The Permian aquifer of Dumfries: groundwater chemistry and age

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BRITISH GEOLOGICAL SURVEY

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Front cover illustration: Galloway cattle grazing in Dumfries & Galloway (photo A A McMillan).

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Executive Summary

The Dumfries aquifer has been studied for over 20 years. However, investigations have been piecemeal and little attempt has been made to bring all the different approaches together. This study, although entirely hydrochemical, aims to help understanding of the groundwater flow within the basin in order to validate (or otherwise) existing hydrogeological conceptual models.

The age and hydrochemistry of groundwater in the Permian sediments of the Dumfries Basin was assessed from 21 groundwater samples and 14 age determinations using CFCs and SF_6. A summary of the important features of the groundwater chemistry is given below.

1. Groundwater is of $Ca-Mg-HCO_3$ type and is moderately mineralised; pH is near neutral. The chemistry is dominated by maritime recharge and the dissolution of carbonate minerals in the sandstone, breccia and drift.

2. Groundwater within the Dumfries basin ranges from older (perhaps greater than 100 years) to modern. Groundwater in the west of the basin within the Doweel Breccia Formation has a large component of modern (less than 10 years) water. In the east of the basin, within the Locharbriggs Formation the groundwater is older, with generally less than 10% modern water (apart from the far south-east edge of the basin where modern groundwater is present).

3. Nitrate concentrations are high (median value of 27 mg/l NO_3 (6.1 mg/l NO_3-N)). The concentration of nitrate is directly related to the age of the groundwater; with older groundwater having low concentrations of nitrate and younger groundwater higher concentrations. The relationship between nitrate and age suggests that recharge currently contains 40-50 mg/l NO_3. Lowest (<10 mg/l NO_3) nitrate concentrations are found in older water in the Locharbriggs formation to the east of the basin.

4. Limited depth sampling suggests that groundwater within the Doweel Breccia Formation in the east of the Basin is stratified. Deeper water tends to be less mineralised than shallow water, and contains lower concentrations of NO_3, Ca, Mg and HCO_3. Although the lower NO_3 concentration can be accounted for by the increased age of the deeper groundwater, the reduced concentration of the other minerals suggests different sources for the deep and shallow groundwater. The deep groundwater may have originated from recharge in another part of the basin, where the drift and lithology produce subtly different chemistry from the shallow, more localised groundwater.

5. Many of hydrochemical variations reflect the geology of the basin. Concentrations of Ca, Mg and HCO_3 are higher in the Doweel Breccia Formation, where the sediments are mainly fluviatile. Concentrations are generally lower within the aeolian sandstones of the Locharbriggs Formation apart from in the south-east where the drift or geology may be sufficiently different from the rest of the Locharbriggs formation to alter groundwater chemistry. Sulphate concentrations increase to the south in both formations, possibly reflecting occurrence of mudstone within the sediment or leakage from the overlying raised beach deposits.

Groundwater flow in the basin is complex. Flow within the Dowell Breccia Formation is relatively rapid and groundwater storage is limited; groundwater is stratified and deeper water may flow considerable distances (>3 km) to abstraction boreholes. Groundwater in the Locharbrigggs Formation is older, suggesting groundwater flow is slower and storage high. A change in water chemistry in the southern outcrop of the Locharbriggs Formation, however, suggests that the flow characteristics may become more like the Doweel Breccia Formation in this area.

1.   INTRODUCTION

The Permian basin of Dumfries is one of Scotland's most important aquifers.   Approximately 11 million cubic metres are abstracted annually, which accounts for 11% of groundwater abstracted in Scotland (Ball, 1999).   Groundwater from the aquifer provides much of the town's domestic and industrial water supply, both through private abstractions and public supply by West of Scotland Water. The aquifer also provides water for two large fish farms, various dairy and arable farms and a mineral water company.

Although the Permian aquifer in Dumfries is heavily exploited, little is known about the hydrochemistry of the aquifer, or the age of groundwater abstracted. In addition, recent geophysical logging in the aquifer has highlighted the complexity of groundwater flow in the western part of the basin (Buckley, 2000). Increased exploitation, the possibility of pollution from economic activity, and the need for proper management of the basin all require improved conceptualisation of existing groundwater flow models (Cheney and MacDonald, 1993).

This study looks at the hydrochemistry of the Dumfries basin. Twenty-one groundwater samples have been taken throughout the basin and analysed for major and minor ions, trace elements and metals. Fourteen samples have been taken for age determination. These data have been interpreted to meet the following objectives:

1.   To identify groundwater residence times within the basin.

2.   To characterise 'baseline' hydrochemistry within the basin.

3.   To identify groundwater flow regimes within the basin.

This study fulfils one of the recommendations of Gaus (1999) who reviewed gaps in knowledge of the Dumfries basin aquifer, and provides supporting evidence of the groundwater flow regime within the basin.

