

Department of Communications,  
Climate Action and Environment



**Environmental  
Monitoring Services at the  
Former Mining Areas of  
Silvermines (Co. Tipperary)  
and Avoca (Co. Wicklow)**

**Avoca Monitoring Report -  
Round 8**

August 2021



**CDM  
Smith**



# Document Control Sheet

<b>Client</b>	Department of Communications, Climate Action and Environment			
<b>Project</b>	Environmental Monitoring of Former Mining Areas of Silvermines and Avoca			
<b>Project No</b>	255416			
<b>Report</b>	Monitoring Report for the Former Mining Area of Avoca August 2021			
<b>Document Reference:</b>	255416/40/DG/39			
<b>Version</b>	<b>Author</b>	<b>Checked</b>	<b>Reviewed</b>	<b>Date</b>
1	██████████	██████	██████	08/12/2021

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# Section 1 Introduction

## 1.1 Objectives and Scope

The Department of Communications, Climate Action and Environment (the Department) appointed CDM Smith Ireland Ltd (CDM Smith) to undertake a programme of environmental monitoring at the closed mine sites of Silvermines and Avoca, commencing in 2018.

The scope of the monitoring programme is defined in the *Environmental Monitoring of Former Mining Areas of Silvermines and Avoca Monitoring Plan*, (Document Ref: 118174/40/DG/01, dated February 2018) and sampling activities were performed in accordance with the programme and procedures set out therein.

The Monitoring Report for the Avoca Mining Area presents an evaluation of the results of the field investigations carried out in August 2021. This report should be read alongside the Avoca Data Report (Document Ref: 255416/40/DG/40, dated September 2021) which contains all field measurements and laboratory analytical results.

## 1.2 Background of Avoca Mining Area

The Avoca mining area is located in the eastern foothills of the Wicklow Mountains, some 55 kilometres south of Dublin. The site includes the East and West Avoca mining areas. The Avoca River divides the East and West Avoca mine sites and runs along the base of the tailings management facility (TMF).

The Avoca Mine site was worked intermittently for approximately 250 years with the extraction of 16 Mt of copper and pyrite ore and on-site processing of concentrates. The mine went into receivership and closed in 1982. Mineral extraction left an environmental legacy that comprises three open pits, over 70 shafts and adits, numerous spoil piles and 25 mine buildings/structures. A number of spoil piles, which have elevated metal levels, and some pit high walls are physically unstable with the potential to collapse. There are also other areas where the ground is unstable and has the potential to subside. Seeps and the water discharges from adits are acidic and metal laden; these discharges impact water quality in the Avoca River.

## 1.3 Catchment Description

The Avoca Mines are located within the Avoca River Catchment which includes an area of 650 km<sup>2</sup>. The East and West Avoca Mines are separated by the Avoca River, which flows through the Vale of Avoca, a noted tourist attraction. To the north of the mines, the Avoca River is formed at the "Meeting of the Waters" by the confluence of the Avonbeg and Avonmore Rivers, while 6.5 km to the south, it is joined by the Aughrim River and flows an additional 7.5 km to the sea at the fishing port of Arklow. Several smaller tributaries join the Avoca River close to the mine water discharges, including Sulphur Brook to the south of East Avoca Mines, and the Valeview and Red Road streams to the north and south respectively of West Avoca Mines.

## 1.4 Geology and Hydrogeology

### 1.4.1 Geology

The mineralised zone at Avoca is hosted in the Ordovician Avoca Formation that consists of tuffs (consolidated volcanic ash) and felsites (volcanic or extrusive igneous rocks) interbedded with slaty mudstones. The rocks trend northeast/southwest and are generally steeply-dipping to the southeast. Tight folds a few hundred metres wide are also present. The main ore zones, from which copper ores and pyrite ( $\text{FeS}_2$ ) were extracted, occur as generally stratiform lenses up to a few tens of metres thick at the top of a sequence of tuffs and felsites.

Numerous shear zones exist and a series of north-south trending faults, one of which (the Great Fault) runs close to the Avoca River and displaces the western orebodies southward relative to the eastern ones.

There are three main ore types:

- Banded sulphides with more than 95% pyrite ( $\text{FeS}_2$ ) accompanied by chalcopyrite ( $\text{CuFeS}_2$ ), sphalerite ( $\text{ZnS}$ ), and galena ( $\text{PbS}$ );
- Vein or disseminated ore invariably associated with silicification and containing pyrite and chalcopyrite; and
- Lead-zinc ore (galena and sphalerite) with banded pyrite.

All three ore types have minor quantities of arsenic and bismuth minerals.

The uppermost 30 to 60 m of the deposits have been oxidised. The most important minerals include iron oxides, chalcocite ( $\text{Cu}_2\text{S}$ ) and covellite ( $\text{CuS}$ ) together with various copper and iron oxides.

### 1.4.2 Hydrogeology

The bedrock is overlain by subsoils derived from glacial till and weathering of bedrock. Subsoils are thin (<2 metres) or absent on hilltops and thicker (>2 metres) along valley floors. The Avoca River valley itself comprises a thick (10-30 metres) sequence of coarse-grained alluvial sediments.

In terms of groundwater yield, the GSI classifies the bedrock in the Avoca mines area as poorly productive: PI - Poor aquifer, generally unproductive except for local zones and Pu - Poor aquifer, generally unproductive.

Overall water movement consists of three primary pathways:

- Surface runoff (overland flow). Within the mines area, surface drainage is influenced by the spoil piles and open pits on both sides of the river. The open pits collect rainwater (directly) and runoff (indirectly);
- Interflow or transition zone (flow in subsoils and/or along the top of bedrock). Near the Avoca River, interflow will enter the alluvium and the Avoca River or emerge as seeps or springs. The transition zone may be only a few metres thick, and is regarded as being more permeable or transmissive than deeper bedrock; and

- "Deep" groundwater flow at Avoca occurs in discrete fractures or fracture zones which represent zones of enhanced permeability. Deep groundwater will also be captured by underground mine workings in the mine area. Near the Avoca River, deep groundwater will also enter the alluvium.

## 1.5 Description of Adit Discharges

Map 1 in [Appendix A](#) shows the adits with active discharges that were sampled and are described in this section.

The **Cronebane Intermediate Adit** (also known as Fathom Stope 43) flows from an opening in the southeast wall of the East Avoca Pit and across the bottom of the pit forming a lake on the southwest end. Two outflow points exist within the lake (53 stope upper end and 53 stope lower end), which both discharge to the 850 Adit. For health and safety reasons, this adit was not sampled. The spring 2019 geotechnical survey by GWP found that the wall of the East Avoca Pit is becoming increasingly unstable and there is a high risk of rockfalls. The survey concluded that to maintain low risk, entry to the East Avoca Pit should be restricted, and limited to a maximum of 8 man-hours per year for essential works only.

The **Cronebane Shallow Adit** discharges on the side of a hill southeast of the East Avoca Pit. The adit is believed to drain the unsaturated workings in the Cronebane and Connary areas. The discharge follows a ferricrete-lined channel which feeds into a culvert and passes under the road. Shortly after passing under the road, the discharge soaks into the ground in a low wooded area (just north of the yellow access gate).

The **Deep Adit** is located northeast of Whites Bridge and is the main mine drainage for East Avoca. The water flows from the portal into a ditch that runs semi-parallel to the Avoca River before discharging into the river. A box culvert was installed at the entrance of the Deep Adit in October 2014 as part of the Avoca Works project. The hydro-morphology of the Deep Adit channel has changed on several occasions in the period 2014-2015 with the full or partial Deep Adit and 850 Adit flow being diverted through the Millrace at different times. Since February 2016, the Deep Adit and 850 Adit flow has discharged to the Avoca River at its normal discharge point. This was due to completed groundworks which were preventing the flow from being diverted to the Millrace channel. It is also noted that flows from the Deep Adit appear to have decreased over time, for reasons that are not clear, but likely connected to changes in the underground workings.

The **850 Adit** is also located northeast of Whites Bridge. In 2009, a significant volume of water was observed issuing from the adit for the first time since more routine investigations began in 2007. This was investigated on behalf of the Department by GWP Consultants who concluded that the water flow is most likely to be due to a collapse inside the mine workings, diverting water from the Deep Adit to higher levels. Since the initial discharge in 2009, flow has been constant observed from the 850 Adit and it was added to the sampling programme in February 2014.

As a result of remediation works at Tigroney over the period from 2014 to 2017, the flow from the 850 Adit is now piped directly to the Deep Adit box culvert, discharging 5 m downstream of the Deep Adit portal (located at the far end of the box culvert). It is not possible to take a sample from inside the 850 Adit as the adit was rehabilitated in 2020 after a geotechnical survey found that stability of the adit had decreased. The 850 Adit flow is now piped to the Deep Adit box culvert and there is no sampling point inside the 850 adit. However, a sample was collected from a

manhole outside of the adit where the 850 Adit flow is piped to the Deep Adit box culvert and an in-situ flow meter is located.

The **Road Adit** is located adjacent to Rathdrum Road at the base of the Ballymurtagh landfill (formerly the Pond Lode Pit). Previously, the Road Adit discharge ran alongside a ditch beside the road and then discharged to the Avoca River just downstream of the Wicklow County Council Yard Gauging Station. Since Autumn 2014, the Road Adit no longer flows along the road and instead goes through a pipe underneath the council yard and discharges directly into the Avoca River above the Wicklow County Council Gauging Station.

The **Ballygahan Adit** is known to have discharged through a 100 mm (4 inch) pipe to the Avoca River over a steep bank just north of the Wicklow County Council Maintenance Yard (hereafter Wicklow co. co. maintenance yard). However, this pipe is no longer visible and there is no longer a point discharge from the Ballygahan Adit to the Avoca river. There are several seeps from the river bank probably due to seeping through the collapsed adit. Due to the relatively high water level in the Avoca River, no visible seeps could be observed during the current monitoring round.

## Section 2 Methodology

### 2.1 Field Sampling Methods

#### 2.1.1 Groundwater Sampling

Seven groundwater monitoring wells were sampled on 16 August 2021. Details of groundwater monitoring locations are listed in Table 1 and illustrated on Map 1 and 2 in [Appendix A](#). No sample was obtained from monitoring well SG104 because the borehole was dry.

- Five monitoring wells were installed in the alluvium in 2007 as part of a previous study for the Department (CDM 2008), as follows:
  - Two nested wells in the Emergency Tailings area, downgradient of the West Avoca pit and slightly side-gradient of the Ballymurtagh Landfill (MWET1 (shallow), and MWET2 (deep));
  - Two nested wells in the Tigroney West spoil area near the Deep Adit (MWDA1 (shallow) and MWDA2 (deep));
  - One shallow well upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments (MWPF1); and
  - Wicklow County Council have a number of monitoring wells, as follows:
    - Three wells installed for Ballymurtagh Landfill monitoring purposes (GW1/05, GW2/05 and SG104), located downgradient of the landfill (in West Avoca) and one located at the toe of the landfill (SG104).

**Table 1 Location of Avoca Groundwater (Borehole) Monitoring Points in August 2021**

Sample ID	Easting	Northing	Water Level	Field Parameters	Sample for Lab Analysis	Owner	Total Depth (mbgl)	Screen Interval (m bgl)
MWDA1	319877	182043	Yes	Yes	Yes	Dept.	12	9.0 – 12
MWDA2	319879	182039	Yes	Yes	Yes	Dept.	24.9	21.9 – 24.9
MWET1	319916	181778	Yes	Yes	Yes	Dept.	10.9	7.8 – 10.6
MWET2	319917	181781	Yes	Yes	Yes	Dept.	21	17 – 20
MWPF1	319678	182296	Yes	Yes	Yes	Dept.	10	4.7 – 7.7
GW1/05	319880	181673	Yes	Yes	Yes	WCC	31	25.0 – 31
GW2/05	319880	181673	Yes	Yes	Yes	WCC	10	4.0 – 10
SG104	319806	181523	Yes	No	No	WCC	26.8	-

Groundwater samples were collected using procedures consistent with the Low Flow Groundwater Sampling Procedure (SOP 1-12) and Groundwater Sampling using Bailers (SOP 1-5) detailed in the monitoring plan. Groundwater was collected using a portable submersible low-flow Wasp® pump where possible, and using bailer fixed-volume purging and sampling where not possible (GW1/05 and GW2/05 only). The static water level was recorded prior to purging and then measured throughout the purging process to monitor drawdown.

Water quality indicator parameters (temperature, pH, ORP, conductivity and dissolved oxygen (DO)) were monitored during low-flow purging using a flow-through cell to minimise oxidation by the atmosphere. Purging continued until the field parameters stabilised. The results were recorded on the Groundwater Purging and Sampling Form every approximately five minutes during the purging process. The physico-chemical field data are summarised in Appendix A of the Data Report.

After the well was purged and stable parameters measured, the flow was reduced for low-flow sample collection. Samples for trace metal analyses were filtered in the field using a 0.45-micron membrane syringe filter before preservation in bottles supplied by the laboratory.

The exceptions to the low-flow sampling procedure were for GW1/05 and GW2/05 where a blockage exists in each well which obstructs access. These samples were collected using single use bailers after greater than three volumes of the well had been purged (calculated as  $\pi r^2 h$  – where  $r$  is the inner casing radius and  $h$  is the height of the water column) and the field parameters had stabilised.

Groundwater levels were measured at seven wells (SG104 was dry) using a portable electronic water level recorder. OTT Orpheus Mini Water Level Loggers continuously monitor hourly hydraulic pressure (water level) and temperature at MWDA1, MWDA2, MWET1, MWET2 and MWPF1. Built-in pressure compensation capillaries compensated hydraulic pressure for the influence of temperature and atmospheric variations. The data were downloaded on site by connecting the logger to a laptop via an infrared interface. Groundwater level data are discussed in Section 6 and the data are contained in Appendix A of the Data Report.

### 2.1.2 Surface Water and Adit Discharge Sampling

Seventeen surface water locations were sampled over 17 and 18 August 2021 as listed in Table 2 and shown on Map 1 and 2 in [Appendix A](#). No sample was collected from the following three locations (not included in Table 2):

1. Ballygahan Adit point discharge; it is possible that related seeps from the Ballygahan Adit were discharging to the Avoca River, but it is not possible to access these seeps in high flow conditions;
2. US Tigroney West; this location was dry at the time of sampling; and
3. Cronebane Intermediate Adit; for H&S reasons, it was not possible to access the location to collect the sample.

Surface water sampling was conducted consistent with the Surface Water Sampling Procedure (SOP 1-1) as detailed in the Monitoring Plan.

The surface water sampling locations were located using a GPS. Photographs were taken of the surface water sampling locations (Appendix B of the Data Report). All sample locations were approached from downstream so that the underlying sediment was not disturbed. Grab samples were collected from a well-mixed portion of the stream, where possible. Due to high flow conditions, composite samples could not be collected on the Avoca River and instead, samples were collected as grab samples from the riverbank.

Samples were collected in new laboratory-provided bottles with the correct preservatives. Sample bottles not requiring filtration (containing no preservatives) were filled directly in the stream. A

container was filled at the same time and transported to the shore for filtering using a 0.45-micron membrane syringe filter before preservation, for the trace metal analysis.

**Table 2 Location of Surface Water Monitoring Points**

Site Name	Sample Site Description	Easting	Northing	Flow Measurement Method	Sample collected (yes/no)
Site T1	Avoca River Location (Upstream of Whites Br.)	319235	182795	Equal to flow recorded at Whites Bridge GS	Yes
Upstream (US) of Whites Bridge	Avoca River Location (between Site T1 and Whites Br.)	319575	182384	Equal to flow recorded at Whites Bridge GS	Yes
Whites Bridge	Avoca River Location (at Whites Br.)	319762	182069	Equal to flow recorded at Whites Bridge GS	Yes
Whites Bridge GS	Avoca River Location (90m downstream of Whites Br.)	319840	182019	Automatic recorder - Whites Bridge GS (Data from EPA)	Yes
Downstream (DS) Deep Adit	Avoca River Location (Downstream of Deep Adit confluence on the Avoca River)	319951	181922	Equal to flow recorded at Whites Bridge GS (plus Deep Adit Conf. discharge)	Yes
Downstream (DS) of Millrace	Avoca River location (Downstream of contaminated Millrace area)	320016	181796	Equal to flow recorded at Whites Bridge GS (plus Deep Adit confluence)	Yes
Upstream (US) of Ballygahan Adit	Avoca River Location (Upstream of Ballygahan Adit discharge)	319936	181633	Equal to flow recorded at Whites Bridge GS (plus Deep Adit confluence)	Yes
Upstream (US) of Road Adit	Avoca River Location (Upstream of Road Adit Discharge on the Avoca River)	319942	181532	Equal to flow recorded at Whites Bridge GS (plus Deep Adit confluence)	Yes
Wicklow County Council Maintenance Yard	Avoca River Location	319939	181445	Equal to flow recorded at Whites Bridge GS (plus Deep Adit confluence and Road Adit confluence)	Yes
Site T5	Avoca River Location (Abandoned Coal Yard)	319972	181114	Equal to flow recorded at Whites Bridge GS (plus Deep Adit confluence and Road Adit confluence)	Yes
Avoca Bridge	Avoca River (Upstream of Avoca Bridge)	320372	179932	Equal to flow recorded at Whites Bridge GS (plus Deep Adit Conf. discharge and Road Adit Confluence discharge)**	Yes
850 Adit	Adit Discharge (at portal)	319850	182123	In-situ permanent flow meter	Yes
Deep Adit (plus 850 Adit)	Adit Discharge (at portal)	319850	182123	OTT Flow meter	Yes
Deep Adit Confluence	Adit Discharge (before entering Avoca River)	319896	181986	Flume	Yes
Road Adit	Adit Discharge (at portal)	319858	181512	In-situ Permanent Flume	Yes
Road Adit Confluence	Adit Discharge (before entering Avoca River)	319942	181513	OTT Flow meter	Yes

Site Name	Sample Site Description	Easting	Northing	Flow Measurement Method	Sample collected (yes/no)
Cronebane Shallow Adit	Adit Discharge	320268	182646	Bucket and Stopwatch	Yes

\*\*The float method was also used at this location, however, on comparison, the data from the gauging station was assessed as more accurate.

Water quality indicator parameters were monitored during sampling using a multi-parameter probe and by collecting the water from the stream profile / location as a composite sample from the stream or discharge when possible; when not possible to collect a composite sample, the sample was collected as a single grab sample into a container and parameters were measured on the stream bank as is typical during high flow conditions. The final stabilised results were recorded using the digital field tablet (Trimble) and are summarised in Appendix A of the Data Report.

### Flow Measurements

Flow was measured at five locations (see Table 2), using various methods depending upon the quantity of flow to be measured and safety concerns.

In addition, data obtained from the EPA for the automatic recorder at Whites Bridge GS (EPA station 10044) was projected to 10 locations. The flow data from the EPA station was selected to match the day and time the samples at each location were collected. Previously, data were also obtained from an EPA automatic recorder at Wicklow County Council Yard GS (EPA station 10045), however, this GS was decommissioned between the 2020 spring high flow and 2020 autumn low flow monitoring events.

Previously, the 850 flow was measured manually, however, this has been replaced by data from the in-situ flow meter installed at the entrance of the 850 Adit in October 2017. Surface water flow results are discussed in Section 5.1 and the data and measurement data are contained in Appendix A of the Data Report. The methods employed included a portable flume (for small to medium discharges) and float method from bridge locations (large flows).

A portable flume was used for small discharges and streams while for very small discrete discharges, a stopwatch, and calibrated volume container was used. At locations with greater flow, flow was measured with an OTT MF Pro digital flow meter. The OTT MF Pro meter digitally calculates and records streamflow. Locations and flow conditions which previously were monitored using a Marsh McBirney meter were monitored with the OTT MF Pro digital flow meter.

The float method is used when it is unsafe to wade into the river. It is the least accurate method, but it provides a reasonable estimate. It is completed by measuring cross-sectional area of the channel from a bridge at regular intervals (approximately 10 locations), along with the time it takes an object to “float” a designated distance. This is repeated at least three times and the average time calculated. The flow at Avoca bridge measured using the float method was 8.84 m<sup>3</sup>/s. This flow was high relative to flow at all other locations along the river, which were approximately 3.75 m<sup>3</sup>/s. Therefore, an estimate of the flow using the flow recorded at Whites Bridge GS plus the flow at the deep adit confluence and road adit confluence was considered more accurate, and used for calculation purposes.

Previously, the flow at Site T1 had been measured by adding the flow of the two upstream tributaries (Avonmore and Avonbeg rivers), which were both measured by the float method from bridges. A H&S review in 2019 found that one of these locations was not suitable to measure the

flow using the float method from the bridge for health and safety reasons. Thus, the flow at Site T1 was estimated using the flow at Whites Bridge GS.

A permanent in-situ flume was installed at the Road Adit in Spring 2021. The data is undergoing validation and quality checks. This data will be available to be included in future monitoring reports.

