Abstract

The hydrochemical, radiochemical, stable isotope, 14C and dissolved noble gas composition of groundwaters has been determined along two profiles across the confined, fissured Chalk aquifer of the London Basin of southern England, and for selected sites in the adjacent Berkshire Basin. During downgradient flow in the London Basin aquifer, the groundwater chemistry is modified by water–rock interactions: congruent and incongruent reaction of the carbonate lithology resulting in enhanced Mg/Ca and Sr/Ca ratios and 13C contents with increased residence times; redox and ion exchange reactions; and towards the centre of the Basin, mixing with a residual saline connate water stored in the Chalk matrix. There is evidence from anomalous water chemistries for a component of vertical leakage from overlying Tertiary beds into the confined aquifer as a result of historical dewatering of the aquifer. Dissolved noble gas contents indicate the climate was up to 4.5° C cooler than at present during recharge of the waters now found in the centres of both Basins; stable isotope (2H and 18O) depletions correspond to this recharge temperature change. For evolved waters having δ 13C > −8‰ PDB a negative linear correlation is demonstrated between derived recharge temperatures and δ 13C values, which is interpreted as mixing between relatively warm, light isotopic, fracture-borne waters and cooler stored waters of the matrix having a 13C signature more or less equilibrated with the Chalk. From geochemical (14C, 4He) age estimates, the abstracted water is interpreted as being either of wholly Holocene/post-Devensian glacial origin, or an admixture of Holocene and Late Pleistocene pre-glacial (cold stage interstadial) recharge. Devensian pleniglacial stage waters of the Last Glacial Maximum are not represented.

1. Introduction and hydrogeological setting

The Chalk is an important groundwater source for public water supply both in the United Kingdom (UK) and in nearby parts of Europe (Edmunds et al., 1992; Downing et al., 1993); it is the most important aquifer in England. In the UK, pumped abstraction of the fissured Chalk aquifer has been extensively developed and used since the 19th century; prior to this, abstraction was generally from springs and hand dug wells in outcrop areas. In the London Basin of SE England, progressive increase in groundwater abstraction since the late 1800s has led to aquifer overexploitation. Groundwater levels in the centre of the Basin have fallen by as much as 70 m since the middle of the last century due to overexploitation (Water Resources Board, 1972). However, in recent decades less water has been pumped from the Chalk beneath Central London, and water levels in the region are gradually recovering (Wilkinson and Brassington, 1991), with enhanced rates of recovery in certain localities through activation of artificial recharge schemes (cf. Kinniburgh et al., 1994). A lesser decline of groundwater levels through pumped abstraction also occurred historically in the adjacent Berkshire Basin (Edmunds et al., 1987).

Groundwater recharge occurs on the northern and southern Chalk outcrops, and in the London Basin the general flow is towards discharge areas in the Lower Thames Valley (Fig. 1). Much of the London Basin is naturally drained by the River Thames reflecting the palaeohydrological development of the Basin (Smith et al., 1976). The recent water resource developments of the Chalk and Tertiary Sands through pumped wells has intercepted the natural discharge, and these abstractions are now the main outlet for the confined area; natural discharge no longer takes place from the central and eastern part of the basins.

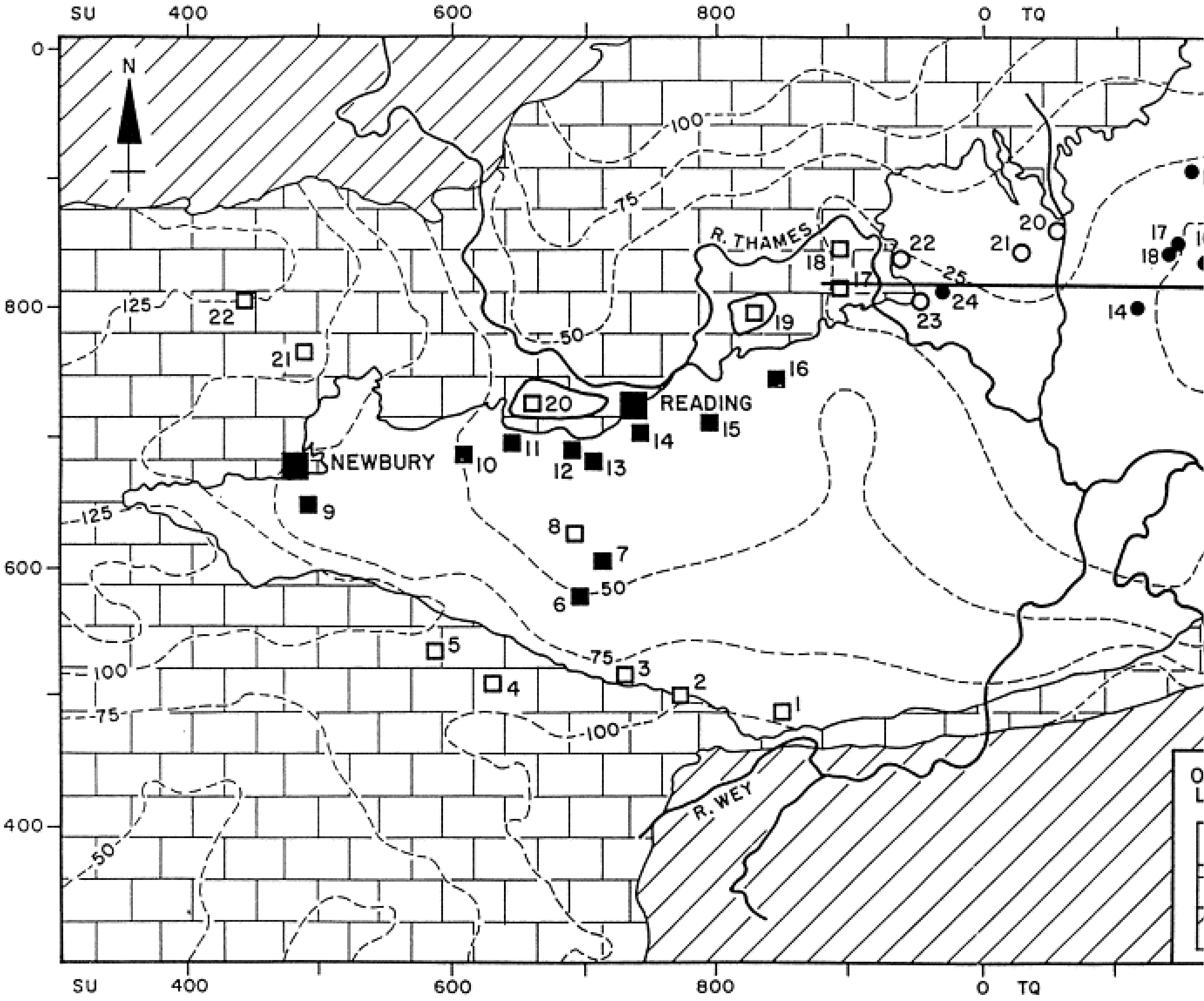

Fig. 1. Geological map showing the locations of the boreholes from which groundwaters from the Chalk of the London Basin (circles) and Berkshire Basin (squares) were sampled. Open symbols indicate groundwaters with δ^{13}C<−8‰ PDB and filled symbols indicate groundwaters with δ^{13}C>−8‰ PDB. Generalised piezometric levels are contoured at intervals of 25 m above mean sea level. The two downgradient sampling lines are shown, one W–E and the second S–N from outcrop into the centre of the London Basin.

View thumbnail images

The geology and hydrogeology of the Chalk aquifer of southern England have been extensively reported (Water Resources Board, 1972; Edmunds et al., 1987; Downing et al., 1993). The London Basin is an eastward plunging synclinorium; the Chalk (Upper Cretaceous) forms the principal aquifer which extends westwards into the hydraulically separate Berkshire Basin. The Upper Chalk (Senonian) Formation varies in thickness between 70 and 170 m and is more fractured, having a higher permeability than both the Middle (Turonian) and Lower (Cenomanian) Chalk. The latter is underlain by, and is generally in hydraulic continuity with, the Upper Greensand (Lower Cretaceous) aquifer. Up to 70 m of Gault Clay (Lower Cretaceous) forms the basal aquitard for both aquifers. The Chalk is overlain unconformably by Lower Eocene strata; the Tertiary Basal Sands (an arenaceous facies at the base of this sequence in the central and eastern parts of the London Basin) are in hydraulic continuity with the Chalk and provide high transmissivity zones which aid recharge. The confined aquifer system is overlain by up to 150 m of low hydraulic permeability Eocene clays (London Clay).

The Chalk is a dual-porosity aquifer which stores relatively immobile water in the fine-grained interstitial porosity of the matrix but transmits water via a more conductive fracture and fissure system. The total porosity is in the range 0.15 to 0.45, and the mean fracture porosity ≈10–3−10–2 (Price, 1987). Matrix permeabilities are low (10–4 to 10–3 m/day) because of the very small pore throat diameters (<1 μ m). In contrast, the primary fissure system imparts permeabilities in the range 0.1 to 1 m/day (Price, 1987), and this constitutes the effective flow system in most of the confined aquifer (Water Resources Board, 1972; Monkhouse, 1995). Enhanced permeabilities up to 200 m/day occur in the weathered zone of the Chalk and for discrete enlarged (secondary) fissures, which occur predominantly close to outcrop in valley axes (e.g., Younger, 1989).

Pore water chemistry may differ significantly from that of fissure water abstracted from boreholes (Edmunds et al., 1973), and diffusive exchange occurs between the very large intergranular storage of matrix waters and the fissure flow (Foster, 1975; Barker and Foster, 1981). The most saline interstitial water in the Chalk is a connate water (sensu stricto), little changed from Cretaceous seawater (Bath and Edmunds, 1981). The salinity of pore waters in the Berkshire Chalk is considered to have resulted predominantly from mixing of fresh waters with residual chlorinity derived from such connate water (Edmunds et al., 1987). A sketch of the proposed evolution of both permeability and salinity development of the confined Chalk aquifer of the Bershire Basin since the initial deposition of the Chalk has been presented recently by Bloomfield (1997).

The London region is an extensively-developed urban area, presenting various possibilities for aquifer pollution. Aquifer overexploitation has led to groundwater quality problems as a result of induced infiltration of poorer quality water sources, e.g., saline intrusion into unconfined Chalk along the Thames Estuary east of the City of London (Water Resources Board, 1972). Interstitial saline waters exist also in the London Clay (200–500 mg/l Cl–; 280–770 mg/l Na+) and Lower Tertiary mudrocks, and dissolution of gypsum and epsomite produces high SO2–4 contents averaging 3000 mg/l (Water Resources Board, 1972; Bath et al., 1989). Vertical drainage of such waters would have significant effect on downgradient quality in the confined aquifer (Ineson and Downing, 1963). Water level recovery has also led to sulphate dissolution in certain localities, as pyrite in overlying Tertiary sediments has been oxidised under unsaturated conditions (Flavin and Joseph, 1983; Payne et al., 1988; Rainey and Rosenbaum, 1989; Kinniburgh et al., 1994). The Berkshire Basin is a more rural location and the Chalk aquifer has been less extensively exploited.