2.   GEOLOGY AND HYROGEOLOGY

The Dumfries aquifer comprises a semi-elliptical basin 25 km long and 10 km wide infilled with more than 1000 m of sediments (Bott and Masson-Smith, 1960) (see Figure 1). The sediments comprise aeolian sandstones and alluvial fan breccias with variable proportions of fluviatile sandstone, siltstone and mudstone. In Dumfries, Permian sediments can be divided into two formations: the Locharbriggs Sandstone formation in the east and the Doweel Breccia Formation in the west (Brookfield, 1978). The Locharbriggs Formation comprises medium- to fine-grained aeolian sandstone with large scale cross bedding. The sandstone consists of sub rounded to very well rounded quartz with less than five percent basalt and feldspar, weakly cemented by silica. The Doweel Breccia Formation consists of coarse- to fine-grained moderately sorted sandy breccias, interbedded with fluviatile sandstone and aeolian sandstone. The clasts within the breccia are derived from surrounding rocks and therefore comprise mainly greywacke mudstone and granite. The breccias thin towards the centre of the basin as sandstones predominate (Brookfield, 1980). Only a small number of boreholes have been drilled in the eastern part of the basin and the geology here is less well understood. Although the geology map indicates sandstones of the Locharbriggs formation to be present throughout the east of the basin, limited trial drilling has shown the presence of breccia and soft marls in the southeast of the basin (Ball, 1994). The basin is faulted along its western edge (British Geological Survey 1996).
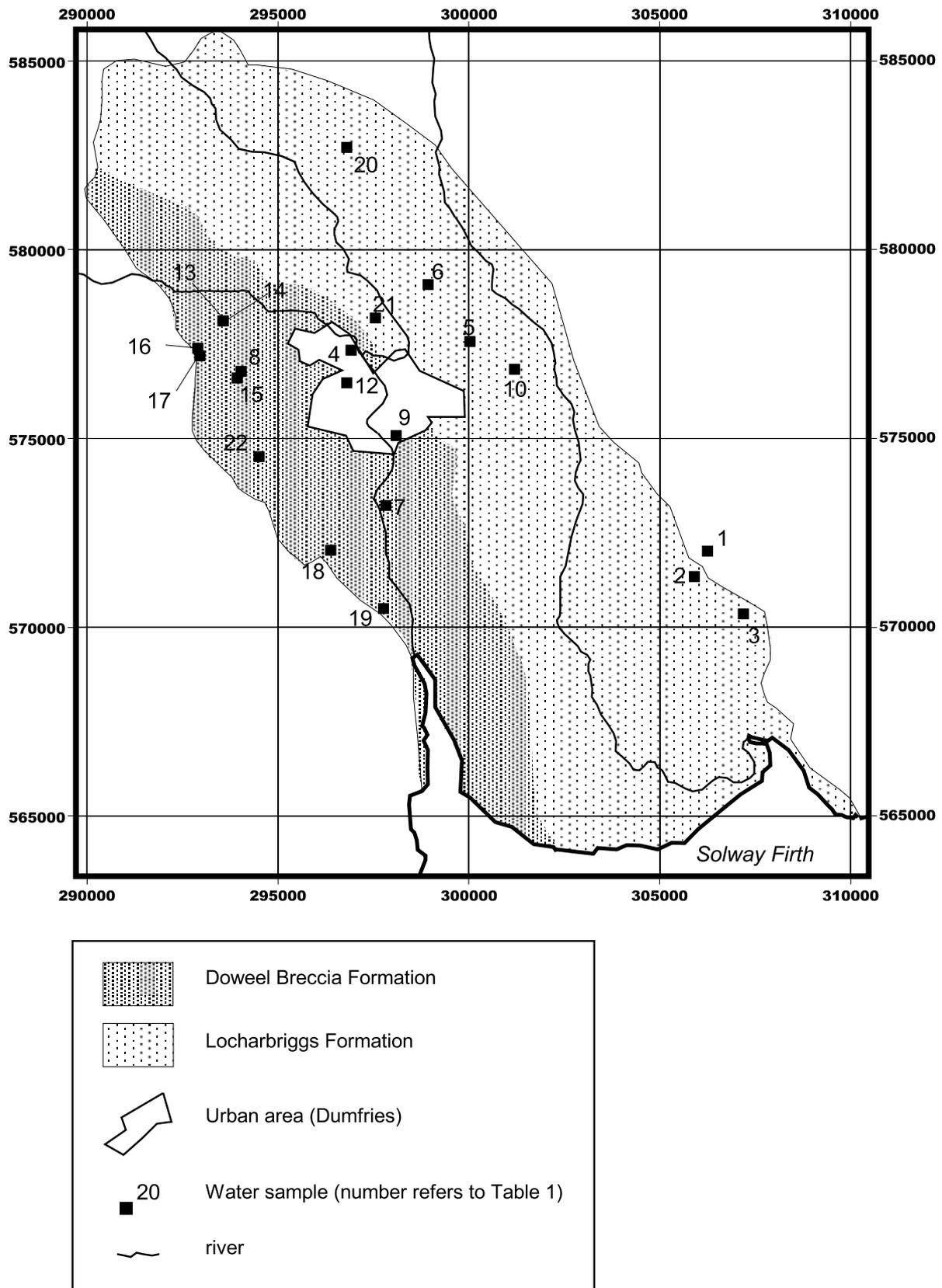
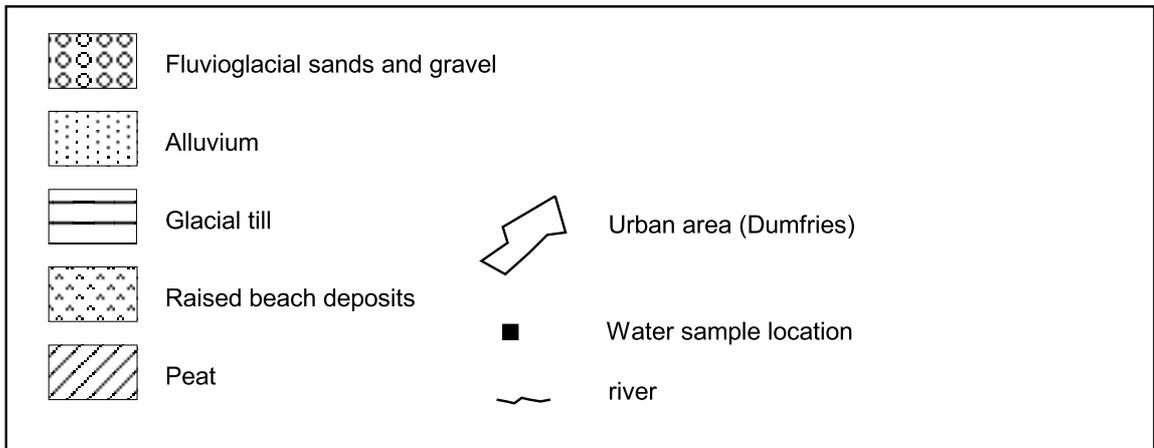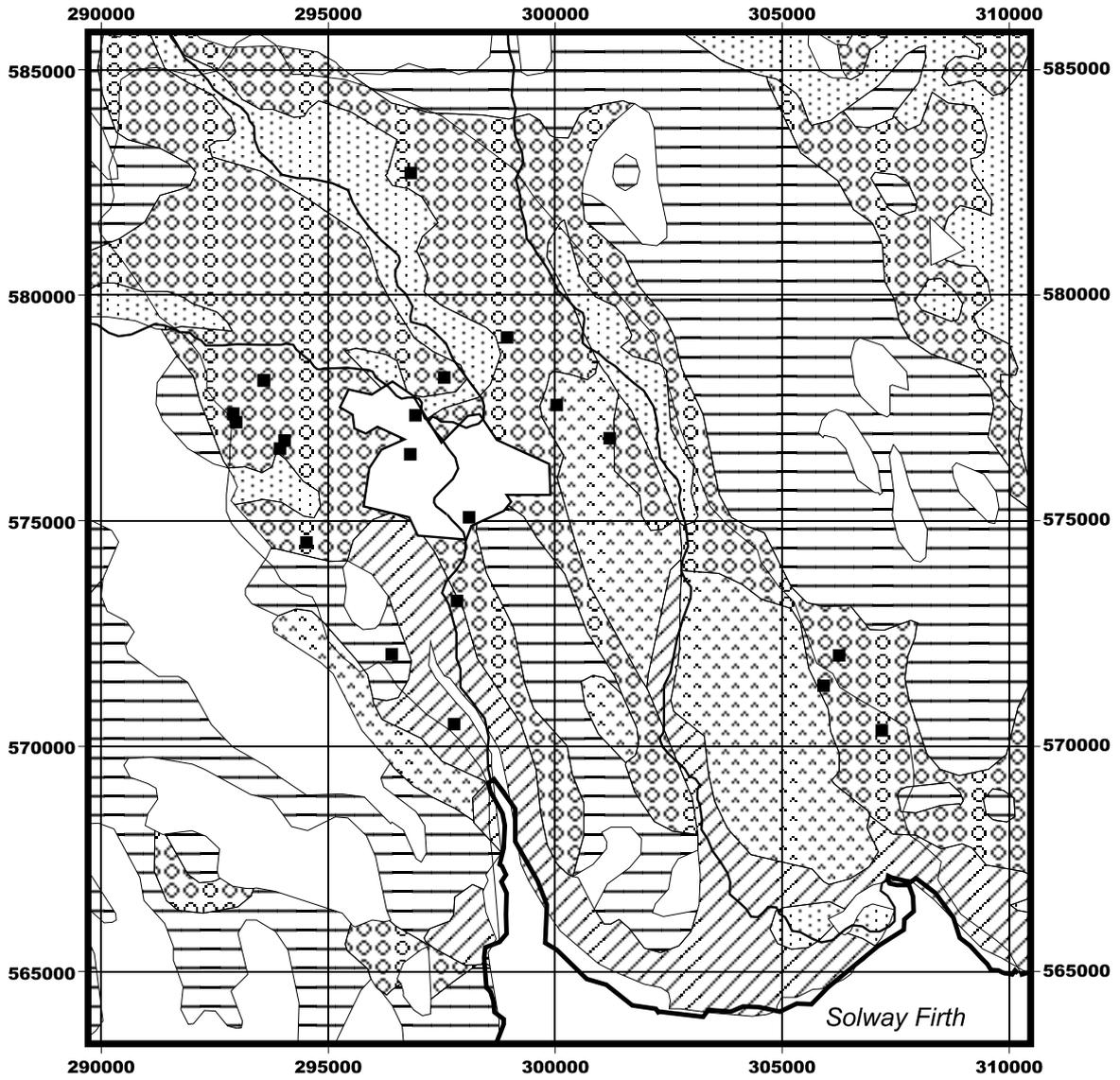**Figure 1**　　　**The geology of the Dumfries Basin and sample locations.**

Figure 2   **Drift map of the Dumfries Basin.**

Bedrock is covered by fluvioglacial sands and gravels, glacial till, alluvium and peat (see Figure 2). Fluvioglacial sands and gravel cover much of the north of the basin and can be up to 30 m thick (Cheney and MacDonald, 1993). Recent mapping in the area suggests that much of the fine material within these deposits originates locally from the Permian sandstones, although pebbles and cobbles are probably derived from harder rocks such as the surrounding greywackeys and granites (Auton pers. comm.). Often the sands and gravels are underlain by thin glacial till (again usually containing a large proportion of local Permian material). Glacial lake deposits are also present, particularly in the vicinity of Dumfries. Thick peat deposits are found under Locharmoss in the southeast of the basin. Peat has a low permeability and may inhibit recharge in this area. Alluvium is present along the River Nith and the Lochar Water. Raised marine, estuarine and beach deposits are present in the south of the basin, and include interbedded layers of clay and silt. The variable composition and thickness of the drift can have a significant impact on recharge to the aquifer. The higher ground of the Terregles area to the north west and the low bedrock ridges that flank the River Nith are covered mainly by thin granular drift.

Groundwater flow in the Permian rocks is governed largely by fracture flow. Investigations have concentrated in the Doweel Breccia Formation (e.g. Robins and Buckley; 1988, Cheney and MacDonald, 1993; Buckley 2000). Measurements of core samples from boreholes from the northern part of the basin indicate that the sandstone has an average porosity of 20% and the breccia of 8% and intergranular hydraulic conductivity of less than 0.5 m/d and 10^{-4} respectively (Cheney and MacDonald, 1993). Limited data from pumping tests give average transmissivity values of 300 m^2/d for the Locharbriggs Formation. Considerably more testing has been carried out in the Doweel Breccia Formation; measurements of transmissivity vary from 9 m^2/d to 4000 m^2/d, with a median of 400 m^2/d (Gaus, 1999). Transmissivity is highest in the Terregles area in the east of the basin. Integrating measured intergranular permeability over the typical length of a borehole (100 m) would suggest transmissivity of 50 m^2/d in the sandstone and 0.01 m^2/d in the breccia. Since this is much less than that measured in pumping tests, secondary flow through fractures must account for much of the groundwater flow.

Understanding of groundwater flow in the Dumfries Basin has been aided by geophysical logging of many of the trial and production boreholes. A summary of the logging carried out in the area is given by Buckley (2000). In the Doweel Breccia formation groundwater flow mainly occurs in fractures between sandstone and breccia layers. Much of the flow in the Hardthorne Road, Terregles and Cargen boreholes comes from only one or two fractures. Various strands of evidence from ongoing (unpublished) BGS work in the area suggest that these fractures may be widespread, and interconnect many of the boreholes drilled into the Doweel Breccia Formation. A tracer test carried out at Hardthorn Rd [NX 9360 7810] proved groundwater flow through a fracture from an observation borehole to the pumping well at a velocity of 200 m/d. Water levels in observation boreholes are known to react rapidly to pumping in a borehole several kilometres away. At Manse Rd, the Golf Course borehole [NX 9588 7562] reacts within a matter of hours to changes in pumping at Manse Rd, while a shallow observation borehole at Manse Rd, which does not penetrate the main fracture zone, is unaffected.

Much less is known about groundwater flow in the sandstones of the Locharbriggs Formation. No geophysical logging has been carried out within the sandstone boreholes and since exploitation has concentrated in the east, there have been no tracer tests.

3.   SAMPLES

Twenty-one water samples were collected from boreholes throughout the basin during November 1999 (Figure 1). Information on the sources are given in Table 1. The majority of samples were taken from pumping boreholes, and represent mixtures of groundwater from various depths. It was only possible to take depth samples at two sites, Hardthorne Rd and Manse Rd. Most of the samples

were collected without contact with the atmosphere. Electrical conductivity (SEC) pH, temperature and alkalinity were measured at the site. Two water samples were taken; both passed through a 0.45 µm filter and one acidified to 1% V/V with concentrated nitric acid. Samples were sent to BGS Wallingford for analysis of major and minor ions. Where a sample could be taken without contact with the atmosphere, samples for Chlorofluorocarbon (CFC) and sulphur hexafluoride (SF_6) determination were taken. These were analysed at Spurenstofflabor in Germany.