### 2.1.3 Field QA/QC Samples

In accordance with the QA/QC Protocols set out in the Monitoring Plan, the following field QA/QC samples were collected (also see Table 3):

- **Groundwater:**
  - One duplicate groundwater sample; and
  - One decontamination blank collected by pumping deionised (DI) water through the groundwater pump after decontamination.
- **Surface Water:**
  - Two duplicate surface water samples; and
  - One decontamination blank collected by pouring DI water over the surface water sampling equipment after decontamination.
- Two certified standard reference materials (SRMs) containing known concentrations of 15 metals were shipped blind to ALS laboratory (the SRM certificate is contained in Appendix E of the Data Report).
- One water blank was collected of the DI water during the sampling event. An additional filtration blank using DI water was collected in to quantify contamination from the filtration procedure.

Sample IDs for the field QA/QC samples are listed in Table 3. The duplicate samples are an independent check on sampling and laboratory precision. The standard reference material is an independent check on laboratory accuracy. The decontamination blank is a check on the decontamination procedures used in the field. These checks are very important and are independent from the QA/QC samples performed by the laboratories (see discussion in Section 3).

**Table 3 Field QA/ QC Sample IDs and Descriptions**

Sample ID	QA/QC Sample Type	Description
AVGD01.17	GW Duplicate	Duplicate of MWET1
AVDB01.17	GW Decontamination blank	DI water (VWR Chemicals: Batch No: 21C104114) Pumped through groundwater pump after final decon at site MWET1)
AVSD01.17	SW Duplicate	Duplicate of Site T1
AVSD02.17	SW Duplicate	Duplicate of Cronbane Shallow Adit
AVDB02.17	SW Decontamination blank	DI water (VWR Chemicals: Batch No: 21C104114) poured over SW composite sample bottle after final decon at Site T1
AVSR01.17	Standard Reference Material	Water ERA "Trace Metals" Lot #P312-740B
AVSR02.17	Standard Reference Material	Water ERA "Trace Metals" Lot #P312-740B
WB01.17	Filtration blank	Deionised water filtered onsite (VWR Chemicals: Batch No: 21C104114)
WB02.17	Water blank	Deionised water (VWR Chemicals: Batch No: 21C104114)

## 2.2 Sample Handling

The waterproof label on each sample container was completed using an indelible marker. The label contained the location, sample ID and date of sample collection. Samples were stored appropriately so they remained representative of the time of sampling. Sufficient ice packs and ice were added to cool the samples.

A chain-of-custody (COC) form was filled out for each sample type at each sampling location. The field staff double-checked that the information recorded on the sample label was consistent with the information on the COC. The COC was placed in a plastic sleeve and placed inside of all shipping and transport containers. All samples were hand delivered or shipped by courier to the laboratory. Samples were packed so that no breakage would occur. Signed COCs are provided in Appendix C of the Data Report.

## 2.3 Laboratory Sample Analysis

Analysis of all water samples was undertaken by ALS Global (formerly ALcontrol). Samples were dispatched from its distribution centre in Dublin and analysed at its facility in north Wales. ALS is accredited by the United Kingdom Accreditation Service (UKAS) in accordance with ISO/IEC 17025:2005 and has also obtained a Certification of Approval by Lloyd's Register Quality Assurance for Environmental Management System Standard ISO 14001:2004.

All samples were analysed for pH, ammoniacal nitrogen as N, sulphate and dissolved metals (Al, Sb, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, V and Zn). Avoca River samples were also analysed for total organic carbon (TOC) and calcium (Ca) to permit assessment of bioavailable concentrations of several metals (further discussed in Section 4.4). The Monitoring Plan provides details on the analytical methods, holding times and reporting limits. Most metals were analysed by ICP-MS to achieve the lowest possible detection limits.

All the laboratory reports and analytical data are contained in Appendix D of the Data Report and discussed in Section 4 of this report.

## 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. In addition, use of blank samples as a DQI is also discussed.

#### 3.1.1 Accuracy

Accuracy is defined as the degree of agreement of a measurement with an accepted reference or true value. The accepted reference is typically a standard reference material (SRM) provided by an established institute or company. The “true” value has been determined by performing multiple analyses by various methods and laboratories. Accuracy is a measure of the bias in a system (i.e., the laboratory procedures). Each measurement performed on a sample is subject to random and systematic error. Accuracy is related to the systematic error. Attempts to assess systematic error are always complicated by the inherent random error of the measurement. Accuracy is quantitative and usually expressed as percent recovery (%R) of a sample result compared to the SRM.

%R is calculated as follows:

$$\%R = \frac{A}{T} \times 100$$

where: %R = Percent recovery  
A = Measured value of analyte (metal) as reported by the laboratory  
T = True value of the analyte in the SRM as reported by the certified institute.

Acceptable quality control (QC) limits are typically between 80 to 120 %R for inorganic methods (i.e., metals in this report). However, the exact acceptable limits depend upon the actual SRM used (see Section 3.2.3). The SRMs used for this project are discussed below.

#### 3.1.2 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.

RPD is calculated as follows:

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

where:

RPD	=	Relative percent difference
D <sub>1</sub>	=	First sample value
D <sub>2</sub>	=	Second sample value (duplicate)

Acceptable RPD values for duplicates generated in the laboratory are usually 65 to 135%. Acceptable RPD values for field duplicates are usually 50 to 150%. The higher values for field duplicates reflects the difficulty in generating homogeneous duplicates in the field. Both field and laboratory duplicates were generated for this project and are discussed below.

### 3.1.3 Blanks

Several different types of “blank” samples may be generated to assist in evaluating general data usability. Periodic analysis of laboratory method blanks ensures there is no carryover of contaminants between samples because of residual contamination on the instrument or from contaminants introduced in the laboratory. Laboratory method blanks are typically laboratory pure water, acids or sand that have been processed through all of the procedures, materials, reagents and labware used for sample preparation and analysis. In addition to the laboratory blanks, decontamination blanks were generated in the field to evaluate the sampling equipment decontamination process. DI water blanks and DI filtration blanks were also analysed. Each of these types of blanks are discussed below.

### 3.1.4 Field QA/QC Samples

Field quality assurance/quality control (QA/QC) samples were submitted to the laboratories and analysed to enable the following evaluations:

- Duplicate Samples: Duplicate groundwater and surface water samples were created in the field and submitted blind to the laboratory (see Table 3 for sample IDs). The results are used to evaluate the combined reproducibility of both the laboratory analyses and field sampling;
- Decontamination Blanks: After the sampling equipment was cleaned, DI water was poured over or pumped through the sampling equipment and collected for laboratory analysis (see Table 3 for sample IDs). Analyses of these samples were used to evaluate the adequacy of the sampling equipment decontamination procedure;
- Standard Reference Material (SRM): Two certified water SRMs were sent blind to the laboratory (Sample IDs AVSR01.17 and AVSR02.17) to evaluate laboratory accuracy. The certified SRM was supplied by ERA Certified Reference Materials and was Lot #P312-740B (Metals). The Certificate of Analysis is provided in the Data Report, Appendix E. The use of a blind or unknown SRM is the only method to independently verify the laboratory accuracy;
- One water blank was collected of the DI water during the sampling event. An additional filtration blank using DI water was collected to quantify any contamination caused by the filtration procedure.

## 3.2 Results of Field QA/QC Samples

### 3.2.1 Duplicates

Three duplicate samples (one groundwater sample and two surface water samples) were generated in the field and sent blind to ALS for analysis. All RPD values were below 15% with four exceptions:

- -20.1% for Site T1 and AVSD01.17 for copper;
- -15.1% for T1 and AVSD01.17 for nickel;
- -62.2% for MWET2 and AVGD 01.17 for copper; and,
- -82.4% recorded for site MWET2 and AVGD01.17 for lead.

The RPDs for the key parameters ranged from -0.7 to 0.0% for aluminium, -8.02 to -82.4% for lead, -62.2 to -0.6% for copper, -1.0 to 5.4% for arsenic and -11.7 to 1.5% for zinc, which were very good.

The highest reported value of the duplicate was selected for interpretive use in Section 4, therefore providing a conservative evaluation.

Table 4 provides the results of the 15 metals for the three duplicate samples and the calculated RPD between each pair of samples. Note if both the original and duplicate results were less than the limit of detection (LOD) then the RPD was zero. If one value was less than the LOD, a value of ½ the LOD was used in the calculation.

All RPD values were below 15% (apart from -20.1% recorded for Site T1 and AVSD01.17 for copper, -15.1% recorded for T1 and AVSD01.17 for nickel and -62.2% recorded for site MWET2 and AVGD 01.17 for copper and -82.4% recorded for site MWET2 and AVGD 01.17 for lead). The RPDs for the key parameters ranged from -0.7 to 0.0% for aluminium, -8.02 to -82.4% for lead, -62.2 to -0.6% for copper, -1.0 to 5.4% for arsenic and -11.7 to 1.5% for zinc, which were very good.

The highest reported value of the duplicate pair was selected for interpretive use in Section 4, therefore providing a conservative evaluation.

**Table 4 Duplicate Pair Reported Values (µg/L) and Calculated % RPD**

Dissolved Metal	LOD (µg/L)	Site T1	AVSD 01.17	% RPD	MWET2	AVGD 01.17	% RPD	Cronbane Shallow Adit	AVSD 02.17	% RPD
Aluminium	<10/<30*	135	136	-0.7	30	30	0.0	295000	297000	-0.7
Antimony	<1/<6*/60*	0.5	0.5	0.0	3	3	0.0	30	30	0.0
Arsenic	<0.5	0.757	0.717	5.4	7.41	7.79	-0.5	87.9	88.8	-1.0
Barium	<0.2	5.63	5.79	-2.8	12	11.3	6.0	6	6	0.0
Cadmium	<0.08	0.04	0.04	0.0	2.12	2.09	1.4	394	389	1.3
Chromium	<1/<6*/60*	0.5	0.5	0.0	3	3	0.0	30	30	0.0

Dissolved Metal	LOD (µg/L)	Site T1	AVSD 01.17	% RPD	MWET2	AVGD 01.17	% RPD	Cronbane Shallow Adit	AVSD 02.17	% RPD
Cobalt	<0.5	0.25	0.25	0.0	118	116	1.7	298	296	0.7
Copper	<0.3	1.12	1.37	20.1	3.95	7.52	-62.2	4610	4640	-0.6
Iron	<19	115	116	-0.9	99300	97800	1.5	186000	188000	-1.1
Lead	<1.2	2.22	2.41	-8.2	0.6	1.44	-82.4	887	905	-2.0
Manganese	<3	5.63	5.78	-2.6	32500	32000	1.6	9110	9220	-1.2
Molybdenum	<3/<18*/	1.5	1.5	0.0	9	9	0.0	90	90	0.0
Nickel	<0.4	0.625	0.727	-15.1	14.4	12.5	14.1	154	172	-11.0
Vanadium	<1/<6*/60*	0.5	0.5	0.0	3	3	0.0	30	30	0.0
Zinc	<1	20.9	23.5	-11.7	5550	5470	1.5	117000	117000	0.0

Notes:

Green highlight indicates an exceedance in the duplicate RPD acceptance criteria

\*The LOD was raised due to a dilution that was carried out on the sample.

### 3.2.2 QA/QC Blank Samples

Table 5 provides the results of the 15 metals for the groundwater decontamination blank (AVDB01.17), surface water decontamination blank (AVDB02.17), the unfiltered deionised water blank (WB02.17) and filtered deionised blank (WB01.17) samples as well as the associated laboratory method blank samples. Most of the reported concentrations were below the limits of detection. Most metals were analysed by ICP-MS to achieve the lowest possible detection limits. The limits of detection in the blank samples ranged from 0.08 to 10 µg/L except for iron (19 µg/L) in cases dilution was required due to high concentrations. Overall, the procedures were adequate and blank samples do not indicate significant contamination. Therefore, all results are considered acceptable for use for their intended purposes. The results are further discussed below.

Table 5 Water Blank and Decontamination Blank Reported Values and Laboratory Method Blanks (µg/L)

Dissolved Metal	LOD (µg/L)	Filt. Blank WB01.17 (µg/L)	Unfilt. Blank WB02.17 (µg/L)	Lab Method Blank (µg/L)	Groundwater Decon blank AVDB01.17 (µg/L)	Lab Method Blank (µg/L)	Surface water Decon blank AVDB02.17 (µg/L)	Lab Method Blank (µg/L)
Sample batch:		210819-95			210819-95		210820-110	
Aluminium	<10	<10	<10	<10	<10	<10	<10	<10
Antimony	<1.0	<1	<1	<1	<1	<1	<1	<1
Arsenic	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Barium	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cadmium	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
Chromium	<1.0	<1	<1	<1	<1	<1	<1	<1
Cobalt	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Copper	<0.3	<0.3	<0.3	<0.3	0.912	<0.3	0.407	<0.3
Iron	<19	<19	<19	<19	<19	<19	<19	<19

Dissolved Metal	LOD (µg/L)	Filt. Blank WB01.17 (µg/L)	Unfilt. Blank WB02.17 (µg/L)	Lab Method Blank (µg/L)	Groundwater Decon blank AVDB01.17 (µg/L)	Lab Method Blank (µg/L)	Surface water Decon blank AVDB02.17 (µg/L)	Lab Method Blank (µg/L)
Sample batch:		210819-95			210819-95		210820-110	
Lead	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.282	<0.2
Manganese	<3.0	<3	3.01	<3	<3	<3	<3	<3
Molybdenum	<3.0	<3	<3	<3	<3	<3	<3	<3
Nickel	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Vanadium	<1.0	<1	<1	<1	<1	<1	<1	<1
Zinc	<1	<1	1.06	<1	1.45	<1	3.53	<1

Notes: Green highlight indicates a detection

### Decontamination Blank Samples

Two decontamination blanks were created by pumping deionised water through the groundwater sampling equipment and over the surface water sampling equipment after decontamination. The two samples were then sent to ALS for analysis.

Detections in the decontamination blanks were observed for three dissolved metals (copper, lead and zinc), with concentrations ranging from 0.282 to 3.53 µg/L. There were detections of dissolved copper and zinc in both the groundwater and surface water decontamination blanks. The surface water decontamination blank also contained dissolved lead.

All detections were less than ten times the LOD.

These low concentrations in the blanks are below the evaluation criteria and do not affect interpretation of results. Overall, the decontamination procedures employed in the field were adequate.

### Sampling Method Blank Samples

To assess the contamination introduced by the field sampling procedure and field filtration procedure, an unfiltered sample of deionised water was collected in the same way as a standard sample (WB02.17) and a filtered sample of deionised water was collected following the same procedure as for a standard sample (WB01.17) (Table 5).

There were no detections in the filtered sample. Zinc and manganese were detected in the unfiltered blank sample. The detections were however all low and less than 10 times the LOD, and there were no other detections for any other metal. This indicates there may be some introduction of zinc and manganese from the deionised water. Overall, the field sampling procedures employed in the field were adequate.

### Laboratory Instrument Blank Samples

The laboratory instrumentation blank data were obtained to determine if contamination occurred within the laboratory (Table 5). There were no detections for any parameter in the lab method blank samples.

The field QA/QC sample results were reviewed for accuracy and precision. The laboratory QA/QC samples and laboratory reports were also reviewed. Overall, the data quality is considered

acceptable, and the data were compared to the assessment criteria and used to perform trend and loading evaluations.

### 3.2.3 Standard Reference Materials

Two certified, water standard reference material (SRM) samples were sent blind to the laboratory (Sample IDs AVSR01.17 and AVSR02.17) to evaluate laboratory accuracy. The ALS laboratory reports are provided in the Data Report. Table 6 summarises the SRM results compared to the acceptance range for the 15 requested metals.

**Table 6 SRM Samples' Reported Values, and SRM certified value and Acceptance Limits (µg/L)**

Dissolved Metal	Certified Value (µg/L)	Acceptance Limits		AVSR01.17 (µg/L)	AVSR02.17 (µg/L)
		Lower (µg/L)	Upper (µg/L)		
Aluminium	3730	3280	4210	3650	3690
Antimony	96.1	83.4	106	89.1	88.8
Arsenic	783	684	861	670	682
Barium	1950	1780	2110	1800	1740
Cadmium	740	658	792	728	730
Chromium	183	167	199	165	179
Cobalt	228	213	253	207	233
Copper	864	785	942	848	920
Iron	2700	2450	3000	2520	2560
Lead	384	348	422	368	386
Manganese	1070	922	1180	934	1000
Molybdenum	219	197	237	194	200
Nickel	429	390	468	411	447
Vanadium	509	463	545	468	512
Zinc	1730	1560	1900	1720	1880

Notes: Green indicates an exceedance in acceptance limits

The concentration of dissolved arsenic, chromium, cobalt and molybdenum were outside of their relative acceptance ranges in AVSR01.17, and the concentration of arsenic and barium were outside of their relative acceptance ranges in AVSR02.17. In all cases, the measured concentrations were lower than the acceptance limits; however, close to the acceptable limit.

All other metals are within their acceptance limits. Arsenic, chromium, cobalt and molybdenum are not priority metals of concern in the current project, however, in the case where there are exceedances of these parameters, it will be considered during the interpretation of the results that the lab may be under-reporting the concentrations of both parameters. Overall, the results show acceptable accuracy by the analytical laboratory

## 3.3 Laboratory QA/QC Samples

### 3.3.1 ALS Laboratory

ALS undertakes quality control and assessment checks to assure the quality of test results. This comprises the following analyses on water samples:

- Analytical quality control (AQC) samples including, certified reference material (CRM), internal reference material (IRM) and matrix spiked material. A minimum of one AQC is

analysed for batch sizes of 20 samples or less, and for batches of greater than 20 samples one AQC is analysed every additional twenty samples or part thereof. These samples are introduced into the sample batch on a random basis, where possible. They are prepared at the same time as the rest of the batch and by the same person who prepares the batch;

- Process blanks: A process blank is included with each batch of samples. These are matrix matched, where possible, and taken through the entire analytical system;
- Instrument blanks: An instrument blank is run to check for contamination within the instrument;
- Independent check standard: An independent check standard is included with every instrumental run of samples. This is prepared from a standard that is sourced separately to the calibration standards and it is used as a check on the validity of the calibration standards. The acceptance criteria for this standard are method specific; and
- Replicate samples (samples tested more than once using the same method) are included at the same frequency as the AQCs.

All ALS laboratory reports were reviewed to ensure that reported values were ISO17025 certified (where relevant) and for any sample deviations. There were no sample deviations, and all samples were analysed within their recommended holding time.

## 3.4 Summary of Data Checks

### 3.4.1 Field Physico-chemical Versus Laboratory Data

Table 7 contains the field and laboratory results for pH and calculated %RPD. The pH measurements in the laboratory were taken from the unpreserved sample and therefore the results do not affect the results of samples from preserved bottles (e.g., metals).

For pH, 18 RPDs were between -10 and +10%, however six RPDs were outside of the range -10 and +10%. Four were within the range 10 to 20%, and indeed, two of these were very close to 10%, at 11.3%, 12.2%. Two readings were outside the -20 to 20% range with readings of -25.7 and 21.0. Recordings of pH in the field are typically lower than the laboratory due to carbon dioxide degassing during transport or within the laboratory itself, however, there were two cases where the pH in the field was slightly higher than the laboratory measured pH, but only one was by greater than -10%, at -25.7% (Table 7).

Overall, the %RPDs between the field and laboratory data are considered satisfactory. Field pH is more representative of actual conditions and is used for interpretive purposes.

**Table 7 Field physico-chemical data and Laboratory Reported Values and Calculated % RPD**

Sample Description	Lab pH	Field pH	% RPD
Site T1	6.98	6.5	7.1
US White Bridge	7.04	5.95	16.8
White Bridge	7.15	6.64	7.4
White Bridge GS	6.96	6.45	7.6
DS Deep Adit	4.91	4.99	-1.6
DS Millrace	6.78	6	12.2

Sample Description	Lab pH	Field pH	% RPD
US Ballygahan Adit	7.02	6.27	11.3
US Road Adit	6.38	6.41	-0.5
850 Adit	3.09	2.88	7.0
Avoca Bridge	6.99	5.80	18.6
Cronebane Shallow Adit	2.79	2.55	9.0
Deep Adit (plus 850)	3.13	2.9	7.6
Deep Adit (plus 850) Conf	3.08	2.91	5.7
Road Adit	4.2	3.9	7.4
Road Adit Conf	4.19	4.07	2.9
Site T5	6.37	5.89	7.8
Wicklow County Council Maintenance Yard	6.41	5.96	7.3
GW1/05	3.77	3.6	4.6
GW2/05	3.75	3.58	4.6
MWDA1	3.19	2.97	7.1
MWDA2	3.5	4.53	-25.7
MWET1	3.48	3.30	5.3
MWET2	6.02	6	0.3
MWPF1	5.22	4.23	21.0

**Notes:**

**Red** indicates an exceedance in acceptance limits

## Section 4 Results and Evaluations

This section provides a statistical summary of the analytical results for groundwater and surface water and a comparison of the analytical results against selected assessment criteria. An evaluation of measured concentrations against bioavailable EQS for key parameters is also provided. An analysis of loading and time trends is provided in Section 5 and groundwater levels are discussed in Section 6. All the laboratory reports and analytical data are contained in Appendix D of the Data Report.

