CatchmentCARE
Community Actions for Resilient Ecosystems

Sampling and Analysis of Groundwater at selected locations on the island of Ireland

Arney Catchment Hydrochemistry Report

UK Research and Innovation/British Geological Survey
Author: F. Papageorgiou & B. Anders & L. Foley, CDM Smith

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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 natural springs across the Arney catchment. The Arney catchment straddles the border between the Republic of Ireland and the United Kingdom (Northern Ireland). This work was completed as part of the CatchmentCARE project.

Six monitoring events were carried out between November 2020 and August 2022:

- November 2020
- May 2021
- October 2021
- March 2022
- June 2022
- August 2022

Up to 16 springs were monitored during each monitoring event, with 81 samples in total collected over the two-year monitoring period.

This report presents the fundamental hydrochemical characteristics of the Arney catchment based on the six 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 Arney catchment straddles the border between the Republic of Ireland and the United Kingdom (Northern Ireland) (Figure 1).

Samples were collected at up to 16 springs across the catchment. The number of data points varies as some springs were dry/not flowing during summer months and one location (Cleggan spring) was monitored only once and then removed from the monitoring programme. The locations and total number of samples are given below and the locations presented in Figure 1:

- Boylans Well (*n* = 6)
- Barran Spring (*n* = 6)
- Barran Spring 2 (*n* = 6)
- Tuam Spring (*n* = 6)
- Ture Rising (*n* = 6)
- Hollywell (*n* = 6)
- Hanging Rock (*n* = 6)
- Cladagh River (*n* = 6)
- Tullyhone Cave (*n* = 5)
- Sulphur Well (*n* = 6)
- Carrickmacsparrow (*n* = 3)
- Mullyard Rising (*n* = 3)
- Marlbank West (*n* = 4)
- Kiltomulty Spring (*n* = 6)
- Mullaghdun Stream (*n* = 5)
- Cleggan Spring (*n* = 1)

From the Corine 2018 Landcover dataset (Corine Landcover 2018), land use across the Arney catchment is predominantly agricultural pastures, with areas of mixed and coniferous forest and some scattered peat bogs in the east. Peat bogs are common in the east of the catchment and coniferous and mixed forests, moors and heathlands are common in the west of the catchment.

Bedrock is comprised of limestones and mudstone, sandstone (Mullaghmore sandstone formation, Glenade sandstone formation and Bellavalley formation) and evaporites are at or close to the surface (GSNI GeoIndex). Shale (Benbulbin shale and Bundoran Shale) and coal lithologies are present in the east. Lacustrine sediments are present surrounding Upper Lough Erne to the north of the catchment (GSI Map Viewer). Details of bedrock geology and mineralogy are presented in Table 1 (GSNI GeoIndex & GSI Map Viewer).

Subsoils across the Arney catchment are largely variable till derived from both limestones and sandstones and shales with some alluvium and peat (GSNI GeoIndex). Soils are predominantly Stagnosols with some leptosols, fluvisols and minor cambisols in the east (UK Soil Observatory). Histosols become more prevalent in the east.

The aquifer across the west of the catchment is complex with regionally important aquifers (karstified) in the east. Aquifers in the east are locally important with flows predominantly in fissures and discontinuities (GSNI GeoIndex). The Arney catchment aquifer vulnerability generally ranges from “high” to “extreme” (GSNI GeoIndex & GSI Map Viewer).

Table 1 Bedrock Geology and Mineralogy

Bedrock Geology	General mineral composition
Bellavally Shale Formation (Mississippian {Asbian}) Grey micrite, shale, laminate evaporite)	Shale: at least 30% clay (Al, Mg, Si) with various amounts of quartz (SiO_2 – can contain minor Li, Na, K and Ti), feldspar (Na, K, Ca, Al, Si, O), carbonates (Na, Ca), iron oxides (Fe) and organic matter (H, O, N, C). Micrite: Calcite ($CaCO_3$)
Mudbank Limestone (Carboniferous)	Limestone: calcium bearing carbonate minerals (Ca, C, O)
Knockmore Limestone member (Mississippian {Asbian}) Pale grey massive fine-grained limestone)	Calcite ($CaCO_3$) and dolomite ($Mg(CO_3)$ and $Ca(CO_3)$)
Glencar Limestone Formation (Mississippian {Holkerian}) Dark fine limestone and calcareous shale)	Dark limestone: Mainly Calcite ($CaCO_3$) with minor pyrite (FeS) Calcareous shale: mainly composed of Calcite ($CaCO_3$) with minor quartz (SiO_2)
Benbulben Shale Formation (Mississippian {Holkerian}) Calcareous shale with minor calcarenite)	Calcareous shale: Calcite ($CaCO_3$), quartz (SiO_2) Calcarenite: calcite (70 %), iron-rich dolomite (25 %), quartz (5 %) and traces of clay minerals (illite).
Glanade Sandstone Formation (Mississippian {Asbian}) Pale orthoquartzitic sandstone	Orthoquartzite is almost exclusively composed of quartz (SiO_2)

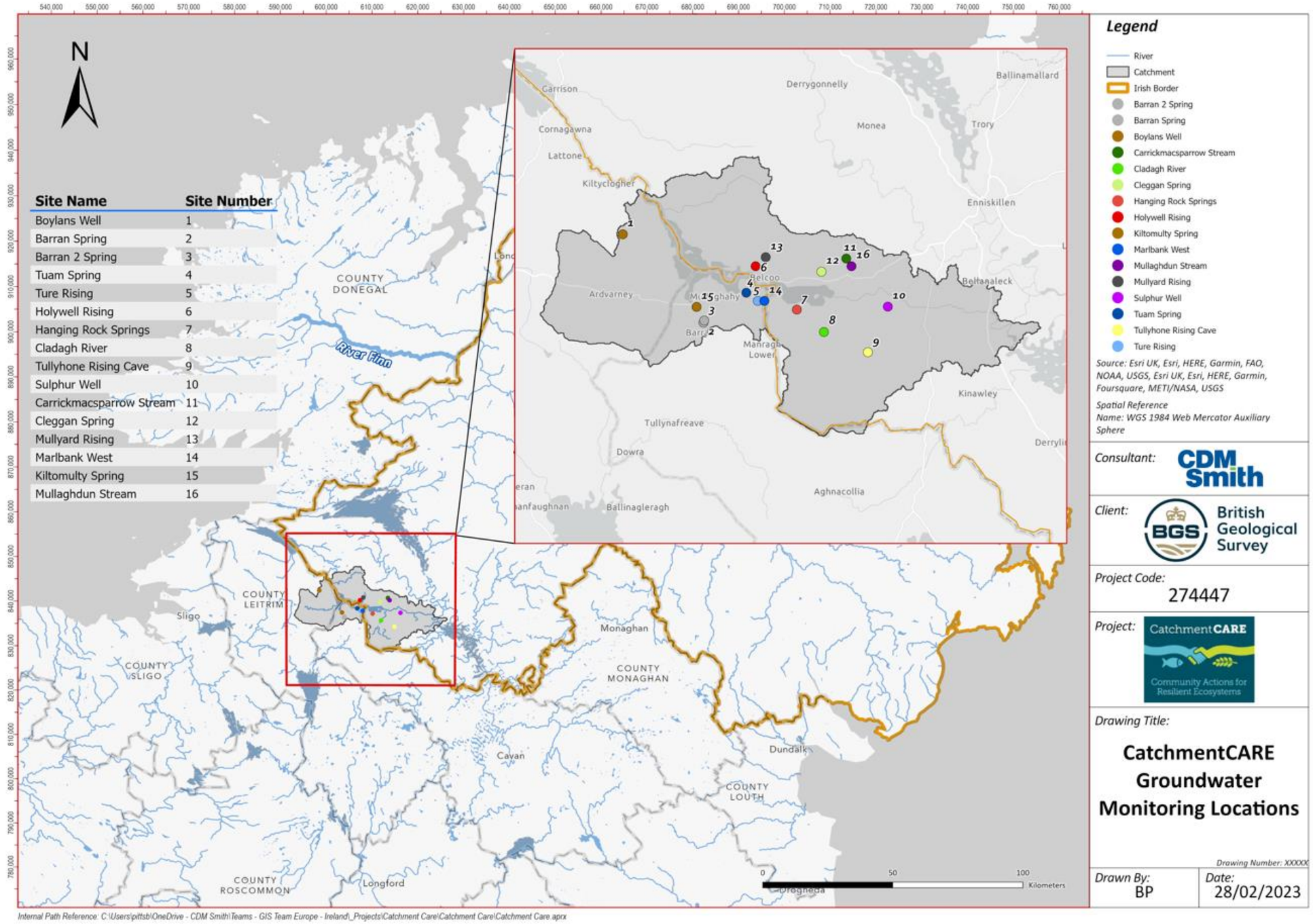

Figure 1: Arney Catchment and Springs Locations

Section 2 Methodology

2.1 Field Sampling Method

Grab samples were taken at all 16 locations.

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

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:

1. Inorganic parameters: 52 parameters, including metals, major anions and cations, macronutrients (nitrogen and phosphorus species), physicochemical parameters (analysed by McQuillan Environmental);
2. Organic parameters: 103 parameters, including pesticides, and insecticides (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:

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

where:

RPD	=	Relative percent difference
D_1	=	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 (by filling two sets of bottles) 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%.

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

		Round 1			Round 2			Round 3		
Sample Description		Kilomulty Spring		% RPD	CCF06 (FSTC Intermediate)		% RPD	CCF07 (F-STC-DEEP)		% RPD
Lab ref		077002	077003		082086	082085		086071	086073	
Date Sampled	Units	19/11/2020			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	13.1	13.8	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
pH	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

		Round 1			Round 2			Round 3		
Sample Description		Kilomulty Spring		% RPD	CCF06 (FSTC Intermediate)		% RPD	CCF07 (F-STC-DEEP)		% RPD
Lab ref		077002	077003		082086	082085		086071	086073	
Date Sampled	Units	19/11/2020			25/05/2021			13/10/2021		
Phosphorus (diss.filt)	ug/l	68.4	34.1	-66.9	<10	<10	0.0	10	20	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	68.8	70.5	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	47.0	47.2	0.4	41.0	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			Round 5			Round 6		
Sample Description		CCD08 (D-DIW-TRANS)		% RPD	FPBH02		% RPD	RW-BH-03		% RPD
Lab ref (MCQ)		101359	101365		105794	105796		108346	108349	
Date Sampled	Units	10/03/2021			16/06/2022			25/08/2022		
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			Round 5			Round 6		
Sample Description		CCD08 (D-DIW-TRANS)		% RPD	FPBH02		% RPD	RW-BH-03		% RPD
Lab ref (MCQ)		101359	101365		105794	105796		108346	108349	
Date Sampled	Units	10/03/2021			16/06/2022			25/08/2022		
Chloride as Cl	mg/l	15.2	33.3	74.6	25.8	25.3	-2.0	19.1	20.4	7
Chromium (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
Iodide*	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
pH	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
TOC	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 monitoring event 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.

3.3 Ionic Balance/Charge Balance

Within a water sample, the amount of positive charges and negative charges should be equal, resulting in an 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. Values of ± 10% are satisfactory for this QA/QC test.

A description of the ionic balance data for the 81 samples is presented below. Of the 81 values, 72 were within ± 10%, with median value of -1.4%. From the remaining ones, two exceeded the ± 10% but were within ± 15% as follows:

- -11.1% (Cladagh River Lab ref: MCQ086108, sampled on 14/11/2021), and
- -12.6 % (Tullyhone Rising Lab ref: MCQ107861, sampled on 16/08/2022).

The remaining five exceeded the ± 15% as follows:

- <-50 (Barran Spring 2 Lab ref: MCQ105876, sampled on 20/06/2022),
- -35.5% (Cladagh River Lab ref: MCQ076996, sampled on 19/11/2022),
- 32.7% (Cladagh River Lab ref: MCQ101361, sampled on 10/03/2022),
- -21% (Boylans Well Lab ref: MCQ105874, sampled on 20/06/2022),
- -39.8% (Kiltomulty Spring Lab ref: MCQ105875, sampled on 20/06/2022), and
- -36.9% (Boylans Well Lab ref: MCQ082185, sampled on 26/05/2021).

The laboratory checked the results for samples with elevated ionic balances and confirmed analysis were correct and data accurate. The laboratory noted that the results with inflated negative ionic balances had high alkalinity, contributing to a high negative anion result. The Boylans Well (Lab ref: MCQ082185, sampled on 26/05/2021, ionic balance -36.9%) had high chloride. The Cladagh River (sample Lab ref: MCQ101361, sampled on 10/03/2022, ionic balance 32.7 %) had high calcium and low content for iron, manganese and sulphate (<5 mg/l).

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 for major and minor elements, and trace elements (metals), 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 81 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
- 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/towardssettingguidelinevaluesfortheprotectionofgroundwaterinireland.html)
- GTV: Groundwater Regulations Threshold Value (S.I. No. 9 of 2010)
- Source: WQS source
- LOD: laboratory analytical limit of detection
- 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 physicochemical water quality parameters along with major and minor elements are contained in Table 4. Table 5 contains the summary statistics of the trace 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 major and minor elements (Table 4):

- Ammonia as N (exceedance no. 18, or 22 %);
- Fluoride (F) (exceedance no. 11, or 14 %);
- Specific electrical conductivity (SEC) (exceedance no. 8, or 10 %);
- Sodium (Na) (exceedance no. 6, or 7.4 %);
- Ortho-Phosphate as P (exceedance no. 6, or 7.4 %);
- Potassium (K) (exceedance no. 3, or 4 %); and;
- Chloride (Cl) (exceedance no. 1, or 1.2 %).

There were exceedances of the respective threshold/WQS for the metals (trace elements) (Table 5):

- Iron (F) (exceedance no. 17, or 21 %);
- Barium (Ba) (exceedance no. 12, or 15 %);
- Manganese (Mn): (exceedance no. 8, or 10%); and;
- Arsenic (As) (exceedance no. 2, or 3 %).