Table 1   Location of samples.

Sample ID	Borehole Name	Easting	Northing	Land use	Depth (m)
1	Townfoot Farm	306250	572000	Pasture	60
2	Holmhead Farm	305900	571330	Pasture	30
3	South Bowerhouse Farm	307190	570340	Pasture	62
4	Nestle Borehole 1	296910	577330	Industrial	183
5	Dundas Chemical	300023	577558	Pasture/Industrial	90
6	Gates Rubber, New Borehole	298930	579060	Industrial	103
7	Galloway Mineral, new borehole	297820	573210	Pasture	150
8	Manse Road P.S.	294020	576770	Pasture	112
9	Larchfield Production	298090	575060	Urban	95
10	Locharmoss BH 1.3	301185	576820	Pasture/Landfill	43
12	Shortridge Laundry	296790	576460	Industrial	48
13	Hardthorne Rd (30 m)	293560	578102	Pasture	127.5
14	Hardthorne Rd (125 m)	293560	578102	Pasture	127.5
15	Manse Rd observation	293923	576590	Pasture	27.4
16	Terregles FF, bottom left	292950	577170	Pasture	122
17	Terregles FF, dog kennel	292890	577370	Pasture	122
18	Cargen Production Bh 1	296380	572030	Pasture	112
19	Greenmerse	297760	570480	Pasture	75
20	Galloberry Farm	296800	582700	Pasture	90
21	Hollywood FF pump10	297540	578170	Pasture	122
22	Dupont DGI 1	294500	574500	Industrial	30

4.   THE AGE OF THE GROUNDWATER

Fourteen samples were analysed for CFC and SF_6 to determine the age of the groundwater within the basin. Appendix 1 gives details of the analysis and interpretation of these data. Analysis of CFC and SF_6 gives two independent measurements of the age of the groundwater. The CFC method cannot be

used for dating where the groundwater has been contaminated by industrial waste, or if the groundwater is highly reducing (Plummer and Busenberg, 1999). The SF_6 method is more susceptible to air contamination during sampling, and SF_6 concentrations can be locally elevated by their use as tracers in the building industry. Table 2 gives the age determinations from both methods. Since the samples are from pumped boreholes and therefore from mixed depths, the age is quoted as the percentage of post 1990 water within pre 1950 groundwater.

Four samples had concentrations above present day atmospheric equilibrium CFC concentrations: samples 8 (Manse Rd PS), 6 (Gates Rubber), 17 (Terregles FF, dog kennel) and 22 (Dupont). Samples 6 and 22 are industrial sites where higher concentrations of CFC may be expected. However, 8 and 17 are in a rural setting, with no obvious source of elevated CFC. The elevated concentrations of CFC may be accounted for by groundwater flow from industrial sites to the borehole. There are no industrial sites in the immediate vicinity, suggesting the presence of a widespread fracture network which allows rapid flow across the aquifer. This is in agreement with the results of geophysical logging, tracer tests and pumping tests described earlier.

SF_6 has also been used to determine groundwater age. For most samples, CFC and SF_6 give similar estimates of age (see Table 2 and Appendix 1). Only two samples, 4 and 19 give substantial differences, where the SF_6 suggests the water is wholly modern, and the CFC indicates the water is older. Since there appears to be no reason why the CFC value should be affected in these two boreholes (i.e. conditions are not reducing), it is assumed that the SF_6 has been subject to inadvertent atmospheric additions during sampling, possibly due (in the case of 19) to the ingress of air into the 50 m hose extension from the wellhead.

The data suggest that groundwater within the Dumfries basin range from perhaps greater than 100 years to modern. The distribution of the age of groundwater in the Dumfries Basin is shown in Figure 3. Groundwater in the west of the basin within the Doweel Breccia Formation has a large component of modern water, although it may become older towards the centre of the basin. In the east of the basin, within the Locharbriggs Formation, the groundwater is considerably older, with generally less than 10% modern groundwater. In the far south-east edge of the basin however, younger groundwater was found. The significance of these ages for understanding the groundwater flow in the basin is discussed later.

To further investigate the age and mixing of water in the Dumfries aquifer it would be helpful to have samples from discrete depths. This would help to isolate the modern and older components within the bulk samples measured at the well head. Taking airtight depth samples suitable for CFC or SF_6 analysis is not trivial, however. A team from BGS is currently working on this issue and hopes to have a reliable field system in the next year.
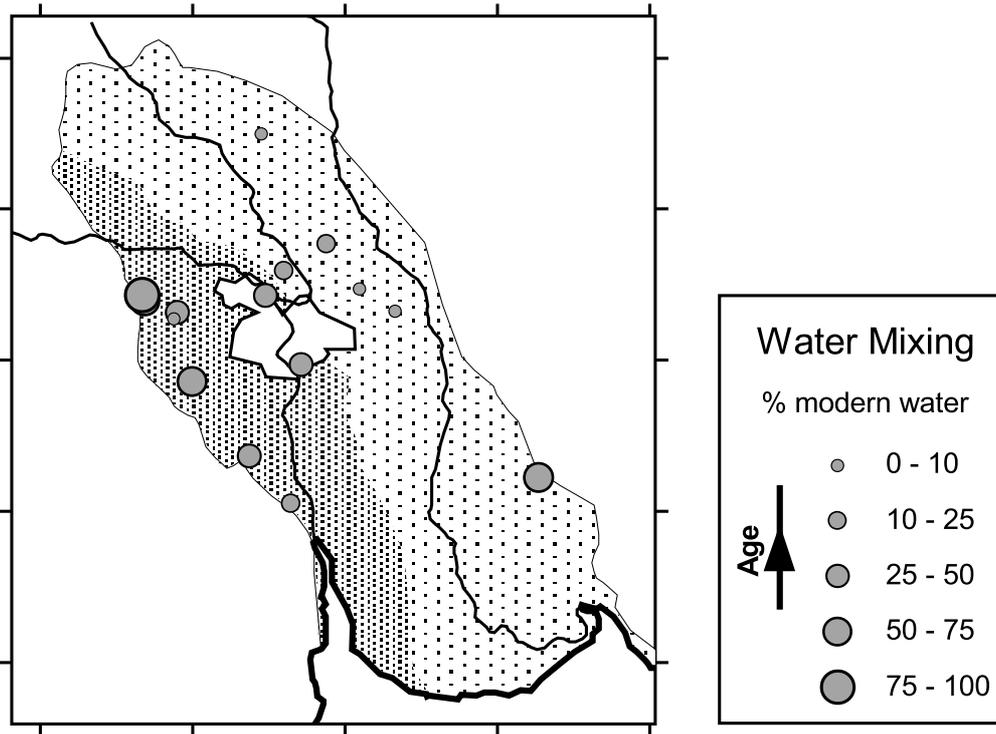
Figure 3 **The age of groundwater in the Dumfries Basin expressed as the proportion of modern (post 1990) water with respect to pre 1950 water.**

Table 2 **Summary of age determinations of groundwater in Dumfries expressed as percentage of 1990 water mixed with pre 1950 water (details in Appendix 1).**

	Percentage of post 1990 water		
Sample ID	**SF$_6$**	**CFC**	**Best estimate**
2	71	65-70	68
4	100	30 - 40	35
5	<5	0 - 5	3
6	15	C*	15
8	46	C	46
9	23	35-40	38
10	17	0 - 5	3
15	69	80 - 100	90
16	62	65 - 70	68
17	90	C	90
18		40 - 45	43
19	86	20 - 25	23
20	<5	0 - 5	3
21	25	20 - 25	23
22	70	C	70

*C denotes likely contamination of sample

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5.   HYDROCHEMISTRY

Maritime recharge and water-rock interaction dominate the chemistry of Dumfries groundwater, although some anthropogenic influence (nitrate) is also noticeable. The composition of samples from Dumfries are given in Table 3. The analyses reveal that groundwater chemistry is predominantly of a Ca-Mg-HCO_3 type; pH is near neutral (measured pH values range from 7.1 to 7.6 with a median of 7.2) and the median temperature of the samples is 9.8°C. Groundwater is not highly mineralised.

The nearest site where rainwater composition is routinely monitored is at Loch Dee [NX 468 779] which is 50 km from the centre of the Dumfries basin. Table 4 shows the weighted mean of rainfall composition from 1986 to 1997. Comparing the composition of rainfall to seawater shows a strong maritime influence. Ratios of Na, Mg and K to Cl in rainwater are all consistent with seawater. Nitrate and SO_4 are highly elevated in rainfall, due to emissions of NO_x and SO_2 from industry and traffic. Calcium is slightly elevated in rainfall which is common, both from natural and anthropogenic origins (Appelo and Postma, 1994). Assuming Cl to be conservative (excluding the obviously contaminated sites), the expected concentrations of major ions in groundwater from recharging rainfall is given in Table 4.

Major ion chemistry of groundwater in Dumfries is summarised on a piper diagram (Figure 4) and a box plot Figure 5. As mentioned above, the chemistry is dominated by Ca-Mg-HCO_3 type waters; elevated high above what would be expected from rainfall alone. The most obvious source is carbonate cements within the sandstone and breccia and also from the overlying drift. The high Mg/Ca ratios in the water samples suggest dolomite predominates, however the groundwater is undersaturated with respect to both calcite and dolomite. The distribution of Ca, Mg and HCO_3 concentrations throughout the basin are broadly similar (Figure 6 and 7). Highest concentrations are found in the north-west of the Doweel Breccia Formation and lowest concentrations within the Locharbriggs formation. In the south-east of the basin, within the Locharbriggs formation, concentrations are found similar to that of the Doweel Breccia Formation, suggesting a possible change in aquifer conditions.