### 4.1 Statistical Summary of Analytical Results

#### 4.1.1 Groundwater Sample Results

Table 8 provides a summary of the reported dissolved concentrations of the seven groundwater samples. Included in the table are the minimum, maximum, mean and standard deviation (SDEV). Where the reported values were below the detection limit, the values were substituted with a value of half the limit of detection and used in the statistical calculations. The highest reported value of the field duplicate pair was used where applicable.

**Table 8 Summary of Dissolved Metal Concentrations in Groundwater**

Dissolved Metal	LOD (µg/L)	Number	Number of Detections	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	SDEV
Aluminium	<10	7	7	15	177000	51686	63556
Antimony	<1/<6 <sup>†</sup>	7	0	-	-	-	-
Arsenic	<0.5/<3 <sup>†</sup>	7	5	0.25	8.69	5.1	3.4
Barium	<0.2	7	7	1.47	11.3	7.3	3.4
Cadmium	<0.08	7	7	0.216	89.1	33.4	30.9
Chromium	<1/<6 <sup>†</sup>	7	2	0.5	13.7	-	-
Cobalt	<0.5	7	6	0.25	316	147	109
Copper	<0.3	7	7	7.52	14600	5140	5408
Iron	<19	7	6	9.5	163000	63289	71295
Lead	<0.2/<1.2 <sup>†</sup>	7	6	0.211	288	47.6	107
Manganese	<3	7	7	16.5	32000	10142	10701
Molybdenum	<3/<18 <sup>†</sup>	7	0	-	-	-	-
Nickel	<0.4	7	7	0.401	131	59.4	48.7
Vanadium	<1/<6 <sup>†</sup>	7	0	0.5	3	-	-
Zinc	<1	7	7	21.7	81100	22332	27743

Where result is <LOD, the minimum value is taken to be half LOD

-No data as two or less detections

<sup>†</sup> Two LODs, higher LOD as LOD was raised due to a dilution that was carried out on the sample

High concentrations of dissolved aluminium, cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc were detected in most of the groundwater samples. The shallow well MWPF1, located upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments generally had the lowest concentrations of most dissolved metals with the exception of the lowest concentration of aluminium (15 µg/L) which was recorded in MWET2 and the lowest concentration of copper (7.52 µg/L) which was recorded in MWET2. MWET1 recorded the highest concentration of aluminium (177,000 µg/L), copper (14,600 µg/L) nickel (131 µg/L) and cobalt (316 µg/L). MWDA2 recorded the

highest concentration of zinc (81,100 µg/L) and MWDA1 recorded the highest concentration cadmium (89.1 µg/L). GW1/05 had the highest concentration of dissolved lead (288 µg/L).

These data are consistent with data recorded during low flow sampling in previous years.

#### 4.1.2 Surface Water Sample Results

Surface water samples were collected from six mine adit discharges and 11 locations along the Avoca River. Table 9 provides a summary of the metal concentrations at the adit discharges. Table 10 provides a summary of the dissolved metals in the river samples. Included in the tables are the minimum, maximum, mean and standard deviation (SDEV). Where the reported values were below the detection limit, the values were substituted with a value of half the limit of detection. The highest reported value of the field duplicate pair was used where applicable.

**Table 9 Summary of Dissolved Metal Concentrations in Adit Discharges**

Dissolved Metal	LOD (µg/L)	Number	Number of Detections	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	SDEV
Aluminium	<10	6	6	10900	297000	80433	108228
Antimony	<6/<60 <sup>†</sup>	6	0	-	-	-	-
Arsenic	<0.5	6	6	12.7	88.8	27.8	30.0
Barium	<20	6	6	6.0	19.7	13.3	5.04
Cadmium	<0.08	6	6	17.7	389	115	139
Chromium	<6	6	0	-	-	-	-
Cobalt	<0.5	6	6	71.8	296	112	90
Copper	<0.3	6	6	350	4640	2364	1688
Iron	<19	6	6	44400	188000	70250	57719
Lead	<0.2	6	6	474	958	783	235
Manganese	<3	6	6	2710	9220	4553	2531
Molybdenum	<18/<180 <sup>†</sup>	6	0	-	-	-	-
Nickel	<0.4	6	6	34.4	172	59.6	55.1
Vanadium	<6/<60 <sup>†</sup>	6	0	-	-	-	-
Zinc	<1	6	6	7540	117000	37168	40635

\*Where result is <LOD, the minimum value is taken to be half LOD

-No data as two or less detections

<sup>†</sup> Two LODs, higher LOD as LOD was raised due to a dilution that was carried out on the sample

The concentrations of dissolved aluminium, arsenic, cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc were high in all adit discharges.

The Cronebane Shallow Adit had the highest concentrations of dissolved aluminium (297,000 µg/L), arsenic (88.8 µg/L), copper (4,640 µg/L), nickel (172 µg/L), cadmium (389 µg/L), chromium (30 µg/L), cobalt (296 µg/L), iron (188,000 µg/L), manganese (9,220 µg/L), nickel (172 µg/L) and zinc (117,000 µg/L). The 850 Adit had the highest concentration of lead (958 µg/L).

#### Avoca River

Table 10 provides a summary of the metal concentrations at 11 locations along the Avoca River.

**Table 10 Summary of Dissolved Metal Concentrations in Surface Water**

Dissolved Metal	LOD (µg/L)	Number	Number of Detections	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	SDEV
Aluminium	<10	11	11	119	1010	284	250
Antimony	<1	11	0	-	-	-	-
Arsenic	<0.5	11	11	0.637	0.782	0.703	0.05
Barium	<0.2	11	11	5.0	5.79	5.34	0.254
Cadmium	<0.08	11	9	0.04	2.66	0.55	0.73
Chromium	<1	11	0	-	-	-	-
Cobalt	<0.5	11	7	0.25	2.51	0.76	0.67
Copper	<0.3	11	11	1.37	80.4	19.9	22.3
Iron	<19	11	11	0.425	608	213	175
Lead	<0.2	11	11	2.06	17.8	4.70	4.47
Manganese	<3	11	11	5.78	88.1	34.4	27.7
Molybdenum	<3	11	0	-	-	-	-
Nickel	<0.4	11	11	0.538	1.89	0.98	0.38
Vanadium	<1	11	0	-	-	-	-
Zinc	<1	11	11	21.4	913	184	252

\*Where result is <LOD, the minimum value is taken to be half LOD

-No data as two or less detections

The concentrations of dissolved metals upgradient of the mining area, at Site T1, were low and in many cases, below the limit of detection.

The dissolved metal concentrations at US Whites Bridge (365m upstream of Whites Bridge) and Whites Bridge (at the bridge) were very similar, with no significant changes. Whites Bridge is typically the first sampling location along the Avoca River within the mining area where increases in metals concentrations are recorded. Concentrations of aluminium, copper and zinc at Whites Bridge (at the bridge) were 119 µg/L, 1.58 µg/L and 26.8 µg/L, respectively.

The concentrations of dissolved metals were variable along the Avoca River. The highest concentration of many dissolved metals was recorded at DS Deep Adit; however, this was likely due to shore sampling of the incompletely mixed upstream plume of Deep Adit discharge. Excluding this sampling location, the highest concentration of dissolved aluminium (295 µg/L) and copper (26.2 µg/L) was recorded at US Road Adit, and the highest dissolved iron (467 µg/L), lead (5.09 µg/L) and manganese (69 µg/L) were recorded at Site T5. This location is downstream of all known discharges and seeps. The highest concentration of zinc (202 µg/L) was recorded at DS Millrace.

Seeps along the stretch where the Ballygahan Adit point discharge was once located were not visible at the time of sampling due to high water level, however an increase in metal concentrations between US Ballygahan Adit and US Road Adit indicate there are inputs in this stretch. The increase in concentrations of the pertinent metals between US Ballygahan Adit and US Road Adit are as follows; aluminium increased from 254 µg/L to 295 µg/L; copper increased from 23.6 µg/L to 26.2 µg/L; lead increased from 3.01 µg/L to 3.04 µg/L; and zinc increased from 128 µg/L to 142 µg/L. Note, iron remained the same, at 174 µg/L at both locations.

The concentration of metals at Site T5, which is downstream of the mining area and adit inputs were elevated, at 260 µg/L for aluminium, 21.3 µg/L for copper, 467 µg/L for iron, 5.09 µg/L for lead, 69

µg/L for manganese, and 201 µg/L for zinc. The concentrations of all metals decreased between Site T5 and Avoca Bridge due to precipitation and attenuation, however, the concentrations of many of the dissolved metals remained elevated at this site, particularly aluminium at 239 µg/L, copper at 17.5 µg/L, lead at 3.92 µg/L and zinc at 151 µg/L.

Note, as referenced above, the samples were collected as grab samples from the riverbank (due to high flows) and may not be representative of concentrations across the entire depth and width of the river. The results are potentially biased high where samples were collected downstream of discharges and on the same side of the river as the discharge, as was the case for:

- D/S Deep Adit and D/S Millrace which are both downstream of and on the same bank as the Deep Adit confluence;
- U/S Road Adit which is downstream and on the same bank as Ballygahan Adit (though it was not located); and
- Wicklow County Council Maintenance Yard and Site T5 which are both downstream and on same bank as Road Adit Confluence.

These findings are discussed in Section 5 where an evaluation of dissolved metal loadings is provided.

## 4.2 Assessment Criteria

### 4.2.1 Groundwater and Surface Water Assessment Criteria

Criteria have been selected to assess the groundwater and surface water data for impact on ecological and human health. The environmental quality standards (EQS) from the European Communities Environmental Objectives (Surface Water) Regulations, 2009 (S.I. 272 of 2009) and amendments provide ecological criteria (Table 11). These include standards for physico-chemical conditions supporting the biological elements, general conditions and standards for specific pollutants. In the case of metals, the EQS refers to the dissolved concentration. The EQS provides an annual average (AA), maximum allowable concentration (MAC) or a 95 percentile (95%-ile). Data are assessed against the MAC or 95%-ile, where possible, as they are the most appropriate for assessment of one value. The AA is used for arsenic, chromium, copper and zinc as there is no specified MAC or 95%-ile. Nickel and lead are also compared to the AA to assess these parameters against the bioavailable EQS (S.I. No. 386 of 2015). To supplement the Irish legislation, screening criteria from Oak Ridge National Laboratory (Suter and Tsao, 1996) were used for aluminium, barium, cobalt, manganese and uranium (Table 11).

Hardness is taken into account when selecting the appropriate EQS value for hardness-dependent metals (copper, zinc and cadmium). The average hardness in the rivers and streams in the Avoca mining area is 31 mg/L CaCO<sub>3</sub> (CDM, 2008) and the appropriate ecological assessment criteria are highlighted in bold in Table 11.

To assess the potential human health risks, the Drinking Water Regulations, 2014 (S.I. No. 122 of 2014) and amendments are utilised and listed in Table 11. These values are the maximum permissible values for a drinking water source. In the case of metals, the standards are for total metals, however, they apply to post-treatment (including filtration) and therefore the dissolved portion is used in the assessment in Section 4.

The Drinking Water Regulations set limits for iron and manganese, but they are categorised as “indicator parameters”. Indicator parameters are not considered to be important human health criteria but rather exceedances can affect the aesthetic quality of drinking water supplies. Iron and manganese are commonly found above the drinking water limit in groundwaters in Ireland and are intermittently above the standard in some surface waters.

The two main receptors for groundwater in the Avoca mining area are surface water bodies and the groundwater resource as a drinking water supply. Therefore, to assess the potential impact of the groundwater quality on relevant groundwater receptors, the same standards and guidelines as discussed for surface water are employed for screening purposes for groundwater (Table 11 and Table 12).

**Table 11 Surface Water and Groundwater Assessment Criteria for Biological Elements**

Parameter	Unit	AA	MAC (or 95%ile)	Source	Description
Ammonia as N	mg/L	0.065	0.14	S.I. No. 272 of 2009	Good status
pH	pH units		> 4.5 and < 9.0	S.I. No. 272 of 2009	Within range
Dissolved Oxygen	% Sat		80 to 120	S.I. No. 272 of 2009	Within range. Only relevant to surface water
Arsenic	µg/L	25	-	S.I. No. 272 of 2009	
Cadmium	µg/L	≤0.08 (Class 1) 0.08 (Class 2) 0.09 (Class 3) 0.15 (Class 4) 0.25 (Class 5)	≤ <b>0.45</b> (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)	S.I. No. 386 of 2015	Hardness measured in mg/L CaCO <sub>3</sub> (Class 1: <40 mg CaCO <sub>3</sub> /l, Class 2: 40 to <50 mg CaCO <sub>3</sub> /l, Class 3: 50 to <100 mg CaCO <sub>3</sub> /l, Class 4: 100 to <200 mg CaCO <sub>3</sub> /l and Class 5: ≥200 mg CaCO <sub>3</sub> /l)
Chromium	µg/L	3.4	-	S.I. No. 272 of 2009	
Copper	µg/L	<b>5</b> or 30	-	S.I. No. 272 of 2009	5 µg/L applies where the water hardness measured in mg/L CaCO <sub>3</sub> is ≤ 100; 30 µg/L applies where the water hardness > 100 mg/L CaCO <sub>3</sub> .
Lead	µg/L	1.2 [1]	14	S.I. No. 386 of 2015	Bioavailable EQS
Nickel	µg/L	<b>4</b> [1]	34	S.I. No. 386 of 2015	Bioavailable EQS
Zinc	µg/L	8 or <b>50</b> or 100	-	S.I. No. 272 of 2009	8 µg/l for water hardness with annual average values ≤ 10 mg/L CaCO <sub>3</sub> ; 50 µg/l for water hardness > 10 mg/L CaCO <sub>3</sub> and ≤ 100 mg/L CaCO <sub>3</sub> ; and 100 µg/l elsewhere.
Supplementary standards:					
Aluminium	µg/L	-	1900	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Barium	µg/L	-	4	Oak Ridge National Laboratory	Invertebrates and Salmon fish
Cobalt	µg/L	-	5.1	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Manganese	µg/L	-	1,100	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids

Notes:

**Bold text** indicates the criteria selected for assessment for ecological health.

[1] These EQS refer to bioavailable concentrations of the substances.

**Table 12 Surface Water and Groundwater Assessment Criteria for Drinking Water**

Parameter	Unit	Parametric value
pH	pH units	>6.5 to <9.5
Conductivity	mS/cm	2.5
Ammonium	mg/L	0.3
Sulphate	mg/L	250
Aluminium	µg/L	200
Antimony	µg/L	5
Arsenic	µg/L	10
Cadmium	µg/L	5
Chromium	µg/L	50
Copper	µg/L	2,000
Iron	µg/L	200
Lead	µg/L	10
Manganese	µg/L	50
Nickel	µg/L	20

## 4.3 Comparison to Assessment Criteria

The groundwater and surface water data are assessed against the relevant criteria for ecological health and drinking water; this is described in Section 4.2.

Table B-2 in [Appendix B](#) highlights the exceedances of the assessment criteria for groundwater and surface water. The exceedances of the assessment criteria in the rivers and streams are reproduced in Table 13 herein. Exceedances of the ecological assessment criteria are highlighted in purple, exceedances of the drinking water criteria are highlighted in blue, and exceedances of both the ecological and drinking water criteria are highlighted in pink. The parameters for which there were exceedances are listed in this section and the parameters of concern (copper, zinc and lead) are discussed further in the following sections.

### 4.3.1 Groundwater Assessment

#### Monitoring wells

The criteria that were exceeded, the assessment criteria threshold and the number of parameters that exceeded each of the criteria are listed below, noting seven groundwater locations were monitored in total.

Parameters for which there were exceedances of the human health criteria only:

- pH (>6.5, <9.5 threshold, two exceedances);
- Specific conductivity (2.5 mS/cm threshold, two exceedances);
- Sulphate (250 mg/l threshold, six exceedances);
- Aluminium (250 µg, one exceedance); and
- Iron (200 µg/l, five exceedances, however this is an indicative parameter only).

Parameters for which there were exceedances of the **ecological criteria only**:

- Cadmium (0.45 µg/l, one exceedance);
- Cobalt (5.1 µg/l, six exceedances);
- Copper (5 µg/l, two exceedances);
- Lead (1.2 µg/l, two exceedances); and
- Zinc (50 µg/l, six exceedances).

Parameters for which there were exceedances of **both human health and ecological criteria**:

- pH (<4.5, >9.5 threshold, five exceedances);
- Ammonia (0.3 mg/l, two exceedances);
- Aluminium (1900 µg, five exceedances);
- Cadmium (5 µg/l, five exceedances);
- Copper (2000 µg/l, four exceedances);
- Lead (10 µg/l, three exceedances);
- Nickel (20 µg/l, five exceedances); and
- Manganese (1100 µg/l, six exceedances, however, this is an indicative parameter only).

The bedrock monitoring well GW1/05 had higher dissolved metal concentrations than its nested, shallow alluvial well GW2/05.

MWPF1, located upgradient of the Deep Adit area and at the eastern margin of the alluvial aquifer, had much lower metal concentrations than the other wells.

### 4.3.2 Surface Water Assessment

#### Adit Discharges

The concentrations of dissolved metal were high in all adit discharges. The criteria that were exceeded, the assessment criteria threshold and the number of parameters that exceeded each of the criteria are listed below, noting there six adit sites were monitored in total.

Parameters for which there were exceedances of the **human health criteria only**:

- Specific conductivity (2.5 mS/cm, one exceedance);
- Sulphate (250 mg/L, six exceedances);
- Arsenic (10 µg/L, five exceedances); and
- Iron (200 µg/L, however, this is an indicative parameter only).

Parameters for which there were exceedances of the **ecological criteria only**:

- Cobalt (5.1 µg/L, six exceedances);
- Copper (5 µg/L, two exceedances) and
- Zinc (50 µg/L, six exceedances).

Parameters for which there were exceedances of **both human health and ecological criteria**:

- pH: (>4.5, <9, six exceedances);
- Aluminium (1900 µg/L, six exceedances);
- Arsenic (25 µg/L, one exceedance);
- Cadmium (5 µg/L, six exceedances);
- Lead (10 µg/L, six exceedances);
- Manganese (1100 µg/L, six exceedances); and
- Nickel (20 µg/L, six exceedances).

### Avoca River

Table 13 provides a summary of the reported values for Avoca River locations that exceeded the ecological and drinking water criteria. The concentrations of dissolved metals in the Avoca River were low in comparison to the groundwater and adit discharges; however, there were some exceedances of both ecological and drinking water criteria.

The criteria that were exceeded, the assessment criteria threshold and the number of parameters that exceeded each of the criteria are listed below, noting 11 river sites were monitored in total.

Parameters for which there were exceedances of the **human health criteria only**:

- pH (<6.5, >9.5, nine exceedances);
- Aluminium (200 µg/L, seven exceedances);
- Iron (200 µg/L, three exceedances, however, this is an indicative parameter only); and
- Manganese (50 µg/L, three exceedances only, however, this is an indicative parameter only).

Parameters for which there were exceedances of the **ecological criteria only**:

- Cadmium (0.45 µg/L, four exceedances);
- Copper (5 µg/L, eight exceedances);
- Lead (1.2 µg/L, 10 exceedances); and
- Zinc (50 µg/L, seven exceedances).

Parameters for which there were exceedances of **both human health and ecological criteria**:

- Lead (10 µg/L, one exceedance).

