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Utilising seasonal variations in hydrogeochemistry and excitation-emission fluorescence to develop a conceptual groundwater flow model with implications for subsidence hazards: an example from Co. Durham, UK

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Abstract Groundwaters were sampled from four research boreholes, a private supply well and a natural karst resurgence in southern County Durham, England. Time series data sets of piezometric levels, groundwater major ions, and fluorescence of dissolved organic matter (DOM) were interpreted in the light of new geological mapping to assess the movement of groundwater and its potential for the dissolution of gypsum. Three distinct groundwater facies were identified representing contact with gypsiferous strata, dolomitic limestone and Quaternary Till. Piezometric data indicated time varying transverse flow across the gypsifeorus strata, which was confirmed from gradational mixing of groundwater types and cation ratios. Fluorescence of dissolved DOM identified variations in protein and fulvic-like acid fluorescence. The former was taken to represent surface derived, short-lived material. Spatial and temporal variations in protein fluorescence offered a means to trace groundwater movement along the regional groundwater gradient and indicated rapid lateral movement of groundwater. It was concluded that gypsum dissolution is occurring beneath the town of Darlington, however, the presence of a thick deposit of Quaternary till effectively confines the small head differences of approximately 1 m, across the gypsum strata beneath the town. Further to the south, the lowering of the ground surface results in a greater upwards flow of water across the gypsum and is used to explain the presence of historic collapse sinkholes.

Keywords Groundwater tracing · Subsidence · Fluorescence · DOM · Gypsum · Karst · County Durham · England

Introduction

The Permian Strata in the environs of Darlington, County Durham, NE England comprise an alternating sequence of marine mudstones, limestones, dolomites and gypsiferous strata (Fig. 1) which accumulated as shallow water detrital and evaporite deposits on the western margins of the Zechstein Basin (Smith 1967).

Although rarely supporting enterable caves, the dolomites and dolomitic limestones exhibit karstic features such as small dolines and stream sinks (Cariney and Hamill 1977). The best examples of karstic phenomena in the UK Permian are related to the gypsiferous deposits and include caves and a wide range of subsidence features. The situation is exemplified in and around the city of Ripon, North Yorkshire, where

Cooper ([1986]) has documented the development of gypsum karst subsidence features and has proposed a generalised geological-hydrogeological model. However, Ripon is not alone in suffering subsidence effects associated with the dissolution of gypsum. Thompson et al. ([1996]) considered other sites situated on the Permian outcrop in Northern England and identified Darlington as an area potentially at risk from gypsum-karst related subsidence. Closed surface depressions and some subsidence-related building damage in the town indicated that the situation warranted further investigation.

The present paper presents an integrated analysis of the geology, hydrogeology (including groundwater quality, groundwater level and natural tracers) with an emphasis on characterising groundwater flow and its potential for gypsum dissolution.
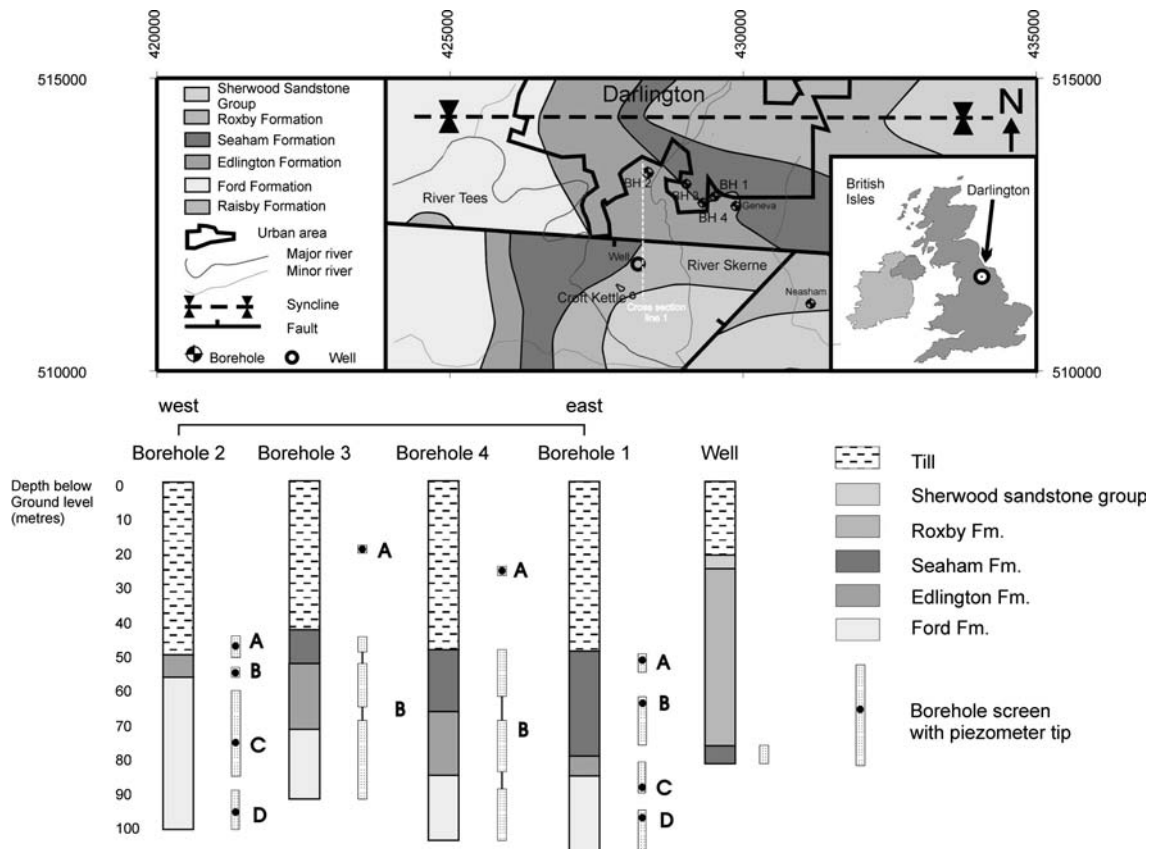
Geology

Succession

The Geological sequence in the Darlington region comprises:

- *Glacial Till* (Quaternary) Comprising reddish brown to greyish brown boulder clay with bands of sand and gravel and laminated and lacustrine clays (approximately 30–50 m thick)
- *Sherwood Sandstone Group* (Triassic) Red-brown sandstone up to 250–300 m thick dominated by siltstone and mudstone at its base.
- *Roxby Formation* (Permian) Red-brown calcareous mudstone with subordinate gypsum beds and about 8 m of gypsum or anhydrite at its base (20–30 m thick).
- *Seaham Formation* (Permian) Thinly bedded pale grey calcitic dolomite 15–20 m thick.
- *Edlington Formation* (or Permian Middle Marl) Red-brown calcareous mudstone with gypsum beds and up to about 30–40 m gypsum or anhydrite at its base (up to 50 m thick).
- *Ford Formation* (Permian) Pale grey and yellow dolomitic limestone (up to 30 m thick).
- *Raisby Formation* (Permian) Pale grey and yellow dolomitic limestone (up to 20 m thick).
- *Marl slate* (Permian) grey organic-rich laminated siltstones and dolomites (up to 5 m thick)
- *Basal Permian Sands* yellow weakly cemented coarse siliceous sand in the north which becomes brecciated dolomites beneath Darlington (up to 30 m thick).

Fig. 1 Geological sketch map of the Darlington area (*top*) with logs of research boreholes and a water supply well

Structure

The geological structure as depicted in Fig. 1 is based on a re-evaluation of the local geology as part of the RO-SES project (see Acknowledgement) by Tony Cooper of the British Geological Survey and Jim Gordon of Darlington Borough Council, which has considerably updated the previous interpretations as shown by the British Geological Survey (1987). In general, the Permian and Triassic strata dip gently E–ESE at around 2–3°. Superimposed on this generalised dip is a prominent but gentle, easterly plunging syncline which underlies most of Darlington.

Two major faults have been newly interpreted. The larger of the two, with a throw of approximately 30 m to the south, passes E–W close to the southern limit of Darlington. The NE–SW trending fault which passes through the confluence of the Rivers Tees and Skerne, has a throw of approximately 8 m.

