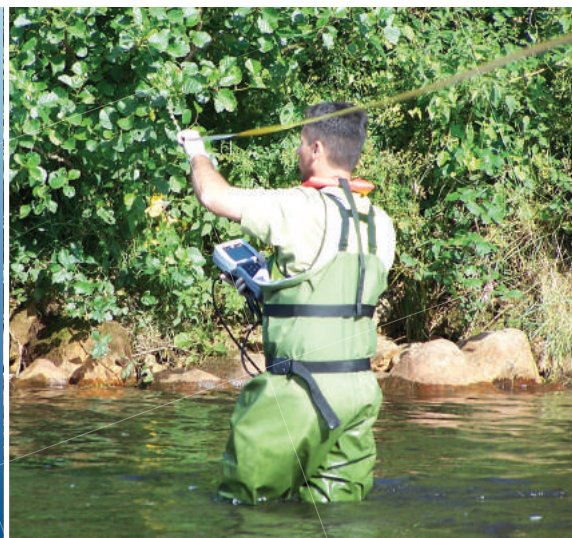


Department of Communications,
Climate Action and Environment



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

**Avoca Monitoring Report -
Round 1**

March 2018



**CDM
Smith**



Document Control Sheet

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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 March 2018. This report should be read alongside the Avoca Data Report (Document Ref: 118174/40/DG/02, dated April 2018) which contains all field observations and laboratory analytical results collected during the monitoring programme.

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 and the Shelton Abbey Tailings Management Facility (TMF) which is located approximately 8 km to the south. The Avoca River divides the East and West Avoca mine sites and runs along the base of 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. In addition, unstable ground is present which has the potential for subsidence. 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 km². 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 Vale View 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 (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 (FeS_2) accompanied by chalcopyrite (CuFeS_2), sphalerite (ZnS), and galena (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 (Cu_2S) and covellite (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 discharge 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.

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. From February 2016 to March 2018, the Deep Adit and 850 Adit flow was discharging 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. Figure 1 illustrates the changing hydro-morphology of the Deep Adit and Millrace area.

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 intermittently observed from the 850 Adit and it was added to the sampling programme in February 2014.

As a result of remediation works onsite, the flow from the 850 Adit is now piped directly to the Deep Adit box culvert, discharging 5-10 m downstream of the Deep Adit portal (located at the far end of the box culvert). A significant flow was observed from the 850 Adit in March 2018.

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** discharges through a 100 mm (4 inch) pipe to the Avoca River over a steep bank just north of the Wicklow County Council Maintenance Yard. There are also some seeps from the river bank probably due to the pipe leaking or flow in the adit not captured by the pipe. No visible discharge from the pipe or seeps from the surrounding area were observed in March 2018.

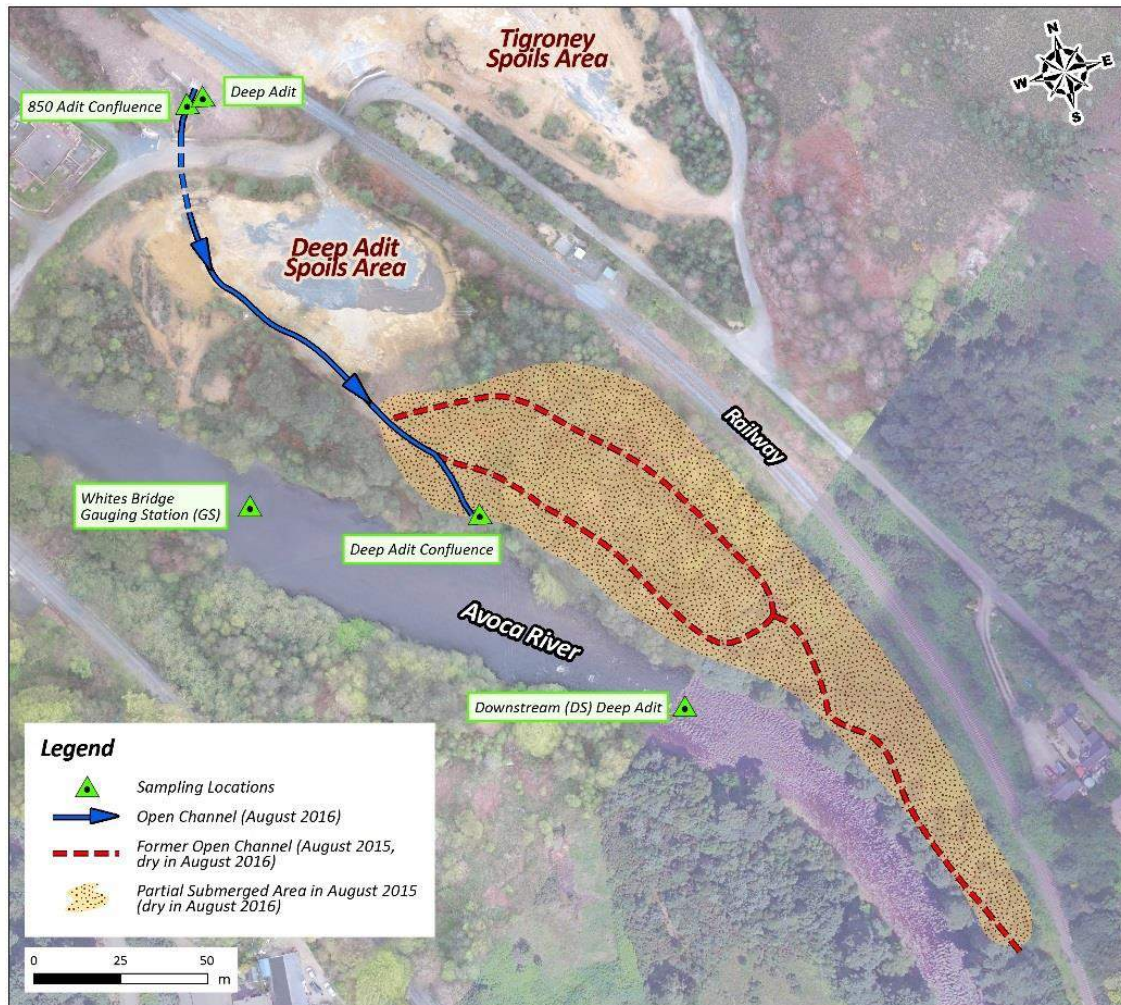


Figure 1 Location of the Deep Adit Confluence Discharge (March 2018)

Section 2

Methodology

2.1 Field Sampling Methods

2.1.1 Groundwater Sampling

Six groundwater monitoring wells were sampled on 7 and 12 March 2018. Details of groundwater monitoring locations are listed in Table 1 and illustrated on Map 2 and 3 in [Appendix A](#). No sample was obtained from monitoring well MWDA2 due to a possible obstruction in the borehole (pump could not be lowered). In future sampling events, designated equipment (tubing with foot valve) will be employed to ensure a representative sample is collected. Also, no sample was obtained from monitoring well SG104 because the borehole was dry.

Monitoring wells installed in the alluvium in 2007 as part of the previous study for the Department (CDM 2008) include:

- 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

The Wicklow County Council monitoring wells are as follows:

- Three of the wells were installed for Ballymurtagh Landfill monitoring purposes (GW1/05, GW2/05 and SG104), which are 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 March 2018

Sample ID	Easting	Northing	Water Level	Field Parameters	Sample for Lab Analysis	Owner	Depth (m-bgl)	Screen Interval (m bgl)
MWDA1	319877	182043	Yes	Yes	Yes	Dept.	12	9.0 – 12
MWDA2	319879	182039	Yes	No	No	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) detailed in the Monitoring Plan. Groundwater was collected using a portable submersible low-flow pump (Grundfos MP1). The static water level was recorded prior to pumping and then measured throughout the purging process to monitor drawdown.

Water quality indicator parameters were monitored in the field during low-flow purging using a flow-through cell to minimise oxidation by the atmosphere. Water quality indicator parameters include temperature, pH, ORP, conductivity and dissolved oxygen (DO). Purging continued until the field parameters stabilised. The results were recorded on the Groundwater Purging and Sampling Form approximately every five minutes during the purging process. The field sheets are contained in Appendix H and 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. New bottles supplied by the laboratories were used for sample collection.

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. Automatic groundwater recorders have been placed in five wells and the data were downloaded. Groundwater level data are discussed in Section 6 and the data are contained in Appendix C of the Data Report.

2.1.2 Surface Water Sampling

Nineteen surface water locations were sampled between 13 and 14 March 2018 as listed in Table 2 and shown on Map 1 and 2 in [Appendix A](#). No sample was collected from Ballygahan Adit because it was dry at the time of sampling. Note that although the adit discharge location was dry at the sampling location, it is possible that related seeps were discharging to the Avoca River. It is not possible to access these seeps in high flow conditions.

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

The predetermined surface water sampling locations were located using a GPS. Photographs were taken of the surface water sampling locations (Appendix D of the Data Report). All sample locations were approached from downstream so that the underlying sediments were not disturbed. Samples were grab samples 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 river bank.

Samples were collected in new laboratory-provided bottles with the correct preservatives. The sample bottles that required no filtering (contained 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?
Site T1	Avoca River Location (Upstream of Whites Br.)	319239	182805	Float method with depth profile from bridge (Avonmore and Avonbeg)	Yes
Upstream (US) of Whites Bridge	Avoca River Location (between Site T1 and Whites Br.)	319584	182389	Equal to flow recorded at Whites Bridge GS	Yes
Whites Bridge	Avoca River Location (at Whites Br.)	319773	182066	Equal to flow recorded at Whites Bridge GS	Yes
Whites Bridge Gauging Station GS (10044)	Avoca River Location (90m downstream of Whites Br.)	319843	182015	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 discharge)	Yes
Upstream (US) of Ballygahan Adit	Avoca River Location (Upstream of Ballygahan Adit discharge)	319936	181633	Equal to flow recorded at Wicklow County Council Maintenance Yard GS (less Road Adit discharge)	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 Wicklow County Council Maintenance Yard GS (less Road Adit discharge)	Yes
Wicklow Co. Co. Maintenance Yard Gauging Station GS	Avoca River Location	319939	181445	Automatic Recorder - Wicklow County Council Maintenance Yard GS (Data from EPA)	Yes
Site T5	Avoca River Location (Abandoned Coal Yard)	319972	181114	Equal to flow recorded at Wicklow County Council Maintenance Yard GS	Yes
Avoca Bridge	Avoca River (Upstream of Avoca Bridge)	320372	179932	Float method with depth profile from bridge	Yes
850 Adit	Adit Discharge (at portal)	319850	182123	Flow Meter	Yes
Deep Adit	Adit Discharge (at portal)	319850	182123	Flow Meter	Yes
Deep Adit Confluence	Adit Discharge (before entering Avoca River)	319896	181986	Flow Meter	Yes
Road Adit	Adit Discharge (at portal)	319858	181512	Equal to flow recorded at Road Adit Conf.	Yes

Site Name	Sample Site Description	Easting	Northing	Flow Measurement Method	Sample collected?
Road Adit Confluence	Adit Discharge (before entering Avoca River)	319942	181513	Flow Meter	Yes
Cronebane Intermediate Adit	Adit Discharge	320320	182749	Flow Meter	Yes
Cronebane Shallow Adit	Adit Discharge	320268	182646	Flume	Yes
Ballygahan Adit	Adit Discharge	319940	181610	No Flow	No
US Tigroney West	Runoff from East Avoca Track	319957	182175	Flow Meter	Yes

Water quality indicator parameters were monitored during sampling by collecting them directly from the stream or discharge when possible, using a multi-parameter probe. The final stabilised results were recorded in the field notebook (Appendix H of the Data Report) and are summarised in Appendix A of the Data Report.

Flow Measurements

Flow was measured at ten locations (see Table 2) using various methods depending upon the quantity of flow to be measured and any safety concerns as detailed in the standard operating procedures in the Monitoring Plan. Data were obtained from the EPA for the automatic recorders at Whites Bridge GS (EPA station 10044) and Wicklow County Council Maintenance Yard GS (EPA Station 10045) and projected to eight locations. Surface water flow results are discussed in Section 5.1 and the data and measurement methodologies are contained in Appendix B of the Data Report. The methods employed included using a portable flume (for small discharges) and a Marsh McBirney meter (flow meter) to measure flow velocities and depths at regular intervals across the streams.

The Float Method was used when it was unsafe to wade into the river. It is the least accurate method but it provides a reasonable estimate. This method requires the measurement and calculation of the cross-sectional area of the channel as well as the time it takes an object to “float” a designated distance. The water depth was measured from a bridge at regular intervals (approximately 10 locations). The float was released into the channel upstream from the beginning of the section and the amount of time it takes the “float” to travel the marked section was recorded. This was repeated at least three times and the average time calculated.

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 was collected; and
 - One decontamination blank was collected by pumping deionised (DI) water through the groundwater pump after decontamination.
- Surface Water:
 - Two duplicate surface water samples; and

- One decontamination blank was collected by pouring DI water over the surface water sampling equipment after decontamination.
- Two certified standard reference materials (SRMs) containing known concentrations of 18 metals were shipped blind to ALS laboratory (the SRM certificate is contained in Appendix G 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 order to try to quantify any contamination caused by 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
AVGD01.10	GW Duplicate	Duplicate of MWET1
AVDB01.10	GW Decontamination blank	DI water (Lennox Lab Supplies: Batch No: 710-7192) Pumped through groundwater pump after final decon at site MWET1)
AVSD01.10	SW Duplicate	Duplicate of Site T1
AVSD02.10	SW Duplicate	Duplicate of Cronebane Intermediate Adit
AVDB02.10	SW Decontamination blank	DI water (Lennox Lab Supplies: Batch No: 710-7192) poured over SW composite sample bottle after final decon at Cronebane Intermediate Adit
AVSR01.10	Standard Reference Material	Water ERA “Trace Metals” Lot #P268-740B
AVSR02.10	Standard Reference Material	Water ERA “Trace Metals” Lot #P268-740B
WB01.10	Filtration blank	Deionised water filtered onsite (Lennox Lab Suppliers. Batch No: 710-7192)
WB02.10	Water blank	Deionised water (Lennox Lab Suppliers. Batch No: 710-7192)

2.2 Sample Handling

One waterproof label for each sample container collected was completed with an indelible, waterproof, marking pen. The label contained the location, sample ID code 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 recorded on the COC record. The COC record was placed in a resealable plastic bag 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 E of the Data Report.

2.3 Laboratory Sample Analysis

Analysis of water samples was undertaken by ALS (formerly ALcontrol). Water (both surface water and groundwater) 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.

For groundwater and surface water, analyses were performed for the following parameters: pH, ammoniacal nitrogen as N, sulphate and dissolved metals including Al, Sb, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, V and Zn. In addition, Total Organic Carbon (TOC) and Calcium (Ca) were analysed on the Avoca River samples to assess bioavailable concentrations of several metals (further discussed in Section 4.2). 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 F 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 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_1 = First sample value
 D_2 = 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 is discussed below.

3.1.4 Field QA/QC Samples

Field 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 AVSR01.10 and AVSR02.10) to evaluate laboratory accuracy. The certified SRM was supplied by ERA Certified Reference Materials and was Lot #P268-740B (Metals). The Certificate of Analysis is provided in Appendix G of the Data Report. 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. 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.

The majority of RPD values were below 50% and the RPDs for the key parameters ranged from 0.4 to 11.1% for aluminium, 1.8 to 10.4% for manganese and 6.2 to 25.6% for zinc which was good. The RPD's for copper were also good but slightly higher for duplicate pair Site T1 and AVSD01.10 with an RPD of 58.7%. Additionally, The RPD for duplicate pair Site T1 and AVSD01.10 exceeded the 50% for lead with a value of 50.5%. These exceedances are probably due to low concentrations, close to the LOD.

The highest reported value of the duplicate pair is 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)	MWET1	AVGDO 1.10	% RPD	Site T1	AVSD0 1.10	% RPD	Crone-bane Inter. Adit	AVSD0 2.10	% RPD
Aluminium	<2	95100	102000	7.0	114	102	-11.1	53500	53300	-0.4
Antimony	<0.1	<1*	<1*	0	<1*	<1*	0	<6*	<1*	0
Arsenic	<0.5	3.58	3.5	-2.3	<0.5	<0.5	0	23.4	17.9	-26.6
Barium	<0.2	3.29	3.55	7.6	7.79	6.83	-13.1	7.22	6	-18.5
Cadmium	<0.08	16.3	16.2	-0.6	0.15	0.123	-19.8	104	69.1	-40.3
Chromium	<1	7.8	7.49	-4.1	<1	<1	0	<6*	<1*	0
Cobalt	<0.15	140	137	-2.2	<0.5*	<0.5*	0	94.6	79.1	-17.8
Copper	<0.3	5920	7310	21.0	1.22	0.666	-58.7	9250	9390	1.5
Iron	<19	66.7	69.6	4.3	74.5	72.1	-3.3	61.3	56.4	-8.3
Lead	<0.2	5.48	5.69	3.8	4.96	2.96	-50.5	1090	903	-18.8
Manganese	<1	6300	6190	-1.8	29.9	27.1	-9.8	2120	1910	-10.4
Molybdenum	<0.5	<3*	<3*	0	<3*	<3*	0	<18*	<3*	0
Nickel	<0.4	68.7	67.2	-2.2	1.04	0.759	-31.2	41.6	34.2	-19.5
Vanadium	<1	<1	<1	0	<1	<1	0	<6*	<1*	0
Zinc	<1	6680	8080	19.0	33.5	25.9	-25.6	29800	28000	-6.2

Notes:

Bold 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 Decontamination Blanks

Two decontamination blanks were created by pumping DI water through (groundwater) and pouring water over (surface water) the sampling equipment after decontamination and sent to ALS for analysis. Table 5 provides the results of the 15 metals for the two decontamination blank samples, the DI water blank and filtration blank samples and the associated laboratory method blank samples. The majority of 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 ranged from 0.08 to 2 µg/l except for iron with a detection limit of 19 µg/l.

Detections were observed for seven dissolved metals ranging from 0.12 to 69.6 µg/l. Two of the metals (dissolved zinc and copper) detected in the decontamination blanks were also detected in the DI water blank (WB02.10). Dissolved zinc was also detected in the DI filtration blank. The concentrations in the decontamination blanks were similar to those found in the DI water blank. Relatively low concentrations of dissolved antimony, cadmium, iron, lead and molybdenum were also found in the decontamination blanks but not the DI water blanks.

None of the parameters which were detected in the decontamination blanks but not detected in the DI water blank samples were greater than ten times the LOD; In AVDB01.10, antimony (1.88 µg/l), cadmium (0.122 µg/l), lead (0.321 µg/l), molybdenum (4.88 µg/l) and in AVDB02.10, iron (69.6 µg/l). Additionally, none of the reported values which were detected in both the DI water blank samples and the decontamination blank were greater than ten times the LOD. All of the detections were less than the assessment criteria outlined in Section 4; therefore, these low concentrations in the blanks do not affect interpretation of results. Overall, the decontamination procedures employed in the field were adequate.

To assess the level of field cross contamination, the concentrations in the decontamination blanks were compared with the concentration in the preceding environmental samples. In AVDB01.10, dissolved cadmium (0.122 µg/l) was 0.8% of the preceding sample, copper (0.677 µg/l) was 0.01%, lead (0.321 µg/l) was 0.1% and, zinc (1.28 µg/l) was 0.02%. Dissolved antimony (1.88 µg/l) and molybdenum (4.88 µg/l) were below the LOD in the preceding sample indicating possible lab cross contamination. In AVDB02.10, dissolved copper (0.117 µg/l), iron (0.07 µg/l) and zinc (2.87 µg/l) were all less than 1% of the preceding sample.

