The comparison between the chalk and the Holderness glacial till water chemistry, North Humberside

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ABSTRACT: The research work was about the hydrochemical of this catchment, in respect of the interactions between the Holderness glacial till and the underlying Chalk. Gross variations in ground water quality in the North Humberside Chalk were recognised and suggested that poor quality water from the Chalk in the Holderness area was an indicator of minimal ground water circulation. This work was devised to resolve outstanding uncertainties of the direct connection between the Holderness glacial till and the underlying Chalk and to improve understanding which has thereby resulted will be of value in the interpretation of the hydrochemical behaviour of this catchment and any similar areas of glacial till underlying Chalk.

KEYWORDS: Chalk, Holderness, Glacial, Till Water, Chemistry, North Humberside.

INTRODUCTION

Catchment is situated at the east side of the Holderness plain of North Humberside, England (Figure 1). The catchment, some 15.5 km sq. in area. The Holderness glacial till in which the boulder clay plain rises imperceptibly towards the coast in the east and the Yorkshire Wolds in the west and north. Relief in the catchment ranges from about 25 m O.D. in the north-east to about 7.5 m O.D., at the exit of the catchment in the south-west, and consequently the majority of the slopes are quite gentle.

The Chalk of the Yorkshire Wolds has long served as a major aquifer in local and regional water resources development. From time to time, therefore, attention has been directed towards water quality as well as quantity. Price and Anderson (2014) found rising of nitrate levels in ground water abstracted from the Chalk aquifer, which is covered by glacial till in the south and east of UK.

Stewart (1984) analysed some water samples from the glacial drift of North Humberside and found that these showed high values of Na, K and Mg. He also suggested that locally drift water may influence water chemistry in the underlying Chalk in a manner suggested by Heathcote (1981) and Elliot et al. (2001) to account for some of the chemical characteristics observed in Chalk ground water in the confined zone. Burn (1980) and Stewart (1984) demonstrated progressive changes in the chemistry of the Chalk ground water southwards below the drift cover and away from the Chalk outcrop of the Northern Wolds.
Catchwater Drain Catchment Till

Sand and gravel deposits cover only relatively small areas of the catchment, forming isolated patches mostly surrounded by sandy loam material developed on the intervening clay. The largest patches occur in the north-western part of the catchment, and at Great Hatfield, Seats Hill, Mapleton, Withernwick, Grange and Manor Farm. Their distribution is shown in Figure 2 which represents the most comprehensive attempt which has so far been made to locate and map the sand/gravel and other coarse, alluvial deposits in the Catchwater Drain catchment. Mechanical examination of the coarser deposits, confirmed by borehole data, has shown that they are either a mixture of sand and gravel or else consist primarily of sand only or, as at North End, of sand surrounded by sandy loam (Bonell, 1971).

Some useful information was derived, however, from the occasional springs and the seepage of ground water associated with the periphery of these patches and which appear to mark the boundary between the sand/gravel and the clay. Such outflows are presumably a result of the superior permeability of the sand/gravel, enabling it to conduct and store ground water better than the surrounding clay. There was plenty of visible evidence of this phenomenon, particularly in fields at Great Hatfield where there was absence of land drains. Seepage, rather than springs, was associated with this area, although on local farmer had reported an active spring which unfortunately was not accessible for observation. In addition, two domestic wells displayed a rapid recovery of water level immediately after a period of use for spraying. Also a spring was noted at the foot of the Withernwick Grange and North End sand deposits, although it was active only during periods of frequent precipitation in winter and early spring.

Patches of sandy loam are found in several places, especially at, and east of, Mount Pleasant, south of Withernwick Grange, and west of Cowden Magna (see Figure 2). This material is usually found peripherally to the most of the sand and gravel areas, e.g. Great Hatfield and Manor Farm. Also there are small patches of loam over gravel around Withernwick, and a fairly widespread distribution of clay mixed with river alluvium throughout the catchment. The loamy and sandy areas cover some hills, for example, at Hatfield Wood Farm, Nortofts Hill and Hedon Hill.