Palaeokarst

As part of this investigation four research boreholes were drilled in the southern part of Darlington where subsidence related building damage has been most severe. Where proven in boreholes, the Edlington Formation varies in thickness from 6 m to 26 m (Table 1) and increases in thickness eastward to achieve 40 m of mostly Anhydrite at Neasham (Fig. 1). The Edlington Formation is recorded in Borehole 2 as 6.5 m of mixed gypsum (about 50%), dolomite siltstone and clay. It lies directly beneath the Till and therefore the top of the unit is not identified. Moving eastwards towards Borehole 3 the unit thickens to 26.1 m. The Unit then thins significantly towards Borehole 1 with a minimum of 6.0 m preserved there. The variation in the thickness of the Edlington Formation over such short distances is probably related to dissolution processes. Karst phenomena which include open and sediment-filled caves and brecciation, are recorded from borehole logs and core (Table 1). Much of the overlying Seaham Formation shows evidence of collapse and foundering as a result of dissolution of the Edlington Formation gypsum. The top of the Ford Formation shows evidence of dedolomitisation, which is frequently associated with gypsum dissolution (Bischoff et al. 1994).

Hydrogeology and groundwater flow

The general hydrostratigraphy of the area consists of a lower aquifer comprising the basal Permian Sands and the Raisby and Ford Formations which is separated from an upper aquifer (comprising the Seaham Formation), by the Edlington Formation which acts as a leaky

Table 1 Dissolution-related phenomena in boreholes on the southern side of Darlington

Geological unit	Borehole 2	Borehole 3	Borehole 4	Borehole 1	Neasham borehole
Till	50.20 m	44.40 m	48.90 m	49.15 m	49 m
Roxby Formation	Absent	Absent	Absent	Absent	Absent
Seaham Formation	Absent	1.4 m recovered only as chippings	18.1 m cavernous and brecciated, completely foundered.	30.70 m brecciated and foundered	Absent
Edlington Formation	~8 m gypsum suboprs at rockhead. much of the gypsum contains clay—possible cave deposits	26.1 m including 16.2 m gypsum, ~3 m of cave deposits with collapse breccia and dissolution residue at base of gypsum, including a 0.5 m open cavity in the gypsum	15.8 including 8.2 m of gypsum 7.0 m in total cave deposits primarily at base (4.2 m) and top (2.6 m).	6.0 m sequence of gypsum containing fragments of overlying Seaham Formation Dolomite	> 18.3 m base not proven . Contained 16.5 m of anhydrite cavity 1.93 m high at base of anhydrite overlying 0.3 m broken gypsum.
Ford Formation	Contact zone very porous and contains material washed in from above, and severely leached dolomite sand.	Upper contact marked by cavities with material washed in from above, and leached dolomite sand.	Contact zone is severely leached and porous with collapse breccia at top.	Contact zone very porous and contains material washed in from above, and severely Leached dolomite sand.	Not penetrated

aquitard (Younger 1995). The degree to which the Edlington Formation acts as an aquitard depends on whether karst has evolved in the gypsum and if subsequent processes have plugged any conduits with sediments. Further to the south and east of Darlington, the Seaham Formation is hydraulically separated from the Triassic Sherwood Sandstone by the intervening Roxby Formation and the argillaceous basal portion of the Sherwood Sandstone Group. The Quaternary Till comprises mostly low permeability boulder clay with occasional higher permeability sand and gravel horizons.

Groundwater contours drawn from boreholes provided by the Environment Agency indicate a gradual fall in the potentiometric surface of the Lower Aquifer from northwest to southeast i.e. from the outcrop areas of the Ford and Raisby Formations situated 5–7 km to the North northeast of Darlington to the valley of the River Tees, 5 km to the south of Darlington (Fig. 2).

Research boreholes (Fig. 1) contained nested piezometers, the hydrographs of which are shown in Fig.3. Groundwater levels measured in the Till (piezometers 3A and 4A) are higher than in the solid rocks below. This is probably owing to the general low permeability of the Till, which is confirmed by the slow recovery of water levels after sampling as seen in 3A (Fig. 3c). Piezometer 4A shows very little variation whatsoever. Although 2A is situated in the Till (just above rockhead), its variation in groundwater levels is almost identical in timing and magnitude to solid geology and therefore probably has a high degree of connection.

The variations in piezometric level in the solid geology over the period of June 1998–February 2000 show strong seasonality with groundwater lows in October with a marked rise in groundwater levels occurring during the winter months.

Piezometric head differences

In both Boreholes 1 and 2, piezometers C and D are situated entirely or in part in the Ford Formation and the similarity in levels and their variation with time indicate hydraulic connection. Piezometers 3B and 4B connect the Ford, Edlington and Seaham Formations through slotted tubes and show similar patterns to Boreholes 1 and 2; the difference in their levels between Boreholes 3 and 4 is attributable to their positions on the hydraulic gradient (Fig. 2).

Borehole 1

Piezometers 1A and 1B show almost identical records, which represents the piezometric level of the upper aquifer i.e. the Seaham Formation. A head difference of 0.25–0.5 m is maintained between this l and the lower aquifer (1C and 1D) by the Edlington Formation. The head difference is generally constant throughout 1998 and 1999 but with a gradual increase during the winter of 1999/2000 (Fig. 6). These data indicate that there may be a component of groundwater flowing upwards from the Ford Formation to the Seaham Formation at this site; the magnitude of which will be influenced by the hydraulic conductivity of the Edlington Formation.

Fig. 2 Regional hydrogeological gradient, interpolated from boreholes in the Ford Formation (1998–1999), indicating general south easterly flow of groundwater towards the River Tees
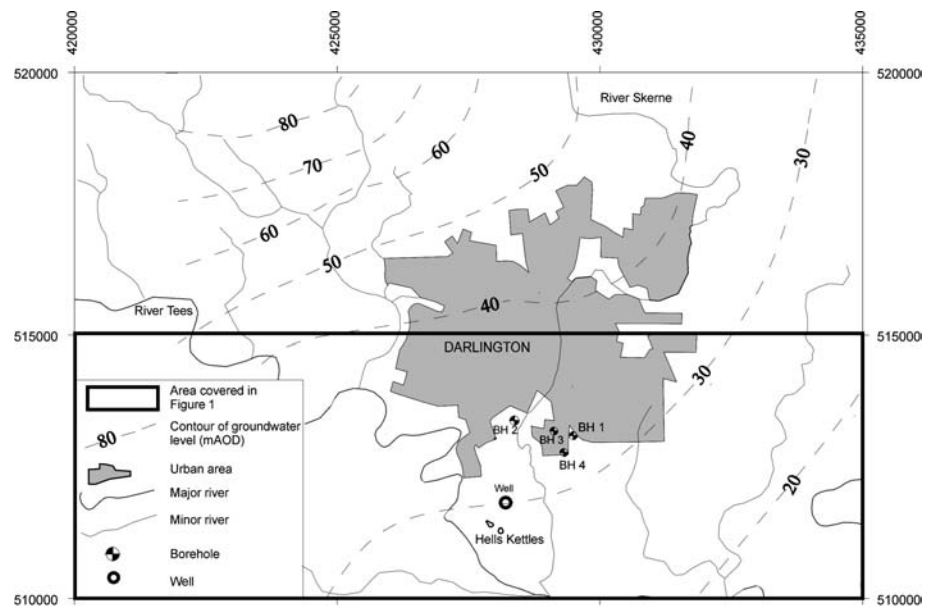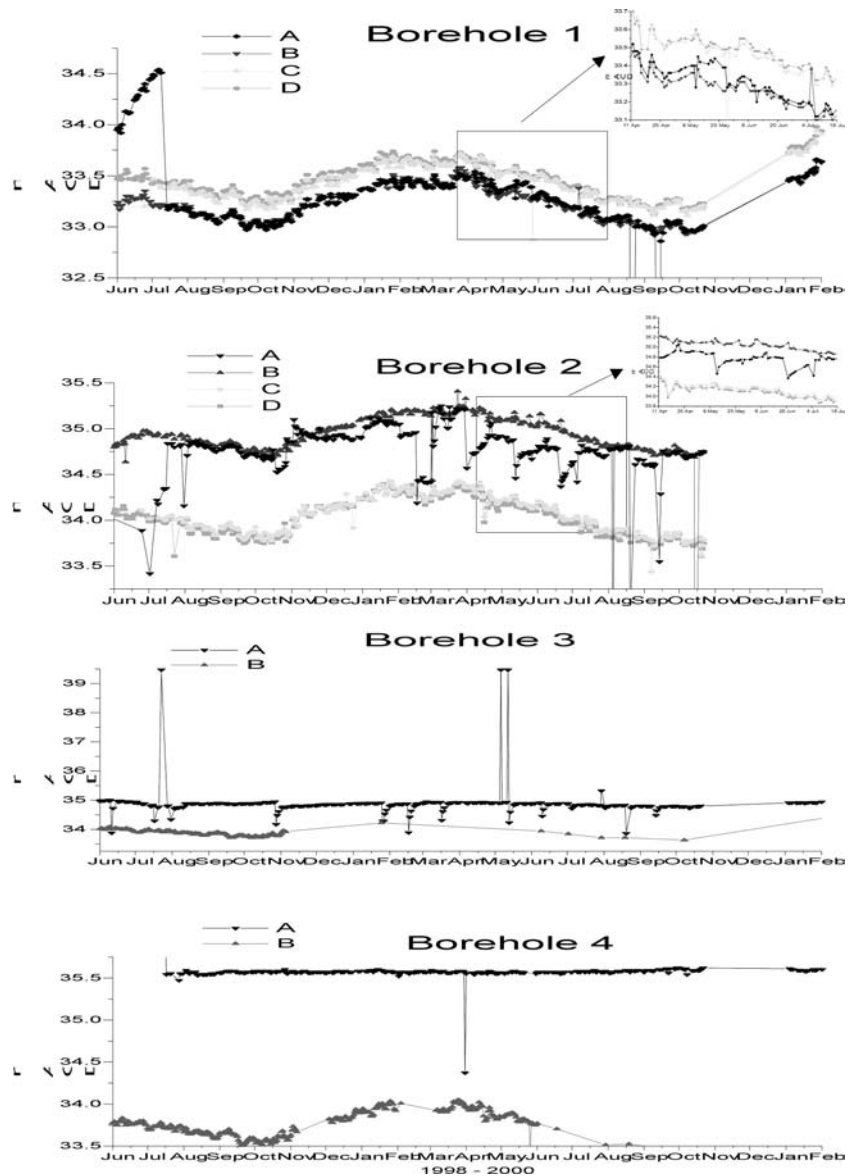
Fig. 3 Piezometric levels from research boreholes 1–4 (1998–2000)

