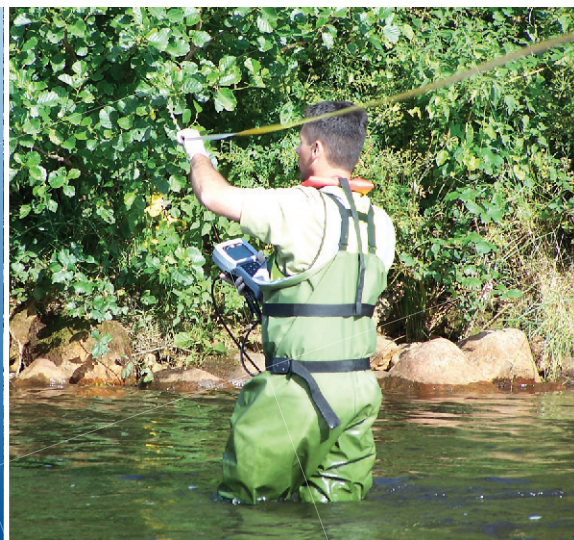


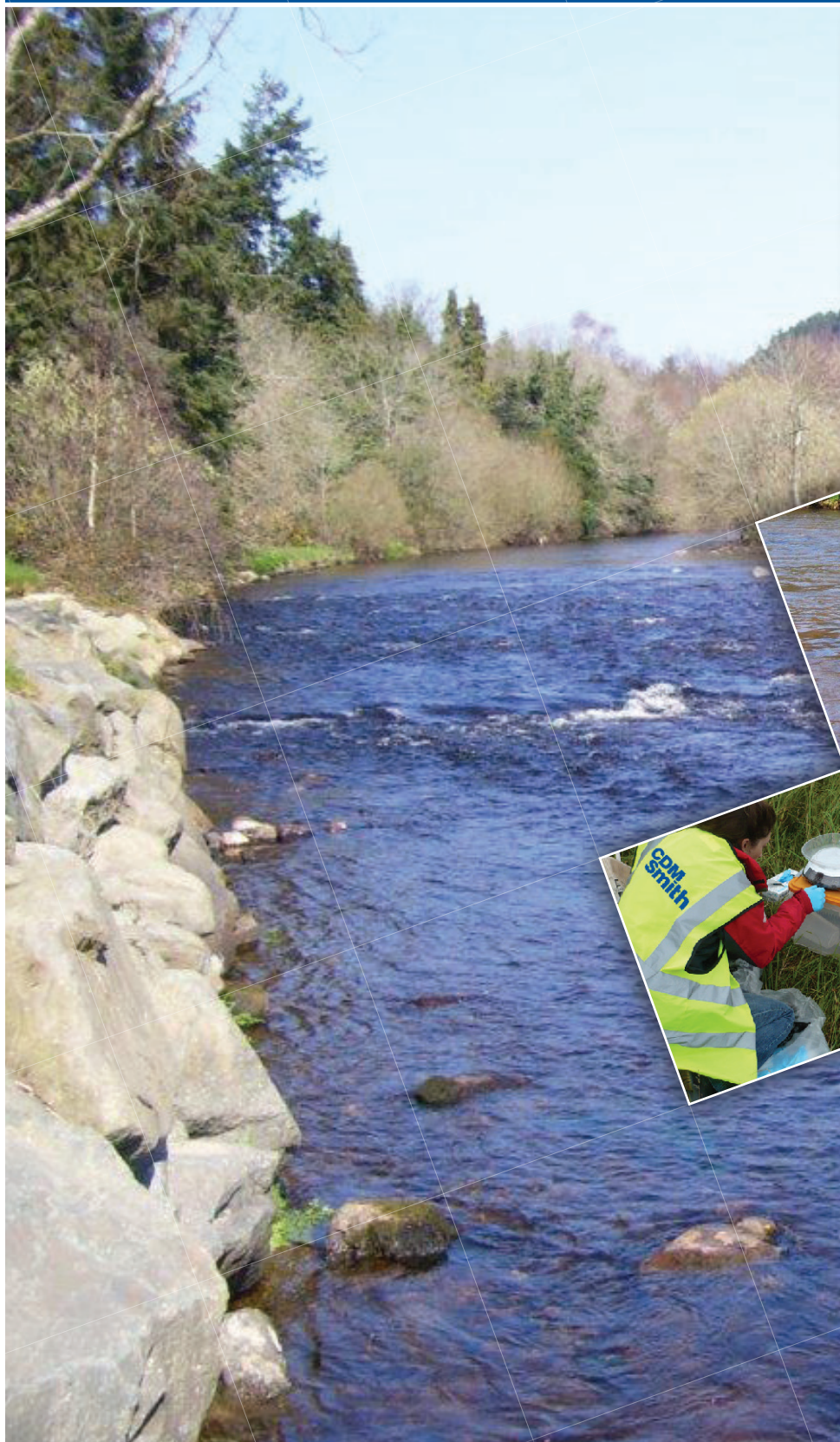
Department of Communications, Energy & Natural Resources



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

**Avoca Monitoring Report
- Round 1 (2015)**

Final



CDM Smith



Document Control Sheet

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Section 1

Introduction

1.1 Objectives and Scope

The Department of Communications, Energy and Natural Resources (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 for a three year period, commencing in 2013.

The scope of the field investigation activities was defined in the *Environmental Monitoring of Former Mining Areas of Silvermines and Avoca Monitoring Plan*, (Document Ref: 95735/40/DG01, dated 26 February 2013) 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 February 2015. This report should be read alongside the Avoca Data Report (Document Ref: 95735/40/DG19, dated May 2015) 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 have impacted the water quality of 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 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.

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 recently installed box culvert entrance into a ditch that runs semi-parallel to the Avoca River before discharging into the river. In September 2014 the adit discharge was mostly diverted into the Millrace through a marshy area to the east of the spoils area. As a result, the Deep Adit discharges both to the Avoca River at its normal discharge point (approximately 170 m from the adit portal) and approximately 20 m downstream of the normal discharge point, through a break in the side of the Millrace. In February 2015 the Deep Adit was not diverted and it was mostly discharging (estimated greater than 90 %) to the Avoca River at its normal discharge point, however there was some ponding of water at the start of the Millrace.

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. This was investigated on behalf of the Department by GWP who concluded that the water flow is most likely to be due to a collapse inside the mine, diverting water from the Deep Adit to higher levels. The flow from 850 Adit passes through a culvert (the “northwest culvert”) under the railway embankment and then joins the Deep Adit discharge channel. 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, it was sampled in February 2015.

The Road Adit is located adjacent to Rathdrum Road at the base of the (closed and capped) Wicklow County Council Ballymurtagh landfill (formerly the Pond Lode Pit). The Road Adit discharge previously flowed through a ditch beside the road and then discharged to the Avoca River just downstream of the Wicklow County Council Yard Gauging Station. Since about October 2014, the Road Adit no longer flows along the road and instead flows through a pipe underneath the council yard and discharges directly into the Avoca River above the Wicklow County Council Gauging Station as shown on Map 3 in [Appendix A](#).

The Spa Adit is located in West Avoca on a hillside approximately 150 m northwest of (and approximately 40 m above) the Wicklow County Council recycling centre. The flow discharges from a break in a pipe which was observed soaking into the ground. As the loads are very low and the discharge does not flow into the Avoca or one of the tributaries within the basin, the importance of the Spa Adit is relatively low.

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 the pipe leaking.

Section 2

Methodology

2.1 Field Sampling Methods

2.1.1 Groundwater Sampling

Nine groundwater monitoring wells in total were sampled, eight were sampled between 9 and 11 February 2015 and one on the 17 February, as listed in Table 1 and shown on Map 2 and 3 in [Appendix A](#).

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
- One shallow well immediately adjacent to and downgradient of the tailings dam at Shelton Abbey (MWSA2).

The Wicklow County Council monitoring wells follow:

- 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 Monitoring Points

Borehole Identifier	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	Yes	Yes	Dept	24.9	21.9 – 24.9
MWET1	319916	181778	Yes	Yes	Yes	Dept	10.9	7.8 – 10.6
MWET2	319917	181781	Yes	Yes	Yes	Dept	21	17 – 20
MWPF1	319678	182296	Yes	Yes	Yes	Dept	10	4.7 – 7.7
MWSA2	321566	175292	Yes	Yes	Yes	Dept	12.6	8.0 – 11
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	Yes	Yes	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 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 had stabilised. The results were recorded approximately every five minutes during the purging process on the Groundwater Purging and Sampling Form. Field sheets are contained in Appendix H and physico-chemical field data are summarised in Appendix A of the Data Report.

After the water had been purged and stable parameters have been 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.

Seven of the wells (MWDA1, MWDA2, MWPF1, MWSA2, GW1/05, GW2/05 and SG104) were unable to be sampled using the low-flow sampling procedure as the pump became stuck in GW1/05 due to an obstruction in the well. The 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 the nine wells using a portable electronic water level recorder. Automatic groundwater recorders have been placed in six 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

Twenty-four surface water locations were sampled on 11, 12, 16 and 17 February 2015, as listed in Table 2 and shown on Map 1 and 2 in [Appendix A](#). At Ballygahan Adit there was insufficient flow to collect a full sample and only dissolved metals were analysed for. No sample was collected from the Millrace as there was very little flow (<10 % of Deep Adit) and it was not discharge to the Avoca River at the time.

A new sampling location called Upstream (US) Road Adit was added to the programme for this round which was upstream of the new Road Adit discharge point and downstream of the Deep Adit discharge on the Avoca River (Map 3 in [Appendix A](#)). The Road Adit discharge was redirected in October 2014 so it now flow directly to the river through a large diameter pipe as shown in Figure 1. This resulted in the discharge point moving 70 metres upstream on the river and therefore upstream of the WCC Maintenance Yard GS location. This meant that there was no sampling location on the Avoca River between the Deep Adit discharge and the Road Adit discharge so the US Road Adit was added.

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 in the field using a GPS. Photographs were taken of the surface water sampling locations (Appendix D of the Data Report). The sample location was approached from downstream so that the underlying sediments are not disturbed. Samples were grab samples collected from a well-mixed

portion of the water stream where possible using a telescopic sampling pole. Note that this is different from the previous round (R4) during low flow in 2014 as composite samples were taken across the channel so that the samples were representative of the Avoca River at a particular location. This does affect the interpretation of the results because the bank samples taken during high flow are not representative of the loadings in the Avoca River; particularly downstream of large discharges such as the Deep Adit and Road Adit. This is discussed further in further detail in Section 5.2.2 Loading Results and Discussion.

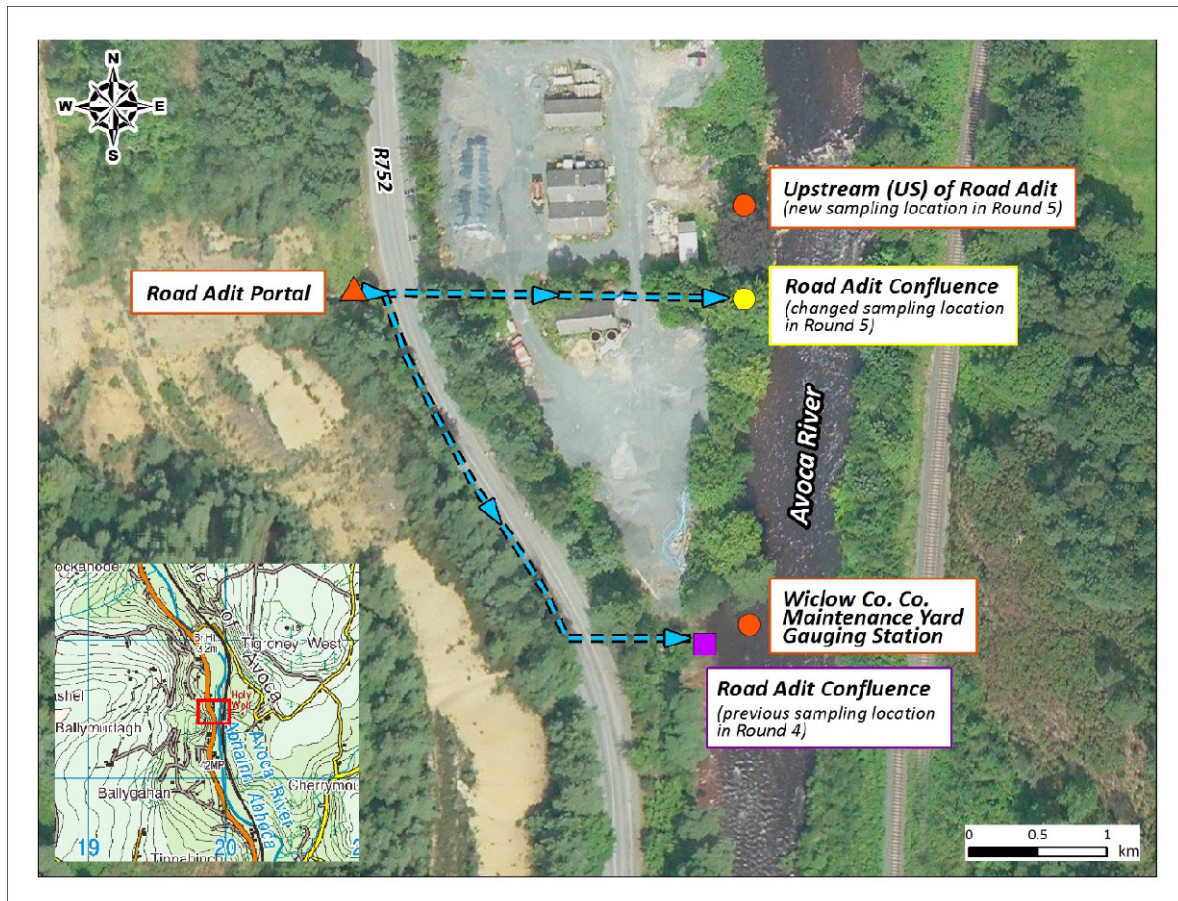


Figure 1 Relocation of the Road Adit discharge in October 2014

Samples were placed into 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.

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.

Table 2 Location of Surface Water Monitoring Points

Site Name	Sample Site Description	Easting	Northing	Flow Measurement Method
Ballinacleish Bridge	Avoca River Location	317197	185010	Flow Meter
Lions Bridge	Avoca River Location	319207	183287	Float Method
Vale View	Tributary of Avoca River	319453	182396	Flow Meter
Site T1	Avoca River Location (Upstream of Whites Br.)	319239	182805	Flow Meter. Calculated
Whites Bridge	Avoca River Location (at Whites Br.)	319773	182066	Equal to flow recorded at Whites Bridge GS
Whites Bridge Gauging Station (GS)	Avoca River Location (90m downstream of Whites Br.)	319843	182015	Automatic recorder Whites Bridge GS
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
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 Co Co. Maintenance Yard GS.
Wicklow Co Co. Maintenance Yard Gauging Station (GS)	Avoca River Location	319939	181445	Automatic Recorder Wicklow Co Co. Maintenance Yard GS
Site T5	Avoca River Location (Abandoned Coal Yard)	319972	181114	Float method
Avoca Bridge	Avoca River above Avoca Bridge	320372	179932	Float method
Upstream (US) of Shelton Abbey	Avoca River Location	320847	175947	Equal to measured flow downstream of Shelton Abbey
Downstream (DS) of Shelton Abbey	Avoca River Location	321939	175213	Float Method used at bridge to fertiliser plant. No flow measured for this location. Float method results from IFI bridge
Sulphur Brook	Tributary of Avoca River	320491	180470	Flow Meter
850 Adit	Adit Discharge (at portal)	319919	182161	Flume
850 Adit Confluence	Adit Discharge (before entering Deep Adit Discharge) – No sample required	319845	182122	No Flow
Deep Adit	Adit Discharge (at portal)	319850	182123	Flume
Deep Adit Confluence	Adit Discharge (before entering Avoca River)	319896	181986	Flow Meter
Millrace	Adit Discharge - branch of Deep Adit (before entering Avoca River)	-	-	Not Recorded
Road Adit	Adit Discharge (at portal)	319858	181512	Not recorded* (permanent flume)
Road Adit Confluence	Adit Discharge (before entering Avoca River)	319942	181513	Flow Meter
Cronebane Intermediate Adit	Adit Discharge	320320	182749	Flume
Cronebane Shallow Adit	Adit Discharge	320268	182646	Flume

Site Name	Sample Site Description	Easting	Northing	Flow Measurement Method
Ballygahan Adit	Adit Discharge	319940	181610	No measurable flow
Spa Adit	Adit Discharge	319637	181747	Bucket and stopwatch
Cronebane Pit Lake	Pit Lake	320933	183402	n/a

* Flow was not recorded at permanent flume, but flow is assumed to be similar to new Road Adit Confluence location as the discharge no longer flows along a ditch.

Flow Measurements

Flow was measured or obtained from EPA records at 17 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. 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. Methods included using a portable flume (for small discharges), a Marsh McBirney meter (flow meter) to measure flow velocities and depths at regular intervals across the streams by wading and for very small discrete discharges, a stop watch and calibrated volume container were used.

The Float Method was used when the location of the river was unsafe to wade. It is the least accurate method but 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 8 locations). The float was released into the channel upstream from the beginning of the section and measured the amount of time it takes the “float” to travel the marked section. This was repeated at least three times and the average time calculated.

Data were obtained from the EPA for the existing automatic recorders at Whites Bridge GS (EPA station 10044) and Wicklow County Council Maintenance Yard (EPA Station 10045).

It should be noted that different methods flow measuring flow are used between the high and flow sampling rounds due to health and safety reasons. For example, during high flow Site T1 is calculated by adding the flows at Ballinacleish Bridge and Lions Bridge, whereas during low flow Site T1 is generally wadable and measured with the flow meter. Also during high flow Site T5 is measured using the float method and estimating the depth profile from the profile measured during the low flow sampling event. Therefore during high flow some of the flow measurement may be less accurate but nevertheless provide good estimates of flow for comparing loadings within the Avoca River.

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
- 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 material containing known concentrations of the 18 metals was shipped blind to ALcontrol 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.
- One filtration blank was collected by filtering DI water into the sample bottle. It 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).

No groundwater decontamination blank was collected as the pump was not operation after being removed from the well and the majority of the groundwater samples were collected using disposable single use bailers.

Table 3 Field QA/ QC Sample IDs and Descriptions

Sample ID	QA/QC Sample Type	Description
AVGD01.5	GW Duplicate	Duplicate of GW1/05
AVSD01.5	SW Duplicate	Duplicate of Deep Adit Confluence
AVSD02.5	SW Duplicate	Duplicate of Avoca Bridge
AVDB02.5	SW Decontamination blank	DI water (Lennox Lab Supplies: Batch No: TE15011GW) poured over SW composite sample bottle after final decon at site Sulphur Brook
AVSR01.5	Standard Reference Material	Wastewater "Trace Metals" by ERA Lot #P234-740A
AVSR02.5	Standard Reference Material	Wastewater "Trace Metals" by ERA Lot #P234-740A
WB01.5	Filtration blank	Deionised water filtered onsite (Lennox Lab Suppliers. Batch No: TE150116W)
WB02.5	Water blank	Deionised water (Lennox Lab Suppliers. Batch No: TE150116W)

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 was 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 specified. 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 ALcontrol. Water (both surface water and groundwater) samples were dispatched from its distribution centre in Dublin and analysed at its facility in North Wales. ALcontrol 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, conductivity, Total Dissolved Solids, ammoniacal nitrogen as N, potassium, sodium, chloride, fluoride, calcium (total and dissolved), magnesium (total and dissolved), nitrate as NO_3 and nitrite as NO_2 , orthophosphate, sulphate, total alkalinity as CaCO_3 , free cyanide, total and dissolved metals including Al, Sb, Ag, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Mo, Ni, Se, Tl, Sn, U, V and Zn. Additionally for surface water, acidity, Total Suspended Solids (TSS) and Chemical Oxygen Demand (COD) were analysed.

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. As noted in the Monitoring Plan, ALcontrol is certified for most of the analyses and the few analyses for which certifications are not available are not critical for comparison to regulatory standards.

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). 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 and the sample filtration process. 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 and collected for laboratory analysis. Note that a groundwater decontamination blank was not collected as the pump was not used and disposable, single use bailers were used for sample collection. Analyses of these samples were used to evaluate the adequacy of the sampling equipment cleaning or decontamination procedure;
- Standard Reference Material (SRM): Two certified water SRMs were sent blind to the laboratory (Sample IDs AVSR01.5 and AVSR02.5) to evaluate laboratory accuracy. The certified SRM was supplied by ERA Certified Reference Materials and was Lot #P234-740A (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; and
- One water blank was collected of the DI water during the sampling event. An additional filtration blank was collected in order to try 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 to ALcontrol for analysis. Table 4 provides the results of the 21 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 detection limit then the RPD was zero. If one value was less than the detection limit the RPD was still calculated using the detection limit value.

The majority of RPD values were below 50 % and the RPDs for the key parameters ranged from 2 to 3 % for aluminium, 2 to 42% for copper and 3 to 16 % zinc which was good.

