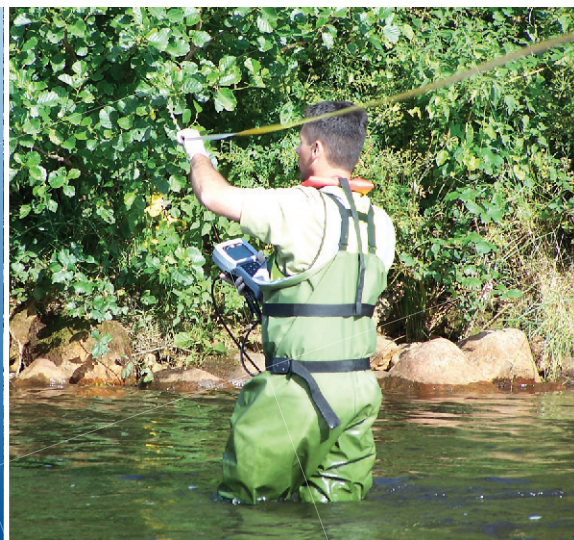


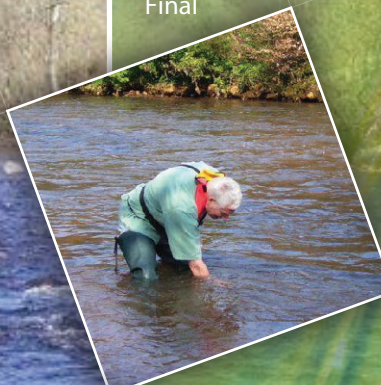
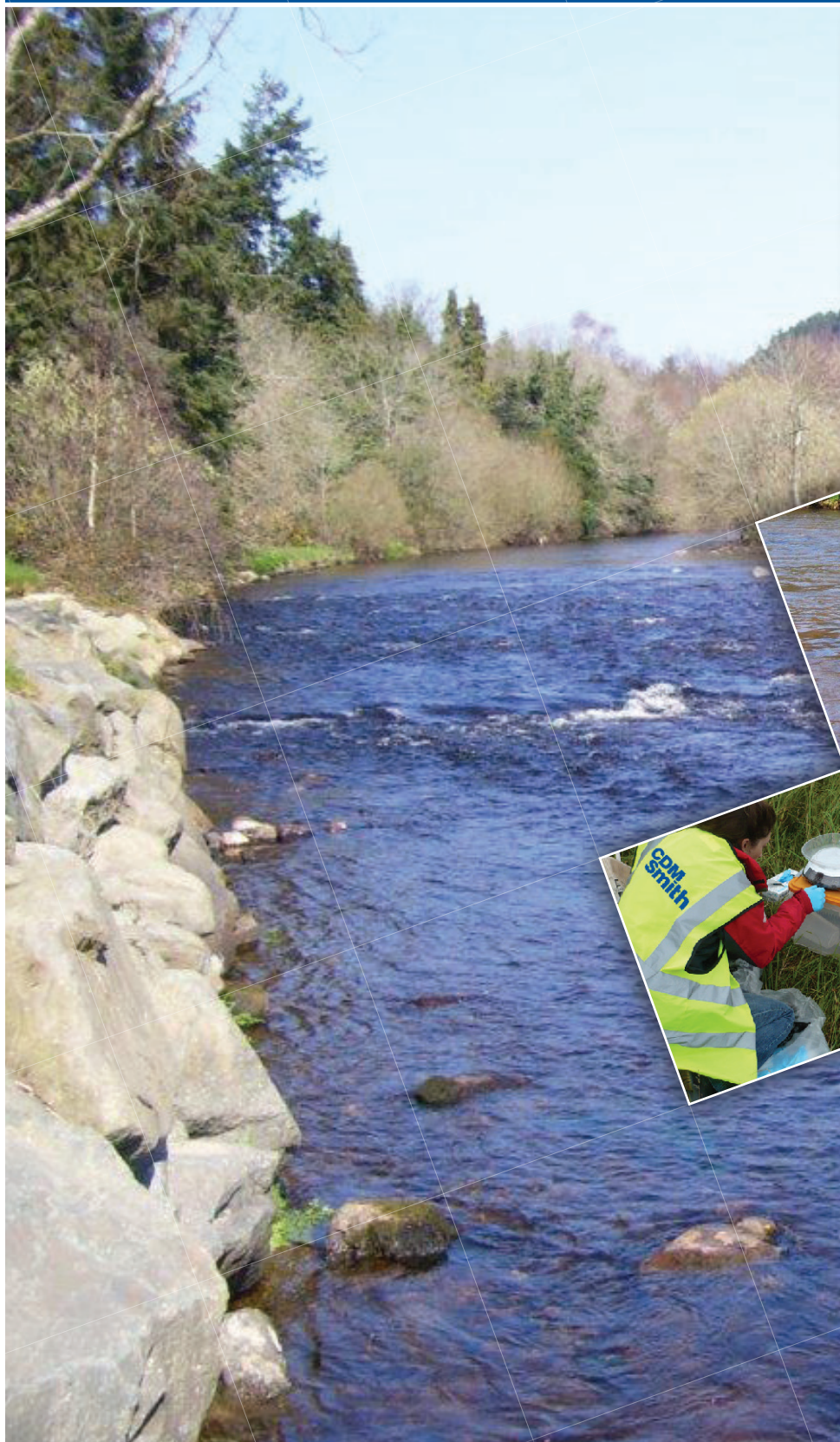
# Department of Communications, Energy & Natural Resources