In this integrated chemical and isotopic study, hydrochemical (major, minor and trace element), radiochemical (U- and Ra-contents, 234U/238U and 228Ra/226Ra activity ratios and including the dissolved radiogenic gas 222Rn), dissolved noble gas (He, Ne, Ar, Kr, Xe), and environmental isotope (2H, 18O, 13C, 14C) contents have been measured along two groundwater flowlines in the fissured UK Chalk of the London Basin, and at further sites in its westward extension into Berkshire complementing a previous well-established profile (Edmunds et al., 1987). These measurements are used to validate the flow directions indicated by piezometric measurements in both aquifers, to study the important hydrogeochemical reactions, groundwater mixing processes, and the controls on water quality, and further provide estimates of both the palaeoclimatic conditions during groundwater recharge and groundwater ages.

2. Groundwater sampling and analytical methods

Groundwaters were sampled along two approximate flowlines (S−N and W−E) from Chalk outcrop to the centre of the London Basin, and at further selected sites in the Berkshire Basin (Fig. 1). The sampling lines were chosen to avoid the possible influences of estuarine saline intrusion in the east of the London Basin, and of artificial recharge projects in the north. Borehole and analytical details can be found in Elliot (1990), along with individual sample results. Relevant field measurements and analytical results are summarised in Table 1Table 2 and Table 3. Borehole locations are given in Table 3. Complementary N–S downgradient chemical trends for the Berkshire Basin have been published previously (Edmunds et al., 1987Edmunds et al., 1992), but more recent data for this Basin are included here. A more regional study of the London Basin Chalk aquifer has been presented recently by Dennis et al. (1997).

Table 1. Field and analytical data (mmol/l) for London Chalk (prefix code: LN) groundwaters

LN	Name	T	pH	Cl	Br	HCO3	SO4	NO3	Li	Na	K	Ca	Mg	Sr	δ 2H	δ 18O	δ 13C	14C	RT	RT	EAI	4He (×10 8)
No.		°C			µmol/l				µmol/l					µmol/l	(1)	(1)	(2)	(3)	°C	±1 SE		cc(STP)/cc
London Chalk: open circles=unevolved groundwater																						
22u	Burnham PS	11.6	6.85	0.85	1.15	5.20	0.47	0.83	0.36	0.67	0.06	3.39	0.21	4.11	-47	-7.4	-14.0	60.8 (4)	9.7	0.5	1.30	5.9
01u	Paynes	11.9	6.80	0.82	1.63	4.44	0.36	0.53	0.63	0.63	0.05	2.84	0.12	4.02	-51	-7.4	-13.6	66.2	12.5	0.7	1.17	6.4
02u	Philips 2	11.6	7.35	0.56	1.38	4.39	0.24	0.38	0.42	0.44	0.04	2.67	0.10	3.30	-48	-7.2	-13.4		11.4	0.9	1.26	5.8
06c	Unigate	13.1	7.35	4.01	5.51	5.31	1.84	0.04	0.39	5.20	0.28	2.25	1.40	42.2	-47	-7.2	-12.8	12.6	10.9	1.0	1.46	267.0
20u	Sanderson 2	20.3	7.05	0.59	1.00	4.97	0.36	0.16	0.68	0.61	0.07	2.57	0.23	15.0	-50	-7.7	-9.9		9.0	1.9	1.32	7.0
23u	Nicholas	14.7	7.00	0.96	2.00	5.25	0.64	0.31	1.12	1.35	0.08	2.89	0.30	11.3	-50	-7.5	-9.6		11.6	0.7	1.65	5.4
05c	Sunlight	13.8	7.30	0.37	0.83	4.84	0.20	0.04	1.18	0.48	0.07	2.17	0.37	15.9	-49		-8.7	14.6	10.2	0.6	1.38	24.8
21c	Pinewood 1	11.8	7.05	0.34	0.56	5.10	0.09	0.04	0.65	0.35	0.05	2.25	0.17	13.0	-49	-7.3	-8.6	20.8	9.8	0.6	1.27	5.3
London Chalk: filled circles=evolved groundwater																						

07c	Harrods 2	13.3	7.50	3.98	6.38	6.18	1.30	0.04	3.75	8.13	0.26	1.12	0.70	20.3	-51	-7.4	-4.8	17.1	9.5	0.8	1.15	572.0
04c	Modeluxe	12.6	7.30	0.51	0.80	4.49	0.32	0.04	2.16	1.22	0.18	1.40	0.70	29.9	-50	-7.4	-3.8	4.5	9.2	0.8	1.25	64.8
03c	BXL Plastics	14.0	7.15	0.40	0.68	5.16	0.23	0.04	2.55	0.48	0.17	1.45	1.07	70.5			-3.6	4.3	9.0	0.5	1.32	9.6
08c	Buchanan Hse	13.9	7.30	3.86		5.56	3.04	0.04		10.66	0.11	1.60	0.93		-52	-7.3	-3.5		8.7	0.7	1.34	287.0
12c	Hornsey Rd	13.7	7.65	1.83		4.80	1.23	0.04		7.13	0.24	0.65	0.59		-54	-7.7	-2.6	1.4	5.8	0.5	1.34	341.0
13c	Kentish Town	13.5	7.60	2.82	5.51	5.97	1.94		5.62	9.96	0.22	0.79	0.49	16.6	-53	-7.8	-2.6	0.8	5.4	0.6	1.50	132.0
24c	Neville	11.2	7.10	0.37	0.93	5.13	0.18	0.04	2.16	0.83	0.16	1.72	0.65	44.3	-48	-7.3	-2.5	1.9	7.8	0.9	1.27	11.5
11c	Unilever 2	13.5	7.25	3.78	6.26	6.36	2.94	0.04	6.20	11.44	0.25	1.42	0.89	24.8	-53	-7.6	-2.5	1.0	6.8	0.6	1.43	244.0
09c	Dorset Hse 2	13.8	7.35	3.92	7.76	5.93	2.77	0.04	6.48	12.83	0.27	1.02	0.74	26.4	-53	-7.8	-2.4	0.8	7.1	0.5	1.38	329.0
19c	Kodak	12.6	6.90	1.47	2.63	6.00	0.76	0.04	5.62	3.92	0.31	1.07	1.25		-50	-7.4	-2.1	3.8(4)	6.8	0.5	1.29	253.0
17c	Glaxo	12.7	7.00	1.69	3.25	6.82	1.86	0.04	6.63	3.70	0.40	1.97	2.07	73.8	-49	-7.4	-1.7	1.1	7.5	0.8	1.40	81.6
10c	Sainsburys	13.5	7.80	4.40	6.63	5.43	1.99	0.06	5.47	10.22	0.25	0.92	0.86	22.4	-51	-7.4	-1.7		7.1	0.5	1.42	242.0
18c	Lyons Tetley	12.5	6.90	1.47	2.75	6.84	2.28	0.04	7.64	4.44	0.42	2.00	2.20	67.9	-51	-7.2	-1.3		6.4	0.6	1.40	144.0

16c	PFW Ltd	12.8	7.00	2.85	5.38	6.80	3.21	0.04	8.36	7.35	0.43	2.05	2.26	63.2	-52	-7.6	-1.2	0.8	5.3	0.9	1.45	356.0
15c	Hoover	12.6	7.35	2.37	4.76	6.36	1.91	0.04	6.63	6.96	0.32	1.00	1.38	40.5	-52	-7.7	-1.1		5.0	0.5	1.45	453.0
14c	Crown Cork	12.8	7.85												-50(4)	-7.7(4)	-0.9	1.1(4)	5.5	0.8	1.25	439.0

Full-size table

Table 2. Field and analytical data (mmol/l) for Berkshire Chalk (prefix code: BK) groundwaters

BK	Name	T	pH	Cl	Br	HCO3	SO4	NO3	Li	Na	K	Ca	Mg	Sr	δ2H	δ18O	δ13C	14C	RT	RT	EAI	4He (×108)
No.		°C			μmol/l				μmol/l					μmol/l	(1)	(1)	(2)	(3)	°C	±1 SE		cc(STP)/cc
Berkshire Chalk: open squares=unevolved groundwater																						
05u	Woodgarston PS	11.1	7.0	0.54		5.30	0.08	0.04		0.37	0.04	2.94	0.09		-48	-7.3	-13.8		9.6	0.5	1.21	5.1
01u	Boxalls Lane PS	11.6	6.90	0.87		5.38	0.85	0.90		1.06	0.15	4.04	0.24		-46	-7.0	-13.7	60.4	9.4	0.5	1.56	4.6
22u	Brightwalton PS	11.1	7.22	0.40		5.34	0.04	0.36		0.37	0.03	3.09 (5)	0.08		-50	-7.7	-13.7	62.1 (5)	10.5	0.5	1.15	4.8
04u	West Ham PS	12.0	7.07	0.59		5.20	0.14	0.52		0.70	0.03	3.19	0.08		-46	-6.9	-13.5	78.5	9.7	0.5	1.22	4.7
08c	Little Pk Fm	12.3	7.55	1.47	1.10 (5)	4.71	0.52	0.04	2.45 (5)	2.35	0.26	1.22	1.13	49.7 (5)	-46	-7.2	-13.4	22.9	6.7	0.7	1.25	208.0
17u	College Ave	11.5	6.98	0.85		5.56	0.40	0.76		0.90	0.07	3.78	0.14		-51	-7.3	-13.3		10.1	0.5	1.19	5.9
19u	Star Works	16.5	7.08	1.52		4.72	2.56	0.04		3.02	0.21	2.97	1.49		-45	-6.7	-13.2	70.7	13.1	0.5	1.28	4.4

02u	Itchell PS	11.2	6.85	0.56		5.03	0.28	0.71		0.43	0.05	3.39	0.16		-45	-7.3	-13.2		9.1	0.6	1.31	5.0
18u	Cookham PS 5	11.5	6.99	0.68		5.59	0.23	0.55		0.62	0.07	3.52	0.15		-50	-7.7	-13.1		10.0	0.5	1.17	6.0
20u	Theale PS	10.8	6.92	0.96	1.25 (5)	6.26	1.31	0.11	1.20 (5)	1.16	0.11	3.84	0.34	16.9 (5)	-48	-7.4	-12.3	55.4 (5)	9.7	0.5	1.12	12.2
03u	Greywell PS	10.5	7.15	0.45	0.69 (5)	5.15	0.16	0.36	0.20 (5)	0.56	0.04	3.07	0.10	3.6(5)	-47	-7.0	-10.1	68.7 (5)	9.6	0.5	1.42	4.8
21u	Chievely PS	10.8	7.20	0.45	0.73 (5)	5.08	0.13	0.52	0.35 (5)	1.28	0.05	2.72 (5)	0.16	4.8(5)	-53	-7.8	-8.1	56.3 (5)	9.1	0.5	1.35	76.9

