (Figure 1-1). Major settlements in the study area include Bradford, Leeds, Huddersfield, Rotherham, Sheffield, and Chesterfield. The M1 and A61 are the major roads within the study area, traversing approximately N-S, whilst the M62 cross-cuts E-W to the south of Leeds. The Pennine Coal Measures are classed as a Secondary A aquifer, supporting only private wells and no public supply points. The main aquifer unit within the Coal Measures consists of discontinuous

beds of sandstone, typically confined at depth by clay-rich strata. The region has been historically mined for coal, with a number of surface and sub-surface workings across the region.

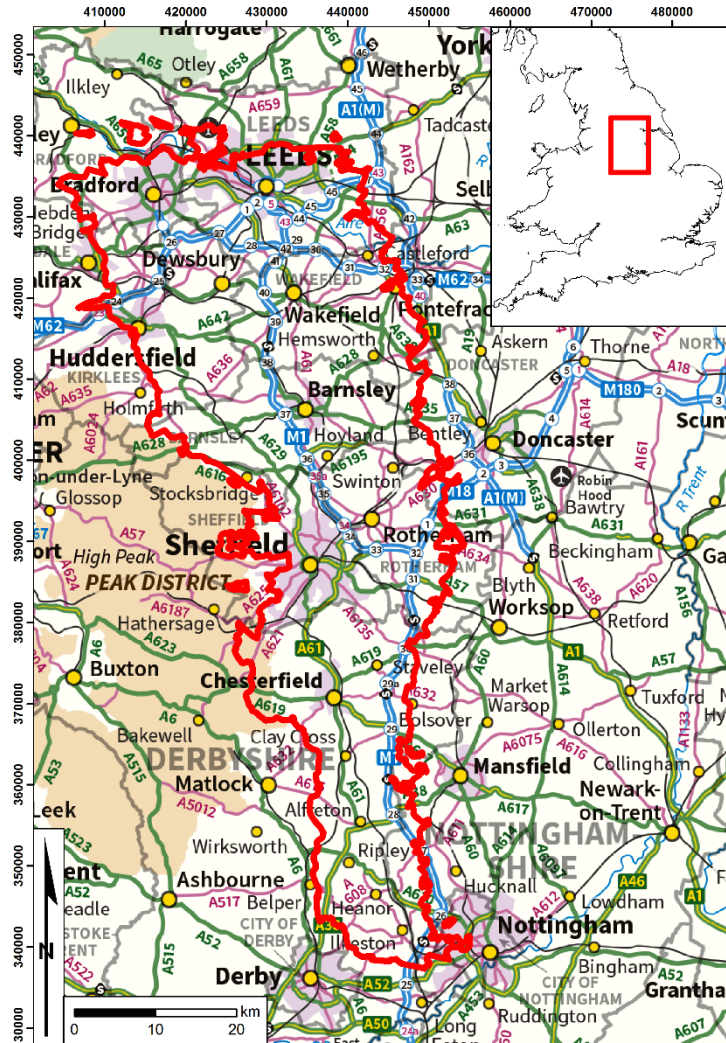


Figure 1-1. Geographical extent of the investigation area, delineated by the red outline. Contains OS data © Crown copyright and database right (2021)

1.3 CURRENT PRESSURES ON GROUNDWATER QUALITY

1.3.1 Coal mining and minewater history

The East Pennine coal field has historically been a major resource in the UK, having produced a total of 21 million tonnes of coal from deep underground and open-cast workings between 1998 and 1999 (Aitkenhead et al., 2002). The East Pennine Coalfield was producing coal up until the closure of both Hatfield and Kellingley Collieries in 2015. Across South Yorkshire and Derbyshire, there were over 200 nationalised coal mines (Northern Mine Research Society, 2021a, b, c). The surface extent of these historical workings can be seen in Figure 1-2. Other mined resources in the region include fireclay and ironstone (Aitkenhead et al., 2002). Notable collieries in the study area include Caphouse, Markham and Blackwell 'A' Winning, Alfreton.

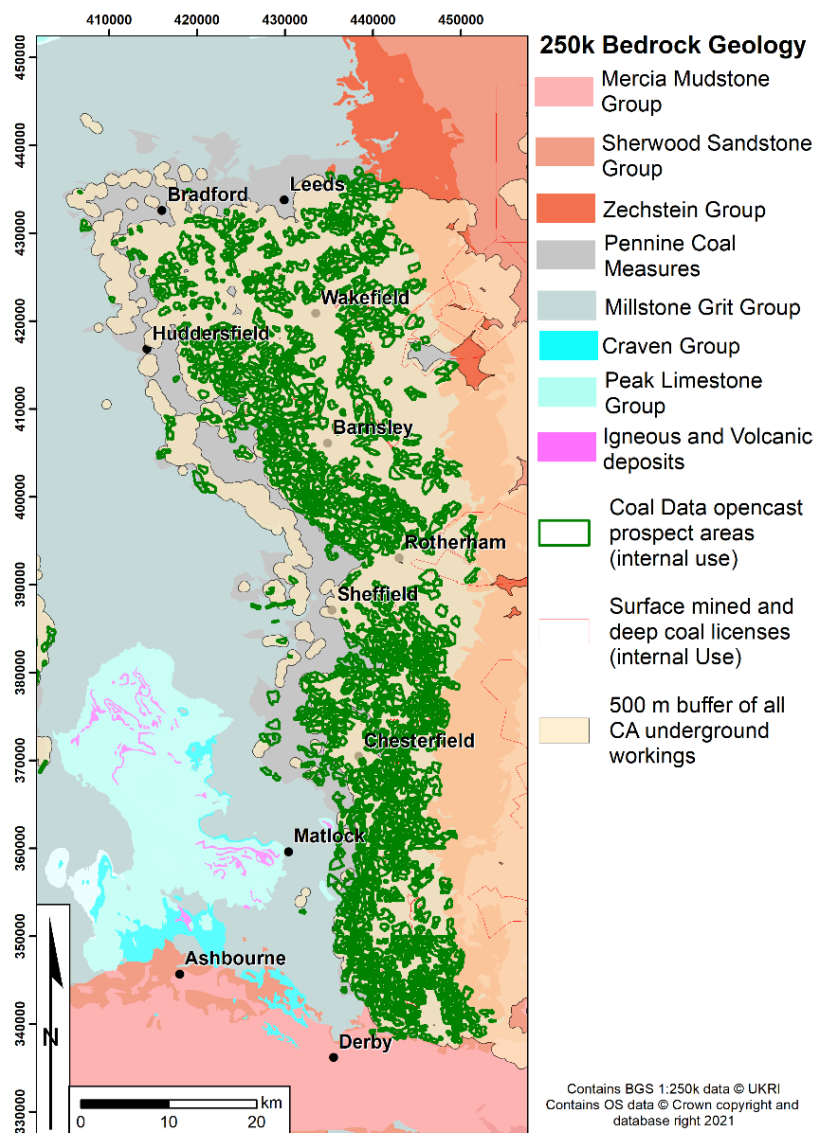


Figure 1-2. Surface extent of coal mines across the study area. Contains BGS data © UKRI 2021 and OS data © Crown copyright and database right 2021

As the coal mining industry progressively closed, dewatering of the workings also ceased, resulting in minewater rebound across much of the eastern extent of the Pennine Coal Measures. This rebound has been a cause for concern with respect to drinking-water quality, especially in the adjacent Sherwood Sandstone aquifer to the east (Allen et al., 1997; Morris, 2005). Many of the collieries through the East Pennine coalfield are hydraulically connected, and have previously been subject to a number of investigations with respect to minewater rebound upon cessation of dewatering activities (Banks, 1997; Burke et al., 2005; Dumpleton et al., 2001; Gandy and Younger, 2007; Gee et al., 2020). Groundwater interaction with these now abandoned mine workings results in acidic and metalliferous rich waters, some of which can be discharged at surface via adits or soughs (Banks, 1997; Younger and Adams, 1997; Younger et al., 2002). The UK Coal Authority manages discharges of acid mine drainage via treatment schemes. Across the wider study area, the Coal Authority manages three treatment sites; Woolley Mine water treatment scheme, Barnsley, and Sheephouse Mine scheme, Stocksbridge, both of which are passive, reed-bed treatment schemes, and the “A” Winning minewater treatment scheme, near Alfreton, (Figure 1-1) where water is pumped to surface and treated in a series of cascades, lagoons and a wetland (Coal Authority, 2017, 2018b, 2021). The “A” Winning site was developed in order to reduce the potential impact of declining water quality on the adjacent Sherwood Sandstone aquifer.

1.3.2 Urban and industrial

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

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

The impacts from urban/industrial activities can be significant to drinking-water supplies. In response to these activities, the Environment Agency has designated a number of Source Protection Zones (SPZs) around major public water supply boreholes. These zones identify the level of risk to the source from contamination from any activity that might cause pollution in the area. There are three main designations:

- “Inner zone – SPZ1: This zone is 50-day travel time of pollutant to source with a 50 metres default minimum radius.
- Outer zone – SPZ2: This zone is 400-day travel time of pollutant to source. This has a 250 or 500 metres minimum radius around the source depending on the amount of water taken.
- Total catchment – SPZ3: This is the 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.”

(EA, 2019)

SPZs for the study area are shown in Figure 1-3. There are very few SPZs on the Pennine Coal Measures (20), with most located towards the west of the study area, south of Huddersfield. They are predominantly SPZ 1 and SPZ 2 designated zones, with one small SPZ 3 zone east of Rotherham. The Sherwood Sandstone and Millstone Grit units, which overlie the PCM in the east of the study area have more numerous SPZs, from Zone 1 to Zone 3 classifications. Within the investigation area, there are a total of 347 licensed abstractions, with over 170 abstracting from Coal Measures sequence, according to the Environment Agency national abstraction licence database (NALD) (Table 1-1). These are all private or industrial abstractions, with one public well.

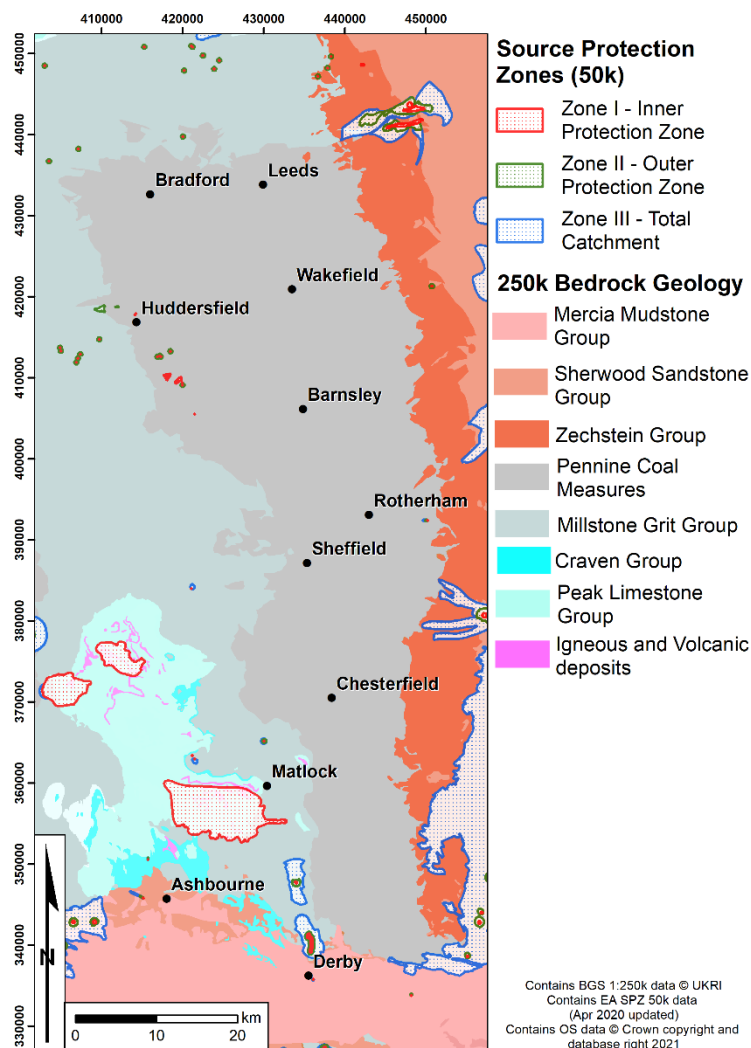


Figure 1-3. Source Protection Zones (SPZs) and geology for the investigation area

Table 1-1. Number of licensed abstractions across the Pennine Coal Measures, divided by type. From NALD © EA 2020

Usage type	Count
Agriculture	23
Water supply	9
Industrial, commercial and public services	133
Amenity	1
Environmental	5

1.3.3 Agriculture

Over 55% of the study area is classified as agricultural land use, principally being divided by arable practices (>30%) and pasture (20%). Within arable practices, the use of nitrogenous fertilisers, pesticides and herbicides pose 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.

Nitrate Vulnerable Zones (NVZ) are one such measures to preserve the water quality from diffuse agricultural pollution. These are areas designated as being at risk from agricultural nitrate pollution. They cover about 55% of land area 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). Strict guidelines for fertiliser use are applied to

agricultural land within these NVZs, in an attempt to protect the groundwater quality (DEFRA, 2018). Much of the investigation area falls under a “Surface Water” designation (Figure 1-4), with a few areas in the south falling under a “Eutrophic Water” classification. There is no “Groundwater” NVZ designation on the Pennine Coal Measures outcrop.

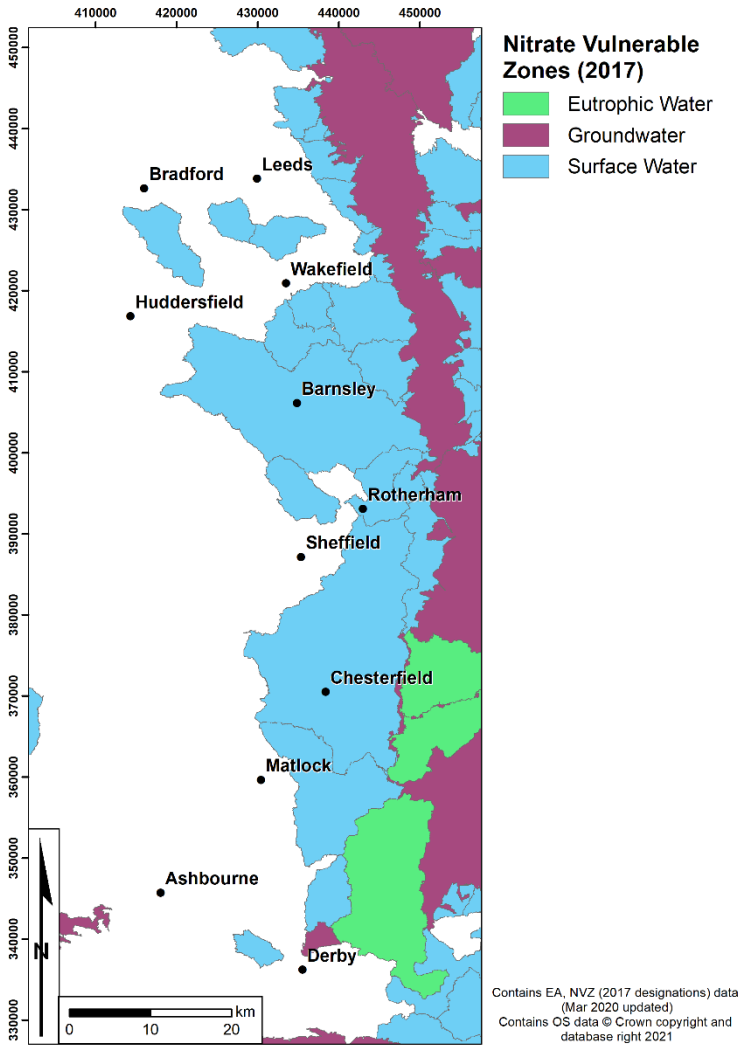


Figure 1-4. Nitrate Vulnerable Zones (NVZs) for the investigation area

1.3.4 Conventional and unconventional hydrocarbon industry

The main focus for this project has been on the onshore oil and gas (OOG) sector and building a better understanding of the compounds in groundwater that could be linked to this industry and that may be present in the aquifer prior to any new OOG activity. There is a long history of OOG in many parts of England, and despite a Government moratorium on high-volume, high-pressure hydraulic fracturing preventing shale gas, conventional and non-conventional OOG that do not involve this activity are continuing.

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, from initial exploration and throughout operation and decommissioning phases.

The study area is situated on the Pennine Coal Measures, historically a major source of coal (Section 1.3.1), and a notable source for “mine gas”: releases of natural gas that naturally build up in abandoned mine workings, derived from the coal. One such site was Markham Colliery (east

of the study area, near Bolsover), operated by Alkane Energy. As of 2006, this is no longer harvesting gas (Banks et al., 2017). Within the study area, wells drilled with the intent to harvest mine gas have principally been exploration wells (Table 1-2).

There are only two conventional gas fields situated in the study area: Calow and Ironville (OGA, 2021a), situated near Chesterfield and Ripley respectively in north Derbyshire. There are a total number of 21 Petroleum Exploration Development Licence (PEDL) areas encompassed by the investigation extent (Figure 1-5) and the area includes 36 onshore wells (OGA, 2021b, c). The number of wells and their intended purpose are shown in Table 1-2.

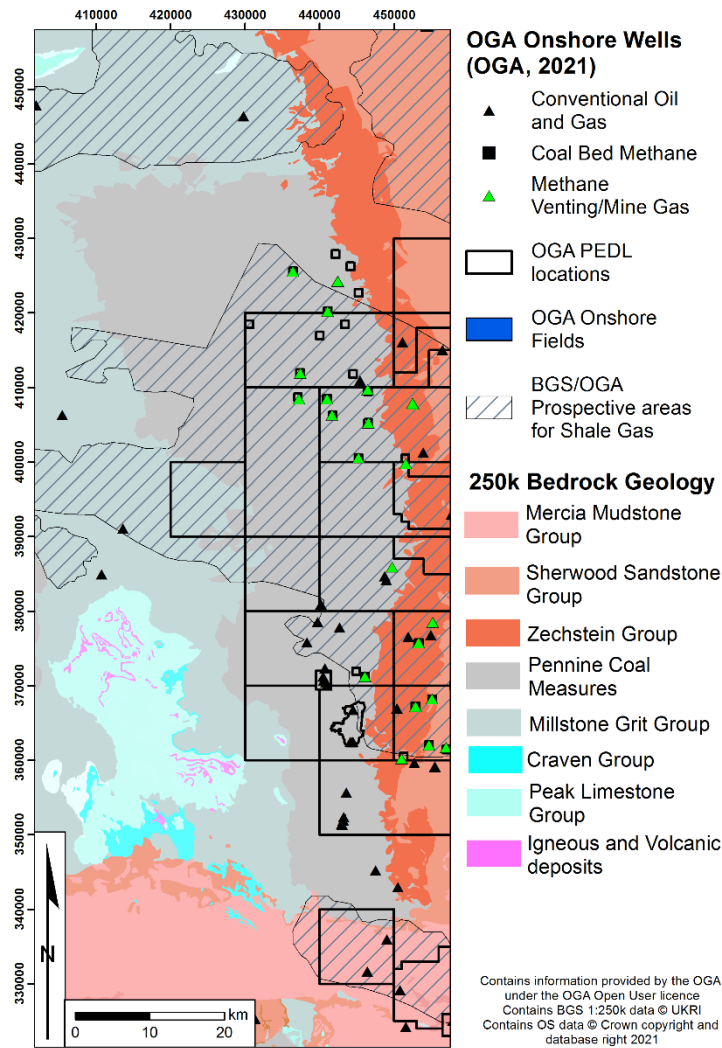


Figure 1-5. OGA data for the investigation area. Map shows onshore wells, PEDL locations, onshore conventional fields, and the joint BGS and OGA dataset for prospective areas for shale gas (data from BGS and OGA (2018); (OGA, 2021a, b, c)). NB: BNG is “British National Grid”

Table 1-2. OOG well types and borehole intention for the study area (shown in Figure 1-1 & Figure 1-5) (OGA, 2021c)

	Conventional oil & gas	Mine gas
Development	3	1
Exploration	17	11
Appraisal	3	1

2 Regional background

2.1 GEOGRAPHICAL SETTING

The extent of the investigation area can be seen in Figure 1-1. The area follows the outcrop of the Coal Measures, approximately 100 km N-S, 45 km E-W (at its widest). The topography for the region is shown in Figure 2-1. To the west of Bradford, Huddersfield, and Sheffield lies the Peak District, which forms a major upland region and divides the Pennine Coal Measures between the East Midlands and the east Cheshire and Manchester regions. Across the study area, the elevation slopes predominantly towards the east, from a high point of 636 m (Kinder Scout, west of Sheffield).

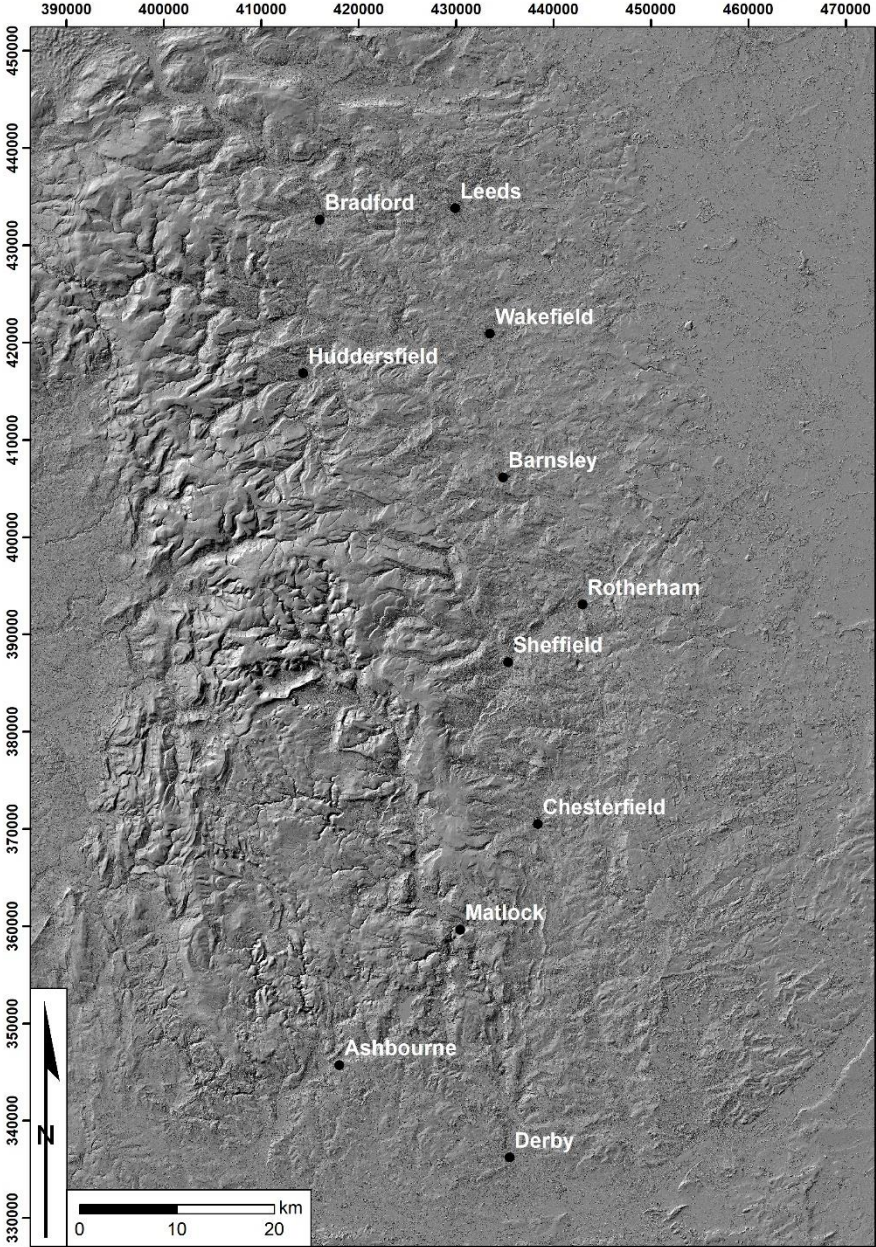


Figure 2-1. Surface topography for the study area (NEXTMap Britain elevation data from Intermap Technologies. Contains OS data © Crown copyright and database right 2021)

2.2 GEOLOGY AND HYDROGEOLOGY

The geology of the east and west Pennines is discussed extensively by Aitkenhead et al. (2002), whilst the hydrogeology is detailed by Jones et al. (2000). The following sections summarise the geology and hydrogeology of the study area.