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

**Avoca Monitoring Report  
- Round 2 (2013)**

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 August 2013. This report should be read alongside the Avoca Data Report (Document Ref: 95735/40/DG08, dated October 2013) 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 km<sup>2</sup>. The East and West Avoca Mines are separated by the Avoca River, which flows through the Vale of Avoca, a noted tourist attraction. To the north of the mines, the Avoca River is formed at the "Meeting of the Waters" by the confluence of the Avonbeg and Avonmore Rivers, while 6.5 km to the south, it is joined by the Aughrim River and flows an additional 7.5 km to the sea at the fishing port of Arklow. Several smaller tributaries join the Avoca River close to the mine water discharges, including Sulphur Brook to the south of East Avoca Mines, and the 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 ( $\text{FeS}_2$ ) were extracted, occur as generally stratiform lenses up to a few tens of metres thick at the top of a sequence of tuffs and felsites.

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

There are three main ore types:

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

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

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

### 1.4.2 Hydrogeology

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

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

Overall water movement consists of three primary pathways:

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

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

## 1.5 Description of Adit Discharges

Map 1 in **Appendix A** shows the adits with active discharge that were sampled and are described in this section.

The Cronebane Intermediate Adit 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 portal into a ditch that runs semi-parallel to the Avoca River before discharging into the river. The Deep Adit discharges directly to the river approximately 170 m from the adit portal. The adit discharge had been previously diverted into a marsh area east of the spoils area (in the first sampling round March 2013). The marsh area has now been blocked off and was completely dried out in August 2013.

The Road Adit is located adjacent to Rathdrum Road at the base of the County Wicklow landfill (formerly the Pond Lode Pit). The Road Adit runs along a ditch beside the road and then discharges to the Avoca River just downstream of the Wicklow County Council Yard Gauging Station.

The Spa Adit is located in West Avoca on a hillside approximately 150 m northwest of (and approximately 40 m above) the County Wicklow recycling centre. The discharge exits from a break in a pipe which was observed soaking into the ground. Because 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 were sampled between 12 and 14 August 2013, 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 Redi-Flo). 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 physio-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.

The only exception to the low-flow sampling procedure was for SG104. Sufficient water was not present in the well to perform the low flow sampling procedure. The sample was collected 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 surface water locations were sampled between 14 and 20 August 2013, as listed in Table 2 and shown on Map 1 and 2 in **Appendix A**.

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). Samples were grab samples collected from a well mixed portion of the water stream where possible. The sample location was approached from downstream so that the underlying sediments are not disturbed.

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.

