Age and quality stratification of groundwater in the Triassic Sherwood Sandstone aquifer of South Yorkshire and the East Midlands, UK

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ABSTRACT

Groundwater from the Triassic Sherwood Sandstone aquifer of the English East Midlands shows a well-documented evolution in chemistry and residence time as it flows downgradient from shallow unconfined conditions to greater depths, confined by Mercia Mudstone. The flow path covers a lateral distance of some 40 km and depths approaching 800 m. The presence of fresh groundwater (Cl = 15 mg/L, Na = 17 mg/L, SO_4 = 144 mg/L, TDS = 500 mg/L) of likely Pleistocene age can be demonstrated down to about 500 m depth in the aquifer, some 10 km downgradient of its confined/unconfined interface. This is amongst the deepest fresh groundwater identified in the UK. Beyond that zone, salinity increases in response to dissolution of gypsum or anhydrite, giving Ca-SO_4 groundwater. Further downgradient still, saline groundwater (TDS = 10 g/L) is encountered in the deepest part of the confined aquifer. Downgradient geochemical evolution and increasing residence time are also observed in the South Yorkshire section of the aquifer, to the north of the East Midlands flow path. Here, analogous sequential geochemical changes are observed, controlled by carbonate and sulphate mineral reactions, redox changes and silicate hydrolysis, with evidence of increased inputs of e.g. Na, Cl and SO_4 from modern pollution at shallow depths in the unconfined aquifer. Redox conditions are more variable in the western part of the South Yorkshire aquifer, due to local confinement or semi-confinement by fine-grained Quaternary deposits overlying the Sherwood Sandstone. Ratios of $\delta^{13}C$ in this section of aquifer increase from −14‰ at outcrop to −11‰ in Mercia-Mudstone-confined conditions as a result of gradual equilibration with aquifer carbonate under closed-system conditions. Ratios of $\delta^{18}O$ and δ^2H become more depleted, reaching −9‰ and −61‰ respectively, suggesting recharge under climatic conditions significantly cooler than the modern era. Increasing residence time is also indicated by increasing concentrations of a number of trace elements (e.g. Li, Rb, Sr, Mo). These transitions are also observed vertically within investigated boreholes in unconfined and semi-confined sections of the aquifer. Deep groundwater (160–170 m depth) from a borehole within the unconfined aquifer of South Yorkshire has $\delta^{18}O$ and δ^2H ratios as depleted as −9.2‰ and −67‰ respectively. Such depth stratification indicates that good-quality palaeowater, likely of Pleistocene age, can exist at depth even in the unconfined Sherwood Sandstone aquifer, and that vertical hydraulic conductivity is much lower than lateral. A paucity of boreholes in the Mercia-Mudstone-confined section of the South Yorkshire aquifer makes estimation of the lateral extent of fresh groundwater there more problematic, though brackish groundwater (Cl = 1300 mg/L, TDS = 5.5 g/L) has been identified 12 km east of the aquifer's confined margin.

1. Introduction

Research on regional groundwater resources and quality in the UK has often focussed on shallow aquifer systems (less than around 100 m depth), because of greater access and use, and greater potential vulnerability to contamination from surface activities. However, interest in the hydrogeochemical conditions at greater depths has increased significantly in recent years, spurred by environmental concerns around new or rejuvenated interests in deep exploration for, for example, unconventional hydrocarbons or radioactive waste disposal. Understanding of groundwater quality and groundwater residence times in deeper aquifers is important for establishing groundwater flow paths, rates and potential pollutant pathways and for determining the three-dimensional extent of groundwater bodies that require protection
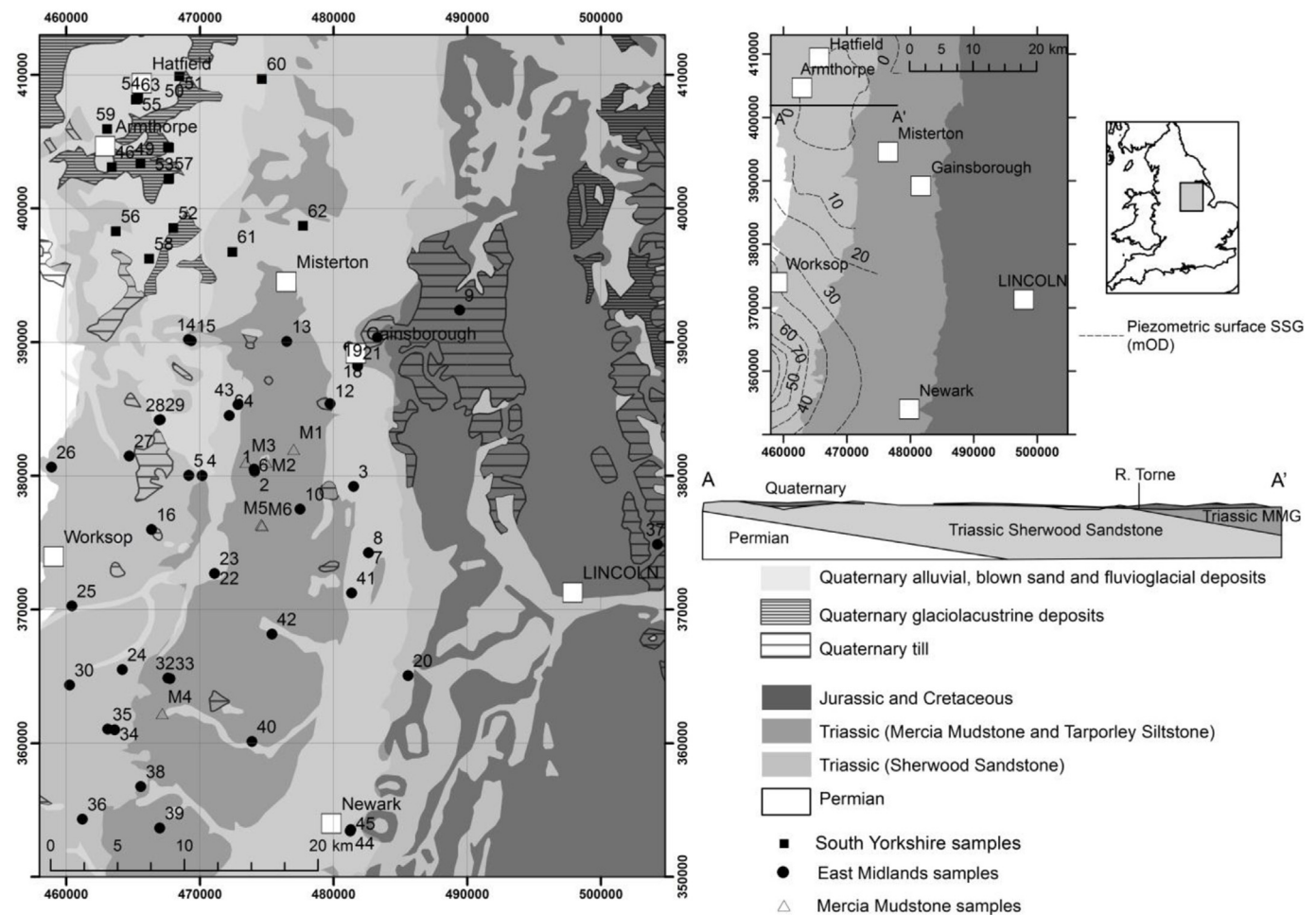
Fig. 1. Geological map showing bedrock and superficial units and locations of groundwater samples (with site numbers) from South Yorkshire and the East Midlands; insets show bedrock geology with piezometric contours on the Sherwood Sandstone aquifer; cross section A–A′ at 10× vertical exaggeration; and national boundaries (SSG: Sherwood Sandstone Group; MMG: Mercia Mudstone Group).

in accordance with European legislation.

The Triassic Sherwood Sandstone of central England is an important regional aquifer. The aquifer is unusual in that it hosts deep potable groundwater, in some places to depths well in excess of 100 m. The East Midlands section of the aquifer is well-documented in terms of groundwater quality and age estimation (e.g. Andrews et al., 1984; Andrews and Lee, 1979; Bath et al., 1979; Bath et al., 1987; Edmunds et al., 1982; Edmunds and Smedley, 2000). It has a recognised flow path that spans some 40 km laterally and extends in depth to around 800 m below ground level (Edmunds and Smedley, 2000), albeit with saline groundwater in the deepest parts of the aquifer at its easterly onshore extent. This paper extends the area of aquifer investigation further north into South Yorkshire (Doncaster area), to an area which has received comparatively little attention. Together with the East Midlands section, the study area covers some 2400 km² (Fig. 1). This paper outlines key regional and depth variations in water chemistry in the aquifer, along with likely controlling processes and residence times estimated from stable isotopes and diagnostic trace elements. The study also summarises the hydrogeochemical data available to estimate the regional extent of the fresh groundwater body and the constraints on its distribution.

2. The Sherwood Sandstone aquifer

The Triassic red-bed Sherwood Sandstone of South Yorkshire, Nottinghamshire and Lincolnshire is a significant source of water for both public and private supply. Investigations have demonstrated geochemical evolution of groundwater from young recharge in the unconfined aquifer in the west, downgradient into the confined aquifer. Water quality consequently changes from relatively high NO₃, SO₄, and Cl water at outcrop to water of good quality with low Cl, NO₃ and SO₄ in the confined part of the aquifer, although SO₄ concentrations progressively increase downgradient beyond the confined/unconfined interface as a result of gypsum or anhydrite dissolution (Edmunds et al., 1982). Studies of stable and radiogenic isotopes have demonstrated an increasing residence time in groundwater further east and with depth, and model ages in excess of 10,000 years have been proposed for the groundwater in the deep confined aquifer (e.g. Edmunds et al., 1982).

The Sherwood Sandstone is largely fluviatile in origin (Ambrose et al., 2014) and comprises red, brown and more rarely green-grey sandstone with interbedded layers and lenses of red-brown mudstone and siltstone. Fining-upwards sequences of breccia, medium-to-fine-grained sandstone, silty sandstone, siltstone and marl are common and a substantial part of the sequence is cross- or parallel-bedded. Laminated sandstone is also present (Gaunt, 1993). Red coloration throughout the Sherwood Sandstone is due to the presence of iron oxide, often as sand-grain coatings and in argillaceous partings. Dolomite is a minor primary mineral and calcite is present in cement, although the sandstone is generally poorly cemented and much of the formation is unconsolidated near the surface. Gypsum is a minor, although widely-scattered constituent, often in association with argillaceous facies (Gaunt, 1993).

Recorded thicknesses of the unconfined Sherwood Sandstone vary from < 100 m thick around Worksop (Nottinghamshire) to 150–180 m near Armthorpe (Yorkshire), to around 220 m near Hatfield (Yorkshire) (Fig. 1).