2.2.1 Bedrock and Superficial geology

The study area comprises Carboniferous to Late Permian/Early Triassic sedimentary sequences, with some igneous and volcanic deposits/intrusions in the southern half of the Peak District. The principal geological units of interest are the Millstone Grit Group, the Pennine Coal Measures, and the Zechstein Group. The Millstone Grit and Pennine Coal Measures form secondary aquifers. The Pennine Coal Measures are subdivided into three major units; the Lower, Middle and Upper Coal Measures. The stratigraphic sequence for the geology of the wider investigation area is shown in Table 2-1. The bedrock geology is shown in Figure 2-2 and Figure 2-3.

The study area sits to the east of the Pennines and Peak District, which forms a topographic high. Situated at the centre of this high (to the west of Matlock) is an outcrop of the Peak Limestone group, a series of fossiliferous and cherty limestones (Cheney, 2007). The Peak Limestone Group is overlain and surrounded by the Millstone Grit Group, aside from some evidence of the Widmerpool Formation (Craven Group) to the south-west of Matlock, and in the vicinity of Ashbourne. The Craven Group consists of the Widmerpool Formation (a pyritic and calcareous mudstone, with interbedded turbidites, tuffs and sandstones) and the Bowland Shale Formation which does not crop out within the study area but is noted to be present at depth in the northern half of the study area (Andrews, 2013; BGS and OGA, 2018). The Millstone Grit consists of coarsening upwards cyclical sequences from siltstones and mudstone to progressively coarser sandstones, capped by coal or palaeosol horizons.

The Pennine Coal Measures Group is subdivided into three distinct units: the Pennine Lower, Middle and Upper Coal Measures. Across the investigation area, all three are at outcrop, with the Upper Coal Measures present only to the east and north of Sheffield. They comprise a series of interbedded siltstones/mudstones, with alternating grey sandstones, and sequences of coal, palaeosols, and ironstones, and volcanic rocks in the base of the Lower Coal Measures sequence (Aitkenhead et al., 2002; Cheney, 2007; Jones et al., 2000). Sandstones within the Pennine Coal Measures are typically thin and discontinuous, but a few units cover a large area (>100 km²); small channels/horizons are typically less than 8 m thick, less than 1 km wide and a few kilometres in length, whilst larger deposits may be in excess of 20 m thick, 20 km wide, and tens of kilometres long (Cheney, 2007; Jones et al., 2000). Sandstone units are at their thickest in the northern half of the Pennine Coal Measures (in South Yorkshire), progressively thinning towards the south and east of the outcrop (towards Nottingham and Derby) (Jones et al., 2000). Notable sandstone members include Wooley Edge Rock, Oaks Rock, the Crawshaw Sandstone (at 55 m thick) and the Wingfield Flags Member (up to 75 m thick) (Cheney, 2007; Jones et al., 2000). The Coal Measures sequence represents dominantly freshwater to brackish alluvial, deltaic and swamp environments, with less common marine shale intercalations (Banks, 1997).

Structurally, the Pennine Coal Measures are heavily jointed and faulted (Figure 2-2), and gently inclined towards the east away from the study area. Many of the sandstone units throughout the Pennine Coal Measures are juxtaposed against mudstones and siltstones, owing to their discontinuous nature (Cheney, 2007; Jones et al., 2000).

The superficial cover across the study area consists of a number of alluvial deposits, with notable glacial deposits just north of the study area (Figure 2-4). Superficial cover has been estimated to reach a maximum thickness of over 25 m in the vicinity of Bradford, but is typically less than 10 m thick or absent across much of the study area (Lawley and Garcia-Bajo, 2010).

Table 2-1. Stratigraphic sequence for the major geology in the wider investigation area (from Aitkenhead et al. (2002); Cheney (2007); Jones et al. (2000), and BGS Lexicon)

Age	Group	Formation	Dominant lithologies	Thickness (m)
Triassic	Mercia Mudstone Group	<i>Undifferentiated for this investigation</i>	Mudstone/siltstone	>200
	Sherwood Sandstone Group	<i>Undifferentiated for this investigation</i>	Coarse, pebbly sandstone	60 – 400
Permian	Zechstein Group	<i>Undifferentiated for this investigation</i>	Dolomitic limestone, limestone, siltstone, mudstone	c. 140
Carboniferous	Pennine Coal Measures group	Pennine Upper Coal Measures Formation	Coal seams, mudstone, siltstone, sandstone	0–160
		Pennine Middle Coal Measures Formation	Coal seams, mudstone, siltstone, sandstone	ca. 200–330
		Pennine Lower Coal Measures Formation	Coal seams, sandstone and mudstone, and basalt	ca. 150–340
	Millstone Grit		Cyclical sequence of siltstones, mudstones, fine- to coarse-sandstones, and subordinate coals/soil horizons	Up to 1075
	Craven Group	Bowland Shale Formation	Organic rich mudstones	Approx. 150
		Widmerpool Formation	Calcareous and fissile mudstone, pyritic, turbidites, sandstones, tuff	110 - >700
	Peak Limestone Group	<i>Undifferentiated for this investigation</i>	Cherty and micritic limestone, fossiliferous limestone, dolomitic limestone, subordinate mudstones and siltstone	200 – 800

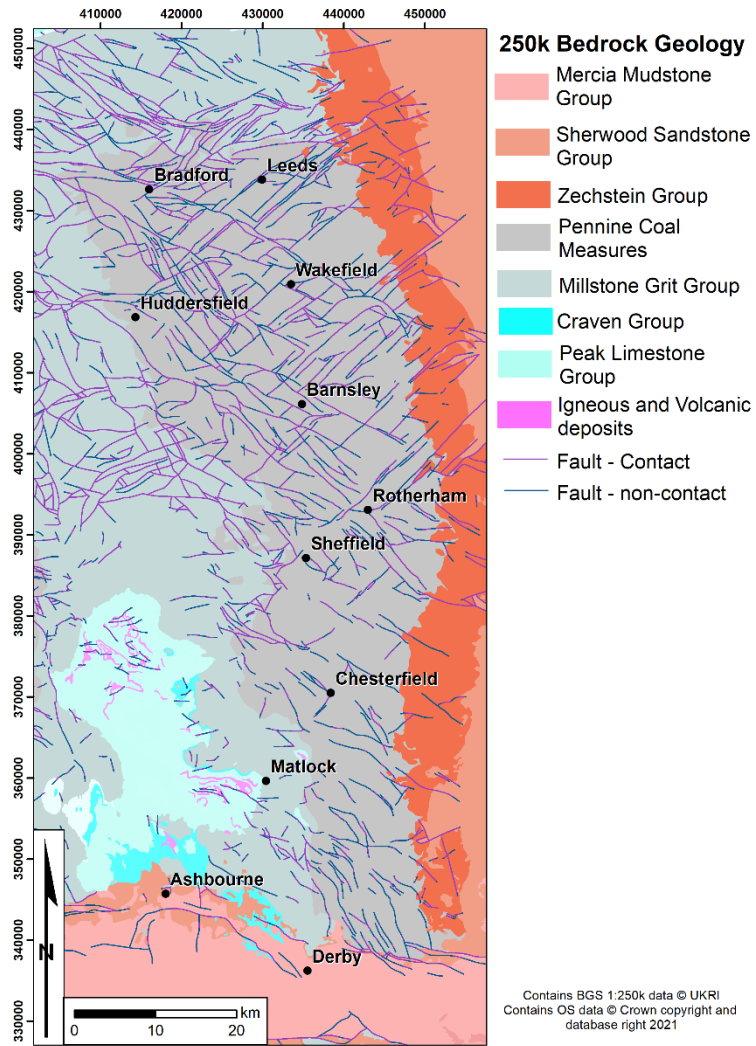


Figure 2-2. Bedrock geology for the investigation area and the wider region; faulting refers to whether or not faults produce contacts between different formations. Contains BGS data © UKRI 2021 and OS data © Crown Copyright and database right 2021

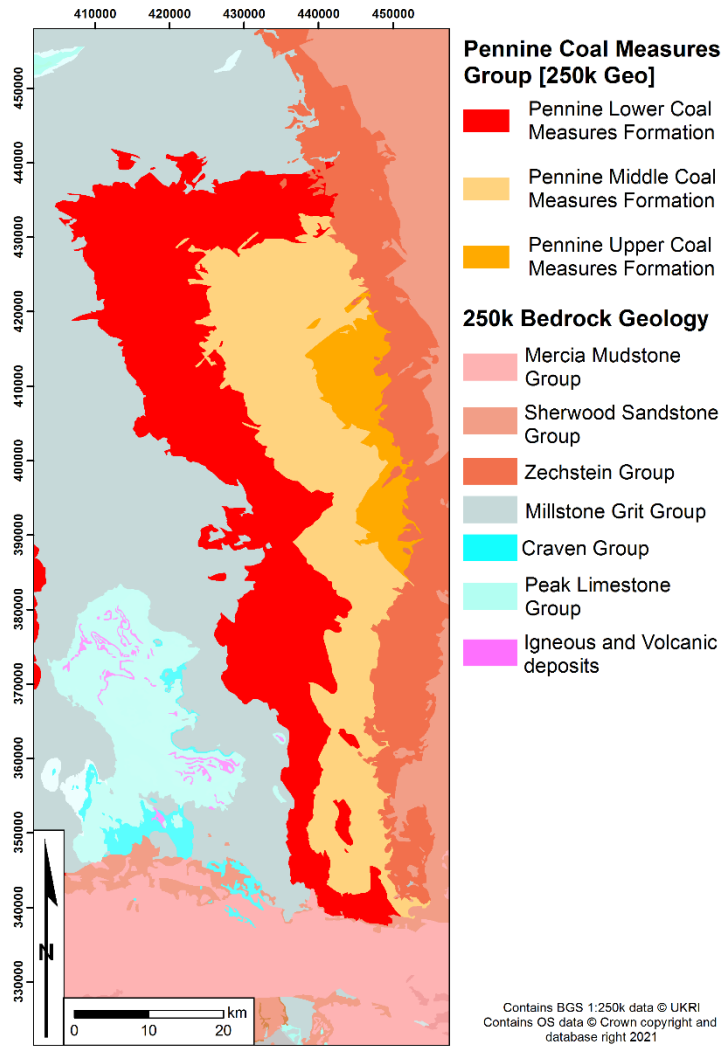


Figure 2-3. 250k Geological map showing differentiation of the Pennine Coal Measures Group into its Upper, Middle and Lower subdivisions

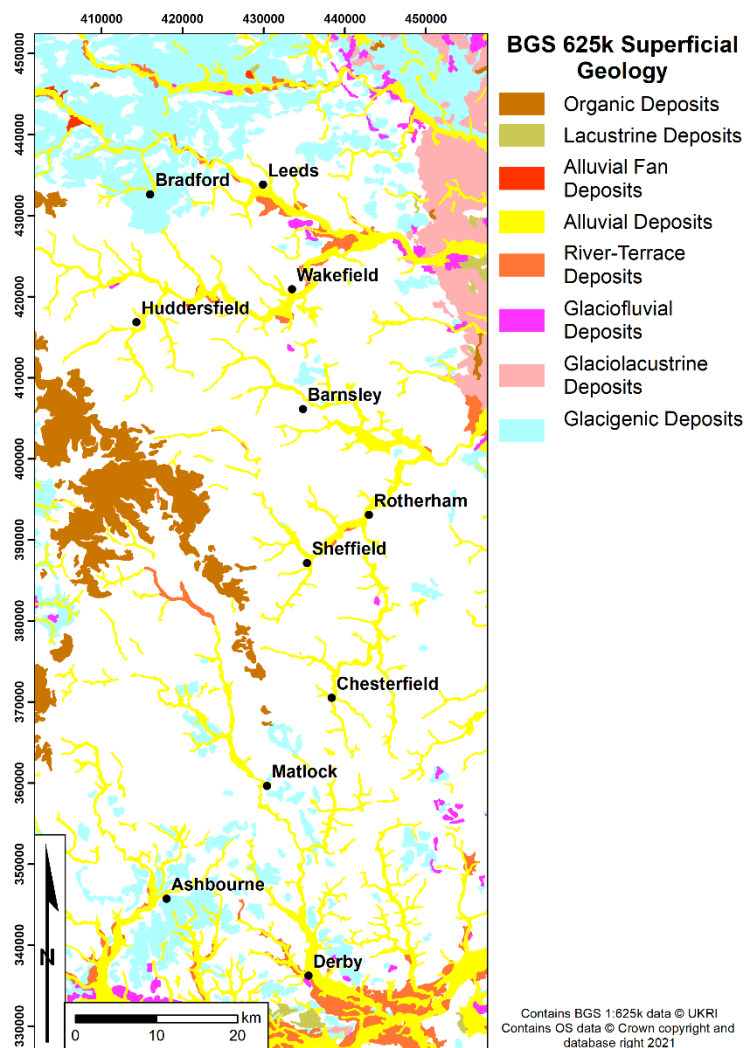


Figure 2-4. Superficial geology for the study area and the wider region

2.2.2 Organic-rich source rocks

There are two key organic source rocks in the study area: the Pennine Coal Measures Group, and the Bowland Shale Formation. The Pennine Coal Measures are most notably a source for coal and minor gas production, which is harvested/collected throughout the region (Figure 1-5). Further to the east, where it becomes confined by the overlying Permo-Triassic sedimentary units, it acts as a reservoir for oil and gas production across the East Midlands oil and gas field (DECC, 2013; Jones et al., 2000).

The Bowland Shale Formation has been considered one of the UK’s potential targets for unconventional hydrocarbons, in the form of shale gas (DECC, 2012). A previous study between BGS and OGA (2018) delineated a prospective area for further investigation, which can be seen on Figure 1-5. There has been no assessment for separation by Loveless et al. (2018) between the Bowland Shale and Pennine Coal Measures, as the study focussed on principal aquifers only.

2.2.3 Hydrogeology

As noted in section 1.2, the Pennine Coal Measures are considered a secondary aquifer (EA and BGS, 2018). The formation supports a number of local private abstractions. The aquifer is “multi-layered”, with discontinuous water-bearing sandstones being confined and isolated from each other by interbedded mudstones and siltstones (Cheney, 2007; Jones et al., 2000). Sandstones tend to be thinner and drier in the Lower and Middle Pennine Coal Measures (Jones et al., 2000), but a number of water-bearing horizons can be found in the Lower and Middle Coal Measures, including the Crawshaw Sandstone and Wingfield Flags members.

Groundwater flow in the Pennine Coal Measures is via fractures, with some intergranular flow within sandstone units. Aquifer properties are typically heterogeneous and anisotropic, and have been heavily modified by a legacy of coal mining. Increased fracturing following subsidence and new connections between once hydraulically isolated units via roadways and mines, has changed the natural behaviour of the Coal Measures (Banks, 1997; Jones et al., 2000). Regional flow is primarily from west to east, but also controlled by the folding and jointing/faulting across the region, alongside the historic mine workings, resulting in a complex 3D and potentially “karstic” like flow regime (Banks, 1997).

Permeabilities for the Pennine Coal Measures are variable and typically greatest in the Upper Coal Measures (up to 3 orders of magnitude greater average permeability than the Lower and Middle Coal Measures). Permeability is greatest in the sandstone horizons, but the mudstones and siltstones can have low values, and act as leaky aquitards (Banks, 1997; Jones et al., 2000). Hydraulic conductivity ranges from 3.8×10^{-5} m/d to 9.4×10^{-4} m/d for the Pennine Lower Coal Measures, 4×10^{-4} m/d to 4×10^{-2} m/d for the Pennine Middle Coal Measures, and 6.4×10^{-6} m/d to 1.7×10^1 m/d for the Pennine Upper Coal Measures. Permeability is affected both by depth and structural features; with increasing overburden pressure, permeability decreases. In the northern half of the study area, jointing and faulting have juxtaposed much of the sandstone units against lower-permeability strata, which result in these discontinuous horizons. Some units may even be hydraulically isolated from any incoming recharge (Jones et al., 2000). To the south, folding has resulted in increased permeabilities along anticlinal folds, allowing recharge to reach much greater depths. The Derbyshire and Nottinghamshire coalfields are historically known to be particularly wet and requiring extensive dewatering (Jones et al., 2000).

Porosity across the Pennine Coal Measures ranges from an average of 11% to 17%, with greater storage typically associated with the sandstone units. Transmissivities range from $0.4 \text{ m}^2/\text{d}$ to $416 \text{ m}^2/\text{d}$, with a median of $16 \text{ m}^2/\text{d}$, as recorded in the BGS Aquifer Properties database (Jones et al., 2000). The Coal Measures have a distinct response curve during pumping tests, where drawdown “creeps” slowly downwards after initially high yields. This is attributed to the prominence of fracture flow and either the interaction with boundary conditions, or an excessive pumping rate (Jones et al., 2000). Historically, the Coal Measures were dewatered in order for mining to proceed at progressively greater depths. For the year of 1972, discharges for the Yorkshire Coal Field totalled $178,000 \text{ m}^3/\text{d}$, whilst in the East Midlands Coalfield, discharges were $41,000 \text{ m}^3/\text{d}$ (Jones et al., 2000). Following the closure of the coal-mining industry, water levels have rebounded across the region, and have been the subject of further study (Burke et al., 2005; Dumbleton et al., 2001; Gandy and Younger, 2007; Gee et al., 2020; Younger and Adams, 1997). More recent abstraction yields range from 0.23 to $6546 \text{ m}^3/\text{d}$, with an interquartile range from $48 \text{ m}^3/\text{d}$ to $655 \text{ m}^3/\text{d}$ (Cheney, 2007).

As stated above, the Coal Measures aquifer has been significantly altered by the impact of the mining industry. With the expansion and mechanisation of the coal-mining industry, a greater number of once-isolated workings became progressively connected, resulting in new hydraulic pathways that could extend tens of kilometres (Banks, 1997; Banks et al., 2017; Jones et al., 2000). The South Yorkshire and East Midlands Coalfields therefore share a somewhat similar setting to that of the Durham region, where a number of expansive workings (“ponds”) can be connected together via open (but now abandoned) roadways. One notable “pond” extends from Morton, via the Blackwell “A” Winning colliery, and towards Calverton colliery in the east (Cheney, 2007). Due to its hydraulic connection with a number of now abandoned workings, and proximity to the Sherwood Sandstone aquifer in the east, abstraction still takes place at the “A” Winning site in order to prevent contamination from the now abandoned workings (Coal Authority, 2018b).

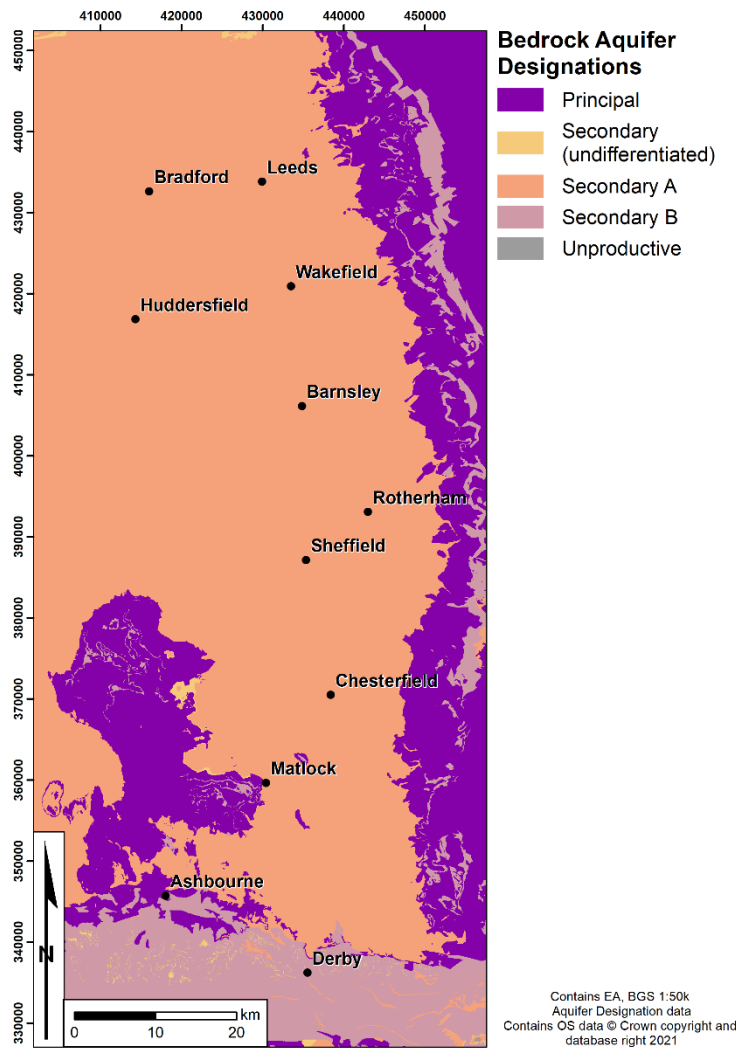


Figure 2-5. Bedrock aquifer designation map for the study area (EA and BGS, 2018)

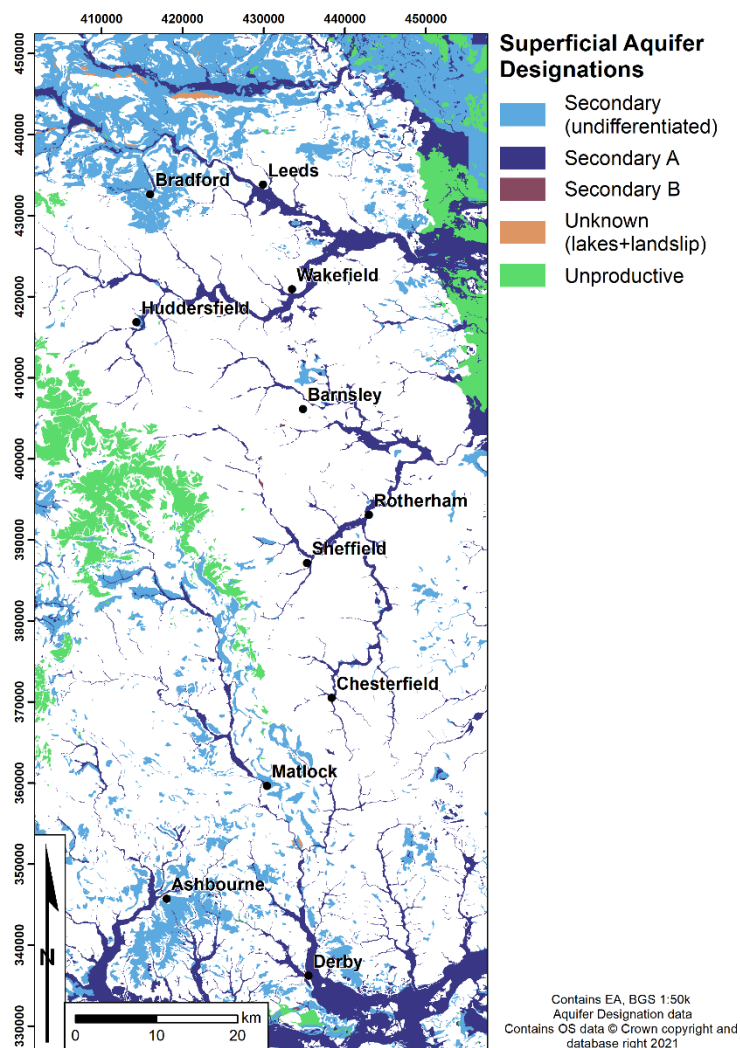


Figure 2-6. Superficial aquifer designation map for the study area (EA and BGS, 2018)

2.3 AQUIFER MINERALOGY

The mineralogy and geological composition of the Pennine Coal Measures is detailed by Aitkenhead et al. (2002). The dominant mineralogy of the sandstones is quartz, with smaller percentages of feldspar, mica and lithic grains (Aitkenhead et al., 2002; Banks, 1997). Sandstones typically have a clay matrix, or may have a secondary calcite cement where clay is absent. Interbedded between these sandstones are a number of clay-rich (including kaolinite) horizons, coal seams and “ironstones”.