There were eight % RPDs that exceeded 50 % as highlighted in Table 4 that ranged from 67.4 to 192%. Seven of the exceedances were for duplicate pair Deep Adit Confluence and AVSD01.5. Some of these differences are likely due to the dilution performed on AVSD01.5 and the different limits of detection for each sample. Each of these duplicate results were checked and confirmed with ALcontrol and they said they were within their duplicate policy margin. 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)	GW1/0 5	AVGD0 1.5	% RPD	Deep Adit Conf.	AVSD0 1.5	% RPD	Avoca Bridge	AVSD0 2.5	% RPD
Aluminium	<2.9	70100	71500	-2.0	77100	79500	-3.1	246	252	-2.4
Antimony	<0.16	<0.16	<0.16	0	<0.16	7.97	-192	<0.16	<0.16	0
Arsenic	<0.12	<0.12	<0.12	0	0.556	2.75	-133	0.408	0.452	-10.2
Barium	<0.03	3.75	3.88	-3.4	4.7	7.47	-45.5	6.25	6.22	0.5
Cadmium	<0.1	16.8	17.2	-2.4	41.4	83.5	-67.4	0.26	0.251	3.5
Chromium	<0.22	1.46	9.01	-144	0.587	<2.2*	-116	0.361	0.312	14.6
Cobalt	<0.06	98.6	100	-1.4	75.9	108	-34.9	0.451	0.463	-2.6
Copper	<0.85	8830	8400	5.0	195	297	-41.5	5.24	5.34	-1.9
Iron	<19	1310	1420	-8.1	58800	60900	-3.5	201	194	3.5
Lead	<0.02	12.9	13.1	-1.5	1760	1790	-1.7	6.56	6.67	-1.7
Manganese	<0.04	5430	5540	-2.0	3320	3440	-3.6	37.6	37.2	1.1
Mercury	<0.01	<0.01	<0.01	0	<0.01	NA	-	<0.01	<0.01	0
Molybdenum	<0.24	<0.24	<0.24	0	<0.24	<2.4*	0	<0.24	<0.24	0
Nickel	<0.15	42.9	43.8	-2.1	27.3	36.7	-29.4	0.811	1.07	-27.5
Selenium	<0.39	<0.39	<0.39	0	<0.39	<3.9*	0	<0.39	<0.39	0
Silver	<1.5	<1.5	1.9	-23.5	<15	<15	0	<1.5	<1.5	0
Thallium	<0.96	<0.96	<0.96	0	1.41	<9.6*	-149	<0.96	<0.96	0
Tin	<0.36	<0.36	<0.36	0	<0.36	10.7	-187	<0.36	<0.36	0
Uranium	<1.5	3.42	3.43	-0.3	7.03	<15*	-72.4	<1.5	<1.5	0
Vanadium	<0.24	<0.24	<0.24	0	<0.24	<2.4*	0	<0.24	<0.24	0
Zinc	<0.41	10100	10500	-3.9	34100	40200	-16.4	87.3	84.8	2.9

Notes:

Bold indicates an exceedance in the Duplicate RPD acceptance criteria

NA analyte not determined by the laboratory

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

3.2.2 Decontamination Blanks

One decontamination blank was created by pouring water over the sampling equipment after decontamination and sent to ALcontrol for analysis. Table 5 provides the results of the 21 metals for the decontamination blank sample along with the results of the DI water blank and filtration blank also created in the field.

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 0.01 to 2.9 µg/l except for iron with a detection limit of 19 µg/l.

Detections were observed for seven dissolved metals ranging from 0.097 to 5.12 µg/l. Five of the metals (antimony, barium, lead, manganese and molybdenum) were also detected in the DI water blank. The levels of detections in the decontamination blanks were similar to those found in the DI water blank.

Dissolved zinc was detected in the decontamination blank (5.12 µg/L) but not the DI water blank. The concentration of dissolved zinc was greater than ten times the detection limit. To assess the level of cross-contamination between samples in the field, the concentrations in the decontamination blanks were compared with the concentration in the preceding environmental samples. Dissolved zinc was detected at only 5 % of the concentration found in the preceding sample (Sulphur Brook 102 µg/l), which was considerably less than the preceding sample and therefore not considered to indicate cross contamination in the field.

The results from the laboratory instrumentation blank were obtained from ALcontrol to determine if any contamination occurred within the laboratory (Table 5). It was noted dissolved antimony, manganese and molybdenum were detected in the method blank and were similar to the concentration in the decontamination blank sample, as follows:

- Three detections of parameters were present in the method blank for Sample Batch 150218-83 that occurred in the decontamination blank from the same batch (see Table 5): antimony 0.639 µg/l, manganese 0.072 µg/l and molybdenum 0.278 µg/l.

Overall, the decontamination blank samples do not indicate any cross-contamination in the field showing that the decontamination procedures were adequate and therefore all the results are considered acceptable.

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

Dissolved Metal	LOD (µg/l)	Filtration Blank WB01.5 (µg/l)	Water Blank WB02.5 (µg/l)	Decon blank AVDB02.5 (µg/l)	Laboratory Method Blank (µg/l)
		<i>Sample batch:</i> 150218-83			
Aluminium	<2.9	<2.9	<2.9	<2.9	NP
Antimony	<0.16	<0.16	0.585	3.27	<i>0.639</i>
Arsenic	<0.12	<0.12	<0.12	<0.12	NP
Barium	<0.03	0.151	0.121	0.097	<0.03
Cadmium	<0.1	<0.1	<0.1	<0.1	NP
Chromium	<0.22	0.242	<0.22	<0.22	<0.22
Cobalt	<0.06	<0.06	0.087	<0.06	<0.06
Copper	<0.85	<0.85	<0.85	<0.85	NP
Iron	<19	<19	<19	<19	NP
Lead	<0.02	<0.02	0.085	0.142	<0.02
Manganese	<0.04	0.05	0.099	0.243	<i>0.072</i>
Mercury	<0.01	<0.01	<0.01	<0.01	NP
Molybdenum	<0.24	<0.24	0.314	0.635	<i>0.278</i>
Nickel	<0.15	<0.15	<0.15	<0.15	NP
Selenium	<0.39	<0.39	0.394	0.971	<0.39
Silver	<1.5	<1.5	<1.5	<1.5	NP
Thallium	<0.96	<0.96	<0.96	<0.96	NP
Tin	<0.36	<0.36	<0.36	<0.36	NP
Uranium	<1.5	<1.5	<1.5	<1.5	NP
Vanadium	<0.24	<0.24	<0.24	<0.24	NP
Zinc	<0.41	<0.41	<0.41	5.12	<0.41

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

NP means result was Not Provided by the laboratory.

3.2.3 Standard Reference Materials

As previously discussed, two certified water SRMs were sent blind to the laboratory (Sample IDs AVSR01.5 and AVSR02.5) to evaluate laboratory accuracy. The ALcontrol 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 18 requested metals.

Reported values for the majority of the metals were within the acceptable ranges. Dissolved aluminium, antimony, arsenic, barium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, selenium, thallium, vanadium and zinc are in excellent agreement with the certified value (%R ranged from 94 to 113 %).

One reported value for dissolved iron was outside of the acceptable range with a % R of 82 %, however the other reported value was within acceptable ranges and therefore the interpretation of the results are not affected. Overall, all of the accuracy of the results was good and results are considered acceptable.

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

Dissolved Metal	Certified Value (µg/l)	Acceptance Limits		AVSR01.5 (µg/l)	% R	AVSR02.5 (µg/l)	% R
		Lower (%)	Upper (%)				
Aluminium	517	87	114	570	110	586	113
Antimony	784	87	111	779	99	780	99
Arsenic	135	87	111	141	104	142	105
Barium	791	91	109	814	103	834	105
Cadmium	136	88	106	127	93	131	96
Chromium	634	91	109	622	98	621	98
Cobalt	550	93	111	563	102	571	104
Copper	816	90	109	799	98	791	97
Iron	840	90	111	793	94	690	82
Lead	649	90	110	672	104	708	109
Manganese	772	92	109	785	102	792	103
Molybdenum	273	90	109	248	91	256	94
Nickel	716	91	109	685	96	684	96
Selenium	660	88	111	618	94	641	97
Silver	772	90	110	>100	-	>100	-
Thallium	606	88	111	637	105	674	111
Vanadium	888	91	107	879	99	874	98
Zinc	895	91	110	901	101	868	97

Notes:

Bold indicates an exceedance in acceptance limits

3.3 Laboratory QA/QC Samples

3.3.1 ALcontrol

ALcontrol undertakes a range of activities associated with both quality control and assessment to assure the quality of test results. Specifically ALcontrol 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;
- Instrument 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 AQC's.

All of the ALcontrol laboratory reports were reviewed to ensure that reported values were ISO17025 certified (where relevant) and for any sample deviations. The sample holding times were exceeded for free cyanide in four samples by three days. Small exceedances are typically considered acceptable from a technical perspective given the conservative nature of holding times.

ALcontrol provided the associated analytical quality control samples (AQC) data. The percentage recovery results for the AQC samples that were run with the regular environmental samples were checked against the individual lower control and upper control limits. All AQC samples run with the environmental samples were within these upper and lower control limits. The results of method blanks were also assessed as described in Section 3.2.2 above.

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 conductivity and provides the calculated %RPD values. 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 conductivity was less than 34 % which is good. The RPDs between laboratory and field pH were also good at less than 30 %. The field pH and conductivity are more representative of actual conditions and are used for interpretive purposes. 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	pH	% RPD	Conductivity @ 20deg.C	Specific Cond. @ 25deg.C	% RPD
	Lab	Field		Lab	Field	
	pH Units			mS/cm		
Cronebane Inter. Adit	3.07	3.21	-4.5	1.11	1.265	-13.1
Cronebane Pit Lake	3.41	2.83	18.6	0.325	0.442	-30.5
Cronebane Shallow Adit	2.88	2.85	1.0	2.98	3.588	-18.5
Deep Adit	3.47	3.56	-2.6	1.25	1.391	-10.7
Deep Adit Confluence	3.28	3.47	-5.6	1.25	1.402	-11.5
Road Adit	4	4.01	-0.2	1.47	1.642	-11.1
Road Adit Confluence	3.98	4.01	-0.8	1.46	1.648	-12.1
Spa Adit	2.81	2.69	4.4	2.19	2.531	-14.4
Ballinacleish Bridge	6.72	5.64	17.5	0.0543	0.055	-1.3
Lions Bridge	6.74	5.87	13.8	0.0562	0.06	-6.5
Site T1	6.61	4.87	30.3	0.0438	0.046	-4.9
Vale View	6.92	6.63	4.3	0.181	0.152	17.4
Whites Bridge	6.94	5.89	16.4	0.0498	0.057	-13.5
Whites Bridge (GS)	6.96	6.08	13.5	0.0508	0.037	31.4
DS Deep Adit	6.02	4.76	23.4	0.0606	0.079	-26.4
Wicklow CO.CO. Main. Yard GS	6.84	5.29	25.6	0.0649	0.092	-34.5
Site T5	7.24	5.72	23.5	0.0605	0.066	-8.7
Avoca Bridge	7.07	5.89	18.2	0.0553	0.06	-8.2
Sulphur Brook	7.32	6.73	8.4	0.141	0.157	-10.7
US Shelton Abbey	7.22	6.39	12.2	0.0935	0.103	-9.7
DS Shelton Abbey	6.6	6.14	7.2	0.097	0.106	-8.9
850 Adit (portal)	2.98	2.87	3.8	1.27	1.49	-15.9
US Road Adit	6.91	5.82	17.1	0.0546	0.061	-11.1
MWDA1	2.91	2.86	1.7	2.21	2.811	-23.9
MWDA2	3.73	3.68	1.3	1.32	1.486	-11.8
MWPF1	4.99	4.77	4.5	0.134	0.154	-13.9
MWET1	3.45	3.4	1.5	1.81	2.087	-14.2
MWET2	6.19	6.16	0.5	2.95	3.416	-14.6
GW1/05	3.83	3.7	3.5	1.44	1.641	-13.0
GW2/05	3.76	3.67	2.4	1.16	1.334	-14.0
SG104	2.93	2.93	0.0	7.16	8.277	-14.5
MWSA2	3.59	4.25	-16.8	2.12	2.355	-10.5

Notes:

Bold indicates an exceedance in acceptance limits

3.4.2 Internal Consistency Analysis

The analyses were checked for internal consistency using both charge balance and mass balance relationships.

The charge balance was calculated as follows:

$$\frac{(\sum(\text{Cations} \times \text{charge}) - \sum(\text{Anions} \times \text{charge}))}{(\sum(\text{Cations} \times \text{charge}) + \sum(\text{Anions} \times \text{charge}))} \times 100\%$$

where, “cations” refers to the molar concentration of positively charged ions (millimoles/L) and “anions” to the molar concentration of negatively charged ions.

The mass balance was calculated using the following relationship:

$$(\text{TDS-Calc} - \text{TDS-Meas})/\text{TDS-Meas} \times 100\%$$

TDS-Calc was calculated by summing the concentrations of all species in mg/l. Adjustments were made in cases where the species that would be formed upon evaporation (laboratory analytical procedure to yield TDS-Meas) was in a different form than that provided by the laboratory. For instance, the bicarbonate concentration was multiplied by a factor of 0.49 to account for loss of carbon dioxide gas during evaporation.

By evaluating both the mass balance and charge balance, conclusions can be drawn about the accuracy and completeness of the analysis. The possible mass balance and charge balance combinations and the corresponding interpretations are shown in Table 8.

The general acceptance criteria for internal consistency are $\pm 10\%$ for both the charge balance and the mass balance. The charge balance was generally within acceptable limits, with most values below 10 % is good, with only three samples outside the range. The mass balance, in the majority of cases (bolded values) did not meet these criteria. Most values were less than 30 %; which overall is very good considering the low pH, high TDS and complex nature of the high metal concentrations of many of the samples. The fact that the mass balance values are mostly negative suggests that either one or more parameters were under-reported by the analytical laboratory and/or one or more parameters present within the samples were not analysed (e.g. silica). There was one site (Vale View) where the mass balance percentage difference was greater than 100%, which also had one of lowest measured TDS values (32.1 mg/l). The TDS result was checked and confirmed with ALcontrol.

Table 8 Charge Balance and Mass Balance Results

Site Description	TDS (Calc) (mg/l)	TDS (Meas) (mg/l)	Cations minus anions	Charge Balance % Diff	Mass Balance % Diff	Conclusion
850 Adit	917	1140	-0.5	-1.8	-19.6	Missing cations
Avoca Bridge	26	90	0.1	7.4	-70.7	Missing anions
Ballinacleish Bridge	26	32.6	0.0	2.9	-20.1	Missing anions
Cronebane Intermediate Adit	894	1160	0.1	0.4	-22.9	Missing anions
Cronebane Pit Lake	156	221	-0.4	-7.9	-29.3	Missing cations
Cronebane Shallow Adit	3812	4970	-4.1	-3.3	-23.3	Missing cations
Deep Adit	1157	1450	1.3	3.5	-20.2	Missing anions
Deep Adit Conf.	1139	1410	0.1	0.3	-19.2	Missing anions
DS Shelton Abbey	48	73	0.2	12.0	-33.6	Missing anions
DS Deep Adit	32	34.7	0.1	7.8	-6.7	Missing anions
GW01/05	1345	1560	0.4	0.9	-13.8	Missing anions
GW2/05	999	1160	-0.1	-0.3	-13.9	Missing cations
Lions Bridge	24	36.8	0.2	22.2	-34.0	Missing anions
MWDA1	2450	3290	-0.1	-0.2	-25.5	Missing cations
MWDA2	1193	1550	0.3	0.7	-23.0	Missing anions
MWET1	1850	2270	-0.5	-0.9	-18.5	Missing cations
MWET2	3207	3580	3.9	3.9	-10.4	Missing anions
MWPF1	77	88	0.0	-1.3	-12.4	Missing cations
MWSA2	2150	2610	0.8	1.2	-17.5	Missing anions
Road Adit	1282	1440	0.2	0.5	-10.9	Missing anions
Road Adit Conf.	1261	1440	-0.9	-2.4	-12.4	Missing cations
SG104	11500	14000	-0.8	-0.2	-17.8	Missing cations
SITE T1	19	21	0.1	15.2	-7.8	Missing anions
Spa Adit	2020	2430	-0.4	-0.6	-16.7	Missing cations
Sulphur Brook	85	87.4	-0.2	-6.1	-2.3	Missing cations
Site T5	32	63	0.0	1.3	-48.6	Missing anions
US Shelton Abbey	54	74	-0.1	-4.8	-27.3	Missing cations
US Road Adit	25	82	0.1	7.8	-69.3	Missing anions
Vale View	82	32.6	-0.1	-4.3	152	Too many anions
WCC Maintenance Yard GS	36	61	0.0	-0.9	-40.9	Missing cations
Whites Bridge	26	31	0.0	4.9	-14.9	Missing anions
Whites Bridge GS	26	28	0.0	2.2	-6.9	Missing anions

Notes:

Bold indicates an exceedance of the acceptance criteria

The specific conductivity (SC) of the solutions can be used to further evaluate the internal consistency. The specific conductivity/total dissolved solids (SC/TDS) ratio of natural waters varies, but typically ranges from ranges from 1 to 1.8. An evaluation can be made of these analyses by examining the ratios of SC/TDS (see Table 9). The low ratios of less than 1 are generally due to samples with high TDS and SC. In these samples, there were also high sulphate values, and at high concentrations of sulphate, ion pairing occurs which results in the SC values being lower (i.e. not all the sulphate will provide independent anions). Vale View had a high SC/TDS-Meas ratio of 4.7 and one of the lowest measured TDS values. At low levels, the relationships are less accurate. The majority of the ratios in Table 9 are within the range for natural waters and therefore the analyses are considered reliable.

Table 9 Comparison of Specific Conductivity to Total Dissolved Solids (SC/TDS) Ratio

Sample Description	Sample Type	Specific Cond.	TDS (Calc)	TDS (Meas)	Ratio	
		(uS/cm)	(mg/l)	(mg/l)	SC/ TDS- Calc	SC/ TDS - Meas
850 Adit	Adit	1490	917	1140	1.6	1.3
Avoca Bridge	SW	60	26	90	2.3	0.7
Ballinacleish Bridge	SW	55	26	32.6	2.1	1.7
Cronebane Intermediate Adit	Adit	1265	894	1160	1.4	1.1
Cronebane Pit Lake	Adit	442	156	221	2.8	2.0
Cronebane Shallow Adit	Adit	3590	3810	4970	0.9	0.7
Deep Adit	Adit	1391	1160	1450	1.2	1.0
Deep Adit Conf.	Adit	1402	1140	1410	1.2	1.0
DS Shelton Abbey	SW	106	48	73	2.2	1.5
DS Deep Adit	SW	79	32	34.7	2.4	2.3
GW1/05	GW	1640	1345	1560	1.2	1.1
GW2/05	GW	1330	999	1160	1.3	1.2
Lions Bridge	SW	60	24	36.8	2.5	1.6
MWDA1	GW	2810	2450	3290	1.1	0.9
MWDA2	GW	1490	1190	1550	1.2	1.0
MWET1	GW	2090	1850	2270	1.1	0.9
MWET2	GW	3470	3207	3580	1.1	1.0
MWPF1	GW	154	77	88	2.0	1.8
MWSA2	GW	2360	2153	2610	1.1	0.9
Road Adit	Adit	1640	1282	1440	1.3	1.1
Road Adit Conf.	Adit	1650	1260	1440	1.3	1.1
SG104	GW	8280	11500	14000	0.7	0.6
Site T1	SW	46	19	21	2.4	2.2
Spa Adit	Adit	2530	2020	2430	1.3	1.0
Sulphur Brook	SW	157	85	87.4	1.8	1.8
Site T5	SW	66	32	63	2.0	1.0
US Shelton Abbey	SW	103	54	74	1.9	1.4
US Road Adit	SW	61	25	82	2.4	0.7
Vale View	SW	152	82	32.6	1.9	4.7
WCC Maintenance Yard GS	SW	92	36	61	2.6	1.5
Whites Bridge	SW	57	26	31	2.2	1.8
Whites Bridge GS	SW	37	26	28	1.4	1.3

Figure 1 shows the relationship between specific conductivity and TDS. There is a strong positive correlation between SC with both the calculated ($R^2=0.95$) and measured ($R^2=0.95$) TDS. The relationship is less strong when the TDS is less than 100 mg/l.

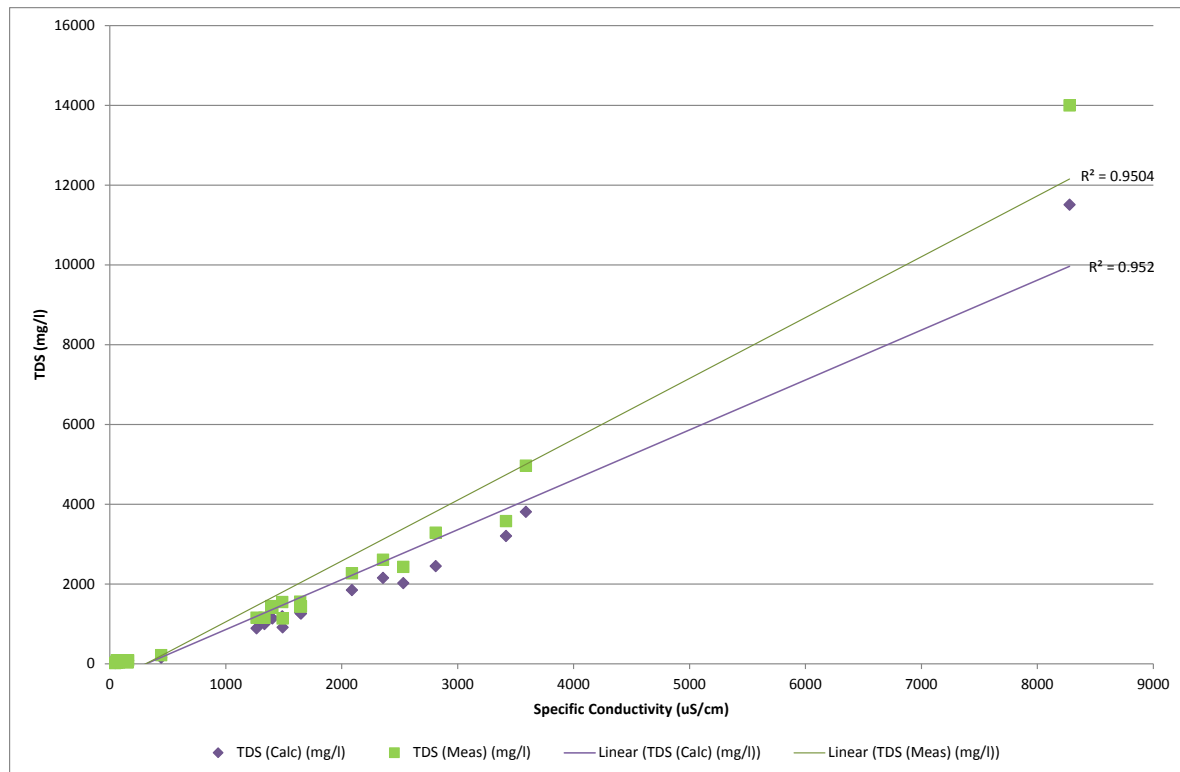


Figure 2 Relationship of Specific Conductivity and Total Dissolved Solids (TDS)

3.4.3 Comparison of Total and Dissolved Metals

Total metals are the concentration of metals determined in an unfiltered sample (combination of metals contained in the solid sediments, colloidal particles and in the dissolved phase), while dissolved metals are those which pass through a 0.45µm membrane filter. Dissolved metals are more biologically available than total metals.