The results from the laboratory instrumentation blank were obtained from ALS to determine if any contamination occurred within the laboratory (Table 5). There were no detections in the laboratory instrumentation blank.

Overall, the decontamination procedures were adequate and blank samples do not indicate any cross-contamination in the field and therefore all the results are considered acceptable and can be used for their intended purposes.

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

Dissolved Metal	LOD (µg/l)	Filt. Blank WB01.10 (µg/l)	Water Blank WB02.10 (µg/l)	Lab Method Blank (µg/l)	Decon blank AVDB01.10 (µg/l)	Lab Method Blank (µg/l)	Decon blank AVDB02.10 (µg/l)	Lab Method Blank (µg/l)
<i>Sample batch:</i>		<i>180310-46</i>			<i>180314-124</i>		<i>180317-36</i>	
Aluminium	<2	<2	<2	<10	<10	<10	<10	<10
Antimony	<0.1	<1	<1	<1.0	1.88	<1.0	<1	<1.0
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	0.12	<0.03	<0.08	<0.08
Chromium	<1	<1	<1	<1.0	<1	<1.0	<1	<1.0
Cobalt	<0.15	<0.15	<0.15	<0.5	<0.5	<0.5	<0.5	<0.5

Dissolved Metal	LOD (µg/l)	Filt. Blank WB01.10 (µg/l)	Water Blank WB02.10 (µg/l)	Lab Method Blank (µg/l)	Decon blank AVDB01.10 (µg/l)	Lab Method Blank (µg/l)	Decon blank AVDB02.10 (µg/l)	Lab Method Blank (µg/l)
Sample batch:		180310-46			180314-124		180317-36	
Copper	<0.3	<0.3	1.74	<0.3	0.68	<0.3	0.975	<0.3
Iron	<19	<19	<19	<0.2	<19	<0.2	0.069	<0.2
Lead	<0.2	<0.2	<0.2	<3.0	0.32	<3.0	<0.2	<3.0
Manganese	<1	<1	<1	<3.0	<3	<3.0	<0.3	<3.0
Molybdenum	<0.5	<0.5	<0.5	<0.4	4.88	<0.4	<3	<0.4
Nickel	<0.4	<0.4	<0.4	<1.0	<0.4	<1.0	<0.4	<1.0
Vanadium	<1	<1	<1	<1.0	<1	<1.0	<1	<1.0
Zinc	<1	1.16	1.99	<10	1.28	<10	2.87	<10

Notes:

Bold indicates a detection

Bold and italics indicates a detection of a parameter also detected in the laboratory method blank.

Italics indicates a detection in the lab method blank that was also detected in a field water or decontamination blank in the same batch

3.2.3 Standard Reference Materials

As previously discussed, two certified water SRMs were sent blind to the laboratory (Sample IDs AVSR01.10 and AVSR02.10) to evaluate laboratory accuracy. The ALS laboratory reports are provided in Appendix F of the Data Report. Table 6 summarises the SRM results and provides the calculated %R values for the 15 requested metals.

Reported values for the majority of the metals were within the acceptable ranges. Dissolved antimony, cadmium, chromium, cobalt, copper, iron, manganese and molybdenum are in excellent agreement with the certified value (%R ranged from 93 to 108%).

One of the reported values for dissolved aluminium (117%), arsenic (86%), barium (109%), lead (123%), vanadium (89%) and zinc (111%) were outside the acceptable range, however the corresponding reported values for the second SRM sample were within acceptable ranges and therefore the interpretation of the results is not affected. Both of the reported values for dissolved nickel were low at 83 and 88%, respectively, which fall outside the expected range. This indicated that there may be bias (low) in the result for nickel and any use of these values should be noted with this observation.

Table 6 SRM Reported Values (µg/l) and Calculated % R

Dissolved Metal	Certified Value (µg/l)	Acceptance Limits		AVSR01.10 (µg/l)	% R	AVSR02.10 (µg/l)	% R
		Lower (%)	Upper (%)				
Aluminium	1020	86	113	1190	117	1040	102
Antimony	702	87	110	669	95	667	95
Arsenic	322	87	110	278	86	310	96
Barium	200	91	108	212	106	217	109
Cadmium	997	89	107	935	94	930	93
Chromium	632	91	109	658	104	654	103
Cobalt	651	93	111	678	104	695	107
Copper	535	91	109	572	107	576	108

Dissolved Metal	Certified Value (µg/l)	Acceptance Limits		AVSR01.10 (µg/l)	% R	AVSR02.10 (µg/l)	% R
		Lower (%)	Upper (%)				
Iron	543	91	111	563	104	551	101
Lead	424	91	110	523	123	454	107
Manganese	668	93	110	677	101	673	101
Molybdenum	397	90	108	391	98	374	94
Nickel	1280	91	109	1060	83	1120	88
Vanadium	1010	91	107	922	91	894	89
Zinc	961	90	110	1010	105	1070	111

Notes:

Bold indicates an exceedance in acceptance limits

3.3 Laboratory QA/QC Samples

3.3.1 ALS Laboratory

ALS undertakes a range of activities associated with both quality control and assessment to assure the quality of test results. Specifically, ALS conduct the following analyses on water samples:

- Analytical Quality Control Samples (AQC) including, Certified Reference Material (CRM), Internal Reference Material (IRM) and Matrix spiked material. For batch sizes of 20 samples or less, a minimum of one AQC and for batches of greater than 20 samples, one AQC every additional twenty samples or part thereof. They 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 was included with each batch of samples. The blanks are matrix matched where possible and were taken through the entire analytical system;
- Instrumental Blanks: An instrument blank was run to check for any contamination within the instrument;
- Independent Check Standard: An independent check standard was included with every instrumental run of samples. This standard is prepared from a separately sourced standard to the calibration standards and is used as a check on the validity of the calibration standards. The acceptance criteria for this standard was method specific; and
- Replicate samples (samples tested more than once using the same method) were included at the same frequency as the AQCs.

All of the ALS laboratory reports were reviewed to ensure that reported values were ISO17025 certified (where relevant) and for any sample deviations. None of the sample holding times were exceeded. ALS provided the associated analytical quality control samples (AQC) data and advised that the AQC samples have two limits, a warning limit and a failure limit. Tests which exceed the failure limit are immediately re-run but tests that exceed the warning limit can still be reported. The test only fails automatically if there are multiple warning limit exceedances. Laboratory analysts check the individual cases where the warning limit is exceeded and report the results if they are satisfied with all other factors involved. The laboratory quality control checks indicate that all results are acceptable for their intended use.

3.4 Summary of Data Checks

3.4.1 Field Physico-chemical Versus Laboratory Data

Table 7 summarises the field and laboratory results for pH and provides the calculated %RPD values between the two results. Note that 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).

The RPDs between laboratory and field pH were very good at less than 10%. Field pH is more representative of actual conditions and is used for interpretive purposes. Recordings of pH in the field are typically lower than the laboratory due to carbon dioxide degassing during transport or within the laboratory itself. Overall, the %RPDs between the field and laboratory data are considered satisfactory.

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

Sample Description	pH Lab	pH Field	% RPD
	pH Units		
850 Adit	2.93	2.94	0.3
Avoca Bridge	6.43	6.29	-2.2
Cronebane Intermediate Adit	2.98	2.96	-0.7
Cronebane Shallow Adit	2.76	2.78	0.7
Deep Adit	3.45	3.44	-0.3
Deep Adit Confluence	3.17	3.18	0.3
DS Deep Adit	5.35	5.47	2.2
DS Millrace	6.27	6.15	-1.9
Road Adit	4.34	4.43	2.1
Road Adit Confluence	4.23	4.58	7.9
Site T1	6.51	6.61	1.5
Site T5	6.32	6.4	1.3
US Ballygahan Adit	6.46	6.52	0.9
US Road Adit	6.42	6.39	-0.5
US Tigroney West	3.91	4.19	6.9
US Whites Bridge	6.62	6.57	-0.8
Wicklow Co. Co. Main. Yard GS	5.75	5.96	3.6
Whites Bridge	6.59	6.64	0.8
Whites Bridge GS	6.43	5.83	-9.8
GW1/05	3.65	3.72	1.9
GW2/05	3.63	3.7	1.9
MWDA1	2.99	2.9	-3.1
MWET1	3.33	3.5	5.0
MWET2	6.17	6.2	0.5
MWPF1	5.09	4.8	-5.9

Notes:

Bold 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 F 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 eight 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. 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	<2	6	5	30*	102,000	47,234	40,839
Antimony	<0.1	6	0	0.3*	3*	-	-
Arsenic	<0.5	6	5	0.25	12.2	6.44	4.42
Barium	<0.2	6	6	1.92	11.4	6.95	3.59
Cadmium	<0.08	6	6	0.29	70.2	22.8	25.3
Chromium	<1	6	2	0.5	8.83	4.36	-
Cobalt	<0.15	6	5	0.25*	140	92.5	49.7
Copper	<0.3	6	5	0.9*	7,530	4,178	3,460
Iron	<19	6	5	9.5*	90,000	30,350	39,186
Lead	<0.2	6	5	0.37	147	33.6	58.4
Manganese	<1	6	6	13.3	30,500	8,359	11,056
Molybdenum	<0.5	6	1	1.5*	9	-	-
Nickel	<0.4	6	6	1.22	68.7	36.0	24.3
Vanadium	<1	6	0	0.5	3*	-	-
Zinc	<1	6	6	32.7	27,700	9,776	9,518

Notes:

If less than LOD minimum value taken to be half LOD.

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

Dissolved aluminium, copper, iron, manganese and zinc were found in significantly high concentrations in the majority of groundwater samples. The shallow well MWPF1 located upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments had the lowest concentrations of dissolved metals. However, the lowest concentration of aluminium (<60 µg/l)

and copper (<1.8 µg/l) was recorded in MWET2 which also had the highest concentrations of iron (90,000 µg/l) and manganese (30,500 µg/l).

MWET1 had the highest concentration of dissolved aluminium (102,000 µg/l) and nickel (68.7 µg/l). The highest concentration of zinc (27,700 µg/l) and cadmium (70.2 µg/l) was recorded in MWDA1. Dissolved arsenic in MWDA1 was reported at 12.2 µg/l and was detected in all other groundwater samples with the exception of MWPF1.

4.1.2 Surface Water Sample Results

Surface water samples were collected for two major categories: the first includes mine adit discharges and the second includes the Avoca River. Table 9 provides a summary of the reported results of the seven adit discharge samples and Table 10 provides a summary of the dissolved metals of the 11 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.

Adit Discharges

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	<2	7	7	10,500	132,000	47,386	42,964
Antimony	<0.1	7	0	3.0*	5.50*	-	-
Arsenic	<0.5	7	6	1.5*	78.7	19.78	26.9
Barium	<0.2	7	7	4.87	20.3	12.18	5.35
Cadmium	<0.08	7	7	5.85	155	63.42	56.4
Chromium	<1	7	0	3.0*	5.5*	-	-
Cobalt	<0.15	7	7	15.5	138	94.21	43.1
Copper	<0.3	7	7	267	9,390	3,663	3,792
Iron	<19	7	7	4,560	134,000	63,466	55,024
Lead	<0.2	7	7	233	1,090	675	329
Manganese	<1	7	7	872	11,300	4,783	4,351
Molybdenum	<0.5	7	0	9.0*	16.5*	-	-
Nickel	<0.4	7	7	7.52	60.0	39.7	18.9
Vanadium	<1	7	0	3.0*	5.50*	-	-
Zinc	<1	7	7	7,000	>31,200	17,257	10,827

Notes:

If less than LOD minimum value taken to be half LOD.

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

Dissolved aluminium, copper, iron, lead, manganese and zinc were found in significantly high concentrations in all of the adit discharges. The Cronebane Shallow Adit had the highest concentrations of dissolved metals including aluminium (132,000 µg/l), cadmium (155 µg/l), cobalt (138 µg/l), nickel (60 µg/l) and zinc (>31,200 µg/l). The highest concentration of iron (134,000 µg/l) and manganese (11,300 µg/l) were recorded at the Road Adit. The Cronebane Intermediate Adit had the highest concentration of dissolved copper (9,390 µg/l).

Dissolved arsenic was detected at all adit discharges with the exception of the Deep Adit. The highest concentration was recorded at Cronebane Shallow Adit (78.7 µg/l). No detections were

recorded for antimony, chromium, molybdenum and vanadium. No sample was collected from the Ballygahan Adit because it was not discharging water in March 2018.

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	<2	11	11	110	515	250	123
Antimony	<0.1	11	0	0.5	0.5	-	-
Arsenic	<0.5	11	3	0.25	0.60	0.30	0.12
Barium	<0.2	11	11	5.82	7.79	6.53	0.69
Cadmium	<0.08	11	8	0.15	1.25	0.38	0.32
Chromium	<1	11	0	0.5	0.5	-	-
Cobalt	<0.15	11	7	0.25	2.81	0.67	0.80
Copper	<0.3	11	9	0.63	76.6	17.2	21.6
Iron	<19	11	11	65.9	2,340	342	670
Lead	<0.2	11	11	3.14	9.75	4.85	2.02
Manganese	<1	11	11	28.3	237	60.9	59.9
Molybdenum	<0.5	11	1	1.5	1.5	-	-
Nickel	<0.4	11	11	0.78	1.84	1.04	0.33
Vanadium	<1	11	0	0.5	0.5	-	-
Zinc	<1	11	11	29.8	388	121	111

Notes:

If less than LOD minimum value taken to be half LOD.

Dissolved metals were detected upgradient of the mining area at Site T1 with concentrations of aluminium at 114 µg/l, copper at 1.22 µg/l, iron at 74.5 µg/l, manganese at 29.9 µg/l and zinc at 33.5 µg/l.

Between Site T1 and US Whites Bridge (365m upstream of the bridge) no significant increases in dissolved metals were recorded. A slight increase in dissolved metals was recorded at Whites Bridge (at the bridge) which 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 were 119 µg/l, 0.6 µg/l and 35.3 µg/l, respectively.

Along the Avoca River the concentrations of dissolved metals were variable; the highest dissolved aluminium (515 µg/l), copper (76.6 µg/l), manganese (70.7 µg/l) and zinc (388 µg/l) were recorded directly downstream of the Deep Adit discharge (DS Deep Adit). Concentrations of dissolved iron (2,340 µg/l) were highest at WCC Maintenance Yard GS (downstream of the Road Adit discharge). Dissolved arsenic was detected at two locations; WCC Maintenance Yard GS (0.602 µg/l) and Whites Bridge (0.501 µg/l). Note that samples were taken as grab samples from the river bank (due to high flows) and may not be representative of concentrations across the entire depth and width of the river.

These findings are discussed further in Section 5 which provides an analysis of dissolved metal loadings.

4.2 Assessment Criteria

4.2.1 Groundwater and Surface Water Assessment Criteria

To assess the analytical results of the groundwater and surface water samples, assessment criteria have been selected to screen reported values for both ecological and human health. To assess ecological criteria, the environmental quality standards (EQS) from the European Communities Environmental Objectives (Surface Water) Regulations, 2009 (S.I. 272 of 2009) and amendments were utilised, as shown in. 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. Compliance with the standards in the surface water regulations is either based on an annual average (AA), a maximum allowable concentration (MAC) or a 95 percentile standard. The MAC or 95 percentile (95%-ile) was selected where possible as the assessment criteria because it is the most appropriate for assessment of one value; however, the AA was used in the absence of the MAC or 95%-ile. Additionally, the AA was selected for lead and zinc to assess these parameters against the bioavailable EQS (S.I. No. 386 of 2015). To supplement the Irish legislation, screening criteria were selected from Oak Ridge National Laboratory (Suter and Tsao, 1996) for certain metals including aluminium, barium, cobalt, manganese and uranium (Table 11).

For hardness-dependent metals copper, zinc and cadmium, the hardness is taken into account when selecting the appropriate EQS value. The average hardness in the rivers and streams in the Avoca mining area was determined to be 31 mg/l CaCO_3 (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, 2007 (S.I. No. 106 of 2007) and amendments were utilised and are listed in Table 12. 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 post treatment (including filtration) and therefore the dissolved portion is used in the assessment in Section 4.

The current Drinking Water Regulations set limit values for iron and manganese but they are categorised as Indicator Parameters. Indicator Parameters are not considered to be important 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 to 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 were utilised 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)	≤ 0.45 (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 ₃ (Class 1: <40 mg CaCO ₃ /l, Class 2: 40 to <50 mg CaCO ₃ /l, Class 3: 50 to <100 mg CaCO ₃ /l, Class 4: 100 to <200 mg CaCO ₃ /l and Class 5: ≥200 mg CaCO ₃ /l)
Chromium	µg/l	3.4	-	S.I. No. 272 of 2009	
Copper	µg/l	5 or 30	-	S.I. No. 272 of 2009	5 µg/l applies where the water hardness measured in mg/l CaCO ₃ is ≤ 100; 30 µg/l applies where the water hardness > 100 mg/l CaCO ₃ .
Lead	µg/l	1.2	14	S.I. No. 386 of 2015	Bioavailable EQS
Nickel	µg/l	4	34	S.I. No. 386 of 2015	Bioavailable EQS
Zinc	µg/l	8 or 50 or 100	-	S.I. No. 272 of 2009	8 µg/l for water hardness with annual average values ≤ 10 mg/l CaCO ₃ ; 50 µg/l for water hardness > 10 mg/l CaCO ₃ and ≤ 100 mg/l CaCO ₃ ; 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 indicates the selected assessment criteria for ecological health**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

Parameter	Unit	Parametric value
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

4.1 Comparison to Assessment Criteria

A comparison of the groundwater and surface water analytical results was made against the relevant assessment criteria for ecological and human health as described in Section 4.2.

Table B-2 in [Appendix B](#) highlights the exceedances of the assessment criteria. Where exceedances of the ecological assessment criteria exist, the result is highlighted in purple, for an exceedance of the human health criteria the result is highlighted in blue. In some cases, the reported values exceeded both the ecological and human health criteria and these results are highlighted in red. The results and exceedances are discussed in this section.

4.1.1 Groundwater Assessment

Monitoring wells

The pH was found to be acidic in the majority of groundwater samples with results ranging from 2.9 to 6.2 (field). All exceeded the acceptable ranges for ecological (4.5 to 9 pH units) and human health (6.5 to 9.5 pH units) criteria, except two locations (MWET2 and MWPF1) which only exceeded the criteria for human health with a pH of 6.2 and 4.8, respectively. The specific conductance ranged from 0.163 to 3.26 mS/cm with the lowest conductivity located at MWPF1 and the highest at MWET2, which exceeded the human health criteria (2.5 mS/cm).

Sulphate levels greatly exceeded the criteria for human health of 250 mg/l in all of the monitoring wells with values ranging from 892 to 2,340 mg/l. One exception was at MWPF1 where sulphate was below the human health assessment criteria with a value of 30.2 mg/l. Ammonia exceeded both the ecological (0.14 mg/l) and human health (0.3 mg/l) assessment criteria in MWDA1 and NWET1 with concentrations ranging from 0.354 to 0.584 mg/l, respectively.

The dissolved metal concentrations were elevated in the majority of the monitoring wells with numerous exceedances of ecological, human health criteria or both, particularly for aluminium, cadmium, copper, iron, manganese, nickel, lead and zinc (Table B-2 in [Appendix B](#) includes the full listing). There were five detections of dissolved arsenic and only MWDA1 with a result of 12.2 µg/l exceeded the human health criteria (10 µg/l).

The dissolved aluminium and copper concentrations at MWET2 (deep) (<60 and <1.8 µg/l) were significantly lower than at MWET1 (shallow) which had concentrations of 102,000 and 7,310 µg/l, respectively. MWET1 exceeded both the ecological and human health criteria for aluminium (1,900 and 200 µg/l) and copper (5 and 2,000 µg/l). This could be explained by the apparent confined nature of MWET2 (heads in MWET2 are higher than in MWET1) and also because MWET1 is screened directly beneath the Emergency Tailings deposits.

