Journal of Hydrology: Regional Studies 28 (2020) 100684

Contents lists available at ScienceDirect

Journal of Hydrology: Regional Studies

journal homepage: www.elsevier.com/locate/ejrh

Characterising variations in the salinity of deep groundwater systems: A case study from Great Britain (GB)

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ARTICLE INFO

Keywords:
Groundwater
Total dissolved solids (TDS)
GB

ABSTRACT

Study region: The study region is Great Britain (GB), a small non-continental island landmass in North West Europe

Study focus: Data for Total Dissolved Solids (TDS) from groundwater samples can be used to characterise regional-scale variations in the quality of deep groundwater systems. Combined with information about typical well-depths, TDS data can be used to identify the presence of currently undeveloped fresh or brackish groundwater at depth that may require protection. This study considers the distribution of TDS with depth relative to sea level in the main GB aquifers and selected other key hydrogeological units, and demonstrates how useful insights can be obtained from data-led analyses of depth variations in groundwater chemistry if the regional context of hydrogeological systems is taken into account.

New hydrogeological insights: In GB, TDS varies over about five orders of magnitude, up to about 330,000 mg/L, with a general increase in mineralisation with depth. Overall, there is a transition from fresh < 1625 mg/L to brackish < 10,000 mg/L groundwater at about 500 m below surface, and from brackish to saline > 10,000 mg/L groundwater at about 700 m. Given that the 95 %tile depth of water wells is about 200 m, it is evident that there is currently undeveloped fresh groundwater at depth across large parts of the study area that may require protection, although it is inferred that TDS is not the only factor limiting exploitation and use of these deeper resources. As in this study, previous data-led analyses of fresh groundwater at depth have typically analysed TDS as depth below surface. However, if TDS data is analysed relative to sea level and in the context of regional hydrogeological information or models, additional insights can be gained on the distribution and controls on fresh groundwater at depth. Projecting TDS data into a 3D hydrogeological model of the study area shows that fresh groundwater at depth exhibits spatial coherence and is generally associated with relatively deep sedimentary basins overlying older, less permeable basement.

1. Introduction

Globally, groundwater provides of the order of one third of all freshwater supplies (Doll et al., 2012, 2014). Two and a half billion people are estimated to depend solely on groundwater for basic daily water needs (UN, 2015) and it sustains the health of many important groundwater-dependent terrestrial ecosystems (Gleeson et al., 2012; Koirala et al., 2017). Fan et al. (2013) have estimated that about one third of the global land surface area has a water table depth or capillary fringe within 3 m of the ground surface, and

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https://doi.org/10.1016/j.ejrh.2020.100684
Received 19 November 2019; Received in revised form 11 February 2020; Accepted 13 March 2020
Available online 25 March 2020

much of the groundwater that is abstracted is from relatively shallow, unconfined groundwater systems of only a few 10 s of metres in depth. However, due to pressure on groundwater resources (Wada et al., 2010; MacDonald et al., 2016) as well as the growing use of the subsurface for other activities, there is an increasing focus on deep groundwater systems for potable water as well as for agricultural irrigation and industrial purposes. For example, across large parts of Africa the need for water security in relation to growing populations and the need to develop resilience to the effects of climate change has led to continental-scale assessments of deep groundwater systems (MacDonald et al., 2012). Throughout many of the major deltas of the world there is a trend towards ever-deeper exploitation of groundwater systems for irrigation and to address natural water quality issues (Lapworth et al., 2018). In the USA, the drive to find groundwater to augment supplies for irrigation and potable use has resulted in an interest in deep groundwater, including brackish groundwater (Kang and Jackson, 2016; Stanton et al., 2017; Ferguson et al., 2018a; Kang et al., 2019; Perrone and Jasschko, 2019).

There are many challenges associated with the development and management of deep groundwater systems. There is the need to consider governance of and access to deep groundwater (Hoogesteger and Wester, 2015), to assess costs of appropriate technologies and implementation of water resource management systems (Harou and Lund, 2008), and to avoid overexploitation of deep aquifers (Wada et al., 2010; Scanlon et al., 2012). In addition, in regions where other activities are undertaken in the deep subsurface, there is also a need to understand the distribution of deep groundwater systems to provide protection of currently unexploited groundwater resources for future use. For example, there is a requirement to understand the vulnerability of deep groundwater systems to activities such as conventional and unconventional onshore hydrocarbon development (Jackson et al., 2013; Cai and Ofterdinger, 2014; Vengosh et al., 2014; Loveless et al., 2018, 2019; McIntosh and Ferguson, 2019), underground nuclear waste storage (Stanfors et al., 1999), and CO_2 sequestration (Newmark et al., 2010). Notwithstanding these challenges, practical constraints on the development and use of deep groundwater are primarily related to an ability to obtain adequate yields of suitable quality water from depth. The aim of the current study is to characterise and better understand regional-scale variations in the quality of deep groundwater systems based on a large set of observational data for Total Dissolved Solids (TDS). Note, the concept of ‘deep groundwater’ and ‘deep groundwater systems’ are here used in a relative not absolute sense and refer to an interval below the current normal depth of active groundwater exploitation, as investigated and described by this study. The concept can also refer to a depth interval relative to a datum, such sea level across a given region, also investigated and described by this study.

A few recent data-led regional- to continental-scale studies have identified low salinity (fresh or brackish) groundwater at depth in the USA using measurements of TDS, and have attempted to estimate volumes of currently undeveloped fresh or brackish groundwater and their susceptibility to pollution from unconventional hydrocarbon development and other potentially polluting sub-surface activates. Analysing the TDS of groundwater samples in California, USA, Kang and Jackson (2016) estimated that useable groundwater volumes could be increased by up to fourfold if groundwater < 3000 ppm TDS was exploited down to a depth of 3 km, but also noted that some of these deep groundwater resources would be vulnerable to conventional and unconventional hydrocarbon extraction. Similarly, Kang et al. (2019) analysed TDS from 17 basins across the southwestern United States and found that in seven of the basins there was ‘useable water’ (defined as < 10,000 ppm TDS) in the ‘deep groundwater’ (defined in their study as depths > 150 m). Stanton et al. (2017) undertook an analysis of brackish groundwater in the USA (defined as a TDS of 1,000–10,000 mg/L) and estimated that almost a third of the subsurface down to a depth of about 900 m contained brackish groundwater. Ferguson et al. (2018a) used TDS data to investigate the depth at which groundwater transitioned from fresh to brackish to saline groundwater defined as fresh < 3000 and brackish < 10,000 mg/L respectively and compared these depth intervals with the depth of hydrocarbon exploitation activities in 28 sedimentary basins across the USA. They noted that, in basins where relatively deep fresh and brackish water is present, groundwater is potentially vulnerable due to the proximity to hydrocarbon development and to waste injection wells.

This study builds on the earlier work to identify the depth of the fresh to brackish groundwater transition for Great Britain (GB); relates this transition to current groundwater resource management and protection depth thresholds; and, considers the implications with respect to vulnerability to potential unconventional hydrocarbon development in GB. It assesses if the transition depth in GB is consistent with those identified in previous studies (Kang and Jackson, 2016; Stanton et al., 2017; Ferguson et al., 2018a; Kang et al., 2019). In addition, it provides additional evidence to test the assertion of Ferguson et al. (2018a) that globally there may be less fresh groundwater than estimated previously (by Gleeson et al. (2016) who assumed that only 6% of water in the upper 2 km was ‘young’, less than 50 years old). Finally, the earlier data-led studies of TDS either implicitly or, in the case of Ferguson et al. (2018a), explicitly did not address depth variations in TDS within individual hydrogeological units, and they did not consider the effects of hydrogeochemical evolution associated with regional groundwater flow or the effects of basin structure on observed TDS depth distributions. This study considers the distribution of TDS with depth relative to sea level in the main GB aquifers and selected other key hydrogeological units, and demonstrates how useful insights can be obtained from data-led (rather than process-driven, e.g. Hanor, 1994a, 1994b; Smedley et al., 2018) analyses of depth variations in groundwater chemistry if the regional context of hydrogeological systems is taken into account.

Following an overview of regulatory limits and definitions of TDS related to groundwater, the hydrogeology of the study area, England, Wales and Scotland (Great Britain), and TDS dataset is briefly introduced and described. Then the depth below surface distribution of TDS is characterised and compared with depths of water wells and with water quality thresholds for fresh and brackish groundwater for the study area and as a function of eight distinct hydrogeological units. The distribution of TDS data is then described spatially and in 3D relative to sea level in order to investigate the spatial coherence of water quality data at depth as a function of the regional geological and hydrogeological setting. Finally, the results are discussed in relation to previous data-led analyses of large TDS datasets and the implications for future systematic analysis of water quality observations from deep groundwater systems are considered.