**Table 13 Summary of Reported Values for Rivers and Streams and the Surface Water Assessment Criteria**

	Date Sampled	pH (field)	Aluminium (diss.filt)	Cadmium (diss.filt)	Copper (diss.filt)	Iron (diss.filt)	Lead (diss.filt)	Manganese (diss.filt)	Zinc (diss.filt)
Sample Description	Units	pH Units	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Ecological Criteria		4.5 to 9	1,900	0.45	5	-	1.2	1,100	50
Drinking water Criteria		6.5 to 9.5	200	5	2000	200	10	50	-
Site T1	17/08/2021	6.5	136	0.04	1.37	116	2.41	5.78	23.5
US Whites Bridge	17/08/2021	5.95	130	0.04	1.49	119	2.18	6.76	21.4
Whites Bridge	17/08/2021	6.64	119	0.0988	1.58	116	2.06	6.48	26.8
Whites Bridge GS	17/08/2021	6.45	147	0.328	5.41	120	2.99	13	37.8
DS Deep Adit	17/08/2021	4.99	1010	2.66	80.4	608	17.8	88.1	913
DS Millrace	17/08/2021	6	247	0.635	18.6	195	4.27	24.7	202
US Ballygahan	17/08/2021	6.27	254	0.352	23.6	174	3.01	28.6	128
US Road Adit	17/08/2021	6.41	295	0.393	26.2	174	3.04	37.5	142
Wicklow County Council	17/08/2021	5.96	285	0.498	21.6	0.425	4.88	58.4	182
Site T5	17/08/2021	5.89	260	0.571	21.3	467	5.09	69	201
Avoca Bridge	17/08/2021	5.80	239	0.428	17.5	249	3.92	40.5	151

**Notes**

Exceeds Ecological Assessment Criteria

Exceeds Drinking water Assessment Criteria

Exceeds both Ecological and Drinking water Criteria

Where result is less than LOD, value in the table is half LOD

## 4.4 Bioavailable EQS Assessment

As discussed in 4.2, a variety of methods incorporate the relationship between hardness and the chronic effects of metals (such as zinc and copper) into the ecological and drinking water thresholds for the metals; the varying metal concentrations for different hardnesses in Table 11 is one such approach. However, advances in scientific understanding and testing of the toxicity of metals in the environment during the past 10 to 15 years has shown that hardness alone is a poor explanation of chronic effects (Environmental Agency, 2015). The European Union Environmental Objectives (Surface Waters) (Amendments) Regulations (S.I. No 386 of 2015) includes annual average EQS for nickel (Ni) and lead (Pb) in freshwater based on “bioavailable” concentrations. “Bioavailability” under the WFD is a combination of physico-chemical factors governing metal behaviour and the biologic receptor (i.e., the route of entry, duration and frequency of exposure). “Bioavailability” should measure what the ecological receptor in the water actually “experiences” (Environmental Agency, 2015).

A tiered approach to assessing bioavailable EQS has been applied in the UK, as follows (Environmental Agency, 2015):

- **Tier 1:** The annual average concentrations (dissolved) are compared to the current single values  $EQS_{bioavailable}$  for Ni (4 µg/L) and Pb (1.2 µg/L). These values are sometimes referred to as “generic  $EQS_{bioavailable}$ ” or “reference  $EQS_{bioavailable}$ ”. Sites with sample results exceeding the  $EQS_{bioavailable}$  progress to Tier 2. Sites with sample results less than the generic  $EQS_{bioavailable}$  are deemed good chemical status for Ni and Pb. However, other metals should be evaluated (see below).
- **Tier 2:** A user-friendly tool, based on integrated biotic ligand models (BLM) which incorporates site-specific data, is used to calculate local bioavailable metal concentrations and local HC5 values (values derived from ecotoxicological data at the 5<sup>th</sup> percentile of a species sensitivity distribution, i.e., this value protects 95% of the species) or local PNEC (predicted no effect concentration). The HC5, PNEC or similar values are used as the scientific basis for developing the  $EQS_{bioavailable}$ . The calculated local bioavailable metal concentration can be compared to the generic  $EQS_{bioavailable}$  and/or the local  $EQS_{bioavailable}$  (or HC5, PNEC, etc.). If the calculated bioavailable metal concentrations show at risk concentrations or exceed the local  $EQS_{bioavailable}$ , the evaluations proceed to Tier 3. User-friendly tools are available to evaluate Cu, Ni, Zn and Pb.
- **Tier 3:** This tier is for “local refinement” if Tier 2 exceedances are observed. These refinements may include consideration of background metal concentrations and running a full (versus user friendly) BLM. Full version BLMs are available for Cu, Mn, Ni, Pb and Zn.
- **Tier 4:** At this tier, the failure of the site to achieve the  $EQS_{bioavailable}$  has been established and appropriate measures to address the situation may be considered.

### 4.4.1 Avoca River Bioavailable EQS Analysis

Appropriate analytical data were collected at the Avoca mining site to enable evaluations of  $EQS_{bioavailable}$  for selected metals. An example evaluation employing the tier 1 and tier 2 steps is as follows:

Tier 1: The current single values generic EQS<sub>bioavailable</sub> for Ni (4 µg/L) and Pb (1.2 µg/L) were based on the most conservative 5<sup>th</sup> percentile no effect concentrations from data available in EU member states (e.g., 4.0 µg/L for Ni was based on 1,553 measured concentrations from Austria). Compared to previous threshold values (S.I. 272 of 2009), the values for EQS<sub>bioavailable</sub> Ni and Pb are much lower (e.g., 4.0 vs 20 µg/L for Ni; 1.2 vs 7.2 µg/L for Pb). Dissolved Pb in the Avoca River exceeded 1.2 µg/L at all locations, though only one location exceeded the 7.2 µg/L (DS Deep Adit at 105 µg/L). Dissolved Ni concentrations in the Avoca River did not exceed the 4 µg/L value at any location. Overall, Cu and Zn are the metals of most concern in the Avoca River when bioavailable concentrations are compared to local HC5 or EQS concentrations (see below evaluation).

Tier 2: Several user-friendly tools are available to assess EQS<sub>bioavailable</sub> values. For this analysis, at the Avoca site, the Bio-met Bioavailability Tool, Version 5.0, June 2019 ([www.bio-met.net](http://www.bio-met.net)), was used. The spreadsheet calculates bioavailability factors, local HC5 values, risk characterisation ratios and local bioavailable metal concentrations. Cu, Zn and Pb can be evaluated in the current Bio-met model. The local bioavailable metal concentrations are compared to the generic EQS<sub>bioavailable</sub>. The generic EQS<sub>bioavailable</sub> values for Pb is 4 µg/L as discussed above (fixed by the WFD). In addition, generic EQS<sub>bioavailable</sub> values for Cu (1 µg/L) and Zn (10.9 µg/L) are included in the Bio-met Bioavailability Tool, but can be adjusted by the user (note, the current EQS values from Table 11 were used for the comparisons in Table 14,). The local bioavailable metal concentrations can also be compared to the local HC5 concentration (as a surrogate for local EQS<sub>bioavailable</sub>). The required input for the Bio-met tool are pH and concentrations of dissolved metals, dissolved organic carbon and calcium at the site. The evaluations for dissolved lead, copper and zinc, the parameters of concern, are presented in Table 14.

**Table 14 Bio-Met Model Results for all Locations on the Avoca River**

Site	Metal	Measured Conc.	HC5	Bioavailable Conc.	Bioavailable Conc. Exceedance of HC5	Measured Conc. Exceedance of current EQS*	Bioavailable Conc. Exceedance of current EQS*
Site T1	Cu	1.37	17.13	0.08	No	No	No
	Zn	23.5	42.32	6.05	No	No	No
	Pb	2.41	15.4	0.19	No	Yes	No
US Whites Bridge	Cu	1.49	6.79	0.22	No	No	No
	Zn	21.4	21.18	11.01	No	No	No
	Pb	2.18	15.29	0.17	No	Yes	No
Whites Bridge	Cu	1.58	24.18	0.07	No	No	No
	Zn	26.8	25.96	11.25	No	No	No
	Pb	2.06	17.31	0.14	No	Yes	No
Whites Bridge GS	Cu	5.41	18.28	0.3	No	Yes	No
	Zn	37.8	42.32	9.74	No	No	No
	Pb	2.99	15.92	0.23	No	Yes	No
DS Deep Adit	Cu	80.4	8.24	9.76	Yes	Yes	Yes
	Zn	913	21.05	473	Yes	Yes	Yes

Site	Metal	Measured Conc.	HC5	Bioavailable Conc.	Bioavailable Conc. Exceedance of HC5	Measured Conc. Exceedance of current EQS*	Bioavailable Conc. Exceedance of current EQS*
	Pb	17.8	18.21	1.17	No	Yes	No
DS Millrace	Cu	18.6	6.79	2.74	No	Yes	No
	Zn	202	21.18	104	Yes	Yes	Yes
	Pb	4.27	15.29	0.34	No	Yes	No
US Ballygahan Adit	Cu	23.6	11.24	2.1	No	Yes	No
	Zn	128	41.14	33.92	No	Yes	No
	Pb	3.01	15.55	0.23	No	Yes	No
US Road Adit	Cu	26.2	16.04	1.63	No	Yes	No
	Zn	142	42.32	36.58	No	Yes	No
	Pb	3.04	17.53	0.21	No	Yes	No
Wicklow Co.Co. Maintenance Yard	Cu	21.6	6.79	3.18	No	Yes	No
	Zn	182	21.18	93.7	Yes	Yes	Yes
	Pb	4.88	15.55	0.38	No	Yes	No
Site T5	Cu	21.3	6.79	3.14	No	Yes	No
	Zn	201	21.18	103	Yes	Yes	Yes
	Pb	5.09	15.29	0.4	No	Yes	No
Avoca Bridge	Cu	17.5	6.79	2.58	No	Yes	No
	Zn	151	21.27	77.4	Yes	Yes	Yes
	Pb	3.92	15.55	0.3	No	Yes	No

\* 1.2 µg/L for Pb, 50 µg/L for Zn and 5 µg/L for Cu

The bioavailable Cu, Zn and Pb concentrations are significantly less than the measured Cu, Zn and Pb concentrations at all 11 sampling locations (Table 14). For Cu, the HC5 (and potential EQS<sub>bioavailable</sub>) is higher all 11 cases (less stringent) than the current EQS of 5 µg/L. For Zn, the HC5 (and potential EQS<sub>bioavailable</sub>) is lower (more conservative) than the current EQS of 50 µg/L at all locations. More conservative HC5 values are caused by low TOC and pH.

For Pb, the HC5 is in all cases higher (less stringent) than the current bioavailable EQS of 1.2 µg/L.

The last three columns of Table 14 are summarised as follows:

- Number of exceedances when comparing measured concentrations to the current EQS: Cu = 8; Zn = 7; Pb = 11
- Number of exceedances when comparing bioavailable concentrations to the HC5: Cu = 1; Zn = 5; Pb = 0
- Number of exceedances when comparing bioavailable concentrations to the current EQS: Cu = 1; Zn = 5; Pb = 0.

The absence of exceedances for lead when comparing the local HC5 and bioavailable concentrations is due to the much higher HC5 values and much lower bioavailable concentrations of Pb. When considering the bioavailable concentration rather than the measured concentration compared to the current EQS, the number of exceedances decreases from eight to one for copper, from seven to five for zinc and from 11 to 0 for lead. The number of exceedances in zinc were similar across all comparisons; this is due to the very high zinc concentrations (measured and bioavailable).

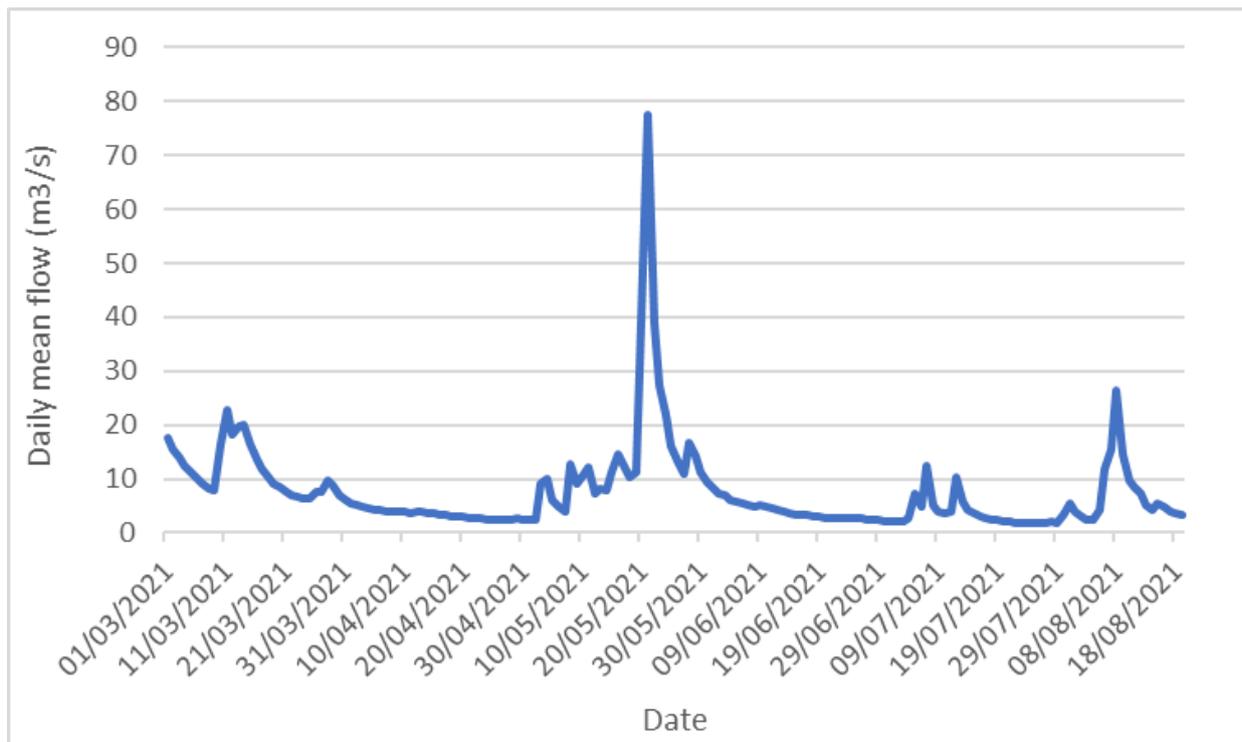
The assessment of bioavailable concentrations indicate that lead is of relatively low concern (due to low bioavailability), while copper, and particularly zinc, are of concern.

## Section 5 Flows, Loads and Trend Analysis

### 5.1 Surface Water Flows

There is one EPA stream flow gauge on the Avoca River near the mine site, Whites Bridge gauging station (GS) (EPA station 10044). There was a second Gauging Station, Wicklow County Council Maintenance Yard GS (EPA Station 10045), however, this was decommissioned in February 2020, and it not included in this report for the purposes of surface water flows. Previous reports have found that the river responds similarly at both gauging stations. Whites Bridge GS is located 90 m downstream of Whites bridge and just upstream of the confluence of the Deep Adit discharge as shown on Map 3 in [Appendix A](#).

Figure 1 shows the flow data (hydrograph) from 01 March 2021 to 19 August 2021 for Whites Bridge GS. The hydrograph shows the flow ranged from a low of approximately 1.67 m<sup>3</sup>/s in late-July to a high of 77.5 m<sup>3</sup>/s in late May. The river is flashy in nature, showing a rapid response to rainfall. The median flow for this period, 4.84 m<sup>3</sup>/s, was nearly half the long-term (2009-2021) median of approximately 8.18 m<sup>3</sup>/s. The lowest flow 1.67 m<sup>3</sup>/s (July) was below the 95%-ile flow (Q95, low flow) for the river (2 m<sup>3</sup>/s).



**Figure 1 Mean Daily Flow (m<sup>3</sup>/s) at Whites Bridge (Station 10044) from 01 March 2021 to 19 August 2021**

Flow was measured in the field as described in Section 2.1.2. Table 15 presents a summary of the results from the flows measured in August 2021. As previously discussed, flow values recorded at the Whites Bridge GS at the time and day of sample collection (see notes for time of collection) were used and reported at a number of locations, as reported in Table 15. Appendix A of the Data Report contains detailed data for each site.

The flow at the Road Adit portal (permanent in-situ flume) was 21.75 L/s, which is within the range of past flows (approximately 6 to 58 l/s (CDM, 2008)). The flow at the Road Adit confluence (flume) was 21.0 l/s. Generally, a small loss in flow is recorded between these two locations, due to loss of flow in the channel and measurement errors.

The 850 Adit discharges to the Deep Adit box culvert and, when flowing, the US Tigroney West drainage channel discharges to the Deep Adit channel directly downstream of the box culvert. Therefore, the flow at the Deep Adit confluence, prior to discharging to the Avoca River, contains the 850 Adit, Deep Adit and US Tigroney West drainage channel, minus any seepage along the channel. There was no flow in US Tigroney West drainage channel at the time of sampling.

The flow at the 850 Adit is recorded by an automatic in-situ recorder installed at the entrance of the 850 Adit in October 2017. Previous data and on-site observations indicated that the in-situ flow meter at the 850 Adit over-estimated the flow. The meter was serviced and calibrated between the Spring and Autumn 2021 monitoring events. The service provider is working with the data to determine a more accurate formula to estimate the flow from the meter. This work was ongoing at the time of production of the report and flow data for the 850 adit had not yet been finalised. The finalised that from this monitoring period should be presented in the next monitoring report. A flow reading was obtained for the sampling event, however, based on visual observation, it is believed that the flow measured by the 850 Adit flow meter in August 2021 was less than the actual flow (i.e., underestimated).

**Table 15 Surface Water Flows Measured in August 2021**

Site Name	Flow m <sup>3</sup> /s	Flow l/s	Date	Method	Notes
Site T1	3.71	3710	17/08/2021	Value for flow estimated to be equal to flow recorded at Whites Bridge GS	GS flow at 13:00
US Whites Bridge	3.71	3710	17/08/2021	Value for flow estimated to be equal to flow recorded at Whites Bridge GS	GS flow at 12:45
Whites Bridge	3.71	3710	17/08/2021	Value for flow estimated to be equal to flow recorded at Whites Bridge GS	GS flow at 11:30
White's Bridge GS	3.71	3710	17/08/2021	Downloaded from EPA Automatic recorder - Whites Bridge GS (Data from EPA)	GS flow at 12:15
DS Deep Adit	3.72	3719	17/08/2021	Value for flow estimated to be equal to flow recorded at Whites Bridge GS (plus Deep Adit Conf. discharge)	GS flow at 12:15
DS Millrace	3.72	3719	17/08/2021	Value for flow estimated to be equal to flow recorded at Whites Bridge GS (plus Deep Adit Conf. discharge)	GS flow at 12:00
US Ballygahan Adit	3.74	3739	17/08/2021	Value for flow estimated to be equal to flow recorded at Whites Bridge GS (plus Deep Adit Conf. discharge)	GS flow at 11:00
US Road Adit	3.74	3739	17/08/2021	Value for flow estimated to be equal to flow recorded at Whites Bridge GS (plus Deep Adit Conf. discharge)	GS flow at 10:45
Wicklow co. co. maintenance yard	3.76	3760	17/08/2021	Value for flow estimated to be equal to flow recorded at Whites Bridge GS (plus Deep Adit Conf. discharge and Road Adit confluence discharge)	GS flow at 10:45
Site T5	3.79	3790	17/08/2021	Value for flow estimated to be equal to flow recorded at Whites Bridge GS (plus Deep Adit Conf. discharge and Road Adit confluence discharge)	GS flow at 10:00
Avoca Bridge	3.82	3820	17/08/2021	Value for flow estimated to be equal to flow recorded at Whites Bridge GS (plus Deep Adit Conf. discharge and Road Adit Confluence discharge)	GS flow at 9:30
850 Adit	0.0033	3.29	18/08/2021	Measured on-site	In-situ flow meter at 10:30
Deep Adit (plus 850)	0.0090	9.0	18/08/2021	Measured on-site	OTT Flow Meter
Deep Adit Confluence	0.0094	9.38	18/08/2021	Measured on-site	Flume
Road Adit	0.0218	21.75	18/08/2021	Measured on-site	Permanently installed flume
Road Adit Confluence	0.0210	21.00	18/08/2021	Measured on-site	OTT Flow Meter
Cronebane Shallow Adit	0.0002	0.18	18/08/2021	Measured on-site	Bucket and stopwatch

## 5.2 Loading Analysis

### 5.2.1 Loading Analysis Methodology

Mass loads (Kg/day) were calculated for the Avoca River, adits and tributaries using flow and concentration data, as follows:

$$\text{Load (Kg/day)} = [C (\mu\text{g/L}) * F (\text{L/day})] / 1,000,000,000 \mu\text{g/kg}$$

where, C = the concentration of the parameter in the water

F = the flow rate of the input

### 5.2.2 Loading Results and Discussion

The calculated mass loads in Table 16 aid with the interpretation of the loading of sulphate and dissolved aluminium, copper, iron, lead and zinc to the Avoca River. From the bioavailability assessment, copper and zinc are the parameters of concern for the Avoca river, and these two parameters are the focus of the below discussion.