The bedrock monitoring well GW1/05 showed higher dissolved metal concentrations than its nested, shallow alluvial well GW2/05. For example, dissolved copper was 7,530 µg/l in GW1/05

and 6,220 µg/l in GW2/05. Both monitoring wells exceeded the ecological and human health criteria for copper (5 and 2,000 µg/l). In GW1/05 and GW2/05, levels of dissolved aluminium (59,100 and 47,100 µg/l), cadmium (27.8 and 18.7 µg/l), manganese (5,320 and 4,110 µg/l) and nickel (50.3 and 39.6 µg/l) exceeded both the ecological assessment criteria and human health assessment criteria respectively.

The groundwater in the shallow well at the Deep Adit area (MWDA1) exceeded the ecological and human health criteria for aluminium (74,900 µg/l), cadmium (70.2 µg/l), copper (3,970 µg/l), lead (46.6 µg/l), manganese (3,910 µg/l) and nickel (40.9 µg/l). Concentrations of dissolved zinc were recorded at 27,700 µg/l which exceeded the ecological assessment criteria (50 µg/l). Note that monitoring well MWDA2 was not sampled in 2018 due to an obstruction in the borehole.

The well located upgradient of the Deep Adit area and at the eastern margin of the alluvial aquifer, MWPF1, had significantly lower metal concentrations than the other wells. However, the human health assessment criteria for dissolved aluminium (200 µg/l) was exceeded with a value of 271 µg/l and the ecological assessment criteria for dissolved copper (5 µg/l) and dissolved barium (4 µg/l) was exceeded with values of 9.51 and 37.7 µg/l, respectively.

4.1.2 Surface Water Assessment

Adit Discharges

The pH was found to be acidic in all adit discharges with results ranging from 2.62 to 4.58 pH (field). All adit discharges exceeded the acceptable ranges for ecological (4.5 to 9 pH units) and human health (6.5 to 9.5 pH units) criteria with the exception of the Road Adit Confluence which only exceeded the human health criteria with a value of 4.58. The specific conductance ranged from 0.334 to 2.402 mS/cm.

Sulphate levels greatly exceeded the criteria for human health of 250 mg/l in all of the adit discharges with values ranging from 563 to 1,370 mg/l. One exception was for the Deep Adit which had a value of 215 µg/l. This value is considered low because previous values (2013-2017) ranged from 781 µg/l to 1,130 µg/l.

Ammonia was detected in four of the adit discharges; 0.32 mg/l at the Cronebane Intermediate Adit, 5.27 mg/l at the Road Adit, 0.529 mg/l at the Cronebane Shallow Adit and 5.16 mg/l at the Road Adit Confluence, all of which exceeded the human and ecological assessment criteria.

The dissolved metal concentrations were high in all of the adit discharges. Numerous exceedances of ecological, human health criteria or both exist for the majority of metals analysed including dissolved aluminium, cadmium, copper, iron, manganese, lead, nickel and zinc (Table B-2 in [Appendix B](#) includes the full listing).

Dissolved zinc ranged from 7,000 to >31,200 µg/l which exceeded the ecological assessment criteria of 50 µg/l. Dissolved aluminium ranged from 10,500 to 132,000 µg/l which exceeded both the ecological (1,900 µg/l) and human health (200 µg/l) criteria. The concentrations of dissolved copper exceeded the ecological assessment criteria (5 µg/l) in all of the adit discharges and also the human health (2,000 µg/l) criteria in the Cronebane Shallow Adit (>6,240 µg/l), the Cronebane Intermediate Adit (9,390 µg/l), the 850 Adit (6,050 µg/l) and the Deep Adit confluence (5,180 µg/l).

Dissolved cadmium (ranging from 5.85 to 155 µg/l) and dissolved lead (ranging from 233 to 1,090 µg/l) exceeded both the ecological and human health criteria. Dissolved nickel ranged from 7.52 to

60 µg/l which exceeded both the ecological and human health criteria of 20 µg/l with one exception; Deep Adit (7.52 µg/l) which exceeded the ecological assessment criteria.

With the exception of the Deep Adit, dissolved arsenic was detected in all of the adit discharges, ranging from 4.44 to 78.7 µg/l. Concentrations in the Cronebane Intermediate Adit (23.4 µg/l), Road Adit (12.4 µg/l) and Road Adit Confluence (10.8 µg/l) exceeded the human health criteria of 10 µg/l. Concentrations in the Cronebane Shallow Adit exceeded the criteria for human health (10 µg/l) and ecological health (25 µg/l) with a recorded value of 78.7 µg/l.

Dissolved iron and manganese were also high in all adit discharges. Iron ranged from 4,560 µg/l to 134,000 µg/l, exceeding the human health assessment criteria of 200 µg/l at every location. Manganese ranged from 872 to 11,300 µg/l which exceeded the criteria for human health (50 µg/l) and the ecological assessment criteria (1,100 µg/l) in all adit discharges except the Deep Adit which only exceeded the human health criteria. Note that iron and manganese are not important criteria for human health (see Section 4.2.1).

A sample was collected upstream of the drainage channel at the recently remediated Tigroney West site. The drainage channel captures runoff from East Avoca that flow along the East Avoca track and discharges it to the Deep Adit channel, downstream of the Deep Adit box culvert. pH exceeded the ecological and human health criteria with a value of 4.19. Dissolved aluminium (6,250 µg/l), cadmium (6.77 µg/l) and lead (306 µg/l) exceeded both the ecological and human health criteria. Dissolved copper and zinc exceeded the ecological health criteria with values of 934 and 2,110 µg/l, respectively.

There were no detections recorded in any of the adit discharges for dissolved antimony, chromium, molybdenum and vanadium.

Avoca River

Table 13 provides a summary of the reported values for river sampling locations in the Avoca Mining area that exceeded the relevant ecological and human health assessment criteria. The pH was found to be below the human health (6.5 to 9.5 pH units) criteria for the majority of rivers and streams ranging from 5.47 to 6.64 pH (field); however, all values were within acceptable ranges for ecological health (4.5 to 9 pH units). The specific conductance was well within the criteria for human health of 2.5 mS/cm ranging from 0.068 to 0.203 mS/cm. Dissolved Oxygen was also within the range for ecological health (80-120 % Sat) ranging from 87.9 (Whites Bridge) to 97.5 (DS Deep Adit). No exceedances were recorded on the Avoca River for ammonia and sulphate.

The dissolved metal concentrations in the Avoca River were low in comparison to the groundwater and the adit discharges; however, several exceedances of both ecological and human health criteria were recorded. Dissolved copper exceeded the ecological criteria (5 µg/l) at all Avoca River locations from Whites Bridge GS to the Avoca Bridge, with results ranging from 8.25 to 76.6 µg/l. The highest dissolved copper concentration was recorded at DS Deep Adit. Similarly, dissolved zinc exceeded the ecological assessment criteria (50 µg/l) from Whites Bridge GS to Avoca Bridge with results ranging from 52.6 to 388 µg/l.

Dissolved cadmium exceeded the ecological assessment criteria (0.45 µg/l) at DS Deep Adit (1.25 µg/l), DS Millrace (0.587 µg/l) and Wicklow County Council Maintenance Yard GS (0.478 µg/l). Dissolved aluminium exceeded the human health criteria at all locations downstream of Whites Bridge GS (except US Ballygahan) with values ranging from 212 to 515 µg/l. Dissolved lead

exceeded the ecological criteria at all sampling locations. Note that the ecological criteria for lead is based on the bioavailable concentration (S.I. No. 386 of 2015; see Table 11).

Dissolved iron exceeded the human health assessment criteria of 200 µg/l at the three locations downstream of the Road Adit confluence with concentrations ranging from 201 to 2,340 µg/l. Dissolved manganese exceeded the criteria for human health (50 µg/l) at Site T5 (65.1 µg/l) and Wicklow County Council Maintenance Yard GS (237 µg/l). Note that iron and manganese are not important criteria for human health (see Section 4.2.1).

Dissolved arsenic, cobalt and nickel were below the ecological and human assessment criteria at all monitoring locations on the Avoca River. Additionally, no detections were recorded for dissolved antimony, chromium, molybdenum and vanadium.

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
Human Health Criteria		6.5 to 9.5	200	5	2000	200	10	50	-
Site T1	13/03/2018	6.61	114	0.15	1.22	74.5	4.96	29.9	33.5
US Whites Bridge	13/03/2018	6.57	110	0.146	0.734	79.9	3.14	28.3	29.8
Whites Bridge	13/03/2018	6.64	119	0.152	0.625	130	3.44	32.1	35.3
Whites Bridge GS	13/03/2018	5.83	337	0.412	17.4	109	3.71	41.1	121
DS Deep Adit	13/03/2018	5.47	515	1.25	76.6	65.9	9.75	70.2	388
DS Millrace	13/03/2018	6.15	328	0.587	30.1	96	5.68	45.6	175
US Ballygahan Adit	13/03/2018	6.52	186	0.194	8.25	114	3.35	35.5	52.6
US Road Adit	13/03/2018	6.39	247	0.28	14.3	135	3.8	42.1	74.2
Site T5	13/03/2018	6.4	243	0.296	11.9	414	4.34	65.1	98.4
WCC Maintenance Yard GS	13/03/2018	5.96	337	0.478	17.5	2340	7.18	237	250
Avoca Bridge	13/03/2018	6.29	212	0.279	10.3	201	4.01	43.3	77

Notes

xx Exceeds Ecological Assessment Criteria

xx Exceeds Human Health Assessment Criteria

xx Exceeds both Ecological and Human Health Criteria

Metals are dissolved

4.2 Bioavailable EQS Assessment

As discussed in 4.2, water quality criteria for metals such as zinc and copper in freshwaters have incorporated hardness in a variety of methods (the different classes shown in Table 11 are one such approach). With the advancement of scientific understanding and testing of the toxicity of metals in the environment during the past 10 to 15 years, hardness alone has been shown to be 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). Overall 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) is 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). Note: no Ni concentrations in the Avoca River exceeded 4 µg/L.
- **Tier 2:** A user friendly tool based upon integrated biotic ligand models (BLM) which incorporates site specific data is used to calculate local bioavailable metal concentrations and local HC5 values (value derived from ecotoxicological data at the 5th 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 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 BLM 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.

4.2.1 Avoca River Bioavailable EQS Analysis

Appropriate analytical data have been 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 follows:

Tier 1: The current single values generic EQS_{bioavailable} for Ni (4 µg/L) and Pb (1.2 µg/L) were based on the most conservative 5th 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_{bioavailable} 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 concentrations in the Avoca River slightly exceed the 1.2 µg/L value at all locations but do not exceed the 7.2 µg/L value except DS Deep Adit. Measured dissolved Ni concentrations in the Avoca River do not exceed the 4 µg/L value. Overall, Cu and Zn concentrations 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 access EQS_{bioavailable} values. For this analysis, at the Avoca site, the Bio-met Bioavailability Tool, Version 4.0, April 2017 (www.bio-met.net), was used. The spreadsheet calculates bioavailability factors, local HC5 values, risk characterisation ratios and local bioavailable metal concentrations. Cu, Zn, Ni and Pb can be evaluated in the current Bio-met model. The local bioavailable metal concentrations are compared to the generic EQS_{bioavailable}. The generic EQS_{bioavailable} values for Pb and Ni are 1.2 and 4 µg/L as discussed above (fixed by the WFD). In addition, generic EQS_{bioavailable} values for Cu (1 µg/L) and Zn (10.9 µg/L) are used in the program (but can be adjusted by the user). Note: these values were not 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_{bioavailable}). Required input for the Bio-met tool includes measured dissolved metal concentrations, pH, dissolved organic carbon concentrations and dissolved calcium concentrations at the site. The evaluations for dissolved copper and zinc, the parameters of concern, are presented in Table 14.

Table 14 Results from the Bio-Met model at 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	1.22	9.52	0.13	No	No	No
	Zn	33.5	15.8	22.5	Yes	No	No
	Pb	4.96	7.54	0.79	No	Yes	No
US Whites Bridge	Cu	0.734	11.4	0.06	No	No	No
	Zn	29.8	19.3	16.3	No	No	No
	Pb	3.14	10.6	0.35	No	Yes	No
Whites Bridge	Cu	0.625	9.52	0.07	No	No	No
	Zn	35.3	16.3	23.0	Yes	No	No
	Pb	3.44	7.54	0.55	No	Yes	No
Whites Bridge GS	Cu	17.4	3.22	5.41	Yes	Yes	Yes
	Zn	121	15.8	82.8	Yes	Yes	Yes
	Pb	3.71	7.58	0.59	No	Yes	No
DS Deep Adit	Cu	76.6	5.62	13.6	Yes	Yes	Yes
	Zn	388	18.8	225	Yes	Yes	Yes
	Pb	9.75	10.6	1.1	No	Yes	No
DS Millrace	Cu	30.1	7.04	4.28	No	Yes	No
	Zn	175	18.2	104	Yes	Yes	Yes
	Pb	5.68	10.6	0.64	No	Yes	No
US Ballygahan Adit	Cu	8.25	3.88	2.13	No	Yes	No
	Zn	52.6	11.6	48.5	Yes	Yes	No
	Pb	3.35	3.84	1.05	No	Yes	No
US Road Adit	Cu	14.3	6.50	2.20	No	Yes	No
	Zn	74.2	15.5	51.6	Yes	Yes	Yes

	Pb	3.8	7.56	0.60	No	Yes	No
Wicklow Co. Co. Main. Yard GS	Cu	17.5	3.22	5.44	Yes	Yes	Yes
	Zn	250	18.3	149	Yes	Yes	Yes
	Pb	7.18	10.6	0.81	No	Yes	No
Site T5	Cu	11.9	3.18	3.75	Yes	Yes	No
	Zn	98.4	11.6	91.5	Yes	Yes	Yes
	Pb	4.34	3.87	1.34	No	Yes	Yes
Avoca Bridge	Cu	10.3	5.23	1.97	No	Yes	No
	Zn	77	15.4	54.0	Yes	Yes	Yes
	Pb	4.01	7.58	0.64	No	Yes	No

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

As shown at the eleven sampling locations on the Avoca River, the bioavailable Cu, Pb and Zn concentrations are significantly less than the measured Cu, Pb and Zn concentrations. For Cu, the HC5 (and potential EQS_{bioavailable}) are in most cases higher (less stringent) than the current EQS of 5 µg/L. For Pb, the HC5 (and potential EQS_{bioavailable}) are in all cases higher (less stringent) than the current EQS of 1.2 µg/L. For Zn, the HC5 (and potential EQS_{bioavailable}) are lower (more stringent) than the current EQS of 50 µg/L. The following summarises the comparisons provided in the last three columns of Table 14.

- Number of exceedances when comparing bioavailable concentrations to the HC5: Cu = 4; Zn = 10; Pb = 0
- Number of exceedances when comparing measured concentrations to the current EQS: Cu = 8; Zn = 8; Pb = 11
- Number of exceedances when comparing bioavailable concentrations to the current EQS: Cu = 3; Zn = 7; Pb = 0

When using local HC5 and bioavailable concentrations, the number of locations with exceedances for Pb is reduced significantly (no locations have exceedances). This is due to the much higher HC5 values and much lower bioavailable concentrations for Pb. When using local HC5 and bioavailable concentrations, the number of locations with exceedances for Cu is also reduced significantly. This is due to the higher HC5 values and lower bioavailable concentrations for Cu. The number of exceedances for Zn is relatively the same for the different comparisons. The large number of exceedances for Zn are caused by the much higher concentrations of Zn compared to Pb and Cu at many locations.

Section 5

Flows, Loads and Trend Analysis

5.1 Surface Water Flows

Two EPA stream flow gauges exist on the Avoca River near the mine site, Whites Bridge GS (EPA station 10044) and the Wicklow County Council Maintenance Yard GS (EPA Station 10045). The Whites Bridge GS is located 90 m downstream of the bridge and just upstream of the confluence of the Deep Adit discharge. The Wicklow County Council Maintenance Yard GS is downstream of both the Deep Adit and the Road Adit as shown on Map 3 in [Appendix A](#).

The flow data from 1 April 2017 to 31 March 2018 for Whites Bridge GS is reproduced in Figure 2 and that for Wicklow County Council Maintenance Yard GS in Figure 3. The hydrographs show the measured flows ranged from 84 m³/s during high flow (March) to approximately 2-3 m³/s during low-flow (May and July). The flashy nature of the river shows a rapid response to rainfall. The median flows for this period of 8.11 m³/s at Whites Bridge GS and 7.62 m³/s at Wicklow County Council Maintenance Yard GS are lower than the long-term (2009-2018) median of approximately 8.5 m³/s and 9.1 m³/s respectively. As expected, the lowest flows were recorded in July and August with a baseline flow of approx. 2 m³/s at Whites bridge GS and 1.6 m³/s at Wicklow County Council Maintenance Yard GS. Note that the 95%-ile flow (low flow) is approximately 2 m³/s at both stations.

The river appears to respond similarly at both gauging stations as can be observed from the peaks in both figures. A discussion of the differences in flow rates between the two gauges is provided in Section 6.4.3.