Coal seams are a notable source of sulphur within the Pennine Coal Measures, with sulphur contents between 0.8 % and 4%. The sulphur is principally organic, but may be present as pyrite. Principal sources of carbonate are in the form of siderite cements and nodules, along with some calcite and ferruginous dolomites (Banks, 1997).

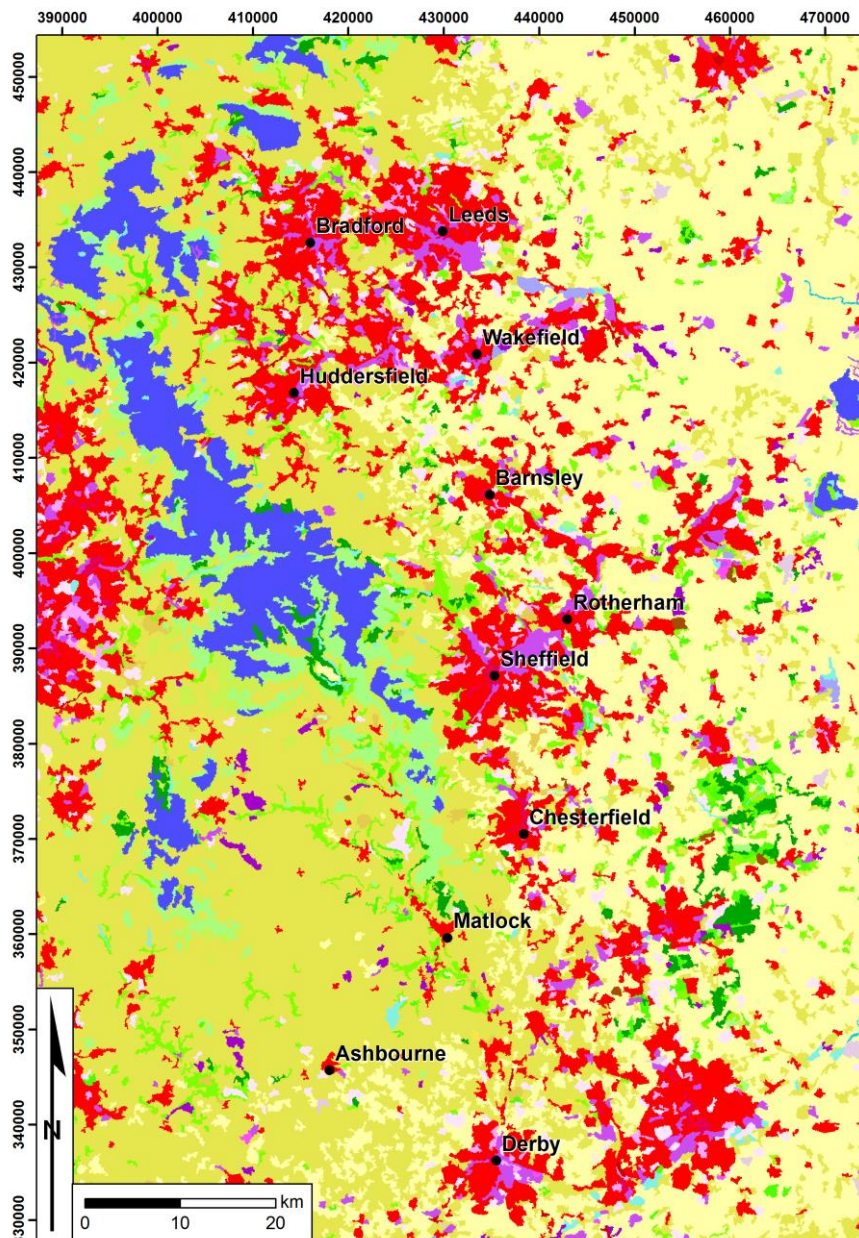
2.4 LAND USE

Land-use data for the study area have been extracted from the CORINE land classification 2018 (CLC 2018) dataset (European Environment Agency, 2019), with a cell size of 100 m x 100 m (Figure 2-7 & Table 2-2). Over 55% of the study area is classified as agricultural land use, principally being divided by arable practices (>30%) and pasture (20%). Urban land use accounts for 37% of the total land cover, with “discontinuous urban fabric” forming the majority of this at 26%. Many of the urban developments are concentrated in the north around Leeds, Bradford, Huddersfield and Wakefield. Sheffield and Rotherham are the major urban centres in the central

portion, whilst the southern half of the study area includes some of the smaller settlements outside of Nottingham and Derby. The extent of the Peak District can be observed in Figure 2-7, to the west, being dominated by Peat Bogs and Moors/Heathland.

Table 2-2. Land classification categories and percentage of total area for the investigation extent shown in Figure 1-1 (from European Environment Agency (2019))

Land Use Classification (CLC 2018 descriptions)	Area (km²)	Percentage total area (%)
Non-irrigated arable land	740.58	30.9
Discontinuous urban fabric	631.62	26.35
Pastures	571.02	23.83
Industrial or commercial units	128.75	5.37
Broad-leaved forest	72.60	3.03
Sport and leisure facilities	69.26	2.89
Green urban areas	38.86	1.62
Moors and heathland	28.42	1.19
Land principally occupied by agriculture, with significant areas of natural vegetation	17.06	0.71
Continuous urban fabric	15.87	0.66
Coniferous forest	10.17	0.42
Natural grasslands	10.15	0.42
Complex cultivation patterns	9.59	0.4
Mixed forest	8.30	0.35
Inland marshes	7.99	0.33
Water bodies	6.88	0.29
Peat bogs	6.82	0.28
Mineral extraction sites	6.13	0.26
Transitional woodland-shrub	5.65	0.24
Road and rail networks and associated land	5.11	0.21
Dump sites	2.47	0.1
Construction sites	1.37	0.06
Airports	1.35	0.06
Sparsely vegetated areas	0.69	0.03
Total	2396.71	100













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|--|--|
|  Airports |  Mineral extraction sites |
|  Broad-leaved forest |  Mixed forest |
|  Complex cultivation patterns |  Moors and heathland |
|  Coniferous forest |  Natural grasslands |
|  Construction sites |  Non-irrigated arable land |
|  Continuous urban fabric |  Pastures |
|  Discontinuous urban fabric |  Peat bogs |
|  Dump sites |  Road and rail networks and associated land |
|  Green urban areas |  Sparsely vegetated areas |
|  Industrial or commercial units |  Sport and leisure facilities |
|  Inland marshes |  Transitional woodland-shrub |
|  Land principally occupied by agriculture, with significant areas of natural vegetation |  Water bodies |

Figure 2-7. CLC (2018) land classification map for the investigation area (European Environment Agency, 2019)

2.5 RAINFALL CHEMISTRY

The average annual rainfall is typically <600 mm, but may reach over 1000 mm to the west, on the elevated plateau of the Peak District (Met Office, 2016). The nearest United Kingdom Eutrophication & Acidifying Network (UKEAN): Precip-net monitoring stations for rainfall chemistry are Wardlow Hay Cop and River Etherow, situated in the Peak District to the west of the study area (DEFRA, 2020a, b, 2021a, b). Summary statistics for recorded rainfall chemistry are shown for 2019 and 2020 for each site (Table 2-3 & Table 2-5 for Wardlow Hay Cop, Table 2-4 & Table 2-6 for River Etherow). Time series data for each site are shown in Appendix 1 (Figure A-1 to Figure A-4).

The total recorded rainfall at Wardlow Hay Cop station was 828 mm in 2019, and 670 mm in 2020 (DEFRA, 2020b, 2021b). The total recorded rainfall at River Etherow was 857 mm in 2019, and 829 mm in 2020 (DEFRA, 2020a, 2021a). The average pH was less than 6.5 for both stations in 2019, and is less than 6 in 2020, with sodium and chloride having the highest concentrations. Recharge inputs, considering evapotranspiration have been calculated and are also presented in the tables below.

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
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
Cl (mg/L)	2.57	15.00	0.01	1.12	7.71
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)
Conductivity (µS/cm)	21.5	93.2	5.12	15.0	-
pH	6.32	7.21	5.46	6.40	-
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
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
Cl (mg/L)	2.79	7.17	0.30	2.10	8.37
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)
Conductivity (µS/cm)	21.5	68.5	4.11	14.7	-
pH	6.46	7.37	5.56	6.38	-
Amount (mm)	40.8	156	3.96	29.7	-

*Assuming NH₄ oxidation to NO₃

Table 2-5. Summary statistics for rainfall chemistry at Wardlow Hay Cop [41773738] (2020)

Solute	Mean	Max	Min	Median	Concentrated mean (enrichment by evapotranspiration, x3)
Ca (mg/L)	0.66	3.99	0.08	0.30	1.98
Mg (mg/L)	0.15	0.66	0.04	0.12	0.46
K (mg/L)	0.11	0.46	0.03	0.08	0.33
Na (mg/L)	1.48	5.56	0.16	1.40	4.43
Cl (mg/L)	2.58	9.26	0.31	2.58	7.73
NO ₃ -N (mg/L)	0.29	0.79	0.06	0.27	2.43* (10.7 as NO ₃)
NH ₄ -N (mg/L)	0.53	1.24	0.12	0.45	-
SO ₄ -S (mg/L)	0.38	1.44	0.11	0.27	1.14 (3.42 as SO ₄)
SO ₄ -S (non-marine, mg/L)	0.26	0.97	0.05	0.22	0.77 (2.3 as SO ₄)
Conductivity (µS/cm)	21.28	67.50	7.56	17.81	-
pH	5.88	6.80	5.10	5.90	-
Amount (mm)	37.21	98.87	1.90	26.46	-

NB: Data to October 2020

*Assuming NH₄ oxidation to NO₃

Table 2-6. Summary statistics for rainfall chemistry at River Etherow [41243988] (2020)

Solute	Mean	Max	Min	Median	Concentrated mean (enrichment by evapotranspiration, x3)
Ca (mg/L)	0.58	5.06	0.07	0.17	1.74
Mg (mg/L)	0.24	1.84	0.03	0.11	0.73
K (mg/L)	0.12	0.76	0.02	0.07	0.37
Na (mg/L)	2.42	17.20	0.10	1.35	7.26
Cl (mg/L)	4.21	31.20	0.19	2.25	12.64
NO ₃ -N (mg/L)	0.39	1.85	0.06	0.30	2.61 (11.5 as NO ₃)
NH ₄ -N (mg/L)	0.48	1.44	0.09	0.40	-
SO ₄ -S (mg/L)	0.53	3.88	0.11	0.31	1.58 (4.73 as SO ₄)
SO ₄ -S (non-marine, mg/L)	0.32	2.44	0.05	0.20	0.96 (2.88 as SO ₄)
Conductivity (µS/cm)	35.32	218.00	6.20	14.27	-
pH	5.87	6.78	5.03	5.81	-
Amount (mm)	41.42	136.46	1.60	26.47	-

NB: Data to October 2020

*Assuming NH₄ oxidation to NO₃

3 Data acquisition and handling

In response to the national restrictions in response to the COVID-19 pandemic, no groundwater sampling has been carried out by the British Geological Survey for the purposes of this investigation. The following geochemical baseline of the Pennine Coal Measures has been assessed using Environment Agency Water Quality Archive (WIMS) data, supplemented in Sections 4 & 5 by information from published studies.

3.1 ENVIRONMENT AGENCY DATA

Extracts of data were taken from the Environment Agency Water Quality Archive (WIMS) from sites located within the Pennine Coal Measures surface expressions. The geographical extent of the WIMS database selection is shown in Figure 1-1, with selected sites shown in Figure 3-1. Extracted data comprised all groundwater samples collected between January 1990 and January 2020. The data were filtered geographically to the surface extent of the Pennine Coal Measures Group and filtered further to the most recent sample at each site with the greatest number of determinands measured. This subset of sample sites was used for mapping and summary statistical evaluation (Figure 3-1 & Table A-1). Some samples/sites were excluded, including targeted surveys, landfill monitoring or pollution response investigations. The total number of sample locations after filtering was 76 sites, with a total of 1595 analyses across 67 parameters.

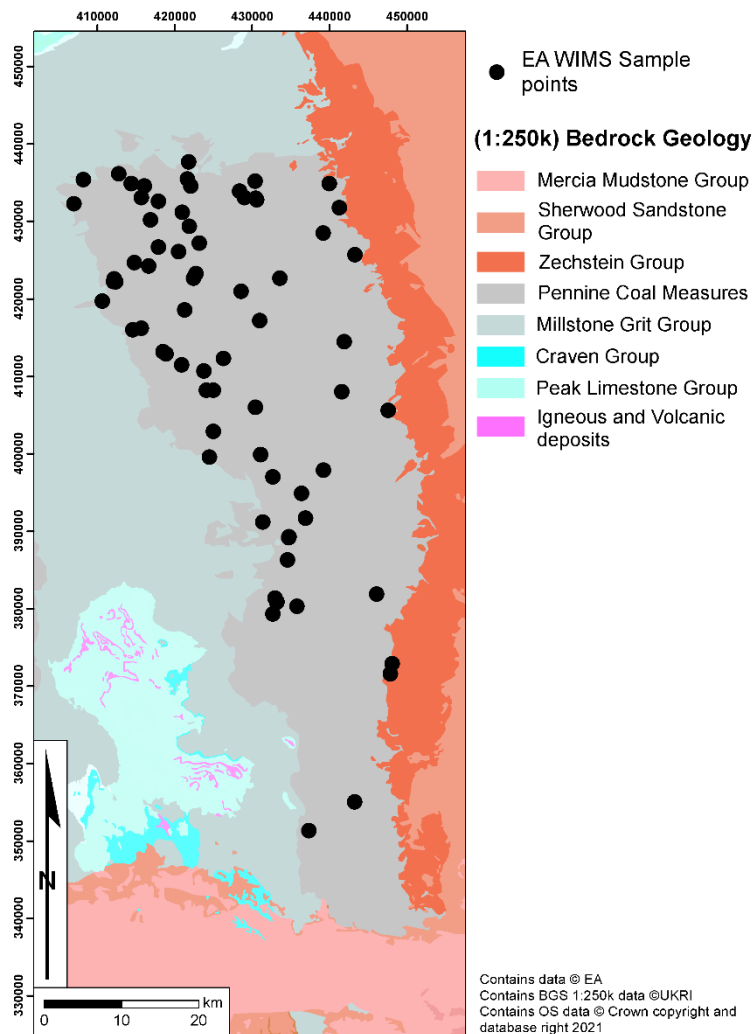


Figure 3-1. Sample locations used from the EA WIMS database for the baseline investigation

Samples were collected without use of a flow cell so data for dissolved oxygen (DO) may not be representative of in-situ aquifer conditions due to potential contact with air. Groundwater temperature was also measured at surface in a sampling container so may in some cases have

been affected by air temperature and may not be reliable. Data for metals used in this report refer to dissolved (filtered to 0.45 µm) concentrations in the WIMS database; filtered data are generally less commonly represented in the WIMS dataset which has inevitably limited the data used in the study.

3.2 STATISTICAL SUMMARY DATA

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 commonly used as an upper cut-off for outlier compositions. 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 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 & 5.

4 Regional hydrogeochemistry

The following section presents the statistical and analytical results from the provided EA WIMS data for the study area. The summarised statistical data are shown in Table 4-1 and Table 4-3.

4.1 FIELD PARAMETERS

Groundwater temperatures in the Pennine Coal Measures range from 7.1 °C to 16.9 °C, with a median of 11.5 °C. The 5th to 95th percentile range is 9.0 °C to 14.3 °C. Groundwater temperatures appear to vary greatly across the study area (Figure 4-1a). Due to sampling methodology, field temperature measurements for WIMS groundwater samples are likely to be affected by the surface air temperature on the day of sampling.

Groundwater pH ranges from 4.90 to 9.30, with a median of 7.26. The 5th to 95th percentile range is 5.86 to 8.24. The pH across much of the study area is near neutral (pH 7), with only a few locations having acidic or alkaline compositions (Figure 4-1b).

The dissolved oxygen (DO) concentration ranges from 2.1 mg/L to 11.9 mg/L, with a median of 5.0 mg/L. The 5th to 95th percentile range is 2.5 mg/L to 9.3 mg/L. The DO data suggest an overall oxic groundwater condition (Figure 4-1c), although this is inconsistent with the ranges of other redox-sensitive species in the dataset (e.g. Fe, Mn, NH₄, NO₃, NO₂, U) which together are indicative of reducing conditions. As mentioned above, field measurements are recorded in open containers; in the case of DO, values would be expected to increase with time in an open top container, and are therefore not representative of the in-situ aquifer condition. The EA WIMS database does not hold records for in-situ Eh values for this area.

Specific Electrical Conductance (SEC at 25 °C) ranges from 207 µS/cm to 2990 µS/cm, with a median of 868 µS/cm. The 5th to 95th percentile range is 391 µS/cm to 2120 µS/cm. SEC is spatially variable with values greater than 2000 µS/cm only observed in the north and central areas (Figure 4-1d), although the number of observations in the south is more limited. The limitations in the spatial coverage to the south of the study area are linked to difficulties in accessing sites as part of the EA monitoring network.

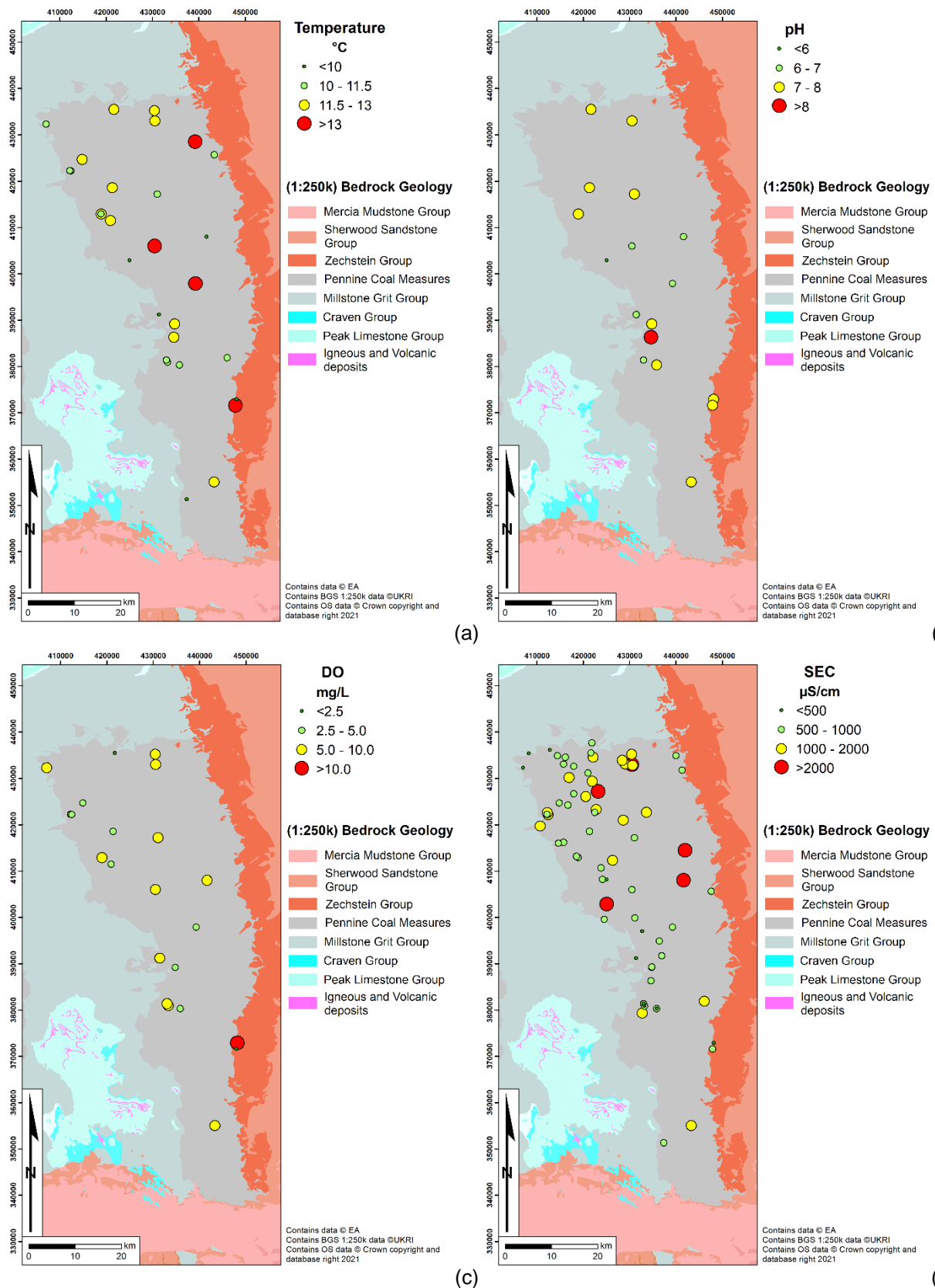


Figure 4-1. Spatial distribution for field measured parameters from EA WIMS data; (a) temperature; (b) pH; (c) dissolved oxygen (DO); (d) SEC

4.2 MAJOR IONS

The limited data for dissolved metals in the WIMS dataset has inevitably affected the quantity of data available for assessment of summary statistics and regional distributions. From available data, dissolved calcium has a concentration range of 21.5 mg/L to 162 mg/L, with a median of 61.6 mg/L. The 5th to 95th percentile range is 25.6 mg/L to 147 mg/L (12 samples, Table 4-1). Assessment of spatial distribution is difficult from the paucity of data (Figure 4-2a).