**Table 16 Summary of Measured Flows and Concentrations and Calculated Loads of Sulphate and Dissolved Metals in Kg/day in the Adits and Avoca River**

Sample Description	Date Sampled	Flow l/s	pH units	Sulphate		Dissolved Aluminium		Dissolved Copper		Dissolved Iron		Dissolved Lead		Dissolved Zinc	
				µg/L	Kg/day	µg/L	Kg/day	µg/L	Kg/day	µg/L	Kg/day	µg/L	Kg/day	µg/L	Kg/day
Site T1	17/08/2021	3710	6.50	1000	321	136	43.6	1.37	0.439	116	37.2	2.41	0.773	23.5	7.53
Upstream (US) of Whites Bridge	17/08/2021	3710	5.95	1000	321	130	41.7	1.49	0.478	119	38.1	2.18	0.699	21.4	6.86
Whites Bridge	17/08/2021	3710	6.64	1000	321	119	38.1	1.58	0.506	116	37.2	2.06	0.660	26.8	8.59
Whites Bridge Gauging Station GS (10044)	17/08/2021	3710	6.45	1000	321	147	47.1	5.41	1.73	120	38.5	2.99	0.958	37.8	12.1
Downstream (DS) Deep Adit	17/08/2021	3719	4.99	24300	7809	1010	325	80	25.8	608	195	18	5.72	913	293
Downstream (DS) of Millrace	17/08/2021	3719	6.00	6700	2153	247	3374	18.60	5.98	195	62.7	4.27	1.37	202	64.9
Upstream (US) Ballygahan Adit	17/08/2021	3739	6.27	5900	1906	254	82.1	23.60	7.62	174	56.2	3.01	0.972	128	41.4
Upstream (US) of Road Adit	17/08/2021	3739	6.41	7300	2359	295	95.3	26.20	8.46	174	56.2	3.0	0.982	142	45.9
Wicklow Co. Co. Maintenance Yard Gauging Station GS	17/08/2021	3760	5.96	10700	3476	285	92.6	21.60	7.02	425	0	4.88	1.59	182	59.1
Site T5	17/08/2021	3790	5.89	12400	4061	260	85.1	21.30	6.98	467	153	5.09	1.67	201	65.8
Avoca Bridge	17/08/2021	3820	5.80	9000	2971	239	78.9	17.50	5.78	249	82.2	3.92	1.29	151	49.8
Cronebane Shallow Adit	18/08/2021	0.18	2.55	2930000	45.6	297000	4.62	4640	0.072	188000	2.92	905	0.014	117000	1.82
Deep Adit (plus 850)	18/08/2021	9.0	2.90	661000	514	53500	41.6	2880	2.24	45400	35.3	941	0.73	31000	24.1

Sample Description	Date Sampled	Flow l/s	pH units	Sulphate		Dissolved Aluminium		Dissolved Copper		Dissolved Iron		Dissolved Lead		Dissolved Zinc	
				µg/L	Kg/day	µg/L	Kg/day	µg/L	Kg/day	µg/L	Kg/day	µg/L	Kg/day	µg/L	Kg/day
850 Adit	18/08/2021	3.29	2.88	691	196	54600	16	3030	0.86	44400	12.6	958	0.27	29500	8.4
Deep Adit Confluence	18/08/2021	9.4	2.91	687000	557	55600	45.1	2920	2.37	45600	37.0	932	0.755	30100	24.4
Road Adit	18/08/2021	21.8	3.90	701000	1317	11000	20.7	350	0.658	48700	91.5	474	0.891	7540	14.2
Road Adit Confluence	18/08/2021	21.0	4.07	708000	1285	10900	19.8	365	0.662	49400	89.6	488	0.885	7870	14.3

### **Loading from Adit Discharges**

The copper and zinc loads at the 850 Adit were 0.86 and 8.4 Kg/day (however, noting that it is believed that the flow meter underestimated the flow). The copper and zinc loads at the Deep Adit (plus 850) were 2.24 and 24.1 Kg/day. This indicates that the loads of copper and zinc loads from the Deep Adit alone were approximately 1.4 and 15.7 Kg/day.

The Deep Adit Confluence comprises flow from the 850 Adit, Deep Adit and the Tigroney West drainage channel, when flowing. The Tigroney West drainage channel was not flowing at the time of monitoring. Dissolved metals loads at the Deep Adit Confluence were estimated at 2.37 Kg/day for copper and 24.4 Kg/day for zinc. Though not observed during this sampling event, there is generally a decrease in metal loads along the Deep Adit channel which is primarily due to a decrease in flow rate caused by infiltration and precipitation along the channel. The average and median loss of flow between the Deep adit portal (including 850 Adit and discharge from Tigroney West) and the Deep Adit Confluence during high flow seasons from 2015-2020 was 17% (3.33 l/s), with range of 1.2 l/s to 6.4 l/s, or 3% to 31%. There was a slight increase in the flow between the two locations (9.0 l/s at Deep Adit+850 Adit and 9.4 at Deep Adit Confluence), however this marginal decrease may be due to field flow measurement error.

The copper and zinc loads at the Road Adit Confluence were 0.662 Kg/day and 14.3 Kg/day, respectively.

The flow from the Cronebane Intermediate Adit was not sampled due to health and safety concerns over rockfall in the Cronebane pit.

The Cronebane Shallow Adit is considered of minor importance in terms of dissolved metals loads to the Avoca River due to both absence of surface flow to the river and low loads (low flow). The flow recorded in August 2021 (0.18 l/s) resulted in the following loads of dissolved metals; 4.62 Kg/day for aluminium, 0.072 Kg/day for copper and 1.82 Kg/day for zinc. This flow is in line with those previously recorded during low flow, e.g. 0.99 l/s in 2020 and 0.18 l/s in 2019 (note, the flow recorded during low flow monitoring in 2020 was higher than usual, at 0.99 l/s).

The Ballygahan Adit discharge was not located at the time of sampling.

### **Avoca River Loadings**

#### *Background Loadings*

Background metals loads upstream of the Avoca Mining Area were calculated using Site T1 data. Figure 2 and Figure 3 show the loads of dissolved zinc, and copper, respectively, at each location along the Avoca River from Site T1 upstream of the mining area to Avoca Bridge (see also Map 1 and 3 in [Appendix A](#)). Composite samples could not be collected due to the flow conditions and therefore loading estimates contain a relatively high level of uncertainty. It is expected that the concentrations (and thus loads) at DS Deep Adit are elevated due to bank sampling and incomplete mixing of the Deep Adit discharge with the stream at this sampling location, leading to inflated results. Due to the very high concentrations and thus loads of metals in this sample, inclusion of these data in the graphs obscures the information for the other sites. To permit full interpretation of the data, Figure 2 and Figure 3 include the load data for DS Deep Adit, while Figure 4 and Figure 5 exclude the load data for DS Deep Adit.

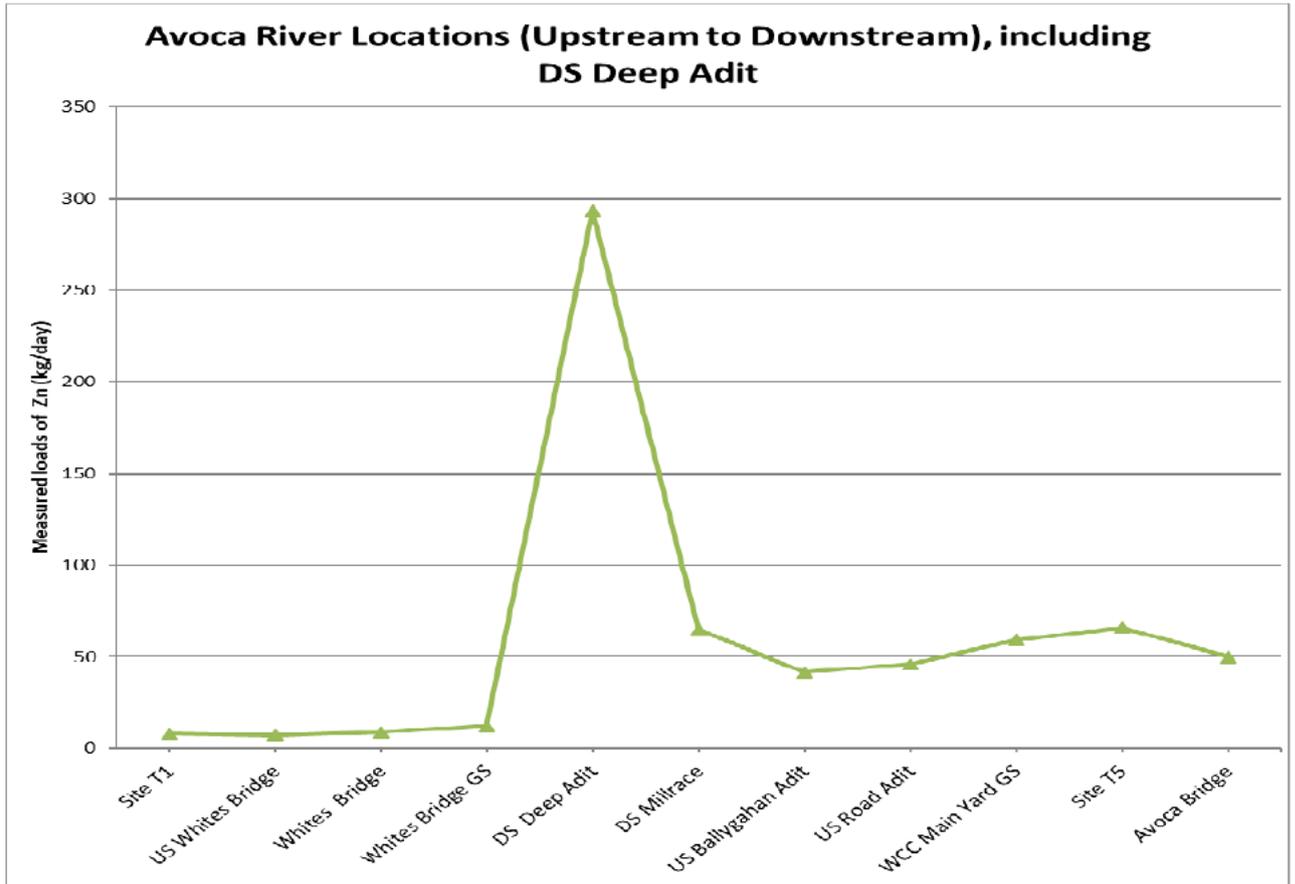


Figure 2 Calculated Loads of Dissolved Zinc (Kg/day) in the Avoca River (including DS Deep Adit) in August 2021

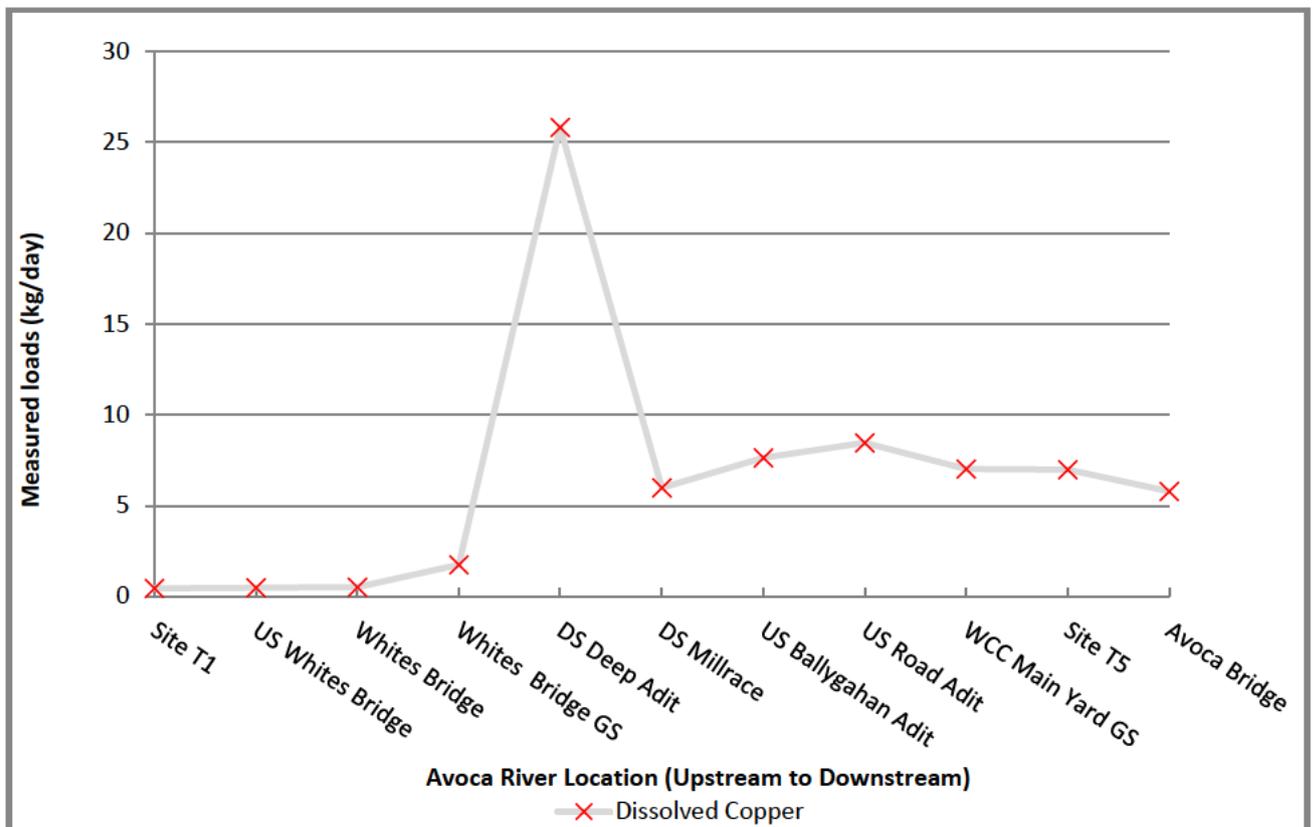


Figure 3 Calculated Loads of Dissolved Copper (Kg/day) in the Avoca River (including DS Deep Adit) in August 2021

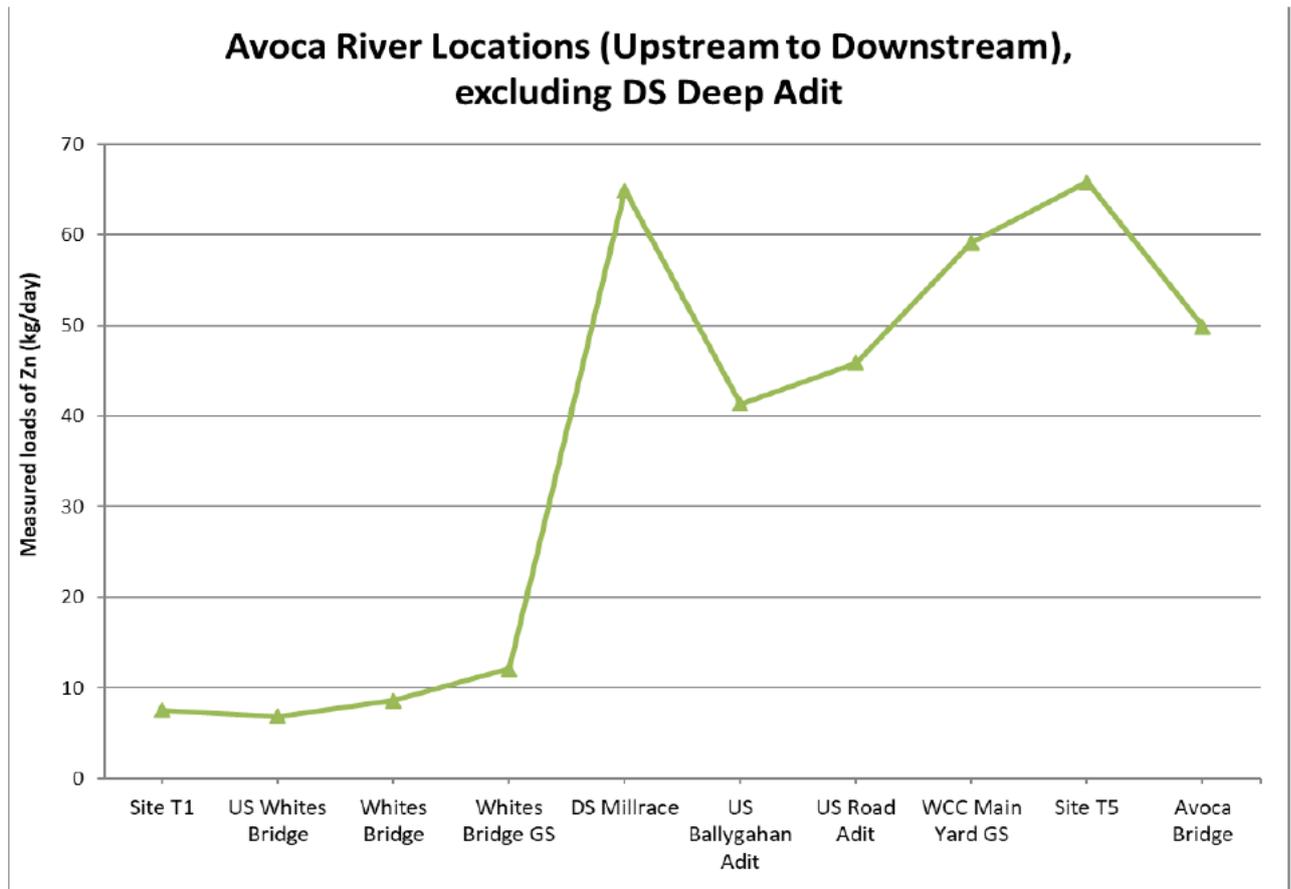


Figure 4 Calculated Loads of and Zinc (Kg/day) in the Avoca River (excluding DS Deep Adit) in August 2021

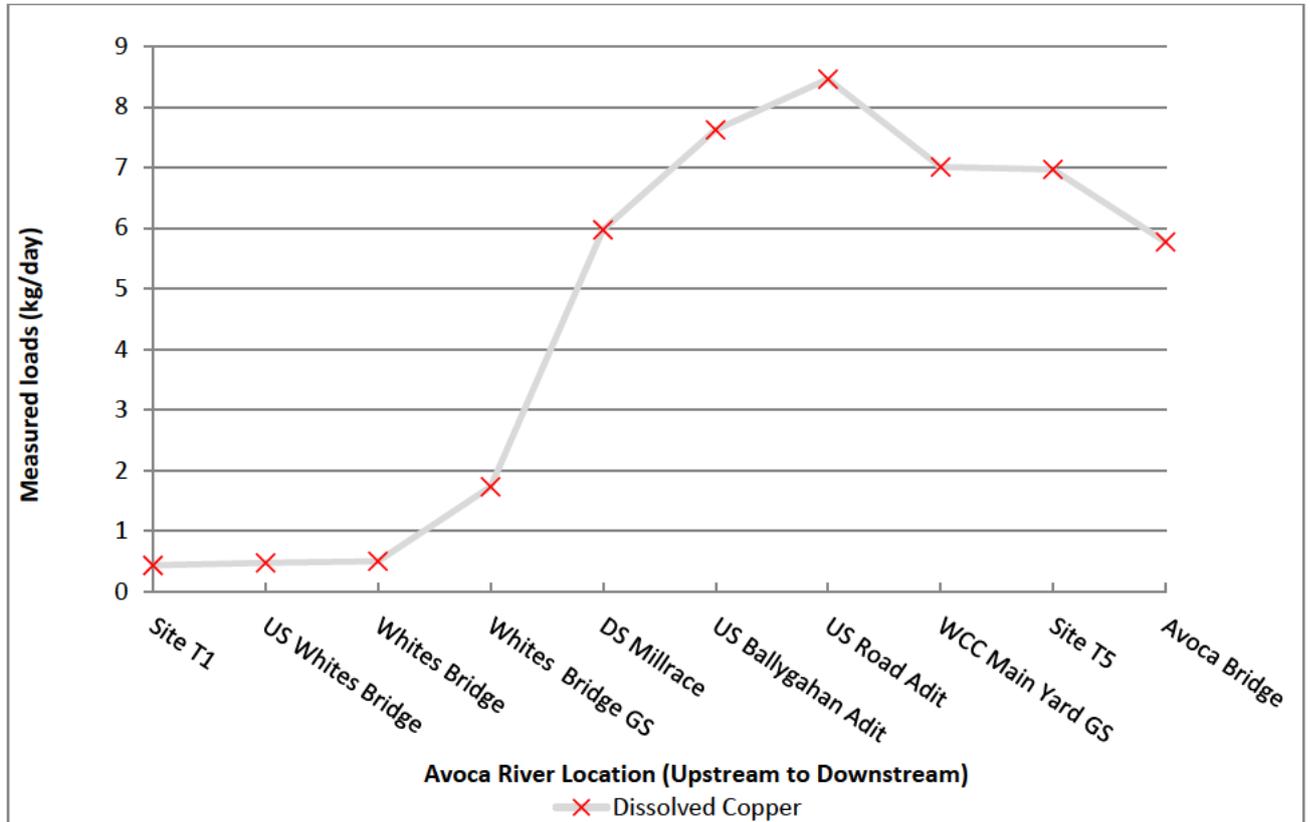


Figure 5 Calculated Loads of Dissolved Copper (Kg/day) in the Avoca River (excluding DS Deep Adit) in August 2021

### *Whites Bridge*

The dissolved metal loads at Site T1, US Whites Bridge and Whites Bridge are comparable. There is little to no increase in metal loads between US Whites Bridge and Whites Bridge. Between Whites Bridge and Whites Bridge GS, there was a slight increase in copper (0.506 Kg/day to 1.73 Kg/day) and zinc (8.59 to 12.1 Kg/day) loads.