## Flow Measurements

Flow was measured at 14 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.

**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	Flow Meter
Vale View	Tributary of Avoca River	319453	182396	Flow Meter
Site T1	Avoca River Location (Upstream of Whites Br.)	319239	182805	Flow Meter
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 (Data from EPA)
Downstream (DS) Deep Adit*	Avoca River Location (Downstream of Deep Adit confluence on the Avoca River)	319951	181922	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 (Data from EPA)
Site T5	Avoca River Location (Abandoned Coal Yard)	319972	181114	Flow Meter
Avoca Bridge	Avoca River above Avoca Bridge	320372	179932	Flow Meter
Upstream of Shelton Abbey	Avoca River Location	320847	175947	Equal to measured flow downstream of Shelton Abbey
Downstream of Shelton Abbey	Avoca River Location	321939	175213	Float Method used at bridge to fertiliser plant
Sulphur Brook	Tributary of Avoca River	320491	180470	Flow Meter
Deep Adit	Adit Discharge	319850	182123	Flume
Road Adit	Adit Discharge	319858	181512	Measured from permanent flume
Cronebane Intermediate Adit	Adit Discharge	320320	182749	Flume
Cronebane Shallow Adit	Adit Discharge	320268	182646	Flume
Ballygahan Adit	Adit Discharge	319940	181610	Bucket and stopwatch
Spa Adit	Adit Discharge	319637	181747	Immeasurable as the flow was too low and the break in the pipe allowing seepage into the ground.
Cronebane Pit Lake	Pit Lake	320933	183402	n/a

\* New locations added to the sampling programme in round 2

An additional method for measuring flow was used when the location of the river was unsafe to wade (Downstream of Shelton Abbey). This method is called the Float Method and 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).

### 2.1.3 Field QA/QC Samples

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

- Groundwater:
  - One duplicate groundwater sample was collected; and
  - One decontamination blank was collected by pumping deionised (DI) water through the groundwater pump after decontamination.
- Surface Water:
  - Two duplicate surface water samples; and
  - One decontamination blank was collected by pouring DI water over the surface water sampling equipment after decontamination.
- Two certified standard reference 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.

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

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

Sample ID	QA/QC Sample Type	Description
AVGD01.2	GW Duplicate	Duplicate of MWET1
AVDB01.2	GW Decontamination blank	DI water though pump after decon after site MWSA2
AVSD01.2	SW Duplicate	Duplicate of Deep Adit
AVSD02.2	SW Duplicate	Duplicate of Site T5
AVDB02.2	SW Decontamination blank	DI water over YSI probes after decon after site Avoca Bridge
AVSR01.2	Standard Reference Material	Phenova Trace Metals Lot #8128-04
AVSR02.2	Standard Reference Material	Phenova Trace Metals Lot #8128-04
WB01.2	Water blank	Deionised water (Lennox Batch TE130701W)



## 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  $\text{NO}_3$  and nitrite as  $\text{NO}_2$ , orthophosphate, sulphate, total alkalinity as  $\text{CaCO}_3$ , 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. The DI water used in the decontamination was also analysed. Each of these types of blanks is discussed below.

### 3.1.4 Field QA/QC Samples

Field QA/QC samples were submitted to the laboratories and analysed to enable the following evaluations:

- Duplicate Samples: Duplicate groundwater and surface water samples were created in the field and submitted blind to the laboratory (see Table 3 for sample IDs). The results are used to evaluate the combined reproducibility of both the laboratory analyses and field sampling;
- Decontamination Blanks: After the sampling equipment was cleaned, DI water was poured over or pumped through the sampling equipment and collected for laboratory analysis. 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 AVSR01.2 and AVSR02.2) to evaluate laboratory accuracy. The certified SRM was supplied by Phenova Certified Reference Materials and was Lot #8128-04 (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
- Water Blank: To ensure that the DI water used for equipment decontamination is analyte free, one water blank sample was collected of the DI water during the sampling event.



## 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 the RPD could not be calculated for the following; if one of the results was less than the detection limit and/or different detection limits were applied due to a dilution of one of the samples in the laboratory. If both the original and duplicate results were less than the detection limit then the RPD was zero.