2. TDS limits of fresh and brackish groundwater

Total dissolved solids (TDS), a measure of inorganic salts and organic substances in solution in a liquid (World Health Organisation, 2011), is a widely reported parameter related to groundwater quality because it provides an indication of the overall degree of mineralisation and hence potability of groundwater. It is usually expressed as mg/L or g/L (weight by volume), but sometimes as ppm or ‰ (weight per weight). TDS is either determined from the weight of dry residue remaining after evaporation of the volatile portion of a sample or can be calculated from the sum of the major ions although often the method used to estimate TDS is unreported or not described. Note that many studies tend to quote electrical conductance (EC) (or Specific Electrical conductance, SEC, defined at 25 °C) in preference to TDS to describe the degree of mineralisation of groundwater (e.g. Kim et al., 2008).

Salinity and overall degree of mineralisation, typically expressed as TDS, tend to increase along groundwater flow paths and with depth (Freeze and Cherry, 1979), and the flow and hydrogeochemical processes effecting the evolution of groundwater mineralisation and quality in sedimentary basins and fractured basement terrains are well-understood (Kreitler, 1989; Palmer and Cherry, 1984; Hanor, 1994a, 1994b; Ferguson et al., 2018b). Variations in groundwater quality, including TDS, arise from a dynamic interplay between depositional and basin evolution processes, and the development of basin-scale to local-scale groundwater flow systems (Toth, 1963, 1999). However, it is only recently that the distribution of TDS data with depth has been the subject of systematic data-led analysis with the specific aim of understanding the location of groundwater quality limits or thresholds with depth (Kang and Jackson, 2016; Stanton et al., 2017; Ferguson et al., 2018a; Kang et al., 2019).

No limits are set for TDS on health grounds. Globally, however, there are a variety of regulatory limits and advisory recommendations for potable groundwater supply based on TDS. In addition, TDS can be used as a guide to protection of groundwater resources. For example, there is a 'desirable limit' for TDS of potable groundwater in India of 500 mg/L, with up to 2000 mg/L permissible in absence of an alternate source Bureau of Indian Standards, 2012). In California, the California State Water Resources Control Board (2016) recommended limit for TDS in public groundwater supply is also 500 mg/L with a short-term limit of 1500 mg/L. Even where no limit is recommended or set, salinities above a certain value are described as unpalatable. For example, the World Health Organisation stating that water with a TDS of less than 600 mg/L is good quality and that over 1000 mg/L it becomes increasingly unpalatable World Health Organisation, 2011). In Australia, the National Health and Medical Research Council (NHMRC, 2011) has set 'aesthetic' guidelines with a groundwater TDS content of less than 600 mg/L regarded as good quality drinking water, 600–900 mg/L fair quality, 900 to 1200 mg/L as poor quality and over 1200 mg/L unacceptable. The EPA (EPA, 2019) states an unenforceable guideline maximum value (National Secondary Drinking Water Regulations) of 500 mg/L for potable groundwater in the USA and also defines underground sources of drinking water that should be protected as sources with a TDS of < 10,000 mg/L.

Similarly, there is little consistency in how brackish and saline groundwater is defined. For example, even though the National Groundwater Association NGWA defines groundwater with a TDS of less than 1000 mg/L as fresh, 1,000–3,000 mg/L as slightly saline and 3000 to 10,000 mg/L as moderately saline (NGWA, 2017), in an assessment of brackish water in the contemporaneous USA, Stanton et al. (2017) defined brackish groundwater as having a TDS range of 1,000–10,000 mg/L. DiGiulio et al. (2018) identified widely differing criteria between 17 states in the USA related to the protection of brackish groundwater in the context of unconventional oil and gas development.

With regard to regulatory limits for potable groundwater supply in the United Kingdom UK, the Council of the European Union directed that the maximum electrical conductance EC or conductivity at 20 °C for potable groundwater should be 2500 μS/cm European Commission, 2000, 2006). This limit has been embodied in the water supply regulations for the UK that specify the maximum admissible concentrations and values for parameters in drinking water for both public supply and private water supplies for human consumption. The UK Technical Advisory Group (UKTAG) on the Water Framework Directive define water in groundwater bodies as 'groundwater [that] is part of an aquifer and is … a long term resource that can be exploited for human activities …', and by implication is of good potable quality (UKTAG, 2012). UKTAG note that there is a lower depth at which groundwater loses value as a potable resource, and for consolidated aquifers the UKTAG guideline for maximum groundwater body thickness is 400 m in the absence of any other information (Table 2 in UKTAG, 2012). By inference, this means that the effective maximum depth of potable groundwater is taken to be 400 m in the absence of any other information. Notwithstanding this, environmental regulators in the UK operate a precautionary principal and seek to protect all groundwater, regardless of whether it is designated as a groundwater body or not, unless groundwater can be denoted as permanently unsuitable for use as a resource.

For the purposes of the present study fresh groundwater is defined as having a TDS of < 1625 mg/L approximately equivalent to < 2500 μS/cm consistent with groundwater legislation in UK and the European Community. In addition, like previous studies van Weert, 2012; Ferguson et al., 2018a), the common convention of Freeze and Cherry (1979) is followed where the maximum TDS for brackish water is defined as 10,000 mg/L. TDS of saline water is taken to be in the range 10,000–100,000 mg/L (with sea water at about 35,000 mg/L), and brine is defined by a TDS in excess of 100,000 mg/L (Freeze and Cherry, 1979).

3. Study area

The GB study area (Fig. 1) consists of a small non-continental island landmass. It is characterised by relatively short but slow groundwater flow paths resulting in saline water occurring in aquifers at relatively small distances down-gradient of outcrop and an absence of extensive confined aquifers containing fresh water (Downing et al., 1987). Deep regional groundwater flow is predominantly through sedimentary basins located above a low permeability basement, where flow is currently controlled by upland divides and lowland, coastal or submarine groundwater sinks. Downing et al. (1987) observed that most groundwaters in GB have

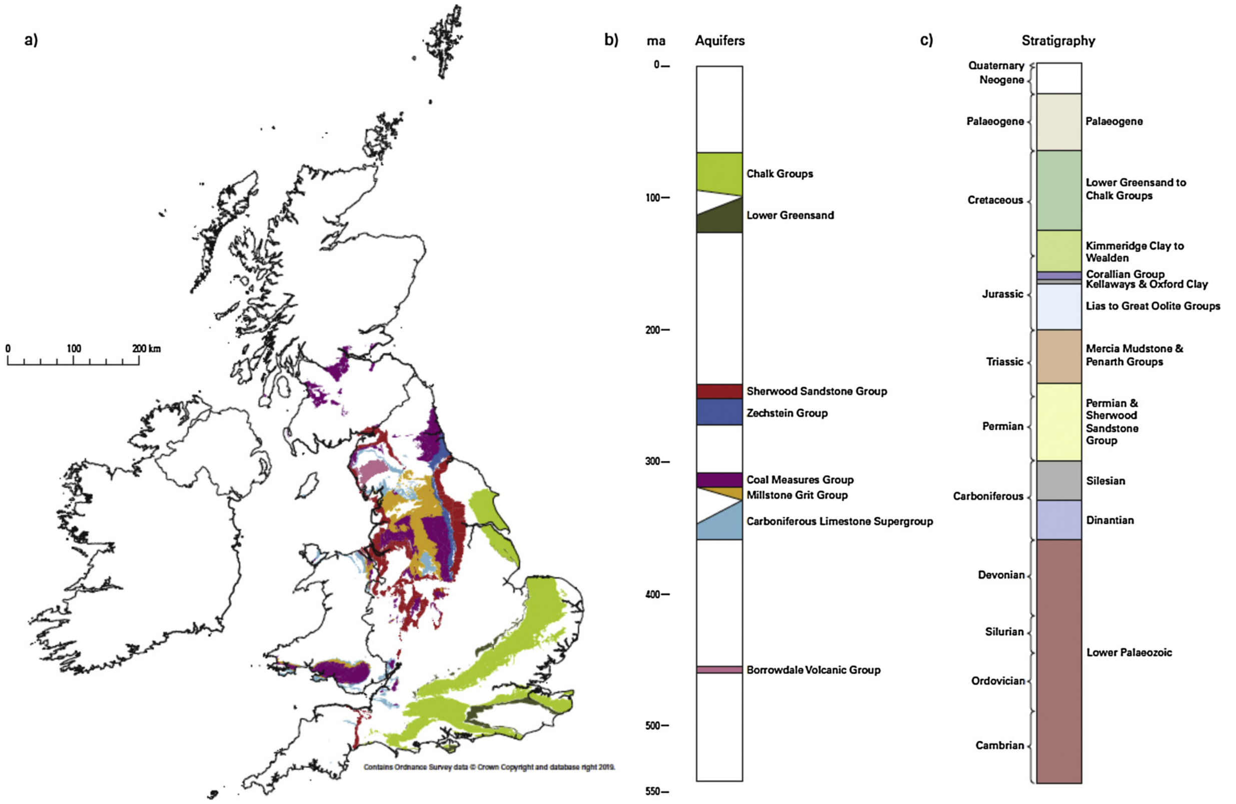

Fig. 1. a. map showing the outcrop of the eight named hydrogeological units, b. the location of the units in the hydrostratigraphic column, and their relationship to c. the stratigraphic units used as the basis for the 3D hydrogeological model and 2D cross-section in Fig. 6.