Beneath the Mercia Mudstone Group (MMG), thicknesses of the Sherwood Sandstone also increase from south to north, from about 120 m in Newhall area (Nottinghamshire), to some 250 m around Misterton, some 300 m at Westwoodside (Yorkshire), and to over 400 m NE of Goole (Yorkshire) (Gaunt, 1993). The depth of the base of the Sherwood Sandstone extends to around 425 m at Sandtoft (South Yorkshire), 500 m at Gainsborough (Lincolnshire) and 800 m at Welton (Lincolnshire).

The Sherwood Sandstone is underlain by Permian mudstones, marls and siltstones with beds of fine sandstone and seams of gypsum, anhydrite and halite. These horizons form a largely impermeable base to the aquifer (Gaunt, 1993).

The Sherwood Sandstone dips gently eastwards (ca. 1°) and in the eastern part of the study area (Fig. 1), is overlain by thick argillaceous sediments of the MMG which confine the aquifer. The MMG is composed of red-brown mudstones and siltstones, which are locally dolomitic and gypsiferous. Anhydrite also occurs as thin beds or veins (Gaunt, 1993). In some areas, the Sherwood Sandstone is overlain by the transitional facies of the Triassic Tarporley Siltstone Formation (part of the MMG, not distinguished in Fig. 1).

Unlike the East Midlands section of the aquifer, where the Sherwood Sandstone has a large outcrop and is unconfined (Edmunds and Smedley, 2000), much of the Triassic succession of South Yorkshire is covered by Quaternary deposits (Fig. 1). Here, only around 10% of the Sherwood Sandstone and Mercia Mudstone crop out at surface. The Quaternary deposits are very variable in composition, ranging from peat and clay to gravel and were deposited in glacial, periglacial, fluvial, glaciolacustrine and aeolian environments. Of particular importance is the Devensian Hemingbrough Formation (formerly named the '25-Foot Drift'), a vast expanse of bedded clay and sand, formed by the infilling of a large lake (Lake Humber) approximately 18,000 years ago (Gaunt, 1993). Most of the glaciolacustrine formation consists of laminated clay, with thin sands generally occurring around the margins. The clay and silts are mainly bluish to reddish-brown and up to 20 m thick. The Hemingbrough Formation is overlain in places by more recent deposits. Sands and gravels are important over the entire area and may locally include clay as a minor component.

The hydrogeology of the South Yorkshire Sherwood Sandstone is in places greatly influenced by the overlying Quaternary deposits since the latter is mainly of low permeability and acts as a locally confining or semi-confining layer. Clayey portions of the Hemingbrough Formation may be particularly important in restricting flow. The vertical leakage of groundwater from the Hemingbrough Formation is unquantified but likely to be small. Vertical leakage of groundwater to the Sherwood Sandstone from the Mercia Mudstone is also thought to be small (vertical hydraulic conductivity estimated around 0.0001 m/day) (Rushton, 2003), except near the MMG interface where the transitional facies of the Tarporley Siltstone Formation occurs. Here, vertical hydraulic conductivity values of 0.002–0.0005 m/day have been reported (Rushton, 2003). Spring flows in this unit also suggest increased hydraulic conductivity.

3. Sampling and analysis

3.1. Pumped groundwater

Sampling and analytical methodology for pumped groundwater samples from the East Midlands have been described by Edmunds and Smedley (2000) and Smedley and Edmunds (2002). From the South Yorkshire part of this study, 17 Sherwood Sandstone pumped groundwater samples were collected from public-supply and private boreholes. Due to limited availability of sampling sites, only 3 boreholes were

sampled in the eastern part of the aquifer where it is confined by sediments of the MMG. Sampling localities for both South Yorkshire and the East Midlands are shown in Fig. 1.

Well-head analysis of pumped groundwaters in South Yorkshire included temperature, specific electrical conductance (SEC at 25 °C), alkalinity (total expressed as HCO_3), pH, Eh and dissolved oxygen (DO); pH, Eh and DO were monitored where possible in an in-line cell to maintain in-situ redox conditions and until stable readings were obtained. Filtered (0.45 μm membrane) samples, consistent with previous campaigns (Edmunds et al., 1982; Edmunds and Smedley, 2000; Smedley and Edmunds, 2002), were collected from each site for laboratory analysis. A colloidal contribution from use of this filter size cannot be ruled out (Kharaka and Hanor, 2014) but the low concentrations of Al observed (generally ≤ 20 μg/L and/or less than detection limit) and the typically strong negative association between observed Fe concentration and observed NO_3 (i.e. redox-rather than colloid-controlled) suggest that this contribution is likely to be small to negligible.

Unacidified aliquots were collected for Cl, NO_3-N and Br by ion chromatography using a Dionex system. Filtered and acidified (1% v/v HNO_3) samples were collected in acid-washed polyethylene bottles for major-cation, SO_4 and trace-element analysis by ICP-AES and ICP-MS. Filtered, acidified (2% v/v HCl) samples were also collected for total As by hydride-generation ICP-AES. Unfiltered samples were collected in glass bottles for $\delta^{18}O$, δ^2H and $\delta^{13}C$ analysis by mass spectrometry.

Calibrations for ICP-AES and ICP-MS were performed using appropriately diluted standards and checked against international reference materials. Ionic charge imbalances were ≤ 6% for all 17 samples. Instrumental drift during ICP-MS analysis was corrected using In and Pt internal standards.

Analyses for six samples of shallow groundwater from the Triassic MMG of the East Midlands (Sites M1–M6) are also described. These were pumped and collected as for the South Yorkshire samples. Sampling localities are also shown in Fig. 1.

3.2. Depth sampling and profiling

Depth sampling was carried out in three public-supply boreholes in South Yorkshire (Sites 47, 54 and 63) and 1 borehole in Gainsborough, Lincolnshire (Site 19) (Fig. 1). These were located in the Sherwood Sandstone, either unconfined or Quaternary-confined in South Yorkshire, and from the MMG-confined aquifer in the East Midlands. Details of the borehole configurations for these sites, along with two further East Midlands boreholes investigated previously (Edmunds and Smedley, 2000) are given in Fig. 2. With the exception of the two shallowest groundwater samples from the Site 19 borehole, all samples were taken from open-hole or slotted-screen sections and are therefore taken to be representative of the specific sampling depths.

In the South Yorkshire boreholes, depth samples were collected mainly from zones where groundwater flow was identified by heat-pulse flow logs (BGS unpublished data). Boreholes at Sites 54 and 47 were pumping at the time of sampling (pump depths 77 m and 42 m below ground level respectively). Heat-pulse flow logging of the borehole at Site 54 showed that about 40% of the water reaching the pump was from above and 60% from below. Heat-pulse flow logging in the borehole at Site 63 showed about equal proportions of flow from above and below the pump.

Site 63 was not being pumped at the time the depth samples were collected but was affected by pumping in the nearby Site 54 borehole at the time, showing evidence of flow in the borehole upwards, downwards and outwards towards the pumping Site 54 borehole.

Depth samples were collected using a stainless-steel depth sampler of 1-L capacity. Aliquots were collected for inorganic chemistry and stable-isotopic analysis, as for the pumped samples.

Downhole geochemical logging was also carried out in the three South Yorkshire boreholes using a Hydrolab sonde, equipped with
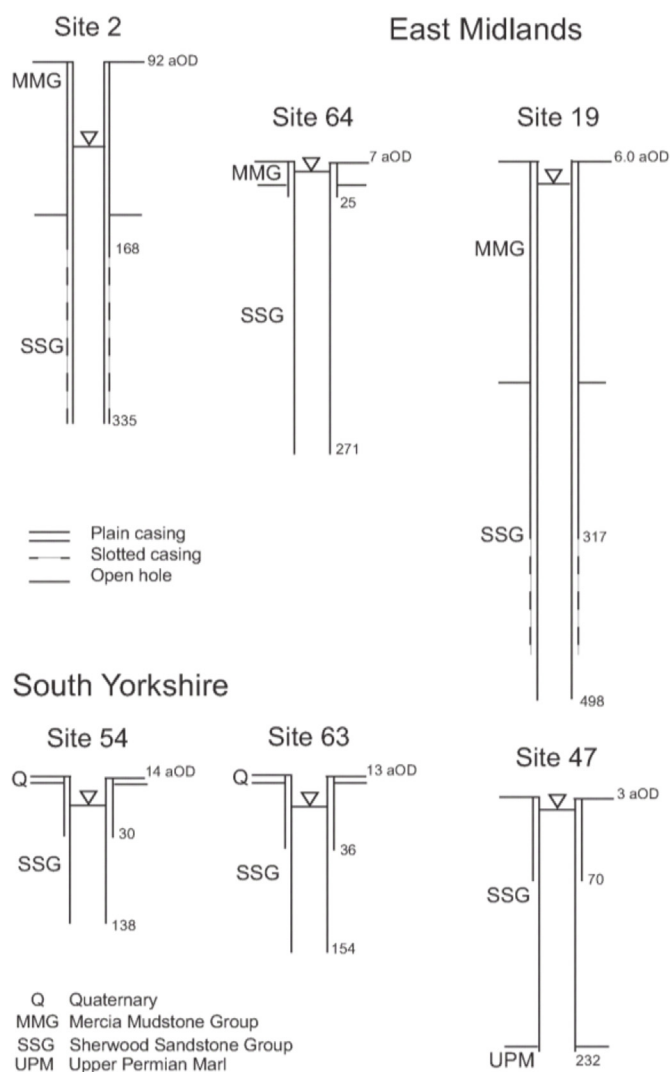
Fig. 2. Details of boreholes from the East Midlands and South Yorkshire sections of the Sherwood Sandstone aquifer used for depth profiling; locations of typical rest water levels are given (units in m).

calibrated sensors for measuring pH, Eh, dissolved oxygen, SEC, temperature and depth. A wide flange above the pump in Site 47 prevented profiling below 42 m depth.

The various sampling campaigns described in this study were conducted over a long interval, ranging from the 1990s for groundwater samples collected from the Mercia Mudstone Group (Sites M1–M6), to 2016 for groundwater depth samples from Gainsborough area (Site 19).

4. Results

4.1. Spatial distributions

Major-, trace-element and isotopic data for the 17 groundwater samples collected from the South Yorkshire part of the aquifer are given in Tables 1 and 2. Results for selected major ions, trace elements and stable isotopes are plotted in Figs. 3 and 4, alongside data for the East Midlands section of the aquifer. South Yorkshire groundwater confined below MMG is distinguished. Distributions are plotted against temperature (taken here to be analogous to residence time) as established and presented in earlier publications (Edmunds et al., 1982; Edmunds and Smedley, 2000; Smedley and Edmunds, 2002) in order to depict chemical variations along the groundwater flow path. It is clear from the plots that the variation in temperature is much smaller than for the

East Midlands as the sampled flow path is much shorter (Fig. 1).

