

## Research papers

## Using environmental tracers to evaluate the preservation of palaeoclimate signals in aquifers of the London Basin, UK

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## ABSTRACT

The concept of aquifer basins as palaeoclimate archives has existed for some decades, yet few detailed studies comparing aquifer types have been carried out. To assess the potential of a particular aquifer as an archive, its hydrogeochemical characteristics must be thoroughly investigated, ideally in comparison to an adjacent aquifer which can be shown to substantially preserve its ice-age endowment at depth. The London Basin (UK) presents such an opportunity, containing two main aquifers of contrasting type: the Chalk, a fractured microporous limestone, and the Lower Greensand, a porous sandstone. Despite intensive exploitation of both, evidence for Devensian (late-glacial) water remains at depth, though this differs between aquifer type. To understand the reasons for this, a suite of environmental tracers has been applied. In addition to hydrochemistry, stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), carbon isotopes ( $\delta^{13}\text{C-DIC}$ ,  $^{14}\text{C-DIC}$ ) and noble gases (He, Ne, Ar, Kr and Xe), two tracers new to the basin (CFCs and  $^{14}\text{C-DOC}$ ) have been used. In effect the Lower Greensand appears to be the 'reference aquifer', preserving recharge from prior to the Last Glacial Maximum (LGM), while the Chalk contains mixed water, with no remaining trace of the undiluted pre-LGM end member even at depth in remote parts of the confined basin. Whereas both aquifers had in the past given maximum  $^{14}\text{C-DIC}$  model ages  $\geq 30$  kyr (the effective limit of that method), in the present study the use of  $^{14}\text{C-DOC}$  has reduced this to 23.4 kyr (Lower Greensand) and 17.2 kyr (Chalk). Similar contrasts in maximum stable isotope depletions ( $-8.2$  ‰ and  $-7.8$  ‰  $\delta^{18}\text{O}$ ) and noble-gas-derived recharge temperature minima ( $2.6^\circ$  and  $4.1^\circ\text{C}$ ) were also observed. CFCs were found at all Chalk sites, with traces detectable even at 40 km from outcrop, so some climate signal degradation appears inevitable throughout the Chalk aquifer of the basin. A correlation between  $^{14}\text{C}$  activity and excess  $^4\text{He}$  suggests that deep saline water in the Lower Greensand could be  $\geq 50$  kyr old. The use of  $^{14}\text{C-DOC}$  in particular appears to be key to understanding how reliable these individual aquifers are as palaeoarchives.

## 1. Introduction

While high-latitude ice cores may be the ultimate hydroclimatic indicator in terms of time resolution, the changes they record may not be synchronous with those occurring at lower latitudes (e.g. Thompson et al., 2005). Although high-resolution proxies like tree-rings and lake sediments can circumvent this limitation, their use can be problematic (e.g. Darling, 2004). Therefore, opportunities to 'ground truth' hydroclimate can be useful. Confined aquifers at the regional scale are often regarded as having this potential (e.g. Edmunds et al., 2004; Kreuzer et al., 2009; Priestley et al., 2020). This means that they are large enough to contain groundwater recharged over millennia or longer,

ideally preserving evidence for past variations in temperature and hydrological regime that can ultimately feed into the validation of climate models.

Approaches to unlocking these aquifer basin palaeoarchives have evolved over time. Originally the emphasis was simply on establishing the age of water in aquifers as a necessary first step, with radiocarbon playing a prominent role (e.g. Hanshaw et al., 1965; Vogel, 1968), though later supplemented by longer-lived radioisotopes (e.g. Bentley et al., 1986; Lehmann et al. 1991) for waters exceeding radiocarbon age ( $>30$  kyr). Stable isotopes as a proxy for recharge temperature conditions were introduced shortly after radiocarbon (e.g. Gat and Issar, 1974; Vogel and Van Urk, 1975). However, ambiguities in interpretation

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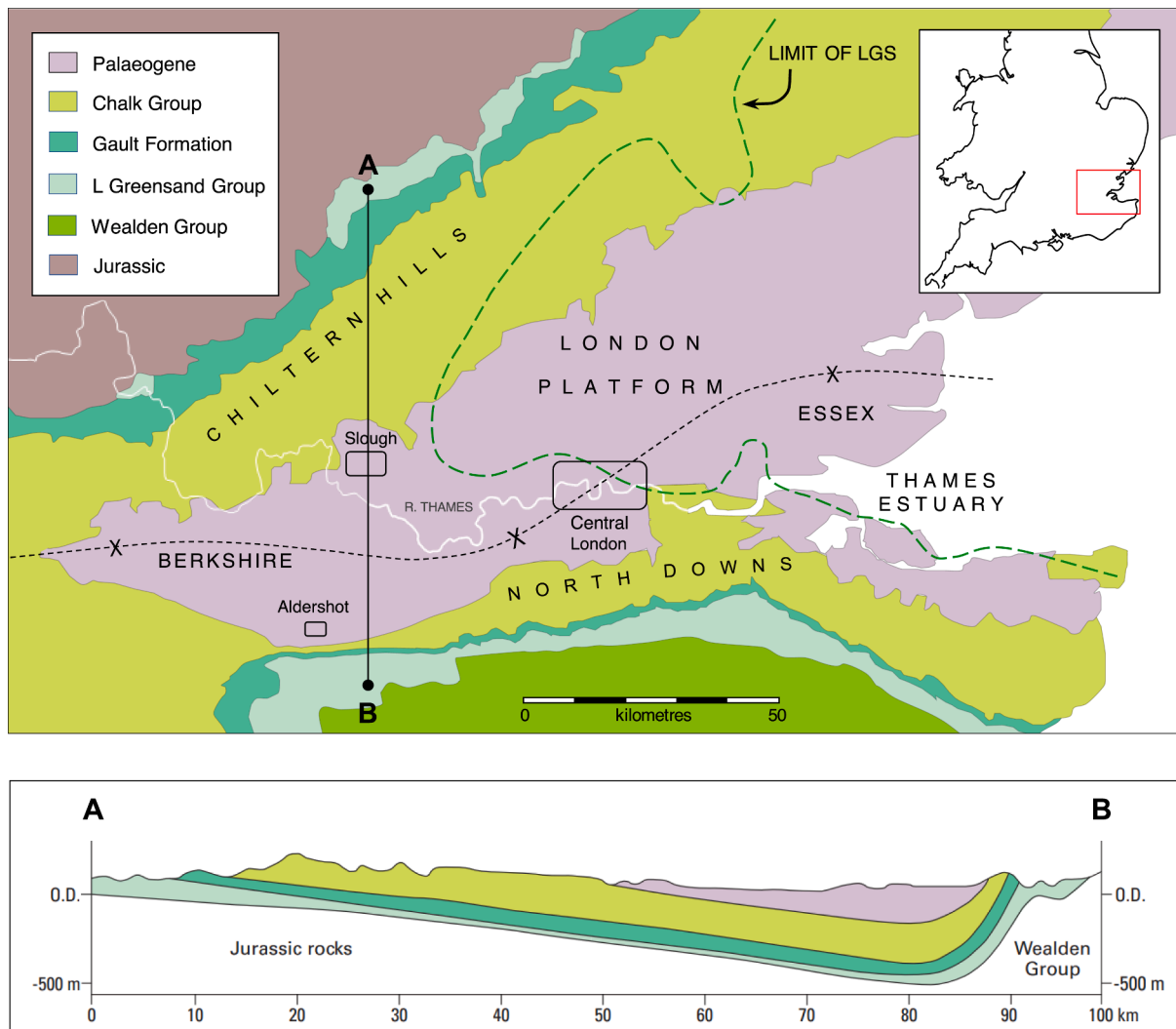


Fig. 1. Basic bedrock geology of the London Basin with synclinal axis and limit of the Lower Greensand around the London Platform indicated. Inset: location of the map area in southern UK. Cross section A–B shows the asymmetry of the basin. Groundwater flow is generally directed from outcrop towards the axis but may be locally perturbed by abstraction (WRB, 1972). Base mapping provided by ESRI.

led to the need for more absolute indicators of palaeotemperature, with noble gas solubility techniques leading the way (Stute et al., 1995; Aeschbach-Hertig et al., 1999). While a wide variety of other environmental tracers (Cook and Herczeg, 1999) may also assist palaeoarchive interpretation, the above methods are still the mainstay.

Any comprehensive study of aquifer palaeoarchive potential requires conjunctive use of a range of environmental tracers. For example, the whole concept of groundwater ‘age’ remains the subject of much debate (e.g. Bethke and Johnson, 2008; Suckow, 2014), insofar as many pumped waters are mixtures which may be of binary, exponential or other type (Matozowski and Zuber, 1982). In such cases a single-figure age derived from a particular indicator is no more than a mean residence time, and to decipher this will probably need more than one age tracer. Then there is the question of just how reliable a particular aquifer may be as a palaeoarchive, which will require detailed consideration of temperature-related phenomena via stable isotopes and noble gas concentrations, ideally related to data from other proxies.

The performance of different aquifer types as palaeoarchives has yet to be much investigated. While studies like those of Edmunds et al. (2004) in Africa and Jiráková et al. (2011) in Europe surveyed a range of confined aquifers and found some divergence in their behaviour relative to palaeorecharge, they were not able to focus in on a detailed comparison of individual aquifer behaviour. The mesoscale London Basin of

southeast England, by contrast, provides an ideal opportunity to investigate this by enabling the comparison of two aquifers with contrasting physico-chemical properties but which must have received a similar endowment of recharge under past climatic conditions owing to the geographical proximity of their outcrops.

The two principal aquifers of the London Basin are the Chalk and the Lower Greensand (LGS). Both aquifers are confined over much of their area by younger strata and at depth contain at least a proportion of palaeowater, defined here as the result of recharge occurring > 12 kyr ago in pre-Holocene times. Despite the undertaking of several radiocarbon-based studies in the late twentieth century to investigate this (Mather et al., 1973; Smith et al., 1976; Dennis et al., 1997; Elliot et al., 1999), researchers have struggled to assign realistic ages to palaeowater in the Chalk owing to its unique lithology (Downing et al. 1979), while largely ignoring the greater palaeoarchive potential of the volumetrically smaller but less-exploited LGS. These studies used environmental tracers variously in the form of hydrochemistry, stable isotopes, noble gases and isotopes of dissolved inorganic carbon (DIC). This paper builds on them by adding two tracers not previously applied in the basin, namely CFCs (chlorofluorocarbons) and  $^{14}\text{C}$ -DOC (radiocarbon activity of dissolved organic carbon). These tracers permit a better understanding of the processes governing apparent groundwater ages in the two aquifers, thereby providing a more secure framework against

which to judge each aquifer's potential as an archive of late-Pleistocene climatic conditions.

## 2. Background

### 2.1. Description of the basin

The London Basin is an approximately E–W trending syncline of asymmetric cross-section (Sumbler, 1996), mostly lying between the hills of the Chilterns and the North Downs (Fig. 1). Some formations in the Palaeogene have aquifer potential, but are limited both in terms of yield and water quality (Bearcock and Smedley, 2010). The principal aquifers are instead found in the underlying Cretaceous. The Chalk (Upper Cretaceous) is present across the whole of the London Basin, though is overlain over approximately half its area by the London Clay aquitard (Eocene), which dominates the Palaeogene sequence (Royse et al., 2012). The underlying LGS (Lower Cretaceous), however, was not deposited across the eastern part of the basin owing to the relatively lower sea level at the time resulting in the emergence of the London Platform.

While the outcrop and therefore recharge area of the Chalk is reasonably large (Fig. 1), that of the LGS is much smaller, particularly on the northern limb of the basin where sediments were deposited in a series of local basins whose hydraulic relationship with the confined aquifer remains somewhat uncertain (Egerton, 1994). Natural discharge from the Chalk occurs slowly through the London Clay aquitard into the River Thames, except where Chalk is exposed directly in the bed of the Thames to the east of London where more rapid flow is possible (WRB, 1972). The natural discharge of the synclinal LGS to the west of London is also assumed to be directed towards the Thames, but at an extremely slow rate given the preservation of artesian conditions in the Slough area (Darling and Lewis, 2021), the current lack of evidence for significant invasion of the Chalk aquifer by LGS water, and the existence of a brackish 'sump' in the deepest part of the LGS (Egerton, 1994).