The majority of RPD values are below 50 %. The RPDs for the key parameters aluminium (1 to 21 %), manganese (0 to 5.4 %) and zinc (1.4 to 2.3 %) are good as they are below 30 %. The RPDs for copper were also good but slightly higher for duplicate pair Deep Adit/AVSD01.2 with an RPD of 39.7 %.

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

Sample Description Dissolved Metal	LOD (µg/l)	MWET1	AVGD01.2	RPD	Deep Adit	AVSD01.2	RPD	Site T5	AVSD02.2	RPD
Aluminium	<2.9	178000	175000	1.70	94500	96700	-2.30	134	166	-21.3
Antimony	<0.16	<0.16	<0.16	0	<1.6*	<0.16	-	<0.16	<0.16	0
Arsenic	<0.12	<0.12	<0.12	0	<0.12	1.29	-7.23	0.273	0.273	0
Barium	<0.03	2.48	2.47	0.40	6.07	4.35	33.0	6.62	6.93	-4.58
Cadmium	<0.1	20.4	20.6	-0.98	89.7	48.3	<b>60.0</b>	0.915	0.931	-1.73
Chromium	<0.22	15.5	15.5	0	<2.2*	0.703	-	0.312	0.262	17.4
Cobalt	<0.06	218	219	-0.46	99.7	84.3	16.7	1.79	1.82	-1.66
Copper	<0.85	10600	10600	0	184	123	39.7	14.7	15.5	-5.30
Iron	<19	131000	129000	1.54	68300	65700	3.88	543	563	-3.62
Lead	<0.02	5.72	5.67	0.88	1990	1710	15.1	4.17	5.04	-18.9
Manganese	<0.04	10200	10200	0	4000	3790	5.39	109	111	-1.82
Mercury	<0.01	<0.01	<0.01	0	<0.01	<0.01	0	0.659	<0.01	<b>194</b>
Molybdenum	<0.24	<0.24	<0.24	0	<2.4*	<0.24	0	<0.24	<0.24	0
Nickel	<0.15	93.5	93.9	-0.43	41.6	29.5	34.0	1.33	1.33	0
Selenium	<0.39	<0.39	<0.39	0	<3.9*	0.947	-	<0.39	<0.39	0
Silver	<1.5	<1.5	<1.5	0	<1.5	<1.5	-0	<1.5	<1.5	0
Thallium	<0.96	1.67	1.88	-11.8	<9.6*	<0.96	0	<0.96	<0.96	0
Tin	<0.36	<0.36	<0.36	0	<3.6*	<0.36	0	<0.36	<0.36	0
Uranium	<1.5	9.76	9.86	-1.02	<15*	7.23	-	<1.5	<1.5	0
Vanadium	<0.24	0.781	0.561	32.8	<2.4*	0.365	-	<0.24	<0.24	0
Zinc	<0.41	13000	12700	2.33	44100	44900	-1.80	350	355	-1.42

Notes:

**Bold** indicates an exceedance in the Duplicate RPD acceptance criteria

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

There were only two RPDs that were above 50 % as highlighted in Table 4, which are cadmium for the Deep Adit/AVSD01.1 (RPD 60 %) sample pair and mercury for the Site T5/AVSD02.2 sample pair

(RPD 194 %). The reported value for Site T5 dissolved mercury was confirmed with ALcontrol, however, this result should be treated with caution as there was no detection in the duplicate or in the total mercury sample. The highest reported value of the duplicate pair is selected for interpretive use in Section 4 therefore providing a conservative evaluation.

### 3.2.2 Decontamination Blanks

Two decontamination blanks were created by pumping water through or 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 two decontamination blank samples along with the results of the DI water 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.

Low level detections were observed for ten dissolved metals ranging from 0.049 to 7.05 µg/l. Three of the metals (chromium, molybdenum and zinc) were also detected in the DI water blank. Detections of dissolved antimony, barium, copper, manganese, nickel, tin and uranium were also found in the decontamination blanks but not the DI water blank.