### *Deep Adit Discharge and Contaminated Millrace Area*

As previously noted, the DS Deep Adit location on the Avoca River is downstream of where the Deep Adit discharges to the Avoca river (Deep Adit Confluence sample) and also a significant section of the contaminated Millrace area. Therefore, the calculated loads at DS Deep Adit assesses the impact of the Deep Adit discharge and the level of diffuse flow and groundwater contribution from the contaminated Millrace area and Deep Adit spoils. As indicated in Figure 4, there is a significant increase in the loads of all metals at DS Deep Adit compared to the upstream sampling locations. As noted before, it is expected that the concentrations (and thus loads) at DS Deep adit are elevated due to bank sampling and incomplete mixing of the Deep Adit discharge with the stream at this sampling location, leading to inflated results.

The contaminated Millrace area located parallel to the Avoca River extends further downstream than the DS Deep Adit sampling location and therefore a sample was also collected downstream of the Millrace area (DS Millrace). Figure 2 and Figure 3 indicate a large decrease in metals loads between DS Deep Adit and DS Millrace, however, the data from Downstream Deep Adit are inflated due to bank sampling. It is not possible to determine if there is an increase or decrease in loads in this section.

Taking into account (i.e., summing) the load at White Bridge GS and Deep Adit Confluence, the actual versus calculated loads at the DS Millrace are 6.0 Kg/day vs 4.1Kg/day for copper and 64.9 Kg/day vs. 36.5 Kg/day for zinc. This difference between the actual and calculated load of metals indicates loading from diffuse sources along this stretch.

### *Ballygahan Adit and Seeps*

The Ballygahan Adit point discharge could not be located at the time of sampling. However, the US Road Adit monitoring point is downstream of the previous location of the point discharge and presumed downstream of any seeps. There were increases in metal loads between US Ballygahan Adit and US Road Adit (Figure 4 and Figure 5). The load of dissolved copper increased from 7.62 Kg/day to 8.46 Kg/day and the dissolved zinc load increased from 41.4 Kg/day to 45.9 Kg/day. These increases indicate additions of the metals into the Avoca river along this section.

### *Road Adit*

The Road Adit is the primary discharge from West Avoca. The Wicklow County Council Maintenance Yard GS sampling location is located downstream of the Road Adit discharge (since October 2014). The sum of the loading at US Road Adit and at the Road Adit Confluence are approximately equal to the loads at Wicklow County Council Maintenance Yard GS.

There is a slight increase dissolved copper and zinc loads increase between WCC Maintenance Yard GS and Site T5, which may indicate diffuse inputs. Further downstream, the loads of all metals decrease between Site T5 and Avoca Bridge due to precipitation and dilution without additional load inputs.

## 5.3 Trend Analysis

### 5.3.1 Historical Trends

This section discusses concentration time trends for dissolved copper and zinc, as from the bioavailability assessment, these are the parameters of concern, at select locations including the Deep Adit, Road Adit and Avoca Bridge. The trends are shown graphically in Figure 6 (Deep Adit), Figure 7 (Road Adit) and Figure 8 (Avoca River at Avoca Bridge). Data for these locations was collected between 2001 and 2003 as part of another project, however, this data showed large variation relative to the data collected as part of the current project since 2007 (which is relatively consistent). In particular, the earlier data contained some extremely high concentrations that have not been observed since. Thus, Figure 6, Figure 7 and Figure 8 show data from 2001 to 2021, and the trend analyses is calculated on data from 2007 to 2021.

Note, as previously discussed, after the box culvert was constructed in October 2014, the 850 Adit flow and the Deep Adit flow were combined so that measurements at the exit to the box culvert (Deep Adit) reflect the flow from the Deep Adit plus the 850 Adit and US Tigroney West.

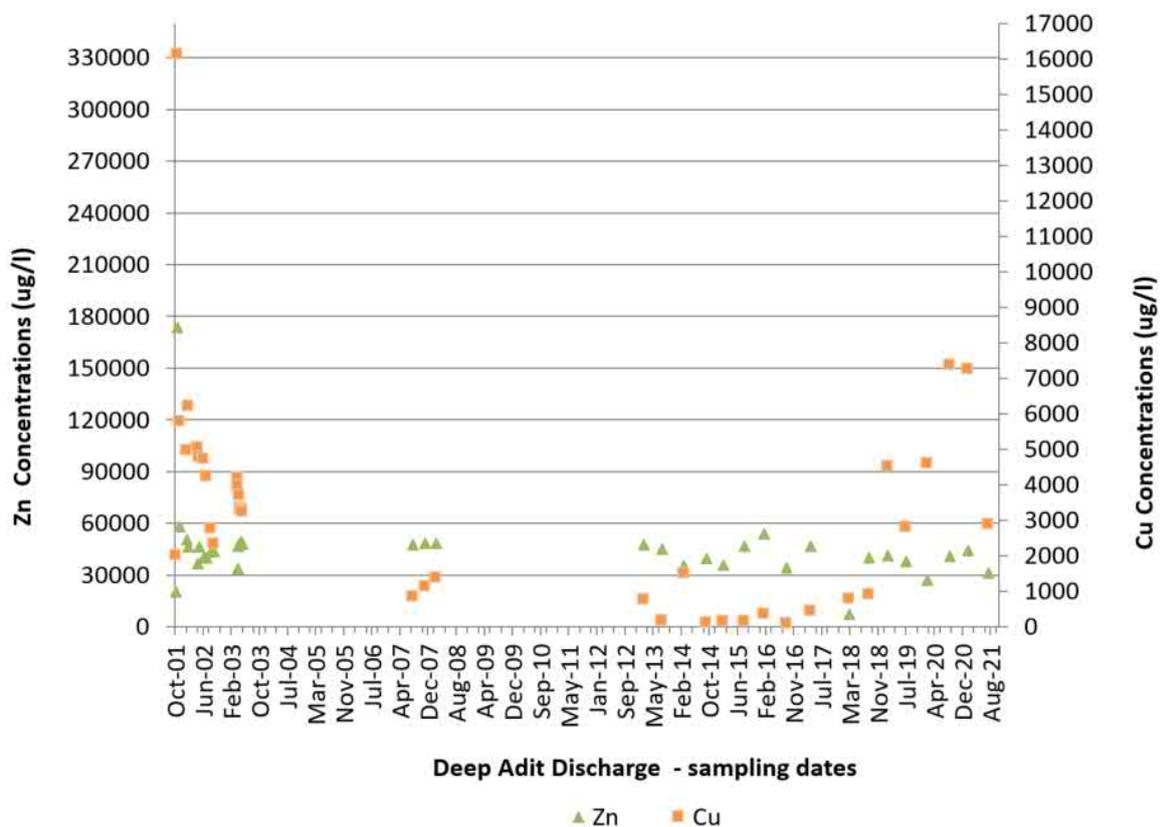


Figure 6 Concentration trends for dissolved copper and zinc within the Deep Adit Discharge (and Deep Adit plus 850 Adit from 2014)

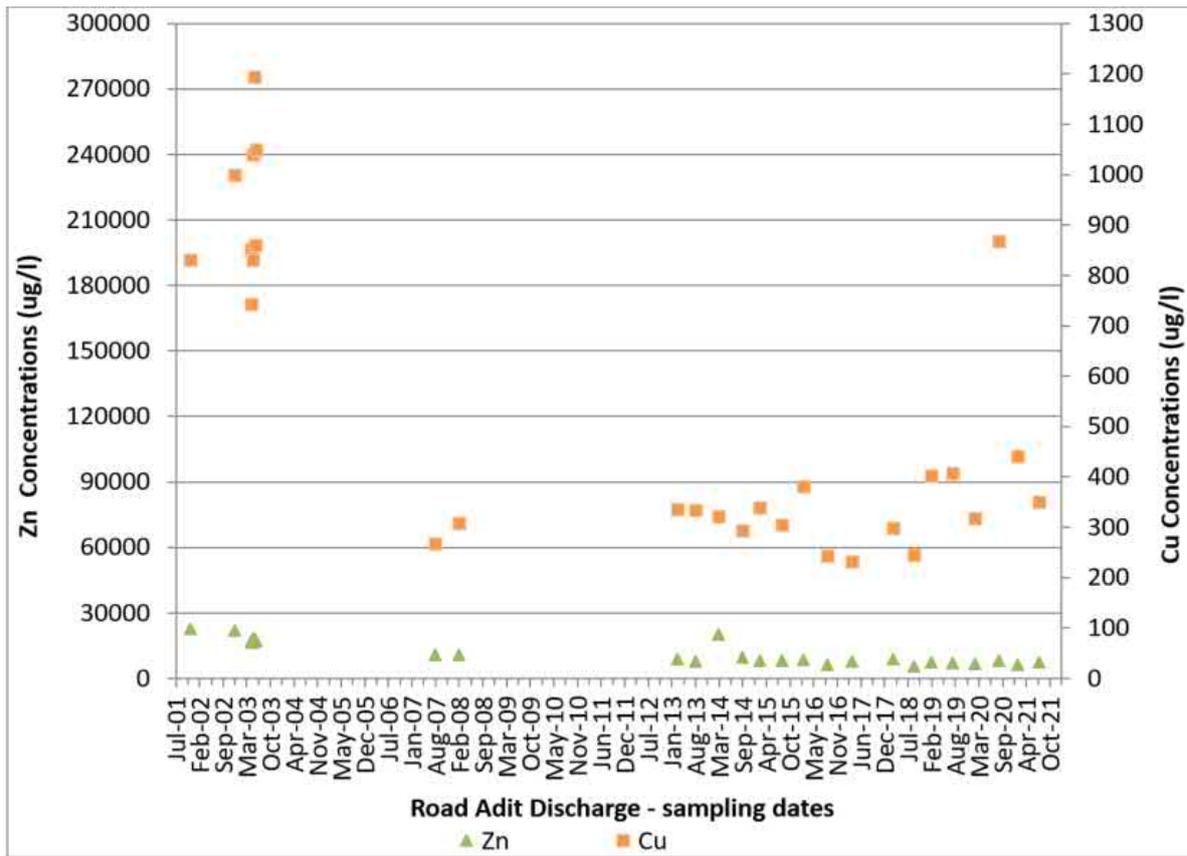


Figure 7 Concentration trends for dissolved copper and zinc within the Road Adit Discharge

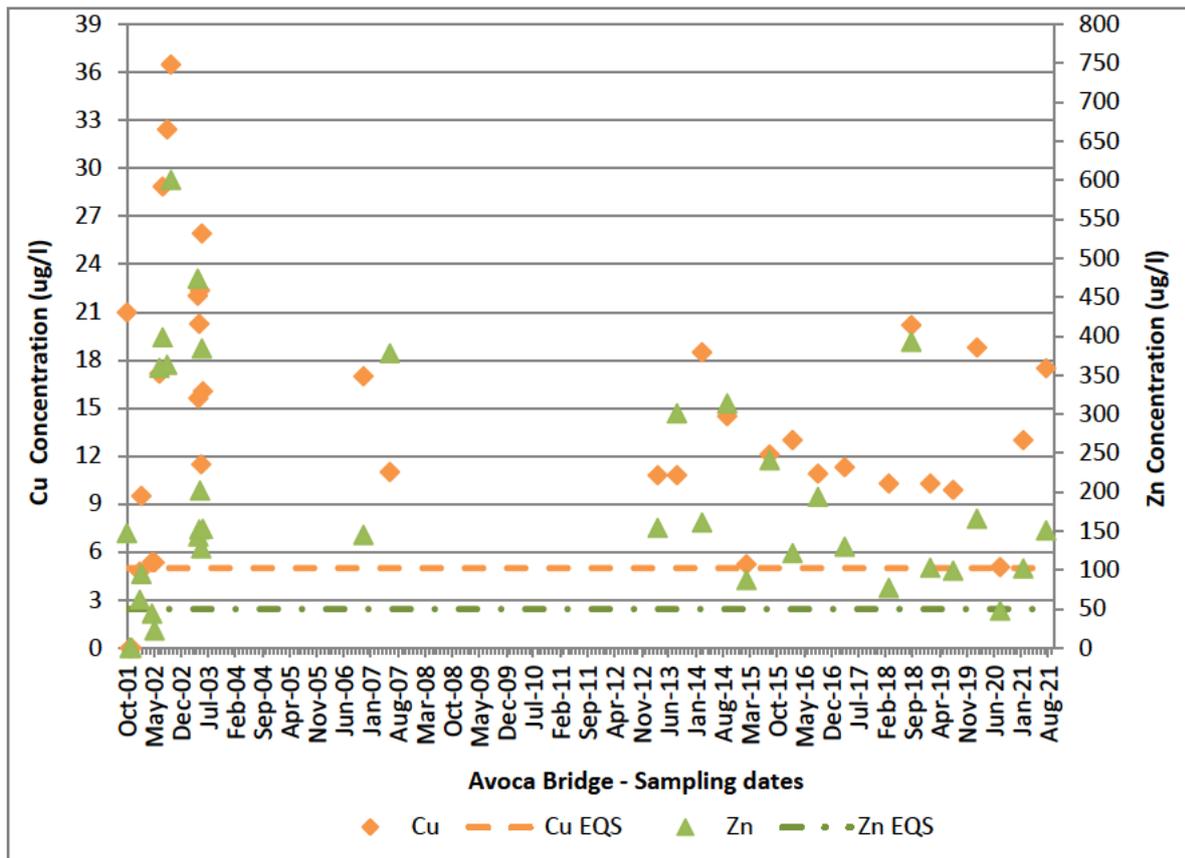


Figure 8 Concentration trends for dissolved copper and zinc at Avoca Bridge compared with the environmental quality objective (EQS)

The Mann-Kendall test was performed to assess statistical trends in the water quality data. The Mann-Kendall test is a non-parametric test that is well suited to use in water quality data analysis. The Mann-Kendall test was performed for dissolved copper, zinc and iron.

The Mann-Kendall test identifies a trend (if one exists) and the probability associated with the trend. Table 17 shows the possible outcomes of the Mann-Kendall trend analysis as applied to the water quality data.

Table 17 Reporting the Mann-Kendall Results

Trend	P value	Trend reported as
Decreasing	$p < 0.05$	Decreasing
	$0.05 \leq p < 0.1$	Likely Decreasing
	$p \geq 0.1$	No Trend
Increasing	$p < 0.05$	Increasing
	$0.05 \leq p < 0.1$	Likely Increasing
	$p \geq 0.1$	No Trend
No Trend	$p = 1$	No Trend

Notes:

Null Hypothesis: The null hypothesis is that there is no trend.

The p-value is the probability that the null hypothesis is true.

The confidence coefficient is 0.95.

The Mann-Kendall test requires the following information for a trend to be calculated: A sample size of at least three values and a maximum of 50% of the sample set is reported as non-detect.

Data has been collected since October 2001. The trend analysis is calculated on data from June 2007 to 2021. The Mann-Kendall test results are presented in Table 18 and facilitate general observations about trends in the water quality of the two main adit discharges and the downstream location of Avoca Bridge.

**Table 18 Mann-Kendall Trend Analysis of data for Deep Adit, Road Adit and Avoca Bridge**

Sample location	Parameter	2007 to 2021		
		P value	S value	Trend
Deep Adit	Copper	0.011	72	Increasing
	Zinc	0.013	-70	Decreasing
	Iron	0.037	-56	Decreasing
Road Adit	Copper	0.046	49	Increasing
	Zinc	0.002	-85	Decreasing
	Iron	<0.001	-91	Decreasing
Avoca Bridge	Copper	0.5	0	No Trend
	Zinc	0.024	-53	Decreasing

**Notes:**

The p-value is the probability that the null hypothesis is true.

The confidence coefficient is 0.95.

The results of the Mann-Kendall analysis for 2007 to August 2021 show:

- There is no trend in dissolved copper at Avoca bridge, while it is increasing at the Deep Adit and increasing at the Road Adit. As noted above, the concentration of dissolved copper at Avoca bridge has been above the ecological assessment criteria of 5 µg/L since mid-2002.
- Dissolved iron is both decreasing in the Deep Adit and in the Road Adit.
- Dissolved zinc is decreasing at all three locations. Dissolved zinc has been above the ecological assessment criteria of 50 µg/L at Avoca Bridge since mid-2002, as shown in Figure 9.

Future monitoring data will be incorporated into the analysis to address the cases where there is currently insufficient statistical evidence to detect a trend.

## Section 6 Groundwater Levels and Groundwater-Surface Water Interaction

### 6.1 Groundwater Levels

Groundwater levels were measured at the seven wells using a portable electronic water level recorder. Table 19 provides the measured depth to groundwater and calculated groundwater elevations. All groundwater level data are contained in Appendix A of the Data Report. The groundwater elevations varied between 25.99 and 27.99 m Ordnance Datum (OD) in the Avoca Mining Area. The groundwater elevations were consistent with the hydraulic gradient towards the Avoca River.

**Table 19 Measured Groundwater Levels and Calculated Elevations August 2021**

Borehole Identifier	Date	Time	Depth to Groundwater (m bTOC)	Depth to Groundwater (m bgs)	Groundwater Elevation (m OD)
MWPF1	16/08/2021	10:23	5.03	4.46	26.46
MWDA2	16/08/2021	10:57	6.32	5.59	26.30
MWDA1	16/08/2021	11:14	4.80	4.20	27.99
MWET2	16/08/2021	12:33	7.30	6.71	26.07
MWET1	16/08/2021	12:37	7.40	6.70	25.99
GW1/05	16/08/2021	13:40	3.20	2.56	27.60
GW2/05	16/08/2021	14:03	3.40	2.57	27.55
SG104	16/08/2021	14:18	Well dry		

**Notes:**

m is metres

OD is Ordnance Datum

bTOC is below top of casing

bgs is below ground surface

The five monitoring wells (MWs) owned by the Department and listed in Table 19 have been equipped with automatic pressure transducers and loggers. It is known that all groundwater flow contours are toward the Avoca River, i.e., the direction of groundwater flow is toward the Avoca River.

Table 19 shows that the groundwater heads of the shallow alluvium monitoring well MWDA1 are higher than the heads of its nested well-pair in the deeper alluvium MWDA2, which suggests an apparent downward hydraulic gradient between the pair. This infers that groundwater containing high concentrations of dissolved metals in the spoils discharge into the alluvial aquifer.

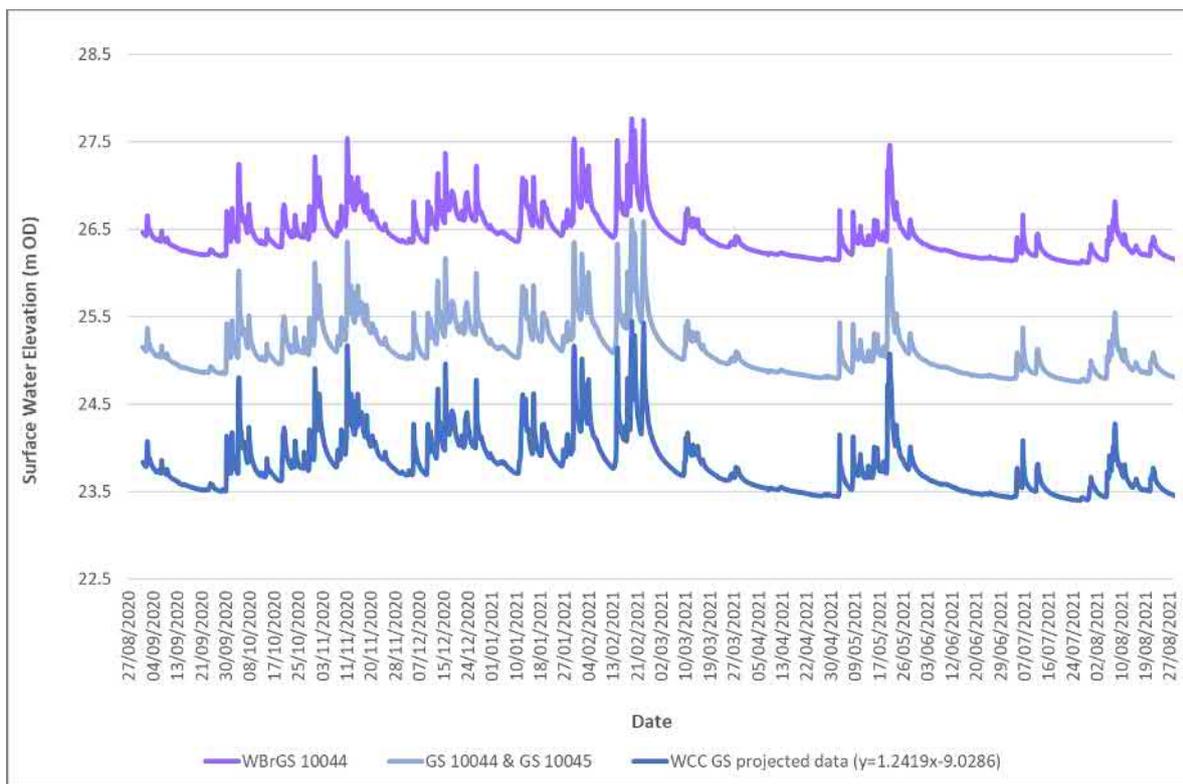
Opposite to MWDA1 and MWDA2, the head is slightly higher in the deep well MWET2 compared to the shallow monitoring well MWET1.