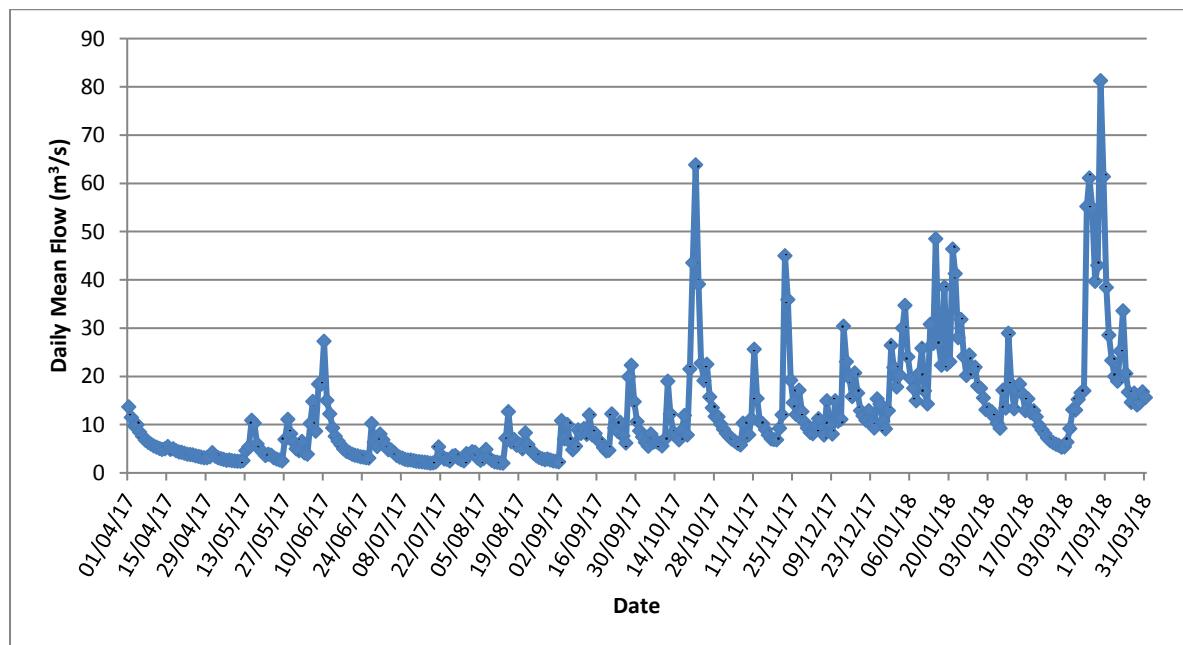


Figure 2 Mean Daily Flow (m³/s) at Whites Bridge (Station 10044) from 1 April 2017 to 31 March 2018

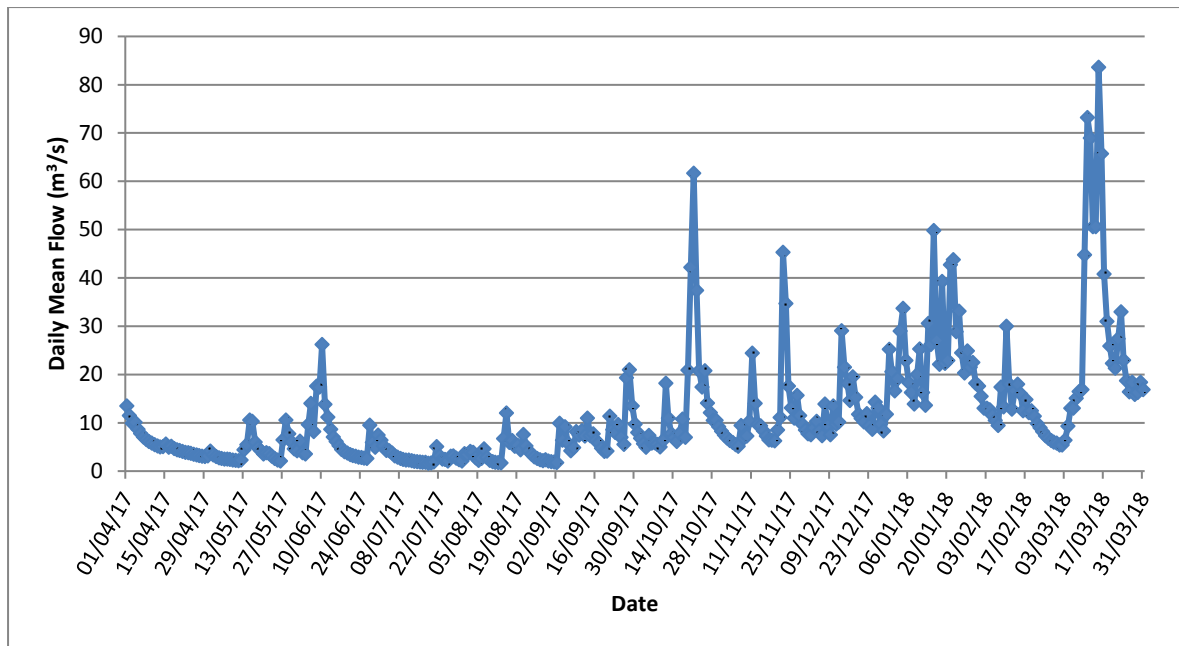


Figure 3 Mean Daily Flow (m³/s) at Wicklow County Council Maintenance Yard (Station 10045) from 1 April 2017 to 31 March 2018

Flow was measured directly in the field using different methodologies depending upon the quantity of flow to be measured and any safety concerns, as described in Section 2.1.2. Table 15 presents a summary of the results from the flows measured in March 2018 at the time of sampling. All flow measurements on the main river channel were performed on the same day; this provides a true representation of hydrogeological activity in the Avoca River. Refer to Appendix B of the Data Report for details of methodologies used per site and associated calculations. Note that a sustained heavy rainfall event on the day of sampling resulted in numerous ephemeral discharges contributing flow to the River.

The measured flow at the Deep Adit of 23.8 l/s is considered relatively high as past records for the Deep Adit range from approximately 10 to 37.5 l/s. The measured flow at the 850 Adit was 33 l/s which is also considered high as the previous recorded maximum flow was 19.3 l/s on 15 February 2016. Note that the 850 Adit discharges to the Deep Adit box culvert and, the US Tigroney west drainage channel (20.1 l/s on 14 March 2018) 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 drainage channel flow.

The measured flow at the Deep Adit confluence was 40.5 l/s which is significantly less than the combined flow upstream (76.9 l/s). The apparent loss of flow between both sampling locations is likely due to:

- The high water level in the deep adit channel resulting in water spilling over the side of the channel at two locations and into the Avoca River;
- Infiltration along the Deep Adit ditch, particularly in areas which are not generally submerged; and
- Inadequate flow measurement location at the Deep Adit confluence (not properly channelised). The measurement should be considered an estimate.

A flow meter was installed at the entrance of the 850 Adit in October 2017. Figure 4 shows the flow rate recorded at hourly intervals for the period 25 October 2017 to 13 July 2018 using a moving average (daily). From October to late December the flow rate is typically below 5 l/s after which point there is a sustained increase in flow which reflects groundwater recharge. The hydrograph also indicates that the adit responds quickly to heavy rainfall events as exemplified by the peak on 16 March. A corresponding peak in river flow is evident in Figure 2 and Figure 3.

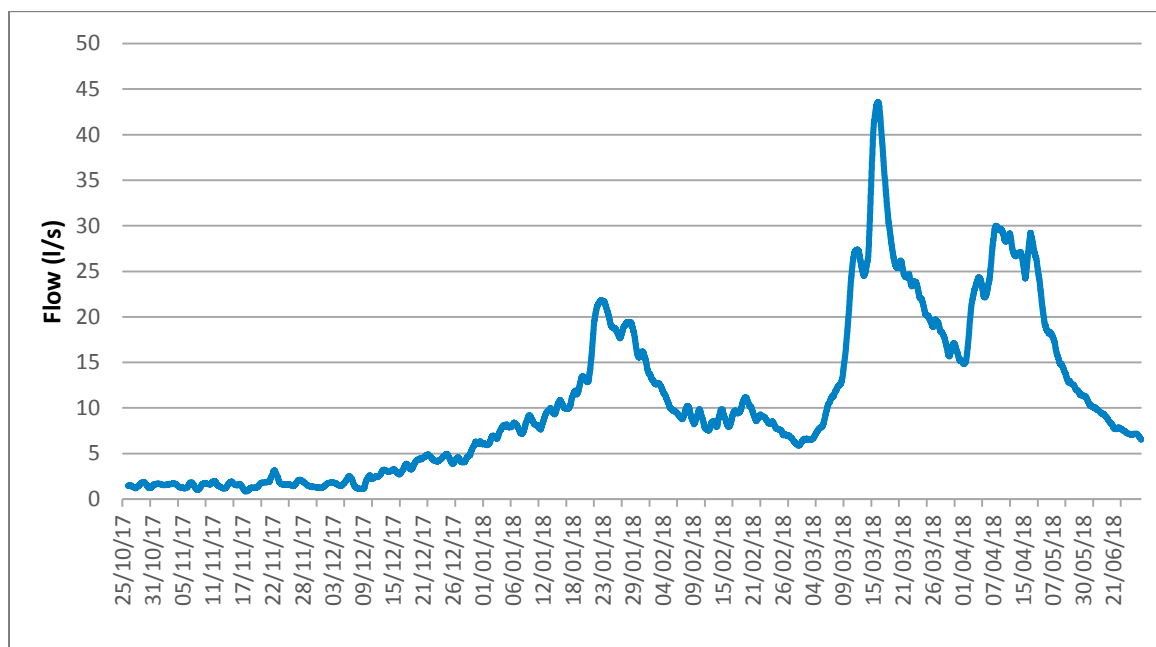


Figure 4 Recorded flow at the 850 Adit entrance from 25 October 2017 to 13 July 2018

The flow was measured at the Road Adit Confluence and the measured flow was 42.7 l/s which is considered high. Past records for the Road Adit range from approximately 6 to 58 l/s (CDM, 2008). At present, it is not possible to calculate the flow at the Road Adit portal (flume) due to the buildup of precipitate. However, due to the short distance between both sampling points, a significant difference in flow rates is unlikely.

Table 15 Surface Water Flows Measured in March 2018

Site Name	Flow m ³ /s	Flow l/s	Date	Notes
Site T1	43.0	43,000	13/03/2018	Combined flow from the Avonmore and Avonbeg river
US Whites Bridge	35.1	35,073	13/03/2018	
Whites Bridge	37.0	37,000	13/03/2018	
White's Bridge GS	37.0	37,000	13/03/2018	
DS Deep Adit	36.8	36,777	13/03/2018	
DS Millrace	45.8	45,773	13/03/2018	
US Ballygahan Adit	49.2	49,200	13/03/2018	
US Road Adit	49.2	49,173	13/03/2018	
Wicklow Co. Co. Main. Yard GS	50.2	50,200	13/03/2018	
Site T5	50.4	50,400	13/03/2018	
Avoca Bridge	56.6	56,600	13/03/2018	
US Tigroney West	0.02	20.1	14/03/2018	Drainage from East Avoca track
850 Adit	0.03	33.0	14/03/2018	
Deep Adit	0.02	23.8	14/03/2018	

Site Name	Flow m ³ /s	Flow l/s	Date	Notes
Deep Adit Confluence	0.04	40.5	14/03/2018	
Road Adit	0.04	42.7	14/03/2018	
Road Adit Confluence	0.04	42.7	14/03/2018	
Cronebane Intermediate Adit	0.01	9.9	14/03/2018	
Cronebane Shallow Adit	0.007	6.7	14/03/2018	

5.2 Loading Analysis

5.2.1 Loading Analysis Methodology

Mass loads (kg/day) were calculated for the Avoca River, the adits, and tributaries using measured 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.

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		Aluminium		Copper		Iron		Lead		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
Avoca Bridge	13/03/2018	56600	6.29	6300	30800	212	1040	10.3	50.4	201	983	4.01	19.6	77	377
DS Deep Adit	13/03/2018	36777	5.47	14600	46400	515	1640	76.6	243	65.9	209	9.75	31	388	1230
DS Millrace	13/03/2018	45773	6.15	7600	30100	328	1300	30.1	119	96	380	5.68	22.5	175	692
Site T1	13/03/2018	43000	6.61	2900	10800	114	424	1.22	4.53	74.5	277	4.96	18.4	33.5	124
Site T5	13/03/2018	50400	6.4	8600	37400	243	1060	11.9	51.8	414	1800	4.34	18.9	98.4	428
US Ballygahan Adit	13/03/2018	49200	6.52	5300	22500	186	791	8.25	35.1	114	485	3.35	14.2	52.6	224
US Road Adit	13/03/2018	49173	6.39	6100	25900	247	1050	14.3	60.8	135	574	3.8	16.1	74.2	315
US Whites Bridge	13/03/2018	35073	6.57	2100	6360	110	333	0.734	2.22	79.9	242	3.14	9.52	29.8	90.3
WCC Main. Yard GS	13/03/2018	50200	5.96	22900	99300	337	1460	17.5	75.9	2340	10100	7.18	31.1	250	1080
Whites Bridge	13/03/2018	37000	6.64	1000	3200	119	380	0.625	2	130	416	3.44	11	35.3	113
Whites Bridge GS	13/03/2018	37000	5.83	6600	21100	337	1080	17.4	55.6	109	348	3.71	11.9	121	387
850 Adit	14/03/2018	33	2.94	859000	2450	60200	172	6050	17.2	17200	49	904	2.58	30000	85.5
Cronebane Inter. Adit	14/03/2018	9.94	2.96	683000	587	53500	45.9	9390	8.06	61300	52.6	1090	0.94	29800	25.6
Cronebane Shallow Adit	14/03/2018	6.7	2.78	1370000	793	132000	76.4	6240	3.61	88500	51.2	683	0.4	31200	18.1
Deep Adit	14/03/2018	23.77	3.44	215000	442	15800	32.4	790	1.62	4560	9.36	869	1.78	7000	14.4
Deep Adit Confluence	14/03/2018	40.49	3.18	563000	1970	49100	172	5180	18.1	10700	37.4	705	2.47	19800	69.3
Road Adit	14/03/2018	42.74	4.43	1280000	4730	10500	38.8	298	1.1	134000	495	240	0.89	8890	32.8
Road Adit Confluence	14/03/2018	42.74	4.58	1250000	4620	10600	39.1	267	0.99	128000	473	233	0.86	8050	29.7
US Tigroney West	14/03/2018	20.08	4.19	154000	267	6250	10.8	934	1.62	1100	1.91	306	0.53	2110	3.66

Loading from Adit Discharges

The Deep Adit had aluminium, copper and zinc loads of 32.4, 1.62 and 14.4 kg/day and the Road Adit had loads of 38.8, 1.1 and 32.8 kg/day, respectively. The Road Adit had sulphate and iron loads of 4,730 kg/day and 495 kg/day, respectively. Calculated loads for the Deep Adit were lower at 442 kg/day and 9.36 kg/day, respectively.

The flow from the Cronebane Intermediate Adit ultimately discharges to the 850 Adit, through the Copse Shaft, approximately 600 m from the entrance of the adit. In March 2018, there was a significant increase in flow between both monitoring points (9.9 to 33 l/s). It should be noted that there was very heavy rainfall at the time of sampling. Accordingly, there was an increase in sulphate (587 kg/day to 2,450 kg/day), aluminium (45.9 kg/day to 172 kg/day), copper (8.06 kg/day to 17.2 kg/day), lead (0.94 kg/day to 2.58 kg/day) and zinc (25.6 kg/day to 85.5 kg/day). Dissolved iron load decreased from 52.6 kg/day to 49 kg/day which is likely due to oxidation and precipitation within the mine workings. Compared to the Deep Adit, the 850 Adit had higher loads of aluminium (172 kg/day and 32.4 kg/day), copper (17.2 kg/day and 1.62 kg/day) iron (49 kg/day and 9.36 kg/day), lead (2.58 kg/day and 1.78 kg/day), zinc (85.5 kg/day and 14.4 kg/day) and sulphate (2,450 kg/day and 442 kg/day).

Significant loads of dissolved metals were calculated for the Tigroney West drainage channel which captures runoff (during rainfall) from the East Avoca track and discharges to the Deep Adit channel, downgradient of the Deep Adit box culvert. As detailed in Table 16, the drainage channel had estimated loads of dissolved aluminium, copper and zinc of 10.8 kg/day, 1.62 kg/day and 3.66 kg/day, respectively.

The Deep Adit confluence comprises flow from the 850 Adit, Deep Adit and the Tigroney West drainage channel. Dissolved metals loads were estimated at 172 kg/day for aluminium, 18.1 kg/day for copper, 37.4 kg/day for iron, 2.47 kg/day for lead and 69.3 kg/day for zinc. There is an apparent significant decrease in metal loads along the Deep Adit channel which is primarily due to a decrease in flow rate (see Section 5.1 for possible causes).

The Cronebane Shallow Adit is considered of secondary 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). A relatively high flow (6.7 l/s) recorded in March 2018 resulted in increased loads of dissolved metals; 76.4 kg/day for aluminium, 3.61 kg/day for copper and 18.1 kg/day for zinc. Ballygahan Adit was dry at the time of sampling.

Avoca River Loadings

Background Loadings

Background loads upstream of the Avoca Mining Area of metals were present which is evident from the calculated loads at Site T1. The dissolved metal loads at Site T1 were 424 kg/day for aluminium, 4.53 kg/day for copper, 277 kg/day for iron, 18.4 kg/day for lead and 124 kg/day for zinc. Figure 5 and Figure 6 graphically show the calculated loads of dissolved aluminium, iron, 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](#)). It is important to note that composite samples could not be collected due to high flow conditions and therefore loading estimates contain a relatively high level of uncertainty.

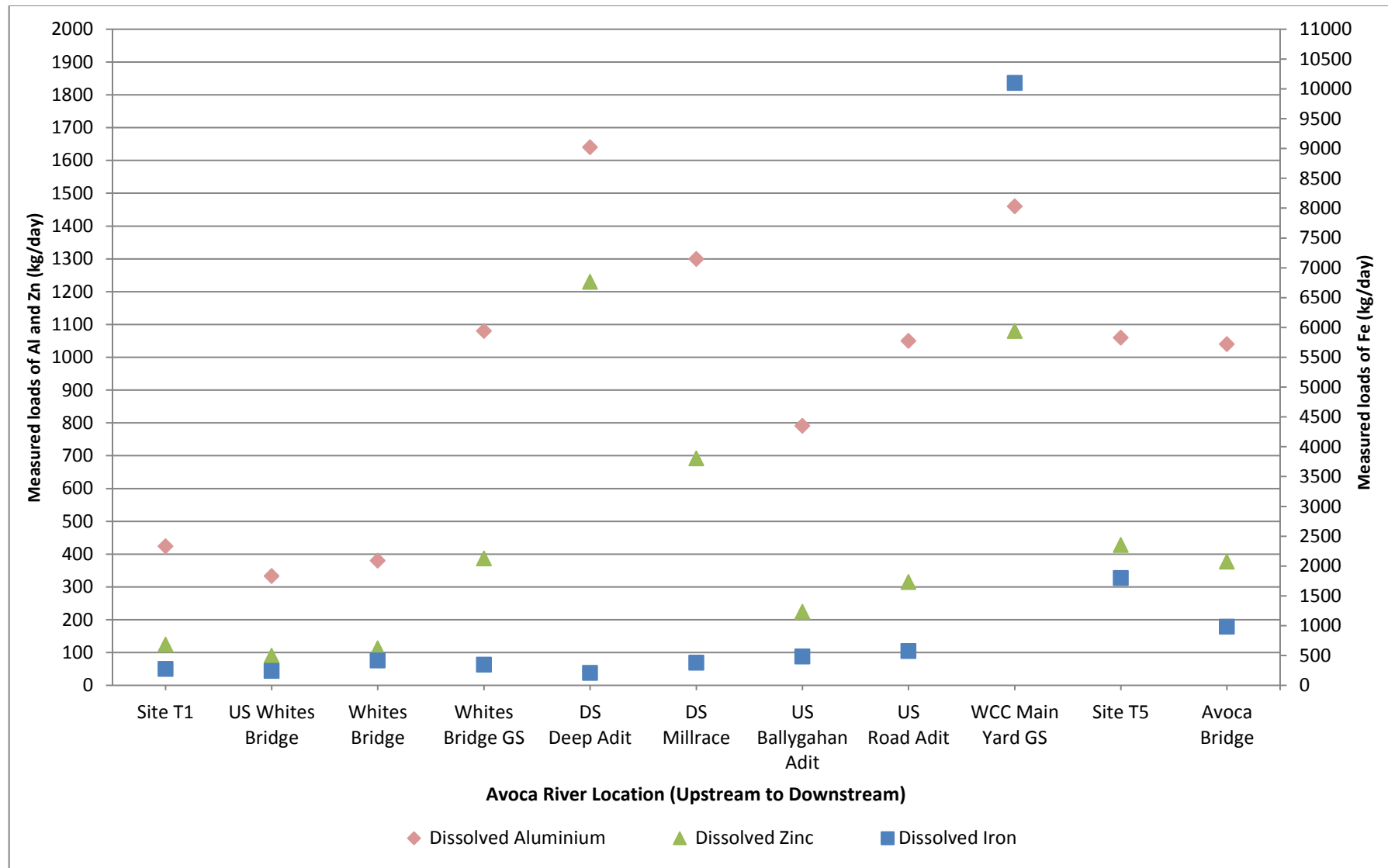


Figure 5 Calculated Loads of Dissolved Aluminium, Iron and Zinc (kg/day) in the Avoca River in March 2018