increasing mineralisation with depth and that their composition lies along the isotope composition ($\delta^{18}0$ / $\delta^{2}H$ ratio) meteoric water line. They interpreted these observations in terms of a geochemical evolution of groundwater along basinal-scale flow lines. Note that groundwater conditions in GB have evolved over a long period of geological time, since at least the beginning of the Cenozoic some 65 million years before present when the landmass emerged from a lengthy phase of marine submergence during the Late Cretaceous (Bath et al., 2006). However, current basin-scale groundwater flow systems reflect the present marine boundary of the British Isles, a relatively recent product of the Holocene transgression following the Last Glacial Maximum at around 15,000 years before the present day, when large parts of the UK continental shelf were subaerially exposed (Downing et al., 1987). Of the TDS observations described below the majority come from eight named, regionally significant geological/hydrostratigraphic units across the study area. The majority are from the two Principal Aquifers in GB, the Cretaceous Chalk (CK) and the Permo-Triassic sandstones of the Sherwood Sandstone Group (SSG) (Allen et al., 1997) (Fig. 1). In addition, there are observations of TDS from the Cretaceous Lower Greensand (LGS), Permian Zechstein (Z) deposits, Carboniferous age Coal Measures (CM), Millstone Grit (MG) and Carboniferous Limestone (CL), and the Ordovician Borrowdale Volcanic Group (BVG). Fig. 1 is a map of the units and their location in a hydrostratigraphic sequence. This hydrostratigraphic sequence is also used in the 3D hydrogeological model described in the methods section below.

4. Data and methods

4.1. Data

Two types of data are used in the study: water well depths (Table 1) and TDS values (Table 2). Water well depths have been obtained from the WellMaster database as described below, and TDS data has been obtained from three sources, namely: the WellMaster database, the UK Geothermal Catalogue; and, from a NIREX study, also described here.

Water well depths are from the British Geological Survey (BGS) WellMaster hydrogeological database, part of the National Well Record Archive for England, Wales and Scotland (BGS, 2018). The WellMaster database holds information on the hydro-lithostratigraphy that wells and boreholes intersect, construction details of wells and boreholes, such as casing and screen, diameters and depths, water quality information, and information on pumping tests performed on the boreholes. Summary statistics for depths of all wells and boreholes in WellMaster are given in Table 1. When the database was accessed in February 2019 the database contained records of the location and depth of 8640 water wells and boreholes for which TDS data was available (Table 1). Spatial coverage of

Table 1
Summary of water well depths (m) for sites with TDS data in the WellMaster database.

Unit	Water well depth (m)					
	No.	Mean	SD	25 %tile	75 %tile	95 %tile
All	8640	81	86	33	107	202
CK	3631	75	55	33	106	153
LGS	470	86	93	37	88	373
SSG	1430	120	96	54	153	305
Z	120	112	283	37	80	165
CM	329	96	78	60	120	231
CL	63	61	59	34	69	160
MG	387	70	60	37	76	200
BVG	0	–	–	–	–	–
Others	2210	63	93	15	77	177

Table 2
Numbers of TDS observations from each of the sources of data by named hydrogeological unit.

Data source	Number of observations									
	All	CK	LGS	SSG	Z	CM	CL	MG	BVG	Others
All	9195	3646	482	1535	176	403	115	478	45	2315
Wellmaster	8640	3631	470	1430	120	329	63	387	0	2210
Geothermal Catalogue	439	15	12	64	56	74	48	91	0	79
NIREX study	116	0	0	41	0	0	4	0	45	26

the wells is focussed on the major aquifers across the region, with data for the two most important aquifers, the Cretaceous Chalk and the Permo-Triassic Sherwood Sandstone Group, accounting for over half the observations in the database, i.e. 3631 and 1430 observations respectively (Table 1). The depths in Table 1 are taken broadly to be indicative of representative intervals of groundwater exploitation across the study area and of differences between the main hydrogeological units described in this study.

Three sources of TDS data have been used for this study. TDS data has been obtained i.) from the UK Geothermal Catalogue (Burley et al., 1984; Rollin, 1987), ii.) from an investigation by NIREX at Sellafield, northwest England in the context of developing a deep sub-surface nuclear waste repository facility (Bath et al., 1996), and iii.) from BGS' WellMaster database (BGS, 2018). Table 2 summaries the number of TDS observations from each of these three sources. The first two sources generally consist of relatively deep observations of TDS, whereas the WellMaster database generally consists of relatively shallow observations of TDS associated with water wells. However, the WellMaster database contains significantly more TDS data than the other two sources of TDS data combined.

The UK Geothermal Catalogue (Burley et al., 1984; Rollin, 1987) is a summary of temperature, heat flow and geochemical data for the UK associated with an extensive characterisation and assessment of geothermal potential in the UK undertaken in the 1980s. It comprises information on well and sample depth, geological formation, and chemical analyses. TDS samples reported in the catalogue were obtained from a range of earlier studies and sources, including springs (and thermal springs), artesian discharges, borehole or well samples, depth samples, pumped samples, and drill stem test samples. The catalogue also includes data from samples obtained from underground mine drainage, primarily from the Carboniferous Coal Measures, however, all samples flagged as underground mine drainage have been excluded from the analysis as it could not be ascertained if those data points represented in-situ observations of TDS. The NIREX study was a major regional investigation of the potential suitability for deep storage of radioactive waste, and TDS observations were made on samples obtained as part of environmental pressure tests, discrete extraction tests, and single packer flow tests on a series of deep boreholes in the Sellafield area (Sutton, 1996). The WellMaster database contains groundwater quality data primarily from relatively shallow boreholes in areas of active groundwater exploitation (BGS, 2018). 8640 sites, or 7.2 %, of the 119,475 springs, wells and boreholes recorded in WellMaster database with known completion depths and named formations have TDS data. However, the manner in which the water sample was obtained is typically unknown. Quality Control (QC) on groundwater TDS data can be undertaken where information on major ion concentrations is available along with TDS. QC was applied to the TDS data from the Geothermal Catalogue. The mean difference between the sum of six major ions (mg/l) and TDS (mg/l) for this datasets is 1.0 % of the recorded TDS. At the time of analysis, NIREX major ions were checked to ensure that they were within 15 % of measured TDS and the ionic charge balance was reported to typically be within +/-5% (Richards and Bath, 1997). The WellMaster database does not hold systematic information related to major ions and no QC was applied to this data source.

There are 9195 TDS observations across the three data sources with 39.6 % of those coming from the Chalk and 16.7 % from the Permo-Triassic sandstones with the majority of these coming from the WellMaster database (Table 2). The WellMaster database provides 94 % of the TDS observations. However, because those observations are from relatively shallow depths compared with those in the other two datasets (the mean sample depth in the WellMaster samples is 81 m compared with 878 m from the Geothermal Catalogue and 751 m for the NIREX observations), there is a systematic bias in the combined dataset towards TDS data from shallow settings.

4.2. Methods

A basic description of the TDS data has been undertaken and TDS values have been plotted as a function of depth below ground level to enable the depth distribution of TDS values to be visualised in the context of characteristic depths of water well and water quality thresholds. The approach of Ferguson et al. (2018a) has been followed where TDS data was binned into 100 m depth intervals and plotted it as box plots to characterise changes in TDS with depth despite the bias towards more shallow observations.