Normally the dissolved metal concentrations would be less than the total metals because they are a portion of the total concentration. This was checked for some of the key metals aluminium, copper, iron and zinc, by calculating ratio of total and dissolved metals to evaluate if the concentrations were distinguishable. Table B-1 in [Appendix B](#) shows the full tabulation of results. The dissolved metals were generally equal to or close to the total metals, indicating that the majority of the aluminium, copper, iron and zinc present were dissolved. For many of the river and stream samples however the total aluminium and iron were significantly higher than the dissolved portion. The total suspended solids in the river and stream samples ranged from <2 to 9 mg/l.

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 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 10 provides a summary of the reported results of the nine 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 10 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	<2.9	9	9	16.2	844000	15300	265000
Antimony	<0.16	9	6	0.08	2.12	0.83	0.79
Arsenic	<0.12	9	2	0.06	16.6	2.48	5.57
Barium	<0.03	9	9	1.08	9.26	5.30	3.06
Cadmium	<0.1	9	9	0.347	99.8	26.9	32.6
Chromium	<0.22	9	9	0.378	24.8	8.20	8.60
Cobalt	<0.06	9	9	0.594	560	152	160
Copper	<0.85	9	9	2.28	87200	14100	28000
Iron	<19	9	9	19.20	92100	36400	35100
Lead	<0.02	9	9	0.263	98.2	22.5	32.20
Manganese	<0.04	9	9	23.10	45500	15300	16600
Mercury	<0.01	9	0	0.005	0.005	-	-
Molybdenum	<0.24	9	2	0.12	0.797	0.22	0.23
Nickel	<0.15	9	9	0.583	205	65.6	60.9
Selenium	<0.39	9	2	0.195	4.31	0.74	1.36
Silver	<1.5	9	0	0.75	0.75	-	-
Thallium	<0.96	9	1	0.48	2.300	-	-
Tin	<0.36	9	3	0.18	1.80	0.46	0.54
Uranium	<1.5	9	8	0.75	50.5	9.70	15.5
Vanadium	<0.24	9	2	0.12	0.931	0.23	0.27
Zinc	<0.41	9	9	38	146000	28300	47100

Notes:

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

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, MWET2 had the lowest concentration of dissolved aluminium (16.2 µg/l) and copper (2.28 µg/l) but was high in dissolved zinc (5,490 µg/l). SG104 is located immediately downgradient of Ballymurtagh Landfill had the highest concentrations of metals especially aluminium, cadmium, nickel and zinc. Dissolved arsenic was only detected in two wells with highest concentration at MWSA2 of 16.6 µg/l.

4.1.2 Surface Water Sample Results

Surface water samples were collected for two major categories: the first includes mine adit discharges and the pit lake and the second includes the Avoca River and tributaries. Table 11 provides a summary of the reported results of the nine adit discharge samples and the one pit lake sample and Table 12 provides a summary of the reported results of the 14 river and stream 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 and Pit Lake

Table 11 Summary of Dissolved Metal Concentrations in Adit Discharges and Pit Lake

Dissolved Metal	LOD (µg/l)	Number	Number of Detections	Minimum (µg/l)	Maximum (µg/l)	Mean (µg/l)	SDEV
Aluminium	<2.9	10	10	8600	295000	84400	86500
Antimony	<0.16	10	4	0.08	7.97	1.50	2.49
Arsenic	<0.12	10	10	0.261	20.9	5.43	6.28
Barium	<0.03	10	10	4.16	16.6	8.15	4.89
Cadmium	<0.1	10	10	7.3	109	45.7	34.0
Chromium	<0.22	10	8	0.587	8.1	2.24	2.44
Cobalt	<0.06	10	10	14.5	198	114	61.0
Copper	<0.85	10	10	147	8520	3220	3270
Iron	<19	10	10	98.9	161000	65200	49700
Lead	<0.02	10	10	84.6	2010	819	708
Manganese	<0.04	10	10	377	13400	5760	3840
Mercury	<0.01	9	0	0.005	0.005	-	-
Molybdenum	<0.24	10	1	0.12	0.284 (1.2*)	0.46	0.513
Nickel	<0.15	10	10	4.51	97.2	44.8	25.0
Selenium	<0.39	10	4	0.195	4.44	0.83	1.311
Silver	<1.5	10	0	0.75	7.5*	-	-
Thallium	<0.96	10	6	0.48	2.88 (4.8*)	2.58	1.65
Tin	<0.36	10	4	0.18	7.22	1.52	2.31
Uranium	<1.5	10	6	0.75	26.6	8.89	6.60
Vanadium	<0.24	10	3	0.12	0.985 (1.2*)	0.63	0.511
Zinc	<0.41	10	10	3110	102000	29000	28600

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. Where there were detections the maximum reported value was presented as the maximum value.

Dissolved aluminium, copper, iron, manganese and zinc were found in significantly high concentrations in the majority of the adit discharges and the pit lake sample. The Cronebane Shallow Adit had the highest concentrations of dissolved metals including aluminium (295,000 µg/l), iron

(161,000 µg/l) and zinc (102,000 µg/l). The lowest dissolved metals concentrations were found in the Cronebane Pit Lake, indicating that there is likely to be a significant rainwater input diluting the concentrations of metals.

Rivers and Streams

Table 12 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	<2.9	14	14	12.2	485	186	126
Antimony	<0.16	14	7	0.08	1.4	0.37	0.409
Arsenic	<0.12	14	14	0.3	0.677	0.41	0.099
Barium	<0.03	14	14	4.6	7.9	6.22	0.912
Cadmium	<0.1	14	11	0.05	0.676	0.25	0.165
Chromium	<0.22	14	13	0.11	0.648	0.37	0.144
Cobalt	<0.06	14	14	0.087	0.956	0.47	0.320
Copper	<0.85	14	12	0.425	21.2	5.37	5.27
Iron	<19	14	13	9.5	465	175	131
Lead	<0.02	14	14	0.093	11.4	5.24	2.86
Manganese	<0.04	14	14	9.66	78.6	37.8	20.1
Mercury	<0.01	14	0	0.005	0.005	-	-
Molybdenum	<0.24	14	5	0.12	0.489	0.23	0.153
Nickel	<0.15	14	14	0.582	1.53	0.88	0.262
Selenium	<0.39	14	3	0.195	0.562	0.26	0.125
Silver	<1.5	14	0	0.75	0.75	-	-
Thallium	<0.96	14	0	0.48	0.48	-	-
Tin	<0.36	14	5	0.18	0.805 (1.18*)	0.38	0.324
Uranium	<1.5	14	0	0.75	0.75	-	-
Vanadium	<0.24	14	0	0.12	0.12	-	-
Zinc	<0.41	14	14	8.95	299	95.4	69.2

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. Where there were detections the maximum reported value was presented as the maximum value.

Dissolved metals were detected upgradient of the mining area at Ballinacleish Bridge and Lions Bridge with concentrations of aluminium at 109 and 113 µg/l, zinc at 45.2 and 52.7 µg/l and iron at 60.1 and 164 µg/l at the respective locations.

Site T1 (upstream of the main mining area) is the first sampling location on the Avoca River with the concentration of dissolved aluminium (169 µg/l) and zinc (21.9 µg/l). Whites Bridge (at the bridge) is the first sampling location along the Avoca River within the mining area where increases in metals concentrations are observed namely; aluminium (252 µg/l) and zinc (84.8 µg/l).

Along the Avoca River the concentrations of dissolved metals were variable; the highest dissolved aluminium was 303 µg/l, the highest dissolved copper was 7.77 µg/l the highest dissolved zinc was 125 µg/l were at WCC Maintenance Yard GS.

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 Table 13. 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. 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 13).

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 CaCO₃ (CDM, 2008) and the appropriate ecological assessment criteria are highlighted in bold in Table 13.

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 14. 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 provide parametric 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 13 and Table 14).

Table 13 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
Ortho-phosphate as P	mg/l	0.035	0.075	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
Free Cyanide	mg/l	0.01	-	S.I. No. 272 of 2009	
Fluoride	mg/l	0.5	-	S.I. No. 272 of 2009	
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. 327 of 2012	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	7.2	-	S.I. No. 327 of 2012	
Mercury	µg/l	0.05	0.07	S.I. No. 327 of 2012	
Nickel	µg/l	20	-	S.I. No. 327 of 2012	
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
Uranium	µg/l	-	2.6	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids

Notes:

Bold indicates the selected assessment criteria for ecological health

Table 14 Surface Water and Groundwater Assessment Criteria for Drinking Water

Parameter	Unit	Parametric value
pH	pH units	>6.5 to <9.5
Chloride	mg/l	250
Conductivity	mS/cm	2.5
Free Cyanide	mg/l	0.05
Ammonium	mg/l	0.3
Fluoride	mg/l	1.5
Nitrate as NO ₃	mg/l	50
Nitrite as NO ₂	mg/l	0.5
Sulphate	mg/l	250
Sodium	mg/l	200
Aluminium	µg/l	200
Antimony	µg/l	5
Arsenic	µg/l	10
Cadmium	µg/l	5
Chromium	µg/l	50
Copper	µg/l	2,000
Iron	µg/l	200
Lead	µg/l	10
Manganese	µg/l	50
Mercury	µg/l	1
Nickel	µg/l	20
Selenium	µg/l	10

4.3 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. The dissolved metal concentrations are assessed as they are more biologically available than total metals and non-dissolved metals are generally removed from drinking water by filtration.

Table B-2 in [Appendix B](#) highlights the exceedances of the assessment criteria. Where there was an exceedance of the ecological assessment criteria, 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 pink. The results and exceedances are discussed in this section.

4.3.1 Groundwater Assessment

The pH was found to be acidic in the majority of groundwater samples with results ranging from 2.86 to 6.16 (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 the two locations with highest pH at MWPF1 with 4.77 pH and MWET2 with 6.16 pH which only exceeded the criteria for human health. The specific conductance ranged from 0.154 to 8.277 mS/cm with the lowest conductivity located at MWPF1 and the highest at SG104. The specific conductance exceeded the human health criteria (2.5 mS/cm) at MWET1, MWET2 and SG104.

Sulphate levels greatly exceeded the criteria for human health of 250 mg/l in all of the monitoring wells with values ranging from 742 to 9,210 mg/l. One exception was at MWPF1 where sulphate was below the human health assessment criteria with a value of 30.4 mg/l. Ammonia exceeded both the ecological (0.14 mg/l) and human health (0.3 mg/l) assessment criteria in 5 monitoring wells with concentrations ranging from 0.559 to 3.01 mg/l. Fluoride was also present in 6 of the monitoring wells sampled, with all values exceeding the ecological (0.5 mg/l) and human health criteria (1.5 mg/l).

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 and zinc (Table B-2 in [Appendix B](#) includes the full listing). There were two detections of dissolved arsenic, only MWSA2 with a result of 16.6 µg/l exceeded only the human health (10 µg/l) criteria.

The dissolved aluminium and copper concentrations at MWET2 (deep) (16.2 and 2.28 µg/l) were significantly lower than at MWET1 (shallow) which had concentrations of 113,000 and 855 µg/l, respectively. MWET1 exceeded both the ecological and human health criteria for aluminium (1,900 and 200 µg/l) and ecological assessment criteria for copper (5 µg/l). This could be because MWET1 is screened directly beneath the Emergency Tailings deposits and there is no flow downward to deeper zone, from shallow zone which is direct communication with tailings deposit (heads in MWET2 are higher than in MWET1).

The bedrock monitoring well GW1/05 showed higher dissolved metal concentrations than its nested, shallow alluvial well GW2/05. For example dissolved copper was 8,830 µg/l in GW1/05 and 6,070 µg/l in GW2/05, both exceeded the ecological and human health criteria for copper (5 and 2000 µg/l). Levels of dissolved lead in GW1/05 exceeded the ecological assessment criteria of 7.2 µg/l and the human health criteria of 10 µg/l, with a value of 13.1 µg/l.

SG104 had the highest levels (compared to the other monitoring wells) of dissolved copper (87,200 µg/l), cadmium (99.8 µg/l) and nickel (205 µg/l) exceeding the ecological and human health criteria. Dissolved cobalt (560 µg/l) and zinc (146,000 µg/l) were also highest in SG104 and exceeded the ecological health criteria. Levels of dissolved lead in SG104 exceeded the ecological assessment criteria of 7.2 µg/l and the human health criteria of 10 µg/l, with a value of 47.9 µg/l.

The groundwater in the shallow well at the Deep Adit area MWDA1 showed higher metal concentrations than at MWDA2 (deep). This was especially the case for dissolved aluminium and copper with concentrations of 192,000 and 18,600 µg/l in MWDA1 and concentrations of 56,600 and 5,420 µg/l in MWDA2, respectively. However, both wells still exceeded the criteria for both ecological and human health for aluminium and copper. MWDA1 exceeded the ecological assessment criteria (3.4 µg/l) and human health criteria (50 µg/l) for chromium with concentrations of 24.8 µg/l.

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 265 µg/l and the ecological assessment criteria for dissolved copper (5 µg/l) was exceeded with a value of 33.6 µg/l.

4.3.2 Surface Water Assessment

Adit Discharges and Pit Lake

The pH was found to be acidic in all adit discharges and the pit lake with results within the range of 2.69 to 4.01 pH (field) which exceeded the acceptable ranges for ecological (4.5 to 9 pH units) and human health (6.5 to 9.5 pH units) criteria. The acidity as HCl ranged from 63.9 mg/l in the Cronebane Pit Lake to 1,760 mg/l in the Cronebane Shallow Adit. The specific conductance ranged from 0.442 to 3.588 mS/cm. There were two exceedances of the human health criteria (2.5 mS/cm) at the Cronebane Shallow Adit and Spa Adit.

Elevated sulphate and ammonia were found at all of the adit discharge locations. Sulphate levels greatly exceeded the criteria for human health of 250 mg/l in all of the adit discharges with values ranging from 647 to 3,010 mg/l. Ammonia was detected in all of the adit discharges and the pit lake which exceeded the ecological criteria (0.14 mg/l) and the human health criteria for ammonia (0.3 mg/l) at all locations, with values ranging from 0.22 to 7.32 mg/l. Concentrations of sulphate (109 mg/l) and ammonia (0.22 mg/l) were generally lower at Cronebane Pit Lake than the adit discharges.

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

Dissolved zinc ranged from 3,110 to 102,000 µg/l which exceeded the ecological assessment criteria of 50 µg/l. Dissolved aluminium ranged from 8,620 to 295,000 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 discharge and pit lake and also the human health (2,000 µg/l) criteria in the Cronebane Shallow Adit, Cronebane Pit Lake, 850 Adit, Ballygahan Adit and Spa Adit where concentrations ranged from 2,150 to 8,520 µg/l.

Dissolved cadmium ranged from 7.3 to 109 µg/l which exceeded both the ecological (0.45 µg/l) and human health (5 µg/l) criteria. Dissolved cobalt ranged from 14.5 to 198 µg/l which exceeded the ecological criteria (5.1 µg/l). Dissolved lead ranged from 84.6 to 2,010 µg/l which exceeded both the ecological (7.2 µg/l) and human health (10 µg/l) criteria. Dissolved nickel ranged from 30.2 to 97.2 µg/l in the adit discharges which exceeded both the ecological and human health criteria of 20 µg/l.

Dissolved arsenic was detected in all of the adit discharges, with Ballygahan Adit (20 µg/l) and Cronebane Shallow Adit (11.2 µg/l) exceeding the criteria human health (10 µg/l) but below the criteria for ecological health (25 µg/l). Dissolved chromium was detected and exceeded the ecological assessment criteria of 3.4 µg/l in Ballygahan Adit, Spa Adit and Cronebane Shallow Adit, ranging from a concentration of 3.41 to 8.1 µg/l.

Dissolved iron and manganese were also high in all adit discharges. Iron ranged from 98.9 to 161,000 µg/l, exceeding the human health assessment criteria of 200 µg/l at each location except Ballygahan Adit. Manganese ranged from 2,580 to 13,400 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. Note that iron and manganese are not important criteria for human health (see Section 4.2.1).

Rivers and Streams

Table 15 provides a summary of the reported values for rivers and streams in the Avoca Mining area that exceeded the relevant ecological and human health assessment criteria. The pH was found to be near neutral in the majority of rivers and streams ranging from 4.76 to 6.73 pH (field) which were within acceptable ranges for ecological criteria (4.5 to 9 pH units). Ballinacleish Bridge, Lions Bridge and all the locations on the Avoca River were below the human health (6.5 to 9.5 pH units) criteria. Acidity was below the limit of detection (<2 mg/l) at all river locations. The specific conductance was well within the criteria for human health of 2.5 mS/cm ranging from 0.037 to 0.157 mS/cm.

Nutrients in the river and stream samples collected were below the limit of detection for ortho-phosphate (<0.02 mg/l) and ammonia (<0.2 mg/l) with a few exceptions. Ammonia was 0.213 and 0.24 mg/l at Ballinacleish Bridge and US Shelton Abbey, respectively, which were above the ecological health criteria of 0.14 mg/l. Ortho-phosphate was 0.0307 mg/l at Sulphur Brook which was below the ecological assessment criteria of 0.075 mg/l.

The dissolved metal concentrations in the rivers and streams were low in comparison to the groundwater and the adit discharges; however, several exceedances of both ecological and human health criteria occurred. Dissolved copper exceeded the ecological criteria (5 µg/l) at White Bridge and all river locations from US Road Adit to the Downstream Shelton Abbey location, with results ranging from 5.34 to 21.2 µg/l. The highest dissolved copper concentration was found in Sulphur Brook. Dissolved zinc exceeded the ecological assessment criteria (50 µg/l) from Whites Bridge on the Avoca River to Downstream Shelton Abbey with results ranging from 69.6 to 299 µg/l, the ecological assessment criteria was also exceeded at Lions bridge with a concentration of 52.7 µg/l. Dissolved aluminium exceeded the human health criteria of 200 µg/l from Whites Bridge to Avoca Bridge 246 to 485 µg/l, however it was below the assessment criteria with a concentration of 136 µg/l at Whites Bridge GS.

Dissolved cadmium exceeded the ecological assessment criteria (0.45 µg/l) at DS Deep Adit with a concentration of 0.676 µg/l. Dissolved lead exceeded the ecological (7.2 µg/l) and human health (10 µg/l) assessment criteria with a concentration of 11.4 µg/l. the ecological assessment criteria for lead was also exceeded at WCC Maintenance Yard and Site T5 with concentrations of 7.75 and 7.47 µg/l, respectively.

Dissolved iron exceeded the human health assessment criteria of 200 µg/l at four locations on the Avoca River with concentration ranging from 201 to 465 µg/l. Dissolved manganese exceeded the criteria for human health (50 µg/l) ranging in concentration from 54.8 to 78.6 µg/l. Note that iron and manganese are not important criteria for human health (see Section 4.2.1).

Table 15 Summary of Reported Values for Rivers and Streams and the Surface Water Assessment Criteria

	Date Sampled	pH (field)	Ammoniacal Nitrogen as N	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	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Ecological Criteria		4.5 to 9	0.14	1,900	0.45	5	-	7.2	1100	50
Human Health Criteria		6.5 to 9.5	0.3	200	5	2000	200	10	50	-
Ballinacleish Bridge	17/02/2015	5.64	0.213	109	<0.1	<0.85	60.1	3.52	23.3	45.2
Lions Bridge	17/02/2015	5.87	<0.2	113	0.162	1.22	164	5.42	21.4	52.7
Site T1	16/02/2015	4.87	<0.2	169	<0.1	<0.85	98.3	5.51	24.2	21.9
Vale View	17/02/2015	6.63	<0.2	12.2	<0.1	1.37	26.5	0.093	9.66	8.95
Whites Bridge	16/02/2015	5.89	<0.2	252	0.251	5.34	194	6.67	37.2	84.8
Whites Bridge GS	16/02/2015	6.08	<0.2	136	0.121	2.01	121	4.45	21.6	84.6
DS Deep Adit	16/02/2015	4.76	<0.2	485	0.676	3.61	372	11.4	45.8	299
US Road Adit	16/02/2015	5.82	<0.2	247	0.219	5.7	140	6	30.3	69.6
WCC Main Yard GS	16/02/2015	5.29	<0.2	303	0.336	7.77	465	7.75	71.3	123
Site T5	16/02/2015	5.72	<0.2	288	0.302	7.71	327	7.47	54.8	106
Sulphur Brook	17/02/2015	6.73	<0.2	28.5	0.315	21.2	<19	4.68	23.9	102
Avoca Bridge	16/02/2015	5.89	<0.2	246	0.26	5.24	201	6.56	37.6	87.3
US Shelton Abbey	11/02/2015	6.39	0.24	101	0.334	6.47	117	1.96	49.1	123

Notes

xx Exceeds Ecological Assessment Criteria

xx Exceeds Human Health Assessment Criteria

xx Exceeds both Ecological and Human Health Criteria

Metals are dissolved

US = upstream, DS = downstream, GS = gauging station

WCC = Wicklow County Council

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 the Deep Adit and was previously just upstream of the Road Adit confluence. As previously discussed and shown on Map 3 in [Appendix A](#), the new discharge location for the Road Adit to the Avoca River (Road Adit Confluence) is upstream of the Wicklow County Council Maintenance Yard GS.

