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ORIGINAL ARTICLE

Tracing sources of carbon in urban groundwater using $\delta^{13}C_{TDIC}$ ratios

J. Rueedi · A. A. Cronin · R. G. Taylor · B. L. Morris

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Abstract Total dissolved inorganic carbon (TDIC) and its stable isotope ratio $\delta^{13}C_{TDIC}$ are used to trace the evolution of the carbon system of groundwater in three UK Permo-Triassic sandstone aquifers. Samples were collected from multilevel piezometers, open boreholes and sewer sampling points in the British Midlands (Nottingham, Birmingham and Doncaster) to evaluate both local and regional variations in $\delta^{13}C_{TDIC}$. $\delta^{13}C$ samples of matrix and pore water have also been analysed in each aquifer to further constrain the interpretations. Combining $\delta^{13}C_{TDIC}$ ratios with measurements of TDIC and pH clearly distinguishes the principal processes underlying the geochemical evolution of groundwater in Triassic sandstone aquifers, where processes can be both natural (e.g. carbonate dissolution) and anthropogenic (sewer-derived recharge). The paper shows that $\delta^{13}C_{TDIC}$ resolves ambiguities that arise from the interpretation of TDIC and pH measurements in isolation. Field measurements demonstrate that, under natural conditions, the carbonate system evolves similarly in each aquifer. An open-system evolution during recharge largely saturates the groundwater with carbonate depending upon its availability in the sandstone matrix. The contribution of sewer exfiltration to urban recharge is readily distinguished by lower pH and higher TDIC values without significant changes in $\delta^{13}C_{TDIC}$.

Keywords Carbon 13 · TDIC · Permo-Triassic sandstone · Sewage · Urban groundwater

J. Rueedi (✉) · A. A. Cronin
Robens Centre for Public and Environmental Health,
Building AW, University of Surrey,
Guildford GU2 7XH, UK
e-mail: joerg.rueedi@eawag.ch

R. G. Taylor
Department of Geography, University College London,
26 Bedford Way, London WC1H 0AP, UK

B. L. Morris
British Geological Survey, Maclean Building,
Crowmarsh Gifford, Wallingford OX10 8BB, UK

Introduction

Fluvially-deposited, red-bed sandstones of Permo-Triassic age form regionally important aquifers throughout Western Europe. In the United Kingdom, the tectonic history of this sandstone formation (the Sherwood Sandstone) has produced a series of regional aquifer systems. Sandstones are fine to coarse-grained in which both matrix and fracture flow occurs (i.e. dual porosity). Groundwater flowing in these sandstone aquifers has played an important role in the development of several major UK cities such as Liverpool, Birmingham, Nottingham, Doncaster and Coventry by supplying water for industrial and potable use for more than 130 years. Recharge sources and pathways in urban sandstone aquifers remain poorly resolved and are the subject of active research (Morris et al. 2006; Taylor et al. 2006; Taylor et al. 2003; Cronin et al. 2003; Tellam and Thomas 2002).

Preliminary interpretation of hydrochemical data involves the description of the concentrations and relative abundances of dissolved major and minor constituents which often can be related to groundwater provenance and flow directions (Bath et al. 1987; Domenico and Schwartz 1998; Edmunds and Smedley 2000; Smedley and Edmunds 2002). The origins of

groundwater and hydrogeochemical processes affecting their chemical evolution cannot always be deduced from changes in major-ion chemistries alone as the same aqueous chemistry can arise through more than one set of processes (Tellam and Lloyd 1986). To resolve potential ambiguities in interpretations further geochemical data such as ion ratios/correlations, characteristic minor/trace determinants, isotopic compositions, downgradient mineralogy and reaction path simulations can be used (Elliot et al. 2001). Isotopes of a given element differ slightly in mass due to different numbers of neutrons in the nucleus (e.g. ^{13}C). Isotopic ratios have proved extremely useful in resolving multiple sources and sinks for dissolved ions, and identifying the downgradient evolution of groundwaters affected by water-rock interaction (e.g. Fritz and Fontes 1980; Clarke and Fritz 1997; Elliot et al. 1999).

Carbonic acid is the most abundant acid in natural water systems and the one most responsible for rock weathering (Langmuir 1997). The isotopes of carbon are ^{12}C, ^{13}C and ^{14}C and their average terrestrial abundances are 98.89, 1.11 and 10^{-10}%, respectively (Fritz and Fontes 1980). Ranges of $\delta^{13}C$ in natural materials are highly variable (e.g. Craig 1953; Burleigh et al. 1984; Langmuir 1997) where $\delta^{13}C$ is usually defined in relation to Vienna-PeeDee Belemnite (V-PDB).

$$\delta^{13}C = \frac{\left(^{13}C/^{12}C\right)_{\text{sample}} - \left(^{13}C/^{12}C\right)_{\text{standard}}}{\left(^{13}C/^{12}C\right)_{\text{standard}}} [\text{V-PDB}] \quad (1)$$

The $\delta^{13}C$ ratio of the total dissolved inorganic carbon content of water ($\delta^{13}C_{TDIC}$) has been used as a tracer in river water systems (e.g. Pawelleck and Veizer 1994) and lakes (e.g. Wachniew and Rozanski 1997). $\delta^{13}C_{TDIC}$ is an excellent tracer of carbonate evolution in groundwater systems because of the large variations in different carbon reservoirs (Clarke and Fritz 1997). Iterative modelling of chemical and isotopic changes during carbonate rock dissolution enables theoretical $\delta^{13}C_{TDIC}$ evolution of a groundwater to be mapped (Deines et al. 1974). This can help to determine whether spring or well waters have evolved under open or closed systems (i.e. with or without a constant supply of soil CO_2).

Despite mounting evidence of groundwater contamination through leaky sewage systems (e.g. Cronin et al 2003; Taylor et al. 2006), the effects of sewage leakage on groundwater ^{13}C remain poorly defined. Fernandes et al. (2005) have shown that application of sewage sludge from a wastewater treatment plant in Brazil has increased the C content of the soil and depleted the soil $\delta^{13}C_{CO_2}$ values due to a $\delta^{13}C$ value of sewage of –23.7‰. In a temperate climate like the UK where the $\delta^{13}C_{TDIC}$ of recharge is in equilibrium with the soil (open system), the similar value of $\delta^{13}C$ sewage will result in an almost unchanged $\delta^{13}C_{TDIC}$ value for the resulting mixture.

Of course, other effects will also affect $\delta^{13}C_{TDIC}$ values in groundwater. As a general rule, reducing conditions give rise to $\delta^{13}C_{TDIC}$ values more enriched in ^{13}C as ^{12}C preferentially binds with hydrogen to form methane. Mineral sources also tend to produce $\delta^{13}C_{TDIC}$ signatures that are enriched in the heavy ^{13}C isotope. Anthropogenic influences also affect $\delta^{13}C_{TDIC}$ values, in particular landfill leachate. Many authors have observed significant increases in these values due to the onset of methanogenesis (e.g. Hackley et al. 1996). North et al. (2004) measured leachate $\delta^{13}C_{TDIC}$ values in excess of +16‰ adjacent to a New Zealand landfill. Organic contamination can also affect carbon isotopic signatures and have been used to assess the degree of biodegradation; these processes and fractionation factors for given compounds are reviewed in Meckenstock et al. (2004).

This paper uses stable carbon isotopic ratios and selected major ion concentrations of groundwater, pore water and aquifer matrix samples to assess and distinguish natural and anthropogenic processes in three urban Permo-Triassic sandstone aquifers in the UK. Processes are considered both in relation to depth and lateral distribution of geochemical observations.

Study area

Doncaster

The Sherwood Sandstone has little topographic expression apart from isolated and subdued ridges on its western (basal) margin (Fig. 1). The aquifer increases in thickness from its western edge, reaching about 175 m to the east of Doncaster where the suburbs and nearby former coal mining villages are located. Quaternary superficial deposits ranging from glacial sand-and-gravel to peat and lacustrine silty clays overlie the sandstones in many places and these can exert a major control on recharge processes, flow patterns and solute/contaminant transport (Smedley and Brewerton 1997). Groundwater flow occurs from west to east following the artificial gradients induced by the water supply wells located outside the urban area.