This observed pattern may be due to changes in the bedrock geology; the sediments within the Doweel Breccia Formation are mainly fluviatile, and therefore probably have a higher component of carbonate cements. Lower concentrations in the Locharbriggs formation, may reflect the aeolian origin of the sediments and therefore a lack of carbonate cement. The composition of the drift may also have an influence on the Permian groundwater. However, recent work in southern Scotland (Stone et al., 1999), showed a very good match between stream sediment geochemistry and underlying geology; implying that drift is generally comprised from local bedrock (maybe within a kilometre). This has also been found by recent drift mapping in Dumfries (see above). Therefore the chemical composition of the drift may not be significantly different to that of the bedrock. Little work has been carried out in Dumfries on the geochemistry of the sandstones and breccia or the drift. McKeever (1992) in a study of the petrology of 17 samples from the Dumfries Basin found that silicate cements prevailed, and that carbonate cement was rare. However, the sample was limited and mainly from outcrop. Samples from other basins in southern Scotland suggested carbonate cements were present and more commonly dolomite than calcite.

Na and Cl concentrations are consistent with rainwater, suggesting no additional sources from the rocks. There are slightly elevated concentrations of Na and Cl towards the south of the basin, although no evidence of significant saline intrusion. The higher concentrations may be due to leakage from poor quality water within the raised beach deposits (Cheney and MacDonald, 1993).

Table 3   **Hydrochemical data from groundwater samples from the Dumfries Basin.**

|	sample ID	1	2	3	4	5	6	7	8	9	10	12	13	14	15	16	17	18	19	20	21	22	25%	50%	75%
mg/l	pH	7.2	7.1	7.4	7.3	7.4	7.3	7.1	7.1	7.0	7.4	7.1	7.0	7.4	7.2	7.2	7.3	7.6	7.1	7.2	7.5	7.0	7.1	7.2	7.4
	TDS	314	493	273	296	136	209	267	311	257	293	255	397	301	464	319	385	303	263	94.3	263	575	230	293	353
	Mg	20.6	19.2	15.5	19.7	7.84	12.7	18.1	21.7	17.6	15.7	17.3	29.2	21.4	29.9	19.8	23.1	19.8	12.9	3.93	16.8	41	15.7	19.2	21.4
	Ca	41.2	86.1	40.2	42	19.4	26.3	38	45.2	35.5	33.8	37	58.5	41.7	70.9	46.6	58.7	41.5	32.4	10.4	36.8	83.3	35.5	41.2	46.6
	Na	14.1	18.4	11.3	12.9	7.3	11.6	11.1	8.9	10.8	23.3	9.4	7.6	9.3	9.6	9.6	10.1	12.9	25.9	8.9	9.6	23.4	9.4	10.8	12.9
	K	3.4	3.3	1.7	1.3	1.2	1.5	1.6	1.5	1.4	3.9	1.2	1.5	1.2	2.7	1.8	1.7	1.9	2.3	1.4	2	2.3	1.4	1.7	2.3
	Cl	24.2	33.1	18.9	20.1	11.5	17	17.8	15.4	17	14.3	16.4	13.7	14.8	14.6	14.3	16.1	22.6	23.4	9.3	14.2	96	14.3	16.4	20.1
	HCO$_3$	147	162	108	159	73.1	112	127	172	117	195	133	232	168	274	188	226	150	122	29.3	157	267	122	157	188
	NO$_3$	44.2	126	47.4	14.7	6.8	8.76	27.7	25.7	27.1	<1.1	18.5	43.8	27.6	44.2	24.2	31.6	27.3	9.01	15.5	6.94	29.4	14.7	27.1	34.7
	SO$_4$	12.8	40.1	26.6	20.3	3.4	14.8	21	16.8	25	2.1	17.8	7.7	12.4	13.9	10.2	13.4	21.2	29.4	9.3	14.6	26.6	12.4	14.8	21.2
	Si	6.6	5.06	3.67	5.5	5.09	4.83	5.13	4.27	5.33	4.71	4.78	3.47	4.86	4.65	4.67	4.07	5.81	5.37	6.3	5.22	6.01	4.67	5.06	5.37
	SI calcite	-0.68	-0.49	-0.62	-0.5	-1.1	-0.89	-0.89	-0.72	-1.1	-0.42	-0.85	-0.55	-0.44	-0.28	-0.53	-0.3	-0.24	-0.92	-1.9	-0.4	-0.34			
	SI dolomite	-1.5	-1.5	-1.5	-1.1	-2.5	-1.9	-2	-1.7	-2	-1.1	-1.9	-1.3	-1.1	-0.85	-1.3	-0.88	-0.67	-2.1	-4.2	-1	-0.84			
µg/l	Br	110	140	70	80	90	80	70	70	80	50	70	60	60	70	60	60	80	110	60	50	220	60	70	80
	F	80	80	70	70	70	100	80	60	80	100	70	60	50	60	60	60	80	80	10	50	40	60	70	80
	I	10	7.3	3.4	3.7	2.8	3.4	2.7	3.4	2.6	5.1	3.8	3.9	3.1	4.3	3	3.2	2.7	2.4	2	2.7	7.5	2.7	3.4	3.9
	Fe	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	70	120	20	30	<20	<20	<20	<20	<20	<20	20	20	20	20
	Mn	0.16	10	0.05	0.05	0.51	0.53	<0.04	0.05	0.06	0.04	0.79	20	5.38	0.41	0.12	<0.04	0.04	0.04	0.15	40	10	0.05	0.15	0.79
	NO$_2$	<19.1	19.1	22.2	11.1	<19.1	19.1	26.5	19.1	13.3	19.1	13.3	30.8	17.6	22	13.2	19.1	19.1	19.1	19.1	17.4	26.1	17.6	19.1	19.7
	NH$_4$	25.7	<12.9	103	25.7	116	12.9	129	<12.9	<12.9	<12.9	<12.9	219	<12.9	<12.9	<12.9	<12.9	<12.9	<12.9	<12.9	<12.9	<12.9	12.9	12.9	25.7
	P	<20	40	20	<20	50	<20	50	20	70	80	20	30	<20	30	<20	<20	40	<20	<20	30	20	20	20	40
	Li	10	10	4.5	5.4	2.6	2.1	2.9	2.1	2.2	3.5	2.8	1.0	3.4	1.5	3.8	1.6	3.9	9.8	2.3	3.0	4.1	2.2	3.0	4.1
	B	20	60	20	10	6.6	20	8.7	10	10	30	9.3	10	9.8	10	10	10	10	10	6.4	7.6	10	9.8	10	10
	Al	1.2	0.4	1.4	0.4	0.8	1.2	0.6	4.8	0.7	1.6	2.9	2.6	1.2	7.0	2.4	0.8	1.0	1.4	1.8	0.7	9.9	0.8	1.2	2.4
	Cr	0.2	0.1	0.3	0.5	0.7	0.2	0.4	0.8	0.3	1.9	0.5	1.8	0.6	0.4	0.4	0.3	0.3	0.4	0.5	0.3	1.7	0.3	0.4	0.6
	Co	0.09	0.18	0.07	0.09	0.04	0.06	0.08	0.11	0.06	0.05	0.08	0.17	0.08	0.14	0.09	0.13	0.07	0.07	0.02	0.09	0.24	0.07	0.08	0.11
	Ni	1.5	2.9	1.2	1.4	0.6	1.3	1.2	1.8	1.3	1.0	1.0	2.7	1.3	2.0	1.4	1.9	1.7	0.9	1.3	1.3	3.8	1.2	1.3	1.8
	Cu	4.2	10	1.5	0.2	0.1	0.2	0.7	5.4	3.4	<0.05	4.8	10	0.8	0.7	0.6	0.7	7.6	2.9	1.1	0.6	0.8	0.6	0.8	4.2
	Zn	5.4	3.1	2.4	4.5	0.5	2.5	1.9	10	4.9	<0.45	7.8	10	2.0	1.8	1.7	1.1	8.6	4.1	7.6	3.8	40	1.9	3.8	7.6
	As	10	4.7	2.2	0.9	0.7	0.4	0.7	1.9	0.7	0.6	1.9	0.7	2.2	0.8	5.8	1.1	1.7	1.7	0.3	0.9	3.1	0.7	1.1	2.2
	Se	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3
	Rb	2.2	2.1	1.3	1.0	0.7	2.8	0.7	0.8	0.8	0.6	0.9	0.8	0.9	1.0	1.2	0.9	1.0	0.6	2.2	1.1	1.6	0.8	1.0	1.3
	Ba	180	120	180	30	10	160	50	50	20	40	30	40	50	70	110	180	20	10	30	30	80	30	50	110
	Pb	0.3	0.24	0.09	0.06	<0.04	0.05	0.09	0.44	0.58	0.05	0.59	0.75	0.18	0.17	0.2	0.2	0.44	0.22	0.55	0.17	0.49	0.09	0.2	0.44
	U	2.17	1.17	0.28	1.56	0.10	1.14	0.37	0.69	0.23	1.44	1.38	0.16	0.92	0.13	1.04	0.51	1.36	1.91	0.11	1.00	0.60	0.28	0.92	1.36
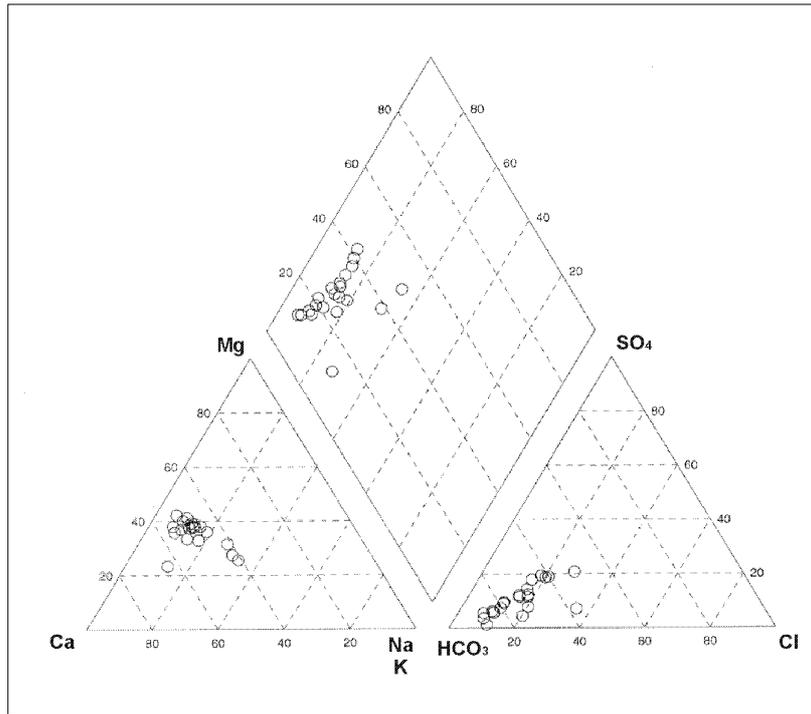
Figure 4   Piper diagram of groundwater in the Dumfries Basin.
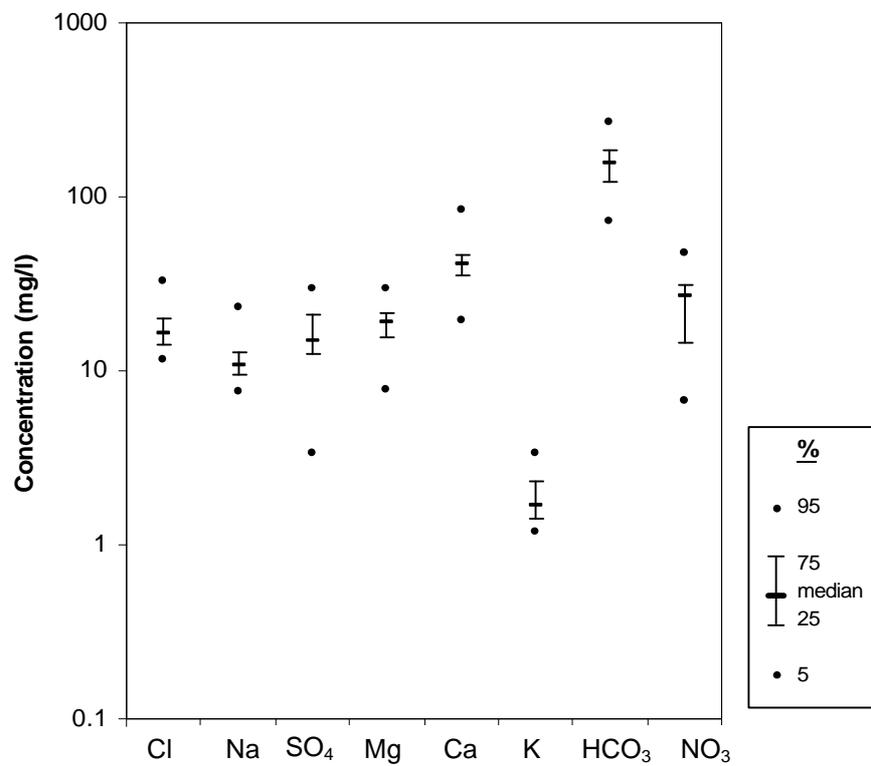