The occurrence of lenses or local stratified deposits of sand, silt or gravel within a particular till and between tills has obvious hydrological significance since these deposits are likely to be more permeable and therefore capable of transmitting water at a much greater rate than are the clay materials.
Data Collection and Instrumentation

The hydrochemical data from the catchment and from the clay and sand/gravel sub-catchments, (Figure 3), are compared with hydrochemical data for the Chalk. Particular attention is paid to Chalk data comparisons with the ground water and stream flow which take place in the Catchwater Drain catchment. These comparisons are made over different time-scales and for different data intervals. In addition, through the detailed analyses of the chemistry of numerous water samples, the chemical "signature" of water in different parts of the catchment is characterised and compared with the chemical characteristics of Chalk water. In this way it is hoped to demonstrate the relationship, between the varying hydrochemical conditions in the underlying Chalk and hydrochemical conditions within the till catchment.
Total Dissolved Solids (TDS)

The concentration of total dissolved solids (TDS) represents a useful compendium of processes occurring in water and was remarkable, in the Catchwater Drain catchment (Table 1), for its very high values which usually ranged between 477 - 795 mg/l. These high concentrations are the result of both natural and man-induced factors, including parent materials, the large number of chalk fragments within the clay, the geologically recent origin of the till and its costal location, and intensive agricultural activity.

TDS values in the catchment stream waters were lower at the catchment outlet and for the clay areas than for the Great Hatfield sandy area. Observed concentrations in fact varied between 564 - 795 mg/l in the Great Hatfield sandy area, 477 - 529 mg/l in the clay areas, and 519 - 750 mg/l at the outlet of the catchment. In wetter periods all values decreased, due to dilution by the greater proportion of quick flow contributing to the stream, and rose during drier periods due to evaporation and the proportionately greater ground water contribution (see Figure 4). It was especially noticeable that, during drier periods, stream water leaving the Great Hatfield sandy area and at the main catchment outlet displayed higher TDS values than in the clay area.

Values of TDS for the confined Chalk aquifer lie between 464 and 849 mg/l and Burn (1980) suggested that values rise rapidly to more than 1000 mg/l as brackish and saline waters are encountered deeper into the confined zone.
Table 1 the range of measured parameters for the catchment surface water and ground water.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Catchwater (mg/L)</th>
<th>Sand water (mg/L)</th>
<th>Clay water (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS</td>
<td>519 - 750</td>
<td>564 - 795</td>
<td>477 - 529</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>309 - 424</td>
<td>318 - 430</td>
<td>217 - 250</td>
</tr>
<tr>
<td>Calcium</td>
<td>118 - 140</td>
<td>135 - 160</td>
<td>93 - 100</td>
</tr>
<tr>
<td>Magnesium</td>
<td>25 - 35</td>
<td>32 - 42</td>
<td>8 - 25</td>
</tr>
<tr>
<td>Calcium hardness</td>
<td>335 - 395</td>
<td>341 - 423</td>
<td>183 - 203</td>
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<tr>
<td>Total hardness</td>
<td>430 - 495</td>
<td>440 - 504</td>
<td>320 - 335</td>
</tr>
<tr>
<td>Sodium</td>
<td>30 - 45</td>
<td>28 - 46</td>
<td>25 - 35</td>
</tr>
<tr>
<td>Potassium</td>
<td>7 - 16</td>
<td>8 - 17</td>
<td>15 - 24</td>
</tr>
<tr>
<td>Chlorite</td>
<td>50 - 74</td>
<td>55 - 86</td>
<td>24 - 55</td>
</tr>
<tr>
<td>Sulphate</td>
<td>80 - 147</td>
<td>70 - 139</td>
<td>137 - 187</td>
</tr>
<tr>
<td>Conductivity (µmhos⁻¹)</td>
<td>835 - 1072</td>
<td>950 - 1085</td>
<td>798 - 860</td>
</tr>
</tbody>
</table>

Fig. 4 The total dissolved solid
Conductivity

Electrical conductivity is the simplest measure of the approximate concentration of soluble salt in water and is often used as a surrogate for TDS concentration. As would be expected, in the catchment were higher during the drier period between July and September 1991 (see Figure 5).