Berkshire Chalk: filled squares=evolved groundwater

09c	Bishop's Green	12.1	7.08	0.25		4.36	0.14	0.23		0.38	0.04	2.46	0.16		-46	-7.2	-7.3		8.4	0.5	1.33	25.4
15c	Toutley PS 2	12.9	7.63	3.47		4.75	0.68	0.04		5.52	0.29	0.97	0.97		-53	-8.1	-6.1	1.4	4.4	0.8	1.40	701.0
16c	Beenham PS 1	11.4	7.36	4.96		5.12	1.31	0.04		5.39	0.28	1.81	1.22		-50	-7.5	-5.6	6.6	5.1	0.5	1.40	486.0
10c	Sterling Green.	11.4	7.18	0.37		4.84	0.22	0.11		0.86	0	2.28	0.43		-47	-7.1	-3.6					
06c	Sherfield Manor	12.7	7.44	0.42		4.84	0.23	0.04		1.17	0.16	1.67	0.87		-46	-7.3	-3.0	3.4(5)	7.5	0.5	1.30	175.0
11c	Ufton Nervet	11.3	7.21	0.42	1.36 (5)	5.07	0.31	0.10	1.53 (5)	1.01	0.11	2.19	0.68	49.7 (5)	-50	-7.2	-3.0	2.6(5)	8.3	0.5	1.30	81.8
13c	Grazeley Ct.	14.4	7.80	2.65		4.71	0.44	0.04	3.46 (5)	4.35	0.24	0.89	1.00	52.5 (5)	-51	-7.6	-2.5		5.4	0.5	1.37	494.0
12	Grazeley PS	11.8	7.45	2.17	3.94 (5)	4.98	0.71	0.04	3.10 (5)	3.30	0.25	1.29	1.28	67.9 (5)	-50	-7.8	-2.1	1.1(5)	6.3	1.0	1.34	405.0

c																						
07c	Lawn Fm	13.5	7.91	7.02		4.80	0.70	0.04	3.17 (5)	9.44	0.24	0.62	0.64	30.8 (5)	-51	-7.7	-1.7		5.7	0.5	1.34	1301.0
14c	Food Res. Inst.	12.4	7.40	3.55	6.76 (5)	5.43	0.47	0.04	3.53 (5)	5.13	0.25	1.08	1.07	49.7 (5)	-51	-7.7	-0.4	1.9(5)	5.7	0.5	1.28	649.0

All chemical analyses in mmol/l unless stated otherwise; c=confined; u=unconfined; PS=Pumping Station; RT=Noble gas recharge temperature; EAI=Excess Air Index; 1SE=1 standard error;(1)‰ relative to SMOW; (2) ‰ relative to PDB; (3) % modern C; (4) Data from Smith et al. (1976) and Downing et al. (1979); (5) Data from Edmunds et al. (1987).

Full-size table

Table 3. Dissolved radioelement contents in London and Berkshire Basin Chalk groundwaters

No.	Name	NGR	U		234U/238U		222Rn*		226Ra		228Ra/226Ra	
			μ g/kg±		(A.R.)±		pCi/kg±		pCi/kg±		(A.R.)	
London Chalk (prefix LN): open circles=unevolved groundwater												
22u	Burnham PS	SU 9295 8290	0.431	0.004	1.38	0.02	72	4	0.03	0.003		
01u	George Paynes	TQ 308 647	0.718	0.004	1.16	0.01	101	6	0.017	0.002	0.573	0.003
02u	Philips 2*	TQ 307 654	0.5015	0.0035	1.225	0.014	193	12	0.03	0.004	0.248	0.003
06c	Unigate Dairies	TQ 305 779	1.241	0.013	1.28	0.02	300	18	0.13	0.006	0.340	0.005
20u	Sanderson 2	TQ 054 851					132	3	0.06	0.004	0.222	0.003
23u	Nicholas Labs.	SU 952 806	0.809	0.007	1.12	0.01	65	1	0.04	0.004	0.604	0.009
05c	Sunlight Laundry	TQ 302 750	0.025	0.001	1.84	0.08	71	2	0.11	0.01	0.292	0.006
21c	Pinewood Studios 1	TQ 018 843	1.113	0.007	0.92	0.01	287	6	0.09	0.005	0.203	0.009
London Chalk (prefix LN): filled circles=evolved groundwater												
07	Harrods 2	TQ 276	0.359	0.004	1.81	0.03	62	6	0.07	0.007		

c		794										
04 c	Modeluxe Linen	TQ 256 705	0.007	0.001	1.54	0.08	108	15	0.10	0.01	0.242	0.005
03 c	BXL Plastics	TQ 299 672	1.508	0.014	2.20	0.02	129	12	0.12	0.01		
08 c	Buchanan House	TQ 290 806	0.083	0.001	1.99	0.04	168	9	0.21	0.013	0.54	0.02
12 c	Hornsey Rd Baths	TQ 307 864	0.105	0.002	2.67	0.05	176	3	0.28	0.01	0.221	0.007
13 c	Kentish Town Baths	TQ 288 847	0.564	0.005	1.89	0.02	87	3	0.10	0.005		
24 c	Neville and Griffin	SU 978 804	0.037	0.001	1.49	0.04	136	16	0.13	0.006	0.224	0.006
11 c	Unilever 2	TQ 315 809	0.999	0.014	1.87	0.03	59	5	0.04	0.005		
09 c	Dorset House 2	TQ 278 820	0.715	0.008	2.04	0.03	86	5	0.04	0.004	B/D	
19 c	Kodak	TQ 146 898	0.136	0.001	1.73	0.02	57	26	0.04	0.005	0.500	0.030
17 c	Glaxo	TQ 1497 8455	1.395	0.009	1.58	0.01	63	11	0.001	0.0005		
10 c	Sainsburys	TQ 316 804	0.451	0.008	1.79	0.04	100	8	0.09	0.007	0.287	0.007
18 c	Lyons Tetley	TQ 146 843	1.184	0.011	1.40	0.02	69	5	0.08	0.007		
16 c	PFW Ltd	TQ 170 834	2.354	0.012	0.99	0.01	61	5	0.059	0.004	0.129	0.005
15 c	Hoover	TQ 167 830	0.328	0.003	1.22	0.02	64	1	0.03	0.003		
14 c	Crown Cork	TQ 110 794	0.026	0.002	3.28	0.25	171	21	0.11	0.009	0.300	0.050

Berkshire Chalk (prefix BK): open squares=unevolved groundwater

05 u	Woodgarston PS	SU 587 550	0.234	0.002	1.32	0.02	120	3	0.07	0.003
01	Boxalls Lane PS	SU 850	0.661	0.008	1.30	0.02	111	3	0.2	0.005

u		480								
22 u	Brightwalton PS	SU 4257 7940	0.194	0.002	1.60	0.02	109	2	0.2	0.005
04 u	West Ham PS	SU 625 523	0.237	0.002	1.29	0.02	84	9	0.07	0.005
08 c	Little Park Farm	SU 6792 6307	0.022	0.0004	4.49	0.11	517	2	0.2	0.01*
17 u	College Avenue PS	SU 883 813	0.867	0.006	1.20	0.01	62	4	0.09	0.005
19 u	Star Works	SU 819 795	1.985	0.011	1.34	0.01	172	1	0.2	0.005
02 u	Itchell PS	SU 775 500	0.494	0.004	1.13	0.01	102	2	0.2	0.01
18 u	Cookham PS 5	SU 880 845	0.687	0.006	1.24	0.01	41	3	0.02	0.002
20 u	Theale PS	SU 645 724	1.093	0.007	1.33	0.01	76	4	0.6	0.10*
03 u	Greywell PS	SU 7227 5135	0.327	0.005	1.27	0.03	100	3	0.2	0.01
21 u	Chievely PS	SU 4763 7515	0.289	0.003	1.42	0.02	87	1	0.1	0.005
Berkshire Chalk (prefix BK): filled squares=evolved groundwater										
09 c	Bishops Green PS 3	SU 501 635	0.453	0.005	1.20	0.02	61	1	0.25	0.05*
15 c	Toutley PS 2	SU 801 704	0.007	0.0002	2.94	0.09	154	18	0.57	0.11*
16 c	Beenham PS 1	SU 851 751	0.332	0.004	1.93	0.03	69	4	0.2	0.005
10 c	Sterling Greengate	SU 598 672	0.009	0.0002	1.89	0.07	50	1	0.3	0.01*
06 c	Sherfield Manor Sch	SU 681 571	0.004	0.0003	1.45	0.14	60	1	0.25	0.05*
11 c	Ufton Nervet PS	SU 6232 6824	0.006	0.0002	1.13	0.06	56	2	0.23	0.04*
13	Grazeley Court	SU 693	0.019	0.0004	2.25	0.07	112	3	1.07	0.04*

c	Farm	674								
12 c	Grazeley PS	SU 6869 6801	0.008	0.0004	2.34	0.14	78	7	0.08	0.003
07 c	Lawn Farm	SU 6998 6011	0.098	0.0003	2.53	0.09	68	1	0.2	0.007*
14 c	Food Res. Institute	SU 7295 6826	0.017	0.0003	1.94	0.05	64	1	0.5	0.007*

NGR=UK National Grid Reference; (A.R.)=activity ratio; PS=Pumping Station; Sch=School.All errors are ±1 σ counting errors, except * which are standard errors (±1 SE) in mean of duplicate samples.Scintillation flask blank is 0.02±0.02 pCi/kg (±1 σ). B/D=below detection limit.N.B. 238U=0.734 U dpm/kg (1 disintegration per minute, dpm =0.45 pCi).

Full-size table

Excepting field parameters (T° C, specific electrical conductivity (SEC), pH, Eh, dissolved O2, and alkalinity) which were determined on site at the well-head, hydrochemical analyses were performed at British Geological Survey (BGS), Wallingford, UK. Samples for analysis of inorganics were 0.45 μm filtered into acid-washed polyethylene bottles, one aliquot being acidified to pH ≤2 by addition of high purity HNO3 for analysis of cations. Analyses for Cl, NO3–N and Br were performed by automated colorimetry on the unacidified aliquot for anions (Cook and Miles, 1980). The cations and also SO4–S were determined by inductively-coupled plasma optical emission spectrometry (ICP–OES; e.g., Miles, 1987).

