



British
Geological
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Baseline groundwater chemistry: the Lower Greensand aquifer of South East England

Environmental Change, Adaptation and Resilience Programme
Open Report OR/21/011



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PROGRAMME

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D Mallin Martin, P L Smedley

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Field photograph of a spring
discharge site within the study
area, sampled by the BGS

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British Geological Survey offices

Environmental Science Centre, Keyworth, Nottingham NG12 5GG

Tel 0115 936 3100

BGS Central Enquiries Desk

Tel 0115 936 3143

email enquiries@bgs.ac.uk

BGS Sales

Tel 0115 936 3241

email sales@bgs.ac.uk

The Lyell Centre, Research Avenue South, Edinburgh EH14 4AP

Tel 0131 667 1000

email scotsales@bgs.ac.uk

Natural History Museum, Cromwell Road, London SW7 5BD

Tel 020 7589 4090

Tel 020 7942 5344/45 email

bgs_london@bgs.ac.uk

Cardiff University, Main Building, Park Place, Cardiff CF10 3AT

Tel 029 2167 4280

Maclean Building, Crowmarsh Gifford, Wallingford OX10 8BB

Tel 01491 838800

Geological Survey of Northern Ireland, Department of Enterprise, Trade & Investment, Dundonald House, Upper Newtownards Road, Ballymiscaw, Belfast BT4 3SB

Tel 01232 666595

www.bgs.ac.uk/gsni/

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

Tel 01793 411500

Fax 01793 411501

www.nerc.ac.uk

UK Research and Innovation, Polaris House, Swindon SN2 1FL

Tel 01793 444000

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Foreword

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

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Summary

This report details the hydrogeochemistry of a broad suite of inorganic and organic analytes in groundwater from the Lower Greensand aquifer of south-east England. The study aims to establish the groundwater baseline chemical compositions, particularly of those analytes that are and could be associated with Onshore Oil and Gas (OOG) activities, in order to facilitate distinction between current compositions and any new industrial contamination from such activities. Analytes of particular interest in this context include indicators of salinity, indicators of redox conditions, dissolved gases including carbon dioxide (CO₂) and methane (CH₄), naturally-occurring radioactive materials (NORM) and organic compounds including volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). Much of the exposed unconfined aquifer is oxic in nature, with groundwater pH controlled by the sporadic presence of calcite within the aquifer matrix. Concentrations of a number of dissolved ions increase along the regional flow path, including Ca, HCO₃, Mg, K, Sr, F, Al, As, Mn, Cu, Ni, Fe and Mn.

The unconfined aquifer is susceptible to a number of anthropogenic impacts. These include diffuse pollution from agricultural activities (indicated by elevated concentrations of nitrate in groundwater across the northern half of the study area), and mobilisation of metals by acidic rainfall recharge in parts of the aquifer where acid-buffering carbonate minerals are absent.

Dissolved organic carbon content of the Lower Greensand groundwater is typically low, with an upper baseline concentration of 4.6 mg/L. Anthropogenic organic chemicals detected as part of this study included chloroform, trichloroethene and chlorodibromomethane, but concentrations detected are orders of magnitude below the drinking-water standard for these compounds and not a cause for concern. Dissolved CH₄ concentrations in the Lower Greensand aquifer are generally low; most samples in the investigation area contained <1 µg/L, except for two locations where concentrations of >300 µg/L were observed (up to 461 µg/L).

1 Introduction

1.1 PROJECT OBJECTIVES

The UK has a mature conventional OOG industry. The 2010s saw an increased interest in exploration for unconventional oil and gas resources, including shale gas, until a moratorium on high-volume, high-pressure hydraulic fracturing in England was imposed by the UK Government in November 2019. Despite this moratorium, the 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 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 new and pre-existing pathways associated with the exploration and production of these unconventional resources (Loveless et al., 2018), a clearer picture of the naturally-occurring and/or already-present 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 collected 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 (reported here), and the Pennine Coal Measures of the East Midlands and South Yorkshire.

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

This report details the baseline chemistry of groundwater in the Lower Greensand aquifer of the Weald (Surrey & West Sussex), of south-east England. As a region with both a principal aquifer, and a mature conventional oil and gas industry (the Weald Basin) with shale-gas exploration potential (Andrews, 2014; DECC, 2012), it was considered an important setting to include within the typologies development.

1.2 STUDY AREA

The extent of the investigation area is shown in Figure 1-1. The study centres on the Reigate, Guildford and Petersfield area. Guildford, Dorking, Petersfield, and Farnham are some of the major urban centres within the study area. Major roads include the A3, A31, and A24. Within this area, the Lower Greensand Group is classified as a principal aquifer, acting as a source for numerous agricultural, public water supply and industrial abstractions. The aquifer is predominantly unconfined where at outcrop, becoming confined to the west, north and south as it dips down the Weald-Artois pericline. The investigation area sits on the edge of the Weald Basin, with a number of conventional oil and gas wells situated to the west, and a several within

the study area. Both the Triassic and Jurassic sequences have been targets for oil and gas in the region (DECC, 2013).

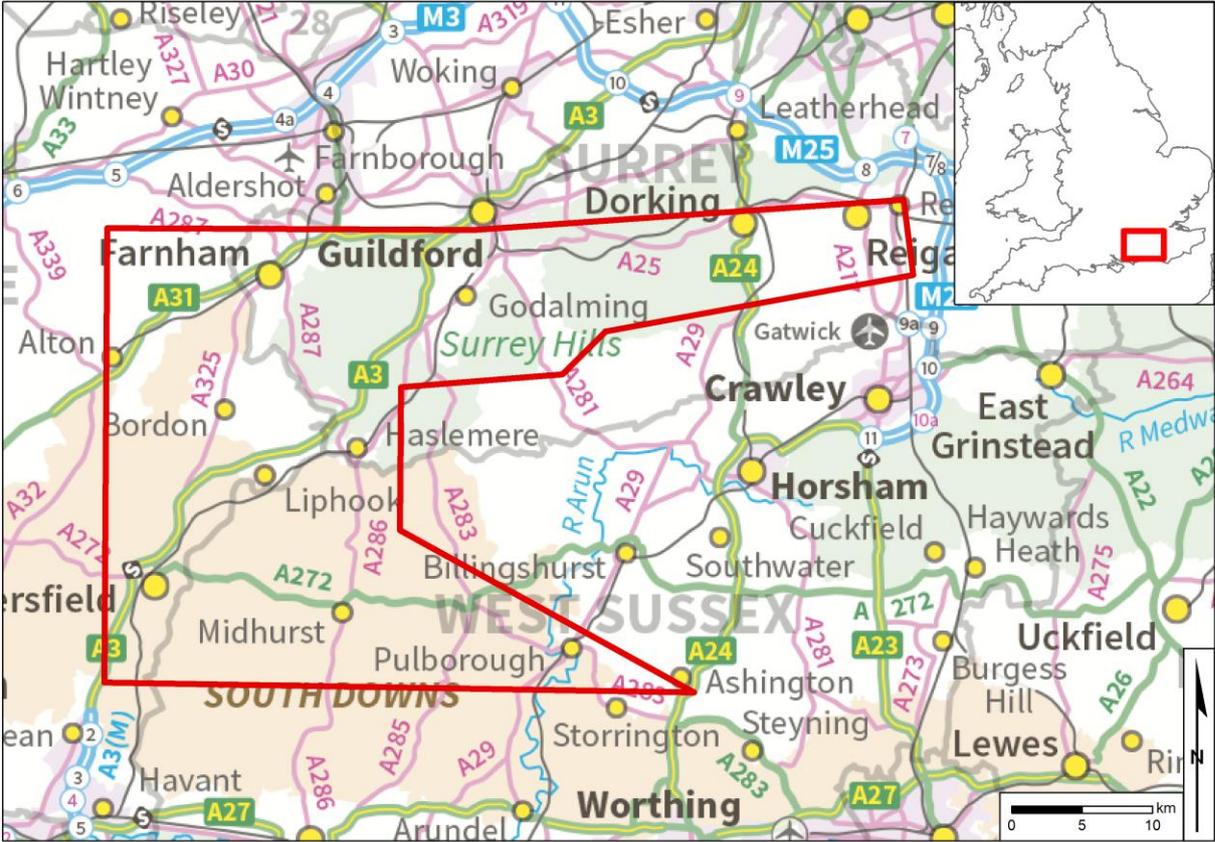


Figure 1-1. Extent of the investigation area, delineated by the red outline. Contains OS data © Crown copyright and database right (2021)

1.3 CURRENT PRESSURES ON GROUNDWATER QUALITY

1.3.1 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.

Urban land use accounts for around 11% of the land cover in the study area (see Section 2.4, Table 2-2). 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 1-2.

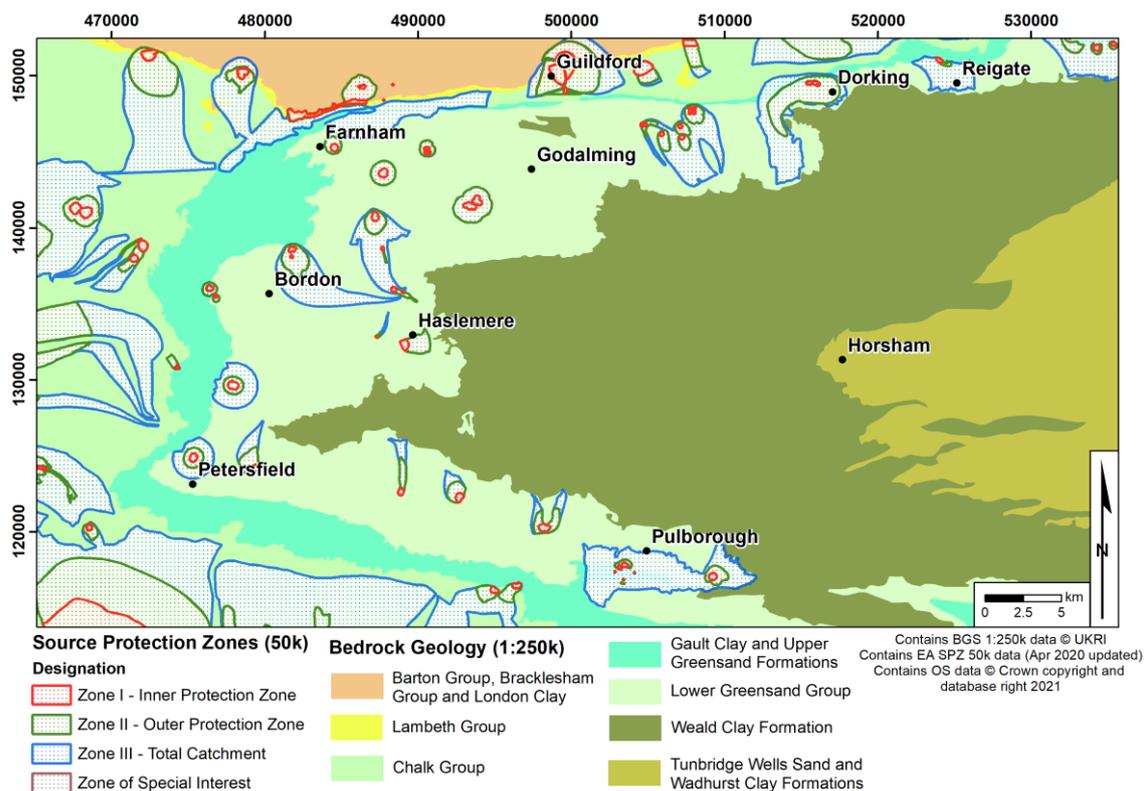


Figure 1-2. Source Protection Zones (SPZs) for the study area.

1.3.2 Agriculture

Within the study area, agriculture and managed grasslands form a principal portion of the land use/cover (>50%) (Table 2-2), and the use of nitrogenous fertilisers, pesticides and herbicides poses a groundwater diffuse-pollution risk. Agricultural practices can impact both water quality and quantity, particularly from large abstractions for irrigation in rural areas during the summer months.

Nitrate vulnerable zones (NVZ) identify areas where additional measures are needed to protect the water quality from diffuse agricultural pollution. These are areas designated as being at risk from agricultural nitrate pollution. They include about 55% of land in England (DEFRA, 2018). Designations are outlined for both groundwater and surface-water bodies at risk (with special designation for surface bodies susceptible to eutrophication). 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 study area is uncategorized, or covered by a Surface Water designation. Only two areas are classified as groundwater-designated NVZs, a strip to the south of Guildford, and a stretch in the Lower Greensand from Petersfield to Pulborough (Figure 1-3). The lack of widespread groundwater NVZ designations may be the combined result of factors included in the NVZ assessment methodology (DEFRA, 2016), which may include observed and forecast nitrate concentrations, the hydrogeology of the area, and the capacity for denitrification (influenced by the presence of reducing conditions).

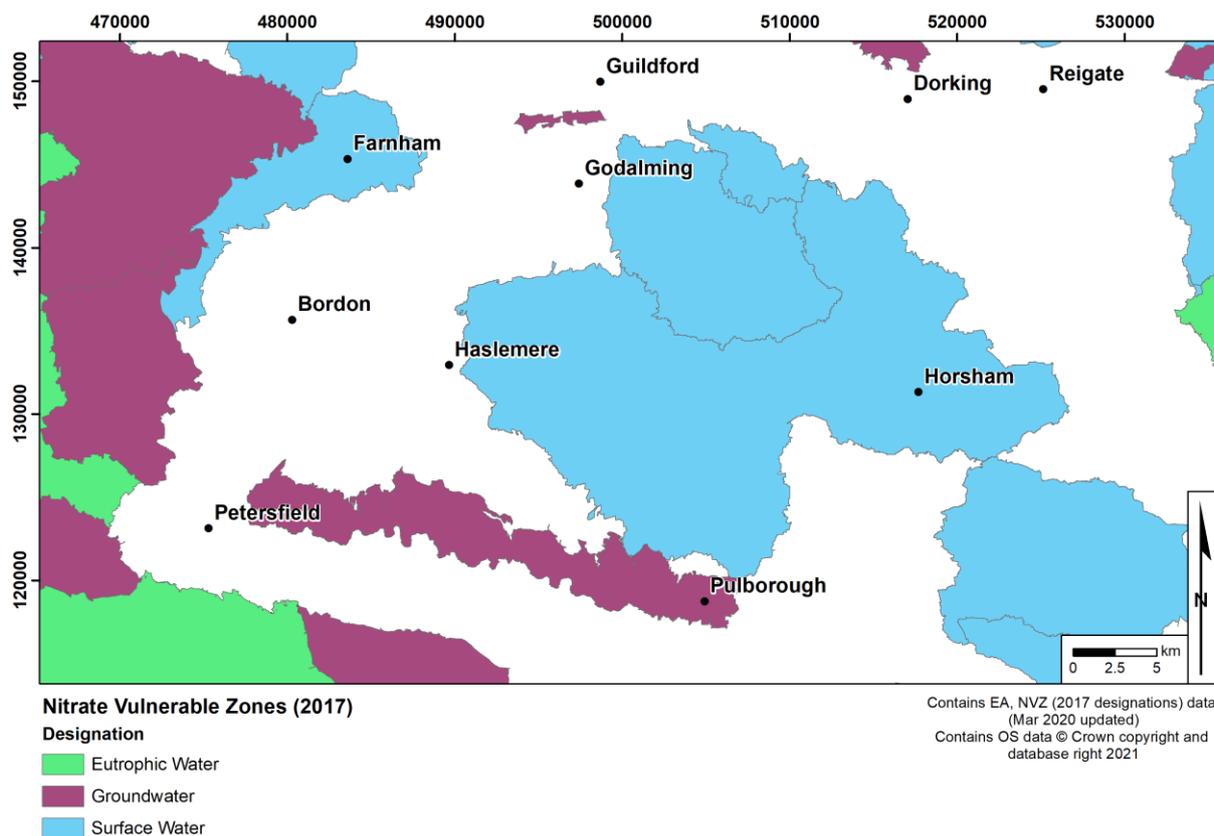


Figure 1-3. Nitrate Vulnerable Zones (NVZs) for the study area

1.3.3 Conventional and unconventional hydrocarbon industry

The main focus for this project is on the onshore oil and gas (OOG) sector, building a better understanding of the compounds in groundwater that can be linked to this industry and may be present in the aquifer prior to any new OOG activity. There is a long history of OOG in many parts of England, 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 investigation, exploration, and throughout operation and decommissioning.

The study area is situated in the Weald Basin, a mature OOG setting in the UK. A total of 13 onshore fields are located in the wider Weald basin, with three in the study area; Brockham, Albury, Humbly Grove (OGA, 2019a). Major reservoir units include the Wealden Sandstone, Great Oolite, Corallian, and Portland Sandstone (Andrews, 2014). Ten Potential Exploration and Development Licence (PEDL) blocks intersect the study area (OGA, 2019b), and 23 OOG wells, all conventional oil and gas, are situated within the investigation area (Figure 1-4 & Table 1-1) (OGA, 2020). The Weald Basin is considered to be a location with potential unconventional shale oil deposits, found within the Jurassic Shale sequence below the study area (Andrews, 2014). Some recent conventional oil and gas exploration has taken place in the local region, including the Horse Hill (east of Horsham) and Broadford Bridge sites (north-east of Pulborough), operated by UK Oil & Gas PLC (UKOG PLC, 2020). Neither exploration sites are situated within the Lower Greensand aquifer.

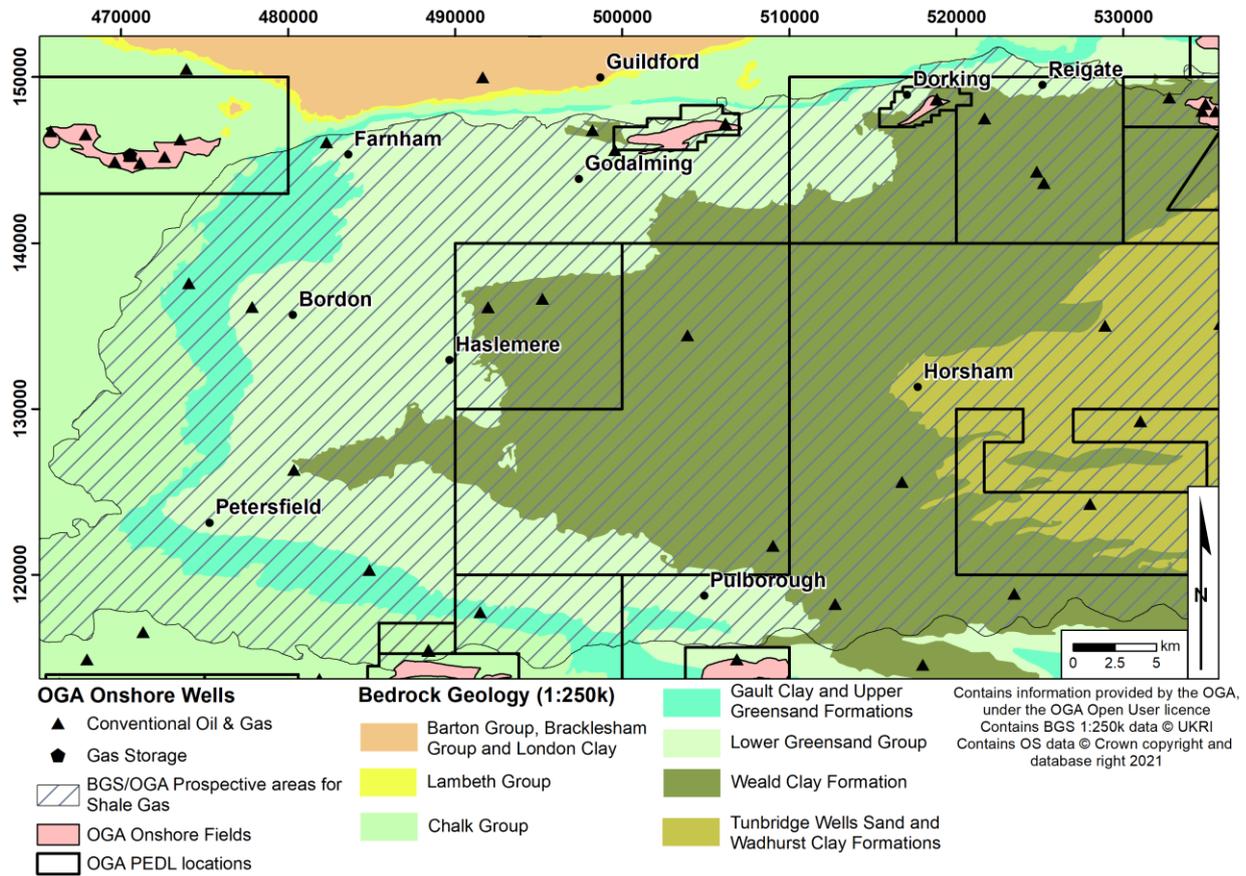


Figure 1-4. OGA data for the investigation area. Map shows onshore wells, PEDL locations, onshore conventional fields, and the joint BGS and OGA dataset for prospective areas for shale gas (data from BGS and OGA (2018); OGA (2019a, 2019b, 2020)).

Table 1-1. OOG well types and borehole intention within the study area (shown in Figure 1-1) (OGA, 2020)

Conventional Oil & Gas	
Development	7
Exploration	12
Appraisal	4

2 Regional background

2.1 GEOGRAPHICAL SETTING

The study area covers 57 km east-west, and 35 km north-south, broadly following the outcrop of the Lower Greensand Group from Reigate down to Pulborough (Figure 1-1). The centre of the area, around Crawley and Horsham, is where the underlying Weald Clay and Wealden Group units crop out, and is not relevant to this investigation. The West of the study area is bounded by Petersfield and Alton, where the Lower Greensand Group becomes confined by the Gault Clay and Upper Greensand Formations.

The topography is shown in Figure 2-1, and is controlled by the geological outcrop of the region. The elevated crag line around Godalming, Haslemere and Pulborough follows the basal boundary of the Lower Greensand Group outcrop (see Section 2.2.1), where it slopes down away towards the west (at a maximum elevation of c. 300 m AOD (above ordnance datum) around Leith Hill, between Dorking and Godalming). The boundary with the Chalk Group at the south, west and north edges of the study area (around Guildford and south of Petersfield) marks the next topographic high feature. The general topography decreases in elevation towards the south.

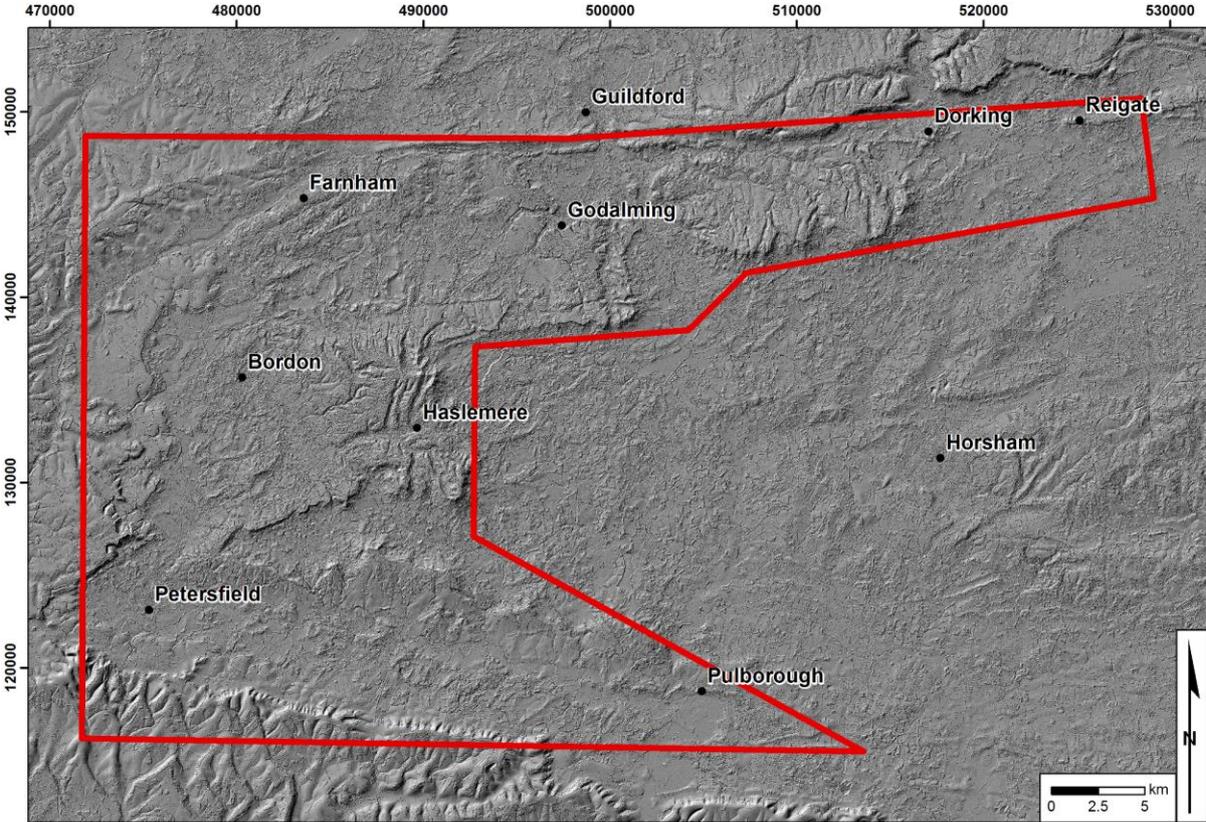


Figure 2-1. Surface topography for the investigation area. (NEXTMap Britain elevation data from Intermap Technologies. Contains OS data © Crown copyright and database right 2020)

2.2 GEOLOGY AND HYDROGEOLOGY

The wider Lower Greensand Group of South East England has been studied previously as part of the EA and BGS Baseline report series (BGS, 2016; Shand et al., 2003). The following section presents a summarised overview of the relevant geology and hydrogeology of the study area. Certain observations by Shand et al. (2003) will not apply to the context of the study area due to the reduced spatial extent of this investigation: Shand et al. (2003) studied the whole Lower Greensand Group of south-east England (including Slough to the north of this investigation, and to the east as far as Maidstone).

2.2.1 Bedrock and Superficial geology

The study area comprises a sequence of Early to Late Cretaceous sandstones, limestones, and clays. The key geological groups of interest are the Wealden Group, the Lower Greensand Group, and the Gault & Upper Greensand formations (Selborne Group) (Figure 2-2). The major aquifer unit in the region is the Lower Greensand Group, which is composed of four formations: the Atherfield Clay Formation, the Hythe Formation, the Sandgate Formation and the Folkestone Formation (Figure 2-3). The stratigraphic sequence and ages for the units are shown in Table 2-1.

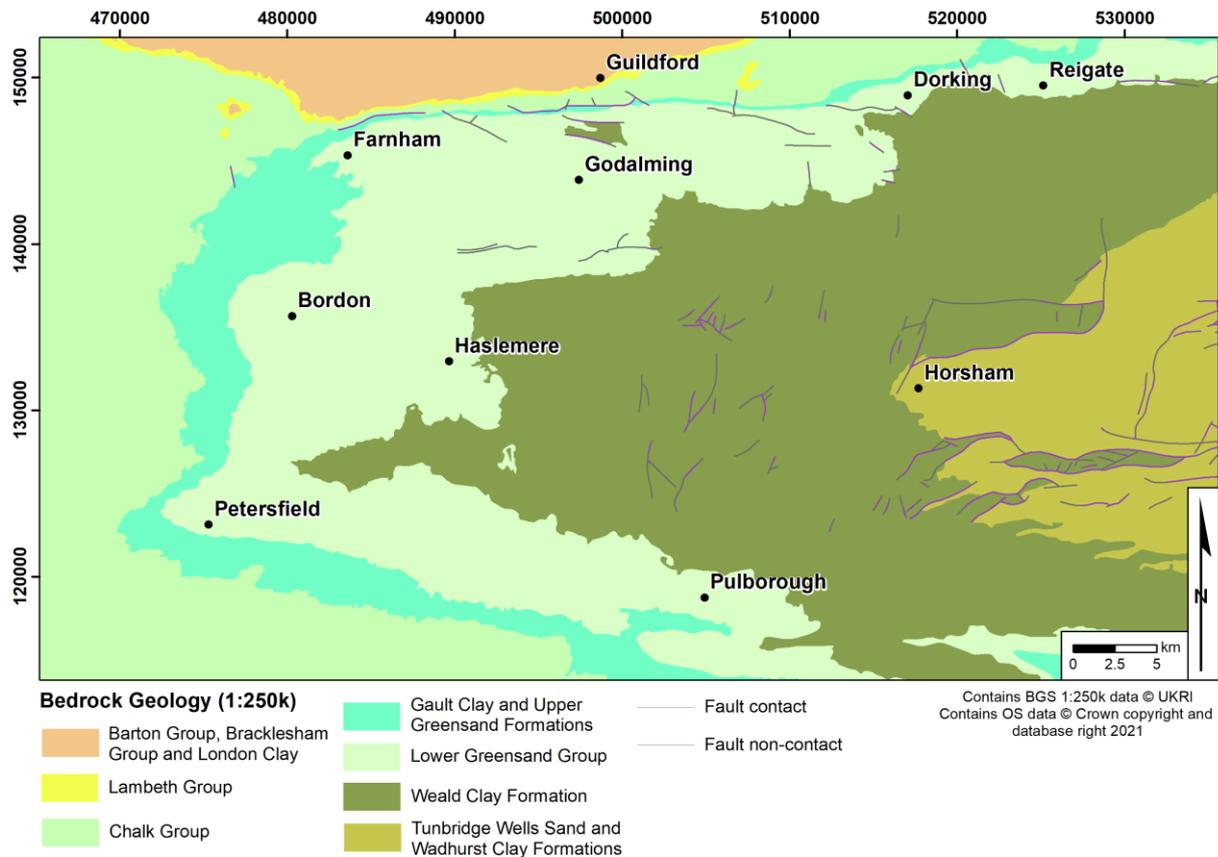


Figure 2-2. Bedrock geology for the study area. The Lower Greensand is undifferentiated at 1:250k scale.

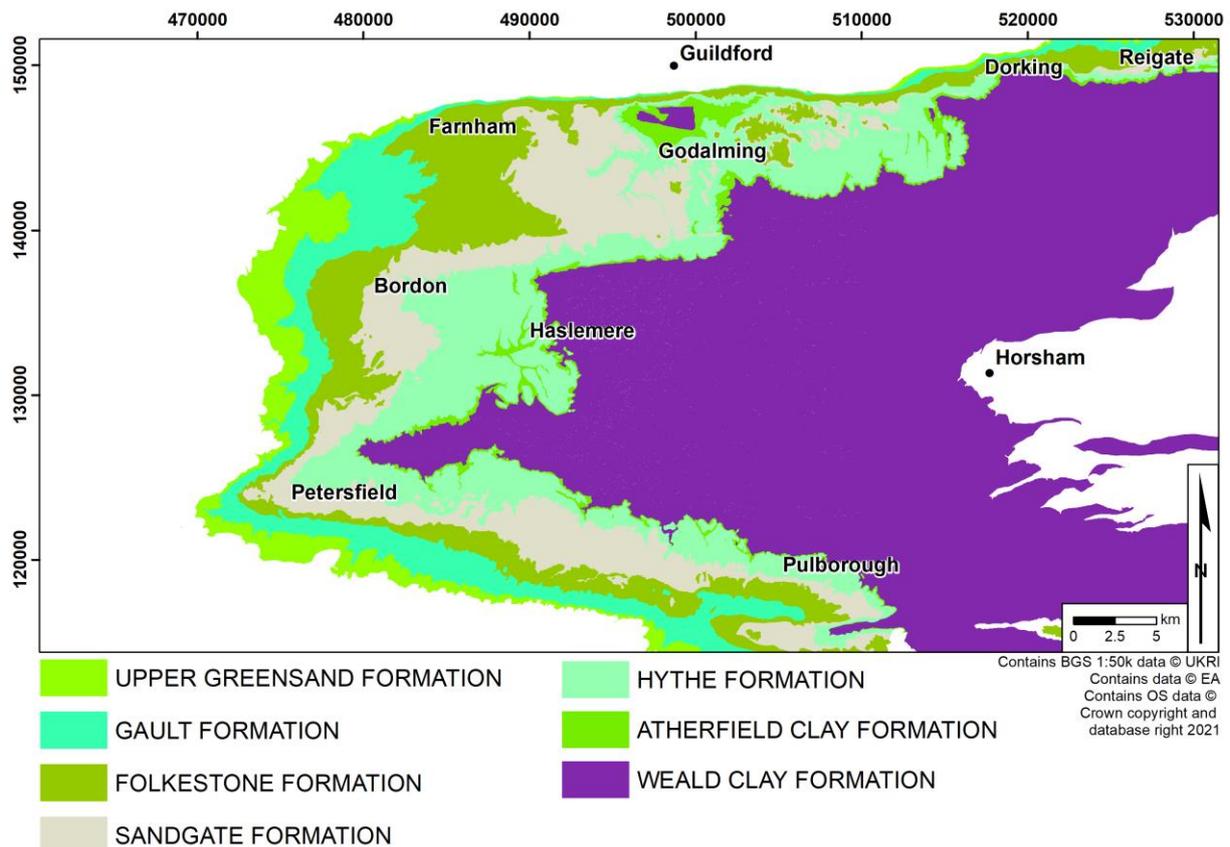


Figure 2-3. Selected formations from BGS 1:50k bedrock geology, showing the subdivisions within the Lower Greensand Group.

The Weald Clay Formation is a dark-grey thinly-bedded shale-mudstone sequence, with subordinate siltstones and fine- to medium-grained sandstones, with some calcareous sandstones and fossiliferous limestones. The upper boundary of the Wealden Clay is a sharp unconformity with the overlying Atherfield Clay Formation of the Lower Greensand Group.

The Atherfield Clay Formation comprises brown/dark grey silty clay, becoming progressively sandier towards the upper boundary with Hythe Formation. In contrast, the Hythe Formation is a predominantly fine-grained sandstone, with a mix of poorly cemented, loamy sandstone towards the base and more well-cemented sandstone towards the top. Glauconite is present within the Hythe Formation, providing its distinctly green colour (weathering to red-yellow at surface), along with well-cemented carbonate-rich beds referred to as “rag”. Above the Hythe Formation, the Sandgate Formation is composed of poorly-sorted glauconitic and limonitic sands, with some evidence of chert towards the base and muddy sandstones throughout the sequence. The Sandgate Formation is overlain by the Folkestone Formation, which is a poorly-consolidated sandstone sequence, with evidence of cross-bedding, ferruginous coatings and ironstone bands, and some minor clay layers draping over major ripple structures (Shand et al., 2003).

The Lower Greensand Group is overlain by the Gault Formation, a blue-grey clay/mudstone formation, sandier at its base, but with notable glauconite, pyrite and phosphatic nodules. The Gault oversteps the Lower Greensand Group north of the investigation area, under the London Basin (Allen et al., 1997).

Table 2-1. Stratigraphic sequence of key units of interest within the study area (from Shand et al. (2003) and the BGS Lexicon).