Figure 5   Box plot of major ions in the groundwater of the Dumfries Basin.

Table 4   Rainwater composition at the Loch Dee rainwater monitoring station (data from http://www.aeat.co.uk/netcen/airqual/welcome/html).

	Sea water (Hem1985)		Rainwater at Loch Dee[*]		Fractionation factor[**]	Conc^n in groundwater from rainwater (mg/l)[***]
	mmol/l	mg/l	µmol/l	mg/l		
Cl	535	19000	125	4.45	0.999	16.4
SO_4	28.1	2700	20.6	1.98	3.13	7.28
NO_3	0.054	3.35	16.6	1.03	1310	3.79
Na	547	10500	107	2.45	0.996	9.02
K	10	390	2.5	0.0975	1.07	0.359
Ca	10.3	410	5.25	0.21	2.19	0.774
Mg	55.6	1350	13.7	0.332	1.05	1.22

[*] weighted mean from 1986 - 1997.

[**] ratio of rainwater to seawater composition defined as $(ion / Cl)_{rain} / (ion / Cl)_{sea}$
[***] assuming chloride is conservative in groundwater

Although sulphate is elevated in rainfall due to acid rain (see Table 4), concentrations of sulphate in groundwater suggest a source additional to rainfall. Higher sulphate concentrations are found in the southern part of the basin and may be associated with the raised beach deposits. No gypsum has been identified from cores within the basin; however sulphides may be present within thin mudstone layers. Low concentrations of sulphate within the northern part of the Locharbriggs Formation may be attributed to the absence of mudstones in the sandstone, or again changes in the composition of the drift. Interestingly, low concentrations are found within the northern portion of the Doweel Breccia Formation, maybe due to an absence of mudstone within the sequence. Potassium concentrations are low and show little change across the basin. The source is probably from K-feldspar, which can comprise up to 10% of the sediments (McKeever, 1992).

Nitrate concentrations are high compared to what would be expected from rainfall inputs alone. The main source of nitrate in the groundwater is likely to be from farming practices, notably NPK fertiliser application. The median value is 27 mg/l NO_3 (6.1 mg/l NO_3-N). The concentration of nitrate shows a good correlation with the age of the groundwater (Figure 8). Groundwater with a high proportion of pre 1950 water has low concentrations of nitrate; samples with a proportion of modern 1990 water have high nitrate. The linear relation between nitrate and the age of the groundwater implies that recharge currently contains 40-50 mg/l NO_3. The regression equation for the data implies that pre 1950s water has 5.5 mg/l NO_3. Much of the fertiliser intensive agriculture and NO_x atmospheric emissions in the UK have occurred since 1950, therefore pre 1950s groundwater are generally assumed to have zero nitrate. The small concentration of nitrate found in the samples with pre 1950s groundwater may be due to the farming practices in Dumfries earlier in the century. The ploughing of established grasslands or the use of unlined slurry pits could have release nitrate into the groundwater pre 1950.
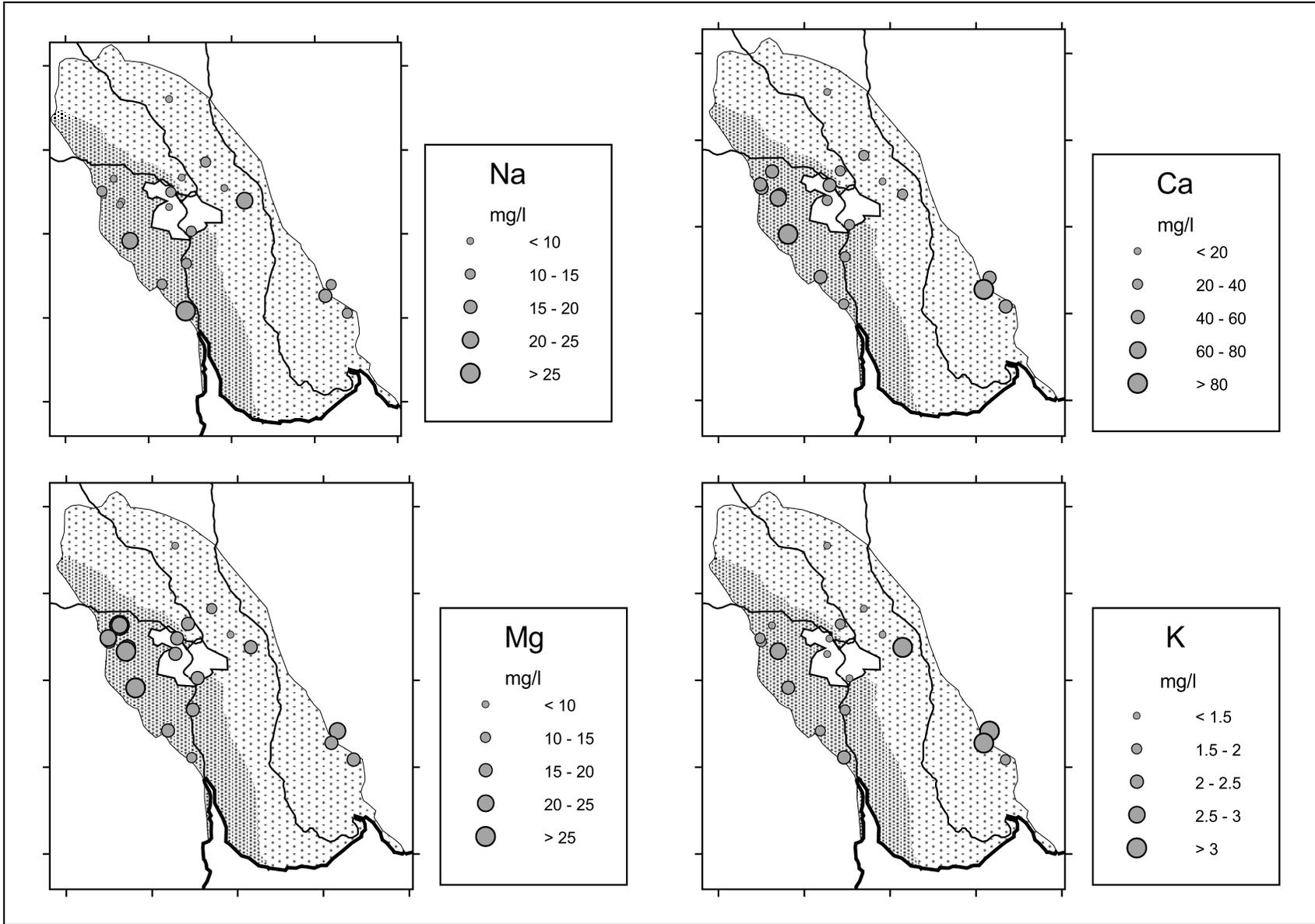
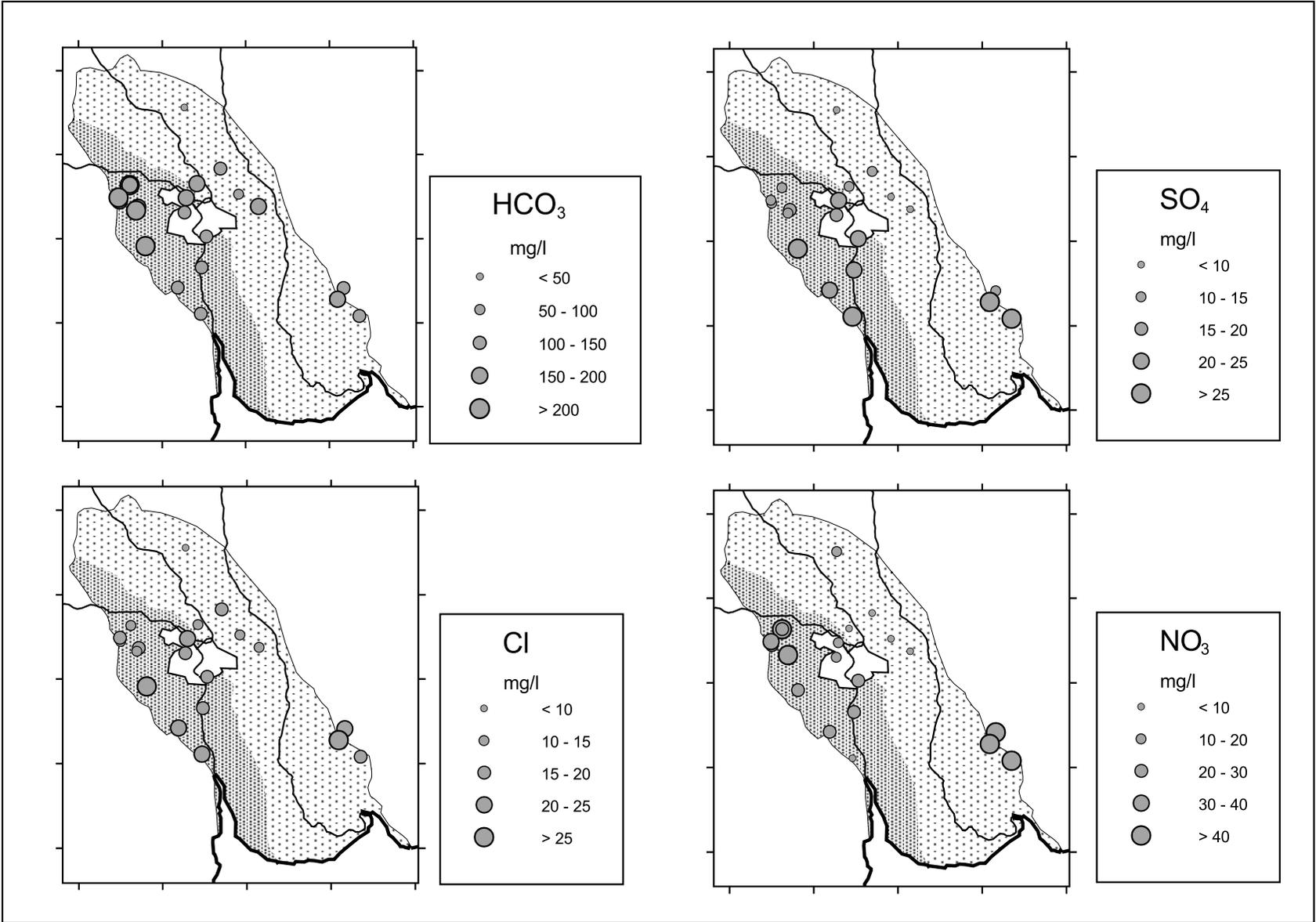**Figure 6   Maps of major ions in groundwater in the Dumfries Basin.**