The Chalk and LGS have contrasting hydrogeological properties. The Chalk is a fractured microporous coccolith limestone, leading to two main disadvantages for a potential palaeoarchive: the high probability of groundwater mixing (Price, 1987), and the potential for extreme dissolution-precipitation exchange between water and rock in the DIC (dissolved inorganic carbon) system (Smith et al., 1976). The consequences are blurring of the age profile, and the compromise of radiocarbon dating based on the conventionally-used  $^{14}\text{C}$ -DIC method. By contrast, the LGS is a better proposition, with largely intergranular flow (Mather et al., 1973) and a much lower potential for DIC exchange. In several respects therefore, the LGS provides a good baseline against which to compare the Chalk when using age tracers.

### 2.2. Previous groundwater age-related studies in the basin

#### 2.2.1. Lower Greensand

As the subsidiary principal aquifer of the London Basin, the LGS has received comparatively little attention from a palaeorecharge point of view. Mather et al. (1973) measured  $^{14}\text{C}$ -DIC on waters from eight sites from N to S across the basin, finding  $^{14}\text{C}$  activities close to or below the detection limit ( $\sim 0.1$  pmc, or percent modern carbon) at two sites, interpreted as indicating ages of  $\geq 24$  kyr. Further  $^{14}\text{C}$ -DIC measurements from the LGS were reported by Evans et al. (1979), this time with stable isotope data showing that waters with low  $^{14}\text{C}$ -DIC activities also possessed more negative  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values, indicating recharge under different climatic conditions. Measurements of  $\delta^{13}\text{C}$ -DIC were used to account for inputs of  $^{14}\text{C}$ -dead carbon from the aquifer matrix (although fundamentally a sandstone aquifer, the LGS contains some calcite cement except where complete de-calcification has occurred). On this basis a minimum age of 29 kyr was assigned to a water from Slough in the areal centre of the basin (Fig. 1). Additional sampling in the early 1990s found the same association of low  $^{14}\text{C}$ -DIC with more negative

$\delta^{18}\text{O}$  and  $\delta^2\text{H}$  (Darling et al., 1997).

#### 2.2.2. Chalk

The first Chalk  $^{14}\text{C}$ -DIC measurements were reported by Smith et al. (1976). Data from 22 sites, all north of the basin axis, were converted to apparent ages using a simple  $\delta^{13}\text{C}$ -based correction. The maximum ages obtained, from sites in central London, were  $> 25$  kyr. Stable O and H isotopes showed a similar association with  $^{14}\text{C}$  as found for the LGS, but to a lesser extent. A reinterpretation of the data with a more sophisticated treatment for the  $^{14}\text{C}$  age correction was published by Downing et al. (1979), but still concluded that groundwater  $> 25$  kyr was present in the deep, less-fractured parts of the basin.

Edmunds et al. (1987) investigated a NW–SE cross-section through the Chalk aquifer in Berkshire, situated towards the western end of the basin, moving from unconfined to confined conditions. Samples from 17 sites were measured for  $^{14}\text{C}$ -DIC, stable O, H and C isotopes and noble gases, in addition to inorganic hydrochemistry (major, minor and selected trace species). Although a range of apparent ages extending to  $> 20$  kyr was obtained by using three different correction models, the one theoretically most applicable to the Chalk (Fontes and Garnier, 1979) gave ages  $\leq 13$  kyr, suggesting that little evidence of palaeorecharge remained in this part of the basin. This conclusion was supported by a lack of consistent  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  depletion, though noble gases, used for the first time in the basin, did give indications of cooler recharge temperatures. Edmunds et al. (1987) recognised the high potential for groundwater mixing in the Chalk, but had at that time no environmental tracer other than the relatively insensitive  $^3\text{H}$  with which to investigate this.

Data from a larger number of sites (35 in total), situated mainly within Greater London and lying both north and south of the River Thames, was reported by Dennis et al. (1997). An attempt to correct  $^{14}\text{C}$ -DIC data for the effects of groundwater mixing was made, and gave maximum apparent ages  $> 37$  kyr, though most were significantly younger. It was noted that the apparently oldest water coincided with the deepest part of the aquifer along the synclinal axis. Limited  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  depletion was observed, in line with the study of Smith et al. (1976). Noble gas recharge temperatures (NGTs) showed a fall of 5–7 °C in the older waters compared to modern recharge. Three of the Dennis et al. (1997) sites were the same as sampled by Smith et al. (1976), and in one case (Waltham Abbey Pumping Station, North London) there was a large discrepancy between the measured  $^{14}\text{C}$  activities. However, the Lea Valley in which Waltham Abbey PS is situated has been the site of large-scale managed aquifer recharge (MAR) activities across the past seven decades (WRB, 1972; Headon et al., 2009), so this seems likely to be responsible.

Elliot et al. (1999) presented new  $^{14}\text{C}$ -DIC data for six sites in the Berkshire Chalk, plus 14 sites across the Greater London area. A further three London sites included a re-sampling of one Smith et al. (1976) site, and two of Dennis et al. (1997). In no case was a significant difference observed. The new Berkshire data extended the Edmunds et al. (1987) transect further southeast, but gave similar contrast between  $^{14}\text{C}$ -DIC values in the confined and unconfined parts of the aquifer. The London data largely followed the plan of W–E and S–N sampling transects terminating in Central London. Both in Berkshire and London, a similar picture emerged of declining  $^{14}\text{C}$  activities, enriched  $\delta^{13}\text{C}$ -DIC,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  depletions, and lower NGTs as the axial zone of the basin was approached. As with previous studies, maximum ages of  $\sim 24$  kyr were inferred, i.e. well into late-Devensian glacial times.

### 2.3. Investigation methods new to the basin

As detailed above, the two main weaknesses of previous studies in the London Basin Chalk were concerned with age ambiguities and the lack of a sensitive indicator showing the degree of penetration of modern water into the confined aquifer. Clearly, for a study of palaeoarchive potential these uncertainties have to be addressed, so two additional

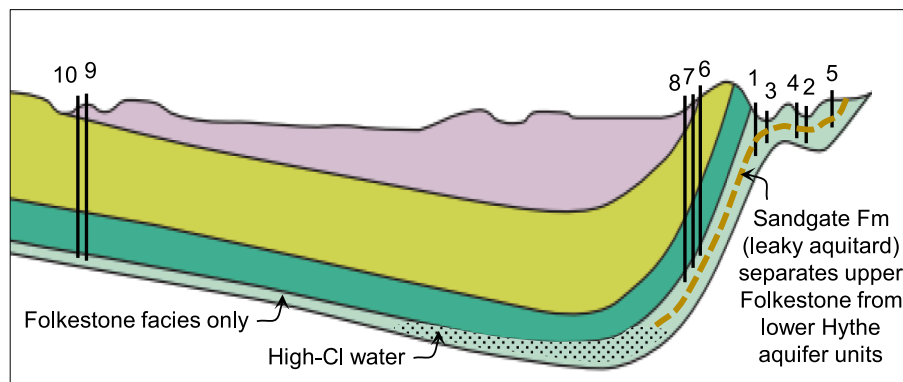


Fig. 2. More detailed cross-section of the LGS aquifer with boreholes projected onto the line of section. Based on information in Morgan-Jones (1985). Geological legend as for Fig. 1.

methods have been applied.

### 2.3.1. CFCs

The CFCs (chlorofluorocarbons) are members of the halocarbon family of non-toxic compounds, traces of which are found in the atmosphere owing to release during industrial processes and refrigerant leakage commencing in the 1930s. The two main compounds are CFC-11 ( $\text{CCl}_3\text{F}$ ) and CFC-12 ( $\text{CCl}_2\text{F}_2$ ). They have accumulated in the atmosphere at a known rate, and although now in decline due to a worldwide ban resulting from their ozone-depleting properties, they remain capable under the right conditions of giving quantitative groundwater age information in the range 0–70 years (Plummer and Busenberg, 2000). This relies on equilibration between the atmosphere and infiltrating rainfall being 'locked in' to groundwater at the time of recharge to the aquifer. Under less favourable conditions (leakage to the aquifer from e.g. refrigeration plants or degreasing operations) they still provide indications of the presence of 'modern' ( $\leq 70$  yr old) groundwater, even if the amount may not be quantifiable (Darling et al., 2012).

CFCs are routinely used for many types of groundwater investigation (Chambers et al., 2019). Their use in the present study primarily focuses on their property of being detectable down to ultra-trace concentrations (Bullister and Weiss, 1988).

### 2.3.2. $^{14}\text{C}$ -DOC

Radiocarbon is frequently used in groundwater investigations (see a general outline in Section S1 of the Supplement to this paper), but conventionally has been carried out on the DIC component of the water (e.g. Tamers, 1975). The initial goal of  $^{14}\text{C}$ -DOC dating is to isolate and measure the FA (fulvic acid or high molecular weight) fraction considered to derive from soil organic matter (Murphy et al., 1989), rather than the HA (humic acid or low molecular weight) fraction that could be derived from various sources, including 'refractory'  $^{14}\text{C}$ -dead carbon present in the aquifer matrix. (However, this would be less significant in the LGS and Chalk, both of which contain generally very low amounts of solid-phase organic carbon: Pacey, 1989; Macleod, 1998) More recent studies have been carried out by other methods of extraction and DOC oxidation that did not differentiate or exclude certain pools of DOC (Heine and Einsiedl, 2021).

The radiocarbon activity of DOC was first investigated as a potential water dating agent more than three decades ago in the Milk River aquifer of western Canada (Murphy et al., 1989; Wassenaar et al., 1991). The principal advantage of  $^{14}\text{C}$ -DOC over  $^{14}\text{C}$ -DIC dating was considered to be the lack of significant dilution of DOC by inputs of dead carbon from the aquifer matrix, and the results largely supported this, with seven of the eight sites yielding a higher  $^{14}\text{C}$  activity for DOC than DIC.

The early promise of  $^{14}\text{C}$ -DOC for groundwater dating based on the Milk River research led to attempts to apply the technique elsewhere in old groundwaters, though usually reporting only a handful of analyses

for individual aquifers. Purdy et al. (1992) published four pairs of analyses from the Aquia and Magothy aquifers in the Atlantic coastal plain of Maryland, USA, showing again that DOC was greater than DIC activity for most sample pairs. Geyer et al. (1993) presented results from 18 sites distributed over three different aquifer types across Germany. In all but one case DOC exceeded DIC activity, thus in line with the previous studies. It had been assumed in previous studies that  $^{14}\text{C}$ -DOC ages could simply be calculated in terms of the  $^{14}\text{C}$  decay curve, with a 100 pmc initial activity (IA), but Geyer et al. (1993) proposed that an IA value in the range 75–95 % might be more appropriate, to reflect mixing of young and older DOC in the recharge zone. Montjotin et al. (1998) studied seven sites in the Mol confined sand aquifer in Belgium, where they too found  $\text{DOC} > \text{DIC}$  activities. Additionally they measured a few unconfined Chalk sites in the Paris Basin, but  $^{14}\text{C}$  activities were high ( $\sim 70$ – $90$  pmc) for both DIC and DOC so of limited relevance to the present study. However they also investigated the IA of DOC in the soil zone of a sand aquifer in the Loire Valley, and concluded that this could vary between 75 and 100 pmc.

Since the 1990s, however, rather few studies have been published, the main challenge appearing anecdotally to be the reliable extraction of sufficient carbon from the very low DOC concentrations typically found in groundwaters. Nevertheless, recently Godfrey et al. (2021) used  $^{14}\text{C}$ -DOC as a way of circumventing the challenge of  $^{14}\text{C}$ -DIC groundwater dating in an active volcanic region of Chile (13 sites), while Thomas et al. (2021) reported  $^{14}\text{C}$ -DOC results from 26 sites in Nevada, USA, derived from volcanic and carbonate aquifers. As with previous studies, both found that for individual sites DOC almost always exceeded DIC activity and therefore gave younger ages, even after allowing for DIC age correction. Godfrey et al. (2021) used varying values of IA based on site-specific assessments of the amount of mixing between DOC reservoirs, but Thomas et al. (2021) concluded that no IA correction for calculating  $^{14}\text{C}$ -DOC ages was necessary in their aquifer system. However, few of the samples in either study gave low  $^{14}\text{C}$ -DOC activities, and there remained a need for more data particularly below the 20 pmc level. The study of Heine and Einsiedl (2021) in a carbonate aquifer contributed a few sub-20 pmc values, reaching a  $^{14}\text{C}$ -DOC minimum of 5.7 pmc. They decided to use a blanket IA value of 85 % to calculate their  $^{14}\text{C}$  DOC ages, which were significantly younger than corrected DIC ages, in line with all the other studies considered above.