Age	Group	Formation	Dominant lithologies	Thickness (m)
Cretaceous	Selborne Group	Upper Greensand Formation	Fine-sandstone, glauconitic	0 - 75
		Gault Formation	Clay or mudstone, glauconitic	90 - 110
	Lower Greensand Group	Folkestone Formation	Medium- to coarse-sands and weak sandstones	3 – 85
		Sandgate Formation	Fine sands, silts, clays, glauconitic	50 - 100
		Hythe Formation	Fine- to medium-sandstone, glauconitic	18 – 100
		Atherfield Clay Formation	Sandy mudstone	6 – 18
	Wealden Group	Weald Clay Formation	Shales, mudstones, some siltstones and sandstones	122 – 460
		Tunbridge Wells Sand Formation	Fine- to medium-sandstone, finely interbedded mudstones and limestones	~75

The regional Weald Anticline is the principal structural feature of interest within the study area. The Lower Greensand Group crops out in the north of the study area around Dorking, Liphook in the west, and Pulborough to the south. In the centre of the study area, around Haslemere and Crawley, the older Wealden Group (in particular, the Weald Clay) outcrops where the Lower Greensand has been eroded away (Allen et al., 1997; Gallois et al., 1992; Shand et al., 2003). Faults have been mapped in the northern half of the study area within the Lower Greensand Group.

The Lower Greensand Group units dip steeply towards the north (Figure 2-4) in the vicinity of Guildford and Dorking, with a shallower westerly dip progressing towards the western edge of the study area. The Group thins down dip to the north and west, obtaining a maximum thickness of 220 m to the west of the Wealden Group outcrop. To the north (around Slough, outside of the study area), where the Lower Greensand Group is overlain by younger deposits, the maximum thickness is 80 m.

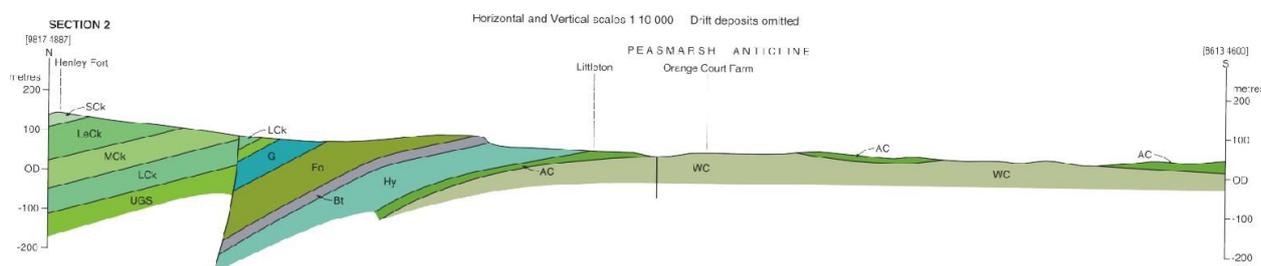


Figure 2-4. N-S geological cross section across the Weald Basin south from Guildford, Surrey; WC: Weald Clay; AC: Atherfield Clay; Hy: Hythe Formation; Bt: Bargate Formation (part of the Sandgate Formation, locally represented); Fo: Folkestone Formation. G: Gault Formation; UGS: Upper Greensand; Ck: Chalk (from Shand et al., 2003)

The superficial geology consists of Alluvial and River terrace deposits, bounding the major surface-water courses across the region, alongside “Residual” (clay/flint/gravel infill deposits) where Chalk is at outcrop, to the north and west of the study area (Figure 2-5). Soils are typically sandy or silty loams, with the most well-draining soils situated over the unconfined sections of the

Hythe and Folkestone formations (Cranfield University, 2021; Shand et al., 2003). Superficial deposits are thin, typically 1 m thick, or absent across much of the study area (Lawley and Garcia-Bajo, 2010) but thicken to the west, typically greater than 5 m at the onset of the “Residual deposits” (Figure 2-5).

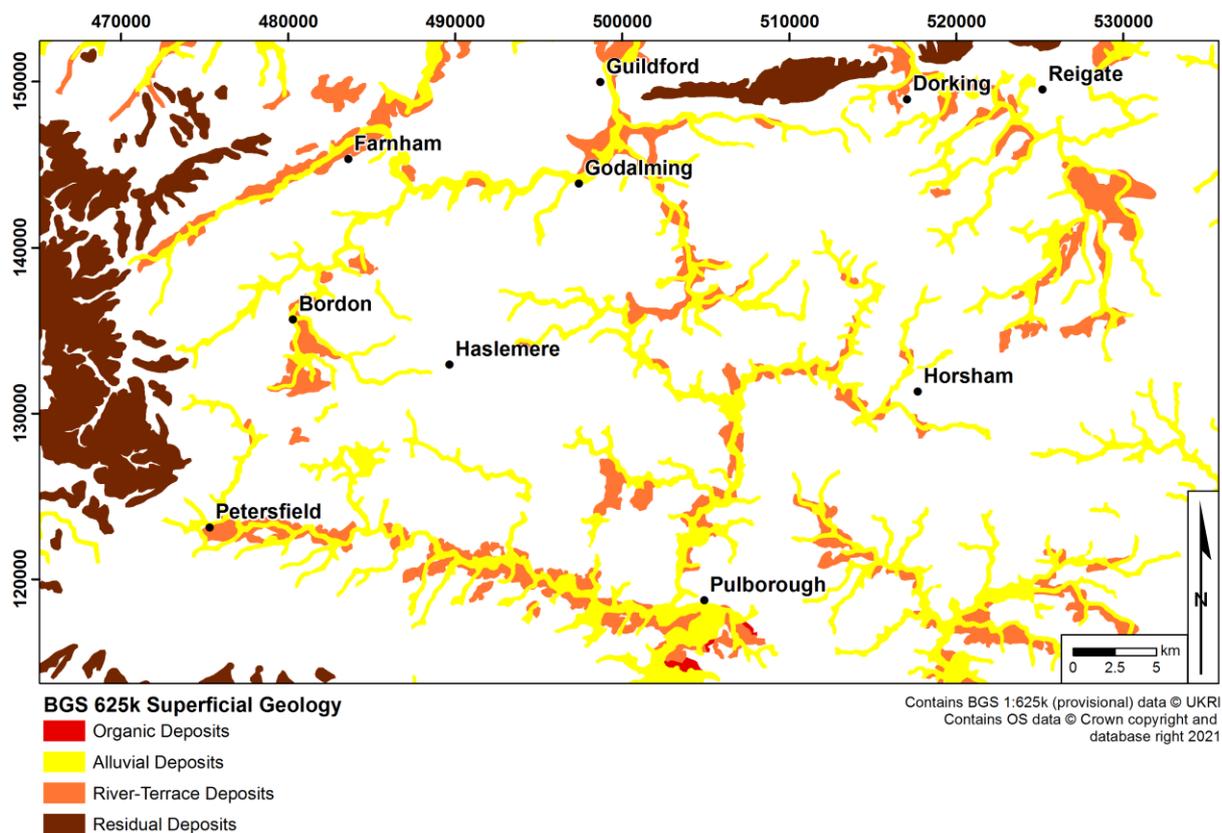


Figure 2-5. Superficial Geology for the study area.

2.2.2 Organic-rich source rocks

The Weald Basin contains a number of organic-rich shale formations, including the Middle and Upper Lias (90 m and 67 m of shale, respectively), the Oxford Clay (67 m of shale), the Corallian Clay (150 m of shale) and the Kimmeridge Clay (550 m of shale). These have been assessed as part of the BGS-led shale resource estimation, commissioned by DECC (Andrews, 2014), and underlie the study area (Figure 1-4). These Jurassic rocks are considered to be source rocks for a number of conventional reservoirs within the Weald Basin, and potential unconventional source rocks for shale oil, with an estimate between 2.2 and 8.6 billion barrels for the entire basin (Andrews, 2014). None of the units crop out within the study area.

Loveless et al. (2018) delineated the vertical separation between the shale-gas source rocks and overlying aquifers on maps which are available online (BGS, 2018). Within the study area, the vertical separation between the Lower Greensand Group and the shallowest Jurassic shale unit, the Kimmeridge Clay, is greater than 800 m (when a thickness for the Lower Greensand principal aquifer of 400 m was assumed, in-line with UK TAG guidance (2012)).

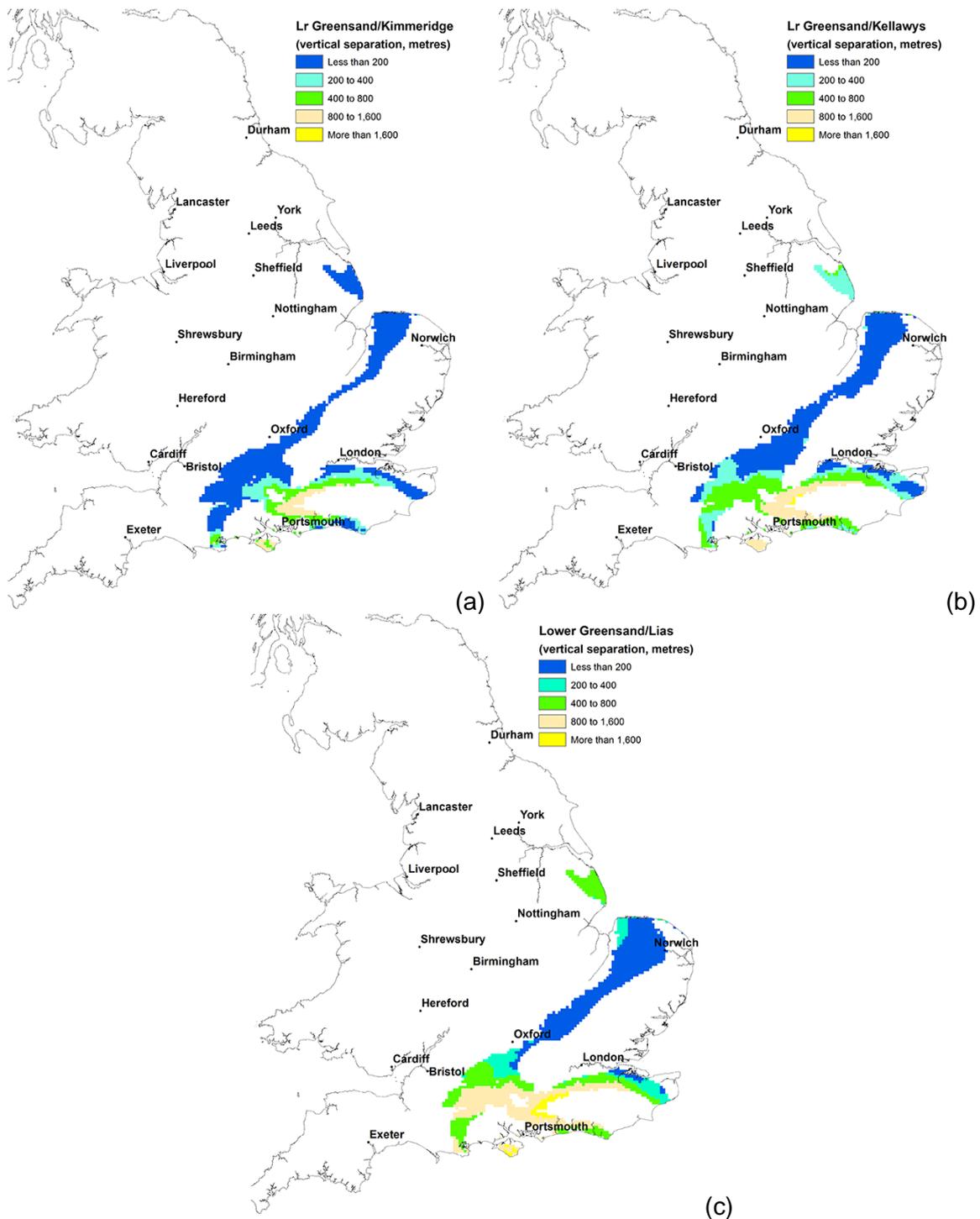


Figure 2-6. Aquifer separation maps for the Lower Greensand Group and a) Kimmeridge Clay; b) Kellawys & Oxford Clay; c) Lias Group (from BGS, 2018; Loveless et al., 2018).

2.2.3 Hydrogeology

The Lower Greensand Group is considered a principal aquifer and supports a number of public and private abstractions (Figure 2-7) (EA and BGS, 2018). The group itself is subdivided into two distinct aquifer units, the Hythe and Folkestone formations, both with differing water chemistries. The two units are separated by the Sandgate Formation, which confines the underlying Hythe Formation (this can be seen in Figure 2-7, where the two Principal aquifers of the Lower Greensand are separated by a band of Secondary A aquifer). However, the Sandgate Formation is not laterally persistent, with some evidence of leakage, so some mixing/connection between the two aquifers may occur (Allen et al., 1997; Shand et al., 2003). Where the Sandgate Formation is locally sandier, it may extend the base or act as part of the overlying Folkestone Formation.

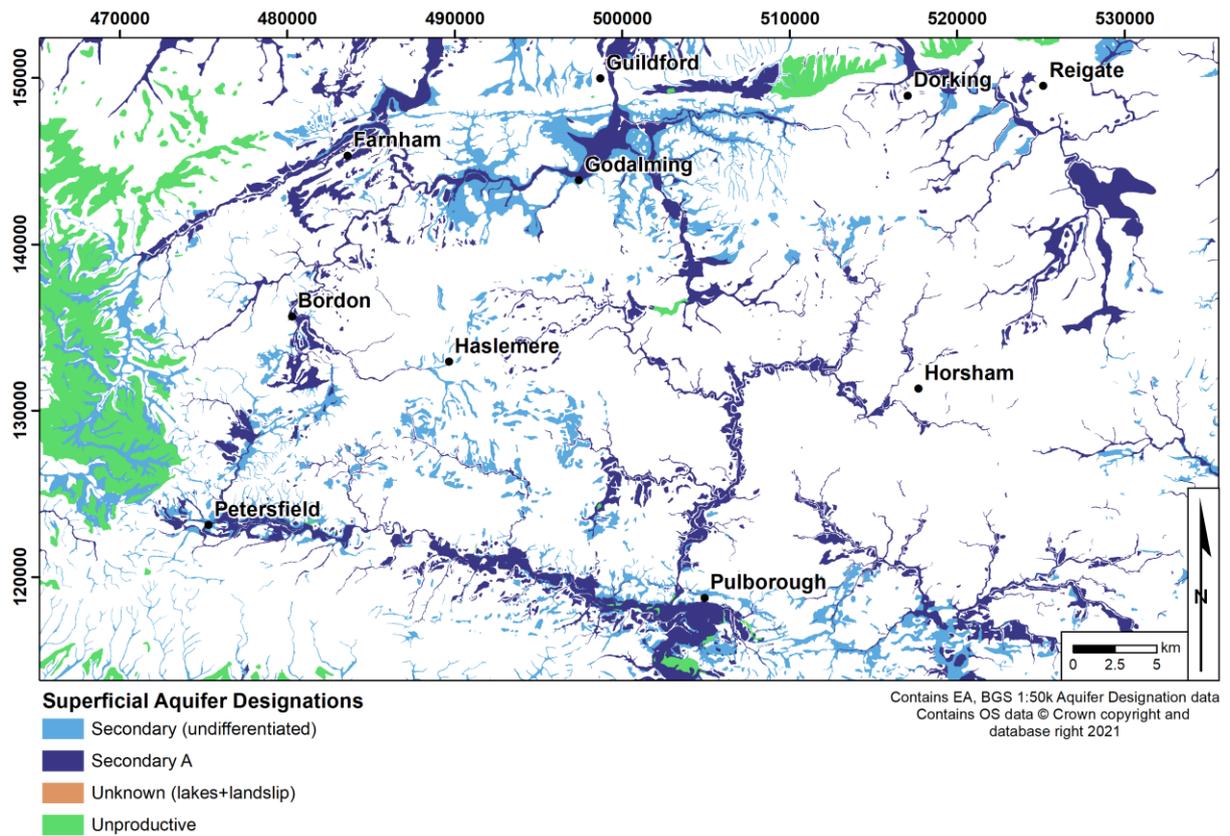
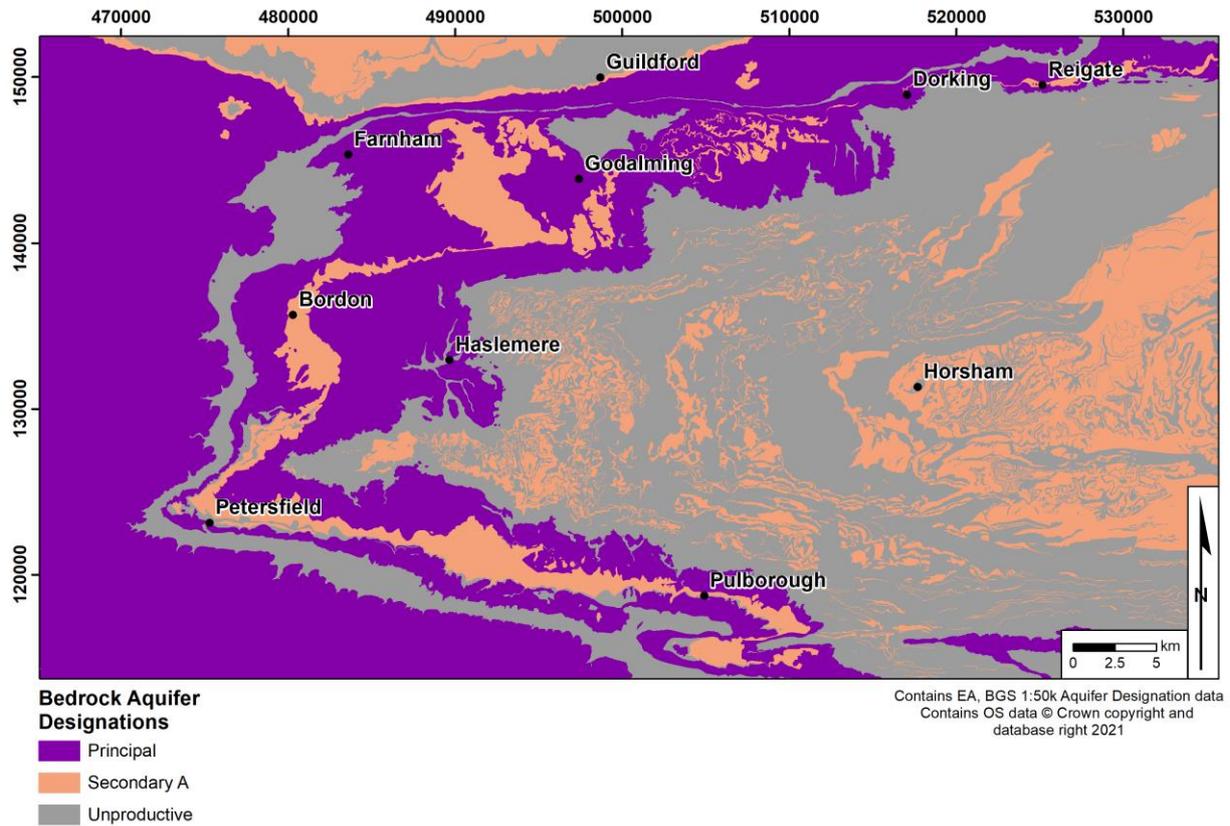


Figure 2-7. EA Aquifer designation maps for Bedrock (top) and Superficial (bottom) geology (EA and BGS, 2018)

The aquifer is unconfined throughout much of the study area along the central axis of the Weald-Artois pericline, but the Lower Greensand aquifer becomes confined towards the north, west and south by the Gault Clay and Upper Greensand formations. The base of the aquifer is defined by the underlying Atherfield Clay Formation. Groundwater levels become artesian with increasing confinement, with the general flow direction away from the exposed Weald Clay Formation and axis of the Weald Pericline. The dominant flow direction is away from Haslemere and Bordon and the boundary with the Weald Clay (Shand et al., 2003). Recharge to the aquifer is via outcropping sections (Morgan-Jones, 1985).

Yields of 76 L/s have been recorded from public supply wells within the undifferentiated Lower Greensand Group (Farrant et al., 2002, from; Shand et al., 2003). Bulk transmissivities for the sequence range from 33 to 3400 m²/d with the geometric mean and median both 270 m²/d. Porosity ranges from 6% to 41%, with a mean of 28% for the Lower Greensand Group (Allen et al., 1997; Shand et al., 2003).

Groundwater flow in the Hythe Formation is controlled by the degree of cementation. Fracture flow dominates in well-cemented zones, whilst intergranular flow dominates in locations with poor cementation. Transmissivities for the Hythe Formation range from 200 m²/day to 1000 m²/day, with values generally being lower in the north, and increasing towards the south of the study area (Allen et al., 1997).

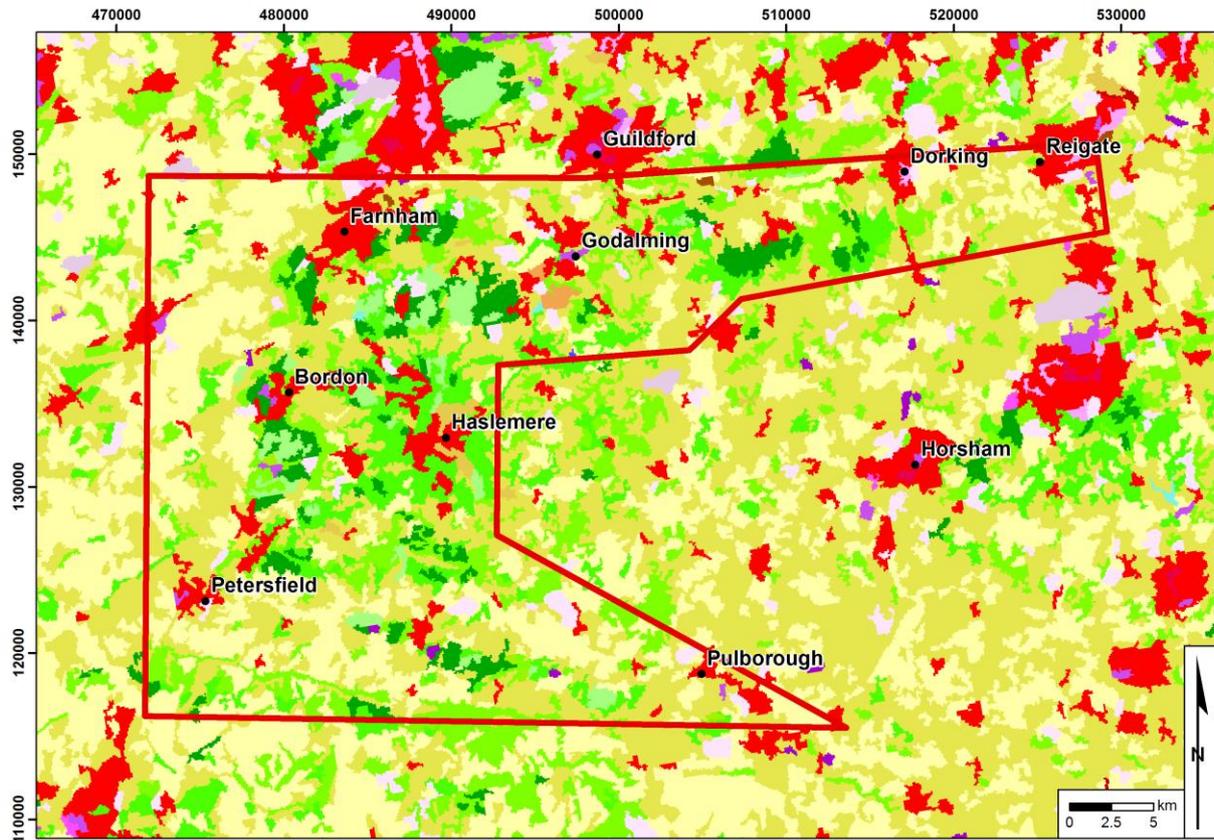
Groundwater flow in the Folkestone Formation is intergranular, with measured transmissivities in the range of 150 m²/day to 1200 m²/day (mean of 260 m²/day) (Allen et al., 1997). Values are typically greatest in the north-west, where the unit is at its thickest, and decrease with aquifer thickness to the north and east. Whilst flow may be considered homogeneous regionally, local variations in the Folkestone Formation, including ironstone beds and nodules, may impact groundwater flow and water levels locally.

2.3 AQUIFER MINERALOGY

The aquifer mineralogy is discussed in detail by Shand et al. (2003); the following section summarises the key details. The dominant mineralogy across the Lower Greensand Group is quartz, with ferruginous coatings found in both the Folkestone and Hythe Formations. Overall carbonate content averages 1% across the Folkestone and Hythe formations, with carbonate cement present in the Hythe (“rag” beds) and Sandgate formations. Glauconitic grains are also common throughout the group, with heavy mineral grains including chromite, magnetite and other iron-rich minerals. Clay minerals in the Lower Greensand Group are typically limited to the Atherfield and Sandgate formations. Only 5–10% of the Hythe Formation minerals are clays, dominantly mica and smectite. A number of precipitates/concretions are also common throughout the group, including ironstones/iron pan deposits, cherts, and phosphatic nodules.

2.4 LAND USE

Land-use data for the study area has 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 2-8 and Table 2-2). Over 50% of the total land use within the study area is agriculture, with 30% dedicated to pasture and livestock. Urban land use cover is only 11% of the total area, most of which is “discontinuous urban fabric”, or smaller settlements. The major urban settlements within the study area are Dorking and Redhill/Reigate in the north-east, Guildford and Farnham in the north/north-west, and Haslemere and Liphook in the centre.



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

Figure 2-8. CLC (2018) land classification map for the investigation area (outlined in red) (European Environment Agency, 2019)

Table 2-2. Land classification categories and percentage of total area for the investigation extent shown in Figure 2-8 (from European Environment Agency, 2019)

Land Use Classification (CLC 2018 descriptions)	Area (km²)	Percentage total area (%)
Pastures	352.69	32.068
Non-irrigated arable land	283.41	25.769
Broad-leaved forest	130.30	11.847
Mixed forest	98.09	8.919
Discontinuous urban fabric	94.30	8.574
Coniferous forest	62.36	5.670
Moors and heathland	28.71	2.610
Sport and leisure facilities	26.82	2.439
Land principally occupied by agriculture, with significant areas of natural vegetation	5.60	0.509
Transitional woodland-shrub	3.99	0.363
Industrial or commercial units	3.67	0.334
Fruit trees and berry plantations	3.23	0.294
Green urban areas	1.79	0.163
Mineral extraction sites	1.63	0.148
Dump sites	0.78	0.071
Complex cultivation patterns	0.75	0.068
Water bodies	0.62	0.056
Natural grasslands	0.38	0.035
Airports	0.28	0.025
Peat bogs	0.22	0.020
Continuous urban fabric	0.19	0.017
Construction sites	0.02	0.002
Total	1099.83	100

2.5 RAINFALL CHEMISTRY

The average annual rainfall across the study area is 950 mm (in the vicinity of the South Downs), and decreases towards the north-east (Met Office, 2016). The nearest UKEAP (United Kingdom Eutrophying & Acidifying Network): Precip-net monitoring station for rainfall chemistry in the study area is Thursley Common, around 10 km to the north of Haslemere [490698, 139919] (DEFRA, 2020a, b). Rainfall chemistry data for the first quarter of 2020 (in line with the dates for groundwater sampling) are presented in Figure A-1, with data for 2019 presented in Figure A-2 (Appendix 1). Summarised statistics for the years 2020 and 2019 are shown in Table 2-3 and Table 2-4 respectively.

The average (both mean and median) pH for rainfall across the study area is below 6, with Na and Cl having the greatest mean concentration across the measured dissolved ions. Total annual rainfall for 2019 was 871.6 mm (DEFRA, 2020a), and the total for January to April 2020 was 266 mm (DEFRA, 2020b). Recharge inputs, considering evapotranspiration have been calculated for this study and are also presented in Table 2-3 and Table 2-4.

Table 2-3. Rainfall chemistry summary statistics for Thursley Common 2 monitoring station [490698, 139919] for the first quarter of 2020 (DEFRA, 2020b)

Solute	mean	min	max	median	Concentrated mean (enrichment by evapotranspiration, x3) (mg/L)
Ca (mg/L)	0.164	0.085	0.24	0.171	0.49
Mg (mg/L)	0.145	0.082	0.21	0.123	0.44
K (mg/L)	0.076	0.059	0.109	0.062	0.23
Na (mg/L)	1.62	0.94	2.35	1.27	4.86
Cl (mg/L)	2.79	1.66	4.1	2.14	8.38
NH ₄ -N (mg/L)	0.222	0.124	0.369	0.183	
NO ₃ -N (mg/L)	0.208	0.109	0.317	0.159	1.29* (5.71 as NO ₃)
SO ₄ -S (mg/L)	0.21	0.146	0.301	0.196	0.63 (1.89 as SO ₄)
SO ₄ -S (non-marine, mg/L)	0.074	0.026	0.117	0.08	0.222 (0.666 as SO ₄)
pH	5.62	5.36	5.92	5.53	
Conductivity (µS/cm)	16.36	12.81	24.1	13.05	
Precipitation (mm)	44.32	0	85.76	46.12	

*Assuming NH₄ oxidation to NO₃

Table 2-4. Rainfall chemistry summary statistics for Thursley Common 2 monitoring station [49061399] for 2019 (DEFRA, 2020a)

Solute	mean	min	max	median	Concentrated mean (enrichment by evapotranspiration, x3) [mg/L]
Ca (mg/L)	0.350	0.089	1.9	0.148	1.05
Mg (mg/L)	0.176	0.057	0.331	0.16	0.53
K (mg/L)	0.132	0.034	0.421	0.098	0.40
Na (mg/L)	1.653	0.271	3.21	1.43	4.96
Cl (mg/L)	2.899	0.426	5.79	2.39	8.70
NH ₄ -N (mg/L)	0.389	0.056	2.7	0.251	
NO ₃ -N (mg/L)	0.374	0.099	1.7	0.284	2.29 (10.13 as NO ₃)
SO ₄ -S(NM) (non-marine, mg/L)	0.187	0.033	0.812	0.147	0.56 (1.68 as SO ₄)
SO ₄ -S (mg/L)	0.325	0.133	1.03	0.263	0.98 (2.94 as SO ₄)
pH	5.98	5.22	6.99	5.93	
Conductivity (µS/cm)	19.88	6.32	49.4	17.74	
Precipitation (mm)	36.32	0	98.52	30.75	

**Assuming NH₄ oxidation to NO₃*

3 Data acquisition and handling

3.1 GROUNDWATER SAMPLING AND ANALYSIS

3.1.1 Sampling procedure

A total of 11 samples were collected across the study area during late February and March 2020, and are shown in Figure 3-1. Some 30 new groundwater samples were originally planned to be collected by BGS, but sampling was cut short by the UK Government COVID-19 restrictions on travel from mid-March, 2020. As a result, new samples form a small component of the dataset, mainly concentrated in the north, but this is complemented by an extensive number of data points provided by the EA from their WIMS water-quality database (see Section 3.2).

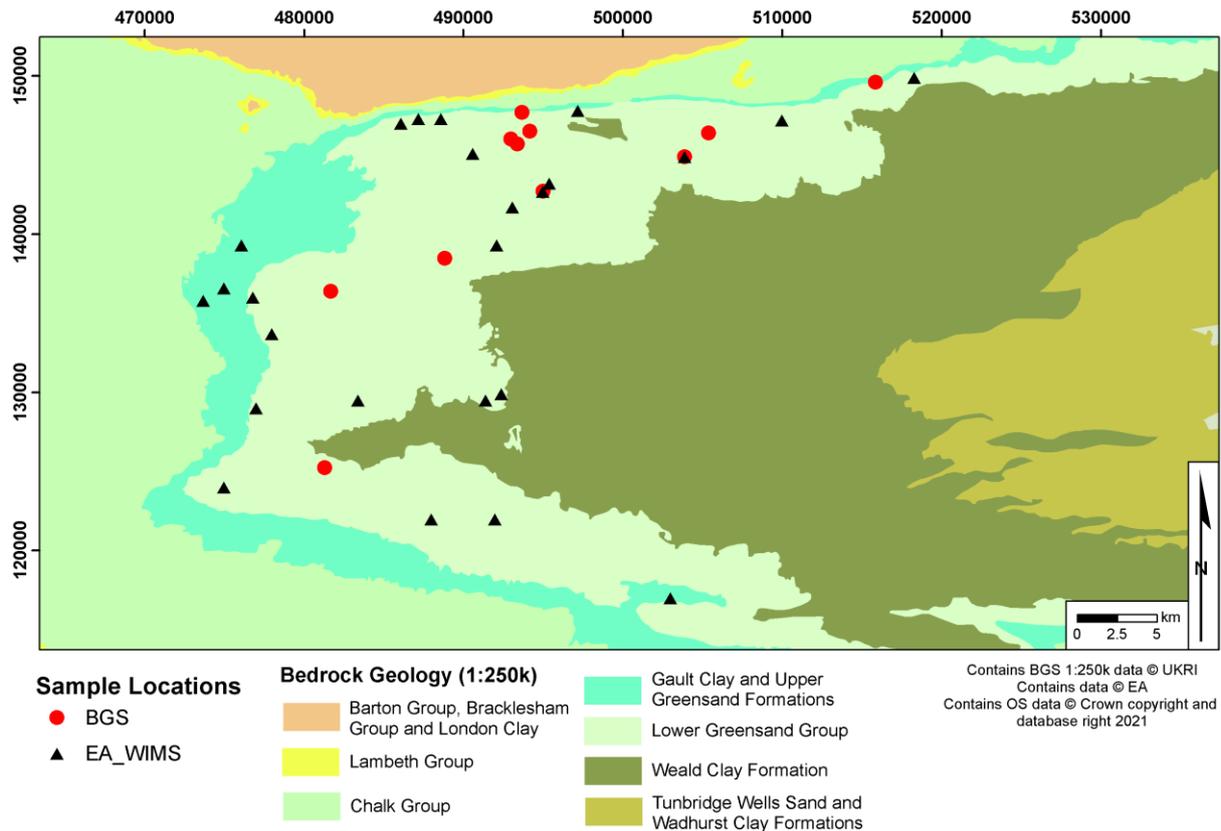


Figure 3-1. Selected EA WIMS sample locations (black), alongside 2020 field samples collected by BGS (red).

Samples and water quality data were collected using existing pumps installed at each site, or using a 12V submersible pump where no infrastructure was present (i.e. springs). Measurements taken at each sampling site included pH, redox potential (Eh), dissolved oxygen (DO), specific electrical conductance (SEC) and temperature. These were recorded from a saturated flow cell to prevent aeration. Alkalinity was also measured on-site by titration against H_2SO_4 . Samples were collected once all water-quality parameters had stabilised.

Samples for major- and trace-element analysis were collected in triple-rinsed LDPE bottles, filtered to $<0.2 \mu m$. Those required for cation and trace-metals analysis were acidified to 1% (v/v) HNO_3 to prevent metal precipitation and minimise sorption onto the container walls. Two separate filtered unacidified aliquots were also collected for analysis of anions and NH_4 .

Samples for organic constituents were collected directly from the sample tap/point where possible, to minimise contact with additional plastic tubing. Samples for non-purgeable organic carbon (NPOC) analysis were filtered through a $0.45 \mu m$ silver-impregnated filter and collected in pre-cleaned glass vials. Additional samples were collected for volatile and semi-volatile organic

carbons (VOC and SVOC), total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH). Samples for dissolved gas analysis (CH₄, C₂H₆ and CO₂) were collected in-line and under pump pressure using a double-valved steel pressure vessel.