Borehole 2

In Borehole 2, a head difference of 0.7–1.2 m is maintained across the base of the Edlington Formation i.e. between Piezometers 2B and 2C (Figs. 3 and 7). The head difference shows a seasonal variability that is greatest in the late summer and early autumn (approximately 1.1 m) and smallest during mid to late winter (approximately 0.7 m). This seasonal variation appears to be controlled by the piezometric level in the Ford Formation, which shows greater variability than the overlying Edlington and basal Till in Borehole 2. These data indicate that there may be a component of groundwater flow downwards from the Till to the Ford Formation, the magnitude of which, as for Borehole 1, will be influenced by the hydraulic conductivity of the Edlington Formation.

Water quality

Water was sampled from all the piezometer tubes in research Boreholes 1–4 using mechanically agitated gravitational lifting tubes manufactured by Waterra. In addition to the research boreholes, water samples were taken from a private supply well and at Croft Kettle (a natural karst resurgence) 3 and 4 km to the south of Darlington, respectively (Fig. 1). Water quality analyses were performed for major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^{2-} and Cl^-) and Sr^{2+}. Figure 4 is a Piper plot of mean values for analyses taken on a 2-week to monthly basis from June 1998 to July 1999. This shows three distinct water types (Table 2).

Table 2 Mean water analyses for samples from all sites

Site		Anions			Cations				TDS
		Cl^-	SO_4^{2-}	HCO_3^-	Mg^{2+}	Ca^{2+}	Na^+	K^+	
2C	Group 1	19.2	504	296	50.3	221	39.7	3.2	1137
2B		19.7	1506	230	88.8	523	74.2	4.8	2456
2A		21.5	1021	291	59.5	369	74.1	8.1	1851
3B		23.1	260	335	29.2	160	31.0	3.1	843
Croft Kettle		29.8	1356	235	100	493	46.3	4.5	2273
well		15.6	762	289	76.2	291	23.9	3.7	1465
Group 1 mean					67.3	343	48.2	4.6	1671
1D	Group 2	20.4	45.9	321	27.0	67.5	25.5	2.5	510
1C		17.1	41.3	283	24.1	61.5	22.9	2.3	452
1B		21.4	159	301	32.7	98.6	36.6	3.4	655
1A		29.4	209	320	33.1	109	54.8	4.1	761
2D		19.4	107	354	42.4	90	32.5	2.8	648
4B		21.7	94.9	334	27.8	81.7	33.6	2.7	597
Group 2 mean					31.2	84.8	34.3	3.0	604
4A	Group 3	96.9	731	454	38.6	79.2	433	9.5	1843
3A		73.7	599	438	35.6	80.3	357	8.9	1593
Group 3 mean		85.3	665	446	37.1	79.8	395	9.2	1718

Table 3 Mean cation ratios for groundwater groups

Groundwater group	Ca/Mg	Ca/Na	Na/K
1	5.0	7.4	10.3
2	2.7	2.5	11.4
3	2.15	0.2	42.9

Group 1

These waters are characterised by relatively high TDS, high ratios of, Ca/Mg and Ca/Na (Table 3), low ratios of Na/K and high ratios SO4/HCO3 which fall in a range from 2B to 3B as shown in Fig. 4. These waters are interpreted as containing dissolved gypsum. Dissolved gypsum in the well and Hells Kettles derive from the Roxby Formation whereas all other group 1 waters contain gypsum dissolved from the Edlington Formation.

Group 2

These waters are derived from Borehole 1 (A, B, C and D) and 4B. They are characterised by relatively low TDS

and low ratios of Ca/Mg, Ca/Na and Na/K and relatively low ratios of SO4/HCO3 which, with the exception of 1A and 1B are tightly grouped towards the bicarbonate corner of Fig. 4. These are interpreted as waters from the Magnesian limestone which have had only limited contact with gypsum; 1A and 1B containing the greater proportions of dissolved gypsum.

Group 3

These waters are derived from the shallow Piezometer tubes 3A and 4A. They are characterised by relatively high TDS, a high ratio of SO4/HCO3, relatively low ratio of Ca/Mg and comparatively very low ratio of Ca/Na. These waters are interpreted as slow moving meteoric recharge which has come into contact with limestone in the Till. Cation exchange of calcium ions for sodium ions in the clays of the Till is considered the likely cause of the low Ca/Na ratio and this seems to be confirmed by the high Na/K ratios of these waters.

The high sulphate content of Type 3 waters appears anomalous as gypsum would not be expected to be present in large quantities in the Till, and the piezo-

Fig. 4 Piper plot of major cations from all sites (1998–2000) indicating three main groundwater facies
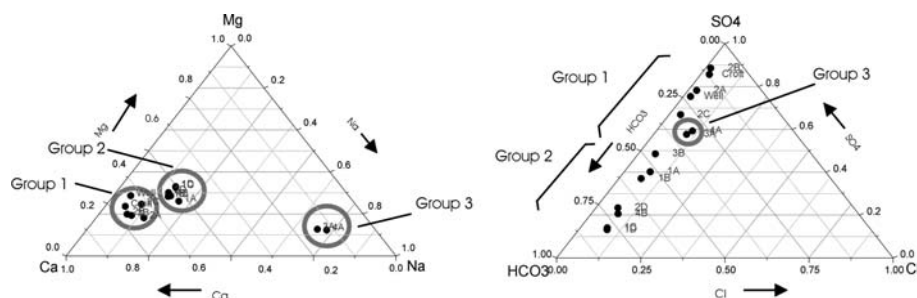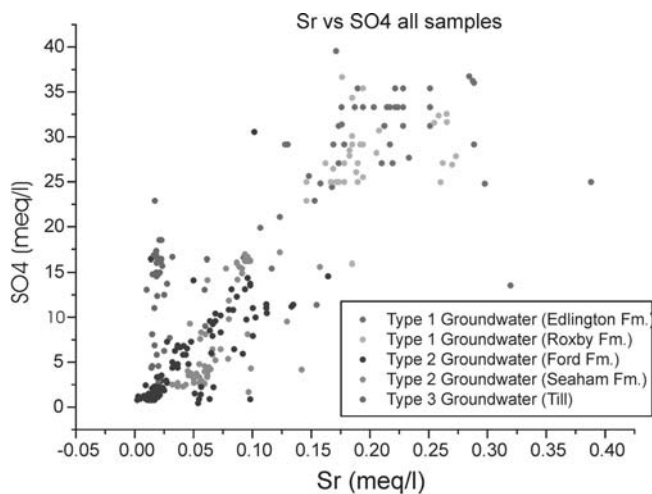
Fig. 5 Concentrations of strontium versus sulphate for all analyses. Note that sulphate concentrations in Type 3 groundwaters vary independent of strontium concentrations