Again the stream waters in the Great Hatfield sandy area displayed higher conductivity (950 - 1080 μmhos⁻¹) than in either the clay area (798 - 860 μmhos⁻¹) or at the main catchment outlet (835 - 1072 μmhos⁻¹). Considered together, however a very similar pattern of behaviour (see Figure 5), reflecting the fact that, once the clay channels had dried out, total catchment stream flow consisted almost entirely of flow from the Great Hatfield sandy area channels.

Fig. 5 The conductivity

Total hardness.

Figure 6 shows that the highest total hardness, approximating that of saline water in the range 440 - 504 mg/l, was found in the Great Hatfield sand area stream water. In comparison, values of 320 – 335 mg/l were measured in the clay area ground water and 430 – 495 mg/l at the outlet of the catchment. Generally, total hardness was higher during dry periods, especially in the
Great Hatfield sub-catchment, where stream water displayed, not only high total hardness compared with that of the clay areas, but also very similar values to that of the main stream at the same time. This again reflects the dominant role of the sandy areas in total catchment stream flow.

Calcium hardness (see Figure 7) was in the range 341 - 423 mg/l for the sandy area stream water, 183 - 203 mg/l for the clay area ground water, and 335 - 395 mg/l at the outlet of the main catchment. Between July and September again, the both Great Hatfield sandy area and the outlet stream waters displayed similarly high calcium hardness in contrast to the clay ground water showed higher calcium hardness, with lower values during the Spring.

![Fig. 6 The total hardness](image_url)
Alkalinity

Alkalinity, the capacity of a solution to neutralise acid, is in the case of most natural water, largely the result of the bicarbonate ion (HCO₃⁻), although carbonate (CO₃²⁻), hydroxide (OH⁻), iron, and silicates can also contribute when the pH is above 9.0, and phosphates will affect alkalinity throughout the normal range of pH. In the case of Chalk ground water, alkalinity is due to bicarbonate and carbonate ions and Burn (1980) suggested that additional bicarbonate may, under some circumstances, be supplied by reactions involving reduction of sulphate or nitrate and that the zones of high alkalinity beneath and near the edge of the Holderness drift probably due to attainment of saturation with respect to calcium down the hydraulic gradient.

The alkalinity of water in the Great Hatfield sandy area was in the range 318 - 430 mg/l, compared with 217 - 250 mg/l in the clay area, and 309 - 424 mg/l for stream water at the outlet of the catchment. As Figure 8 shows, high alkalinity is found during the summer with lower values during the spring.

This higher alkalinity indicates that the source of this water may be saline water confined under the glacial till and moving upward through lenses of sands and gravels. In this respect it is significant that the comparative Chalk water shows similar high levels of alkalinity, i.e. 253 - 438 mg/l. Certainly a down dip increase in the bicarbonate ion, together with a fall in the free CO₂ content, was recorded by Ineson and Downing (1963), the increase in both bicarbonate and calcium and magnesium ions and the corresponding decrease in the free CO₂ content being in nearly equivalent proportion.
Fig. 8 The alkalinity

Calcium and Magnesium

Earlier analyses of Chalk ground water in North Humberside have shown that the concentration of calcium broadly parallels that of alkalinity, total hardness, and other ion concentrations, e.g. magnesium and sodium. Stewart (1984) pointed out that in the confined zone, calcium values in excess of 120 mg/l are found in the extreme south-east of Holderness. Also Burn (1980) and Stewart (1984) found a rapid rise in magnesium towards the coast in the confined zone, with values rising to 70 mg/l at Aldbrough, some 5.0 km southeast of the catchment. This rapid increase in magnesium east of the River Hull was attributed to mixing with brackish and saline waters in the Holderness Chalk. An area of higher magnesium north and west of Beverley is believed to result from recharge through the glacial till introducing magnesium into the Chalk water.