As for the East Midlands, the main influences on chemical composition of the groundwater are mineral-water interaction, notably reaction with carbonate and gypsum and redox reactions. Pollution also appears to have had a role in the unconfined part of the aquifer. Stable isotopes give an indication of groundwater residence time. Distributions of NO_3 may have been influenced to some extent by denitrification under reducing conditions, although absence of agricultural/urban contaminants in confined groundwater is also doubtless a factor. In the East Midlands section, the aquifer's capacity to reduce oxidised species is considered to be generally low, with concentrations of naturally-occurring dissolved organic carbon typically ≤ 0.15 mg/L and solid forms rare or absent (Edmunds et al., 1982).

Compositions of groundwater from six samples in the poorly-permeable MMG of the East Midlands (Table 3) indicate relatively high concentrations of Ca, Mg, SO_4, K, Li, Sr and B in particular in the groundwater compared to the Sherwood Sandstone groundwater. The high concentrations are consistent with dissolution of gypsum and clay minerals which are abundant in the argillaceous deposits (Howard et al., 2008). The compositions indicate the likely influence of vertical recharge from the MMG on the chemistry of groundwater in the underlying Sherwood Sandstone, although they are not distinguishable from groundwaters in gypsiferous and/or marl horizons within the Sherwood Sandstone aquifer itself.

Carbonate reaction: variations in pH, HCO_3, Ca and Mg are largely controlled throughout the Sherwood Sandstone aquifer by reaction with carbonate minerals in the sandstone matrix. Groundwater pH is buffered between 7.2 and 8.0 (Table 1). The groundwaters are saturated throughout with respect to both calcite and dolomite, although one of the confined groundwater samples is oversaturated with respect to calcite (SI 0.48). Molar Mg/Ca ratios range between 0.64 and 0.8 in the groundwaters from unconfined or Quaternary-(semi)-confined aquifer but two of the samples from the MMG-confined aquifer have lower ratios of around 0.4. Ratios of just less than 1 would be expected from equilibration with both calcite and dolomite, applicable to most of the South Yorkshire samples. The lower ratios in the two MMG-confined groundwater samples are mainly attributable to increase in Ca. These are both from relatively shallow boreholes which penetrate only the upper part of the Sherwood Sandstone. This increase could be due to leakage of gypsum-reacted groundwater from the overlying MMG, although dissolution of gypsum/anhydrite within the topmost Sherwood Sandstone, in a region where little groundwater pumping has occurred due to low demand, is a potential alternative explanation. Low Mg/Ca ratios observed in the deeper section of the East Midlands part of the aquifer have been attributed previously to an intraformation dedolomitisation reaction, involving dissolution of gypsum/anhydrite and associated precipitation of calcite (Edmunds et al., 1982). Gypsum dissolution also has been postulated for Sherwood Sandstone groundwater in the Birmingham area (Jackson and Lloyd, 1983) and northwest England (Kimblin, 1995).

Reaction of carbonate minerals is also evident from the trend in $\delta^{13}C$ values across the aquifer in the South Yorkshire section. Samples of pumped groundwater from the western unconfined/semi-confined aquifer have ratios of −15 to −12‰ (Table 2), whilst MMG-confined sandstone groundwaters have ratios of around −11‰. Progressive reaction of groundwater with freshwater diagenetic calcite ($\delta^{13}C$ ratio of around −7‰) or primary marine dolomite ($\delta^{13}C$ of ca. 0 to −3‰) (Edmunds et al., 1982) under closed or semi-closed conditions would explain the trend towards a more enriched $\delta^{13}C$ composition down the groundwater flow gradient.

Strontium is also likely to derive largely by carbonate dissolution, although as noted above, the highest Sr concentrations observed (up to 1.6 mg/L) in the confined aquifer may be additionally derived by dissolution of gypsum.

Sulphate reaction: SO_4 concentrations range between 8 and 65 mg/L in groundwaters from the western part of South Yorkshire with no

Table 1
Chemical data for groundwater samples from the Sherwood Sandstone, Doncaster area.

Site	Depth mbgl	Temp °C	pH	Eh mV	DO mg/L	SEC μS/cm	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO₃ mg/L	SO₄ mg/L	Cl mg/L	NO₃-N mg/L	NO₂-N μg/L	Si mg/L
Site 46	120	10.0	7.83	382	< 0.1	588	52.4	23.7	20.0	2.51	151	27.6	55.0	9.01	76	3.8
Site 47	232	10.6	7.62	120	< 0.1	462	49.6	19.8	10.8	2.66	223	23.3	20.1	0.17	< 30	4.1
Site 48	137	10.5	7.23	117	< 0.1	484	52.7	23.5	9.6	2.19	246	22.7	15.3	0.25	92	4.1
Site 49	155	10.6	7.31	317	< 0.1	537	66.4	25.8	8.6	2.47	232	48.9	21.5	2.77	37	4.4
Site 50	180	11.1	7.87	395	0.6	384	38.0	16.1	9.9	1.82	129	20.9	21.6	6.48	< 30	4.1
Site 51	180	10.8	7.89	399	1.5	478	50.9	20.8	12.5	3.35	138	47.7	25.3	9.31	< 30	4.2
Site 52	61	9.0	7.51	375	4.7	477	61.8	24.2	11.4	2.74	232	31.2	20.6	6.39	< 30	4.1
Site 53	140	10.8	7.79	291	6.8	392	43.8	18.4	7.5	1.75	196	7.6	14.9	0.25	< 30	3.8
Site 54	137	10.6	7.78	397	< 0.1	499	53.2	22.0	10.7	2.68	138	65.7	26.5	4.86	< 30	4.3
Site 55	137	10.5	7.99	396	< 0.1	497	50.9	20.7	12.4	3.19	104	58.3	30.5	11.2	< 30	4.2
Site 56	120	10.4	7.99	411	< 0.1	386	38.8	16.7	10.5	1.67	121	30.8	23.3	7.25	< 30	3.9
Site 57	140	10.6	7.74	220	0.0	471	50.0	21.6	12.9	2.00	193	28.5	22.7	5.15	< 30	3.7
Site 58	170	11.0	7.96	404	< 0.1	411	42.3	20.7	9.8	2.13	171	21.5	13.0	2.82	< 30	3.9
Site 59	165	10.1	7.79	395	1.0	519	53.7	22.3	15.0	2.84	103	62.9	28.8	14.0	< 30	4.9
Site 60	72	9.5	7.91		< 0.1	833	113	30.1	16.0	8.79	209	232	21.3	0.07	< 30	3.7
Site 61	< 30	10.2	6.67	70	< 0.1	480	48.5	25.9	8.0	6.64	165	92.7	11.1	< 0.02	< 30	3.6
Site 62	91	10.4	7.48		< 0.1	765	98.3	28.0	19.1	6.24	175	2400	15.1	0.10	< 30	4.0

SEC: specific electrical conductance at 25 °C; DO: dissolved oxygen; mbgl: metres below ground level.

discernible distinction between outcrop groundwaters and those (semi-) confined by Quaternary deposits. As with Ca, SO₄ concentrations are higher at between 93 and 240 mg/L in the MMG-confined aquifer. The increase is also in response to dissolution of gypsum or anhydrite. The high concentrations of B in these two shallowest groundwater samples (95.6 μg/L and 42.8 μg/L; Table 2) would also be consistent with dissolution of gypsum or anhydrite, either in situ or via vertical leakage. All the South Yorkshire groundwaters are undersaturated with respect to gypsum and none reaches the concentrations or near-saturated state of the deep East Midlands groundwaters (Edmunds et al., 1982).

Groundwaters in the western part of the South Yorkshire aquifer are mainly supersaturated with respect to barite, the Ba source possibly deriving from carbonate minerals, while the MMG-confined groundwaters are at equilibrium with respect to barite. The trend suggests somewhat slow kinetics of barite precipitation with equilibrium only achieved in longer-residence groundwaters.

Silicate reaction: despite the dominance of silicate minerals in the Sherwood Sandstone, the significance of reaction with these is relatively small compared to that of carbonates. Sodium concentrations range between 8 and 20 mg/L (Fig. 3), much likely to be of atmospheric origin. Only a very small increase (a few mg/L) in concentrations in the MMG-confined groundwater is apparent, alkali feldspar the main likely source of the increase.

Potassium concentrations are slightly higher in the MMG-confined aquifer (6.2–8.8 mg/L compared to 1.7–3.2 mg/L in the west). Here, reaction of alkali feldspar (Bath et al., 1987) or clay minerals may be responsible. Some K in the unconfined groundwaters may also be pollution-derived (see below). Increasing concentrations of Li are also evident in the MMG-confined groundwaters (Fig. 4). Reaction with alkali feldspar and clay minerals are thought to be the main sources (Edmunds and Smedley, 2000; Tardy et al., 1972).

Lithium concentrations increase linearly throughout the East Midlands aquifer and do not appear to be buffered by mineral saturation. Rubidium shows a similar increase in concentration downgradient (Table 2). Dissolved Si concentrations are relatively uniform (3.6–4.2 mg/L) throughout the South Yorkshire part of the aquifer (Table 2). Ion-exchange reactions on clays may account for some of the element variations observed, but are probably unimportant relative to carbonate and sulphate mineral reactions.