metric data show a pressure gradient indicating downwards flow from the Till. The source of the sulphate is illuminated in Fig.5, which plots strontium against sulphate for all analyses. Strontium concentrations correlate well with sulphate for groundwaters from groups 1 and 2 whose water quality analyses, taken together, indicate a series with increasing quantities of dissolved gypsum. It is known that strontium substitutes for calcium in the gypsum lattice and therefore the strontium data in Fig. 5 confirm the interpretations made from analyses for the major ions (Fig. 4). Group 3 waters have sulphate concentrations which might indicate dissolved gypsum; however, there is no association with strontium. It is suggested therefore that the sulphate present in group 3 waters has a source other than the dissolution of gypsum. Oxidation of iron pyrite is a potential for the sulphate in the Till. Coal seams rich in pyrite crop out just to the north of the area and the abundant coal fragments in the Till in the study area are likely to derive from this source.

Comparison of water quality with head differences

Borehole 1

The piezometric data from Borehole 1 suggested the potential for groundwater to flow upwards across the Edlington Formation. If this were so it might be expected that water from 1B showed traces of dissolved gypsum. Table 2 and Fig. 4 show that both 1A and 1B are transitional between groundwater groups 1 and 2. Piezometer 1A has higher mean SO_4 concentrations than 1B but it is not immediately adjacent to the Edlington Formation (Fig. 1). However, mean Sr/SO_4 ratios of for 1A and 1B of 78.3 and 68.0, respectively, indicate slight strontium

depletion and thus enhancement of non-gypsum derived sulphate in groundwater from 1A. This is supported by Na/K ratios of 13.3 and 10.7 for 1A and 1B showing enrichment of sodium in 1A which, as indicated for 3A and 4A, is associated with Till-derived waters.

Borehole 2

Piezometric data for Borehole 2 suggested that groundwater may be flowing downwards from the Till across the Edlington Formation. The screened section of Piezometer 2B lies in the gypsum at the base of the Edlington Formation and contains the highest recorded sulphate concentrations of this research. Although 2C is within the Ford Formation, it is classified with Group 1 groundwaters i.e. containing dissolved gypsum (situated towards the HCO_3 end of the Group 1 range in Fig. 4). It thus appears that groundwater is flowing down through the Edlington Formation where it dissolves gypsum before proceeding to enter the Ford Formation and mix with the water there.

Piezometer 2A is situated at the base of the Till but gave mean SO_4/Sr and Na/K ratios of 145 and 9.16, respectively, which when compared to the other data indicate dissolution of gypsum and a lack of sodium enrichment from Till-derived waters (i.e. dissimilar to 3A and 4A). Therefore, the high sulphate in 2A is considered to be associated with gypsum dissolution even though piezometric data indicate that water is flowing downwards. This apparent anomaly is interpreted as an artefact of sampling. Field experience showed that the recovery of the water level in 2A, drawn down during sampling, was very slow (Fig. 3). Given the close proximity of 2A to the top of the Edlington, it is likely that sampling temporarily reversed the local hydraulic gradient such that water flowed from the Edlington upwards towards 2A, resulting in water samples containing dissolved gypsum.

Boreholes 3 and 4

Water samples from the deep piezometers in Boreholes 3 and 4 (3B and 4B) are less easily clearly interpreted. Piezometer tubes were slotted at three horizons thus connecting the Ford, Edlington and Seaham Formations (Fig. 1) with 3B open to almost the entire thickness of the Edlington Formation. Water from 3B is transitional between groundwater Groups 1 and 2 (Fig. 4 and Table 2) whereas water from 4B is clearly associated with groundwater Group 2. This is probably related to differences in the thickness of the Edlington exposed in the borehole and variations of rock mass characteristics between the boreholes. Neither 3B nor 4B show appreciable mixing of Till-derived waters.

Annual variations in water quality

Piezometric and water quality data from Borehole 1 and Borehole 2 indicate that water is flowing through the Edlington Formation and dissolving gypsum. The rate of dissolution will be related to the degree of undersaturation (with respect to gypsum) of the incoming water and the rate of water flow. Piezometric data from Boreholes 1 and 2 indicate a seasonally variable head difference across the Edlington Formation which is controlled by the water level in the Ford Formation. If water is flowing through the Edlington Formation, then a seasonal variation in water quality influenced by the dissolution of gypsum might be expected in Piezometers 1B and 2C. Piezometer 1B, situated in the Seaham Formation, taps water, which may have travelled up through the Edlington Formation, and 2C, situated in the Ford Formation, samples water which may have travelled downwards through the Edlington Formation.

Borehole 1

Figure 6 shows head differences across the Edlington Formation with water quality indices for Piezometers 1A, 1B and 1C. This shows that all measured water quality indices generally vary synchronously which suggests either a single source for the water or mixing of waters whose qualities vary similarly with time. All the species may be derived from different sources, however, sulphate and strontium in particular would, in this

Fig. 6 Intra-annual variations in water quality indices and head difference across the Edlington (gypsiferous) Formation in Borehole 1
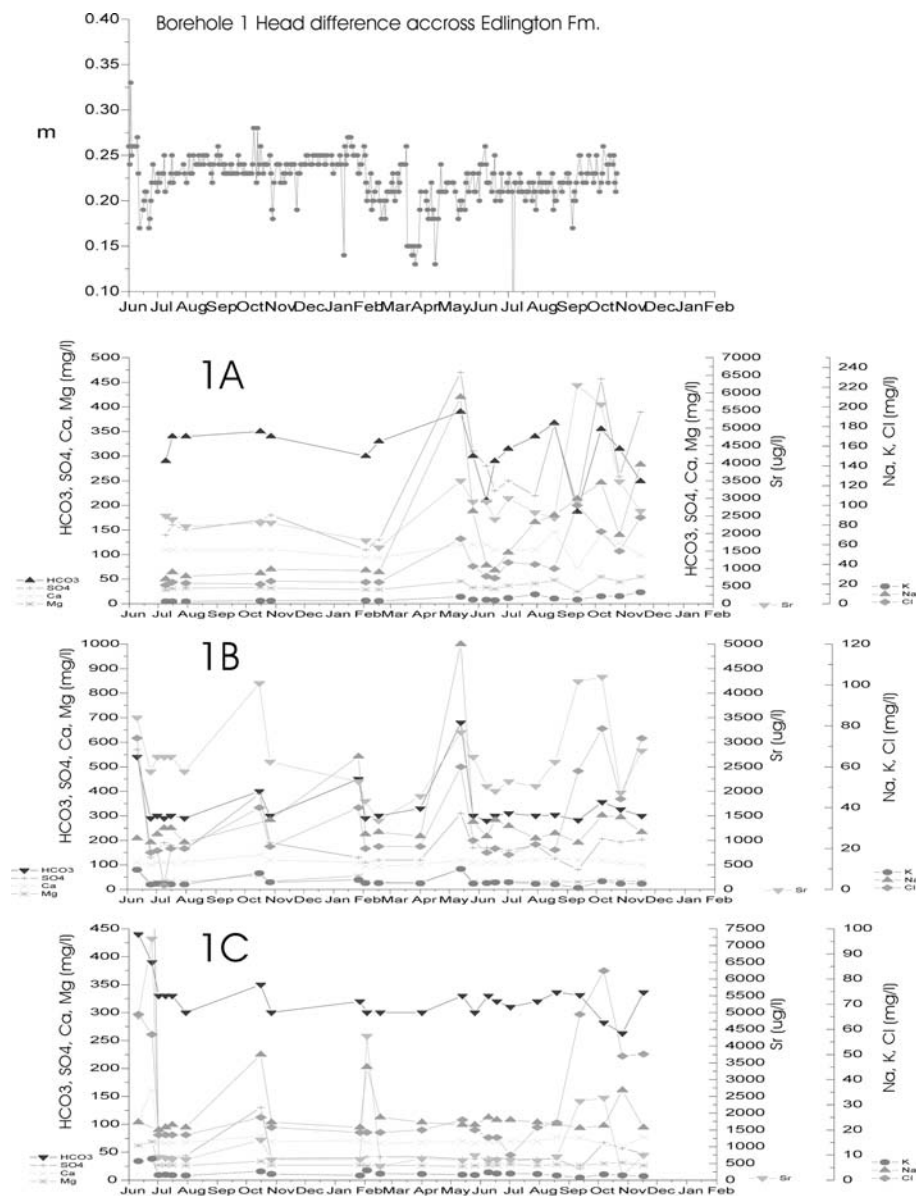
artesian setting, indicate dissolution of the gypsum of the Edlington Formation beneath. The variation of Sr^{2+}, and SO_4^{2-} in 1A and 1B appear to correlate with the head differences across the Edlington Formation. There is a general decrease in sulphate and strontium concentrations throughout the winter of 1998 and 1999, which then recover in the late summer and autumn of 1999. The prominent peak of all indices in late May 1999 appears to follow a sharp rise in head difference during a period of otherwise depressed head difference. This is interpreted as an increased residence time within the Edlington Formation. There may be a lag between the depression in head difference and the appearance of dissolved gypsum in 1A and 2A but the sampling frequency was not high enough to quantify any such effect.