In total there were fifteen low level detections of dissolved metals in the decontamination blanks. Only two of these were greater than ten times the detection limit, manganese in AVDB01.2 (0.557 µg/l) and antimony in AVDB02.1 (2.99 µg/l). All of the detections including manganese and antimony were significantly less than the assessment criteria outlined in Section 4; therefore, these low concentrations in the blanks do not affect interpretation of results.

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. The concentrations in the blanks were generally less than 10% of the concentration in the preceding environmental samples. Three exceptions were the detection of chromium, molybdenum and nickel in AVDB01.2 which were determined to be 133%, 32% and 12% of the preceding environmental sample, respectively. Chromium and molybdenum were detected in the DI water blank and dissolved nickel was only slightly above the detection limit and therefore the detections are not indicative of cross-contamination.

The results from the laboratory instrumentation blank were obtained from ALcontrol to determine if any contamination occurred within the laboratory (Table 5). One detection in the method blank from Sample Batch 130816-44 was 0.395 µg/l of dissolved molybdenum. Dissolved molybdenum was detected in the water blank and the decontamination blank in the same sample batch at similar concentrations ranging from 0.322 to 0.33 µg/l. Six detections of parameters were present in method blank for Sample Batch 130821-36 that occurred in the decontamination blank from the same batch (see Table 5): dissolved antimony 0.953 µg/l, barium 0.221 µg/l, chromium 0.424 µg/l, manganese 0.329 µg/l, molybdenum 0.488 µg/l and tin 0.457 µg/l.

It was noted that the parameters detected in the method blanks for both sample batches were similar to those in the decontamination blank samples. This issue will be discussed with the laboratory in further detail prior to the next sampling round.

Overall, the decontamination blank samples do not indicate any cross-contamination in the field and the detections were significantly less than the assessment criteria outlined in Section 4 and therefore the results are considered acceptable.

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

Sample Description	LOD (µg/l)	Water Blank WB01.2 (µg/l)	Decon blank AVDB01.2 (µg/l)	Laboratory Method Blank W-10403 (µg/l)	Decon blank AVDB02.2 (µg/l)	Laboratory Method Blank W-10423 (µg/l)
Dissolved Metal						
Sample batch:		130816-44			130821-36	
Aluminium	<2.9	<2.9	<2.9	NP	<2.9	NP
Antimony	<0.16	<0.16	<0.16	0.7	<b>2.99</b>	0.953
Arsenic	<0.12	<0.12	<0.12	<0.12	<0.12	0.313
Barium	<0.03	<0.03	<b>0.12</b>	<0.03	<b>0.049</b>	0.221
Cadmium	<0.1	<0.1	<0.1	NP	<0.1	NP
Chromium	<0.22	<b>0.309</b>	<b>0.696</b>	<0.22	<b>0.382</b>	0.424
Cobalt	<0.06	<0.06	<0.06	NP	<0.06	NP
Copper	<0.85	<0.85	<b>1.1</b>	<0.85	<0.85	<0.85
Iron	<19	<19	<19	NP	<19	NP
Lead	<0.02	<0.02	<0.02	<0.02	<0.02	0.227
Manganese	<0.04	<0.04	<b>0.557</b>	<0.04	<b>0.125</b>	0.329
Mercury	<0.01	<0.01	<0.01	NP	<0.01	NP
Molybdenum	<0.24	<b>0.322</b>	<b>0.33</b>	0.395	<b>1.06</b>	0.488
Nickel	<0.15	<0.15	<b>0.181</b>	<0.15	<0.15	0.465
Selenium	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39
Silver	<1.5	<1.5	<1.5	NP	<1.5	NP
Thallium	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96
Tin	<0.36	<0.36	<0.36	<0.36	<b>0.739</b>	0.457
Uranium	<1.5	<1.5	<1.5	<1.5	<b>1.71</b>	<1.5
Vanadium	<0.24	<0.24	<0.24	NP	<0.24	NP
Zinc	<0.41	<b>12.8</b>	<b>7.05</b>	<0.41	<b>0.98</b>	<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 AVSR01.2 and AVSR02.2) 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 dissolved aluminium, antimony, arsenic, barium, chromium, cobalt, copper, lead, manganese, nickel, selenium, thallium and zinc are in excellent agreement with the certified value (%R ranged from 91 to 114 %).