GW1/05 and GW2/05 are located closer to the western alluvial margin, and approximately 95 m to the south-southeast of the MWET1/ET2 well cluster. The groundwater elevation recorded in August 2021 in the alluvial well GW2/05 (27.55mOD) and top of bedrock well GW1/05 (27.860 mOD) were very similar.

## 6.2 Surface Water Levels

As described in Section 5.1 Surface Water Flows, there were two EPA stream flow gauges on the Avoca River near the mine site: Whites Bridge GS (EPA station 10044) and the Wicklow County Council Maintenance Yard (EPA Station 10045). Wicklow County Council Maintenance Yard (EPA Station 10045) was decommissioned in February 2020. Hourly water level data for Whites Bridge GS (EPA station 10044) for the entire monitoring period were obtained from the EPA. Previous data has shown that the river responds similarly at both gauging stations. An analysis of previous water level data for the two locations found there was a predictable relationship between the water level at Whites Bridge GS (EPA station 10044) and the Wicklow County Council Maintenance Yard (EPA Station 10045);  $y=1.2419x-9.0286$ , where  $y$  is the level at Wicklow County Council Maintenance Yard and  $x$  is the level at Whites Bridge GS, with excellent correlation between values ( $r^2=1$ ). This equation was used to predict the Wicklow County Council Maintenance Yard using the Whites Bridge GS levels. The distance between the two gauging stations is approximately 470 metres. The measured and extrapolated water elevations from 01 September 2020 to 31 August 2021 are reproduced in Figure 9. The calculated elevations (average) of the Avoca River at the mid-point between the two automatic flow gauges are also shown in Figure 11.

Previous data has shown that the average gradient between the two gauges is 0.006. Streambed characteristics and the elevations both influence the flow rates and help define any apparent losses or gains in river flow.



**Figure 9 Elevation of the Avoca River at GS 10044 Whites Bridge and GS Wicklow County Council Maintenance Yard 10045 (projected) and their interpolated mid-point level to represent the river at the Deep Adit Area from 01 September 2020 to 31 August 2021**

## 6.3 Groundwater-Surface Water Interaction

Groundwater gradients to the Avoca River were calculated using the estimated groundwater elevations and corresponding river water elevations for the same date and time. The locations of the monitoring wells with respect to the gauging station locations on the Avoca River are shown on Map 3 in [Appendix A](#). The appropriate river gauges were selected as follows:

- For MWDA1, MWDA2 and MWPF1, the river water elevation was taken from the EPA gauge located at Whites Bridge GS (GS 10044);
- MWET1, MWET2, GW1/05 and GW2/05 are approximately equidistant between the two gauges. To take account of the gradient between the two gauges, the river water elevation can be estimated using the Whites Bridge GS (GS 10044) and the projected Wicklow County Council Maintenance Yard GS (GS 10045) by selecting a midpoint water level; and
- For SG104 the predicted water elevation from Wicklow County Council Maintenance Yard (GS 10045) would be used; however, the monitoring well was dry at the time of sampling.

Table 20 summarises the resulting hydraulic gradient data between the monitoring well clusters and the Avoca River during the sampling event (16 August 2021) and shows an estimated gradient from the wells to the river at the time of sample collection.

These values are all positive, i.e., the direction of flow is from the groundwater towards the river. The gradients are comparable to those recorded during previous years low flow sampling campaigns carried out in August/September, and of greater magnitude than the values generally recorded during high flow monitoring.

**Table 20 Groundwater Gradients in August 2021**

Borehole Identifier	Date	Time	Groundwater Elevation (m OD)	Water Elevation at Perpendicular Stream Point (m OD)	Distance to Perpendicular Stream Point	Gradient
MWPF1	16/08/2021	10:23	26.46	26.265	40	0.004
MWDA2	16/08/2021	10:57	26.3	26.261	40	0.001
MWDA1	16/08/2021	11:14	27.99	26.261	72	0.043
MWET2	16/08/2021	12:33	26.07*	24.917**	72	0.016
MWET1	16/08/2021	12:37	25.99*	24.917**	44	0.015
GW1/05	16/08/2021	13:40	27.6*	24.915**	74	0.036
GW2/05	16/08/2021	14:03	27.55*	24.915**	74	0.036
SG104	16/08/2021	14:18	Dry	Dry	Not calculated	

\* Monitoring Well elevations were based on a GPS survey and therefore may be less accurate

\*\* Estimated elevations based on two surface water gauges

The hydraulic communication between the river and groundwater is of primary importance in reviewing potential contaminant loads to the river from diffuse groundwater flow. Where a positive hydraulic gradient from the alluvial aquifer to the river is present (i.e., the head in the aquifer is higher than in the river), the Avoca River is a net gaining river.

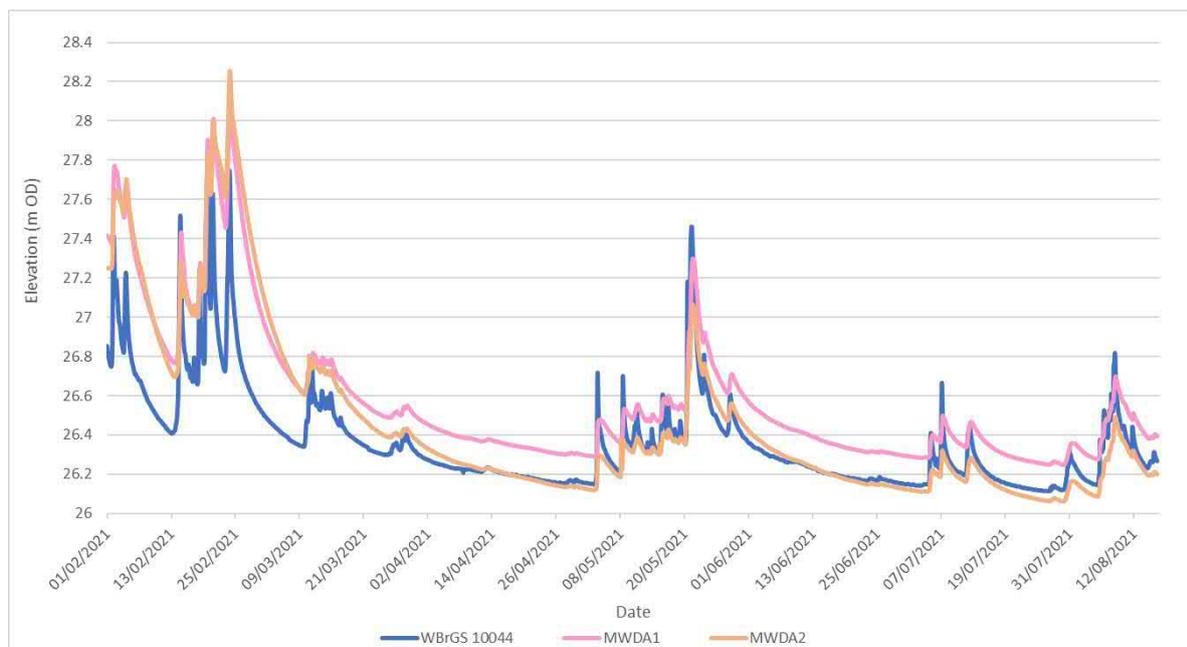
Groundwater elevation data were plotted against the recorded elevations of the Avoca River as shown in Figure 10 for the Deep Adit area and Figure 11 for the Emergency Tailings area. Both

figures demonstrate the direct relationship between the river stage and the groundwater levels in both areas. Rises in river levels are simultaneously accompanied by rises in groundwater levels.

Both figures show that there were several significant hydrological (rainfall) events which resulted in groundwater levels rising. For example, groundwater levels rose by approximately over 75 cm (MWDA1 (78 m) and MWDA2 (60 m)) on 20/21 May 2021. This peak was in response to river levels which rose by 96 cm during the same event. In general, the head observed in the monitoring wells is above the water levels in the river. However, the opposite can occur for major increases of the water level in the river, which follow periods of low to moderate rainfall (illustrated by individual rises in water level).

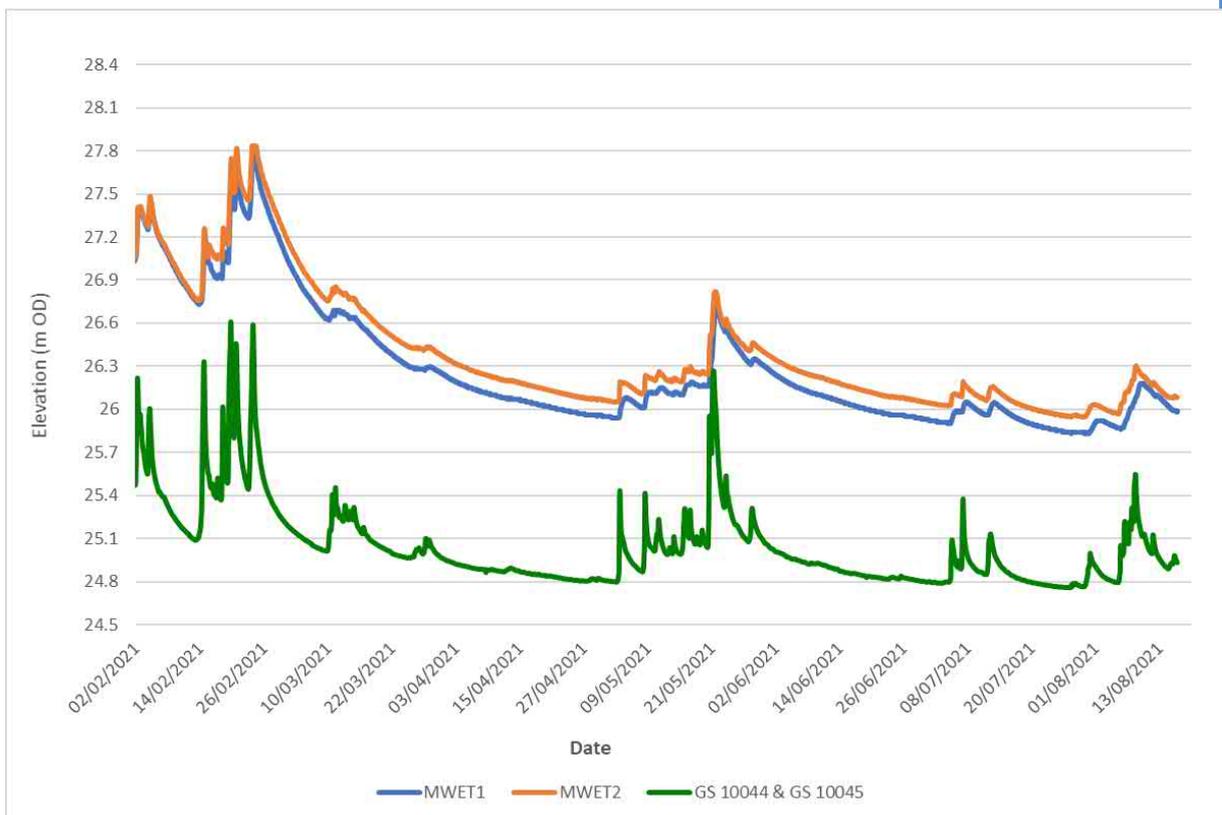
The implication is that the spoil and the alluvial areas on both sides of the river contribute contaminant load to the river. However, Figure 10 (Deep Adit area) shows that a negative gradient occurs on occasion between both MWDA1 and MWDA2 and the river during periods of high flow, particularly when a major rise in river water level follows a period of low or moderate rainfall, as mentioned previously. This phenomenon highlights the slower response of the alluvium compared to the faster response of the river. For example, the rise in river level on 20/21 May 2021 resulted in higher water elevation in the river than in the wells the MWDA2 and MWDA1 wells (i.e., negative gradient), indicating that water moved from river into the surrounding alluvium spoils at this time.

The projected elevation of the river was higher than that of MWDA2 (i.e., negative gradient) occasionally during the monitoring period (Figure 10). In turn, negative gradients occurred infrequently for the shallower well MWDA1. The average gradient at MWDA1 during the period measured was 0.005m. The average positive gradient indicates that shallow groundwater in the Deep Adit area was discharging to the Avoca River for the majority of the monitoring period. The gradient is comparable to that normally measured between the river and MWDA1, allowing climatic variability (rainfall and evaporation) etc.



**Figure 10 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044) at the Deep Adit Area from 01 February to 16 August 2021**

Except for one occasion for MWET1 on 28 July 2021, only positive gradients were observed for MWET1 and MWET2 with a minimum positive gradient of 0.003m (MWET1) and a maximum of 0.029m (MWET2). The average gradients of MWET1 and MWET2 were 0.016 and 0.019 respectively for the period 01 February to 16 August 2021. Note, the elevations are based on the GPS survey of the boreholes and the river water elevations were estimated using both the Whites Bridge GS elevation and the projected Wicklow County Council Maintenance Yard because they are located equidistance between the gauges.



**Figure 11 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044 & 10045) at the Emergency Tailings Area from 01 February to 16 August 2021**

## 6.4 Summary of Diffuse Loading

Diffuse flow from the Avoca mining area discharges to the Avoca River from a combination of sources including groundwater, ditch infiltration and infiltration on spoil piles. This section provides a summary of the evidence of diffuse loading to the Avoca River from three sources, as follows:

- Point source and diffuse loading analysis;
- Groundwater gradients; and
- Surface water flow data at the EPA Gauging Station.

### 6.4.1 Point Source and Diffuse Loading

The analysis of loading to the Avoca River is discussed in Section 5.2.2, Loading Results and Discussion, and can be summarised as follows using the zinc loading as an example:

- Between Site T1 (7.5 Kg/day) to US Whites Bridge (6.9 Kg/day), the zinc load remained approximately the same.
- Between US Whites Bridge and Whites Bridge, the zinc load increased from 6.9 to 8.6 Kg/day which is a 25% increase. Between Whites Bridge and Whites Bridge GS, the zinc load increased from 8.6 to 12 Kg/day, which is an additional 41% increase. The only surface water input in this segment is from the Valeview tributary which discharges negligible zinc to the river and is no longer monitored. This indicates that the increase in loading is due to diffuse sources.
- The zinc load increased from 12 Kg/day at Whites Bridge GS to 293 Kg/day at DS Deep Adit. As discussed, the elevated value at DS Deep Adit was likely due to sampling of an incompletely mixed plume of Deep Adit discharge and collection of a grab sample from the bank vs a composite sample across the river. Therefore, it is more representative to compare the Whites Bridge GS loads with the DS Millrace loads. Between Whites Bridge GS and DS Millrace on the Avoca River, the zinc load increased from 12 to 65 Kg/day, an 436% increase. The Deep Adit (plus 850) contributed 24 Kg/day to the river at the confluence. The remaining load of ~29 Kg/day is due to diffuse flow/loading. This conclusion is supported by the calculated groundwater gradients in this river stretch;
- Between DS Millrace and US Ballygahan Adit on the Avoca River, zinc loads decrease from 65 to 41.4 Kg/day, which is likely due to precipitation and further mixing of the Deep Adit discharge;
- Between US Ballygahan Adit and US Road Adit dissolved zinc increased by 11% from 41.4 to 46 Kg/day. The Ballygahan Adit is located within this river stretch, however, its discharge could not be located in August 2021. This increase in load between these two locations is likely due to input from the Ballygahan adit, and possibly also other seeps;
- Between US Road Adit and Wicklow County Council Maintenance Yard GS, the zinc load increased from 46 to 59.1 Kg/day. As discussed, the elevated value at Wicklow County Council Maintenance Yard GS was likely due to sampling of an incompletely mixed plume of Road Adit and collection of a grab sample from the bank vs a composite sample across the river. Therefore, it is more representative to compare the US Road Adit loads with Site T5 loads. The loads at the Wicklow County Council Maintenance Yard GS would likely be similar to Site T5 or perhaps a little higher due to precipitation. The zinc load at Site T5 was 66 Kg/day. The Road Adit (confluence sample) contributed 14.3 Kg/day of zinc load between these two locations. Thus, the expected load at Wicklow County Council Maintenance Yard GS is 60 Kg/day. The remaining 6 kg is due to diffuse sources in the stretch between US Road Adit and Site T5.
- The zinc load at Avoca Bridge, which is downstream of Wicklow County Council Maintenance Yard, was 50 Kg/day. This shows that there is no significant loading below Wicklow County Council Maintenance Yard. The decrease in load is due to additional precipitation and dilution without additions of metals.

## 6.4.2 Groundwater Gradients

There were some negative gradients for the deeper groundwater well (MWDA2) in the Deep Adit area for periods during the time period, e.g., in May 2021. However, overall, the groundwater

gradients were predominantly positive, indicating that the Avoca River was a net gaining river from the alluvium in the Deep Adit area and the Emergency Tailings area during the monitoring period. The implication is that the spoil and alluvial areas on both sides of the river contribute contaminant load to the river.

### 6.4.3 Surface Water Flow Data at the EPA Gauging Stations

Flow records were examined to examine whether the Avoca River was a losing or gaining river between Whites Bridge GS and the former Wicklow County Council Maintenance Yard GS (see Map 3 in [Appendix A](#) for locations).

Discharge measurements in open channel cross-sections are all subject to some level of error. It is not possible to predict the error, but an indication can be derived from the deviation plots. The deviation plots compare the measured flow against the rating curve flow.

As discussed in the Round 1 report of February 2018, deviation plots were obtained from the EPA for the Whites Bridge GS and the Wicklow County Council Maintenance Yard GS. The total number of flow measurements at Whites Bridge GS was 26 and the difference between the measured flow and the flow rating curve ranged from 0.010 to 1.22 m<sup>3</sup>/s (or 0.1 to 6.7 %). The total number of flow measurements at Council Yard GS was 20 and the difference between the measured flow and the flow rating curve ranged from 0.010 to 0.418 m<sup>3</sup>/s (or 0.4 to 12.7 %).

Data have shown that the mean daily flows at the two gauging stations are relatively similar with the percentage difference ranging from 0 to 16% with an average difference of 6%. It is not possible to draw conclusions using the gauge data as to whether the stretch of river between the two gauges is consistently and in general a gaining or a losing river.

Tracer tests conducted during low flow in 2016 (June – August, when flows ranged from 3.75 to 5.5 m<sup>3</sup>/s) found that the flow between Whites Bridge and downstream of the Millrace increased during two tests (19 to 22 %) and decreased during two tests (-7.3 and -2.2 %). The flow between downstream of the Millrace and downstream of the Road Adit confluence decreased by 10 % during one test. All of these values are within the accuracy of flow measurements and therefore definitive conclusions concerning gaining and losing conditions cannot be made; however, mass balances for copper, iron and zinc showed very significant increases in all four tests between Whites Bridge and downstream of the Millrace (ranging from 59 % to 475 %) and the one test between downstream of the Millrace and downstream of the Road Adit (49 % to 149 %). These tracer test results show that the mass load from diffuse flow is very significant.

### 6.4.4 Diffuse Loading Conclusion

Overall, the interaction between the Avoca River and groundwater is very dynamic. The quantity of diffuse loading varies along each river stretch with the greatest evidence of diffuse loading between Whites Bridge GS and DS Millrace, and US Ballygahan Adit and Upstream Road Adit.

The groundwater gradients are predominantly positive which suggests that the Avoca River is a net gaining river from the alluvium in the Deep Adit area and the Emergency Tailings area during the monitoring period. The implication is that the spoil and the alluvial areas on both sides of the river contribute contaminant load to the river. This is evident in the measured zinc load results during the August 2021 sampling event.

The findings of the August 2021 sampling event are supported by the *Avoca River Tracer Study Report* (Document Ref: 95735/40/DG/31; dated December 2016) which provides a detailed assessment of the extent and location of diffuse contamination. The tracer study found that diffuse flow loading (e.g., groundwater, ditch infiltration, infiltration on spoil piles) accounted for a significant proportion of the total dissolved metal load in the Avoca River. In the upper section of the study area (approximately Whites Bridge to downstream of the contaminated millrace area) diffuse loads were on average, 41%, 46% and 28% of the total load, respectively, for copper, iron and zinc. In the lower section of the study area (approximately downstream of the contaminated Millrace area to the abandoned coal yard), the extent of diffuse loading increased to 51%, 61% and 61% of the total load, respectively, for copper, iron and zinc.

## Section 7 Summary and Recommendations

### 7.1 Summary of Findings

Seven groundwater monitoring wells were sampled in August 2021 (one well was dry). Surface water was sampled at 17 locations, with flow measured at six locations and an EPA gauging station and projected to an additional ten locations from the EPA gauging station. The field QA/QC sample results were reviewed for accuracy and precision. The laboratory QA/QC samples and laboratory reports were also reviewed. Overall, the data quality is considered acceptable, and the data was compared to the assessment criteria and used to perform trend and loading evaluations.