In order to understand the spatial and 3D distribution of TDS, the TDS data has also been analysed relative to sea level (in the UK sea level is defined by a datum, the Ordnance Datum, OD, Bradshaw et al. (2015) taken to be the long-term average of sea levels recorded at the Newlyn Tide Gauge). To assess the nature of any spatial correlation in fresh and brackish groundwater at depth, TDS observations below the 95 %tile depth relative to sea level have been mapped and the location of fresh, brackish and saline groundwater samples highlighted. In addition, the TDS data has also been visualised as 2D sections through a 3D hydrogeological model of the study area (Newell, 2019) to qualitatively investigate the influence of geological/hydrogeological setting on the presence of fresh and brackish groundwater at depth. The hydrogeological model is based on a simplified hydrostratigraphic sequence for the study area, and the relationship between this and the eight named hydrogeological units for which there is TDS data is shown in Fig. 1. TDS data is projected into two representative sections through the 3D hydrogeological model of the study area. To enhance the visualisation of TDS data in the 2D sections, a lateral clipping domain of 50 km on each side of the cross-sections has been applied. TDS values lying within this clipping plane were projected onto the hydrogeological cross-sections. While this projection process increases the density of data shown on the cross-sections, the hydrostratigraphic context of the TDS points might undergo some migration, depending on the direction of projection relative to the structural dip.

5. Results

TDS varies over about five orders of magnitude (Table 3, Fig. 2a. At depths down to 100 m TDS varies over about three orders of magnitude from about 10 to > 10,000 mg/L, while at a depth of 1 km it varies from about 1000 to > 100,000 mg/L Fig. 2a). There is a general increase in mineralisation of groundwater with depth defined by a general increase in the minimum value of TDS for a given depth interval. The maximum observed TDS, at just over 330,000 mg/L, is approximately one order of magnitude higher than that of seawater and is for a sample from the Zechstein unit from about 1.8 km depth, although samples with a similar order of magnitude TDS are found from depths of a few hundred metres to over 2 km.

5.1. Depth distribution of TDS related to interval of active groundwater exploitation

The mean depth of all water wells with data is 81 m and the 95 %tile is 202 m (Table 1) with systematic differences in the depth of water wells between the two main aquifers. For example, the mean depth of water wells in the Chalk is 75 m compared with 120 m for the Permo-Triassic Sandstones, and the equivalent 95 %tiles are 153 m and 305 m. The 95 %tile of all water wells is indicated on Figs. 2a by the dark blue interval. Even though most TDS observations of fresh groundwater are within the zone of active groundwater exploitation, there are many TDS observations where fresh or brackish groundwater water is present below 202 m (Fig. 2a). Table 4 summarises the number and percentage of observations where TDS data indicate fresh or brackish conditions below the current intervals of exploitation. There are 917 TDS observations, 10.0 % of all the TDS observations, below the 95 %tile depth of water wells. Of these observations, 454, 4.9 % of all the TDS samples, are of fresh groundwater, with about another 1.1 % being brackish groundwater. It is inferred from these observations that current groundwater exploitation in GB is not necessarily limited just by TDS changes with depth, other limiting factorsmay include specific water quality issues (Kinniburgh et al., 1994), relatively

Table 3
Summary of TDS data by hydrogeological unit.

Unit	Number of observations	TDS (mg/L)						
		Mean	SD	Min.	25 %tile	75 %tile	95 %tile	Max.
All	9195	4,757	26,916	1	300	625	6,612	331,135
CK	3,646	676	1,493	3	318	540	1,453	35,287
LGS	482	375	680	9	160	361	850	8,820
SSG	1,535	3,062	20,740	10	253	530	2,911	299,714
Z	176	75,515	122,579	13	457	182,945	319,052	331,135
CM	403	12,319	35,064	87	380	1,240	96,052	279,511
CL	116	19,446	36,978	39	400	10,921	98,986	205,957
MG	478	12,394	40,937	60	240	767	99,539	317,298
BVG	48	40,156	36,978	108	22,000	60,344	96,480	181,000
Others	2,311	3,429	17,544	1	325	715	6,354	315,711

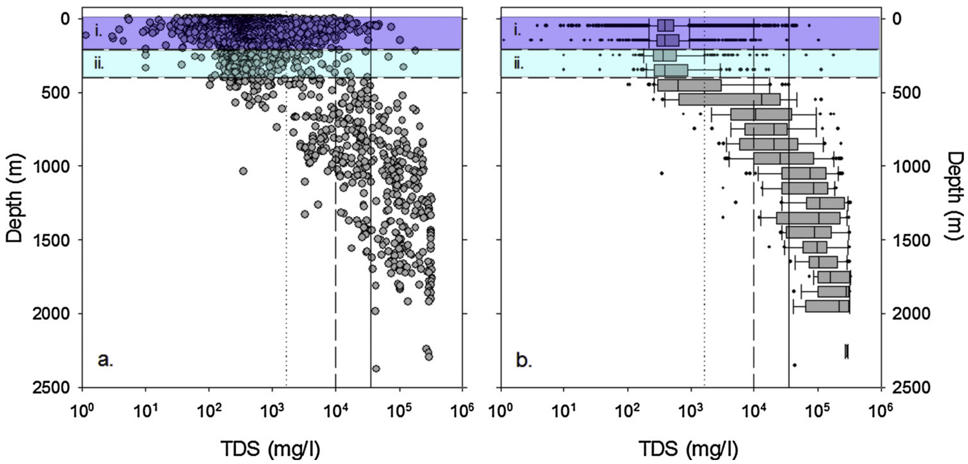

Fig. 2. TDS depth plots. a. scatter plot and b. binned TDS data showing i. 95 %tile of water well depths (202 m) and ii. UKTAG groundwater body deepest advisable limit (400 m). Vertical lines illustrate fresh (dotted line) and brackish (dashed line) groundwater thresholds and seawater (solid line).

Table 4
Number and percentage of sites that are fresh TDS < 1625 mg/L or brackish TDS > 1625 mg/L and < 10,000 mg/L below the 95 %tile depth of water well and below 400 m for each hydrogeological unit.

Unit	Number (%age of total) of observations						
	Total	> 95 %tile unit depth	> 95 %tile unit depth & fresh	> 95 %tile unit depth & brackish	> 400 m	> 400 m & fresh	> 400 m & brackish
CK	3,646 (39.5 %)	218 (6.0 %)	204 (5.6 %)	11 (0.3 %)	8 (0.2 %)	3 (0.1 %)	5 (0.1 %)
LGS	482 (5.2 %)	32 (6.6 %)	30 (6.2 %)	2 (0.4 %)	23 (4.8 %)	21 (4.4 %)	2 (0.4 %)
SSG	1,535 (16.7 %)	127 (8.3 %)	82 (5.3 %)	19 (1.2 %)	61 (4%)	23 (1.5 %)	12 (0.8 %)
Z	176 (1.9 %)	60(34.1 %)	6 (3.4 %)	1 (0.6 %)	54 (30.7 %)	0	1 (0.6 %)
CM	403 (4.4 %)	86(21.3 %)	14 (3.5 %)	7 (1.7 %)	70 (17.4 %)	0	6 (1.5 %)
CL	116 (1.3 %)	52 (44.8 %)	3 (0.6 %)	20 (17.2 %)	50 (43.1 %)	2 (0.4 %)	21 (4.4 %)
MG	478 (5.2 %)	110 (95.7 %)	20 (17.4 %)	26 (22.6 %)	89 (77.4 %)	2 (1.7 %)	25 (21.7 %)
BVG	48 (0.5 %)	43 (89.6 %)	0 (0%)	0 (0%)	43 (89.6 %)	0	2 (4.2 %)
Others	2,311 (25.1 %)	189 (8.2 %)	95 (4.1 %)	15 (0.6 %)	84 (3.6 %)	4 (0.2 %)	4 (0.2 %)
Total	9195	917 (10.0 %)	454 (4.9 %)	101 (1.1 %)	482 (5.2 %)	55 (0.6 %)	78 (0.8 %)

low groundwater yields (Abesser and Lewis, 2015), and the relative cost of development of deep groundwater sources (Johns and Özdemiroğlu, 2007; Charalambous, 2019).