Redox processes: in the East Midlands section, confined conditions only occur as a result of MMG cover and the groundwaters show a clear evolution from oxic to anoxic conditions as the groundwater flows downgradient. By contrast, locally confining conditions occur in the South Yorkshire aquifer section where the piezometric surface lies in the Quaternary deposits (especially the Hemingbrough Formation), as well as in the MMG cover. This more patchy distribution of aquifer

Table 2
Trace-element and stable-isotopic data for groundwater samples from the Sherwood Sandstone, Doncaster area.

| Site	Sr μg/L	Ba μg/L	Fe μg/L	Mn μg/L	As μg/L	Br μg/L	Li μg/L	B μg/L	Al μg/L	Cr μg/L	Co μg/L	Ni μg/L	Cu μg/L	Zn μg/L	Rb μg/L	Mo μg/L	Sb μg/L	U μg/L	δ¹⁸O ‰	δ²H ‰	δ¹³C ‰
Site 46	81	414	< 3	36	< 2	370	8.2	11.7	< 7	< 0.4	0.11	0.12	3.3	6.6	2.46	< 0.05	0.04	0.40	−7.9	−55	−13.4
Site 47	121	546	365	161	< 2	70	16	18.5	< 7	< 0.4	0.09	2.93	1.1	2.3	2.40	0.38	0.07	0.52	−7.9	−58	−14.1
Site 48	199	567	493	122	< 2	60	17	16.0	< 7	< 0.4	0.08	3.66	1.4	1.4	2.19	0.25	0.08	0.45	−8.1	−54	−15.1
Site 49	149	264	< 3	79	< 2	60	16	16.5	< 7	< 0.4	0.11	0.24	0.3	6.3	2.00	0.08	< 0.03	1.72	−8.1	−55	−13.8
Site 50	43	104	< 3	11	< 2	< 50	7.1	14.9	7.3	1.0	0.07	0.19	16.2	13.7	2.16	0.24	0.15	1.09	−8.1	−55	−12.3
Site 51	49	104	< 3	2.8	< 2	70	7.2	17.4	9.0	0.8	0.06	0.48	19.4	14.1	2.18	0.24	0.11	1.01	−7.9	−56	−12.0
Site 52	66	554	22	36	< 2	230	10.4	20.5	< 7	< 0.4	0.09	0.24	1.1	84	1.39	4.69	0.14	0.91	−7.9	−55	−13.0
Site 53	37	810	53	28	< 2	80	10.3	8.7	18.9	< 0.4	0.08	0.66	2.7	4.7	1.24	0.93	0.13	0.39	−7.7	−55	−14.1
Site 54	140	304	< 3	2.4	< 2	70	5.7	20.8	12.9	0.5	0.13	0.19	20.5	9.0	2.25	< 0.05	0.07	0.68	−7.9	−58	−13.2
Site 55	152	251	5.3	3.0	< 2	80	5.1	18.6	21.8	0.5	0.09	0.13	10.5	11.1	1.99	0.10	0.08	0.43	−8.1	−55	−14.1
Site 56	29	513	4.7	12	7.0	70	4.1	11.6	7.6	0.4	0.05	< 0.12	11.4	6.0	1.21	0.04	0.12	< 0.35	−7.8	−55	−13.9
Site 57	46	426	50	20	< 2	70	11.0	15.6	< 7	< 0.4	0.09	0.51	8.8	7.5	1.35	2.76	0.09	0.63	−8.1	−54	−13.0
Site 58	49	421	< 3	0.5	< 2	< 50	8.9	16.7	7.0	< 0.4	0.04	0.17	11.2	10.8	1.97	0.07	0.03	0.89	−8.0	−55	−12.8
Site 59	61	90	6.0	0.7	< 2	100	5.9	20.7	7.7	0.6	0.07	0.20	23.3	8.2	1.28	< 0.05	< 0.03	< 0.35	−8.3	−59	−13.1
Site 60	1410	24	103	216	< 2	120	32	95.6	9.4	< 0.4	0.22	1.24	1.3	237	6.82	2.55	0.43	5.88	−8.6	−59	−13.2
Site 61	506	24	764	11	< 2	90	18	19.3	9.9	< 0.4	< 0.04	5.69	< 0.2	23	3.61	1.88	< 0.03	0.39	−9.0	−60	−11.1
Site 62	1560	13	673	19	< 2	100	59	42.8	15.9	11.1	0.33	6.70	0.8	1080	6.38	1.63	0.07	0.61	−9.0	−61	−11.4

‰: relative to SMOW.
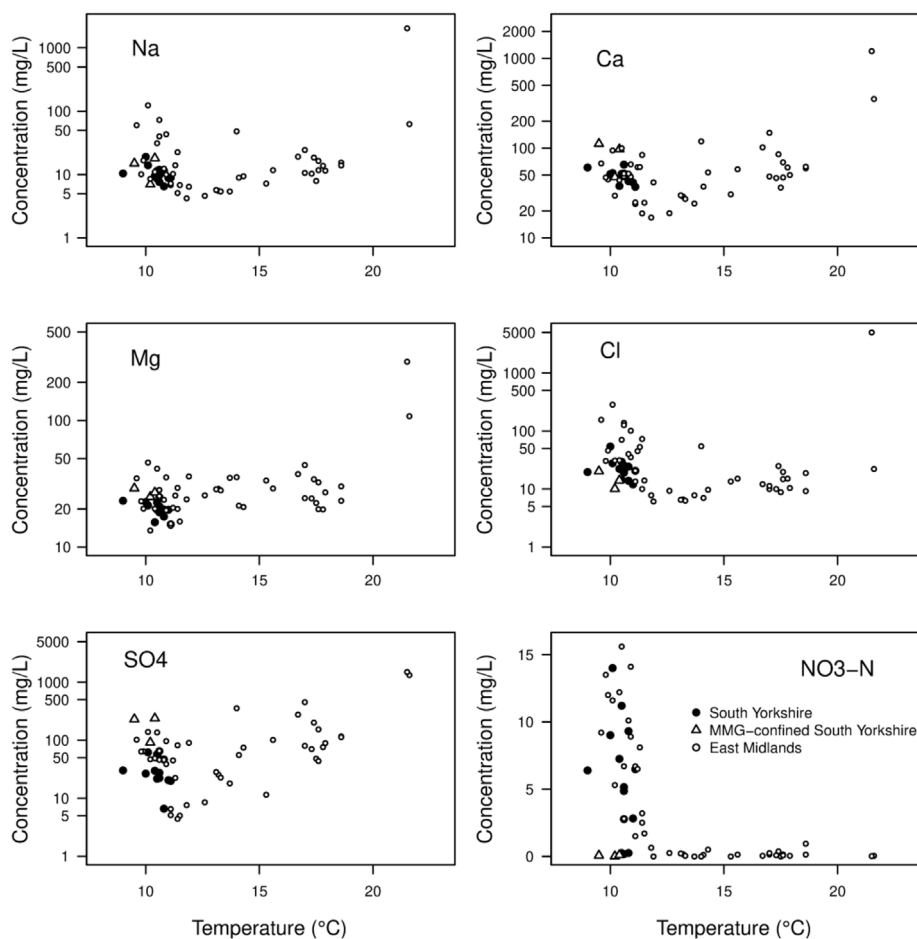
Fig. 3. Variation in major-ion composition of groundwater from South Yorkshire and the East Midlands with increasing temperature (residence time).

confinement means that the geographical trend in redox chemistry is much less distinct. Nonetheless, variations in redox conditions do occur and are an important control on the mobility of many solutes.

Oxic South Yorkshire groundwater has Eh values in the range 291–411 mV with dissolved-oxygen (DO) concentrations up to 6.8 mg/L. Redox potential was measured at only one of the MMG-confined sites. This gave a low value of 70 mV.

Concentrations of reduced sulphur were not determined in the groundwater samples from the region, but were detectable by smell at six localities in the East Midlands section. Olfactory sulphide was not noted in the South Yorkshire section.

Concentrations of dissolved Fe and Mn are low in the oxic groundwaters but increase in anoxic conditions, reaching maxima of 764 µg/L and 216 µg/L respectively in the confined aquifer (Table 1; Fig. 4). The main sources are likely to be Fe and Mn oxides in the sandstone matrix, but ferroan calcite may be an additional source of Fe (II).

Molybdenum is also most likely to be derived from Fe oxide in the sandstone coatings and has a relatively high concentration in the reducing waters (> 1.6 µg/L Table 2). Concentrations locally reach up to 4.7 µg/L (Fig. 4). Molybdenum concentrations only decrease in the deeper, most evolved groundwaters in the East Midlands section, likely linked to formation of sulphide minerals (Smedley and Edmunds, 2002).

Arsenic concentrations reach a maximum of 6.5 µg/L in the oxic part of the South Yorkshire aquifer (Table 2). This aligns with the observations in the East Midlands section, where the maximum observed concentration was 13 µg/L in relatively evolved oxic groundwaters (Smedley and Edmunds, 2002). Here, pH-dependent sorption/

desorption reactions with Fe-oxide surfaces were implicated.

Uranium reaches a maximum concentration of 5.9 µg/L in the most evolved, reducing groundwater from the MMG-confined aquifer. Uranium mobility may be enhanced by the formation of soluble U-carbonate species. In the East Midlands section, U concentrations progressively decrease under reducing conditions as a result of the reduced solubility of U(IV) species. This is not observed in the South Yorkshire pumped groundwater samples and suggests that conditions in the parts of the aquifer investigated are insufficiently reducing to initiate U reduction to the U(IV) form and initiate precipitation/coprecipitation reactions (e.g. as uraninite or U-bearing carbonate) or sorption to metal oxides.

Pollution: groundwater from the oxic unconfined aquifer shows evidence of pollution from agricultural and industrial sources. Concentrations of NO_3-N are highest in the oxic groundwaters from the outcrop zone (maximum observed 14 mg/L in South Yorkshire; 15.6 mg/L in the East Midlands section) (Table 1, Fig. 3). Concentrations are uniformly low (less than 0.1 mg/L) in the MMG-confined zone and usually low in the Quaternary-covered sections. Whether the lower concentrations are related to denitrification or lack of initial pollutant inputs is unclear. The Sherwood Sandstone is known to have a paucity of reducing agents (e.g. organic carbon, sulphide minerals) to drive denitrification across most of the aquifer (Edmunds et al., 1982; Smedley and Edmunds, 2002) and so this may not be an important control (Wilson et al., 1994). Concentrations of nitrite (Table 1), a potential indicator of denitrification, are also low in the reducing waters. However, both factors may be involved.

Chloride derives initially from rainfall but the observed concentrations in the groundwater have likely been enhanced by agricultural and
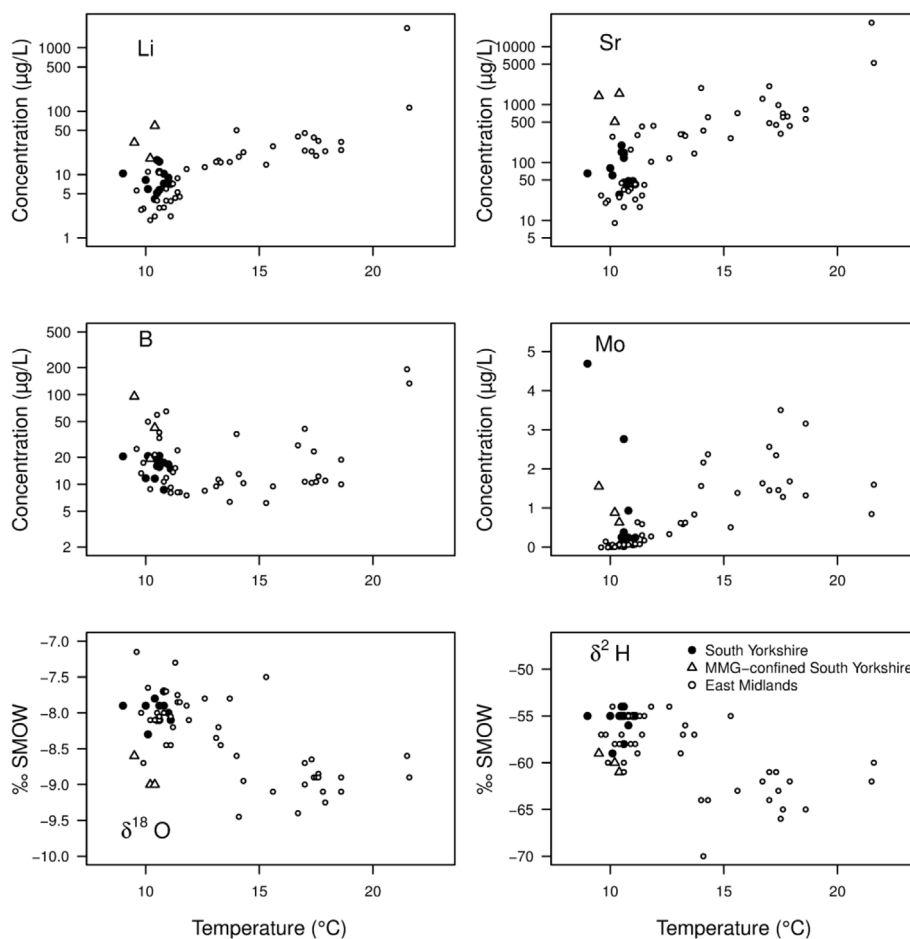
Fig. 4. Variation in concentrations of selected trace elements and stable-isotopic compositions with increasing temperature (residence time).