3.1.2 Sample analysis

Analysis of samples was carried out BGS. Analysis of major cations and trace elements was carried out by ICP-MS and of anions by ion chromatography. Additional methods included colorimetry for NH₄, and gas chromatography for dissolved CH₄ and CO₂. Non-purgeable organic carbon (NPOC) was determined by combustion using an organic carbon analyser.

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

VOC determination was by direct aqueous injection purge-and-trap GC-MS, whilst PAH determination was by solvent extraction followed by GC-MS.

3.2 ENVIRONMENT AGENCY DATA

Extracts of data were taken from the Environment Agency WIMS database from sites located within the Lower Greensand and Gault Clay surface expressions. The geographical extent of the WIMS database selection is shown in Figure 1-1 and 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 Lower Greensand and Gault Clay groups, representing the unconfined and confined Lower Greensand respectively. The most recent and complete data for each sample site were selected for mapping and summary statistical evaluation. Sites from targeted surveys, landfill monitoring or pollution response investigations were excluded. Complete criteria for the filtering process can be found in Appendix 2 (Table A-1 & Table A-2).

Charge imbalances were checked to assess any obvious problems in data quality. Imbalances were typically less than 10% although balances were not calculable in cases where major-ion analyses were incomplete. Samples from the filtered WIMS dataset were not omitted where major-ion data were incomplete.

The data extracted from the Environment Agency WIMS database was then combined with the analytical results from the samples collected by BGS. A summary of the two datasets is shown in Table 3-1.

Table 3-1. Summary of filtered data

Summary of filtered data	BGS	EA WIMS
Number of individual records	2696	990
Number of sample sites	11	26
Number of unique analytes across samples	223	67

3.3 STATISTICAL SUMMARY DATA

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

Kaplan-Meier (K-M) and regression-on-order statistics (ROS), both of which are suitable for datasets with multiple detection limits (Helsel, 2005; Lee and Helsel, 2005b, 2007).

The K-M method calculates the rank of the data, 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 data contain $>80\%$ 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 5.1 and 5.1.3.

4 Regional hydrogeochemistry

The following section presents the statistical and analytical results from the combined WIMS data and the field sampling conducted by the BGS. It summarises the results for both the confined and unconfined aquifer sections. The statistical summary data are presented in Table 4-1.

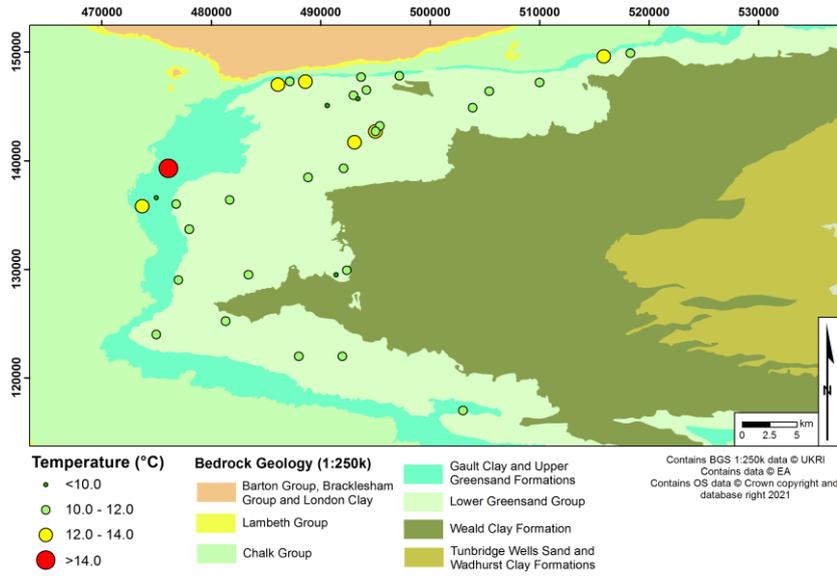
4.1 FIELD-DETERMINED PARAMETERS

Groundwater temperatures for the aquifer range from 3.67 °C to 14.9 °C, with a median of 11 °C. The 5th to 95th percentile range is 9.62 °C to 12.4 °C. Temperatures are primarily between 10 °C and 14 °C across much of the Lower Greensand aquifer, in both the unconfined (eastwards) and confined (westwards) setting, showing very little difference between the two settings (Figure 4-1a). The anomalous 14.9°C value is derived from the EA WIMS dataset. Field measurements for WIMS samples are taken in a container at surface, so temperature readings are likely to be affected by the surface air temperature on the day of sampling.

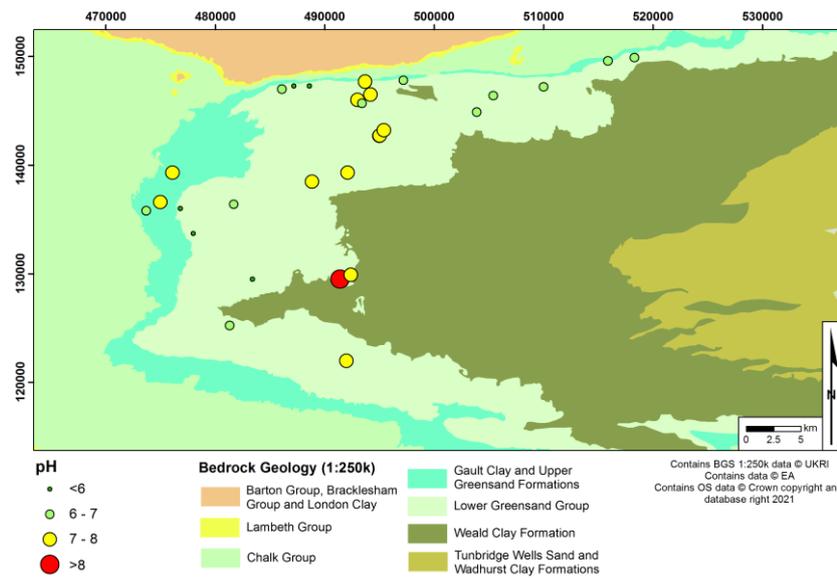
Values for pH range from 4.5 to 8.1 across the aquifer, with a median of 6.87. The 5th to 95th percentile range is 5.19 to 7.8. The limited data do not provide evidence for spatial trends (Figure 4-1b).

Dissolved oxygen (DO) results for the aquifer range from <0.5 mg/L to 12.6 mg/L, with a median of 8.55 mg/L. The 5th to 95th percentile range is 0.565 mg/L to 12.1 mg/L. The DO content of the water is mostly >5 mg/L across the aquifer, with values of 10 mg/L and higher recorded close to the boundary with the Weald Clay Formation (Figure 4-1c). Observations of redox potential (Eh) range from 141 mV to 472 mV, with a median of 356 mV. However, Eh data were only monitored for the BGS field samples. As mentioned above, field measurements are recorded in open containers for EA WIMS samples; in the case of DO, such measurements are not likely to be representative of the in-situ aquifer condition. The EA WIMS database does not hold records for Eh for this area. Spatial trends are therefore difficult to assess, although the observed values indicate the full range of redox conditions (from reducing to oxidising) are present (Figure 4-1d).

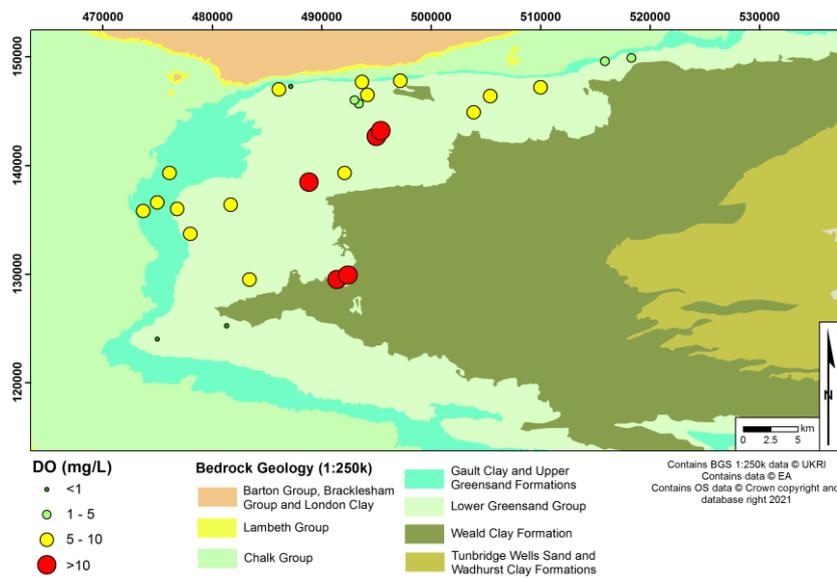
Specific electrical conductance (SEC, at 25°C) across the aquifer ranges from 150 µS/cm to 838 µS/cm, with a median of 430 µS/cm. The 5th to 95th percentile ranges from 165 µS/cm to 768 µS/cm. There is a cluster of high (>650 µS/cm) values in the north of the study area around Godalming and Farnham (Figure 4-1e). SEC values are lower (<250 µS/cm) in the Haslemere and Bordon areas, increasing towards the north. Limited data points in the southern half of the study area do not allow for robust conclusions to be drawn for this section.



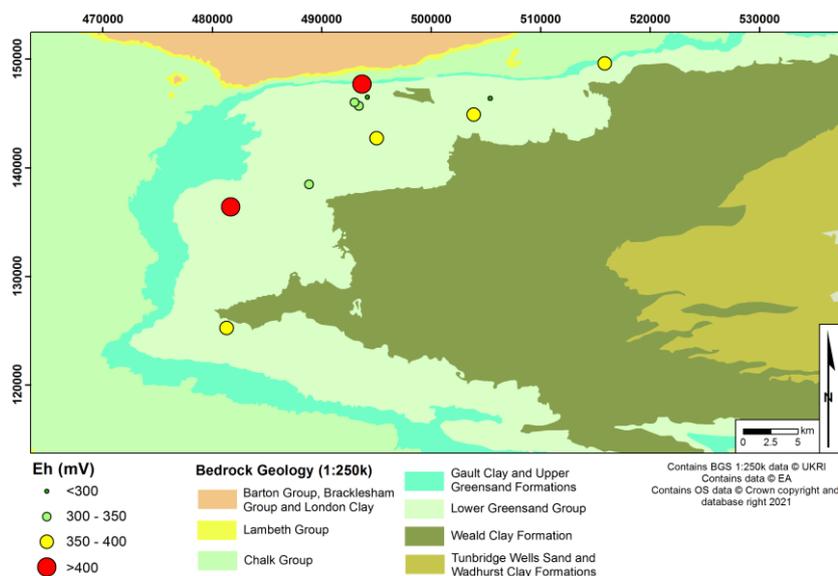
(a)



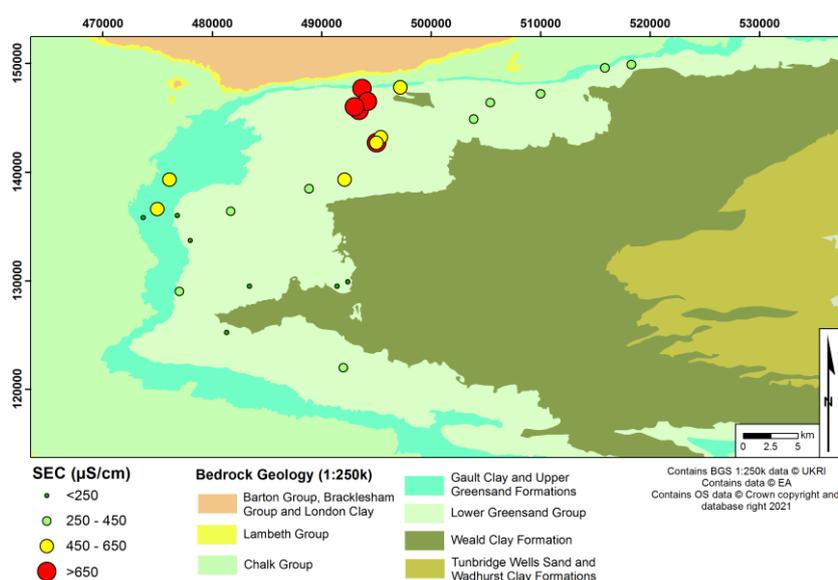
(b)



(c)



(d)



(e)

Figure 4-1. Geographical distribution of in-field measured water quality properties; (a) groundwater temperatures; (b) pH; (c) dissolved oxygen (DO); (d) redox potential (Eh); (e) specific electrical conductivity (SEC).

4.2 MAJOR IONS

The calcium concentration ranges from 12.4 mg/L to 138 mg/L, with a median of 54.1 mg/L. The 5th to 95th percentile range is 13.4 mg/L to 126 mg/L. Concentrations appear to increase from the centre of the study area towards the north, from <20 mg/L to in excess of 50 mg/L (Figure 4-2a). There is a cluster of concentrations >100 mg/L to the north-west of Godalming.

The magnesium concentration ranges from 1.55 mg/L to 9.6 mg/L, with a median of 3.08 mg/L. the 5th to 95th percentile range is 1.63 mg/L to 8.74 mg/L. In the northern half of the study area (from Dorking, Godalming and Farnham), concentrations can be seen to increase towards the confined setting of the Lower Greensand aquifer (Figure 4-2b). There appears to be no clear spatial trend in the central and southern portion of the study area.

Sodium concentration ranges from 5.8 mg/L to 28.9 mg/L, with a median of 10.4 mg/L. The 5th to 95th percentile range is 6.14 mg/L to 24.7 mg/L. Sodium concentrations are typically below 15 mg/L across much of the study area, with elevated concentrations to the north-west of Godalming (>15 mg/L) (Figure 4-2c).

Potassium concentrations range from 0.97 mg/L to 25.1 mg/L, with a median of 2.7 mg/L. The 5th to 95th percentile range is 1 mg/L to 16.5 mg/L. Concentrations appear to be typically <3 mg/L in much of the central and northern portion of the aquifer, marginally increasing (between 3 mg/L and 7 mg/L) towards the confining Gault Clay and Upper Greensand Formations (Figure 4-2d). A few elevated concentrations (>7 mg/L) are present to the north-west of Godalming.

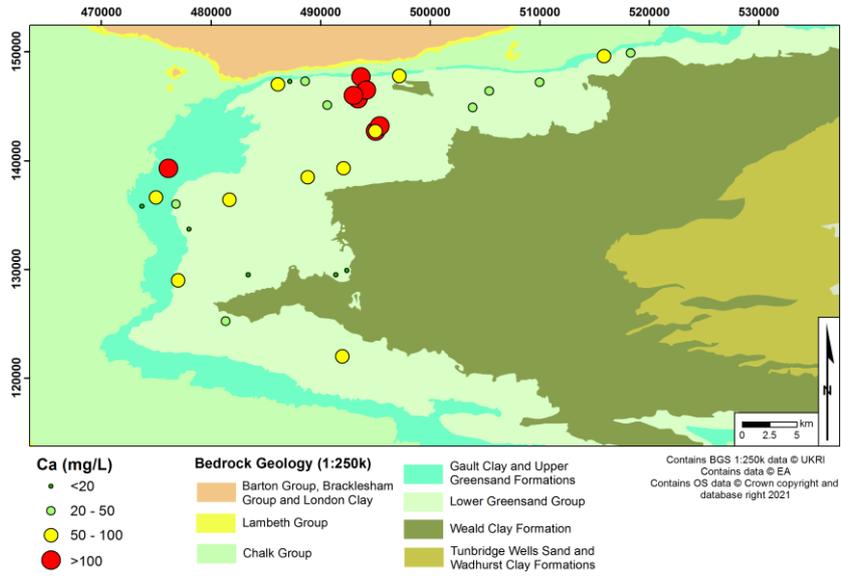
Chloride concentrations range from 11.4 mg/L to 59.7 mg/L, with a median of 20 mg/L. The 5th to 95th percentile range is 12.6 mg/L to 40.6 mg/L. Concentrations are notably above 30 mg/L in the region north-west of Godalming. From the central to southern half of the study area, the concentrations are predominantly less than 20 mg/L, with a few locations between 20 mg/L and 30 mg/L (Figure 4-2e).

Alkalinity (as HCO₃) ranges from <6.1 mg/L to 387 mg/L, with a median of 146 mg/L. The 5th to 95th percentile range is 18.3 mg/L to 316 mg/L. Concentrations are typically above 100 mg/L in the north and north-western part of the study area, with a cluster of concentrations greater than 200 mg/L in the vicinity of Godalming in the north (Figure 4-2f). Concentrations also appear to be higher in the confined setting, although the number of sample points is limited.

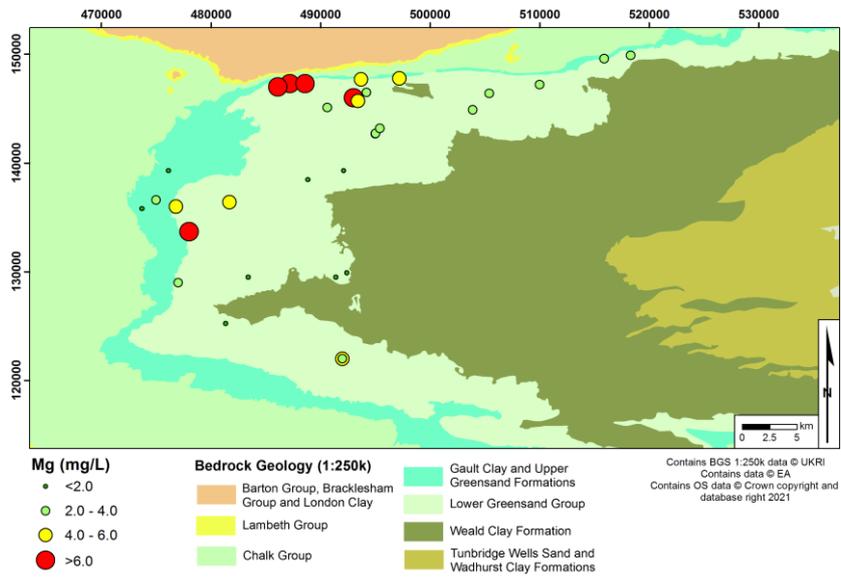
Sulphate (SO₄) concentrations range between <10 mg/L and 107 mg/L, with a median of 27.6 mg/L. The 5th to 95th percentile range is 14.9 mg/L to 80.6 mg/L. Only a few locations in the combined WIMS and BGS dataset have concentrations above 50 mg/L, centred around Godalming, and towards Farnham (Figure 4-2g).

Nitrate (NO₃) concentrations range between <0.06 mg/L to 155 mg/L, with a median of 22.5 mg/L. The 5th to 95th percentile range is 2.58 mg/L to 77.2 mg/L. Nitrate concentrations are greatest in the north of the study area (although data points in the south are limited), and in this area are above 25 mg/L (Figure 4-2h). The few samples in the confined setting to the west and south have concentrations less than 25 mg/L. Nitrate concentrations have been plotted against a backdrop of the NVZs (Section 1.3.2), and are shown in Figure 4-3. Nearly all sites located within the NVZs (8 locations) have nitrate concentrations less than 50 mg/L, aside from one site in the north of the study area.

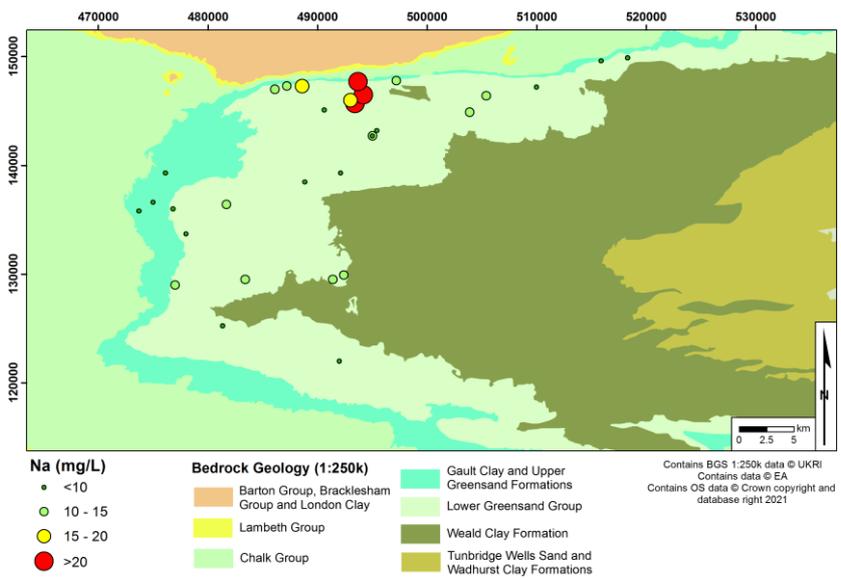
Silica (reported as Si) concentrations range between 2.56 mg/L and 13.6 mg/L, with a median of 5.88 mg/L. The 5th to 95th percentile is 4.37 mg/L to 11.2 mg/L. Concentrations are typically between 5 and 7 mg/L in the northern portion of the study area, with some isolated locations greater than 7 mg/L (Figure 4-2i).



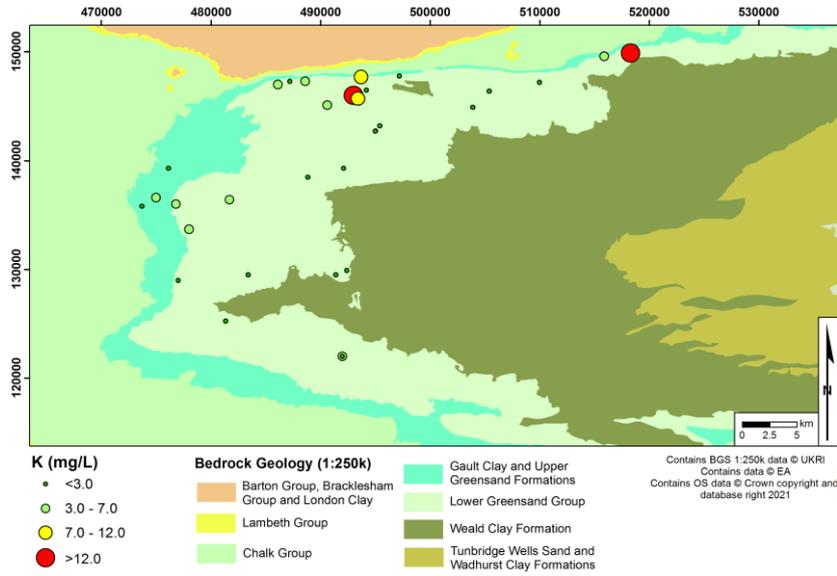
(a)



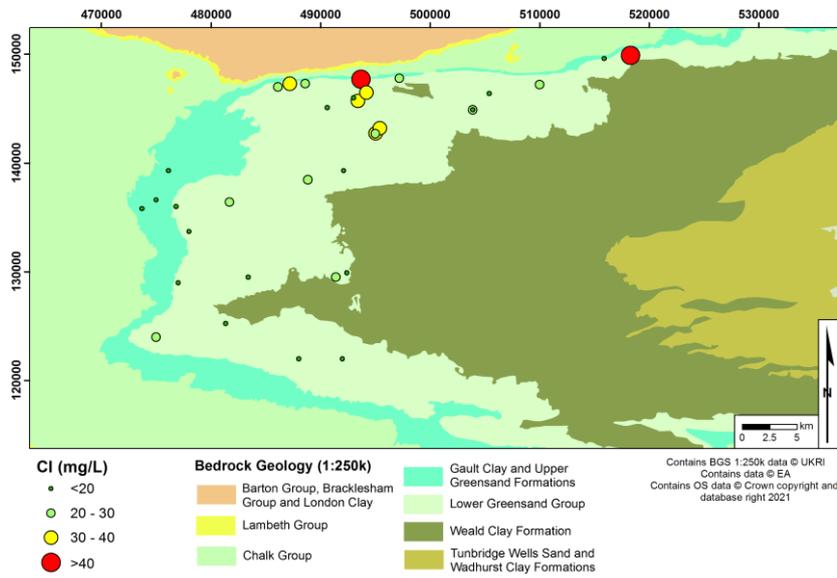
(b)



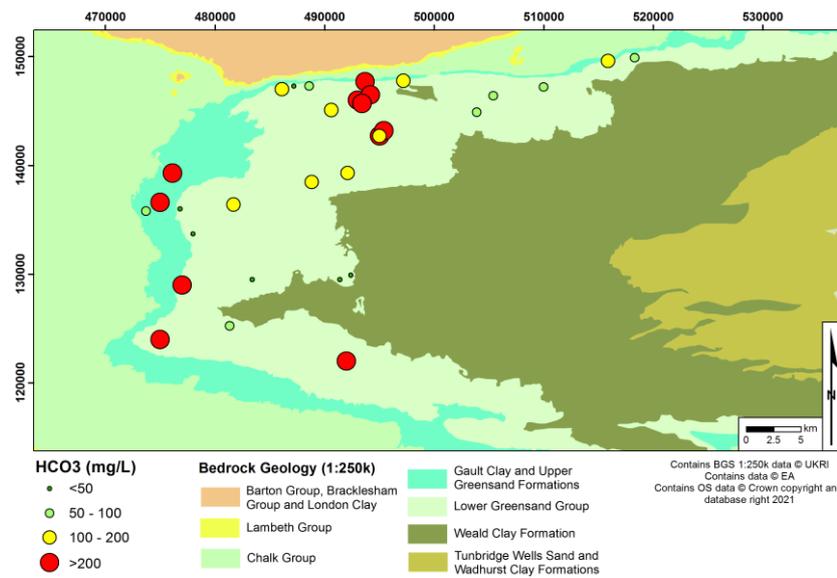
(c)



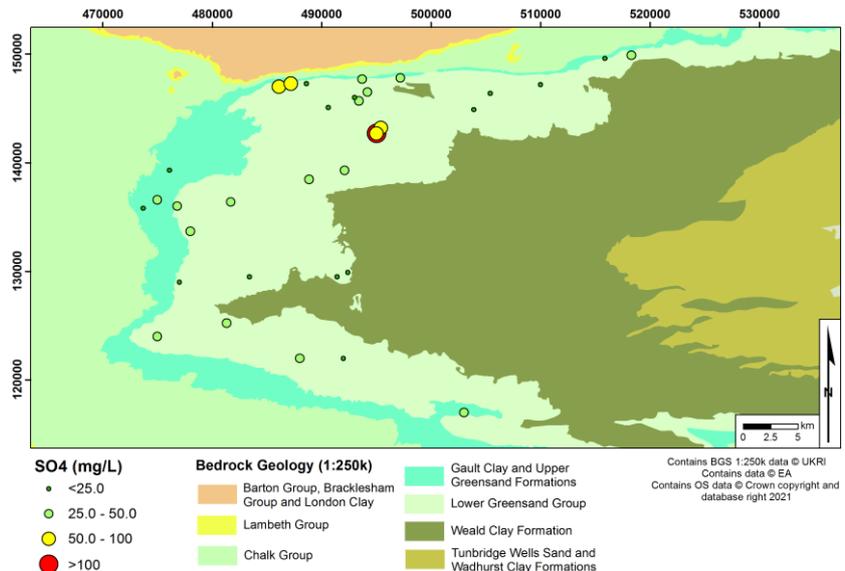
(d)



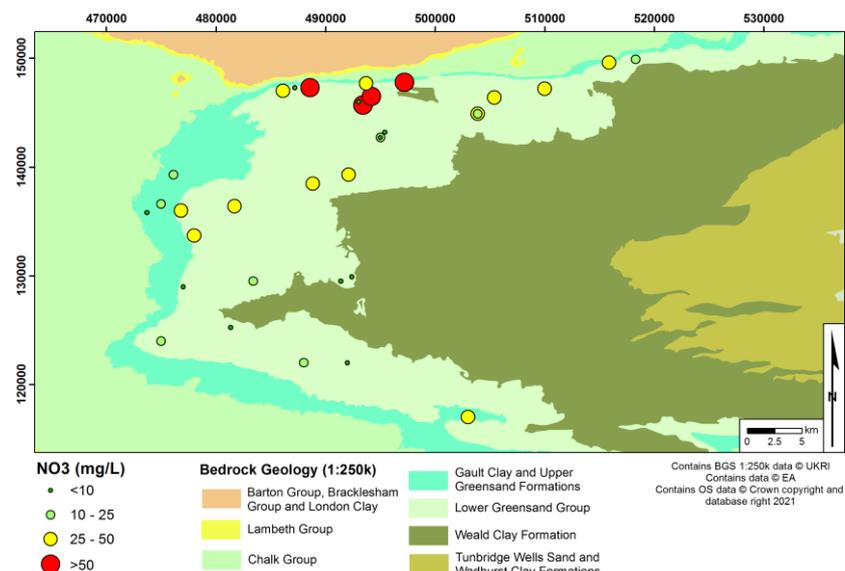
(e)



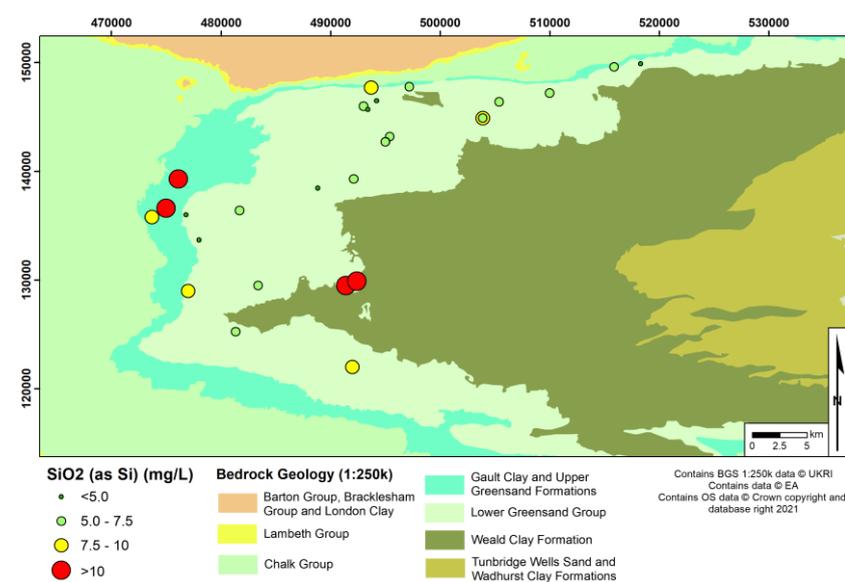
(f)



(g)



(h)



(i)

Figure 4-2. Spatial distribution of major ion concentrations across the study area; (a) calcium; (b) magnesium; (c) sodium; (d) potassium; (e) chloride; (f) bicarbonate; (g) sulphate; (h) nitrate; (i) silica (reported as silicon)

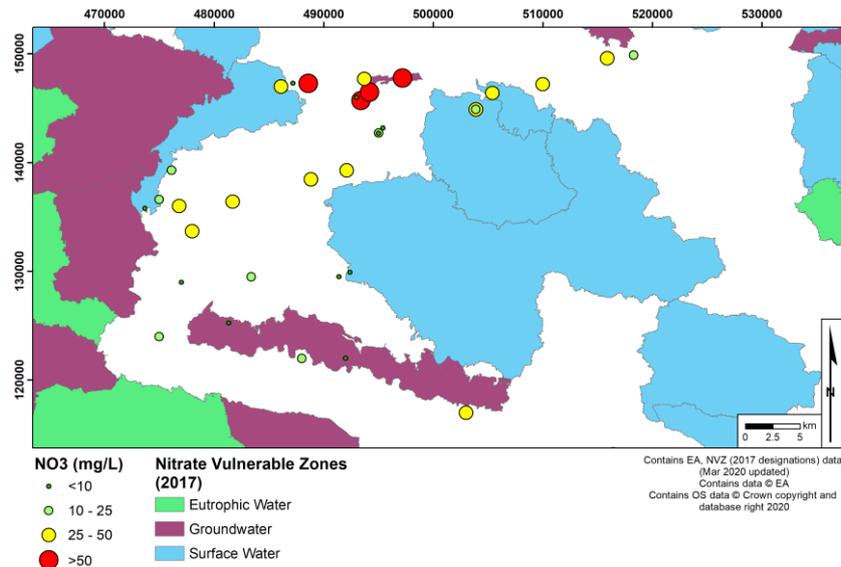


Figure 4-3. Comparison of nitrate concentrations and NVZs (DEFRA, 2018)

Samples with complete sets of data for major-ions (a total of 33 locations) have been summarised in a Piper Plot (Figure 4-4.). There is a clear grouping of samples with Ca-HCO₃ water type, with low relative percentages of Mg, and Na + K. There is a cluster of samples with high relative concentrations of SO₄ and Cl, indicating a more mixed-type. These occur in the north of the study area (Figure 4-2). Similar water types have been observed for the Lower Greensand by Shand et al. (2003).

Box plots and cumulative-probability plots showing distributions for the major ions are shown in Figure 4-5. & Figure 4-6.

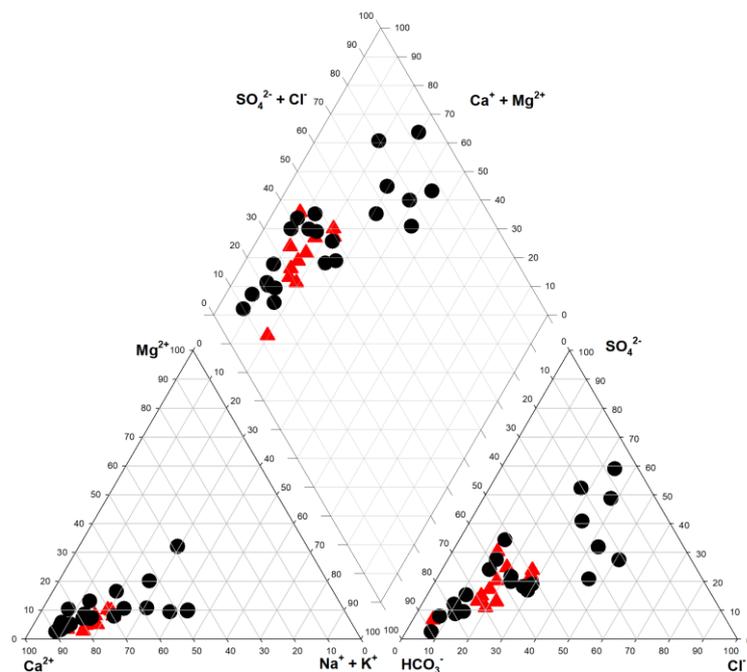


Figure 4-4. Piper plot for EA-WIMS (Black) and BGS (red) groundwater samples from the Lower Greensand Aquifer.