The water quality indices for 1C (in the Ford and Edlington Formation, Fig. 1) show a much lower variation in species concentrations which do not correlate with head difference across the Edlington and do not reveal the peak in May/June 1999. The peaks in Sr^{2+} and Na^+ in 1C during February 1999 are unexplained and a $+9.75\%$ ionic balance suggests analytical error.

The mean annual water quality data (Table 2) are related to dissolution of gypsum in the Edlington Formation such that 1C and 1D (not shown in Fig. 6) contain about one quarter the concentration of sulphate and strontium as compared to 1B and have significantly lower TDS Ca^{2+} Mg^{2+} and Na^+.

Fig. 7 Intra-annual variations in water quality indices and head difference across the Edlington (gypsiferous) Formation in Borehole 2
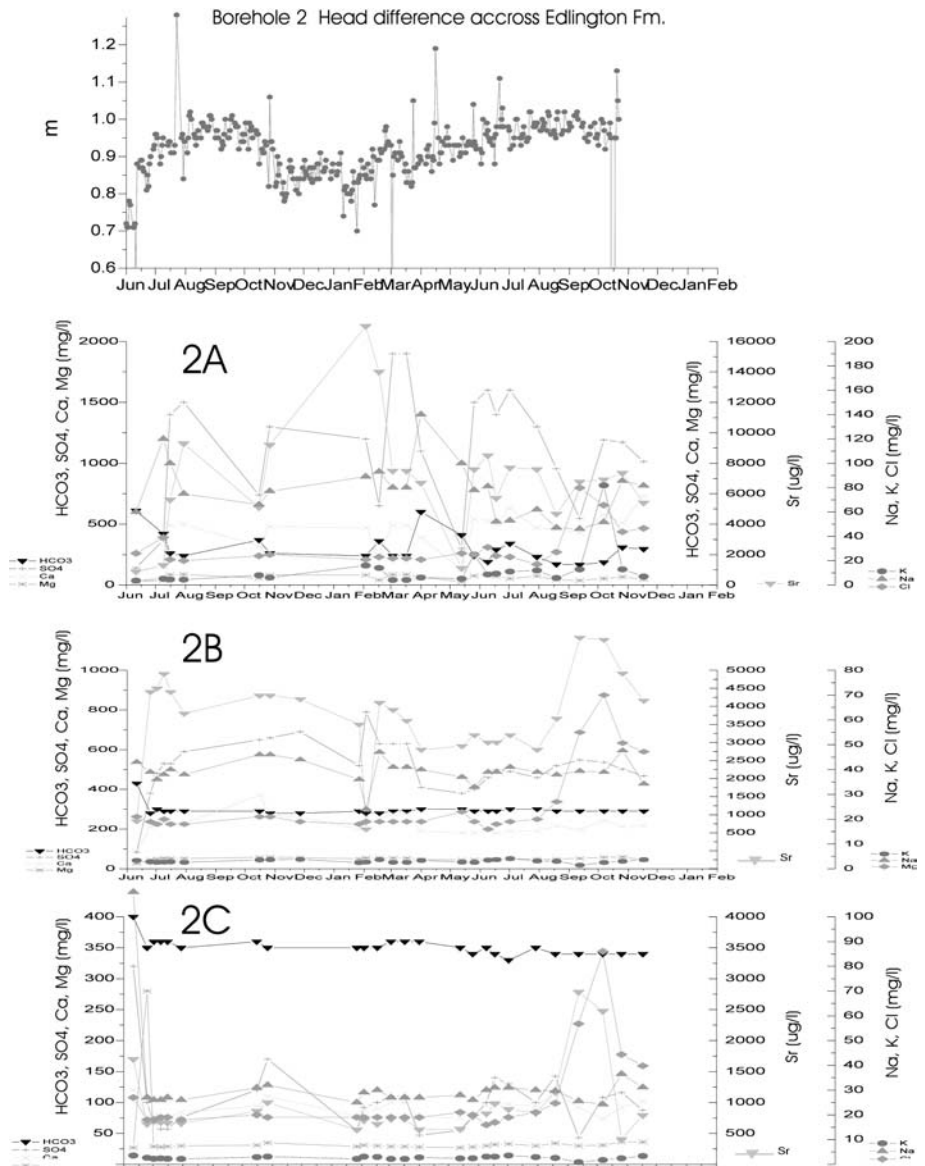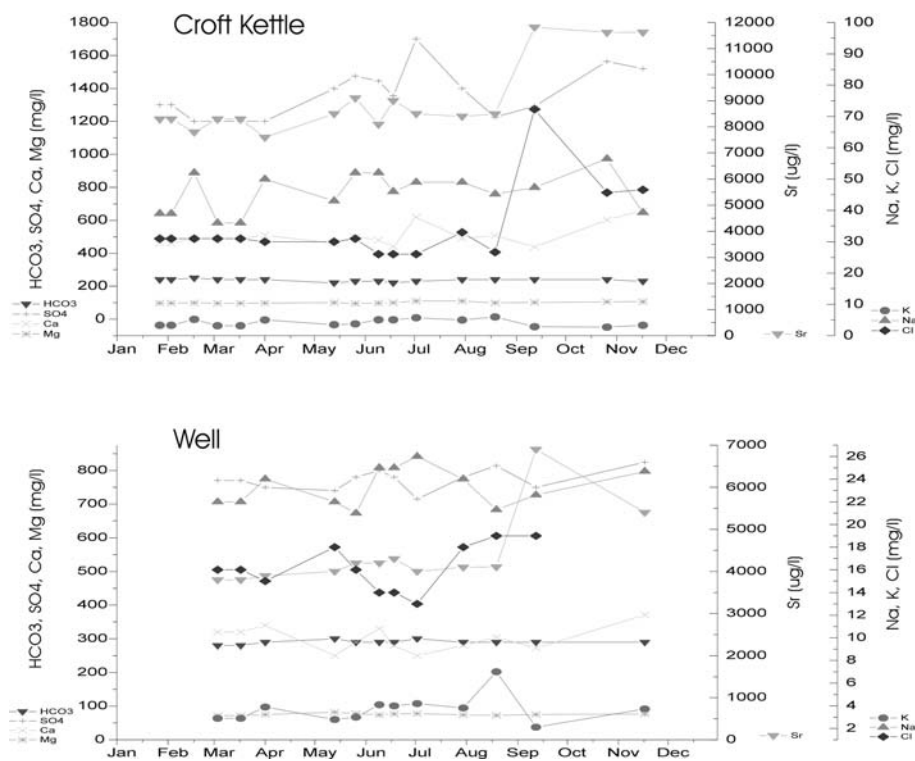
Borehole 2

The same data for piezometer 2C (Fig. 7) show a sympathetic relationship of Ca^{2+}, SO_4^{2-}, Sr^{2+} and Cl^- with head difference across the Edlington Formation. This is interpreted as downward flowing water travelling through the Edlington and dissolving gypsum before mixing with the water in the Ford Formation. The rate of dissolution varies intra-annually and is controlled by the head difference across the Edlington.