Radiochemical analyses were performed in the School of Chemistry, University of Bath, UK. Water samples for the determination of total dissolved U-content and 234U/238U activity ratio were collected in 60-l acid-washed polyethylene containers. On collection, samples were acidified to pH<2 and a 236U tracer spike (8.91±0.08 dpm) added to quantify the chemical yield of U extraction, in addition to 900 mg of Fe3+ carrier. In the laboratory, U was co-precipitated with Fe3+ under alkaline conditions, then separated from Fe, Ca, Mg and other elements in the precipitate by solvent extraction and ion-exchange procedures (Andrews and Kay, 1983). The extracted U was then electro-deposited onto a steel planchet and its activity counted in a silicon surface barrier α-spectrometer. Samples for dissolved radiogenic 222Rn determination were collected in gas-tight throughflow bottles with sealable inlet and outlet tubes. The 222Rn was outgassed into a scintillation flask using a N2 stream and its activity determined by α-scintillation counting. Samples for Ra determinations were filtered (0.45 μm) into a 5 l acid-washed container, and acidified. Recovered samples for 226Ra contents were transferred to glass de-emanation bottles and 222Rn outgassed using N2. The bottles were sealed and left one month for ingrowth of 222Rn to its equilibrium activity with 226Ra, subsequently determined as for dissolved Rn samples. Samples for Ra activity ratios were recovered using the MnO2 powder scavenging method, subsequently leached with 2N HNO3 and co-precipitated as Ba(Ra)SO4. Radium isotope activities were then counted using a hyperpure (Li-drifted) Ge γ-ray spectrometer (cf. Michel et al., 1981).

Water samples for stable isotope analyses (2H, 18O, 13C) were collected in glass bottles, and δ-values subsequently analysed at BGS Wallingford using a VG Micromass 602E mass spectrometer and related to the SMOW or PDB standards. 14C and again δ 13C were determined on BaCO3 precipitated from 60–120 l samples, and analysed at the UK Natural Environment Research Council (NERC) Radiocarbon Laboratory, East Kilbride. 14C was determined radiometrically by liquid scintillation counting after conversion to benzene (IAEA, 1968).

For noble gas analyses, replicate 5 ml samples were collected in Cu tubes under pressurised flow conditions to avoid air contamination and sample degassing. The tubes were then closed by swaging clamps. Noble gases were determined by isotope dilution mass-spectrometry after vacuum extraction and separation by adsorption on charcoal (Andrews and Lee, 1979; Elliot, 1990).

Thermodynamic calculations of hydrochemical speciation and mineral saturation indices were performed using the geochemical code WATEQ4F (Ball et al., 1987) updated for trace element species including U (Ball et al., 1981).

3. Results and discussion

In the following discussions, for each Basin the groundwaters are further subdivided into two groups based on their 13C contents: (i) a younger and less evolved group with δ 13C<−8‰ PDB; and (ii) an older and more evolved group with δ 13C>−8‰ PDB. The less evolved groundwaters are identified on all figures by open symbols, and the evolved group by filled symbols. The basis for, and significance of, this subdivision are explained in the text. The principal changes in hydrogeochemistry taking place along the principal axes (W−E and S−N; Fig. 1) for hydraulic gradients into the centre of the London Basin are illustrated in Fig. 2Fig. 3Fig. 4Fig. 5Fig. 6Fig. 7Fig. 8Fig. 9.

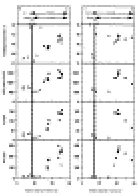

Fig. 2. Downgradient trends in sampling temperature, electrical conductivity and major ions (Na, Cl) along the W−E and S−N sampling lines across the London Basin.

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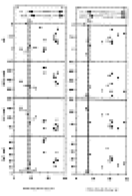

Fig. 3. Downgradient trends in carbonate system parameters (pH, HCO3, Ca, Mg) along the W−E and S−N sampling lines across the London Basin.

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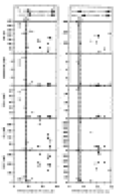

Fig. 4. Downgradient trends in redox system parameters (Eh, dO2, NO3, Fetotal,SO4) along the W−E and S−N sampling lines across the London Basin.

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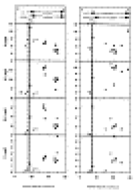

Fig. 5. Downgradient trends in minor element concentrations (Si, K, Sr, F) along the W–E and S–N sampling lines across the London Basin.

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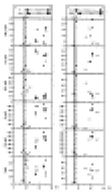

Fig. 6. Downgradient trends in minor and trace element concentrations (Mntotal, Li, Ba, B, Br, Itotal) along the W–E and S–N sampling lines across the London Basin.

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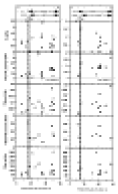

Fig. 7. Downgradient trends in radieolement contents and activities (U, 234U/238U, 226Ra, 228Ra/226Ra, 222Rn) along the W–E and S–N sampling lines across the London Basin.

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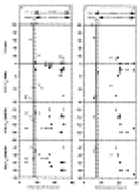

Fig. 8. Downgradient trends in environmental isotopic parameters (14C, 13C, 18O, 2H) along the W–E and S–N sampling lines across the London Basin.

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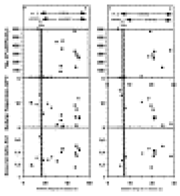

Fig. 9. Downgradient trends in dissolved gas parameters (4He, RT, EAI) along the W–E and S–N sampling lines across the London Basin.

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3.1. Hydrogeochemical changes downgradient and groundwater evolution in the London Basin

The overall chemical trends across both the Berkshire and London Basins may be discussed relative to Cl^- as a conservative element. The unconfined and peripherally-confined zones of the London Basin show low salinity groundwaters with SEC <1000 μS/cm, Na ≤30 mg/l and Cl ≤35 mg/l (Fig. 2). In the confined aquifer these concentrations increase progressively in a downgradient direction. In the Berkshire Basin, which has not been influenced by major overexploitation, there is a progressive downgradient increase in Cl^- to ≈200 mg/l in the deepest groundwaters caused by mixing with residual formation water and which attains a maximum Cl^- concentration of approximately one-tenth that of seawater (Edmunds et al., 1987); a similar increase along the flowgradient is seen in the London Basin waters (Fig. 2). In the London Basin, maximum Cl^- concentrations also are ≈150 mg/l. Thus in the Chalk, increases in Cl^- downgradient may be used as an indicator of groundwater evolution, predominantly reflecting the progressive admixing of original formation water salinity in evolved groundwater. The apparent salinity decrease along the S–N sampling line (Fig. 2) for waters sampled northwards from central London (i.e., at distances >20 km along the line of section) traces flow coming from northern recharge.

The molar ratio of Br^-/Cl^- may be used to help characterise the source and evolution of the dissolved Cl^- as marine and evaporite sources have characteristic signatures (cf. Richter and Kreitler, 1993; Edmunds, 1996). Fig. 10a shows that most waters have Br^-/Cl^- ratios close to the marine value (≈1.5×10^{-3}), confirming the seawater provenance of the chlorinity in downgradient waters, and indicating that even recharge waters reflect the marine aerosol ratio. In contrast to Cl^- and Br^-, other major and minor ion concentrations have been modified by geochemical reactions during groundwater migration. Concentrations of the alkali metals (Na, K and also Li) generally increase downgradient from outcrop (Fig. 2 and Fig. 5 and Fig. 6). The peak in Na^+ values is displaced along the lines of sections relative to the peak of Cl^- (Fig. 2), and there is an apparent excess over simply seawater admixture which is also shown for Li^+ (Fig. 10b,c). The degree to which the Na^+/Cl^- ratio exceeds the marine input molar ratio (≈0.86) is a measure of the extent of cation exchange of Ca^{2+} and/or Mg^{2+} for equivalent Na^+. From mass balance considerations, Elliot (1990) estimated that 50% of the dissolved Na^+-contents in waters from the centre of the London Basin may be so derived, whereas the estimate for the Berkshire Basin is only 14% (Edmunds et al., 1987). Similar clay mineralogies occur in both Basins, with high cation exchange capacity smectite and illite in nodular horizons and marl bands throughout the Upper and Middle Chalk but illite dominant in the Lower Chalk (Morgan-Jones, 1977), so that the differing estimates may reflect longer residence times or the extent of greater interaction with overlying Tertiary beds in the London Basin.

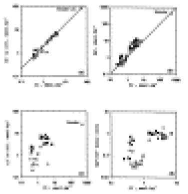

Fig. 10. Logarithmic plots of relationships between concentrations (mmol.kg^{-1}) of chemical species: (a) Br^- versus Cl^-; (b) Na^+ versus Cl^-; (c) Li^+ versus Cl^-. The solid line is the concentration/dilution line for seawater composition (or an unfractionated marine aerosol). (d) Molar Mg^{2+}/Ca^{2+} ratio versus Cl^-. Note the increase in ratio prior to any chlorinity increase in the unevolved waters.

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Elliot (1990, his Figures 7.12 and 7.14) argues from "anomalous" water chemistry for some Berkshire Chalk sites and more generally from Cl^- vs. SEC relationships identified for both Basins, that there is a component of vertical leakage from the overlying Tertiary cover into the Chalk aquifer of the London Basin. An admixture of ≤10% of vertical leakage waters from the overlying semi-permeable cover can account for SO_4 concentrations in the central London Basin (Ineson and Downing, 1963; Water Resources Board, 1972; Elliot, 1990).

Downgradient changes in dissolved HCO_3, pH, Ca, Mg, Sr (and $\delta^{13}C$) reflect reactions with carbonate minerals. Groundwaters tend to become rapidly saturated with calcite; the Mg^{2+}/Ca^{2+} ratio (Fig. 10d) increases progressively during groundwater evolution, reaching a maximum value of around unity consistent with equilibrium with both calcite and dolomite (Edmunds et al., 1987) and supported by mineral saturation indices (Elliot, 1990). Significantly, the Mg^{2+}/Ca^{2+} ratio increase occurs initially independently of Cl^- in the unevolved freshwaters (Fig. 10d). For these waters in both Basins, the molar ratio of $(Ca-SO_4)/HCO_3$ corrected assuming gypsum dissolution to be the source of dissolved SO_4 (Morgan-Jones, 1977) is approximately 1:2 indicating the congruent dissolution of calcite according to the equation $CaCO_3(s)+H_2CO_3=Ca^{2+}+2HCO_3^-$ (Fig. 11a). The average $\delta^{13}C$ value for soil CO_2 in Britain is −26.1±0.3‰ (Smith et al., 1976), and that for the Chalk matrix is 2.3±0.5‰ (Scholle, 1977; Downing et al., 1979; Bath and Edmunds, 1981). Congruent dissolution of calcite by dissolved soil CO_2 would therefore produce HCO_3^- with a $\delta^{13}C$ value ≈−12‰ (see Eq. (A.1)) A large group of the least evolved waters have $\delta^{13}C$ ≈−13.5‰ in acceptable agreement with the end result of congruent reaction between dissolved soil CO_2 and the carbonate matrix in the unconfined aquifer. Both Mg and Sr contents subsequently increase by incongruent reaction: an enhancement of both the $Mg/(Ca-SO_4)$ and $Sr/(Ca-SO_4)$ molar ratios with more positive $\delta^{13}C$ values than ≈−13.5‰ is evident (Fig. 11b,c) and indicates the importance of concurrent dissolution–precipitation processes in the carbonate system (Edmunds et al., 1987; Kloppmann et al., 1994). Thus, generally the ratios Mg^{2+}/Ca^{2+} and Sr^{2+}/Ca^{2+} may be used as a separate indicator of groundwater evolution, since their increase is initially independent of Cl^- in the unevolved waters as a result of time-dependent water–rock interaction and/or mixing with an evolved freshwater. Water–rock interaction similarly explains the general downgradient increase in $\delta^{13}C$ of evolved waters (Fig. 8). Leakage of waters from the confining Tertiary cover may also enhance Mg and Sr contents (cf. sites BK08, BK19, BK20, LN06, Fig. 11b,c; Bath et al., 1989).