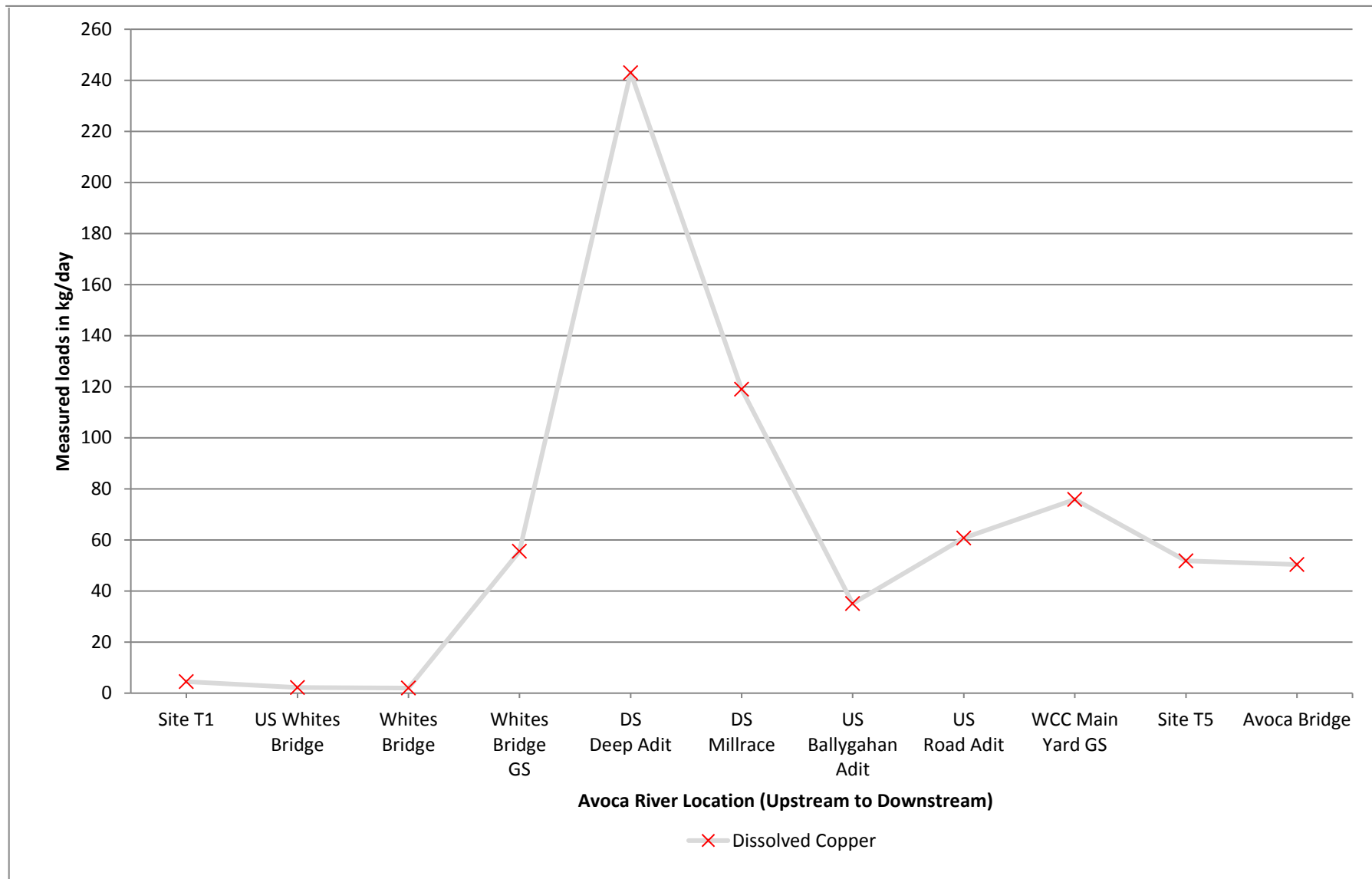


Figure 6 Calculated Loads of Dissolved Copper (kg/day) in the Avoca River in March 2018

Whites Bridge

At sampling location US Whites Bridge which is located approximately 365m upstream of the bridge, there is a slight decrease in dissolved metal loads compared to Site T1 which is likely due to the overestimation of flow at Site T1. High flow conditions resulted in the flow rate at T1 being calculated using the float method on the upstream Avonmore and Avonbeg tributaries. Further downstream at Whites Bridge there is an increase with loads of dissolved aluminium at 380 kg/day, iron at 416 kg/day and zinc at 113 kg/day. There was a negligible difference in dissolved lead and copper loads. Between Whites Bridge and Whites Bridge GS, aluminium increased by 700 kg/day, copper by 53.6 kg/day, lead by 0.9 kg/day and zinc by 274 kg/day. The dissolved iron load decreased by 68 kg/day likely due to precipitation.

Deep Adit Discharge and Contaminated Millrace Area

The DS Deep Adit location on the Avoca River is downstream of the Deep Adit discharge (Deep Adit Confluence sample) and 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 5 and Figure 6, a significant increase in loads occurs at DS Deep Adit compared to the upstream sampling location (Whites Bridge GS) with increases in aluminium (1,080 kg/day to 1,640 kg/day), copper (55.6 kg/day to 243 kg/day), lead (11.9 kg/day to 31 kg/day) and zinc (387 kg/day to 1,230 kg/day). Sulphate loads increased by 25,300 kg/day.

Taking into account the calculated dissolved metal loads at the Deep Adit Confluence the loading results at DS Deep Adit would be expected to be lower. The additional dissolved metal load indicates that the contamination of the alluvial material in the Millrace area are a secondary source of diffuse load to the Avoca River. Note that the contaminated Millrace area located parallel to the Avoca River extended further downstream than the DS Deep Adit sampling location and therefore a sample was also collected at DS Millrace. Dissolved metal loads at the DS Millrace sampling location decreased for aluminium (1,640 kg/day to 1,300 kg/day), copper (243 kg/day to 119 kg/day), lead (31 kg/day to 22.5 kg/day) and zinc (1,230 kg/day to 692 kg/day). This decrease is likely due to further dilution of the Deep Adit discharge and metal precipitation.

Between DS Millrace and US Ballygahan Adit, dissolved aluminium decreased by 509 kg/day, copper by 83.9 kg/day, and zinc by 468 kg/day (see Figure 5). In contrast, the calculated dissolved iron load increased from 380 kg/day to 485 kg/day indicating a diffuse source of dissolved iron within this river stretch.

Ballygahan Adit and Seeps

In order to assess the groundwater seeps which, discharge to the River in close proximity to the Ballygahan Adit (dry at the time of sampling), samples were collected upstream (US Ballygahan Adit) and downstream (US Road Adit). Increases were calculated for the following dissolved metals; aluminium (791 kg/day to 1,050 kg/day), copper (35.1 kg/day to 60.8 kg/day), iron (485 kg/day to 574 kg/day), lead (14.2 kg/day to 16.1 kg/day) and zinc (224 kg/day to 315 kg/day).

Road Adit Discharge

The Road Adit is the primary discharge from West Avoca. Upstream of the Road Adit Confluence (US Road Adit), dissolved metal loads were calculated as follows; aluminium (1,050 kg/day), copper (60.8 kg/day), iron (574 kg/day), lead (16.1 kg/day) and zinc (315 kg/day).

The Wicklow County Council Maintenance Yard GS sampling location is located downstream of the Road Adit discharge since October 2014. Taking into account the loadings at US Road Adit and at the Road Adit Confluence the loads would be expected to be 1,088 kg/day for aluminium, 61.9 kg/day for copper and 348 kg/day for zinc. However, the calculated loadings at Wicklow County Maintenance Yard GS were higher for aluminium (1,460 kg/day), copper (75.9 kg/day) and zinc (1,080 kg/day).

The increase in loads at Wicklow County Council Maintenance Yard GS can be attributed to the Road Adit which discharges to the Avoca River approximately 65m upstream and may have undergone limited dilution. This is the primary cause of the very high and overestimated iron load (10,100 kg/day). The additional or unexplained increase can be attributed to diffuse groundwater flow which is consistent with the findings of a dye tracer study undertaken on the Avoca River in September 2016.

Further downstream at Site T5 and Avoca Bridge dissolved metal loads decrease significantly which is likely due to precipitation and further dilution of the Road Adit discharge.

5.3 Trend Analysis

5.3.1 Historical Trends

This section discusses concentration time trends for select locations including the Deep Adit, the Road Adit and one location on the Avoca River for selected parameters (dissolved copper, zinc and iron). The trends are shown graphically in Figure 7 (Deep Adit from October 2001 to March 2018), Figure 8 (Deep Adit from October 2001 to March 2018, excluding high values recorded in November 2001), Figure 9 (Road Adit from October 2001 to March 2018) and Figure 10 (Avoca River at Avoca Bridge from October 2001 to March 2018).

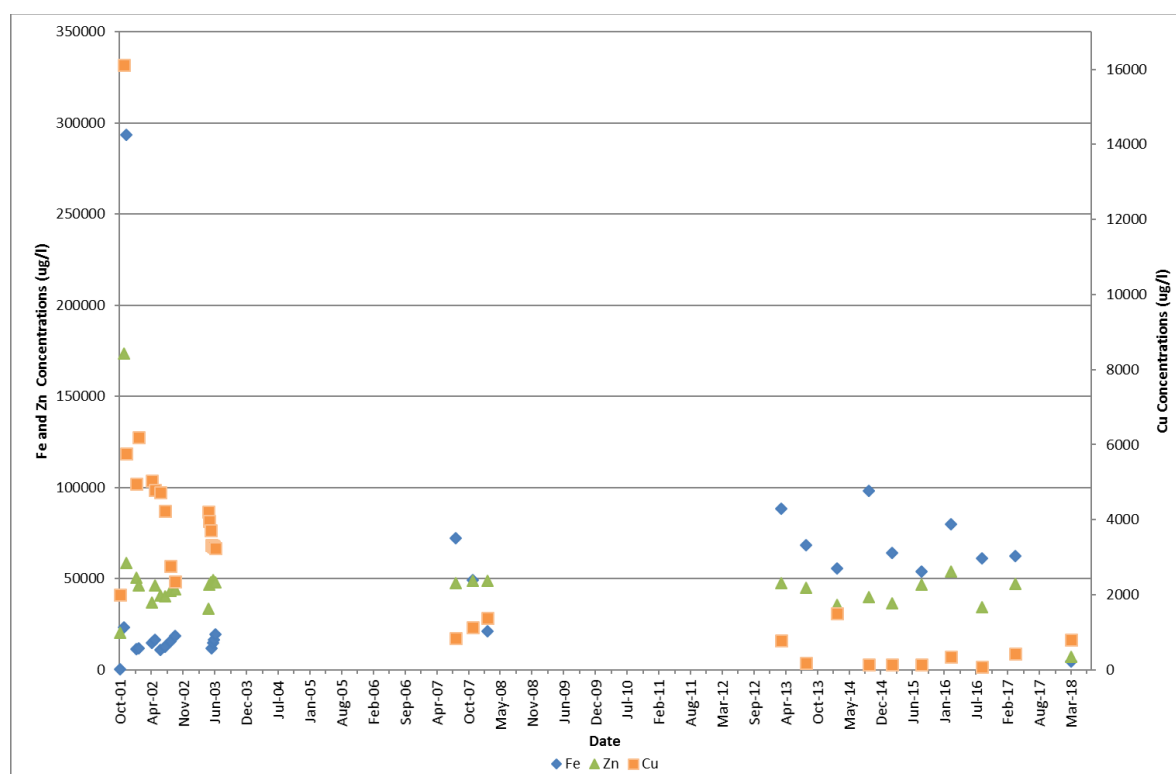


Figure 7 Concentration trends for dissolved copper, zinc and iron within the Deep Adit Discharge (Oct 2001 to March 2018)

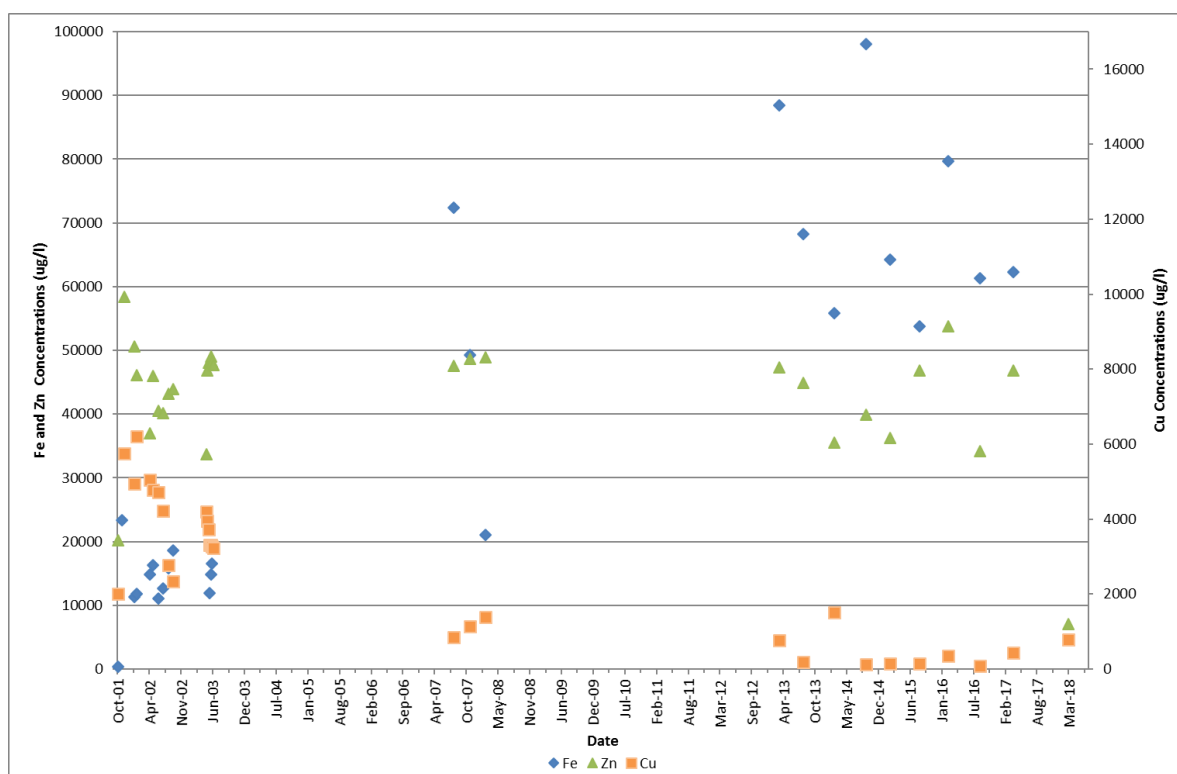


Figure 8 Concentration trends for dissolved copper, zinc and iron within the Deep Adit Discharge (Oct 2001 to March 2018), excluding high values recorded in November 2001

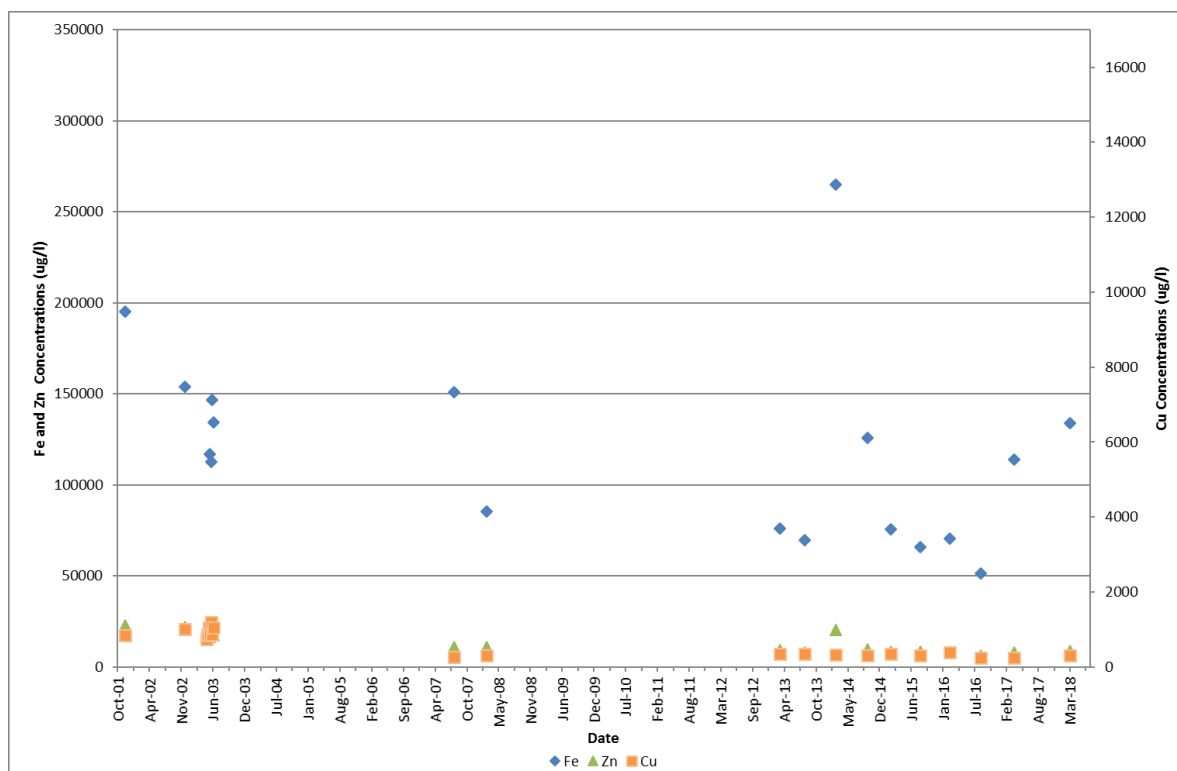


Figure 9 Concentration trends for dissolved copper, zinc and iron within the Road Adit Discharge (Oct 2001 to March 2018)

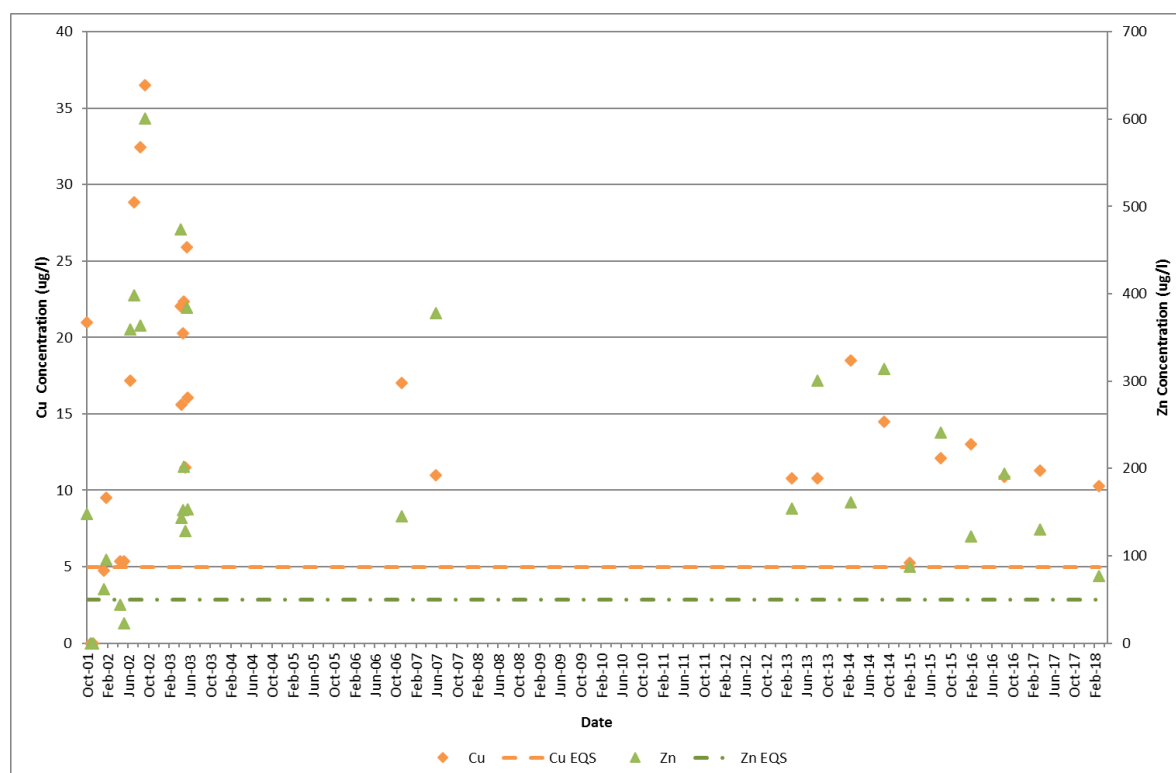


Figure 10 Concentration trends for dissolved copper and zinc at Avoca Bridge compared with the environmental quality objective (EQS) (Oct 2001 to March 2018)

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 results in the identification of 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 value and a maximum of 50% of the sample set is reported as non-detect.