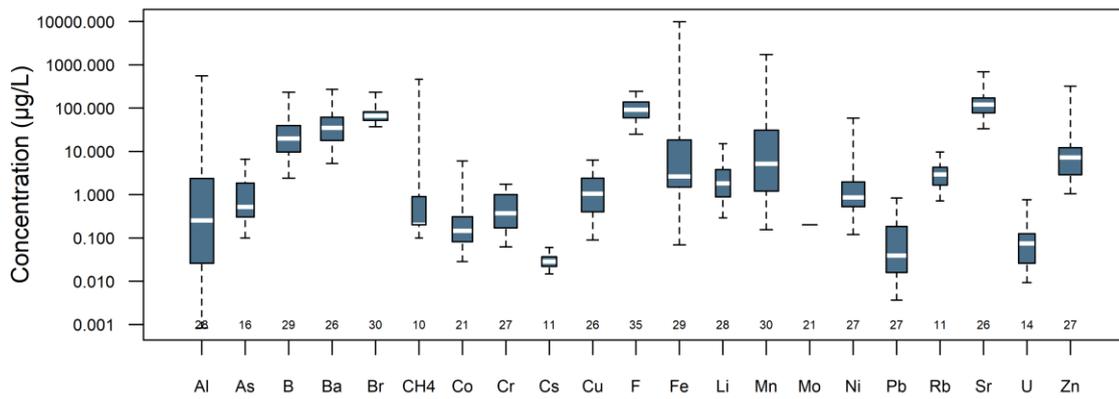
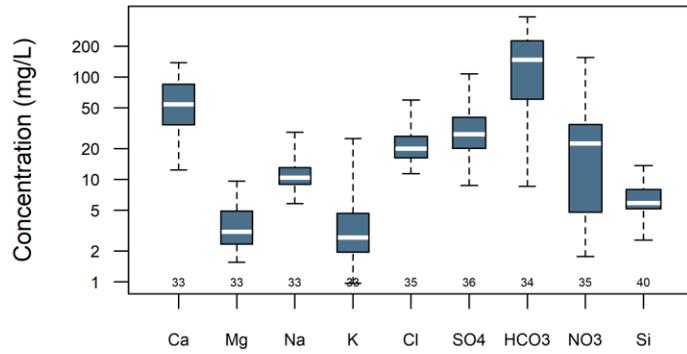


Figure 4-5. Box plot of major ions (top) and minor and trace elements (bottom); number of analyses given for each box

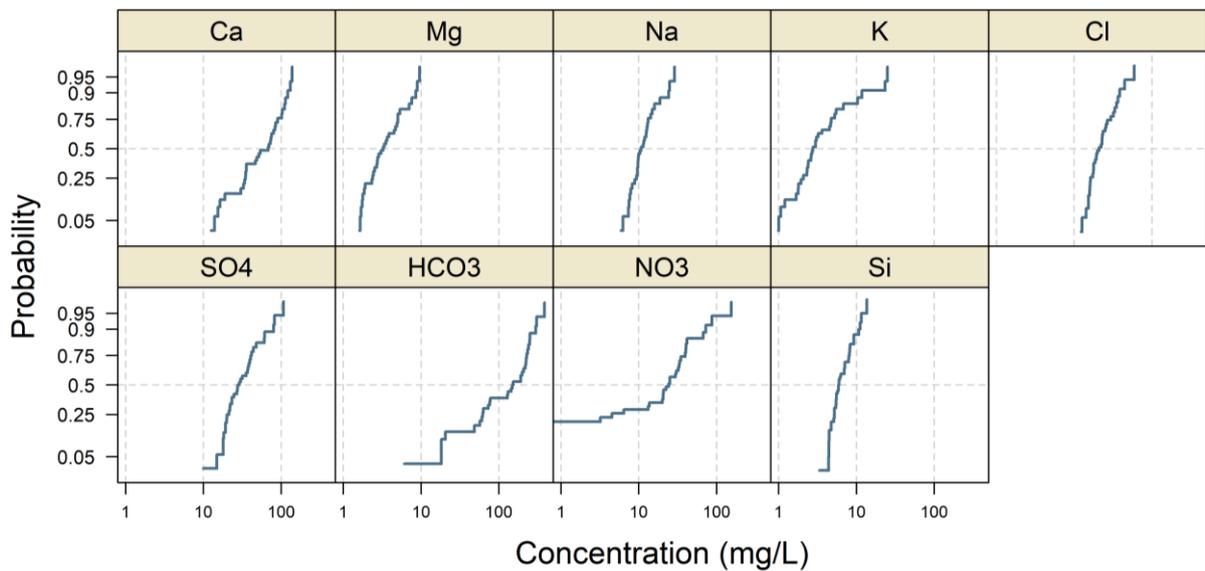
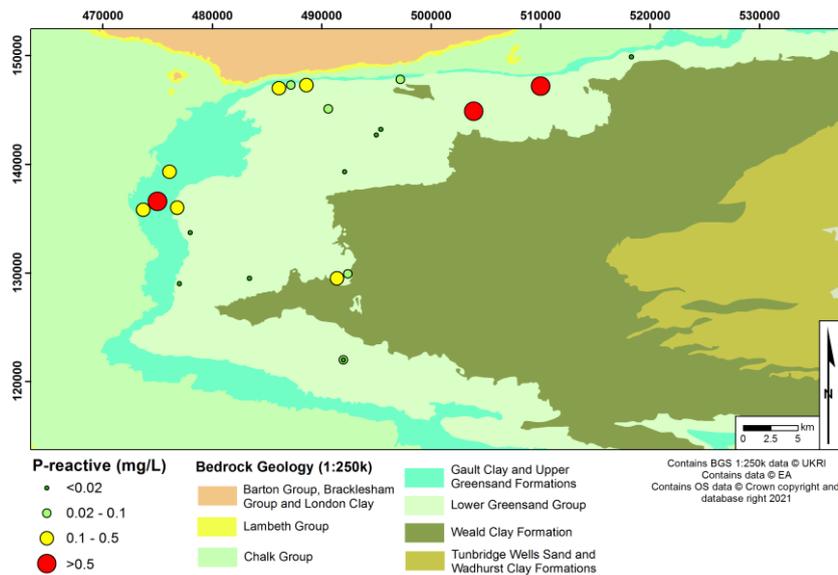


Figure 4-6. Cumulative-probability plots for major ions

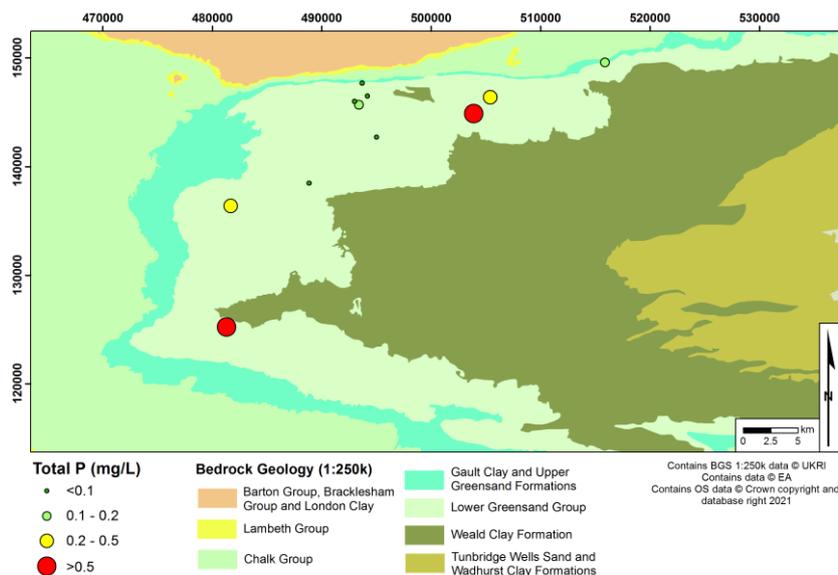
4.3 MINOR AND TRACE ELEMENTS

4.3.1 Phosphorus

Phosphorus (reactive/orthophosphate expressed as P, referred to as P-R, and measured by colorimetry) has a median concentration of 0.0475 mg/L, with a range of <0.01 mg/L to 0.955 mg/L. The 5th to 95th percentile range is 0.00436 mg/L to 0.71 mg/L. Spatial distribution for P-R is presented in Figure 4-7.a. Concentrations of total dissolved phosphorus (as P) were determined by BGS from different sites, using a different analytical method (ICP-MS) and are presented separately in Figure 4-7.b. Concentrations of total dissolved phosphorus range from <0.02 mg/L to 0.95 mg/L, with a median of 0.11 mg/L. The 5th to 95th percentile range is 0.0269 mg/L to 0.85 mg/L. P-reactive appears to have higher concentrations towards the confined edge of the aquifer, with concentrations above 0.1 mg/L (Figure 4-7.a). Much of the unconfined Lower Greensand aquifer has P-Reactive concentrations close to or less than 0.1 mg/L. There are too few data for total dissolved phosphorus to draw conclusions (Figure 4-7.b).



(a)



(b)

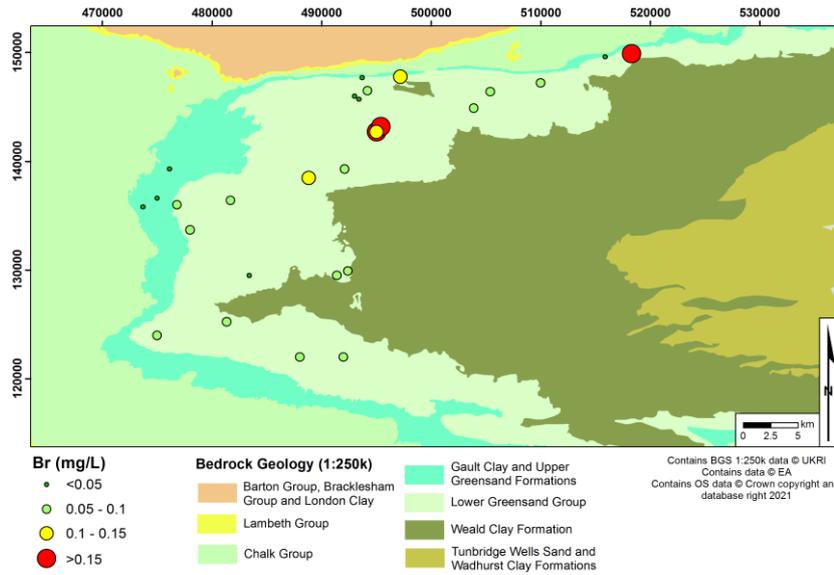
Figure 4-7. Spatial distributions across the study area for (a) P-reactive, and (b) total dissolved phosphorus

4.3.2 Halogens

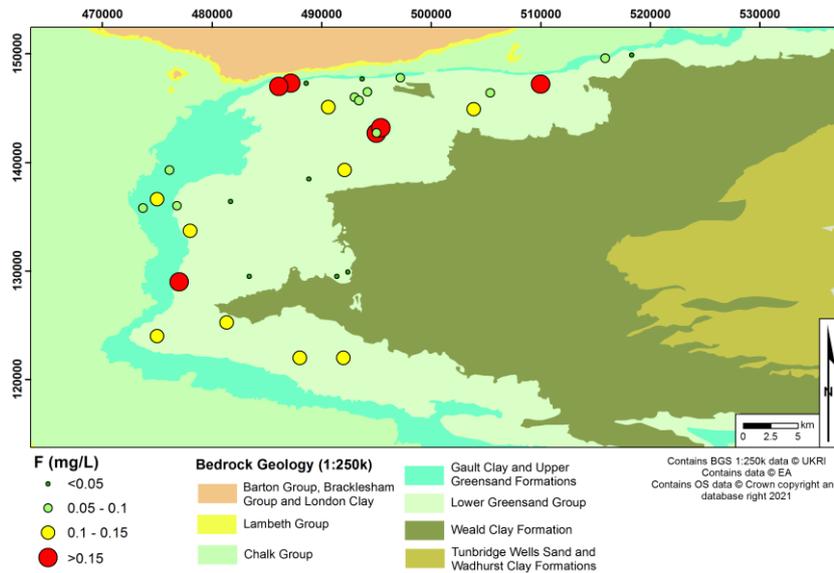
Bromide has a concentration range of <0.05 mg/L to 0.234 mg/L, with a median of 0.0658 mg/L. The 5th to 95th percentile range is 0.0382 mg/L to 0.195 mg/L. Bromide concentrations are greater in the unconfined aquifer, and lower in the confined setting to the north and west (Figure 4-8a).

Fluoride concentrations range from <0.05 mg/L to 0.245 mg/L, with a median of 0.091 mg/L. The 5th to 95th percentile range is 0.0298 mg/L to 0.215 mg/L. The lowest fluoride concentrations can be observed towards the centre of the study area (west of Haslemere). Concentrations are greatest (typically >0.05 mg/L in the north and west (Figure 4-8b).

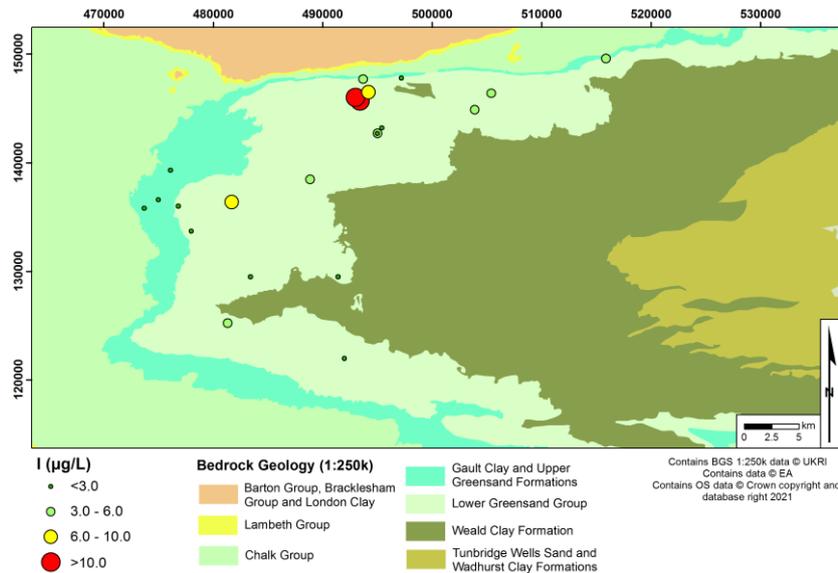
Iodine concentrations range from <3 µg/L to 14.6 µg/L, with a median of 3.09 µg/L. The 5th to 95th percentile range is 1.07 µg/L to 10.1 µg/L. Iodine concentrations are greatest in a cluster in the north of the study area (close to Godalming), with a grouping of low concentration values in the confined setting to the west (Figure 4-8c). Concentrations are typically <6 µg/L across the wider aquifer.



(a)



(b)



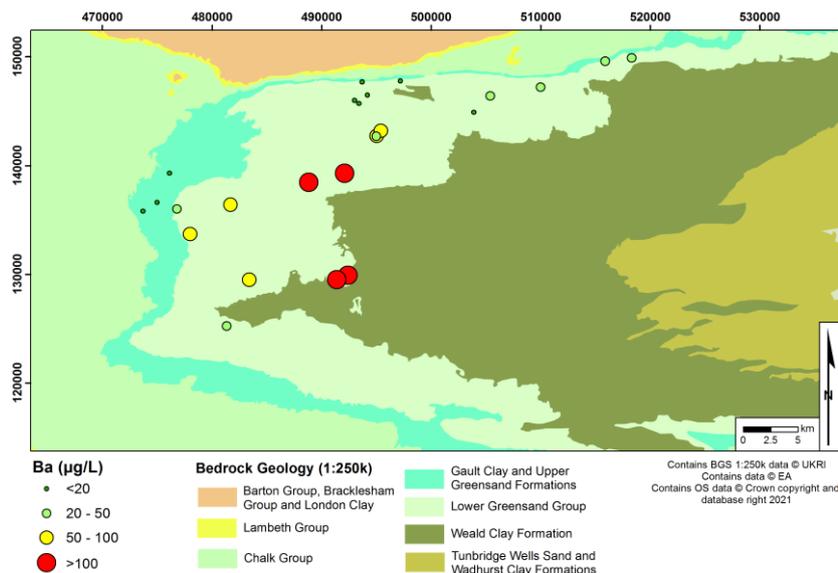
(c)

Figure 4-8. Spatial distributions for halogen group elements across the study area; (a) bromide; (b) fluoride; (c) iodine.

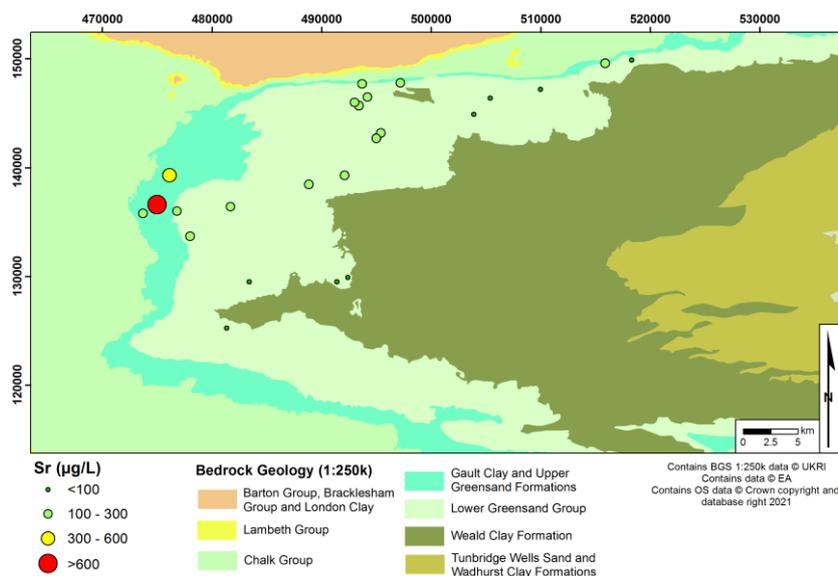
4.3.3 Alkaline-earth metals

Barium has a concentration range of <math><10\ \mu\text{g/L}</math> to 272 $\mu\text{g/L}</math>, with a median of 35.1 $\mu\text{g/L}</math>. The 5th to 95th percentile range is 5.6 $\mu\text{g/L}</math> to 111 $\mu\text{g/L}</math>. Barium concentrations are greatest in the centre of the study area (>50 $\mu\text{g/L}</math>), with lower values observed in the confined settings towards the west and a cluster <math><20\ \mu\text{g/L}</math> close to Godalming (Figure 4-9a). Concentrations appear to decrease to the north, south and west from the high concentrations in the centre of the study area.$$$$$

Strontium concentrations range from 33.3 $\mu\text{g/L}</math> to 694 $\mu\text{g/L}</math>, with a median of 120 $\mu\text{g/L}</math>. The 5th to 95th percentile range is 56.5 $\mu\text{g/L}</math> to 408 $\mu\text{g/L}</math>. Concentrations between 100 $\mu\text{g/L}</math> and 300 $\mu\text{g/L}</math> can be observed in the Godalming to Farnham region, with a notable decrease to <math><100\ \mu\text{g/L}</math> towards the east and due south (Figure 4-9b). Limited data indicate an increase in Sr concentration into the confined setting in the west and far south.$$$$$$$



(a)



(b)

Figure 4-9. Spatial distribution of (a) barium and (b) strontium across the study area

4.3.4 Alkali metals

Rubidium has a concentration range of 0.71 µg/L to 9.58 µg/L, with a median of 2.94 µg/L. The 5th to 95th percentile range is 0.83 µg/L to 7.21 µg/L. Rb concentrations appear greatest (>3 µg/L) in the northern half of the study area (Figure 4-10). Data points are limited towards the south, but appear to be of lower concentrations than those in the North.

Lithium concentrations were observed to be below detection limit across the aquifer, with 26 out of 28 non-detects (<100 µg/L for EA WIMS data, <8 µg/L for BGS collected samples). Caesium is only detected in two instances across the aquifer, with 9 out of 11 samples below detection limit (<0.05 µg/L). Maximum concentrations recorded for both Li and Cs are shown in Table 4-1. There were no Cs data in the EA WIMS database.

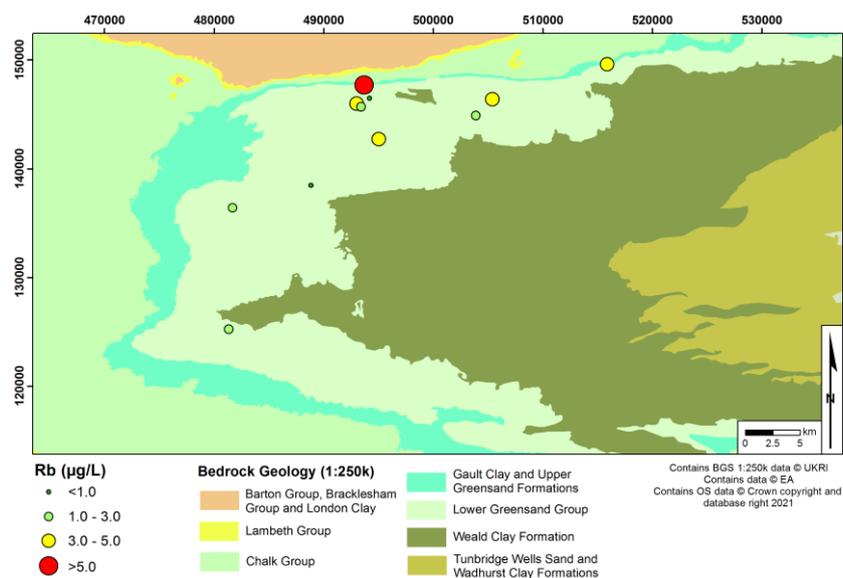
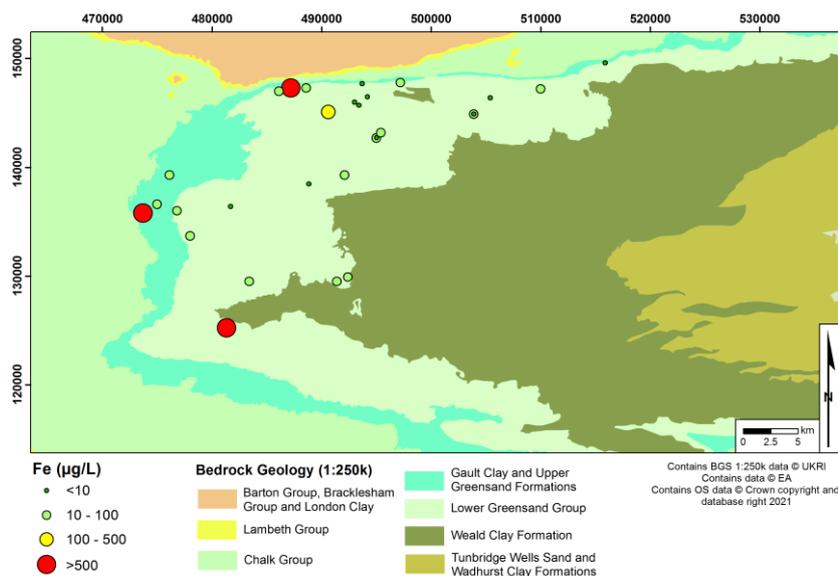


Figure 4-10. Spatial distribution of rubidium concentrations across the Lower Greensand Aquifer

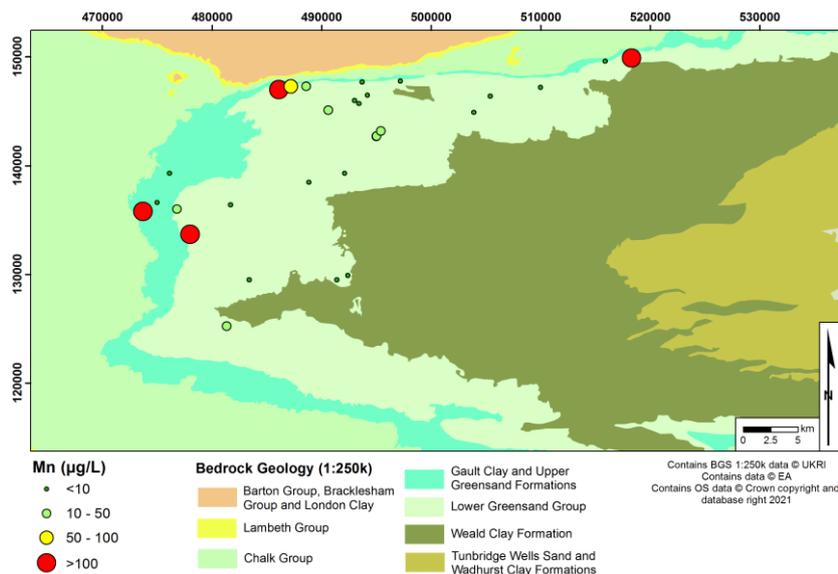
4.3.5 Iron and manganese

The concentration range for iron across the aquifer is <30 µg/L to 9910 µg/L, with a median of 2.64 µg/L. The 5th to 95th percentile range is 0.274 µg/L to 2400 µg/L. There appears to be no clear spatial trend of Fe concentration across the aquifer (Figure 4-11a).

Manganese has a concentration range of <10 µg/L to 1720 µg/L, with a median of 5.15 µg/L. The 5th to 95th percentile range is 0.393 µg/L to 315 µg/L. Mn concentrations are typically below 10 µg/L across much of the aquifer with only a few isolated locations >10 µg/L (Figure 4-11b).



(a)



(b)

Figure 4-11. Spatial distribution of (a) Iron and (b) Manganese concentrations across the study area.

4.3.6 Other trace elements

Aluminium has a concentration range from <2 µg/L to 554 µg/L, with a median of 0.251 µg/L. The 5th to 95th percentile range is 0.00193 µg/L to 38 µg/L. Much of the unconfined Lower Greensand aquifer has recorded Al concentrations <5 µg/L, with elevated concentrations within the confined setting to the west and north (Figure 4-12a). Only 8 samples had recorded values above detection limit.

Ammonium (NH₄) has a concentration range of <0.0038 to 0.0956 mg/L, with a median of 0.00866 mg/L. The 5th to 95th percentile is 0.00174 mg/L to 0.0767 mg/L. NH₄ concentrations appear to be elevated (>0.02 mg/L) in the northern half of the study area, with concentrations between 0.01 mg/L and 0.02 mg/L across much of the south and west (Figure 4-12b). A few elevated values >0.05 mg/L can be seen in the north and west.

Arsenic concentrations across the study area range from <1 µg/L to 6.63 µg/L, with a median of 0.515 µg/L. The 5th to 95th percentile range is 0.115 µg/L to 5.4 µg/L. Concentrations across the

north of the study area are typically below 1 µg/L (Figure 4-12c). A small grouping of values between 1 µg/L and 5 µg/L is observed to the west in the confined setting, with only one location, close to the Weald Clay Formation, showing a recorded concentration > 5 µg/L.

Chromium concentrations range from <0.05 µg/L to 1.73 µg/L, with a median of 0.373 µg/L. The 5th to 95th percentile range is 0.0737 µg/L to 1.61 µg/L. Cr concentrations appear to be above 1 µg/L throughout the centre of the study area, but is <0.5 µg/L in the confined setting in the west (Figure 4-12d). There are no clear spatial trends across the aquifer.

Copper has a concentration range of <0.1 µg/L to 6.3 µg/L, with a median of 1.05 µg/L. The 5th to 95th percentile range is 0.183 µg/L to 4.43 µg/L. Copper concentrations are <1.0 µg/L across much of the aquifer, with elevated concentrations (>1.5 µg/L) between Farnham and Godalming, and to the far north, south and west in proximity to (or within) the confined setting (Figure 4-12e).

Cobalt shows a concentration range of <1 µg/L to 5.99 µg/L, with a median of 0.145 µg/L. The 5th to 95th percentile range is 0.031 µg/L to 2.11 µg/L. Cobalt concentrations appear low across the aquifer as a whole, with no large spatial changes (Figure 4-12f). Two sites in the west of the study area show evidence of high concentrations (>1.5 µg/L), but do not appear to be tied to any trends from the unconfined setting.

Nickel has a concentration range from <0.5 µg/L to 58.9 µg/L, with a median of 0.86 µg/L. The 5th to 95th percentile range is 0.208 µg/L to 10.9 µg/L. Much of the aquifer has a concentration of less than 1 µg/L, with marginally higher concentrations (1.0 – 5.0 µg/L, with some locations >5.0 µg/L) towards the northwest, and at the edge of the confined aquifer in the west (Figure 4-12g).

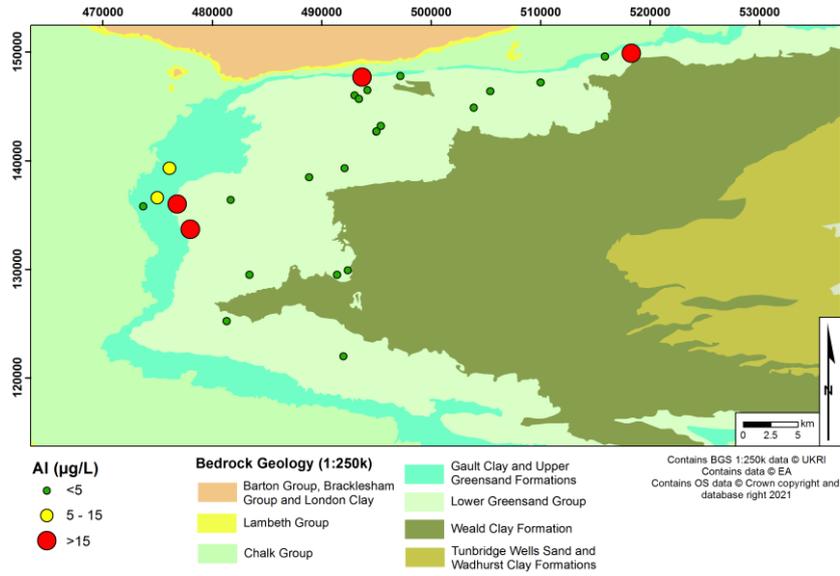
Uranium has a concentration range from <0.009 µg/L to 0.763 µg/L, with a median of 0.0745 µg/L. The 5th to 95th percentile range is 0.0131 µg/L to 0.427 µg/L. The central region of the study area (in the vicinity of Haslemere, Godalming and Bordon) has concentrations >0.1 µg/L. Limited sample points in the south do not allow any spatial trends to be observed (Figure 4-12h).

Vanadium has a concentration range from <0.04 µg/L to 3.59 µg/L, with a median of 0.52 µg/L. The 5th to 95th percentile range is 0.201 µg/L to 1.23 µg/L with no clear spatial trends (Figure 4-12i).

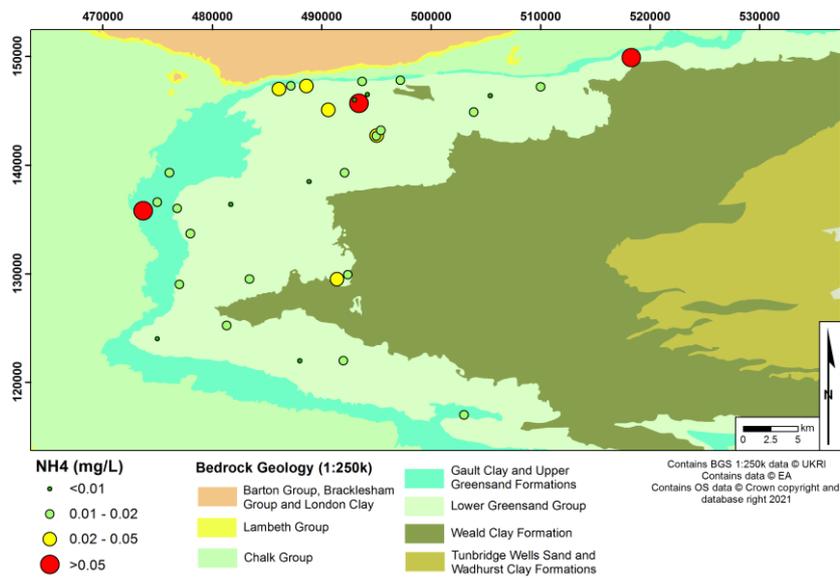
Yttrium has a concentration range from <0.006 µg/L to 0.065 µg/L, with a median of 0.009 µg/L. The 5th to 95th percentile range is 0.00164 µg/L to 0.0585 µg/L. Yttrium concentrations appear to increase away from the boundary with the Weald Clay (Figure 4-12j).

Zinc has a concentration range from <5 µg/L to 321 µg/L, with a median of 7.16 µg/L. The 5th to 95th percentile range is 1.26 µg/L to 90.4 µg/L. Zinc concentrations appear to increase from the north of the study area, towards the west (Figure 4-12k). Concentrations are greatest (>20 µg/L) at the furthest edge of the confined setting, by the Gault Clay and Upper Greensand formations, but two sites close to the Weald Clay boundary also show concentrations >20 µg/L.

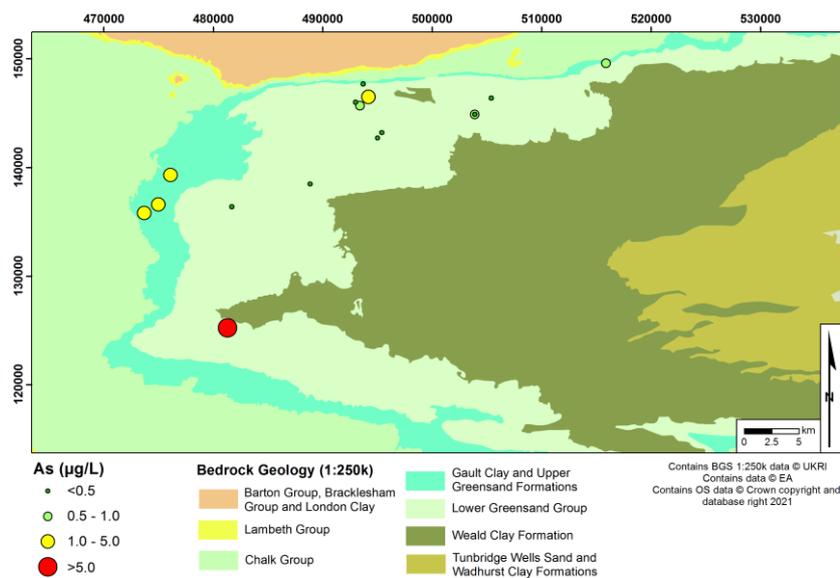
Box plots and cumulative-probability plots for selected minor and trace elements are shown in Figure 4-5 and Figure 4-13 respectively.