Magnesium has a concentration range of 9.0 mg/L to 99.2 mg/L, with a median of 37.7 mg/L. The 5th to 95th percentile range is 10.1 mg/L to 84.7 mg/L. As with calcium, there are a limited number of analyses for magnesium within the study area (Figure 4-2b). Concentrations for magnesium appear to increase towards the east, appearing to be greatest (>45 mg/L) closest to the boundary with the Zechstein Group, albeit with one sample at the boundary showing a concentration <30 mg/L.

Sodium has a concentration range of 18.1 mg/L to 213 mg/L, with a median of 87.4 mg/L. The 5th to 95th percentile range is 23.9 mg/L to 185 mg/L. Concentrations are relatively low across the wider study area (<100 mg/L), with a few isolated locations with concentrations >100 mg/L (Figure 4-2c). The limited number of sample points limits the assessment of spatial trends.

Potassium concentrations range from 2.58 mg/L to 13.2 mg/L, with a median of 4.36 mg/L. The 5th to 95th percentile range is 3.0 mg/L to 13.1 mg/L. From the limited number of samples available, potassium concentrations can be seen to increase towards the east and south away from Bradford in the north-east (Figure 4-2d). Concentrations are greatest (>7 mg/L) in the far south (to the east of Matlock), and to the east of Wakefield and Barnsley.

Chloride has a concentration range of 10.2 mg/L to 323 mg/L, with a median of 58 mg/L. The 5th to 95th percentile range is 19.3 mg/L to 178 mg/L. Chloride concentrations appear greatest in the northern half of the study area, but the sampling density is also greater north of Sheffield and Rotherham (Figure 4-2e). Chloride concentrations are locally elevated (with concentrations >150 mg/L) in isolated locations. Much of the wider aquifer appears to have concentrations <150 mg/L.

Alkalinity (expressed as HCO₃) ranges from <12 mg/L to 1170 mg/L, with a median of 311 mg/L. The 5th to 95th percentile range is 41.5 mg/L to 643 mg/L. HCO₃ concentrations are typically between 150 mg/L to 600 mg/L across the wider Pennine Coal Measures (Figure 4-2f). There are a few isolated locations with concentrations greater than 600 mg/L to the north of Huddersfield. Within the northern half of the study area, concentrations also appear to increase from <150 mg/L to above 300 mg/L towards the east away from the boundary with the Millstone Grit Group.

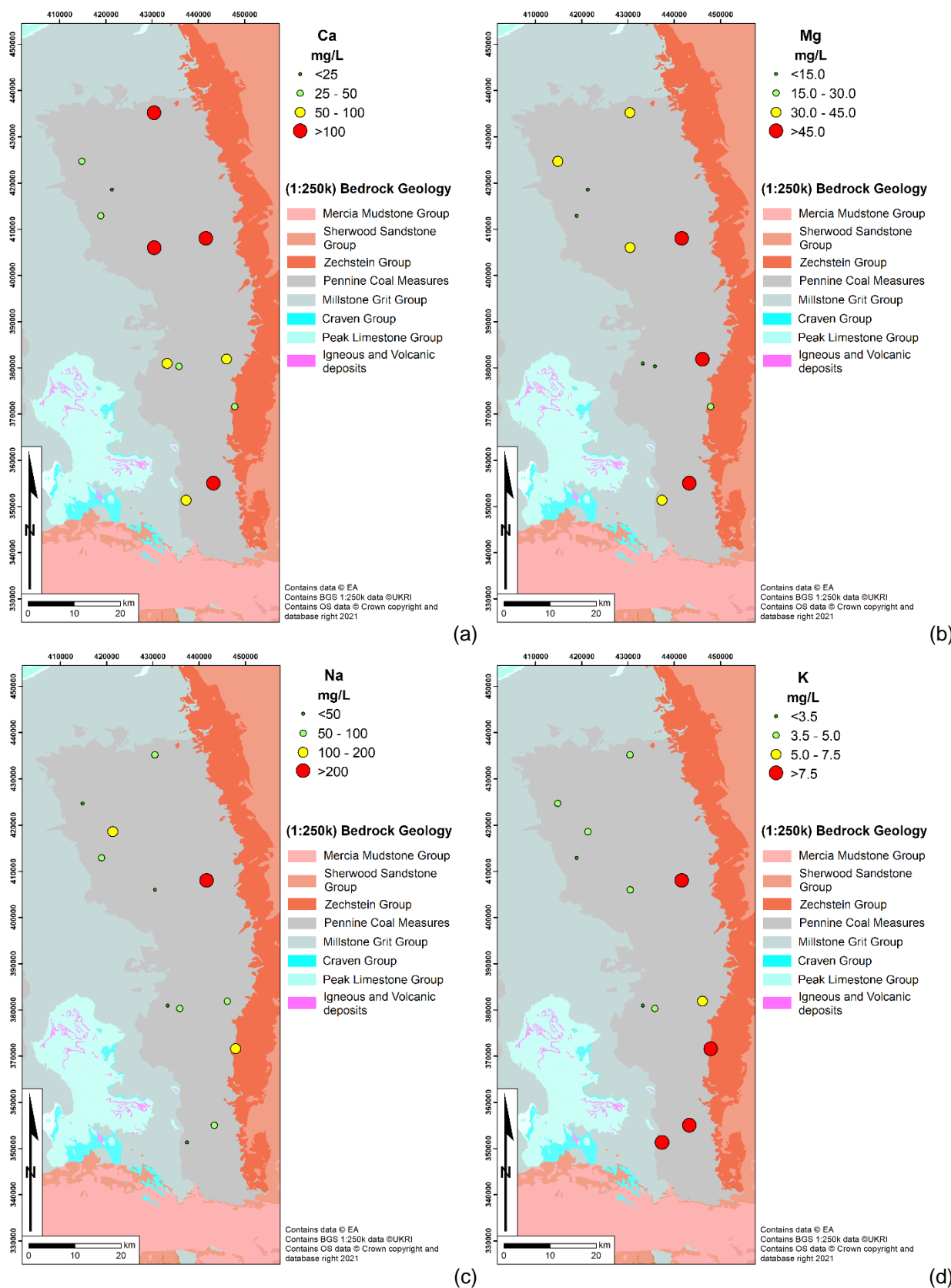
Nitrate (as NO₃) has a concentration range of <0.86 mg/L to 35.4 mg/L, and a median of 0.823 mg/L. The 5th to 95th percentile range is 0.31 mg/L to 11.4 mg/L. Nitrate concentrations across the Pennine Coal Measures are mostly low (<10 mg/L), with only one site in the centre of the study area having a concentration greater than 25 mg/L (Figure 4-2g). No sites exceed the 50 mg/L drinking-water standard (UK Gov., 2018).

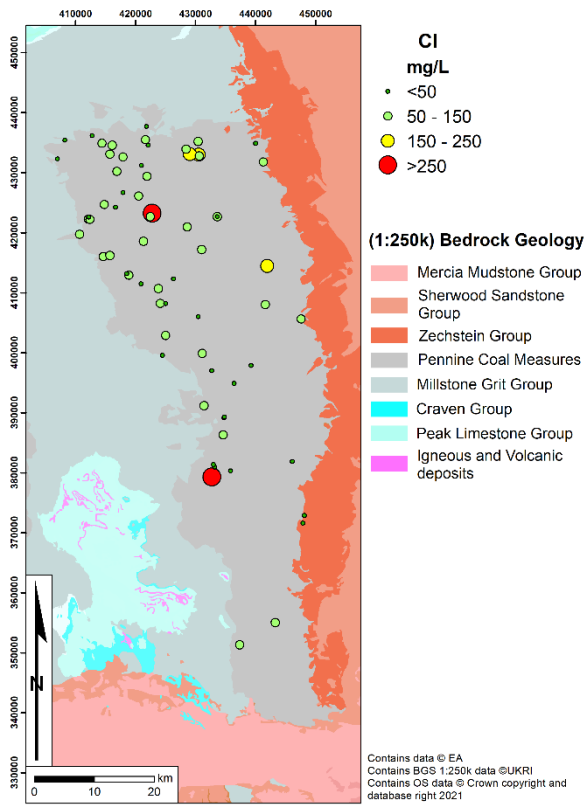
Sulphate concentrations range from <10 mg/L to 1920 mg/L, with a median of 87.5 mg/L. The 5th to 95th percentile range is 8.01 mg/L to 528 mg/L. Sulphate concentrations are predominantly <250 mg/L in the west of the study area (Figure 4-2h). Concentrations are greatest (>500 mg/L) near Rotherham and to the north of Wakefield. Sampling density is greatest in the northern half of the study area so very few conclusions about spatial trends can be drawn about the southern half of the study area.

Silicon (as Si) concentrations range from 2.52 mg/L to 11.1 mg/L, with a median of 7.20 mg/L. The 5th to 95th percentile range is 4.54 mg/L to 10.8 mg/L. Silicon does not appear to show any clear trends or changes across the study area, with concentrations >5.0 mg/L across much of the north and south (Figure 4-2i).

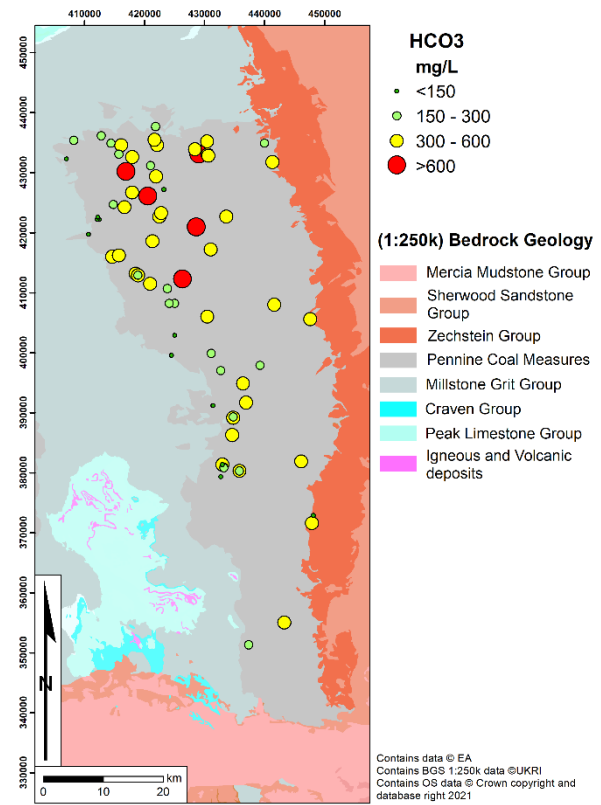
Samples with a complete suite of major-ion concentrations (Ca, Mg, Na, K, Cl, SO₄, HCO₃) have been plotted on a Piper diagram (Figure 4-3). Only 12 samples had a full set of dissolved major-ion data, so classification of the water types across the wider aquifer has not been attempted. A number of samples show evidence for a Ca-Mg-HCO₃ water type, but there is also a trend towards Ca-Mg-SO₄ type waters. A few samples are of Na-HCO₃ type.

Box plots and cumulative-probability plots showing statistical distributions for the major ions are shown in Figure 4-4 & Figure 4-5.

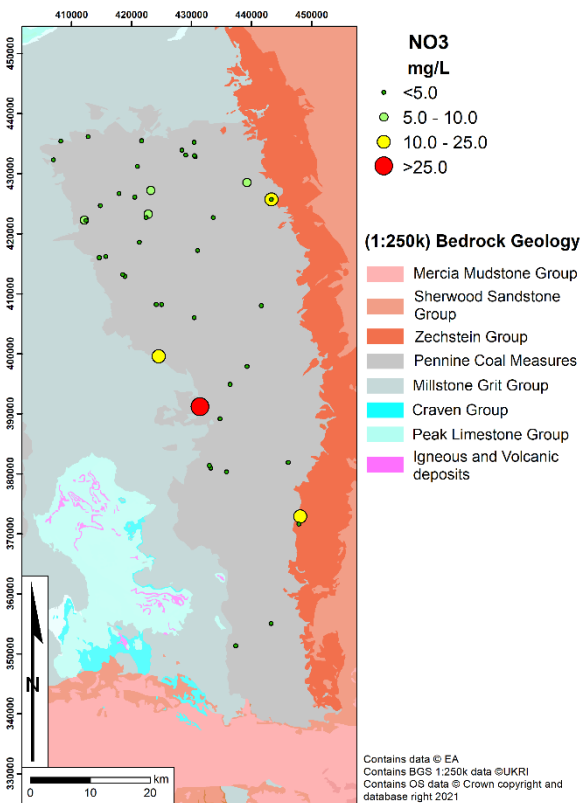




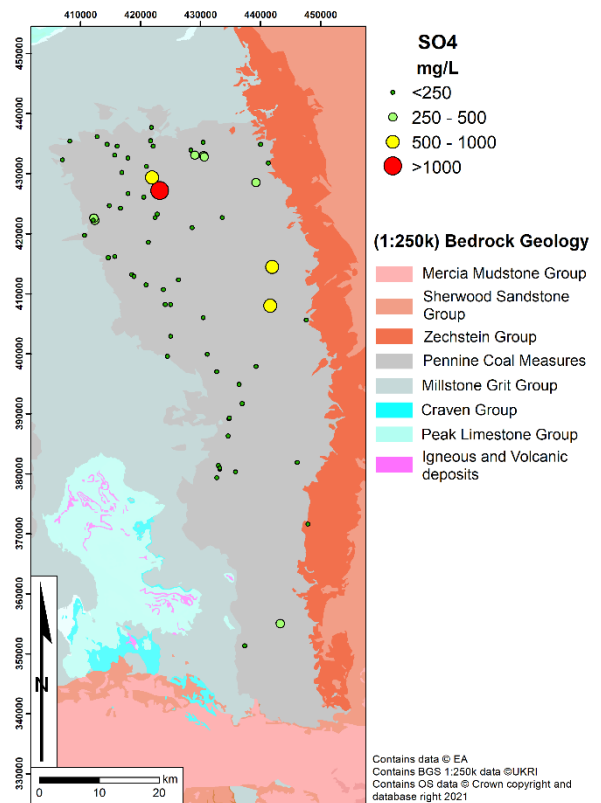
(e)



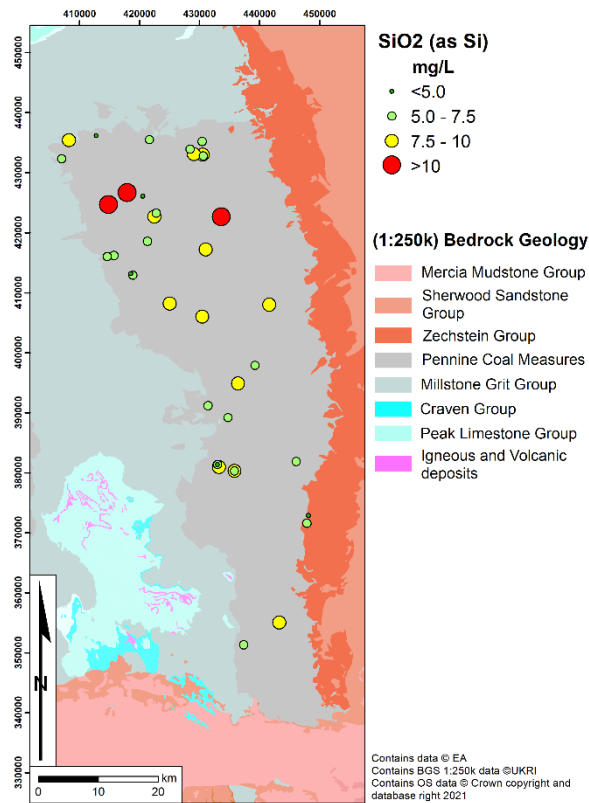
(f)



(g)



(h)



(i)

Figure 4-2. Spatial distribution for major ions in groundwater; (a) calcium; (b) magnesium; (c) sodium; (d) potassium; (e) chloride; (f) bicarbonate; (g) nitrate; (h) sulphate; (i) silicon

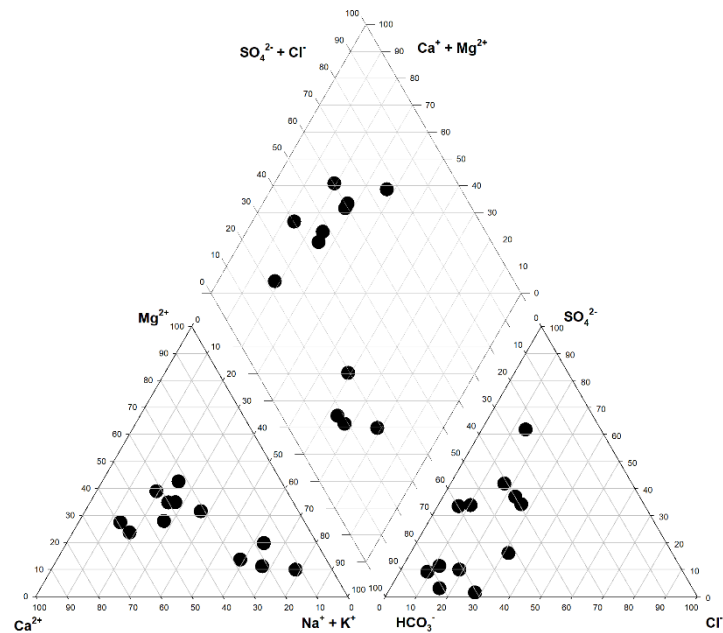


Figure 4-3. Piper plot for EA-WIMS samples for the Pennine Coal Measures aquifer

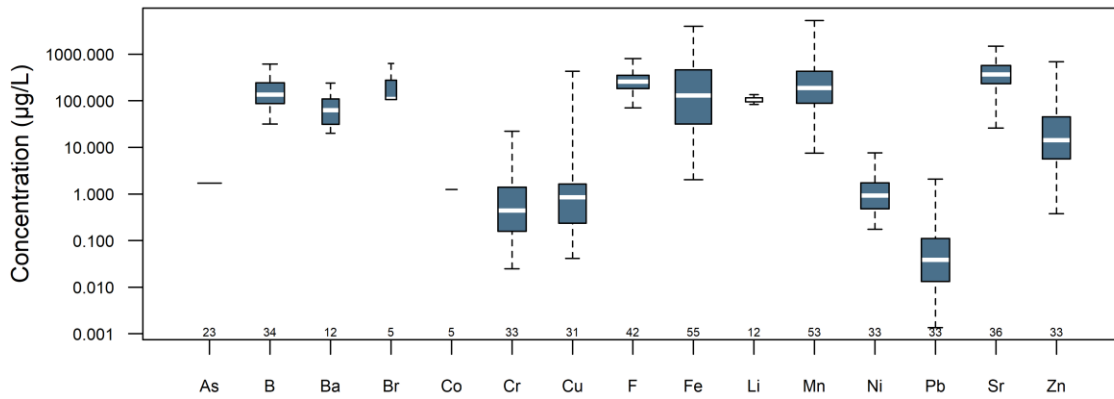
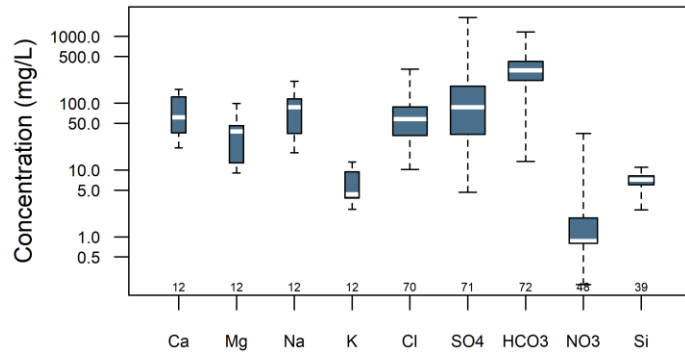


Figure 4-4. Box plots for major ions (top) and select minor and trace elements (bottom); number of analyses given for each box

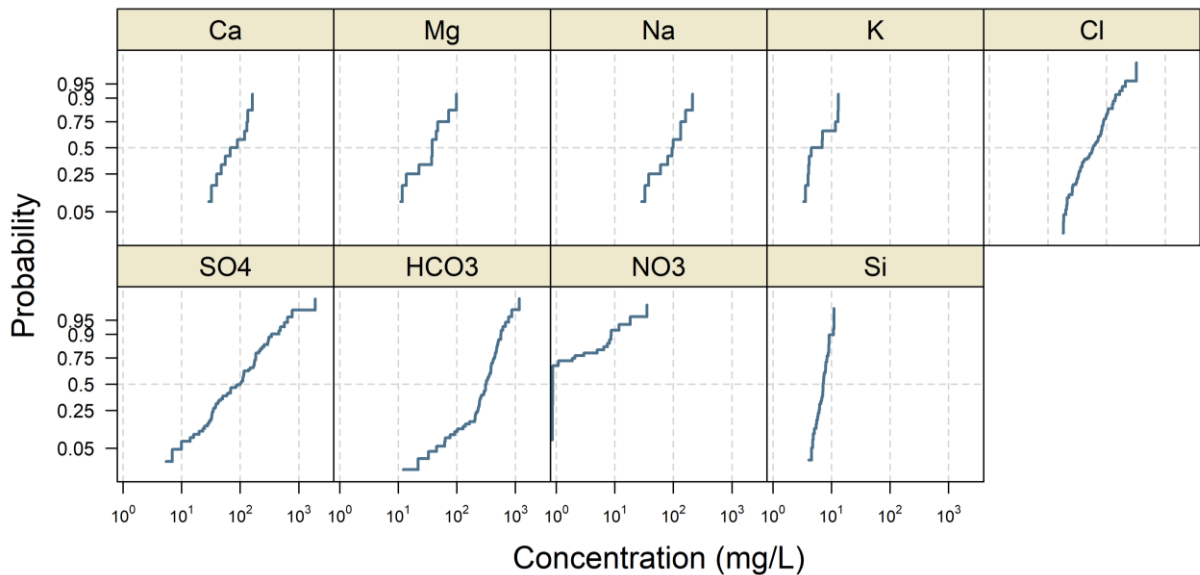


Figure 4-5. Cumulative-probability plots for major ions

4.3 MINOR IONS AND TRACE ELEMENTS

4.3.1 Phosphorus

Phosphorus (reactive/orthophosphate as P) has a concentration range of <0.01 to 1.2 mg/L, with a median also <0.01 mg/L. The 95th percentile is 0.0348 mg/L. Only 5 sites had concentrations of P-reactive above detection limits, with concentrations across the wider aquifer predominantly <0.01 mg/L. There is no clear evidence for a trend in P-reactive concentrations across the study area (Figure 4-6).