Trend analyses were conducted for all data since October 2001 because data were available for all the sample locations from that date onwards. Analyses on data since June 2007 were also carried out to determine if there were any trends in more recent data, which also eliminated the high results in 2001/2002. The Mann-Kendall test results for both time periods 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	October 2001 to March 2018			June 2007 to March 2018		
		P value	S value	Trend	P value	S value	Trend
Deep Adit	Copper	<0.001	-341	Decreasing	0.1	-22	No trend
	Zinc	0.20	-51	No trend	0.04	-30	Decreasing
	Iron	0.001	154	Increasing	0.29	-10	No trend
Road Adit	Copper	0.001	-102	Decreasing	0.27	-10	No trend
	Zinc	<0.001	-134	Decreasing	0.04	-26	Decreasing
	Iron	0.009	-63	Decreasing	0.19	-14	No trend
Avoca Bridge	Copper	0.09	-69	Possibly decreasing	0.23	-6	No trend
	Zinc	0.460	-6	No trend	0.03	-25	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 October 2001 to March 2018 show that:

- Dissolved copper concentrations are decreasing in the Deep Adit and there is no trend for dissolved zinc. However, dissolved iron is increasing in the Deep Adit.
- Dissolved copper, dissolved zinc and dissolved iron are decreasing in the Road Adit. These trends can also be inferred from Figure 7 and Figure 9.
- Dissolved copper concentrations are possibly decreasing at the Avoca Bridge. This trend can also be inferred from Figure 10. The ecological assessment criteria (or EQS) are also shown on the graph for reference. Dissolved copper has been above the ecological assessment criteria of 5 µg/l since mid-2002.

The results of the Mann-Kendall analysis for June 2007 to March 2018 show that:

- Dissolved zinc is decreasing in the Deep Adit and the Road Adit.
- Dissolved zinc is decreasing at Avoca Bridge. Dissolved zinc has been above the ecological assessment criteria of 50 µg/l since mid-2002, as shown in Figure 10.

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

5.3.2 Seasonal Trends

Table 19 shows the seasonal variation between the concentrations of dissolved metals and the calculated loads observed between the high flow sampling events in March 2013, February 2014, February 2015, February 2016 and March 2017, and the low flow sampling events in August 2013, September 2014, August 2015 and August/September 2016. The following points detail the March 2018 sampling event (high flow) in the context of previous results:

- In March 2018, the flow rates at the Deep Adit (23.8 l/s), Road Adit (42.7 l/s) and Avoca Bridge (56,600 l/s) were comparatively high. Concentrations of dissolved iron (4,560 µg/l),

zinc (7,000 µg/l) and aluminium (15,800 µg/l) at the Deep Adit were significantly lower than previous monitoring rounds as shown in Table 19. In contrast, dissolved copper was higher than average with a value of 790 µg/l. Because of the relatively low concentrations, dissolved metal loads were lower than previous rounds for aluminium, iron and zinc. The dissolved copper load at the Deep Adit was 1.62 kg/day which is higher than average.

- At the Road Adit, concentrations of dissolved copper (298 µg/l), aluminium (10,500 µg/l) and zinc (8,890 µg/l) were relatively high but below average. Dissolved iron was above average with a value of 134,000 µg/l. Calculated loads of dissolved copper and iron were above average with estimated values of 1.1 kg/day and 495 kg/day, respectively. Calculated loads of dissolved aluminium (38.8 kg/day) and zinc (32.8 kg/day) were below average but nonetheless significant.
- Concentrations of dissolved aluminium (212 µg/l), copper (10.3 µg/l) and iron (201 µg/l) at Avoca Bridge were similar to previous high flow sampling results with dissolved aluminium being above average. Dissolved zinc was lower than previous results with a value of 77 µg/l. Estimated dissolved metal loads for aluminium (1,040 kg/day) copper (50.4 kg/day) and zinc (377 kg/day) were significantly greater than previous loadings, primarily due to the high flow conditions. Dissolved iron load (983 kg/day) was close to the previous maximum value recorded (1,010 kg/day).

Table 19 Seasonal Variation of Concentrations and Calculated Loads of Dissolved Metals in the Adits and at Avoca Bridge from 2013-2017

		Deep Adit				Road Adit				Avoca Bridge			
		High Flow		Low Flow		High Flow		Low Flow		High Flow		Low Flow	
Flow (l/s)	Min	12		10.4		17.4		8.34		10,350		1,940	
	Max	29.2		19.5		56.2		18		24,000		3,298	
	Average	20		15.1		33.5		14.1		16,969		2,872	
units		µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day
Aluminium	Min	71,600	87.9	68,500	61.6	10,000	15	10,900	7.85	152	140	93.1	25.8
	Max	98,800	249	106,000	179	15,000	72.8	16,400	24.3	246	427	161	37
	Average	84,100	138	87,850	118	12,900	39.6	14,050	17.7	174	259	121	29
Copper	Min	147	0.2	85.2	61.6	232	0.35	244	0.18	5.24	9.1	10.8	1.81
	Max	1,500	2.9	184	0.21	382	1.6	335	0.46	18.5	38.4	14.5	4.06
	Average	640	1.17	135	0.17	328	0.97	295	0.37	11.8	17.9	12.1	3.05
Iron	Min	55,800	73	53,800	55.1	70,400	171	51,500	37.1	153	158	161	38.9
	Max	88,500	223	98,100	148	265,000	1290	126,000	196	485	1,010	232	52.1
	Average	70,100	116	70,375	92.8	120,220	461	78,200	102	275	431	190	46
Zinc	Min	35,500	52	34,200	30.7	7,960	12	6,300	4.54	87	116	194	50.5
	Max	53,800	119	46,800	78.8	20,100	97.6	9,810	15.3	161	334	314	88
	Average	43,960	70.0	41,450	55.2	10,804	38.9	8,053	10.2	131	191	263	64.1

Section 6

Groundwater Levels and Groundwater-Surface Water Interaction

6.1 Groundwater Levels

Groundwater levels were measured at the eight wells using a portable electronic water level recorder. Table 20 provides the measured depth to groundwater and calculated groundwater elevations. All groundwater level data are contained in Appendix C of the Data Report. The groundwater elevations varied between 26.06 to 27.87 m Ordnance Datum (OD) in the Avoca Mining Area. These groundwater elevations were between 0 to 0.9 metres higher than the elevations measured in March 2017 with the exception of GW2/05 which was 0.45 m lower. The groundwater elevations were consistent with the hydraulic gradient towards the Avoca River.

Table 20 Measured Groundwater Levels and Calculated Elevations March 2018

Borehole Identifier	Date	Time	Depth to Groundwater (m bTOC)	Depth to Groundwater (m bgs)	Groundwater Elevation (m OD)
MWDA1	12/03/2018	11:45	5.23	4.63	27.56
MWDA2	12/03/2018	11:10	5.31	4.58	27.31
MWET1	12/03/2018	14:45	6.43	5.86	26.96
MWET2	12/03/2018	15:30	6.34	5.64	27.03*
MWPF1	12/03/2018	9:15	3.62	3.03	27.87*
GW1/05	07/03/2018	12:10	4.74	4.10	26.06*
GW2/05	07/03/2018	11:35	4.87	4.04	26.08*
SG104	07/03/2018	13:30	Dry	Unknown	-

Notes:

m is metres

OD is Ordnance Datum

bTOC is below top of casing

bgs is below ground surface

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

Automatic pressure transducers and loggers have been installed in the five wells owned by the Department. Figure 11 shows the groundwater elevations of the five wells located in the Avoca Mining Area from 27 March 2017 to 11 March 2018. For MWET2, no data are available for the period 27 March 2017 to 24 May 2017 due to a logger malfunction. Note that the datalogger MWSA2 (Shelton Abbey) was removed in March 2018. Data for MWSA2 is provided in Appendix C of the corresponding Data Report.

Table 20 and Figure 11 show that the heads are higher in the shallow alluvium monitoring well MWDA1 with respect to 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, discharges into the alluvial aquifer.

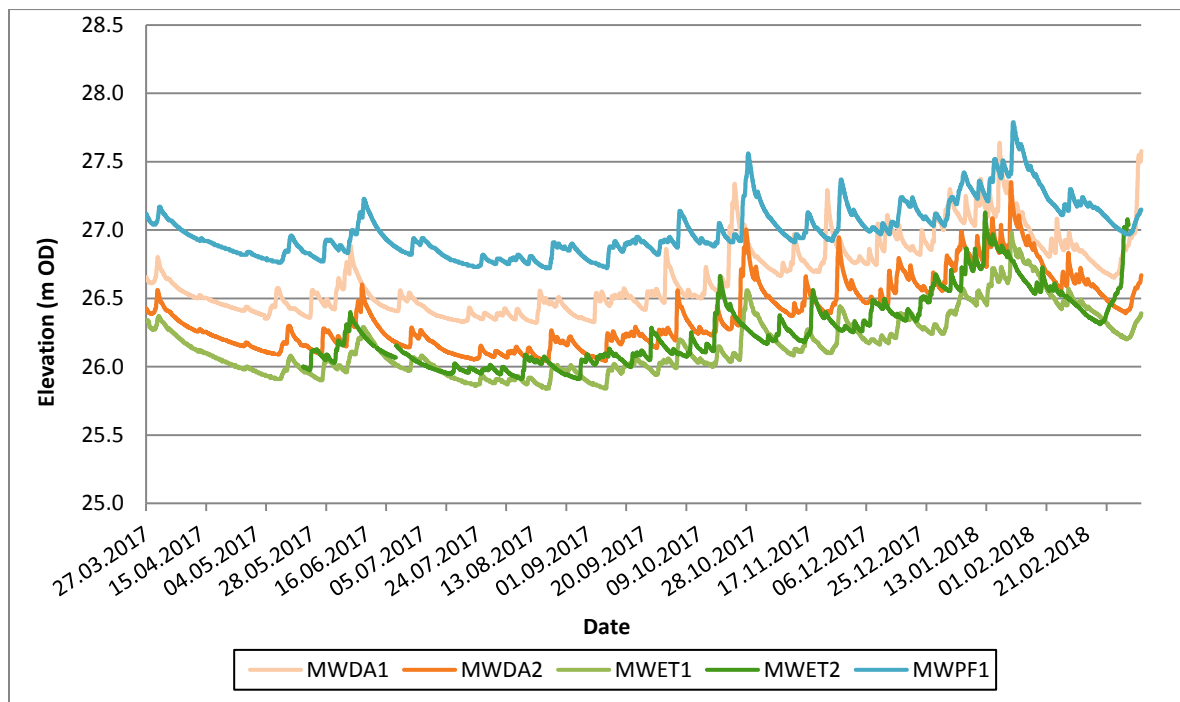


Figure 11 Groundwater Elevations in the Avoca Mining Area from 27 Mar 2017 to 11 March 2018

In contrast to MWDA1 and MWDA2, the head is slightly greater 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. There was a negligible difference between the alluvial well GW2/05 and top of bedrock (GW1/05) at this location in March 2018 (Figure 11).

6.2 Surface Water Levels

As described in Section 5.1 Surface Water Flows, there are 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 GS (EPA Station 10045). The measured water elevations from 28 March 2017 to 7 March 2018 for Whites Bridge GS and Wicklow County Council Maintenance Yard GS are reproduced in Figure 12. Additionally, the calculated elevations of the Avoca River at the mid-point between the two automatic flow gauges are shown in Figure 12. The figure demonstrates that the river appears to respond similarly at both gauging stations.

The distance between the two gauging stations is approximately 470 metres. The measured surface water elevations were used to calculate the average gradient between the two gauges for the monitoring period, which was 0.006. Streambed characteristics and the elevations both influence the flow rates and help define any apparent losses or gains in river flow.

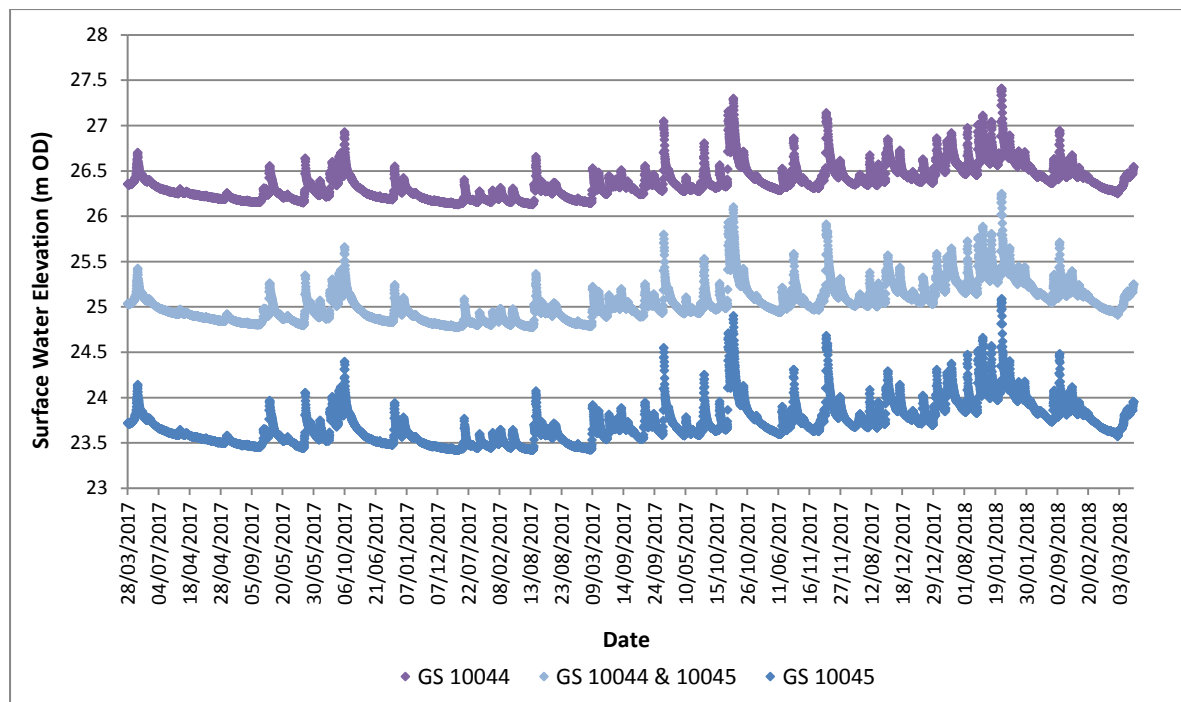


Figure 12 Elevation of the Avoca River at GS 10044 and GS 10045 at the Deep Adit Area from 28 March 2017 to 7 March 2018

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 both the Whites Bridge GS (GS 10044) and the Wicklow County Council Maintenance Yard GS (GS 10045) by selecting a midpoint water level. The estimated surface water elevations for the emergency tailing area for the period 28 March 2017 to 7 March 2018 are displayed on Figure 12 (GS 10044 & GS 10045); and
- For SG104 the water elevation from Wicklow Maintenance Yard County Council (GS 10045) would be used; however, the monitoring well was dry at the time of sampling.

Table 21 summarises resulting hydraulic gradient data between the monitoring well clusters and the Avoca River during the sampling event and, shows an estimated gradient from the wells to the river at the time of sample collection in March 2018. These values are similar to previous rounds in both direction and magnitude with an estimated mean gradient of 0.015, 0.009 and 0.022 for MWDA1, MWDA2 and MWPF1, respectively.

Table 21 Calculated Groundwater Gradients for March 2018

Borehole Identifier	Date	Time	Groundwater Elevation (m OD)	Water Elevation at Perpendicular Stream Point (m OD)	Distance to Perpendicular Stream Point (m)	Gradient
MWDA1	12/03/2018	11:45	27.56	26.95	40	0.015
MWDA2	12/03/2018	11:10	27.31	26.95	40	0.009
MWET1	12/03/2018	14:45	26.96*	25.74**	72	0.030
MWET2	12/03/2018	15:30	27.03*	25.73**	72	0.032
MWPF1	12/03/2018	9:15	27.87	26.98	44	0.022
GW1/05	07/03/2018	12:10	26.06*	25.16**	74	0.023
GW2/05	07/03/2018	11:35	26.08*	25.16**	74	0.023
SG104	07/03/2018	13:30	-	23.86	142	-

* 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.

Hourly water level data for both gauges on the Avoca River (Whites Bridge GS (EPA station 10044) and the Wicklow County Council Maintenance Yard GS (EPA Station 10045)) were obtained for the monitoring period from the EPA. Groundwater elevation data were plotted against the recorded elevations of the Avoca River as shown in Figure 13 for the Deep Adit area and Figure 15 for the Emergency Tailings area. Both figures demonstrate that there is a direct relationship between the river stage and the groundwater levels in both areas. Rises in river levels are 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 0.7 metres between 15 and 17 October 2017. This peak was in response to river levels which rose by up to 0.7 metres during the same event. From October 2017 to January 2018, groundwater levels gradually increase in the Deep Adit area and the Emergency Tailings area. A decrease in groundwater and surface water (river) levels occur in February and March 2018.

Figure 14 and Figure 16 show the calculated gradient to the Avoca River at the Deep Adit area (MWDA1, MWDA2) and the Emergency Tailings area (MWET1, MWET2) from 28 March 2017 to 7 March 2018 based on hourly elevation data. Both figures show that as river stages change 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 in both areas 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.

However, Figure 14 (Deep Adit area) shows that a negative gradient occurs during periods of high flow, particularly when there was a rapid rise in water level. From 26 to 19 November 2017, a significant hydrological (rainfall) event resulted in groundwater levels rising in MWDA1 and MWDA2 by approximately 0.6 metres. A negative gradient of up to -0.022 and -0.014 can be

observed during this period between the river and MWDA2 and MWDA1, respectively. From the beginning of May 2017 to the end of July 2017 gradients are predominantly negative for MWDA2. The minimum gradient for MWDA2 was -0.018 while the average was -0.001. For MWDA1 which is the shallower well, a positive gradient existed for approximately 95% of the monitoring period. The findings indicate that shallow groundwater in the Deep Adit area is likely discharging to the Avoca River for the majority of the monitoring period.

For MWET1 and MWET2, only positive gradients were observed during the monitoring period with a minimum gradient of 0.003 (MWET2) and a maximum of 0.03 (MWET2). Note that 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 Wicklow County Council Maintenance Yard gauges because they are located equidistance between the gauges.