Fig. 11. (a) $(Ca-SO_4)$ plotted against HCO_3 molar concentrations for evolved and unevolved groundwaters, showing the stoichiometry of carbonate dissolution. Additional data (triangular symbols) have been included from the Berkshire Chalk study of Edmunds et al. (1987); (b) $Mg/(Ca-SO_4)$ and (c) $Sr/(Ca-SO_4)$ molar ratios (i.e., the mMg/mCa and mSr/mCa ratios corrected for gypsum dissolution) plotted against $\delta^{13}C$(‰) for the unevolved waters. The apparent negative correlation for the marked sites could relate to significant admixture of Mg- and Sr-rich leakage waters from the Tertiary cover (cf. Kloppmann et al., 1994).

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3.2. Redox system

Measured redox potentials, Eh, are +250 to +320 mV in unconfined London waters, but decrease to around +100 mV more or less coincident with aquifer confinement (Fig. 4). Dissolved O_2 concentrations are 5–7 mg/l in the unconfined aquifer, falling to <1 mg/l upon aquifer confinement and <0.2 mg/l throughout much of the confined sections. Nitrate concentrations are around 50 mg/l in the unconfined waters, falling to zero more or less coincident with aquifer confinement and generally remaining below detection limits throughout the confined section. A redox barrier therefore exists in the confined sections (shown in Fig. 2, Fig. 3, Fig. 4, Fig. 5, Fig. 6, Fig. 7, Fig. 8 and Fig. 9) coincident with the drop in Eh values to around +100 mV. Total dissolved Fe concentrations (≤0.45 μ m fraction) are below the detection limit of ~1 μ g/l in unconfined oxygenated waters, but increase in the anaerobic confined aquifer to ≥0.1 mg/l. Sulphate concentrations are unrelated to the redox conditions, but may help in stabilising dissolved Fe contents as FeSO04 under reducing conditions. Despite the presence of traces of dissolved sulphide in the reducing zone of the Berkshire Chalk (Edmunds et al., 1984), SO4 reduction is generally considered negligible in the Chalk. Kimblin and Johnson (1992Kimblin and Johnson, 1994) have inferred that active SO4 reduction occurs in the London Chalk based on a decrease in interstitial SO2–4 contents with depth from the overlying Basal Sands aquifer into the underlying Chalk. However, a concomitant diminution for other species concentrations (Kinniburgh et al., 1994, their Figure 11) suggests a dilution effect (Elliot and Younger, 1994). Some variation in Fe(total), Eh and SO4 levels for sites in Central London (Fig. 4) are further suggestive of localised admixture of more oxidising waters percolating through the Tertiary cover.

3.3. Trace and minor elements in the London Basin groundwaters

Several minor and trace elements (K, Sr, F, Ba, Li, Mn, B, I) have been identified as being diagnostic of the chemical evolution of groundwater in the Chalk of the Berkshire Basin (Edmunds et al., 1987); these are briefly described here to follow trends within the London Basin.

Variations in potassium concentrations are associated with Mg2+ in the initial stages of aquifer confinement; the strong increase prior to a salinity increase probably reflects K+ release during freshwater diagenesis of clay minerals in the Chalk. The most saline interstitial formation waters of the Berkshire Chalk are relatively depleted in K+, which was incorporated into the clays during early diagenesis (Edmunds et al., 1987); the decrease in K+ accompanying Na+ increase in the more saline waters relates to progressive admixture of this connate water component. Peak values in K+ occur prior to the peak in Na+ levels, and are displaced slightly downgradient of Mg2+; the K-decrease towards Central London along the W–E profile indicates an ion-exchange sequence.

Two modes of strontium occurrence in the Berkshire Chalk groundwaters are proposed by Edmunds et al. (1987): (i) very high values of Sr2+ in (saline) interstitial pore fluids are related to early diagenetic reactions of original aragonite and high-Mg calcite; (ii) continuous and active diagenesis of the resultant low-Mg calcite in the Chalk by groundwater flow leads to the significant increase in Sr2+ at nearly constant values of Cl–. The initial abrupt increase in Sr2+ contents on aquifer confinement in the London Basin is associated with Mg2+, and can be related to this latter process of continuous freshwater diagenesis of the Chalk. Sr2+ concentrations in the deep London Basin groundwaters (2 mg/l) are slightly lower compared with 4 mg/l in Berkshire.

Fluoride shows an initial increase in values that can be related to progressive reaction with the Chalk matrix. The most likely source of F– is the reaction of apatite (or fluorapatite), present as an accessory mineral especially in the Upper Chalk. Fluoride concentrations generally increase to around 2 mg/l in the centre of the Basin (Fig. 5), controlled by solubility with respect to fluorite.

The abrupt increase in barium with confined conditions may also relate to active freshwater diagenesis of the Chalk (Fig. 6). Mineral equilibrium calculations indicate that barite (BaSO4) solubility may control Ba2+ concentrations.

Lithium concentrations generally display the same trends as Sr2+ and K+. The initial increase reflects freshwater diagenesis of the Chalk, with preferential release of Li+ from clay or carbonate minerals. In the confined waters there is an increase in the Li+/Na+ ratios towards values similar to those found in evolved connate waters of the Berkshire Basin (Edmunds et al., 1987).

Manganese occurs at concentrations of 100–200 mg/kg in the Berkshire Chalk (Edmunds et al., 1987) and is released during carbonate dissolution. In view of the low concentrations in the unconfined groundwaters (Fig. 6) Mn2+ is evidently removed from groundwater by oxidation.

The main source of boron relates to the increase in groundwater salinity: molar B/Cl ratios are around 6 × 10–3 in freshwaters, rising to values of 0.01–0.02 (higher than seawater ≈7.6 × 10–3).

Iodine concentrations increase on aquifer confinement before any increase in Cl– (Fig. 2 and Fig. 6). I– may be released during oxidation of organic matter, or during the reaction of fluoroapatite. There is a general broad increase in iodide concentrations following the rise in salinity.

3.4. Dissolved radioelements

Uranium and Th contents of the Chalk sediment are generally low: ≤1 μg/g U and ≤1.5 μg/g Th (Cuttell et al., 1986; Edmunds et al., 1987; Younger and Elliot, 1995), although higher concentrations may be locally present in phosphatic zones especially in the Upper Chalk (Pacey, 1984). Dissolved radioelement contents and activity ratios (U, 234U/238U, 226Ra, 228Ra/226Ra, 222Rn) from both Basins are presented in Table 3; 234U and 228Ra contents may be derived from these values.

Total dissolved U concentrations are relatively high in the oxygenated waters of the London Basin, up to 2.35 μg/l (Fig. 7). Lower concentrations (<0.5 μg/l) occur generally under the reducing conditions of the confined aquifer (Eh<+100 mV). However, U mineral solubility controls are not apparent: all waters remain significantly undersaturated in the common U minerals coffinite (USiO4) and uraninite (UO2), although the latter has been suggested as the control in the most reducing waters of the Chalk aquifers of the Paris and northern Germany Basins (Kloppmann et al., 1996). The corresponding pattern in the 234U/238U activity ratio values for the London Chalk is a general progressive increase from around 1.2 at aquifer outcrop to >2 in the centre of the confined basin (Fig. 7). This may reflect the preferential solution of 234U under reducing conditions by an α-recoil mechanism (Kigoshi, 1971; Andrews and Kay, 1983).

A similar pattern for U is found in the Berkshire Basin groundwaters: dissolved U concentrations range over 0.004–2.0 μg/l, and again display a bimodal distribution reflecting the redox control. In the oxidising (Eh≤+250 mV) aquifer, U contents are >0.1 μg/l with a geometric mean of 0.35 μg/l (n=11); under reducing conditions (Eh<0, averaging –30 mV) towards the centre of the confined Basin, U concentrations are <0.1 μg/l, with a geometric mean of 0.0095 μg/l (n=9), but again with no apparent U mineral solubility control. The highest U concentrations in the oxidising aquifer (>1 μg/l) are found at Theale (BK20) and Star Works (BK19) where there is evidence of a mixing of water from overlying Tertiary deposits (Fig. 12; cf. Elliot, 1990; Bath et al., 1989). A broad trend to increasing U with salinity in the confined waters may reflect progressive admixture of a connate component. Again samples have significantly enhanced 234U/238U activity ratios (>1.0) with values of around 1.3 in the high-U content, oxidising part of the aquifer, but much greater enhanced values (≥2.0) occurring in the low-U content waters in the centre of the Basin related again to recoil solution of 234U under reducing conditions.

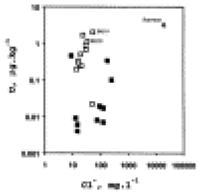

Fig. 12. Logarithmic plot of relationship between concentrations of U versus Cl in the Berkshire Basin waters. The two sites marked are Theale (BK19) and Star Works (BK20), both peripherally-confined samples.

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Dissolved 226Ra activities range over 0.001–0.28 pCi/l, with a modal value of around 0.04 pCi/l. There are no significant trends in dissolved 226Ra activities, nor in 228Ra/226Ra activity ratios along the flow gradients (Fig. 7): mean values are 0.069 ± 0.039 pCi/l and 0.33 ± 0.15 (1 σ , n=22), respectively. The constant 228Ra/226Ra activity ratio may reflect the micro-distribution of Th in relation to U at the rock–water interface (cf. King et al., 1982; Nordstrom et al., 1985) and would suggest a Th/U (weight) ratio of 1.00 ± 0.45, similar to cited values of around 1.5 in the Berkshire Chalk (Edmunds et al., 1987). Ra-226 activities in the Berkshire waters range over 0.02–1.07 pCi/l with a modal value of 0.2 pCi/l and mean value of 0.26 ± 0.24 (1 σ , n=22), again with no significant variation over the Basin but with generally higher levels than for the London Basin.

Dissolved 222Rn activities are variable across the London Basin (Fig. 7). Activities from both Basins generally range between 40–517 pCi/l, and the data display two log-normal distributions with modal values of 65 and 106 pCi/l, and corresponding geometric means of 66 ± 10 pCi/l (1 σ , n=25) and 125(+45,–33) (1 σ , n=18) respectively, for a discriminatory 222Rn threshold activity of 90 pCi/l. The Chalk is predominantly a fracture-flow system with regard to regional groundwater abstraction; geochemical modelling of these Rn-contents following Andrews et al. (1986) allows estimation of in situ fracture aperture dimensions (Elliot, 1990; Younger and Elliot, 1995). For a rock U content in the Chalk, [U]r=0.1 μ g/g (Cuttell et al., 1986), a 222Rn content of 66 pCi/l could be derived by flow in fractures with widths of around 100 μ m, more or less appropriate for the primary fissures system (Price et al., 1996). Higher 222Rn contents might be associated with U-rich phosphatic zones or flow in a system with smaller fracture apertures.