5.2. Depth of fresh to brackish groundwater transition

In their analysis of the depth of transition between fresh and brackish groundwater across the contiguous USA, Ferguson et al. (2018a) plotted TDS against depth as box plots in successive 100 m depth intervals so that the TDS data could be readily compared with depth intervals of interest while accounting for a systematic bias towards shallow samples. Fig. 2b is such a plot for TDS data for the current study area with the mean TDS in each 100 m depth interval indicated by the central line in each box and whisker plot. Again, as in Figs. 2a, in Fig. 2b the 95 %tile of all water wells is indicated by the dark blue interval and the UKTAG groundwater deepest advisable limit, down to 400 m, is indicated by the base of the pale blue interval. For each 100 m depth interval down to 500 m the mean TDS of the binned data is less than the maximum admissible concentration for potable groundwater supplies in England 1625 mg/L, i.e. the intervals down to 500 m represent predominantly fresh groundwater Fig. 2b). From 500 m down to a depth of 700 m TDS is consistent with predominantly brackish groundwater conditions. Below 700 m, the TDS data indicates groundwater is saline and that it becomes progressively more saline with depth, so that below 1 km the mean TDS of the binned data exceeds that of seawater (~35,000 mg/L).

Most water wells and boreholes recorded in the WellMaster database are within the 400 m depth interval defined by UKTAG (2012) as the maximum base of groundwater bodies. This indicates some consistency between current depths of groundwater exploitation and the current UKTAG definition of the effective base of groundwater bodies. However, there are a small number of observations where TDS values indicate that there is fresh and brackish groundwater below 400 m (Fig.2, Table 4). There are 55

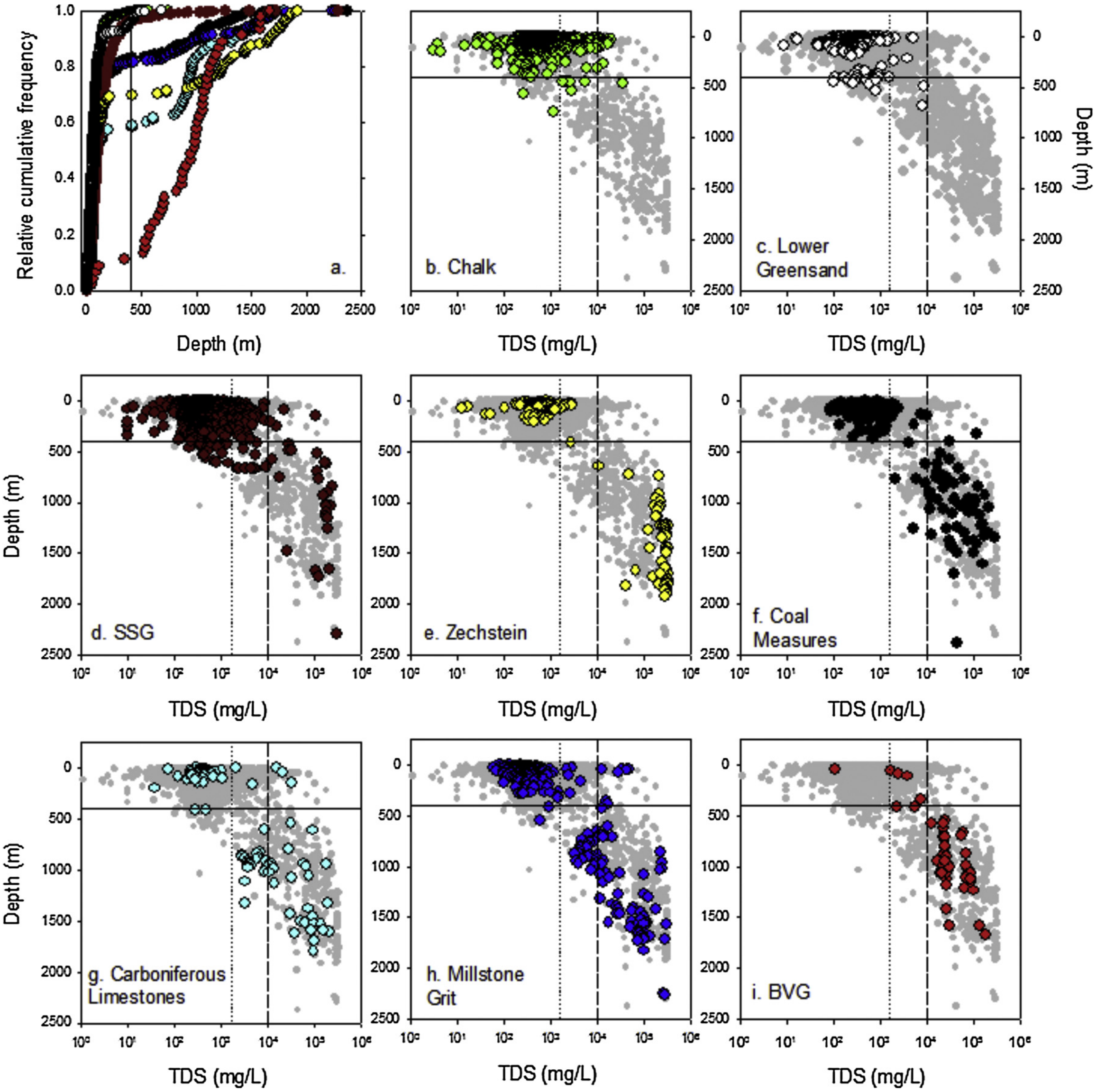

Fig. 3. a. Cumulative frequency plots of sample depths, and, b. to i., TDS depth plots for each named hydrogeological units. Vertical lines indicate fresh (dotted) and brackish (dashed) groundwater thresholds. The vertical (a.) and horizontal solid (b. to i.) lines indicates the current maximum regulatory depth to potable water (400 m) in the study area (UKTAG, 2012). Symbol colours in 3a correspond to samples in hydrogeological units in Figs. 3b to 3i.

observations (0.6 % of all TDS samples) below 400 m depth that indicate fresh groundwater conditions and 78 TDS observations (0.8 % of all TDS samples) that indicate brackish groundwater conditions below 400 m. Given these, albeit limited, observations, and the distribution of binned TDS data in Fig. 2b, it is inferred that if a precautionary approach is taken to the definition of the effective base to groundwater bodies in the UK then this threshold might be more appropriately set at 500 m, rather than at the current 400 m (UKTAG, 2012).

5.3. TDS as a function of hydrostratigraphy and hydrogeological setting

Fig. 3 shows the depth distribution of TDS as a function of the eight named hydrostratigraphic units. Very high values of TDS appear to occur broadly independent of depth and are found in all named units with the exception of the Lower Greensand that, like the Chalk, hasn't been sampled at depths greater than a few hundred metres (Fig. 3). However, in all units except the Borrowdale Volcanic Group, high values of TDS are unusual and the majority of the TDS observations are below the TDS of seawater (Table 3). There are differences in the TDS distributions between the different hydrogeological units (Fig. 3, Table 3). For example, the mean TDS of measurements from the Chalk (676 mg/L) and Lower Greensand (375 mg/L) are about two orders of magnitude less than the

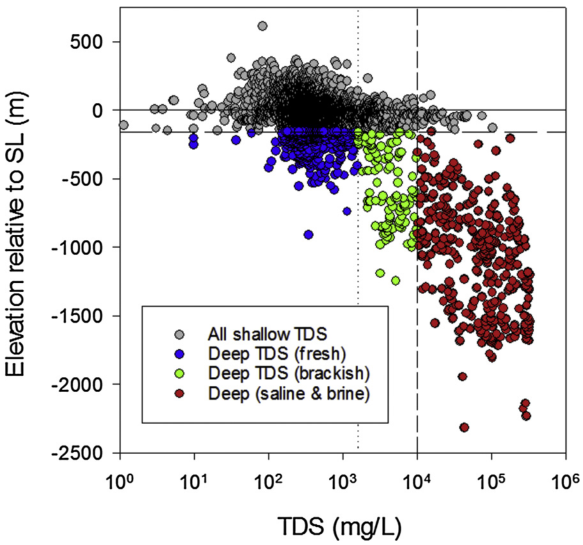

Fig. 4. TDS relative to sea level (horizontal solid line) and the 95 %tile of observation depths relative to sea level (horizontal long dash). Vertical lines indicate fresh (dotted) and brackish (short dash) groundwater thresholds. Deep TDS observations of fresh (blue), brackish (green) and saline and brines (red) that are plotted in Fig. 5 are highlighted. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mean TDS of samples from the Zechstein (75,515 mg/L) and the Borrowdale Volcanic Group (40,156 mg/L). This reflects systematic differences in the depth of occurrence and sampling of the units (Loveless et al., 2018) (Fig. 3a), differences in the hydrogeological setting where the units are found, as well as differences in the characteristic hydrogeochemistry of the units. Although all units have observations of brackish groundwater below the UKTAG groundwater deepest advisable limit at 400 m, there are no records of fresh groundwater below this depth in the Zechstein, Coal Measures, and Borrowdale Volcanic units (Fig. 3, Table 4).

