Appendix 10 Technical Note:

Review of Spatial Factors Controlling Water Discolouration in England and Wales

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1. Introduction

1.1 Background

Severn Trent Water Ltd (STWL) and Hafren Dyfrdwy Ltd (HDL) have proposed to the Water Forum that the ability to bring discolouration complaints down, to levels similar to those received by water companies in southern and eastern England, is compromised by raw water quality. Furthermore, they link these issues with raw water quality to geological factors. The Water Forum has requested independent verification that their view of an east/west divide in discolouration, due to geology, is based on sound science. ESI Ltd was asked in July 2018 to provide that verification.

1.2 Raw Water Discolouration

A study of raw water discolouration focuses on the chemistry of manganese and on the corrosiveness of water (which affects iron mains). Manganese concentrations alone may not be a direct cause of discolouration, but it can be made harder to treat when the raw water is soft, or when it forms complexes with organic matter. Low mineralisation, and low pH also promote the corrosion of iron mains.

1.3 This Technical Note

This technical note comprises an archive of the findings for this project. Section 2 reviews the data sets referred to in verifying the existence of the south east/north west divide. Section 3 presents a non-technical summary that can be communicated with the Water Forum.

2. Data Review

2.1 Bedrock and Superficial Geology

For context, a geological timescale is shown in Figure Error! No text of specified style in document..1, with the age ranges of the nationally most important aquifers marked on. Figure Error! No text of specified style in document..2 shows a map of the nationally most important bedrock aquifers overlaid upon the geological age of the bedrock. The age of bedrock is key in this context because the older rocks (in the north and west of England and Wales) have been subjected to orogenic processes (heat and pressure) and are therefore harder than the more recent rocks (in the south and east of England).

Harder rocks in the north and west form poor aquifers and promote runoff, hence the main contribution to water supply is as surface water inputs to valley reservoirs. In the south and east the rocks are softer and have open porosity so that they contribute a significant groundwater resource.

It is also worth noting the distribution of peat bodies in superficial geology (Figure Error! **No text of specified style in document..3**) in the uplands of England and Wales (there are extensive areas of peat in the Somerset Levels and the East Anglian Fens, but these are not important in water supply catchments). Peat (especially dry peat) releases dissolved organic matter to water.

The water supply area of STWL straddles the boundary between the softer Mesozoic rocks in the south east and the harder Palaeozoic rocks in the north west. Notably, the Bamford and Elan Valley sources (which generate most discolouration complaints within STWL's supply zone) are in the far north and west of the area respectively. There is extensive peat in the Bamford catchment, though not so much in the Elan Valley catchment.

2.2 Baseflow Index / Runoff Proportion

Harder rocks have lower permeability and effective porosity which makes them poor aquifers, and the proportion of rainfall falling on these areas infiltration vs runoff (the baseflow index) is lower. Runoff prevents the water coming into contact with the rock mass, the process which tends to impart mineralisation to the water.

Figure Error! No text of specified style in document..4 shows a map of baseflow index for soils across England and Wales. This very clearly shows a divide between the north and west (low baseflow index) and the south and east (high baseflow index).

Baseflow index is not dependent on slope, so the steeper slopes of the hills of the north and west (see Figure Error! No text of specified style in document..3) further promote runoff at the expense of infiltration. Figure Error! No text of specified style in document..5 maps the runoff coefficient (the amount of rainfall that becomes runoff before interacting with the soil zone).

The water supply area of STWL has a relatively low baseflow index, though the slopes are mostly quite shallow so the runoff coefficients are quite low. This is the case except for the catchments feeding the Bamford and Elan Valley sources.

2.3 Surface Water Quality Data

2.3.1.1 2.3.1 Spatial Averages

A water quality dataset has been obtained from the Environment Agency ('Historic UK Water Quality Sampling Harmonised Monitoring Scheme Detailed Data') (HMS). This is not the same as the more comprehensive and up-to-date Open WIMS dataset but is a subset, which was available at the time of writing this report. 'The sampling network includes 230 sites which are mainly located at the tidal limits of major rivers or at the points of confluence of significant tributaries. The information held within the HMS includes data on: Oxygen and ammonia, Nutrients, List II metals and Pesticides. The Harmonised Monitoring Scheme (HMS) was established to provide an archive of water quality data for the UK.'