## 3. Site locations, sampling and analysis

### 3.1. Site locations

LGS sites (1–10) divide into two groups: those in the shallow, partially-confined Hythe Formation on the southern edge of the basin (1–5), and those in the stratigraphically overlying but deep and fully-confined Folkestone Formation (6–10). This is illustrated in Fig. 2,

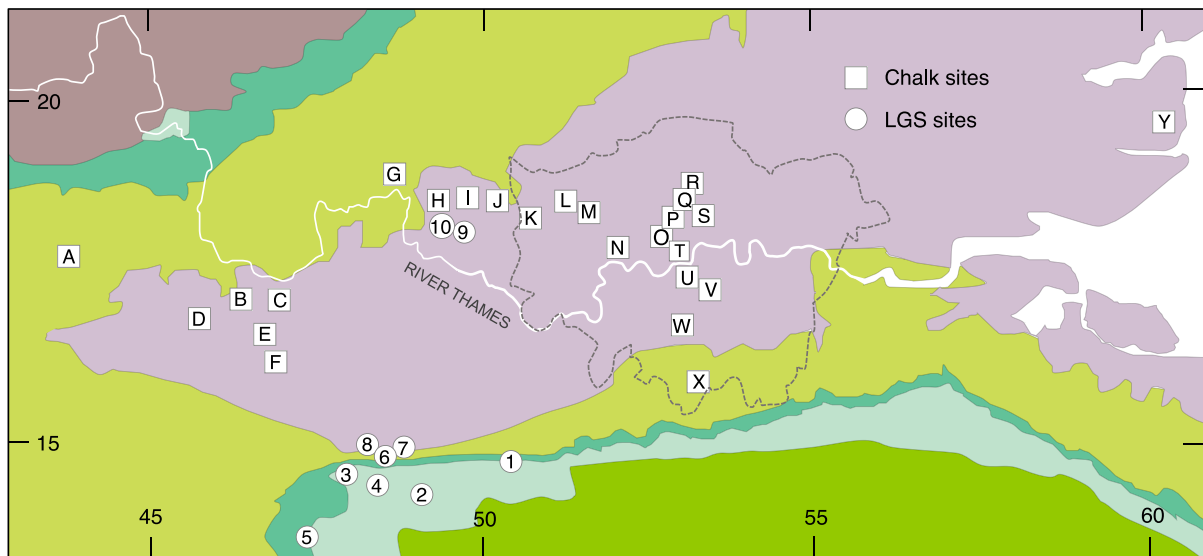


Fig. 3. Location of sampling sites relative to the Greater London boundary (dashed line). Geological legend as for Fig. 1. 50-km grid shown. Base mapping provided by ESRI.

Table 1

Site location details and results of field measurements. Aquifer information: WC – White Chalk Group, GC – Grey Chalk Group, F – LGS Folkestone Formation (Fm), H – LGS Hythe Fm, U – Upnor Fm, T – Thanet Fm, conf – confined, s/conf – semi-confined, unc – unconfined.

Site name	Site ID	Aquifer unit	Date	NGR		Temp °C	pH	SEC µS/cm	DO mg/L
				E	N				
<i>Chalk</i>									
Eastbury Grange <sup>a</sup>	A	WC/GC - unc	Mar-97	435905	179960	10.7	7.22	–	9.80
Ufton Nervet PS <sup>a</sup>	B	WC - conf	Mar-97	462300	168260	10.9	7.20	623	0.20
Grazeley PS <sup>ab</sup>	C	WC - conf	Mar-97	468602	167905	11.8	7.40	782	0.20
Old Mill Hotel <sup>a</sup>	D	U/WC - conf	Mar-97	459095	166242	11.8	7.35	540	0.20
Mortimer PS <sup>a</sup>	E	WC - conf	Mar-97	467207	164232	12.5	7.49	–	<0.10
Little Park Farm <sup>a</sup>	F	U/WC - conf	Mar-97	467902	163052	12.1	7.45	619	0.20
Bourne End PS	G	WC - unc	Jan-98	489191	188132	11.0	6.90	554	10.7
Burnham Beeches GC	H	WC - conf	Aug-14	493700	183960	12.8	6.97	688	6.10
Stoke Park GC	I	WC - conf	Jul-14	496729	182767	11.3	7.20	302	4.61
Pinewood Studios	J	WC - conf	Jul-14	501812	184293	12.2	7.02	261	0.39
Stockley Pines GC	K	WC - conf	Jul-14	507539	180389	19.0	7.47	337	0.13
Glaxo Greenford <sup>c</sup>	L	WC - conf	Mar-97	514975	184535	13.0	7.00	1040	–
Ealing GC	M	WC - conf	Jul-14	517349	182729	12.6	7.64	595	0.15
Chiswick Park	N	WC - conf	Jul-14	519741	178747	16.5	7.83	1206	0.23
Kensington Gardens	O	WC - conf	Jun-14	526698	180690	14.3	7.56	1647	0.19
Regents Park	P	WC - conf	Jun-14	527647	182819	13.0	7.49	1367	0.38
Dorset House <sup>c</sup>	Q	WC - conf	Mar-97	527800	181987	14.5	7.35	1506	<0.10
Kentish Town Baths <sup>c</sup>	R	WC - conf	Mar-97	528793	184764	14.0	7.60	1149	–
Sadlers Wells	S	WC - conf	Jun-14	531640	182881	13.6	7.40	862	0.10
Dolphin Square	T	WC - conf	Oct-13	529500	178026	13.8	7.31	1037	0.19
Sunlight Laundry Brixton	U	WC - conf	Jun-14	530210	174990	14.0	7.02	1246	0.22
Dulwich & Sydenham GC	V	WC - conf	Aug-14	533656	172780	13.5	7.34	541	0.09
Mitcham GC	W	WC - conf	Aug-14	528451	167584	12.4	7.15	568	1.49
Kenley WTW	X	WC/GC - unc	Oct-13	532777	159974	10.9	7.15	522	5.25
Wraywick Farm	Y	T - conf	Nov-19	599205	199185	9.3	8.46	2617	0.16
<i>Lower Greensand</i>									
Netley Mill PS	1	H - unconf	Oct-14	507918	147853	11.2	6.46	239	4.30
Mousehill PS	2	H - s/conf	Oct-14	493917	141690	10.8	7.56	387	–
The Bourne PS	3	H - s/conf	Jul-14	484395	145594	11.6	7.10	491	7.61
Tilford Meads PS	4	H - s/conf	Jul-14	487678	143597	11.0	7.52	324	0.10
Oakhanger PS	5	H - s/conf	Jul-14	476352	135992	13.0	8.05	260	0.07
Tongham PS	6	F - conf	Jul-14	487769	148390	20.4	7.87	464	0.10
Tongham Moor PS	7	F - conf	Jul-14	488358	149435	22.4	7.87	451	0.13
Boxalls Lane PS	8	F - conf	Jul-14	486438	149204	21.7	7.91	544	0.13
GSK Horlicks Slough	9	F - conf	Jul-14	497300	180490	17.7	7.82	549	0.09
Slough Estates No 7	10	F - conf	Jul-14	494641	181932	17.3	7.89	673	0.08

<sup>a</sup>pH and DO values from Edmunds et al. (1987).

<sup>b</sup>SEC value from Grazeley Court Farm.

<sup>c</sup>pH values from Elliot et al. (1999).

**Table 2**

Concentrations of chlorofluorocarbons (CFCs) and noble gases dissolved in groundwaters from the London Basin. Values for recharge temperature (NGT) and excess air (EA) calculated from the noble gas data using the iNoble program (Matsumoto, 2015). Excess  $^4\text{He}$  calculated by subtraction of NGT and EA components (values assumed where not available). STP (Standard Temperature and Pressure) refers to 0 °C and 1 atm.

Site ID	CFC-12 pmol/L	CFC-11 pmol/L	He cm <sup>3</sup> STP/g ×10 <sup>-8</sup>	Ne ×10 <sup>-7</sup>	Ar ×10 <sup>-4</sup>	Kr ×10 <sup>-8</sup>	Xe ×10 <sup>-8</sup>	NGT °C	EA cm <sup>3</sup> STP/kg	$^4\text{He}_{\text{exc}}$ cm <sup>3</sup> STP/g ×10 <sup>-8</sup>
<i>Chalk</i>										
A	–	–	5.07	2.36	4.08	9.90	1.27	9.2	1.8	0.0
B <sup>a</sup>	203	6.37	29.6 <sup>a</sup>	–	–	–	–	–	–	23.3
C <sup>b</sup>	0.53	1.31	143	–	–	–	–	–	–	137
D	0.58	1.36	35.7	2.79	4.28	11.2	1.48	6.2	3.7	29.1
E	0.17	0.21	–	–	–	–	–	–	–	–
F	0.54	1.83	85.2	–	–	–	–	–	–	78.9
G	13.2	103	11.6	2.88	3.96	9.47	1.49	11.4	4.8	4.6
H	21.9	65.1	5.23	2.26	3.69	8.99	1.46	11.6	1.4	0.0
I	184	104	8.09	2.31	3.76	9.29	1.47	10.7	1.6	2.6
J	117	65.7	9.27	2.42	4.01	10.1	1.58	8.0	1.9	3.6
K	2.11	6.18	14.3	2.04	3.45	8.58	1.30	13.1	0.4	9.5
L	–	–	81.6 <sup>c</sup>	–	–	–	–	–	–	75.3
M	1.09	4.87	380	3.29	4.78	11.7	1.82	4.4	6.2	372
N	0.94	2.93	427	2.47	4.29	11.0	1.77	5.1	1.8	421
O	1.80	1.99	345	3.39	4.88	11.9	1.79	4.1	6.7	337
P	2.18	1.35	66.3	2.57	4.47	11.3	1.79	4.1	2.3	60.3
Q	–	–	329 <sup>c</sup>	2.16 <sup>d</sup>	4.64 <sup>d</sup>	9.95 <sup>d</sup>	1.71 <sup>d</sup>	4.4	0.2	324
R	–	–	132 <sup>c</sup>	–	–	–	–	–	–	126
S	0.30	1.32	38.7	2.45	3.81	11.1	1.69	6.7	1.8	33.1
T	1.95	3.40	116	2.25	3.81	9.44	1.47	9.9	1.2	111
U	1.33	4.24	70.9	3.11	4.56	11.0	1.68	5.7	4.5	63.9
V	0.08	0.07	58.3	3.34	4.61	11.0	1.71	6.6	6.8	50.1
W	42.8	54.7	9.45	2.71	4.08	9.84	1.54	9.4	3.7	2.9
X	3.39	61.1	13.7	3.03	4.01	9.45	1.47	11.9	5.6	6.9
Y	0.04	0.09	586	2.50	4.46	11.2	1.69	4.4	1.9	580
<i>Lower Greensand</i>										
1	2.45	24.82	9.0	3.08	4.38	9.65	1.36	10.3	5.9	2.0
2	<0.03	0.18	12.8	2.46	3.94	9.68	1.48	9.5	2.3	4.2
3	0.37	<0.01	17.1	2.37	4.02	9.25	1.34	10.1	2.0	11.3
4	0.49	0.09	15.0	2.52	4.29	9.32	1.56	8.8	2.6	9.0
5	–	–	11.0	2.66	4.18	9.51	1.38	9.7	3.5	3.4
6	<0.03	0.08	521	3.05	4.80	11.8	1.89	3.4	4.8	515
7	<0.03	<0.01	785	2.68	4.89	11.7	1.71	3.2	7.3	778
8	<0.03	0.07	915	2.97	4.99	11.8	1.74	3.0	4.4	909
9	0.11	0.12	686	2.78	4.91	12.2	1.71	2.6	3.3	680
10	0.14	0.19	1090	4.09	5.60	12.6	1.82	2.7	10.5	1083

<sup>a</sup>Data from Edmunds et al. (1987).

<sup>b</sup>Results from Grazeley Court Farm.

<sup>c</sup>Data from Elliot et al. (1999).

<sup>d</sup>Data from Dennis et al. (1997).

while the geographic locations are shown in Fig. 3 and site data reported in Table 1.