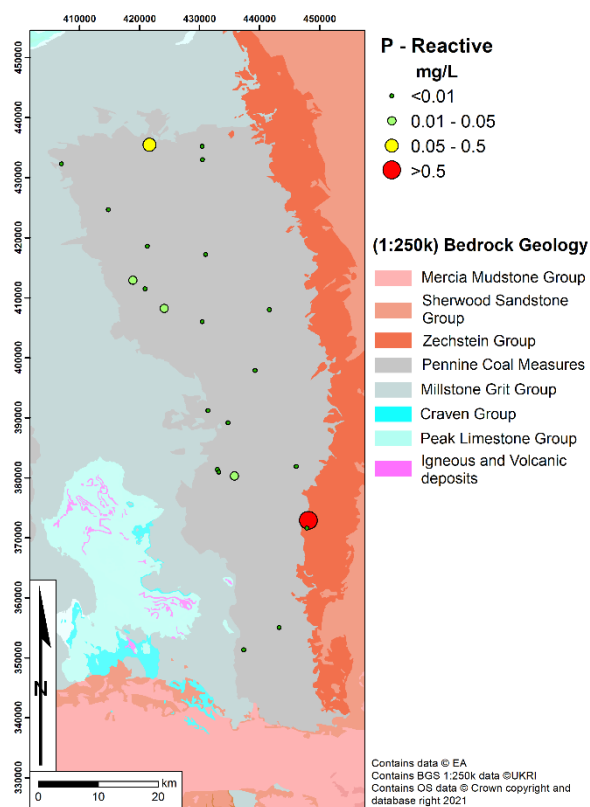


Figure 4-6. Spatial distribution for P-reactive

4.3.2 Halogens

Fluoride concentrations range from <0.05 mg/L to 0.81 mg/L, with a median of 0.258 mg/L. The 5th to 95th percentile range is 0.0973 mg/L to 0.52 mg/L. Fluoride concentrations are typically between 0.1 mg/L and 0.5 mg/L across much of the aquifer, with a few elevated concentrations towards the western edge of the study area (Figure 4-7). Concentrations are fairly constant across the aquifer and show little variation spatially.

Iodine was only detected in one instance from the filtered dataset, with four additional samples being non-detects (<3 µg/L). Bromide was only present in five samples, which are insufficient to draw any wider conclusions.

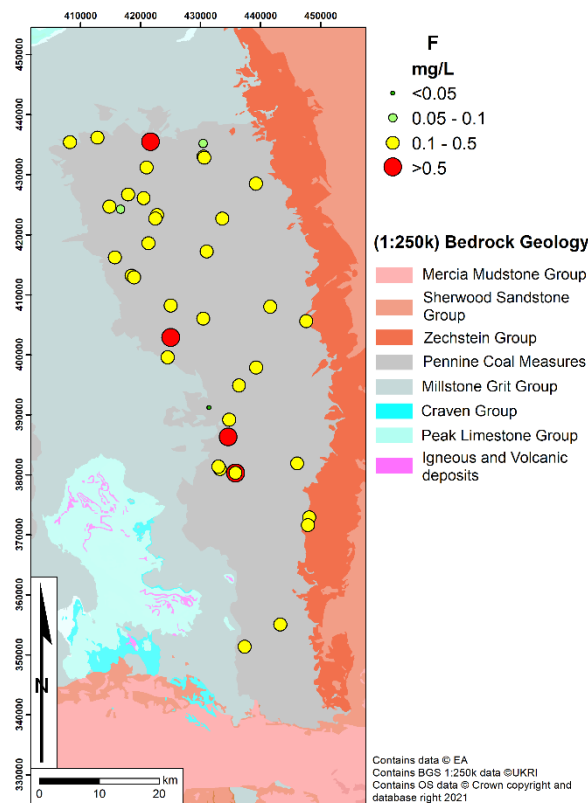


Figure 4-7. Spatial distribution for concentrations of fluoride

4.3.3 Alkali metals

Lithium concentrations detected in the aquifer were below detection limit ($<100 \mu\text{g/L}$) for 10 out of the 12 samples within the filtered dataset, with two positive detections (Table 4-1). Cs and Rb were not measured.

4.3.4 Alkaline earth metals

Barium concentrations range from $20.1 \mu\text{g/L}$ to $240 \mu\text{g/L}$, with a median of $62.4 \mu\text{g/L}$. The 5th to 95th percentile range is $21.6 \mu\text{g/L}$ to $203 \mu\text{g/L}$. Barium concentrations appear to vary across the study area, and with only a few sample points (12), no definitive spatial trends can be drawn (Figure 4-8a).

Strontium has a median concentration of $369 \mu\text{g/L}$, and a range of $26 \mu\text{g/L}$ to $1480 \mu\text{g/L}$. The 5th to 95th percentile range is $70.8 \mu\text{g/L}$ to $1020 \mu\text{g/L}$. Sr concentrations are relatively high in the north-east (Figure 4-8b).

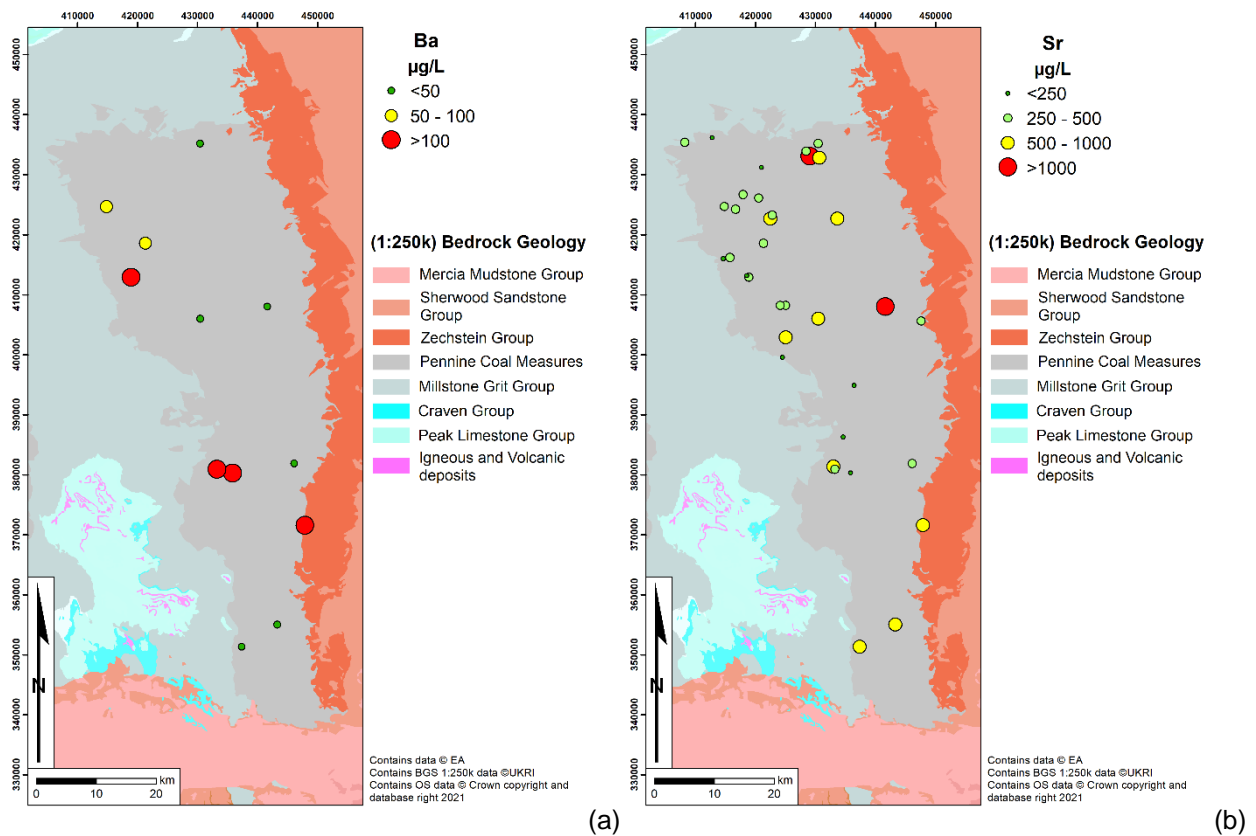


Figure 4-8. Spatial distribution for concentrations of alkaline earth elements; (a) barium; (b) strontium

4.3.5 Iron and manganese

Iron concentrations range from <30 µg/L to 3970 µg/L, with a median of 129 µg/L. The 5th to 95th percentile range is 5.4 µg/L to 2860 µg/L. Iron concentrations across the study area appear to be variable (Figure 4-9a). Concentrations are typically above 100 µg/L between Bradford and Huddersfield in the north of the study area, and over 200 µg/L in the east of the study area, in proximity to the boundary with the Zechstein Group.

Manganese concentrations range from <10 µg/L to 5290 µg/L, with a median of 189 µg/L. The 5th to 95th percentile range is 12.4 µg/L to 2110 µg/L. Concentrations greater than 1500 µg/L are mostly found in sites to the north (Figure 4-9b).

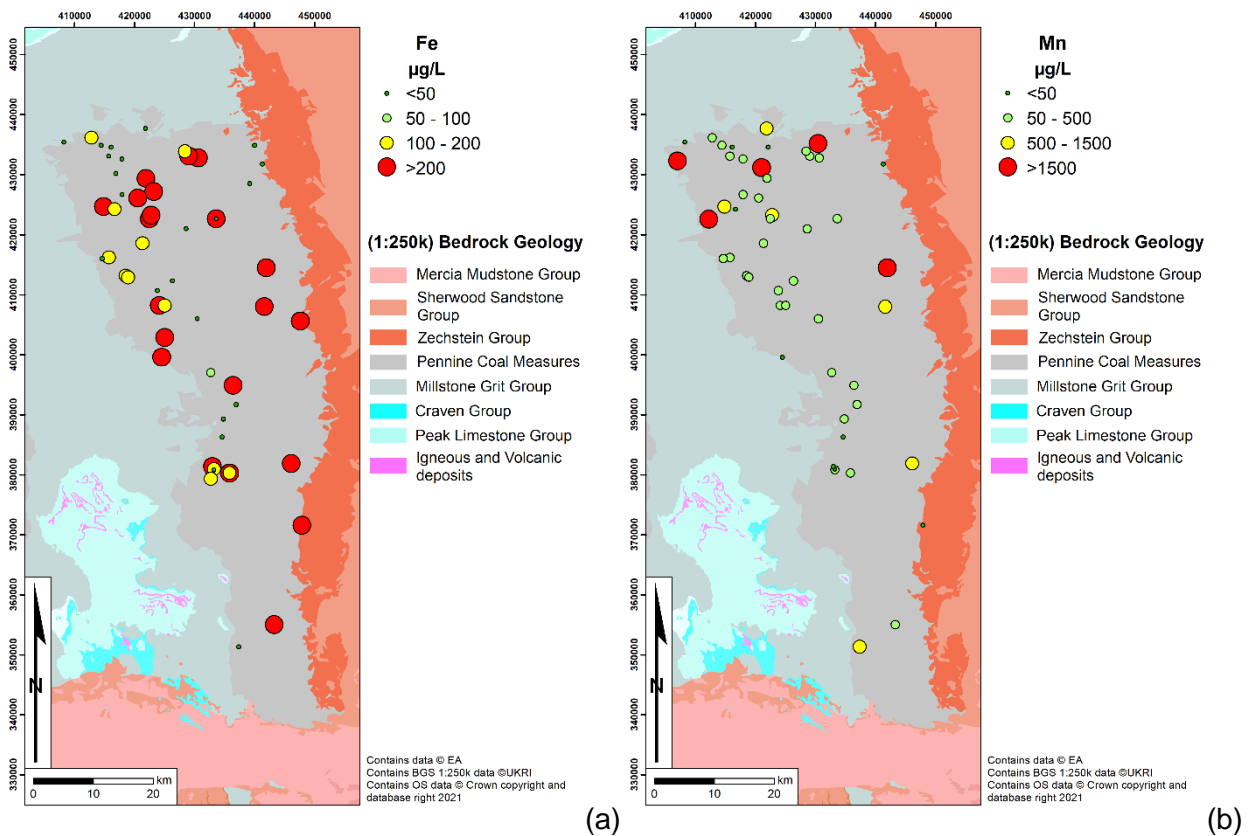


Figure 4-9. Spatial distributions of iron (a) and manganese (b) across the study area

4.3.6 Other selected ions and trace elements

Ammonium (as NH_4) has a concentration range of <0.04 mg/L to 10.5 mg/L, with a median of 0.341 mg/L. The 5th to 95th percentile range is <0.04 mg/L to 4.89 mg/L. NH_4 concentrations are lowest (<0.5 mg/L) in the centre and east of the study area (near Sheffield), and increase towards the northern half (Figure 4-10a). 27 sites (out of 76) show evidence of exceeding the 0.5 mg/L drinking-water standard (UK Gov., 2018). Within the northern half of the study area, concentrations are typically greater in the east than the west, with a general increase from <0.5 mg/L around Bradford to between 0.5 mg/L and 10 mg/L between Leeds and Wakefield.

Boron has a median concentration of 136 $\mu\text{g/L}$, and a concentration range of <100 $\mu\text{g/L}$ to 613 $\mu\text{g/L}$. The 5th to 95th percentile range is 46.2 $\mu\text{g/L}$ to 541 $\mu\text{g/L}$. B concentrations in the north of the study area are typically >200 $\mu\text{g/L}$ (around Leeds and Bradford), and are lower south of Huddersfield (Figure 4-10b) with a few sites in the centre and south of the study area with concentrations above 400 $\mu\text{g/L}$, although these do not show any spatial correlation. There are only a few locations sampled in the far south of the study area.

Copper has a concentration range of <0.5 $\mu\text{g/L}$ to 428 $\mu\text{g/L}$, with a median of 0.85 $\mu\text{g/L}$. The 5th to 95th percentile range is <0.5 $\mu\text{g/L}$ to 4.72 $\mu\text{g/L}$. Concentrations across much of the study appear to be below 1 $\mu\text{g/L}$, with elevated concentrations in a few locations (Figure 4-10c). There are more sites with higher concentrations between Huddersfield, Leeds and Bradford, and immediately south of Sheffield. There do not appear to be any clear regional trends across the study area.

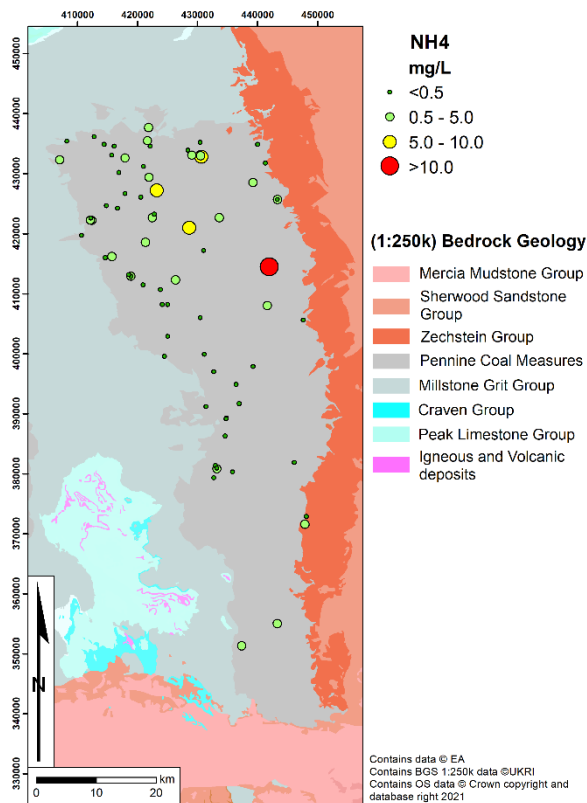
Chromium has a concentration range of <0.5 $\mu\text{g/L}$ to 22.2 $\mu\text{g/L}$, with a median of 0.44 $\mu\text{g/L}$. The 5th to 95th percentile range is <0.5 $\mu\text{g/L}$ to 3.58 $\mu\text{g/L}$. Cr concentrations are <1 $\mu\text{g/L}$ in the southern half of the study area, and with more locations with higher concentrations towards the north, in the vicinity of Huddersfield and Bradford (Figure 4-10d). The north-west corner has the highest concentrations in the region.

Nickel concentrations range from <0.5 $\mu\text{g/L}$ to 7.64 $\mu\text{g/L}$, with a median of 0.92 $\mu\text{g/L}$. The 5th to 95th percentile range is <0.5 $\mu\text{g/L}$ to 4.56 $\mu\text{g/L}$. Concentrations across the aquifer are typically below 5 $\mu\text{g/L}$, with only 2 locations with concentrations greater than 5 $\mu\text{g/L}$ (Figure 4-10e).

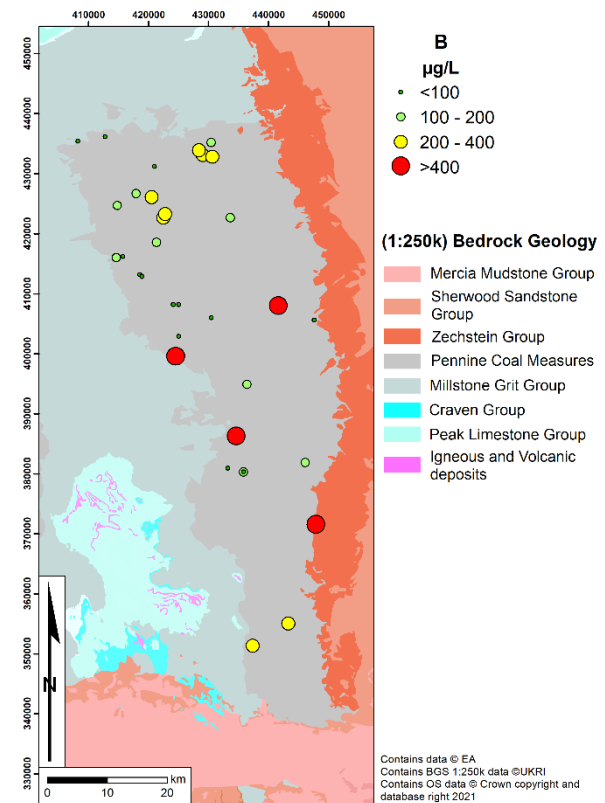
Nitrite concentrations range from <0.013 mg/L to 0.519 mg/L, and have a median of 0.00239 mg/L. The 95th percentile 0.22 mg/L. Concentrations are <0.1 mg/L across most of the study area (Figure 4-10f).

Zinc has a concentration range of <5 µg/L to 685 µg/L, with a median of 14.2 µg/L. The 5th to 95th percentile range is <5 µg/L to 379 µg/L. Concentrations are <50 µg/L across much of the wider study area, but with isolated locations with elevated concentrations in the west and north (Figure 4-10g).

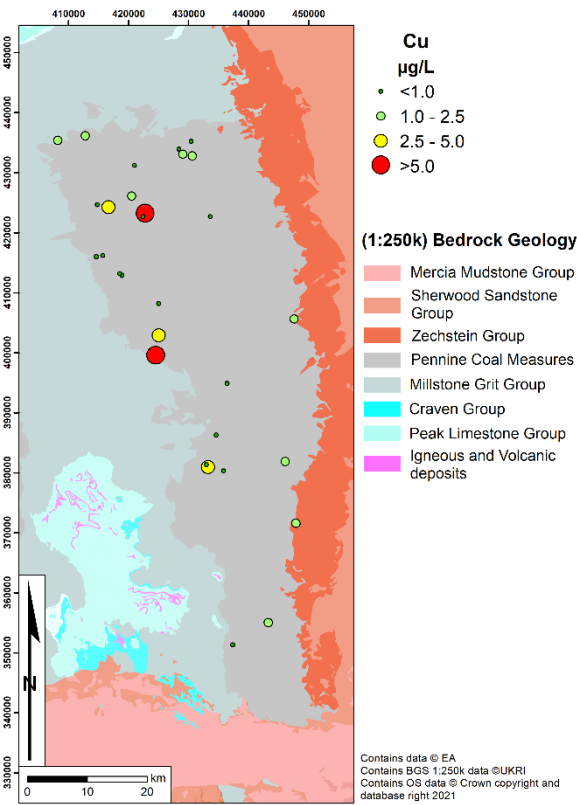
Box plots and cumulative-probability plots for a number of minor and trace elements are shown in Figure 4-4 and Figure 4-11 respectively.



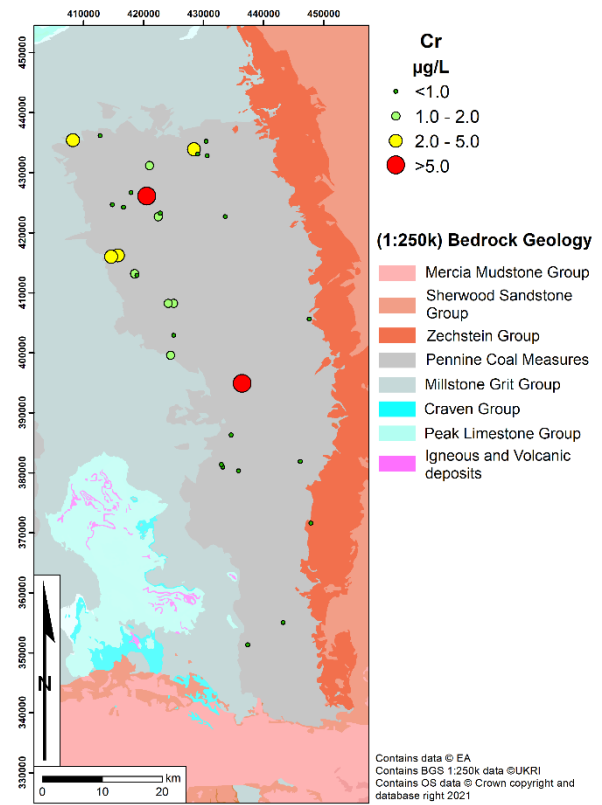
(a)



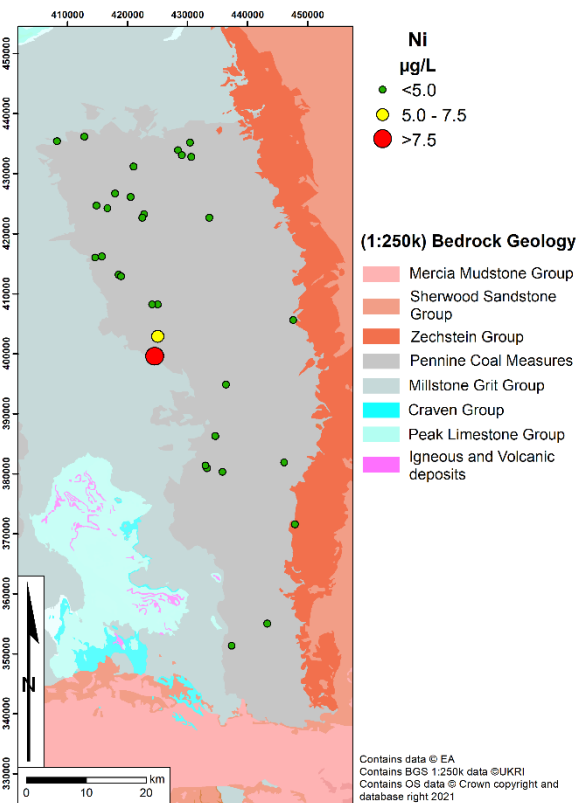
(b)



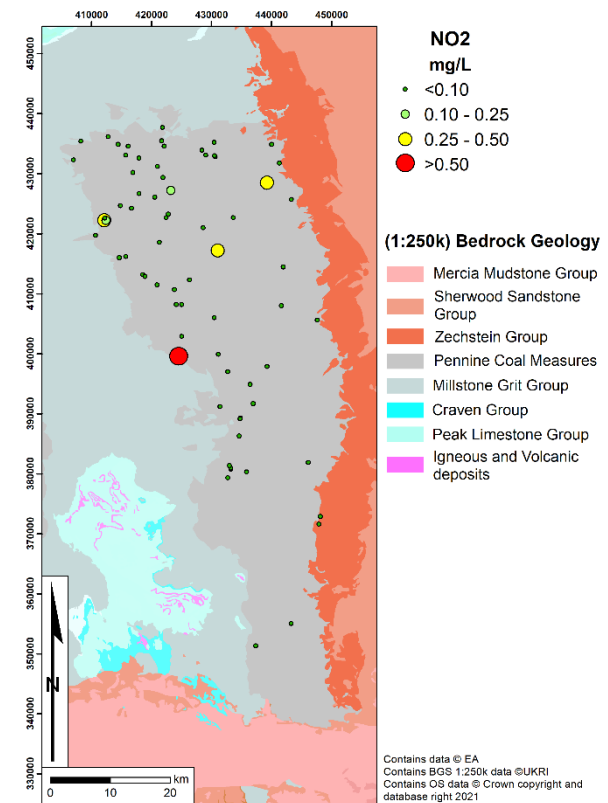
(c)