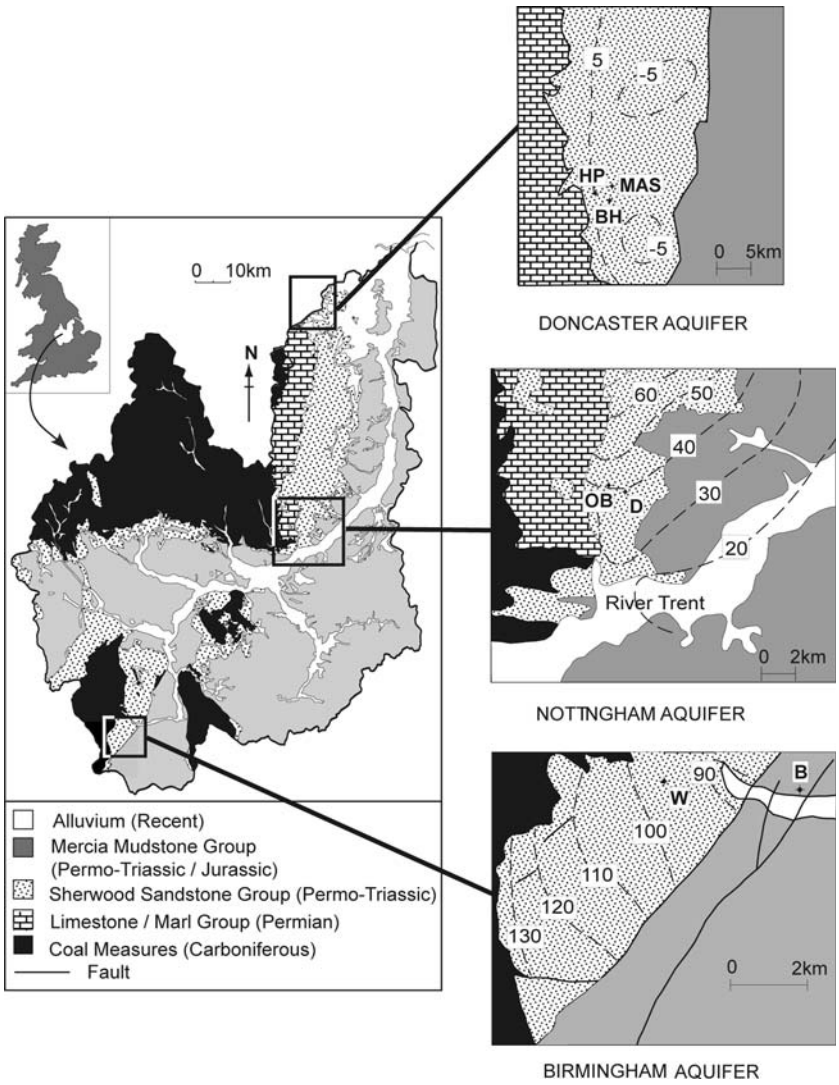

Fig. 1 Location and geology of the Trent River Basin, England. The *upper right hand box* shows the geology of Doncaster at an expanded scale, the *middle box* denotes Nottingham while the *lower right hand box* shows the geology of the Birmingham area at the same scale. Piezometric water levels are denoted by the *dashed lines* with associated labels m relative to Ordnance Datum. These *expanded boxes* also show multilevel piezometer locations as (+) crosses

Hydraulic conductivities are between 2 and 11 m/day ($2.3–12.7 \times 10^{-5}$ ms^{-1}), typically ranging between 3 and 5 m/day ($3.5–5.8 \times 10^{-5}$ ms^{-1}). The chosen sampling sites, Haslam Park (HP), Bolton Hill (BH) and McAuley School (MAS), are all located in Bessacarr-Cantley, a suburb of Doncaster. This area was chosen because it is located down-gradient of the historical town centre of Doncaster and because the Quaternary deposits are thin to non-existent across much of the suburb. The sites are part of a set of five, all of which are located where the sandstone is either at outcrop or below thin permeable sands and gravels.

Nottingham

The city is underlain by a sedimentary sequence (Carboniferous to Triassic) of limestones, marls, sandstone and mudstone that dip generally 1.5°–4° toward the SE (Charsley et al. 1990). The Sherwood sandstone is underlain by Permian marls and, in the southern and eastern areas, overlain by the Mercia Mudstone, providing similar confining conditions to those southeast of the Birmingham fault. Extensive Quaternary superficial deposits in the Trent valley consists of till, sand and gravel, silt and clay. The thickness of these deposits is generally less than 5 m but can be up to 10 m locally. Beneath much of the city of Nottingham the aquifer is unconfined and found at shallow depths. Regionally, groundwater in the Sherwood Sandstone flows toward the Trent River system. Figure 1 shows that the two sampling sites in Nottingham, Daybrook (D) and Old Basford (OB) are both located in the unconfined part of the aquifer.

Birmingham

Permo-Triassic sandstones form the principal aquifers also in the Trent River Basin of central England

(Fig. 1). The Birmingham Sherwood Sandstone aquifer is overlain by Quaternary glacial deposits of 0–40 m thickness in west Birmingham and these can produce locally confined conditions (Ford and Tellam 1994). The aquifer is confined by the Triassic Mercia Mudstone to the southeast of the Birmingham fault. This fault restricts but does not totally eliminate groundwater flow between confined and unconfined aquifer sections, as evidenced by comparison of piezometric surfaces on either side of the fault (Jackson and Lloyd 1983). The Birmingham plateau has the Trent and its tributaries to the North and East and the Severn and its tributaries to the West and South. The two sampling sites were chosen in the unconfined Witton (W) and confined Bromford (B) areas.

Much research has been carried out in these aquifers (Bath et al. 1987; Edmunds et al. 1982; Edmunds and Smedley 2000; Smedley and Edmunds 2002) though these previous studies have usually employed shallow monitoring piezometers and/or pre-existing deep abstraction boreholes (often of uncertain depth and construction). Large screened intervals and ambient vertical flow in such boreholes masks depth-specific trends through the mixing of waters from several horizons (Parker et al. 1982). This deficiency in the ability to distinguish depth specific variations, led to the installation of the three multilevel piezometers in Nottingham, two in Birmingham (Taylor et al. 2003) and the five in Doncaster (Rueedi et al. 2004). All of the multilevels were installed in open holes 50–90 m deep, drilled by air-flush and each has 7–10 sampling ports. Bentonite clay seals (1–3 m thick) separate each sampling interval.

Methodology

Conceptual model

Much research has been done on the use of stable carbon isotopes to distinguish evolution pathways of groundwater (Fritz and Fontes 1980; Clarke and Fritz 1997). Figure 2 shows a conceptual representation of six different pathways groundwater can undergo in the subsurface and how these pathways can be uniquely distinguished by using pH, TDIC, and $\delta^{13}C_{TDIC}$. For more detailed explanations on pathways 1–4 please refer to Fritz and Fontes (1980), Clarke and Fritz (1997) or Langmuir (1997).

1. During groundwater recharge infiltrating water is in constant contact with the surrounding CO_2 of plant root origin and the soil matrix. Following this evolutionary pathway, commonly referred to as open system conditions, TDIC in groundwater is assumed to be in equilibrium with both soil CO_2 and rock matrix (Fritz and Fontes 1980). Therefore, there is continuous exchange between the dissolved calcite from the matrix and the water percolating through the unsaturated zone. Due to the much larger reservoir of carbon in the soil, $\delta^{13}C_{TDIC}$ is in equilibrium with the soil CO_2. An increase in pH corresponds with an increase of TDIC because a greater proportion of dissolved carbon is in the states of HCO_3^- and CO_3^{2-}. The observed discrepancy between the $\delta^{13}C$ ratio of the observed TDIC in the water sample and the $\delta^{13}C$ ratio of soil CO_2 (dotted lines in Fig. 2) increases with increasing pH because the isotopic fractionation increases for carbonic acid species dominating at high pH (CO_3^{2-}) with the biggest differences evident in the pH range of 6–7. Note that the curves displayed in Fig. 2 for open evolution are independent of the initial pH.
2. If calcite saturation is not reached during groundwater recharge carbon evolution will continue in the absence of soil CO_2 provided there is sufficient calcite present in the aquifer matrix. Following this evolutionary pathway, commonly referred to as closed system conditions, only slight changes in both TDIC and $\delta^{13}C_{TDIC}$ with increasing pH are possible (Fritz and Fontes 1980). Principally, dissolution of carbonate cement increases the $\delta^{13}C$ ratios in the groundwater as the matrix mineral C is more enriched in the heavy isotope (^{13}C). Note that, in addition to $\delta^{13}C$ values for the soil and matrix, the curves for closed system evolution displayed in Fig. 2 require an initial pH, TDIC and $\delta^{13}C_{TDIC}$ of the sample that defines the initial mass balance at the groundwater table.
3. Dissolution of gypsum is a minor process in the Permo-Triassic sandstone (Smedley and Edmunds 2002) but can influence the carbon system. In groundwater saturated with calcite, gypsum dissolution leads to the precipitation of calcite and a decrease in pH since the bivalent sulphate anion (fully deprotonated) is the dominant form of aqueous sulphate at near-neutral pH. In order to make this point clear the reaction displayed below is shown in Eq. 2 in two steps. Firstly, dissolution of gypsum to obtain only dissolved ions and then the precipitation of calcite. In Fig. 2, this pathway follows the closed system lines (pathway 2) but in the opposite direction.

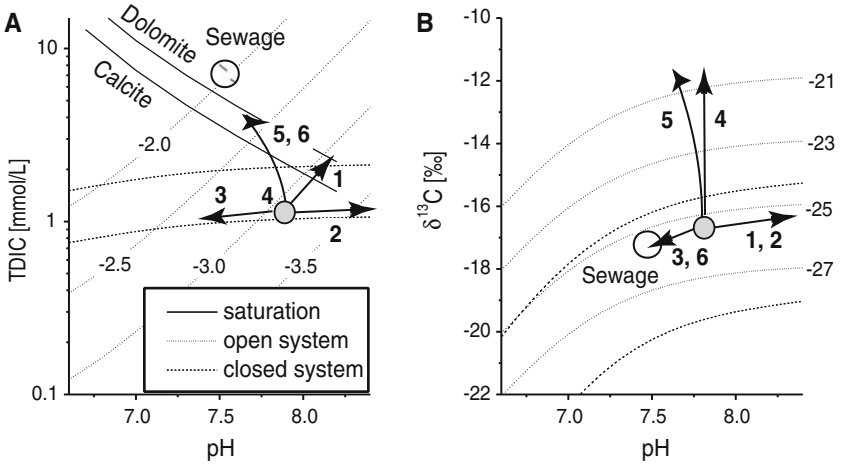

Fig. 2 TDIC and $\delta^{13}C_{TDIC}$ values (‰ w.r.t. VPDB) versus pH for four water evolution pathways in the carbonate system. (1) open system with indicated log values of CO_2 partial pressure and $\delta^{13}C_{CO_2}$; (2) closed system with initial (closing) pH of 7.6 and closing CO_2 partial pressure of 1×10^{-3} and 2×10^{-3}, $\delta^{13}C$ of soil CO_2 of –16 and –20‰ and a $\delta^{13}C$ of the aquifer matrix of –3‰; (3) congruent gypsum dissolution or dedolomitisation; (4) cation exchange; and (5) sewage admixture. The open and closed system and carbonate cement relationships were calculated after Langmuir (1997) and Clarke and Fritz (1997)

$$CaSO_4 \cdot 2H_2O + HCO_3^- \Rightarrow SO_4^{2-} + 2H_2O + Ca^{2+} + HCO_3^- \Rightarrow SO_4^{2-} + 2H_2O + CaCO_3 + H^+ \quad (2)$$