Chalk sites (A–Y) can also be divided into two basic groupings: the western basin in Berkshire (A–F) and the central basin beneath Greater London (G–X). Three sites are wholly unconfined (A, G, X). The remaining site (Y) is in the far east of the confined basin (Fig. 3). Site data are given in Table 1. All sampled boreholes abstract from formations in the White Chalk Subgroup (Middle and Upper Chalk in older literature) except for the three unconfined sites which include some Grey Chalk (formerly Lower Chalk) strata, and a few other confined sites D, F and Y where boreholes may barely penetrate the Upper Chalk but are screened in the immediately overlying thin sands and gravels at the base of the Palaeogene beneath the London Clay, relying on hydraulic continuity with the Chalk to yield sufficient water.

### 3.2. Sampling

All samples were collected at or close to borehole wellheads, except at Site 3 (LGS), where the sampling point is ~500 m from the source. Boreholes were sampled after temperature, pH, alkalinity, specific electrical conductivity (SEC) and dissolved oxygen (DO) had stabilised.

Values are reported in Table 1. Samples for chemistry,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$ -DIC were collected in HDPE bottles. Samples for  $^{14}\text{C}$ -DIC were collected in 1-litre glass bottles, while those for  $^{14}\text{C}$ -DOC were either collected in 50-litre polyethylene drums, or more recently in 2.5 L amber glass bottles with polycone tops. CFC samples were collected under water according to the method described in IAEA (2006), while noble gas samples were taken in clamped 10 mm o.d. copper tubes.

To check the  $\delta^{13}\text{C}$  values of soil  $\text{CO}_2$ , necessary for  $^{14}\text{C}$ -DIC age correction, some soil gas sample pairs were collected in pre-evacuated glass bulbs from the outcrops of the Chalk and LGS using a hollow spike sampler.

### 3.3. Processing samples for $^{14}\text{C}$ -DOC measurement

Samples taken in 1997–98 were prepared by extraction of the HMW compounds (humic and fulvic acids) from approximately 50 L of groundwater by adsorption onto a DEAE-cellulose resin. The HMW compounds were eluted from the resin using 0.5 M NaOH. The eluant was acidified to pH 1 with HCl to precipitate the humic acid (HA) fraction while the fulvic acid (FA) fraction remained in the eluant. Analysis of the fulvic acid fraction was carried out by AMS at NERC-RCF

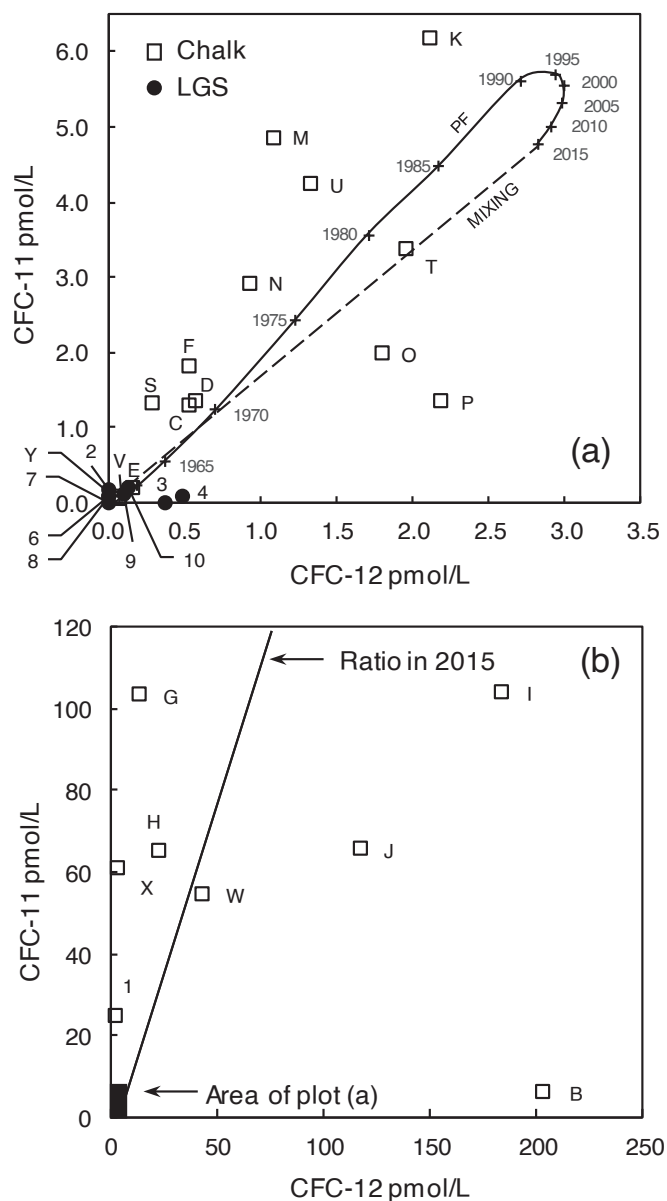


Fig. 4. CFC cross-plots for groundwaters of the London basin, with mixing line and piston flow (PF) curve with recharge year indicated, based on data from USGS (2021).

at East Kilbride, Scotland. Here, samples were decanted leaving approximately 5 ml of FA-rich solution in the sample bottles (no obvious HA precipitate was observed). Measured supernatant sample volumes were rotary-evaporated in acid-washed, sample-rinsed glassware, until a few ml of solution remained. This solution was quantitatively transferred to pre-weighed, acid-washed glass beakers and dried in a freeze dryer. Known weights of dried solids were converted to CO<sub>2</sub> either by combustion using an elemental analyser (samples from sites A, L, Q and R), or under vacuum in sealed quartz tubes in the presence of CuO and Ag wire (sites B, C, D, E and F).

For samples taken in 2013–14, four 2.5 L glass bottles were collected per site. Initially, aliquots of 2.5–8.0 L of whole sample water were subjected to rotary evaporation and prepared to dried solids as described above. Inorganic carbon was removed from the dried solids by fumigation with concentrated HCl in an evacuated (<0.1 bar) desiccator at 62 °C. Known weights of dried solids were converted to CO<sub>2</sub> using an elemental analyser. Later, after difficulties with obtaining sufficient carbon for analysis from some sites, seven available reserve water

samples were submitted to the Research and Development department at Beta Analytic, Miami, USA. Here, aliquots of up to 1 L of incrementally-filtered sample water were subject to UV oxidation (UVox), in the presence of oxygen gas, and the resulting CO<sub>2</sub> was collected for <sup>14</sup>C and <sup>δ</sup><sup>13</sup>C analysis. Further details of the UVox method as performed at Beta Analytic are provided in Section S2 of the Supplement.

The CO<sub>2</sub> from all three preparation methods was cryogenically purified prior to conversion to graphite using Fe/Zn reduction.

### 3.4. Analysis

Inorganic hydrochemistry was determined by the Centre for Environmental Geochemistry at the British Geological Survey (BGS) in Keyworth using ICP mass spectrometry and ion chromatography. CFCs and noble gases were measured at BGS-Wallingford, by gas chromatography and quadrupole mass spectrometry respectively. O and H stable isotope ratios were determined by dual-inlet isotope ratio mass spectrometry (IRMS) at the Stable Isotope Facility at BGS-Keyworth, while most samples for <sup>14</sup>C-DIC and -DOC were analysed by AMS (accelerator mass spectrometry) at NERC-RCF in East Kilbride, although a subset was measured for <sup>14</sup>C-DOC via the Research and Development laboratory of Beta Analytic in Miami, Florida using AMS. During the AMS sample preparation, separate aliquots of CO<sub>2</sub> were taken and measured for <sup>δ</sup><sup>13</sup>C by dual-inlet IRMS, where sample size allowed.

CFC detection limits were 0.01 and 0.03 pmol/L for CFC-11 and CFC-12 respectively. Average measurement precisions for noble gases were 3.5 % (He), 1.5 % (Ne), 2.0 % (Ar), 2.2 % (Kr) and 5.4 % (Xe). Typical stable isotope precisions were ±0.1 ‰ (δ<sup>18</sup>O), ±1‰ (δ<sup>2</sup>H) and ±0.2 ‰ (δ<sup>13</sup>C-DIC). Measurement precisions (1σ) for radiocarbon averaged ±0.23 pmc (<sup>14</sup>C-DIC) and ±0.38 pmc (<sup>14</sup>C-DOC).

## 4. Results

### 4.1. Hydrochemistry

Since the primary focus of this paper is on isotopic and trace-gas indicators, inorganic hydrochemistry is reported and briefly interpreted in Section S3 of the Supplement.

### 4.2. Dissolved gases

CFC data (Table 2) are cross-plotted at different scales in Fig. 4a and 4b. The first plot shows those results (from ~75 % of the sites) in the context of the atmospheric input curve (USGS, 2021), here converted to dissolved concentration and therefore equivalent to a piston (plug) flow model (Fig. 4a). (Although London is a megacity, Darling and Goody (2007) found no evidence for any local atmospheric enhancement effect preserved in soil gases, unlike for example the study of Ho et al. (1998) in the New York area). All except one of the LGS sites have low or undetectable concentrations, partly obscuring a few Chalk sites on the plot, namely E (Berkshire), V (South London) and Y (eastern Essex). Apart from these low-concentration sites, one sample T falls on the binary mixing line between modern and old groundwater. Otherwise, all remaining 'low' Chalk sites show evidence of modest CFC enhancement usually in CFC-11, which is more soluble in water than CFC-12. The effect is seen across urban and rural areas alike.

Remaining sites show some very high concentrations of both CFCs, though with CFC-12 reaching the most elevated values at Sites I, J and S (Fig. 4b). The sole LGS site to show major CFC enhancement, Site 1, is the only wholly unconfined site measured in the LGS aquifer. The high Chalk sites are mostly at or near the edge of confinement by Palaeogene cover. However, despite the existence of some high CFC concentrations, these are only relative and even the highest value falls far below the general dissolved organic water quality action level of 0.1 µg/L in drinking water.

**Table 3**

C, O and H environmental isotopes for London Basin groundwaters. DOC concentrations were measured by TOC analyser, except for the samples measured by UV-vis in the UVox DOC conversion, where values are inferred from the analysis of only the conjugated/aromatic DOC. Where samples were measured twice for DOC isotopes, the average value is given (the individual measurements are reported with their laboratory publication codes in Table S1).

Site ID	Dissolved inorganic carbon			Dissolved organic carbon			Stable isotopes	
	DIC	<sup>14</sup> C-DIC	δ <sup>13</sup> C-DIC	DOC	<sup>14</sup> C-DOC	δ <sup>13</sup> C-DOC	δ <sup>18</sup> O	δ <sup>2</sup> H
	mg/L	pmc	‰ VPDB	mg/L	pmc	‰ VPDB	‰ VSMOW	
<i>Chalk</i>								
A	224	–	–14.8	0.9	76.2 <sup>a</sup>	–27.7	–7.07	–45.7
B	322	2.6	–3.6	0.6	59.5 <sup>a</sup>	–	–7.22	–46.5
C	301	1.1	–3.0	0.7	43.6 <sup>a</sup>	–26.3	–7.26	–48.2
D	326	5.8	–4.8	1.0	38.9 <sup>a</sup>	–26.3	–7.23	–47.0
E	268	11.7	–7.3	1.2	33.5 <sup>a</sup>	–26.5	–7.43	–49.0
F	323	23.4	–9.7	–	41.1 <sup>a</sup>	–26.5	–7.14	–47.2
G	132	57.5	–13.2	0.7	77.8 <sup>a</sup>	–27.3	–7.27	–48.6
H	361	52.1	–10.0	0.6	56.3 <sup>c</sup>	–29.0	–7.19	–48.1
I	319	45.2	–12.5	0.6	94.0 <sup>c</sup>	–	–6.77	–46.6
J	299	23.8	–9.3	–	–	–	–7.15	–47.9
K	335	43.1	–4.9	3.2	84.1 <sup>b</sup>	–31.9	–6.13	–43.3
L	416	1.1	–2.1	1.1	22.6 <sup>a</sup>	–26.6	–7.39	–49.4
M	356	0.4	–0.4	0.6	26.1 <sup>c</sup>	–26.2	–7.18	–49.6
N	334	1.1	–1.6	0.6	15.8 <sup>c</sup>	–28.2	–7.83	–52.1
O	383	0.6	–1.6	0.6	23.3 <sup>c</sup>	–	–7.82	–51.9
P	418	0.4	–2.2	–	–	–	–7.70	–52.1
Q	362	0.8	–1.4	1.2	10.6 <sup>a</sup>	–26.2	–7.82	–53.0
R	364	0.8	–2.4	1.3	16.9 <sup>a</sup>	–26.4	–7.78	–53.1
S	412	26.1	–5.5	1.3	52.2 <sup>b</sup>	–36.9	–6.66	–46.0
T	322	46.8	–7.9	–	–	–	–6.69	–45.0
U	346	16.3	–8.9	5.7	46.9 <sup>b</sup>	–36.6	–6.77	–45.2
V	308	7.1	–7.2	3.3	19.0 <sup>b</sup>	–40.5	–7.56	–50.0
W	277	39.3	–9.7	0.60	53.3 <sup>c</sup>	–23.9	–7.14	–46.9
X	302	58.1	–13.4	5.2	35.3 <sup>b</sup>	–29.1	–7.16	–47.1
Y	421	–	–5.6	–	–	–	–7.78	–49.1
<i>Lower Greensand</i>								
1	71	77.3	–17.5	0.2	67.3 <sup>b</sup>	–32.4	–7.08	–45.8
2	60	36.8	–12.4	0.9	50.7 <sup>b</sup>	–28.7	–6.90	–45.4
3	245	38.3	–12.6	0.59	65.6 <sup>c</sup>	–	–6.90	–46.1
4	162	23.5	–11.5	0.5	19.5 <sup>b</sup>	–25.5	–6.89	–45.2
5	131	23.6	–16.3	0.9	24.5 <sup>b</sup>	–15.1	–6.08	–39.4
6	149	8.0	–16.1	0.4	13.6 <sup>b</sup>	–24.1	–7.69	–51.8
7	172	1.8	–16.0	0.4	7.4 <sup>b</sup>	–23.2	–7.46	–49.2
8	154	<0.1	–15.9	0.1	6.0 <sup>b</sup>	–24.4	–7.58	–50.8
9	244	<0.1	–11.7	0.9	9.2 <sup>b</sup>	–26.7	–8.22	–56.0
10	226	<0.1	–10.7	0.4	5.0 <sup>b</sup>	–33.6	–8.08	–54.2