The above data suggest that gypsum is being actively dissolved from within the Edlington Formation at both the Borehole 1 and Borehole 2 sites. The former groundwater (probably a small proportion of the flow) is moving upwards from the Ford Formation across the Edlington Formation and mixing with water containing dissolved gypsum with water in the Seaham Formation. The latter water is moving downwards across the Edlington Formation dissolving gypsum and mixing with the Ford Formation. A prominent 'event' in May 1999 is manifest as a sharp decrease in water quality indices in 2A suggesting this is a recharge event with low salinity meteoric water. The signature of dissolved gypsum in 2B shows a gradual rise through late May and June.

Croft Kettle and well

Seasonal variations in the water quality of Hells Kettles and the well are shown in Fig. 8. These data are similar to the deep piezometers 1D and 2D and 1C and 2C (Figs. 6 and 7) and show general stability. Croft Kettle and the well show rises in strontium, sulphate and sodium during May and June (see discussion below on natural tracers). A rise in calcium is seen in the well but is absent from Croft Kettle. The water quality, particularly sulphate and calcium in Croft Kettle, may be difficult to interpret because of the effects of sulphate reducing bacteria and sulphide oxidising bacteria and the activity of the alga *Chara hispida* which removes calcium from the water by secreting a calcite.

Summary

Water quality and piezometric data indicate that groundwater flows upwards from the Ford Formation and across the gypsifeous Edlington Formation near Borehole 1 and downwards from across the Edlington, the till near Borehole 2. Variations in groundwater quality indices appear to be related on a seasonal basis to head differences across the Edlington Formation.

Dissolved organic matter (DOM)

Dissolved organic matter including proteins and organic acids (derived from the decay of soil matter) are a natural component of many groundwaters. In UK, concentrations of these components typically range from

Fig. 8 Intra-annual variations in water quality indices in Croft Kettle and the water supply well

1 mg/L to 15 mg/L (Tipping et al. 1997). Baker and Lamont-Black (2001) made an initial study of the fluorescence of groundwaters in the sites described in this study (for a detailed description of the methodology, see Baker and Lamont-Black 2001). The interpretations of groundwater flow are used below to interpret groundwater flow and explore the use of DOM as a natural tracer in this karst system.

Figure 9 shows time-series of protein and fulvic-like acid (FLA) intensities (which act as a proxies for concentration) and Fig. 10 plots these data as protein fluorescence intensity against the ratio of protein to FLA intensity. Boreholes 3 and 4 are not considered because the sampling regime was half as frequent as the other sites and are therefore, not directly comparable, however, mean values are considered.

Changes in fluorescence intensity through the sampling season are represented in Fig. 9. Two periods of high fluorescence intensity occur which broadly correlate with peaks in fluorescence wavelength identified in Baker and Lamont-Black (2001). The most intense peak occurs in autumn and is probably associated with autumn recharge, a secondary peak in May/early June event is less intense but more distinct. The intensity and timing of both events is shown in Table 4.

Plotting the ratio of protein to FLA intensity (Fig. 10) follows Baker (2001), and permits the identification of different water sources based on fluorescence properties. Baker (2001) identifies waters, which have high protein intensity and low protein/fulvic ratio as being typical of sewage impacted water. Waters derived from the two trends in protein and FLA fluorescence intensities (Fig. 10) are apparent. Samples from 1A and 2A are characterised by a low gradient, suggesting waters of high protein intensity and low protein/FLA ratio. Values observed at these sites are typical of those of sewage impacted rivers of Baker (2001) and suggest that these samples might be similarly impacted from overlying leaking sewage systems. All other sample sites are characterised by a higher protein/FLA like fluorescence ratio. Figure 9 clearly demonstrates that water samples