Clearly this does not contain specific groundwater quality datasets, though in the high baseflow catchments of the south and east of England river water quality is, in part, reflective of regional outcrop groundwater quality.

The dataset was queried to establish arithmetic mean concentrations¹ of the following determinands: pH, colour, manganese, dissolved organic carbon, and calcium. Maps of mean concentration are shown in Figure Error! No text of specified style in document..6 to Figure Error! No text of specified style in document..10. Date ranges and frequency vary for different sites and different determinands.

The distribution of data points reflects the positions of major confluences, so this should only be used to look at the broader scale patterns in relation to the river catchments of England and Wales, not the detailed pattern within the STWL area itself.

The spatial distribution of water quality data shows that the highest (>60th centile) manganese concentrations (Figure Error**! No text of specified style in document..6**) are generally found in the north and west, though there are locations with high manganese around the Wash (high peat) and in Surrey and Sussex.

Furthermore, with the exception of a cluster of high colour results along the River Lee, the highest (>80th centile) colour results are found in the north and south west of England (Figure Error! **No text of specified style in document..7**). There are many moderately high (60-80th centile) results in the south east and East Anglia, but river water at these locations is mostly not used for water supply, and colour results is not a characteristic of the groundwater that provides baseflow to these rivers. The distribution of high colour results is visually similar to the distribution of dissolved organic carbon concentrations (Figure Error! **No text of specified style in document..8**).

Review of the distribution of calcium (Figure Error! No text of specified style in document..9) shows that there is a very clear north west - south east contrast in hardness. The groundwater-dominated catchments of south and east England have high hardness, while the runoff-dominated catchments in the north and west yield soft water.

Therefore, there is a clear overlap of a) the distribution of high manganese in river waters, b) concentrations of dissolved organic carbon, and c) soft water in the north and west of England and Wales. All of these are factors that cause difficulties with manganese removal from raw water relative to concentrations of un-complexed manganese in soft water from south and east England.

The distributions of calcium and pH (Figure Error! **No text of specified style in document..10**) can be used to qualitatively show the likely distribution of Langelier index (LI): where the water is low in calcium and the pH is low the LI is more likely to be negative. The distribution of soft, low pH water is also focussed on the north and west so that the risk factors for corrosion of iron water mains are also higher in that area.

2.3.1.2 Transient Variation

Arithmetic mean results are shown in the maps of Section 2.3.1.1. These show spatial variability, but not transient changes in water quality. This is important to note because the more flashy nature of upland catchments leads to greater variability in water quality.

To illustrate these factors, transient datasets from five of the HMS monitoring locations have been extracted and plotted for manganese concentration, dissolved organic carbon, calcium concentration and pH. These factors highlight the discolouration risk factors. The sites were chosen as follows.

- River Don at Halfpenny Bridge (just downstream of Sheffield) the River Don drains the Dark Park like the catchment of Bamford WTW (River Noe and Ladybower Reservoir). The monitoring site is 21 km east of Bamford.
- River Derwent at Church Wilne (just downstream of Derby). The Bamford WTW catchment is in the upper Derwent catchment, but is only a small part of it. The monitoring site is 57 km south of Bamford.
- River Wye at Glyn Footbridge (just downstream of Rhyader). The Elan Valley Reservoirs are just upstream of the monitoring point, though their catchment forms a small part of the Wye catchment here.

¹ Arithmetic mean concentrations are used as these are relatively simple to calculate given the huge amount of data. Use of the geometric mean would be more representative but would be disproportionately time consuming in context of the desired outcome of this project.

- River Thames at the NSWC Intake Egham (probably the intake for the west London Reservoirs, but not certain). This monitoring point is chosen as an indication of the water quality in the south and east from a mixed permeable (Cotswolds and Berkshire Downs Chalk) and clay (Oxford Clay, Gault Clay) catchment.
- River Itchen at The White Swan (downstream of Eastleigh and Winchester). This monitoring point is chosen as an indication of the water quality from an entirely chalk groundwater-fed river.

Variability in manganese concentrations is clearly greatest in the rivers with upland catchments: the Don and Wye (Figure Error! **No text of specified style in document..11**). Variability is low in the rivers with the lowland catchments: the Thames and Itchen, while the Derwent shows intermediate variability. Dissolved organic concentrations do not seem to show the same pattern - possibly influenced by treated sewage discharges in the catchments.