The flow record from 1 October 2014 to 31 March 2015 of Whites Bridge GS is reproduced in Figure 2 and for Wicklow County Council Maintenance Yard GS from 1 October 2014 to 23 February 2015 in Figure 3. The figures show the measured flows ranged from $>65 \text{ m}^3/\text{s}$ following rainfall events to approximately $2.6\text{--}4 \text{ m}^3/\text{s}$ during low-flow. The river typically shows a rapid response to rainfall. The median flows for this period of approximately $12.4 \text{ m}^3/\text{s}$ at Whites Bridge GS and $13.1 \text{ m}^3/\text{s}$ at Wicklow County Council Maintenance Yard GS are higher than the long term median of approximately $8.6 \text{ m}^3/\text{s}$ and $9.5 \text{ m}^3/\text{s}$ respectively (CDM Smith, 2015), which reflects the high levels of rainfall during the monitoring period. Flow in November was particularly high with the daily mean flow recorded at $68.5 \text{ m}^3/\text{s}$ on 15 November 2014.

The river appears to respond similarly to rainfall at both gauging stations as can be observed in both figures. The peaks in the graphs in response to rainfall events appear to be similar. A discussion of the differences in flow rates between the two gauges is provided in Section 6.4.3 Surface Water Flow Data at the EPA Gauging Stations.

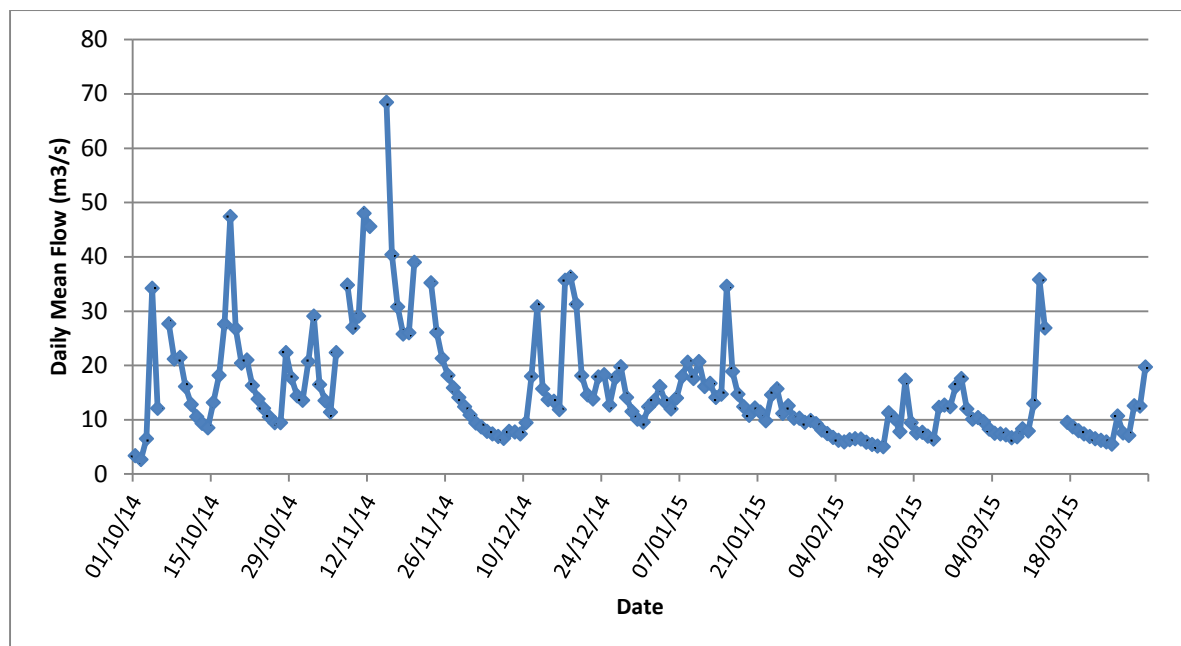


Figure 3 Mean Daily Flow (m³/s) at Whites Bridge (Station 10044) from 1 Oct 2014 to 31 Mar 2015

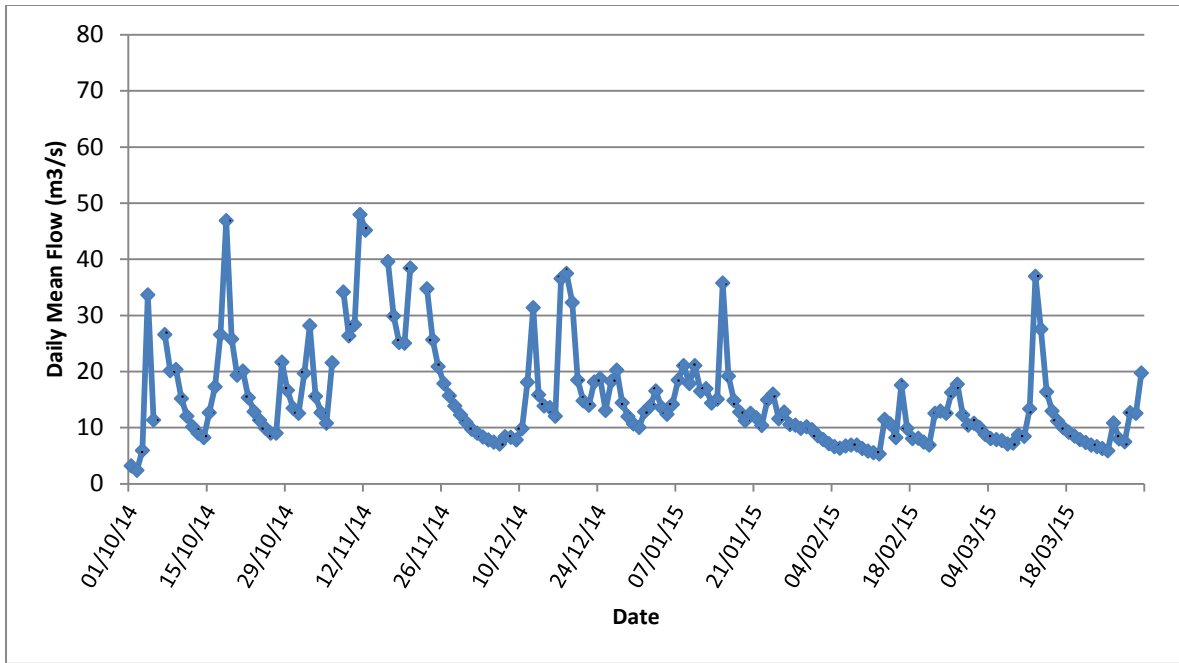


Figure 4 Mean Daily Flow (m3/s) at Wicklow County Council Maintenance Yard (Station 10045) from 1 Oct 2014 to 24 Feb 2015

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 Surface Water Sampling. Table 16 presents as a summary of the results from the flows measured in February 2015 at the time of sampling. It is noted that all of the flow measurements on the main channel were carried out on the same day. This gives a true representation of hydrogeological activity in the Avoca River and the average flow measurements reflect this. Appendix B of the Data Report contains details of methodologies used per site and associated calculations.

The measured flow at the Deep Adit of 16.7 l/s is considered a moderate flow as past records for the Deep Adit ranged from approximately 10 to 37.5 l/s. This reflects the relatively low levels of rainfall in February. There was a very low flow issuing from the 850 Adit at 0.30 l/s. The combined flow of the Deep Adit and the 850 Adit was calculated to be 17 l/s. The flow was also measured at the Deep Adit Confluence (Deep Adit + 850 Adit) prior to it discharging to the river and the measured flow was 13.1 l/s which is slightly less than the combined flow of the two adits. Note this location is not ideal for measuring flow as it is not properly channelised and the measurement should be considered an estimate. This indicates that there is a loss of flow which is likely due to; dispersed flow along the channel, infiltration into the channel bed and diversion into the millrace (estimated to be <10%). Note that there was no sample collected from the Millrace, as any flow was likely seeping to groundwater. The water was pooled in the Millrace approximately 10 m from the Deep Adit channel and flow was unable to be measured at this location.

The flow was measured at the Road Adit Confluence prior to the adit discharging to the river and the measured flow was 56.5 l/s. Flow was not recorded at the Road Adit Portal during this sampling event but the flow is assumed to be similar to the measured flow at the Road Adit Confluence as

the Road Adit now flows through a pipe directly into the river rather than through a ditch alongside the road.

Table 16 Surface Water Flow Value Measured in February 2015

Site Name	Flow m ³ /s	Flow l/s	Date	Notes
Ballinacleish Bridge	2.70	2700	17/02/2015	
Lions Bridge	7.83	7830	17/02/2015	
Vale View	0.02	18	17/02/2015	
Site T1	10.5	10500	16/02/2015	Flow on 17/2/2015 less than 16/2/2015
White's Bridge GS	17.3	17300	16/02/2015	Note that flow on 11/02/2015 was 5.55 m ³ /s
DS Deep Adit	17.3	17300	16/02/2015	
Upstream of Road Adit	17.6	17600	16/02/2015	
Wicklow Co Co. Maintenance Yard GS	17.6	17600	16/02/2015	
Site T5	16.1	16200	16/02/2015	
Avoca Bridge	20.1	20100	16/02/2015	
Upstream of Shelton Abbey	10.2	10200	11/02/2015	
Downstream of Shelton Abbey	10.2	10200	11/02/2015	
Sulphur Brook	0.157	157	17/02/2015	
850 Adit	0.0003	0.30	12/02/2015	
850 Adit Confluence	-	-	12/02/2015	No measurable flow
Deep Adit	0.017	16.7	12/02/2015	
Deep Adit Confluence	0.013	13.1	12/02/2015	
Millrace	-	-	12/02/2015	No measurable flow
Road Adit	-	-	12/02/2015	Height from flume not recorded
Road Adit Confluence	0.056	56.5	02/12/2015	
Cronebane Intermediate Adit	0.005	5.1	11/02/2015	
Cronebane Shallow Adit	0.0003	0.31	11/02/2015	
Ballygahan Adit	-	-	12/02/2015	No measurable flow
Spa Adit	0.00001	0.012	12/02/2015	
Cronebane Pit Lake	n/a	n/a	11/02/2015	

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 17 aid with the interpretation of the loading of sulphate and dissolved aluminium, copper, iron, lead and zinc to the Avoca River.

Table 17 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
Cronebane Inter. Adit	11/02/2015	5.08	3.21	647000	284	47500	20.8	1900	0.830	87100	38.2	1270	0.560	29300	12.90
Cronebane Shallow Adit	11/02/2015	0.31	2.85	3010000	81	295000	7.96	8520	0.230	161000	4.34	1140	0.030	102000	2.75
Deep Adit	12/02/2015	16.66	3.56	864000	1240	85600	123	147	0.210	64200	92.4	2010	2.89	36300	52.2
Deep Adit Confluence	12/02/2015	13.07	3.47	862000	974	79500	90	297	0.34	60900	69	1790	2.02	40200	45.4
Road Adit Confluence	12/02/2015	56.49	4.01	890000	4340	12000	58.6	322	1.570	75900	370	344	1.68	8150	39.8
Spa Adit	12/02/2015	0.01	2.69	1580000	2	156000	0.2	7570	0.010	108000	0	89	0.000	12500	0.0
850 Adit	12/02/2015	0.30	2.83	711000	18	70700	1.8	4830	0.13	17800	0	862	0.020	26500	0.7
Ballinaclesh Bridge	17/02/2015	2705	5.64	1000	234	109	25.5	0.425	0.10	60.10	14	3.52	0.820	45.2	10.6
Lions Bridge	17/02/2015	7830	5.87	1000	677	113	76.4	1.22	0.830	164	111	5.42	3.670	52.7	35.70
Site T1	16/02/2015	10500	4.87	1000	907	169	153	0.425	0.39	98.30	89.2	5.51	5.0	21.9	19.90
Vale View	17/02/2015	18.16	6.63	15500	24	12.2	0.02	1.37	0.000	26.50	0.0	0.093	0.000	8.95	0.01
Whites Bridge	16/02/2015	17300	5.89	1000	1490	252	377	5.34	7.98	194	290	6.67	9.970	84.8	127
Whites Bridge GS	16/02/2015	17300	6.08	1000	1490	136	203	2.01	3.00	121	181	4.45	6.650	84.6	126
DS Deep Adit	16/02/2015	17300	4.76	9700	14500	485	725	3.61	5.40	372	556	11.4	17.0	299	447
US Road Adit	16/02/2015	17600	5.82	1000	1520	247	376	5.7	8.67	140	213	6	9.12	69.6	106
WCC Main. Yard GS	16/02/2015	17600	5.29	10000	15200	303	461	7.77	11.8	465	707	7.75	11.8	123	187
Site T5	16/02/2015	16148	5.72	7500	10500	288	402	7.71	10.8	327	456	7.47	10.4	106	148
Avoca Bridge	16/02/2015	20096	5.89	1000	1740	246	427	5.24	9.10	201	349	6.56	11.4	87.3	152
Sulphur Brook	17/02/2015	157	6.73	11700	159	28.5	0.4	21.2	0.29	9.50	0.10	4.68	0.060	102	1.40
US Shelton Abbey	11/02/2015	10168	6.39	12100	10600	101	88.7	6.47	5.68	117	103	1.96	1.720	123	108
DS Shelton Abbey	11/02/2015	10168	6.14	13300	11700	116	102	6.72	5.90	151	133	1.89	1.660	127	112

Loading from Adit Discharges

The Deep Adit Confluence had aluminium, copper and zinc loads of 90, 0.34 and 45.4 kg/day and the Road Adit Confluence had loads of 58.6, 1.57 and 39.8 kg/day, respectively. The Road Adit Confluence had a higher load of sulphate with 4,340 kg/day and dissolved iron with 370 kg/day and the Deep Adit had 974 kg/day sulphate and 69 kg/day of iron. The 850 Adit had significantly lower loadings than the Deep Adit which reflects the very low flow conditions measured at this location.

To determine if there was any apparent loss of sulphate or metals loading along the Deep Adit ditch, the flow and loading results were summed up for the Deep Adit and 850 Adit portal samples and compared with the measured loads at the Deep Adit Confluence (Table 17). The recorded flow was lower further downstream which is likely due to the difficulties in measuring the flows as the discharge was dispersed and flowing several different directions. Also, there is likely infiltration occurring in the channel including a small flow (<10%) seeping to groundwater at the Millrace channel. The concentrations of sulphate and the dissolved metals were slightly lower in the Deep Adit confluence compared to the Deep Adit Portal with the exception of dissolved copper and dissolved zinc which were slightly higher. The loading of aluminium and iron in particular were lower at the Deep Adit Confluence (total aluminium 90 kg/day and iron 69 kg/day) when compared with the Deep Adit portal (aluminium 123 kg/day and iron 92.4 kg/day). The sulphate load also decreased downstream of the portal from 1,240 to 974 kg/day. The decreases in loads are likely due to the loss of flow which can be attributed to the difficulties in measuring the flows or from infiltration along the ditch.

The Cronebane Intermediate Adit had dissolved metals loads of 20.8 kg/day for aluminium, 38.2 kg/day iron and 12.9 kg/day zinc. The Cronebane Shallow Adit and Spa Adit were of minor importance in terms of dissolved metals loads to the Avoca, either because of absence of surface flow to the river or due to low loads (either low concentrations or low flows). Loads from these adits range from 0.2 to 7.96 kg/day for aluminium and 0.01 to 0.23 kg/day for copper. Loads from the Ballygahan Adit could not be calculated because the flow was too low to measure and but a sample was collected.

Avoca River Loadings

Background loads upstream of the Avoca Mining Area of metals were present which is evident from the calculated loads at Ballinacleish Bridge, Lions Bridge and Site T1. The dissolved metal loads at Site T1 were 153 kg/day for aluminium, 0.39 kg/day for copper, 89.2 kg/day for iron, 5.0 kg/day for lead and 19.9 kg/day for zinc. Figure 4 graphically shows the calculated loads of dissolved aluminium, copper, iron and zinc 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](#)).

Compared to upgradient locations, an increase in loads occurs at Whites Bridge with loads of dissolved aluminium at 377 kg/day, iron at 290 kg/day, zinc at 127 kg/day and copper at 7.98 kg/day. There was a significant decrease in dissolved aluminium 203 kg/day, iron 181 kg/day and copper 3 kg/day loads, 90 metres downstream at Whites Bridge GS.

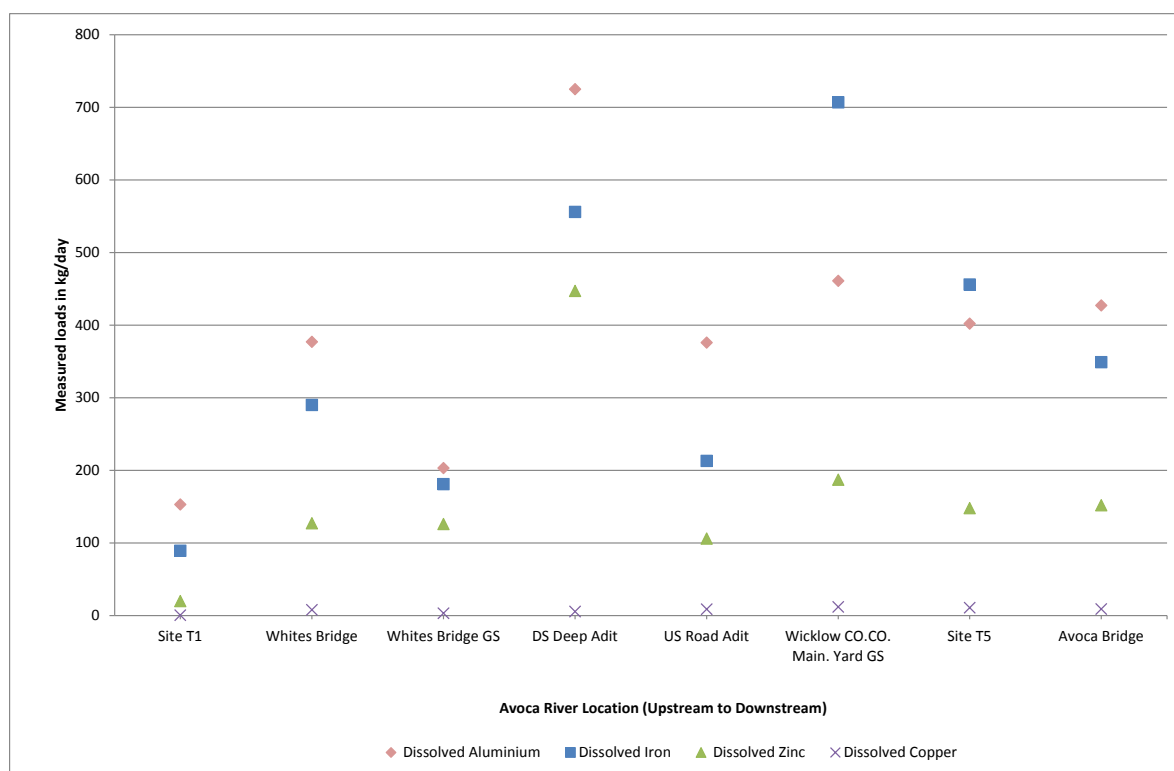


Figure 5 Calculated Loads of Dissolved Aluminium, Iron, Zinc and Copper in kg/day in Avoca River in February 2015

The DS Deep Adit location is on the Avoca River is downstream of the Deep Adit discharge, therefore the loads would be expected to be 293 kg/day for aluminium, 250 kg/day for iron and 171.4 kg/day for zinc to account for the loading at Whites Bridge GS (203 kg/day aluminium, 181 kg/day iron and 126 kg/day zinc) and the Deep Adit Confluence (90 kg/day aluminium, 69 kg/day iron and 45.4 kg/day zinc). However, the loadings were determined to be significantly higher at DS Deep Adit with 725 kg/day aluminium, 556 kg/day iron and 447 kg/day zinc. The DS Deep Adit sample was collected from the river bank and so the discharge is unlikely to be fully mixed with the Avoca River therefore the loadings are an overestimation of the actual loads in the Avoca River at the DS Deep Adit location. Composite samples taken along a transect at this location during low flow in Round 4 and 6 which provide more representative results.

Further downstream on the Avoca River at US Road Adit on the Avoca River, the measured loads were closer to the expected loads with 376 kg/day for aluminium, 213 kg/day for iron and 106 kg/day for zinc; however, aluminium was higher than expected whereas iron and zinc were lower. At the US Road Adit location, the Deep Adit discharge is better mixed with the Avoca River.