4. Once the groundwater sample is saturated with respect to calcite congruent gypsum dissolution (Eq. 3 with a and b being the stochiometric coefficients to ensure mass balance) and/or dedolomitisation (Eq. 4) can continue the isotopic exchange with the rock matrix and further increase the $\delta^{13}C_{TDIC}$. This occurs because dolomite with an enriched $\delta^{13}C$ ratio (of the rock matrix) is continuously dissolved and calcite with a depleted $\delta^{13}C$ ratio (from TDIC) is precipitated where the influence of $\delta^{13}C$ depletion due to fractionation as a result of calcite precipitation is small compared to large differences between the $\delta^{13}C$ of rock matrix and TDIC. Provided the sample was previously saturated, these two processes leave both pH and TDIC constant.

$$a CaSO_4 \cdot 2H_2O + b CaMg(CO_3)_2 \Rightarrow 2b CaCO_3 + 2H_2O + (a-b)Ca^{2+} + bMg^{2+} + aSO_4^{2-} \quad (3)$$

$$Ca^{2+} + CaMg(CO_3)_2 \Rightarrow 2CaCO_3 + Mg^{2+} \quad (4)$$

5. Cation exchange is able to affect the carbon system continuously by removing Ca^{2+} and Mg^{2+} from the aqueous phase and replacing these with Na^+ (and K^+). As a result, dissolution of calcite and dolomite continues and adds Ca^{2+} and Mg^{2+} to the solution until eventually saturation with respect to these minerals is reached. Cation exchange occurs mostly with clay minerals and requires an associated sodium source in these minerals (Appelo and Postma 1993). If groundwater is undersaturated with respect to calcite, hydrochemical evolution of groundwater will proceed along an evolution pathway similar to path 2. After saturation with respect of calcite is reached evolution of the carbon system is an increase of TDIC together with a decrease of pH and an increase of $\delta^{13}C_{TDIC}$ as indicated with evolution path 5 in Fig. 2.
6. The admixture of sewage with its lower pH and high alkalinity to a groundwater with a natural background signature increases TDIC and decreases pH. If the recharging water is undersaturated with respect to calcite (Fig. 2), an admixture of sewage leads to a 'hook-shaped curve' in the TDIC-pH plot. If the recharge is already saturated the evolution will follow the calcite saturation line.

Sampling and measurement techniques

Results presented in this work originate from two separate projects that were performed to assess the impact of urban settlements on the Triassic Sandstone formation in the UK. Note that sampling and measurement techniques are not the same for these two projects. However, standard techniques and procedures were used and both isotope laboratories are

regularly cross checking their results against international standards (NBS and IAEA).

All wells and piezometers were purged for a minimum of three to five well volumes and isotopic samples were only taken after well head parameters (temperature, pH, electrical conductivity, redox conditions) had stabilised. Alkalinity was analysed on-site by titration and all measurements were transformed to TDIC according to the pH values.

The Doncaster samples were collected in 60 ml glass bottles with polycone tops. Samples were then stored at 4°C until analysis, which was within 2 weeks after sampling. The total dissolved inorganic carbon (TDIC) was converted into CO_2 gas by direct acidification of the water sample with 80% H_3PO_4 and the gas was purified under vacuum by a series of cryogenic cold traps. This procedure was found to be most reliable to insure that no fractionation occurs during the process due to incomplete CO_2 recovery. The procedure was regularly tested with internal standards. The CO_2 was then isolated and analysed on a dual-inlet isotope ratio mass spectrometer (VG-Optima) to give its isotopic composition ($^{13}C/^{12}C$).

Due to health and safety concerns connected with on-site sampling, only few sewage samples were analysed for pH and alkalinity on-site. The others were only analysed in the lab and, therefore, have to be treated with care. A pH comparison between the two methods showed a decrease of 0.5-1 pH between sampling and lab analysis.

Birmingham and Nottingham water samples were collected in 1.5 ml crimp top vials that were analysed by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) on a PDZ Europa 20-20. The reference standard for $\delta^{13}C_{TDIC}$ analyses was NBS-19 (National Bureau of Standards limestone standard) that is traceable to the Vienna Pee Dee Belemnite primary standard (V-PDB). Water samples were analysed in triplicate to determine the instrumental precision (1 SD ~ 0.05‰).

Porewaters from Doncaster were extracted by centrifuging at 15,000 rpm and then analysed as above by dual-inlet IRMS. $\delta^{13}C_{TDIC}$ analysis was also carried out on the rock matrix from cores taken during borehole drilling in the Sherwood Sandstone in all four study areas. The bulk rock samples were crushed to a grain size between 250 and 425 μm and then acidified under vacuum by addition of phosphoric acid. The subsequent gas analyses were carried out by GC-IRMS for the Birmingham and Nottingham sets and by dual-inlet IRMS for the Doncaster samples, as described above. Mineralogy analysis was not performed on these samples. $\delta^{13}C_{TDIC}$ values in aerobic systems will be strongly influenced by the $\delta^{13}C$ of the soil CO_2 though various constraints did not permit soil measurements to be made as part of this work.

Saturation with respect to calcite, dolomite and gypsum were calculated on NETPATH 2.0 and using the Debie-Huckel approximation (Plummer et al. 1994).

Results and discussion

Detailed evaluations of the geochemical trends in the Permo-Triassic sandstone are given in Taylor et al. (2006) for Nottingham and Birmingham and in Morris et al. (2006) for Doncaster. Chemical data can be found in Table 1 for all parameters relevant to this paper. The focus of this study is the carbon system with supporting evidence to illustrate key hydrochemical processes occurring in the Permo-Triassic sandstone. New $\delta^{13}C_{matrix}$ values from these areas are presented in Table 2 and compared with other ratios measured in the Permo-Triassic sandstone (Table 3) as for future reference e.g. to correct radiocarbon groundwater ages. Such sizeable variation in the matrix values is surprising though not dissimilar to that found in other studies (Table 3). Bath et al. (1979) postulate that the wide range in $\delta^{13}C_{matrix}$ values reflects a minor secondary precipitate carbonate being more susceptible to solution than the primary carbonate cement. Other studies showed that the large range is due to the difference in $\delta^{13}C_{matrix}$ for dolomite (~0 to –3‰) whereas secondary calcite has more depleted $\delta^{13}C_{matrix}$ values than that of primary calcite, often taken as close to –10‰ (Edmunds et al. 1982; Evans et al. 1983).

Sewage

Sewer leakage has been found to influence water quality at the majority of the sites. Regular positive detections of bacterial and viral indicators of faecal origin have been found in both aquifers (Powell et al. 2003, Cronin et al. 2005) where they have been explained by a small but rapid flow component transporting sewer-derived leakage to depth (Cronin et al. 2003; Taylor et al. 2004; Morris et al. 2006). Rueedi et al. (2006) have used mass balance calculations of sewer-derived indicators detected in the Doncaster multilevels to estimate that sewer exfiltration makes up ca. 5–20% of total groundwater recharge. Yang et al. (1999) estimated sewer leakage rates of 3–14% of total annual recharge in Nottingham. Hence, sewer leakage has potentially a major influence on carbon evolution.

Table 1 Major hydrochemical composition of water samples from Doncaster and Daybrook, Nottingham