Imeson (1970) pointed out that magnesium concentrations in the catchment generally ranged between 12 and 48 mg/l and like the concentrations of some other ions, were related to hydrometeorology conditions, i.e. magnesium in the catchment decreased with increasing discharge and decreasing pH. These concentrations were relatively high compared with those from other areas studied by Imeson and are probably related to the large number of magnesium limestone fragments in the glacial till.

The main variation in magnesium concentration, in common with that of most other ions, therefore appears to reflect the varying proportions of surface and ground water discharge. This
may possibly reflect changing carbonate equilibria, since magnesium concentration correlates more significantly with pH than with other parameter. It may be that magnesium concentration in the catchment is influenced by fertiliser application in spring and autumn, as is the concentration of other ions such as sodium and calcium.

Both ground water and stream water in the Great Hatfield sandy area contained calcium and magnesium concentrations similar to that of the Chalk ground water classified as brackish/saline by Burn (1980) and Stewart (1984). During the summer (see Figure 9) the calcium concentration reached 160 mg/l and the magnesium concentration 42 mg/l in the sandy area, 140 mg/l and 35 mg/l respectively in the outlet stream water, and 100 mg/l and 25 mg/l respectively in the clay water, while comparative values for Chalk water were 163 mg/l and 30 mg/l. In wetter periods the ion concentrations were reduced to 93 mg/l for calcium and 8 mg/l for magnesium in the clay ground water, 135 mg/l and 32 mg/l respectively in the Great Hatfield stream water, and 118 mg/l and 25 mg/l respectively in the stream water at the outlet of the catchment.

Fig. 9 The calcium ion concentration
Sodium and Potassium

Sodium, the most abundant of the alkali metals, forms highly soluble minerals and once in solution does not experience important complexing or precipitation. The principal sources of sodium are rainfall contaminated by salt sea spray, interstitial connate or saline water, the sodium minerals, e.g. feldspar, halite, cation exchange involving clay minerals, and agricultural fertilisers. Foster (2000) also found the effect of agriculture on ground water.

A general increase of sodium east and south-east of the River Hull by Burn (1980) and is believed to have resulted, at least in part, from an increase of ion exchange in the vicinity of the River Hull and further east in the brackish waters of Holderness. Through this process, calcium and magnesium ions have been preferentially adsorbed onto the clay surfaces while the sodium has been liberated into the ground water (Michel, 1986). Stewart (1984) also found that, east of the River Hull, sodium values increase rapidly to 40-90 mg/l. Chalk waters in Holderness may reflect contributions from percolation through the till and mixing with brackish/saline waters. Vlahovic and Sumanovac (2015) found unclear results whether the main aquifer lies within the superficial deposits or within the underlying carbonate rock.

Fig. 10 The magnesium ion concentration
Fig. 11 The sodium ion concentration

Fig. 12 The potassium ion concentration
Imeson (1970) found that hydrometeorological factors accounted for only a small part of the sodium variation.

In most natural water the concentration of potassium is much lower than that of sodium, which tends to remain in solution rather persistently once it has been liberated from silica mineral structures. Potassium, however, is liberated with greater difficulty from silicate minerals and exhibits a strong tendency to be reincorporated into solid weathering products, especially certain clay minerals.

Potassium, like sodium, can take part in ion exchange reactions and the local high values at and near the Chalk outcrop may be derived from fertiliser applications. Potassium concentrations have also been found to increase rapidly eastwards from the River Hull to between 10 and 53 mg/l.