In continental sedimentary basins, deep groundwater circulation is controlled by the elevation of the major outflow points from the basins relative to the location and elevation of the recharge areas (Toth, 1963). However, for sedimentary basins in non-continental island landmasses, such as the UK, groundwater discharge to the coast is an important control on deep groundwater circulation. Downing et al. (1987) have previously described this phenomenon for the UK. Consequently, plotting the TDS data relative to sea level is important because it enables assessments to be made of the extent to which current sea level acts as a major base level control on current regional groundwater circulation in the UK. However, this means that in the following description of the TDS data it is necessary to modify the definition of deep groundwater. Previously, deep groundwater was defined as groundwater occupying an interval below the current normal depth of active groundwater exploitation, for example below the 95 %tile of well depths for a given aquifer across a given region. However, for the purposes of considering TDS data in the context of regional hydrogeological flow to the coast deep groundwater is defined as groundwater below the 95 %tile of all sample depths relative to sea level, the reference level for the model.

The TDS data for GB has been plotted as a function of sea level (Fig. 4), the distribution of deep (relative to sea level) fresh, brackish and saline TDS has been mapped to investigate spatial coherence in the data (Fig. 5), it has been projected into sections through the 3D hydrostratigraphical model of the study area (Fig. 6), and is described in the context of regionally important structural features shown in Figs. 5 and 6 and described in Table 5. Fig. 4 shows the depth distribution of TDS data relative to sea level, with the boundaries between fresh and brackish groundwater indicated by vertical dotted and dashed lines respectively. As expected, most fresh groundwater is found above sea level (solid horizontal line in Fig. 4). However, there are many deep fresh groundwater observations below the 95 %tile of all depths relative to sea level (i.e. 157.6 m below sea level as indicated by the long-dashed horizontal line). Although some brackish groundwater is present above sea level, in contrast to the fresh groundwater observations, most brackish groundwater observations are between sea level and the 95 %tile of depth relative to sea level. With the exception of two samples, all saline groundwater and brines are found below sea level, and the overwhelming majority of these are found below the 95 %tile of depth relative to sea level. This distribution of groundwater quality with depth is consistent with the observation that in the study area the majority of fresh groundwater is associated with contemporary groundwater recharge and circulation associated with current base levels (Downing et al., 1987; Edmunds and Smedley, 2000; Smedley et al., 2018) and controlled by groundwater flow and discharge to rivers (Toth, 1963) or to the sea (Edmunds et al., 2001a, 2001b). To investigate the regional distribution of TDS below the 95 %tile of all sample depths relative to sea level but unrelated to specific aquifers, observations of fresh (blue), brackish (green), and saline to brine (red) groundwater highlighted in Fig. 4 have been mapped spatially in Fig. 5.

Where deep fresh groundwater is present it is generally spatially coherent and is characteristically associated with relatively deep sedimentary basins (Fig. 5 and Table 5). For example, there are clusters of observations of fresh groundwater present at depth in the Chalk and Lower Greensand aquifer of the Wessex Basin in southern England, in the Permo-Triassic sandstones of the Worcester and

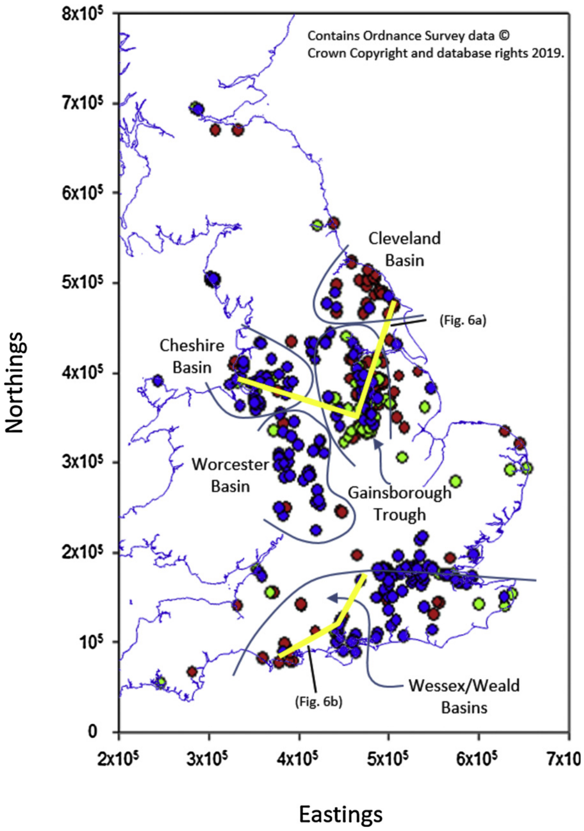

Fig. 5. Spatial distribution of fresh (blue), brackish (green) and saline (red) groundwater based on samples below the 95 %tile observation depths relative to sea level. The generalised outlines of selected major basins (blue lines) across the study area are indicated, as are the locations of the two cross-sections (yellow lines) shown in Fig. 6. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

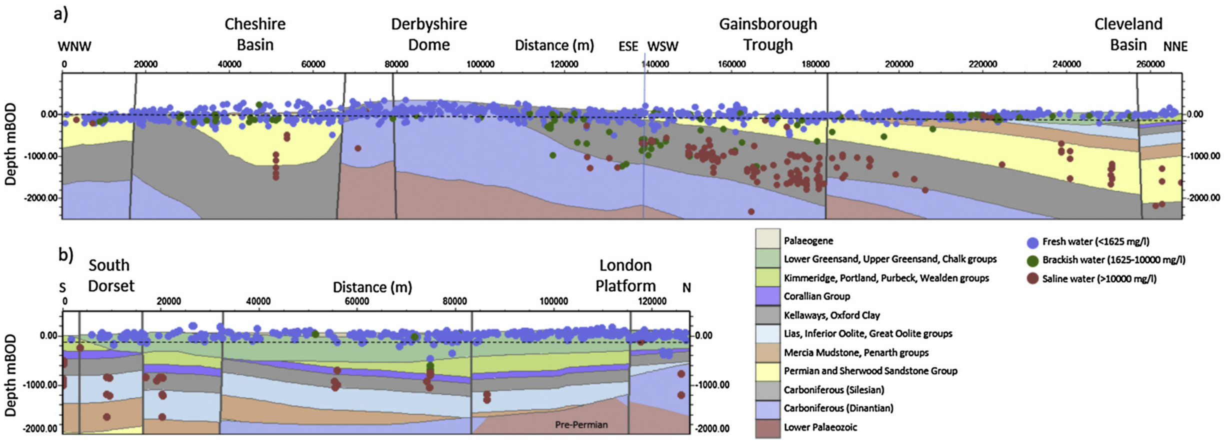

Fig. 6. Cross sections showing 3D distribution of TDS as a function of generalised basin structure and stratigraphy in a. northern and b. southern England. The location of the sections is shown on Fig. 5. Sections are shown with 10x vertical exaggeration. Depth in both sections in metres below OD (mbOD). The hydrostratigraphy and how it relates to the eight named units is also detailed in Fig. 1. The 95 %tile observation depth relative to sea level is indicated by a dashed line in the sections.

Cheshire Basins in central and NW England, and in the Permo-Triassic sandstones of the Gainsborough Trough. Basin-scale hydrogeological controls on the distribution of deep brackish groundwater are less evident, and there does not appear to be a systematic spatial coincidence between fresh and brackish water at depth. For example, there is no apparent systematic coincidence between fresh and brackish groundwater in the Chalk of the Wessex Basin or the Sherwood Sandstone Group of the Worcester Basin, although

Table 5
Brief descriptions of the geological settings and structural features discussed in the study.

