

Sampling and Analysis of Groundwater at selected locations on the island of Ireland Blackwater Catchment Hydrochemistry Report

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Blackwater Catchment Hydrochemistry Report









An Roinn Tithíochta, Rialtais Áitiúil agus Oidhreachta Department of Housing, Local Government and Heritage

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Section 1 Introduction

1.1 Background

The British Geological Survey (BGS) appointed CDM Smith Ireland Ltd (CDM Smith) to undertake a programme of groundwater monitoring at locations across the Blackwater catchment. This work was completed as part of the CatchmentCARE project.

Four (no. 4) monitoring events were carried out between October 2021 and August 2022:

- October 2021
- March 2022
- June 2022
- August 2022

Up to nine monitoring wells were sampled during each monitoring event as newly drilled wells were added to the monitoring programme during successive monitoring events, and wells were drop due redundancy in sampling the same groundwater body. In total, 24 samples were collected over the two-year monitoring period.

This report presents the fundamental hydrochemical characteristics of the Blackwater catchment based on the four monitoring events. The hydrochemistry across the catchment is summarised, an initial assessment of the water types is provided and potential anthropogenic pressures in the catchment are discussed.

1.2 Site Background

The Blackwater catchment is situated on the border between the Republic of Ireland (ROI) and Northern Ireland spanning south Tyrone, west Armagh and north Co. Monaghan (Figure 1). Samples were collected in three locations across the catchment. All samples from any one location are grouped together for analysis and interpretation purposes in this report. The locations/groups and total number of samples per group are given below and presented in Figure 1:

- Group 1: Trimble Farm (n= 10)
- Group 2: Hughes Farm (n = 6)
- Group 3: Anacramp (n = 8)

The Corine 2018 Landcover dataset indicates that the land use across the Blackwater catchment is predominantly agricultural pastures (<u>Corine Landcover 2018</u>). Throughout the catchment, discontinuous urban fabrics are common and small scattered patches of mixed and coniferous forests are present.

The soils are generally poorly drained fine loam and drift with alluvium in some areas (EPAMaps, data available for Republic of Ireland only). Subsoils across the south of the catchment are

largely variable till derived from limestone, sandstone and shale with alluvium and some raised peat especially south of Lough Neagh (<u>GSI Map Viewer; UK Soil Observatory</u>).

Bedrock is at or close to surface comprising predominantly of limestones and sandstones in the west (<u>GSI Map Viewer; GSNI GeoIndex</u>). Subsoil permeability is generally low (<u>EPAMaps</u>).

The aquifer is largely 'Bp' (poor potential productivity fracture flow) in the north of the catchment, extending to 'Bh' (high potential productivity fracture flow with karstic element) or 'Lm' (generally moderately productive) to the south of the catchment (<u>GSI Map Viewer; GSNI GeoIndex</u>). Aquifer vulnerability is generally low in the south of the catchment (<u>GSI Map Viewer; GSNI Viewer</u>) and southwest of Lough Neagh with moderate elsewhere with some smaller areas of higher vulnerability, particularly in the NI section (<u>GSNI GeoIndex</u>).



Figure 1: Blackwater Catchment Location

Location	Bedrock Geology (GSNI 1:250,000)	General mineral composition
Trimble farm (west catchment)	Clogher Valley Formation	Argillaceous: Aluminosilicates
	(Interbedded Argillaceous rock	(AlNa ₁₂ SiO ₅), clay minerals
	and subordinate limestone	(kaolinite (Al ₂ O ₃ 2SiO ₂ ·2H ₂ O),
	(Tournaisian))	montmorillonite-smectite
		(OH)4Si ₈ Al ₄ O ₂ O·nH ₂ O), illite ((K,H
		₃O)(Al,Mg,Fe) 2(Si,Al)
		$4O_{10}[(OH)_2 \cdot (H_2O)])$, chlorite
		((Mg,Fe) ₃ (Si,Al) 4O ₁₀ (OH)
		2·(Mg,Fe)₃(OH) ₆))
Anacramp (center catchment)	Maydown Limestone Formation	Argillaceous: Aluminosilicates
	(Argillaceous, muddy limestone	(AlNa ₁₂ SiO ₅), clay minerals
	(Absian))	(kaolinite ($AI_2O_3 2SiO_2 \cdot 2H_2O$).
		Limestone: Calcite (CaCO ₃)
Hughes Farm (east catchment)	Sherwood Sandstone Group	Sandstone: Silica (SiO ₂) 93-94%,
		Aluminium oxide (Al ₂ O ₃) 1.4-
		1.5%, Iron (Fe ₂ O ₃) 1.5-1.6%, CaO
		0.8-0.9%, Na₂O &(K 1.0-1.2%,
		MgO 0.2-0.25%

Section 2 Methodology

2.1 Field Sampling Method

Groundwater samples were collected using either the low-flow technique or fixed volume technique. Ground water purging and sampling was carried out using pumps as follows:

- Bladder pump (low flow purge and sample method);
- Peristaltic pump (low flow purge and sample method); or
- Suction pump (fixed volume purge).

Groundwater levels were measured at all wells prior to pumping using a portable electronic water level meter and the initial static water level was recorded.

Field water quality parameters (temperature, pH, oxidation-reduction potential (ORP), conductivity and dissolved oxygen (DO)) were measured at all wells.

For low flow monitoring, the field water quality parameters were monitored in the field during low-flow purging using a flow-through cell to minimise oxidation by the atmosphere. Purging continued until the water quality indicator parameters stabilised (pH < \pm 0.1; specific electrical conductivity < 3%; temperature < \pm 0.1 ° C). The water level was measured throughout the purging process to monitor drawdown. The field data were recorded in a Survey123 Groundwater Purging and Sampling Survey digital form using a handheld portable electronic device every approximately three-five minutes during the purging process. After the well was purged and stable parameters measured, the flow was reduced for low-flow sample collection (500 ml / minute).

Fixed volume purging was carried out by purging three times volume of the complete water column in the well. The well was then allowed to recharge before sampling using either the peristaltic pump or suction pump.

All samples for trace metal analyses were filtered in the field using a 0.45-micron membrane filter before filling bottles containing nitric acid preservative. New bottles supplied by the laboratories were used for sample collection.

2.2 Laboratory Analysis

Analysis of water samples was undertaken by McQuillan Environmental, Antrim, Northern Ireland, United Kingdom and Element Materials Technology (Element), Deeside, United Kingdom. Both laboratories are accredited by the United Kingdom Accreditation Service (UKAS) in accordance with ISO/IEC 17025:2005.

Water samples were either collected by a courier on the day of sampling (McQuillan Environmental) or dispatch by DHL to Element in UK.