Fig. 9 Time series FLA and protein fluorescence intensity data for Boreholes 1, 2, Croft Kettle and the supply well
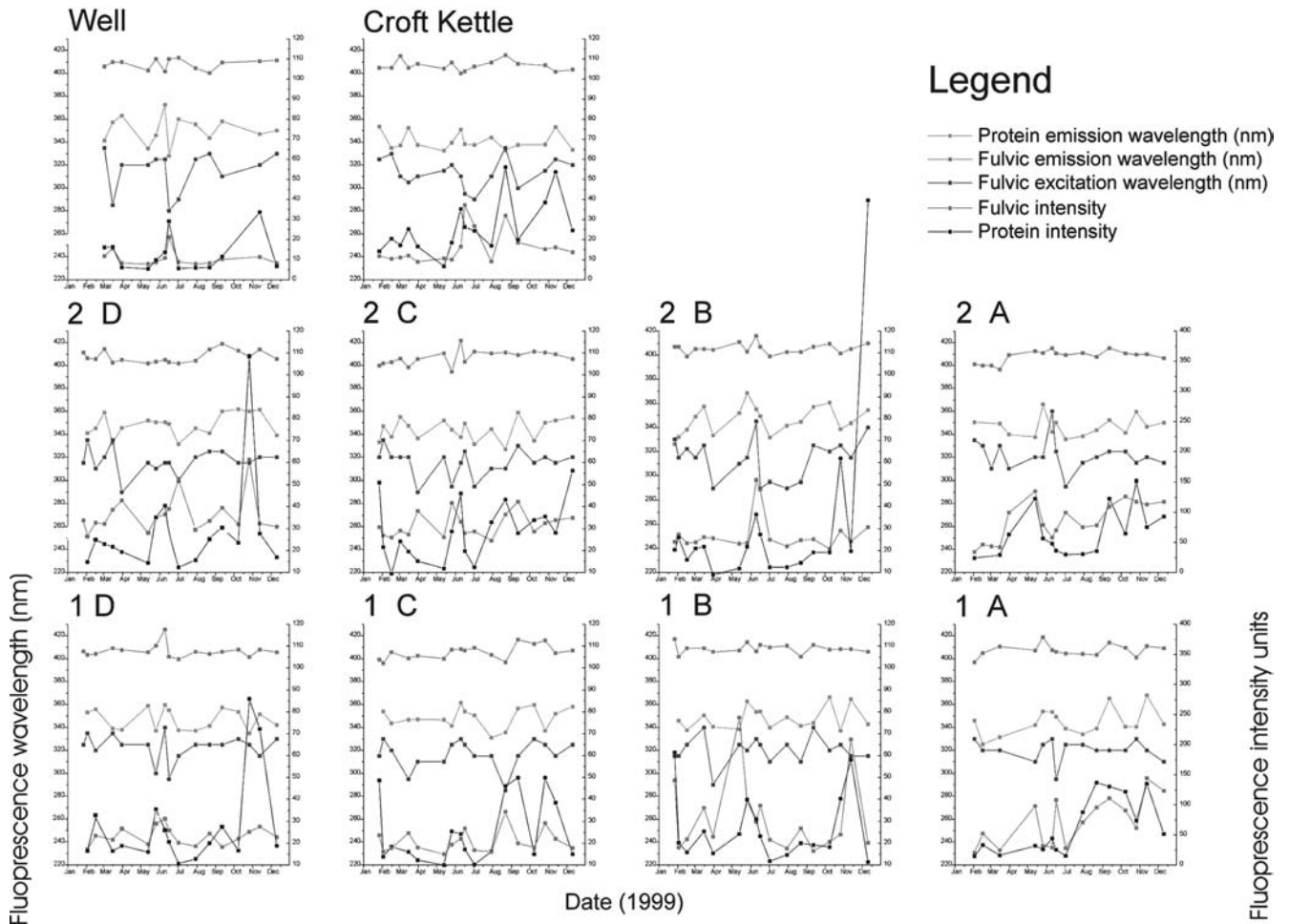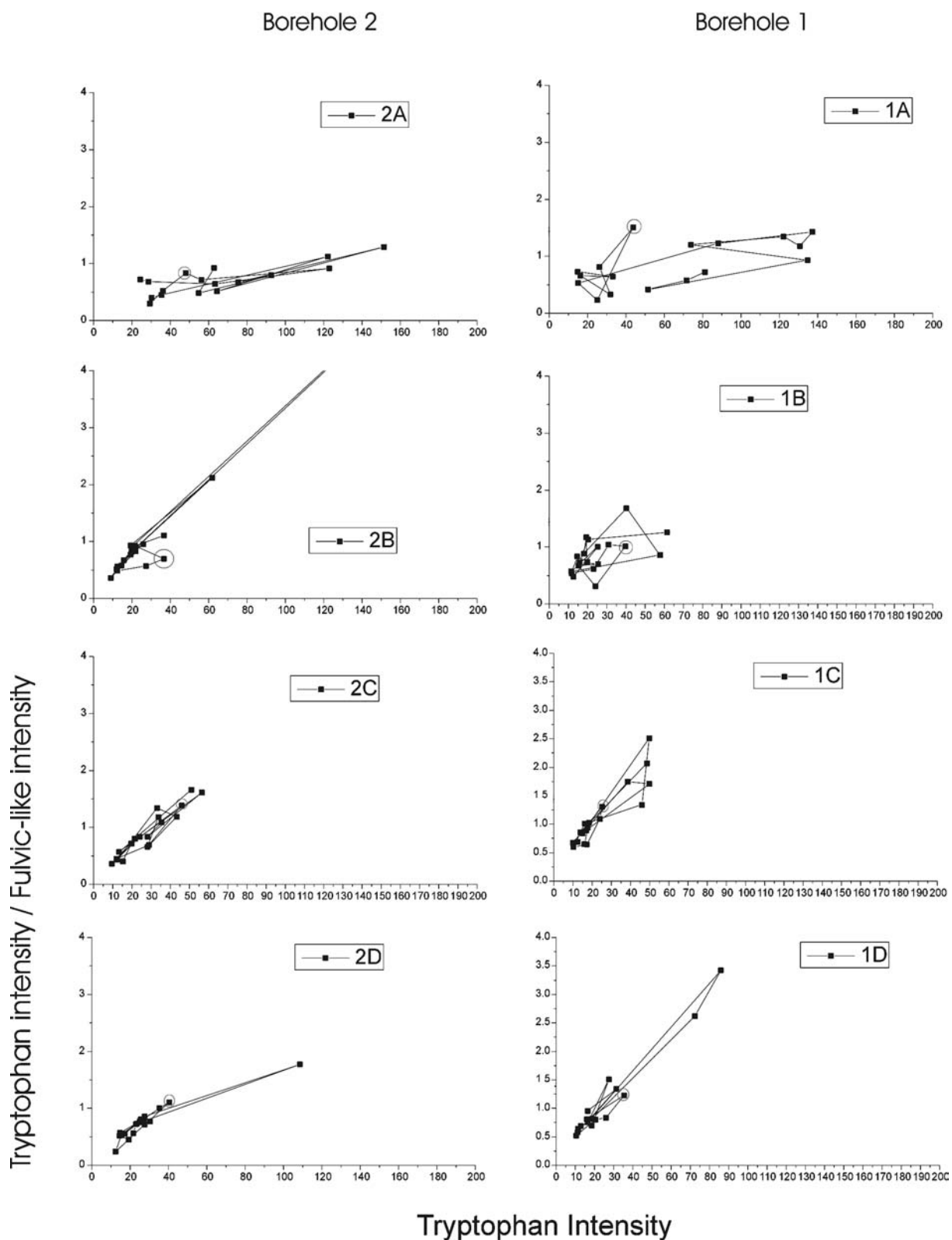
Fig. 10 Tryptophan (protein) intensity versus tryptophan: FLA intensity ratio (after Baker 2001) for Boreholes 1 and 2. *Circles* indicate the groundwater 'event' of May–June 1999

from 1A and 2A have a different organic fingerprint than the other sites.

Mean annual variations

Mean annual data for protein and FLA fluorescence intensity (Table 4) indicate a strong hydrostratigraphical control on the concentrations of DOM. Piezometers 1A, 2A (also 3A and 4A not shown) show significantly higher intensities of protein and fulvic acid than the rest of the sample set. The association of these piezometers is that they are all situated either in the Till or close to Rockhead and are, thus, in closer contact with the ground surface.

In the solid geology, mean annual protein intensities in Croft Kettle and boreholes 1 and 2 are similar, whereas the well shows a significantly lower protein fluorescence intensity. FLA mean annual fluorescence intensity for the solid geology sites show a pattern similar to protein intensities but Croft Kettle joins the well at the low intensity end of the range and Borehole 2 shows somewhat higher FLA fluorescence intensities than Borehole 1. The source of this variation is not immediately apparent.

Intra-annual variations in fluorescence

A general feature of the fluorescence intensities is a general covariance of protein and FLA fluorescence intensities and a gradual rise during late summer and autumn. It has been suggested for karst systems that this relates to the flushing into the groundwater system of organic matter that has accumulated in the soil during the summer (Emblanche et al. 1998). In addition to this

seasonal trend, a prominent peak in fluorescence intensities is observed in most sites during late May to late June 1999 (Fig. 9). This peak in intensities is also accompanied by a marked increase in the variation of fluorescence wavelengths. Previous research has suggested that protein-rich waters are 'young' in age because of the relatively rapid breakdown of protein in the natural environment (Emblanche et al. 1998). Therefore, the intensity peak may relate to an event or short-lived series of events during the spring. The effects of this 'event' are not limited to fluorescence, but correlate with increased variability in the water quality in all the borehole piezometers and in the well and Croft Kettle (Figs. 6 and 7). The event is also picked up in the hydrograph of Borehole 1 (Fig. 3) such that the water level of 1A rises sharply during mid-May and the effect is seen as a reduction in the head difference across the Edlington Formation at this time (Fig. 6). The same rise is not recorded in piezometer 2A because of the effects of a draw-down following sampling on 13th May. However, circumstantial evidence for an unusual rise in water pressure in 2A is shown by the much faster recovery of 2A after this sampling occasion as compared to other post sampling recoveries.

Given the relatively discrete nature of the 'event' during May–June we have attempted to trace its movement through the groundwater system using DOM to learn more about the groundwater flow beneath Darlington. Unlike designed tracing events, however, there are many unknowns, such as the original composition of the material, the precise time and conditions under which it was applied, its initial concentration and the exact spatial extent of its application. Therefore, the interpretations to be drawn regarding the groundwater flow are purely qualitative. As shown in Table 4, there are discrete peaks spread over a period of about

Table 4 Date and value of protein and FLA intensity peaks for the May–June 1999 event and mean annual intensity values

Sample site	Protein			FLA		
	May–June intensity peak		Mean annual value	May–June intensity peak		Mean annual value
	Date	Value		Date	Value	
1A	10th June	43.9	64.5	16th June	108	78.0
1B	26th May	39.8	25.6	13th May	77.4	31.5
1C	26th May	25.3	24.2	16th June	26.8	20.8
1D	26th May	35.4	26.0	10th June	31.1	22.8
2A	13th May	122	64.6	13th May	135	84.6
2B	10th June	36.6	30.4	10th June	52.1	27.7
2C	10th June	46.0	27.7	26th May	41.7	31.0
2D	10th June	40.5	28.1	2nd July	52.4	36.1
3A	N/A	N/A	50.0	N/A	N/A	105
3B	N/A	N/A	31.7	N/A	N/A	27.7
4A	N/A	N/A	45.5	N/A	N/A	116
4B	N/A	N/A	37.6	N/A	N/A	35.8
Well	16th June	29.2	14.2	16th June	21.0	11.1
Croft Kettle	10th June	35.2	25.2	16th June	37.2	15.8

6 weeks. A more frequent sampling regime would have revealed more detail, however, these data show:

Protein variations

The protein intensity peak is the most distinct signature of the fluorescence signals, it appears earliest in Borehole 2A on the13th of May, followed by peaks on the 10th of June in 2B, 2C and 2D. In Borehole 1it also appears in 1A on the 13th of May, then again on the 10th of June. It appears consistently in 1C and 1D on the 10th of June. Croft Kettle also displays the peak on the 10th of June and it is last seen on 16th of June in the well.