<sup>a</sup>DEAE cellulose method.

<sup>b</sup>Evaporation method.

<sup>c</sup>UV-vis method.

For Ne, Ar, Kr and Xe (Table 2), only subtle variations are apparent, but are interpretable in terms of surface equilibration temperature (NGT – Stute and Schlosser, 1993) and excess air (EA – Heaton and Vogel, 1981) values prevailing at the time of recharge, here calculated using the closed-system equilibration (CE) method of Aeschbach-Hertig et al. (2000). In contrast, He values range over three orders of magnitude, presumably owing to the age-related accumulation of <sup>4</sup>He. Not surprisingly therefore, the highest He values are associated with the deeper confined sites in both aquifers: Site Y in the Chalk and Site 10 in the LGS (586 × 10<sup>–8</sup> and 1090 × 10<sup>–8</sup> cm<sup>3</sup>STP/g respectively). However, to fully reflect the excess <sup>4</sup>He component due to accumulation, subtractions for the NGT and EA components need to be applied, resulting in slightly lower <sup>4</sup>He<sub>exc</sub> values (Table 2).

#### 4.3. Isotopes

Data for δ<sup>18</sup>O and δ<sup>2</sup>H (Table 3) generally adhere closely to Craig's (1961) global meteoric water line (Fig. 5a). The LGS data have the greatest range, partly due to the geographical spread of sites but also to palaeoclimatic factors considered further in the Discussion. The Chalk data are more scattered, especially site K, which would conventionally be interpreted as providing evidence of evaporative modification. This

and other aspects are considered further in the Discussion.

In terms of DIC isotopes (Table 3), LGS waters show rather little change in δ<sup>13</sup>C but reach a maximum <sup>14</sup>C activity of ~80 pmc (Fig. 5 b). Chalk samples, however, show a generally good correlation between <sup>14</sup>C and δ<sup>13</sup>C, attributable to water-rock interaction and commonly observed by other studies (Smith et al., 1976; Dennis et al., 1997; Elliot et al., 1999). For the same reason, maximum <sup>14</sup>C activities are no higher than ~60 pmc. The implications for residence time calculation are considered further in the Discussion below.

In contrast, Chalk maximum DOC activities reach 94 pmc (Table 3, Fig. 5c) presumably because of the lack of significant water-rock interaction. Some 75 % of the data lie within the δ<sup>13</sup>C range of –23 to –30 ‰, typical of temperate zone soil organic carbon (Smith and Chalk, 2021). In this study, the evaporation method for concentrating DOC tended on occasion to produce more negative δ<sup>13</sup>C-DOC values, but mainly for the Chalk rather than the LGS. This was probably due to the higher DIC concentration in Chalk samples requiring longer HCl fumigation times to remove all contaminant DIC from the dried solids after rotary evaporation, which may have oxidised and fractionated the FA fraction. However, this was not a problem with the UVox preparation method, at least in those samples yielding sufficient CO<sub>2</sub> gas for both <sup>14</sup>C and δ<sup>13</sup>C determination.



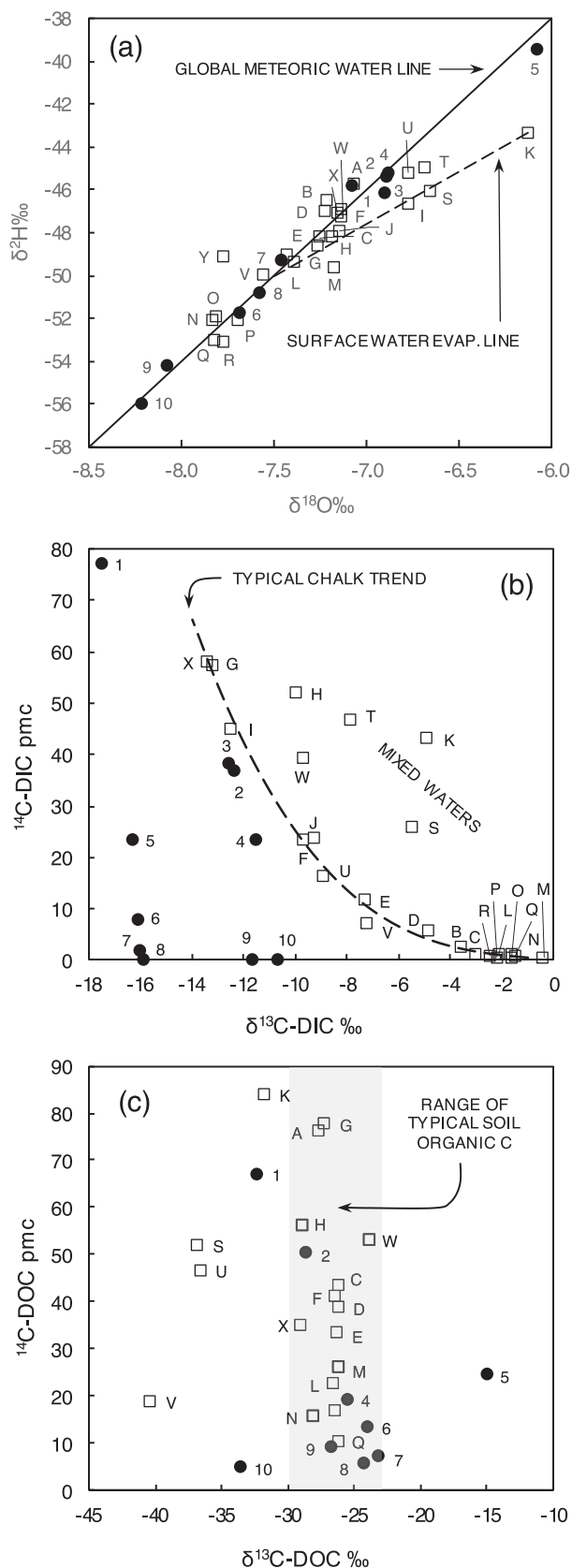


Fig. 5. O, H and C isotopes in groundwaters of the London Basin. Aquifer symbols as Fig. 4.

Soil  $\delta^{13}\text{C}$ -CO<sub>2</sub> values averaged  $-26.1$  ‰ and  $-24.9$  ‰ for the Chalk and LGS respectively (Table S4).

## 5. Discussion

### 5.1. Provenance of recharge to the aquifers

One premise of this study is that inputs of stable O and H isotopes from rainfall vary in a predictable way across the basin, as inferred from the UK groundwater isotope map of Darling et al. (2003) but further developed for the LGS by Darling and Lewis (2021), who considered that inputs from the northern and southern LGS outcrops consistently differ by  $\sim 0.5$  ‰ in  $\delta^{18}\text{O}$  (see their Fig. 2). Superimposed on any areal differences is a further displacement due to palaeoclimatic shifts in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , operating beyond the Holocene-Pleistocene boundary some 12 kyr ago. Thus LGS sites with  $^{14}\text{C}$  activities of  $< 20$  pmc have more negative stable isotope values: the Aldershot sites 6, 7 and 8 on the southern limb of the LGS syncline, and the Slough sites 9 and 10 in the N–S geographical centre of the basin. The reason for the negative displacement between the Aldershot and Slough samples is thought to be due to Slough lying at or near the termination of a flowline deriving from the northern limb of the syncline (Darling and Lewis, 2021).

A similar age depletion effect operates to an extent in the Chalk: for example, lowest  $^{14}\text{C}$  activities are associated with samples more negative than the 30-year (1990–2019) weighted mean of  $-7.3$  ‰  $\delta^{18}\text{O}$  and  $-49$  ‰  $\delta^2\text{H}$  for rainfall observed at the Wallingford GNIP (Global Network of Isotopes in Precipitation) station 70 km west of central London. However, there is no discernible north–south divide in the data partly because the Chalk outcrop in the basin is more extensive but also more constricted from N to S than that of the LGS. Nonetheless, the scatter in the Chalk  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values is inherently greater than for the LGS. While recharge mechanisms to the two aquifers are different (predictable piston-flow infiltration to the LGS, less-predictable mixing and matrix–fracture exchange in the Chalk unsaturated zone), any intra-aquifer differences would presumably be smoothed out in confinement. Instead, the scatter must reflect the almost infinite possibilities for mixing in the Chalk aquifer between waters of different ages, conceivably further influenced by the effects of differing pumping rates as previously proposed for dissolved CH<sub>4</sub> by Darling and Goodydy (2006).

Could different LGS and Chalk infiltration mechanisms lead to inter-aquifer selection in groundwater isotope composition, to the extent that peak palaeowater isotope depletions might differ between the aquifers? It was shown by Darling et al. (2003) that there was no bias within measurement error between weighted mean isotope values in rainfall and local Chalk groundwaters around the Wallingford GNIP station, but for the LGS there are no similar data. Notwithstanding this, comparisons between Chalk and LGS groundwaters from the same area can be attempted. There are rather few suitable Chalk-LGS pairs (here taken as being within 10 km, known stable isotope values, unconfined and/or of known Holocene age), but details of available pairs around the perimeter of the London Basin are provided in Section S4 of the Supplement. While there are signs of geographical variation as expected, there is no evidence of systematic difference between LGS and Chalk stable isotope values for individual pairs, so it is therefore concluded that no significant Holocene selection bias exists, and by implication also in the late-Devensian.

### 5.2. Anthropogenic inputs

#### 5.2.1. Modern tracers

Early studies of both the Chalk and the LGS reported tritium ( $^3\text{H}$ ) data as the only contemporaneously available technique for identifying the presence of ‘modern’ recharge (i.e., since the aerial thermonuclear testing of the mid-1960s). In both aquifers detectable  $^3\text{H}$  activities were found in the unconfined sections as expected, but also in some apparently old, confined Chalk groundwaters (Smith et al., 1976), and in the

**Table 4**  
Groundwater ages derived from <sup>14</sup>C measurements of DIC and DOC in Chalk and LGS waters from the London Basin.