A statistical summary of the analytical results for groundwater and surface water was prepared and results were compared to assessment criteria. Analyses of loading, concentration time trends and groundwater levels were also conducted.

The overall conclusions are as follows:

- The dissolved metal concentrations were elevated in the majority of the monitoring wells and adit discharges with numerous exceedances of ecological criteria, drinking water criteria or both, particularly for dissolved aluminium, arsenic, cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc. Sulphate levels also greatly exceeded the criteria for drinking water in six of the seven monitoring wells and all adit discharges.
- The shallow well MWPF1 located upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments had the lowest concentration of dissolved metals among all the monitoring wells. The highest concentrations of dissolved aluminium, nickel and copper were recorded in MWET1 (Emergency Tailings area), and the highest concentration of dissolved zinc was recorded at MWDA2 (Deep Adit spoils area). The highest concentration of dissolved lead was recorded in GW1/05.
- Of the adits, Cronebane Shallow Adit was the adit discharge with the highest concentrations of dissolved aluminium, copper, cadmium, iron, nickel and zinc. The Cronebane Shallow Adit is of minor importance in terms of metals loads to the Avoca River because of its low flows and the absence of direct flow to the river.
- The highest concentration of dissolved lead was recorded at the 850 Adit.
- The Deep Adit (plus 850) and Road Adit had significant dissolved metal loads which were discharging to the Avoca River. The Deep Adit (plus 850) had copper, zinc and lead loads of 2.24, 24.1 and 0.73 Kg/day, respectively. The calculated loads for the Road Adit were lower at 0.66 Kg/day for copper, 14.2 Kg/day for zinc and 0.891 Kg/day for lead.
- Dissolved metal concentrations in the Avoca River were low in comparison to the groundwater and adit discharges; however, there were multiple exceedances of both the ecological and drinking water criteria, namely for dissolved aluminium, copper, iron, lead, manganese and zinc. Dissolved copper exceeded the ecological criteria (5 µg/L) at Whites Bridge GS and all river locations downstream of this location, with results ranging from 5.41 to 80.4 µg/L. Dissolved zinc exceeded the ecological assessment criteria (50 µg/L) at DS Deep Adit and all downstream river locations with results ranging from 128 to 913 µg/L.

Dissolved lead exceeded the ecological criteria (1.2 µg/L) at all locations on the Avoca River including the upstream location T1. When calculated bioavailable concentrations and local HC5 values are used for evaluations, the number of locations with exceedances for copper and lead reduced significantly. The highest value for dissolved iron (608 µg/L) was recorded at DS Deep Adit. It is noted that the concentrations and loads at this location may be inflated due to sampling of the incompletely mixed discharge plume and bank sampling.

- Evaluations of EQS<sub>bioavailable</sub> for Zn, Cu and Pb were undertaken at the 11 Avoca River monitoring locations. The bioavailable Cu, Zn and Pb concentrations are significantly less than the measured Cu, Zn and Pb concentrations. For Cu, the HC5 (and potential EQS<sub>bioavailable</sub>) is higher in all cases (less stringent) than the current EQS of 5 µg/L. For Zn, the HC5 (and potential EQS<sub>bioavailable</sub>) are lower (more stringent) than the current EQS of 50 µg/L for all locations. For Pb, the HC5 are higher (less stringent) in all cases than the current bioavailable EQS of 1.2 µg/L. The number of exceedances when using the various thresholds (HC5 and EQS) and concentrations (measured and bioavailable) were also compared. When using local HC5 and bioavailable concentrations, there were no exceedances for lead, the number of locations with exceedances for Cu were lower, and the number of locations with zinc exceedances decreased only slightly, by two locations, due to the very high values of measured and bioavailable zinc.
- The Mann-Kendall trend analysis for the period June 2007 to February 2021 indicates there is no trend in dissolved copper at Avoca bridge, while it is increasing at the Deep Adit and increasing at the Road Adit. Dissolved iron is likely decreasing in the Deep Adit and decreasing in the Road Adit, and dissolved zinc is decreasing at all three locations.
- As river stages change, the hydraulic gradients to or from the river also change. Gradients are predominantly positive which suggests that the Avoca River is a net gaining river from the alluvium during the monitoring period. The implication is that the spoil and the alluvial areas either side of the river contribute contaminant load to the river. This is especially evident in the measured zinc load results, in the stretches of river between Whites Bridge GS and DS Millrace, and US Ballygahan Adit and Upstream Road Adit.

## 7.2 Recommendations for the Monitoring Programme

It is recommended that monitoring be continued to assess point and diffuse discharges to the Avoca River.

## Section 8 References

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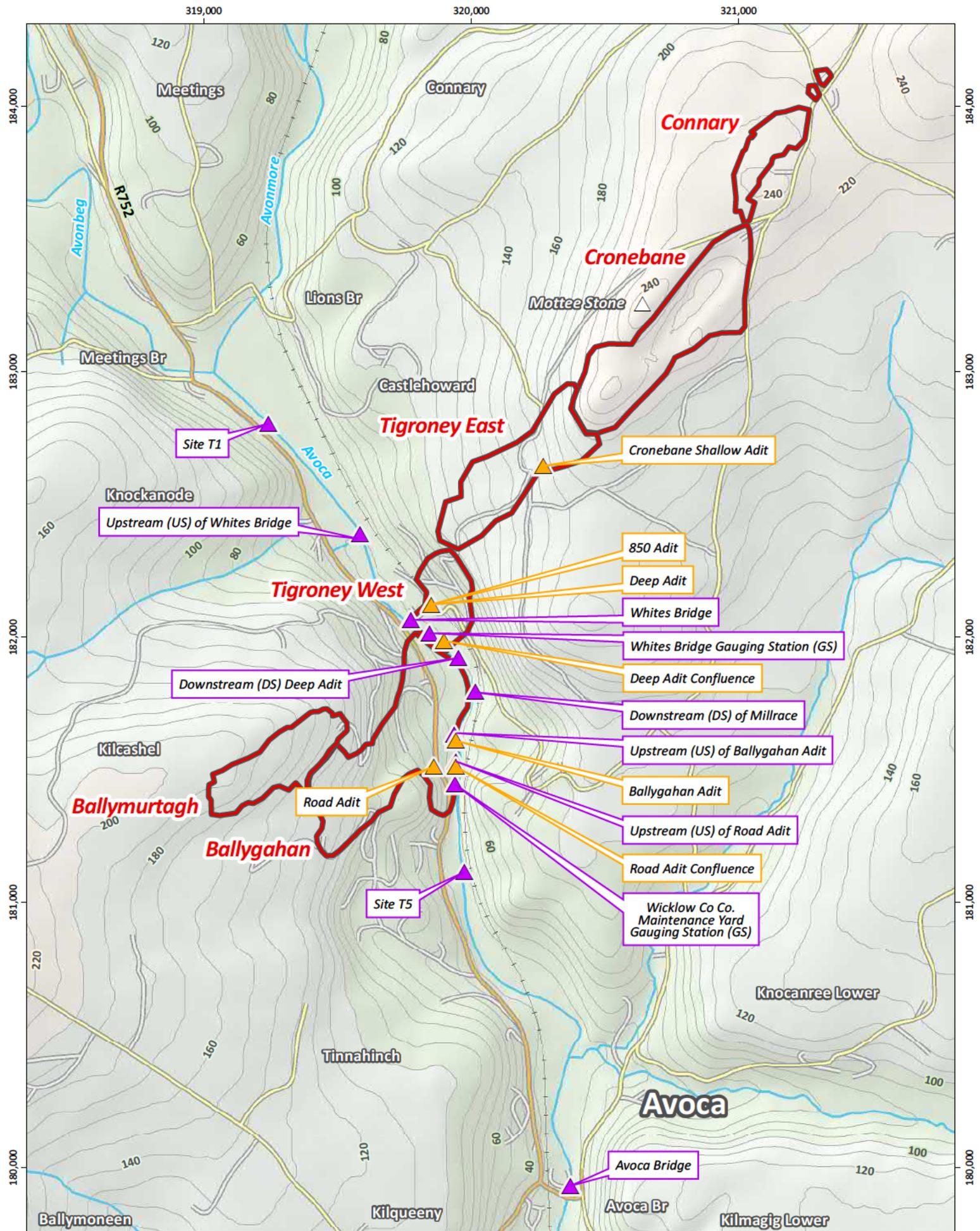
Hedberg, Y., Herting, G. and Odnevall Wallinder, I. (2011). Risks of using membrane filtration for trace metal analysis and assessing the dissolved metal fraction of aqueous media. A study on zinc, copper and nickel. *Environmental Pollution*, 159, 1144-1150.

Suter, G.W. II and Tsao, C.L. (1996). Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Aquatic Biota: 1996 Revision. Oak Ridge, Tennessee: Oak Ridge National Laboratory.

# Appendix A

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## Figures



### Map 1 - Avoca - Main Area

Drawn by: SM Date: 01/02/2021  
 Internal Project Reference: Q:\118000-118499\118174\40 Documents Generated\GIS\02\_GIS\_Tasks\01\_Monitoring\_Plan\_Report\_2020\MXD\01\_AvocaMon1.mxd  
 Source: © Ordnance Survey Ireland. All rights reserved. Licence No AR 0095918



### Legend

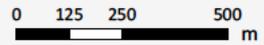
#### Sampling Locations

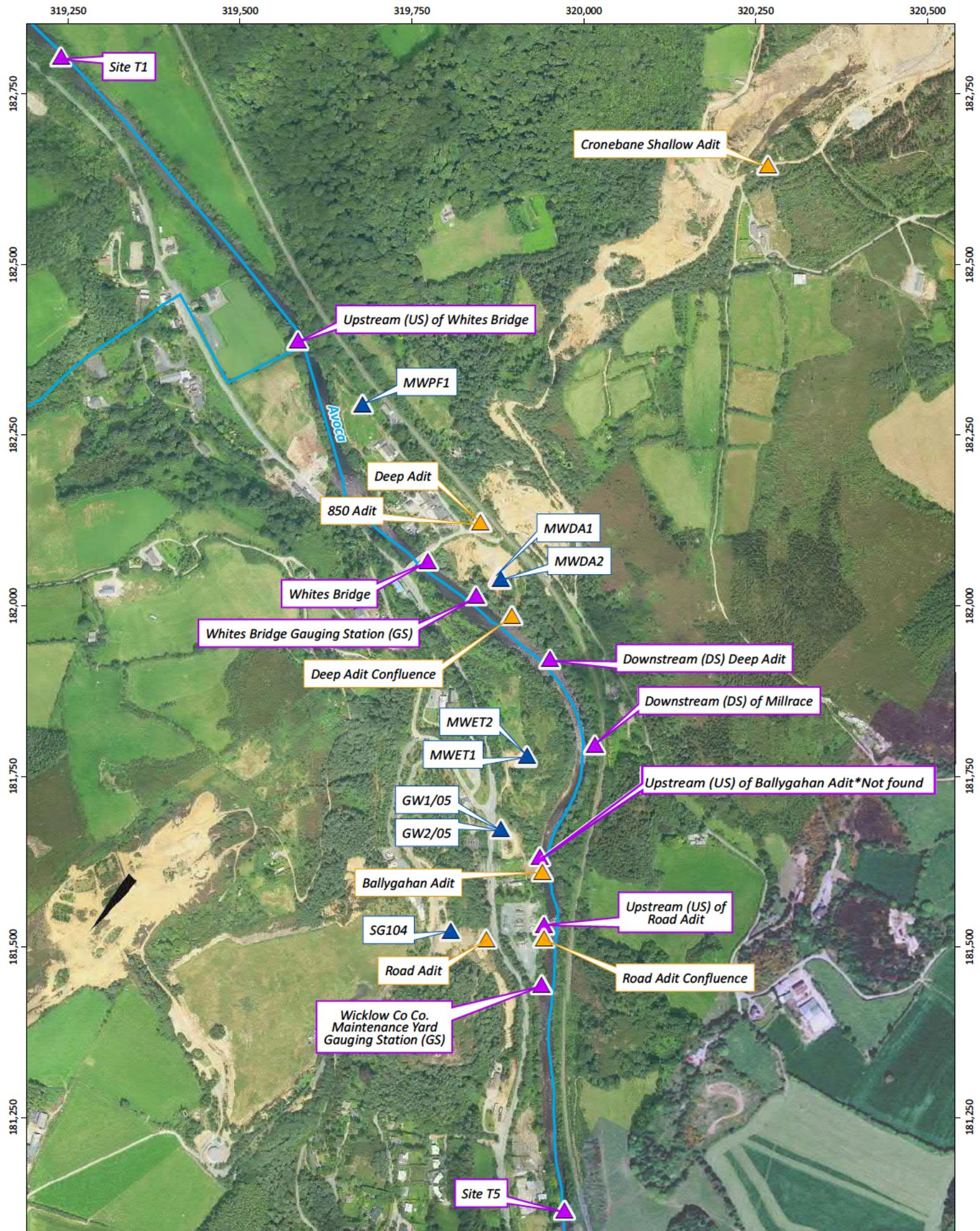
- ▲ Surface water (Rivers and Streams)
- ▲ Surface water (Adit discharges)

#### Mines

- ⬭ Mining Area
- Rivers

Scale is 1:18,000





### Map 3 - Avoca - Main Area - Surface Water and Groundwater

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 Internal Project Reference: Q:\118000-118499\118174\  
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 Plan\_Report\_2021\MXD\03\_AvocaMonSWGWMxd  
 Source: © DCENR Lidar Survey (2007)



#### Legend

##### Sampling Locations

- ▲ Surface water (Adit discharge)
- ▲ Surface water (Rivers and Streams)
- ▲ Groundwater (Borehole)

— Rivers



Scale is 1:7,000  
 0 50 100  
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## Appendix B

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### Analytical Data Tables and Assessment Criteria

			Total Organic Carbon	Ammoniacal Nitrogen as N	Oxygen, dissolved (field)	Specific Conductance @ 25°C (field)	Sulphate	Aluminium (diss.filt)	Antimony (diss.filt)	Arsenic (diss.filt)	Barium (diss.filt)	Cadmium (diss.filt)	Calcium (diss.filt)	Chromium (diss.filt)	Cobalt (diss.filt)	Copper (diss.filt)	Iron (diss.filt)	Lead (diss.filt)	Manganese (diss.filt)	Molybdenum (diss.filt)	Nickel (diss.filt)	Vanadium (diss.filt)	Zinc (diss.filt)	
Units			mg/l	mg/l	% Sat	pH (in ts)	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	
Ecolog cal Criteria			0.14	80 to 120*	4.5 to 9	2.5	250	300	5	25	4	0.45	-	3.4	5.1	5	-	1.2	1100	-	20	-	50	
Human Health Criteria			0.3	80 to 120*	6.5 to 9.5	2.5	250	300	10	25	4	5	-	50	-	2000	200	20	50	-	20	-	-	
Sample Description	Type	Date Sampled																						
Site T1	R ve	17/08/2021	6.39	0.1	88.2	6.5	0.046	1	136	0.5	0.217	5.79	0.04	2720	0.5	0.25	1.37	116	2.41	5.78	1.5	0.227	0.5	23.5
US Wn tes B - dee	R ve	17/08/2021	6.53	0.1	88.3	6.50	0.047	1	130	0.5	0.162	5.37	0.04	2720	0.5	0.25	1.49	115	2.18	6.78	1.5	0.538	0.5	21.4
Wn tes B - dee	R ve	17/08/2021	7.22	0.1	97.7	6.64	0.050	1	119	0.5	0.752	5	0.0988	2740	0.5	0.25	1.58	116	2.06	6.48	1.5	0.684	0.5	26.8
Wn tes B - dee GS	R ve	17/08/2021	6.76	0.1	103	6.45	0.052	1	147	0.5	0.782	5.23	0.328	3020	0.5	0.25	5.41	120	2.99	13	1.5	0.658	0.5	37.8
US Deep Ad 1	R ve	17/08/2021	7.7	0.1	101	4.99	0.079	24.3	3010	0.5	0.617	5.23	7.66	2960	0.5	2.51	80.4	508	17.8	88.1	1.5	1.89	0.5	913
US M 1 - dee	R ve	17/08/2021	6.55	0.1	106	6	0.059	6.7	247	0.5	0.671	5.03	0.036	2880	0.5	0.561	18.6	4.27	24.7	1.5	0.929	0.5	202	
US Ballynaham	R ve	17/08/2021	6.65	0.1	93.8	6.27	0.061	5.9	254	0.5	0.736	5.23	0.352	3090	0.5	0.579	23.6	174	3.01	28.6	1.5	0.93	0.5	128
US Ballynaham Ad 1	R ve	17/08/2021	6.65	0.1	93.8	6.27	0.061	5.9	254	0.5	0.736	5.23	0.352	3090	0.5	0.579	23.6	174	3.01	28.6	1.5	0.93	0.5	128
US Road ad 1	R ve	17/08/2021	7.4	0.1	102	6.51	0.070	7.7	295	0.5	0.642	5.28	0.393	3090	0.5	0.721	26.2	174	3.04	37.5	1.5	0.831	0.5	142
W klow Coco	R ve	17/08/2021	6.66	0.1	104	5.96	0.077	10.7	285	0.5	0.751	5.41	0.498	3.47	0.5	0.598	21.6	0.475	4.88	58.4	1.5	1.09	0.5	182
Site TE	R ve	17/08/2021	6.53	0.1	104	5.80	0.071	12.4	268	0.5	0.715	5.37	0.578	3720	0.5	1.24	21.3	467	5.09	98	1.5	1.34	0.5	201
Avoca B - dee	R ve	17/08/2021	6.67	0.1	96.9	5.80	0.063	9	239	0.5	0.65	5.77	0.428	3290	0.5	0.699	17.5	249	3.92	40.5	1.5	1.15	0.5	151
C onebane Shallow Ad 1	Ad t	18/08/2021	0.508	39.6	2.55	3.70	2930	237000	30	88.8	6	389		30	296	4640	183000	905	9220	90	172	30	117000	
BSO Ad 1	Ad t	18/08/2021	0.27	87.8	2.88	1.37	691	54600	3	13.1	11.8	89.5		3	78.1	3030	44400	958	2730	9	89.1	3	29500	
Deep Ad 1 (plus BSO)	Ad t	18/08/2021	0.1	91.7	2.9	1.33	661	53500	3	12.7	12	86.9		3	75.8	2880	45400	941	2710	9	88.6	3	31000	
Deep Ad 1 Conf	Ad t	18/08/2021	0.1	90.8	2.91	1.37	687	55600	3	13.1	11.6	85.9		3	77.3	2920	45600	932	2770	9	88.6	3	31000	
Road Ad 1	Ad t	18/08/2021	8.17	84.7	3.9	1.40	701	11000	3	19.8	18.4	177		3	71.8	350	48700	474	4820	9	94.4	3	7540	
Road Ad 1 Conf	Ad t	18/08/2021	8.35	82.6	4.07	1.37	708	10900	3	19.6	19.7	18		3	74.7	365	49400	488	5070	9	94.9	3	7870	
US T roney West	Ad t	17/08/2021	6.65	0.1	101	6.27	0.061	5.9	254	0.5	0.736	5.23	0.352	3090	0.5	0.579	23.6	174	3.01	28.6	1.5	0.93	0.5	128
GW105	GW	16/08/2021	0.1	47	3.6	1.52	1020		3	1.7	7.67	37.7		3	129	8110	32800	288	5020	9	53.4	3	16300	
GW205	GW	16/08/2021	0.1	53.6	3.58	1.42	831	48400	3	1.5	1.47	21.2		3	97	6830	176	0.6	4050	9	46.5	3	8330	
MWDA1	GW	16/08/2021	0.333	8.1	2.97	1.50	853	72000	3	8.69	8.77	89.1		3	84.6	5880	3290	26.7	4770	9	57.6	3	31200	
MWDA2	GW	16/08/2021	0.1	12.2	4.53	1.55	1010	9950	3	3.55	10.6	52.9		3	267	512	163000	3.65	14800	9	116	3	81100	
MWE11	GW	16/08/2021	0.594	8.6	3.30	2.56	1910	177000	3	2.24	5.05	35.6		3	11.7	316	14600	146000	15.3	9550	9	131	3	13000
MWE12	GW	16/08/2021	0.1	10.1	6	2.65	2170	15	3	7.79	11.3	2.09		3	116	7.52	97900	1.44	12000	9	12.5	3	5470	
MWPF1	GW	16/08/2021	0.1	88.4	4.23	0.16	27.5	18	3	0.25	6.08	0.216		3	0.25	21.6	9.5	0.211	16.5	1.5	0.402	0.5	21.7	

Green indicates higher values used from duplicate pair  
 W Exceeds Ecolog cal Assessment C te a  
 W Exceeds Human Health Assessment C te a  
 W Exceeds both Ecolog cal and Human Health C te a  
 W Less than the Limit of Detect on (LOD) - Value taken to be 0.5 of the LOD  
 - Not analysed or no assessment c te a  
 \* Only applies to ve s o st exams (e. not d scha ges)



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