The Wicklow Co. Co. Maintenance Yard GS is located downstream of the Road Adit discharge since October 2014. The loads would be expected to be 435 kg/day for aluminium, 583 kg/day for iron and 146 kg/day for zinc to account for the loading at US Road Adit (376 kg/day aluminium, 213 kg/day iron and 106 kg/day zinc) and the Road Adit Confluence (58.6 kg/day aluminium, 370 kg/day iron and 39.8 kg/day zinc). However, the loadings were determined to be slightly higher at Wicklow Co. Co. Maintenance Yard GS with 461 kg/day aluminium, 707 kg/day for iron and 187 kg/day for zinc. At Wicklow Co. Co. Maintenance Yard GS, the Road Adit discharge is not fully

mixed with the Avoca River and because the sample was collected from the river bank the loadings are likely overestimated at this location.

Site T5 is located further downstream where the Road Adit discharge is mixed better with the Avoca River, which is also evident as the measured loads were similar to what would be expected with 402 kg/day for aluminium, 456 kg/day for iron and 148 kg/day for zinc.

There was an apparent increase in the dissolved aluminium, iron and zinc loads from 88.7 kg/day for aluminium, 103 kg/day for iron and 108 kg/day for zinc from US Shelton Abbey to 102 kg/day for aluminium, 133 kg/day for iron and 112 kg/day for zinc DS Shelton Abbey. The calculated loads for dissolved copper and lead were similar at the upstream and downstream locations of Shelton Abbey.

Two tributaries to the Avoca River were sampled: Vale View and Sulphur Brook. Both tributaries had insignificant loads relative to the adit discharges, with the highest loading of 1.4 kg/day for zinc at Sulphur Brook.

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 including dissolved copper, zinc and iron. The trends are shown graphically in Figure 5 (Deep Adit from Oct 2001 to Feb 2015), Figure 6 (Road Adit from Oct 2001 to Feb 2015) and Figure 7 (Avoca River at Avoca Bridge from Oct 2001 to Feb 2015).

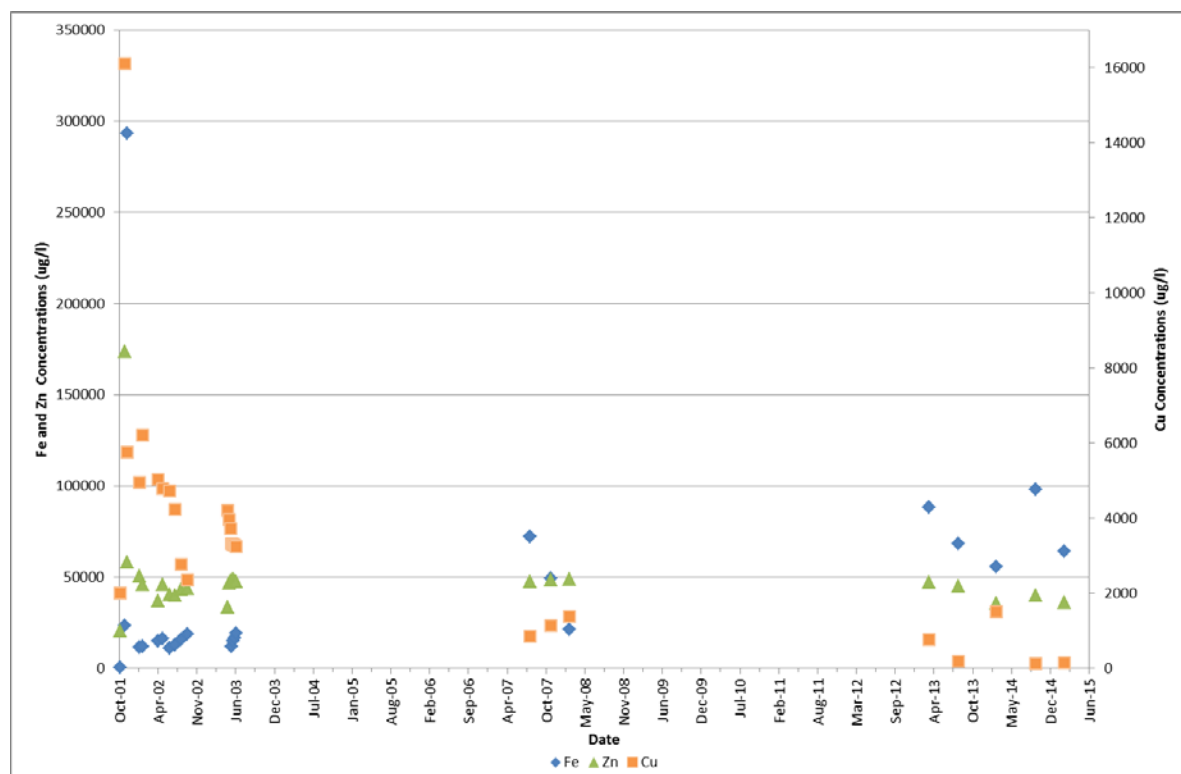


Figure 6 Concentration trends for dissolved copper, zinc and iron within the Deep Adit Discharge (Oct 2001 to Feb 2015)

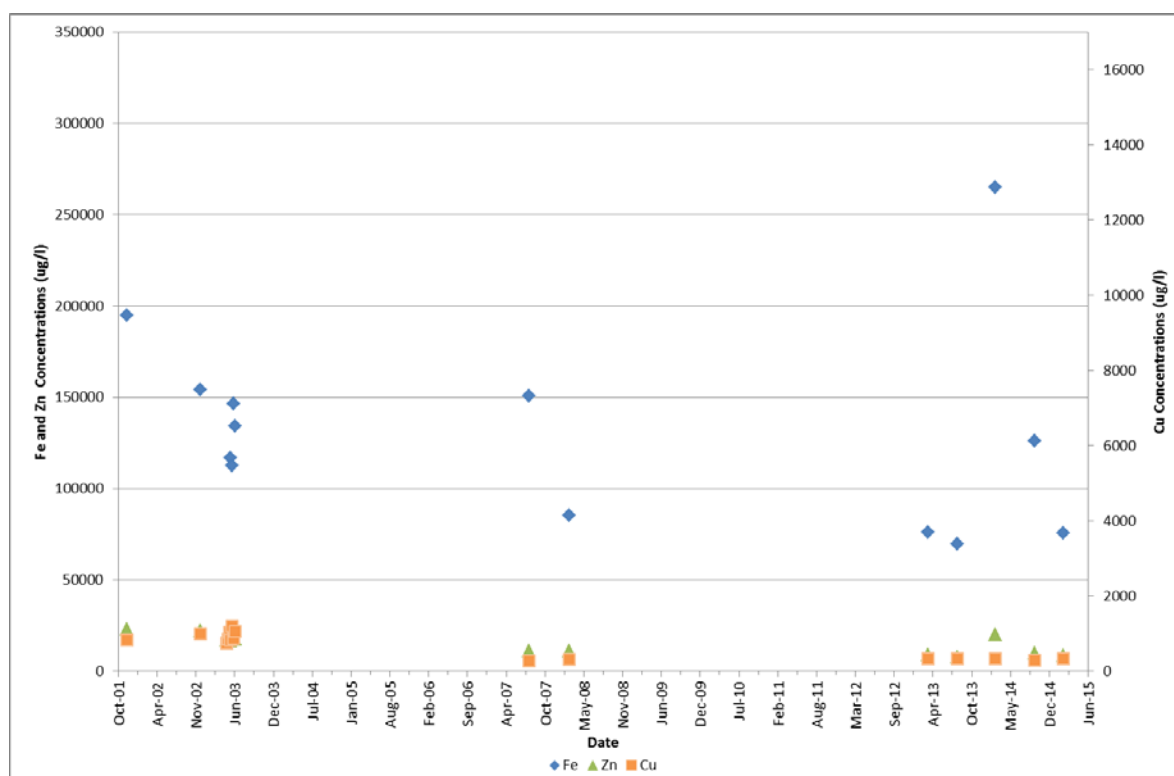


Figure 7 Concentration trends for dissolved copper, zinc and iron within the Road Adit Discharge (Oct 2001 to Feb 2015)

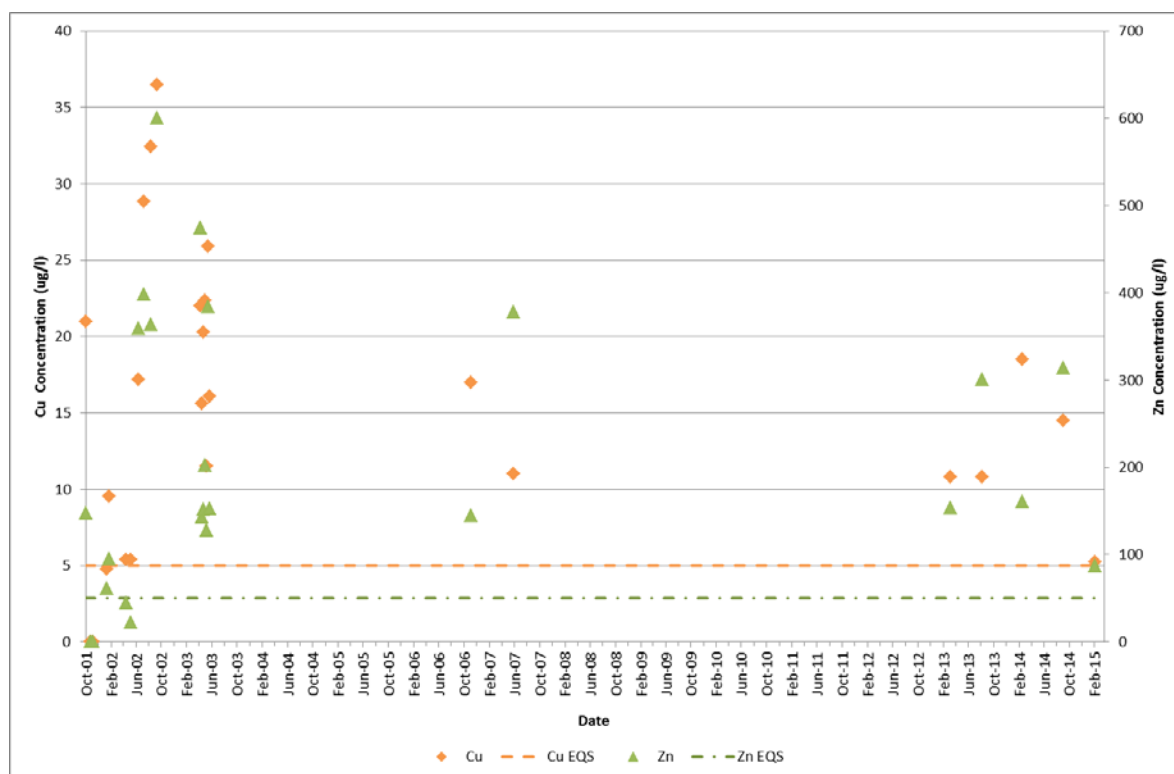


Figure 8 Concentration trends for dissolved copper and zinc at Avoca Bridge compared with the environmental quality objective (EQS) (Oct 2001 to Feb 2015)

The Mann-Kendall test was performed on the surface water sampling locations 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 of that trend being real. Table 18 shows the possible outcomes of the Mann-Kendall trend analysis as applied to the water quality data.

Table 18 Reporting the Mann-Kendall Results

Trend	P value	Trend reported as
Decreasing	$0 \leq p < 0.05$	Decreasing
	$0.05 \leq p < 0.1$	Likely Decreasing
	$p \geq 0.1$	No Trend
Increasing	$0 \leq p < 0.05$	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.

Trend analysis was conducted for all data since the October 2001 because data were available for all of the sample locations from that date onwards. Analysis of data since June 2007 was 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 19 and facilitate general observations about trends in the water quality of the two main adit discharges and the downstream location of Avoca Bridge.

Table 19 Mann-Kendall Trend Analysis of data for Deep Adit, Road Adit and Avoca Bridge

Sample location	Parameter	October 2001 to February 2015			June 2007 to February 2015		
		P value	S value	Trend	P value	S value	Trend
Deep Adit	Copper	0.0000001	-239	Decreasing	0.1328	-10	No Trend
	Zinc	0.3139	-23	No Trend	0.0177	-18	Decreasing
	Iron	0.0004	129	Increasing	0.3553	4	No Trend
Road Adit	Copper	0.0396	-40	Decreasing	0.1838	7	No Trend
	Zinc	0.0013	-68	Decreasing	0.2740	-5	No Trend
	Iron	0.0384	-30	Decreasing	0.2740	-5	No Trend
Avoca Bridge	Copper	0.2717	-24	No Trend	0.4242	-2	No Trend
	Zinc	0.1990	33	No Trend	0.2262	-5	No Trend

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 February 2015 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. These trends can also be inferred from Figure 5 and 6.

The results of the Mann-Kendall analysis for June 2007 to February 2015, show that dissolved zinc is decreasing in the Deep Adit and that there were no other trends for dissolved zinc, iron or copper for this time period in the adit discharges.

Figure 7 displays the results for dissolved copper and zinc in the Avoca River at Avoca Bridge which is downstream of the main Avoca Mining Area, from 2001 to present. No statistically significant trend was present for dissolved zinc or dissolved copper for both the 2001-2015 period and the 2007-2015 period. Dissolved copper and zinc concentrations at Avoca Bridge were their lowest since mid-2002 with concentrations of 5.24 and 87.3 µg/l, respectively. 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 and dissolved zinc above the ecological assessment criteria of 50 µg/l since mid-2002.

5.3.2 Seasonal Trends

Table 20 shows the seasonal variation between the concentrations of dissolved metals and the calculated loads observed between the high flow sampling events in March 2013 (R1), February 2014 (R3) and February 2015 (R5) and the low flow sampling events in August 2013 (R2) and September 2014 (R4). As can be observed from Table 20, the concentrations of dissolved aluminium, copper, iron and zinc were very similar in each sampling event with a few exceptions. Dissolved copper in the Deep Adit was significantly lower in concentration in August 2013, September 2014 compared with the high flow sampling, however it was also quite low in February 2015 when the flow in the Deep Adit was lower than other winter sampling events. The concentration of dissolved iron at Avoca Bridge is quite variable and dissolved zinc is higher in concentration during the low flow sampling events in August 2013 and September 2014.

Table 20 also shows that the calculated loads of dissolved aluminium, copper, iron and zinc were all significantly lower in August 2013 and September 2014 due to the low flow conditions. Similar flow conditions measured at the Deep Adit in February 2015 resulted in relatively low calculated loads of dissolved metals.

Table 20 Seasonal Variation of Concentrations and Calculated Loads of Dissolved Metals in the Adits and at Avoca Bridge from 2013-2015

Sample Description	Date Sampled	Flow l/s	Aluminium		Copper		Iron		Zinc	
			µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day
Deep Adit	R1 15/03/2013	29.2	98800	249	770	1.9	88500	223	47300	119
	R2 15/08/2013	13	96700	110	184	0.21	68300	77.4	44900	50.9
	R3 27/02/2014	22.2	71600	138	1500	2.9	55800	107	35500	68.2
	R4 16/09/2014	17.5	80200	121	130	0.2	98100	148	39900	60.3
	R5 12/02/2015	16.7	85600	123	147	0.2	64200	92	36300	52
Road Adit	R1 15/03/2013	28.9	14900	37.2	366	0.9	76100	190	9140	22.8
	R2 15/08/2013	15.6	16400	22.1	335	0.45	69500	93.9	7810	10.5
	R3 27/02/2014	56.2	15000	72.8	321	1.6	265000	1290	20100	97.6
	R4 16/09/2014	18	15600	24.3	294	0.46	126000	196	9810	15.3
	R5 12/02/2015	-	12400	-	339	-	75600	-	8350	-
Avoca Bridge	R1 20/03/2013	12000	162	167	10.8	11.2	153	158	154	159
	R2 20/08/2013	1940*	161	27	10.8	1.81	232	38.9	301	50.5
	R3 04/03/2014	24000	152	315	18.5	38.4	485	1010	161	334
	R4 17/09/2014	3240	93.1	26.1	14.5	4.06	182	51	314	88
	R5 16/02/2015	20096	246	427.1	5.24	9.10	201	349	87	151.6

Notes:

*Unrepresentative flows resulted in an underestimate of the sulphate and dissolved metals loadings at Avoca Bridge

Section 6

Groundwater Levels and Groundwater-Surface Water Interaction

6.1 Groundwater Levels

Groundwater levels were measured at the nine wells using a portable electronic water level recorder prior to purging. Table 21 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 25.85 to 32.79 m Ordnance Datum (OD) in the Avoca Mining Area. These groundwater elevations were between 0.1 to 0.3 metres higher than the elevations measured in September 2014 with the exception of SG104 which was 0.3m lower. The groundwater elevations were consistent with the hydraulic gradient towards the Avoca River. MWSA2 is located downgradient of Shelton Abbey Tailings which is in a different part of the catchment and the groundwater elevation is much lower than that of the West and East Avoca.

Table 21 Measured Groundwater Levels and Calculated Elevation February 2015

Borehole Identifier	Date	Time	Depth to Groundwater (m bTOC)	Depth to Groundwater (m bgs)	Groundwater Elevation (m OD)
MWDA1	10/02/2015	16:40	6.23	5.63	26.56
MWDA2	10/02/2015	17:26	6.28	5.55	26.34
MWPF1	10/02/2015	13:38	4.53	3.94	26.96
MWET1	09/02/2015	10:52	7.17	6.6	26.22*
MWET2	09/02/2015	11:49	7.05	6.35	26.32*
GW1/05	09/02/2015	16:10	4.95	4.31	25.85*
GW2/05	09/02/2015	15:30	5.00	4.17	25.95*
SG104	10/02/2015	10:50	25.38	unknown	32.79*
MWSA2	11/02/2015	15:32	8.53	8.25	1.64

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 six wells owned by the Department. Figure 8 shows the groundwater elevations of four of the five wells located in the Avoca Mining Area from 1 October 2014 to 31 March 2015. Figure 9 shows the groundwater elevation at MWSA2 at Shelton Abbey Tailings Facility between 1 October 2014 to 31 March 2015. Due to a data logger malfunction data are missing for MWPF1 for the entire monitoring period. Data are missing for MWDA1 from 17 March 2015 to 31 March 2015 due to data logger repairs and MWET1 from 5 March 2015 to 31 March 2015 due to battery failure.

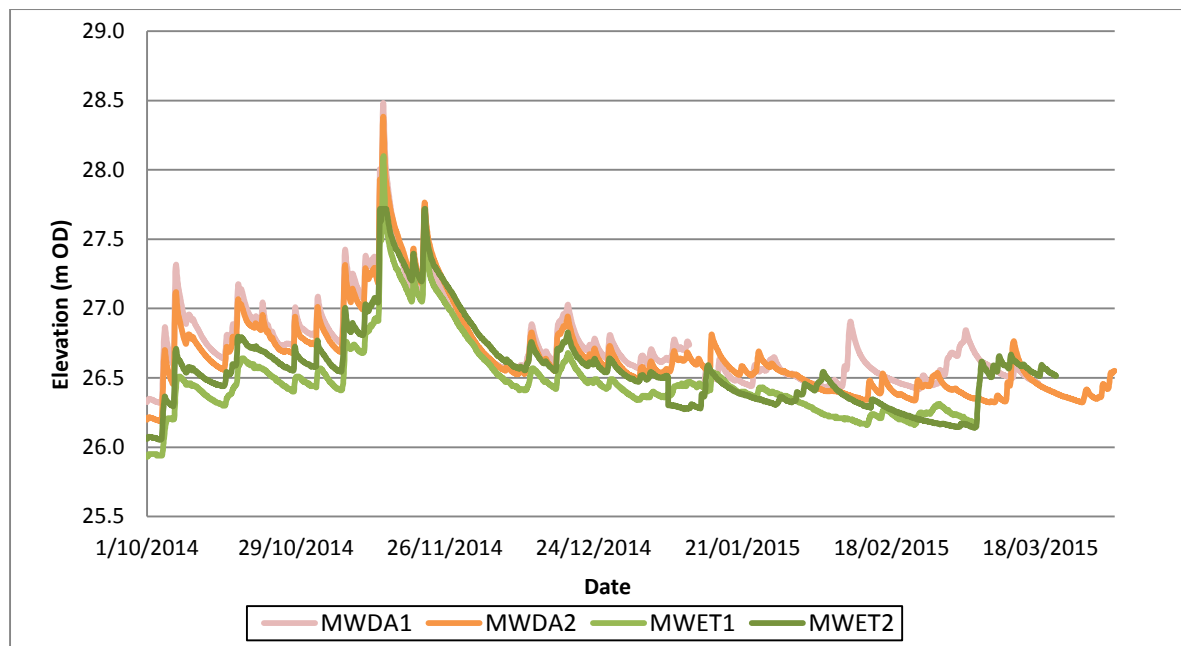


Figure 9 Groundwater Elevations in the Avoca Mining Area from 1 Oct 2014 to 31 Mar 2015

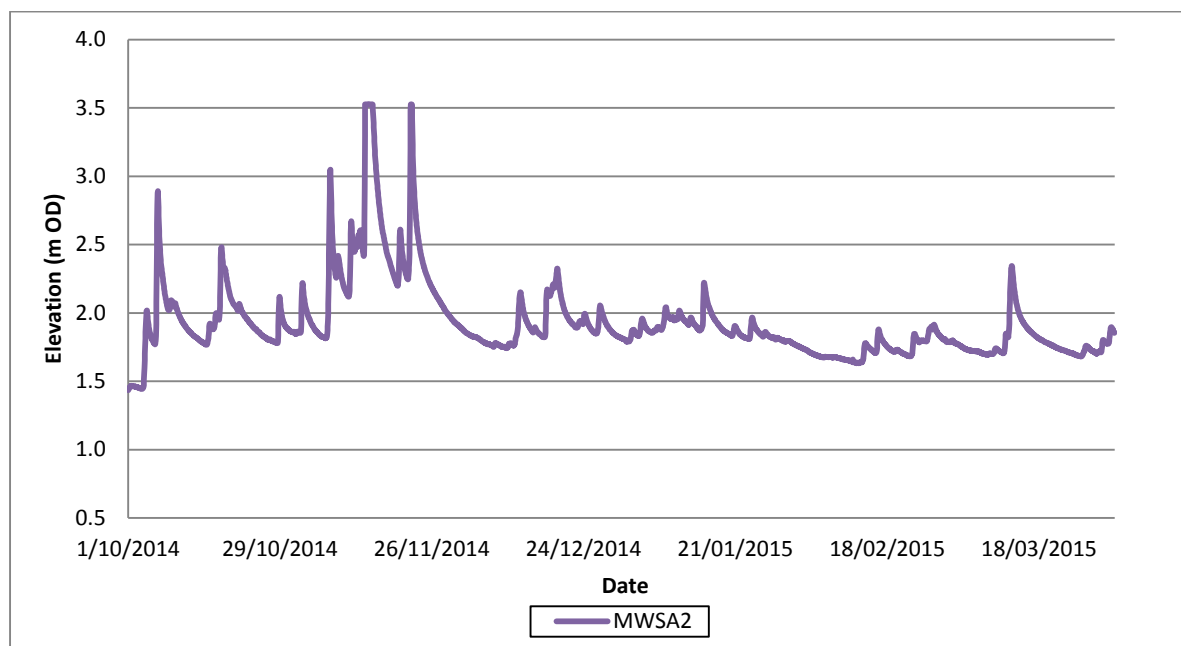


Figure 10 Groundwater Elevation at Shelton Abbey from 1 Oct 2014 to 31 Mar 2015

Figure 8 shows 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, which infers that groundwater in the spoils discharges into the alluvial aquifer. The water level at MWDA1 in February and March 2015 is inconsistent with long term trends and it deviates uncharacteristically from MWDA2 on several occasions. Also the groundwater levels appear to rise before any rise in surface water levels recorded on the Avoca River for the same period, as shown in Figure 10, which is uncharacteristic

for MWDA1,. Furthermore, the manual measurement taken on the 10 February 2015 was 0.41 m greater than the instantaneous value recorded for the time. It is recommended that data for this time MWDA1 data from February and March 2015 is used with caution.