Imeson (1980) found that the summer increase in potassium concentration in the catchment differed from that in this other two study rivers, on the North York’s Moor and the Yorkshire Wolds, in having low concentrations in wet periods. In the present work (see Figure 11 and 12) the stream water in the catchment showed a high concentration of sodium and potassium during the summer and early autumn. In the sandy area stream, sodium concentrations of (28 - 46 mg/l) and potassium concentrations of (8 - 17 mg/l) were recorded. For the clay ground water, values of sodium were in the range 25 - 35 mg/l and of potassium 15 -24 mg/l, and at the main catchment outlet, 30 - 45 mg/l for sodium and 7 - 16 mg/l for potassium. For comparative Chalk ground water, the values were 31 - 58 mg/l and 9 - 25 mg/l.

The higher values for the Great Hatfield area may possibly be attributed to the greater ground water contribution in this part of the catchment.

**Sulphate and Chloride**

Sulphate is a major dissolved constituent in polluted air, as a result of numerous industrial and power-generation processes, and is transferred to catchment waters via the precipitation process. It is also produced from the use of fertilisers, from the decomposition of organic material, and from the
solution of sulphides in pyritiferous sediments. However, Llyod et al (1981) found out that the selenite and pyrite are virtually absent from the sands and gravels of some other tills in eastern England, so that the hydrochemical composition of the Great Hatfield and catchment flows in summer must presumably be attributed to another source.

As Figure 13 illustrates, the sulphate concentrations in the catchment waters in the summer varied markedly between the clay ground water and the stream water draining from the sand at Great Hatfield. The range in the former was between 137 mg/l and 187 mg/l, with several minor peaks corresponding to runoff variations and possibly the application of fertilisers. In the sandy area of the Great Hatfield, on the other hand, the stream water not only showed lower sulphate concentrations throughout the summer, with values ranging from 70 mg/l to 139 mg/l, but also showed a fairly steady increase in concentration for much of the time, which may have reflected the increasing ground water contribution to the stream from this area. The variation at the outlet of the catchment was very similar to that in the sandy area, with sulphate concentrations ranging from 80 mg/l to 147 mg/l.

The chloride in catchment waters is derived mainly from ancient sea water entrapped in sediments, the solution of halite and related minerals in evaporite deposits, the concentration by evaporation of chloride contributed by rain or snow, and the solution of dry fallout from the atmosphere. The chloride content of rain in coastal areas commonly ranges between 3 and 6 ppm, diminishing rapidly to 1 ppm or less 100 miles inland.

Figure 14 shows that the chloride concentration increased gradually during the summer period in the Great Hatfield sandy area and at the catchment outlet, ranging between 55 and 85 mg/l for the former, and between 50 and 74 mg/l for the latter. Whereas the clay waters displayed a range of 24 - 55 mg/l, the range for the Chalk water was between 65 and 110 mg/l. These data
therefore also indicate a close relation between the Chalk and sand area waters, as well as the strong correlation between the latter and the water at the catchment outlet.

![Chloride Concentration Graph](image)

**Fig. 14 The chloride ion concentration**

**Comparisons of Water Chemistry**

Various graphical methods have been used by different workers in order to characterise the chemistry of water samples, or in other words, to identify their chemical "signatures". Of these, the use of trilinear diagrams is one of the best known. In this method cations and anions are plotted separately in triangular fields which show the percentage contribution of each ion to the total concentration of ions. Subsequently the plotting position on each triangular field is projected onto a diamond-shaped field and the point of intersection, which is sometimes represented as a circle whose diameter is proportional to the TDS concentration, then indicates the hydrochemical facies of the water type.

Such a diagram, incorporating all the chemical analyses discussed, is shown in Figure 15. This illustrates clearly that all the water samples from the sandy area plot as being calcium-bicarbonate type, which is characteristic of the Chalk water. Furthermore, it will be seen that most of the plotting positions for the sandy waters overlapped those for the Chalk water in both the cation and anion fields. This coincidence indicates strongly that these waters are likely to be derived from the same environmental source.
Fig. 15 The trilinear diagram for cations and anions in the catchment and Chalk waters.