The laboratory monitored parameters fall into three groups:

- Inorganic parameters: 52 parameters, including metals, major anions and cations, macronutrients (nitrogen and phosphorus species), physico-chemical parameters (analysed by McQuillan Environmental);
- 2. Organic parameters: up to 216 parameters, including pesticides and herbicides (analysed by Element); and
- 3. Microbial parameters: *E. coli*, total coliforms and *Clostridium Perfringens* (analysed by McQuillan Environmental).

Section 3 Data Quality and Usability Evaluation

3.1 Introduction

Laboratory data quality and usability were assessed using data quality indicators (DQIs). Data "usability" means that the data are acceptable to use for their intended purpose and associated evaluations. The DQIs for assessing data are expressed in terms of precision and accuracy. These DQIs provide a mechanism to evaluate and measure laboratory data quality throughout the project. The definitions and methods of measurement of precision and accuracy are discussed below.

3.2 Precision

Precision is the measurement of the ability to obtain the same value on re-analysis of a sample (i.e., the reproducibility of the data). The closer the results of the measurements are together, the greater is the precision. Precision is not related to accuracy or the true values in the sample; instead, precision is focused upon the random errors inherent in the analysis that result from the measurement process and are compounded by the sample vagaries. Precision is measured by analysing two portions of the sample (sample and duplicate) and then comparing the results. This comparison can be expressed in terms of relative percent difference (RPD). RPD is calculated as the difference between the two measurements divided by the average of the two measurements, as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2) \ x \ 0.5} \ x \ 100$$

where:

RPD	=	Relative percent difference
D1	=	First sample value
D ₂	=	Second sample value (duplicate)

Acceptable RPD values for field duplicates are usually 50 % to 150 %. Field duplicates were generated for this project. One field duplicate was collected each round, totalling six for the project.

3.2.1 Field QA/QC Samples

The results are used to evaluate the combined reproducibility of both the laboratory analyses and field sampling.

One duplicate sample per round was generated in the field and sent blind to McQuillan Environmental for analysis. Table 2 (monitoring events 1, 2 & 3) and Table 3 (monitoring events 4, 5 & 6) provide the results of 52 parameters and the calculated RPD between each pair of samples. Note, where both the original and duplicate result are less than the limit of detection (LOD), the RPD is zero. Where only one value is less than the LOD, half of the LOD value is used to permit calculation of the RPD; in such cases the "0.5 X <LOD" value is indicated by grey fill. Table cells with a blue fill indicates an RPD greater than 50% but less than 150%. Yellow filled cells indicates an RPD greater than 150%.

		Ro	und 1		Roun	id 2		Rou	Round 3	
Sample Description		Kilomu	Ity Spring		CCF06 Interme	(FSTC diate)		CCF07 DE		
				% R			% R			% R
Lab ref		077002	077003	B	082086	082085	PD	086071	086073	Dd
Date Sampled	Units	19/1	1/2020		25/05/	/2021		13/10	/2021	
Alkalinity, Bicarbonate as CaCO3	mg/l	399	407	2.0	170	195	13.7	140	135	-3.6
Alkalinity, Total	mg/l	404	410	1.5	199	198	-0.5	148	138	-7.0
Aluminium (diss.filt)	ug/l	11.3	5	-77.3	<10	<10	0	19.1	18	-5.9
Ammonia as N	mg/l	0.37	0.39	5.3	< 0.11	<0.11	0	0.34	0.055	-144
Anions	ueq/l	9440	9530	0.9	5,900	5,900	0	4,600	4,340	-5.8
Arsenic (diss.filt)	ug/l	12.8	12	-6.5	<0.5	<0.5	0	<0.5	<0.5	0
Barium (diss.filt)	ug/l	267	252	-5.8	87.3	86.3	-1.2	27.2	27.1	-0.4
Boron (diss.filt)	ug/l	18.8	23.8	23.5	13	5	-88.9	<10	<10	0.0
Bromide	mg/l	0.207	0.207	0	0.202	0.207	2.4	0.0873	0.0994	13.0
Cadmium (diss.filt)	ug/l	<0.08	<0.08	0	<0.08	<0.08	0	<0.08	<0.08	0
Caesium, Dissolved	ug/l	<1.0	<1.0	0	< 1.0	<1	0	< 1.0	< 1.0	0
Calcium (diss.filt)	mg/l	120	121	0.4	49.6	50	0.8	13.058	13.788	5.4
Cations	ueq/l	9570	9580	0.1	5,600	5,700	1.8	4,190	4,300	2.6
Cerium, Dissolved*	ug/l	<1.0	<1.0	0	< 1.0	< 1.0	0.0	-	-	-
Chloride as Cl	mg/l	37	39.1	5.5	33.1	33.5	1.2	27.7	25.0	-10.2
Chromium (diss.filt)	ug/l	<1	<1	0	<1	<1	0	<1	<1	0
Cobalt (diss.filt)	ug/l	<0.5	<0.5	0	<0.5	<0.5	0	<0.5	<0.5	0
Copper (diss.filt)	ug/l	0.338	0.15	-77.0	<0.3	<0.3	0	<0.3	<0.3	0
Dissolved Organic Carbon	mg/l	5.07	5.28	4.1	3.08	3.53	13.6	< 2.0	< 2.0	0
Electrical Conductivity	uS/cm	885	894	1.0	557	559	0.4	442	439	-0.7
Fluoride as F	mg/l	0.45	0.455	1.1	0.59	0.58	-1.7	1.67	1.65	-1.2
Iodide*	mg/l	<0.1	<0.1	0	<0.1	<0.1	0.0	-	-	-
Ionic Balance	%	0.6	0.3	-66.7	-2.6	-1.7	-41.9	-4.7	-0.5	-162
Iron (diss.filt)	mg/l	9.39	9.47	0.8	0.167	0.15	-10.7	<0.019	<0.019	0
Lead (diss.filt)	ug/l	<0.2	<0.2	0	<0.2	<0.2	0	<0.2	<0.2	0
Lithium (diss.filt)	ug/l	7.69	8.04	4.5	19.8	19.8	0	12.4	12.7	2.4
Magnesium (diss.filt)	mg/l	22.7	22.6	-0.4	13	13.4	3.0	4.17	4.31	3.3
Manganese (diss.filt)	ug/l	93.3	90.7	-2.8	34.7	34.2	-1.5	8.73	8.05	-8.1
Mercury (diss.filt)	ug/l	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01	0
Nickel (diss.filt)	ug/l	1.21	1.15	-5.1	<0.4	<0.4	0	<0.4	<0.4	0
Nitrate as N	mg/l	0.58	0.04	-174	<0.08	<0.08	0	0.13	0.09	-36.4
Nitrite as N	mg/l	<0.05	<0.05	0	< 0.05	< 0.05	0	< 0.05	< 0.05	0
Nitrogen, Total	mg/l	<1	<1	0	<1	<1	0	<1	<1	0
рН	Units	6.8	6.92	1.7	7.82	7.84	0.3	8.47	8.53	0.7
Phosphate, Ortho as P	mg/l	<0.07	<0.07	0.0	< 0.07	< 0.07	0.0	<0.02	<0.02	0