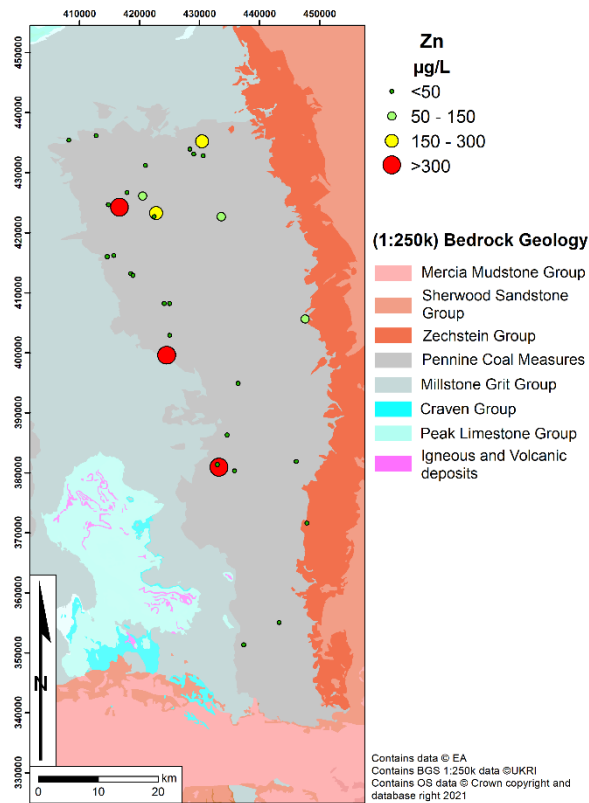
(d)



(e)



(f)



(g)

Figure 4-10. Spatial distribution for concentrations of selected minor and trace elements; (a) ammonium; (b) boron; (c) copper; (d) chromium; (e) nickel; (f) nitrite; (g) zinc

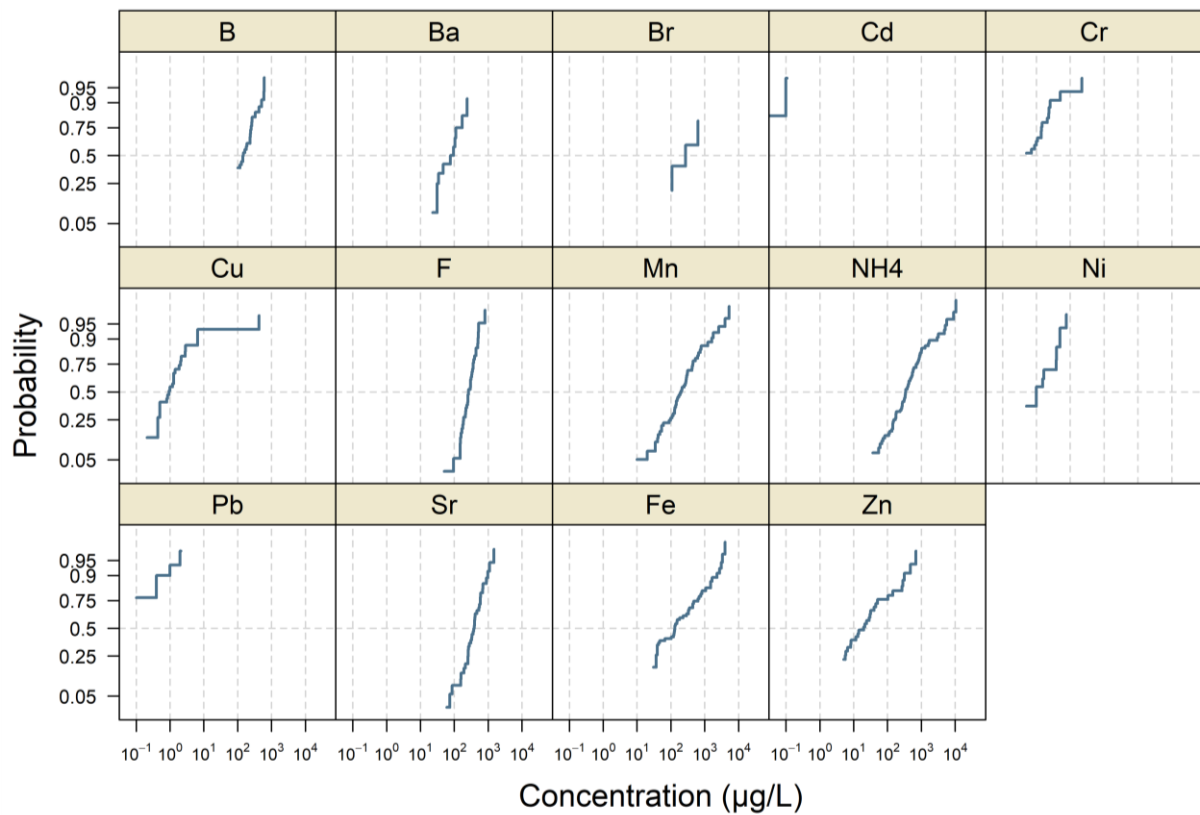


Figure 4-11. Cumulative-probability plot for selected trace elements

Table 4-1. Statistical summary data including percentiles (5th–95th) for inorganic analytes in groundwater from the Pennine Coal Measures aquifer from the EA WIMS database

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
DO	mg/L	22	0	2.12	5.44	11.9	2.47	2.58	3.8	5.01	6.46	9	9.32
SEC	µS/cm	72	0	207	982	2990	391	440	600	868	1100	1770	2120
pH		17	0	4.90	7.19	9.30	5.86	6.10	6.89	7.26	7.65	7.86	8.24
Temperature	°C	30	0	7.1	11.6	16.9	9.0	9.7	10.6	11.5	12.4	13.7	14.3
Ag	µg/L	5	5	<1		<1							
Al	µg/L	12	12	<10		<10							
As	µg/L	23	22	<1		1.71							
B	µg/L	34	12	<100	190	613	46.2	57.7	88.7	136	241	396	541
Ba	µg/L	12	0	20.1	82.6	240	21.6	23.6	31.3	62.4	108	167	203
Be	µg/L	5	5	<1		<1							
Br	µg/L	5	0	0.106	0.246	0.635	0.106	0.106	0.107	0.109	0.275	0.491	0.563
Ca	mg/L	12	0	21.5	77.4	162	25.6	29.3	37.7	61.6	122	134	147
Cd	µg/L	33	30	<0.01		0.107							
Cl	mg/L	70	0	10.2	72.3	323	19.3	21.3	33.1	58	87.6	132	178
Co	µg/L	5	4	<1	1.25								
Cr	µg/L	33	18	<0.5	1.52	22.2	0.0535	0.0747	0.159	0.44	1.4	2.34	3.58
Cu	µg/L	31	10	<0.5	14.9	428	0.0944	0.145	0.236	0.85	1.64	2.86	4.72
F	mg/L	42	3	<0.05	0.288	0.81	0.0973	0.149	0.183	0.258	0.35	0.494	0.52
Fe	µg/L	55	17	<30	521	3970	5.4	10.1	31.6	129	460	1600	2860
HCO ₃	mg/L	72	1	<12	332	1170	41.5	78.4	222	311	421	562	643
I	µg/L	5	4	<3		3.5							
K	mg/L	12	0	2.58	6.53	13.2	3	3.38	3.9	4.36	8.22	12.9	13.1
Li	µg/L	12	10	<100		136							
Mg	mg/L	12	0	9	37.1	99.2	10.1	11.1	13.3	37.7	45.4	70.2	84.7
Mn	µg/L	53	3	<10	506	5290	12.4	34.5	89	189	427	1140	2110

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
Mo	µg/L	5	5	<3		<3							
Na	mg/L	12	0	18.1	88.4	213	23.9	29	36.7	87.4	108	159	185
NH ₄	mg/L	76	6	<0.037	0.908	10.5	0.0363	0.0582	0.151	0.341	0.702	1.66	4.89
Ni	µg/L	33	25	<0.5	1.58	7.64	0.267	0.301	0.482	0.92	1.74	3.84	4.56
NO ₂	mg/L	76	60	<0.013	0.0334	0.519	5.98E-05	0.000132	0.000527	0.00239	0.012	0.0493	0.22
NO ₃	mg/L	48	19	<0.86	3.11	35.4	0.31	0.442	0.823	0.864	1.9	8.24	11.4
Pb	µg/L	33	29	<0.1		2.09							
P-reactive	mg/L	24	19	<0.01	0.0551	1.2	4.10E-06	1.09E-05	5.40E-05	0.000413	0.00312	0.0274	0.0348
Sb	µg/L	5	5	<1		<1							
Se	µg/L	23	21	<1		5							
Si	mg/L	39	0	2.52	7.18	11.1	4.54	4.89	6.03	7.2	8.23	9.12	10.8
Sn	µg/L	5	5	<2		<2							
SO ₄	mg/L	71	2	<10	160	1920	8.01	16	34.1	87.5	180	309	528
Sr	µg/L	36	0	26	429	1480	70.8	120	243	369	564	800	1020
Ti	µg/L	5	5	<2		<2							
U	µg/L	8	8	<0.5		<0.5							
V	µg/L	5	5	<2		<2							
Zn	µg/L	33	7	<5	80.7	685	0.993	1.71	5.66	14.2	45.4	281	379

NB: ncens = number of censored data (below detection limit)

4.4 ORGANIC CHEMISTRY

A number of organic analytes were included in the filtered EA WIMS dataset, but most analyses are non-detects; the few detections observed for given analytes are shown in Table 4-2. Complete summary statistics for all organic analytes included in the filtered EA WIMS dataset are shown in Table 4-3. A minority of sites showed detections of PAHs and VOCs (MTBE and BTEX compounds).

Table 4-2. Detected organic compounds and number of detections from filtered EA WIMS dataset

Analyte	Number of detections
Acenaphthene	1
Benzene	1
Benzo(a)pyrene	1
Benzo(g,h,i)perylene	1
Benzo(k)fluoranthene	1
Dimethylbenzene: Sum of isomers (1;3- 1;4-): [m+p xylene]	3
Ethylbenzene	2
Fluoranthene	1
MTBE:- [Methyl tert-butyl ether]	4
Toluene:- [Methylbenzene]	3

Data for both dissolved organic carbon (DOC) and total organic carbon (TOC) were present in the filtered dataset. DOC concentrations range from 0.41 mg/L to 6.92 mg/L, with a median of 1.09 mg/L. The 5th to 95th percentile range is 0.546 mg/L to 5.22 mg/L. DOC concentrations are relatively low across the study area, typically 1.5 mg/L or less (Figure 4-12a).

TOC concentrations range from <0.5 mg/L to 15.3 mg/L, with a median of 1.6 mg/L. The 5th to 95th percentile range is 0.515 mg/L to 6.45 mg/L. There are no samples in the south of the study area (besides 2 in the vicinity of Sheffield), so no conclusions can be drawn for this area (Figure 4-12b). TOC concentrations in the north appear to show isolated areas with elevated concentrations, against a background of sites with concentrations <2.5 mg/L.

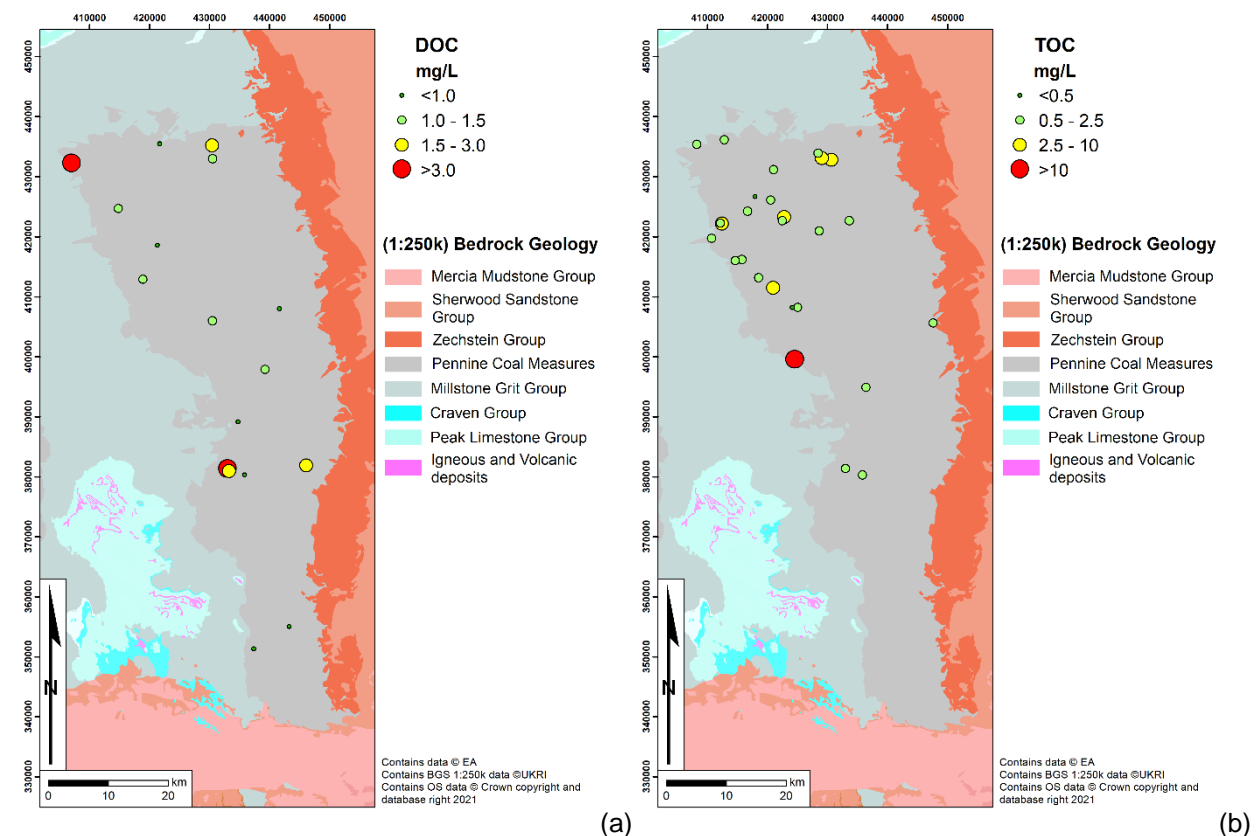


Figure 4-12. Spatial distributions for concentrations of (a) DOC and (b) TOC across the study area

Table 4-3. Statistical summary data including percentiles (5th–95th) for organic analytes in groundwater from the Pennine Coal Measures aquifer from the EA WIMS database

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
Acenaphthene	µg/L	7	6	<0.01	NA	0.181							
Acenaphthylene	µg/L	7	7	<0.01	NA	<0.01							
Benzene	µg/L	35	34	<0.1	NA	0.1							
Benzo(a)pyrene	µg/L	8	7	<0.01	NA	0.007							
Benzo(b)fluoranthene	µg/L	7	7	<0.01	NA	<0.01							
Benzo(e)pyrene	µg/L	1	1	<0.01	NA	<0.01							
Benzo(g;h;i)perylene	µg/L	8	7	<0.01	NA	0.012							
Benzo(k)fluoranthene	µg/L	8	7	<0.01	NA	0.006							
Dibenzo(a,h)anthracene	µg/L	7	7	<0.01	NA	<0.01							
Dimethylbenzene: Sum of isomers (1;3- 1;4-): [m+p xylene]	µg/L	33	30	<0.1	NA	3.55							
DOC	mg/L	17	0	0.41	1.63	6.92	0.546	0.64	0.83	1.09	1.55	3	5.22
Ethylbenzene	µg/L	34	32	<0.1	NA	1.04							
Fluoranthene	µg/L	8	7	<0.01	NA	0.013							
Fluorene	µg/L	7	7	<0.01	NA	<0.01							
Hexachlorobenzene	µg/L	8	8	<0.001	NA	<0.01							
MTBE:- [Methyl tert-butyl ether]	µg/L	32	28	<0.1	NA	1.36							
Naphthalene	µg/L	28	28	<0.01	NA	<0.3							
n-ButylBenzene:- [1-Phenylbutane]	µg/L	21	21	<0.1	NA	<0.2							
n-Propylbenzene:- [1-phenylpropane]	µg/L	21	21	<0.1	NA	<0.1							
Perylene	µg/L	1	1	<0.01	NA	<0.01							
Phenanthrene	µg/L	7	7	<0.01	NA	<0.01							
Pyrene	µg/L	7	7	<0.01	NA	<0.01							
TOC	mg/L	27	2	<0.5	2.46	15.3	0.515	0.764	1.14	1.6	2.22	4.46	6.45
Toluene:- [Methylbenzene]	µg/L	35	32	<0.1	NA	0.54							

5 Geochemical controls

5.1 INORGANIC GEOCHEMISTRY

5.1.1 Recharge and anthropogenic inputs

Recharge to the Pennine Coal Measures is predominantly via infiltration to exposed outcrop areas. Recharge chemical compositions have been estimated in Table 2-3 to Table 2-6, from the closest available Defra PRECIP-Net monitoring stations (DEFRA, 2020a, b, 2021a, b). Na and Cl dominate the estimated recharge chemistry, with concentrated means for Cl ranging from 7.71 mg/L to 12.64 mg/L, and a range of 4.29 mg/L to 7.26 mg/L for Na, across 2019 and 2020.

Comparing these data against concentrations observed from the filtered WIMS dataset, averages for Na are around 16-19 times greater in groundwater, and around 7-10 times greater for Cl. Of all the aquifers in the UK, the Pennine Coal Measures have been observed as the most saline at shallow depths (EA, 2020).

Estimated annual NO₃ concentrations in infiltrating recharge are estimated to be between 9.96 mg/L to 11.8 mg/L, at the high end of the range for NO₃ concentration in the groundwater (5.54 mg/L). (10th–90th percentile: 0.46–12 mg/L). Average SO₄ concentrations are low for infiltrating recharge, ranging from 2.88 mg/L to 4.73 mg/L (total sulphate) (Table 2-3 to Table 2-6), around 2%–4% of the median concentration observed in the aquifer (Table 4-1). As with Na and Cl, SO₄ is principally derived from interactions with the aquifer matrix. The principal source of elevated SO₄ is abandoned coal-mine workings, now flooded as groundwater levels have rebounded, and taken up the SO₄ generated by oxidation of pyrite (Banks, 1997; Banks et al., 1997; Younger et al., 2002).

5.1.2 Geochemical reactions

The groundwater chemistry within the Pennine Coal Measures aquifer is predominantly controlled by aquifer water-rock interactions and the impact of historical coal-mining activities, although relationships are complex and processes non-trivial to determine. The chemistry is characterised by a large range of pH values (4.9–9.3) and typically high dissolved-solids contents (SEC up to 6030 µS/cm).

The groundwater is overwhelmingly reducing with low concentrations of NO₃ in most, and high concentrations of dissolved Fe and NH₄ and some high concentrations of Mn. Low concentrations of dissolved U and V further support the reducing condition, albeit with few analyses available for these trace elements. Distributions of dissolved N species suggest an important role for denitrification (decrease in concentration of NO₃), supported by the detection of nitrite (NO₂), as well as nitrate reduction (generation of NH₄). These are all likely to be favoured by the abundance of organic carbon in both the solid and aqueous phases (TOC up to 15.3 mg/L). Low concentrations of NO₃ relative to the estimated values in infiltrating recharge (Section 5.1.1) also support this inference. Abundance of SO₄ in particular is indicative of oxidation of sulphide minerals in parts of the sedimentary sequence and the variation in pH supports the variable influence of buffering by carbonate minerals including calcite.

The groundwaters are variably of Ca-Mg-HCO₃, Ca-Mg-SO₄ and Na-HCO₃ types (Figure 4-3). Similar water chemistry types were observed by Banks (1997). Calcite dissolution and interaction with clays are possible sources for the dominant Ca-Mg-HCO₃ waters. Na-HCO₃ waters may be influenced by ion-exchange reactions on clays, and Ca-Mg-SO₄ waters from the oxidation of sulphide minerals. Relatively high observed molar Mg/Ca ratios (range 0.4 to 1.3) are consistent with clay dissolution/exchange reactions. The elevated sulphate concentrations (>500 mg/L) are prevalent in the northern half of the area, and are likely linked to abandoned mine workings.

Where possible to model mineral equilibrium from groundwater data available, most are slightly undersaturated with respect to calcite and more strongly undersaturated with dolomite. Most are saturated with respect to quartz which is a possible control on the concentrations of Si. As a result of the high concentrations of SO₄, a majority of samples are saturated with respect to barite. This is shown by the strong negative relationship between Ba and SO₄ (Figure 5-1a). Barium also has

a somewhat less well-defined positive relationship with pH (Figure 5-1b). All groundwaters are undersaturated with respect to fluorite.

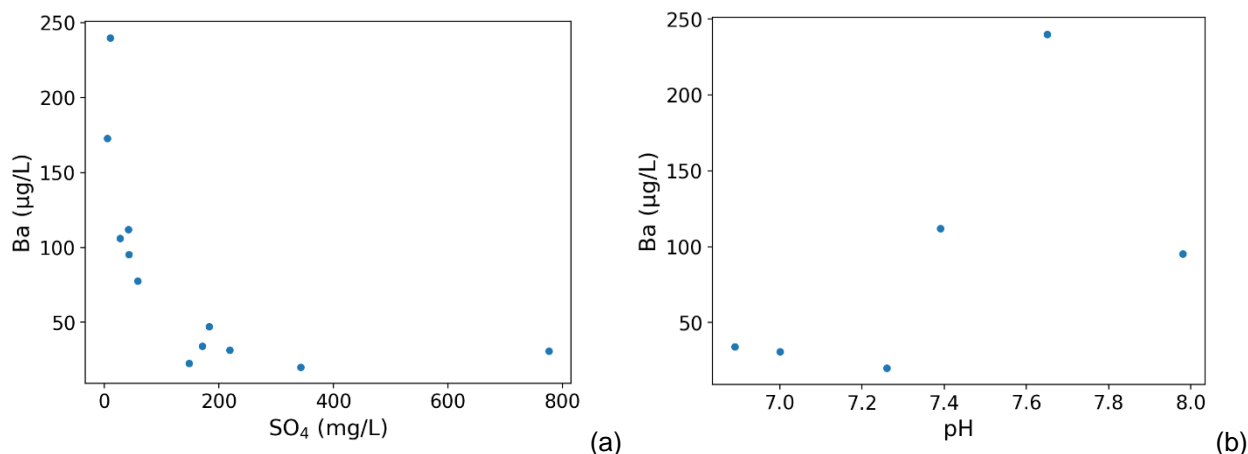


Figure 5-1. Relationship between barium concentration and (a) sulphate concentration, and (b) pH

Low concentrations of SO_4 in the Coal Measures groundwater have been attributed to SO_4 reduction, with resultant increased alkalinity, resulting from oxidation of organic carbon (Banks, 1997). Only a few of the groundwater analyses provided by the WIMS dataset (7 samples) in this study show low concentrations of SO_4 (<10 mg/L) as would follow from a control of SO_4 reduction; rather, high concentrations of SO_4 are much more typical and indicative instead of the oxidation of sulphide minerals. Sulphate reduction is inferred for groundwater from a few sites, but the dataset suggests the impact is localised.