Table 3
Chemical data for shallow groundwater from the Mercia Mudstone Group of the East Midlands.

Site	Well depth mbgl	pH	SEC µS/cm	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO₃ mg/L	Cl mg/L	SO₄ mg/L	NO₃-N mg/L	Li µg/L	B µg/L	Sr µg/L	δ³⁴S ‰
M1		7.03	2450	579	74.1	33.1	5.60	380	41.6	1250	3.88	77	240	5030	15.8
M2		7.70	966	64.6	48.4	24.9	6.20	188	55.2	158	11.9	18	120	106	
M3		7.52	1185	95.4	46.8	29.0	72.3	467	70.8	104	9.68	19	200	515	4.0
M4		7.18	603	61.6	30.3	11.7	24.3	230	26.8	81.0	8.90	< 7	79	70	
M5	4.1	7.30	589	63.0	24.3	18.8	23.3	249	23.4	75.3	5.00	20	200	250	
M6	3.7	7.19	1770	131	58.9	152	51.2	389	338	130	15.1	20	90	1040	9.6

Concentrations of Al all < 100 µg/L.

industrial pollution. The highest observed Cl concentration in the South Yorkshire groundwater is 55 mg/L (Table 1). This sample also has relatively high SEC, Na and Br concentrations (Tables 1 and 2). The site is close to the former Markham Main colliery and is likely to have been influenced by recharge of mine drainage into the local river. Bromide (370 µg/L in the sample) is commonly concentrated in organic materials (e.g. coal) and the high concentration is consistent with mine drainage influence at the site. Concentrations of Cl are low in the MMG-confined aquifer (< 22 mg/L) and illustrate the unpolluted condition of groundwater with longer residence time further down the flow path.

It has been suggested that SO₄ concentrations in the unconfined East Midlands aquifer are also derived from modern anthropogenic sources, including atmospheric and agricultural (Edmunds et al., 1982; Edmunds and Smedley, 2000). Concentrations in the South Yorkshire section are not as high as some of the East Midlands oxic groundwaters (Fig. 3) but some of the SO₄ in the unconfined aquifer is likely to derive from similar pollutant sources.

Residence time: Various groundwater dating studies using ¹⁴C, ³He, ³⁶Cl and stable-isotopic data combined with major- and trace-element data (Andrews, 1983; Andrews et al., 1994; Bath et al., 1979; Edmunds et al., 1982), have provided evidence for increasing groundwater residence time ('age') with distance down the Sherwood Sandstone flow gradient. The oldest groundwater in the deepest confined parts of the aquifer was estimated to have recharged in excess of 30,000 years ago. Oxygen and deuterium isotopic compositions are distinctly more depleted than modern recharge in these confined, long-residence-time groundwaters from the East Midlands (δ¹⁸O more negative than −8.4‰, δ²H more negative than −60‰) (Edmunds and Smedley, 2000). This trend is also seen in the South Yorkshire section: MMG-confined groundwaters have δ¹⁸O values as depleted as −9.0‰ and δ²H ‰ as depleted as −61‰ (Fig. 4). Although quantitative age dating tools were not used for the South Yorkshire samples, the δ¹⁸O and δ²H values obtained suggest the MMG-confined groundwater is older (cooler recharge) than the samples taken to the west of the MMG cover.
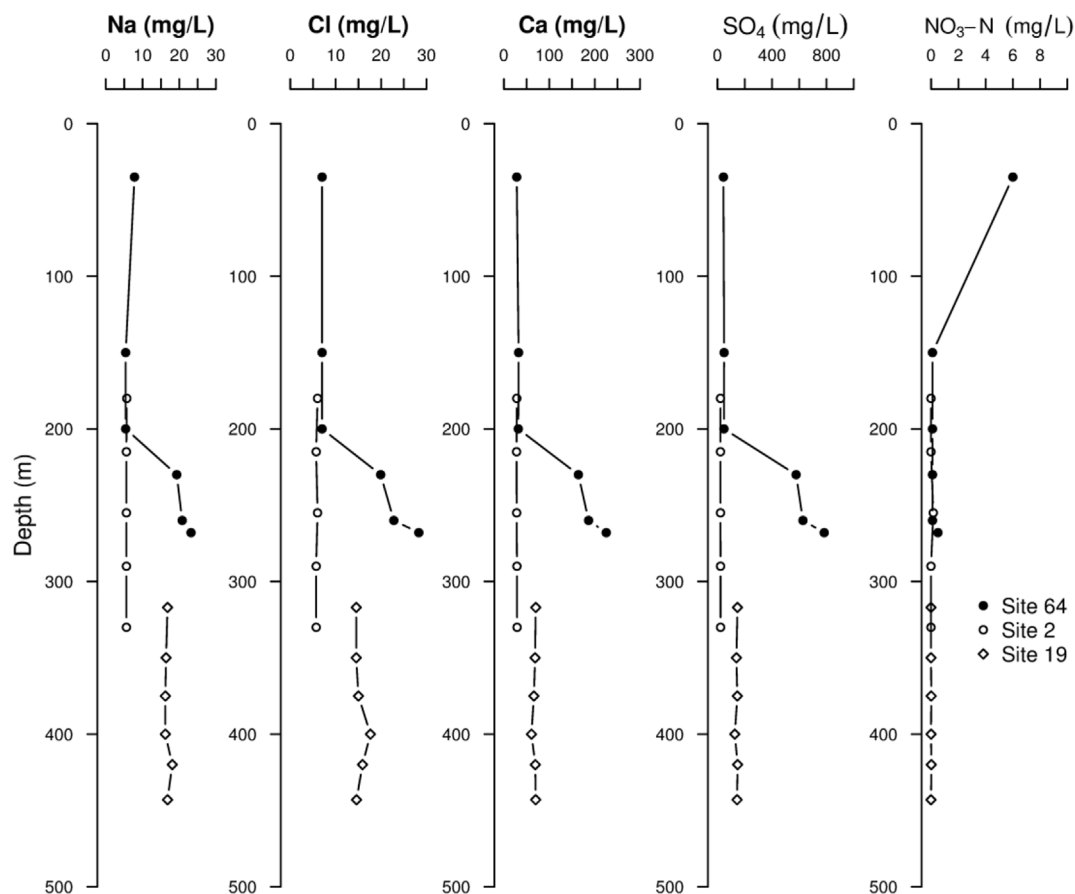
Fig. 5. Profiles of groundwater major-ion chemistry in three boreholes from the East Midlands (Sites 2, 19 and 64) (all sampled under static conditions); depths are relative to ground level.

Values more depleted than $-9‰$ and $-60‰$ respectively have been linked to Pleistocene age groundwater (Edmunds and Smedley, 2000).

4.2. Depth variations

4.2.1. East Midlands profiles

Groundwater chemical profiles for three boreholes (Sites 2, 19, 64) in the MMG-confined section of the East Midlands aquifer are shown in Figs. 5 and 6. Site 19 is the furthest downgradient, located at Gainsborough (Fig. 1). The two shallowest samples from Site 19 were taken within casing and so, although given in Tables 1 and 2 for completeness, are not displayed in Figs. 5 and 6 as their representativeness of in-situ groundwater conditions is uncertain.

Sites 2 and 19 show remarkably little variation in chemical composition with depth over the depth intervals sampled. Each has groundwater with concentrations of Na and Cl < 20 mg/L and of $SO_4 < 200$ mg/L (Fig. 5). This suggests that fresh water (within potable limits for these solutes) extends to around 250 m (borehole depth 335 m) and 450 m (borehole depth 500 m) in the boreholes respectively. Lack of stratification in these boreholes is also demonstrated for several trace elements (Fig. 6).

Groundwater from Site 2 has $\delta^{18}O$ values around $-8.5‰$ and δ^2H around $-60‰$, older than modern recharge (Darling et al., 1997) and previously interpreted as of Holocene age (Edmunds and Smedley, 2000) (Fig. 6). By contrast, ratios of $\delta^{18}O$ and δ^2H are more strongly depleted in groundwater from Site 19 ($-9.2‰$ and $-62‰$ respectively). Ratios of $\delta^{13}C$ are also enriched ($-10‰$), indicating significant carbonate mineral (calcite or dolomite) reaction.

The profile for Site 64 does show some stratification, with a relatively sharp interface at around 200 m depth (Figs. 5 and 6).

Concentrations of Ca, SO_4 and Sr undergo the greatest increases and are consistent with increasing dissolution of gypsum or anhydrite in the deeper section. The shallower part of the Site 64 borehole has $\delta^{18}O$ and δ^2H values respectively around $-8.4‰$ and $-64‰$. Radiocarbon data yielded an interpreted Holocene age for groundwater in this section (Edmunds and Smedley, 2000). Groundwater in the deeper part of the Site 64 borehole (200–250 m depth) has a more strongly depleted isotopic signature ($\delta^{18}O$ $-9.2‰$, δ^2H $-65‰$). Radiocarbon data from this section showed a range 4.6–17.3 pmc ($\delta^{13}C$ -7.8 to $-0.8‰$), interpreted to have a Pleistocene age, around 17,100 a BP (Edmunds and Smedley, 2000). The calibration provided by the ^{14}C data for Site 64 deep groundwater support the conclusion that the groundwater in Site 19 borehole is also of Pleistocene age.