In contrast to MWDA1 and MWDA2 the head is slightly greater in the deep well MWET2 compared to the shallow monitoring well MWET1. The water level data for MWET2 in January, February and March 2015 is inconsistent with long term trends and it deviates uncharacteristically from the water levels recorded in MWET1 on several occasions. Furthermore, several rapid increases and decreases in water level are present in the data which are unlikely to represent real water level fluctuations and are inconsistent with water level recordings in the surrounding wells as shown in Figure 8. Further analysis of temperature recordings for this period revealed somewhat erratic behaviour implying that the data the logger was recording was inaccurate. It is therefore concluded that measurement accuracy of MWET2 may have been distorted by battery issues and it is recommended that data for January to March 2015 is used with caution.

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 marginal downward gradient between the alluvial well GW2/05 and top of bedrock (GW1/05) at this location (Table 21).

MWPF1 was replaced with a new data logger and all the loggers were serviced by CDM Smith in July 2015. New OTT firmware was installed, the batteries were replaced, the water levels were recalibrated and the outside of the instruments were cleaned.

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 1 November 2014 to 31 March 2015 for Whites Bridge GS and Wicklow County Council Maintenance Yard GS are reproduced in Figure 10. The figure demonstrates that the river appears to respond similarly to rainfall 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 which was 0.006 for the monitoring period. Streambed characteristics and the elevations both influence the flow rates and help define any apparent losses or gains in river flow.

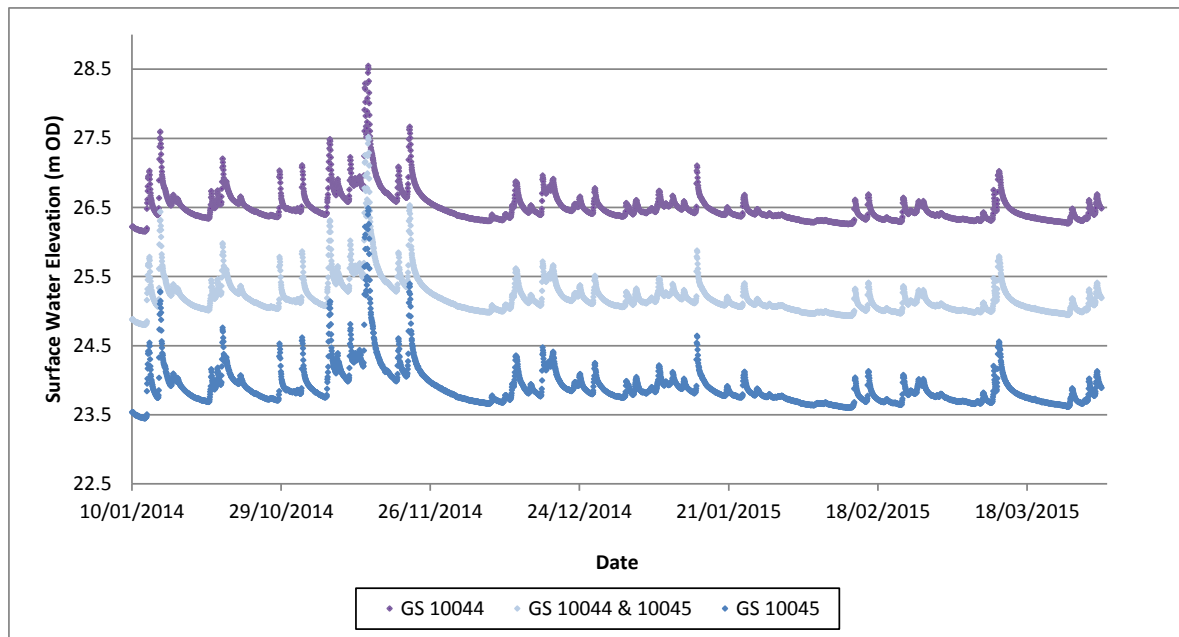


Figure 11 Elevation of the Avoca River at GS 10044 and GS 10045 at the Deep Adit Area from 1 October 2014 to 31 March 2015

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 located approximately equidistance between the two gauges. To take account of the gradient between the two gauges, the river water elevation was estimated using both the Whites Bridge GS (GS 10044) and the Wicklow Maintenance Yard County Council GS (GS 10045) by selecting a midpoint water level. The estimated surface water elevations for the emergency tailing area are also displayed on Figure 10 (GS 10044 & GS 10045);
- For SG104 the water elevation from Wicklow Maintenance Yard County Council was used (GS 10045); and
- The river water level at MWSA2 was unable to be determined because there are no gauges available at a nearby location.

Table 22 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 February 2015.

Table 22 Calculated Groundwater Gradients for February 2015

Borehole Identifier	Date	Time	Groundwater Elevation (m OD)	Water Elevation at Perpendicular Stream Point (m OD)	Distance to Perpendicular Stream Point (m)	Gradient
MWDA1	10/02/2015	16:40	26.56	26.28	40	0.007
MWDA2	10/2/2015	17:26	26.34	26.28	40	0.002
MWPF1	10/2/2015	13:38	26.96	26.28	44	0.015
MWET1	10/2/2015	10:52	26.22*	24.96**	72	0.018
MWET2	9/2/2015	11:49	26.32*	24.96**	72	0.019
GW1/05	9/2/2015	16:10	25.85*	24.96**	74	0.012
GW2/05	9/2/2015	15:30	25.95*	24.96**	74	0.013
SG104	9/2/2015	10:50	32.79	23.63	142	0.065
MWSA2	10/2/2015	15:32	1.64	Not available	45	Not available

* 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 from the EPA for the monitoring period. Groundwater elevation data were plotted against the recorded elevations of the Avoca River as shown in Figure 11 for the deep adit area and Figure 13 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.

Rainfall totals were higher than the Long-Term-Average (LTA) for the majority of meteorological stations in November (Met Eireann, 2014). Both Figure 11 and Figure 13 show that several significant hydrological (rainfall) events occurred in October and November 2014 which resulted in groundwater levels rising. For example groundwater levels rose by approximately 1.2 metres between 13 and 14 November. This peak was in response to river levels which rose by up to 1.7 metres during the same event. High groundwater levels were recorded at the beginning of the monitoring period due to the occurrence of numerous high rainfall events. However, relatively low levels of rainfall in the second half of the monitoring period resulted in an overall decrease in groundwater levels at the Deep Adit area and the emergency tailings area. The majority of rainfall stations in the east of the country reported approximately two-thirds or less of their expected rainfall total for February (Met Eireann, 2015).

Figure 12 and Figure 14 show the calculated gradient to the Avoca River at the Deep Adit area (MWDA1, MWDA2) and the emergency tailings area (MWET1, MWET2) from 1 October 2014 to 31 March 2015 based on hourly elevation data. Both figures show that as river stages change

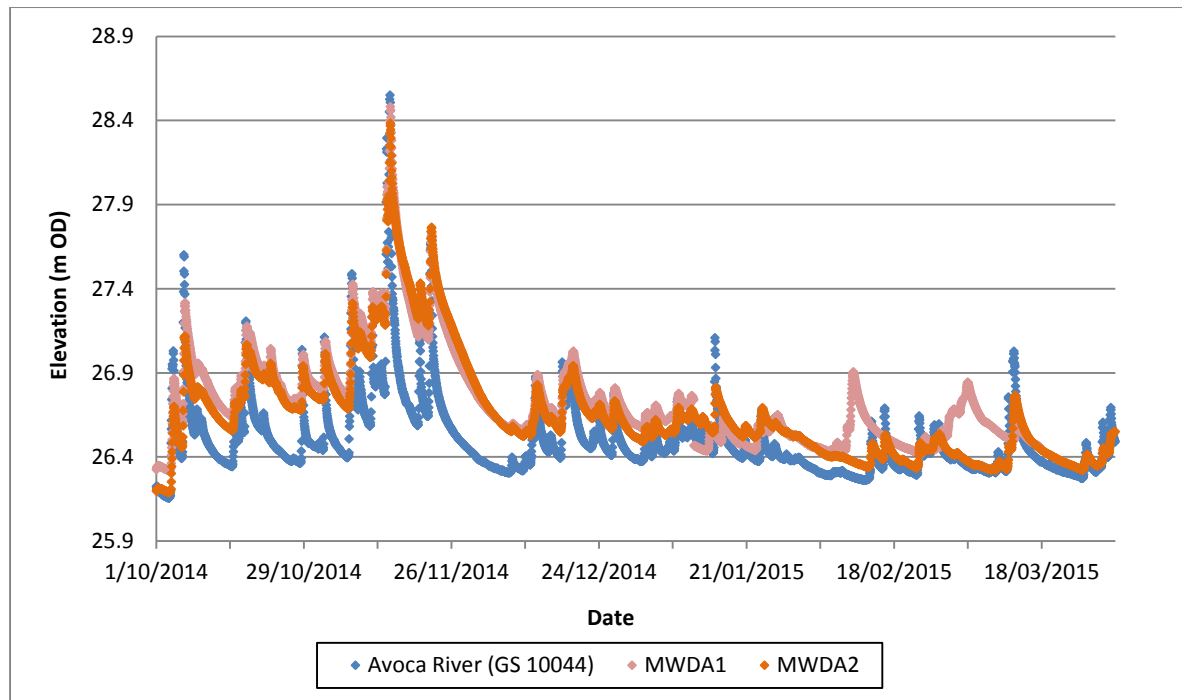


Figure 12 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044) at the Deep Adit Area from 1 Oct 2014 to 31 Mar 2015

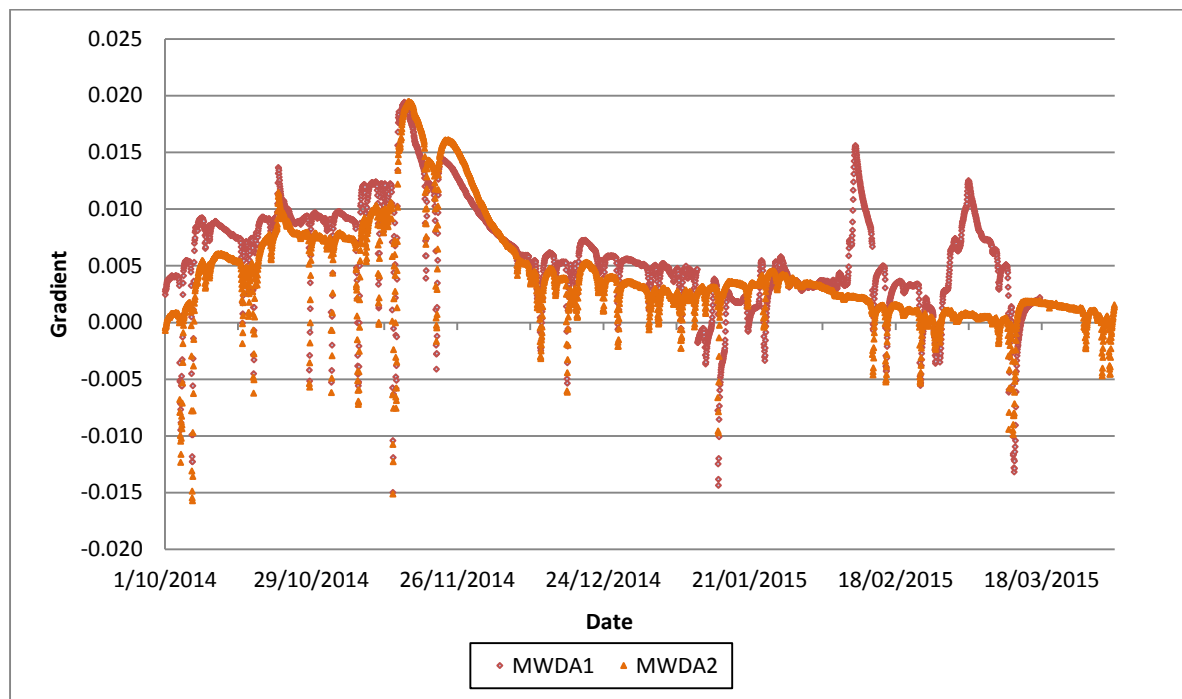


Figure 13 Calculated Groundwater Gradient to the Avoca River at the Deep Adit Area from 1 Oct 2014 to 31 Mar 2015

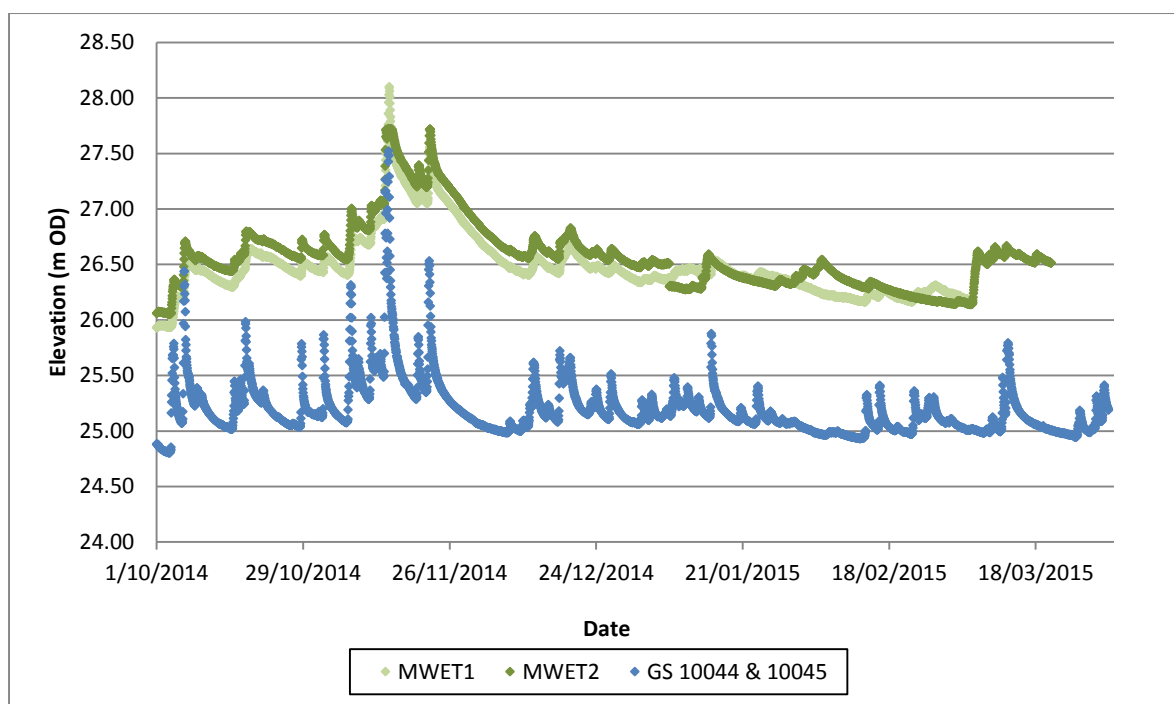


Figure 14 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044 & 10045) at the Emergency Tailings Area from 1 Oct 2014 to 31 Mar 2015

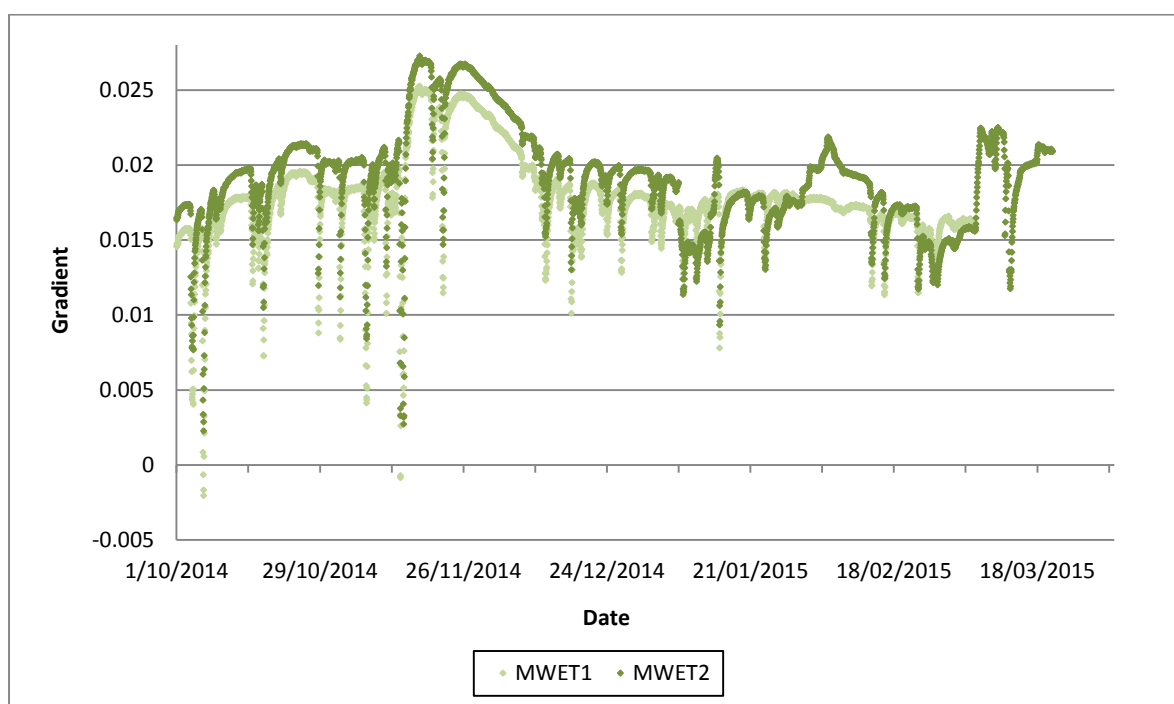


Figure 15 Calculated Groundwater Gradient to the Avoca River at the Emergency Tailings Area from 1 Oct 2014 to 31 Mar 2015

hydraulic gradients to or from the river also change. However, 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. As discussed in Section 6.1, water level data for MWDA1 (Feb and March) and MWET1 (Jan, Feb and March) should be used with caution.

However, Figures 11 and 12 shows that a negative gradient occurs during periods of high flow for short periods of time, particularly when there was a rapid rise in water level. On 13 and 14 November a significant hydrological (rainfall) event resulted in groundwater levels rising in MWDA1 and MWDA2 by approximately 1.2 metres. A negative gradient can be observed during this period between the river and both wells, as shown in Figure 12. During the 13 and 14 November period the river water level also rose (approximately 1.7 metres) but more rapidly which resulted in water moving into the monitoring well area, apparent from the rise in groundwater levels. It is likely the river water moved into an unsaturated zone, which could result in mobilising new metals if they were not exposed before. A similar hydrological event occurred on 4 and 6 October. MWDA2 which is located in the deeper alluvium appears to respond less to the river than MWDA1 and may be more seasonally influenced (e.g. aquifer storage). A positive gradient existed for over 90% of the monitoring period for MWDA2 with a minimum gradient of minus 0.016 and an average gradient of 0.004. For MWET1 and MWET2 positive gradients exist for the entirety of the monitoring period with the exception of MWET1 on 6 and 11 of November when the gradient was minus 0.002 and 0.0008 respectively. This was in response to a rapid rise in water level as shown in Figure 13. An average gradient of 0.017 (MWET1) and 0.019 (MWET2) was observed during the monitoring period. Note that the elevations are based on a GPS survey of the boreholes and the river water elevations were estimated using both the Whites Bridge GS elevation and the Wicklow Maintenance Yard County Council gauges because they are located equidistance between the gauges so the calculated gradients may be less accurate.