Ion-exchange reactions have been concluded to have had an impact in groundwater across parts of the Midlands and South Yorkshire Coal Measures aquifer, especially between Ca and Na. Ion exchange is noted to occur in coincidence with the onset of SO_4 reduction (Banks, 1997). Clay matrices are typical within the water-bearing sandstones of the Pennine Coal Measures (Section 2.3), and are likely to be a notable medium for ion-exchange reactions, where strongly reducing conditions occur.

The concentrations of Fe exceed the 200 $\mu\text{g/L}$ drinking-water standard (UK Gov., 2018) in many of the Coal Measures groundwaters (21 out of 55 sites). Sources for iron include iron oxide, pyrite and possibly siderite, the products of oxidised pyrite being derived from now-abandoned coal mine workings following flooding and rebound of groundwater levels (Burke et al., 2005; Gandy and Younger, 2007; Gee et al., 2020; Younger et al., 2002). Mobility of ferrous Fe is a function of mildly reducing conditions in the groundwater, although it is also linked to pyrite oxidation and associated acid mine drainage from old mine discharges, which is currently treated by the Coal Authority (Banks et al., 1997; Coal Authority, 2021).

5.1.3 Changes downgradient

A number of solutes increase from west to east across the study area, in line with the regional flow direction. These include Ca, Mg, K, and SO_4 and associated SEC. Solute concentrations are likely to increase with the increased water-rock reaction, flow into deeper parts of the aquifer, and interaction with a much higher density of abandoned mine workings (Figure 1-2). Solute concentrations can increase not only with increased residence time, but also by mixing with deeper, more saline waters (Aitkenhead et al., 2002; Banks, 1997). This has been observed by Banks (1997) at a number of deep wells (>150 m) in the Sheffield area, and may also play a role in the relatively high SEC values recorded in some of the groundwaters in the current study (Figure 4-1d). Additionally, the extent of historical coal mining increases in density from west to east across the study area (Coal Authority, 2018a), which is also likely to have an impact, notably on the increasing concentrations of SO_4 . These abandoned coal mines offer potential new pathways for hydraulic flow and connection with deeper groundwaters. In contrast, Ba concentrations can be seen to decrease from west to east (Figure 4-8a) across the study area, the upper limits controlled by barite solubility.

Banks (1997) identified two groups of more reducing waters at greater depths within the Pennine Coal Measures aquifer, which have not been identifiable with confidence within the context of the current study and data. These two groups were distinguished by their elevated alkalinity and Na (group ii, in Banks, 1997) and increased Cl concentrations (group iii, in Banks, 1997). Whilst there is evidence for both these types of waters in the current WIMS dataset, they cannot necessarily be fully resolved with the Banks (1997) data.

5.2 ORGANIC GEOCHEMISTRY AND DISSOLVED GASES

Concentrations of organic carbon in Coal Measures groundwater have a median of 1.09 mg/L for DOC and 1.92 mg/L for TOC, although the mean and maximum values for TOC are large (5.37 mg/L and 20.9 mg/L respectively). Potential origins include industrial, urban and agricultural pollution, although the organic-rich nature of the aquifer could also be consistent with a substantially natural origin for both.

A total of 10 PAH and VOC compounds have been detected within the extracted dataset. The highest observed concentrations detected include dimethylbenzene (3.55 µg/L), ethylbenzene (1.04 µg/L) and MTBE (1.36 µg/L). The organic-rich coal beds within the aquifer are potentially a source of soluble organic compounds, including PAH and VOCs.

Coal seams are also a possible source of dissolved methane, although no data were provided for dissolved methane (or CO₂) in the WIMS dataset, as this is not routinely monitored by the Environment Agency. Considering that mine gas has historically been explored and exploited across the area to the east (Section 1.3.4, Table 1-2), there is evidence of methane presence at some sites. Within the literature, authors have identified methane in groundwater, with a range of 16.5 µg/L to 9000 µg/L reported by Banks et al. (2017), and 0.8 to 9 µg/L observed by Bell et al. (2016).

5.3 PROXIMITY TO ONSHORE OIL AND GAS ACTIVITIES

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, 2021c), and measurements within the buffer zone were extracted. The number of measurements, and the range of data extracted, are shown in Table 5-1, Figure 5-2 & Figure 5-3.

Table 5-1. Selected intersecting analytes within 1 km of the OGA (2021c) onshore wells dataset

Analyte	Number of intersects (n)	Range of extracted data
Na	2	100 – 213 mg/L
Cl	3	88.7 – 131 mg/L
SO ₄	3	115 – 776 mg/L
DOC	2	0.88 – 0.93 mg/L
TOC	1	1.82 mg/L

There are very few sites from the filtered WIMS dataset that intersect with the 1-km buffer zone (a maximum of 3). From the limited data, it appears that the inorganic analytes are of relatively high concentration, whilst the organic analytes do not appear as elevated. The OGA onshore wells dataset identifies that the vast majority of drilled boreholes are found in the east of the study area. This may explain the correlation with the high concentration of inorganic analytes, as concentrations have been seen to increase from west to east with the regional flow direction (Section 5.1.3). However, the insufficient number of intersecting locations prevents any statistically robust evaluation of a relationship between proximity to onshore oil and gas wells and the reported hydrogeochemistry. 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.

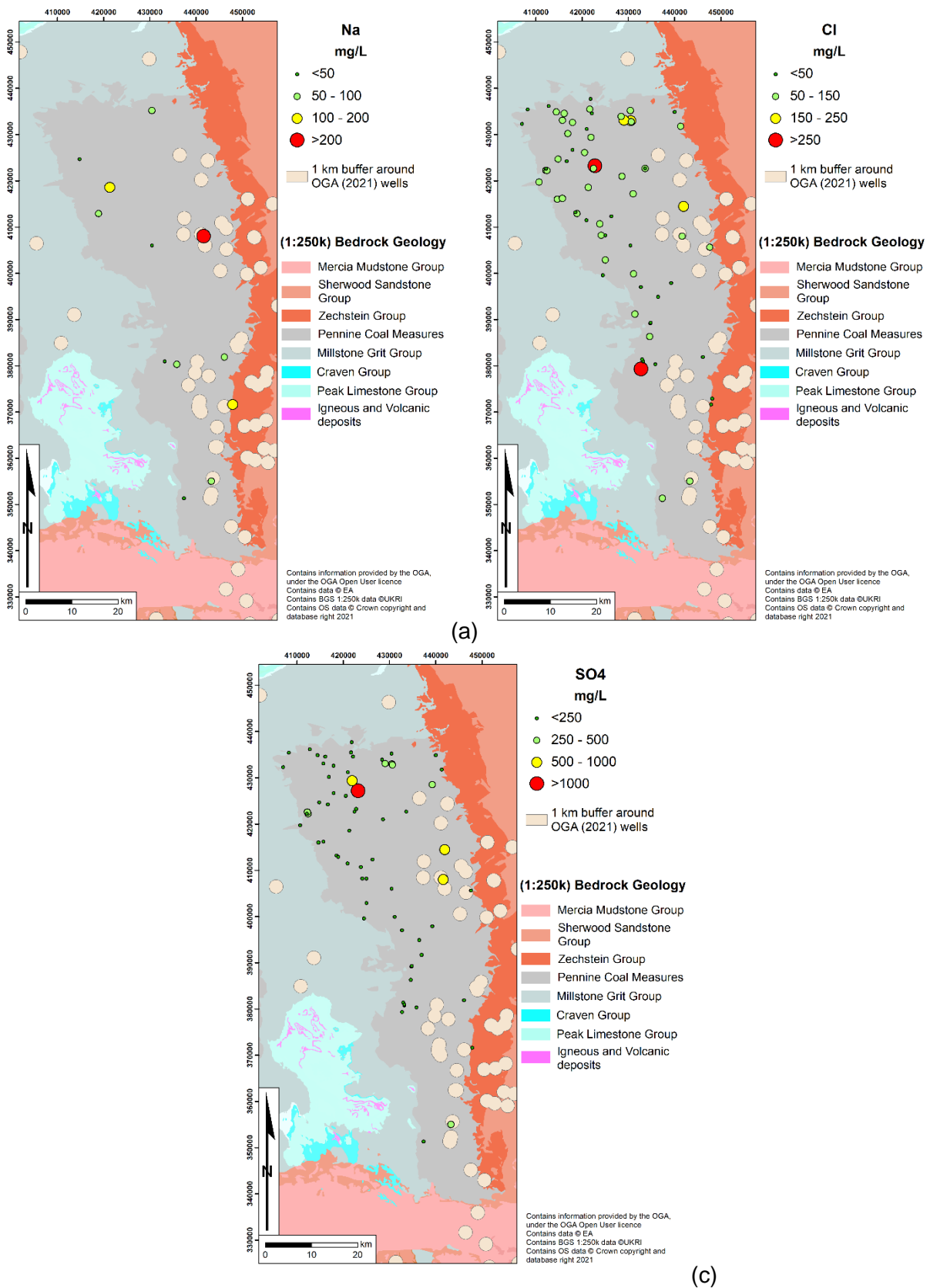


Figure 5-2. Select inorganic analytes and their proximity to OGA (2021c) wells across the study area: (a) sodium; (b) chloride; (c) sulphate

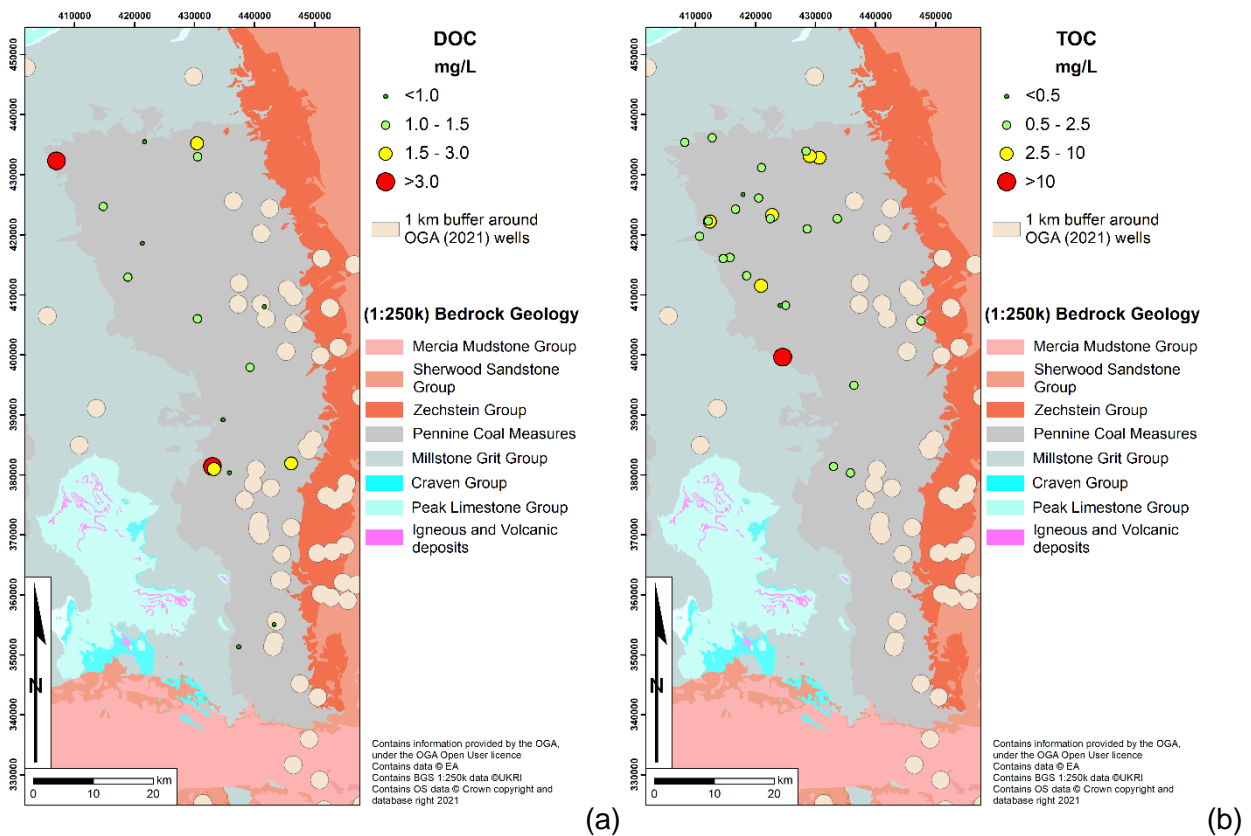


Figure 5-3. Select organic analytes and their proximity to OGA (2021c) wells across the study area: (a) DOC; (b) TOC

5.4 TEMPORAL VARIATION

Of the data from WIMS with sufficient analyses to investigate a time series, relatively few show trends with time and where trends can be inferred, few are consistent across sites. Many show a large variation in concentrations of major ions within sites (Figure 5-4 to Figure 5-6). Overall, the data in Figure 5-4 to Figure 5-6 demonstrate the high concentrations of dissolved solids (e.g. Cl, Na, SO₄, alkalinity), the range of pH values (mildly acidic to mildly alkaline) and a dominance of reducing groundwater conditions (elevated concentrations of Fe, Mn, NH₄, low concentrations of NO₃ - Total Oxidised Nitrogen, U). High concentrations of SO₄ in many are consistent with pyrite oxidation (Figure 5-4 to Figure 5-6) and point away from a significant influence of SO₄ reduction.

400B0135

Detect ○ Non-detect ○

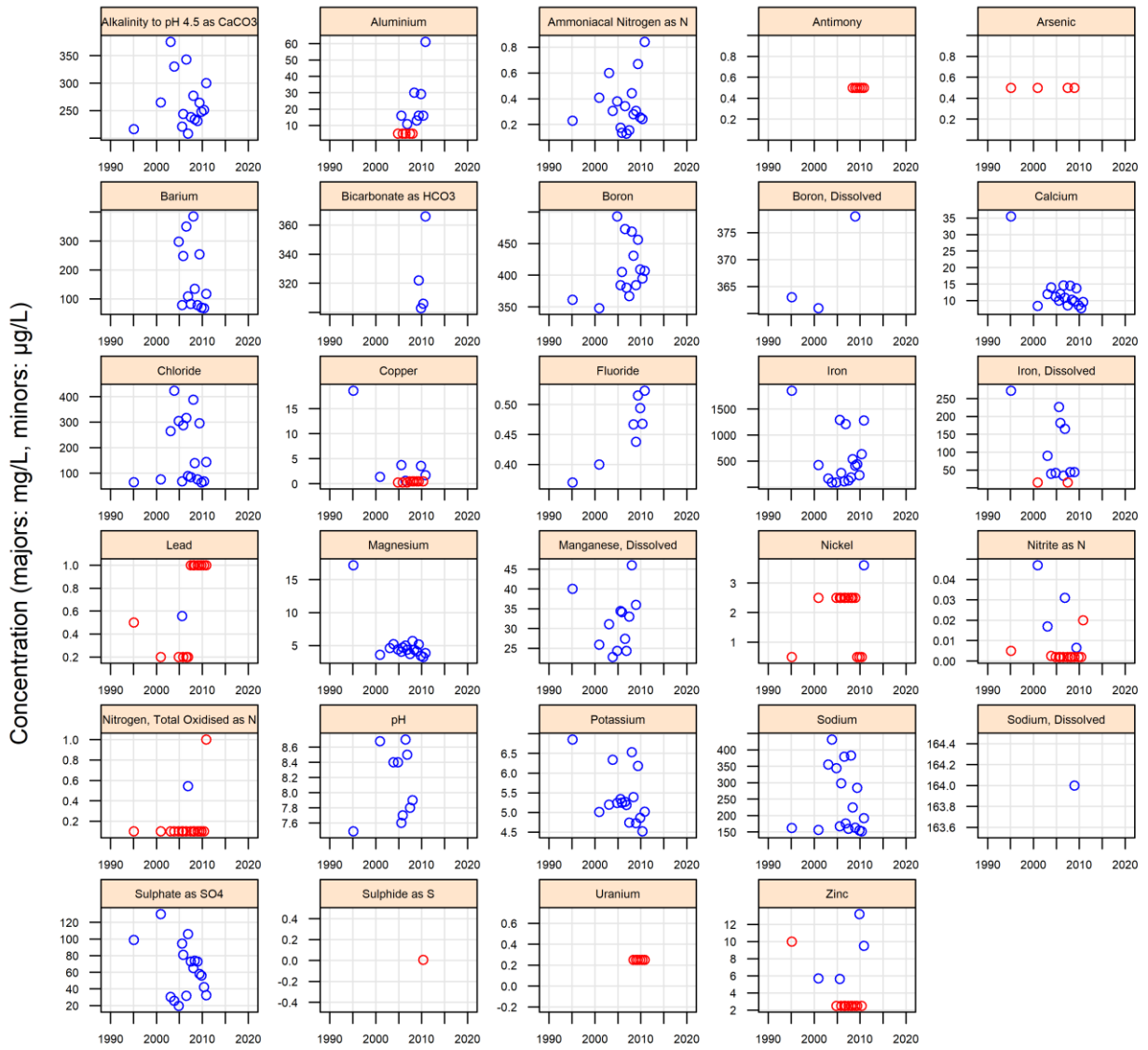


Figure 5-4. Temporal variation in selected analytes in groundwater samples from indicative site 400B0135 from the Pennine Coal Measures aquifer, EA-WIMS data (Ca, Mg, Na, K, NO₃-N, HCO₃, SO₄, S, F as mg/L; trace elements as µg/L)

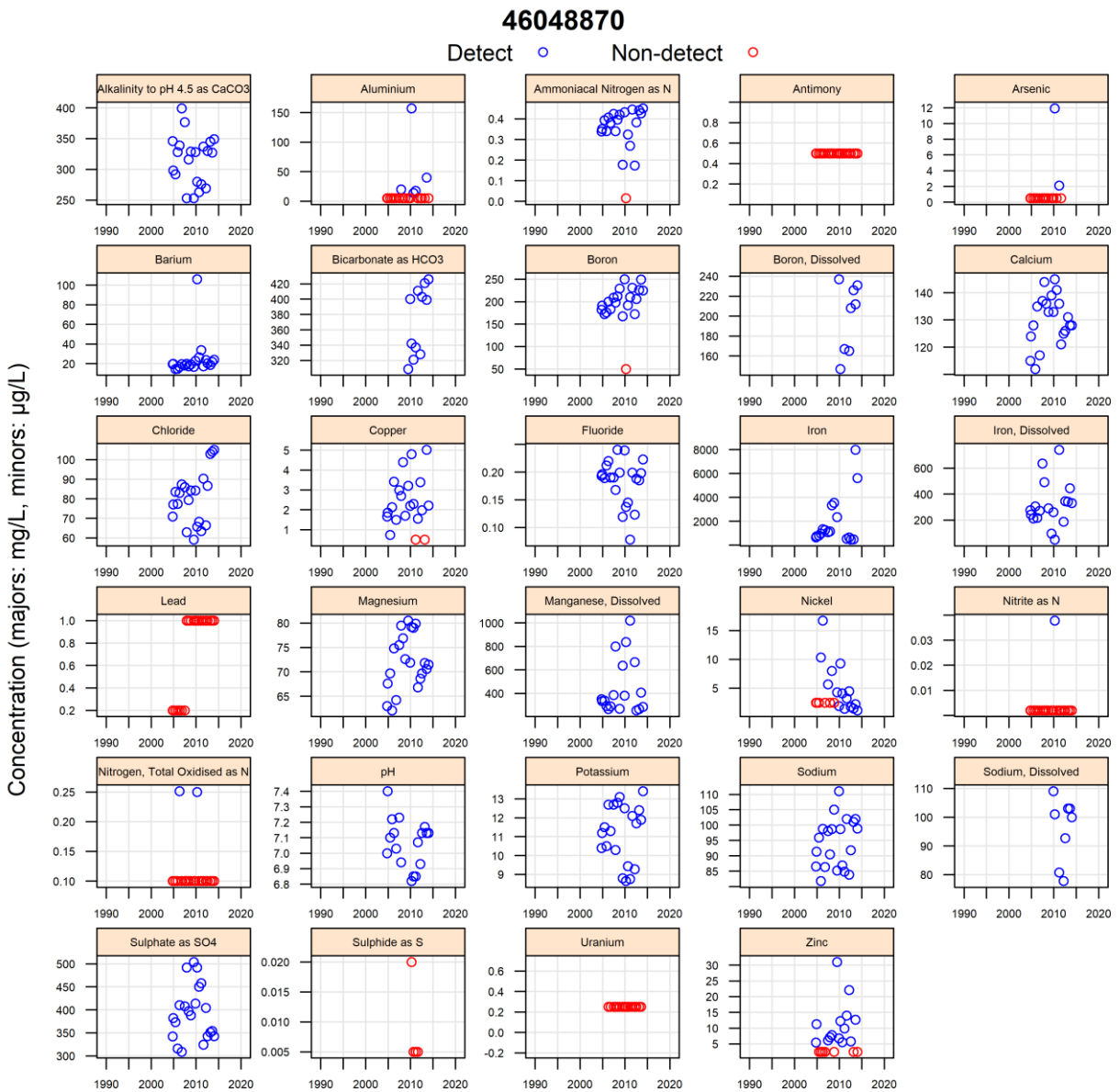


Figure 5-5. Temporal variation in selected analytes in groundwater samples from indicative site 46048870 from the Pennine Coal Measures aquifer, EA-WIMS data (Ca, Mg, Na, K, NO₃-N, HCO₃, SO₄, S, F as mg/L; trace elements as µg/L)

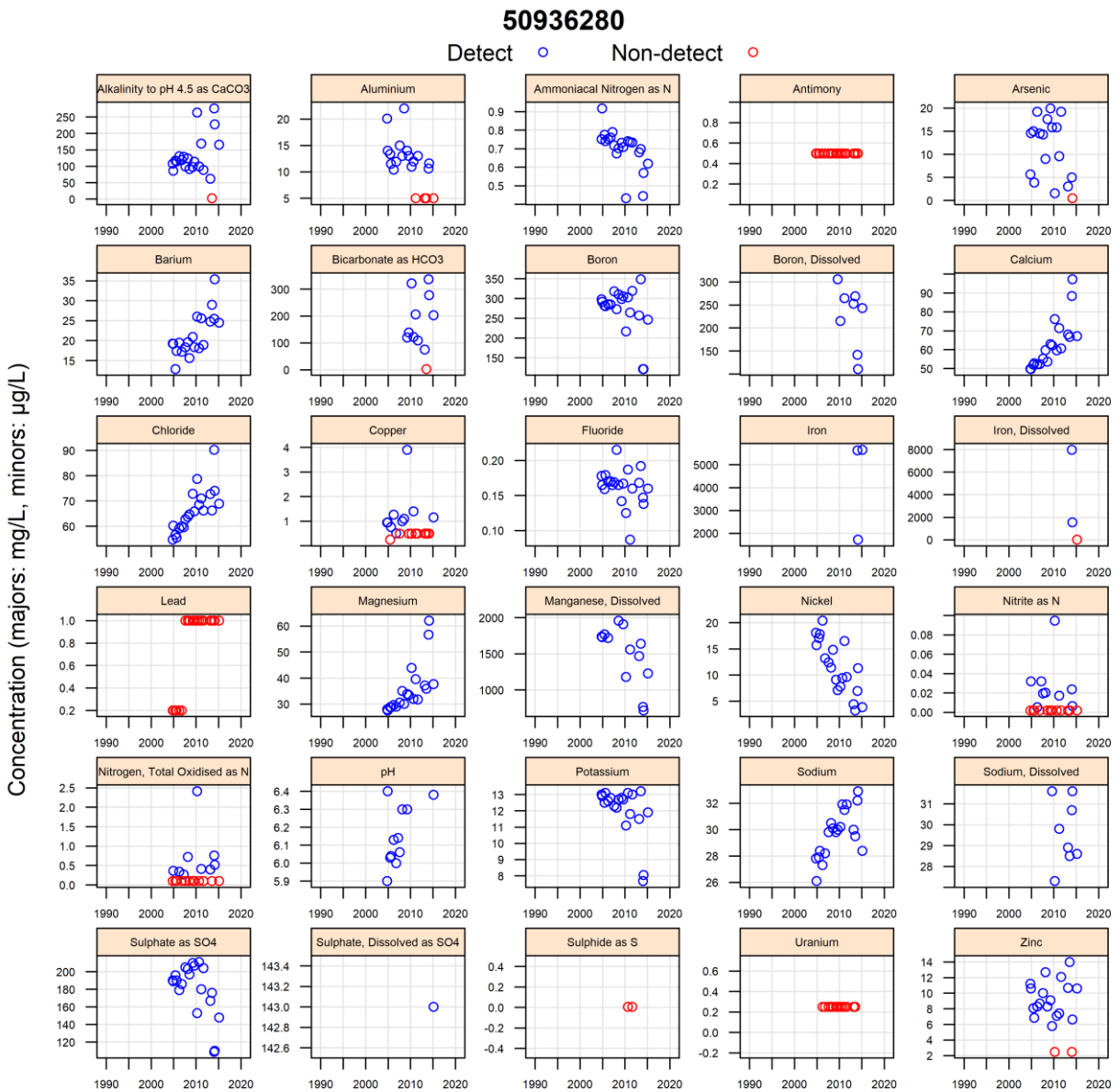


Figure 5-6. Temporal variation in selected analytes in groundwater samples from indicative site 50936280 from the Pennine Coal Measures aquifer, EA-WIMS data (Ca, Mg, Na, K, NO₃-N, HCO₃, SO₄, S, F as mg/L; trace elements as µg/L)

6 Baseline characteristics of the Pennine Coal Measures aquifer

6.1 INORGANIC CHEMICAL COMPOSITIONS

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. 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. In the context of a pre-new OOG development baseline, this will likely serve as an ideal starting point, considering the pre-existing conditions influenced both by the water-rock interactions and the anthropogenic activities within the region.