4.2.2. South Yorkshire profiles

Three investigated boreholes in South Yorkshire (Sites 47, 54 and 63), all from the west of the MMG cover in the unconfined or semi-confined aquifer, demonstrate clear vertical stratification in chemical composition and redox status. At Sites 54 and 63, downhole geochemical logging (not shown) revealed that the groundwater is oxidising (dissolved oxygen > 5 mg/L, Eh close to 300 mV) with SEC values around 800 µS/cm at < 80 m depth. At deeper levels than this, the groundwater becomes more reducing and with lower SEC values (≤ 340 µS/cm). The groundwater throughout each profile is fresh, with SEC mainly determined by Ca and SO_4 (Tables 4 and 5). However, the shallowest part in each borehole shows relatively high concentrations of Na, Cl, SO_4 and NO_3 (Fig. 7), all of which are indicative of modern pollutant inputs, as suggested for the East Midlands (Smedley and Edmunds, 2002). The two boreholes show similar trends with depth but the interface between higher-SEC water and low-SEC water is sharper in
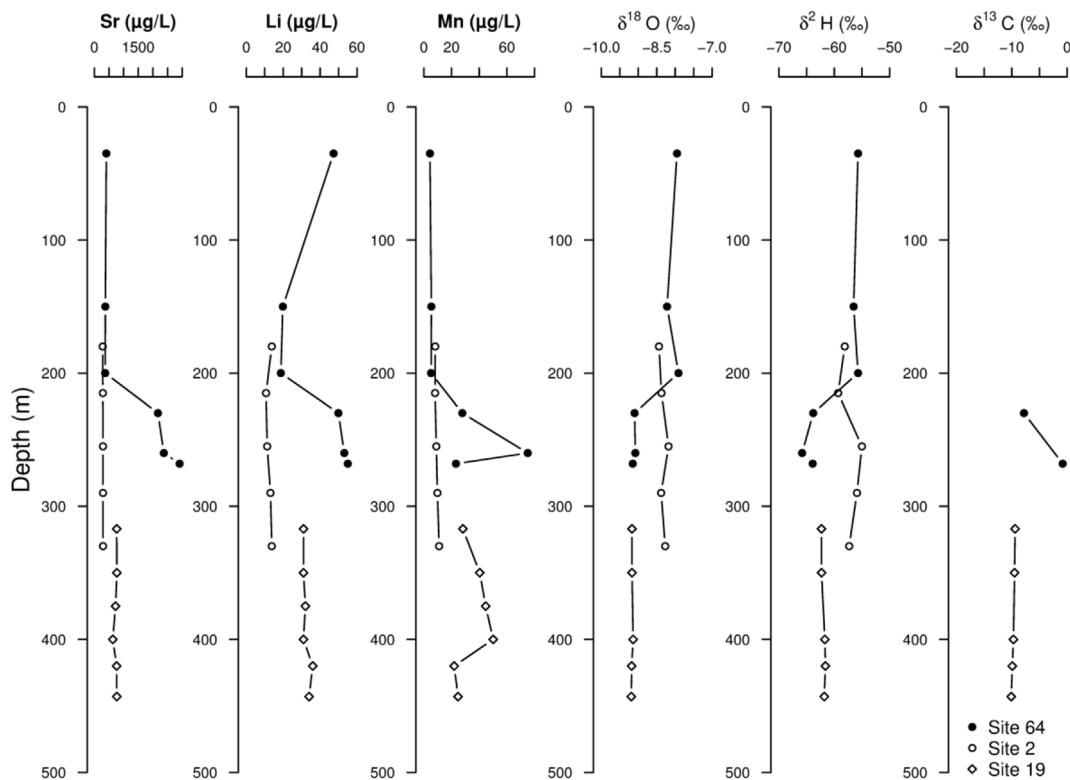
Fig. 6. Profiles of selected trace elements and stable isotopes in groundwater from the East Midlands (Sites 2, 19 and 64); depths are relative to ground level.

Table 4
Depth samples from Site 54.

Analyte	Unit	55 m	62 m	66 m	74 m	92 m	124 m	130 m
pH*		7.52	7.56	7.47	7.44	8.32	8.42	8.44
Ca	mg/L	99.0	101	101	91.9	26.7	27.3	25.5
Mg	mg/L	36.3	37.1	37.1	34	14	20.3	21.3
Na	mg/L	19.6	19.6	18.8	16.8	7.1	7.1	7.4
K	mg/L	6.1	6.0	5.6	4.5	2.1	3.8	5.3
HCO$_3$	mg/L	229	222	219	195	126	181	182
Cl	mg/L	53	57.2	56.3	51	13.3	11.4	12.2
SO$_4$	mg/L	145	151	154	146	13.0	12.7	15.1
NO$_3$-N	mg/L	11.4	11.6	10.8	8.3	2.8	< 0.3	< 0.3
NO$_2$-N	µg/L	4.0	7.0	23	30	< 4	7.0	< 4
NH$_4$-N	mg/L	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Si	µg/L	4.9	4.8	4.8	4.8	3.9	3.8	3.5
Sr	µg/L	73	71	72	77	217	515	470
Ba	µg/L	62	54	52	62	458	305	172
Fe	µg/L	110	51	56	28	16	25	53
Mn	µg/L	30	18	9.0	11	5	7	17
Li	µg/L	5.2	6.3	5.1	4.4	7.7	19.3	20.8
Rb	µg/L	3.2	3.4	3.3	3.0	2.0	3.3	4.4
Cs	µg/L	0.09	0.36	0.11	0.08	0.04	0.05	0.06
B	µg/L	51	61	42	28	< 16	18	19
Cr	µg/L	0.58	0.53	0.58	0.4	0.63	0.2	0.32
Co	µg/L	0.31	0.38	0.42	0.27	0.06	0.13	0.07
Ni	µg/L	3.56	3.26	3.05	2.34	1.09	0.83	0.86
Cu	µg/L	5.03	4.37	4.15	2.42	< 1.4	< 1.4	< 1.4
Zn	µg/L	35.9	26.8	36.1	17.8	6.66	5.20	9.20
Zr	µg/L	2.2	2.3	< 1.2	3.0	2.1	6.1	< 1.2
Mo	µg/L	0.04	0.07	0.06	0.06	0.19	0.6	0.8
Pb	µg/L	1.44	0.46	2.0	0.48	0.32	0.15	0.74
Sb	µg/L	0.22	0.17	0.18	0.24	< 0.17	0.21	0.27
U	µg/L	0.30	0.30	0.28	0.23	0.96	3.51	5.45
δ^{18}O	‰	−8.5	−8.6	−8.0	−8.5	−8.1	−8.4	−8.1
δ^{2}H	‰	−61	−60	−57	−60	−57	−58	−55
δ^{13}C	‰	−14.8	−14.8					

Rn in pumped discharge: 11.7 Bq/L. Concentrations of Al all < 15 µg/L. Depths refer to metres below ground level (elevation 14 m above OD). δ^{18}O, δ^{2}H relative to SMOW; δ^{13}C relative to PDB. *pH values determined using a downhole multi-parameter sonde.

Table 5

Depth samples and one discharge sample (pump depth 76 m below ground level) from Site 63.

Analyte	Unit	Discharge	60 m	62 m	74 m	80 m	86 m	100 m	126 m	132 m	140 m
pH*			7.48	7.51	8.02	8.10	8.12	8.18	8.28	8.28	8.40
Ca	mg/L	53.8	95.5	89.2	79.4	29.2	24	20.6	23.8	25.5	25.6
Mg	mg/L	21.5	37.5	33.2	29.5	13.5	11.4	11	14.7	15.7	15.7
Na	mg/L	14.5	41.8	18.2	16.2	10.8	9.6	9.9	16.7	18.7	24.5
K	mg/L	2.82	4.06	3.37	2.97	2.54	2.48	3.14	5.35	5.85	6.15
HCO_3	mg/L	105	116	112	108	103	93	108	174	185	188
Cl	mg/L	31.7	52.4	45.2	41.4	17.7	15.1	11	11.9	12.2	12.9
SO_4	mg/L	75.3	165	152	129	20.6	13	9.7	12.1	13.6	17.1
NO_3-N	mg/L	15.5	25.8	24.7	22.3	7.2	6.7	2.8	< 0.3	< 0.3	< 0.3
NO_2-N	µg/L	4	14	11	6	7	6	4	6	< 4	< 4
NH_4-N	mg/L	< 0.02	0.03	< 0.02	< 0.02	0.02	0.02	< 0.02	< 0.02	< 0.02	< 0.02
Si	mg/L	4.2	4.7	4.6	4.5	4.0	3.8	3.7	3.6	3.6	3.7
Sr	µg/L	124	85	126	68	162	174	262	405	438	455
Ba	µg/L	92	40	42	40	144	170	158	117	102	116
Fe	µg/L	15	18	38	21	19	19	84	169	79	6.0
Mn	µg/L	5	31	24	8	8	4	13	36	17	3
Li	µg/L	6.8	6.1	5	4.6	7.7	6.7	11.7	25.6	28.8	31.5
Rb	µg/L	2.3	3	2.9	2.6	2.1	2.0	2.2	3.7	4.0	4.5
B	µg/L	16	44	17	< 16	< 16	< 16	23	32	37	44
Cr	µg/L	0.35	0.66	0.64	0.46	0.45	0.32	0.61	0.36	0.21	0.53
Co	µg/L	0.1	0.2	0.17	0.16	0.08	0.04	0.06	0.06	0.05	0.05
Ni	µg/L	3.4	4.73	2.27	1.91	4.63	1.18	1.78	0.69	0.8	0.53
Cu	µg/L	8.35	10.2	4.44	1.90	6.11	2.32	4.53	< 1.4	29.7	< 1.4
Zn	µg/L	27.6	83.5	31.8	20.5	24.1	23.1	13.0	7.07	25.9	2.61
Mo	µg/L	0.11	0.13	0.05	0.04	0.19	0.13	0.27	0.39	0.41	0.87
Pb	µg/L	0.32	2.01	0.58	0.3	0.64	0.51	0.60	0.26	1.38	< 0.2
U	µg/L	0.37	0.08	0.06	0.08	0.51	0.55	1.00	2.48	2.69	0.23
Rn	Bq/L	12.6									
$\delta^{18}O$	‰	−8.5	−8.4	−8.4	−8.3	−8.2	−8.4	−8.0	−8.0	−8.1	−8.2
δ^2H	‰	−58	−59	−58	−61	−57	−56	−54	−58	−55	−54
$\delta^{13}C$	‰							−13.1	−13.2	−13.9	−14.3	−15.2

Concentrations of Al all < 15 µg/L. Depths refer to metres below ground level (elevation 9 m above OD). $\delta^{18}O$, δ^2H relative to SMOW; $\delta^{13}C$ relative to PDB. *pH values determined using a downhole multi-parameter sonde.

the pumped borehole at Site 54 than 63 (static) as water is drawn in by the pump.