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 analyses of loadings to the Avoca River are 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 Whites Bridge, zinc load increased from 19.9 to 127 kg/day which is an 84 % increase. The only surface water input in this segment is from Vale View which contributes very little load (0.01 kg/day). This indicates that the increase in loading is primarily due to diffuse load;
- Between Whites Bridge and Whites Bridge GS, zinc load is similar with 127 kg/day at the bridge and 126 kg/day at the gauging station. This shows that there was greater diffuse load contributing to the Avoca River upstream of the bridge location and no apparent additional diffuse load between these locations;

- Between Whites Bridge GS and US Road Adit on the Avoca River, zinc load decreases slightly from 126 to 106 kg/day which is a 15 % decrease;
- Between US Road Adit and WCC Maintenance Yard GS, zinc load increases from 106 to 187 kg/day. The Road Adit (confluence sample) contributed 39.8 kg/day of the load. The zinc load was higher than expected at this location because the Road Adit discharge was not fully mixed; and
- Between WCC Maintenance Yard GS and Site T5, zinc load decreased from 187 to 148 kg/day, showing that the Road Adit was better mixed with the Avoca River.

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.

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 WCC 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 taken 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 Council Yard GS. The deviation plots show the difference between the recorded flow and manual gauged measurements. The total number of manual gauging's 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 manual gauging's 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 similar during the monitoring period with the percentage difference ranging from 0 to 8 % which is likely to be within the margin of error determined from the deviation plots. Therefore 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 it has been shown that the Avoca River and its interaction groundwater is very dynamic. The quantity of diffuse loading varies along each river stretch with the greatest evidence of diffuse loading just above Whites Bridge.

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 of the diffuse loading is that the spoil and the alluvial areas on both sides of the river contribute contaminant load to the river. For example, upstream of Whites Bridge there is greater evidence of diffuse flow as it accounts for approximately 84 % of the increased dissolved zinc load. Dissolved zinc exceeded the ecological assessment criteria (50 µg/l) from Whites Bridge on the Avoca River to Downstream Shelton Abbey with results ranging from 67.9 to 299 µg/l. The dissolved zinc result at Whites Bridge was 84.8 µg/l and the primary source was from diffuse flow upstream of the Deep Adit discharge into the Avoca River.

Section 7

Summary and Recommendations

7.1 Summary of Findings

Nine groundwater monitoring wells were sampled and analysed in February 2015 and water levels were measured. Twenty-four surface water locations were sampled and analysed in February 2015 with flows measured at 17 of the locations. The field QA/QC sample results were reviewed for accuracy and precision. The laboratory QC/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. Sulphate levels greatly exceeded the criteria for human health in the majority of 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. SG104 located immediately downgradient of Ballymurtagh Landfill had the highest concentrations of dissolved metals especially aluminium, cadmium, nickel and zinc.
- The Cronebane Shallow Adit was the adit discharge with the highest concentrations of metals including aluminium, cadmium and zinc. The Cronebane Shallow, Ballygahan and Spa adits are of minor importance in terms of metals loads to the Avoca, either because of absence of direct flow to the river or due to low concentrations and/ or flows.
- In the Avoca River and tributaries, 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 copper, zinc and aluminium. Dissolved copper exceeded the ecological criteria (5 µg/l) at White Bridge and all river locations from US Road Adit to the Downstream Shelton Abbey location, with results ranging from 5.34 to 21.2 µg/l. Dissolved zinc exceeded the ecological assessment criteria (50 µg/l) from Whites Bridge on the Avoca River to Downstream Shelton Abbey with results ranging from 69.6 to 299 µg/l, the ecological assessment criteria was also exceeded at Lions bridge with a concentration of 52.7 µg/l. Dissolved aluminium exceeded the human health criteria of 200 µg/l from Whites Bridge to Avoca Bridge 246 to 485 µg/l, however it was below the assessment criteria with a concentration of 136 µg/l at Whites Bridge GS.

- There was an apparent loss of sulphate, dissolved iron and aluminium load from the Deep Adit Confluence when compared to the Deep Adit portal sample. This is likely due to the precipitation of iron and other metals along the ditch. The decreases in loads at the confluence are likely due to the loss of flow which can be attributed to the difficulties in measuring the flows at the confluence or from infiltration.
- The results of the Mann-Kendall analysis for 2007-2015 period, show that dissolved zinc is decreasing in the Deep Adit and that there were no other trends for dissolved zinc, iron or copper for this time period in the adit discharges. At Avoca Bridge no statistically significant trend was present for dissolved zinc or dissolved copper for both the 2001-2015 period and the 2007-2015 period. Dissolved copper and zinc concentrations at Avoca Bridge were at their lowest since mid-2002.
- 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, with only a few short term negative gradients during higher flows. 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 Site T1 and Whites Bridge where the diffuse load accounts for a large portion of the zinc loading to the Avoca River.

7.2 Recommendations for the Monitoring Programme

Based on the data analysis and above conclusions no recommendations are made at this time. However, it is intended that as an additional item of work all of the data and evaluations for the three year monitoring programme will be reviewed and summarised after the sixth round of sampling and recommendations for the monitoring programme will be made at that stage.

Section 8

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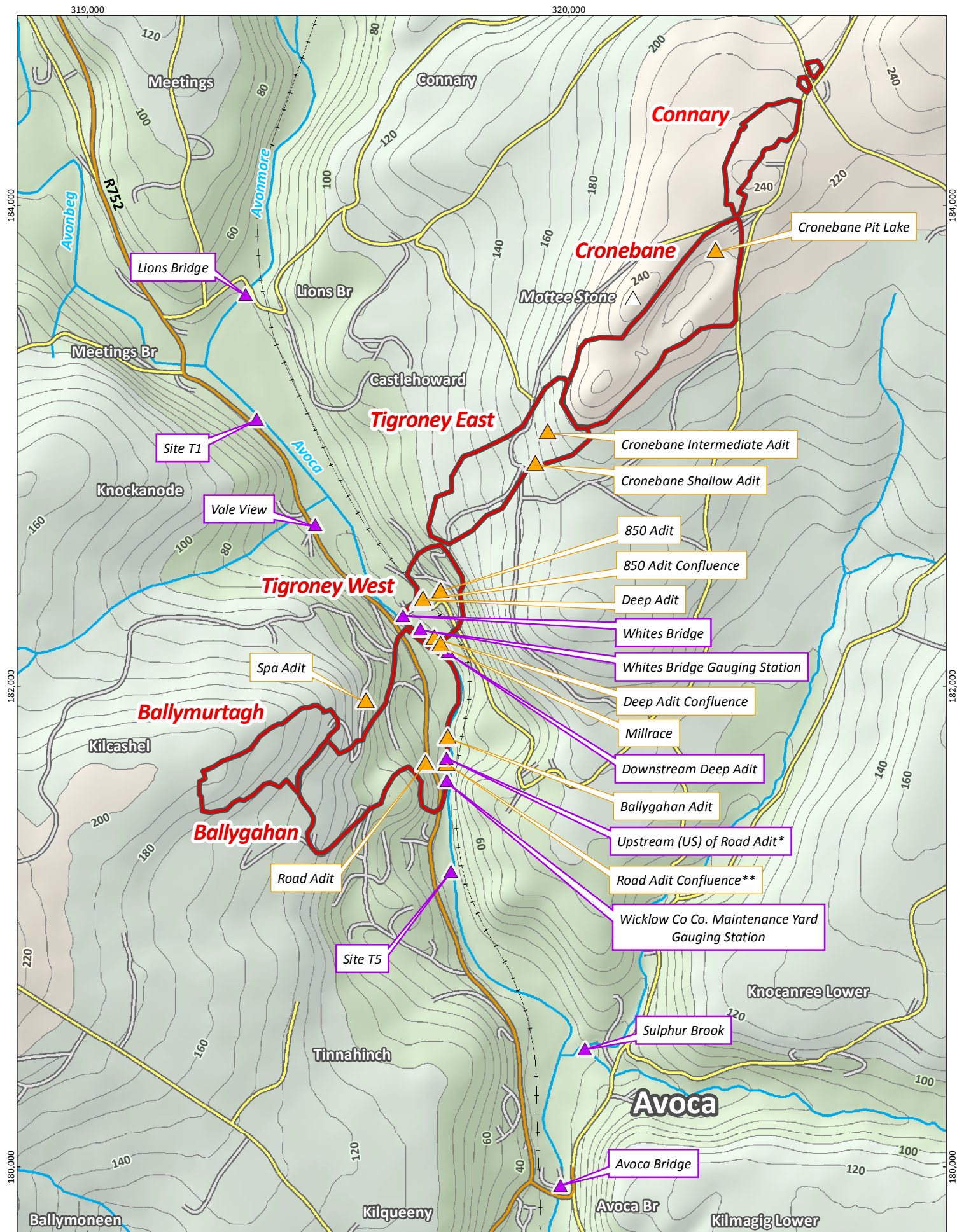
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Appendix A

Figures



Map 1 - Avoca - Main Area

Drawn by: OC Date: 19/08/2015

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CDM Smith

Legend

Sampling Locations

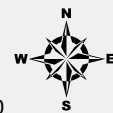
- Surface water (Rivers and Streams)
- Surface water (Adit discharges)

* New sampling location in Round 5

** Changed sampling location in Round 5

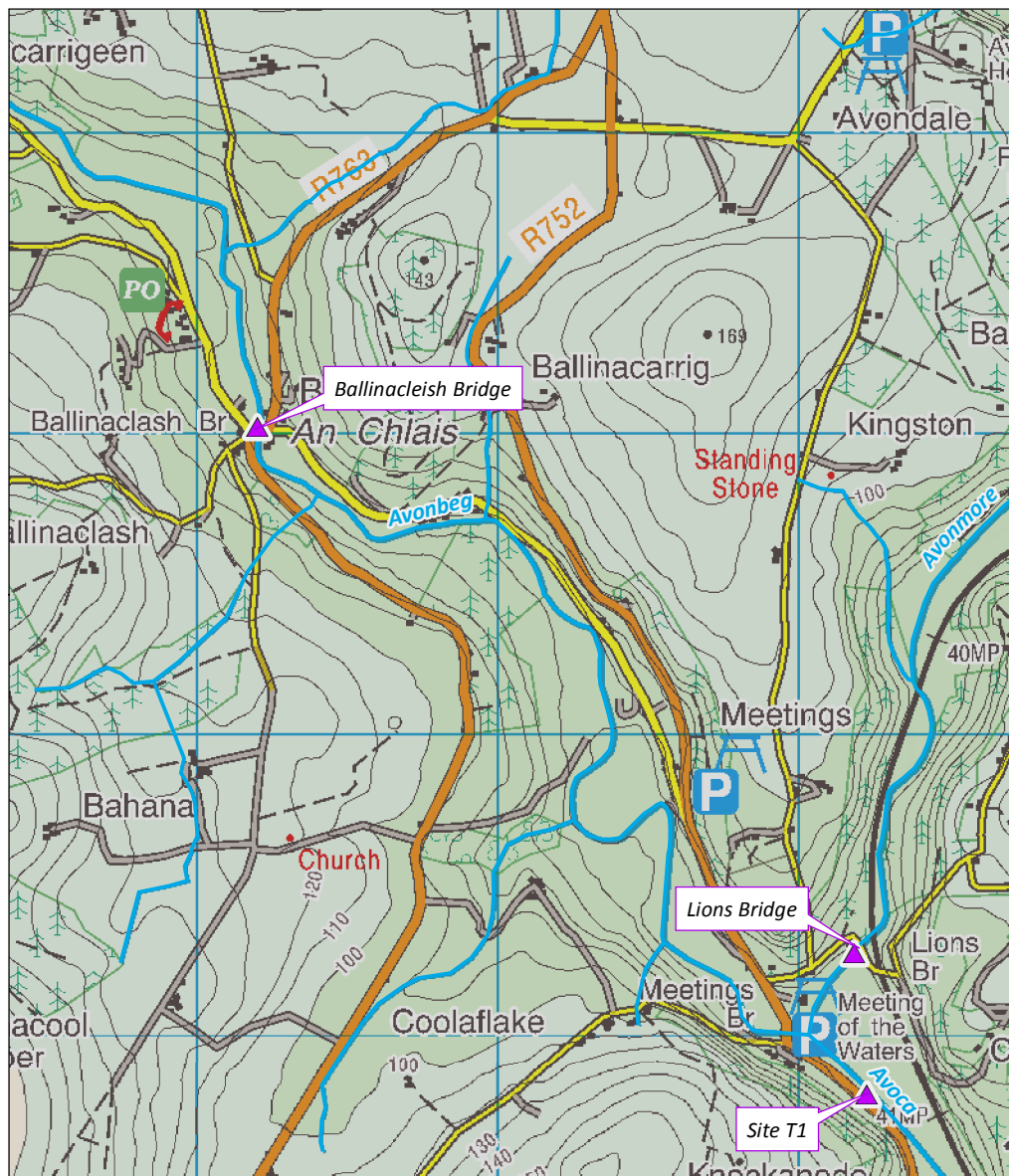
Mines

- Mining Areas
- Rivers

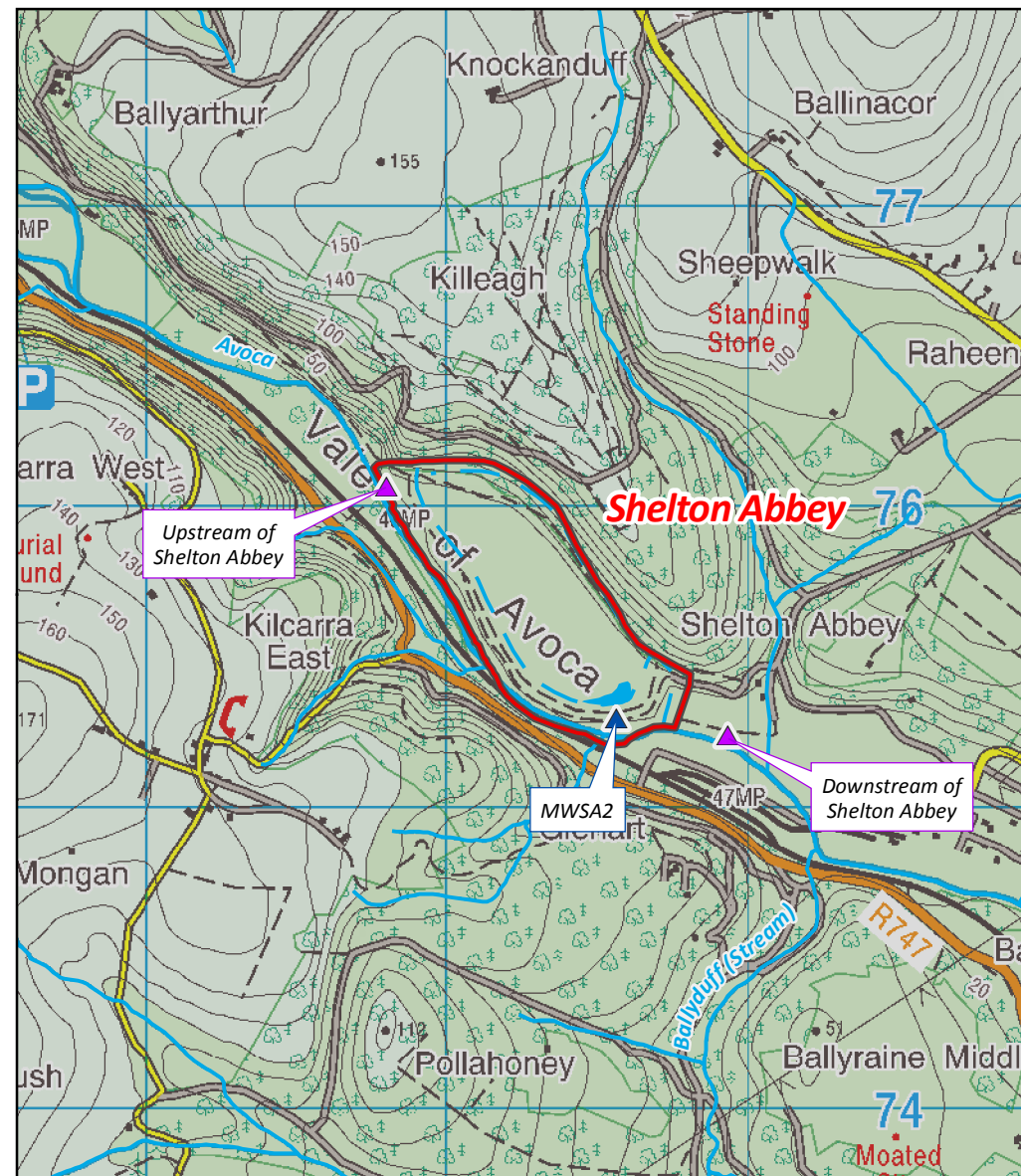


Scale is 1:18,000

0 125 250 500 m



Ballinacleish



Shelton Abbey

Map 2 - Avoca - Ballinacleish and Shelton Abbey

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Legend

Sampling Locations

- ▲ Surface water (Rivers and Streams)
- ▲ Surface water (Adit discharges)
- ▲ Groundwater (Shelton Abbey)

Mines

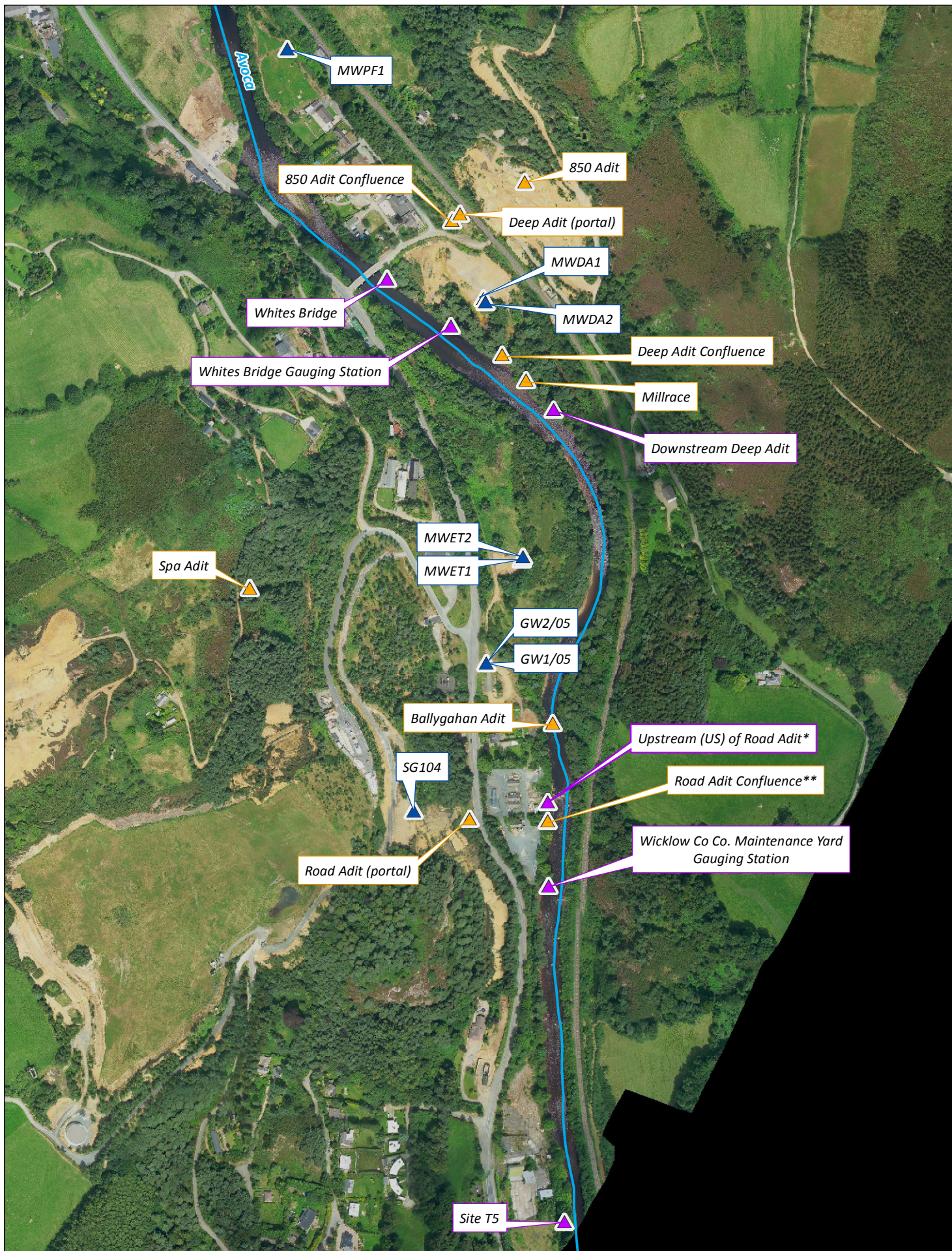
- Mining Area

— Rivers

Scale is 1:25,000

0 250 500 1,000 m





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

Drawn by: OC/LG Date: 19/08/2015

Internal Project Reference: Q:\95500-95999\95735\
40 Documents Generated\GIS\02_GIS_Tasks\12_MonRptR5\
MXD\03_AvocaMonGW.mxd

Source: © DCENR Lidar Survey (2007)