Figure 7   **Maps of major cations in groundwater in the Dumfries Basin.**

The farm boreholes in the south east of the basin have the highest nitrate; these three boreholes are all located on dairy farms close to the farm buildings. The very high nitrate may be due to local contamination around the farm, rather than regional contamination of the aquifer. Lowest nitrate concentrations are found in the older water in the Locharbriggs formation in the east of the basin where nitrate concentrations are generally less than 10 mg/l (2.26 mg/l NO_3-N).

Si is the most abundant component of the rocks in Dumfries; therefore a ready supply of Si is potentially available for dissolution. The concentration of Si is limited by the low solubility of quartz rather than the supply of source material. At 25°C quartz has a solubility of 6 mg/l (Hem, 1985). Concentrations are similar throughout the basin, ranging from 3.5 mg/l to 6.6 mg/l with a median value of 5.1 mg/l. In a study of the trace elements in the groundwater of the Permian of northern England and Southern Scotland, Edmunds et al. (1989) found groundwaters to be oversaturated with respect to quartz.

Iron and manganese levels are low throughout the aquifer. Iron is generally below the detection limit of 0.02 mg/l, with manganese <0.04 mg/l. The solubility of these two minerals is strongly redox controlled particularly at near neutral pH. Significant dissolution of iron and manganese will only occur under reducing conditions even though iron is present as haematite within the sediments (which gives the rocks the characteristic red colour).

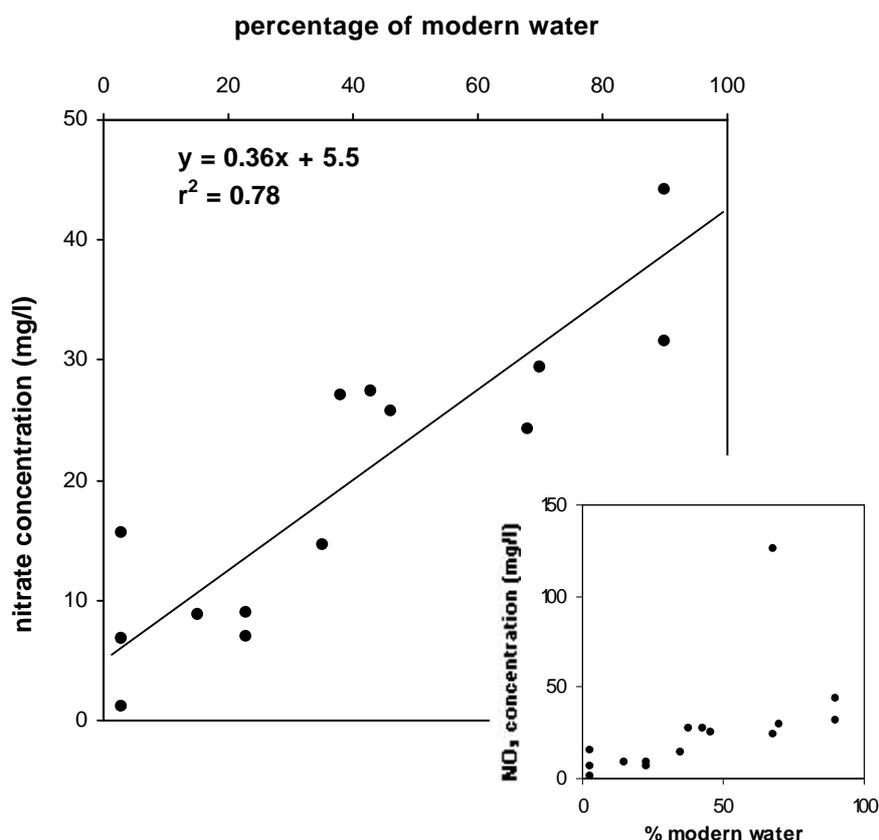percentage of modern water

$y = 0.36x + 5.5$
$r^2 = 0.78$

Figure 8   **Relation of nitrate to the proportion of modern water in groundwater. The insert shows all the data and the main graph and regression equation excludes the outlier.**

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6.   CHANGES WITH DEPTH

Depth samples were taken at two sites. At Hardthorne Rd, where there is strong groundwater flow within the borehole, two inflows were sampled, one from 125 mbgl (sample 14) and another from 30 mbgl (sample 13). The water from these two inflows flows out of the borehole at a fracture at 60 mbgl. The strong flow within the borehole is probably due to pumping elsewhere in the basin. Two samples were taken at the Manse Rd site. One sample (8) was taken from the production borehole where the water primary flows into the borehole from a fracture at about 110 m bgl; and a second sample (15) from a 30 m deep observation borehole drilled 190 m away.