Protein fluorescence intensity acts as a proxy for concentration. The highest intensity during the May–June event was recorded in 2A which also records the earliest arrival of the peak. The lowest intensity is recorded in the well which also shows the latest arrival of the peak. These intensity maxima also show the highest deviations from mean annual levels. In summary:

– Protein intensities peak in 1B, 1C and 1D on the 26th of May and in 2 B, 2C, and 2D on the 10th of June.
– Protein in 1A shows two peaks—13th of May and 10th of June.
– Protein intensities peak in 2B, 2C and 2D on the 10th of June and therefore, lag behind Borehole 1.
– Potein shows a single peak in 2A on the13th of May.
– Protein peaks in Croft Kettle on the 10th of June.
– Protein peaks in the well on the 13th of June.

FLA variations

The variation in FLA intensity is generally synchronous with protein with the exception of 2D which lags the protein peak by about 2 weeks.

The FLA intensity signal is more varied than the protein intensity. It appears as a single and double peak. As a single peak it is exemplified by the records from 2B and the well and also occurs in 1C, 1D, 2A, 2C, 2D and Croft Kettle. Double peaks occur in 1A and 1B which, together with 2A record the first appearance of the signal on the13th of May. The peak is then recorded in 2C on the 26th of May; in 1D and 2B on 10th June and 1A, 1B, 1C, Croft Kettle and the Well on the 16th of June and finally in 2D on 2nd of July (an FLA peak is also seen at this time in 2A). The strength of the peak relative to mean annual levels for each piezometer is similar to the relationship for protein intensities such that the well and Borehole 2 show generally stronger peaks than Borehole 1, with 1A being the weakest.

The timing of FLA peaks in relation to the protein peak is inconsistent, compared to the generally more discrete protein peaks. FLA peaks are synchronous in 2A, 2B and the well (strong FA signals); the FLA peak lags behind the protein peak in 1C, 1D, 2D and Croft. These lag peaks are in general weaker than the synchronous peaks. In 2C the FA peak appears to arrive before the protein intensity peak.

Protein and FLA fluorescence wavelengths show an increased variability (especially in excitation wavelength) during the May–June event. The timing, and polarity of peaks and troughs in excitation and emission wavelengths appears complex. There seems to be no clear relationship between variations in excitation and emission wavelength and intensity. However, all intensity peaks are associated with a general pattern of increased variation in emission wavelength.

Generalised conceptual model of groundwater flow

Much data has been presented in the preceding sections and can be summarised thus:

– Regional groundwater flow is from the northwest to the southeast.
– Three groups of groundwater relating to contact with the Till and Permian strata with and without gypsum are recognised from major ions and cation ratios.
– Water quality and annual variations therein relate to transverse flow across gypsiferous strata.
– The most northwesterly site, Borehole 2, reveals weak, generally downward flow across the gypsum; a few hundred metres SSE Borehole 1 reveals weak, generally upwards flow across the gypsum; several hundred metres to the south the well and Croft Kettle reveal strong upwards flow across the gypsum.
– Prominent variations in water quality are associated with a groundwater event in May 1999; water quality indices show a prominent peak in 1A and 1B following a period when the head difference was depressed due to higher pressures in the overlying Till. Water flowing downwards at 2A shows a distinct meteoric influence and salinities in 2B (underneath the gypsum) show a depression and then gradual re-establishment of the gypsum signal.
– Distinct seasonal variations are seen in DOM intensities with a rise during the winter months and a discrete set of peaks associated with an event in May–June 1999.

Tracing with DOM

Protein intensities reveal a slightly simpler variation than FLA intensities. This may be owing to the fact that they are relatively short lived. The first arrival of the May–June protein intensity peak, on the 13th of May is seen strongly in 2A and very weakly in 1A. This corre-

lates with the meteoric signal recorded in 2A following a rise in the piezometric level in the groundwater at rockhead note in 1A and suspected in 2A. This peak is followed by the remaining piezometers in Borehole 1, then Borehole 2 and Croft Kettle and finally the well.

In Borehole 1 the flow is generally upwards through the Edlington Formation; the two peaks in protein and FLA in 1A probably relate to an initial surface derived signal at the beginning of the event; then following the re-establishment of 'normal' upwards flow the DOM signal is seen again having flowed through the Edlington Formation from the Ford Formation beneath.

With a generally SSE water flow (Fig. 2) it might be expected that Croft Kettle would be last to show the peak. However, the well lags behind (precise timing is impossible owing to the frequency of sampling). The well is situated just to the south of the major EW fault (Fig. 1) which has its downthrow side to the south, such that the Seaham Formation is adjacent to the Edlington Formation. In this area the groundwater is confined with a local discharge in Croft Kettle. Therefore, flow towards the well will be slow and governed by its modest abstractions, whereas the flow from the Ford Formation crosses the fault and into the Seaham Formation, down the regional hydraulic gradient to discharge in Croft Kettle.

The most discrete intensity peaks of FLA and protein are shown in the Piezometers 2B and 1C, the well and Croft Kettle. These show a general synchronicity of all DOM and water quality indices. This may be due to the small thickness of the aquifer that is sampled by these piezometers, thus limiting the possibility of mixing. Screen lengths in the well and 2B are relatively short (Fig. 1) and they are positioned in the top of the Ford Formation which is porous, leached (dedolomitised) just beneath a gypsum horizon (Table 1). Croft Kettle is not a borehole, however, the Roxby Formation, through which the sinkhole penetrates, is composed of marls with gypsum or anhydrite at its base. The base of the sinkhole, therefore, probably rests in the gypsum and dedolomitised portion of the Seaham Formation and represents a sample of water from fairly limited vertical extent.

Subsidence hazards

The formation of Hells Kettles was recorded as having taken place in 1197 by a catastrophic collapse. This is the only direct evidence of karst related subsidence in the area. Transverse flow karstification (Klimchouk 1996) is the likely cause of the subsidence in this location. Further north under Darlington itself, karst features are recorded in borehole logs i.e. clay filled cavities in the gypsum, brecciation of the overlying Seaham Formation

and circumstantially in the form of dedolomitisation of the underlying Ford Formation. However, these features appear to be relict palaeokarst features and the conditions required for significant contemporary gypsum dissolution do not appear to have been met. Martinez et al. (1998) list four criteria required for evaporite dissolution i.e.:

1. Presence of an evaporite deposit.
2. Presence of water undersaturated with respect to the evaporite mineral.
3. Energy to drive water through the system.
4. Presence of an outlet for groundwater containing dissolved evaporite.

These conditions have been met, and the data sets presented indicate that dissolution of gypsum is taking place beneath Darlington. However, whether or not this represents a hazard in terms of subsidence will be related to a wide range of other factors. The main factor of interest in this study is the rate of gypsum dissolution and how widespread it is. Owing to its relatively high solubility, the most significant risk for rapid dissolution of gypsum occurs in the transverse flow setting. There is a gradual increase in artesian pressure from the southern part of Darlington to the Tees Valley to the south. In the vicinity of Borehole 2 there is general downwards flow across the gypsum, this becomes slightly artesian at the site of Borehole 1. Travelling further south the supply borehole at the farm has an artesian head of approximately 3–4 m; and there are some natural discharges at Hells Kettles and near the banks of the Tees at Croft and elsewhere. It appears therefore that the thick confining layer or Till beneath Darlington effectively confines the groundwater and prevents significant transverse flow across the gypsum. The presence of river gravels and a thinner quaternary sequence in the Tees flood plain may be responsible for allowing the discharge of gypsiferous groundwaters thus allowing dissolution which resulted in the formation of Hells Kettles. Thus, it may be reasonably concluded that gypsum dissolution does not present a risk of subsidence in Darlington.

Conclusions

The above data sets have brought together information on geology and time-series data on groundwater levels, groundwater heads, water quality and DOM. The groundwater flow pattern has been conceptually identified using a combination of piezometric data, major ions and variations in fluorescence of DOM. This integrated approach has proved a useful tool in understanding water flow in an area which is overlain by a thick series of Quaternary deposits.

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