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

Test	Units	LOD	WQS	Source	Min*	Mean	Max	Median	97.7th percentile	No. Samples	No. Detections	% Detections	No. WQS Exceedances	% WQS Exceedances
Ammonia as N	mg/l	0.11	0.065	GTV 2016	0.120	0.238	4.18	0.055	1.23	81	81	100	18	22
Fluoride	mg/l	0.024	1	IGV 2003	0.020	67.9	5450	0.050	5.46	81	74	91	11	14
Specific Electrical Conductivity	µS/cm	1	800	GTV 2016	2.50	476	1160	437	1140	81	81	100	8	10
Sodium	mg/l	0.145	150	GTV 2010	3.07	26.2	232	7.52	220	81	100	100	6	7.4
Ortho-phosphate as P	mg/l	<0.02 or <0.07	0.035	GTV 2016	0.010	0.025	0.360	0.010	0.048	81	81	100	6	7.4
Potassium	mg/l	0.174	5	IGV 2003	0.291	1.48	8.23	1.02	5.80	81	81	100	3	4
Chloride	mg/l	0.35	187.5	GTV 2016	4.99	23.1	232	13.4	92.1	81	81	100	1	1.2
Total Dissolved Solids	mg/l	<3	1000	IGV 2003	72.0	277	693	243	654	81	81	100	0	0
pH (field)	-	-	<6.5, >9.5	-	6.70	7.40	8.40	7.30	8.40	81	-	-	0	0
Oxidation reduction potential (ORP) (field)	mV	-	-	-	-625	-93.9	332	-114	281	81	-	-	-	-
Dissolved oxygen (field)	mg/l	-	-	-	0.320	6.69	13.1	7.96	12.0	81	-	-	-	-
Total phosphorus	ug/l	<20	No WQS	-	20.2	52.7	458	32.2	201	57	44	77	-	-

Test	Units	LOD	WQS	Source	Min*	Mean	Max	Median	97.7th percentile	No. Samples	No. Detections	% Detections	No. WQS Exceedances	% WQS Exceedances
Magnesium	mg/l	0.101	50	IGV 2003	1.01	8.30	36.1	5.21	29.5	81	81	100	0	0
Calcium	mg/l	0.101	200	IGV 2003	11.6	63.3	129	65.1	121	81	79	98	0	0
Sulphate	mg/l	5	187.5	GTV 2016	5.09	13.8	135	2.50	115	81	33	41	0	0
Alkalinity as $CaCO_3$	mg/l	5	NO WQS	No WQS	33.5	214	399	210	382	81	81	100	0	0
Nitrate (as N)	mg/l	0.08	37.5	GTV 2016	0.09	0.471	2.31	0.300	1.96	81	64	79	0	0
Total organic carbon	mg/l	1.5	No WQS	-	0.36	16.7	83.0	7.53	76.0	81	64	80	-	-
Dissolved organic carbon	mg/l	1.5	No WQS	-	1.18	17.3	83.0	7.90	82.0	8	70	86	-	-
Nitrite (as N)	mg/l	0.05	No WQS	-	-	-	-	-	-	81	0	-	-	-

*Minimum result above detection limit

Table 5 Summary statistics of metals (trace elements)

Test	Units	LOD	WQS	Source	Min*	Mean	Max	Median	97.7th percentile	No. Samples	No. Detections	% Detections	No. WQS Exceedances	% WQS Exceedances
Iron	mg/l	0.019	0.20	IGV 2003	0.020	0.530	9.39	0.052	8.54	81	53	65	17	21
Barium	ug/l	0.20	100	IGV 2003	6.02	82.7	743	24.4	716	81	81	100	12	15
Arsenic	ug/l	0.50	7.50	GTV 2016	0.533	0.655	12.8	0.25	6.42	81	7	9	2	2.5
Manganese	ug/l	3.00	50.0	IGV 2003	3.00	15.7	115	3.68	95.8	81	43	53	8	10
Uranium	ug/l	0.50	9.00	IGV 2003	0.511	0.271	0.550	0.25	0.540	81	6	7	0	0
Aluminium	ug/l	10.0	150	GTV 2016	11.2	18.8	150	5.00	84.0	81	32	40	0	0
Zinc	ug/l	1.00	75.0	GTV 2016	1.10	2.24	14.8	1.90	7.44	81	68	84	0	0
Boron	ug/l	10.0	750	GTV 2010	10.3	79.0	744	5.00	733	81	35	43	0	0
Bromide	ug/l	0.060	No WQS	No WQS	0.063	0.115	0.979	0.030	0.942	81	29	36	0	0
Cadmium	ug/l	0.080	3.75	GTV 2010	-	-	-	-	-	81	0	0	0	0
Chromium	ug/l	1.00	37.5	GTV 2016	-	-	-	-	-	81	0	0	0	0
Caesium	ug/l	1.00	No WQS	No WQS	5.90	-	5.90	-	-	81	1	1	0	0
Copper	ug/l	0.30	1500	GTV 2010	0.30	0.460	7.25	0.30	1.10	81	41	50	0	0
Lithium	ug/l	1.00	No WQS	No WQS	1.02	8.59	69.2	-	66.9	81	36	45	0	0
Nickel	ug/l	0.400	15	GTV 2010	0.412	0.530	5.13	0.420	1.25	81	42	52	0	0

Test	Units	LOD	WQS	Source	Min*	Mean	Max	Median	97.7th percentile	No. Samples	No. Detections	% Detections	No. WQS Exceedances	% WQS Exceedances
Lead	ug/l	0.100	7.5	GTV 2016	0.203	0.105	0.329	0.10	0.203	81	3	4	4	0
Selenium	ug/l	1.00	No WQS	-	1.03	0.550	2.86	0.50	1.11	81	3	4	-	-
Strontium	ug/l	1.00	No WQS	-	42.1	688	3910	152	3,883	81	81	100	-	-

*Minimum result above detection limit

Section 5 Water Physiochemical Characteristics and Water Type

This section provides analysis and interpretation of water physicochemical characteristics and the water types for each of 15 springs. Note, analysis and interpretation are not provided for Cleggan spring at which only one sample was collected. The 15 springs are:

- Barran Spring;
- Barran Spring 2;
- Boylans Well;
- Carrickmacsparrow;
- Cladagh River;
- Hanging Rock;
- Hollywell Rising;
- Kiltomulty Spring;
- Marlbank West;
- Mullyard Rising;
- Sulphur Well;
- Tuam Spring;
- Tullyhone Rising;
- Ture Rising; and,
- Mullaghdun Spring.

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, oxidation-reduction potential 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, for which there were three detections at one site at a minimum, is provided below.

5.1.1 Calcium

- Calcium (Ca) concentrations within the Arney catchment range from 11.6 mg/L at Sulphur Well to 128 mg/L at Tuam Spring (Figure 2).
- The widest interquartile range of concentrations occur at Barran Spring, Mullyard Rising and Ture Rising.
- Generally, the highest calcium concentrations occur at Kiltomulty Spring, Marlbank West, Tuam Spring and Mullaghdun.
- The lowest calcium concentrations occur at Sulphur Well.

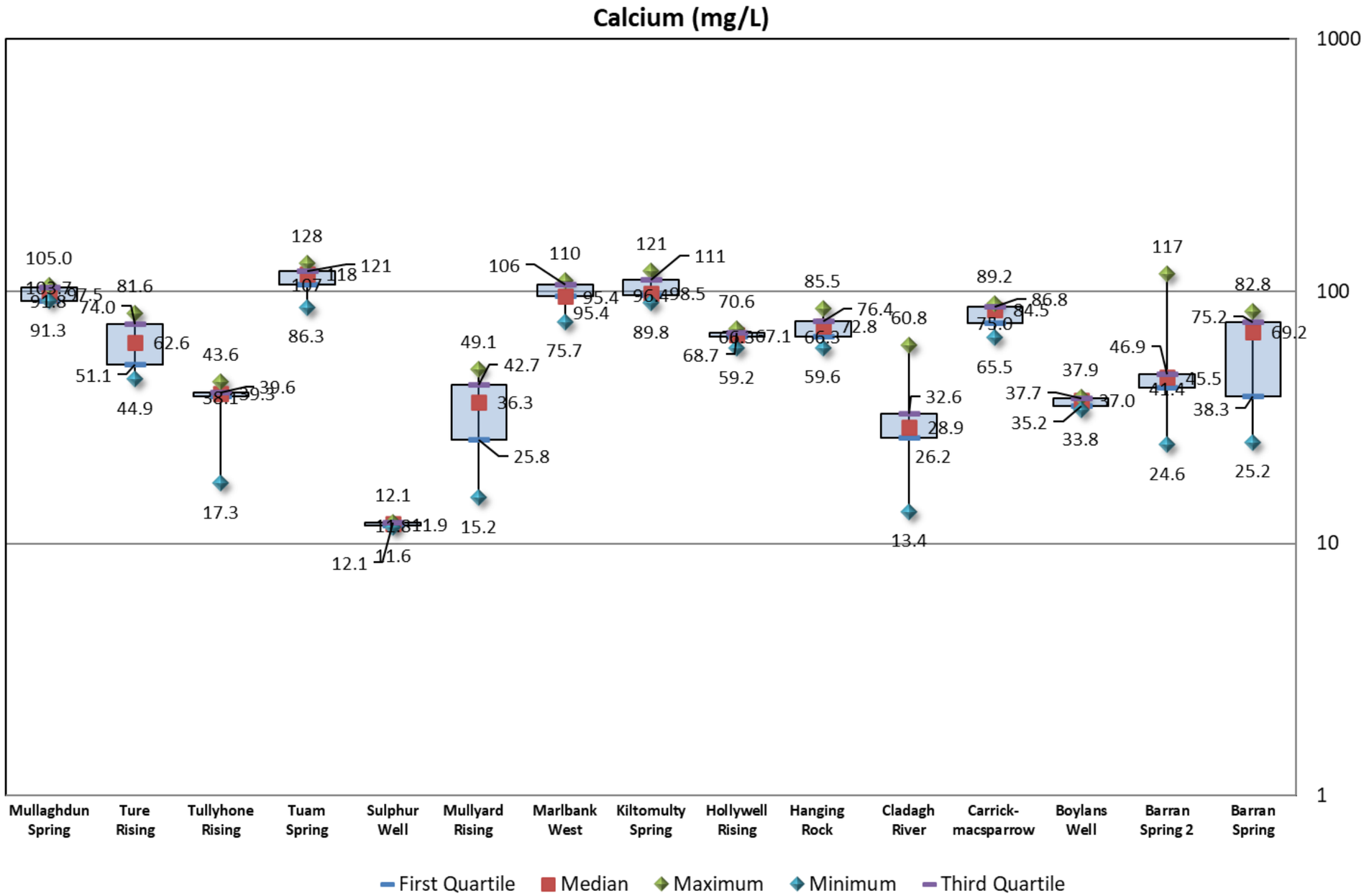

Figure 2: Calcium (Ca) boxplot with log scale y-axis

5.1.2 Sodium

- Sodium (Na) concentrations within the Arney catchment range from 3.07 mg/L at Cladagh River, to 232 mg/L at Sulphur Well (Figure 3).
- Relatively high sodium concentrations occur at Sulphur Well (median: 215 mg/L), followed by Boylans Well (median: 45.7 mg/L).
- The median concentrations at all other locations range from ~5 to 17 mg/L.

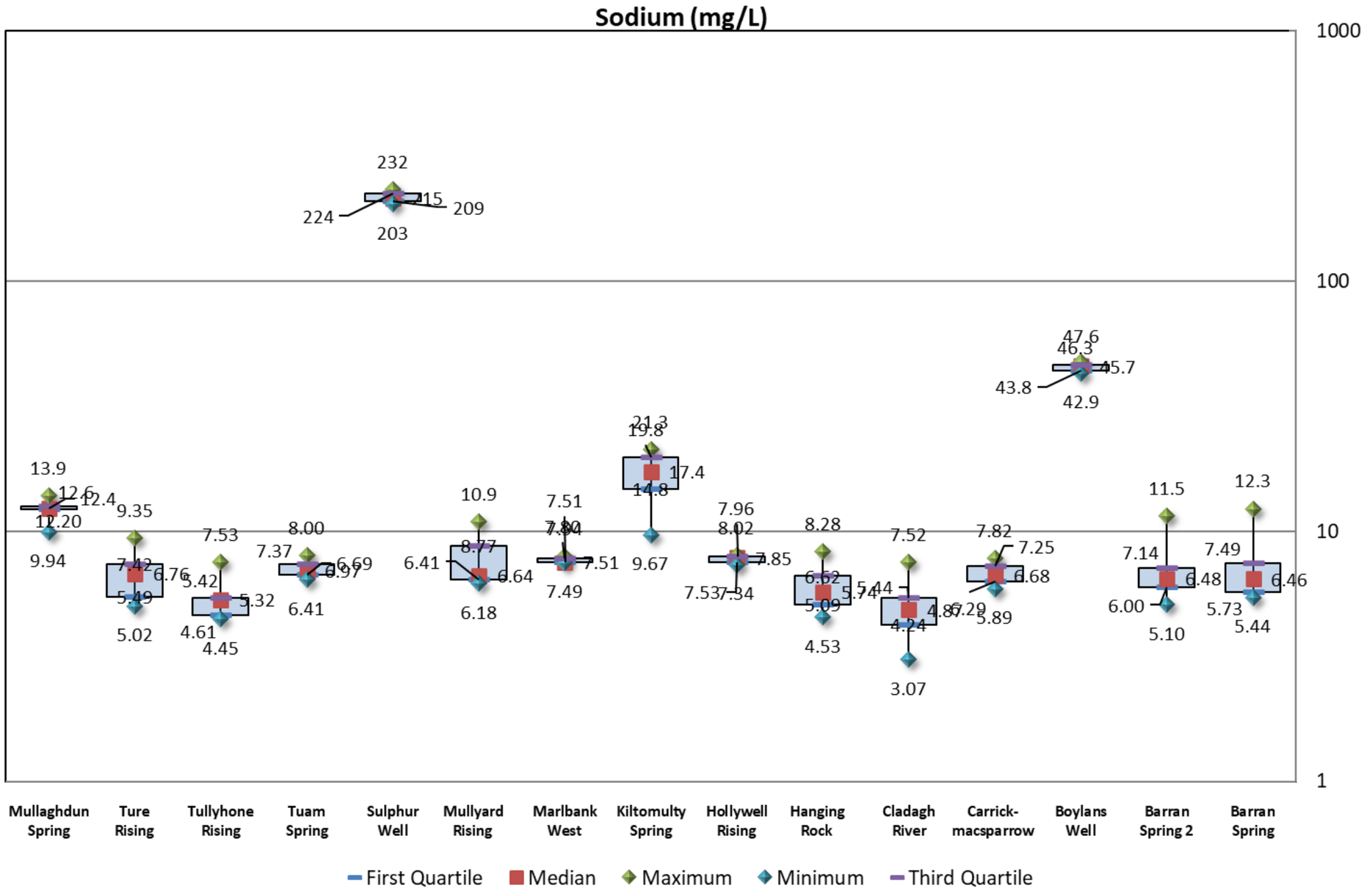

Figure 3: Sodium (Na) boxplot with log scale y-axis

5.1.3 Chloride

- Chloride (Cl) concentrations within the Arney catchment range from 4.99 mg/L at Hanging Rock Spring, to 232 mg/L at Boylans Well (Figure 4).
- Generally, the highest chloride concentrations occur at Sulphur Well, followed by Kiltomulty spring.

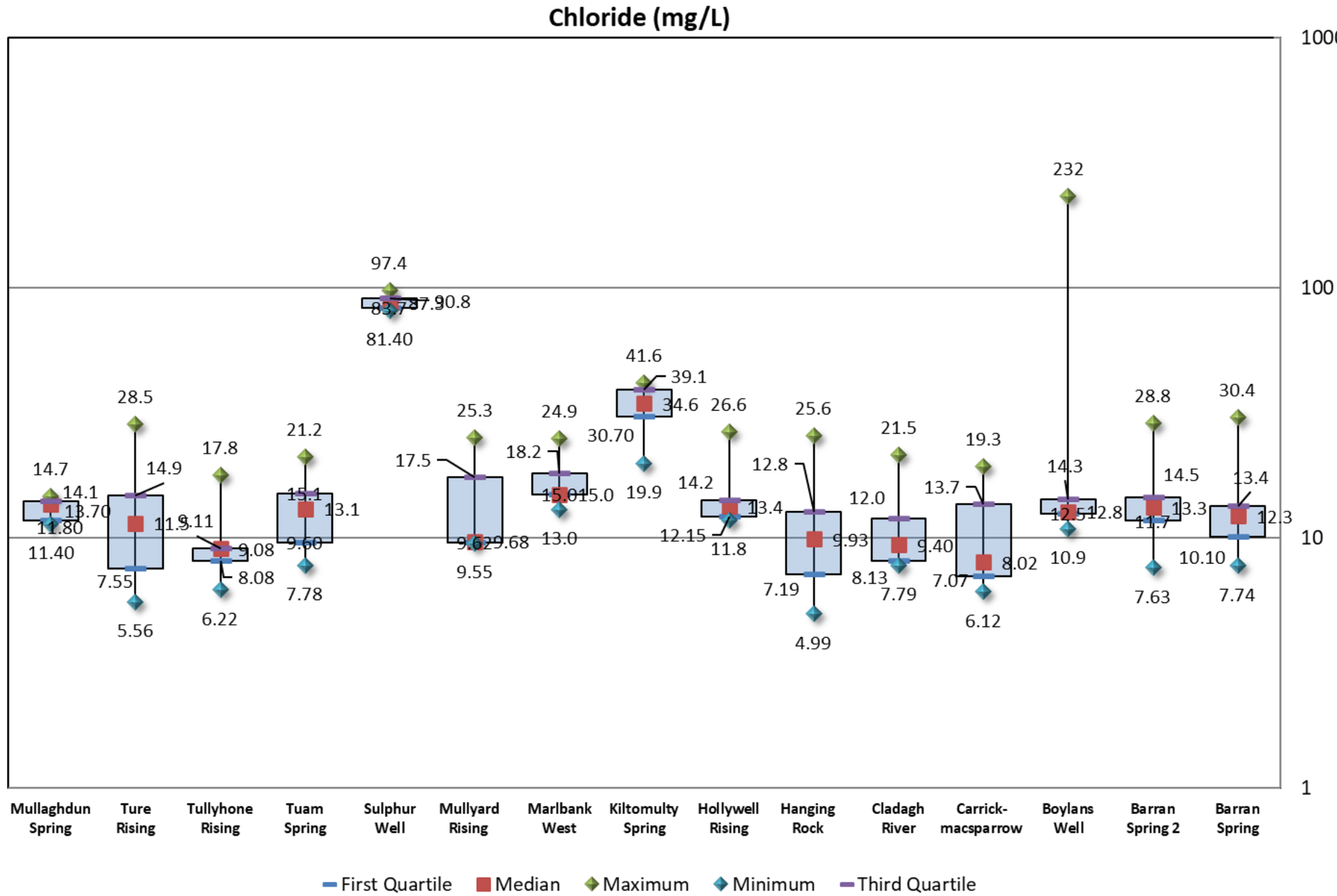

Figure 4: Chloride (Cl) boxplot with log scale y-axis

5.1.4 Potassium

- Potassium (K) concentrations within the Arney catchment range from 0.29 mg/L at Tullyhone Rising, to 8.23 mg/L at Kiltomulty Spring (Figure 5).
- The lowest values are recorded at Tullyhone Rising followed by Cladagh River.
- Highest potassium concentrations generally occur at Kiltomulty Spring, followed by Boylans Well.
- The lowest potassium concentrations generally occur at Tullyhone Rising and Cladagh River.