Table 2 Duplicate data and associated RPD (%), monitoring events 1,2 & 3

		Ro	und 1		Roun	d 2		Rou			
Sample Description		Kilomulty Spring			CCF06 Interme	(FSTC diate)		CCF07 DE	(F-STC- EP)		
Lab ref	Units	077002	077003 1/2020	% RPD	082086	082085	% RPD	086071 13/10	086073	% RPD	
Phosphorus (diss.filt)	ug/l	68.4	34.1	-66.9	<10	<10	0.0	10	2021	66.7	
Potassium (diss.filt)	mg/l	8.23	8.21	-0.2	11.9	12	0.8	7.05	7.47	5.8	
Selenium (diss.filt)	ug/l	<1	<1	0	<1	<1	0	<1	<1	0	
Sodium (diss.filt)	mg/l	21.3	21.2	-0.5	39.8	40.8	2.5	68.80	70.50	2.4	
Strontium (diss. filt)	ug/l	1750	1700	-2.9	424	420	-0.9	236	234	-0.9	
Sulphate as SO4	mg/l	11.5	11.2	-2.6	47.00	47.20	0.4	41.00	41.80	1.9	
Total Dissolved Solids	mg/l	528	526	-0.4	343	345	0.6	245	229	-6.8	
Total Organic Carbon	mg/l	4.14	4.14	0	2.43	2.46	1.2	1	0.09	-167	
Total Oxidised Nitrogen as N	mg/l	0.58	0.04	-174	< 0.08	< 0.08	0	0.13	1	154	
True Colour	mg/l Pt/Co	14.4	6.78	-72.0	<1	<1	0	<1	<1	0	
Turbidity	ntu	92.1	88.8	-3.6	3.21	3.64	12.6	0.93	1.03	10.2	
Uranium (diss.filt)	ug/l	<0.5	<0.5	0	17.9	18	0.6	10.9	10.7	-1.9	
Zinc (diss.filt)	ug/l	1.6	2.77	53.5	1.67	0.5	-108	6.53	3.14	-70.1	

* Removed following absence of detections in any well

Table 3 Duplicate data and associated RPD (%), monitoring events 4, 5 & 6

			Round 4		F	lound 5		Round 6			
Sample Description		CCD08 (D-DIW-TRANS)		%	FPBI	102	%	RW-BH-03		%	
Lab ref (MCQ)		10135 9	10136 5	RPD	105794	10579 6	RPD	108346	10834 9	RPD	
Date Sampled	Units	10/03	/2021		16/06,	16/06/2022		25/08/			
Alkalinity, Bicarbonate as CaCO3	mg/l	70.6	90	24.2	250	295	16.5	133	84.7	-44	
Alkalinity, Total	mg/l	70.3	89.6	24.1	280	274	-2.2	119	105	-13	
Aluminium (diss.filt)	ug/l	<10	<10	0	11.3	5	-77.3	17.1	21.9	25	
Ammonia as N	mg/l	0.055	0.14	87.2	<0.11	<0.11	0	<0.11	<0.11	0	
Anions	ueq/l	2820	3890	31.9	6720	6580	-2.1	3050	2850	-7	
Arsenic (diss.filt)	ug/l	<0.5	<0.5	0	0.674	0.882	26.7	1.77	1.8	2	
Barium (diss.filt)	ug/l	79.9	77.8	-2.7	163	163	0	25	24.3	-3	
Boron (diss.filt)	ug/l	18.9	11.5	-48.7	11.6	10.5	-10.0	<10	<10	0	
Bromide	mg/l	0.0866	0.102	16.3	0.114	0.116	1.7	0.071	0.104	38	
Cadmium (diss.filt)	ug/l	0.125	0.04	-103	<0.08	<0.08	0	<0.08	<0.08	0	
Caesium, Dissolved	ug/l	<1.0	<1.0	0	<1.0	<1.0	0	1	1	0	
Calcium (diss.filt)	mg/l	31.7	41	25.6	54	55	1.8	27.3	26.4	-3	
Cations	ueq/l	2480	3240	26.6	6350	6500	2.3	2540	2490	-2	
Cerium, Dissolved*	ug/l	-	-	-	-	-	-	-	-	-	

			Round 4		R	ound 5				
Sample Description		CCI (D-DIW	D08 -TRANS)	%	FPBF	102	%	RW-BH-03		%
		10135	10136	RPE		10579	RPE		10834	RPE
Lab ref (MCQ)		9	5		105794	6		108346	9	
Date Sampled	Units	10/03	/2021		16/06/	2022		25/08/	_	
Chloride as Cl	mg/l	15.2	33.3	74.6	25.8	25.3	-2.0	19.1	20.4	7
(diss.filt)	ug/l	<1	<1	0	1.05	1.13	7.3	<1	<1	0
Cobalt (diss.filt)	ug/l	<0.5	<0.5	0	<0.5	<0.5	0	3.81	3.83	1
Copper (diss.filt)	ug/l	0.388	1.93	133	1.93	2.04	5.5	<0.3	<0.3	0
DOC	mg/l	10	3.1	-105	3.4	3.4	0	4.7	3.5	-29
Electrical Conductivity	uS/cm	298	410	31.6	643	642	-0.2	285	260	-9
Fluoride as F	mg/l	0.0614	0.022	-94.5	0.304	0.286	-6.1	0.0698	0.764	167
lodide*	mg/l	-	-	-	-	-	-	-	-	-
Ionic Balance	%	-6.5	-9.1	33.3	-2.8	-0.6	-129	-9.3	-6.6	-34
Iron (diss.filt)	mg/l	<0.019	<0.019	0	<0.019	<0.019	0	10.9	11.2	3
Lead (diss.filt)	ug/l	0.1	0.208	70.1	0.343	0.325	-5.4	<0.2	<0.2	0
Lithium (diss.filt)	ug/l	<1	<1	0	26.1	26.1	0	1.65	1.78	8
Magnesium (diss.filt)	mg/l	5.45	5.91	8.1	20	20.5	2.5	1.82	1.74	-4
Manganese (diss.filt)	ug/l	3.23	241	195	23.8	23.1	-3.0	1320	1290	-2
Mercury (diss.filt)	ug/l	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01	0
Nickel (diss.filt)	ug/l	0.585	0.481	-19.5	1.03	1.29	22.4	3.15	3.16	0
Nitrate as N	mg/l	9.46	13	31.5	0.1	0.1	0	<0.08	<0.08	0
Nitrite as N	mg/l	<0.05	<0.05	0	<0.05	<0.05	0	<0.05	<0.05	0
Nitrogen, Total	mg/l	9.22	12.5	30.2	<1	<1	0	<1	<1	0
рН	Units	6.22	6.18	-0.6	7.87	7.87	0	6.56	6.47	-1
Phosphate, Ortho as P	mg/l	<0.02	<0.02	0	<0.02	<0.02	0	<0.02	<0.02	0
Phosphorus (diss.filt)	ug/l	10	23.6	81.0	<20	<20	0	77.9	75.7	-3
Potassium (diss.filt)	mg/l	0.833	4.8	141	23.3	23.8	2.1	<0.87	<0.87	0
Selenium (diss.filt)	ug/l	<1	<1	0	<1	<1	0	<1	<1	0
Sodium (diss.filt)	mg/l	9.65	12.9	28.8	32.5	33.4	2.7	8.82	8.74	-1
Strontium (diss. filt)	ug/l	140	166	17.0	1240	1250	0.8	68.4	67.7	-1
Sulphate as SO4	mg/l	14.8	11.1	-28.6	18.3	18.1	-1.1	6.46	8.3	25
TDS	mg/l	152	263	53.5	367	374	1.9	167	163	-2
тос	mg/l	2.8	15	137	3.3	3.2	-3.1	5	3.7	-30
TON as N	mg/l	9.46	13	31.5	0.1	0.1	0	<0.08	<0.08	0
True Colour	mg/l Pt/Co	0.5	2.1	123	4.48	4.47	-0.2	12.2	45	115
Turbidity	ntu	0.616	0.427	-36.2	0.452	0.359	-22.9	64.4	81.8	24
Uranium (diss.filt)	ug/l	<0.5	<0.5	0	46.8	46.7	-0.2	1.03	1.06	3
Zinc (diss.filt)	ug/l	9.91	8.4	-16.5	3.44	3.49	1.4	16.5	10.3	-46