Structural feature	Geological setting	References
Cheshire Basin	The Cheshire Basin is a half-graben structure bounded to the SE by a major fault system. It contains a thick sequence of Permo-Triassic sandstones beneath a cover of Late Triassic mudstone and evaporite. Within the basin groundwater circulation is controlled by a combination of relatively low permeability units and high angle extensional fault systems, with regional groundwater flow in a general NW direction across the basin from the high ground in the S and SE of the basin.	Downing et al. (1987); Aitkenhead et al. (2002); Plant et al. (1999)
Cleveland Basin	The Cleveland Basin is an inverted Jurassic basin. Inversion is thought to have occurred largely intra-Jurassic and intra Cretaceous, and locally controls thickness variations in the regionally important Chalk aquifer. Groundwater flow in the Chalk is from high ground in the W and NW towards the coast to the E.	Kent, 1980; Gale and Rutter, 2006.
Derbyshire Dome	The Derbyshire Dome consists of a structurally uplifted Carboniferous shallow-water carbonates controlled by major basement fault systems.	Aitkenhead et al. (2002); Stone et al. (2010)
Gainsborough Trough	The Gainsborough Trough consists of a half-graben structure fault-bounded to the NE and preserving a series of up to 4 km thick Carboniferous sediments to the SW. Above these, and dipping eastwards towards the N Sea are Permian and younger sediments including the regionally important Sherwood Sandstone Group (SSG) and Zechstein (Z) aquifers. Groundwater recharge occurs over the higher ground to the west and flows down dip toward the N Sea.	Downing et al. (1987); Edmunds, and Smedley, 2000; Pharaoh et al. (2011)
London Platform	The London Platform is a structural high or divide separating the Late Palaeozoic/ Mesozoic extensional basins of the English Midlands from the Wessex and Weald basins. The thin cover of Cretaceous and Tertiary deposits was folded during Alpine inversion to form the synclinal London Basin.	Sumbler (2011)
Wessex Basin and Weald	The Wessex Basin comprises a series of linked extensional basins filled with strata of Permian to Tertiary age covering southern England and adjacent offshore areas. The present structural configuration reflects Alpine compression with the Chalk and Lower Greensand forming large-scale fold structures and steep monoclines above reverse reactivated faults. Chalk is recharged around the high ground towards the N of the Basin and generally flows S towards the centre of the Basin and towards the English Channel.	Allen and Crane (2017)
Worcester Basin	The Worcester Basin is a N–S trending graben structure that separates the Welsh Palaeozoic Massif from the London Platform. It contains Permo-Triassic sandstones (SSG) beneath a cover of Late Triassic/Jurassic mudstone. The regional flow pattern is controlled by high piezometric heads to the W, N and E.	Hains and Horton (1969); Downing et al. (1987)

there does appear to be both fresh and brackish groundwater at depth in the Sherwood Sandstone Group of the Cheshire Basin and the Gainsborough Trough. Similarly, observations of deep saline groundwater and brines appear to be most spatially coherent within the Cleveland Basin, the Gainsborough Trough and at the western end of the Wessex Basin. Previous work indicates that groundwater in GB is primarily meteoric. Downing (1987) noted that, throughout GB, formation waters have probably been replaced by fresh groundwater recharge several times, and that current day changes in groundwater down-hydraulic gradient in most of the aquifer systems are a response to the evolution of water along flow lines. Downing et al., 1987 noted only one example of a residual connate (*sensu stricto*) water had been found to date in the Chalk of E Anglia (Edmunds, 1986; Younger et al., 2015).

In summary: fresh groundwater is present below the 95 %tile depth relative to sea level in all the Basins (with the exception of the Cleveland Basin); brackish groundwater is present in the Cheshire Basin and the Gainsborough Trough; and, saline groundwater and brines are present within the Cleveland Basin, Cheshire Basin, the Gainsborough Trough and the Wessex Basin. Consequently, it is inferred that differences in the details of the regional hydrogeological setting and evolution of meteoric water in the respective basins are important controls on the spatial distribution of TDS with depth. This inference is supported by consideration of 2D sections through the 3D hydrogeological model.

Fig. 6 illustrates two sections, one running SSW from the coast of eastern England, across the Gainsborough Trough and then turning WNW through the northern end of the Cheshire Basin to the coast in NW England (Fig. 6a). The second section that runs SW from the north-eastern end of the Wessex Basin, across the western end of the Weald anticline, through the centre of the Wessex Basin and out to the south coast of England (Fig. 6b). The sections show large-scale basin structures associated with the hydrostratigraphy, as well as the locations of TDS samples (colour coded according to TDS) and the depth of the 95 %tile of observations relative to sea level. In the northern section fresh and brackish groundwater is present below the 95 %tile of observations relative to sea level in the Cheshire Basin to the west, and in the Gainsborough Trough to the east of the Derbyshire Dome, a regional topographic high (Fig. 6a). The relatively fresh groundwater in the Gainsborough Trough in both the Sherwood Sandstone Group and other units appears to be associated with previously documented relatively deep groundwater circulation Gainsborough Trough and inferred to be driven by elevated hydraulic heads across the neighbouring topographic high (Downing et al., 1987). Within the fault-bounded Cheshire Basin a continuous sequence of sandstones to depths of in excess of 1 km have enabled groundwater circulation to develop, again inferred to be driven by heads in the topographic highs at the margins of the Basin (Plant et al., 1999). In contrast, at the NNE end of the same section (Fig. 6a), fresh groundwater is effectively absent at depth. Here the Chalk (dark green unit in Fig. 6a) aquifer is present and is relatively thin compared with the Sherwood Sandstone Group aquifer at the WNW end of the section. This combined with an absence of significant relief and consequently low regional head gradients (Gale and Rutter, 2006) is inferred to contribute to an absence of fresh groundwater below the 95 %tile of observations relative to sea level in the Cleveland Basin.

In the southern section, the Chalk and Lower Greensand aquifer is at its thickest and deepest throughout the central part of the section across the Wessex Basin (Loveless et al., 2018) (Fig. 6b). Here fresh and brackish groundwater is present at or below the 95 %tile of observations relative to sea level, and is inferred to be driven by elevated heads at local topographic highs at the margins of the Basin (Allen and Crane, 2017). Whereas at the far southern end of the section (Fig. 6b), fresh groundwater is generally absent at depth where the Chalk is thinner, and the potential for groundwater circulation has been limited by the presence of older, less permeable units such as the Oxford Clay and Lias (dark grey and pale blue respectively in Fig. 6b) near the surface (Allen and Crane, 2017).

6. Discussion

6.1. Some implications for UK groundwater resources and protection

As noted above, given the presence of, albeit limited, fresh groundwater in GB's two major aquifers below the current advisory base of groundwater bodies in the UK (UKTAG, 2012) (Fig. 2b), the base of groundwater bodies in the UK might be more appropriately taken to be at 500 m. An implication of this is that under current legislation groundwater down to this depth would need to be both protected and restored to 'good status'. Under the implementation guidance associated with the European Water Framework Directive (European Commission, 2000) and the daughter Groundwater Directive (European Commission, 2006) the environmental objectives of 'preventing deterioration of, and protecting, enhancing and restoring good groundwater status' would apply to all bodies of groundwater down to this depth interval.

An additional implication of a deepened advisory base of groundwater bodies is that it would reduce the separation between the base of potential future groundwater bodies and the depth of interest for future development of unconventional hydrocarbons. Ferguson et al. (2018a) used their analysis of TDS to not only analyse the relationship between water well depths and salinity transitions in the USA, but also to quantify the separation between the interval of fresh groundwater resources and the depth of onshore hydrocarbon development and other potentially polluting sub-surface activities. Although the latter is not a focus of the present study, the results here can be related to the concept of 3D groundwater vulnerability (Loveless et al., 2019) and the concept of 'safe separation' between fresh groundwater requiring protection and onshore hydrocarbon development below aquifers, including potential shale gas development in the UK (Loveless et al., 2018). Currently, high pressure high volume fracking for shale gas is banned above 1 km depth (1.2 km under designated protected land such as National Parks) in England. This is equivalent to a minimum 600 m separation with the current default base of groundwater bodies, a separation of about 800 m between the 95 %tile depth of water wells in the WellMaster database, and a separation of just over 900 m with mean water well depths. There is still a lack of consensus as to what constitutes a 'safe separation' between groundwater requiring protection and an interval of shale gas development below a body of groundwater (Loveless et al., 2018). In a study of the separation of the base of aquifers and the top of underlying shale units in England and Wales, Loveless et al. (2018) assessed the implications of 'safe separation' intervals for different aquifer-shale pairs in the UK. They analysed 'safe separation' distances of 600 m and 1000 m, representative of the maximum height of induced hydraulic fractures and of natural hydraulic fractures Davies et al., 2012). In the context of the current study, assuming the same 'safe separation' intervals as Loveless et al. (2018), a slightly deepened depth to base of groundwater bodies of 500 m would mean that there would be no unambiguously 'safe separation' for shale gas development at depths down to 1.1 km based on the maximum height of induced hydraulic fractures. Similarly, there would be no 'safe separation' for shale gas development at depths down to 1.5 km based on the maximum height of natural hydraulic fractures (Davies et al., 2012; Loveless et al., 2018).