Variability in calcium concentrations is similar (relative to the mean concentration), but pH in the upland catchments has the greatest variability (Figure Error! **No text of specified style in document..12**). pH in the River Wye is very variable, in particular.

Hence it is not just the spatial variability of concentrations that is important in controlling risk of discolouration, but also the flashy nature of low permeability catchments that controls transient variability of water quality parameters.

2.4 Groundwater Quality

Section 2.3 deals with surface water quality; with the implication that the water quality of high baseflow lowland catchments reflects to a degree groundwater chemistry.

The Permo-Triassic Sandstone aquifer forms a significant water resource for STWL and some of the other northern water companies (United Utilities in particular). This is well-known to locally yield groundwater with high concentrations of manganese (e.g. at STWL's Milford source). The chalk and other limestone aquifers, used by the southern and eastern water companies, do not generally have a manganese concentration issues as commonly as the Permo-Triassic Sandstone.

The British Geological Survey has produced many studies that explore baseline groundwater quality of English and Welsh aquifers (though the single Welsh report is not of relevance to this report). Table Error! **No text of specified style in document..1** collates the maximum, 97.7th and 95th percentile concentrations of manganese and dissolved organic carbon (DOC), the minimum and median concentration of calcium, and the minimum and median pH value, which are the key factors that promote discolouration risk, for the most important aquifers of England.

When comparing the water quality from Permo-Triassic sandstone aquifer with the others, the critical difference is the elevated concentration of manganese. Peak concentrations (max and 97.7th percentile) are typically an order of magnitude greater in groundwater from the Permo-Triassic sandstone - in particular those aquifers of the north west – than in other aquifers. In general, peak DOC concentrations from the Permo-Triassic sandstone are also higher, and minimum pH and calcium concentrations (i.e. hardness) are lower than in other aquifers.

Aquifer**	Area**	Stat.***	Mn (mg/l)	DOC (mg/l)	Stat.	Calcium (mg/l)	Field pH
Permo- Triassic sandstones	Staffordshire & Worcestershire	Max: 97.7 th :	0.224 0.103	8.9 7.9	Min: Med:	25.6 68.2	5.70 7.21
	Shropshire	Max: 97.7 th :	1.480 0.870	1.6 1.5	Min: Med:	25.4 76.0	5.20 7.32
	Vale of York	Max: 97.7 th :	1.400 1.155	19.2 18.7	Min: Med:	55.3 140.0	6.49 7.26

Aquifer**	Area**	Stat.***	Mn (mg/l)	DOC (mg/l)	Stat.	Calcium (mg/l)	Field pH
	West Cheshire &	Max:	6.120	5.0	Min:	4.4	7.00
	Wirral	97.7 th :	2.327	5.0	Med:	74.0	7.51
	Manchester &	Max:	6.000	6.7	Min:	12.0	6.0
	East Cheshire	97.7 th :	3.193	6.4	Med:	77.5	7.2
	Liverpool &	Max:	2.990	17.5	Min:	25.6	5.88
	Rufford	97.7 th :	2.236	16.7	Med:	87.2	7.19
	Devon and	Max:	0.234	6.5	Min:	1.6	5.14
	Somerset	95 th :	0.111	0.6	Med:	72.2	6.91
Chalk	Dorset	Max: 97.7 th :	0.555 0.150	4.2 3.8	Min: Med:	50.0 105.0	6.94 7.22
	Hampshire	Max: 95 th :	0.726 0.002	1.2 1.1	Min: Med:	94.4 105.0	6.88 7.11
	North Downs, Kent & East Surrey	Max: 97.7 th :	0.013 0.004	4.6 4.1	Min: Med:	61.9 117.0	6.40 7.20
	Chilterns (Colne & Lee catchments)	Max: 97.7 th :	0.040 0.014	3.1 3.0	Min: Med:	106.0 125.0	6.94 7.20
	Great Ouse catchment (East Anglia)	Max: 97.7 th :	0.102 0.049	4.1 3.5	Min: Med:	81.0 128.0	6.60 7.10
	Yorkshire & N.	Max:	0.057	8.6	Min:	62.4	6.34
	Humberside	97.7 th :	0.017	8.2	Med:	106.0	7.28
Other	Cotswolds	Max:	0.018	5.4	Min:	14.4	6.40
limestones		97.7 th :	0.013	5.2	Med:	96.9	7.20
	Lincolnshire	Max:	0.110	5.5	Min:	95.5	7.1
	Limestone	97.7 th :	0.080	5.1	Med:	161.5	7.3
	Corallian of Oxfordshire & Wiltshire	Max: 97.7 th :	0.466 0.391	8.7 5.8	Min: Med:	2.5 103.0	6.63 7.32
	Corallian of the	Max:	0.109	n/a	Min:	48.8	6.96
	Vale of Pickering	95 th :	0.012	n/a	Med:	108.0	7.30
	Magnesian	Max:	1.290	11.1	Min:	10.3	6.93
	Limestone	95th:	0.270	4.9	Med:	92.0	7.24
Lower	Southern	Max:	0.100	10.1	Min:	9.3	5.80
Greensand	England	97.7 th :	0.075	9.7	Med:	51.7	7.18