Location multilevel wells	Date	Depth mbgl	pH field	pH lab	SEC µS/cm	T °C	*K* mg/l	Na mg/l	Ca mg/l	Mg mg/l	HCO_3^- field mg/l	HCO_3^- lab mg/l	Cl mg/l	SO_4 mg/l	NH_4–N mg/l	TDN-N mg/l	DOC mg/l	Sr mg/l
Haslam Park 2	9/9/2004	10.1	7.55		387	11.3	3.72	6.25	35.2	16	90.2		10.1	38.5	0.0113	8.46	4.73	0.0844
Haslam Park 2	9/9/2004	13.98	7.89		519	11.1	4.32	8.85	48.2	20.6	120.1		21.2	59.8	0.0684	8.49	2.14	0.0759
Haslam Park 2	9/9/2004	19.09	7.88		515	11.3	4.48	8.81	48.9	19.8	124.3		22.3	59.3	<0.006	7.46	2	0.0644
Haslam Park 2	9/9/2004	27.09	7.74		488	11	3.85	8.03	45	18.6	117.0		19.9	53.2	<0.006	8.98	1.89	0.0705
Haslam Park 2	9/9/2004	35.13	7.8		398	11	2.27	9.14	36.1	12.8	28.5		32	44	<0.006	11.5	1.27	0.0176
Haslam Park 2	9/9/2004	45.17	7.91		288	11	1.51	6.57	24.4	9.23	48.8		17.7	22.2	0.0213	8.33	0.77	0.0215
Haslam Park 2	9/9/2004	60.7	7.71		309	11.1	1.94	7.61	28	10.9	73.1		14.9	22.1	0.0087	7.91	1.27	0.0427
Bolton Hill	7/9/2004	16.41	7.45		767	10.5	12.4	16.1	91.7	33.6	295.0		31.4	96.3	<0.01	4.08	2.55	0.0903
Bolton Hill	7/9/2004	22.39	7.53		843	11.8	11.2	18.8	87.6	33.7	299.9		33.6	86.7	<0.01	4.78	1.65	0.0511
Bolton Hill	7/9/2004	28.98	7.82		984	11.1	8.6	23.9	101	38.5	243.8		69.3	143	0.272	6.07	1.62	0.0348
Bolton Hill	7/9/2004	34.96	7.95		988	11.1	6.11	19.8	105	36.9	153.6		106	147	<0.01	4.96	1.15	0.0399
Bolton Hill	7/9/2004	39.97	7.94		908	11	6.32	16.5	91.7	35.5	129.2		98.6	140	0.109	6.05	0.97	0.0357
Bolton Hill	7/9/2004	45.34	7.87		571	10.8	6.39	12.3	55	21	92.6		48.4	75.8	<0.01	7.64	1.2	0.0354
Bolton Hill	7/9/2004	51.33	7.89		574	10	2.42	10.1	56.7	22.8	97.5		43	73.4	0.234	9.99	1.55	0.0471
McAuley School	10/9/2004	9.07	6.96		619	12	2.65	44.3	38.9	22.2	246.2		11.8	25	0.301	7.23	5.57	0.102
McAuley School	10/9/2004	14.04	7.44		645	11	5.07	16.6	68.6	23.4	241.4		21	46.8	<0.01	4.94	2.42	0.053
McAuley School	10/9/2004	21.17	7.34		640	11.2	4.03	27.5	57.8	23	247.5		13	47.1	<0.01	6.86	2.68	0.0645
McAuley School	10/9/2004	28.17	7.87		668	11.4	4.81	11.2	79.1	23.5	140.2		14.2	134	0.286	9.4	2.81	0.0333
McAuley School	10/9/2004	35.7	7.95		649	11.6	3.86	19.8	69.2	22	157.3		23.6	109	0.407	5.46	1.58	0.0302
McAuley School	10/9/2004	45.24	7.87		609	11.6	2.93	20.6	59.4	17.9	71.9		25.7	98.7	0.044	17.7	0.71	0.0279
McAuley School	10/9/2004	60.53	7.86		402	13.1	2.18	12.8	38.4	11	51.2		31.7	38	<0.01	11	3.86	0.028
Pore water																		
Core 1		30.2		7.89			7.4	21.9	71.3	23.2		120.8	71.5	97.5	0.01			0.0408
Core 2		29.5		7.86			8.7	23.1	73.7	24.1		119	88.5	95.1	<0.01	14.8		0.0401
Core 3		16.25		7.92			7.4	17.3	70.3	28		145.1	163	67.4	<0.01	6.52		0.0588
Core 4		10.6		7.91			6.7	17.4	80.8	39.9		150	232	57.1	<0.01	14.5		0.146
Core 5		9.9		8			6.4	13.1	95	41.3		145.1	259	41.5	<0.01	21.3		0.218
Regional wells																		
Racecourse	6/9/2004		7.26		416	11.6	1.81	11.4	42.5	15.8	158.1		17.9	24.3	0.025	1.2	0.65	0.0359
Peglars	7/9/2004		7.61		739	18.2	4.82	16.7	72.4	34.1	196.9		38.3	108	<0.01	7.59	2.31	0.209
Cantley Water Towers	8/9/2004		6.96		394	10.9	7.48	24.5	69.4	21.7	157.3		65	69.1	<0.01	9.01	1.94	0.0351
Warning Tounge Lane	9/9/2004		8.27		757	11	5.95	16.2	74.8	33.7	118.2		50.5	148	<0.01	9.23	1.59	0.0623
Gatewood Grange	8/9/2004		7.43		793	11.9	1.49	22.1	88	26.7	195.0		54.1	86.5	<0.01	12.6	1.92	0.0329
Nutwell BH2	10/9/2004		7.61		517	17	2.65	10.9	54.9	22.2	223.7		21.4	27.9	0.028	1.02	1.81	0.13
Armthorpe	10/9/2004		7.45		572		2.51	20.2	49.6	20.8	99.4	101	37.7	66.4	<0.01	12.6	1.03	0.055
Nottingham multilevel																		
Daybrook	3/11/2000	12.12	6.06		238	10.5	2.7	8.8	17.1	9.1	27		12.5	43.2	<0.1	6.7	12.1	6.06
Daybrook	3/11/2000	16.00	7.07		1239	9.6	5.3	51.8	120.0	49.7	195		202.0	145.0	<0.1	11.5	16.0	7.07
Daybrook	3/11/2000	19.09	7.2		1331	9.6	3.7	69.3	122.0	51.9	199		228.0	148.0	<0.1	11.1	19.1	7.2

Table 1 continued

Location multilevel wells	Date	Depth mbgl	pH field	pH lab	SEC µS/cm	T °C	*K* mg/l	Na mg/l	Ca mg/l	Mg mg/l	HCO_3^- field mg/l	HCO_3^- lab mg/l	Cl mg/l	SO_4 mg/l	NH_4–N mg/l	TDN-N mg/l	DOC mg/l	Sr mg/l
Nottingham multilevel																		
Daybrook	3/11/2000	21.05	7.52		1309	10.4	3.3	63.5	120.0	51.7	221		212.0	151.0	<0.1	11.5	21.1	7.52
Daybrook	3/11/2000	25.00	7.47		954	11	1.9	25.3	99.3	45.9	250		110.0	132.0	<0.1	13.1	25.0	7.47
Daybrook	3/11/2000	28.15	7.5		908	10.9	1.8	21.1	96.4	44.8	240		94.6	130.0	<0.1	13.3	28.2	7.5
Daybrook	3/11/2000	30.94	7.56		698	10.6	1.8	15.4	72.4	33.1	178		62.2	92.4	<0.1	12.0	30.9	7.56
Daybrook	3/11/2000	35.00	7.43		777	10.7	1.6	17.8	80.4	38.5	195		73.1	107.0	<0.1	12.5	35.0	7.43
Daybrook	3/11/2000	40.05	7.62		524	10.8	1.3	12.7	50.8	25.5	140		42.2	50.5	<0.1	10.0	40.1	7.62
Daybrook	3/11/2000	46.10	7.52		530	11	1.4	13.2	50.4	23.6	153		45.0	41.5	<0.1	9.5	46.1	7.52
Sewage samples		Time																
Burnham Close	29/7/2003	14:00		7.69	840	18.1	13.9	79.7	57.4	23.2		382	66.6	90.8	24.5		38.6	0.0925
Everingham Road	29/7/2003	15:45		7.49	1000	17.8	20.2	116	53.2	24.5		456	104	88.7	34.5		68.8	0.109
Everingham Road 1	4/11/2004	12:15	8.35	7.65	1348	18	18.2	131	50.9	23.7		482	76.5	104	36.1		83.9	0.0942
Everingham Road 2	4/11/2004	13:00	8.22	7.47	1289	17.9	18	108	50.1	23.3		454	74.3	79.6	31.7		46.6	0.0954
Everingham Road 5	4/11.2004	16:05	8.12	7.17	1405	17.4	31	116	52.6	23.9		503	94.7	83.1	45		84.9	0.104
Everingham Road 7	4/11/2004	18:55	8.15	7.42	1240	17.8	21.9	88.8	51.2	22.8		465	85.7	70.6	47		51.8	0.103
Everingham Road 10	4/11/2004	00:30	8.15	7.5	1266	18.3	22.6	82.3	52	23.4		523	83.2	67.5	60.4		106	0.105
Everingham Road 11	5/11/2004	06:40	8.07	8.2	1387	16.9	20.5	67.4	55	23.8		537	84.3	59.9	66.6		26.3	0.115
Everingham Road 13	5/11/2004	09:55	8.54	7.58	1387	18.1	21.9	103	49.3	23.2		584	77.9	86.4	74.2		132	0.0965
Warning Tongue Lane	25/7.2003	12:30		7.79	940	19.8	22.3	128	51.3	23.7		566	74.5	94.5	44.4		106	0.106
Warning Tongue Lane 1	4/11/2004	11:40	8.42	7.44	1182	18.2	15.6	133	58.1	24.7		492	69.4	98.6	21.9		69.9	0.126
Warning Tongue Lane 2	4/11/2004	12:45	8.44	7.71	1081	18	18.3	88.8	55.5	24.1		398	70.9	83.8	30.9		92.3	0.125
Warning Tongue Lane 5	4/11/2004	15:40	8.15	7.4	1026	17.8	16.7	63.4	52	22.4		422	68.1	64	31.3		66.6	0.119
Warning Tongue Lane 7	4/11/2004	18:10	8.25	7.55	1155	17.6	24	98.9	49.9	24		464	87.3	78.3	44		48.1	0.115
Warning Tongue Lane 10	4/11/2004	00:00	8.38	8.18	1108	18.2	21.2	66.4	52	22.8		544	73.4	63.9	68.3		48.3	0.128
Warning Tongue Lane 11	5/11/2004	06:05	8.44	8.23	793	16.8	62.9	47.4	65.1	25.6		524	47.1	76.5	61.3		21.6	0.173
Warning Tongue Lane 13	5/11/2004	09:30	8.61	7.37	1165	18.8	21.6	111	51	24.2		512	69.2	88.3	53.9		158	0.104