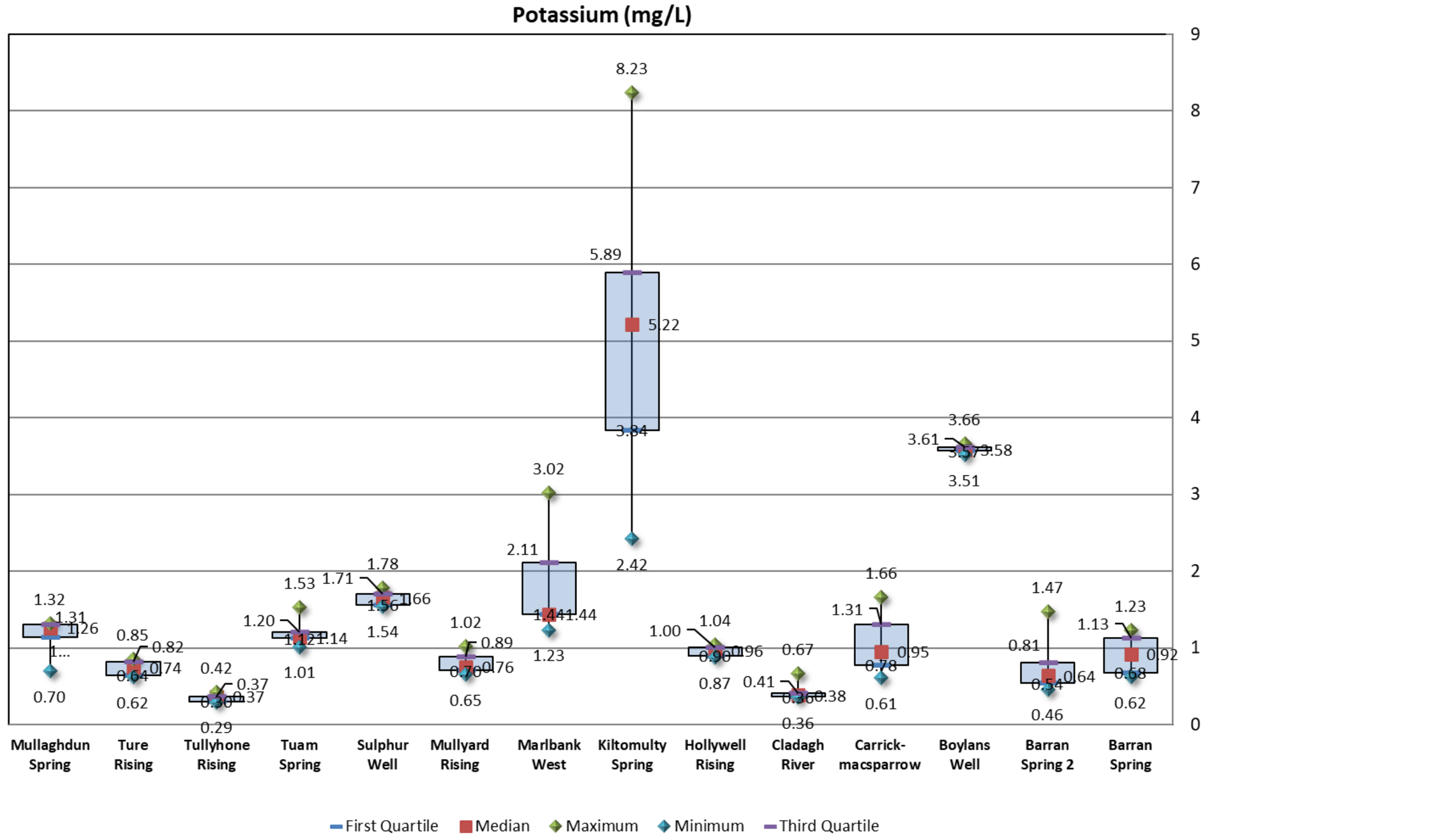

Figure 5: Potassium (K) boxplot

5.1.5 Sulphate

- Sulphate (SO_4) concentration within the Arney catchment ranges from <LOD (5 mg/L, included as 2.50 mg/L in the graph) at most locations, to 135 mg/L at Sulphur Well (Figure 6).
- The highest sulphate concentrations occur at Sulphur Well, followed by Mullaghdun Spring.
- All values at Barran Spring, Carrickmacsparrow, Mullyard Rising and Tuam Spring are <LOD. At Ture Rising, Tullyhone Rising, Hanging Rock and Boylans Well most values are <LOD.

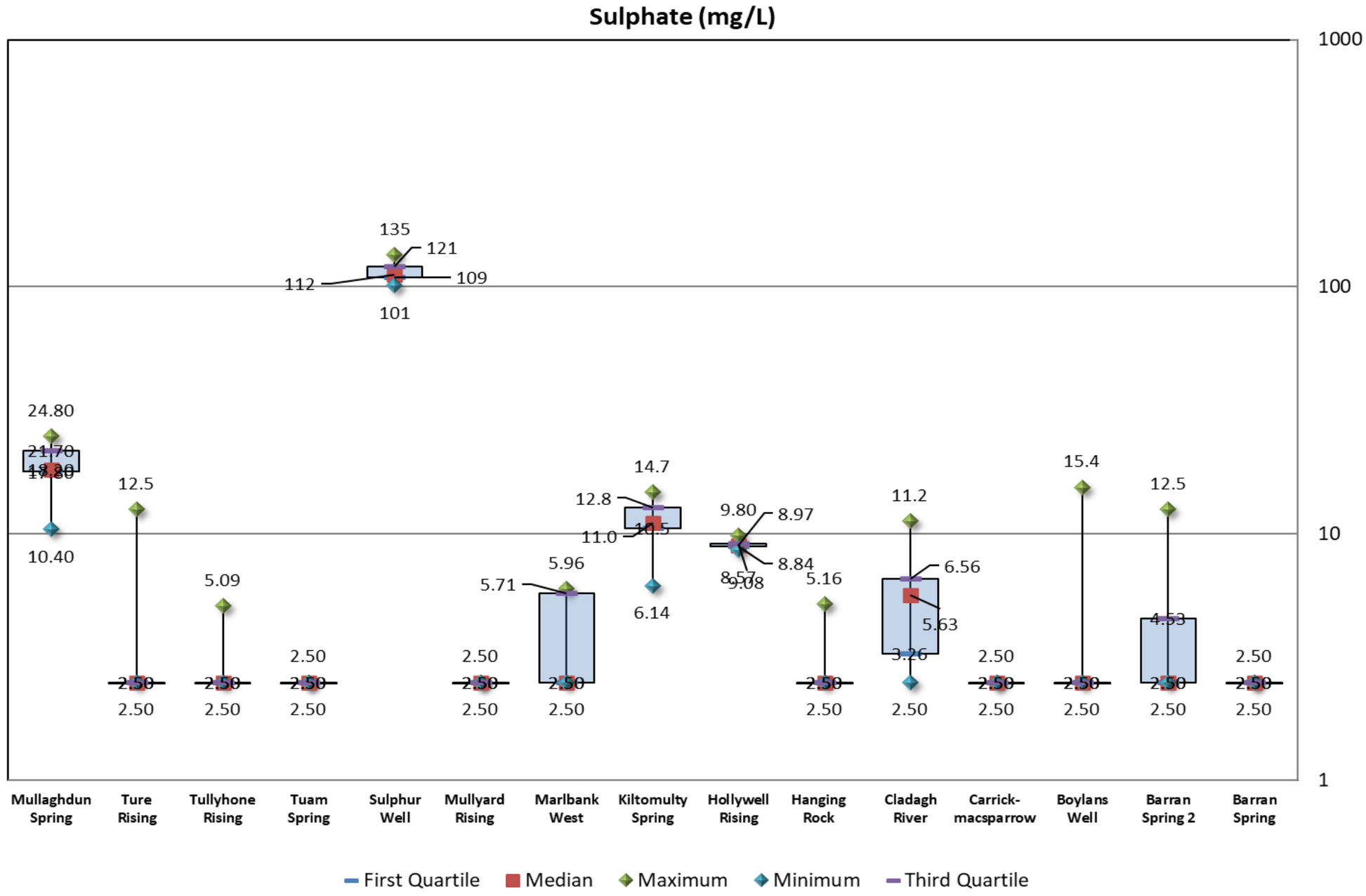

Figure 6: Sulphate (SO_4) boxplot with log scale y-axis

5.1.6 Fluoride

- Fluoride (F) within the Arney catchment ranges from <LOD (0.02 mg/L, included in the chart as 0.01 mg/L) at Barran Spring 2, Hanging Rock, Mullyard Rising and Tullyhone Rising, to 5.46 mg/L at Sulphur Well (Figure 7).
- The highest concentrations of fluoride occur at Sulphur Well. Lower, but still relatively high fluoride concentrations occur at Mullaghdun Spring, Kiltomulty Spring and Boylans Well. The fluoride concentrations at all other 11 wells are relatively lower.

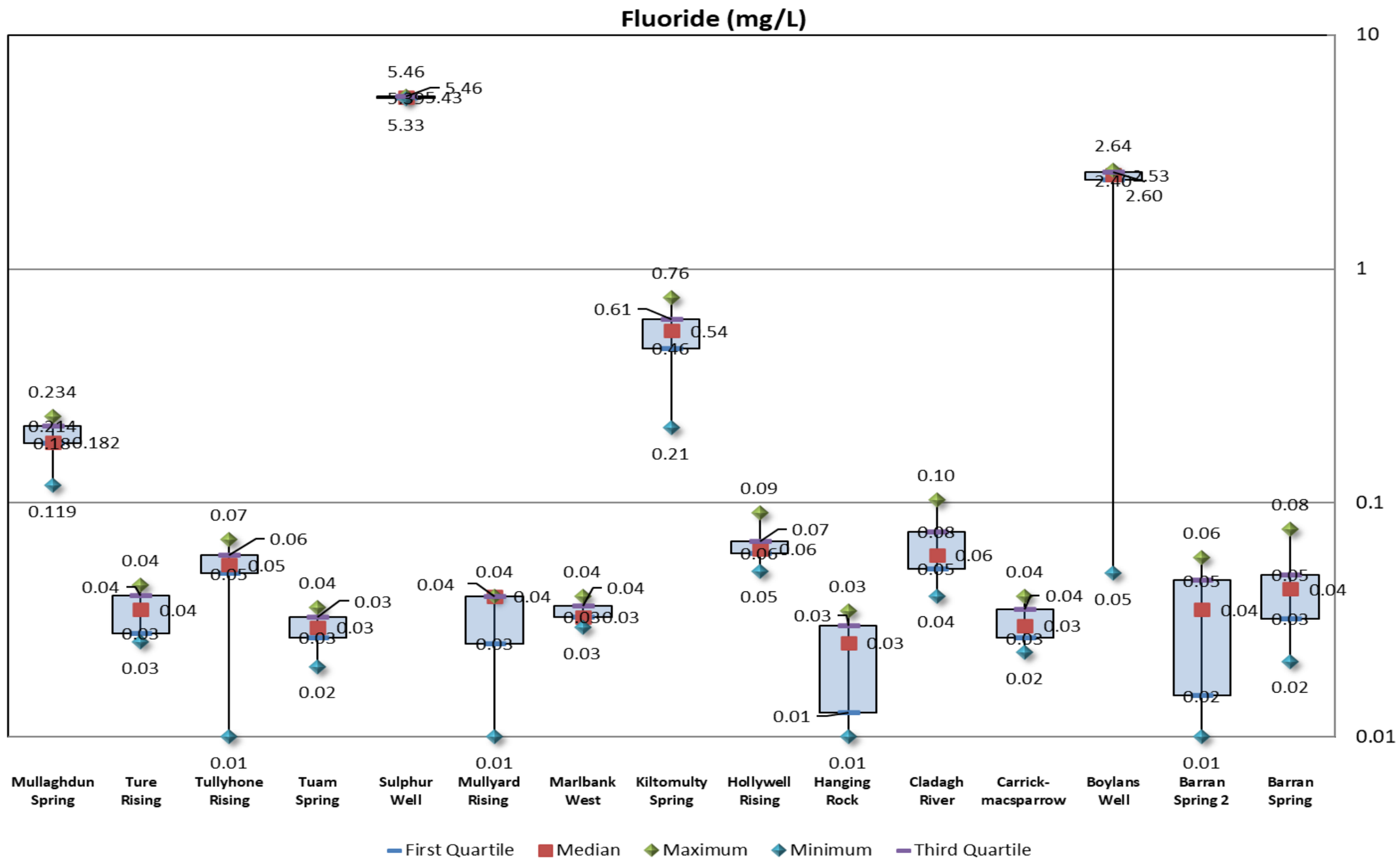

Figure 7: Fluoride (F) boxplot

5.1.7 Nitrate (NO_3 as N)

- Nitrate (NO_3) concentrations within the Arney catchment range from <LOD (0.08 mg/L, included in the graph as 0.04 mg/L) at most springs to 2.01 mg/L at Kiltomulty Spring (Figure 8).
- Generally, the lowest nitrate concentrations occur at Hollywell Rising.
- Generally, relatively higher nitrate concentrations (median >0.50 mg/L) occur at:
  - Tulllyhone Rising;
  - Mullyard Rising;
  - Marlbank West;
  - Kiltomulty Spring;
  - Hanging Rock; and
  - Carrickmacsparrow.