3.5. Carbonate system evolution and carbon isotope (13C, 14C) systematics

The total dissolved inorganic C (TDIC) is equivalent to the groundwater HCO3 content for the observed pH-range. Most samples are close to calcite saturation, with saturation indices (SIcalcite) in the range –0.2 to +0.1. There is generally little variation in TDIC although some increase is observed for the most evolved waters of the London Basin (Fig. 3 and Fig. 13a). The slightly higher concentrations in HCO–3 for evolved waters may be caused either by oxidation of organic matter, carbonate dissolution driven by cation exchange and the common ion effect, or by incongruent reaction of the carbonate matrix. Oxidation of organic matter must be small because 13C contents increase with alkalinity (Fig. 13a), whereas alkalinity derived from organic matter oxidation would have depleted 13C contents (Thorstenson et al., 1979). Ion exchange-induced dissolution of the primary marine carbonate of the matrix is also likely limited in this aquifer, reflected in only a slight increase of 0.2–0.5 pH units for the most evolved groundwaters (Fig. 3). Adjustment of HCO–3 at equilibrium due to incongruent reaction is the likely explanation. A large group of the least evolved waters in both Basins (Fig. 13a,b) have δ 13C values ≈–13.5‰, in acceptable agreement with simple congruent reaction between dissolved soil–CO2 and the carbonate matrix. Groundwater evolution then takes place generally under closed-system conditions with respect to atmospheric CO2. Heavier isotopic contents >–13.5‰ must involve incongruent reaction with the Chalk under a closed system.

Fig. 13. (a) Alkalinity of groundwater vs 13C of TDIC for London and Berkshire groundwaters; (b) 13C of TDIC vs Cl^{-} content; (c) 14C of TDIC (% modern C) vs 13C. Lines A, B1 and B2 are explained fully in the text.

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As for the Berkshire Basin, the predominant cause of alkalinity increase is therefore either incongruent dissolution/precipitation processes leading towards 13C equilibration with the Chalk matrix and/or mixing between water in the fracture flow system and evolved 13C-equilibrated interstitial waters. Alkalinity values up to 6.5 mmol/l (400 mg/l) have been reported for extracted Chalk porewaters from a borehole in the Berkshire Basin (Edmunds et al., 1987), comparable with the alkalinity for the most evolved groundwaters in the London Basin (Fig. 3). However, for the deepest groundwater samples attaining a temperature of ≈15° C (Table 1 and Table 2), TDIC in equilibrium with the matrix would be ≈0.4‰ lighter than the solid calcite (Mook, 1980), i.e., δ 13C ≈1.9±0.5‰. The trends in Fig. 13a,b show that for the most evolved waters δ 13C ≈ −1.0‰. Either the interstitial water end-member for the mixing series (the RT/ δ 13C relationship, Fig. 14) is not fully equilibrated with the matrix or interstitial surfaces have undergone isotopic exchange during prolonged groundwater flow such that they do not exactly reflect the bulk Chalk value.

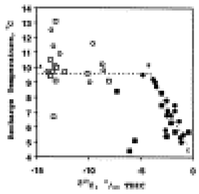

Fig. 14. Noble gas derived recharge temperatures vs 13C of TDIC (° /oo relative PDB) for London and Berkshire groundwaters. Lines AB and BC are explained fully in the text.

View thumbnail images

Downgradient trends in C isotopic contents of TDIC in the London Basin clearly show heavier δ 13C values corresponding with diminishing values of 14C activities towards the centre of the Basin (Fig. 8 and Fig. 13c). Groundwaters with more than 50% modern C after congruent dissolution must be of recent origin, and some of these may contain an input of 14C from thermonuclear weapon tests. Under closed (to CO2 input) system conditions, decay of 14C from an activity of 50% modern C in those groundwaters which have attained δ 13C ≈−13.5‰ by congruent dissolution of calcite in the soil zone, would evolve as indicated by line A on Fig. 13c and the positions of such groundwaters after ageing for up to 11.4 ka are indicated by the dotted lines. Significantly, the sites apparently following this evolution trend (e.g., LN06, Fig. 13c) are those considered to be affected by leakage from the Tertiary strata (Fig. 11b,c) which may bring in 14C-aged waters (i.e., delayed in their passage through the cover) without a concomitant δ 13C-evolved signature. Groundwaters which also involve some incongruent exchange of C-isotopes would evolve as indicated by curve B1. The more evolved waters (δ 13C ≥−8.0‰) have clearly undergone incongruent exchange and/or mixing with an evolved 13C-rich TDIC source. Their 14C specific activities decrease towards insignificant values as δ 13C increases. Mixed signatures may occur where high 14C-content waters mix directly with more evolved waters giving curve B2 (Fig. 13c), possibly due to admixing of a rapid flow path from recharge into the aquifer or as result of a faulty borehole lining giving rise to bypass flow; however, the two sites following this curve are both unconfined Chalk sites (BK03 and BK21) and may simply reflect open system evolution.

3.6. Groundwater temperatures and recharge conditions

The temperatures at which recharge waters are equilibrated with air in the unsaturated zone may be determined from the noble gas contents of groundwaters, and generally reflect annually-averaged values (Andrews and Lee, 1979; Herzberg and Mazor, 1979; Stute and Sonntag, 1992). The abundances of Ne, Ar, Kr and Xe dissolved during equilibration of recharge water with air are determined by their solubility/temperature relationships, generally decreasing with increasing temperature (e.g., Benson and Krause, 1976). In temperate latitudes, potential effects of insolation in the subsurface (e.g., Herzberg and Mazor, 1979; Rudolph et al., 1984; Heaton et al., 1986) are minor and the recharge temperatures more or less directly reflect surface conditions. Mean values of the recharge temperature (RT) for the Chalk waters, corrected for any excess air present (EAI is the excess air index normalised to dissolved Ne contents; Andrews, 1992), are reported in Table 1 and Table 2 and are plotted versus δ 13C of the TDIC in Fig. 14. RTs for waters with δ 13C <-8.0‰ are (with one exception) ≥9° C as compared with the modern long-term (30 a) mean annual air temperature at Kew Gardens (London) of 10.5° C (WMO, 1971), although this latter value is influenced by its urban environment and the natural value would be somewhat lower. Those RTs which are ≥11° C indicate that the groundwater either was re-equilibrated with air close to the collection point or (more unlikely) the sample is dominated by a rapid infiltration of summer recharge. The former case may occur as a consequence of the pump not being sufficiently immersed below the dynamic water level.

Significantly cooler RTs occur downgradient towards the centre of the London Basin (Fig. 9) and similar waters are present in the Berkshire Basin (Table 2), suggesting recharge under a colder climate than present. Simplistic adoption of their radiocarbon ages (Table 4) assuming a piston-flow aquifer suggests recharge potentially through the Devensian Last Glacial Maximimum (LGM) period, occurring around 18 ka BP in the UK. The lack of apparent ages between around 13 and 17 ka ago for sampled groundwater (Elliot, 1990) has also been noted for groundwaters from the East Midlands Trias (Andrews and Lee, 1979; Bath et al., 1979; Andrews et al., 1984 and [Andrews et al., 1994]) and also the Lower Greensand and Lincolnshire Limestone aquifers (Darling et al., 1997). This might be ascribed simply to a hiatus of reduced infiltration due to permafrost conditions over the recharge zones during the last pleniglaciation ([Younger, 1989] and [Younger, 1993]). However, a linear mixing-line between δ 13C and RT (line BC, Fig. 14) is demonstrated in the Chalk waters, and from geochemical considerations it may be argued that this reflects admixture between Holocene or very recent infiltration (fracture-borne) with evolved water stored in the matrix porosity of the Chalk. Most of the groundwaters with δ 13C more positive than −8.0‰ lie on this linear mixing trend: over the δ 13C range −4‰ to 0‰, RT is directly proportional to δ 13C. This is attributed to mixing of low 13C content waters recharged at ≈9.5° C (line AB, Fig. 14) with stored interstitial waters which had been recharged at ≈5° C (i.e., around 4.5° C cooler than during the Holocene), and which were 13C-equilibrated with the matrix.

Table 4. Modelling of carbon-14 data for London and Berkshire Basin Chalk groundwaters

No	Name	13C	14C	Model ages in ka					
		(1)	(2)	(a)	(b)	(c)	(d)	(e)	(f)
London Chalk: unevolved groundwater									
LN22 u	Burnham PS	-14.0	60.8 (3)	3.8	-0.01	-0.9	-0.8	-2.0	-1.0
					100	111	110	127	112
LN01 u	Payne	-13.6	66.2	3.1	-0.6	-1.8	-1.7	-2.7	-1.8

						107	124	123	139	124
LN06	c	Unigate Dairies	-12.8	12.6	16.8	11.9	11.6	11.6	11.0	11.4
LN05	c	Sunlight Laundry	-8.7	14.6	15.5	10.8	7.7	7.7	7.3	7.5
LN21	c	Pinewood Studios 1	-8.6	20.8	12.6	8.4	4.7	4.7	4.3	4.6
London Chalk: evolved groundwater										
LN07	c	Harrods 2	-4.8	17.1	14.3	9.2	2.8	2.6	2.2	2.7
LN04	c	Modeluxe Linen	-3.8	4.5	25.8	21.0	13.9	13.8	13.4	12.6
LN08	c	Buchanan House	-3.6	4.3	25.7	21.0	12.5	12.2	11.9	12.6
LN12	c	Hornsey Rd Baths	-2.6	1.4	35.0	29.7	20.4	20.0	19.7	20.7
LN13	c	Kentish Town Baths	-2.6	0.8	39.6	34.4	25.0	24.7	24.3	24.9
LN24	c	Neville and Griffen	-2.5	1.9	32.4	28.1	17.7	17.5	17.1	17.6
LN11	c	Unilever plc 2	-2.5	1.0	37.7	33.0	23.0	22.6	22.3	22.9
LN09	c	Dorset House 2	-2.4	0.8	39.5	34.7	24.7	24.3	23.9	24.6
LN19	c	Kodak plc	-2.1	3.8 (3)	26.7	22.9	11.2	10.8	10.5	11.2
LN17	c	Glaxo plc	-1.7	1.1	39.5	35.3	22.2	21.7	21.3	22.1
LN14	c	Crown Cork plc	-0.9	1.1 (3)	36.9	32.7	20.7	20.3	19.9	20.7
Berkshire Chalk: unevolved groundwater										
BK01	u	Boxalls Lane PS	-13.7	60.4	3.8	-0.1	-1.0	-0.9	-1.9	-1.0
						101	112	112	126	112
BK22	u	Brightwalton PS	-13.7	62.1 (4)	3.6	-1.0	-1.2	-1.1	-2.2	-1.0
						113	116	114	130	113
BK04	u	West Ham PS	-13.5	78.5	1.7	-2.7	-3.2	-3.2	-4.1	-3.3
						138	148	147	164	150
BK08	c	Little Park Farm	-13.4	22.9	11.9	6.7	6.9	7.0	6.1	6.8
BK19	u	Star Works	-13.2	70.7	2.5	-1.9	-2.5	-2.5	-3.2	-2.6
						126	136	136	148	140
BK20	u	Theale PS	-12.3	55.4 (4)	4.5	0.6	-1.0	-1.0	-1.3	-1.1