Site ID	<sup>14</sup> C- pmc		DIC age kyr	DOC age kyr	
	DIC	DOC		IA/100 pmc	IA/85 pmc
<b>Chalk</b>					
			$\delta^{13}\text{C}_{\text{carb}} = +2.5\text{‰}$		
A	–	76.2	modern (assumed)	2.3	0.9
B	2.6	59.5	17.2	4.3	3.0
C	1.1	43.6	23.4	6.9	5.5
D	5.8	38.9	12.1	7.8	6.5
E	11.7	33.5	8.8	9.0	7.7
F	23.4	41.1	4.9	7.3	6.0
G	57.5	77.8	modern	2.1	0.7
H	52.1	56.3	0.4	4.8	3.4
I	45.2	94.0	1.4	0.5	modern
J	23.8	–	5.2	–	–
K	43.1	84.1	modern	1.4	0.1
L	1.1	22.6	21.8	12.3	10.9
M	0.4	26.1	29.9	11.1	9.8
N	1.1	15.8	20.6	15.3	13.9
O	0.6	23.3	26.5	12.1	10.7
P	0.4	–	29.7	–	–
Q	0.8	10.6	22.8	18.5	17.2
R	0.8	16.9	24.9	14.7	13.4
S	26.1	52.2	0.4	5.4	4.0
T	46.8	–	modern	–	–
U	16.3	46.9	7.3	6.3	4.9
V	7.1	19.0	12.7	13.7	12.4
W	39.3	53.3	0.9	5.2	3.9
X	58.1	35.3	modern	8.6	7.3
<b>Lower Greensand</b>					
			$\delta^{13}\text{C}_{\text{carb}} = 0\text{‰}$	$\delta^{13}\text{C}_{\text{carb}} = -5\text{‰}$	
			modern	modern	
1	77.3	67.3	modern	modern	3.3
2	36.8	33.8	2.4	modern	5.6
3	38.3	65.6	2.2	modern	3.5
4	23.5	19.5	5.2	2.0	13.5
5	23.6	24.5	8.3	7.1	11.6
6	8.0	13.6	17.2	15.9	16.5
7	1.8	7.4	29.2	27.8	21.6
8	<0.1	6.0	<30	<30	23.2
9	<0.1	9.2	<30	<30	19.7
10	<0.1	5.0	<30	<30	24.8

part-confined Hythe Formation beneath the southern LGS outcrop, though the deeper Folkestone Formation remained tritium-free within measurement error (Mather et al. (1973)). In the present study measurement of <sup>3</sup>H, currently only present in rainfall at activities of a few TU (tritium units), was replaced by CFCs as a by-now much more sensitive indicator of the presence of modern recharge.

Fig. 4 shows just how pervasive CFC enhancement is in the Chalk aquifer. For nearly all sites, confined or not, CFCs cannot be used for reliable age estimation. Instead their value lies in showing just how far anthropogenic contamination may have penetrated the aquifer. By contrast, while three LGS sites provided some evidence of enhancement (especially the unconfined Site 1, Fig. 4b), some of the others had values below detection, particularly from the deep (>500 m bgl) sites around Aldershot (Sites 6, 7 and 8, Fig. 4a), implying that these waters are unaffected by any mixing with modern water.

5.2.2. Induced binary mixing in the Chalk aquifer

Beyond the general conclusion based on a variety of tracers that most Chalk groundwater has to a certain extent been heterogenised by processes promoted by its extensive fracture porosity, it is clear in a few cases that simple binary mixing is occurring. The plot of <sup>14</sup>C-DIC vs <sup>13</sup>C-DIC (Fig. 5b) picks out particularly sites K, S and T as falling on a mixing trend between young and old water. These sites, plus I and U, also have the most positive <sup>18</sup>O values (Fig. 5a), suggesting all have an input of surface water. At Site T situated a few hundred metres from the River

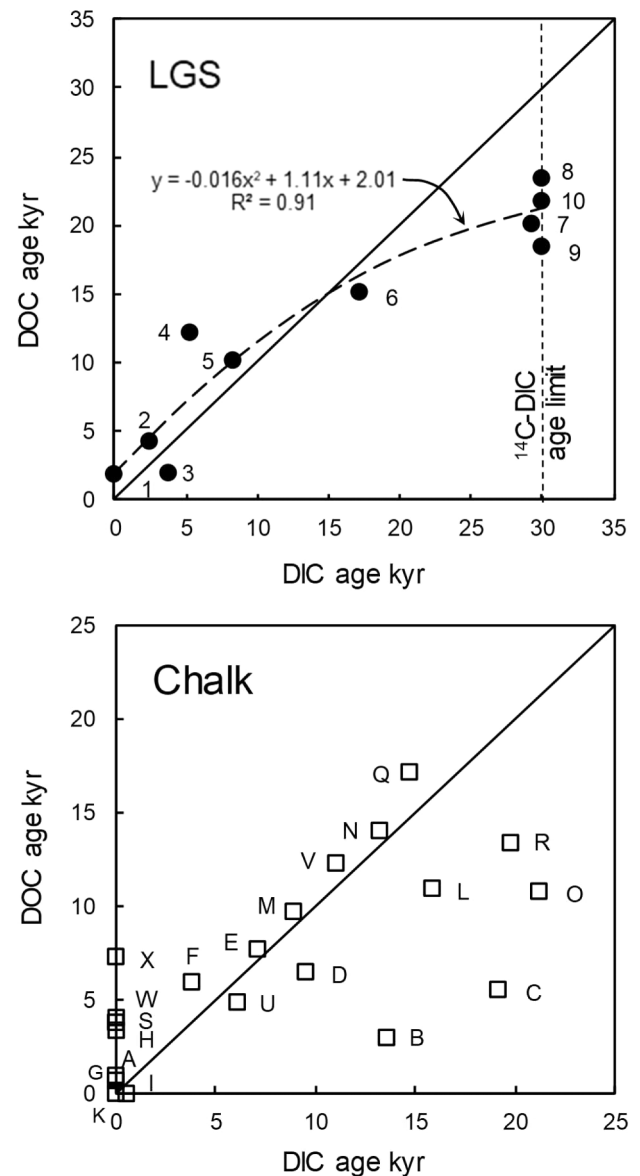


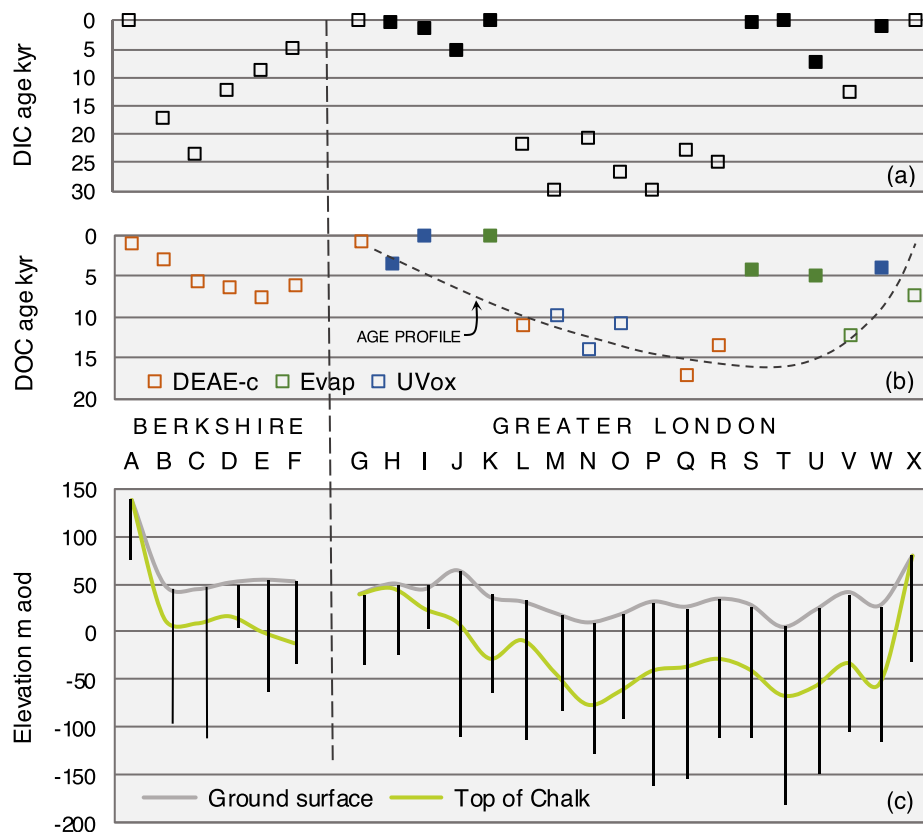
Fig. 6. Comparison of <sup>14</sup>C-DIC and <sup>14</sup>C-DOC model ages for groundwaters of the London Basin.

Thames on reclaimed marshland this is clearly a possibility, while Site K lies a similar distance from flooded gravel pits and the Grand Union canal. Site S lies at the southern end of the New River, a large aqueduct supplying London with water since the seventeenth century which ended in filter ponds adjacent to the site. While the aqueduct now terminates a few kilometres to the north, the observed isotope effects may be a legacy of this former activity. Sites H and W also show evidence for mixing (Fig. 5b), but this is more likely due to their positions near the edge of confinement where they may receive a certain amount of concentrated surface runoff from the clays of the overlying Palaeogene, probably explaining their high CFC excesses, as also noted earlier for Sites I and J (Fig. 4b).

5.3. Old groundwater

5.3.1. DIC and DOC stable isotopes

The DIC system All <sup>13</sup>C-DIC values appear consistent with an ultimate derivation from the reaction between soil or rock carbonate minerals and the weak carbonic acid produced by the solution of soil CO<sub>2</sub> by infiltrating rainwater: in other words, there is no evidence for



**Fig. 7.** Schematic comparison between (a) Chalk DIC and (b) DOC ages relative to basic geology (c), in Berkshire and across Greater London (see Fig. 3). Ages are plotted in reverse order in (a) and (b) to allow easier comparison with the borehole information (c). Filled symbols represent mixed samples (see 5.2.2). The three different DOC extraction methods used in the study are identified: DEAE-c – DEAE cellulose, Evap – evaporation, UVox – ultra-violet oxidation. A tentative age profile beneath the city has been added to plot b. Distances between sites not to scale. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

anthropogenic  $^{13}\text{C}$  inputs affecting any of the sites.

Soil  $\text{CO}_2$  in temperate climates is commonly assigned a  $\delta^{13}\text{C}$  value of  $-25\text{‰}$  (e.g. Fontes and Garnier, 1979). Limited soil gas sampling (Table S4) gave results of  $\sim -26\text{‰}$  (Chalk) and  $\sim -25\text{‰}$  (LGS), so these values are retained for  $^{14}\text{C}$ -DIC age correction.

The  $\delta^{13}\text{C}$  of soil and rock carbonate ( $\delta^{13}\text{C}$ -carb) is less well constrained. There are almost no data on the  $\delta^{13}\text{C}$ -carb values of the carbonate cement of the LGS matrix. Evans et al. (1979) found some highly variable values in core from the Warlingham stratigraphic borehole a few kilometres southeast of Site X, but concluded that ‘...the carbonate in the aquifer is predominantly of marine origin with a  $\delta^{13}\text{C}$  close to zero’.

Smith et al. (1976) assumed a Chalk  $\delta^{13}\text{C}$ -carb value of  $+2.35\text{‰}$ , close to the bulk value of  $\sim +2.5\text{‰}$  since attributed to the White Chalk in Southern England on the basis of numerous cliff and borehole core profiles collated by Jarvis et al. (2006). Although it was hypothesised by Smith et al. (1976) that the reactive surfaces of individual Chalk coccoliths are slowly becoming less positive in  $\delta^{13}\text{C}$  owing to prolonged exchange with DIC, there is no clear evidence that this has occurred on a significant scale. Data from Smith et al. (1976), Dennis et al. (1997) and the present study all show Chalk  $\delta^{13}\text{C}$ -DIC values peaking in the range  $-0.5$  to  $0\text{‰}$ , which would be consistent with a water reaching equilibrium with a Chalk matrix having a value of  $+2.5\text{‰}$   $\delta^{13}\text{C}$  (Kloppmann et al., 1998).

The evolutionary path of DIC in each aquifer will tend to diverge after the initial carbonate dissolution. The 1:1 reaction between soil  $\text{CO}_2$  of  $\delta^{13}\text{C} \sim -25\text{‰}$  and calcite  $\sim 0\text{‰}$  leads initially to  $\delta^{13}\text{C}$ -DIC values of around  $-13\text{‰}$  (Fontes and Garnier, 1979). Open-system conditions provide the potential for further re-equilibration with soil  $\text{CO}_2$  thus decreasing  $\delta^{13}\text{C}$ -DIC values. For Chalk groundwaters, this is limited by the large excess of carbonate available, so it is unusual to see values  $< -15\text{‰}$ . In the poorly-buffered LGS, values down to  $< -20\text{‰}$  are known

(e.g. Darling and Goody, 2006) but more normally lie in the range  $-12$  to  $-16\text{‰}$ . Closed-system conditions, which tend to occur under confinement, allow further interaction between the DIC and the rock, leading to the point where  $\delta^{13}\text{C}$ -DIC values in the Chalk can approach those of the rock matrix (see previous paragraph). This is considered to be very largely due to dissolution–reprecipitation processes rather than isotopic re-equilibration, which is an extremely slow process (Evans et al., 1979). In the LGS, however, the process is much more limited owing to the relative scarcity of carbonate in the rock.