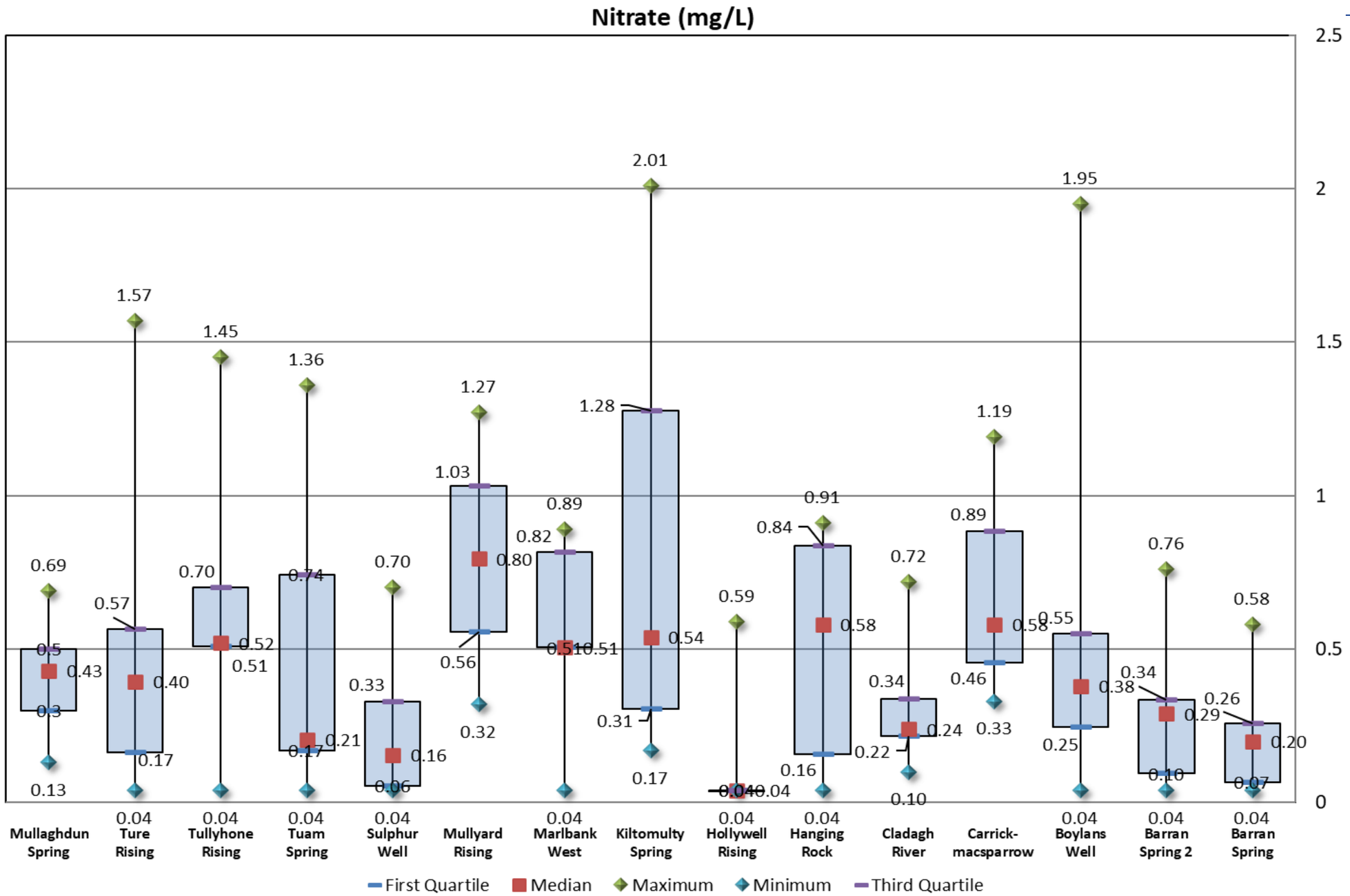

Figure 8: Nitrate (NO_3 as N) boxplot

5.2 Major and Minor (Trace) Elements

A summary of the concentration patterns of major and minor (trace) elements, for which there were three detections at one site at a minimum, is provided below.

5.2.1 Dissolved Iron

- Dissolved iron (Fe) concentrations within the Arney catchment range from <LOD (0.02 mg/L, included in the graph as 0.01 mg/L) to 9.39 mg/L Kiltomulty Spring (Figure 9).
- The highest iron concentrations occur at Kiltomulty Spring.
- Relatively low concentrations (values mostly <LOD) occur at Mullaghdun Spring, Tuam Spring and Hollywell Rising. The lowest iron concentrations occur at Sulphur Well (all values <LOD).

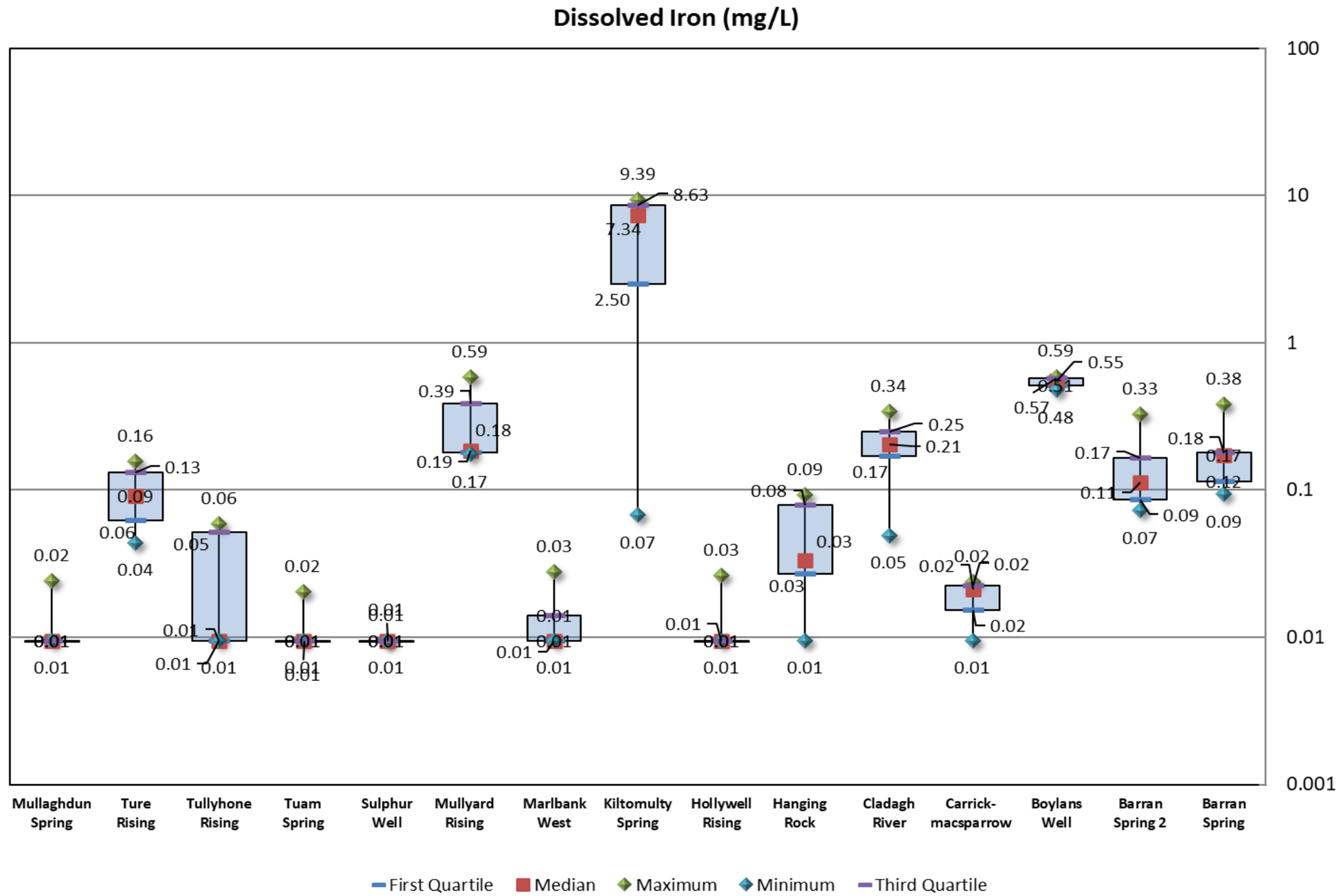

Figure 9: Dissolved Iron (Fe) boxplot with log scale y-axis

5.2.2 Dissolved Aluminium

- Dissolved aluminium (Al) concentrations within the Arney catchment range from <LOD (10.0 ug/L, included in the graph as 5.00 ug/L) at all locations except Ture Rising, Mullyard Rising and Barran Spring, to 150 ug/L at Barran Spring 2 (Figure 10).
- Generally, relatively higher aluminium concentrations occur at Barran Spring, Barran Spring 2, Cladagh River, Mullyard Rising and Ture Rising.
- For the below springs, most or all recorded aluminium values are <LOD (with maximum of one value greater than the LOD):
  - Mullaghdun Spring;
  - Tullyhone Rising;
  - Sulphur Well;
  - Tuam Spring;
  - Hollywell Rising;
  - Kiltomulty;
  - Boylans Well; and
  - Carrickmacsparrow.

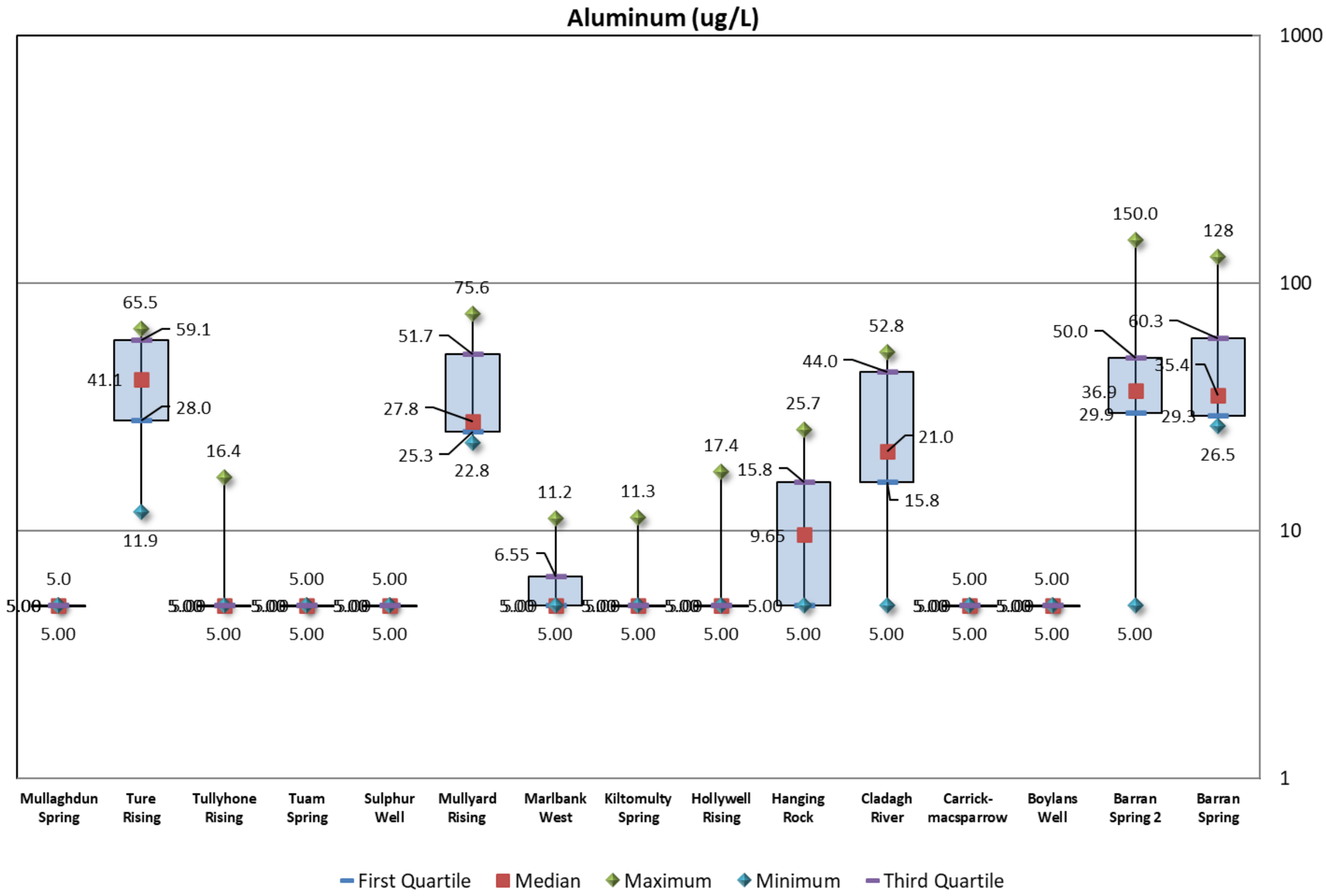

Figure 10: Aluminium (Al) boxplot with log scale y-axis

5.2.3 Dissolved Magnesium

- Magnesium (Mg) concentrations within the Arney catchment range from 1.01 mg/L at Cladagh River to 36.1 mg/L at Kiltomulty Spring (Figure 11).
- The widest interquartile range of concentrations occurs at Kiltomulty Spring. Also, relatively higher concentrations of magnesium occur at Kiltomulty Spring compared to all other springs.
- Similar and relatively high magnesium concentrations occur at Sulphur Well and Boylans Well. Somewhat lower, but also relatively high magnesium concentrations also occur at Mullaghdun Spring. Magnesium concentrations at all other springs are relatively lower.

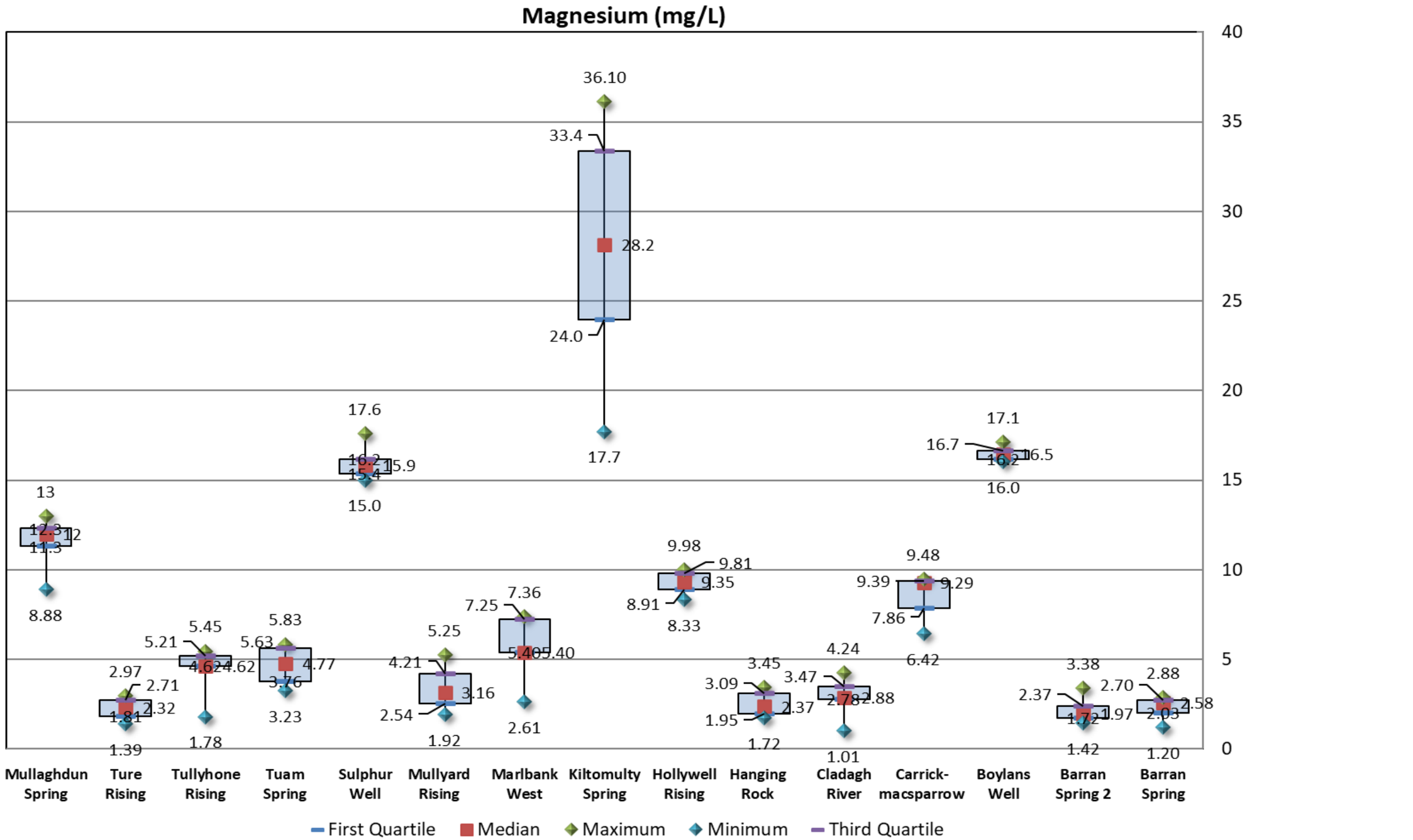

Figure 11: Magnesium (Mg) boxplot

5.2.4 Dissolved Barium

- Dissolved barium (Ba) concentrations within the Arney catchment range from 6.02 ug/L at Carrickmacsparrow, to 743 ug/L at Boylans Well (Figure 12).
- The highest Barium concentrations occur at Boylans (median: 706 ug/L), followed by Kiltomulty Spring (median: 139 ug/L).
- The lowest barium concentrations occur at Carrickmacsparrow (median: 7.13 ug/L).
- The median barium concentration of all other springs ranges from 9.48 ug/L to 35.5 ug/L.