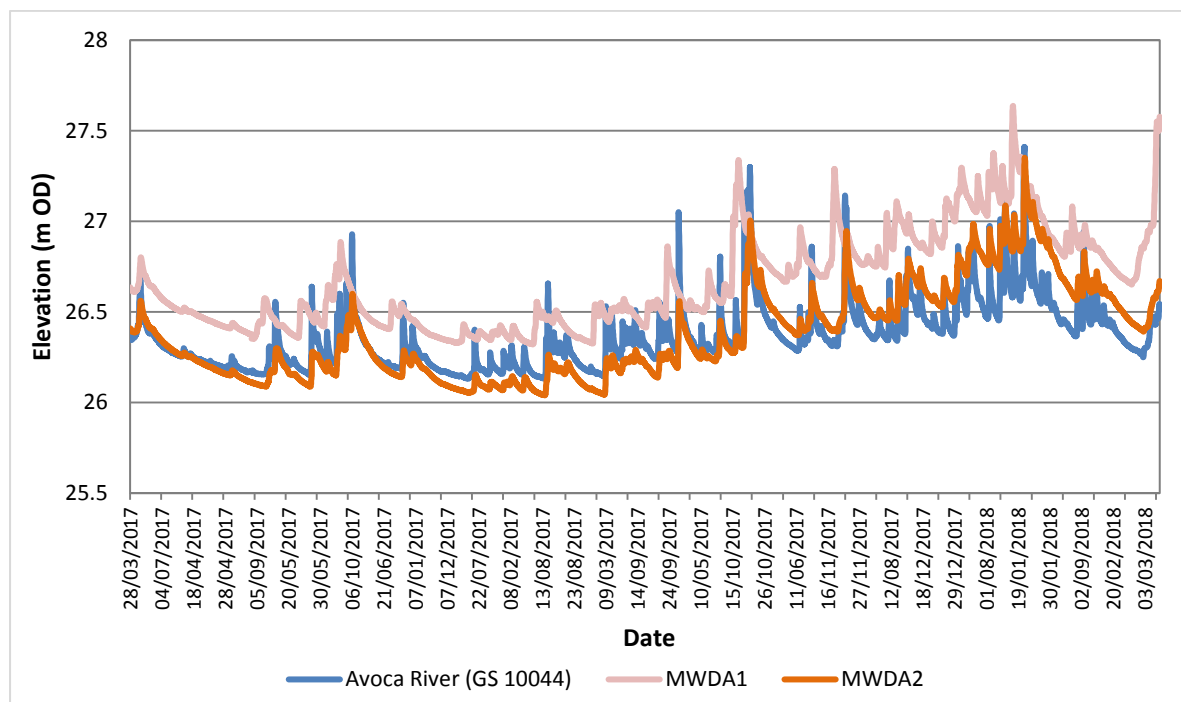


Figure 13 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044) at the Deep Adit Area from 28 March 2017 to 7 March 2018

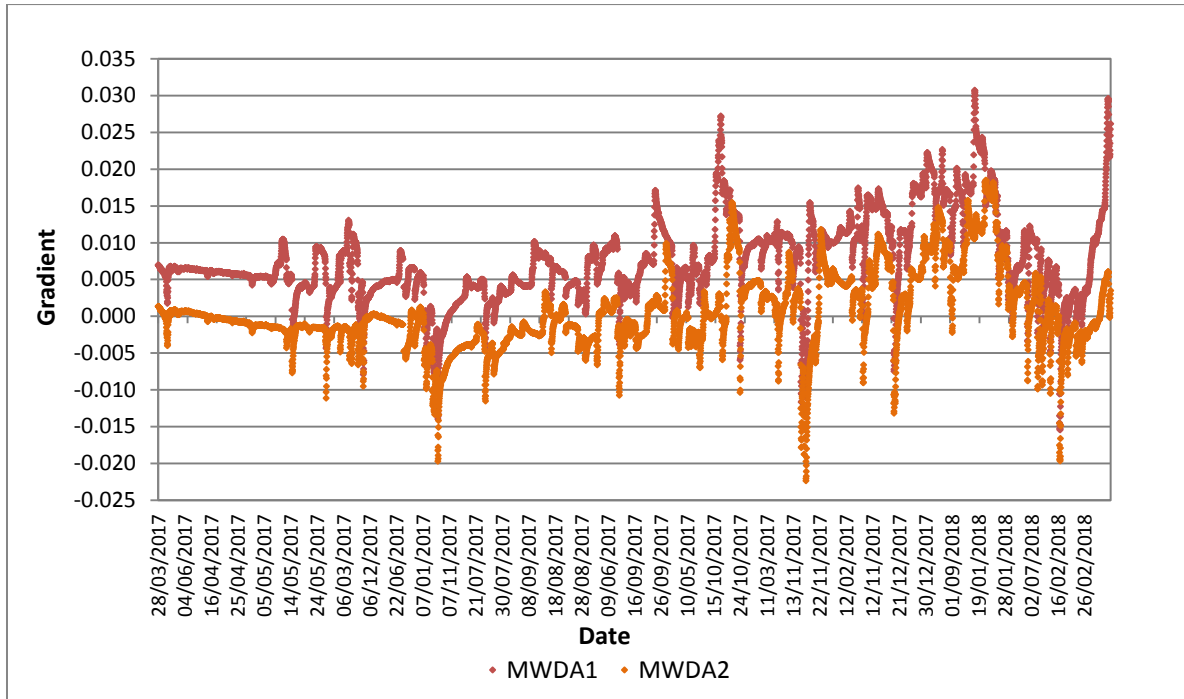


Figure 14 Calculated Groundwater Gradient to the Avoca River at the Deep Adit Area from 28 March 2017 to 7 March 2018

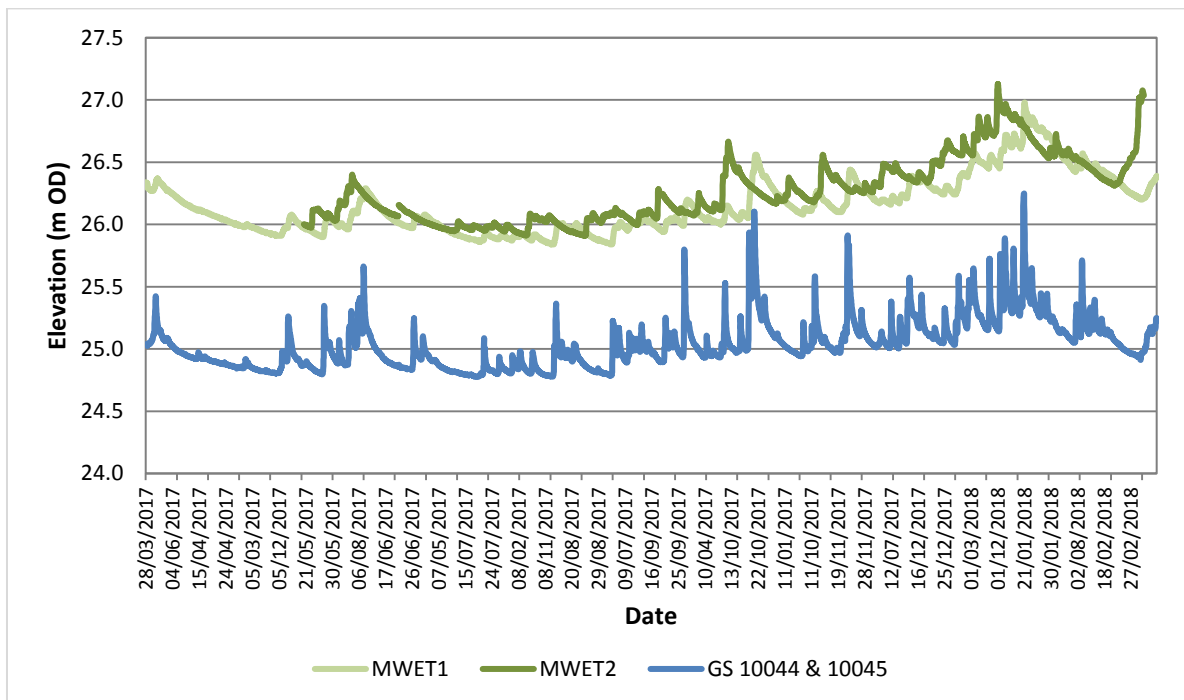


Figure 15 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044 & 10045) at the Emergency Tailings Area from 28 March 2017 to 7 March 2018

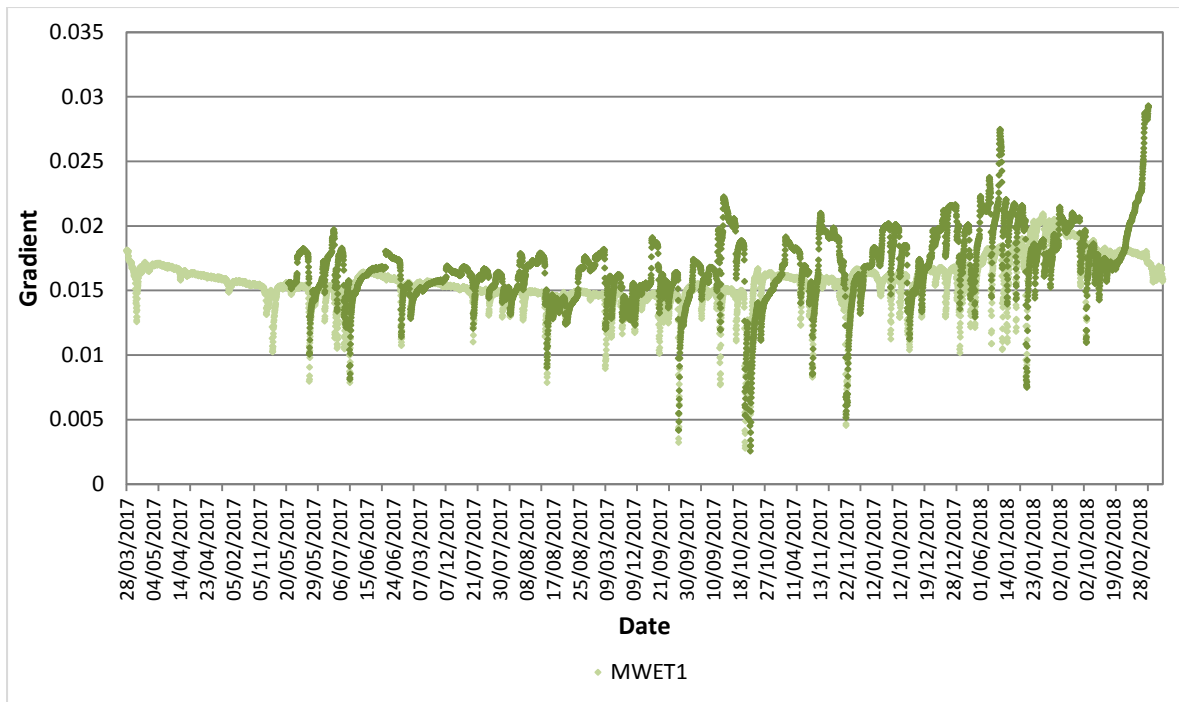


Figure 16 Calculated Groundwater Gradient to the Avoca River at the Emergency Tailings Area from 28 March 2017 to 7 March 2018

6.4 Summary of Diffuse Loading

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

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

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 to US Whites Bridge, there is a slight decrease in zinc load from 124 to 90.3 kg/day which is likely due to an overestimation of flow at Site T1. Between US Whites Bridge and Whites Bridge, zinc load increased from 90.3 to 113 kg/day which is a 25 % increase. The only surface water input in this segment is from Vale View (estimated to be 92.7 l/s). Historically, the Vale View tributary has discharged very low zinc loads to the Avoca River. This indicates that the increase in loading is primarily due to diffuse load;
- Between Whites Bridge and Whites Bridge GS (approx. 90 m), zinc load increases from 113 kg/day to 387 kg/day. No surface water inputs (point sources) exist within this river stretch and therefore, the increase in zinc load is due to diffuse load from the adjacent mining area (e.g. particularly the adjacent Deep Adit spoils area). This conclusion is supported by the calculated groundwater gradients in this river stretch (see section 6.4.2);
- Between Whites Bridge GS and DS Deep Adit on the Avoca River, the zinc load increases significantly from 387 to 1,230 kg/day. The Deep Adit (confluence sample) contributed 69.3 kg/day of the load. The zinc concentration at DS Deep Adit may be overestimated (bank sample) and therefore the estimated load may not be representative of conditions across the entire depth and width of the river. However, previous loading results indicate that there is a significant level of diffuse flow entering the river from the Deep Adit spoils and/or the contaminated Millrace area which is contributing to the zinc load of the River. Between DS Deep Adit and DS Millrace there is a 44% decrease in zinc load which is likely due to the overestimated zinc concentration at DS Deep Adit and the further dilution of the Deep Adit discharge at DS Millrace;
- Between DS Millrace and US Ballygahan Adit on the Avoca River, zinc loads decrease from 692 to 224 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 increases by 41% from 224 to 315 kg/day. The Ballygahan Adit is located within this river stretch and was dry in March 2018. Groundwater seeps also exist in this area and are the likely cause of the increase in dissolved zinc;

- Between US Road Adit and Wicklow County Council Maintenance Yard GS, the zinc load significantly increases from 315 to 1,080 kg/day. The Road Adit (confluence sample) contributed 32.8 kg/day of the total load. This increase is likely a combination of diffuse contamination and incomplete mixing (bank sample) of the Road Adit discharge; and
- Between Wicklow County Council Maintenance Yard GS and Site T5, the zinc load decreased from 1,080 to 428 kg/day which is a closer to the expected load downstream of the Road Adit confluence.

6.4.2 Groundwater Gradients

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. However, negative gradients existed for the deeper groundwater well (MWDA2) in the deep adit area for a prolonged period from the beginning of May to the end of July 2017. The implication is that deeper groundwater in the deep adit area does not discharge directly to the Avoca River during periods of sustained low flow.

6.4.3 Surface Water Flow Data at the EPA Gauging Stations

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

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. The 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 m³/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 m³/s (or 0.4 to 12.7 %).

The mean daily flow at the two stations were relatively similar during the monitoring period with the percentage difference ranging from 0 to 25% with an average difference of 6%. Note that the difference between the daily mean flows on 13 March 2018, which was the day the Avoca River was sampled, was 24% which may indicate that the River was gaining between the two river gauges at the time of sampling. Additionally, numerous ephemeral flows were observed within this stretch caused by a substantial heavy rainfall event. However, it is not possible to draw any conclusions using the gauge data at this time as to whether the stretch of river between the two gauges is a gaining or a losing river. In the future when the rating curve is improved and the margin of error is reduced it may be possible to make a determination.

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 Deep Adit and between US Ballygahan Adit and US Road Adit.

The groundwater gradients are predominantly positive which also 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 from the March 2018 sampling event (e.g. between Whites Bridge and Whites Bridge GS).

The findings from the March 2018 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

Six groundwater monitoring wells were sampled and analysed in March 2018 and water levels were measured. Nineteen surface water locations were sampled with flows measured at ten of the locations and projected to an additional nine from the EPA automatic gauges. 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 can be used to compare to the assessment criteria and 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 provided.

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, human health criteria or both, particularly for dissolved aluminium, cadmium, copper, iron, manganese, nickel and zinc. As well, sulphate levels greatly exceeded the criteria for human health in five of the six monitoring wells.
- 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. The highest concentrations of dissolved aluminium and nickel were recorded in MWET1 (Emergency Tailings area). The highest concentration of dissolved cadmium and zinc was recorded at MWDA1, located in the Deep Adit spoils area. GW1/05 had the highest concentration of copper.
- The Cronebane Shallow Adit was the adit discharge with the highest concentrations of dissolved metals including aluminium, cadmium, nickel and zinc. The Cronebane Shallow Adit is of minor importance in terms of metals loads to the Avoca River, because of absence of direct flow to the river and low concentrations and/ or flows.
- The Deep Adit, 850 Adit and Road Adit had significant dissolved metal loads which were discharging to the Avoca River. The Deep Adit had aluminium, copper and zinc loads of 32.4, 1.62 and 14.4 kg/day. The 850 Adit had loads of 172, 17.2 and 85.5 kg/day, respectively. The calculated loads for the Road Adit were lower at 38.8 kg/day for aluminium, 1.1 kg/day for copper and 32.8 kg/day for zinc.
- In the Avoca River dissolved metal concentrations were low in comparison to the groundwater and the adit discharges; however, multiple exceedances of both the ecological and human health criteria occurred, namely for dissolved aluminium, cadmium, copper, lead, manganese and zinc. Dissolved copper exceeded the ecological criteria (5 µg/l) at DS

Deep Adit and all river locations from Whites Bridge GS to Avoca Bridge, with results ranging from 8.25 to 76.6 µg/l. Similarly, dissolved zinc exceeded the ecological assessment criteria (50 µg/l) at all river locations from Whites Bridge GS to Avoca Bridge with results ranging from 52.6 to 388 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 are reduced significantly (e.g. lead has no exceedances). Dissolved cadmium exceeded the ecological assessment criteria of 0.45 µg/l at the monitoring point located downstream of both the Deep Adit discharge and the contaminated Millrace. The highest value for dissolved iron was recorded at 2,340 µg/l at Wicklow County Council Maintenance Yard GS located downstream of the Road Adit discharge on the Avoca River.

- The results of the Mann-Kendall analysis for October 2001 to March 2018 show that dissolved copper concentrations are decreasing in the Deep Adit and there is no trend for dissolved zinc. Dissolved iron however is increasing in the Deep Adit. Dissolved copper, dissolved zinc and dissolved iron were decreasing in the Road Adit. At Avoca Bridge, no statistically significant trend was present for dissolved zinc for the 2001-2018 period; however, dissolved zinc was decreasing for the 2007-2018 period. Dissolved copper was possibly decreasing for the 2001-2018 period and no trend was present for the 2007-2018 period.
- As river stages change 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 and Whites Bridge GS and between US Ballygahan Adit and US Road Adit.
- Evaluations of EQS_{bioavailable} for Zn and Cu were undertaken at the eleven Avoca River monitoring locations. The bioavailable Cu and Zn concentrations are significantly less than the measured Cu and Zn concentrations. For Cu, the HC5 (and potential EQS_{bioavailable}) are in most cases higher (less stringent) than the current EQS of 5 µg/L. For Zn, the HC5 (and potential EQS_{bioavailable}) are lower (more stringent) than the current EQS of 50 µg/L. As shown, use of EQS_{bioavailable} values results in the adjustment (reduction) to the number of exceedances for Cu at four sites (e.g. Avoca Bridge). Due to the very high concentrations on zinc, most of the sites exceed both the current EQS (50 µg/L) and the calculated HC5 value.

7.2 Recommendations for the Monitoring Programme

It is recommended that the groundwater monitoring well, MWDA2, is sampled in future monitoring rounds with designated tubing and a foot valve. No further recommendations for the monitoring programme are proposed at this time.

Section 8

References

CDM (2008). Feasibility Study for Management and Remediation of the Avoca Mining Site. Report prepared for Department of Communications, Energy and Natural Resources.

CDM Smith (2013). Monitoring Report for the Avoca Mining Area Round 1 2013. June 2013. Document Reference: 95735/DG/06. Report prepared for Department of Communications, Energy and Natural Resources.

CDM Smith (2016). Avoca River Tracer study. December 2016. Document Reference: 95735/DG/31. Report prepared for Department of Communications, Climate Action and Environment.

Environment Agency (2015). Technical Guidance to Implement Bioavailability-Based Environmental Quality Standards for Metals. April 2015. Environment Agency, Bristol, UK.

European Communities Drinking Water Regulations, 2007 (S.I. No. 106 of 2007).