* Removed following absence of detections in any well

The majority of RPD values were below 50%. In total, 26 of the 312 (i.e., 8%) of RPD > 50% but less than 150%. There were seven instances of RPD > 150%. With one exception, these exceedances/high RPDs were generally associated with low concentrations and often with one value being at the LOD (and thus 0.5 x LOD used for the calculation). For Manganese in the Round four duplicate, the recorded concentration were 3.23 ug/L and 241 ug/L. All other parameters for these two duplicates are in line with expected values for a duplicate pair. The manganese concentrations were checked with the laboratory who confirmed their accuracy and suggested the deviation was due to a contamination issue at some point.

Overall, the duplicate %RPD data are considered satisfactory and useable for the intended evaluations.

3.3 Ionic Balance/Charge Balance

Within a water sample, the amounts of positive charges and negative charges should be equal, resulting in a charge balance or ionic balance of close to zero. Determining the ionic balance of a sample is a useful means of checking the laboratory analysis of ions have been carried out correctly and all major ions were analysed. Values of \pm 10% are satisfactory for this QA/QC test.

Of the 24 values, 23 were within the \pm 10%, with median value of -3.5 %.

The ionic balance Trimble Farm on 14/06/2022 (Lab ref: MCQ105667) was -15.2 %.

The laboratory checked the results for samples with elevated ionic balances and confirmed analysis were correct and data accurate.

Overall, the ionic balances were acceptable indicating good and complete analysis, with all major anions and cations analysed.

Section 4 Data Summary & Interpretation

4.1 Summary Statistics

This section provides a statistical summary of the analytical results and a comparison of the analytical results against selected assessment criteria. Where the reported values were below the detection limit (<LOD), the values were substituted with a value of half the limit of detection (0.5 x <LOD). The summary statistics apply to all 24 samples collected during the six monitoring events across all wells.

The summary statistics presented are briefly described below:

- WQS: water quality standard value/threshold to which the results are compared (either IGV or GTV, as below)
- IGV: EPA Interim Guide Value (Towards Setting Guideline Values For The Protection Of Groundwater In Ireland – Interim Report http://www.epa.ie/pubs/advice/water/ground/towardssettingguidelinevaluesfortheprote ctionofgroundwaterinireland.html)
- GTV: Groundwater Regulations Threshold Value (S.I. No. 9 of 2010)
- LOD: laboratory analytical limit of detection
- Source: WQS source
- Min: minimum detected value above the LOD
- Mean: mean of dataset
- Maximum: maximum value detected
- Median: median value of dataset
- 97.7th percentile: 97.7th percentile of dataset
- No. of Samples: number of samples analysed for this parameter
- No. of WQS Exceedances: number of exceedances of the WQS threshold
- % of WQS Exceedances: percentage of values above the WQS threshold
- No. of Detections: number of values above the detection limit
- % of WQS Detections: percentage of values above the limit of detection

Summary statistics of the field physico-chemical water quality parameters along with major and minor elements are contained in Table 4. Table 5: Summary statistics of metals (trace elements)

Exceedances of the respective WQS are indicated by orange highlight of the number and percentage WQS exceedance.

There were exceedances of the respective threshold/WQS for the following field parameters, and major and minor elements:

- Ammonia (N) (exceedance no. 10 or 42 %);
- Specific electrical conductivity (SEC) (exceedance no. 7 or 29 %);
- Sulphate (SO₄) (exceedance no. 6 or 25 %);
- Total Dissolved Solids (TDS) (exceedance no. 6 or 25 %);
- Magnesium (Mg) (exceedance no. 6 or 25 %);
- Calcium (Ca) (exceedance no. 6 or 25 %); and
- Fluoride (F) (exceedance no. 4 or 16.7 %).

There were exceedances of the respective threshold/WQS for the metals (trace elements):

- Iron (Fe) (exceedance no. 24 or 100 %);
- Barium (Ba) (exceedance no. 14 or 58 %);
- Manganese (Mn) (exceedance no. 9 or 38 %);
- Arsenic (As) (exceedance no. 1 or 4.2 %); and
- Aluminium (Al) (exceedance no. 1 or 4.2 %).