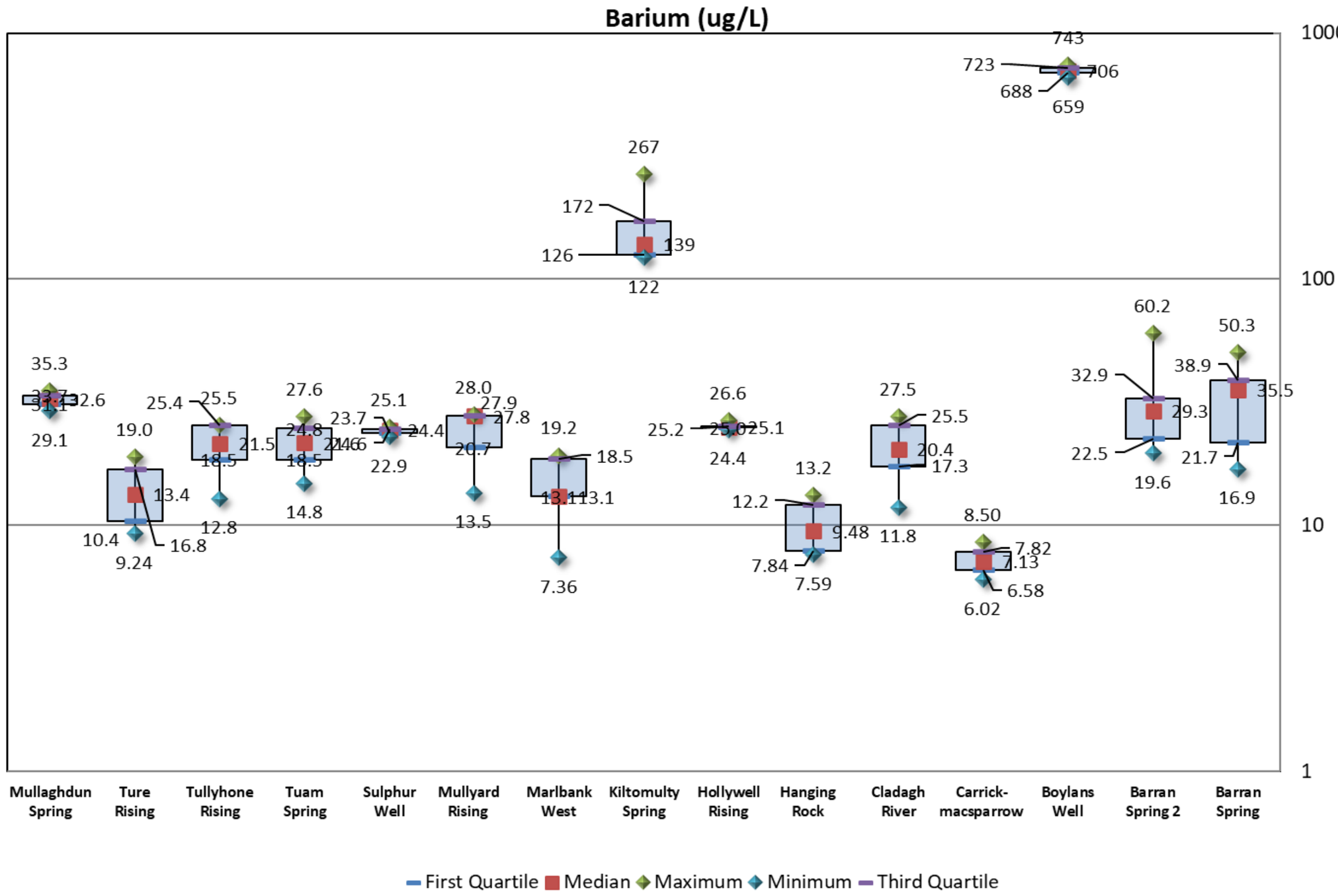

Figure 12: Barium (Ba) boxplot with log scale y-axis

5.2.5 Dissolved Nickel

- Dissolved nickel (Ni) concentrations within the Arney catchment range from <LOD (0.04 ug/L, included in the graph as 0.02 ug/L) at most springs, to 5.13 ug/L at Kiltomulty Spring (Figure 13).
- Generally, the highest nickel concentrations occur at Barran Spring (median: 0.99 ug/L) and Kiltomulty Spring (median: 0.97 ug/L).
- At Tullyhone Rising, Sulphur Well, Marlbank West and Boylans Well, all values are <LOD.
- The median nickel concentration at all other wells ranges from 0.20 ug/L to 0.67 ug/L.

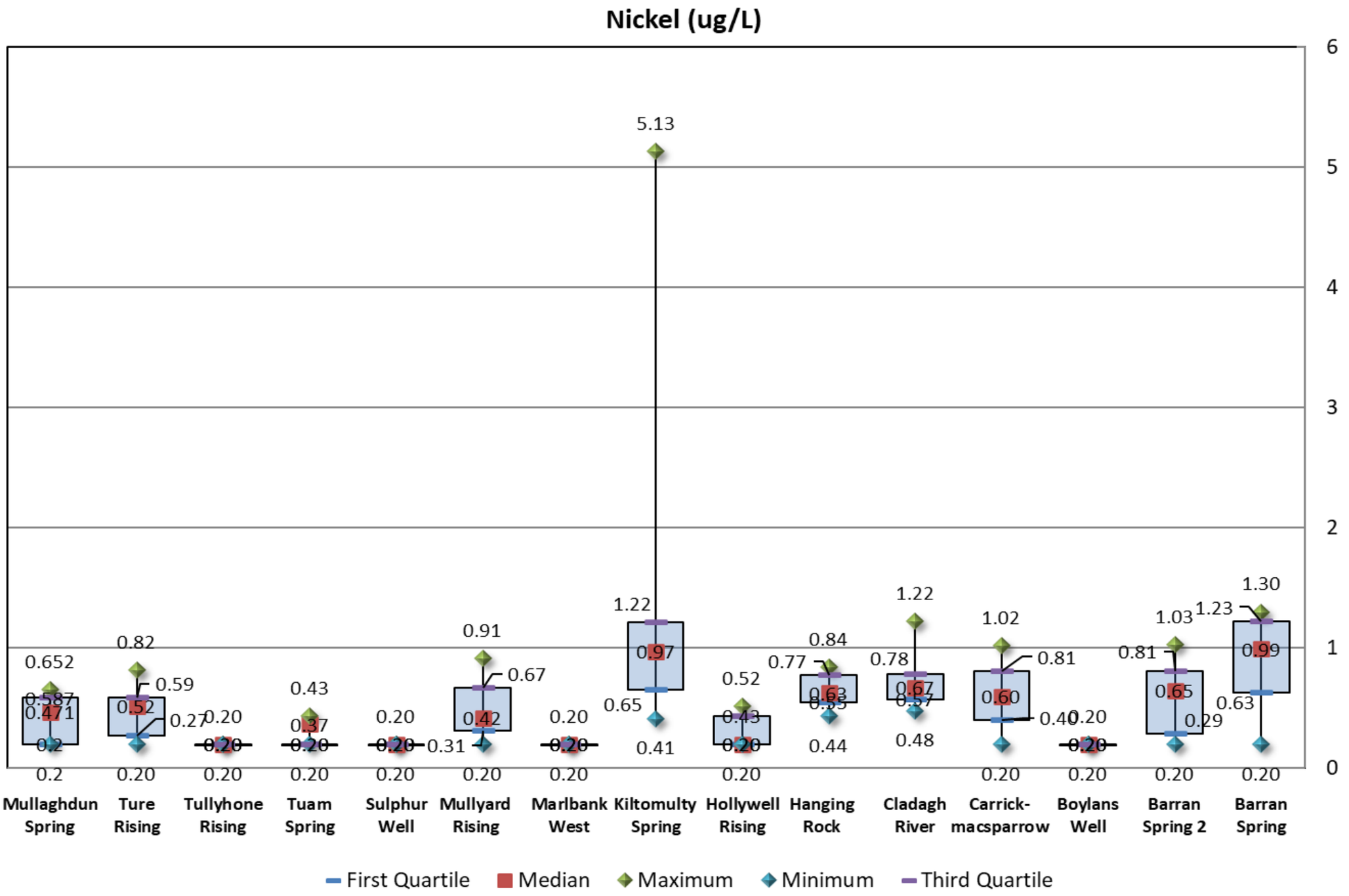

Figure 13: Nickel (Ni) boxplot

5.2.6 Dissolved Zinc

- Dissolved zinc (Zn) concentrations within the Arney catchment range from <LOD (1 ug/L, included in the graph as 0.5 ug/L) at Barran Spring 2, Boylans Well, Carrickmacsparrow, Hollywell Rising, Kiltomulty Spring, Sulphur Well, Tuam Spring and Tullyhone Rising, to 14.8 ug/L at Kiltomulty Spring (Figure 14).
- Median zinc concentrations across all springs range 0.50 ug/L and 2.57 ug/L.

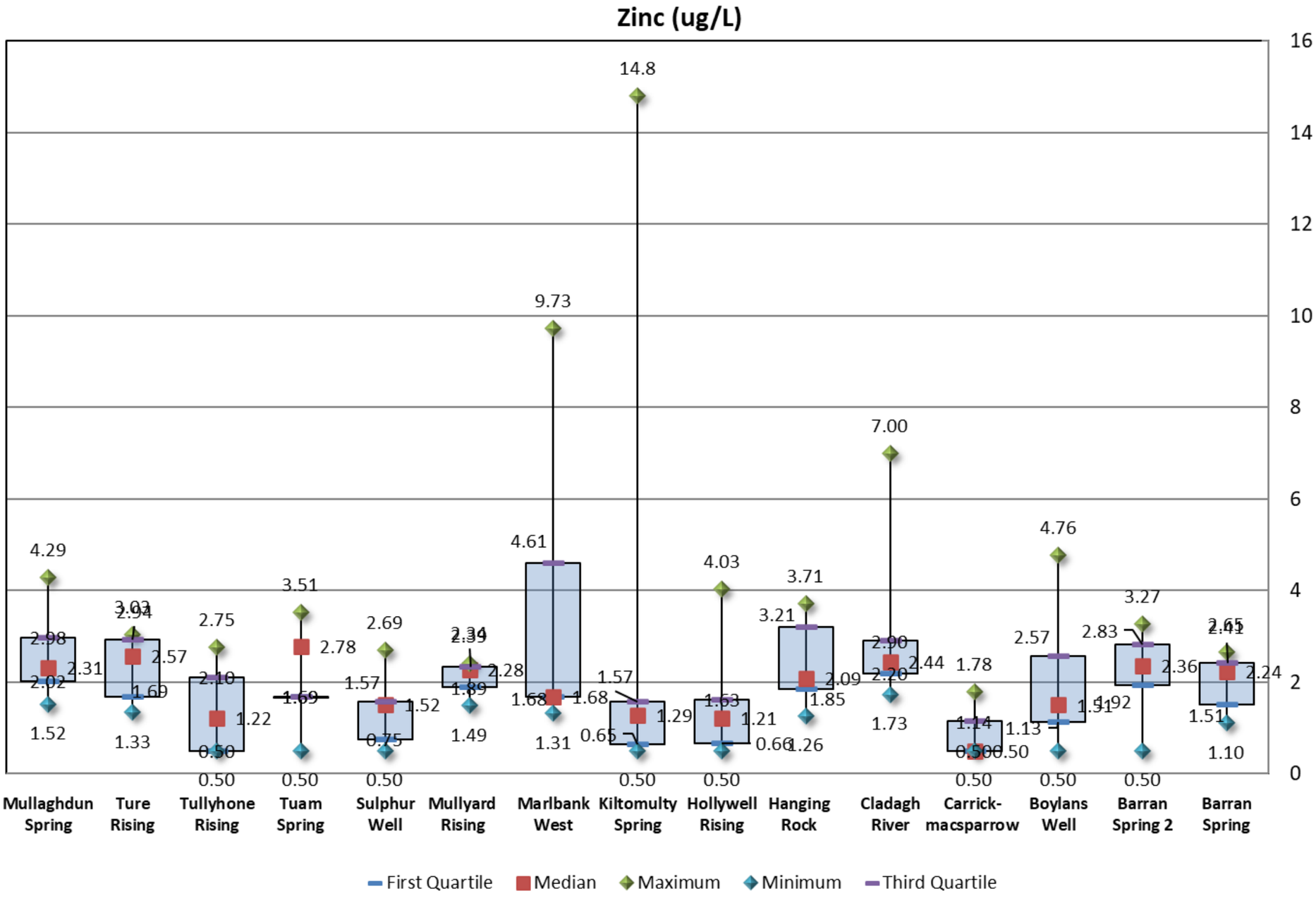

Figure 14: Zinc (Zn) boxplot with log scale y-axis

5.2.7 Dissolved Strontium

- Strontium (Sr) concentrations within the Arney catchment range from 47.3 ug/L at Barran Spring, to 3,910 ug/L at Sulphur Well (Figure 15).
- Generally, the highest strontium concentrations occur at Sulphur Well (median: 3,830 ug/L) followed by Kiltomulty Spring (median: 1,865 ug/L) and Boylans Well (median: 2,035 ug/L), followed by Mullaghdun Spring (median: 1,210 ug/L).
- The median strontium concentration at all other springs ranges from 73.7 ug/L (Ture Rising) to 256 ug/L (Hollywell Rising).