Conditions in Site 47 borehole appear to become anoxic at shallower depth than at the other two boreholes; dissolved oxygen diminishes to very low concentrations at around 30 m depth (Table 6). Pumped groundwater from this borehole (pump depth 42 m) is also anoxic (DO < 0.1 mg/L, Eh 120 mV) and suggests that below the depth measured, conditions become more reducing still.

As for the profiles in the confined East Midlands aquifer, groundwater at depth in the Site 47 borehole has low Cl concentration (< 18 mg/L) (Table 6; Fig. 7). Such low values are consistent with recharge in a pre-industrial pre-agricultural era (Edmunds et al., 1982; Jackson and Lloyd, 1983).

Fig. 8 shows that concentrations of a number of trace elements, including Sr, Li, Mn and Mo increase with depth in groundwater from borehole Sites 54 and 63. The build-up of these elements with depth suggests an increasing reaction with aquifer minerals (carbonates, clays, gypsum, iron oxide) as a result of increasing residence time (Fig. 4).

Uranium concentrations in samples from sites 54 and 63 also increase with increasing depth, reaching a maximum of 5.5 µg/L at 130 m in the former (Table 4). The concentration is lower in the deepest sample analysed from Site 63 at 140 m depth. The concentrations are relatively high in groundwater where redox conditions are mildly reducing (e.g. NO_3-N < 3 mg/L) and pH is alkaline (above about 8.2; Tables 4 and 5), both of which are likely to have played a role in U mobilisation. The speciation of U in the deeper groundwater samples is uncertain but U(VI) likely remains stable under the mildly reducing conditions. A pH-dependent desorption of U(VI) from e.g. metal oxides, abundant as surface mineral coatings, is a possible mechanism (Barnett et al., 2002; Wang et al., 2015). Further release of U may be afforded by the partial reductive dissolution of the iron oxides themselves. The concentrations of U in the reducing groundwater are not exceptional but are comparatively high by British groundwater standards (Shand et al., 2007). The same applies to the activities of Rn determined in the two boreholes (11.7 and 12.6 Bq/L respectively; Tables 4 and 5), which are likely associated with the U (Andrews, 1983).

Fig. 8 also shows the distribution of $\delta^{18}O$ and δ^2H values with depth in these boreholes. Little variation is seen in $\delta^{18}O$ and δ^2H in samples from Sites 54 and 63 but both isotopic ratios become markedly more depleted with depth in Site 47. The deepest groundwater at that site has the signature of a palaeowater (recharged in cooler conditions). The $\delta^{13}C$ ratio also becomes more enriched with depth in this borehole (−11.5‰; Table 6), and suggests that reaction with carbonate minerals has progressed with increased groundwater depth.

The stratification of chemical and isotopic compositions with depth in the boreholes investigated mirrors closely the situation seen in samples collected spatially across the aquifer and demonstrates the three-dimensional pattern of groundwater quality and evolution with increasing residence time. Groundwater 'ageing' occurs both with depth and with lateral distance from the recharge zone and has a large impact on resulting groundwater chemistry.

5. Discussion

5.1. Groundwater age distributions

Many studies of sandstone aquifers have demonstrated downgradient evolution of groundwater as residence times and effects of rock reaction increase (e.g. Bath et al., 1979; Celle-Jeanton et al., 2009; Chapelle and Knobel, 1983; Edmunds et al., 1982; Edmunds et al., 2003; Hidalgo and Cruz-Sanjulian, 2001). As noted above, groundwater ages in the deep confined East Midlands section have been estimated at greater than 30,000 years using a number of isotopic techniques and
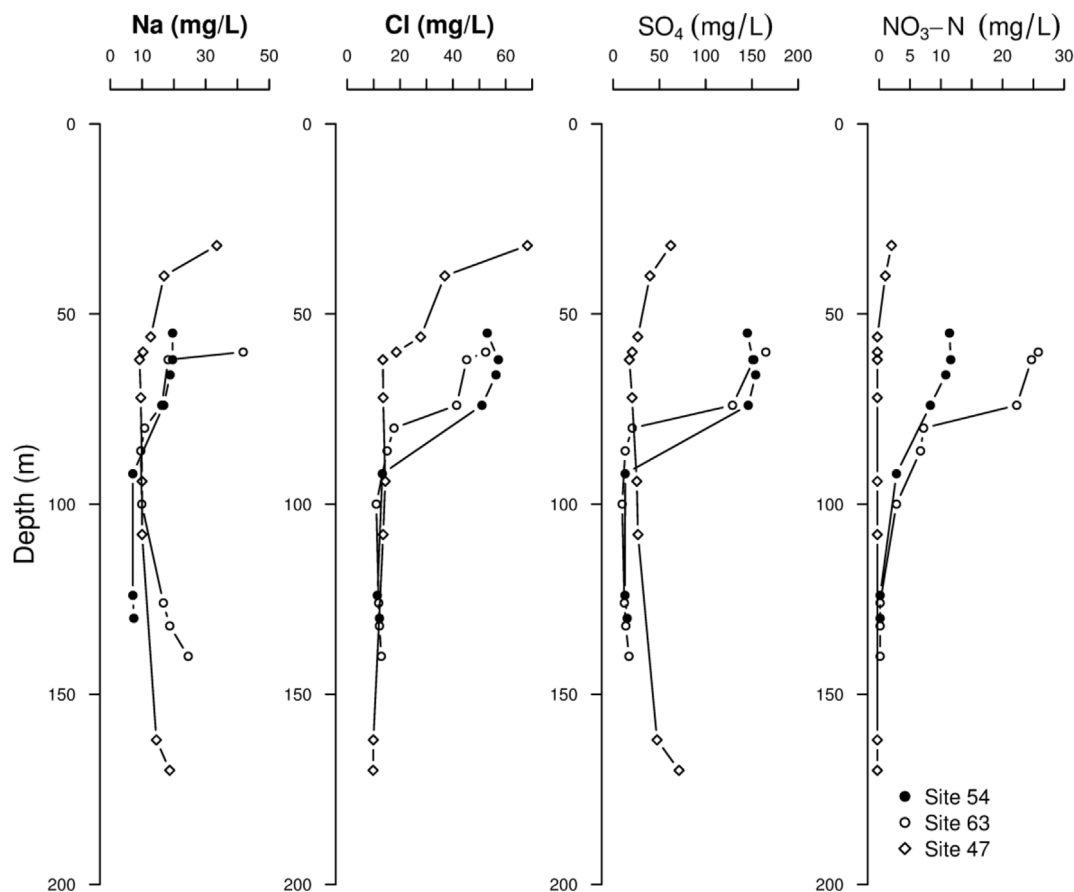
Fig. 7. Profiles of groundwater major-ion chemistry from three boreholes in South Yorkshire. Site 63 was static at the time of sampling; Sites 47 and 54 were pumping at depths 42 m and 77 m respectively; depths are relative to ground level.

this study indicates that MMG-confined groundwater in the South Yorkshire section is also likely of Pleistocene age. Geochemical reactions along the flow path produce sequential changes in the concentrations and expected speciation of many solutes. This study has indicated that chemical changes, with some significant increases in residence time, are also apparent within the aquifer with increasing depth. Table 7 summarises the stable-isotopic character of groundwater

from the studied boreholes over different depth ranges. Palaeowaters ($\delta^{18}O$ values more depleted than -9‰ and δ^2H more depleted than -60‰) occur at depth in boreholes at Sites 47, 19 and 64. These are considered to be Pleistocene signatures, in line with previous studies in the region. Two of these sites are from the confined East Midlands section, but one is from the unconfined aquifer in South Yorkshire. This indicates that, even in unconfined groundwater conditions, vertical

Table 6
Depth samples from Site 47 (static at time of sampling).

	Unit	32 m	40 m	56 m	60 m	62 m	72 m	94 m	108 m	162 m	170 m
pH*		7.42	7.32								
Ca	mg/L	65.2	58.5	53.6	48.5	46.7	45.7	41.4	39.4	37.5	40.5
Mg	mg/L	24.3	20.4	17.9	19.1	19.1	21.3	21.2	21.2	16.1	15.4
Na	mg/L	33.5	16.9	12.7	10.3	9.2	9.6	10.0	10.0	14.5	18.7
K	mg/L	10.9	6.00	2.89	2.48	2.43	2.81	3.16	3.42	4.63	4.93
HCO$_3$	mg/L	228	228	222	234	237	243	193	215	176	164
Cl	mg/L	68.2	36.9	27.8	18.6	13.5	13.6	14.4	13.6	9.9	9.8
SO$_4$	mg/L	62.2	39.8	26.6	20.6	17.5	20.4	25.5	26.8	47.4	71.2
NO$_3$-N	mg/L	2.0	1.0	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
NH$_4$-N	mg/L	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Si	mg/L	4.2	4.4	4.5	4.1	3.9	3.7	3.6	3.5	3.6	3.6
Li	µg/L	9	9	9	16	17	21	22	23	25	25
Sr	µg/L	53	43	41	122	159	203	235	281	177	210
Ba	µg/L	426	562	610	564	517	506	453	409	260	163
Fe	µg/L	38	< 3	< 3	353	440	533	473	425	133	100
Mn	µg/L	225	253	248	158	118	79	52	33	15	12
$\delta^{18}O$	‰	−8.1	−7.8	−8.0		−8.2	−7.9	−8.3	−8.3	−8.8	−9.2
δ^2H	‰	−57	−56	−55		−56	−59	−59	−60	−66	−67
$\delta^{13}C$	‰	−14.7		−14.0			−13.8		−13.3		−11.5