Test	Units	LOD	wqs	Source	Min*	Mean	Max	Median	97.7 th percentile	No. samples	No. detections	% Detections	No. WQS Exceedances	% WQA Exceedances
Ammonia as N	mg/l	<0.11	0.065	GTV 2016	0.110	0.106	0.360	0.055	0.281	24	10	42%	10	42%
Electrical Conductivity	uS/cm	<1	800	GTV 2016	452	1116	2690	746	2690	24	24	100%	7	29%
Sulphate as SO4	mg/l	<5	187.5	GTV 2016	12.3	432	2050	60	1833	24	24	100%	6	25%
Calcium Dis	mg/l	<0.201	200	IGV 2003	37.4	177	549	103	537	24	24	100%	6	25%
Total Dissolved Solids (TDS)	mg/l	<3	1000	IGV 2003	251	892	2540	446	2535	24	24	100%	6	25%
Magnesium (Dissolved)	mg/l	<0.101	50	IGV 2003	6.3	41.7	107.0	22.65	107.0	24	24	100.00%	6	25%
Fluoride as F	mg/l	<0.02	1	IGV 2003	0.100	0.53	1.84	0.284	1.81	24	24	100%	4	17%
Nitrite as N	mg/l	<0.05	0.375	GTV 2016	-	-	-	-	-	24	0	-	0	-
Phosphate, Ortho as P	mg/l	<0.02	0.035	GTV 2016	-	-	-	-	-	24	0	-	0	-
Nitrate as N	mg/l	<0.08	37.5	GTV 2016	0.080	0.11	0.49	0.04	0.41	24	8	33%	0	0%
Potassium (Dissolved)	mg/l	<0.17	5	IGV 2003	1.03	2.62	4.79	2.255	4.57	24	24	100%	0	0%
Sodium (Dissolved)	mg/l	<0.145	150	GTV 2010	10.5	24.0	39.4	24.2	39.0	24	24	100%	0	0%
Chloride as Cl	mg/l	<0.35	187.5	GTV 2016	12.0	17.0	33.2	16.3	26.4	24	24	100%	0	0%
рН	Units	-	<6.5, >905	IGV 2003	7.01	7.28	7.74	7.15	7.71	24	24	100%	0	0%
Cations	ueq/l	-	No WQS	-	4620	13423	35900	8085	35371	24	-	-	-	-
Anions	ueq/l	ueq/l	No WQS	-	5070	15002	47300	8380	42592	24	-	-	-	-
Ionic Balance	%	<-50%	No WQS	-	-15.2	-4.29	0.80	-3.50	-0.36	24	-	-	-	-
Dissolved Oxygen	mg/l	-	No WQS	-	0.150	2.35	9.07	1.84	7.31	24	-	-	-	-

Table 4: Summary statistics of field parameters, and major and minor elements

Test	Units	LOD	wqs	Source	Min*	Mean	Max	Median	97.7 th percentile	No. samples	No. detections	% Detections	No. WQS Exceedances	% WQA Exceedances
Total Oxidised Nitrogen (TON) as N	mg/l	<0.08	No WQS	-	0.080	0.14	1.00	0.04	0.73	24	8	33%	-	-
Organic Carbon, Total	mg/l	<2	No WQS	-	0.170	17.6	82.0	2.15	78.8	24	14	58%	-	-
True Colour	mg/l Pt/Co	<1	No WQS	-	1.20	1.39	4.60	0.50	4.51	23	9	39%	-	-
Nitrogen, Total	mg/l	<1	No WQS	-	-	-	1.24	-	-	24	1	4%	-	-
Turbidity	ntu	<0.1	No WQS	-	1.53	13.5	92.3	4.70	63.6	24	24	100%	-	-
Dissolved Organic Carbon	mg/l	<2	No WQS	-	2.00	17.1	82.0	1.50	78.8	24	12	50%	-	-
Total phosphorus	ug/l	<20	No WQS	-	21.3	30.2	161	15.7	121	24	12	50%	-	-
**Alkalinity, Bicarbonate as CaCO3	mg/l	-	No WQS	-	187	276	385	257	383	23	23	100%	-	-
Alkalinity, Total as CaCO ₃	mg/l	<5	No WQS	-	189	276	378	262	373	24	24	100%	-	-

*Minimum result above detection limit

**One value of <2 mg/l (LOD) removed as erroneous outlier

Table 5: Summary statistics of metals	s (trace elements)
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Test	Units	LOD	wqs	Source	Min*	Mean	Max	Median	97.7th percentile	No. Sample s	No. Detection s	% Detections	No. WQS Exceedance s	% WQS Exceedance s
Iron	mg/l	<0.019	0.2	IGV 2003	0.3	39.3	341	0.792	305	24	24	100%	24	100%
Barium	ug/l	<0.2	100	IGV 2003	1.0	123	360	135	327	24	24	100%	14	58%
Manganese	ug/l	<3	50	IGV 2003	3.5	157	804	29.1	706	24	22	96%	9	38%
Arsenic	ug/l	<0.5	7.5	GTV 2016	0.6	1.8	8.1	0.25	6.8	24	11	46%	1	4%
Aluminiu m	ug/l	<10	150	GTV 2016	15.2	6.3	23.9	5.00	19.5	23	2	8.7%	0	0%
Boron	ug/l	<10	750	GTV 2010	15.3	255	581	153	565	24	24	100%	0	0%
Lithium	ug/l	<1	No WQS	-	1.1	26.8	74.4	21.5	72.4	24	24	100%	-	-
Strontium	ug/l	<1	No WQS	-	296	7,577	24,600	3,760	24,494	24	24	100%	-	-
Copper	ug/l	<0.3	1500	GTV 2010	0.150	0.185	0.689	0.150	0.565	24	19	79.%	0	0%
Nickel	ug/l	<0.4	15	GTV 2010	0.458	0.377	1.76	0.200	1.31	24	8	33.3%	0	0%
Uranium	ug/l	<0.5	9	IGV 2003	0.581	0.366	0.819	0.250	0.737	24	6	25%	0	0%
Bromide	mg/l	<0.06	No WQS	-	0.2	0.1	0.2	0.06	0.1	24	17	77%	-	-
Lead	ug/l	<0.2	7.5	GTV 2016	0.3	-	0.3	-	-	24	1	4.2%	0	0%
Cobalt	ug/l	<0.5/ <0.096	No WQS	-	-		0.321	-	-	24	2	8.33%	-	-
Cadmium	ug/l	<0.08	3.75	GTV 2010	-	-	-	-	-	24	0	0%	0	0%
Chromium	ug/l	<1	37.5	GTV 2016	-	-	-	-	-	24	0	0%	0	0%
Mercury	ug/l	<0.01	0.75	GTV 2016	-	-	-	-	-	24	0	0%	0	0%
***Caesium	ug/l	<1	No WQS	-	-	-	-	-	-	9	0	0%	-	-
Cerium	ug/l	<1	No WQS	-	-	-	-	-	-	24	0	0%	-	-
Selenium	ug/l	<1	No WQS	-	-	-	-	-	-	24	0	0%	-	-

*Minimum result above detection limit

One value of 235 ug/l removed as erroneous outlier *Analysis omitted after second round due to non-detects across all monitoring locations in project

Section 5 Water Physiochemical Characteristics and Water Type

This section provides analysis and interpretation of water physicochemical characteristics and the water types. For the purposes of assessing the water physicochemical characteristics and assessing the water types, the wells are divided in five groups. Each group represents a cluster of wells which are in close geographical proximity within the catchment. The three groups are:

- Group 1: Anacramp;
- Group 2: Hughes Farm;
- Group 3: Trimble Farm

The following are assessed in this section:

- Water chemistry:
 - Major cations and anions, with box plots and interpretation in Section 5.1, and
 - Major and minor (/trace) constituents, with box plots and interpretation in Section 5.2.
- Water physiochemistry, via assessment of alkalinity, ORP and pH with box plots and interpretation in Section 5.3.1; and
- Water type, by piper diagram assessment of major ions in Section 5.3.2;

5.1 Major Cations and Anions

A summary of the concentration pattern of each of the major cations and anions is provided below.