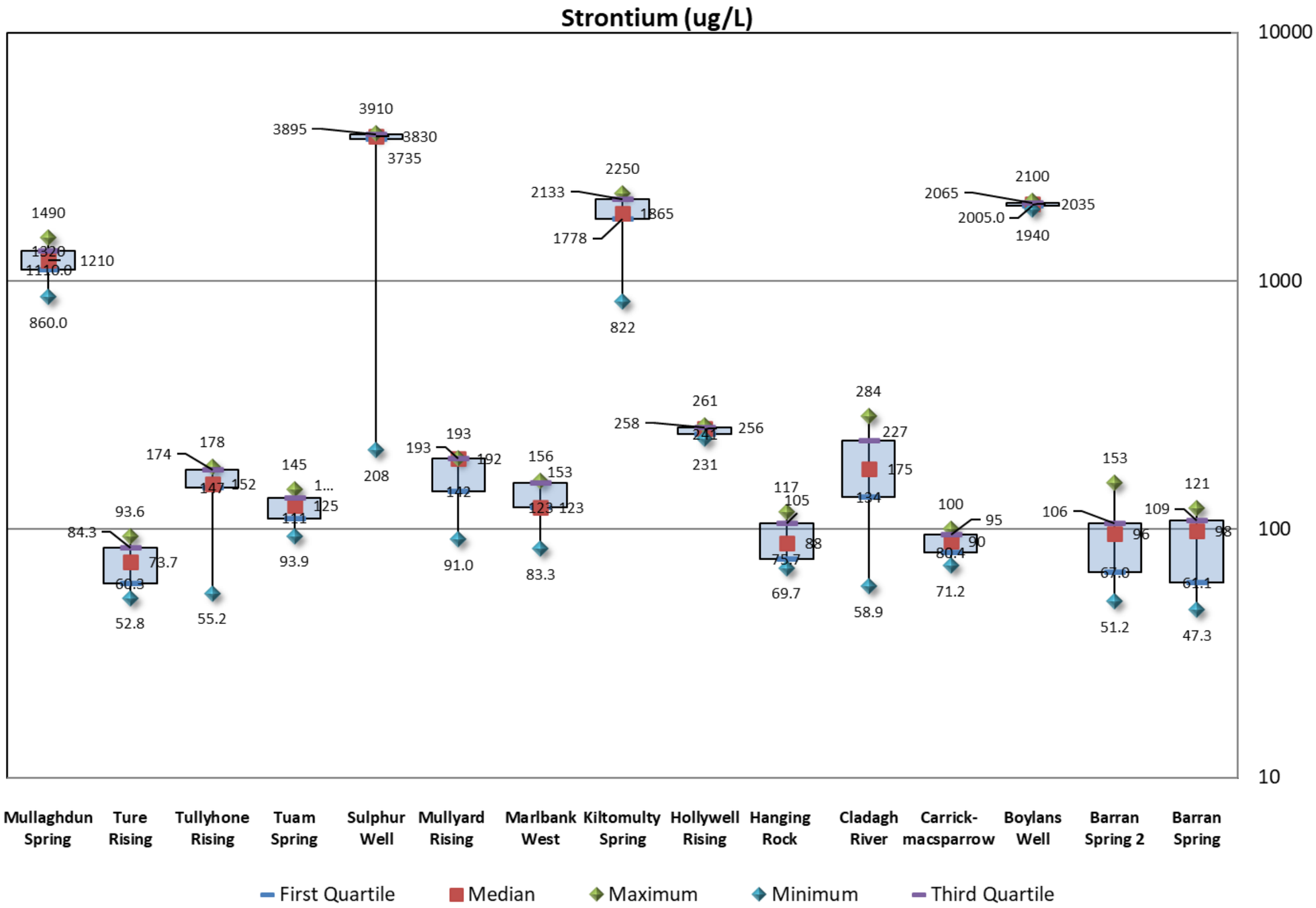

Figure 15: Strontium (Sr) boxplot with log scale y-axis

5.2.8 Dissolved Copper

- Dissolved copper (Cu) concentrations within the Arney catchment range from <LOD (0.3 ug/L, included in the graph as 0.15 ug/L) at all springs to 7.25 ug/L at Kiltomulty Spring (Figure 16).
- Concentrations of copper across the catchment are generally low (<1 ug/L).

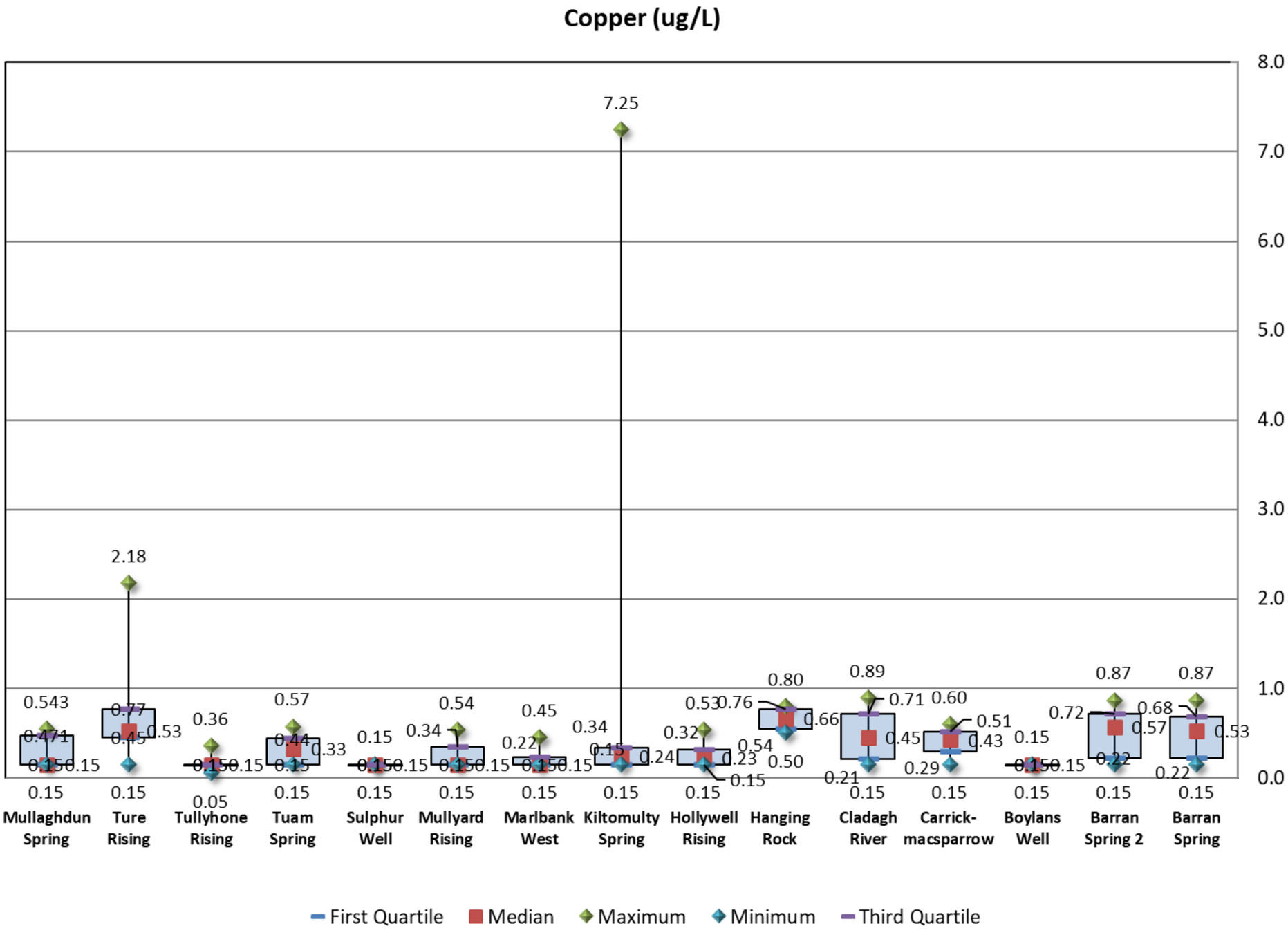

Figure 16 Copper (Cu) boxplot

5.2.9 Dissolved Manganese

- Manganese (Mn) concentrations within the Arney catchment range from <LOD (3.00 ug/L, included in the graph as 1.50 ug/L) at Barran Spring, Cladagh River, Hanging Rock, Marlbank West, Sulphur Well, Tuam Spring, Tullyhone Rising, and Ture Rising, to 115 ug/L at Kiltomulty Spring (Figure 17).
- Generally, the highest concentrations of dissolved manganese are found at Kiltomulty Spring.
- At Hanging Rock, Marlbank West, Tullyhone Rising and Ture Rising, all concentrations are <LOD. At each of Cladagh River, Sulphur Well and Tuam Spring, all except one recorded manganese concentration are <LOD.

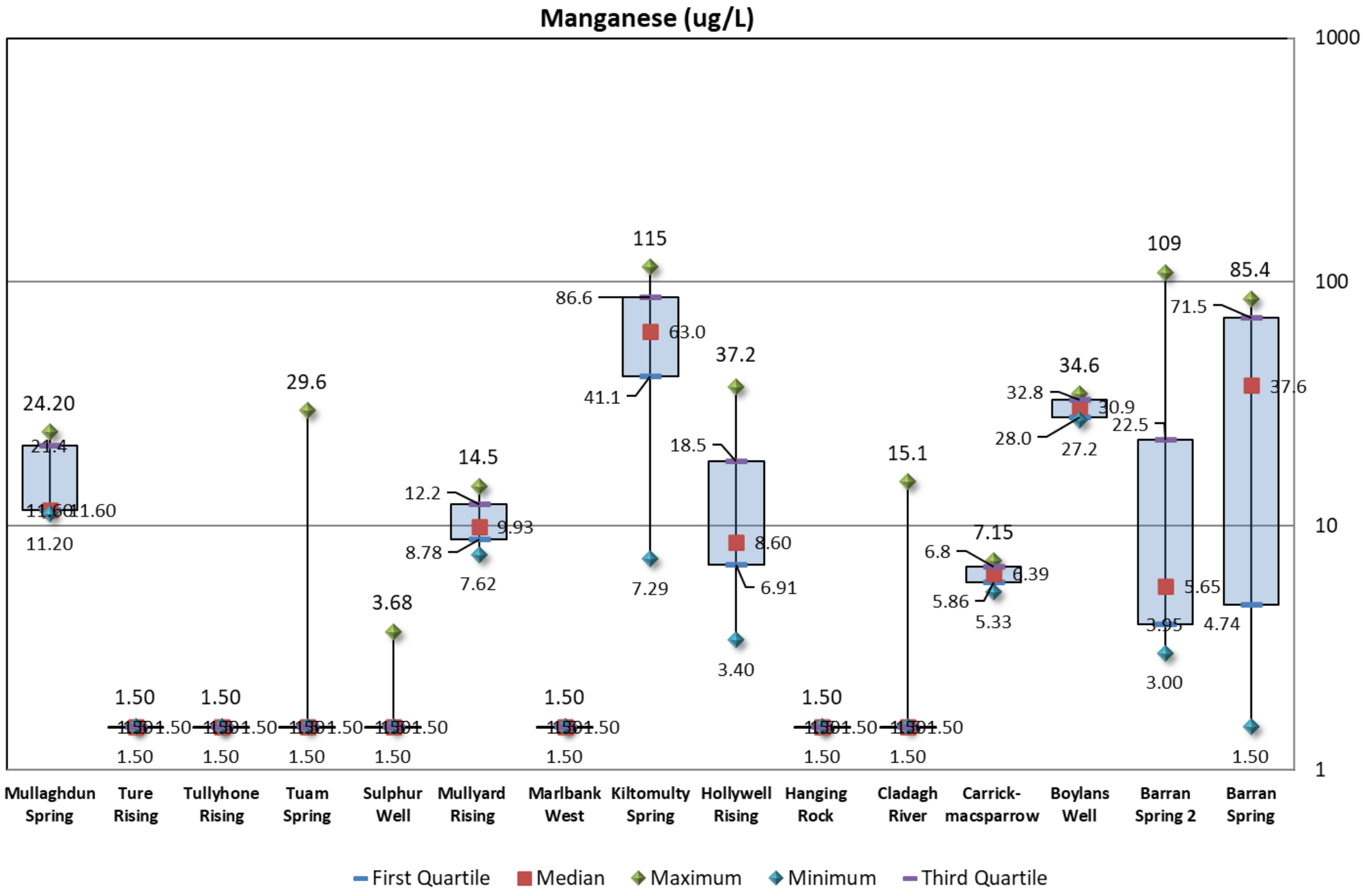

Figure 17: Manganese (Mn) boxplot with log scale y-axis

5.2.10 Dissolved Lithium

- Dissolved lithium (Li) concentrations within the Arney catchment range from <LOD (1.00 ug/L, included in the graph as 0.50 ug/L) at Barran Spring, Barran Spring 2, Carrickmacsparrow, Cladagh River, Marlbank West, Mullyard Rising, Tuam Spring, Tullyhone Rising and Ture Rising, to 69.1 ug/L at Sulphur Well (Figure 18).

- The highest lithium concentrations occur at Sulphur Well (median: 66.1 ug/L), followed by Boylans Well (median: 31.0 ug/L), followed by Kiltomulty Spring (median: 7.97 ug/L) and Mullaghdun Spring (median: 4.59 ug/L). The median lithium concentration across all other locations ranges from 0.50 ug/L to 1.85 ug/L.

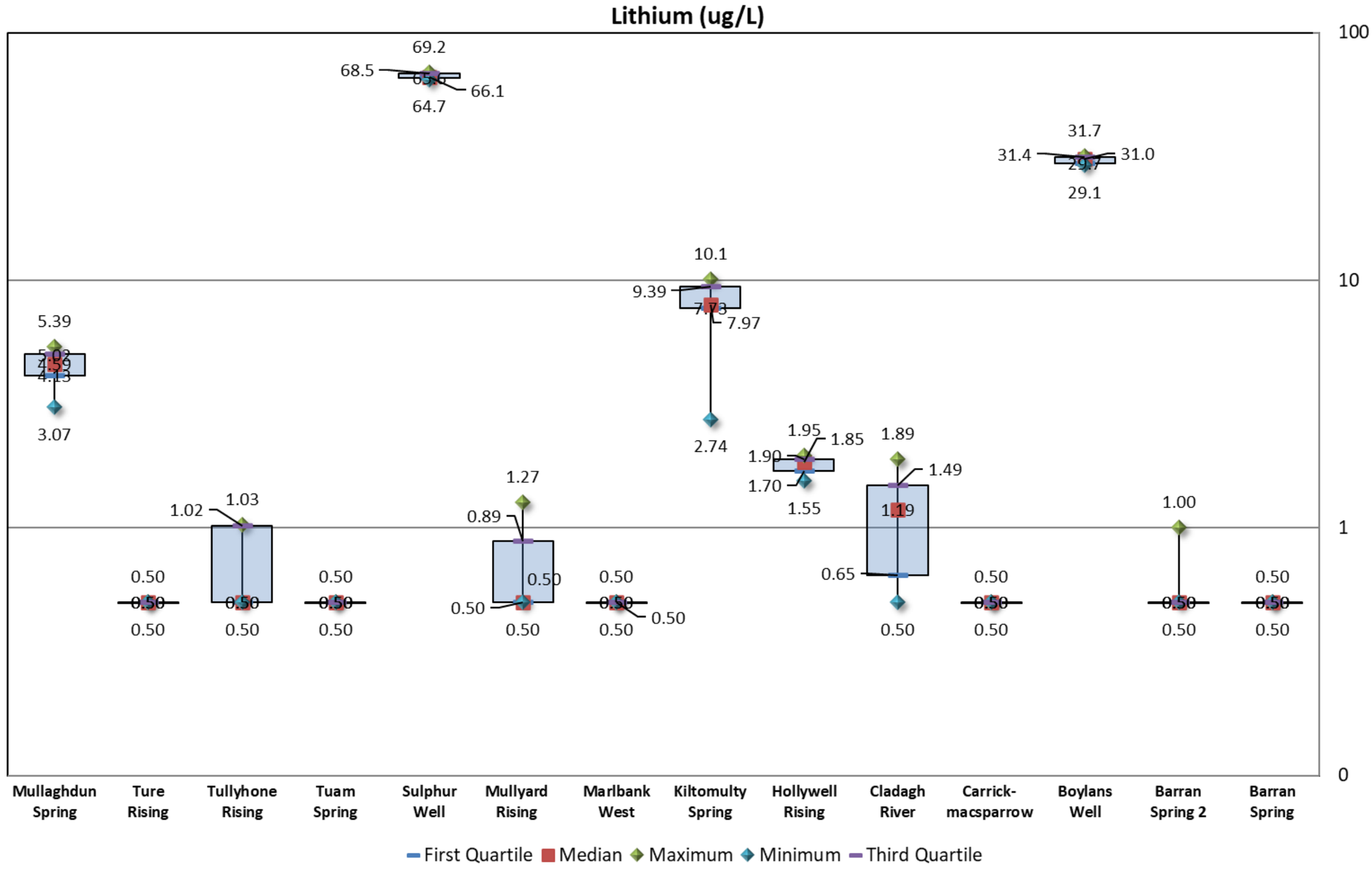

Figure 18: Lithium (Li) boxplot

5.2.11 Dissolved Uranium

- Dissolved uranium (U) concentrations within the Arney ranges from <LOD (0.50 ug/L, included in the graph as 0.250 ug/L) at all springs to 0.54 ug/l at Hollywell Rising (Figure 18).
- With the exception of Marlbank West and Hollywell Rising, all recorded uranium concentrations across the catchment are <LOD.
- The highest uranium concentrations occur at Hollywell Rising.