Sampling dates are shown in the second column and depths of the multilevel wells are shown in the third column

Table 2 $\delta^{13}C$ ratios and logarithmic saturation indexes of all samples used in the paper

Location	Depth mbgl	$\delta^{13}C‰$-PDB	Log SI		
			Calcite	Dolomite	Gypsum
Doncaster multilevels					
Haslam Park 2	10.1	–17.36	–0.577	–1.352	–2.194
Haslam Park 2	13.98	–15.99	–0.015	–0.256	–1.92
Haslam Park 2	19.09	–16.27	0	–0.246	–1.917
Haslam Park 2	27.09	–17.64	–0.197	–0.638	–1.986
Haslam Park 2	35.13	–18.25	–0.82	–1.95	–2.117
Haslam Park 2	45.17	–17.92	–0.618	–1.519	–2.53
Haslam Park 2	60.7	–16.54	–0.588	–1.445	–2.491
Bolton Hill	16.41	–16.78	0.146	–0.012	–1.55
Bolton Hill	22.39	–16.91	0.235	0.211	–1.614
Bolton Hill	28.98	–17.31	0.458	0.641	–1.372
Bolton Hill	34.96	–17.07	0.405	0.502	–1.34
Bolton Hill	39.97	–16.93	0.271	0.274	–1.398
Bolton Hill	45.34	–15.9	–0.107	–0.493	–1.779
Bolton Hill	51.33	–15.45	–0.065	–0.402	–1.782
McAuley School	9.07	–17.79	–0.707	–0.861	–2.396
McAuley School	14.04	–15.08	–0.027	–0.382	–1.919
McAuley School	21.17	–16.31	–0.184	–0.625	–1.98
McAuley School	28.17	–16.79	0.202	0.026	–1.436
McAuley School	35.7	–17.96	0.286	0.228	–1.566
McAuley School	45.24	–15.67	–0.18	–0.728	–1.644
McAuley School	60.53	–16.38	–0.448	–1.262	–2.16
Pore water					
Core 1	30.2	–10.76	0.115	–0.115	–1.607
Core 2	29.5	–12.46	0.091	–0.162	–1.610
Core 3	16.25	–11.34	0.217	0.175	–1.783
Core 4	10.6	–13.52	0.263	0.362	–1.836
Core 5	9.9	–12.83	0.402	0.582	–1.920
Matrix					
Haslam Park 2	–10	–2.96			
Haslam Park 2	–16	–4.96			
Haslam Park 2	–30	–6.29			
Haslam Park 2	–60	–6.64			
Bolton Hill	–23.6	–6.89			
Bolton Hill	–36	–5.85			
McAuley School	–20	–6.6			
McAuley School	–30.5	–5.88			
McAuley School	–51	–7.19			
Nottingham					
Daybrook	12.12	–15.3	–2.885	–5.912	–2.388
Daybrook	16.00	–12.8	–0.353	–0.971	–1.333
Daybrook	19.09	–14.7	–1.987	–4.226	–1.322
Daybrook	21.05	–14.4	0.147	0.061	–1.339
Daybrook	25.00	–15.3	0.109	0.026	–1.426
Daybrook	28.15	–15	0.112	0.031	–1.436
Daybrook	30.94	–8.4	–0.049	–0.304	–1.640
Daybrook	35.00	–8.7	–0.106	–0.396	–1.558
Daybrook	40.05	–13.4	–0.204	–0.571	–1.988
Daybrook	46.10	–12.9	–0.261	–0.712	–2.071
Old Basford	8.24	–14	–0.035	–0.217	–1.473
Old Basford	11.25		0.279	0.462	–1.515
Old Basford	15.24	–15	–0.041	–0.226	–1.544
Old Basford	18.25	–15.2	0.127	0.112	–1.736
Old Basford	22.33	–13.5	–0.098	–0.394	–1.557
Old Basford	26.15	–14.4	0.353	0.554	–1.774
Old Basford	30.42	–12.3	0.128	0.065	–1.969
Old Basford	35.37	–6.6	0.592	1.355	–2.463
Old Basford	39.38	–7.5	0.120	0.360	–2.398

Table 2 continued

Location	Depth mbgl	δ^{13}C‰-PDB	Log SI		
			Calcite	Dolomite	Gypsum
Old Basford	42.44		0.558	1.125	–1.971
Old Basford	48.62	–6.9	0.152	0.282	–2.267
Birmingham					
Bromford	9.41		0.351	0.176	–0.036
Bromford	12.61	–6.4	0.135	–0.281	–0.019
Bromford	18.61	–7.8	0.138	–0.259	–0.025
Bromford	76.28	–9.2	0.565	0.671	0.004
Bromford	81.31	–9.9	0.517	0.573	0.008
Bromford	90.79	–9	0.046	–0.429	–0.001
Witton	9.56	–13.7	–0.192	–1.769	–1.814
Witton	13.79		–0.150	–1.437	–1.723
Witton	16.24	–14.8	–0.354	–1.843	–1.691
Witton	21.92		–0.220	–1.223	–1.129
Witton	26.91	–13.8	–0.220	–1.427	–0.895
Witton	34.94	–13.8	–0.020	–1.159	–0.824
Witton	38.95	–14.2	–0.366	–1.806	–1.002
Witton	42.06	–14.3	–0.338	–1.011	–1.114
Witton	47.07	–14.3	–0.282	–1.080	–1.141
Regional wells					
Racecourse		–14.87	–0.542	–1.364	–2.328
Peglars		–14.85	0.151	0.233	–1.602
Cantley Water Towers		–13.86	–0.695	–1.755	–1.752
Warning Tounge lane		–14.12	0.473	0.744	–1.440
Gatewood Grange		–14.77	–0.036	–0.433	–1.595
Nutwell BH2		–14.31	0.122	0.091	–2.222
Armthorpe		–15.28	–0.513	–1.245	–1.876
Sewage samples					
Brunham Close		–19.39	0.393*	0.621*	–1.794*
Everingham road		–20.05	0.219*	0.356*	–1.861*
Everingham road 1			1.04	2.012	–1.83
Everingham road 2			0.904	1.736	–1.927
Everingham road 5			0.815	1.539	–1.901
Everingham road 7			0.856	1.618	–1.971
Birmingham					
Witton	52.14	–13.8	–0.089	–1.364	–2.460
Witton	60.43	–14.3	–0.073	–1.423	–2.056
Everingham road 10			0.911	1.742	–1.998
Everingham road 11			0.854	1.589	–2.022
Everingham road 13			1.259	2.462	–1.948
Warning Tongue Lane		–14.3	0.604*	1.158*	–1.873*
Warning Tongue lane 1			1.175	2.247	–1.799
Warning Tongue lane 2			1.097	2.096	–1.86
Warning Tongue lane 5			0.839	1.569	–1.981
Warning Tongue lane 7			0.93	1.798	–1.944
Warning Tongue lane 10			1.134	2.178	–2.027
Warning Tongue lane 11			1.246	2.335	–1.861
Warning Tongue lane 13			1.296	2.55	–1.914

*Lab pH used for calculation of saturation index

In Doncaster, a subset of sewage samples that were analysed for major and minor ion hydrochemistry was also analysed for δ^{13}C (Fig. 3). The much higher TDIC values of these sewer samples are distinct from the multilevel and regional well results. However, when compared with the lines of calcite and dolomite saturation the sewage samples are oversaturated with respect to both minerals (Fig. 3). How this occurs is yet unclear. However, it is likely to originate from the mixture of the different water sources, some with high pH and others with high bicarbonate content. In order to compare field and lab measurements of pH, pH

Table 3 Comparison of $\delta^{13}C$ matrix ranges (‰ V-PDB) from other studies on Permo-Triassic sandstone aquifers in Great Britain

Range of $\delta^{13}C_{matrix}$	Reference
–0.2 to –10.8	This study
–5.5 to –11.7	Bath et al. (1979)
–7.9 to –10.7	Jackson and Lloyd (1983)
0 to –7	Edmunds et al. (1982)
–2.2 to –9.9	Evans et al. (1983)
–4.5	Tellam (1994)

values were measured on-site in one of the field campaigns though laboratory measurements were undertaken for all samples (Table 1). The range of the measured field pH ($N = 14$) is displayed within the shaded area in Fig. 3a. It indicates that the initial composition of sewage is even more oversaturated with respect to calcite and dolomite than the samples analysed in the laboratory, possibly due to calcite precipitation in the unacidified sample used for alkalinity titration, which is conducted by automated titrimetry. This possible process is indicated with the dotted lines for closed system evolution (evolution path 2 in Fig. 2). Figure 3b shows that the $\delta^{13}C$ values spread over a rather large range. The $\delta^{13}C$ ratios in the actual sewer may be marginally more depleted than the sampled values if calcite precipitation occurred in the sampling bottle. The $\delta^{13}C_{TDIC}$ values of the original sewage samples were, therefore, higher than the measurements displayed in Fig. 3.