5.1.1 Calcium

- Calcium (Ca) concentrations within the Blackwater Catchment range from 36.3 mg/L at Group 2: Hughes Farm to 549 mg/L at Group 3: Trimble Farm (Figure 2).
- The groups display distinct patterns of Ca concentrations.
- The widest range of values occurs at Group 3: Trimble Farm and Group 2: Hughes Farm shows the narrowest range of values.
- Interquartile ranges do not overlap for any of the three locations. Group 2: Hughes Farm has relatively lower calcium concentrations, Group 1: Anacramp has mid-range concentrations and Group 3: Trimble Farm recorded the highest calcium concentrations.



Figure 2: Calcium (Ca) boxplot, where x-axis is the well group and log scale y-axis

5.1.2 Magnesium

- Magnesium (Mg) concentrations within the Blackwater catchment ranged from 6.29 mg/L to 107 mg/L in Group 3: Trimble Farm (Figure 3).
- Group 3: Trimble Farm displays the highest range in magnesium concentrations.
- The narrowest range of concentrations was observed in samples from Group 2: Hughes Farm.
- The interquartile ranges overlap for all three locations, indicting similarity in recorded magnesium concentrations.



Figure 3: Magnesium (Mg) boxplot, where x-axis is the well group

5.1.3 Sodium

- Sodium (Na) concentrations within the Blackwater catchment range from 10.5 mg/L at Group 1: Anacramp to 39.4 mg/L at Group 2: Hughes Farm (Figure 2).
- Generally, higher sodium concentrations were observed at Group 3: Trimble Farm and Group 2: Hughes Farm.
- Group 1: Anacramp shows the narrowest range of values while the ranges at the other two locations are similar and larger.
- All groups display similarly sodium concentrations in the low concentration range. Interquartile ranges overlap for all three locations.

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Sodium (mg/L)

Figure 4: Sodium (Na) boxplot, where x-axis is the well group

5.1.4 Chloride

- Chloride (Cl) concentrations within the Blackwater Catchment ranged from 12.0 mg/L at to 33.2 mg/L at Group 1: Anacramp (Figure 5).
- All three groups have similar median concentrations; however, Group 1: Anacramp and Group 3: Trimble Farm are similar to each other and both distinct from Group 2: Hughes Farm when considered interquartile ranges.



Figure 5: Chloride (Cl) boxplot, where x-axis is the well group

5.1.5 Potassium

- Potassium (K) concentrations within the Blackwater catchment ranged from 1.03 mg/L at Group 1: Anacramp, to 4.79 mg/L at Group 3: Trimble Farm (Figure 6).
- Group 2: Hughes Farm and Group 1: Anacramp has relatively narrow ranges and low concentrations, while Group 3: Trimble Farm has relatively wider ranges.
- Generally, higher concentrations of potassium are recorded at Group 3: Trimble Farm and lower concentrations at Group 1: Anacramp and Group 2: Hughes Farm.
- Group 1: Anacramp and Group 2: Hughes Farm had very similar K concentration patterns.



Potassium (mg/L)

Figure 6: Potassium (K) boxplot, where x-axis is the well group

5.1.6 Sulphate

- Sulphate (SO₄) concentrations within the Blackwater catchment ranged from 12.3 mg/L at Group 2: Hughes Farm to 2,050 mg/L at Group 3: Trimble Farm (Figure 7).
- The widest range of values occurred at Group 3: Trimble Farm while Group 2: Hughes Farm shows the narrowest range of values.
- All groups displayed distinct patterns of sulphate concentrations. Interquartile ranges do not overlap at any of the three locations.

 The lowest concentrations were recorded at Group 2: Hughes Farm and highest concentrations at Group 3: Trimble Farm, with intermediate concentrations at Group 1: Anacramp.



Sulphate (mg/L)

Figure 7: Sulphate (SO₄) boxplot, where x-axis is the well group and y-axis is log scale

5.1.7 Fluoride

- Fluoride (F) concentrations within the Blackwater catchment ranged from 0.1 mg/L at Group 2: Hughes Farm to 1.84 mg/L at Group 1: Anacramp (Figure 8).
- Group 2: Hughes Farm had the narrowest range concentrations, while the widest range of concentrations was observed in samples obtained from Group 1: Anacramp.
- Generally, higher concentrations of dissolved F were recorded at Group 1: Anacramp with lower interquartile concentrations Group 3: Trimble Farm. Values at Group 2: Hughes Farm were consistently low. The concentrations at Group 2: Hughes Farm were distinct from that at Group 1: Anacramp and Group 3: Trimble Farm. The range of concentrations at Group 1: Anacramp and Group 3: Trimble Farm overlapped.



Figure 8: Fluoride (F) boxplot, where x-axis is the well group

5.1.8 Nitrate (NO₃ as N)

- Nitrate (NO₃) concentrations within the Blackwater catchment ranged from <LOD (0.08 mg/L, included in the graph as 0.04 mg/L) at all locations, to 0.490 mg/L at Group 3: Trimble Farm (Figure 9).
- The widest interquartile range of values occurred at Group 3: Trimble Farm, while Group 1: Anacramp had the narrowest range of values with all records below the limit of detections.
- The highest nitrate concentrations were observed at Group 3: Trimble Farm.



Figure 9: Nitrate (NO₃ as N) boxplot, where x-axis is the well group

5.2 Major and Minor (Trace) Elements

A summary of the concentration patterns of major and minor (trace) elements for which there were detections at one site at a minimum is provided below. The data are grouped based on clusters of wells, as previously discussed.

5.2.1 Dissolved Iron

- Dissolved iron (Fe) concentrations within the Blackwater catchment ranged from 0.273 mg/L at Group 2: Hughes Farm to 341 mg/L at Group 1: Anacramp (Figure 10).
- Group 3: Trimble Farm had the narrowest interquartile range of concentrations, while the widest range of interquartile concentrations was observed in samples obtained from Group 1: Anacramp.
- Generally, higher concentrations of dissolved Fe were recorded at Group 1: Anacramp with lower interquartile concentrations at Group 2: Hughes Farm and Group 3: Trimble Farm. The interquartile ranges of all three locations overlap indicating overlap in concentration ranges.