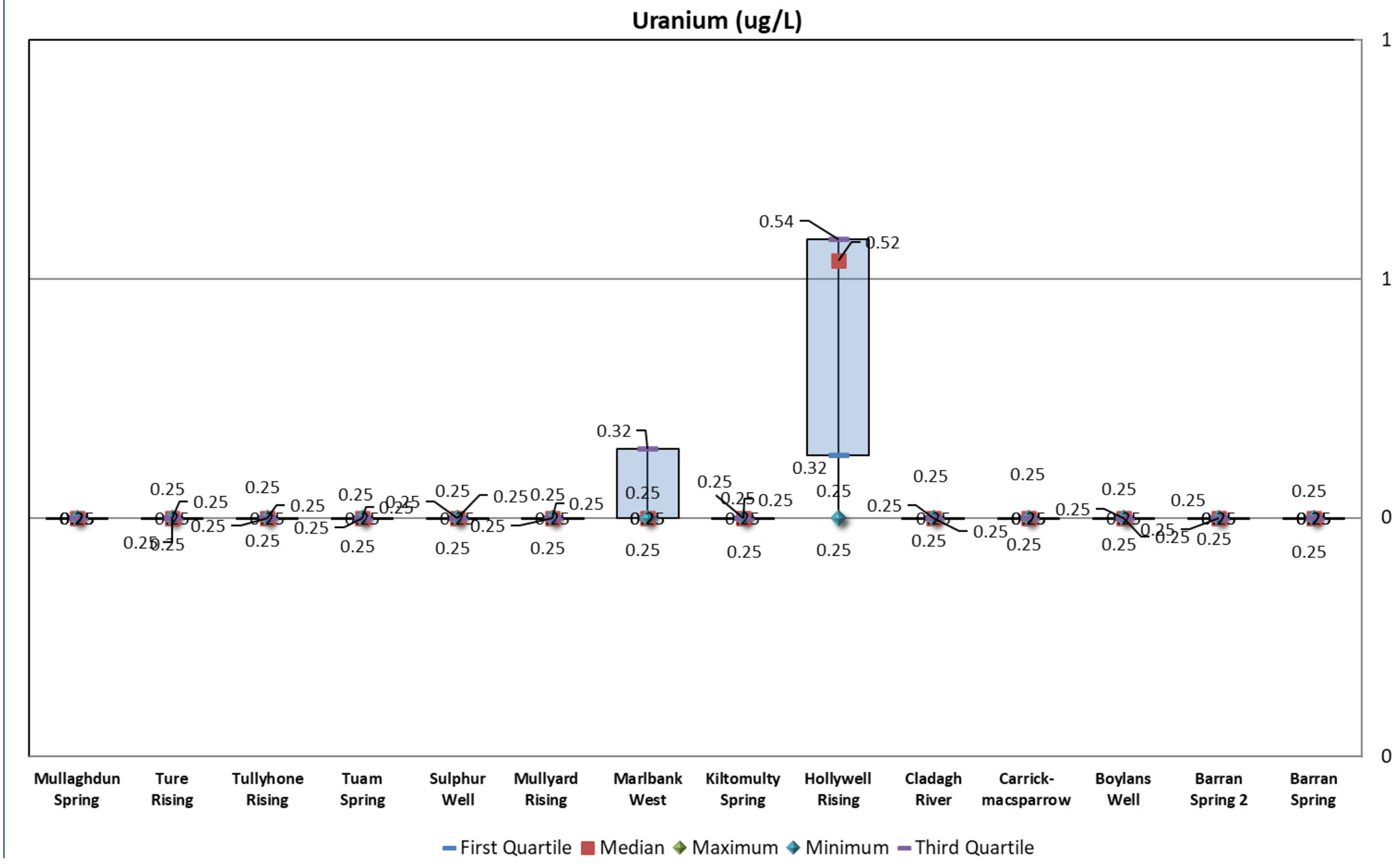

Figure 19: Uranium (U) boxplot

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 oxidation reduction potential (ORP) are presented below.

Alkalinity (Bicarbonate a $CaCO_3$)

- The alkalinity within the Arney catchment ranges from 33.5 mg/L at Cladagh River, to 399 mg/L at Kiltomulty Spring (Figure 19).
- Generally, the lowest alkalinities occur at Cladagh River (median: 78.0 mg/L), followed by Mullyard Rising (median: 97.1 mg/L).
- Generally intermediate alkalinities for this catchment (i.e., median range from 115 to 169 mg/L) occur at Barran Spring, Barran Spring 2, Tullyhone Rising and Ture Rising.
- The median alkalinity at all remaining springs ranges from 200 mg/L to 381 mg/L.

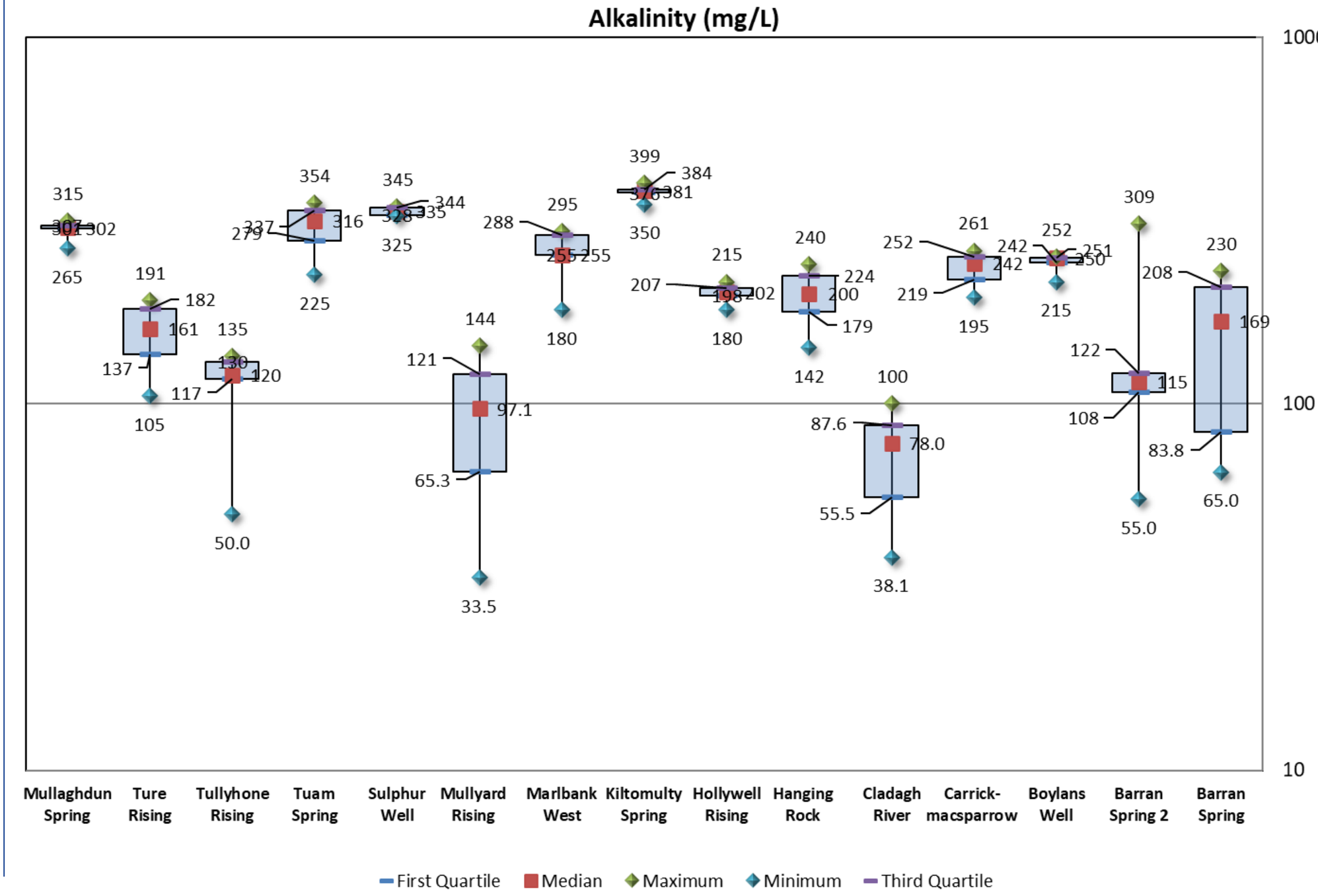

Figure 20: Alkalinity (Bicarbonate as $CaCO_3$) boxplot with log scale y-axis

Oxidation-reduction potential (ORP)

- The oxidation-reduction potential (ORP) within the Arney catchment ranges from -625 mV in Kiltomulty Spring, to 332 mV at Ture Rising (Figure 20).
- At Hollywell Rising and Hanging Rock, ~50% of the ORP values are negative and 50% are positive, indicting more reducing conditions during 50% of the monitoring events and more oxidizing conditions during the other 50% of monitoring events. At both locations, reducing conditions, when they occur, are more pronounced (more negative ORP values) than the oxidizing conditions when oxidizing conditions occur. That is, the ORP range at Hollywell Rising extends from relatively strongly reducing (-511 mV) to relatively more weakly (relatively lower value on the positive scale) oxidizing (221 mV).
- With the exception of Hollywell Rising and Hanging Rock, generally, the ORP is more frequently negative than positive across the catchment. This indicates that reducing conditions are more prevalent than oxidizing conditions.

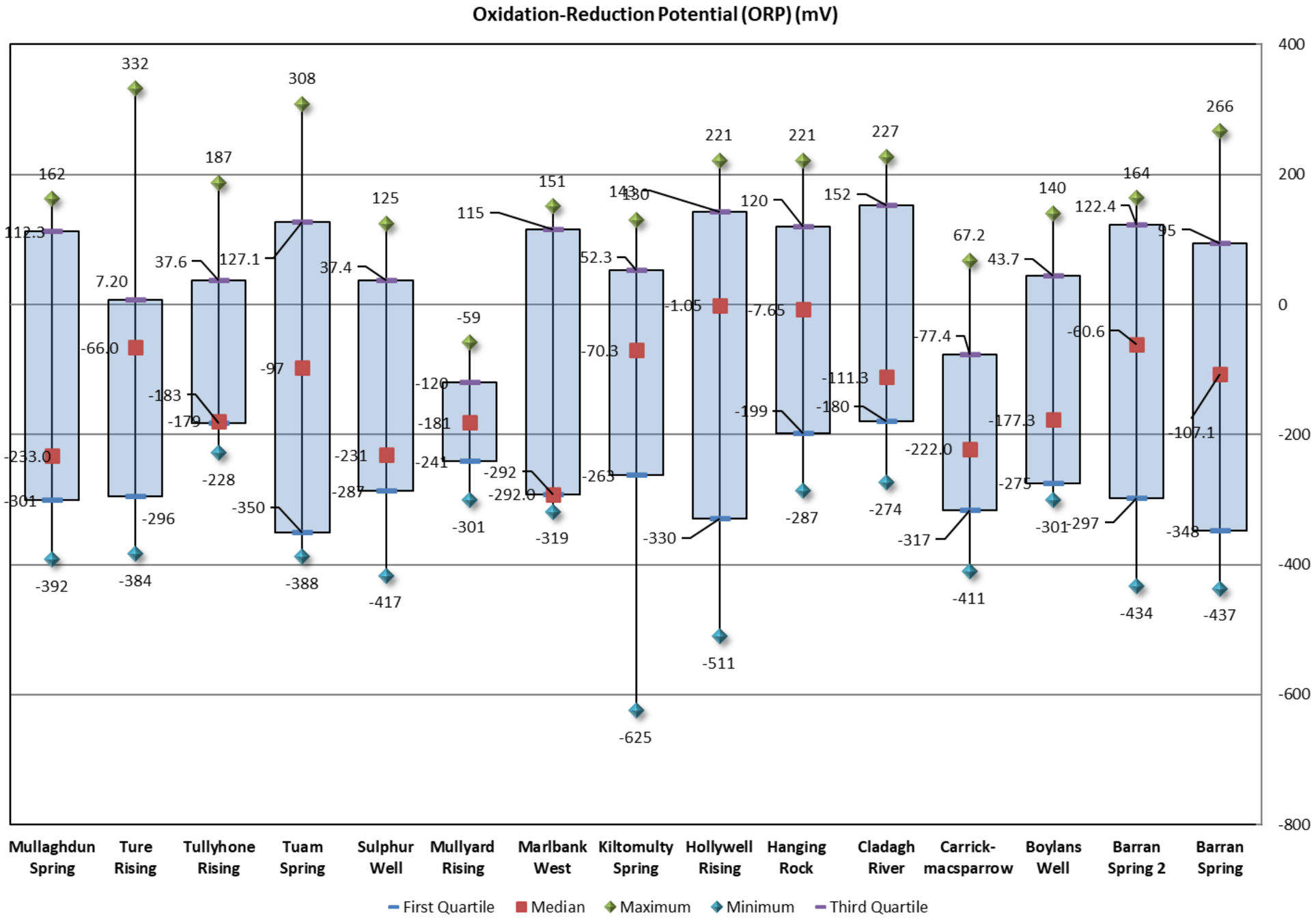

Figure 21: Oxidation-Reduction Potential (ORP) boxplot

pH

- The pH within the Arney catchment ranges from 6.66 at Barran Spring 2, to 8.40 at Carrickmacsparrow Spring (Figure 22).
- Relatively high pH values (interquartile range >8.0) occur at Carrickmacsparrow, Sulphur Well and Tullyhone Rising. Somewhat lower, but still relatively (for this catchment) high pH values (interquartile range >7.5 and largely <8.0) occur at Boylans Well, Cladagh River and Mullaghdun Spring.
- Relatively lower pH values (interquartile range <7.5) occur across the remaining 10 locations.

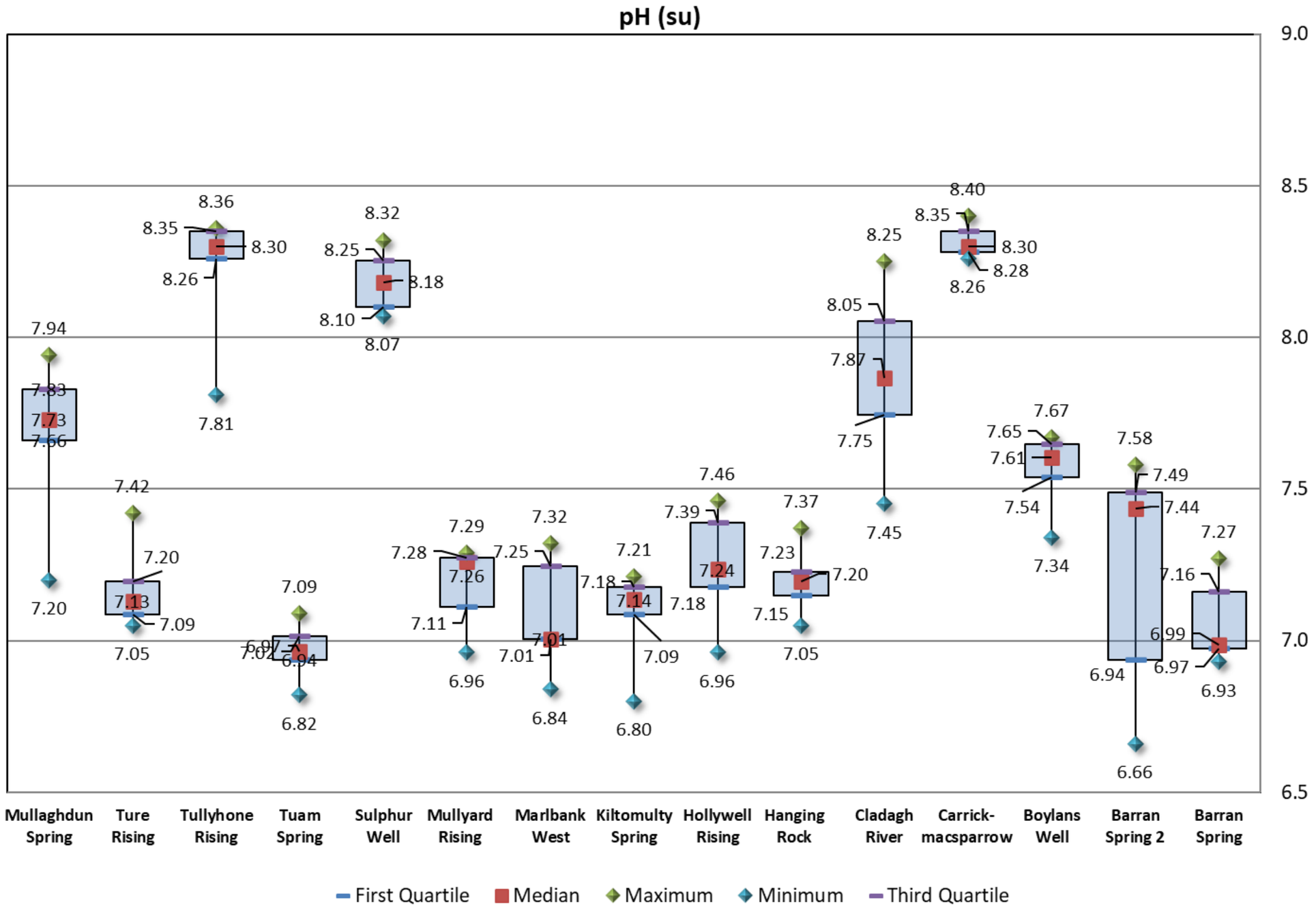

Figure 22: pH boxplot

5.3.2 Water Type

Piper diagrams are used to determine the water type across the Arney catchment. An illustration of the interpretation of piper diagrams is presented in Figure 23

Overall, the groundwater in the Arney catchment is calcium (predominantly)-magnesium (relatively less compared to calcium) bicarbonate (Ca-Mg-HCO_3) type, with some samples mixed type of groundwater and a few plotting on the Na-K-HCO_3 type (

Figure 24).