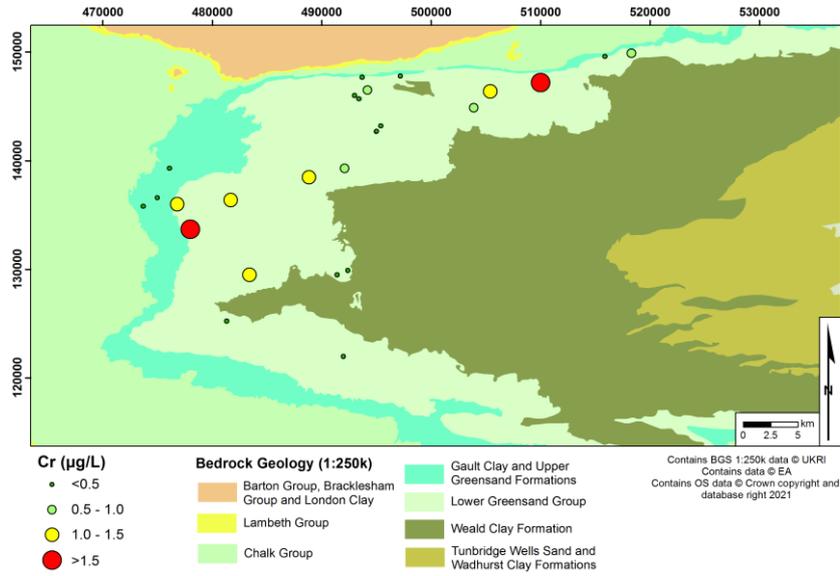
(a)



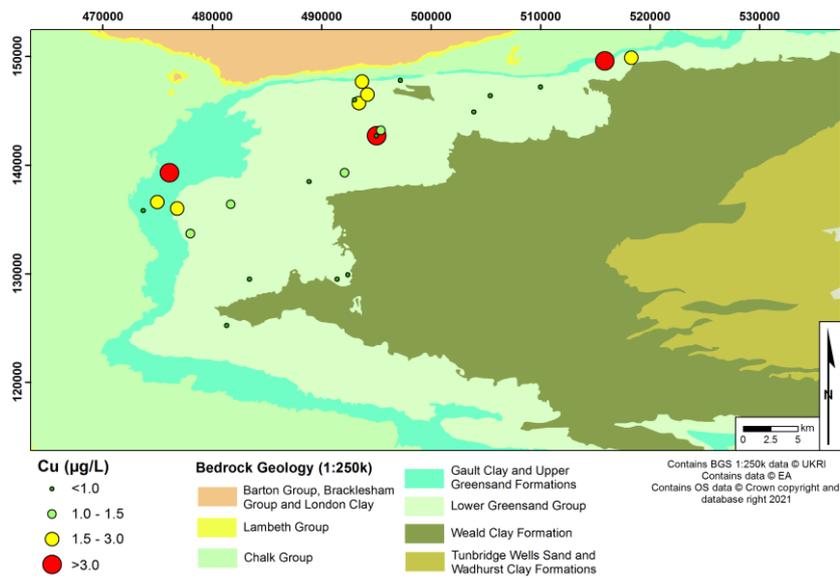
(b)



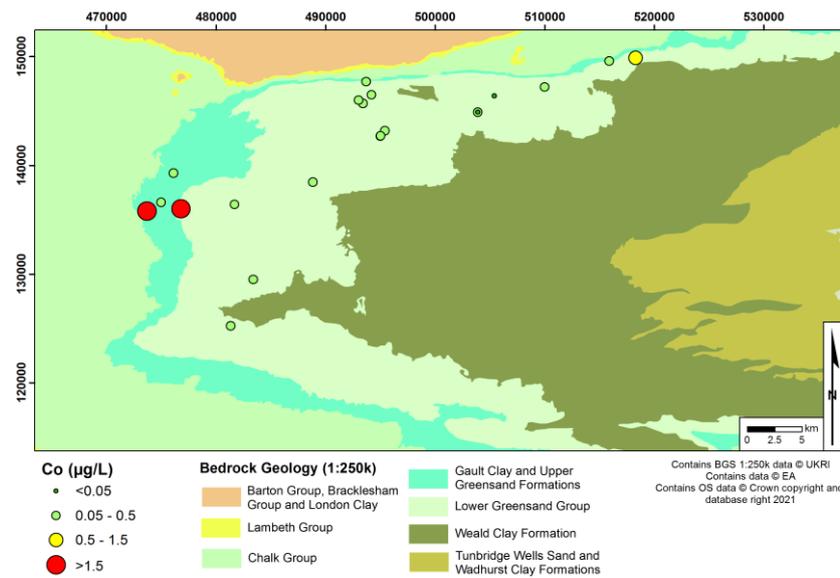
(c)



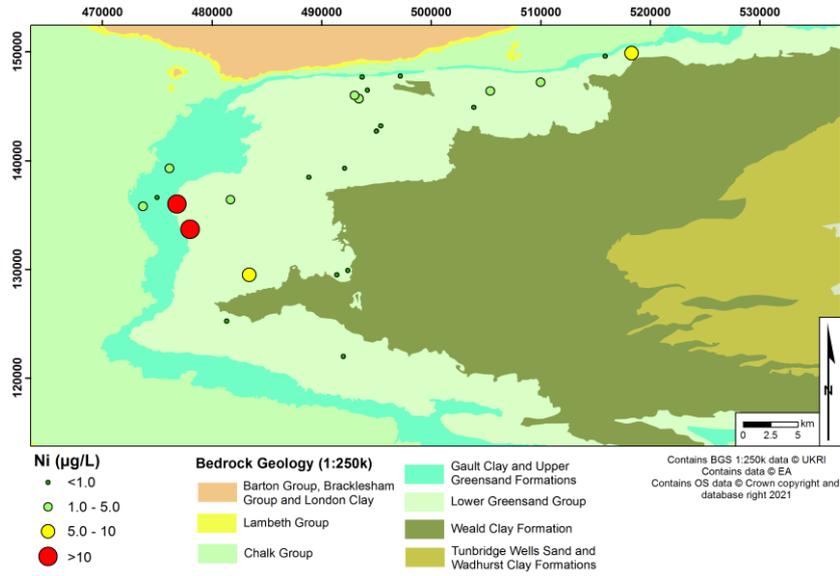
(d)



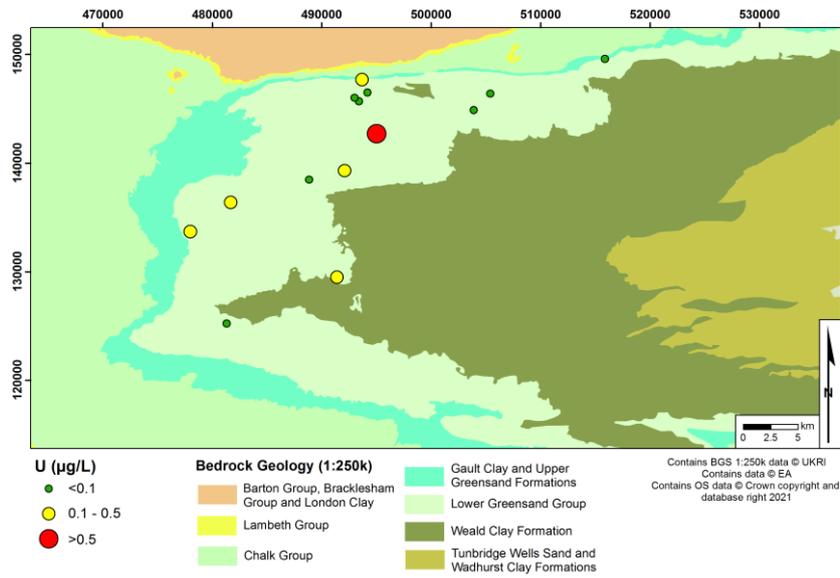
(e)



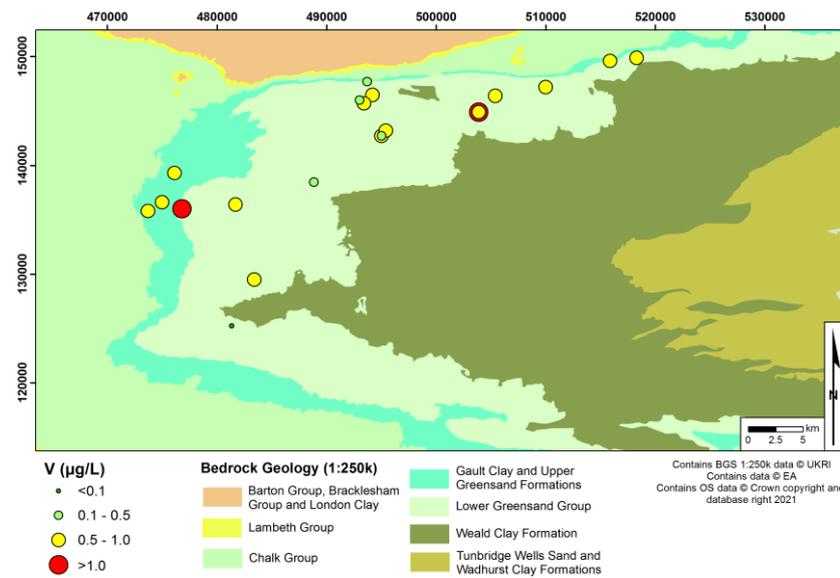
(f)



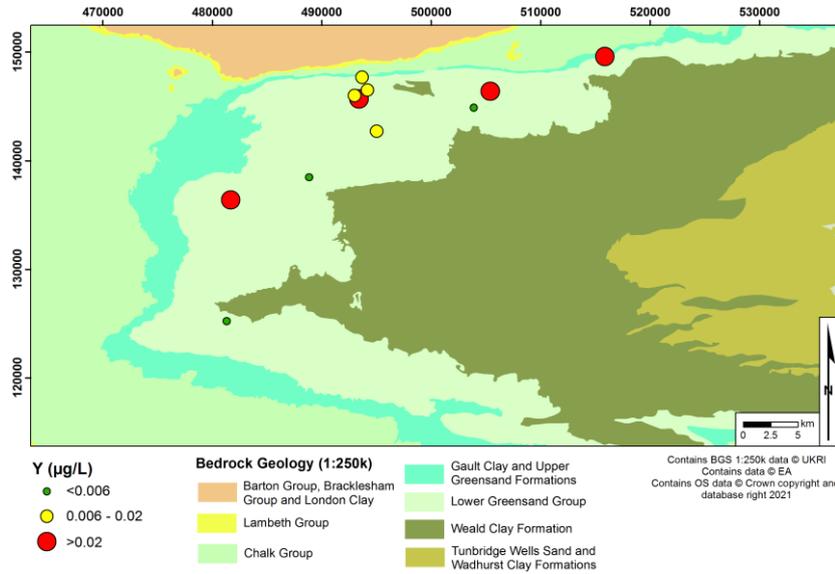
(g)



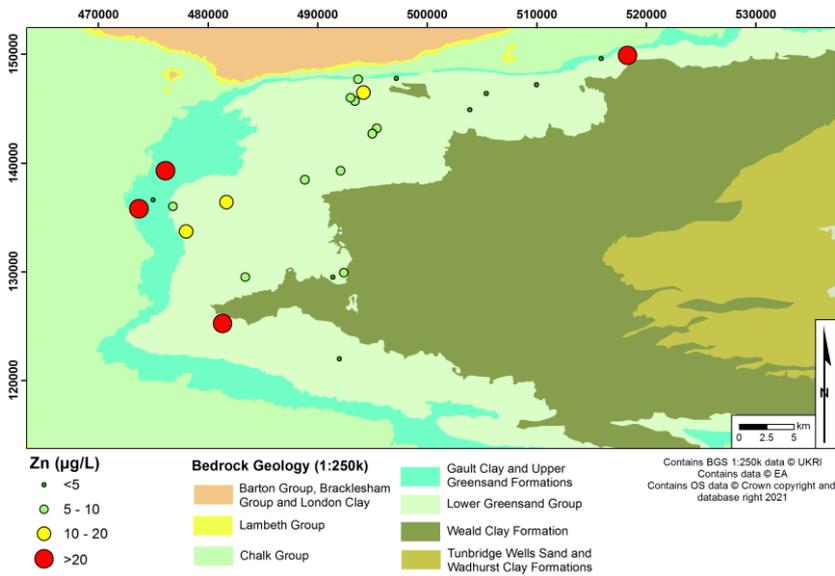
(h)



(i)



(j)



(k)

Figure 4-12 Spatial distributions of select minor and trace elements across the study area; (a) aluminium; (b) ammonium; (c) arsenic; (d) chromium; (e) copper; (f) cobalt; (g) nickel; (h) uranium; (i) vanadium; (j) yttrium; (k) zinc

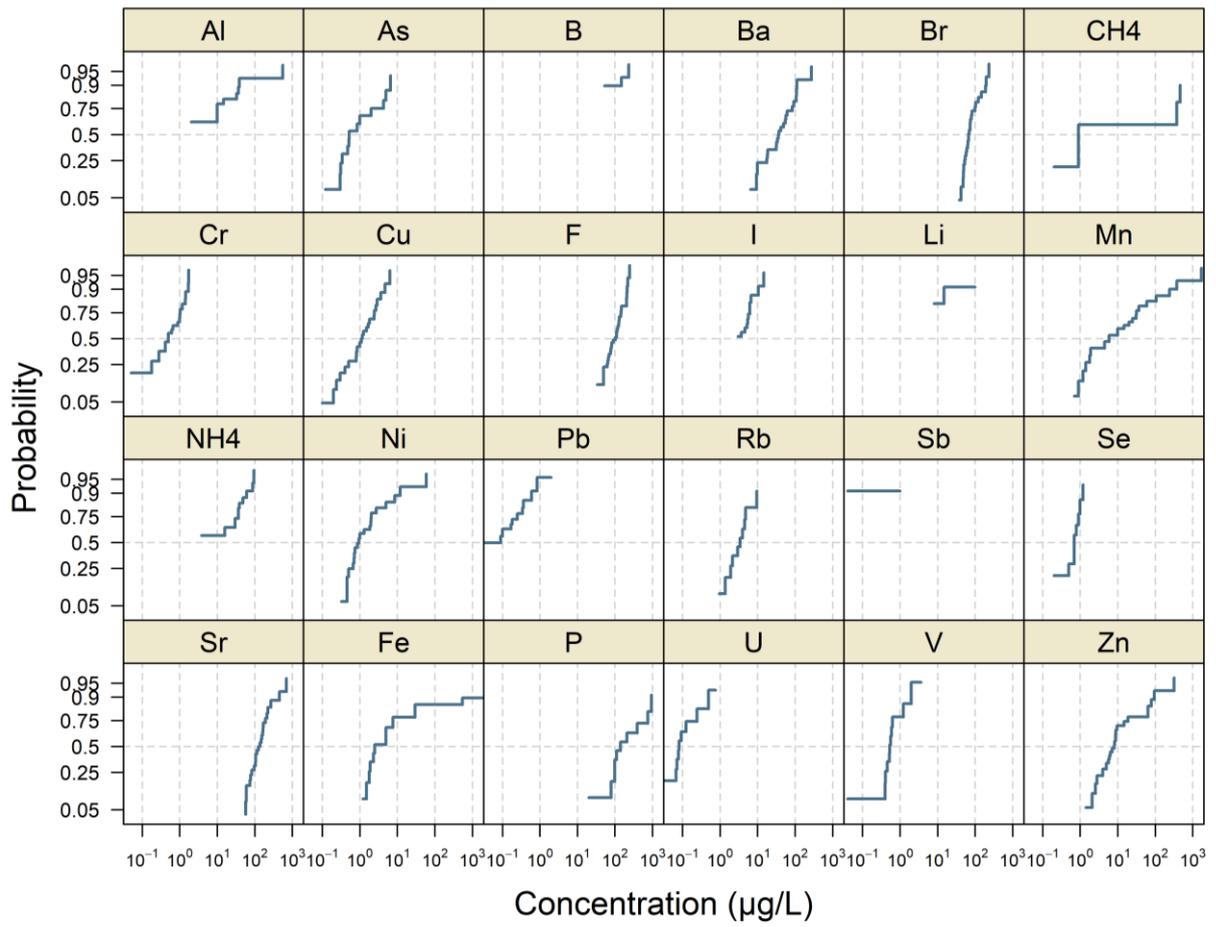


Figure 4-13. Cumulative-probability plots for select minor and trace elements

Table 4-1. Statistical summary data including percentiles (5th–95th) for inorganic analytes in groundwater from the Lower Greensand aquifer from the EA WIMS database and new samples collected and analysed by BGS

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
Temperature	°C	36	0	3.67	11	14.9	9.62	10.2	10.6	11	11.6	12.2	12.4
pH		31	0	4.5	6.82	8.1	5.19	5.61	6.46	6.87	7.52	7.78	7.8
DO	mg/L	29	1	<0.5	7.56	12.6	0.565	1.34	6.13	8.55	9.85	11	12.1
Eh	mV	11	0	141	345	472	218	296	331	356	379	410	441
SEC (at 25°C)	µS/cm	28	0	150	422	838	165	180	263	430	535	682	768
Ag	µg/L	21	21	<0.2		<1							
Al	µg/L	28	20	<2	25	554	0.00193	0.00445	0.0288	0.251	2.18	34.1	38
As	µg/L	16	2	<1	1.5	6.63	0.115	0.177	0.308	0.515	1.78	4.65	5.4
B	µg/L	29	26	<53		234							
Ba	µg/L	26	3	<10	51.3	272	5.6	7.31	17.7	35.1	60.8	108	111
Be	µg/L	21	21	<0.08		<1							
Bi	µg/L	11	11	<0.08		<0.08							
Br	mg/L	30	3	<0.05	0.0823	0.234	0.0382	0.0418	0.0521	0.0658	0.0813	0.151	0.195
Ca	mg/L	33	0	12.4	62.3	138	13.4	15.7	34.1	54.1	85.1	114	126
Cd	µg/L	27	18	<0.006	0.0244	0.344	0.000394	0.000656	0.00142	0.00464	0.0192	0.0415	0.0722
Ce	µg/L	11	11	<0.009		<0.009							
Cl	mg/L	35	0	11.4	23.4	59.7	12.6	14.7	16.2	20	26.4	36.2	40.6
Co	µg/L	21	7	<1	0.581	5.99	0.031	0.048	0.081	0.145	0.308	1.2	2.11
Cr	µg/L	27	11	<0.05	0.601	1.73	0.0737	0.0974	0.168	0.373	1	1.43	1.63
Cs	µg/L	11	9	<0.05		0.06							
Cu	µg/L	26	3	<0.1	1.53	6.3	0.183	0.22	0.427	1.05	2.26	3.25	4.43
Dy	µg/L	11	9	<0.003		0.005							
Er	µg/L	11	9	<0.003		0.014							
Eu	µg/L	11	10	<0.003		0.003							
F	mg/L	35	6	<0.05	0.106	0.245	0.0298	0.0348	0.0592	0.091	0.138	0.208	0.215

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
Fe	µg/L	29	15	<30	501	9910	0.274	0.633	1.5	2.64	18.4	276	2400
Ga	µg/L	11	11	<0.2		<0.2							
Gd	µg/L	11	9	<0.005		0.041							
HCO ₃	mg/L	45	2	<6.1	155	387	18.3	24.2	62.4	146	229	280	316
Hf	µg/L	11	11	<0.007		<0.007							
Hg	µg/L	4	4	<0.01		<0.01							
Ho	µg/L	11	11	<0.003		<0.003							
HPO ₄	mg/L	11	2	<0.05	0.698	2.8	0.039	0.0511	0.131	0.314	0.859	1.95	2.38
I	µg/L	23	12	<3	4.15	14.6	1.07	1.3	1.92	3.09	5.6	6.62	10.1
K	mg/L	33	0	0.97	4.64	25.1	1	1.1	1.95	2.7	4.66	9.69	16.5
La	µg/L	11	10	<0.007		0.008							
Li	µg/L	28	26	<8		15							
Lu	µg/L	11	10	<0.003		0.013							
Mg	mg/L	33	0	1.55	3.84	9.6	1.63	1.71	2.34	3.08	4.92	7.49	8.74
Mn	µg/L	30	9	<10	90.6	1720	0.393	0.67	1.25	5.15	29.4	119	315
Mo	µg/L	21	20	<0.2		0.2							
Na	mg/L	33	0	5.8	12	28.9	6.14	7.41	8.94	10.4	13	18.2	24.7
Nb	µg/L	11	11	<0.03		<0.03							
Nd	µg/L	11	10	<0.02		0.03							
NH ₄	mg/L	33	24	<0.0038	0.0187	0.0956	0.00174	0.00251	0.00451	0.00866	0.0198	0.0471	0.0767
Ni	µg/L	27	5	<0.5	3.94	58.9	0.208	0.277	0.524	0.86	1.98	6.45	10.9
NO ₂	mg/L	32	27	<0.01		0.115							
NO ₃	mg/L	35	7	<0.06	28.2	155	2.58	3.31	4.78	22.5	34.4	57.4	77.2
P (total)	mg/L	11	1	<0.02	0.26	0.95	0.0269	0.04	0.08	0.11	0.3	0.75	0.85
Pb	µg/L	27	17	<0.03	0.148	0.839	0.00605	0.00743	0.0174	0.0393	0.181	0.359	0.585
Pr	µg/L	11	11	<0.003		<0.003							
P-reactive	mg/L	22	8	<0.01	0.159	0.955	0.00436	0.00599	0.0141	0.0475	0.15	0.568	0.71
Rb	µg/L	11	0	0.71	3.32	9.58	0.83	0.95	1.66	2.94	4.3	4.84	7.21

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
S (total)	mg/L	11	0	7.8	13.6	38.4	8	8.2	8.75	10.9	13.9	18.1	28.2
Sb	µg/L	21	20	<0.04		0.06							
Se	µg/L	15	6	<0.2	0.577	1.2	0.195	0.214	0.323	0.5	0.75	1.02	1.13
Si (as Si)	mg/L	40	0	2.56	6.56	13.6	4.37	4.42	5.19	5.88	7.97	9.45	11.2
Sm	µg/L	11	11	<0.007		<0.007							
Sn	µg/L	21	21	<0.08		<2							
SO ₄	mg/L	36	1	<10	34.3	107	14.9	18	20.1	27.6	40	61.2	80.6
Sr	µg/L	26	0	33.3	159	694	56.5	58.5	79.1	120	170	247	408
Ta	µg/L	11	11	<0.006		<0.006							
Tb	µg/L	11	11	<0.004		<0.004							
TDS	mg/L	11	0	167	400	633	177	186	227	336	570	626	630
Th	µg/L	11	11	<0.03		<0.03							
Ti	µg/L	21	18	<0.07		3							
Tl	µg/L	11	11	<0.03		<0.03							
Tm	µg/L	11	10	<0.003		0.004							
U	µg/L	14	5	<0.009	0.127	0.763	0.0131	0.0163	0.0342	0.0745	0.117	0.21	0.427
V	µg/L	21	10	<0.04	0.688	3.59	0.201	0.276	0.4	0.52	0.63	1.15	1.23
W	µg/L	11	11	<0.06		<0.06							
Y	µg/L	11	3	<0.006	0.0187	0.065	0.00164	0.00209	0.00504	0.009	0.024	0.052	0.0585
Yb	µg/L	11	8	<0.004	0.00506	0.043	5.31E-06	8.50E-06	3.65E-05	0.000208	0.0029 2	0.006	0.0245
Zn	µg/L	27	3	<5	26.5	321	1.26	1.71	2.87	7.16	12.2	70	90.4
Zr	µg/L	11	10	<0.009		0.009							

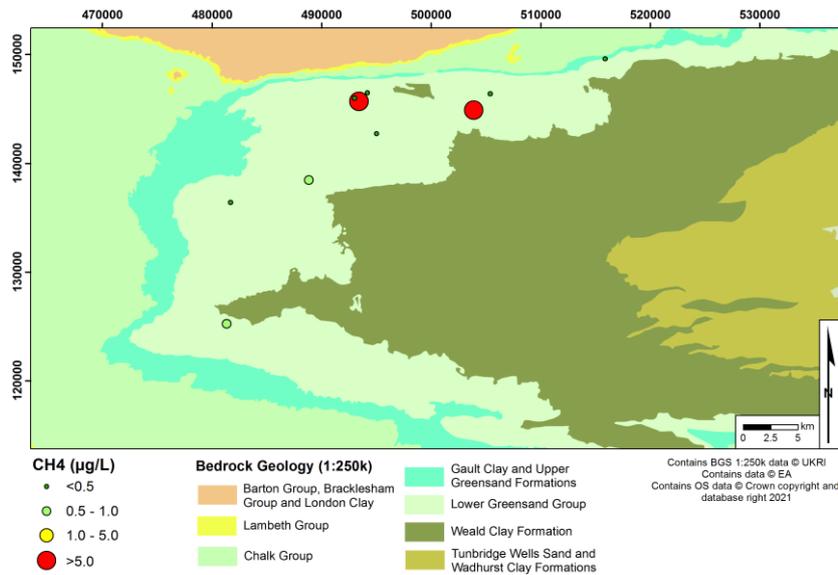
NB: ncens = number censored

4.4 DISSOLVED GASES

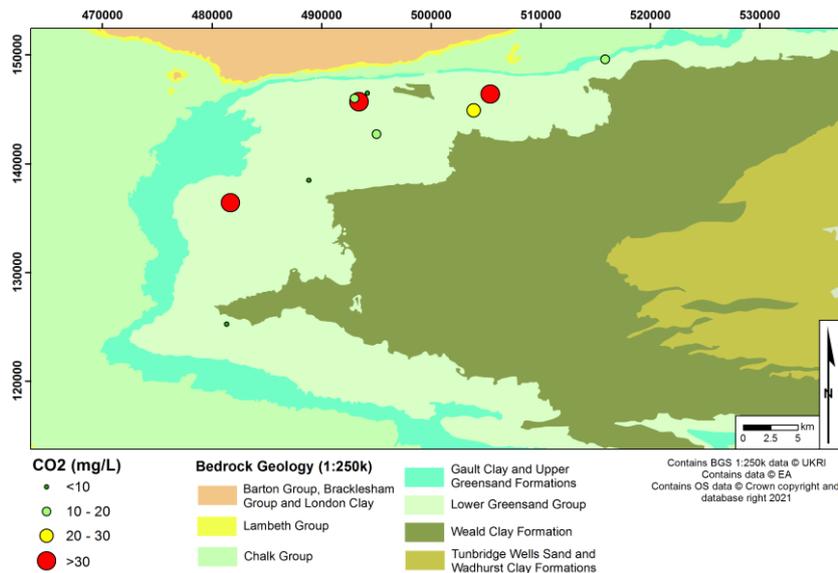
Three dissolved gases have been sampled and analysed for as part of the recent BGS sampling campaign: methane, ethane and CO₂. Although there are limited data, the summary statistics for each are presented in Table 4-2, with detailed descriptions below.

The observed concentration range for methane ranged from 0.1 µg/L to 461 µg/L, with a median of 0.2 µg/L. The 10th to 95th percentile range is 0.1 µg/L to 422 µg/L. There do not appear to be any spatial trends although few data are available for the confined aquifer (Figure 4-14a). Only two samples showed evidence of ethane, with a maximum concentration of 5.1 µg/L. These correlated with the two samples with methane concentrations >300 µg/L.

CO₂ has a concentration range of 5.4 mg/L to 47.1 mg/L, with a median of 17.6 mg/L. The 5th to 95th percentile range is 6.16 mg/l to 42.3 mg/L. CO₂ concentrations appear variable across the aquifer (Figure 4-14b).



(a)



(b)

Figure 4-14. Spatial distribution of selected dissolved gases across the study area: (a) methane and; (b) carbon dioxide.

Table 4-2. Statistical summary data including percentiles (5th–95th) dissolved gases in groundwater from the Lower Greensand aquifer from new samples collected and analysed by BGS.

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
C ₂ H ₆	µg/L	10	8	<1	2.66	5.1	1.37	1.5	1.83	2.39	3.1	4.29	4.69
CH ₄	µg/L	10	0	0.1	83.8	461	0.1	0.1	0.2	0.2	0.9	383	422
CO ₂	mg/L	10	0	5.4	20.6	47.1	6.16	6.93	9.95	17.6	29	37.6	42.3

NB: ncens = number censored

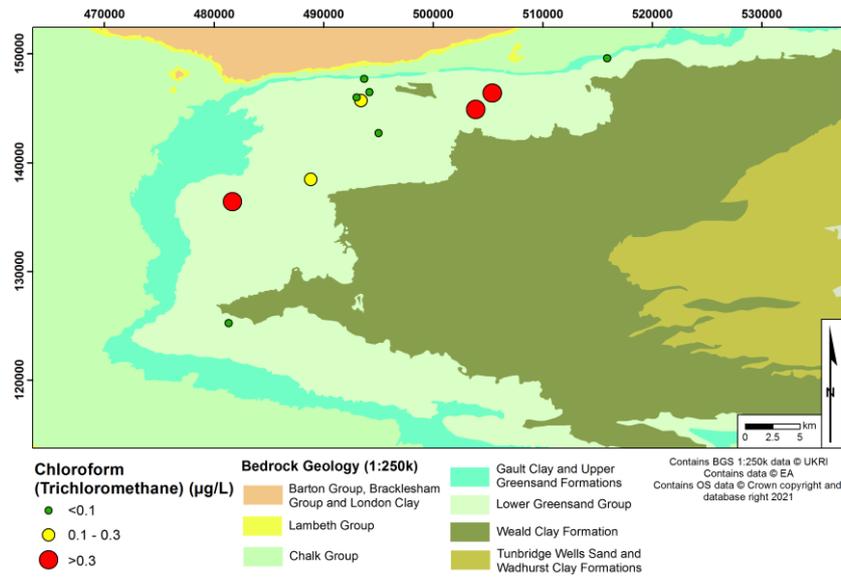
4.5 ORGANIC GEOCHEMISTRY

4.5.1 TPH, volatile/semi-volatile organic carbon and PAH compounds

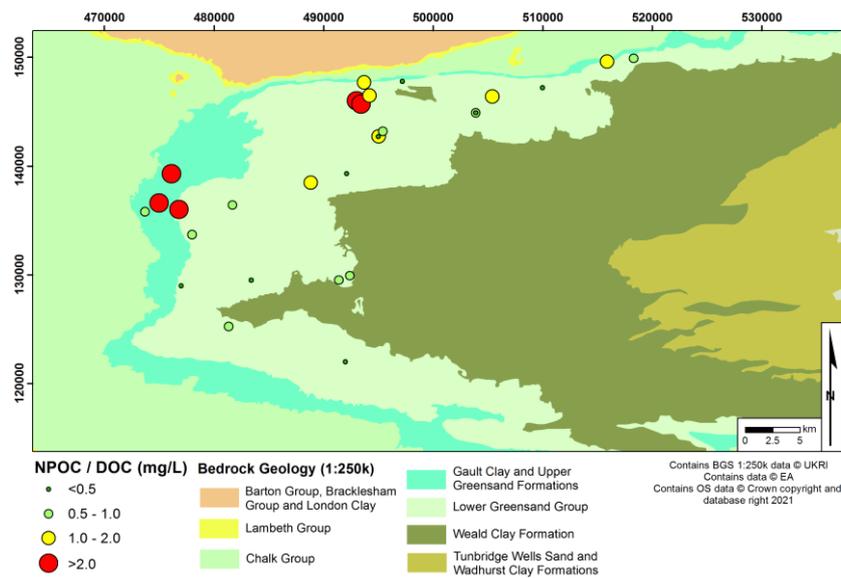
The summary statistics for a number of organic compounds can be seen in Table 4-3. Only one compound, chloroform, had a significant number of detects. The only two other compounds which were detected were trichloroethene and chlorodibromomethane, both only with one detection each (Table 4-3).

Chloroform had a total of 5 detections across the aquifer, with a range from <0.1 µg/L to 0.48 µg/L. The 5th to 95th percentile range is 0.0302 µg/L to 0.457 µg/L. Chloroform appears to be present in isolated locations (Figure 4-15a). The two locations in the north of the study area >0.3 µg/L were both taken from spring sites.

In addition to targeted organic analyses, organic carbon content of the groundwater has been represented in the dataset by combining the NPOC content of samples collected by BGS with the reported Dissolved Organic Carbon (DOC) content of samples reported in the WIMS database. These combined BGS-WIMS organic carbon results show a concentration range of 0.21 mg/L to 5.96 mg/L, with a median of 0.85 mg/L. The 5th to 95th percentile range is 0.22 mg/L to 4.6 mg/L. There appears to be no clear spatial distribution across the aquifer from the few data available (Figure 4-15b), aside from two cluster of higher concentrations (>0.3 mg/L) in the confined western setting, and close to Godalming/Farnham in the North. Total Organic Carbon (TOC) has been omitted as only six samples were selected following the criteria outlined in Section 3.2.



(a)



(b)

Figure 4-15. Spatial distribution of select organic compounds across the study area: (a) chloroform; (b) NPOC/DOC.

Table 4-3. Statistical summary data including percentiles (5th–95th) for organic compounds in groundwater from the Lower Greensand aquifer from the EA WIMS database and new samples collected and analysed by BGS.