							113	112	117	114
BK03	u	Greywell PS	-10.1	68.7 (4)	2.8	-1.7	-4.1	-4.1	-4.5	-4.3
						123	165	164	172	167
BK21	u	Chievely PS	-8.1	56.3 (4)	4.4	-0.2	-3.9	-3.9	-4.3	-4.0
						102	161	161	168	163
Berkshire Chalk: evolved groundwater										
BK15	c	Toutley PS 2	-6.1	1.4	35.0	29.8	24.8	24.8	24.4	24.7
BK16	c	Beenham PS 1	-5.6	6.6	22.1	17.3	11.5	11.5	11.1	11.3
BK06	c	Sherfield Manor School	-3.0	3.4 (4)	27.6	22.6	13.7	13.4	13.1	13.6
BK11	c	Ufton Nervet	-3.0	2.6 (4)	29.8	25.2	15.9	15.7	15.4	15.8
BK12	c	Grazeley PS	-2.1	1.1 (4)	36.9	32.0	21.5	21.2	20.8	21.4
BK14	c	Food Res. Institute	-0.4	1.9 (4)	32.4	27.5	12.9	12.2	11.9	12.8

PS=Pumping Station; (1) ‰ rel. PDB; (2) % modern carbon (pmc); c=confined; u=unconfined (3) from Smith et al. (1976) and Downing et al. (1979); (4) from Edmunds et al. (1987).Model details: (a) calculated for equilibration of TDIC with soil CO2 (open system or uncorrected age); (b) calculated for 50% of TDIC derived from rock carbonate (Tamers, 1967); (c) calculated for isotope dilution of 13C and 14C by rock carbonate (Pearson and Hanshaw, 1970); (d) calculated for initial derivation of 50% of TDIC from rock carbonate (see (a)), followed by incongruent exchange between TDIC and rock carbonate (Evans et al., 1979); (e) calculated for initial congruent dissolution of rock carbonate involving no decay, followed by incongruent mixing with 14C-dead pore fluids in equilibrium with the carbonate matrix (see Appendix A); (f) calculated for chemical evolution from recharge conditions to the observed groundwater pH, TDIC, and d13C values of the groundwater (Reardon and Fritz, 1978).Where corrected model ages are negative reflecting modern ages, then the next line represents an estimate of the samples initial activity (% modern C).

Full-size table

It is envisaged that the cold end-member signature for admixture (C, Fig. 14) substantially replaced previous matrix storage via diffusional exchange from fissure waters during extended cold periods. Partial exchange between fissure and matrix waters would mean that the composition of downgradient fracture fluids may be similar to that of the adjacent matrix fluids because of this diffusive exchange, but with limited storage of the signature. Recharge of stored waters at this reduced temperature for the Chalk interstitial fluids must have required an extended time period because this exchange is a relatively slow process. The characteristic time required for total replacement of the matrix fluid by fracture fluid with a different composition may be assessed through a diffusion exchange model or a simple box model of exchange (e.g., Barker and Foster, 1981; Domenico and Robbins, 1985). Such models show that there is a gradual dilution in time and space of matrix solute contents caused by continuous replacement of dilute groundwater in the fracture system. In the case of Cl–, solute diffusion is essentially unidirectional from matrix to fractures. The interdiffusion of H218O and H216O molecules for a significant step change (glacial signature) of $\Delta(\delta$ 18O)=+3‰ in 18O content of the colder higher content infiltrating water relative to the pore water during cooler recharge conditions, would require many thousands of years to change the signature stored in the pore fluids of large matrix blocks.

Palaeoclimatic curves derived from studies of fossil Coleopteran (beetle) assemblages for southern England (Coope, 1977; Atkinson et al., 1987) show that extended cold conditions, on average about 5° C colder than during the Holocene, existed during the Late Pleistocene Upton Warren and Chelford Interstadials prior to the LGM and occurring between 80 and 26 ka ago. A similar RT difference has been observed between Holocene and (pre-LGM) Late Pleistocene recharge in the East Midlands Triassic Sandstone (Andrews and Lee, 1979; Bath et al., 1979; Andrews et al., 1984; Wilson et al., 1994). Geochemical and isotopic evidence has shown that there was adequate precipitation during the Late Pleistocene interstadials to maintain aquifer recharge in the East Midlands Trias (Andrews et al., 1994). These are more likely periods for recharge and replacement of the pore fluids of the Chalk in the immediate geological past (cf. Lockwood, 1979) than during the LGM itself which extended for only a few thousand years and for which the temperature difference with the Holocene was about 11° C. Moreover, it is considered unlikely that recharge was substantial during the LGM pleniglaciation when in southern Britain frozen ground periglacial conditions (Watson, 1977; [Younger, 1989] and [Younger, 1993]) may have reduced infiltration and when precipitation would have been low. Thus, the time span of the interstadials may have been long enough to permit significant recharge and replacement of pore fluids, and also to allow establishment of C-isotope equilbrium between TDIC in the porefluids and the Chalk. The abrupt warming which ended the LGM about 13 ka ago would then have permitted rapid infiltration of the fracture system by water at ≈10° C, which would have progressively mixed with colder and earlier recharge stored in the fissures and matrix of the Chalk.

The line AB (Fig. 14) for groundwaters with δ 13C <−8.0 ‰ may reflect either incongruent dissolution of the Chalk (cf. Fig. 11b,c) under present climatic conditions throughout the Holocene, and/or progressive mixing of recent fracture-borne waters with a component of (relatively 13C evolved) stored water recharged during the Holocene. If the latter case, then the observed RT decrease for two sites with less 13C-evolved water than point B (Fig. 14) might be tentatively explained as the result of the of the transient signature of climatic deterioration of the Loch Lomond Stadial (which occurred soon after the initial Holocene postglacial warming) stored via partial exchange. Alternatively this might be disregarded as an artefact of either rapid flow in the aquifer or of sampling, mixing older, cold recharge component with more recent waters.

Similar mean Δ RT∼−5° C for palaeowaters relative to modern waters both for the UK Trias and the Chalk, may be argued as support for the interpretation of a cold stage pre-LGM emplacement age for the waters. Comparable decreases in RT and hence surface temperatures of 5−7° C relative to modern values elsewhere in Europe have also been derived from groundwaters 14C-dated to the last glacial period (Rudolph et al., 1984; Deak et al., 1987; Stute and Deak, 1989).

3.7. Stable isotopes of water

Excepting geothermal aquifers, in groundwater investigations it can be generally assumed that δ 2H and δ 18O are conservative properties of the water mass during subsurface flow which are related to the isotopic composition of the long-term weighted average precipitation at recharge, dependent also on surface temperature (Gat, 1971).

Darling and Bath (1988) show for a southern Chalk site that the regional aquifer has an isotopic composition similar in value to weighted average rainfall and (lysimeter drainage) infiltration. The UK Chalk groundwaters in the present study cluster along the the Global Meteoric Water Line (GMWL) defined originally by Craig (1961; Fig. 15a). Such signatures for both modern groundwaters and palaeowaters suggest that the 2H excess, defined as d= δ 2H−8 δ 18O, has not changed significantly.

This may imply that comparatively there has been no substantial change in relative humidity over the oceanic source of the precipitation for the dated periods (Merlivat and Jouzel, 1979), although as argued above this implication does not relate to the pleniglacial LGM stage (cf. Rozanski, 1985). However, isotopic signatures from other UK palaeowaters similarly plot along the GMWL (Darling et al., 1997).

Fig. 15. (a) 18O–2H plot for London and Berkshire groundwaters. the Global Meteoric Water Line is defined by δ 2H=8. δ 18O+10; (b) 18O vs noble gas derived recharge temperature (RT) of groundwater. A relative isotopic change of δ 18O 1.4‰ corresponds to an RT change of 8.5° C; (c) 18O vs Cl-contents.

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The evolved Chalk waters typically show lighter isotopic signatures (Fig. 15a), related also to cooler RTs established by the noble gas method (Fig. 8 and Fig. 9 and Fig. 15b). The slope of the δ 18O vs RT change is 0.16‰ per ° C (Fig. 15b). The scatter on this relationship is large and may be attributed to the complexity of the palaeorecharge and mixing processes in the Chalk as discussed above. The δ 18O/RT relationship further north in England is 0.19‰ per ° C (E. Midlands Triassic Sandstone; Andrews, 1993). These temperature relationships for groundwaters from specific UK localities are significantly different from that defined originally in modern rainfall by Dansgaard (1964) at 0.7‰ per ° C (confirmed as (0.59±0.09)‰ per ° C for European stations by Rozanski et al., 1992). This latter value, however, relates to a spatial relationship between long-term annual average values of δ 18O and temperature at globally-distributed stations in the Global Network for Isotopes in Precipitation (GNIP) maintained by the International Atomic Energy Agency and World Meteorological Organisation (IAEA/WMO).

Wallingford (Oxfordshire, UK) approximately 20 km NE of Reading is the nearest relevant IAEA/WMO GNIP site, for which there is a continuous temporal record of monthly mean 18O for rainfall and surface temperature (T) measurements covering the period 1982–1995. A singular gap in this record (November 1989) can be filled by the long-term mean monthly value. At this location, the slope δ 18O/T for the short term (monthly) relationship of δ 18O vs. T over this period is (0.24±0.04)‰ per ° C close to the δ 18O/RT relationship suggested in the Chalk groundwaters. Two longer term temporal relations between δ 18O in rainfall and surface temperature at a give location have been proposed as providing more relevant relationships for climatic investigations in groundwaters. Siegenthaler and Oeschger (1980) have suggested that, as there are a large range of "climates" within an annual cycle, using long-term seasonal relationships (monthly values averaged over several years) at a location may be relevant for palaeoclimatic applications. Most recently Rozanski et al. (1992Rozanski et al., 1993) have suggested that the long-term interannual changes of δ 18O and T at a location are climatically more relevant, which for a European stations composite time-series curve yields a relationship of (0.63±0.04)‰ per ° C close to the spatial relation. For Wallingford, the δ 18O/T slope of the long-term seasonal relationship is (0.22±0.04)‰ per ° C, whereas for the long-term interannual changes the relationship is (0.47±0.08)‰ per ° C.