**The DOC system** This should in theory be much less variable than the DIC. Values of  $\delta^{13}\text{C}$ -DOC measured on the FA fraction of soil zone water were not measured during this project, but are assumed to have values  $\leq -25\text{‰}$  based on other studies from the UK (e.g. McTiernan et al., 1999; Palmer et al., 2001) owing to a lack of fractionation during solution. Both the LGS and the Chalk have very low matrix organic contents:  $\leq 0.2\%$  by weight in the Hythe Formation (Macleod, 1998) and  $< 0.1\%$  for the White Chalk (Pacey, 1989), most of which is assumed to be highly refractory and therefore unlikely to influence the DOC in terms of its isotopic composition.

### 5.3.2. DIC and DOC groundwater ages

Calculated  $^{14}\text{C}$  ages are reported in Table 4. The DIC ages are corrected by the Evans et al. (1979) model, first developed for the LGS. (While the Fontes and Garnier (1979) model was considered for the Chalk, erratic performance at higher  $\delta^{13}\text{C}$ -DIC values (Edmunds et al., 1987) ruled it out for this study.) LGS ages have here been modelled with two different  $\delta^{13}\text{C}$ -carb values because of some uncertainty over the appropriate value to use (see earlier), though at an average difference of 2 kyr the effect is only small for a 5‰ difference in  $\delta^{13}\text{C}$ -carb. DOC ages are calculated with two different IA values: the ‘traditional’ 100 pmc, and the 85 pmc value used by Heine and Einsiedl (2021) for their Jurassic carbonate aquifer. Table 4 shows that when an 85 pmc value is

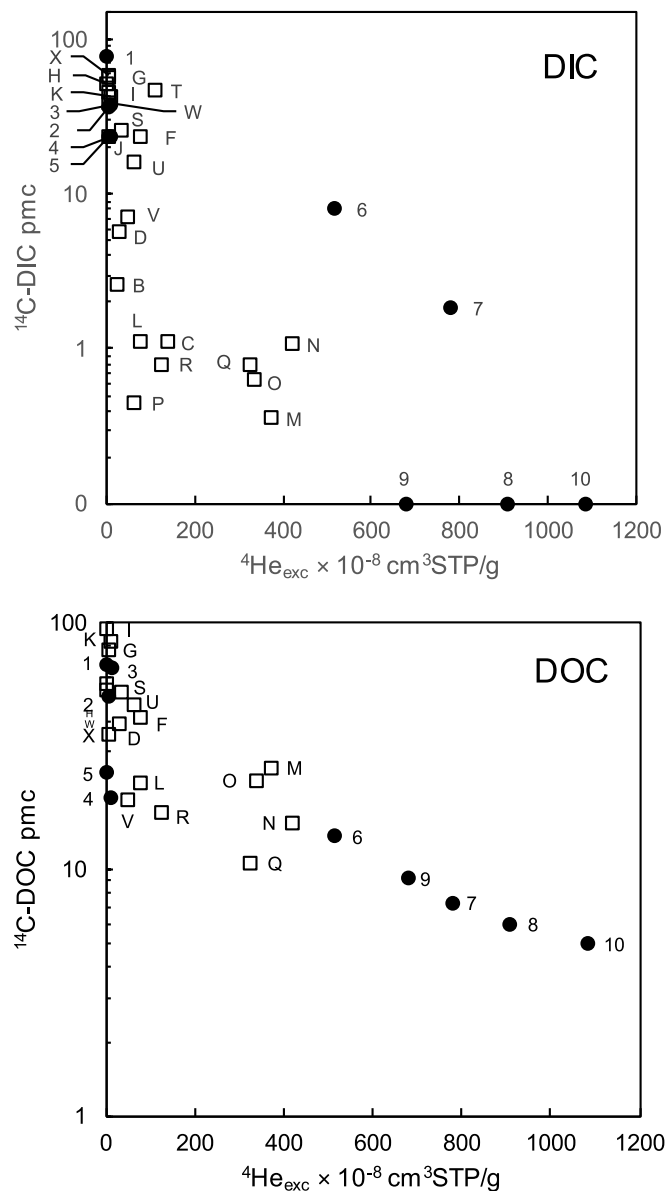


Fig. 8. Relationships of  $^{14}\text{C}$ -DIC and  $^{14}\text{C}$ -DOC activities with excess  $^4\text{He}$  in groundwaters of the London Basin. Aquifer symbols as Fig. 4.

used, ages at the unconfined sites A, G and 1 are 1.3 kyr closer to modern, so this is the preferred IA for the present study. Ages calculating in excess of the effective 30 kyr limit for DIC dating are reported as '>30 kyr'. The limit for DOC dates should in theory be higher, perhaps 35 kyr because of the reduction in dead carbon inputs, but none of the DOC ages reported here exceeds 25 kyr.

In the LGS aquifer, DOC ages tend initially to exceed DIC ages but cross over at about 15 kyr until the 30 kyr DIC dating barrier is reached, at which point the maximum DOC age is  $\sim 25$  kyr (Fig. 6). This could represent the age limit for fresh water in the LGS of the London Basin, although there are indications that older saline waters exist (5.4 below). The Chalk plot shows much more scatter, as already demonstrated for example by  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  (Fig. 5a), though with most samples falling on or below the 1:1 line. While a DIC-DOC age calibration curve can be attempted for the LGS (Fig. 6), clearly this would not be meaningful for the Chalk. Instead it may be more useful to compare Chalk DIC and DOC ages in relation to the basin geology (Fig. 7a-c). The DIC ages (7a) show reasonably well that residence times increase at depth under central London (as expected) but have an unlikely distribution along the

Berkshire section. DOC ages, however, compare well with the geology in both Berkshire and Greater London (7b). Some of the variation could be due to the differing borehole depths (7c): boreholes are normally left unlined in the Chalk, potentially allowing mixing from multiple horizons in the deeper boreholes. For both DIC and DOC, the apparent ages of mixed samples are reduced by modern water influx (5.2.2). Otherwise, virtually all DOC ages are younger than 15 kyr, while DIC ages range up to 30 kyr. A tentative age profile curve has been added to the DOC ages (Fig. 7b). Its shape partly reflects the asymmetric nature of the basin, but also suggests that representative  $^{14}\text{C}$ -DOC ages can be obtained using any of the three preparation methods used during the study.

### 5.3.3. Recharge temperatures

NGTs from the LGS cover the range 10.3–2.6  $^{\circ}\text{C}$  (Table 2), and despite the small number of samples it is clear that this dataset is highly bimodal, reflecting the hydrochemistry as depicted in Fig. S2. Apart from an outlier at 10.5  $\text{cm}^3\text{STP}/\text{kg}$  (Site 10), EA values average 4.0  $\text{cm}^3\text{STP}/\text{kg}$ , similar to results from other Lower Cretaceous confined sandstones in Norfolk, eastern England (Ingram et al., 2007).

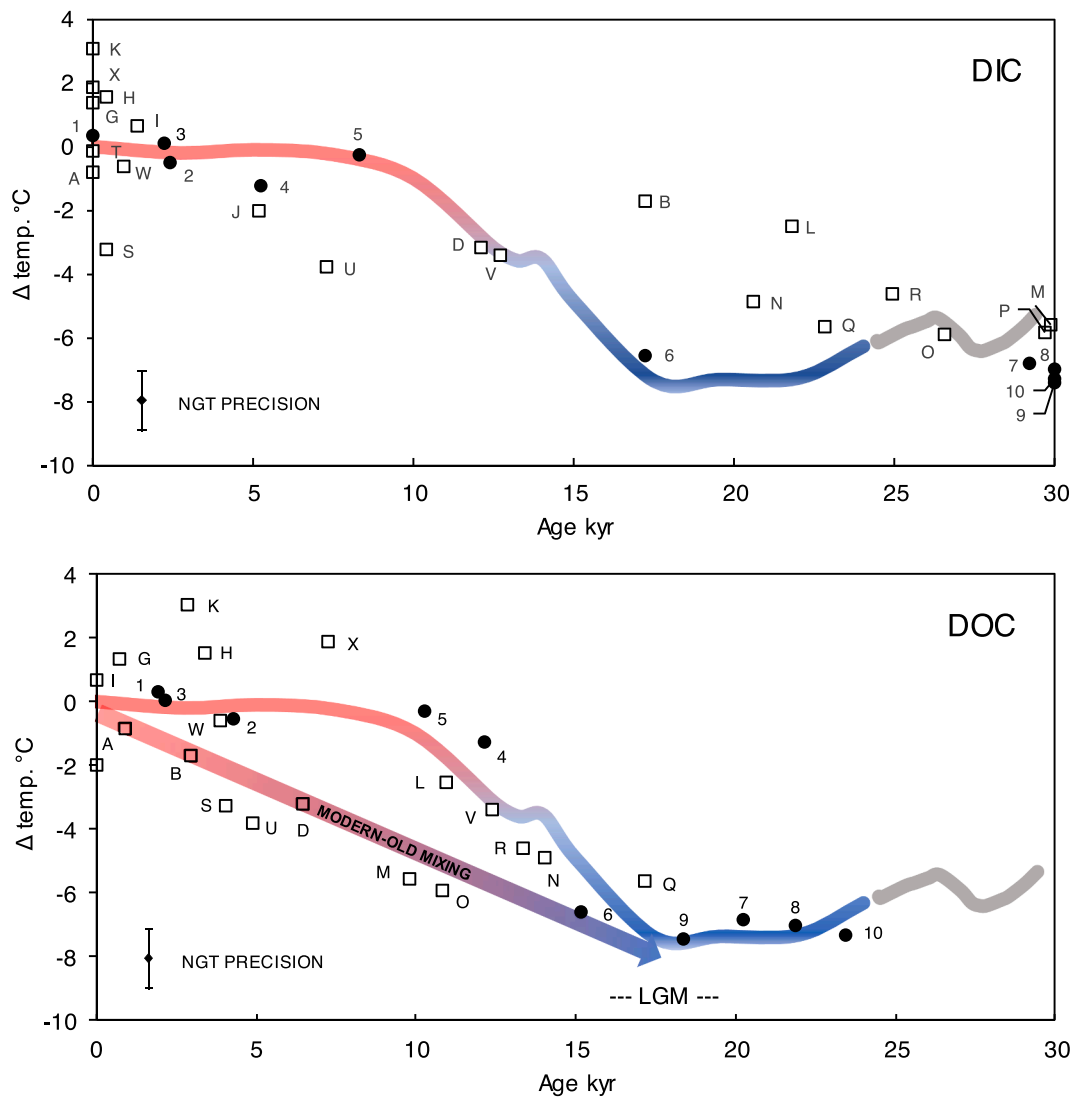
Chalk NGT values range from 13.1 down to 4.1  $^{\circ}\text{C}$  (Table 2), with a fairly even spread across the range. The highest NGT of 13.1  $^{\circ}\text{C}$  is from K, a site already identified as showing mixing with surface water (5.2.2), so this is likely to have perturbed the noble gas ratios also. Otherwise, since the mean annual air temperature (MAAT) in southern England is  $\sim 10^{\circ}\text{C}$ , maximum NGTs of around this value would be expected. Of the four sites with NGTs  $\geq 10^{\circ}\text{C}$ , all are unconfined or near the edge of confinement (G, H, I and X). Conversely, the four sites yielding the lowest NGTs ( $\leq 4.5^{\circ}\text{C}$ ) are all sites at least 20 km into confinement (O, P, Q, Y). EA values average 3.1  $\text{cm}^3\text{STP}/\text{kg}$  (sd 2.1). While this is approximately twice the mean value from the unconfined Chalk in West Berkshire (Darling et al., 2017), there is little evidence to associate higher EA with cooler NGT values, so with the exception of temperature, recharge conditions seem likely to have remained similar, with no evidence for a marked increase in rainfall intensity such as inferred by Zhu and Kipfer (2010).