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
>C10-C12	µg/L	11	11	<5	NA	<5							
>C12-C16	µg/L	11	11	<10	NA	<10							
>C16-C21	µg/L	11	11	<10	NA	<10							
>C21-C35	µg/L	11	11	<10	NA	<10							
>C5-C6	µg/L	11	11	<10	NA	<10							
>C5-EC7	µg/L	11	11	<10	NA	<10							
>C6-C8	µg/L	11	11	<10	NA	<10							
>C8-C10	µg/L	11	11	<10	NA	<10							
>EC10-EC12	µg/L	11	11	<5	NA	<5							
>EC12-EC16	µg/L	11	11	<10	NA	<10							
>EC16-EC21	µg/L	11	11	<10	NA	<10							
>EC21-EC35	µg/L	11	11	<10	NA	<10							
>EC7-EC8	µg/L	11	11	<10	NA	<10							
>EC8-EC10	µg/L	11	11	<10	NA	<10							
1;1-Dichloroethane	µg/L	11	11	<0.1	NA	<0.1							
1;1-Dichloroethene	µg/L	11	11	<0.1	NA	<0.1							
1;1-Dichloropropene	µg/L	11	11	<0.1	NA	<0.1							
1;1;1-Trichloroethane	µg/L	11	11	<0.1	NA	<0.1							
1;1;1;2-Tetrachloroethane	µg/L	11	11	<0.1	NA	<0.1							
1;1;2-Trichloroethane	µg/L	11	11	<0.1	NA	<0.1							
1;1;2;2-Tetrachloroethane	µg/L	11	11	<0.1	NA	<0.1							
1;2-Dibromo-3-chloropropane	µg/L	11	11	<0.1	NA	<0.1							
1;2-Dibromoethane	µg/L	11	11	<0.1	NA	<0.1							
1;2-Dichlorobenzene	µg/L	22	22	<0.1	NA	<1							
1;2-Dichloroethane	µg/L	11	11	<0.1	NA	<0.1							
1;2-Dichloropropane	µg/L	11	11	<0.1	NA	<0.1							
1;2-Dimethylbenzene (o-Xylene)	µg/L	22	22	<0.1	NA	<5							
1;2;3-Trichlorobenzene	µg/L	11	11	<0.1	NA	<0.5							
1;2;3-Trichloropropane	µg/L	11	11	<0.1	NA	<0.5							
1;2;3-Trimethylbenzene	µg/L	11	11	<0.1	NA	<0.1							
1;2;4-Trichlorobenzene	µg/L	22	22	<0.1	NA	<1							
1;2;4-Trimethylbenzene	µg/L	11	11	<0.1	NA	<0.1							
1;3-Dichlorobenzene	µg/L	22	22	<0.1	NA	<1							

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
1,3-Dichloropropane	µg/L	11	11	<0.1	NA	<0.1							
1,3,5-Trichlorobenzene	µg/L	11	11	<0.1	NA	<0.1							
1,3,5-Trimethylbenzene (Mesitylene)	µg/L	11	11	<0.1	NA	<0.1							
1,4-Dichlorobenzene	µg/L	22	22	<0.1	NA	<1							
2-Chloronaphthalene	µg/L	11	11	<1	NA	<1							
2-Chlorophenol	µg/L	11	11	<1	NA	<1							
2-Chlorotoluene (1-Chloro-2-methylbenzene)	µg/L	11	11	<0.1	NA	<0.1							
2-Methylnaphthalene	µg/L	11	11	<1	NA	<1							
2-Methylphenol	µg/L	11	11	<0.5	NA	<0.5							
2-Nitroaniline	µg/L	11	11	<1	NA	<1							
2-Nitrophenol	µg/L	11	11	<0.5	NA	<0.5							
2,2-Dichloropropane	µg/L	11	11	<0.1	NA	<0.1							
2,4-Dichlorophenol	µg/L	11	11	<0.5	NA	<0.5							
2,4-Dimethylphenol	µg/L	11	11	<1	NA	<1							
2,4-Dinitrotoluene	µg/L	11	11	<0.5	NA	<0.5							
2,4,5-Trichlorophenol	µg/L	11	11	<0.5	NA	<0.5							
2,4,6-Trichlorophenol	µg/L	11	11	<1	NA	<1							
2,6-Dinitrotoluene	µg/L	11	11	<1	NA	<1							
3-Chlorotoluene(1-Chloro-3-methylbenzene)	µg/L	11	11	<0.1	NA	<0.1							
3-Nitroaniline	µg/L	11	11	<1	NA	<1							
4-Bromophenylphenylether	µg/L	11	11	<1	NA	<1							
4-Chloro-3-methylphenol	µg/L	11	11	<0.5	NA	<0.5							
4-Chloroaniline	µg/L	11	11	<1	NA	<1							
4-Chlorophenylphenylether	µg/L	11	11	<1	NA	<1							
4-Chlorotoluene(1-Chloro-4-methylbenzene)	µg/L	11	11	<0.1	NA	<0.1							
4-Isopropyltoluene (4-methyl-Isopropylbenzene)	µg/L	11	11	<0.1	NA	<0.1							
4-Methylphenol	µg/L	11	11	<1	NA	<1							
4-Nitroaniline	µg/L	11	11	<0.5	NA	<0.5							
4-Nitrophenol	µg/L	11	11	<10	NA	<10							
Acenaphthene	µg/L	31	31	<0.01	NA	<1							
Acenaphthylene	µg/L	35	35	<0.01	NA	<0.5							
Anthracene	µg/L	22	22	<0.01	NA	<0.5							
Azobenzene	µg/L	11	11	<0.5	NA	<0.5							

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
Benzene	µg/L	36	36	<0.02	NA	<5							
Benzo(a)anthracene	µg/L	22	22	<0.01	NA	<0.5							
Benzo(a)pyrene	µg/L	26	26	<0.00022	NA	<0.01							
Benzo(b)fluoranthene	µg/L	26	26	<0.00052	NA	<0.01							
Benzo(b.k)fluoranthene	µg/L	11	11	<1	NA	<1							
Benzo(e)pyrene	µg/L	18	18	<0.01	NA	<0.01							
Benzo(g;h;i)perylene	µg/L	37	37	<4e-04	NA	<0.5							
Benzo(k)fluoranthene	µg/L	26	26	<0.00047	NA	<0.01							
Bis(2-chloroethoxy)methane	µg/L	11	11	<0.5	NA	<0.5							
Bis(2-chloroethyl)ether	µg/L	11	11	<1	NA	<1							
Bis(2-ethylhexyl) phthalate	µg/L	11	11	<5	NA	<5							
Bromobenzene	µg/L	11	11	<0.1	NA	<0.1							
Bromochloromethane	µg/L	11	11	<0.1	NA	<0.1							
Bromodichloromethane	µg/L	11	11	<0.1	NA	<0.1							
Bromoform (Tribromomethane)	µg/L	11	11	<0.1	NA	<0.1							
Butylbenzyl phthalate	µg/L	11	11	<1	NA	<1							
Carbazole	µg/L	11	11	<0.5	NA	<0.5							
Carbon Disulphide	µg/L	11	11	<0.1	NA	<0.1							
Carbon tetrachloride (Tetrachloromethane)	µg/L	11	11	<0.1	NA	<0.1							
Chlorobenzene	µg/L	11	11	<0.1	NA	<0.1							
Chlorodibromomethane	µg/L	11	10	<0.1	NA	0.1							
Chloroform(Trichloromethane)	µg/L	11	6	<0.1	0.188	0.48	0.0302	0.0368	0.0585	0.0966	0.308	0.435	0.457
Chloromethane(Methyl Chloride)	µg/L	11	11	<0.1	NA	<0.5							
Chrysene	µg/L	22	22	<0.01	NA	<0.5							
cis-1;2-Dichloroethylene(cis-1;2-Dichloroethene)	µg/L	11	11	<0.1	NA	<0.1							
cis-1;3-Dichloropropylene(cis-1;3-Dichloropropene)	µg/L	11	11	<0.1	NA	<0.1							
Di-n-butyl phthalate	µg/L	11	11	<1.5	NA	<1.5							
Di-n-Octyl phthalate	µg/L	11	11	<1	NA	<1							
Dibenzo(a;h)anthracene	µg/L	35	35	<0.01	NA	<0.5							
Dibenzofuran	µg/L	11	11	<0.5	NA	<0.5							
Dibromomethane	µg/L	11	11	<0.1	NA	<0.5							
Dichloromethane (Methylene Dichloride)	µg/L	11	11	<0.2	NA	<0.5							
Diethyl phthalate	µg/L	11	11	<1	NA	<1							
Dimethyl phthalate	µg/L	11	11	<1	NA	<1							

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
Dimethylbenzene: Sum of isomers (1;3-1;4-) (m+p xylene)	µg/L	23	23	<0.1	NA	<0.2							
Ethyl tert-butyl ether (ETBE)	µg/L	11	11	<0.1	NA	<0.1							
Ethylbenzene	µg/L	34	34	<0.1	NA	<5							
Fluoranthene	µg/L	37	37	<0.00084	NA	<0.5							
Fluorene	µg/L	35	35	<0.01	NA	<0.5							
Hexachlorobenzene	µg/L	18	18	<0.001	NA	<1							
Hexachlorobutadiene	µg/L	22	22	<0.1	NA	<1							
Hexachlorocyclopentadiene	µg/L	11	11	<1	NA	<1							
Hexachloroethane	µg/L	22	22	<0.1	NA	<1							
Indeno(1;2;3-cd)pyrene	µg/L	11	11	<0.01	NA	<0.01							
Isophorone	µg/L	11	11	<0.5	NA	<0.5							
Isopropylbenzene	µg/L	11	11	<0.1	NA	<0.1							
m/p-Xylene	µg/L	11	11	<5	NA	<5							
MTBE (Methyl tert-butyl ether)	µg/L	33	33	<0.1	NA	<5							
n-ButylBenzene(1-Phenylbutane)	µg/L	11	11	<0.1	NA	<0.1							
N-nitrosodi-n-propylamine	µg/L	11	11	<0.5	NA	<0.5							
n-Propylbenzene (1-phenylpropane)	µg/L	11	11	<0.1	NA	<0.1							
Naphthalene	µg/L	35	35	<0.01	NA	<1							
Nitrobenzene	µg/L	11	11	<1	NA	<1							
NPOC	mg/L	29	0	0.21	1.32	5.96	0.22	0.236	0.35	0.85	1.48	3.46	4.6
Pentachlorophenol	µg/L	11	11	<1	NA	<1							
Perylene	µg/L	18	18	<0.01	NA	<0.01							
Phenanthrene	µg/L	35	35	<0.01	NA	<0.5							
Phenol	µg/L	11	11	<1	NA	<1							
Pyrene	µg/L	35	35	<0.01	NA	<0.5							
sec-Butylbenzene(1-Methylpropylbenzene)	µg/L	11	11	<0.1	NA	<0.1							
Styrene (Vinylbenzene)	µg/L	11	11	<0.1	NA	<0.1							
tert-Amyl methyl ether	µg/L	11	11	<0.1	NA	<0.1							
tert-Butylbenzene (1;1-Dimethylethyl)benzene)	µg/L	11	11	<0.1	NA	<0.1							
Tetrachloroethylene (Perchloroethylene)	µg/L	11	11	<0.1	NA	<0.1							
TOC	µg/L	6	1	<1	0.774	1.21	0.6	0.6	0.623	0.697	0.805	1.02	1.12
Toluene (Methylbenzene)	µg/L	34	34	<0.1	NA	<5							
Total aliphatics and aromatics (C5-35)	µg/L	11	11	<10	NA	<10							
Total aliphatics C5-35	µg/L	11	11	<10	NA	<10							

Analyte	Units	n	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
Total aromatics C5-35	µg/L	11	11	<10	NA	<10							
trans-1;2-Dichloroethylene (trans-1;2-Dichloroethene)	µg/L	11	11	<0.1	NA	<0.5							
trans-1;3-Dichloropropylene (trans-1;3-Dichloropropene)	µg/L	11	11	<0.5	NA	<10							
Trichloroethylene (Trichloroethene)	µg/L	11	10	<0.1	NA	0.2							
Trichlorofluoromethane	µg/L	11	11	<0.1	NA	<0.1							
Vinyl chloride (Chloroethylene)	µg/L	11	11	<0.1	NA	<0.1							

NB: ncens = number censored

NB: NPOC analysis by BGS and WIMS DOC analysis are combined and reported as NPOC in the table.

5 Geochemical controls

The chemical compositions of groundwater in the Lower Greensand formations show many of the features identified in previous studies of the Weald aquifers, including presence of acidic water in some areas, redox-induced downgradient chemical changes and influences of nitrate pollution in some unconfined aquifer sections. However, it has not been possible to identify specific aquifer sources for given sites (Hythe/Folkestone/Sandgate) or compare data from the current study with those from previous works (e.g. Shand et al., 2003) as WIMS data were supplied in location-anonymised form. This account therefore necessarily presents only a generalised overview of the geochemical variations in the groundwaters.

5.1 INORGANIC GEOCHEMISTRY

5.1.1 Recharge and anthropogenic inputs

Rainfall chemistry and inferred recharge inputs are outlined in section 2.5 and Table 2-3 & Table 2-4. Infiltrating rainfall provides notable inputs of Na, Cl and NO₃ into the aquifer, but measured concentrations across the aquifer indicate additional sources. Estimated atmospheric inputs of NO₃ in recharge are in the region of 10 mg/L (Table 2-3 and Table 2-4), whilst average (median) concentrations across the aquifer are 22.5 mg/L, over twice as great. NO₃ concentrations are typically greater in the northern half of the study area (Figure 4-2h). NO₃ concentrations are likely elevated (greater than estimated recharge inputs) due to local agricultural activity and diffuse inputs into the aquifer. Nitrate (NO₃) concentrations also appear to be lower in NVZs (Figure 4-3), but are also typically less than 50 mg/L (the drinking-water standard) in areas not covered by these designated zones.

Alongside NO₃, a number of ions also show a marked increase in concentration compared to likely recharge compositions, including Na (2.5x greater in the aquifer), Cl (2.7x greater), and SO₄ (12x greater). Such increases could also suggest possible anthropogenic sources, especially for Cl, although water-rock interaction is also a likely factor.

Concentrations of halogens (F, Br, I) are low across the aquifer, and are likely derived from atmospheric inputs. The range of concentrations observed in this study correlates with those recorded by Shand et al. (2003). Fluoride can be seen to increase in concentration moving away from the centre of the study area, which may indicate some minor dissolution of F-bearing minerals such as apatite.

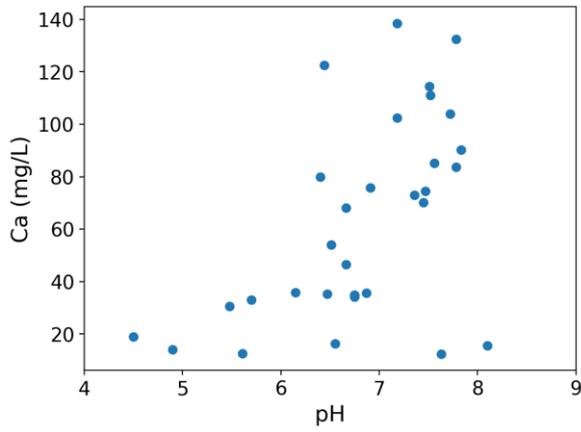
5.1.2 Water-rock interaction

The water in the Lower Greensand aquifer from the study area is fresh, with SEC values <1000 μS/cm, and a median of 443 μS/cm. The dominant water chemistry types in the Lower Greensand aquifer are Ca-HCO₃ and mixed Ca-Cl-SO₄ types (Figure 4-4). Shand et al. (2003) identified Na-HCO₃ groundwater compositions, although that study included samples from the deeper confined aquifer (e.g. Slough), which are not represented in the current study.

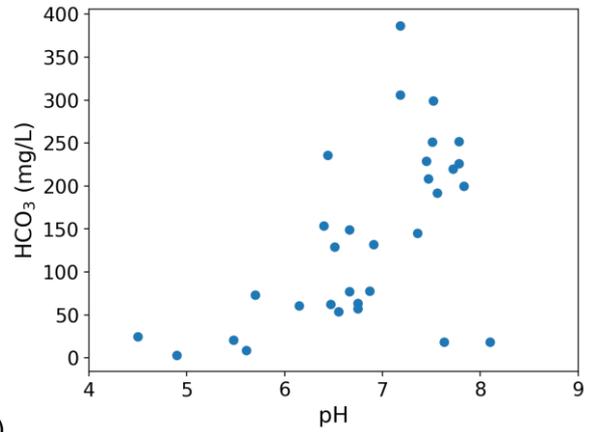
As recharge is typically acidic (pH <6), and with limited carbonate mineral content in the unconfined greensand and superficial cover to buffer groundwater pH (Sections 2.2.1 & 2.3), the aquifer is at increased risk of mobilisation of contaminants, especially metals (Morgan-Jones, 1985; Shand et al., 2003).

Within this investigation, the range in observed pH values in the groundwater is consistent with sporadic occurrence of calcite in the greensand and higher pH values coincide with higher concentrations of Ca, HCO₃ and Sr (Figure 5-1a, b & c), as well as increased SEC. Groundwater with neutral to alkaline pH values (>7) is typically saturated with respect to calcite. Both Mg and K can be seen to be greatest at lower pH values, generally decreasing with increasing pH (Figure 5-1d & e). For other ions (Na, Al, As, Mn, Fe, Si), there are no clear correlations with pH (Figure 5-1f to i). Higher concentrations of a number of these ions at lower pH values may be attributed to dissolution of silicate minerals such as clays (micas etc) and feldspars under acidic conditions

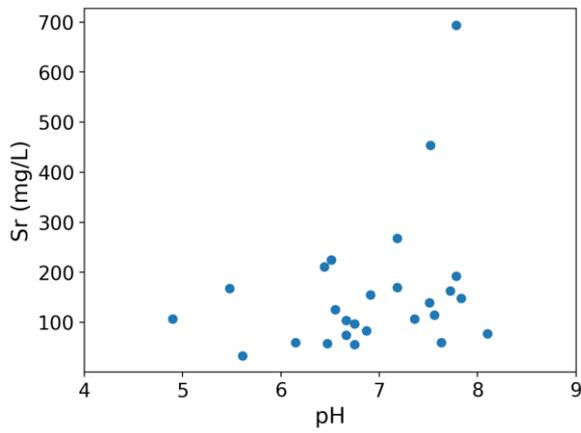
(silicate hydrolysis). Shand et al. (2003) did find increased concentrations of a number of major and minor ions (e.g. Mg, Ca, K, Si, Al, Mn, Pb) in acidic porewaters from the unsaturated zone in the study area.



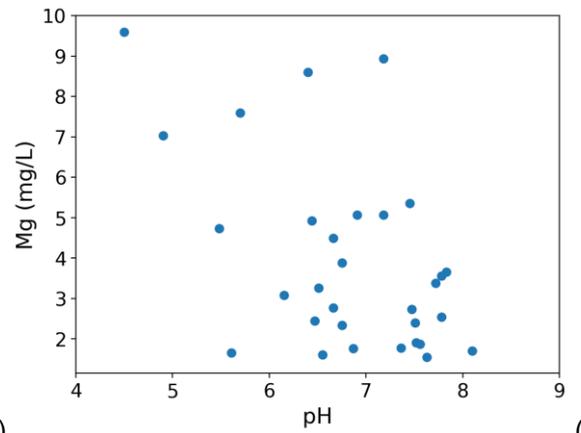
(a)



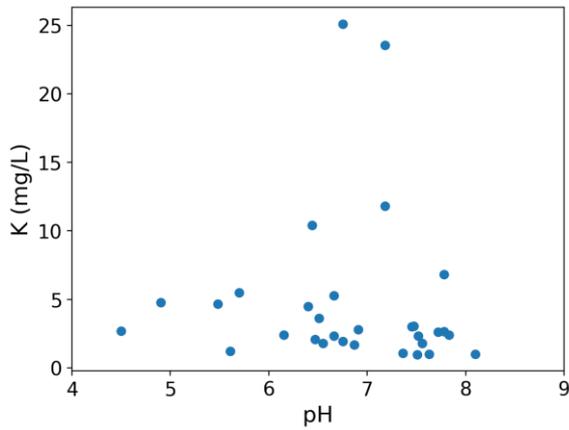
(b)



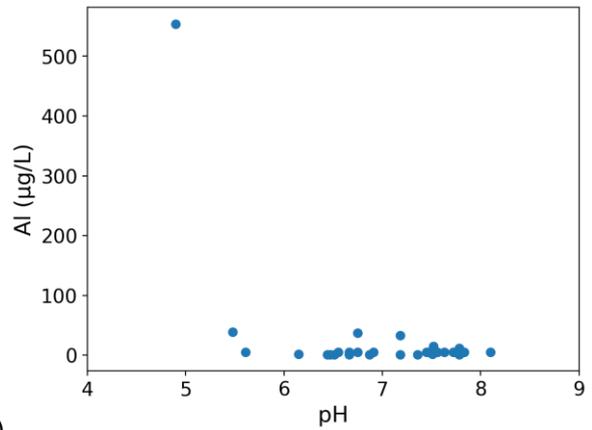
(c)



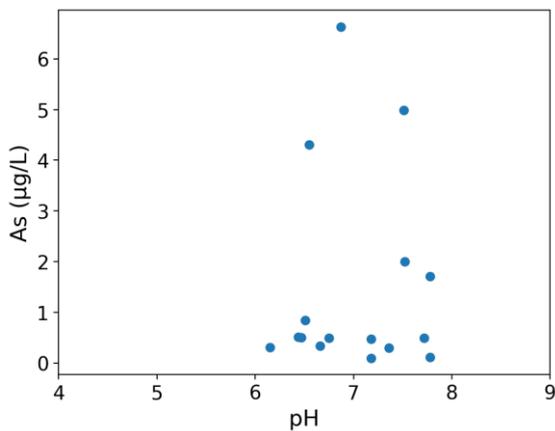
(d)



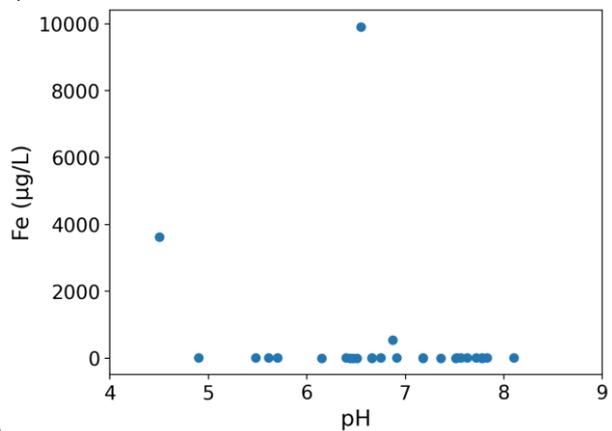
(e)



(f)



(g)



(h)

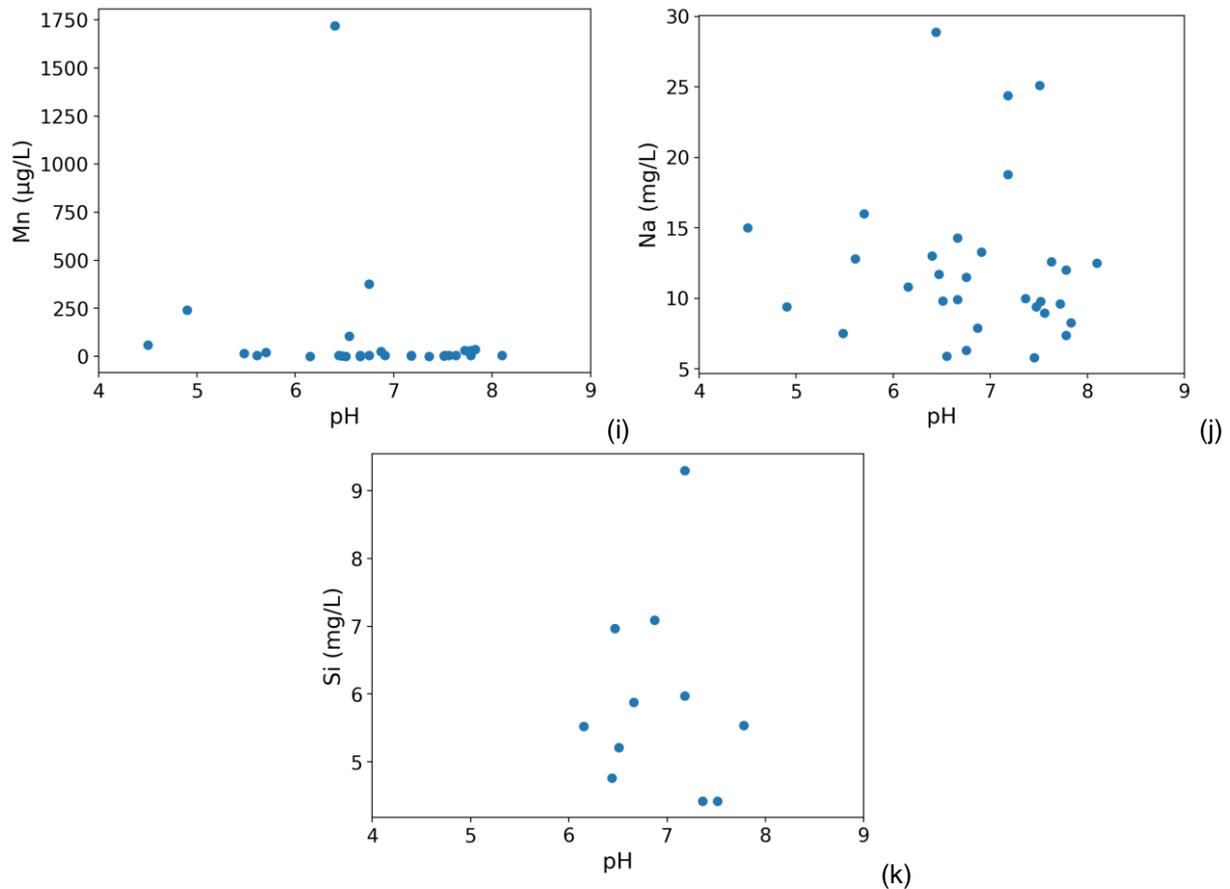


Figure 5-1. Selected ions compared to their associated pH values; (a) calcium; (b) bicarbonate; (c) strontium; (d) magnesium; (e) potassium; (f) aluminium; (g) arsenic; (h) iron; (i) manganese; (j) sodium; (k) silicon.

It is difficult to assess the differences in conditions between the confined and unconfined aquifer, as few samples from the confined Lower Greensand were available for this study. In an attempt to determine whether an assessment could be made on the impact of confining conditions, samples were differentiated based on their location with respect to BGS 1:50k geology (Figure 5-2). Only Ca and HCO_3 showed any clear indication of the impact that confinement has on the hydrogeochemistry – other ions did not show a clear relationship, especially with redox condition indicator species (Section 5.1.3), so further distinction has not been carried out. It can be seen that confined samples typically have a pH above 6.5, and follow the trend of increasing Ca and HCO_3 concentrations with increasing pH. Unconfined samples show evidence of a range of pH values, but include samples notably more acidic than those in the confined setting, as a result of acidic rainfall infiltration. More alkaline samples will likely be those which have longer residence times, and may be trending towards confining conditions.

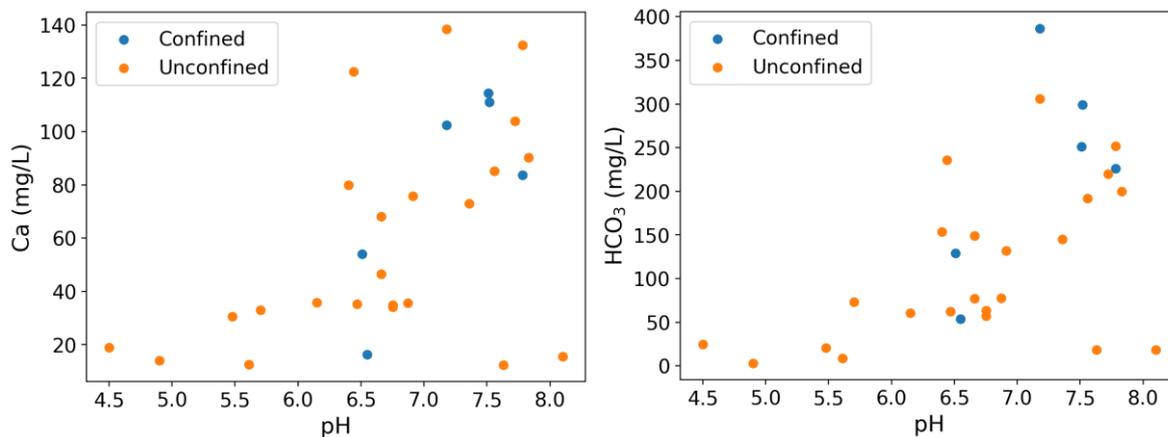


Figure 5-2. Plots of Ca (left) and HCO₃ (right) against pH for EA WIMS and BGS collected samples. Samples have been distinguished based on their hydrogeological setting (confined or unconfined).

Shand et al. (2003) determined that with increasing confinement and residence time, ion-exchange reactions took place, increasing the concentration of sodium relative to calcium. The same trends have not been observed during this study, due to the reduced scope of the study area in comparison to that covered by Shand et al. (2003). Na/Ca molar ratios range from 0.88 to 0.072, with a median of 0.17. The relationship between Na and Ca concentrations (in milliequivalents) is shown in Figure 5-3, whilst spatial variation of the Na/Ca molar ratio is shown in Figure 5-4. With distance away from the Weald Clay (down the flow path), the molar ratio of Na/Ca can be seen to decrease away from an elevated high of >0.75, to 0.25 or less in the north. Ca concentrations can be seen to increase towards the north away from the Weald Clay boundary (Figure 4-2a), indicating that dissolution of Ca bearing minerals is occurring rather than ion-exchange, which would be represented by an increase in Na concentrations relative to Ca. The higher ratios at the boundary with the Weald Clay are likely recharge controlled, owing to the relatively high inputs of Na from rainfall (Table 2-3 & Table 2-4). Such ion-exchange reactions are only likely to take place much further to the north away from the study area (near Slough), in the deep confined Lower Greensand aquifer.

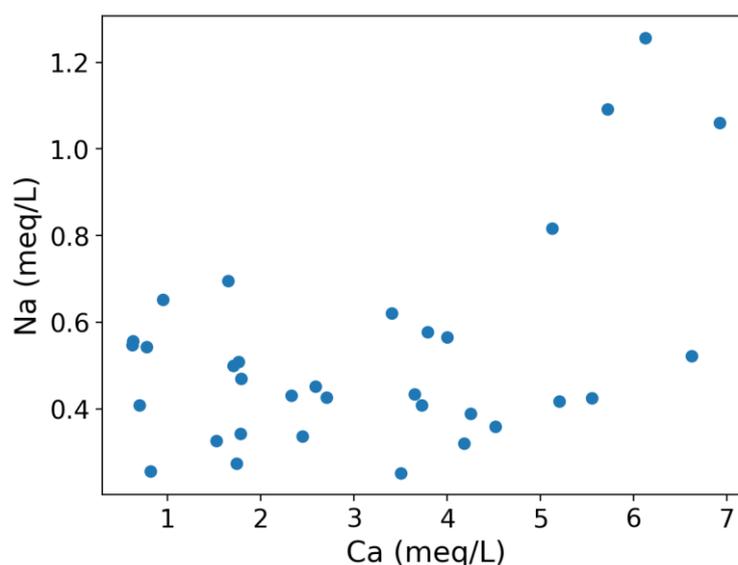


Figure 5-3. Plot of sodium against calcium (in meq/L) for groundwater in the study area

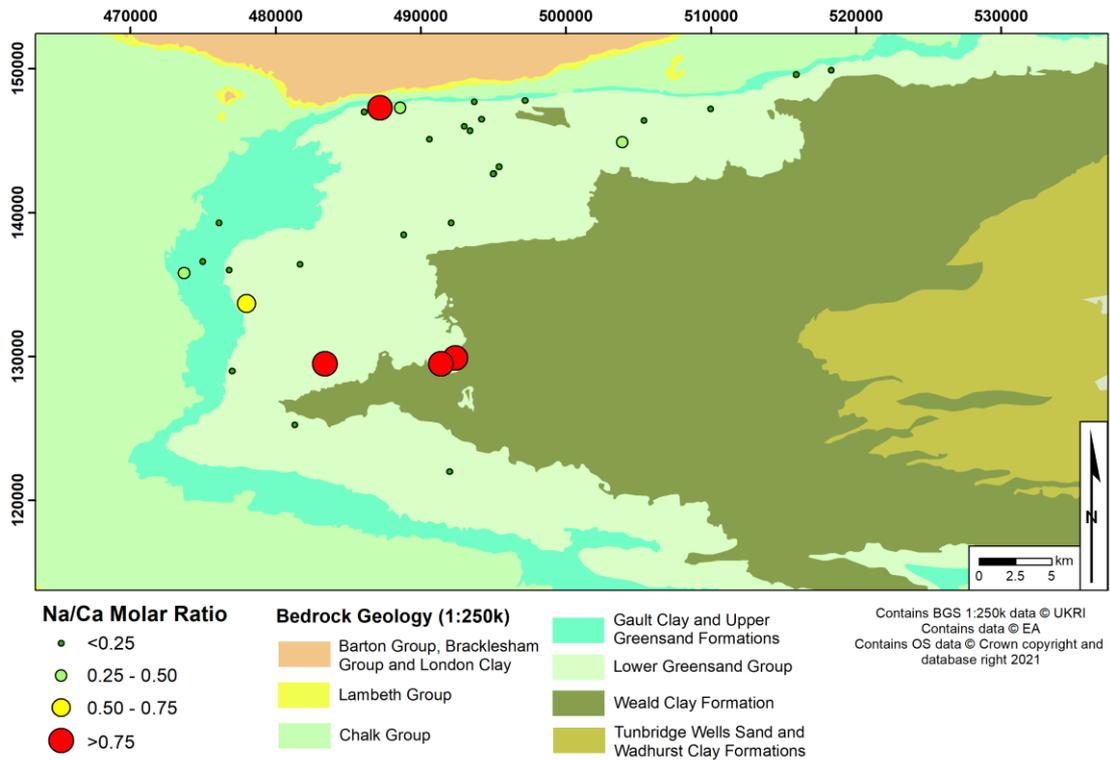
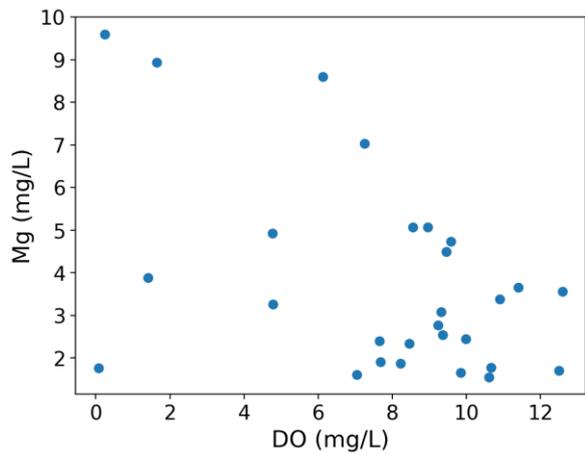


Figure 5-4. Spatial distribution of Na/Ca molar ratios across the study area

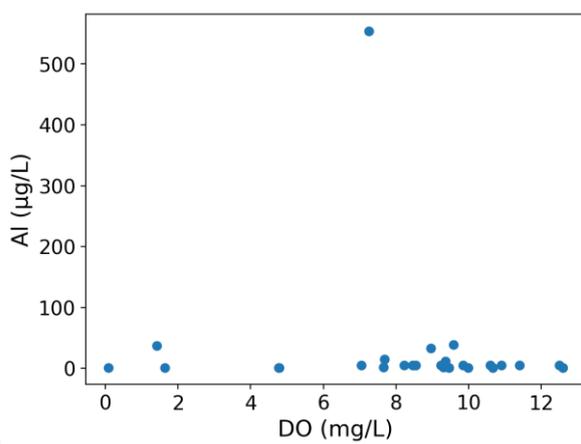
5.1.3 Changes downgradient

Although much of the Lower Greensand aquifer can be seen to be relatively fresh (SEC $<1000 \mu\text{S}/\text{cm}$), observations by Shand et al. (2003) identified that the geochemistry of the Lower Greensand aquifer changes along the flow path, as it becomes progressively confined. It was noted that water became more reducing with confinement (Eh and DO decreasing). The field data collected as part of this study (from both BGS and WIMS data sources) are insufficient to demonstrate a clear declining trend away from the boundary with the Weald Clay. There are no Eh records for the fully confined Lower Greensand aquifer within the WIMS and BGS dataset, whilst DO shows evidence of only a slight decrease ($>10 \text{ mg}/\text{L}$ to between $5 \text{ mg}/\text{L}$ and $10 \text{ mg}/\text{L}$). This slight decrease indicates a change towards sub-oxic conditions down the flow path.

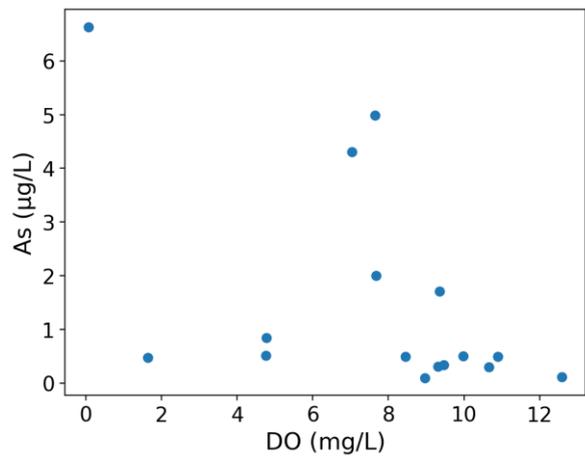
Within this study, only Mg shows a negative correlation with DO, with concentrations increasing as DO decreases (Figure 5-5a). Trends are less clear or well defined for a number of other ions (Figure 5-5). Nitrate concentrations show some positive correlation with DO (Figure 5-5i), likely correlated with anthropogenic inputs of nitrate in recent recharge to the unconfined, oxic portion of the Lower Greensand aquifer. However, as indicated in the previous section, there are only a few locations representative of the confined Lower Greensand setting, so the trends of Shand et al. (2003) are not reproduced to the same extent in this study.