Dissolved Iron (mg/L)



Figure 10: Dissolved Iron (Fe) boxplot, where x-axis is the well group and y-axis is log scale

5.2.2 Dissolved Aluminium

- Dissolved aluminium (Al) concentrations within the Blackwater catchment ranged from <LOD (10 ug/L, included in the graph as 5 ug/L) at all groups to 23.9 ug/L at Group 2: Hughes Farm (Figure 11).
- Group 2: Hughes Farm had the widest range of concentrations, while concentrations at Group 1: Anacramp and Group 3: Trimble Farm were largely below the limit of detection.

Aluminum (ug/L)



Figure 11: Aluminium (AI) boxplot, where x-axis is the well group and y-axis log scale

5.2.3 Dissolved Barium

- Dissolved barium (Ba) concentrations within the Blackwater catchment ranged from 0.985 ug/L at Group 3: Trimble Farm to 360 ug/L at Group 1: Anacramp (Figure 12).
- Group 3: Trimble Farm and Group 1: Anacramp had relatively wide ranges of barium concentrations while a relatively narrow range of concentrations was observed in samples obtained from Group 2: Hughes Farm.
- The interquartile ranges of all groups overlap, however, Group : Trimble Farm had a lower median concentration than Group 2: Hughes Farm and Group 1: Anacramp (which were similar).



Barium (ug/L)

Figure 12: Barium (Ba) boxplot, where x-axis is the well group and y-axis are log scale

5.2.4 Dissolved Nickel

- Dissolved nickel (Ni) concentrations within the Blackwater catchment ranged from <LOD (0.4 ug/L, included in the graph as 0.2 ug/L) at all groups to 1.76 ug/L at Group 1: Anacramp (Figure 13).
- All records at Group 2 Hughes Farm were <LOD. The range of concentrations at the other two locations were overlapping and similar.



Nickel (ug/L)

Figure 13: Nickel (Ni) boxplot, where x-axis is the well group

5.2.5 **Dissolved Zinc**

- Dissolved zinc (Zn) concentrations within the Blackwater catchment ranged from <LOD (1 ug/L, included in the graph as 0.5 ug/L) at all groups to 21.1 ug/L at Group 1: Anacramp (Figure 14).
- Group 1: Anacramp had the widest range of concentrations, followed by Group 3: Trimble Farm. The narrowest range of concentrations was observed for Group 2: Hughes Farm.
- The concentration ranges of all three groups overlap.





Figure 14: Zinc (Zn) boxplot, where x-axis is the well group

5.2.6 Dissolved Strontium

- Strontium (Sr) concentrations within the Blackwater catchment ranged from 296 ug/L at Group 2: Hughes Farm to 24,600 ug/L at Group 1: Anacramp (Figure 15).
- Higher concentrations of dissolved strontium were recorded in samples from wells in Group 1: Anacramp and Group 3: Trimble Farm. Lower and more consistent strontium concentrations were recorded in samples from Group 2: Hughes Farm.
- Group 1: Anacramp had the widest range of strontium concentrations, while the narrowest range was observed in samples obtained from Group 3: Trimble Farm.

Strontium (ug/L)



Figure 15: Strontium (Sr) boxplot, where x-axis is the well group

5.2.7 Dissolved Manganese

- Manganese (Mn) concentrations within the catchment ranged from <LOD (3 ug/L, included in the graph as 1.5 ug/L) to 804 ug/L, both at Group 1: Anacramp (Figure 16).
- Generally, higher concentrations of dissolved manganese were recorded in samples from wells in Group 1: Anacramp and Group 3: Trimble Farm, with lower concentrations at Group 2: Hughes Farm.
- Samples from wells in Group 1: Anacramp had the widest range of manganese concentrations, while the narrowest range of manganese concentrations was observed in samples obtained from wells in Group 2: Hughes Farm.



Figure 16: Manganese (Mn) boxplot, where x-axis is the well group and y-axis are log scale

5.2.8 Dissolved Lithium

- Dissolved lithium (Li) concentrations within the catchment ranged from 1.11 ug/L at Group 3: Trimble Farm to 74.4 ug/L at Group 1: Anacramp (Figure 17).
- Group 1: Anacramp had the widest range of concentrations, while the narrowest range of concentrations was observed for Group 2: Hughes Farm.
- The concentration ranges of all three groups overlap.



Figure 17: Lithium (Li) boxplot, where x-axis is the well group

5.2.9 Dissolved Uranium

- Dissolved uranium (U) concentrations within the catchment ranged from the LOD 0.5 ug/l (reported as 0.5 x LOD, or 0.250 ug/L in the graph below) at all groups to 0.819 ug/L at Group 3: Trimble Farm (Figure 18).
- Uranium concentrations at Group 2: Anacramp were mostly low (most values <LOD).
 Some higher concentrations were recorded at the other two locations. The interquartile range of all site locations overlapped (due to non-detects (<LOD) at each location).

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Figure 18: Uranium (U) boxplot, where x-axis is the well group

5.3 Physicochemical Characteristics and Water Types

5.3.1 Water physiochemistry: Alkalinity, Oxidation-Reduction Potential (ORP) & pH

A summary of water chemistry parameters alkalinity, pH and redox are presented below.

Alkalinity (Bicarbonate as CaCO₃)

- Alkalinity within the catchment ranged from 187 mg/L in Group 3: Trimble Farm to 385 mg/L in Group 1: Anacramp (Figure 19).
- Group 3: Trimble Farm and Group 1: Anacramp had relatively wide ranges of alkalinities, while that at Group 2: Hughes Farm was relatively narrow.
- Higher alkalinities were recorded in wells in Group 1: Anacramp and the concentration pattern at this site was distinct from the other two sites (which themselves overlapped).

Alkalinity (mg/L)



Figure 19: Alkalinity (Bicarbonate as CaCO₃) boxplot, where x-axis is the well group

Redox (oxidation-reduction potential, ORP)

- All redox values across the catchment were negative indicating reducing conditions.
- The redox within the catchment ranged from -501 mv in Group 2: Hughes Farm (indicating sulphate reducing conditions) to -3 mv in Group 3: Trimble Farm (Figure 19).
- Wells in Group 1: Anacramp had the lowest redox potential and thus the most reducing conditions. Wells in Group 3: Trimble Farm had the highest redox potential of the three locations, though still negative and thus still indicating a reducing environment.



Figure 20 Redox boxplot, where x-axis is the well group

рΗ

- The pH ranged from 7.01 at Group 3: Trimble farm to 7.74 at Group 1: Anacramp (Figure 21).
- Generally, higher pH values were seen at Group 2: Hughes Farm and lower pH values at Group 3: Trimble Farm.
- The mean and interquartile ranges of pH of the three groups were distinct.



Figure 21: pH boxplot, where x-axis is the well group

5.3.2 Water Type

Piper diagrams are used to determine the water type in the Blackwater catchment and in each cluster of wells within the catchment. An illustration of the interpretation of piper diagrams is presented in Figure 22.