### 5.3.4. Helium-4 accumulation

Accumulation of  $^4\text{He}$  in older groundwaters is commonly observed (e.g. Solomon, 2000). In addition to in-aquifer production from radioactive decay of U-Th series minerals,  $^4\text{He}$  may be supplemented by a flux from deeper strata, and therefore He accumulation rates are aquifer-specific rather than carrying absolute age implications. Nevertheless, in a given aquifer unit an inverse relationship between  $^4\text{He}_{\text{exc}}$  and  $^{14}\text{C}$  activity would be expected for waters not exceeding radiocarbon age, and Fig. 8 confirms this to be the case for the London basin. There is a relationship, rather better for  $^{14}\text{C}$ -DOC than -DIC, especially in the Chalk where there is a large scatter below the 1 pmc level. By contrast, the LGS data are much more constrained, with a major difference between the sites in the Hythe and Folkestone units. This may be due to easier escape of  $^4\text{He}$  from the semi-confined Hythe compared to the fully-confined Folkestone.

### 5.4. Preservation of the palaeorecharge signal

The deep confined sites of the LGS would be inherently more likely to retain a record of late-Devensian recharge than the heavily fractured Chalk. The comparative thinness of the Folkestone aquifer unit (Fig. 1) would also favour the preservation of piston flow rather than the mixing that often characterises the Chalk (4.2, 5.2.2). However, the question arises as to what extent intensive abstraction from the Chalk may have perturbed any natural palaeowater preservation. While it is certain that Chalk groundwater flow lines beneath central London have been modified by pumping (WRB, 1972), the extent is difficult to assess since isotopic methods have only been available in recent decades. The scarce 'time lapse' radiocarbon evidence (outlined in 2.2.2 above) did not usually show significant change, but the time gaps would only have been



**Fig. 9.** Noble gas recharge temperatures plotted versus  $^{14}\text{C}$ -DIC and  $^{14}\text{C}$ -DOC ages of groundwaters of the London Basin, but converted into  $\Delta$ -temperature values assuming a modern MAAT of  $10^\circ\text{C}$ . Also shown is the global mean surface  $\Delta$ -temperature curve from Osman et al. (2021), extended from 24 to 30 kyr by inference from the Vostok ice core record (<https://cdiac.ess-dive.lbl.gov/ftp/trends/temp/vostok/vostok.1999.temp.dat>). Aquifer symbols as for Fig. 4.

~20 years. The present paper reports two sites (J and U) also sampled by Elliot et al. (1999) again about 20 years previously; in both cases the new AMS-measured  $^{14}\text{C}$ -DIC activity was slightly lower than the older decay-counted value, so perhaps a technique-based phenomenon rather than a real change.

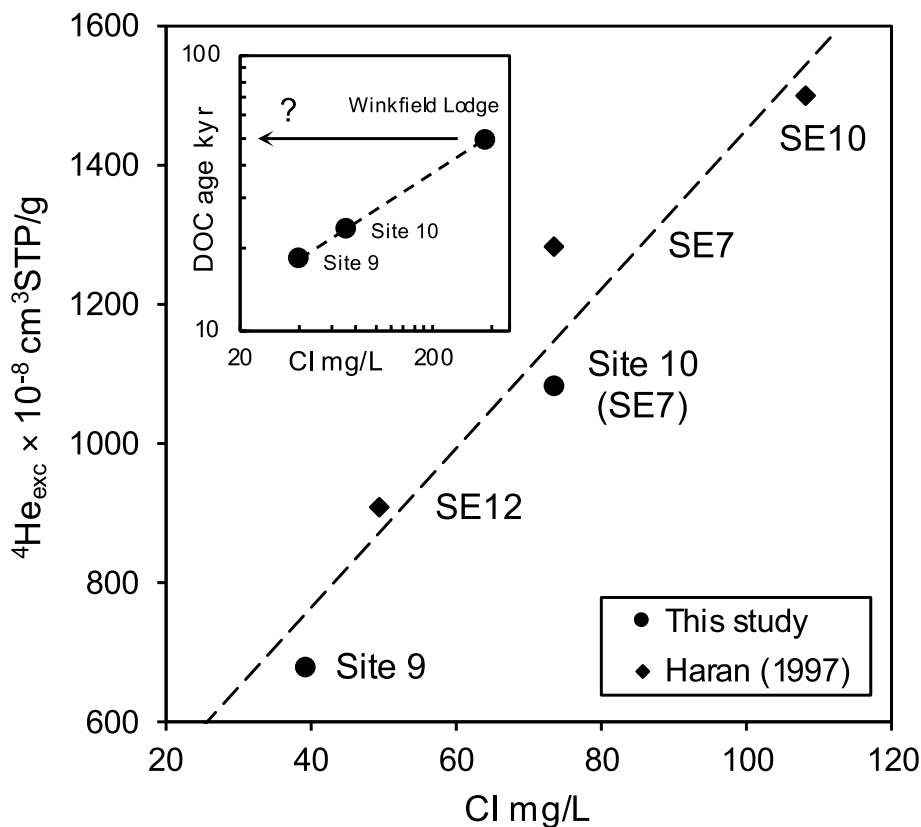
An effective way of testing the two aquifers as palaeoclimate archives is to plot the model ages from Table 4 in relation to  $\Delta$ -temperature values derived from NGT values in Table 2 and assuming a late-Holocene MAAT of  $10^\circ\text{C}$  (Fig. 9). Also shown on the figure is the global surface temperature-change curve covering the past 24 kyr (Osman et al., 2021), a period including the Last Glacial Maximum (LGM) at 15–20 kyr. Although the curve is based on  $^{14}\text{C}$  results calibrated to calendar years while the water ages are uncalibrated, the plot is sufficient to show that DOC ages are more in agreement with it than the DIC ages, some of which appear too old for their temperatures. In the LGS, DOC ages divide between the Hythe (Holocene) and Folkestone (late-Devensian) units. The DOC ages for the Chalk by comparison tend to plot below the curve in its post-LGM section, suggesting mixing between modern and late-Pleistocene waters. However, DOC ages are not wholly without issues. The main example of this is at the unconfined Chalk site X where the DOC age is 7.6 kyr but DIC gives a much more likely ‘modern’ age (see also Fig. 7).

The NGT difference of  $\sim 7^\circ\text{C}$  shown by the LGS samples coincides with the temperature curve of Osman et al. (2021), implying that late-Pleistocene recharge is well-preserved at depth. A similar difference in NGT values between Holocene and Pleistocene recharge was found for the Triassic sandstone aquifer in the East Midlands of England, also considered to preserve palaeowater effectively (Bath et al., 1979).

Despite the LGS possessing apparently good palaeoarchive properties, a question remaining about the aquifer is the age of the residual saline water known to lie in the axial zone from historic borehole evidence (Egerton, 1994), but which is otherwise unexploited or tested in modern times. It was proposed by Darling and Lewis (2021) that hydrochemical data from the Slough area reveal evidence of mixing with this brackish water. A plot of  $^4\text{He}_{\text{exc}}$  vs Cl for four sites in the area, including Sites 9 and 10, shows a well-correlated mixing trend (Fig. 10). Given the equally good correlation between  $^{14}\text{C}$ -DOC and  $^4\text{He}$  in Fig. 8, extrapolation on a DOC age vs Cl plot suggests that water close to the centre of the saline zone at 375 mg/L Cl (legacy value for Winkfield Lodge: Prestwich, 1895) could have an age of  $\sim 50$  kyr (inset to Fig. 10).

##### 5.5. The wider basin east of London

The London Basin continues to broaden until around the Thames



**Fig. 10.** Plot of new and legacy data showing a good correlation between Cl and excess  $^4\text{He}$  for four LGS sites in the Slough area of the London Basin. Assuming the  $^4\text{He} / ^{14}\text{C}$ -DOC relationship from Fig. 8 holds, an age of  $\sim 50$  kyr can be inferred for the most saline water known from the area to the SW (inset). (See above-mentioned references for further information.)

Estuary the confining Palaeogene cover is  $\sim 90$  km wide from north to south (Fig. 1). While the LGS is largely absent, the Chalk remains present across the basin. To test the theory that older, less-mixed Chalk groundwater might still be preserved at depth in the eastern axial zone of the basin (Fig. 1), a borehole (Site Y, Fig. 3) was sampled on the Dengie peninsula of coastal Essex, the area most remote from the Chalk outcrop. However, as Tables 2 and 3 show, values of  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$ -DIC were all comparable to waters from other deep confined Chalk sites, while the presence of CFCs, albeit at very low concentrations, was another similarity. Although at  $586 \times 10^{-8}$  ccSTP/g the concentration of  $^4\text{He}$  was the highest Chalk value found during this study, slightly higher values were reported for some Berkshire sites by Elliot et al. (1999). These results from Dengie therefore strongly suggest that the degradation of the palaeoclimatic signal identified in the aquifer beneath London extends throughout the confined Chalk of the whole onshore London Basin.

## 6. Conclusions

Earlier studies of the age of groundwater in the principal aquifers of the London Basin (Chalk and Lower Greensand) established that both still contained evidence of recharge in late-Devensian (last ice age) times, but left much doubt over the maximum ages and therefore degree of preservation of these remnants. The present study has provided more robust and reliable water age characterisation with the aid of techniques new to the basin, specifically chlorofluorocarbons (CFCs) and the radiocarbon activity of dissolved organic carbon ( $^{14}\text{C}$ -DOC). Measuring the latter presented some technical challenges at the low DOC concentrations encountered, but comparable results using three different extraction methods appear to validate the DOC dating approach.

Most significantly, all  $^{14}\text{C}$ -DOC activities have been above the limit of

detection, whereas the corresponding  $^{14}\text{C}$ -DIC activities have sometimes been below this level, rendering it only possible to assign a model age of ' $\geq 30$  kyr' to these waters. Minimum  $^{14}\text{C}$ -DOC activities found for the Chalk and LGS were 10.6 and 5.0 pmc respectively, providing a degree of headroom above the detection limit and consequently usually resulting in younger ages than the corresponding  $^{14}\text{C}$ -DIC values (a phenomenon commonly observed in similar studies). On this basis the oldest Chalk groundwater identified was  $\sim 17$  kyr and the oldest LGS water  $\sim 23$  kyr. A similar level of discrepancy was shown by climate-related stable isotope depletions, the LGS reaching a minimum of  $-8.2$  ‰  $\delta^{18}\text{O}$  compared to  $-7.8$  ‰ for the Chalk, and noble gas-derived recharge temperatures giving minima of  $2.6$  °C (LGS) and  $4.1$  °C (Chalk).

Despite the exact meaning of groundwater 'age' being debatable, it seems likely that the LGS substantially preserves its ice-age recharge endowment at depth, but that this has disappeared from the Chalk leaving evidence of its previous existence inferable only from mixing relationships. The susceptibility of the Chalk to mixing has been well demonstrated by this study, particularly by the detection of CFCs throughout the confined aquifer, even at 40 km from outcrop. Although some of this may have been promoted by large-scale pumping from the aquifer, the Chalk's highly fractured nature would probably have led to much the same outcome even under natural flow gradients.

While there must now be little expectation of finding relict Devensian recharge anywhere in the Chalk of the London Basin, the LGS has been shown to have good potential as a palaeoarchive. In particular, future research could help to unravel the relationship between the deep fresh-water boreholes and the brackish water along the basin axis, which may preserve evidence of earlier Devensian recharge under a warmer climate.

More broadly, the results from this study when compared to LGM cooling effects preserved in other archive aquifers are similar to those

included in the [Arppe and Karhu \(2010\)](#) survey of  $\delta^{18}\text{O}$  depletion in European groundwaters, and the [Seltzer et al. \(2021\)](#) survey of low-to-medium-latitude noble gas temperatures worldwide. This provides additional evidence that the LGS aquifer performs well as a palaeoarchive.

### CRedit authorship contribution statement

**W. George Darling:** Conceptualization, Methodology, Investigation, Writing – original draft. **Daren C. Gooddy:** Methodology, Investigation, Writing – review & editing. **Pauline L. Gulliver:** Methodology, Investigation, Writing – review & editing. **Amy M. Scott:** Validation, Writing – review & editing. **Sean P. Ahearn:** Validation, Writing – review & editing.

### Declaration of Competing Interest

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

### Data availability

Data will be made available on request.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2022.128972>.

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