Doncaster

Plots A–E in Fig. 4 show depth-specific trends in relevant geochemical parameters for all three Doncaster multilevel piezometers. DOC and Sr^{2+} (Fig. 4d, e respectively) are both derived not only from carbon system evolution but also in sewage in amounts exceeding natural background concentrations. Mean sewage values of DOC and Sr^{2+} are 67 and 0.11 mg/l, respectively, whereas rural well background mean values are 3.66 and 0.03 mg/l (Table 1). On the pathway from sewage system to the actual sampling location, DOC could undergo dilution (with uncontaminated recharge from precipitation), adsorption and/or oxidation/reduction processes, where the latter processes would be capable of influencing $\delta^{13}C$ signatures in groundwater. However, both DOC and Sr^{2+} values observed in the most shallow piezometer are of the order of ten times lower than the concentrations in raw sewage, a proportion that is similar to the estimated contribution of sewage to the total recharge (Rueedi et al. 2006). Dilution therefore seems to be the dominant process affecting sewage-derived DOC on the transport to the groundwater table. The results displayed in Fig. 4d suggest that the sharp decrease of DOC in the top 10–15 m of the aquifer is due to either adsorption or oxidation. Reduction is not possible throughout the entire depth of the aquifer because all groundwater samples from multilevel wells had dissolved oxygen concentrations between 5 and 11 mg/l and redox potentials were in a range of +250 to +450 mV. The natural background of strontium in Triassic sandstone wells may come from incongruent dissolution of impure carbonate cements (Edmunds and Morgan-Jones 1976; Taylor et al. 2006). Figure 4e shows a decrease in strontium concentrations with depth that is significantly different from the sewage contribution.

The TDIC-pH plot displayed in Fig. 4g demonstrates that only open system evolution (as displayed with dotted lines) is occurring under natural, uncontaminated conditions with CO_2 partial pressures in the unsaturated zones consistently in a range of $10^{-2.5}$–

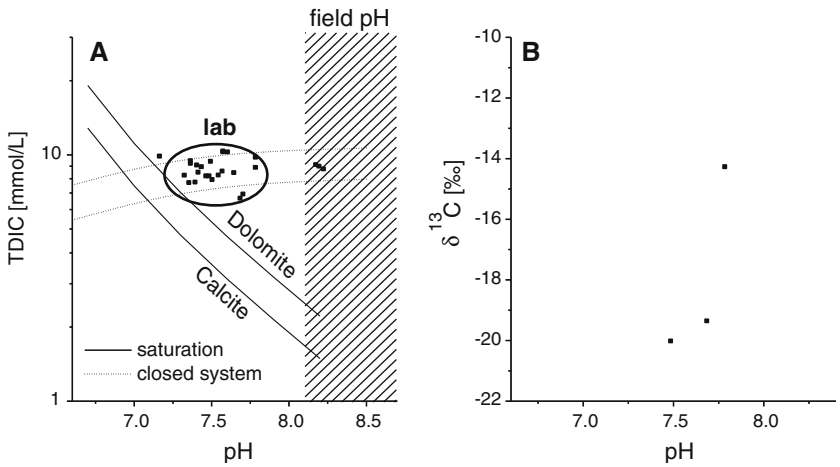

Fig. 3 Plot of TDIC and $\delta^{13}C_{TDIC}$ versus pH of sewage samples taken in Doncaster and measured in the lab. The *shaded area* indicates the range of pH values measured in the field ($N = 14$). *Full lines* indicate calcite and dolomite saturation and *dotted lines* indicate a closed system evolution when calcite is precipitated. Initial values of TDIC at pH 8.4 (of field samples) were about 8 and 10.4 mg/l

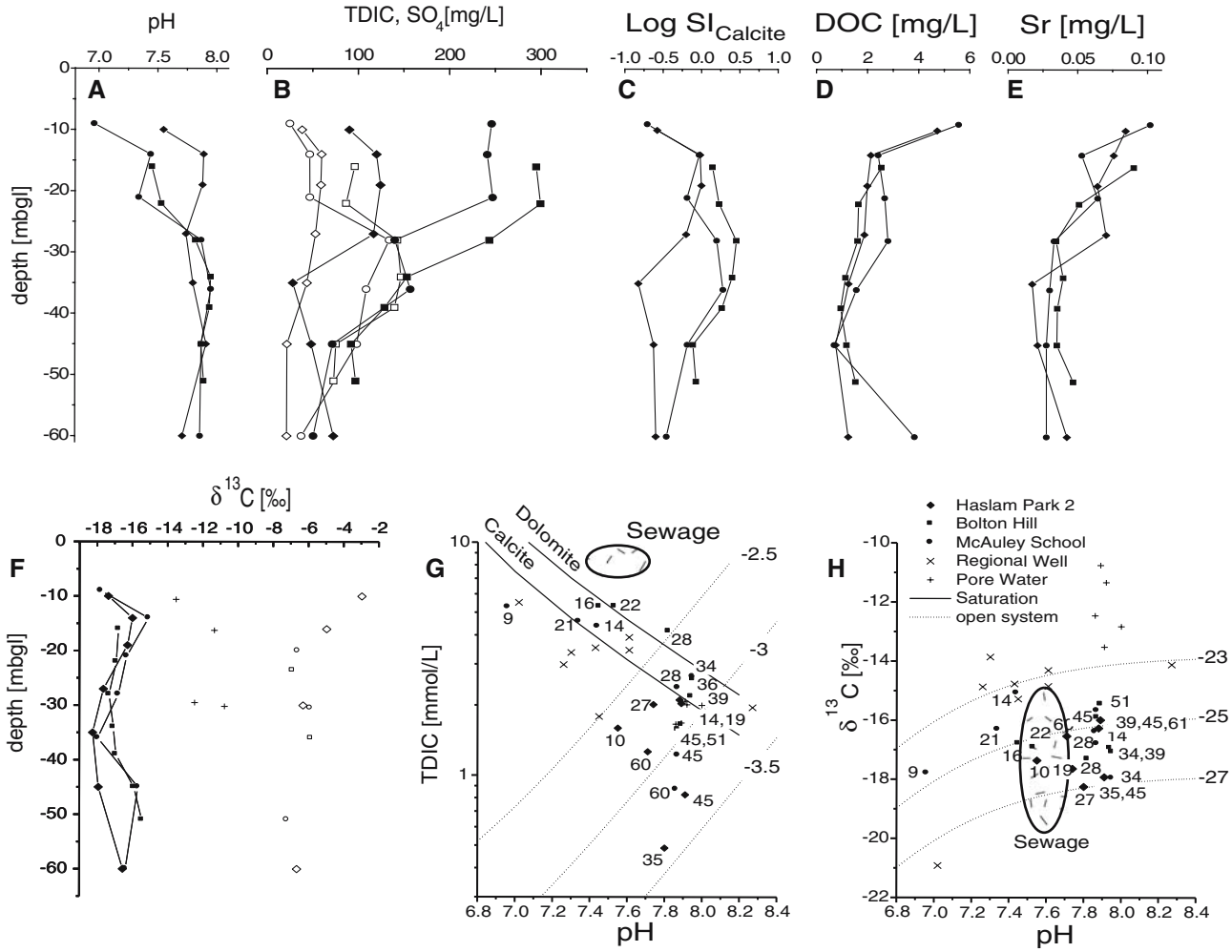

Fig. 4 Depth profiles of the multilevel piezometer sites in Doncaster with the depths of each sampling port given beside the corresponding marker. Haslam Park 2 is depicted with *diamonds*, Bolton Hill with *squares* and McAuley School with *circles*. **a** pH; **b** TDIC (*full symbols*) and SO_4^{2-} (*open symbols*); **c** calcite saturation index SI; **d** Dissolved organic carbon; **e** Sr^{2+}; and **f** $\delta^{13}C$ ratios of groundwater (*full symbols*), rock matrix (*open symbols*) and pore water (*crosses*). **g** and **h** TDIC versus pH and $\delta^{13}C_{TDIC}$ versus pH, respectively, including labelled equilibrium lines for open system evolution (*dotted lines*), saturation lines (*full lines*) and typical range of sewage samples shown with the *dashed circle*. Regional wells are indicated with *X's* and depths are in meters below ground level (mbgl)

$10^{-3.5}$ (evolution path 1 in Fig. 2). Deep uncontaminated samples are found to be undersaturated with respect to calcite indicating either limited amounts of calcite cement and/or relatively high flow velocities. A similar observation was made on three cores taken during drilling of the multilevel wells. There is a general trend of carbonate system evolution with a line of mixing between deep, uncontaminated groundwaters and typical sewage composition as indicated with the shaded circle (evolution path 6 in Fig. 2). The regional wells, of which the sewage contribution is unknown, appear to represent a mixture between the different intervals of the multilevel. An alternative hypothesis is that the very mixed disposition of the data may be influenced by the degree of cementation present at different depths and in different locations of the aquifer. The relative positioning of the samples may be associated with the availability of calcite to drive samples towards saturation. However, this is less likely as the presence of cements would strongly affect pH values (increase) while only modestly increasing TDIC values. Also it is unlikely to be due to depth variation in matrix values as Fig. 4f shows little variation in matrix $\delta^{13}C$ ratios below 15 m depth. In general, the groundwater trend line shows large increases in TDIC and little pH change and so is more similar to evolution path 6 rather than only path 1, as displayed in Fig. 2.