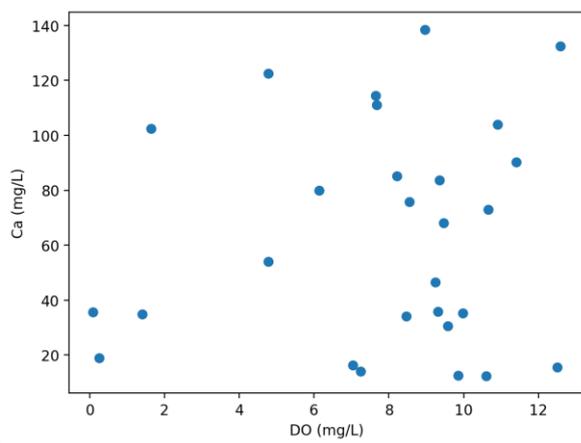
(a)



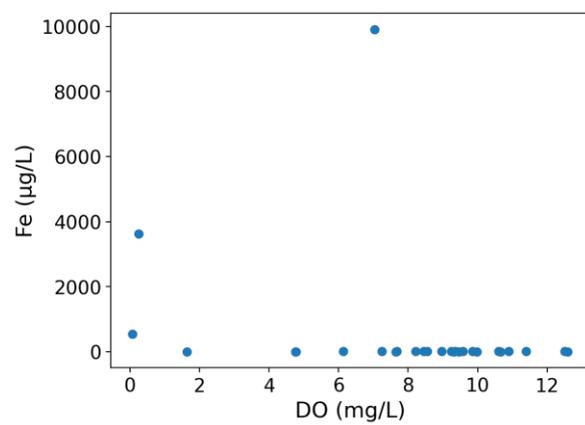
(b)



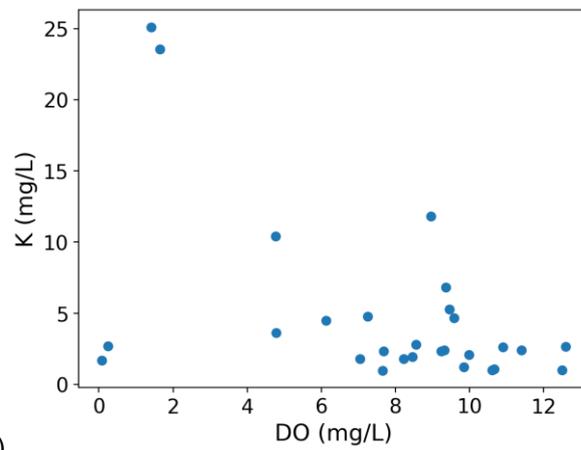
(c)



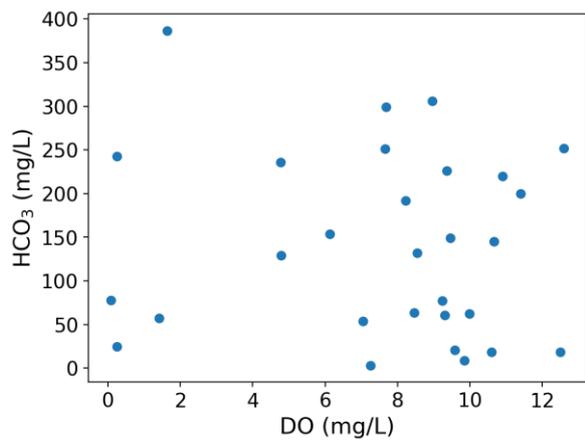
(d)



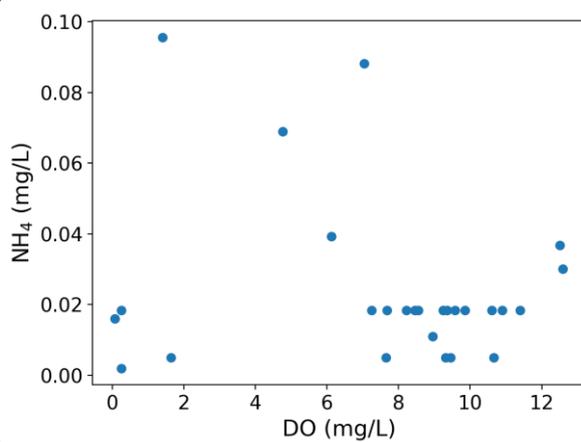
(e)



(f)



(g)



(h)

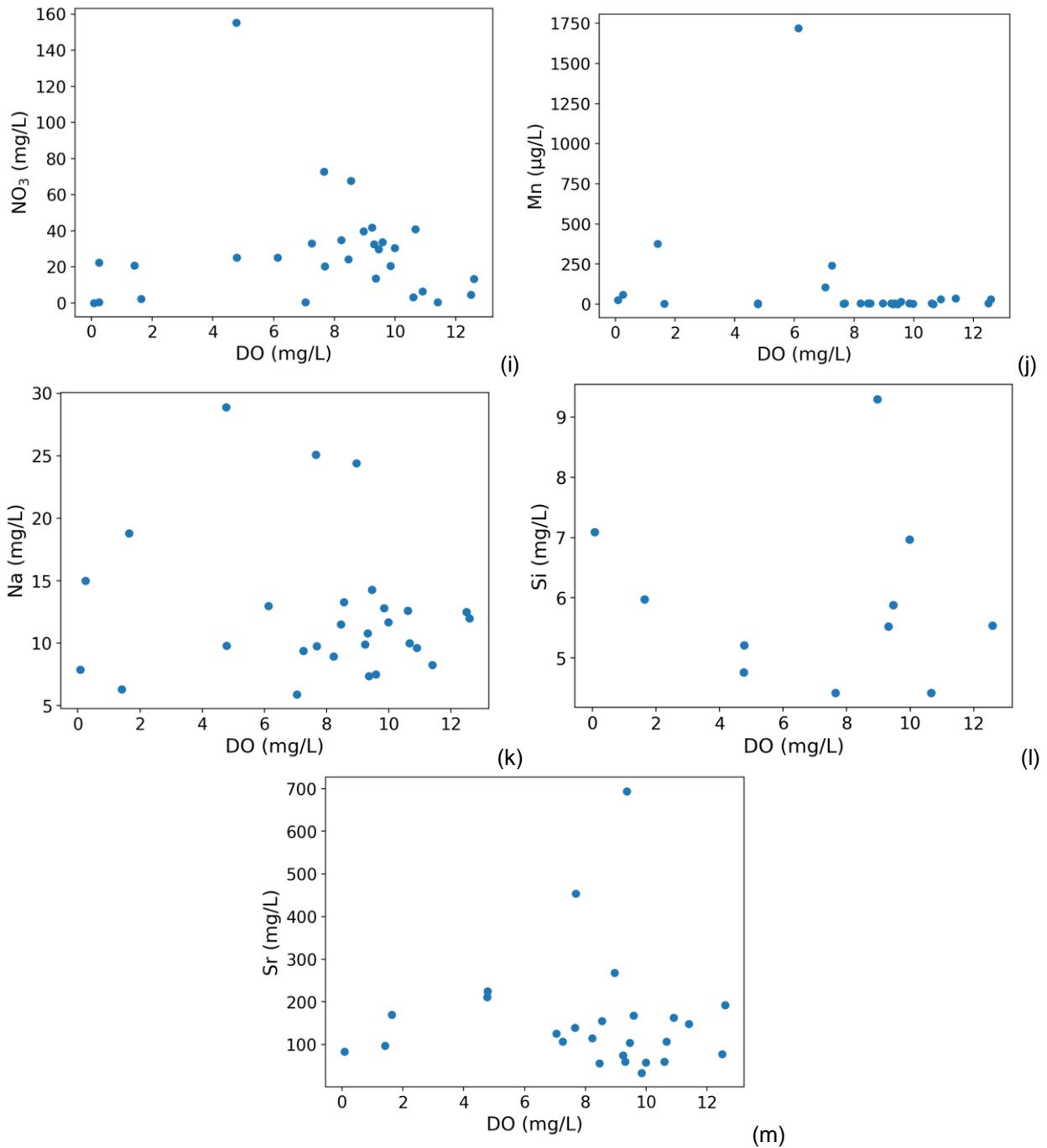


Figure 5-5. Plots of selected ions against their associated dissolved oxygen results; (a) magnesium; (b) aluminium; (c) arsenic; (d) calcium; (e) iron; (f) potassium; (g) bicarbonate; (h) ammonium; (i) nitrate; (j) manganese; (k) sodium; (l) silicon; (m) strontium

A number of dissolved ions can be seen to increase along the regional flow path from the centre of the study area, to the north and west. Both alkalinity and calcium increase progressively towards the north of the study area and in the confined setting towards the west (Figure 4-2a & Figure 4-2f). This further highlights the progressive dissolution of the limited calcite present within the Lower Greensand aquifer along the regional flow path. Other major ions which increase towards the north and towards the confined setting are Cl, K, and SO₄. Minor ions which show an increase in concentration towards the north and west include Sr, F, Al, As, Mn, Cu and Ni. These highlight the dissolution of both silicate and heavy minerals, with increasing residence time across the aquifer. Phosphorus (reactive) can be seen to increase away from the centre of the study area as well (Figure 4-7a), likely derived from phosphatic nodules and grains within the Lower Greensand aquifer (Shand et al., 2003). Fe and Mn both show signs of minor increases in concentration into the confined setting, which may be the result of reductive dissolution of the

glauconite, iron-rich precipitates and heavy minerals. The data are limited by the relatively high detection limits recorded from the WIMS database (Table 5-1).

Table 5-1. Select examples of the different detection limits for BGS analysed samples and those held within the EA WIMS database

Analyte	BGS field sampling	EA WIMS dataset
Li	<7 µg/L	<100 µg/L
Al	<2 µg/L	<10 µg/L
As	<0.1 µg/L	<1 µg/L
NH ₄	<0.01 mg/L	<0.03678 mg/L

5.1.4 Temporal variation

Time-series groundwater chemistry data extracted from WIMS, show that few sites have been monitored from the confined sections of the Lower Greensand aquifer in the study area. Figure 5-6 to Figure 5-8 shows a selection of data from selected sites as indicative of temporal variation in the unconfined sections.

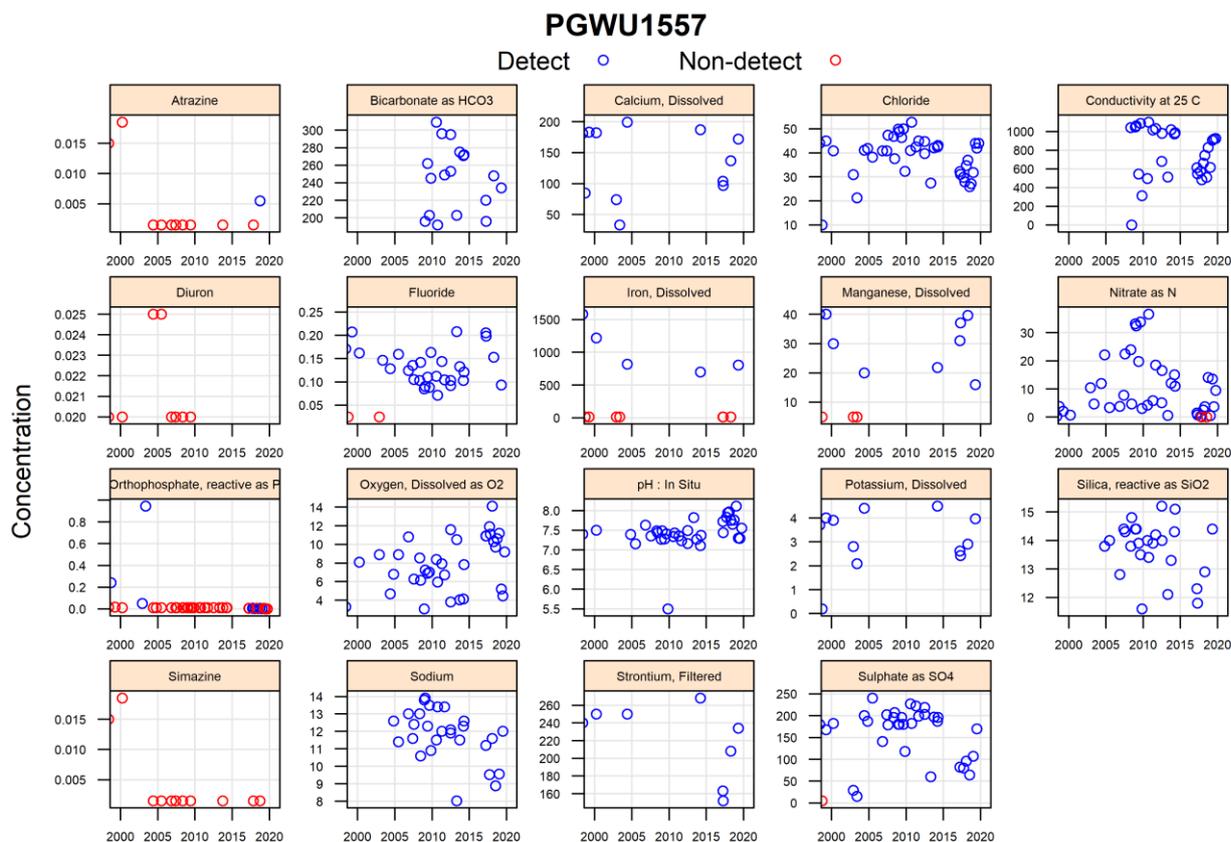


Figure 5-6. Temporal variation in selected analytes in groundwater samples from indicative site PGWU1557 from the Lower Greensand aquifer, EA-WIMS data (Ca, Mg, Na, K, nitrate, bicarbonate, SiO₂, SO₄, F, DO, P as mg/L; trace elements, organics as µg/L, SEC as µS/cm)

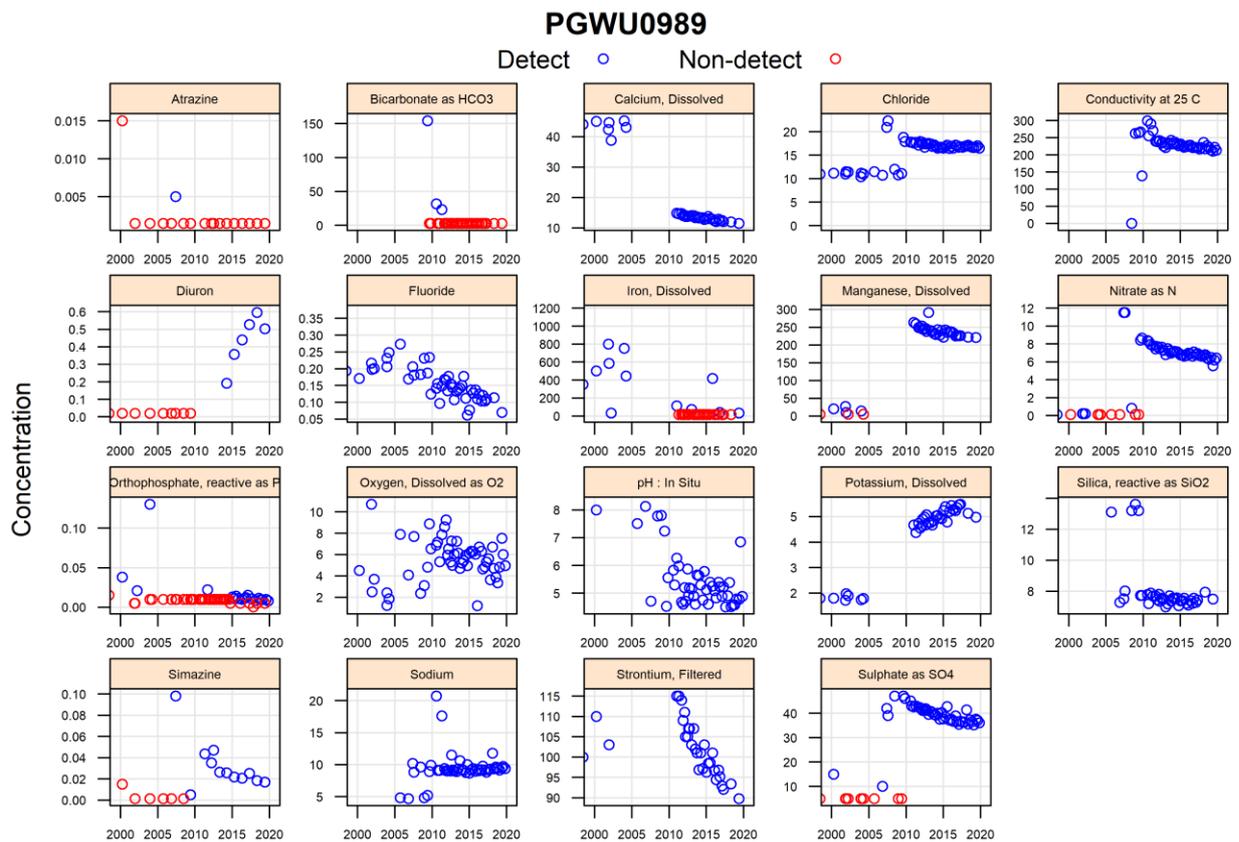


Figure 5-7. Temporal variation in selected analytes in groundwater samples from indicative site PGWU0989 from the Lower Greensand aquifer, EA-WIMS data (Ca, Mg, Na, K, nitrate, bicarbonate, SiO₂, SO₄, F, DO, P as mg/L; trace elements, organics as µg/L, SEC as µS/cm)

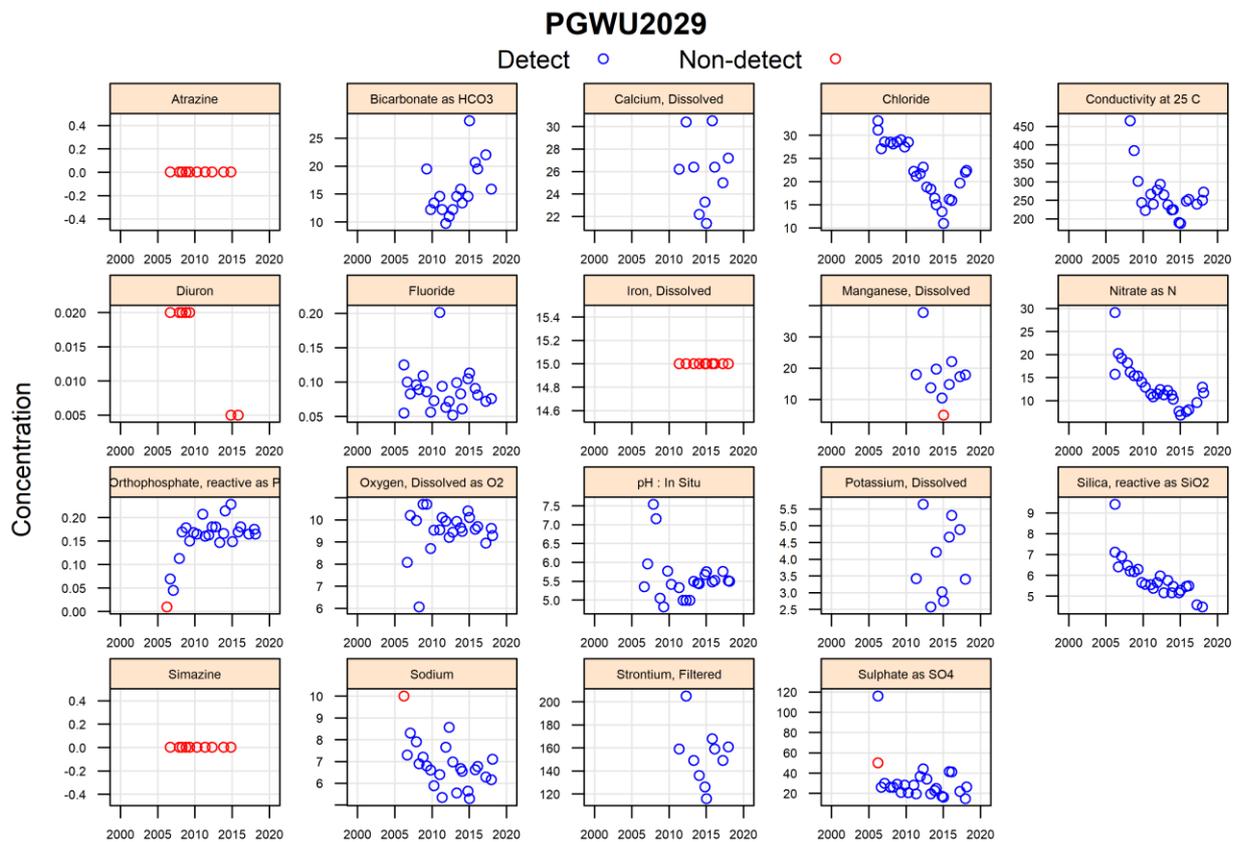


Figure 5-8. Temporal variation in selected analytes in groundwater samples from indicative site PGWU2029 from the Lower Greensand aquifer, EA-WIMS data (Ca, Mg, Na, K, nitrate, bicarbonate, SiO₂, SO₄, F, DO, P as mg/L; trace elements, organics as µg/L, SEC as µS/cm)

Site PGWU1557 is also a pH-neutral Ca-HCO₃ water with a relatively high concentration of dissolved SO₄ (Figure 5-6). The groundwater is oxic with consistently high concentrations of nitrate.

Site PGWU0989 shows a trend towards decreasing pH (8 to <5) over the 20 years of monitoring (Figure 5-7). Low alkalinity (as HCO₃), low and reducing concentrations of Ca and Sr, and low SEC suggest declining influence of carbonate mineral reaction, consistent with the development of acidic conditions. Increase in K concentrations may reflect acid dissolution of K-bearing minerals such as clays. Groundwater has been consistently oxic over the period. A possible step change in compositions appears to have occurred in around 2007 at the site, for reasons which are unclear. Appearance of the herbicides diuron and simazine after this time suggest agricultural/urban pollution, although concentrations of NO₃ and SO₄ declined slightly over the same time period, pointing to complexities in sources and processes.

Site PGWU2029 also has groundwater which has become increasingly acidic over time (7.5 to 5.5); concentrations of Ca and HCO₃ are low and concentrations of Cl, NO₃, SiO₂, Sr and SEC have decreased as the groundwater has become more acidic (Figure 5-8). A decline in carbonate mineral reaction is indicated with time. Groundwater is oxic; concentrations of dissolved Fe are low (below detection limit), though the presence of dissolved Mn may be due to the acidic dissolution of Mn oxides or carbonates. No detections of diuron, atrazine or simazine have been noted at the site (Figure 5-8).

5.2 ORGANIC GEOCHEMISTRY

5.2.1 Dissolved organic carbon and organic carbon compounds

The dissolved organic content of groundwater in the Lower Greensand aquifer is relatively low, with a median value of 0.85 mg/L, and a 95th percentile of 4.6 mg/L. The average is notably lower than reported by Shand et al. (2003) (median of 2.7 mg/L), but the range of data is comparable. Elevated NPOC concentrations are noted in the region between Godalming and Farnham, as well as in the north and to the west where the Lower Greensand becomes confined. The overall low concentration of organic carbon in the aquifer is likely due to its paucity in both the soil and aquifer sources, with locally elevated concentrations due to modern anthropogenic pollution. Organic carbon content appears to increase away from the boundary with the Weald Clay (downgradient), with samples in the west and north typically having the higher concentrations (>2 mg/L) of NPOC. This may be the result of continued dissolution of any organic carbon along the regional flow path.

The low organic carbon content is also demonstrated by the limited number of detections for PAHs, VOC/SVOC and TPH compounds. Only three compounds were detected, including trichloroethene, chlorodibromomethane and chloroform, of which only chloroform had a sufficient number of detections for statistical analysis. Concentrations of these organic contaminants in the Lower Greensand aquifer have been assessed by Manamsa et al. (2016). All were less than 10 µg/L, across a total of 1288 detections at 78 sampled sites. These included a number of compounds such as tetrachloroethene, trichloroethene, carbamazepine and caffeine.

5.2.2 Dissolved methane

A limited number of dissolved gas samples (10) were collected as part of this study. From the data gathered, there appear to be no spatial trends in the concentration of dissolved methane in the Lower Greensand aquifer, so these have been compared with the results obtained by Bell et al. (2016), and are shown in Figure 5-9. Combining the two datasets, it can be seen that concentrations increase marginally towards the confined aquifer in the north and west. However, concentrations are very low, with a maximum of 22 µg/L recorded by Bell et al. (2016), around 98% lower than the lower explosive limit (1600 µg/L) that Bell et al. (2016) used. Two samples collected as part of this study show concentrations >300 µg/L (maximum 461 µg/L), but do not appear to be associated with any spatial trends, or abstraction use.

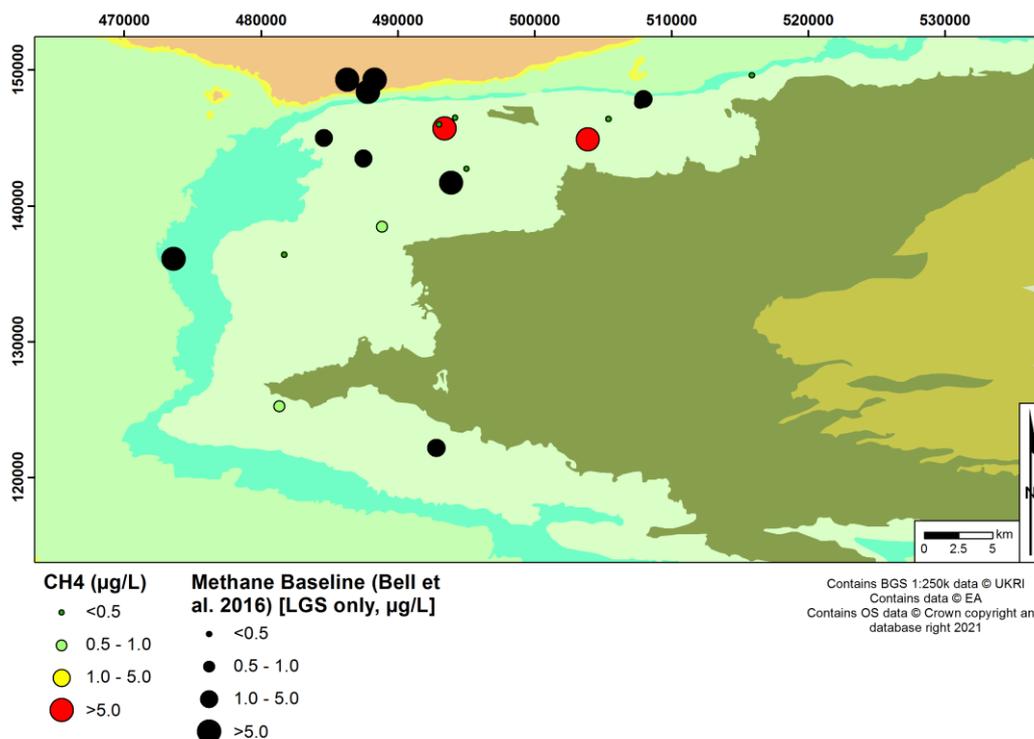


Figure 5-9. Methane samples collected as part of this investigation and from Bell et al. (2016), NB: LGS refers to Lower Greensand

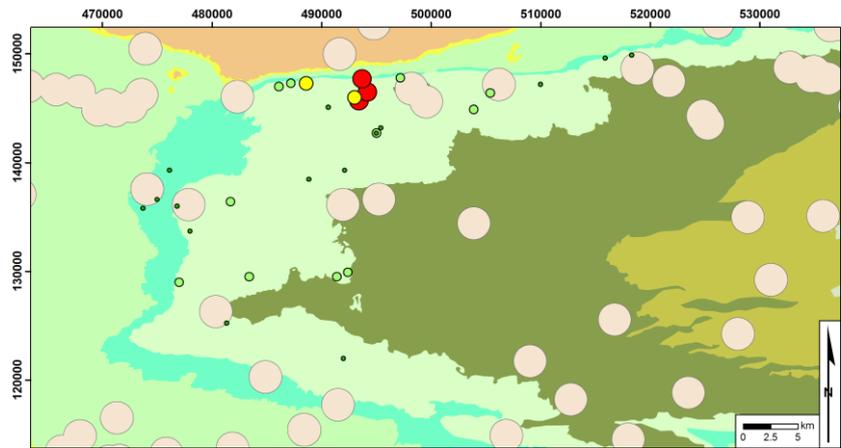
5.3 PROXIMITY TO ONSHORE OIL AND GAS ACTIVITIES

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 (associated with saline groundwater and a few select organic compounds) in Table 5-2 were plotted against a 1 km buffer around the OGA Onshore well dataset (OGA, 2020), and measurements within the buffer zone were extracted. The number of measurements, and the range of data extracted, are shown in Table 5-2, as well as in Figure 5-10 & Figure 5-11.

There are very few intersecting sites within the Lower Greensand aquifer (6) and not all have a full suite of analytes. There are not enough intersecting locations to allow a statistically robust evaluation to be drawn of a relationship between proximity to onshore oil and gas wells and the reported hydrochemistry. The geochemical controls highlighted in Sections 5.1 and 5.2 have a much greater impact on the observed distribution of data than a proximity to oil and gas developments.

Table 5-2. Selected intersecting analytes within 1 km of the OGA (2020) onshore wells dataset

Analyte	Number of intersects (n)	Range of extracted data
Na	6	6.3 – 13.3 mg/L
Cl	6	15.4 – 44.8 mg/L
SO ₄	6	23.3 – 41.9 mg/L
CH ₄ (BGS/WIMS)	2	0.2 – 0.9 µg/L
CH ₄ (incl. Bell et al. (2016))	4	0.2 – 1.6 µg/L
NPOC	6	0.35 – 5.96 mg/L
Chloroform	2	0.05 – 0.48 µg/L

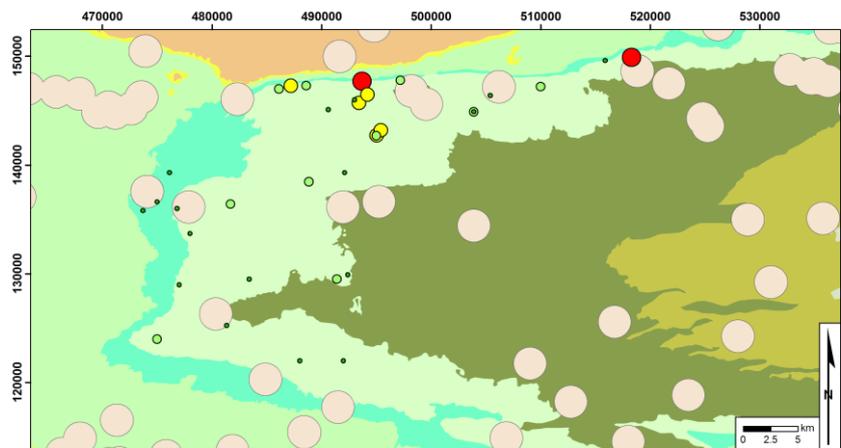


Na (mg/L) 1 km buffer from OGA Wells

- <10
- 10 - 15
- 15 - 20
- >20

Contains information provided by the OGA,
under the OGA Open User licence
Contains data © EA
Contains BGS 1:250k data © UKRI
Contains OS data © Crown copyright and
database right 2020

(a)

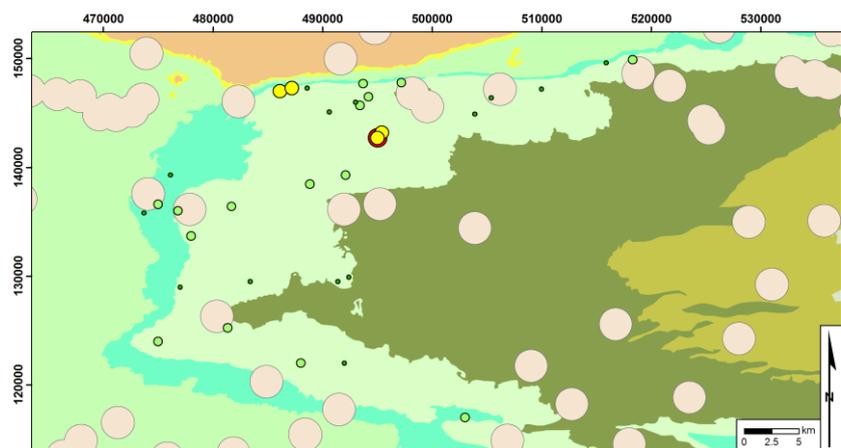


Cl (mg/L) 1 km buffer from OGA Wells

- <20
- 20 - 30
- 30 - 40
- >40

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(b)



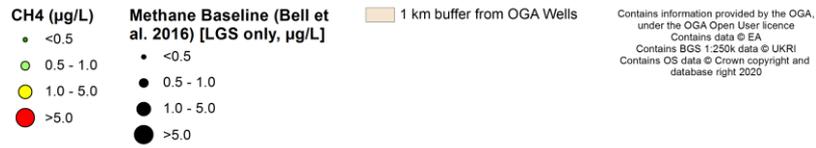
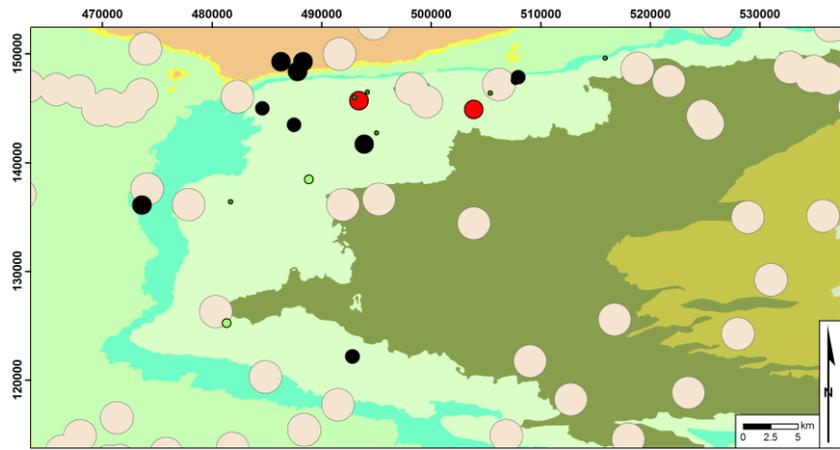
SO4 (mg/L) 1 km buffer from OGA Wells

- <25.0
- 25.0 - 50.0
- 50.0 - 100
- >100

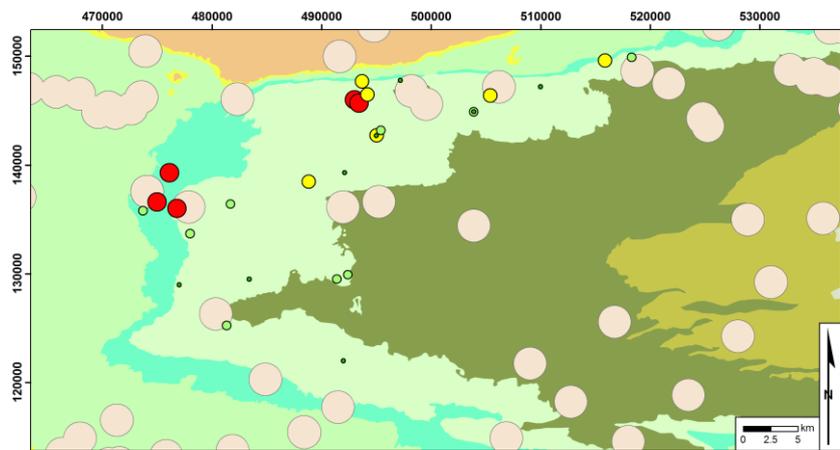
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(c)

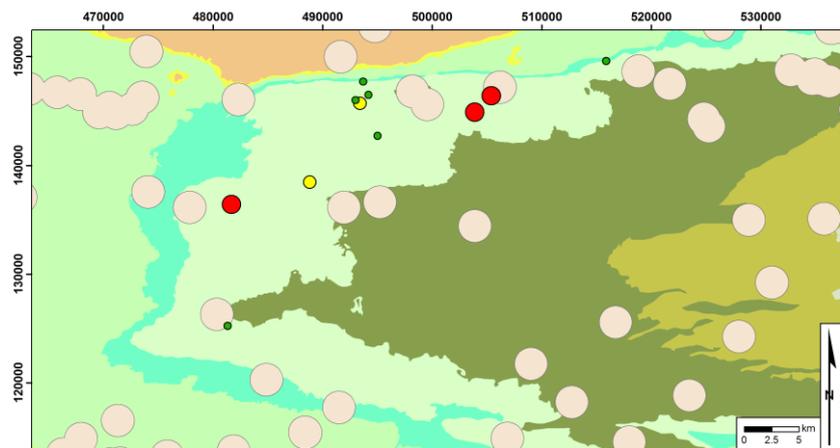
Figure 5-10. Selected inorganic analytes and their proximity to OGA (2020) wells across the study area: a) sodium; b) chloride; c) sulphate



(a)



(b)



(c)

Figure 5-11. Selected organic analytes and their proximity to OGA (2020) wells across the study area: a) methane, including data from Bell et al. (2016); b) NPOC; c) chloroform

6 Baseline characteristics of the Lower Greensand 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 and associated national legislation 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. 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 Lower Greensand Group aquifer, in the vicinity of Dorking, Godalming, and Petersfield, is largely derived from rainfall recharge. Rainfall introduces a number of principal ions in high concentrations, including Na and Cl, alongside some minor concentrations of SO₄, NO₃, Ca and Mg. pH values on infiltrating recharge are low (pH 6 or less), which in turn results in a number of water-rock interactions taking place under acidic conditions.