The change of major ion chemistry with depth is shown on Figure 9 (data in Table 3). Both sites show a similar pattern. The deeper waters have display less mineralisation than the shallow waters, reflected by the lower TDS, although sulphate and to a lesser extent, chloride concentrations are slightly elevated in the deeper samples. Age samples could only be determined for the Manse Rd site where the deeper water was considerably older than the shallow water. Not surprisingly, nitrate
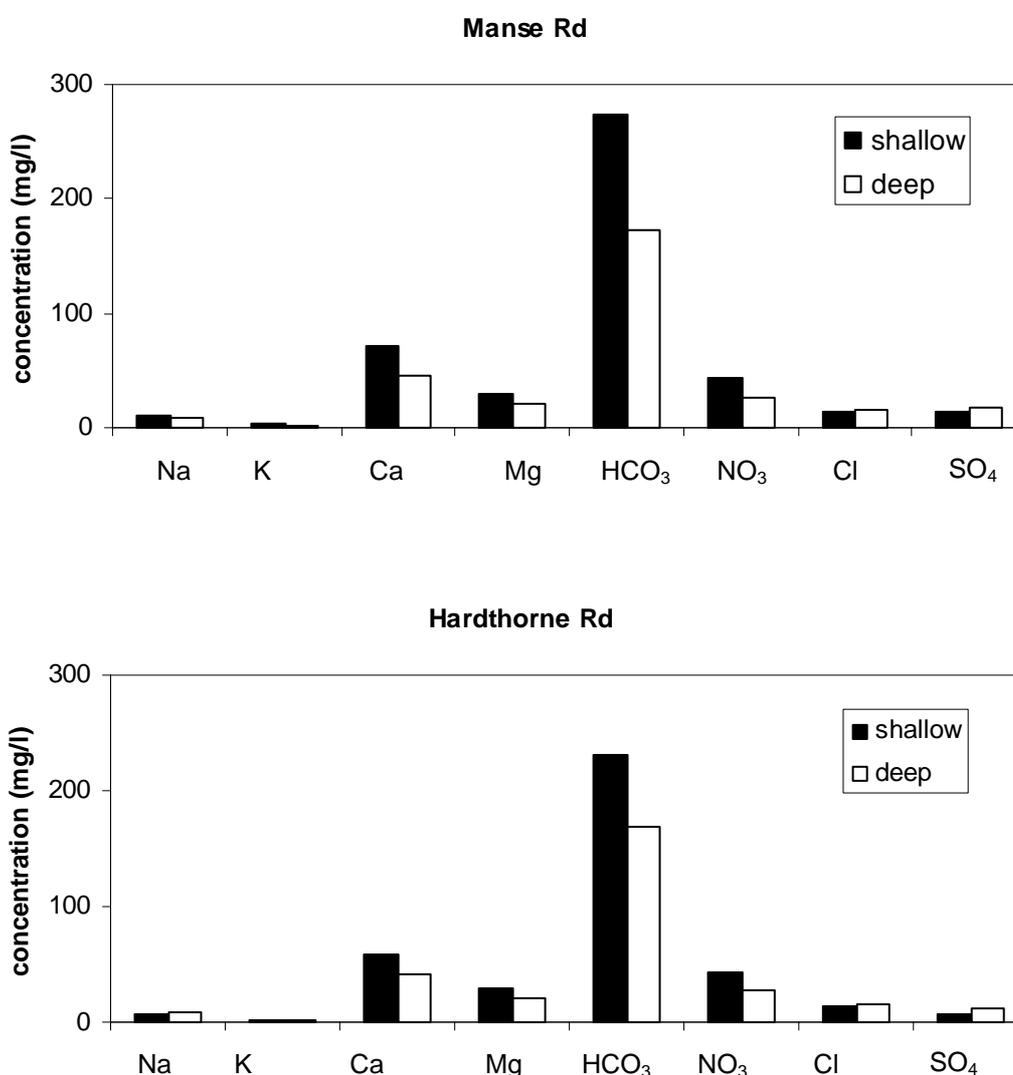

Figure 9   **The relative change of major ions with depth. Shallow samples are from fractures approximately 30 m, and deep samples from fractures at 100 – 130 m.**

decreases markedly with depth - from 44 mg/l NO_3 to approximately 27 mg/l NO_3 in both cases. This supports the evidence above that nitrate concentrations are higher in younger groundwater than older groundwater. However, nitrate is not the only constituent that decreases with depth: K, Ca, Mg and HCO_3 also reduce with depth suggesting that the groundwater is from a different source to the shallow younger water. The deeper groundwater may not be infiltrating from directly above, but moving laterally through the aquifer at depth from an area with different drift or geochemistry.

The two sites are located in the Doweel Breccia Formation, which comprises interbeds of breccia, fluviatile sandstone and aeolian sanstone. Therefore, changes in hydrochemistry with depth probably reflect the stratification of the aquifer and fracture flow from a small number of highly permeable horizons as indicated by the borehole geophysics (see earlier).

7.   TRENDS WITH TIME

There is not a large historical database of hydrochemical analyses for groundwater in the Dumfries basin. This makes it difficult to analyse trends and identify potential threats. The best historical dataset is from the Manse Rd production borehole where nitrate concentrations have been measured periodically since 1989. From 1992 to 1995, samples were taken at least fortnightly. These data have been averaged for each year, to highlight any long term trends in nitrate. Figure 10 indicates that average nitrate concentrations have increased from 22 mg/l (4.97 mg/l NO_3-N) in 1989 to more than 26 mg/l (5.87 NO_3-N) in 1999, although there is a marked variance in nitrate concentration measured throughout the year. As younger, nitrate rich water moves through the aquifer, nitrate concentrations are likely to continue rising. Intermittent data from the Cargen borehole since 1996 also indicates a rise in nitrate concentrations. It is essential to continue monitoring nitrate throughout the aquifer to identify these long-term trends.
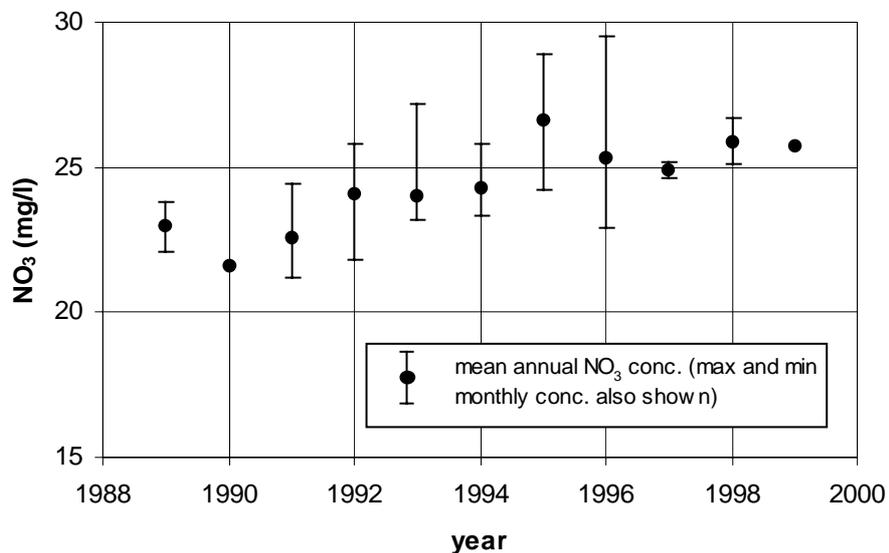

Figure 10   Average annual nitrate concentration in the Manse Rd borehole 1989-1999. Data from West of Scotland Water.

8. IMPLICATIONS FOR UNDERSTANDING THE HYDROGEOLOGY

Much of the hydrochemistry of the Dumfries Basin can be explained by the geology of the area as interpreted by Brookfield (1978). In the Doweel Breccia Formation, the enhanced concentrations of HCO_3, Mg and Ca in groundwater are probably due to carbonate cementation in the fluviatile sediments and the overlying drift. However, the mineralisation of the groundwater is low, and they are undersaturated with respect to calcite and dolomite, indicating that the proportion of carbonate cement is low or the groundwater hydrogeochemically immature. Bicarbonate, Mg and Ca concentrations in groundwater are generally lower within the Locharbriggs Formation, indicating a lower proportion of carbonate cement. However, concentrations increase in the south-east of the basin, possibly indicating that the geology changes here towards fluviatile sediments. Logging of the Stragglingwath test borehole [NY 0680 6980] in this area (Ball, 1994) showed the presence of mudstone and thin conglomerate

The hydrochemical study has supported the general conception that groundwater flow in the basin is complex. Groundwater flow within the Doweel Breccia Formation is rapid and stratified and groundwater storage is limited. There is generally a high proportion of modern (post 1990) groundwater in the Doweel Breccia Formation. The breccia has low porosity and intergranular hydraulic conductivity. Although sandstone layers have a higher porosity, they are generally thin. The high yields of the boreholes are therefore met from fracture flow which may transport groundwater from far afield. The aquifer is stratified. Groundwater flowing at depth appears not to be derived from rainwater infiltrating through the rocks and drift directly above (hence lower mineralisation and different hydrochemistry at depth).

Older groundwater is present in the Locharbriggs Formation, even in shallow boreholes; here much of the groundwater is pre 1950. This suggests that groundwater flow in the Locharbriggs Formation is slower and less dependent on recent recharge than the Doweel Breccia Formation. This is consistent with the high porosity of the sandstones which allows large quantities of groundwater to be stored in the Locharbriggs Formation. The change in water chemistry to the south of the basin, however, suggests that the flow characteristics of the aquifer may change and become more like the Doweel Breccia Formation.

9. IMPLICATIONS FOR AQUIFER DEVELOPMENT

Development for public water supply has concentrated in the Doweel Breccia Formation in the west of the basin. Here, groundwater flow is through highly permeable widely spaced fractures, the aquifer is stratified and groundwater storage is low. Consequently, although yields are high, boreholes rely on a large component of modern water to sustain their flow. There is evidence to suggest that modern recharge contains 40-50 mg/l NO_3. Hence, NO_3 levels within the pumped boreholes have risen and may continue to rise. The stratification of the aquifer and high flows at depth, suggest that groundwater may travel laterally for large distances (>3 km) to sustain borehole yields.

From the limited data, groundwater within the Locharbriggs Sandstone Formation appears to be considerably older than groundwater in the Doweel Breccia Formation. The high porosity of the sandstone, and absence of breccia mean that much groundwater is stored, but yields are possibly lower due to the absence of flow horizons at breccia/sandstone interfaces. Little exploration has been undertaken in the Locharbriggs Formation to measure aquifer properties. Development within the Locharbriggs formation may provide a low nitrate source of groundwater, but from lower yielding boreholes. In the south of the basin, however, breccia may again be present; but groundwater is younger and higher in nitrate. To protect the long-term sustainability of low nitrate sources in the Locharbriggs formation, the extent of nitrate concentrations already in the unsaturated zone would need to be measured and nitrate inputs to the aquifer possibly controlled.

10.   RECOMMENDATIONS FOR FUTURE WORK

The current study has provided useful insight into the chemistry, age and flow of groundwater within the Dumfries Basin. It has highlighted several gaps in knowledge which could be addressed.