Groundwater in the Pennine Coal Measures aquifer of the Midlands and South Yorkshire is derived from rainfall recharge, but shows signs of significant impacts by a legacy of coal mining across the region, as well as interaction with the aquifer matrix. Rainfall introduces inputs of elevated inputs of Na and Cl, alongside more minor inputs of Ca, Mg, NO₃ and SO₄. Of those ions measured for rainfall, only NO₃ is observed to have a lower concentration within the aquifer, and is concluded to be evidence of the reducing conditions and limited agricultural inputs.

Water types are dominantly Ca-Mg-HCO₃ and Ca-Mg-SO₄, with minor evidence for Na-K-HCO₃ type waters in isolated locations. These compositions are principally influenced by the aquifer mineralogy, consisting of limited calcite cement and clays, alongside oxidised sulphide minerals exposed within abandoned mining infrastructure. The average pH of rainfall recharge is <6.5, but this is buffered by the presence of carbonate minerals (calcite, siderite) within some areas of the aquifer matrix, resulting in a range of pH values but broadly centred on neutral compositions. Interaction with now flooded mine workings leads to high concentrations of Fe, Mn and SO₄ within the groundwater, often which can exceed drinking-water standards (UK Gov., 2018).

Groundwater shows evidence of predominantly reducing conditions, shown by high concentrations of Fe, Mg, NH₄, and low concentrations of NO₃. High alkalinity in some groundwater samples are consistent with redox reactions involving oxidation of organic carbon.

6.2 ORGANIC CHEMICAL COMPOSITIONS

DOC and TOC across the aquifer are generally low but with a 95th percentile of 5.22 mg/L for DOC, and 6.45 mg/L for TOC. Sources of organic C could be anthropogenic (industrial, including from coal mines, or domestic) or aquifer-derived, but elevated concentrations are not inconsistent with a natural origin from the organic-rich aquifer.

There are only a few occurrences of PAH and VOC compounds within this study, with concentrations considered to be linked the abundant coal resources within the aquifer, although they could also be sourced from modern anthropogenic sources.

Whilst no WIMS dissolved-gas data have been available as part of this study, previous investigations (Banks, 1997; Banks et al., 2017; Bell et al., 2016), alongside a history of mine-gas exploration (Figure 1-5 and Banks et al. (2017)), have identified the occurrence of methane across the aquifer, with up to 9 mg/L dissolved in groundwater.

The reliance on groundwater data solely from the WIMS database, even with careful screening to exclude sites with sampling purpose codes indicating pollution incidents/sources, inevitably risks inclusion of sites impacted by industrial or other pollution. This is inferred to be the case with respect to uncommon occurrences of PAHs, BTEX and MTBE in this study. The Coal Measures aquifer is located substantially below urban and industrial areas of northern England, and so the influences of urban and industrial pollutants on regional groundwater chemistry increase. In the context of potential future OOG-type developments, such contaminants in groundwater constitute a component of the current baseline condition. Appropriate care needs to be taken with interpreting distributions of organic compounds in groundwater in this context.

7 Conclusions

The Pennine Coal Measures aquifer of the East Midlands and South Yorkshire, in the vicinity of Leeds, Sheffield and north Derbyshire, is a secondary aquifer (EA and BGS, 2018) used for a number of private and industrial abstractions. The aquifer structure is complex, with water-bearing sandstone horizons interbedded with mudstones and coal seams. Sandstone horizons are composed of quartz, feldspar, mica and lithic grains in a clay matrix with minor and sporadic calcite. Hydraulic flow throughout the aquifer is influenced by widespread faulting and jointing, and the legacy of coal mining across the region. Groundwater becomes progressively confined towards the east as a result of the interbedded sequence and confining mudstones and coal seams.

The aquifer is recharged by rainfall, providing inputs of solutes including Na, Cl and NO_3 into the aquifer. Groundwater chemistries include Ca-Mg- HCO_3 , Ca-Mg- SO_4 , and Na- HCO_3 . Reaction with carbonates (calcite, siderite), clays and sulphides form the dominant sources for Ca, Mg, Na, Fe, SO_4 and HCO_3 and shape the groundwater chemistry. Groundwater pH varies from acidic to alkaline (4.9–9.3) with a neutral median value (7.26). Groundwaters are typically moderately to highly reducing, controlled by redox reactions including denitrification and nitrate reduction and reductive dissolution of Fe and Mn oxides. These reactions lead to typically low concentrations of NO_3 , high concentrations of NH_4 , Fe and Mn and slightly elevated concentrations of NO_2 . The commonly high concentrations of dissolved SO_4 result from oxidation of sulphide minerals, especially pyrite, in the organic-rich sediments and mobilisation of the reaction products in rising groundwaters as a result of groundwater rebound. High Na and Cl concentrations, along with elevated SEC values (up to 2990 $\mu\text{S}/\text{cm}$), provide some evidence for mixing with more mineralised fluids associated with the deep mines at a few isolated locations, typically those situated within the deeper section of the Pennine Coal Measures.

DOC and TOC present in the groundwater are likely derived from the organic matter including coal seams found within the aquifer. Only a small number of PAH and VOC compounds were detected in the WIMS dataset used for this study, and highlighted evidence of anthropogenic pollution for a few select analytes. Previous investigations by Bell et al. (2016) and Banks et al. (2017) have indicated dissolved methane concentrations up to 9 mg/L, which are likely derived from redox reactions involving the coal seams.

Appendix 1 Time-series plots for Precip-NET stations



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

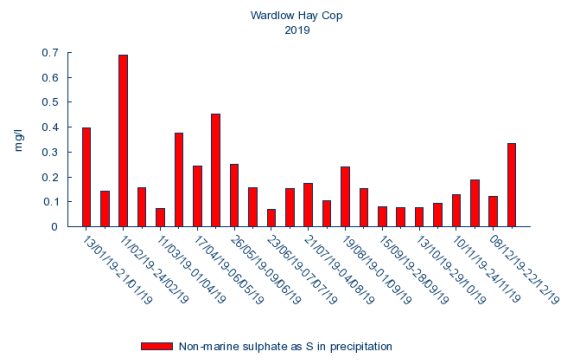
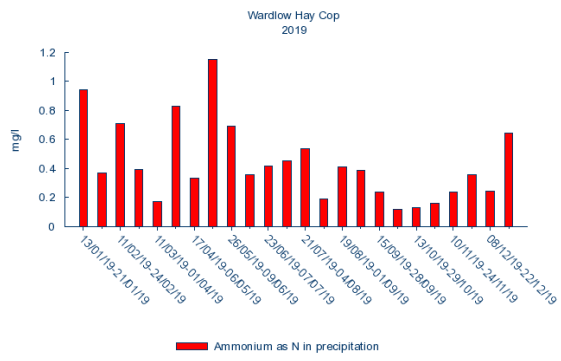
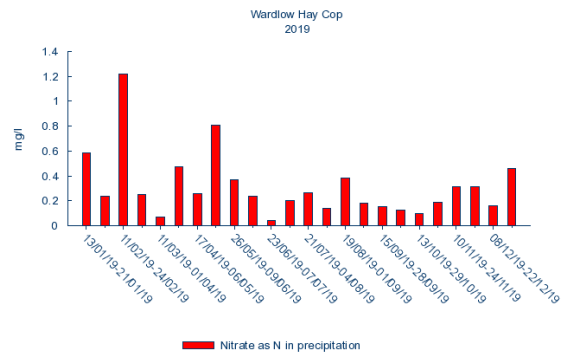
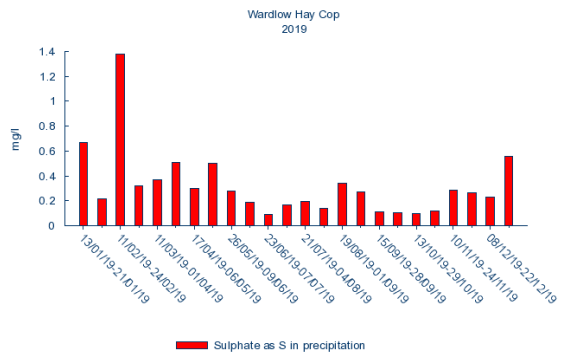


Figure A-1. (cont)



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

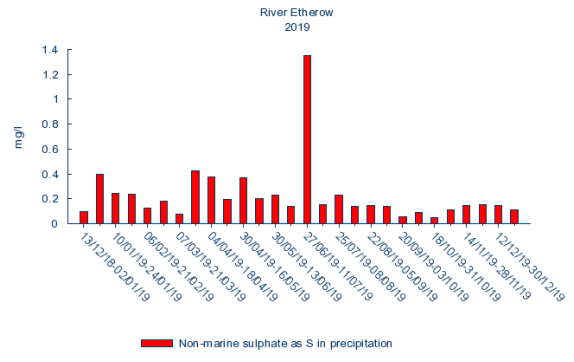
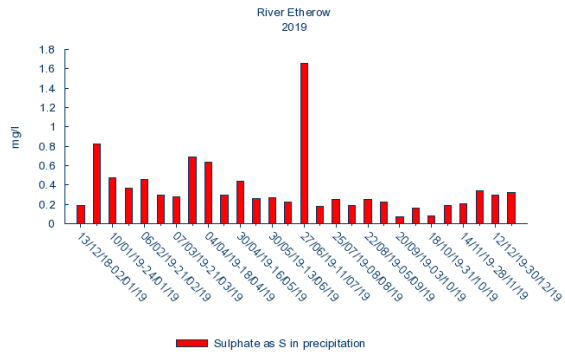
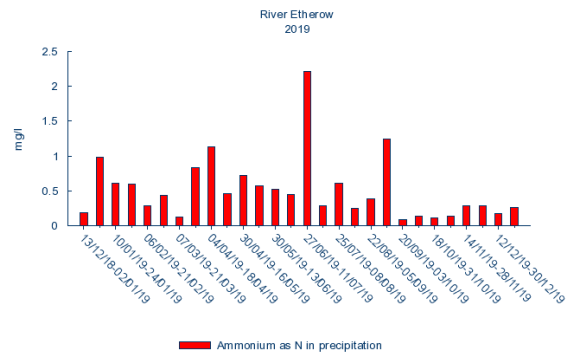
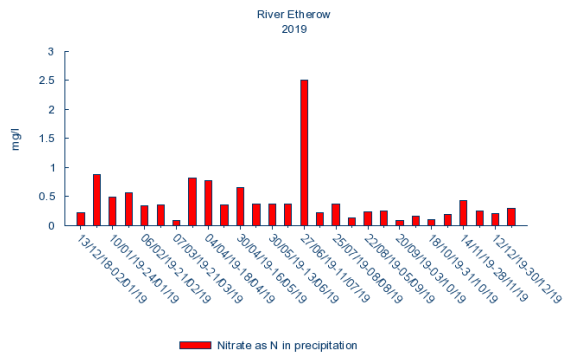


Figure A-2. (cont.)



Figure A-3. Time-series plots for Wardlow Hay Cop (2020) (DEFRA, 2021b)

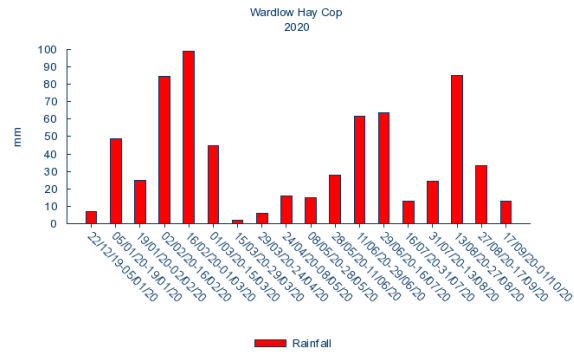
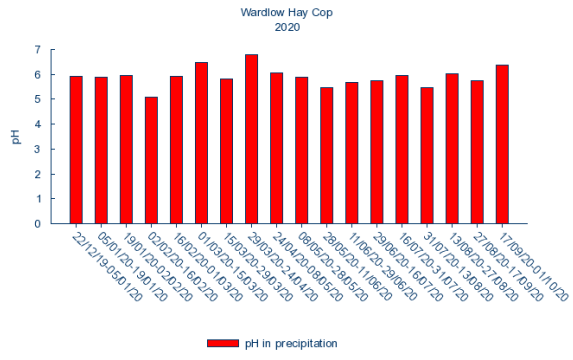
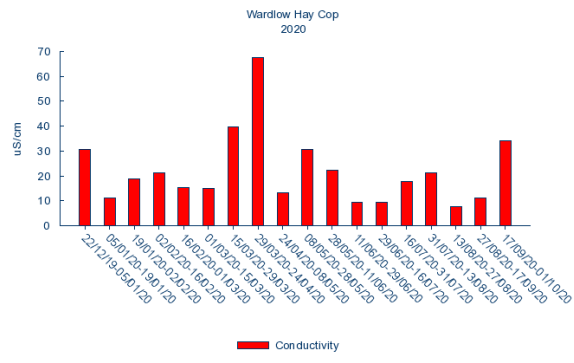
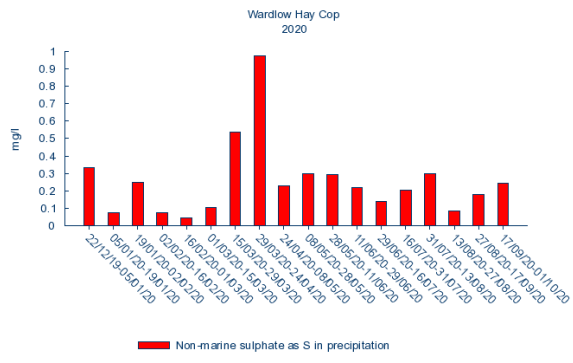


Figure A-3. (cont)

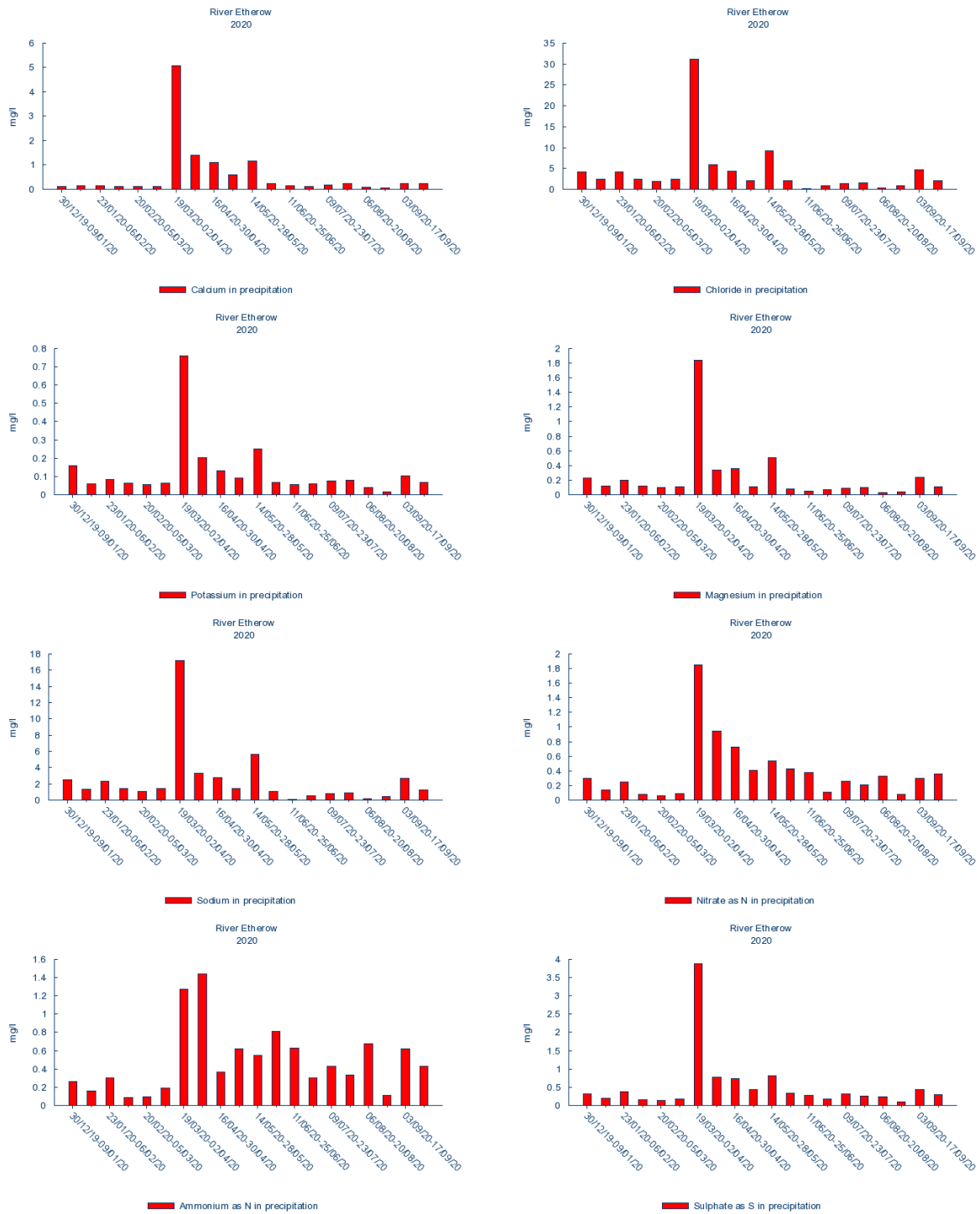


Figure A-4. Time-series plots for River Etherow (2020) (DEFRA, 2021a)

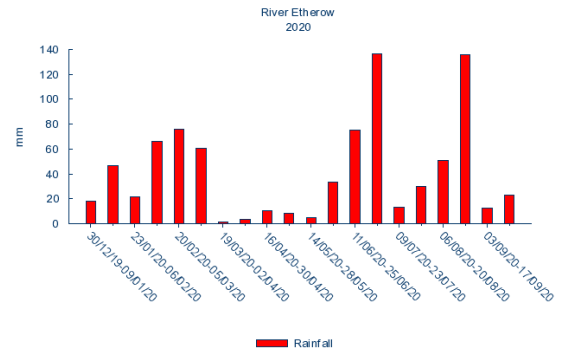
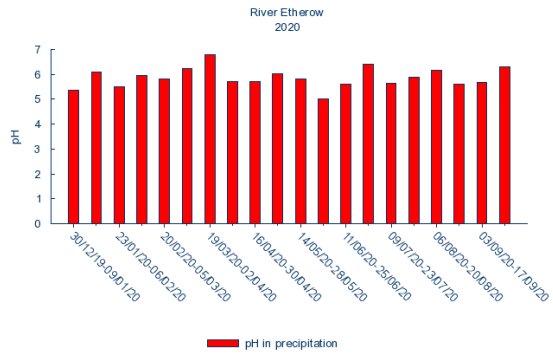
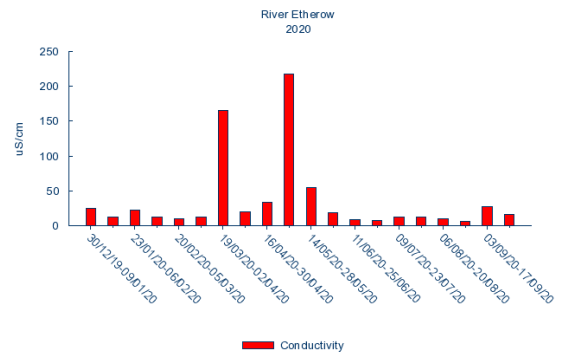
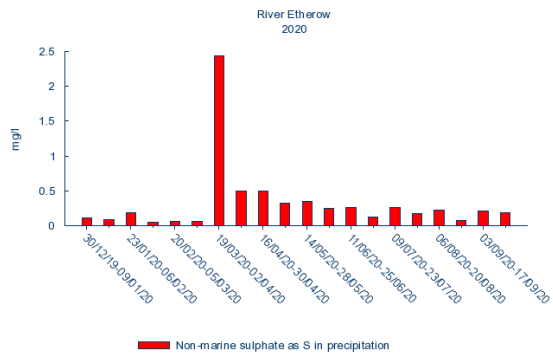


Figure A-4. (cont)

Appendix 2 WIMS database filter criteria

Table A-1. WIMS Database filter criteria

Site location	Purpose description	Date criteria
Pennine Coal Measures 1:250k Geology shapefile	Environmental monitoring (GQA & RE only)	Most complete suite of analyses for each location
	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)	

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