**CDM
Smith**

Legend

Sampling Locations

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

— Rivers

* New sampling location in Round 5
** Changed sampling location in Round 5



Scale is 1:5,000

0 50 100
m

Appendix B

Analytical Data Tables and Assessment Criteria

Table B-1 Comparison of Total versus Dissolved Metals R5

Sample Description	Date Sampled	Suspended solids, Total	Aluminium (tot.unfilt)	Aluminium (diss.filt)	Ratio diss to total Aluminium	Copper (tot.unfilt)	Copper (diss.filt)	Ratio diss to total Copper	Iron (tot.unfilt)	Iron (diss.filt)	Ratio diss to total Iron	Zinc (tot.unfilt)	Zinc (diss.filt)	Ratio diss to total Lead
		Units mg/l	µg/l	µg/l		µg/l	µg/l		µg/l	µg/l		µg/l	µg/l	
850 Adit	12/02/2015	<2	64800	70700	1.09	3430	4830	1.41	17700	17800	1.01	25200	26500	1.05
Avoca Bridge	16/02/2015	2.5	369	246	0.67	9.16	5.24	0.57	415	201	0.48	124	87.3	0.70
Ballinaclesh Bridge	17/02/2015	<2	125	109	0.87	2	0.425	0.21	100	60.1	0.60	24.8	45.2	1.82
Cronebane Intermediate Adit	11/02/2015	9	57300	47500	0.83	2290	1900	0.83	88600	87100	0.98	34800	29300	0.84
Cronebane Pit Lake	11/02/2015	<2	8450	8620	1.02	2200	2150	0.98	1870	1720	0.92	2890	3110	1.08
Cronebane Shallow Adit	11/02/2015	2.5	295000	295000	1.00	5550	8520	1.54	166000	161000	0.97	60000	102000	1.70
Deep Adit	12/02/2015	<2	90600	85600	0.94	183	147	0.80	61100	64200	1.05	39900	36300	0.91
Deep Adit Conf.	12/02/2015	<2	81500	77100	0.95	235	195	0.83	64400	58800	0.91	36100	34100	0.94
DS Shelton Abbey	11/02/2015	2	378	116	0.31	17.9	6.72	0.38	339	151	0.45	165	127	0.77
DS Deep Adit	16/02/2015	4.5	886	485	0.55	5.68	3.61	0.64	851	372	0.44	382	299	0.78
GW01/05	17/02/2015	-	69800	70100	1.00	10500	8830	0.84	2030	1310	0.65	11400	10100	0.89
GW2/05	09/02/2015	-	49400	45500	0.92	8590	6070	0.71	7590	82.5	0.01	7760	5840	0.75
Lions Bridge	17/02/2015	5	140	113	0.81	2	1.22	0.61	243.0	164	0.67	39.2	52.7	1.34
MWDA1	10/02/2015	-	210000	192000	0.91	18800	18600	0.99	59600	48300	0.81	48600	44600	0.92
MWDA2	11/02/2015	-	66900	56600	0.85	4480	5420	1.21	65400	50200	0.77	41500	38800	0.93
MWET1	09/02/2015	-	128000	113000	0.88	11800	855	0.07	101000	100,000	0.99	10500	890	0.08
MWET2	09/02/2015	-	98.9	16.2	0.16	21.2	2.28	0.11	111000	92100	0.83	4680	5490	1.17
MWPF1	10/02/2015	-	438	265	0.61	79.2	33.6	0.42	221	19.2	0.09	89.3	38	0.43
MWSA2	11/02/2015	-	70300	60100	0.85	277	95.5	0.34	88200	71800	0.81	3320	2760	0.83
Road Adit	12/02/2015	<2	12000	12400	1.03	356	339	0.95	93000	75600	0.81	8640	8350	0.97
Road Adit Conf.	12/02/2015	<2	13000	12000	0.92	390	322	0.83	80800	75900	0.94	9250	8150	0.88
SG104	10/02/2015	-	942000	844000	0.90	70700	87200	1.23	50800	27800	0.55	122000	146000	1.20
SITE T1	16/02/2015	<2	217	169	0.78	2	0.425	0.21	205	98.3	0.48	24.9	21.9	0.88
Spa Adit	12/02/2015	2	161000	156000	0.97	8880	7570	0.85	108000	108000	1.00	13100	12500	0.95
Sulphur Brook	17/02/2015	<2	97.6	28.5	0.29	32.2	21.2	0.66	59.1	9.5	0.16	96.8	102	1.05
Site T5	16/02/2015	2.5	385	288	0.75	10.9	7.71	0.71	554	327	0.59	140	106	0.76
US Shelton Abbey	11/02/2015	2.5	307	101	0.33	11.2	6.47	0.58	263	117	0.44	144	123	0.85
US Road Adit	16/02/2015	3	389	247	0.63	9.53	5.7	0.60	411	140	0.34	100	69.6	0.70
Vale View	17/02/2015	<2	25	12.2	0.49	2	1.37	0.69	67.8	26.5	0.39	8.4	8.95	1.07
WCC Maintenance Yard GS	16/02/2015	<4	436	303	0.69	11.7	7.77	0.66	792	465	0.59	166	123	0.74
Whites Bridge	16/02/2015	3.5	211	131	0.62	2	1.69	0.85	321	136	0.42	39.9	30.1	0.75
Whites Bridge GS	16/02/2015	<2	204	136	0.67	2	2.01	1.01	282	121	0.43	49.4	84.6	1.71

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

Table B-2 Comparison of Groundwater and Surface Water Results to Assessment Criteria R5

Sample Description	Type	Date Sampled Units	Specific Conductance @ deg.C (field) mS/cm																	
			Acidity as HCL mg/l	Alkalinity, Total as CaCO3 mg/l	Hardness as CaCO3 mg/l	Ammoniacal Nitrogen as N mg/l	Chloride mg/l	COD, unfiltered mg/l	Cyanide, Free mg/l	Dissolved solids, Total mg/l	Fluoride mg/l	Nitrate as NO3 mg/l	Nitrite as NO2 mg/l	Oxygen, dissolved (field) % Sat	pH (field) pH Units	Phosphate (ortho) as P mg/l	Sulphate mg/l	Sodium (diss.filt) mg/l	Suspended solids, Total mg/l	
Ecological Criteria			-	-	-	0.14	-	-	0.01	-	0.5	-	-	80 to 120*	4.5 to 9	0.075	-	-	-	
Human Health Criteria			-	-	-	0.3	250	-	2.5	0.05	-	1.5	50	0.5	6.5 to 9.5	-	250	200	-	
GW2/05	GW	09/02/2015	-	1	1	0.1	15.3	-	1.334	0.025	1160	0.25	6.94	0.025	51.9	3.67	0.01	742	9.92	-
MWET1	GW	09/02/2015	-	1	1	0.632	23.1	-	2.087	0.025	2270	43.2	0.15	0.025	3.6	3.4	0.01	1400	15	-
MWET2	GW	09/02/2015	-	1	1	0.559	14.6	-	3.416	0.025	3580	29.8	0.15	0.025	1.8	6.16	0.01	2290	24.5	-
MWDA1	GW	10/02/2015	-	1	1	0.689	12.6	-	2.811	0.025	3290	3.91	0.15	0.025	8.2	2.86	0.01	1930	8.42	-
MWPF1	GW	10/02/2015	-	1	1	0.1	15.5	-	0.154	0.025	88	0.25	7.3	0.025	80	4.77	0.01	30.4	8.91	-
SG104	GW	10/02/2015	-	1	1	3.01	14.7	-	8.277	0.025	14000	9.42	0.15	0.025	54	2.93	0.01	9210	6.89	-
MWDA2	GW	11/02/2015	-	1	1	0.1	13.8	-	1.486	0.025	1550	21.9	0.824	0.078	13	3.68	0.01	885	11.5	-
MWSA2	GW	11/02/2015	-	1	1	1.03	14.8	-	2.355	0.025	2610	25.1	0.15	0.025	8.8	4.25	0.01	1560	9.56	-
GW01/05	GW	17/02/2015	-	1	1	0.1	13.9	-	1.641	0.025	1560	0.25	8.48	0.025	35.9	3.7	0.01	1010	10.5	-
Cronebane Pit Lake	Pit Lake	11/02/2015	63.9	1	1	0.22	10.4	3.5	0.442	0.025	221	0.25	2.8	0.025	89.4	2.83	0.01	109	5.64	-
Cronebane Intermediate Adit	Adit	11/02/2015	374	1	1	0.496	13.7	12.7	1.265	0.025	1160	4.64	0.15	0.025	3.2	3.21	0.01	647	8.73	1
Cronebane Shallow Adit	Adit	11/02/2015	1760	1	1	0.705	15.2	29.5	3.588	0.025	4970	16.5	0.15	0.025	38.3	2.85	0.01	3010	6.62	2.5
850 Adit	Adit	12/02/2015	369	1	1	0.443	12.8	12.1	1.5	0.025	1140	4.41	0.477	0.025	97.8	2.83	0.01	711	7.7	-
Deep Adit	Adit	12/02/2015	422	1	1	0.281	13.4	17.1	1.391	0.025	1450	1.13	0.15	0.025	37.7	3.56	0.01	864	7.64	1
Deep Adit Conf.	Adit	12/02/2015	429	1	1	0.4	14.1	15.1	1.402	0.025	1410	1.31	0.15	0.025	77.6	3.47	0.01	862	7.63	1
Road Adit	Adit	12/02/2015	221	1	1	7.31	30.3	33.2	1.642	0.025	1440	29	3.92	0.073	29.2	4.01	0.01	890	39.7	1
Road Adit Conf.	Adit	12/02/2015	203	1	1	7.32	31.7	28.1	1.648	0.025	1440	28.5	3.87	0.074	79.7	4.01	0.01	890	22.1	1
Ballygahan Adit	Adit	12/02/2016	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Spa Adit	Adit	12/02/2015	934	1	1	0.921	10.4	30.4	2.531	0.025	2430	16.8	0.529	0.025	78.2	2.69	0.01	1580	6.42	2
Ballinacleish Bridge	River	17/02/2015	2	7	9	0.213	7.7	9.64	0.055	0.025	32.6	0.25	3.82	0.025	102.8	5.64	0.01	1	4.75	1
Lions Bridge	River	17/02/2015	2	1	1	0.1	8.7	16.9	0.06	0.025	36.8	0.25	3.24	0.025	102.6	5.87	0.01	1	5.65	5
Site T1	River	16/02/2015	2	1	1	0.1	7.6	20.9	0.046	0.025	21	0.25	2.18	0.025	100.5	4.87	0.01	1	4.36	1
Vale View	River	17/02/2015	2	26.5	32	0.1	13	3.5	0.152	0.025	32.6	0.25	12.5	0.025	102.5	6.63	0.01	15.5	6.69	1
Whites Bridge	River	16/02/2015	2	7	9	0.1	8.8	16	0.057	0.025	31	0.25	2.43	0.025	98.9	5.89	0.01	1	5.21	3.5
Whites Bridge GS	River	16/02/2015	2	7.5	9	0.1	8.6	19.3	0.037	0.025	28	0.25	2.43	0.025	100.1	6.08	0.01	1	5.06	1
DS Deep Adit	River	16/02/2015	2	1	1	0.1	8.5	11.2	0.079	0.025	34.7	0.25	2.4	0.025	100.3	4.76	0.01	9.7	5.23	4.5
US Road Adit	River	16/02/2015	2	6.5	8	0.1	8.3	8.92	0.061	0.025	82	0.25	2.25	0.025	99.7	5.82	0.01	1	5.01	3
WCC Maintenance Yard GS	River	16/02/2015	2	5.5	7	0.1	8.6	8.5	0.092	0.025	61	0.25	2.68	0.025	100.5	5.29	0.01	10	5.21	2
Site T5	River	16/02/2015	2	5	6	0.1	8.5	16.4	0.066	0.025	63	0.25	2.62	0.025	99.9	5.72	0.01	7.5	5.13	2.5
Sulphur Brook	River	17/02/2015	2	22.5	27	0.1	15.2	3.5	0.157	0.025	87.4	0.25	20.5	0.025	101.8	6.73	0.0307	11.7	8.67	1
Avoca Bridge	River	16/02/2015	2	7	9	0.1	8.7	18.3	0.06	0.025	90	0.25	2.32	0.025	100.1	5.89	0.01	1	5.06	2.5
US Shelton Abbey	River	11/02/2015	2	13	16	0.24	10.1	8.65	0.103	0.025	74	0.25	7.76	0.025	95.2	6.39	0.01	12.1	6.82	2.5
DS Shelton Abbey	River	11/02/2015	2	1	1	0.1	9.9	9.33	0.106	0.025	73	0.25	7.67	0.025	101.3	6.14	0.01	13.3	6.94	2

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 LOD
- Not analysed or no assessment criteria
* Only applies to rivers or streams (i.e. not discharges or groundwater)
** Qualifier - result should be used with caution

Table B-2 Comparison of Groundwater and Surface Water Results to Assessment Criteria R5

Sample Description	Type	Date Sampled Units	Aluminium (diss.filt) µg/l	Antimony (diss.filt) µg/l	Arsenic (diss.filt) µg/l	Barium (diss.filt) µg/l	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	Mercury (diss.filt) µg/l	Molybdenum (diss.filt) µg/l	Nickel (diss.filt) µg/l	Selenium (diss.filt) µg/l	Silver (diss.filt) µg/l	Thallium (diss.filt) µg/l	Tin (diss.filt) µg/l	Uranium (diss.filt) µg/l	Vanadium (diss.filt) µg/l	Zinc (diss.filt) µg/l
Ecological Criteria			1,900	-	25	4	0.45	3.4	5.1	5	-	7.2	1100	0.07	-	20	-	-	-	-	2.6	-	50
Human Health Criteria			200	5	10	-	5	50	-	2000	200	10	50	1	-	20	10	-	-	-	-	-	-
GW2/05	GW	09/02/2015	45500	0.644	0.06	1.08	12.7	0.881	67.4	6070	82.5	0.277	3430	0.005	0.12	31.6	0.195	0.75	0.48	0.711	2.71	0.12	5840
MWET1	GW	09/02/2015	113000	2.12	0.06	2.59	16.7	13.7	148	855	>100,000	6.11	664	0.005	0.797	63.9	0.195	0.75	2.3	1.8	8.43	0.12	890
MWET2	GW	09/02/2015	16.2	0.629	5.29	7.6	1.66	1.66	106	2.28	92100	0.873	36000	0.005	0.364	14.4	4.31	0.75	0.48	0.576	1.9	0.12	5490
MWDA1	GW	10/02/2015	192000	0.78	0.06	2.64	50.2	24.8	114	18600	48300	98.2	11600	0.005	0.12	62.5	0.195	0.75	0.48	0.18	8.86	0.3	44600
MWPF1	GW	10/02/2015	265	2.06	0.06	8.64	0.347	0.378	0.594	33.6	19.2	0.263	23.1	0.005	0.12	0.583	0.195	0.75	0.48	0.18	0.75	0.12	38
SG104	GW	10/02/2015	844000	0.998	0.06	9.26	99.8	16.6	560	87200	27800	47.9	45500	0.005	0.12	205	0.195	0.75	0.48	0.18	50.5	0.12	146000
MWDA2	GW	11/02/2015	56600	0.08	0.06	4.31	42.7	1.49	121	5420	50200	11.6	8390	0.005	0.12	61.2	0.195	0.75	0.48	0.18	5.22	0.12	38800
MWSA2	GW	11/02/2015	60100	0.08	16.6	7.96	1.44	5.12	147	95.5	71800	24.3	26700	0.005	0.12	107	0.979	0.75	0.48	0.18	5.76	0.931	2760
GW01/05	GW	17/02/2015	71500	0.08	0.06	3.75	17.2	9.01	100	8830	1420	13.1	5540	0.005	0.12	43.8	0.195	0.75	0.48	0.18	3.43	0.12	10500
Cronebane Pit Lake	Pit Lake	11/02/2015	8620	0.08	0.261	7.59	7.3	0.696	14.5	2150	1720	254	377	0.005	0.12	4.51	0.195	0.75	0.48	0.18	0.75	0.12	3110
Cronebane Intermediate Adit	Adit	11/02/2015	47500	0.08	4.12	6.69	66.6	1.37	62	1900	87100	1270	2580	0.005	0.12	34.4	0.798	0.75	2.88	0.18	7.85	0.985	29300
Cronebane Shallow Adit	Adit	11/02/2015	295000	0.08	11.2	4.95	109	8.1	198	8520	161000	1140	8670	0.005	0.12	97.2	0.195	0.75	1.89	0.18	26.6	0.965	102000
850 Adit	Adit	12/02/2015	70700	1.3	5.06	6.64	55.3	0.86	73.9	4830	17800	862	3060	0.005	0.284	34.6	0.927	7.5	2.05	1.08	8.3	0.12	26500
Deep Adit	Adit	12/02/2015	85600	0.423	1.13	4.16	42.3	0.712	79.9	147	64200	2010	3580	0.005	0.12	30.2	0.927	7.5	1.28	0.447	8.12	0.319	36300
Deep Adit Conf.	Adit	12/02/2015	79500	7.97	2.75	4.7	83.5	0.587	108	297	60900	1790	3440	0.005	0.12	36.7	0.195	7.5	1.41	0.18	7.03	0.12	40200
Road Adit	Adit	12/02/2015	12400	0.8	4	16.6	11.4	1.1	113	339	75600	342	7770	0.005	1.2	45.9	0.195	7.5	4.8	1.8	7.5	1.2	8350
Road Adit Conf.	Adit	12/02/2015	12000	3.41	4.57	16.1	11.9	1.1	114	322	75900	344	7530	0.005	1.2	45.7	0.195	7.5	4.8	7.22	7.5	1.2	8150
Ballygahan Adit	Adit	12/02/2016	77000	0.8	20.9	9.76	48.8	3.41	185	6140	98.9	84.6	13400	-	1.2	72.5	4.44	7.5	4.8	3.74	7.5	1.2	23300
Spa Adit	Adit	12/02/2015	156000	0.08	0.358	4.29	20.7	4.5	191	7570	108000	89	7130	0.005	0.12	46.3	0.195	7.5	1.38	0.18	7.78	0.12	12500
Ballinacleish Bridge	River	17/02/2015	109	0.08	0.333	7.9	0.05	0.466	0.229	0.425	60.1	3.52	23.3	0.005	0.12	0.67	0.195	0.75	0.48	0.18	0.75	0.12	45.2
Lions Bridge	River	17/02/2015	113	0.08	0.677	4.6	0.162	0.561	0.121	1.22	164	5.42	21.4	0.005	0.12	0.741	0.562	0.75	0.48	0.18	0.75	0.12	52.7
Site T1	River	16/02/2015	169	0.937	0.382	7.24	0.05	0.233	0.229	0.425	98.3	5.51	24.2	0.005	0.432	0.582	0.195	0.75	0.48	0.805	0.75	0.12	21.9
Vale View	River	17/02/2015	12.2	0.08	0.346	7.32	0.05	0.414	0.087	1.37	26.5	0.093	9.66	0.005	0.12	0.738	0.456	0.75	0.48	0.18	0.75	0.12	8.95
Whites Bridge	River	16/02/2015	252	1.4	0.487	5.54	0.251	0.312	0.463	5.34	194	6.67	37.2	0.005	0.46	1.53	0.195	0.75	0.48	1.18	0.75	0.12	84.8
Whites Bridge GS	River	16/02/2015	136	0.596	0.432	5.44	0.121	0.26	0.187	2.01	121	4.45	21.6	0.005	0.4	0.682	0.195	0.75	0.48	0.51	0.75	0.12	84.6
DS Deep Adit	River	16/02/2015	485	0.38	0.37	5.7	0.676	0.23	0.94	3.61	372	11.4	45.8	0.005	0.296	0.963	0.195	0.75	0.48	0.363	0.75	0.12	299
US Road Adit	River	16/02/2015	247	0.08	0.436	6.31	0.219	0.11	0.345	5.7	140	6	30.3	0.005	0.12	0.682	0.195	0.75	0.48	0.18	0.75	0.12	69.6
WCC Maintenance Yard GS	River	16/02/2015	303	0.221	0.45	6.33	0.336	0.4	0.927	7.77	465	7.75	71.3	0.005	0.12	1.22	0.195	0.75	0.48	0.18	0.75	0.12	123
Site T5	River	16/02/2015	288	0.345	0.475	6.29	0.302	0.275	0.751	7.71	327	7.47	54.8	0.005	0.12	0.835	0.425	0.75	0.48	0.18	0.75	0.12	106
Sulphur Brook	River	17/02/2015	28.5	0.733	0.318	7.08	0.315	0.363	0.221	21.2	9.5	4.68	23.9	0.005	0.489	0.737	0.195	0.75	0.48	0.792	0.75	0.12	102
Avoca Bridge	River	16/02/2015	246	0.08	0.408	6.25	0.26	0.361	0.451	5.24	201	6.56	37.6	0.005	0.12	0.811	0.195	0.75	0.48	0.18	0.75	0.12	87.3
US Shelton Abbey	River	11/02/2015	101	0.08	0.3	5.45	0.334	0.648	0.685	6.47	117	1.96	49.1	0.005	0.12	0.947	0.195	0.75	0.48	0.18	0.75	0.12	123
DS Shelton Abbey	River	11/02/2015	116	0.08	0.312	5.57	0.312	0.491	0.956	6.72	151	1.89	78.6	0.005	0.12	1.13	0.195	0.75	0.48	0.18	0.75	0.12	127

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 LOD
- Not analysed or no assessment criteria
* Only applies to rivers or streams (i.e. not discharges or groundwater)
** Qualifier - result should be used with caution