* Further investigation of the stratification of the aquifer (both in the east and west) by targeting water sampling to inflows measured by geophysical logs. New sampling techniques will allow CFC depth samples to be taken in unpumped boreholes.

* Investigation of the recharge to the aquifer, particularly the link between groundwater in the drift and in the Permian sandstones.

* Investigation of the nitrate input to the aquifer, particularly the concentrations of nitrate in modern recharge throughout the basin. Several nitrate profiles could be measured in the unsaturated zone.

* Test drilling in the Locharbriggs formation to assess aquifer properties. Both the northern area where nitrate is low, and the southeast of the basin, where the geology appears to change.

* Controlled tracer tests from borehole to borehole may highlight information on groundwater flow patterns particularly in the Doweel Breccia Formation.

* Investigate the drift water quality throughout the Basin and in particular the Raised Beach Deposits.

* Data collection should lead towards the development of a groundwater model. Stream flows and groundwater levels should be monitored, and the interaction between rivers and aquifer assessed. The outflow from the aquifer is not known, since the interface between the drift and the Permian in the Solway Firth is uncertain. Once sufficient data has accrued, a groundwater model should be developed.

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APPENDIX 1: RESULTS OF CFC AND SF$_6$ ANALYSIS

Chlorofluorocarbons (CFCs)

The raw data for CFC-11, CFC-12 and CFC-113 are given in Table A1. Given that peak modern values for recharge at 10°C are 5.6 (CFC-11), 2.9 (CFC-12) and 0.55 (CFC-113) pmol/l it is apparent that certain sites (D99/4, D99/8, D99/11 and D99/22, mainly in industrial or landfilled areas) exceed these concentrations for all three species and therefore cannot be used for dating purposes.

Table A1   CFC results for Dumfries Basin sites. Concentrations in pmol/l.

Sample No	Site Name	CFC-11		CFC-12		CFC-113	
		value	±	value	±	value	±
D99/2	Holmhead Fm	4.3	0.3	2.2	0.2	0.73	0.05
D99/4	Nestle #1	8.2	0.5	1.2	0.1	0.22	0.05
D99/5	Dundas Chemical	0.07	0.05	0.01	0.05	0.03	0.05
D99/6	Gates Rubber new b/h	11	2	7.9	0.4	2.6	0.6
D99/8	Manse Rd PS Dumfries	>70	-	17	2	2.1	0.6
D99/9	Larchfield Production	4	0.2	1	0.1	0.32	0.05
D99/10	Locharmoss #1.3	0.51	0.05	0.02	0.05	5.6	1.2
D99/11	Locharmoss #1.6	8.1	0.5	3.2	0.2	6.5	1.3
D99/15	Manse Rd obs	7	0.4	2.9	0.2	3.7	0.8
D99/16	Terregles, bottom left	6.2	0.4	2.1	0.2	0.62	0.05
D99/17	Terregles, dog kennel	9.6	0.5	3	0.1	1	0.1
D99/18	Cargen Prod #1	2.8	0.2	1.2	0.1	3.8	0.8
D99/19	Greenmerse	0.31	0.05	0.68	0.05	0.03	0.05
D99/20	Gallaberry Fm	0.35	0.05	0.02	0.05	<0.01	-
D99/21	Hollywood FF pump 10	0.16	0.05	0.78	0.05	0.01	0.05
D99/22	Dupont DGI 1	>200	-	20	4	1.5	0.2

While CFC concentrations in groundwater are raised by contamination, they can be lowered by degradation under low-oxygen conditions. A possible index of this could be a low ratio of nitrate to alkalinity (~0.02 or less) resulting from denitrification. Sites not already suffering major CFC contamination where this could be ocurring include D99/4, D99/5, D99/10, D99/19 and D99/21. The effect of lowering CFC concentrations is to increase the apparent bulk age of the sample, so all these sites could be giving greater than actual ages. Of course, nitrate can be naturally low without denitrification, and where this is the situation, the CFC 'ages' are likely to be reliable.

The fact that there are three CFC species provides a degree of 'redundancy' in calculating ages. Ideally each species will give around the same date for a sample, but this is rather rarely the case in reality. The most usual contaminant is CFC-113, and indeed at nine out of sixteen sites this species is present at concentrations above present-day. Where the other species are present at below present-day concentrations, the presence of high CFC-113 is generally taken to be evidence of a waste-water contribution (e.g. this could be the case for sites D99/2 and D99/18). CFC-12 tends to be the most reliable of the 3 species for age estimation because it is less affected by degradation than CFC-11, and is also less likely to be supplemented by contamination than CFC-11 and CFC-113.

CFC data can be used as a 'bulk-age' or 'proportion-of-mixing' indicator. The nature of the Dumfries aquifer (see main text) makes it likely that most of the waters are mixed. For the purposes of the calculations in Table A2 it is assumed that pre 1950 CFC-free water (Cook and Solomon, 1997) is mixing with 'young' water a few years old. The table shows that waters range from apparently largely young (D99/15, Manse Road) to unequivocally old (D99/20, Gallaberry Farm). Reservations concerning each site are given in the *Comments* column.

Table A2   **CFC concentrations interpreted in terms of the percentage of young (1990s) water mixed with pre-1950 water.**

Site Name	Area Type	Apparent % of young water	Comments
Holmhead Fm	Pasture	65-75	113 suggests some waste water,
Nestle #1	Industrial	30-40	11 shows contam, low TON, interpret with caution
Dundas Chemical	Past./Industrial	0-5	Low TON, interpret with caution
Gates Rubber new b/h	Industrial	contam.	Moderate contam, no age possible using CFCs
Manse Rd PS Dumfries	Pasture	contam.	High contam, no age possible using CFCs
Larchfield Production	Urban	35-40	No contra-indications
Locharmoss #1.3	Past./Landfill	0-5	113 suggests some waste water, low TON, caution
Locharmoss #1.6	Past./Landfill	contam.	Moderate contam, no age possible using CFCs
Manse Rd obs	Pasture	80-100	All species at or near max uncontam values
Terregles, bottom left	Pasture	65-70	11 and 113 contaminated, interpret 12 with caution
Terregles, dog kennel	Pasture	100	All species at or above max uncontam values
Cargen Prod #1	Pasture	40-45	113 suggests some waste water, otherwise OK
Greenmerse	Pasture	20-25	Low TON, interpret with caution
Gallaberry Fm	Pasture	0-5	No contra-indications
Hollywood FF pump 10	Pasture	20-25	Low TON, interpret with caution
Dupont DGI 1	Industrial	contam.	Highly contaminated, no age possible using CFCs

SF$_6$ (sulphur hexafluoride)

In an attempt to deal with the two CFC problem areas identified above (contamination and degradation), the analysing laboratory (Spurenstofflabor) measured the SF$_6$ content of each sample. The rationale behind this was that SF$_6$ is an atmospherically well-mixed tracer like CFCs, but is a much less common pollutant and also much less easy to degrade.

Table A3 shows the results of SF$_6$ analysis converted to percentage of young water compared to the CFC results. All the CFC-contaminated sites yield 'real' results, ranging from 15% young water at D9/6 (Gates Rubber) to 100% young at D99/11 (Locharmoss 1.6). Sites with possible reducing conditions gave mixed results: in the case of D99/4 and D99/19 (Nestle No 1 and Greenmerse) there is a large disparity between the ages suggesting degradation of CFCs, but for D99/5, D99/10 and D99/21 (Dundas Chemical, Locharmoss 1.3 and Hollywod FF pump 10) there is fair-to-good agreement, indicating that degradation has not been a problem and that the low nitrate is 'genuine'. Otherwise, for the five remaining sites (Cargen was not measured for SF6) with evidence of neither gross contamination nor degradation, agreement is mostly close; where less good (D99/9 and D99/15) the site is either urban (Larchfield Production) or associated with a CFC-contaminated site (Manse Road Observation), with the probably enhanced CFCs giving what appear to be somewhat too high percentages of young water.

Table A3 **Comparison of SF$_6$ and CFC results expressed as the percentage of young (1990s) water mixed with pre-1950 water.**

Sample No	Site Name	Type of Area	Percentage of Young Water	
			SF$_6$	CFC
D99/2	Holmhead Fm	Pasture	71	65-75
D99/4	Nestle #1	Industrial	100	30-40
D99/5	Dundas Chemical	Past./Industrial	<5	0-5
D99/6	Gates Rubber new b/h	Industrial	15	C
D99/8	Manse Rd PS Dumfries	Pasture	46	C
D99/9	Larchfield Production	Urban	23	35-40
D99/10	Locharmoss #1.3	Past./Landfill	17	0-5
D99/11	Locharmoss #1.6	Past./Landfill	100	C
D99/15	Manse Rd obs	Pasture	69	80-100
D99/16	Terregles, bottom left	Pasture	62	65-70
D99/17	Terregles, dog kennel	Pasture	90	C
D99/18	Cargen Prod #1	Pasture		40-45
D99/19	Greenmerse	Pasture	86	20-25
D99/20	Gallaberry Fm	Pasture	<5	0-5
D99/21	Hollywood FF pump 10	Pasture	25	20-25
D99/22	Dupont DGI 1	Industrial	70	C

Conclusions

1.   On the basis of their CFC and SF_6 contents, the groundwaters sampled in the Dumfries basin range from old (perhaps over 100 years) to wholly modern.

2.   CFCs are unlikely to provide residence time information on or near industrial or landfilled sites, but they may have an important tracer function.

3.   It helps to have information on redox conditions (DO or Eh) in order to judge whether low CFC concentrations are likely to be real or degraded.

4.   The use of SF_6 should be considered in situations where CFC contamination or degradation are suspected.

References

Cook P G and Solomon D K 1997.   Recent advances in dating young groundwater: chlorfluorocarbons, ^{3}H/^{3}He and ^{85}Kr. *Journal of Hydrology*, **191,** 245-265.