Concentrations of Al all < 100 µg/L. Depths refer to metres below ground level (elevation 3 m above OD). $\delta^{18}O$, δ^2H relative to SMOW; $\delta^{13}C$ relative to PDB. *pH values determined using a multi-parameter sonde.
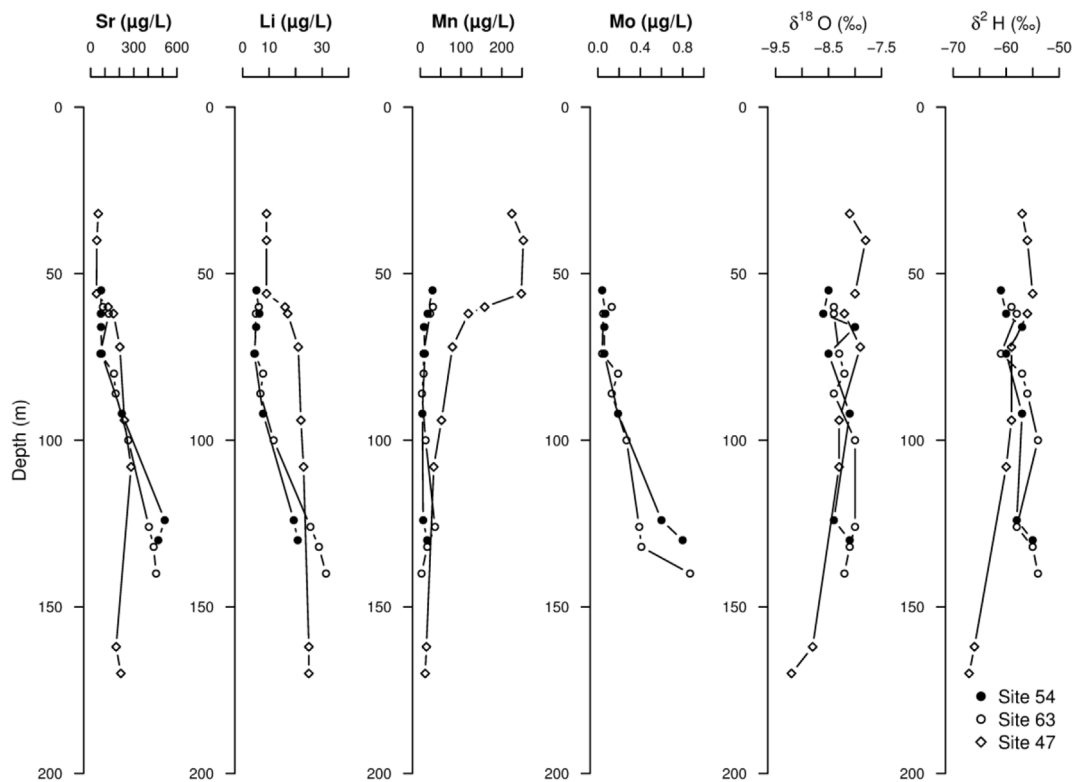
Fig. 8. Profiles of selected trace elements and stable isotopes from three boreholes in South Yorkshire (Sites 54, 63 and 47); depths are relative to ground level.

Table 7
Average stable-isotopic compositions of groundwater in borehole sections taken from depth samples with estimated groundwater residence times based on regression equations from Edmunds and Smedley (2000) (ibid for ^{14}C data source).

Site	Well depth mbgl	Range	δ^{18}O ‰	δ^2H ‰	δ^{13}C ‰	[14]C age years	Cs years	Li years	Mn years	Mo years	Rb years	Sr years	δ^{13}C years
64	280	< 200 m	−8.0	−56.0				31,000	10,000			16,000	
64		> 200 m	−9.1	−64.5		17,100		58,000	163,000			125,000	
2	335		−8.3	−57.1	−8.3	7200		13,600	27,000			11,000	
19	500		−9.2	−61.9	−9.7		24,000	35,300	134,000	22,200	36,500	33,500	23,000
54	137	< 80 m	−8.4	−59.5	−14.8		5500	5600		modern	15,200	modern	
54		> 80 m	−8.2	−56.7				17,300		142,600	15,300	16,300	
63	150	< 80 m	−8.4	−58.1	−13.1			7500	44,000	1000	7500	3000	
63		> 80 m	−8.1	−55.7	−14.5			31,300	66,000	7700		18,000	
47	232	< 150 m	−8.1	−57.4	−14.0			17,100	160,000			modern	modern
47		> 150 m	−9.0	−66.5	−11.5			27,300	14,600			3000	6700

flow rates can be small such that at > 150 m depth (Site 47), palaeo-water of greater than ca. 10,000 years is preserved. As residence times in the deep confined East Midlands aquifer are some 30,000 years or more at 20 km downgradient of the outcrop (Lincoln area), this implies that vertical flow rates in the deeper aquifer may be at least an order of magnitude smaller than horizontal flow rates.

A number of dissolved trace elements not constrained by mineral solubility controls have revealed time-dependent increases in this aquifer system as a result of weathering reactions (e.g. Li, Sr, Rb, Mn, Mo). These have been used as proxy indicators of residence time in the absence of radiogenic isotope data or to add to the body of dating evidence, or indeed to extend the range of ^{14}C dating capability (Edmunds and Smedley, 2000). Application of these proxy indicators to the depth samples collected from the selected South Yorkshire and East Midlands boreholes yields a range of model ages shown in Table 7.

The results indicate some large variability in model ages, although most of the deep palaeowaters have correspondingly larger values. Many sites show a degree of consistency between different trace elements but it is clear from the discrepancies that some significant

caution is needed in application of the chemical age dating approach beyond the East Midlands section of aquifer. Model ages for Mn tend to be overreported compared to the other trace elements for given depths, probably because Mn shows reactive behaviour in the South Yorkshire aquifer (Fig. 7) that differs from the East Midlands profile used for calibration.

5.2. Extent of the freshwater aquifer

Downgradient evolution in groundwater chemistry leads to an eventual increase in salinity, with concentrations of Na and Cl respectively of 2000 mg/L and 5000 mg/L at depths of 800 m, at Welton, some 40 km downgradient of the confined/unconfined Sherwood Sandstone interface. This groundwater has been interpreted as old, highly evolved groundwater (Edmunds et al., 1982; Smedley and Edmunds, 2002), although its salinity is less than that of seawater. Along the flow path before this saline interface is reached, groundwater solute concentrations increase progressively, largely in response to carbonate and evaporite mineral reactions. In the Corringham area, 20 km east of the

confined/unconfined interface, groundwater is brackish, but salinity is controlled by concentrations of Ca and SO_4 due to gypsum dissolution (Ca = 350 mg/L, SO_4 = 1330 mg/L). Even this far down the flow gradient, the concentration of Cl remains very low at 22 mg/L (Edmunds and Smedley, 2000).

In the boreholes at Gainsborough, evidence especially from Site 19, shows that fresh groundwater (17 mg/L Na; 15 mg/L Cl; 144 mg/L SO_4) can be found down to around 500 m depth. This is the approximate base of the aquifer at this location.

Further north, in the South Yorkshire aquifer, the paucity of boreholes in the MMG-confined section makes estimation of the extent of freshwater there more difficult, although the lack of boreholes may be an indication of poorer water quality (and/or yields) in that section. BGS records for a 500 m-deep borehole at Scunthorpe, some 12 km east of the MMG/Sherwood Sandstone interface in South Yorkshire, indicate the presence of brackish groundwater there with a Cl concentration of 1300 mg/L and TDS of 5500 mg/L. This suggests that the freshwater is less extensive eastwards than in the East Midlands section.

Understanding the extent of freshwater in aquifers is a key requirement for groundwater management and protection under European legislation. Article 5 of the European Water Framework Directive (WFD) requires delineation of groundwater bodies, defined as bodies of water that constitute an actual or potential resource, and that for example are not of poor quality due to salinity. The UK-TAG (2011) report on groundwater body delineation recommends a maximum depth consideration for groundwater bodies as 400 m below surface, although it includes a requirement to consider local variations. In the case of the East Midlands aquifer, resource protection clearly needs to cover a larger depth range than this current recommendation advocates (i.e. to 500 m, the base of the aquifer), at least in the aquifer section considered in this study.

6. Conclusions

This study shows the distribution and range of groundwater chemical compositions in the Sherwood Sandstone aquifer of the English East Midlands and South Yorkshire, generated by water-rock interaction processes, variable inputs of modern pollutants and variable groundwater residence time. Pollutant inputs are demonstrated by relatively high concentrations of Na, Cl and NO_3 (for example) in the shallow unconfined aquifer but these diminish downgradient and with depth as impacts of anthropogenic inputs diminish. Mineral geochemical reactions are dominated by carbonate (calcite, dolomite) and evaporite (gypsum, anhydrite) minerals, with a dedolomitisation reaction involving gypsum dissolution leading to increasing dissolved SO_4 concentrations downgradient and at depth. Increased concentrations of Sr and enriched $\delta^{13}C$ values are also manifestations of this time-dependent reaction. Silicate hydrolysis reactions (e.g. of feldspar and clays) also occur. These result in increased concentrations of K, Rb and Li (for example) with time but are not a principal influence on the dominant major ions.

Redox changes affect the chemical compositions of the redox-sensitive solutes (e.g. NO_3, Fe, Mn, Mo, U). In the South Yorkshire aquifer, redox changes are much less regular spatially than in the East Midlands section because of the influence of the superficial Quaternary deposits, most notably the clay-dominant glaciolacustrine Hemingbrough Formation. Across the aquifer, NO_3 concentrations diminish under reducing conditions, while concentrations of Fe, Mn and Mo increase. Distributions of NO_3 may have been influenced to some extent by denitrification under reducing conditions, but the aquifer's capacity to reduce oxidised species is likely to be low. In South Yorkshire, concentrations of U increase (up to around 6 μg/L) under mildly reducing conditions, close to the confined/unconfined interface or in the transition from oxic to anoxic conditions within a borehole. In the East Midlands section, concentrations reach similar maxima, but are lower under the more strongly reducing conditions observed in the deep

confined aquifer, likely as changing U redox speciation reduces mobility. The time-dependent increases in concentrations of trace elements such as Mn, Li, Rb and Sr have been used as proxy indicators of groundwater residence time in the East Midlands and South Yorkshire aquifer. These give groundwater model ages broadly consistent with inferences from stable-isotopic results, but with a variability providing uncertainty and requiring caution with their interpretation.

Groundwater samples from discrete depths in investigated boreholes from both the unconfined and confined aquifer sections have revealed the presence of isotopically distinct groundwater at depth ($\delta^{18}O$ more depleted than $-9‰$, δ^2H more depleted than $-60‰$, $\delta^{13}C$ more enriched than $-12‰$). Depth of occurrence varies, but is typically more than 150 m depth in the unconfined/semi-confined aquifer of South Yorkshire. The groundwater has the O, H and C stable-isotopic character of a palaeowater, considered of Pleistocene age.

A three-dimensional pattern of groundwater geochemical evolution is therefore identified, where increasing groundwater residence time occurs both laterally with downgradient flow and vertically with depth. The vertical stratification of groundwater quality in the Sherwood Sandstone aquifer indicates that even in unconfined conditions in the western part of the aquifer, unpolluted fresh, low-NO_3, old groundwater is present at depth (> 150 m). The confined Sherwood Sandstone aquifer of the East Midlands contains the deepest recorded fresh groundwater in the UK, with low-salinity palaeowater occurring at depths down to some 500 m. Such deep fresh groundwater bodies extend beyond the current regulatory scope for protection under WFD legislation, and provide challenges for water management, especially as new pressures from exploitation of the deep subsurface, for example for hydrocarbons, produce new threats to groundwater quality.

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