The narrow ranges of $\delta^{13}C$ ratios in both groundwater (–15 to –19‰) and aquifer matrix (–3 to –7‰) along with the pore water samples (–11 to –14‰)

plotted in Fig. 4f–h indicate that there is a distinction between mobile (or effective) and immobile porosity. When calcite is present in the pore system (≈15–30 mbgl), the immobile water is in equilibrium with the calcite matrix (Fig. 4g) with a corresponding enriched $\delta^{13}C$ ratio of about 3‰ (Fig. 4h) and the groundwater samples are saturated with respect to calcite (so no TDIC gradient from mineral to aqueous water). Furthermore, the pH of both mobile and immobile water is equal (Fig. 4h). This observed difference between groundwater samples and pore water samples of approximately 5‰ can only be explained by diffusive exchange of carbon isotopes between mobile and immobile water. In the shallower water sample (10 mbgl) where the groundwater sample shows undersaturation with respect to calcite and a matrix $\delta^{13}C$ of about –3‰ the $\delta^{13}C$ ratio of the pore water sample is much closer to the groundwater sample but not the same. This indicates that an exchange between matrix and groundwater occurs but that it is much smaller than in the deeper levels. Under similar conditions as in the deeper levels, the pore water should have a $\delta^{13}C$ ratio of approximately –8‰ rather than the observed –14‰. This reduced exchange could originate from a limited accessibility of the existing calcite matrix and/or from higher flow velocities. These two mechanisms would explain why some samples from Haslam Park and some regional samples (with integrated samples) are undersaturated with respect to calcite even though all matrix samples contained calcite.

In Fig. 4g the regional wells tend to plot to the top left (higher TDIC and lower pH) of the deep multilevel samples, indeed closer to the shallow contaminated wells than the deeper multilevel samples. The $\delta^{13}C$ ratios of the regional wells are more enriched in ^{13}C than the multilevel samples. This increase in $\delta^{13}C$ could originate from permanent but very slow admixture of carbon from the immobile phase by diffusive exchange. However, as discussed above, dedolomitisation or congruent dissolution of gypsum with subsequent precipitation of calcite (evolution path 4 in Fig. 2) can lead to this kind of evolution of the carbonate system. The fact that these integrated samples contain a larger mixture of waters representing different flow paths could add to the discrepancy between samples from regional and multilevel wells.

Nottingham

Figure 5 (plots A, B and C) graphs pH and TDIC, sulphate concentrations and calcite saturation indices for both of the Nottingham multilevel piezometers. TDIC and pH values as well as the saturation indexes (Fig. 5e) at Daybrook indicate that all samples have previously undergone an open system evolution (evolution path 1 in Fig. 2) with partial pressures of soil CO_2 in the range of 10^{-2}–10^{-3} and $\delta^{13}C$ ratios between –21 and –24‰ leading to $\delta^{13}C_{TDIC}$ ratios in the range of –13 to –16‰ (Fig. 5f). Compared to the Doncaster samples these samples are all near the calcite saturation line indicating considerable accessible amounts of calcite cement in sandstone and/or lower flow velocities, an observation that is confirmed by core samples from this region that are all well cemented. A shift to more enriched $\delta^{13}C$ signatures between 30.71 and 34.98 mbgl points to a potential dominance of dolomite or gypsum dissolution over calcite and subsequent ongoing calcite precipitation (pathways 3 or 4). At Old Basford vertical evolution of pH, TDIC and sulphate (Fig. 5a–c) are very similar to the Daybrook site. However, $\delta^{13}C_{TDIC}$ signatures increase slowly (–15.2 to –12.3‰) from 18.0 to 30.3 mbgl and then rise significantly to –6.6 to –7.5‰ from 35.1 to 39.3 m below ground level (mbgl) (Fig. 5d). The rock matrix $\delta^{13}C$ signatures show high values in the upper part of the aquifer and these decrease to slightly lower ratios with depth. Congruent dissolution of gypsum cannot be responsible for the considerable enriched $\delta^{13}C_{TDIC}$ ratios because sulphate concentrations are consistently lower in the deep levels. Therefore, $\delta^{13}C$ signatures are considered to reflect enrichment due to dedolomitisation (evolution path 4 in Fig. 2). The absence of matrix $\delta^{13}C$ values at these depths prevents confirmation of this assertion but the observed increasing Mg/Ca ratios are consistent with this hypothesis (Taylor et al. 2006). Interestingly, the same pattern of shallow multilevels with slightly more elevated TDIC values and lower pH than deeper multilevel samples (evolution path 4 in Fig. 2) is also evident from the Nottingham results though the points bunch more closely in Fig. 5e than in the Doncaster case study.

Birmingham

Figure 6 (plots A, B and C) graphs pH and TDIC, sulphate concentrations and calcite saturation indices for both of the Birmingham multilevel piezometers. $\delta^{13}C_{TDIC}$ signatures at the unconfined site Witton are within a narrow range between –13 and –15‰ (Fig. 6f) that is indicative of solely open system evolution and/or sewage contamination. However, the very high TDIC values observed for most of the levels is a strong indication that sewage contamination (evolution path 6 in Fig. 2) plays a dominant role to depths of about 50 m. Below that, open system evo-

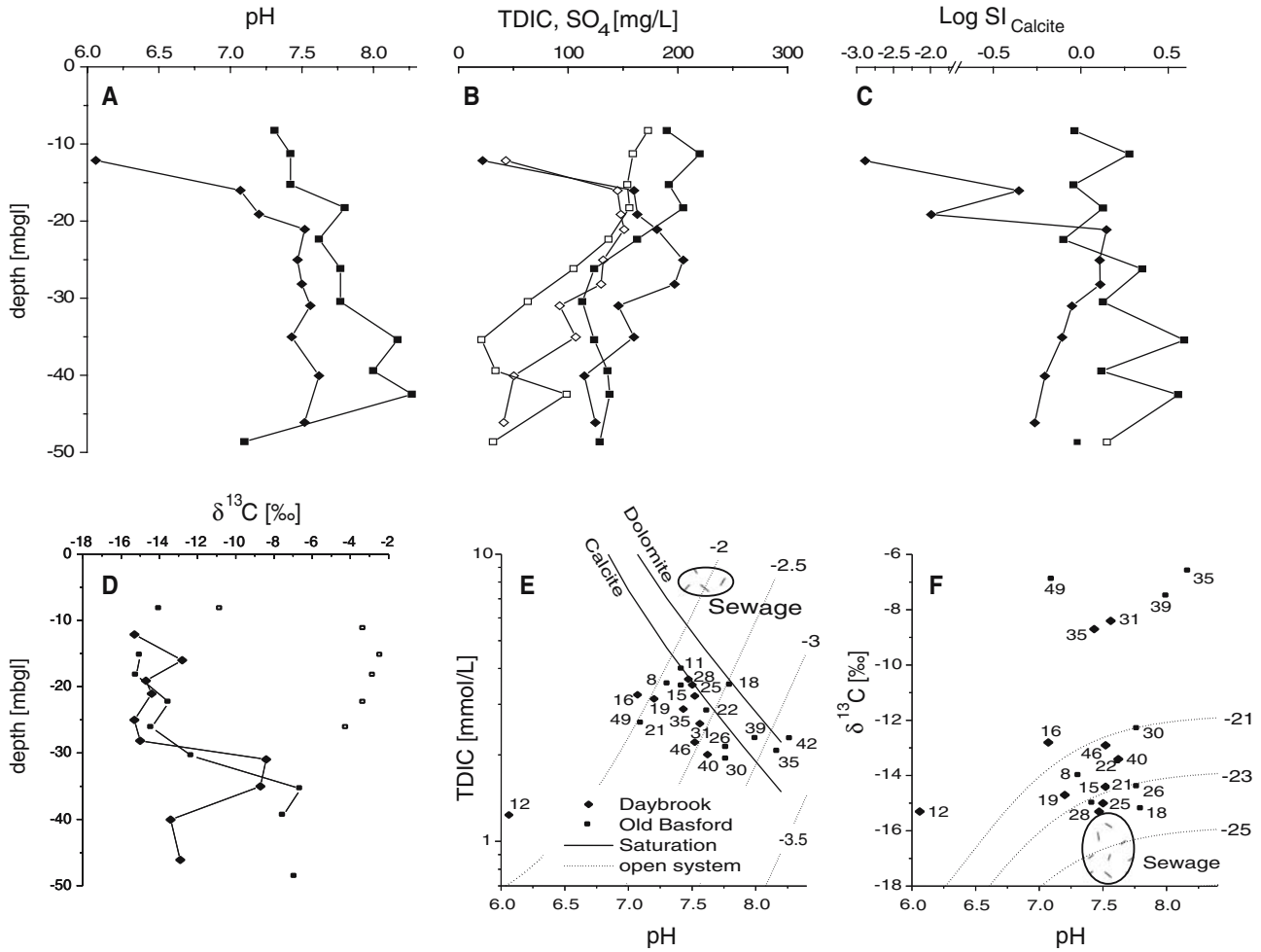

Fig. 5 Depth profiles of the multilevel piezometer sites in Nottingham with the depths of each sampling port given beside the corresponding marker. Daybrook is depicted with *diamonds* and Old Basford with *squares*. **a** pH; **b** TDIC (*full symbols*) and SO_4^{2-} (*open symbols*); **c** calcite saturation index SI and **d** $\delta^{13}C$ ratios of groundwater (*full symbols*) and rock matrix (*open symbols*). **e** and **f** TDIC versus pH, respectively $\delta^{13}C_{TDIC}$ vs. pH, including labelled equilibrium lines for open system evolution (*dotted lines*), saturation lines (*full lines*) and typical range of sewage samples shown with the *dashed circle*

lution alone under soil CO_2 pressures of 10^{-2}–$10^{-2.5}$ and soil $\delta^{13}C$ ratios of about –22‰ can explain the observations. Elevated sulphate concentrations (among other sewage indicators) in the central multilevel intervals led Taylor et al. (2006) to conclude these values are strongly influenced by sewage recharge (Fig. 6b). The TDIC of almost all of the Witton samples is slightly less than the shaded circle that represents the results of the Doncaster sewer sampling (Fig. 6e). Sewer exfiltration influences can be seen here with samples again following the evolution line 6 of Fig. 2. The visualisation of this trend is complicated here though by the fact that the Birmingham samples seem to show slight, though consistently low pH values (by ~0.1 unit), potentially due to a systemic error with the specific pH meter though calibration of the meter was carried out daily.