Many of the water samples from the clay areas of the catchment plotted in the same cation field as did the Chalk water, i.e. calcium type, while the remainder plotted very close to the boundary of this field in the area signifying "No dominant type". This is an entirely consistent plotting pattern given the predominance of chalk fragments in the so-called "chalky boulder clay". In the anion field, however, all the clay area samples plotted in the "No dominant type" position, in contrast to the Chalk water which plotted exclusively in the bicarbonate field. In other words, the clay waters contained more sulphate than the Chalk water. Accordingly, in the combined field, all the clay area samples plotted within the calcium-sodium-chloride field and outside the calcium-bicarbonate field occupied by the Chalk and the sandy water plotting positions. This confirms that the clay waters belong to a different hydrochemical facies than the Chalk and sandy area waters.

The catchment outlet stream displays a very close relation to the sandy area waters. The combined plotting position in Figure 15 locates the catchment stream water as belonging to the calcium-bicarbonate facies. This is consistent with the repeated evidence, which indicates that, for much of the summer low flow period, the main stream water was draining almost entirely from the sandy area at Great Hatfield.

Although trilinear diagrams probably represent the most frequently used graphical approach to the identification of hydrochemical facies, Stiff diagrams may provide an even more effective visual approach. The graphical method devised by Stiff (1951) uses four parallel horizontal axes and one vertical axis, with concentrations being expressed in equivalents per million.
Stiff diagrams for the main water sites are plotted (see Figure 16 and Table 2). These display an obviously close similarity in ion pattern between the Chalk and sandy area waters and again, the catchment outlet stream pattern shows a similarly close relation to those of the sandy waters. The clay area waters, however, have very different patterns to that of the Chalk and sandy waters. This further confirms the evidence of the trilinear diagrams that the clay waters derive from a different environment that the Chalk or sand waters. Another useful diagram, commonly used in the U.S.A. to distinguish between water types, is the bar graph (see Figure 17), showing cation and anion concentrations in equivalents per million.

Table 2 the selected cations and anions parameters for the catchment surface water and ground water, and for the Chalk water.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Catchwater(epm)</th>
<th>Sand water(epm)</th>
<th>Clay water(epm)</th>
<th>Chalk(epm)</th>
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</thead>
<tbody>
<tr>
<td>Ca</td>
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<td>6.4</td>
<td>4.0</td>
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</tr>
<tr>
<td>Mg</td>
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<td>1.8</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Na+K</td>
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<td>2.3</td>
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</tr>
<tr>
<td>Cl</td>
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<tr>
<td>HCO3</td>
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<tr>
<td>SO4</td>
<td>2.0</td>
<td>2.1</td>
<td>3.0</td>
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</table>

Fig. 16 The stiff diagrams for selected cations and anions in the catchment and Chalk waters.
CONCLUSION

In summary, the chemical analyses of stream water and ground water within the catchment indicate that, during the summer low flow period, waters in the Great Hatfield sandy area generally showed higher ion concentrations than those in the clay area, were most, if not all, the stream channels dried out or became stagnant. Comparisons between the catchment and the underlying Chalk, show that the water chemistry of the Great Hatfield sandy area is very closely related to that of the Chalk ground water.

In the context of a classification of hydrochemical facies, it was shown clearly that the water samples from the sandy area are exclusively of the calcium-bicarbonate type, which is characteristic of the Chalk water and suggests strongly that these waters are likely to be derived from the same environmental source. The clay water sample, in contrast, were of the calcium-sodium-sulphate type. Stiff diagrams and bar graphs also confirmed the close similarities between the chemistry of the Great Hatfield waters and those of the Chalk and the much weaker relationship between the clay area waters and the Chalk water.

Fig. 17 The bar graphs for selected cations and anions in the catchment and Chalk waters.
Finally, it may be concluded that the very close relation, which has been demonstrated, between the water chemistry of the Chalk and the Great Hatfield sandy area lends strong evidence of the direct hydrochemical connection between the Chalk and the sandy area at Great Hatfield and that this results in an upward movement of ground water from the underlying Chalk into the Great Hatfield sandy area through interconnecting bodies of sand and gravel.

REFERENCE