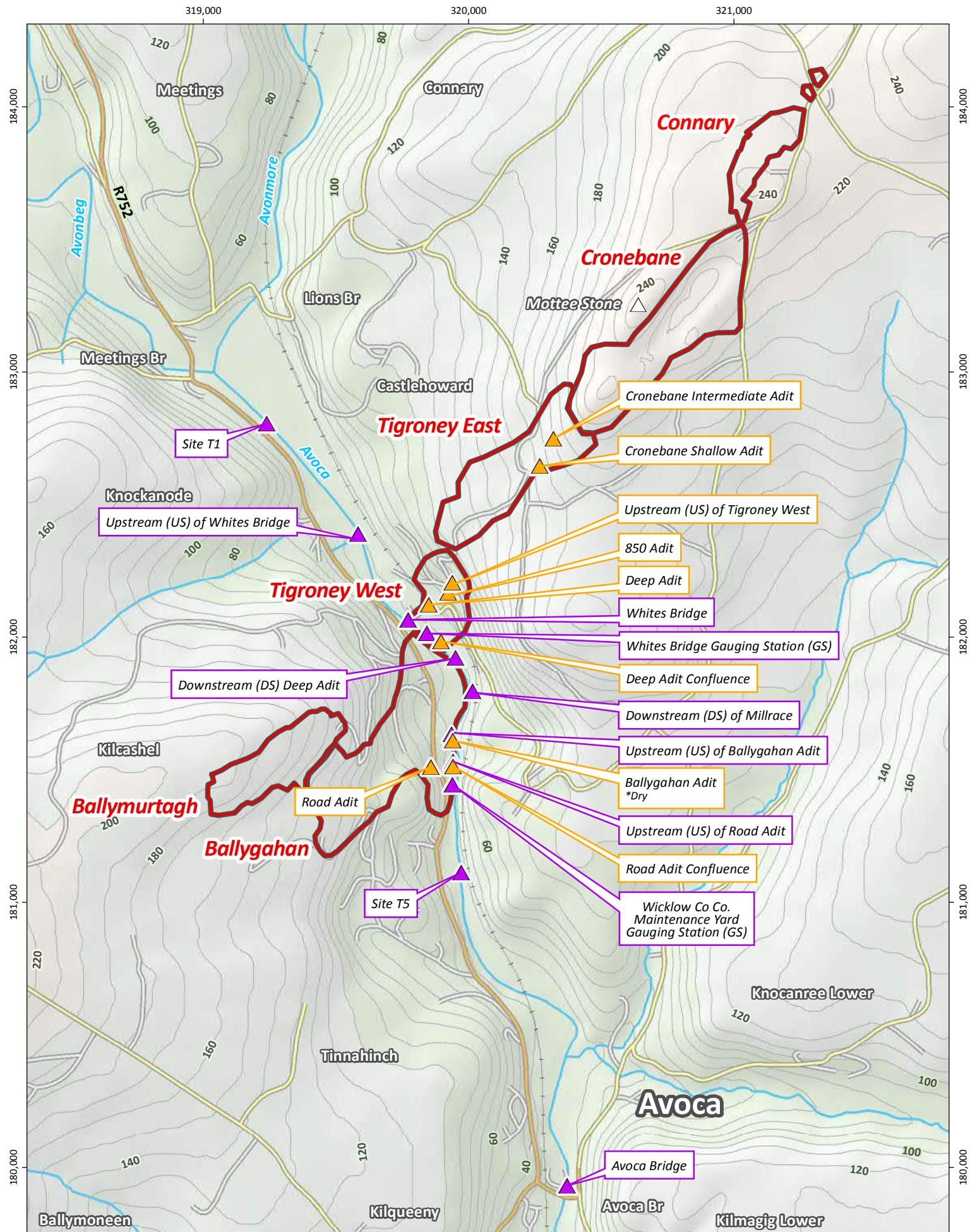
European Communities Environmental Objectives (Surface Water) Regulations, 2009 (S.I. 272 of 2009).

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

Figures



Map 1 - Avoca - Main Area

Drawn by: OC Date: 30/04/2018

Internal Project Reference: Q:\118000-118499\118174\40 Documents Generated\GIS\02_GIS_Tasks\04_MonReport_R1\MXD\01_AvocaMon1.mxd

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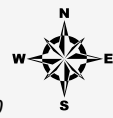
Legend

Sampling Locations

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

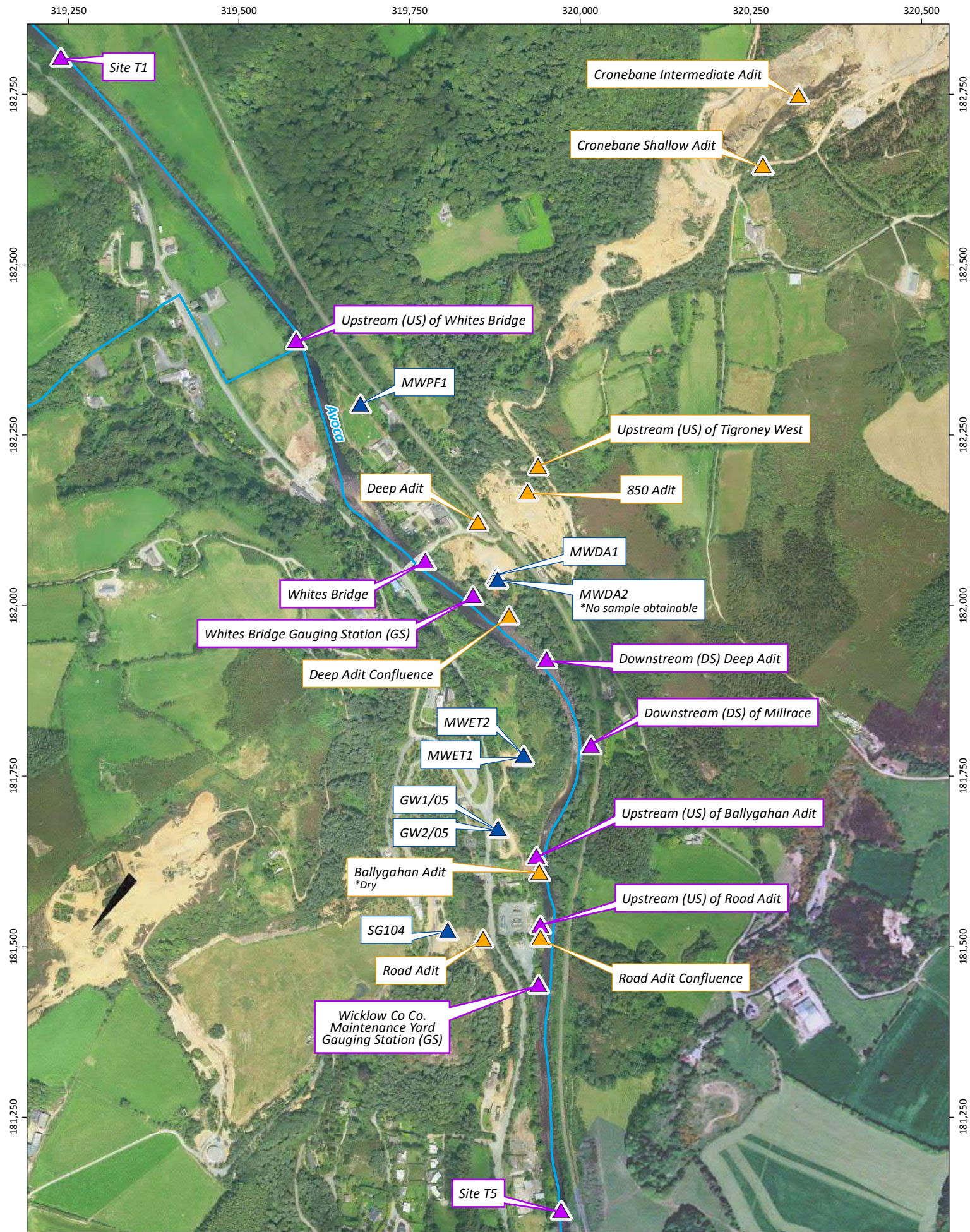
Mines

- Mining Area
- Rivers



Scale is 1:18,000

0 125 250 500 m



Map 2 - Avoca - Main Area - Surface Water and Groundwater

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Internal Project Reference: Q:\118000-118499\118174\40 Documents Generated\GIS\02_GIS_Tasks\04_MonReport_R1\MXD\02_AvocaMonSWGWMxd

Source: © DCENR Lidar Survey (2007)

**CDM
Smith**

Legend

Sampling Locations

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

— Rivers



Scale is 1:7,000

0 50 100 m

Appendix B

Analytical Data Tables and Assessment Criteria

Table B-1 Comparison of Groundwater and
Surface Water Results to Assessment Criteria R1 (2018)

Sample Description	Type	Date Sampled Units	Total Organic Carbon mg/l	Ammoniacal Nitrogen as N mg/l	Oxygen, dissolved (field) % Sat	pH (field) pH Units	Specific Conductance @ deg.C (field) mS/cm	Sulphate mg/l	Aluminium (diss.filt) µg/l	Antimony (diss.filt) µg/l	Arsenic (diss.filt) µg/l	Barium (diss.filt) µg/l	Calcium (diss.filt) µg/l
Ecological Criteria			-	0.14	80 to 120*	4.5 to 9	-	-	1,900	-	25	4	-
Human Health Criteria			-	0.3	-	6.5 to 9.5	2.5	250	200	5	10	-	-
GW1/05	GW	07/03/2018	-	0.1	26.0	3.72	1.644	1080	59100	0.3	9.89	7.27	-
GW2/05	GW	07/03/2018	-	0.1	50.2	3.7	1.542	986	47100	0.3	4.63	1.92	-
MWDA1	GW	12/03/2018	-	0.354	3.9	2.9	1.719	892	74900	3	12.2	8.04	-
MWET1	GW	12/03/2018	-	0.584	26.0	3.5	1.968	1270	102000	0.5	3.58	3.55	-
MWET2	GW	12/03/2018	-	0.1	50.2	6.2	3.26	2340	30	3	8.11	11.4	-
MWPF1	GW	12/03/2018	-	0.1	99.2	4.8	0.163	30.2	271	0.5	0.25	9.51	-
AVOCA BRIDGE	River	13/03/2018	3.1	0.1	95.5	6.29	0.0685	6.3	212	0.5	0.25	6.28	3.9
DS DEEP ADIT	River	13/03/2018	4.25	0.1	97.5	5.47	0.0854	14.6	515	0.5	0.25	5.82	2.5
DS MILLRACE	River	13/03/2018	4.39	0.1	96.7	6.15	0.0728	7.6	328	0.5	0.25	5.98	2.5
SITE T1	River	13/03/2018	3.62	0.1	96.4	6.61	0.0693	2.9	114	0.5	0.25	7.79	2.76
SITE T5	River	13/03/2018	1.5	0.1	95.4	6.4	0.0742	8.6	243	0.5	0.25	7.71	4.2
US BALLYGAHAN ADIT	River	13/03/2018	1.5	0.1	96.8	6.52	0.0677	5.3	186	0.5	0.25	6.19	3.94
US ROAD ADIT	River	13/03/2018	3.15	0.1	96.3	6.39	0.0698	6.1	247	0.5	0.25	6.08	3.99
US WHITES BRIDGE	River	13/03/2018	3.89	0.1	96.9	6.57	0.0684	2.1	110	0.5	0.25	6.45	2.7
WCC MAIN YARD GS	River	13/03/2018	4.11	0.1	97.3	5.96	0.116	22.9	337	0.5	0.602	6.15	6.72
WHITES BRIDGE	River	13/03/2018	3.13	0.1	87.9	6.64	0.203	1	119	0.5	0.501	6.24	4.36
WHITES BRIDGE GS	River	13/03/2018	3.22	0.1	96.1	5.83	0.0733	6.6	337	0.5	0.25	7.16	3.88
850 Adit	Adit	14/03/2018	-	0.1	71.7	2.94	1.607	859	60200	3	7.2	10	-
Cronebane Inter. Adit	Adit	14/03/2018	-	0.32	3.7	2.96	1.398	683	53500	3	23.4	7.22	-
Cronebane Shallow Adit	Adit	14/03/2018	-	0.529	60.5	2.78	2.182	1370	132000	3	78.7	4.87	-
Deep Adit	Adit	14/03/2018	-	0.1	57.7	3.44	0.556	215	15800	3	1.5	20.3	-
Deep Adit Conf	Adit	14/03/2018	-	0.1	92.1	3.18	1.12	563	49100	3	4.44	12	-
Road Adit	Adit	14/03/2018	-	5.27	25	4.43	2.073	1280	10500	5.5	12.4	16.3	-
Road Adit Conf	Adit	14/03/2018	-	5.16	77	4.58	2.402	1250	10600	3	10.8	14.6	-
US Tigroney West	Adit	14/03/2018	-	0.1	96.3	4.19	0.334	154	6250	0.5	1.74	12.3	-

xx Exceeds Ecological Assessment Criteria

xx Exceeds Human Health Assessment Criteria

xx Exceeds both Ecological and Human Health Criteria

xx Less than the Limit of Detection (LOD) - Value taken to be 0.5 of the

- Not analysed or no assessment criteria

* Only applies to rivers or streams (i.e. not discharges)

Table B-1 Comparison of Groundwater and
Surface Water Results to Assessment Criteria R1 (2018)

Sample Description	Type	Date Sampled	Cadmium (diss.filt) µg/l	Chromium (diss.filt) µg/l	Cobalt (diss.filt) µg/l	Copper (diss.filt) µg/l	Iron (diss.filt) µg/l	Lead (diss.filt) µg/l	Manganese (diss.filt) µg/l	Molybdenum (diss.filt) µg/l	Nickel (diss.filt) µg/l	Vanadium (diss.filt) µg/l	Zinc (diss.filt) µg/l
		Units											
Ecological Criteria			0.45	3.4	5.1	5	-	1.2	1,100	-	4	-	50
Human Health Criteria			5	50	-	2000	200	10	50	-	20	-	-
GW1/05	GW	07/03/2018	27.8	3	121	7530	13400	147	5320	1.5	50.3	3	11200
GW2/05	GW	07/03/2018	18.7	3	87.1	6220	112	0.6	4110	7.87	39.6	3	6350
MWDA1	GW	12/03/2018	70.2	8.83	87.6	3970	8980	46.6	3910	9	40.9	3	27700
MWET1	GW	12/03/2018	16.3	7.8	140	7310	69600	5.69	6300	1.5	68.7	0.5	8080
MWET2	GW	12/03/2018	3.53	3	119	0.9	90000	1.22	30500	9	15	3	5290
MWPF1	GW	12/03/2018	0.288	0.5	0.25	37.7	9.5	0.374	13.3	1.5	1.22	0.5	32.7
AVOCA BRIDGE	River	13/03/2018	0.279	0.5	0.25	10.3	201	4.01	43.3	1.5	0.992	0.5	77
DS DEEP ADIT	River	13/03/2018	1.25	0.5	1.46	76.6	65.9	9.75	70.2	1.5	1.46	0.5	388
DS MILLRACE	River	13/03/2018	0.587	0.5	0.653	30.1	96	5.68	45.6	1.5	0.983	0.5	175
SITE T1	River	13/03/2018	0.15	0.5	0.25	1.22	74.5	4.96	29.9	1.5	1.04	0.5	33.5
SITE T5	River	13/03/2018	0.296	0.5	0.699	11.9	414	4.34	65.1	1.5	0.998	0.5	98.4
US BALLYGAHAN ADIT	River	13/03/2018	0.194	0.5	0.25	8.25	114	3.35	35.5	1.5	0.795	0.5	52.6
US ROAD ADIT	River	13/03/2018	0.28	0.5	0.25	14.3	135	3.8	42.1	1.5	0.935	0.5	74.2
US WHITES BRIDGE	River	13/03/2018	0.146	0.5	0.25	0.734	79.9	3.14	28.3	1.5	0.793	0.5	29.8
WCC MAIN YARD GS	River	13/03/2018	0.478	0.5	2.81	17.5	2340	7.18	237	1.5	1.84	0.5	250
WHITES BRIDGE	River	13/03/2018	0.152	0.5	0.25	0.625	130	3.44	32.1	1.5	0.784	0.5	35.3
WHITES BRIDGE GS	River	13/03/2018	0.412	0.5	0.25	17.4	109	3.71	41.1	1.5	0.798	0.5	121
850 Adit	Adit	14/03/2018	90.8	3	96.7	6050	17200	904	3070	9	36.2	3	30000
Cronebane Inter. Adit	Adit	14/03/2018	104	3	94.6	9390	61300	1090	2120	9	41.6	3	29800
Cronebane Shallow Adit	Adit	14/03/2018	155	3	138	>6240	88500	683	3200	9	60	3	>31200
Deep Adit	Adit	14/03/2018	21	3	15.5	790	4560	869	872	9	7.52	3	7000
Deep Adit Conf	Adit	14/03/2018	60.3	3	62.7	5180	10700	705	2120	9	24.2	3	19800
Road Adit	Adit	14/03/2018	7	5.5	130	298	134000	240	11300	16.5	57.7	5.5	8890
Road Adit Conf	Adit	14/03/2018	5.85	3	122	267	128000	233	10800	9	50.9	3	8050
US Tigroney West	Adit	14/03/2018	6.77	0.5	8.71	934	1100	306	653	1.5	5.12	0.5	2110

xx Exceeds Ecological Assessment Criteria

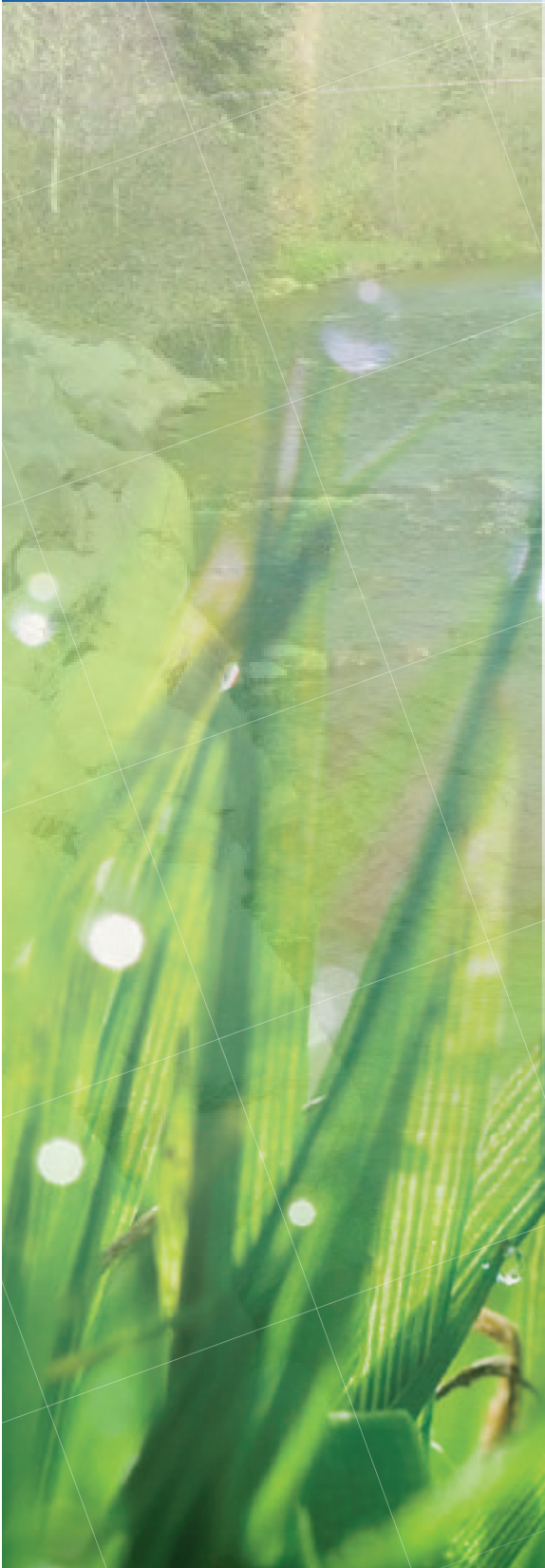
xx Exceeds Human Health Assessment Criteria

xx Exceeds both Ecological and Human Health Criteria

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- Not analysed or no assessment criteria

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