The TDIC-pH plot (Fig. 6e) indicates that the groundwater at Bromford, Birmingham evolved under open conditions only, showing similar partial pressures of soil CO_2 as observed in Doncaster ($10^{-2.5}$–$10^{-3.5}$). $\delta^{13}C_{TDIC}$ values decrease mainly in the top 30 m (–6.5 to –9.5‰) and remain in a narrow range for deeper wells. Overall, they agree well with the vertical trend in matrix $\delta^{13}C$ values where the difference between the two ratios should be approximately 3‰ (Fig. 6d). The higher ratios at this well are a consequence of congruent gypsum dissolution leading to gypsum saturation, with SO_4^{2-} levels in this well of more than 1,000 mg/l (Fig. 6b). The results show that sewer influences is of minor importance in this piezometer. This observation coincides well with the fact that this well is confined and also that it is located in an industrial area.

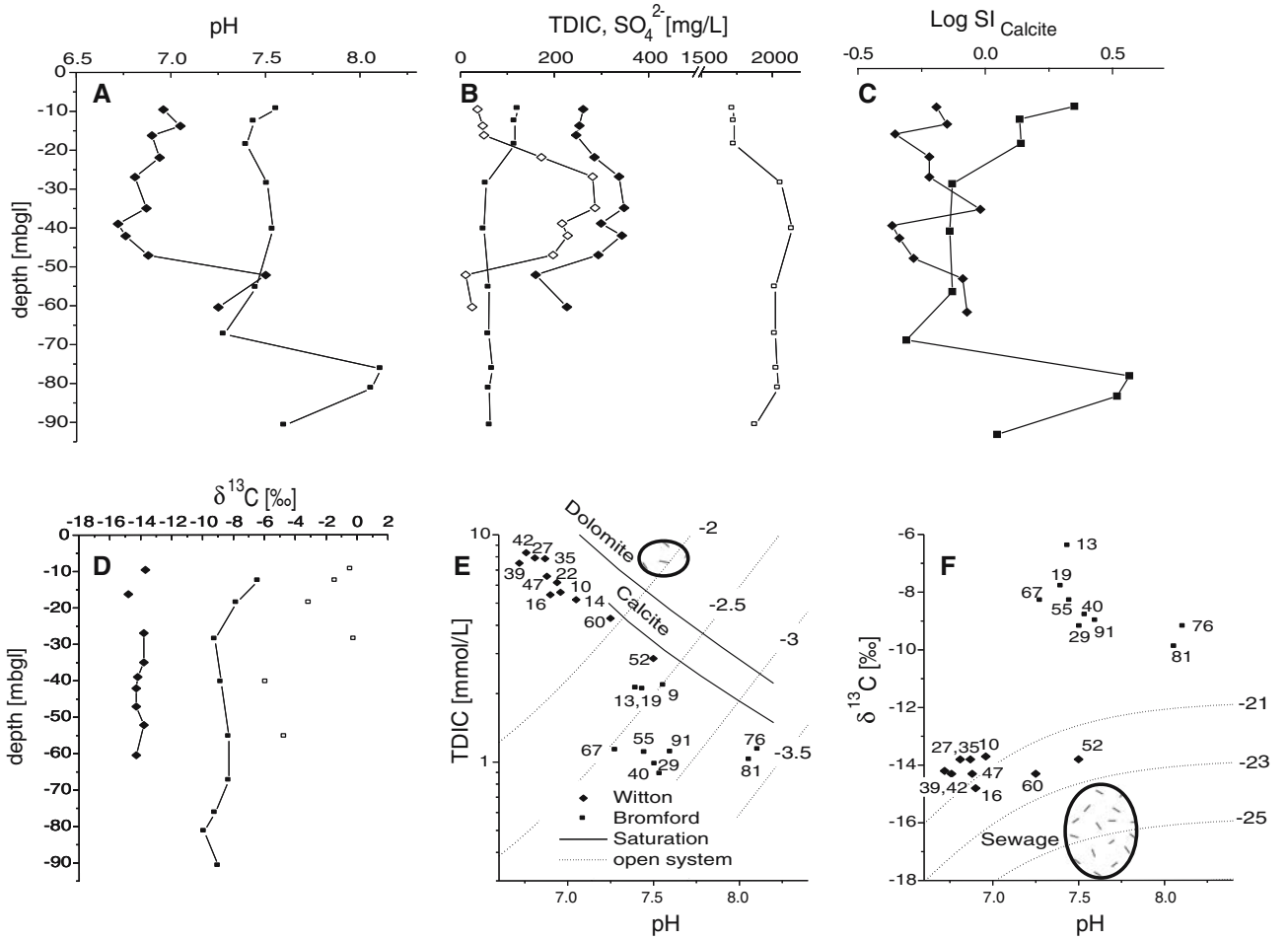

Fig. 6 Depth profiles of the multilevel piezometer sites in Birmingham with the depths of each sampling port given beside the corresponding marker. Witton is depicted with *diamonds* and Bromford with *squares*. **a** pH; **b** TDIC (*full symbols*) and SO_4^{2-} (*open symbols*); **c** calcite saturation index SI and **d** $\delta^{13}C$ ratios of groundwater (*full symbols*) and rock matrix (*open symbols*). **e** and **f** TDIC versus pH, respectively $\delta^{13}C_{TDIC}$ versus pH, including labelled equilibrium lines for open system evolution (*dotted lines*), saturation lines (*full lines*) and typical range of sewage samples shown with the *dashed circle*

Synthesis of $\delta^{13}C_{TDIC}$ inferences in Triassic sandstone aquifers

The carbon system of all samples taken from the different Triassic sandstone aquifers naturally starts with dissolution of CO_2 and calcite under open system conditions in the unsaturated zone (evolution path 1 in Fig. 2). Typical partial pressures for uncontaminated samples in Doncaster, Birmingham and Nottingham were found to be between 0.0032 ($10^{-2.5}$) and 0.00032 ($10^{-3.5}$) bar. The range of $\delta^{13}C$ ratios found in shallow groundwaters are also within quite a narrow range (–14 to –19‰) corresponding well with an assumed $\delta^{13}C$ soil gas ratio of –23 to –27‰. Natural evolution of groundwater chemistry through congruent gypsum dissolution and/or dedolomitisation is subsequently able to influence the carbon system. Both reactions do not affect the pH but they result in a strong increase of $\delta^{13}C_{TDIC}$ (evolution path 4 in Fig. 2). The observable trend to decreasing $\delta^{13}C$ ratios of bulk rock matrix with depth confirms this observation. If only gypsum dissolution occurred the evolution would be distinguishable because it led to decreasing values of pH, TDIC and $\delta^{13}C$ of dissolved carbon (evolution path 3). The range of $\delta^{13}C$ ratios of aquifer matrix are variable but similar for all five sites (Table 2) and correspond well with the variation in ranges documented in literature (Table 3).

Besides the natural processes, urban contamination through leaking sewage systems has been shown to considerably alter the carbon system by adding sewage-derived bicarbonate leading to a decrease of the pH (evolution path 5 in Fig. 2). Using only major hydrochemical parameters this path is not readily distinguishable from natural pathways but using the $\delta^{13}C$ ratios of groundwater samples a clear and consistent distinction can be made.

Conclusions

Field studies of the Triassic sandstone aquifer (Sherwood Sandstone Group) at three locations in the UK (Birmingham, Doncaster, Nottingham) show that the stable isotopes of carbon measured in parallel with the standard water parameters measured at the wellhead can clearly distinguish natural from anthropogenic geochemical processes responsible for dissolved inorganic carbon in groundwater. In Birmingham, Nottingham and Doncaster natural evolution involves an equilibration of recharging water with soil CO_2, having typical partial pressures of 0.00032–0.0032 bar and $\delta^{13}C$ ratios between –23 and –27‰. Depending on the aquifer material, congruent dissolution of gypsum and/or dolomite leads to increasing $\delta^{13}C$ ratios in groundwater and decreasing $\delta^{13}C$ ratios of (bulk) aquifer matrix through secondary calcite. Admixture of sewage can be traced because it increases the TDIC and decreases the pH but has a minimal impact on $\delta^{13}C_{TDIC}$. The effect of sewage on the $\delta^{13}C$ ratio of recharging water, however, depends strongly on the $\delta^{13}C$ signature of the soil CO_2 and the $\delta^{13}C$ signature of raw sewage. As the latter varies considerably, further research is required to constrain the isotopic signature of this source of carbon.

Depth profiles from multilevel monitoring wells have led to an improved understanding of different geochemical processes affecting groundwater and have enabled a determination of depth of contamination via leaking sewer systems. Fully penetrating wells, in comparison, represent a mixture of waters integrated over a much larger depth interval, and though diluted, the influence of sewage was still observed. However, mixture of different evolution pathways through integration over the full depth of an open well complicates straightforward interpretations. Overall, the evidence and interpretations presented here reinforce the microbiological, mass balance and age indicator work that all suggest components of younger recharge (with an important sewer-derived component) reaching significant depths of the Permo-Triassic sandstone. Hence, despite the qualitative nature of carbon stable isotopic ratio studies their use, along with the examination of the whole carbonate system, can lead to a more complete understanding of horizontal and vertical extent of urban contamination.

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