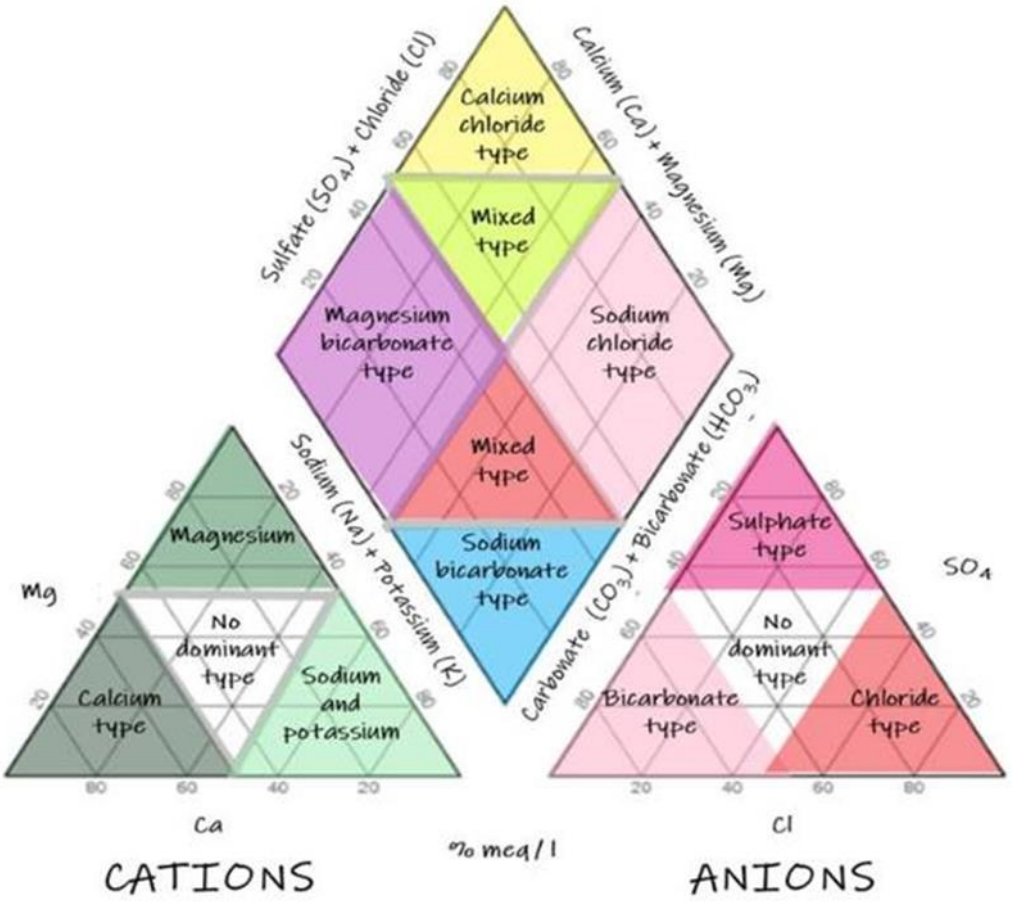

Figure 23: Piper diagram interpretation

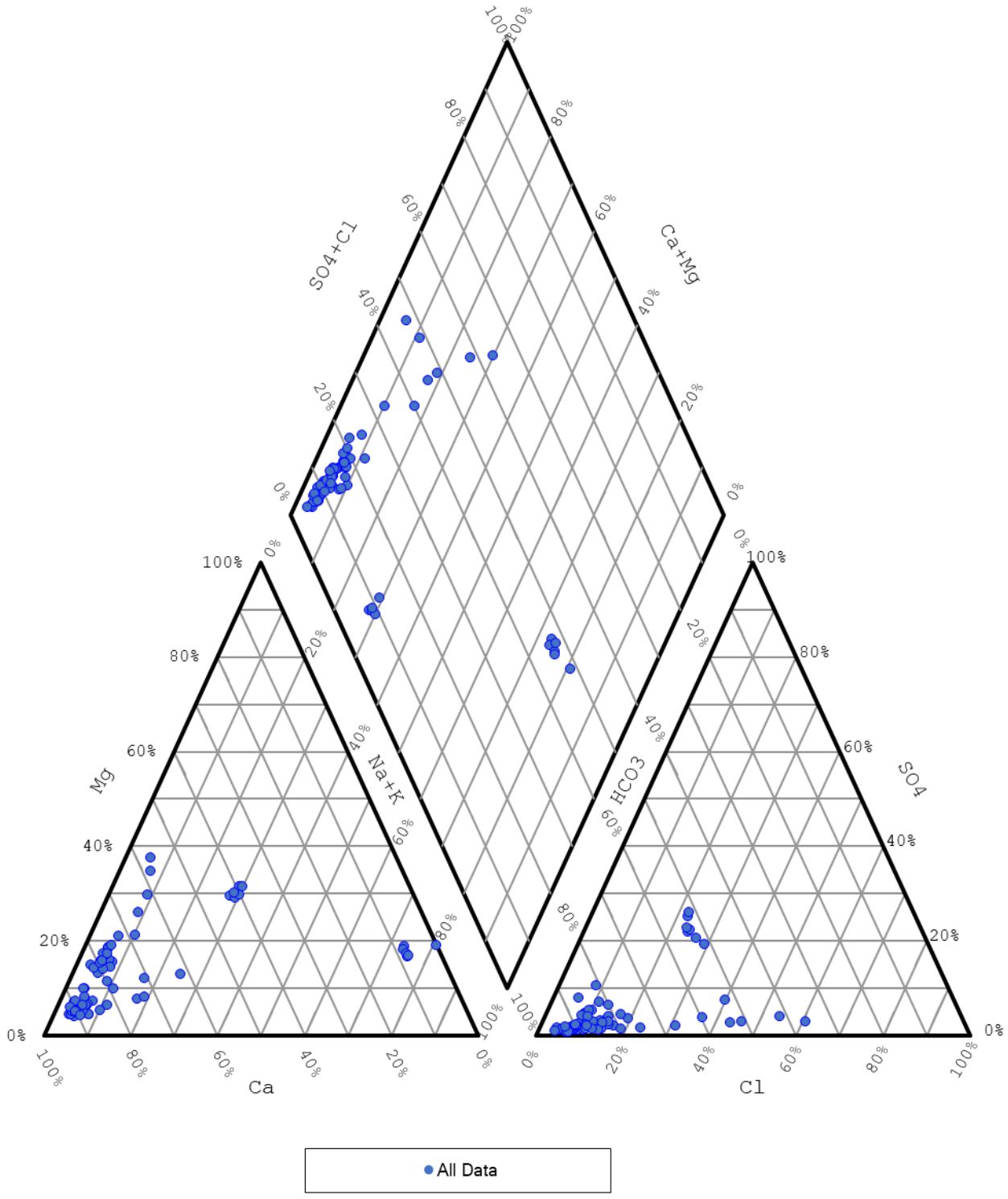

Figure 24: Piper diagram of all samples

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

- Seven springs (were monitored in Round 3 (November 2021) for 103 organic parameters including MCPA (<0.01 ug/L) and cypermethrin in November 2021:

- Mullyard Rising;
- Kiltomulty;
- Boylans well;
- Barran spring;
- Sulphur well; and
- Carrickmacsparrow spring.

There were no detections of any organic parameters monitored.

5.4.2 Microbial parameters

Microbial parameters *E. coli*, total coliforms and *Clostridium Perfringens* were monitored at all spring locations during the last four monitoring events (i.e. monitoring event 3 through 6).

There were detections of microbial parameters of microbial parameters at all locations during all monitoring events (Table 6). The limit of detection for these parameters is zero, all values above zero are a detection and the minimum reportable and reported value is zero. In Table 6, a greater than sign (>) indicates the value was higher than the maximum limit of quantification and the maximum limit of quantification (i.e., 80 or 150 as appropriate) is included for calculation purposes.

Table 6 Microbial Parameters Summary Statistics

Test	Units	Mean	Max	Median	97.7th percentile	No. Samples	No. Detections	% Detections
E. Coli	cfu/100 ml	36	>80	25	>80	57	45	79
Total coliforms	cfu/100 ml	54	>80	>80	>80	57	54	95
Clostridium Perfringens	cfu/100 ml	39	>150	10	>150	57	41	72

As there are four microbial samples per spring location, box plots are not appropriate for assessment of the microbial parameters. Table 7 presents the number and % of detections of microbial parameter at each spring, where *n* = 4 for all sites (except Cleggan spring for which *n* = 1). Total coliforms are naturally present in soils and do not in themselves indicate an anthropogenic input. *E. coli* and *Clostridium perfringens* occur in the digestive tract of humans and domestic and wild animals and indicate contamination with human/animal waste.

Table 7 Summary of exceedances of microbial parameters at each spring

	Total coliforms		*E. coli*		*Clostridium perfringens*	
Spring name	No detections	% detections	No detections	% detections	No detections	% detections
Barran Spring	4	100%	4	100%	4	100%
Barran Spring 2	4	100%	3	75%	3	75%
Boylans Well	4	100%	1	25%	0	0%
Carrickmacsparrow	2	50%	2	50%	2	50%

	Total coliforms		*E. coli*		*Clostridium perfringens*	
Spring name	No detections	% detections	No detections	% detections	No detections	% detections
Cladagh River	4	100%	4	100%	4	100%
Cleggan Spring	1	25%	1	25%	1	25%
Hanging Rock	4	100%	4	100%	3	75%
Holywell Rising	4	100%	2	50%	2	50%
Kiltomulty Spring	3	75%	1	25%	2	50%
Marlbank West	3	75%	3	75%	2	50%
Mullaghdun Spring	4	100%	4	100%	4	100%
Mullyard Rising	2	50%	2	50%	2	50%
Sulphur Well	3	75%	2	50%	1	25%
Tuam Spring	4	100%	4	100%	4	100%
Tullyhone Rising	4	100%	4	100%	3	75%
Ture Rising	3	75%	3	75%	3	75%

Section 6 Summary and Recommendations

6.1 Water Type

Overall, the groundwater in the Arney catchment is calcium-magnesium bicarbonate (Ca-Mg-HCO_3) and mostly Ca-bicarbonate type, with some samples mixed type of groundwater and a few plotting on the Na-K-HCO_3 type.

6.2 Exceedances, Pressures & Pollution Indicators

Land use across the Arney catchment is predominantly agricultural pastures, with areas of mixed and coniferous forest and some scattered peat bogs in the east (Corine Landcover 2018). Peat bogs are common in the east of the catchment and coniferous and mixed forests, moors and heathlands are common in the west of the catchment. The Arney catchment aquifer vulnerability generally ranges from "high" to "extreme" (GSNI GeoIndex).

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

- Ammonia as N (exceedance no. 18, or 22 %);
- Fluoride (F) (exceedance no. 11, or 14 %);
- Specific electrical conductivity (SEC) (exceedance no. 8, or 10 %);
- Sodium (Na) (exceedance no. 6, or 7.4 %);
- Ortho-phosphate as P (exceedance no. 6, or 7.4 %);
- Potassium (K) (exceedance no. 3, or 4 %); and;
- Chloride (Cl) (exceedance no. 1, or 1.2 %).

There were exceedances of the respective threshold/WQS for the following minor elements:

- Iron (Fe) (exceedance no. 17, or 21 %);
- Manganese (Mn): (exceedance no. 8, or 10%); and;
- Arsenic (As) (exceedance no. 2, or 3 %).
- Barium

The locations of the exceedances of WQS thresholds are outlined in Table 8, with yellow fill indicating relatively few exceedances of the relative threshold (1 exceedance only) and orange fill indicating higher numbers of exceedances (2 of more exceedances).

Table 8 Exceedances of WQS parameters relative to sampling location

Parameter	Manganese	Specific Electrical Conductivity	Ammonia	Fluoride	Sodium	Ortho-P	Chloride	Potassium	Iron	Barium	Arsenic
Barran Spring											
Barran Spring 2											
Boylans Well											
Cladagh River											
Hanging Rock											
Kiltomulty Spring											
Marlbank West											
Mullyard Spring											
Mullaghdun Spring											
Sulphur Well											

Some of these elevated concentrations may relate to aquifer hydrochemistry and others may relate to catchment land use practices. Sodium, potassium, barium and iron bearing minerals are common in the bedrock geology across the catchment (Table 1). Arsenic (Kiltomulty spring) may be related to geology or may be due to an anthropogenic pressure and input.

Fluoride (Boylans wells, Cladagh River and Sulphur well) is relatively rare in nature and likely anthropogenic in origin. Fluoride may be associated with domestic waste water treatment systems.

The exceedances of ammonia and specific electrical conductivity may be due to peaty soils/subsoils or of anthropogenic origin. Ortho-phosphate, chloride and manganese exceedances are unlikely to be due to natural geology or soils/subsoils. Elevated ammonia, ortho-phosphate and potassium may be associated with fertiliser use. Elevated manganese requires reducing conditions, indicating organic carbon in the system which may be derived from animal waste (manure), human waste (domestic waste water treatment) or peat.

There were no detections of MCPA (<0.01 ug/L) or any other organic parameter monitored.

E. coli and *Clostridium perfringens* occur across the catchment, indicating groundwater contamination with animal or human waste.

Excluding the microbial parameters, the largest number of parameters with exceedances occur at Cladagh River (nine parameters with one or more exceedance of their respective threshold and Kiltomulty Spring (seven parameters with one or more exceedance of their respective threshold) (Table 8).

The data indicate that the groundwater in the catchment is impacted by anthropogenic pressures. From the parameters, these pressures may be/include agricultural practices and/or domestic waste water systems and/or peat.

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 body. 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., microbial parameters, ammonia, ortho-phosphate, fluoride, etc.). It is recommended that cyanide is added as an indicator peat bog impacts.

It is recommended that further assessments be carried out to provide insight on the potential sources of anthropogenic contamination (i.e., pressures). Along with cyanide, total organic carbon, ammonia, ORP, colour and total suspended solids may also be considered to assess the impact of peat on groundwater in the catchment. Phosphorus concentrations might be assessed 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); ORP, 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 springs (including assessment of fluoride at Boylans Well and Sulphur Well, ammonia in Boylans Well, Cladagh River, Kiltomulty Spring and Sulphur Well). Further work might include probability plots or other statistical methods to develop background values when a larger dataset is available.

Section 7 References

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

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