However, to relate the δ 18O/RT groundwater relationships to the climatic relationships seen in rainfall potential changes of δ 18O of the ocean in the past must be taken into account (Heaton et al., 1986; Rozanski et al., 1992). Both Elliot (1990) and Hiscock et al. (1996) have argued that under glacial climatic conditions an additional isotopic shift of 1–1.7‰ to that observed in the UK Chalk palaeowaters might be necessary to compensate for the enhanced 18O of the ocean (i.e., N Atalantic) source of the precipitation during the LGM caused by glacial build-up of 16O-enriched ice sheets on the continents (Shackleton, 1977; Ruddiman and McIntyre, 1984; Bradley, 1985; Raymo et al., 1990). For the East Anglian Chalk, Hiscock et al. (1996) suggest that this correction equates the observed relative isotopic shift in their palaeowaters to a decrease in mean surface air temperature of 4.5° C when using the relationship δ 18O/T=0.6‰ per ° C; this brings their isotopic estimate of surface temperature at recharge seemingly in better agreement with decreases of 5–7° C in recharge temperatures for the Pleistocene period deduced from noble gas studies. Nevertheless, it is important again to note that the example UK study of Andrews and Lee (1979) cited by Hiscock et al. (1996) actually equates this degree of decrease in noble gas-derived recharge temperatures relative to modern values to interstadial (pre-LGM) and not pleniglacial (LGM) recharge. In the case of stable isotope δ 18O signatures, decreases for the source ocean ~0.5‰ are more appropriate for interstadials (e.g., Raymo et al., 1990). For the Chalk aquifer, this latter correction to the observed relationship (Fig. 15b) would suggest δ 18O/RT≈0.21‰ per ° C, which is in line with long-term seasonal estimate in rainfall at Wallingford rather than the corresponding interannual estimate at this site.

The relationship between δ 18O and dissolved Cl^- (Fig. 15c) suggests freshwater mixing with a saline component having an isotopically lighter signature, and supporting the suggestion that the stored component was recharged during cooler climatic conditions.

3.8. Corrected C-14 (geochemical) ages

Groundwater residence times based on 14C activity of the TDIC may be estimated provided that dilution of the 14C by inactive C of the Chalk matrix can be evaluated. Many correction models have been proposed (Mook, 1980; Fontes, 1983) which are based on chemical evolution and/or isotope dilution of 13C/12C derived from soil CO2 through interaction with aquifer solids. The results of age calculations with several models described in the literature are given in Table 4, together with a newly-adopted model (Model (e), Table 4) which is based on mixing effects in the dual-porosity Chalk aquifer and which is described in detail in Appendix A.

Groundwaters have been sub-divided in Table 4 according to the previously used δ 13C criterion (unevolved vs. evolved waters), which corresponds also to subdivision into groups with RTs greater than and less than ≈9.5° C, respectively. All of the applied correction models (which are essentially based on isotope dilution) suggest Holocene or modern ages for unevolved (light δ 13C) waters; their ages range from modern to ≈11 ka. It may be noted that ages corrected according to the method of Tamers (1967) (i.e., Table 4, column (b)) are undercorrected by up to 10 ka in comparison with models which account for incongruent dissolution processes. The latter models (Table 4, columns (c), (d), (e) and (f)) suggest ages which agree within ±1.0 ka. These models also generally produce negative ages for modern groundwaters. In such cases, a second row of data shows the 14C activity (% modern C) of atmospheric CO2 to produce nearly zero groundwater ages. These values are well within the range of 14C contamination of atmospheric CO2 by nuclear weapons testing since 1956 and suggest that the groundwaters are very recent.

All of the evolved (heavy δ 13C) groundwaters have modelled ages which suggest Late Pleistocene recharge. The oldest modelled ages range from 20 to 25 ka; uncertainties due to 14C determination are generally about ±1.0 ka. It may be concluded that the pore waters corresponding to evolved groundwaters were recharged at least several thousand years prior to the maximum of the Devensian glaciation. The age data are therefore consistent with the line BC (Fig. 14) being due to mixing of recent water with older matrix and/or fracture stored fluids pore waters; i.e., a mixing line between evolved Holocene waters (RT≈9.5° C; δ 13C≈−4.5‰ PDB) with interstitial waters (RT≈5.0° C; δ 13C≈−1.0‰ PDB) which were recharged ≥20 ka ago.

3.9. Helium content

The 4He content of freshwater equilibrated with the atmosphere at 10° C is 4.5 × 10−8 cm3 STP gas/cm3 H2O. The Chalk water contents range from 5 to 1000 × 10−8 cm3 STP gas/cm3 H2O. Fig. 16a,b shows that 4He generally increases both with 13C content of the TDIC and Cl− concentration and decreases with 14C (Fig. 16c), i.e., 4He can be used as another ageing parameter. Radiogenic 4He is accumulated in static or migrating groundwater due to the dissolution of the flux of 4He produced by radioelement (U, Th) decay in the regional crust. The aquifer intergranular matrix porosity is 0.35. Solids U and Th contents are 0.1–0.3 ppm. The time required for accumulation of 10−5 cm3 of 4He per cm3 of water if all of the generated He is dissolved in the pore fluids is ≈35 Ma, i.e., the order of magnitude of the age of the Formation. As the residence time of the bulk of the pore fluids in the Upper Chalk is unlikely to be greater than ≈0.1 Ma, the contribution of such in-situ (aquifer) generated He to the He-content of the fluids is negligible in comparison with the observed He-contents, and sources of He external to the aquifer are implicated (Heaton, 1984). Groundwater ages may be estimated from the relation [He]=tr.F/(o.h), where [He] is the 4He-content of the groundwater, tr is its residence time in the aquifer, F is the crustal flux of He, o is the aquifer porosity and h is its thickness (Andrews et al., 1985). For an average total crustal He-flux of ≈3.3 × 10−6 cm3/cm2/a (O'Nions and Oxburgh, 1983), the residence time of central Basin pore fluids with 10−5 cm3/cm3 of He is about 21 ka for a full aquifer thickness of 200 m, i.e., the same order of magnitude as the 14C residence times discussed above.

Fig. 16. (a) Radiogenic 4He content vs 13C of TDIC (‰ relative PDB). AEW−Air Equilibrated Water (@10° C, 4He=4.5 × 10−8 cm3 gas(STP). cm−3 H2O); (b) 4He (10−8 cm3(STP).cm−3) versus Cl− (mmol.kg−1); (c) 4He (10−8 cm3(STP).cm−3) versus 14C (% modern C).

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4. Conclusions

Downgradient hydrogeochemical trends in the London Basin reflect: (i) active water−rock interaction, mainly involving both congruent and incongruent carbonate dissolution and redox processes; (ii) admixture of a stored palaeowater recharged during the cold stage interstadial preceding the last glaciation; (iii) exchange with a small amount of higher chlorinity water originating from the original (connate water) pore fluids; (iv) leakage of water from overlying beds as a consequence of aquifer overexploitation.

Modelled 14C ages indicate the presence of pre-Last Glacial Maximum (LGM) stage Late Pleistocene waters in the Chalk aquifers of both the London and Berkshire Basins. This is supported by noble gas recharge temperature (RT) signatures and by O and H stable isotope ratios. The 4He contents of the groundwaters may be explained by dissolution of the whole crustal He-flux; and indicate maximum groundwater ages of the same order of magnitude as corrected 14C ages. The younger waters have evolved initially by congruent reaction between soil CO2 and the near-surface Chalk matrix and downgradient predominantly by incongruent dissolution of the solid Chalk matrix through reaction along flow lines. Towards the centres of both Basins their evolution has also involved admixture between fracture-borne and (Holocene) stored matrix waters, producing groundwaters with δ 13C in the range −12‰ to −8‰. Noble gas-derived recharge temperatures for groundwaters with δ 13C values more positive than −8‰ are linearly correlated with their dissolved 13C content, and the balance of the geochemical evidence indicates mixing between younger fracture-borne waters and older (pre-Devensian glacial age) pore fluids of the adjacent matrix. The recharge temperature difference between the Holocene and Late Pleistocene waters of ≈4.5° C is similar to that observed in the East Midlands Trias and other European aquifers which are reservoirs for palaeowaters of pre-LGM age.

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Appendix A.

The simple model for column (e) of Table 4, was developed in this study particularly for application to a dual-porosity aquifer such as the Chalk which rapidly achieves carbonate saturation. It assumes that congruent dissolution occurs rapidly (i.e., with no significant 14C decay) in the unsaturated zone, yielding the initial fracture waters. The initial activity, Aoc, of the TDIC at the end of open system congruent dissolution is:

(A.1)

$$A_{oc} = (A_g + {}^{14}\varepsilon_{ag} + A_r) / 2$$

where Ag is the 14C specific activity of soil gas CO2, Ar is that for rock carbonate and 14 ε ag is the fractionation of 14C in dissolved H2CO3 relative to soil−CO2. Incongruent dissolution/precipitation occurs mainly in the confined aquifer under closed system conditions with respect to soil−CO2, moving the 13C isotopic signatures towards the rock value. Equivalently (as assumed here) mixing then occurs between the TDIC of the initial fracture and rock-equilibrated pore waters to predominate the 13C-isotope evolution.

For an end-member pore water which is 14C-dead and is equilibrated with the solid carbonate phase, the fraction, fc, of the initial fracture water which is present in the mixture of end-member waters of equivalent overall C-concentration, may be simply estimated from (e.g., Faure, 1986):

(A.2)

$$f_c = (\delta_p - \delta_{\mathrm{TDIC}}) / (\delta_p - \delta_c)$$

where δ p is δ 13C for the matrix pore fluid, δ TDIC is the δ 13C value of the TDIC and δ c is δ 13C at the end of congruent dissolution and may be calculated from:

(A.3)

$$\delta_c = (\delta_a + \delta_r) / 2 = (\delta_g + {}^{13}\varepsilon_{ag} + \delta_r) / 2$$

where δ a, δ g and δ r are the δ 13C values for H2CO3, soil CO2 and rock, respectively, and 13 ε ag is the fractionation of dissolved H2CO3 relative to soil CO2. For equilibration of the dissolved bicarbonate of the pore fluids with the matrix carbonate δ p=(δ r+13 ε bc), and on substitution in Eq. (A.2)we obtain:

(A.4)

$$f_c = (\delta_r + {}^{13}\varepsilon_{bc} - \delta_{TDIC}) / (\delta_r + {}^{13}\varepsilon_{bc} - \delta_c)$$

where 13 ε bc is the fractionation of dissolved bicarbonate relative to solid carbonate. The 14C activity, ATDIC*, of the groundwater TDIC corrected for the effect of mixing with the 14C-dead pore fluid end-member is then:

(A.5)

$$A_{TDIC*} = A_{TDIC} / f_c$$

where ATDIC is the measured activity of the groundwater TDIC. The corrected 14C age, t, of the groundwater TDIC is then:

(A.6)

$$t = \ln(A_{oc} / A_{TDIC*}) / \lambda$$

where λ is the decay constant for 14C.

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