6.2. Comparison with previous studies

The depth distribution of TDS data across the study area is broadly consistent with that described in previous data-led analyses of TDS data from the USA (Kang and Jackson, 2016; Ferguson et al., 2018a; Kang et al., 2019). In all cases there is a general increase in mineralisation of groundwater with depth associated with a general increase in the minimum value of TDS for a given depth interval, and variability in TDS is greatest at relatively shallow levels and decreases with depth. There is a common upper bound to TDS for the different study areas irrespective of depth at about 330,000 mg/L. These very high values of TDS, well above that of seawater, are consistent with groundwater that is supersaturated with respect to halite (Hanor, 1994a, 1994b; Ferguson et al., 2018b).

It is not possible to make direct comparisons between the depth of transitions between fresh and brackish groundwater in the present study and the findings of the previous studies from the USA (Kang and Jackson, 2016; Stanton et al., 2017; Ferguson et al., 2018a; Kang et al., 2019) as the studies differ slightly in their respective definitions of groundwater quality. However, the inferred average transition from fresh to brackish groundwater is broadly consistent with those of the previous studies. In particular, the average depth of the transition at about 500 m for the present study (Fig. 2b) is very similar to the equivalent average transition depth of 550 m across large parts of the USA found by Ferguson et al. (2018a). This is significant in that it provides new, additional confirmation of the observation of Ferguson et al. (2018a) that their transition depth was relatively shallow compared with previous global estimates of the average transition depth (Gleeson et al., 2016). Ferguson et al. (2018a) asserted that, if their observations could be extrapolated globally it would suggested that there may be considerably less fresh groundwater available than estimated by Gleeson et al. (2016). The findings of this case study appear to support that assertion.

6.3. Role of data-led studies in understanding deep regional groundwater quality

Our observation, that deep fresh groundwater is present in relatively deep sedimentary basins, is consistent with the concept of groundwater as a geologic agent (Toth, 1999). Specifically, that local- to national-scale variations in TDS result from the long-term interaction between local- to national-scale chemical processes, and groundwater flow processes driven by head differences associated with topographic relief. In a global study of the relationship between the age and depth of groundwater, Jasechko et al. (2017) have shown that fossil waters (water recharged at least 12,000 years ago, prior to the Holocene) comprise a significant proportion of groundwater stored in the top 1 km of the crust and the majority of groundwater abstracted from wells deeper than 250 m. However, based on measurements of tritium, they also noted that much younger (post-1953 recharge) waters were also present in half of the wells that were dominated by fossil groundwater. Although there is no comparable systematic set of data on groundwater ages for deep samples from the GB study area, deep groundwater flow is known to have been influenced by Quaternary history, evolving relationships between basins and coastlines, and by geological structure For example, Bath et al. (2006) explained the relatively uniform salinity depth profile down to about 1700 m in the low permeability basement of NW England as due to repeated cycles of Quaternary recharge. Black and Barker (2016) subsequently supported this interpretation when they estimated lower recharge temperatures and described relict high hydraulic heads to a depth of 1100 m across the same region. The long coastline of the study area is a major influence on groundwater systems Black and Brightman, 1996) with groundwater being significantly impacted by changing sea levels. Sea levels have probably been lower than present for the last 100,000 years, reaching their minimum of about 125 m below current levels during the Last Glacial Maximum, although the lowest groundwater base levels during this period, controlled by palaeo-topography, have been estimated to be about 65 below current sea level (Edmunds et al., 2001b). These lowered sea levels caused freshwater recharge of saline aquifers at the coastline (Black and Barker, 2016; Edmunds et al., 2001a, 2001b) with groundwater in higher permeability units coming into equilibrium with the changing boundary conditions more quickly than in lower permeability units (Black and Brightman, 1996).

Clearly, data-led analyses of TDS, such as presented here, do not provide information about groundwater ages or direct insights into the origins of freshwater at depth. However, when combined with conceptual or numerical models of regional-scale hydrogeology they can provide useful information for water resource management agencies and policymakes to make more informed decisions related to groundwater resource development plans and the protection of deep groundwater resources. The approaches to TDS data exploration and analysis described here (analysis of TDS with respect to depth of current groundwater exploitation and with respect to sea level in the context of regional hydrogeological models) are applicable regardless of hydrogeological setting, and could be applied equally effectively wherever there are depth changes in groundwater TDS, including, for example, coastal delta systems. For large continental sedimentary basins, data-led analysis of depth variations in TDS in the context of a consistent hydrostratigraphy of a given basin may improve the interpretation of the TDS data. In such settings, analysis of TDS relative to a basin-specific base level, such as the level of the lowest flow gauge in the basin, would be more appropriate than using sea level as a reference. More generally, analysis of TDS as a function of regional groundwater base levels in addition to depth below ground level may provide additional insights in to the possible controls on TDS. In addition, studies from other regions and hydrogeological environments are encouraged in order to add new evidence for establishing representative depths for the transition from fresh to brackish groundwater and hence contribute to a more refined global estimate of the availability of fresh groundwater.

7. Conclusions

- In the study area, TDS varies over about five orders of magnitude, with a general increase in mineralisation with depth.
- The interval of active groundwater exploitation in GB is typically down to about 200 m and most groundwater in this interval is fresh or brackish. However, there is evidence for fresh and brackish groundwater water below this interval. Almost 5% of all the TDS samples indicate fresh groundwater below about 200 m, with about another 1% being brackish groundwater. It is inferred from these observations that current groundwater exploitation in GB is not necessarily limited just by TDS at depth, but may also be limited by other factors such as relatively low groundwater yields, other water quality considerations, e.g. potability limits for specific determinands, and the relative cost of development and pumping from deep groundwater sources.
- Based on averaged TDS values for 100 m depth intervals, there is a transition from fresh to brackish groundwater at 500 m, and from brackish to saline groundwater at 700 m. Below 700 m, groundwater becomes progressively saline with depth, so that below 1 km mean TDS exceeds that of seawater (~ 35,000 mg/L).
- This depth distribution of TDS data across the GB study area is consistent with previous data-led analyses from the USA. The average depth of transition from fresh to brackish groundwater is consistent with that found by Ferguson et al. (2018a) for the USA, and supports their assertion that globally there may be considerably less fresh groundwater available than previously estimated by Gleeson et al. (2016) based on assumptions of groundwater age.
- In the UK, a maximum effective base to groundwater bodies has been defined, in the absence of any other information, at 400 m (UKTAG, 2012). However, there are a small number of TDS observations of fresh and brackish groundwater below 400 m. Given these observations, it is inferred that if a precautionary approach is taken then this threshold might be more appropriately set at 500 m.
- There are differences in the TDS distributions between the hydrogeological units in GB. For example, the mean TDS of measurements from the Chalk (676 mg/L) and Lower Greensand (375 mg/L) are about two orders of magnitude less than the mean TDS of samples from the Zechstein (75,515 mg/L) and the Borrowdale Volcanic Group (41,544 mg/L). This reflects systematic differences in the depth of occurrence and samples in the units, differences in the hydrogeological settings where the units are

found, and differences in the characteristic hydrogeochemistry of the units.

- When the TDS data for GB is analysed relative to sea level and the deep TDS observations are mapped, fresh and brackish groundwater exhibits some spatial coherence as a function of regional geological and hydrogeological setting. Spatially coherent fresh and brackish groundwater at depth tends to be associated with relatively deep sedimentary basins overlying older, less permeable basement. It is inferred from this observation that differences in the regional hydrogeological setting and hydrogeological evolution of the respective basins are important controls on the distribution of fresh and groundwater at depth.

CRediT authorship contribution statement

J.P. Bloomfield: Conceptualization, Formal analysis, Writing - original draft, Writing - review & editing. **M.A. Lewis:** Data curation, Formal analysis, Writing - original draft, Writing - review & editing. **A.J. Newell:** Visualization, Writing - original draft. **S.E. Loveless:** Conceptualization, Writing - original draft. **M.E. Stuart:** Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ejrh.2020.100684.

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