* Some baseline reports tabulate data from oxidising and reducing aquifer environments separately. Here, it is assumed that only the groundwater from oxidising environments are representative of groundwater going into public water supply.

** Links to sources: <u>https://www.bgs.ac.uk/research/groundwater/quality/BaselineUK/baselineEngWales.html</u>

*** Most reports contain the 97.7th percentile statistic and not the 95th percentile. Reports for the sandstones of Devon and Somerset, Chalk of Hampshire, Corallian of the Vale of Pickering, and Magnesian Limestone, only give the 95th percentile.



* The aquifers marked here provide most of the groundwater abstracted for public supply in England and Wales. The Environment Agency and Natural Resources Wales define additional 'Principal Aquifers' that are worth protecting, but which are of secondary importance in terms of abstraction (these are: Crag [Palaeogene, Norfolk], Spilsby Sandstione [Lincolnshire's equivalent to the Lower Greensand aquifer], Carboniferous Limestone [of Northern England, and North and South Wales], and the Fell Sandstone {Carboniferous of Northumberland]).



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Don
Thames
Wye
Derwent
Itchen



Dissolved Organic Carbon

Don
Thames
Wye
Derwent
Itchen

Calcium



Don
Thames
Wye
Derwent
Itchen





Don
Thames
Wye
Derwent
Itchen

3. Summary

Discoloration of water in public water supplies can arise from ineffective treatment of dissolved manganese or corrosion of iron water mains (amongst other things). Treatment for manganese removal from raw water can be compromised if the water is soft, and/or it has high dissolved organic carbon concentrations. Corrosion of iron mains can be promoted by low pH and soft waters.

Spatial distributions of these risk factors have been mapped and reviewed. A clear divide is seen in that the waters of the north and west of England and Wales tend to have high manganese concentrations, low hardness, higher dissolved organic carbon, and lower pH. In addition, intermittent runoff from the steep slopes of the north and west lead to more variable water quality. Higher variability can lead to more frequent breaches of drinking water standards for a given level of treatment.

The main cause of all these factors is the underlying geology - the rocks of the north and west of England and Wales are older and have been subjected to high temperatures and pressures within the Earth's crust. This has led to these rocks becoming hard; they are resistant to erosion, so the topography is steeper. Aquifer properties of these rocks can also be poor so economic levels of groundwater abstraction cannot be developed. Therefore, rainfall runs quickly off the ground surface and is captured in surface water reservoirs. In the south and east of England the rocks are younger and have only been lightly altered. Topography is less steep, so groundwater recharge is higher, and better aquifer characteristics mean that groundwater can be exploited for public supply.

As rainfall infiltration passes through soils the pH increases, and as the resultant groundwater passes through the subsurface the water becomes more mineralised and less soft. Dissolved organic carbon may also be lost. Hence the factors that compromise manganese treatment are lessened with residence in the subsurface. This then, favours the south and east of England as an area where manganese treatment is less likely to fail.

Geological factors also control the distribution of manganese-rich groundwater in water supply aquifers. The Permo-Triassic Sandstones of the Midlands and North West England are particularly prone to high dissolved manganese concentrations compared to other aquifers.