Water types within the aquifer consist dominantly of Ca-HCO₃, but may locally also be Ca-Cl-SO₄ mixed type waters. The Lower Greensand contains very little calcite or carbonate material (average of 1% across both the Hythe and Folkestone formations) which can buffer these incoming acidic recharge waters (Shand et al., 2003). However, as groundwater progressively flows away from the boundary with the Weald Clay towards the north and west, concentrations of Ca and HCO₃ increase slowly, indicating that what limited calcite is available is being dissolved. In turn, pH values at a number of sites have been seen to decrease gradually over time within the study area, indicating the gradual decline in available carbonate material. Dissolution of silicate minerals (clays and feldspars) is a likely origin of a number of major and minor ions including Mg, K, Al, As, and Cu, whilst increases in Fe and Mn are likely the result of dissolution of the abundant glauconite and heavy minerals (including precipitates).

The confined conditions within the Lower Greensand aquifer, both within the group (confinement of the Hythe Formation by the Sandgate Formation) and by the Gault Clay and Upper Greensand formations have not been possible to explore in great detail due to the limited number of sample points within these settings, and the anonymised nature of the supplied WIMS data. Previous studies by Shand et al. (2003) indicated a gradual shift from calcite dissolution towards ion-exchange reactions of Na for Ca with increasing confinement, but such evidence has not been present in this investigation. There is minor evidence of a decrease in DO content towards the north and west of the study area, showing a slight shift towards more reducing conditions. This shift towards more reducing conditions can also be seen by the increases in both Fe and Mn concentrations towards the west where a number of confined samples have been obtained, both of which are typically controlled by redox conditions.

The anthropogenic inputs to the aquifer are clearly demonstrated by the high concentrations of NO₃ and NH₄. Concentrations are highest in the north of the study area, where there appears to be more urban developments. However, there appears to be evidence of a gradual reduction in NO₃ over time at a number of locations within the aquifer (Figure 5-8), which may be a result of a shift in agricultural practices across the region.

6.2 DISSOLVED GAS COMPOSITIONS

Sampling for dissolved gases is typically not undertaken within routine groundwater sampling and analysis, often owed to the difficulties in collecting and analysing the samples. This study, alongside previous work by Bell et al. (2016), has been able to establish a baseline assessment for methane within the study area, a notable component within OOG activities. Concentrations across the Lower Greensand aquifer are low, with Bell et al. (2016) observing a maximum concentration of 22 µg/L, whilst this study observed two locations with concentrations over 300 µg/L, with an observed maximum of 461 µg/L. In the absence of organic source material within the Lower Greensand, or within the superficial deposits, methane is most likely derived from biogenic activity in the shallow subsurface. Concentrations do not appear to correlate with redox indicators (DO and Eh), and are most likely locally controlled by other factors unrelated to the activity.

CO₂ appears to increase down the flow path, likely increasing in conjunction with calcite dissolution. Concentrations ranged from 5.4 mg/L to 47.1 mg/L showing an increase in concentration away from the Weald Clay boundary.

6.3 ORGANIC BASELINE

Organic carbon concentrations within the Lower Greensand are low, with the upper limit (95th percentile) of NPOC at 4.6 mg/L, and TOC with an upper limit of 1.12 mg/L. NPOC concentrations appear to increase downgradient, which may be linked to increased residence time and dissolution of the limited amounts of organic carbon within the aquifer.

Within this study, only one organic compound was detected in sufficient quantities to contribute to the statistical assessment of organic compounds in the groundwater. Chloroform detections are likely associated with discharges of treated water. This compound, along with only 2 other detected compounds, is anthropogenic in origin. Pesticides such as diuron, atrazine and simazine were detected when reviewing time-series data for selected sites but did not contribute to the wider baseline assessment. Investigations by Manamsa et al. (2016) detected a number (1288 detections across the wider aquifer) of micro-organic pollutants within the Lower Greensand aquifer, consisting of a number of agricultural, pharmaceutical and personal-use compounds (e.g. caffeine). Likely sources for these organic pollutants are from widespread agricultural activities (diffuse sources), leakage from sewerage networks, and surface discharges and run-off. As highlighted by Shand et al. (2003), the Lower Greensand aquifer is susceptible to surface (anthropogenic) pollution, associated with its low alkalinity and buffering properties, alongside the limited superficial cover and well-draining soils.

In terms of environmental protection, detection of these compounds signals a departure from natural baseline conditions. In terms of assessment for any future subsurface activities, their detection under the current conditions needs to be noted.

7 Conclusions

The Lower Greensand aquifer, in the vicinity of Dorking, Godalming and Petersfield, serves as an important resource for groundwater in south-east England, including for drinking-water purposes. The aquifer consists of two primary water-bearing horizons (the Hythe and Folkestone formations), composed of clean quartz sands and glauconitic grains, limited calcite, and minor feldspar and clays. These two strata are separated by the Sandgate Formation, which may locally confine the underlying Hythe Formation. The aquifer is principally unconfined within much of the study area, becoming completely confined to the north, west and south by the Gault Clay and Upper Greensand formations.

The aquifer is recharged by rainfall, and groundwater is relatively fresh (SEC <1000 $\mu\text{S}/\text{cm}$) across much of the study area. Dominant water chemistry types are Ca-HCO₃, but evidence of some mixed types (Ca-Cl-SO₄) have also been identified. Infiltrating rainfall brings notable components of Na and Cl in to the aquifer, and is typically acidic. Groundwater pH across the aquifer is typically <7, due to the limited buffering capacity of the aquifer (limited/sporadic presence of calcite). The aquifer is typically at risk of mobilising a number of metals (e.g. Mg, Ca, K, Si, Al, Mn, Pb) through dissolution of feldspar and micas by silicate dissolution reactions. Ca and HCO₃ can be seen to increase along the regional flow path, indicating the dissolution of the limited calcite available within the aquifer. Increases in Mg, K, Sr, F, Al, As, Mn, Cu, Ni, Fe and Mn towards the north and west suggest gradual dissolution of silicate and heavy minerals and iron oxides.

Within this study, the impact of intra-group confining conditions (confinement of the Hythe by the Sandgate Formation) have not been distinguishable in great detail. Groundwater towards the north and west, where becoming fully confined by the Gault Clay and Upper Greensand formations, shows evidence of a slight loss of DO and a shift towards Fe- and Mn-reducing conditions. However, much of the aquifer is oxic and reducing conditions are not necessarily observed.

Anthropogenic inputs have been observed including elevated concentrations of nitrate, and organic pollutants such as chloroform. Dissolved organic carbon content in groundwater across the aquifer is relatively low, owing to limited sources in both the superficial cover and within the Lower Greensand group itself. Methane concentrations are low across the study area, showing slight increases towards confining conditions in the north, but this study predominantly found values <0.1 $\mu\text{g}/\text{L}$.

Appendix 1 Time-series plots for Precip-NET stations

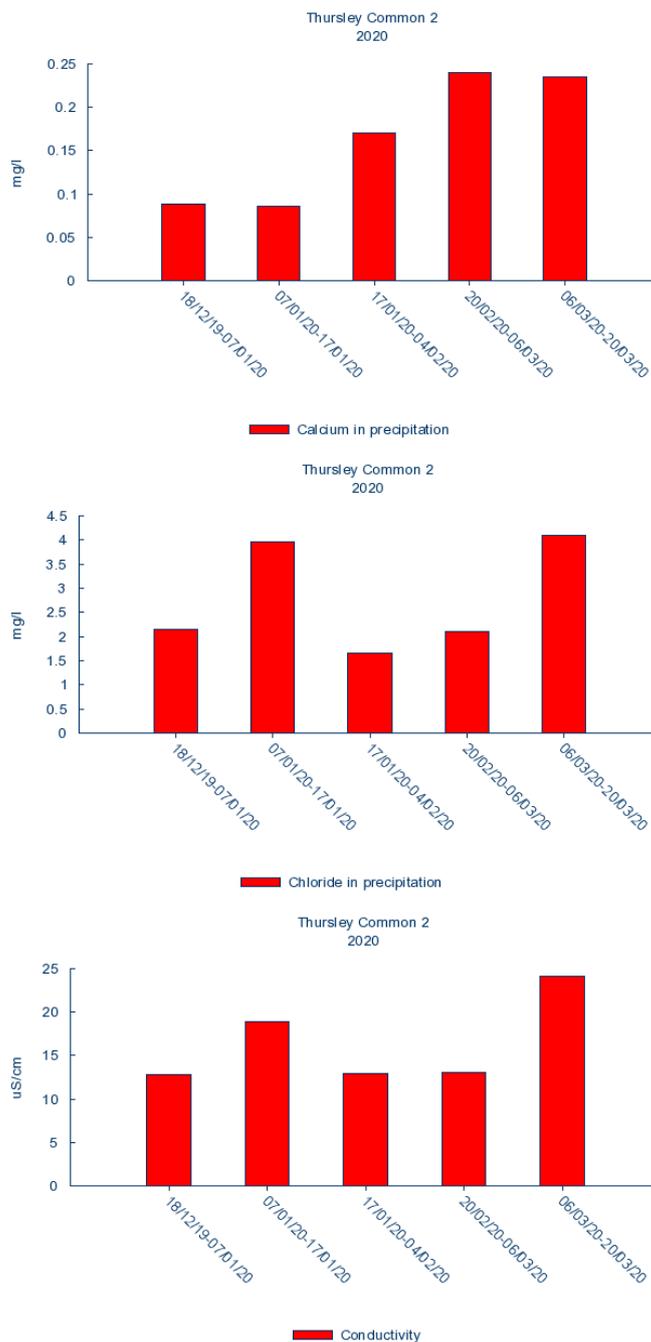
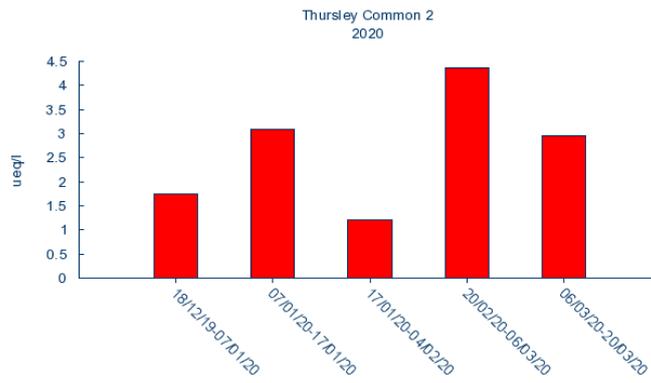
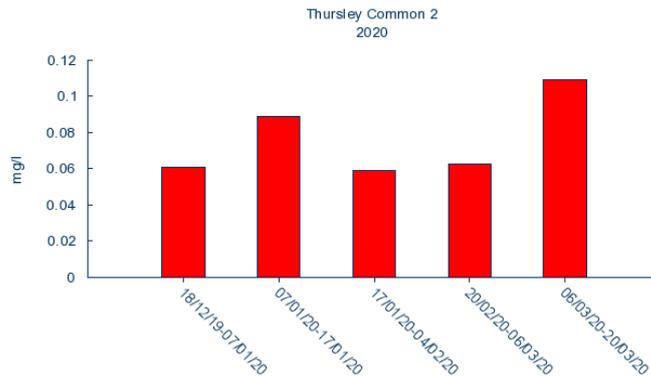


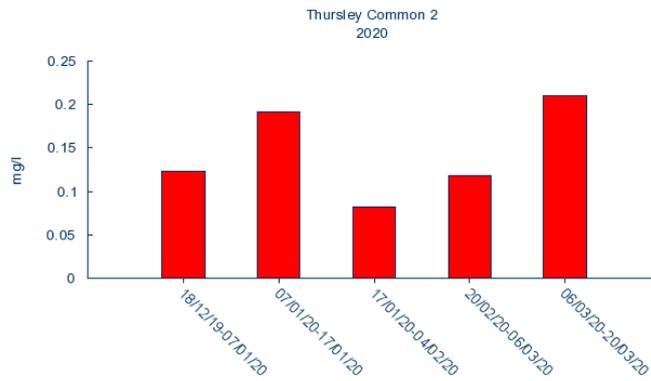
Figure A-1. Monthly precipitation chemistry for Thursley Common 2 monitoring station (2020) (from DEFRA, 2020b)



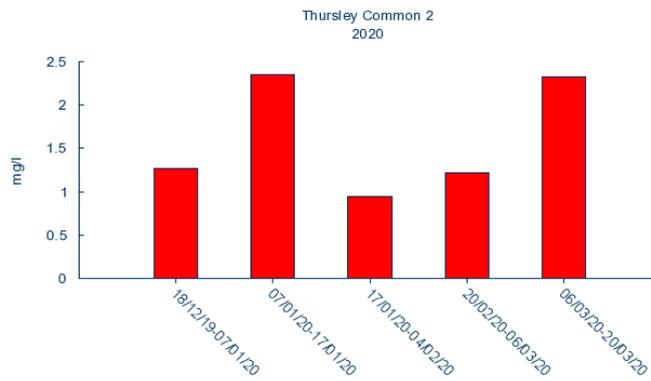
Acidity in precipitation



Potassium in precipitation



Magnesium in precipitation



Sodium in precipitation

Figure A-1. (cont)

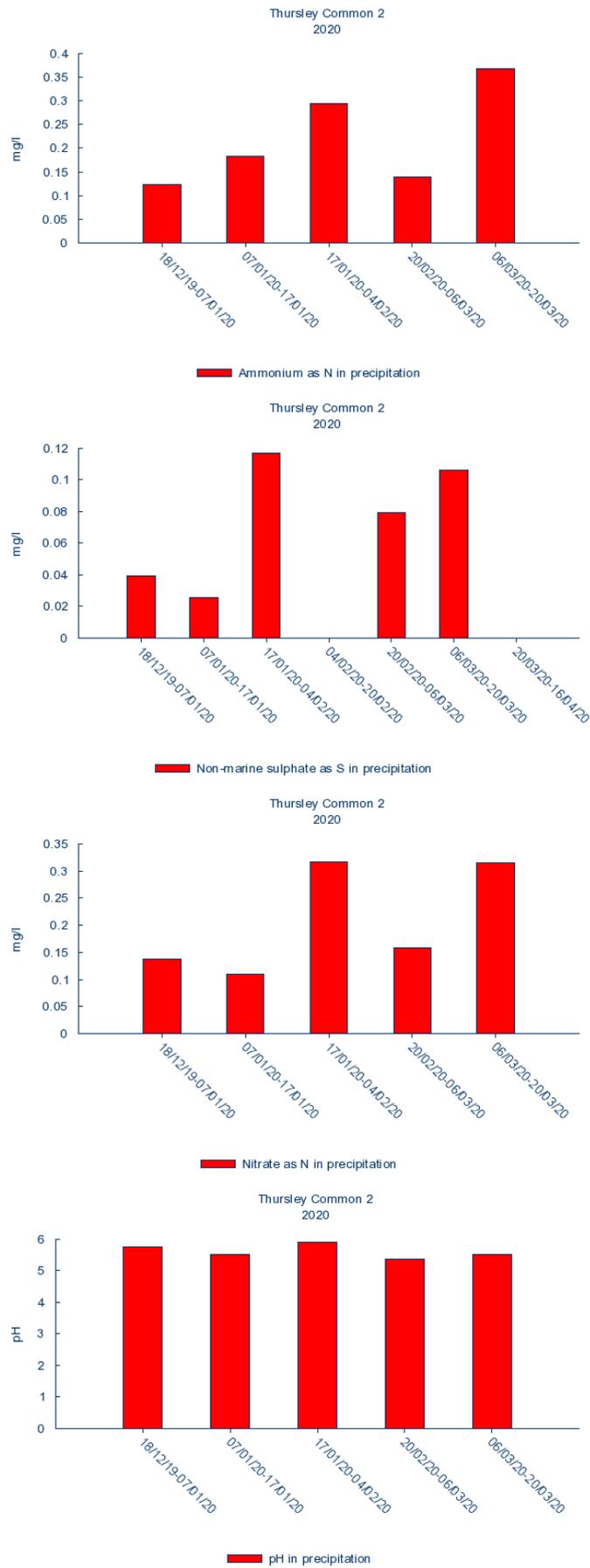


Figure A-1. (cont)

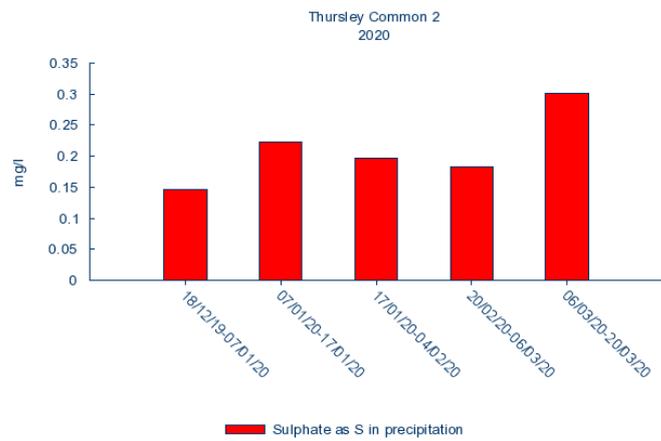
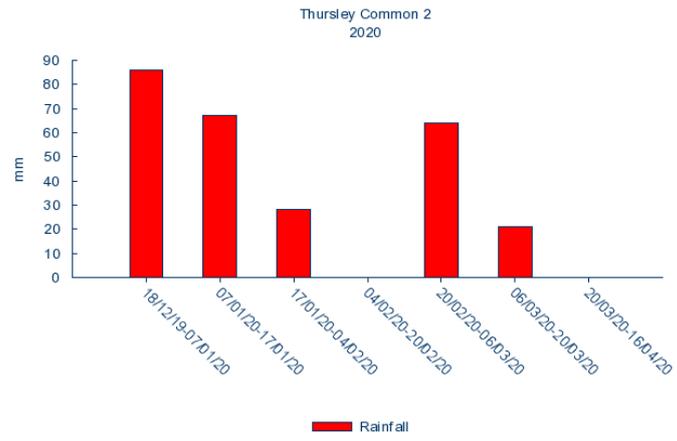
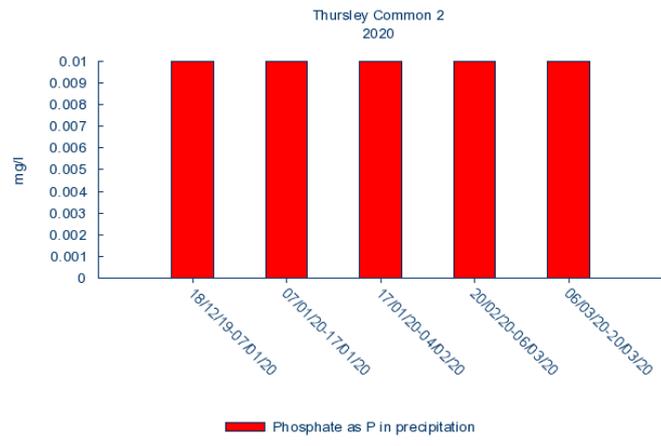


Figure A-1. (cont)

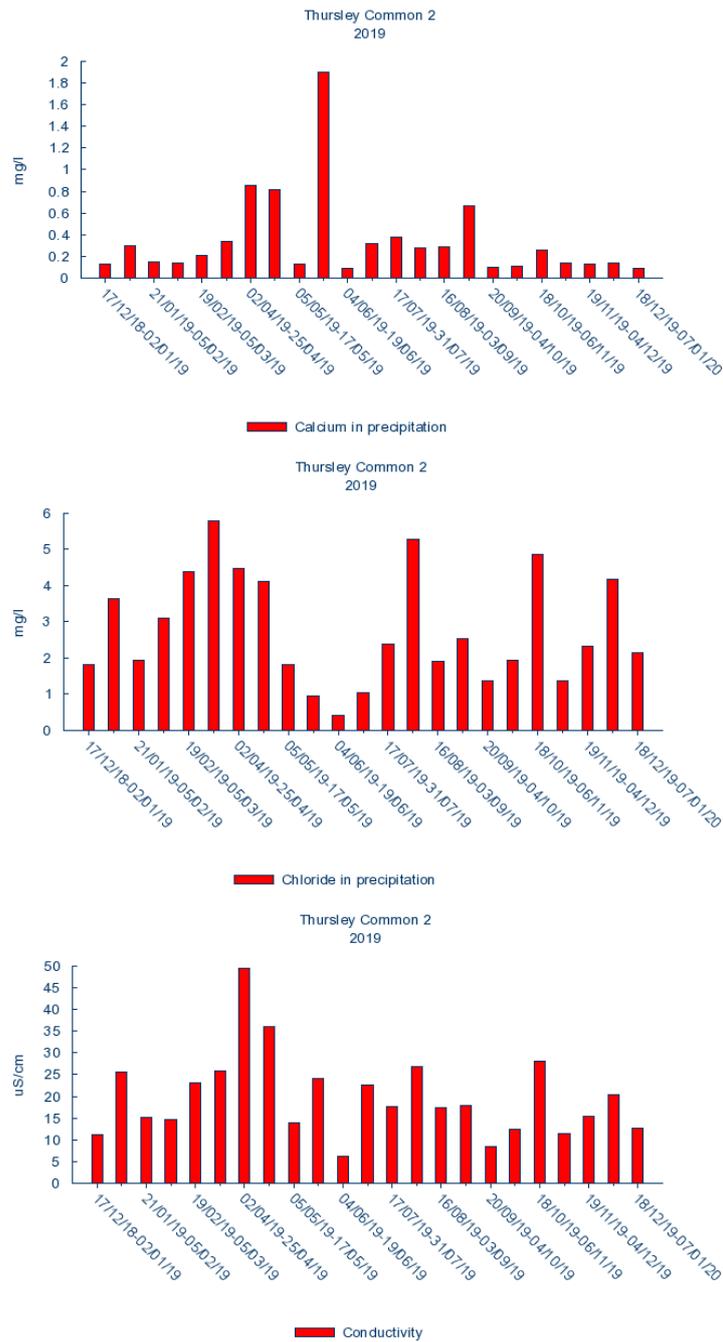


Figure A-2. Monthly precipitation chemistry for Thursley Common 2 monitoring station (2019) (From DEFRA (2020a))

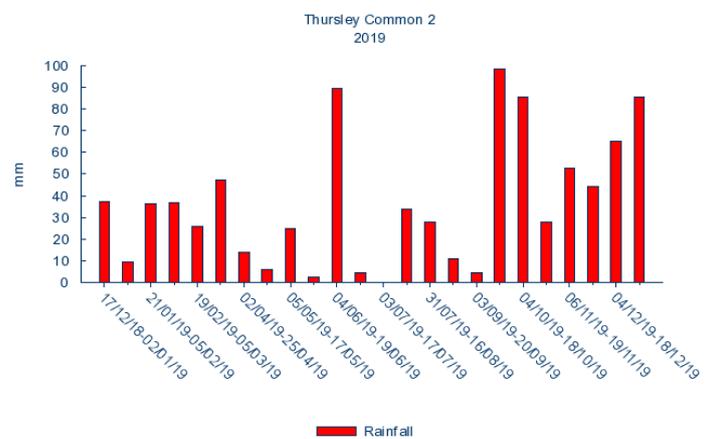
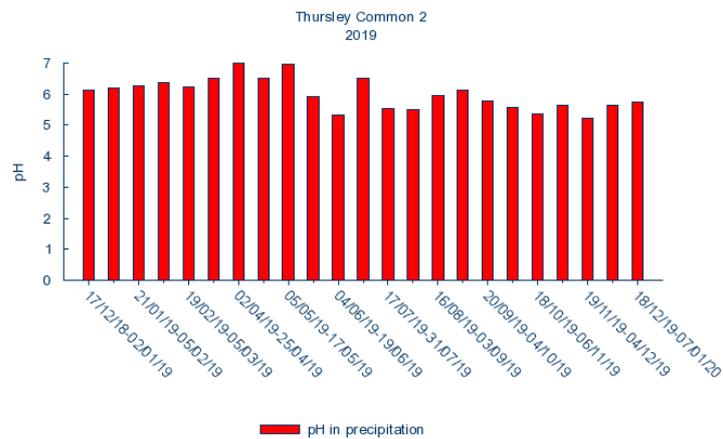
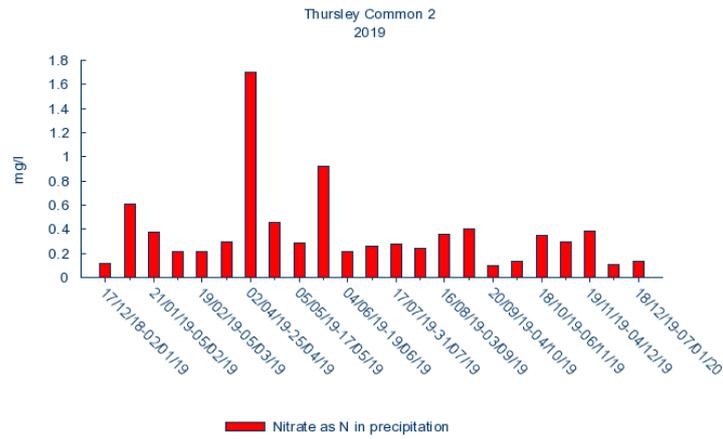
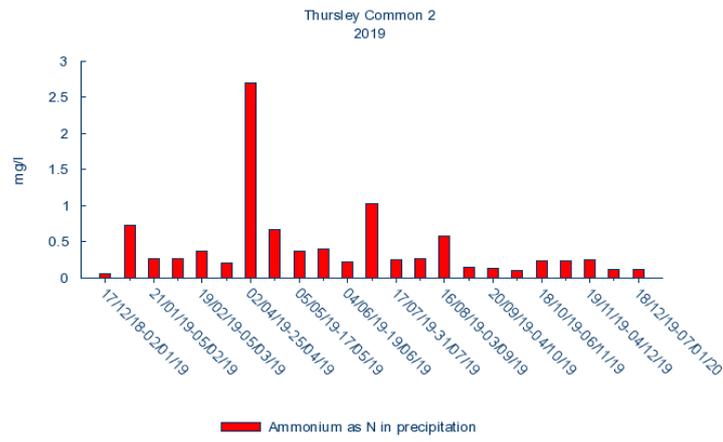


Figure A-2. (cont)

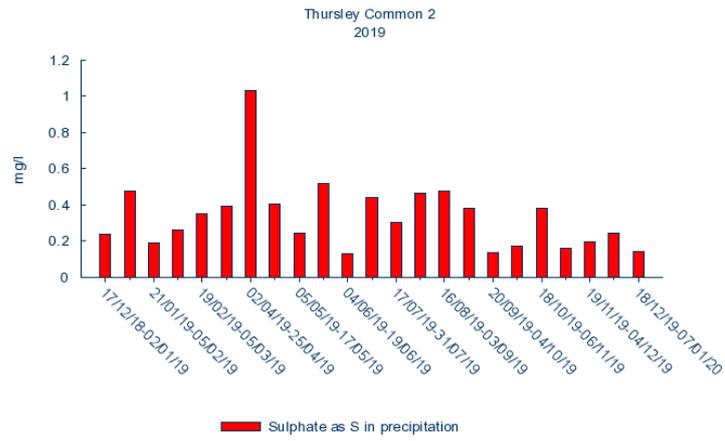
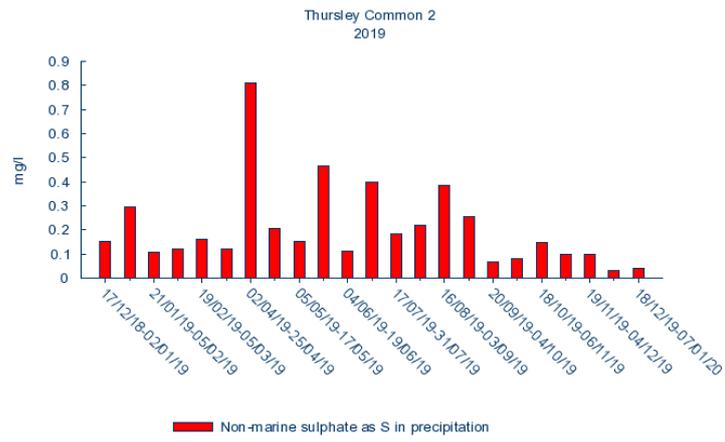


Figure A-2. (cont)

Appendix 2 WIMS database filter criteria

Table A-1. WIMS Database filter criteria

Site location	Purpose description	Date criteria
Lower Greensand Group 1:250k Geology Shapefile	Environmental monitoring (GQA & RE only)	Most complete suite of analyses for each location
Gault clay formation 1:250k Geology Shapefile	Environmental monitoring statutory (EU directives)	
Upper Greensand formation 1:250k Geology Shapefile	Monitoring (national agency policy)	
	Monitoring (UK Govt policy - not GQA or RE)	
	Planned formal non-statutory (permit/env mon)	
	Planned investigation (local monitoring)	

GQA: general quality assessment; RE: river ecosystem

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

Organic determinands	Inorganic determinands
>C10-C12	Temperature
>C12-C16	pH
>C16-C21	DO
>C21-C35	Eh
>C5-C6	SEC
>C5-EC7	Ag
>C6-C8	Al
>C8-C10	As
>EC10-EC12	B
>EC12-EC16	Ba
>EC16-EC21	Be
>EC21-EC35	Bi
>EC7-EC8	Br
>EC8-EC10	Ca
1;1-Dichloroethane	Cd
1;1-Dichloroethylene :- [1;1-Dichloroethene]	Ce
1;1-Dichloropropylene :- [1;1-Dichloropropene]	Cl
1;1;1-Trichloroethane	Co
1;1;1;2-Tetrachloroethane	CO ₂
1;1;2-Trichloroethane	Cr
1;1;2;2-Tetrachloroethane	Cs
1;2-Dibromo-3-chloropropane	Cu
1;2-Dibromoethane	Dy
1;2-Dichlorobenzene	Er
1;2-Dichloroethane	Eu
1;2-Dichloropropane	F
1;2-Dimethylbenzene :- [o-Xylene]	Fe
1;2;3-Trichlorobenzene	Ga
1;2;3-Trichloropropane	Gd
1;2;3-Trimethylbenzene	HCO ₃
1;2;4-Trichlorobenzene	Hf
1;2;4-Trimethylbenzene	Hg
1;3-Dichlorobenzene	Ho
1;3-Dichloropropane	HPO ₄
1;3;5-Trichlorobenzene	I
1;3;5-Trimethylbenzene :- [Mesitylene]	K
1;4-Dichlorobenzene	La
2-Chloronaphthalene	Li
2-Chlorophenol	Lu
2-Chlorotoluene :- [1-Chloro-2-methylbenzene]	Mg
2-Methylnaphthalene	Mn
2-Methylphenol	Mo
2-Nitroaniline	Na
2-Nitrophenol	Nb

Organic determinands	Inorganic determinands
2;2-Dichloropropane	Nd
2;4-Dichlorophenol	NH ₄
2;4-Dimethylphenol	Ni
2;4-Dinitrotoluene	NO ₂
2;4;5-Trichlorophenol	NO ₃
2;4;6-Trichlorophenol	Total P
2;6-Dinitrotoluene	Pb
3-Chlorotoluene :- [1-Chloro-3-methylbenzene]	Pr
3-Nitroaniline	P-reactive
4-Bromophenylphenylether	Rb
4-Chloro-3-methylphenol	Sb
4-Chloroaniline	Se
4-Chlorophenylphenylether	Si
4-Chlorotoluene :- [1-Chloro-4-methylbenzene]	Sm
4-Isopropyltoluene :- [4-methyl-Isopropylbenzene]	Sn
4-Methylphenol	SO ₄
4-Nitroaniline	Sr
4-Nitrophenol	Ta
Acenaphthene	Tb
Acenaphthylene	TDS
Anthracene	Th
Azobenzene	Ti
Benzene	Tl
Benzo(a)anthracene	Tm
Benzo(a)pyrene	U
Benzo(b)fluoranthene	V
Benzo(b.k)fluoranthene	W
Benzo(e)pyrene	Y
Benzo(g,h,i)perylene	Yb
Benzo(k)fluoranthene	Zn
Bis(2-chloroethoxy)methane	Zr
Bis(2-chloroethyl)ether	
Bis(2-ethylhexyl) phthalate	
Bromobenzene	
Bromochloromethane	
Bromodichloromethane	
Bromoform :- [Tribromomethane]	
Butylbenzyl phthalate	
Carbazole	
Carbon Disulphide	
Carbon tetrachloride :- [Tetrachloromethane]	
Chlorobenzene	
Chlorodibromomethane	
Chloroform :- [Trichloromethane]	
Chloromethane :- [Methyl Chloride]	

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

Organic determinands**Inorganic determinands**

Total aromatics C5-35

trans-1;2-Dichloroethylene :- [trans-1;2-Dichloroethene]

trans-1;3-Dichloropropylene :- [trans-1;3-Dichloropropene]

Trichloroethylene :- [Trichloroethene]

Trichlorofluoromethane

Vinyl chloride :- [Chloroethylene]

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