Overall, the groundwater in the Blackwater catchment appears to be of the magnesium bicarbonate (Mg-HCO₃) type; however some samples appear to be of a calcium-bicarbonate type of groundwater with a number plotting on the Ca-Cl type and the Mg and SO₄ types (



Figure 24).

pH (su)

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Figure 22 Piper Diagram Interpretation





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Figure 24: Piper diagram for the grouped wells

5.4 Organic and Microbial Parameters

A number of organic parameters and microbial parameters were monitored as pollution indicator parameters. These included pesticides and herbicides.

5.4.1 Organic parameters

Organic parameters were monitored at two wells in Round 6 (August 2022), shallow wells CCB06 (BW-Anacramp-Transition) and CCB03 (BW-Trimble Farm-Transition). A range of organic parameters, pesticides and insecticides were analysed, including cypermethrin (<100 µg/l).

There was one detection of each of the herbicides monuron (0.02 μ g/l) and glyphosate (0.40 μ g/l) in BW-Anacramp-Transition. The concentration of glyphosate exceeded the Groundwater Directive (S.I. No. 366/2016) limit of 0.075 μ g/l.

There were no detections of the other 216 parameters analysed.

5.4.2 Microbial parameters

Microbial parameters were also monitored in the two shallowest wells, CCB06 (BW-Anacramp-Transition) and CCB03 (BW-Trimble Farm-Transition), during in Round 6 (August 2022).

There were no detections of any microbial parameter in BW-Anacramp-Transition.

Total coliforms and *E. coli* were detected at low levels in BW-Trimble Farm-Transition (10 and 6 cfu/100 ml, respectively).

Section 6 Summary and Recommendations

6.1 Water Type

The groundwater in the Blackwater catchment is $Mg/Ca-HCO_3$ type; however, some samples are no-dominant type of groundwater with a number of samples being Ca-SO₄/Cl type.

6.2 Exceedances, Pressures & Pollution Indicators

The Blackwater catchment is predominantly agricultural pastures, with low aquifer vulnerability (ROI dataset).

There were exceedances of the respective WQS threshold for the following physicochemical parameters, and major and minor elements:

- Ammonia (N) (exceedance no. 10 or 42 %);
- Specific electrical conductivity (SEC) (exceedance no. 7 or 29 %);
- Total dissolved solids (TDS) (exceedance no. 6 or 25 %);
- Magnesium (Mg) (exceedance no. 6 or 25 %);
- Calcium (Ca) (exceedance no. 6 or 25 %);
- Sulphate (SO₄) (exceedance no. 6 or 25 %); and,
- Fluoride (F) (exceedance no. 4 or 17 %).

There were exceedances of the respective threshold/WQS for the metals (trace elements):

- Iron (Fe) (exceedance no. 24 or 100 %);
- Barium (Ba) (exceedance no. 14 or 58 %);
- Manganese (Mn) (exceedance no. 9 or 38 %); and
- Arsenic (As) (exceedance no. 1 or 4.2 %).

Some of these elevated concentrations may relate to aquifer hydrochemistry (e.g., potentially iron) and others may relate to catchment land use practices (e.g. possibly ammonia).

The locations of the exceedances of WQS thresholds are outlined in Table 6, with orange fill indicating >5% of values exceed the threshold (% of exceedances).

Parameter	lron	Barium	Manganese	Specific electrical conductivity (SEC)	Ammonia	Sulphate	Calcium	Magnesium	Total Dissolved Solids (TDS)	Fluoride	Arsenic
Group 1: Anacramp											
Group 2: Hughes Farm											
Group 3: Trimble Farm											

Table 6 Exceedances of WQS parameters relative to well group/well location

Iron, calcium and magnesium-bearing minerals are common in the bedrock geology across the catchment (Table 1). Manganese may also be found in the geology in the catchment. Manganese is mobilized from minerals under reducing conditions. The oxidation-reduction potential indicates generally reducing conditions at all locations.

Barium is relatively common in sandstone, however, some of the detections, particularly at Group 1: Anacramp and Group 3: Trimble farm, may be anthropogenic (either residual from construction of the wells and/or from anthropogenic inputs).

The arsenic exceedances at Group 2: Hughes Farm may be due to sedimentary rock type.

Fluoride (at Group 1: Anacramp) is relatively rare in nature and likely to be of anthropogenic origin. Fluoride may be associated with domestic waste water treatment systems. There was one detection of each of the herbicides monuron ($0.02 \mu g/l$) and glyphosate ($0.40 \mu g/l$) at this location, in the well CCB06 (BW-Anacramp-Transition). The concentration of glyphosate exceeded the Groundwater Directive (S.I. No. 366/2016) limit of 0.075 $\mu g/l$. There were also exceedances of specific electrical conductivity and ammonia, which may be associated with agricultural practices and/or domestic waste water treatment systems.

There were a relatively high number of exceedances of a relatively large number of parameters at Group 3: Trimble Farm, including parameters that might be indicative of anthropogenic pressures (ammonia, sulphate, TDS and specific electrical conductivity (SEC)). Total coliforms and *E. coli* were also detected at this location, in well CCB03 (BW-Trimble Farm-Transition) (10 and 6 cfu/100 ml, respectively) during round 6 (August 2022). These parameters may be associated with agricultural practices and/or domestic waste water treatment systems.

The data indicate that anthropogenic pressure(s) may be impacting the water quality at Group 3: Trimble Farm and Group 1: Anacramp. The data suggest that the pressure(s) may be agriculture and/or domestic wastewater treatment systems. It should be noted that these conclusions are based on a relatively small dataset. Additional monitoring should take place to carry out further assessments and determine/confirm any pressures on the groundwater bodies.

6.3 Recommendations

It is recommended that monitoring is continued to develop a robust baseline dataset and to assess and characterize the pressures on the groundwater bodies, where they exist, particularly at locations Anacramp and Trimble Farm. This programme should be guided by the results of this project and include at a minimum the parameters that indicate anthropogenic pressures for which there were exceedances/detections (i.e., herbicides, microbial parameters, ammonia etc.).

It is recommended that further assessments be carried out to provide insight on the potential sources of anthropogenic contamination (i.e., pressures). This might include assessments of phosphorus concentrations relative to background values to assess the impact of agricultural practices (e.g., land spreading of fertilizer (manure) can result in elevated phosphorus). Other assessments might consider further the concentrations of fluoride (which may indicate household/domestic waste); total organic carbon; nitrate; ammonia and total dissolved solids, as well as the ratios of chloride to bicarbonate, sodium to calcium and sulfate to bicarbonate.

Further work might include better definitions of individual wells and probability plots or other statistical methods to develop background values when a larger dataset is available.

Section 7 References

Corine Landcover 2018. Available at: <u>https://land.copernicus.eu/pan-european/corine-land-cover/clc2018</u> (Accessed: February 7, 2023).

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