One of the reported values for dissolved molybdenum, iron and silver (ID AVSR02.2) are low at 82 %, 87 % and 78 % and just fall out of the acceptable range. However, the second reported values are within the acceptable range and therefore it is considered that results are usable.

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

Sample Description Dissolved Metal	Certified Value (µg/l)	Acceptance Limits (%)	AVSR01.2 (µg/l)	% R	AVSR02.2 (µg/l)	% R
Aluminium	2640	82.6 -116	2740	104	2860	108
Antimony	605	70.2 -120	568	94	627	104
Arsenic	672	84.1 -117	678	101	729	108
Barium	1710	86.5 -113	1860	109	1660	97
Cadmium	423	85.1 -113	374	88	416	98
Chromium	765	87.2 -113	763	100	769	101
Cobalt	346	87.6 -112	352	102	394	114
Copper	637	90.0 -110	635	100	682	107
Iron	1560	88.5 -113	1360	<b>87</b>	1450	93
Lead	245	85.3 -114	235	96	244	100
Manganese	805	89.8 -111	791	98	811	101
Molybdenum	337	84.3 -115	275	<b>82</b>	337	100
Nickel	644	89.9 -112	627	97	671	104
Selenium	1820	79.7 -116	1950	107	1680	92
Silver	399	86.0 -115	310	<b>78</b>	357	89
Thallium	466	79.8 -121	449	96	464	100
Vanadium	1480	87.8 -112	1370	93	1310	89
Zinc	1980	86.4 -115	1900	96	1800	91

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 was 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.

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 total dissolved solids in four samples by one day. 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 physio-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 29 % which is good. The RPDs between laboratory and field pH were also good and generally less than 18 % which is very good. The field pH and conductivity are more representative of actual conditions and is used for interpretive purposes. Overall the %RPDs between the field and laboratory data are considered satisfactory.



**Table 7 Field physio-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		
MWDA1	3.17	2.94	7.5	1.81	2.154	-17.4
MWDA2	3.84	3.66	4.8	1.33	1.588	-17.7
MWPF1	5.15	4.66	10.0	0.143	0.153	-6.8
SG104	2.99	3.03	-1.3	7.79	9.071	-15.2
GW1/05	3.9	3.82	2.1	1.82	2.423	-28.4
GW2/05	3.73	3.56	4.7	1.07	1.43	-28.8
MWET1	3.34	3.31	0.9	2.23	2.595	-15.1
MWET2	6.02	6.11	-1.5	2.48	3.493	-33.9
MWSA2	3.73	3.94	-5.5	2.2	2.174	1.2
Ballygahan Adit	3.13	3.1	1.0	2.08	2.342	-11.8
Cronebane Inter. Adit	3.26	2.89	12.0	1.04	1.121	-7.5
Cronebane Pit Lake	3.22	3.11	3.5	0.503	0.563	-11.3
Cronebane Shallow Adit	2.84	2.52	11.9	3.7	4.22	-13.1
Deep Adit	3.45	3.52	-2.0	1.36	1.483	-8.7
Road Adit	3.9	3.72	4.7	1.43	1.565	-9.0
Spa Adit	ND	2.6	-	ND	2.882	-
Ballinacleish Bridge	6.63	5.5*	18.6	0.0391	0.043	-9.5
DS Deep Adit	6.8	6.33	7.2	0.0616	0.067	-8.4
Lions Bridge	7.25	7.28	-0.4	0.0717	0.078	-8.4
Site T1	6.86	6.71	2.2	0.0519	0.056	-7.6
Whites Bridge	6.88	6.84	0.6	0.0604	0.07	-14.7
Whites Bridge GS	6.95	6.97	-0.3	0.0598	0.066	-9.9
Wicklow CO.CO. Main. Yard GS	6.56	6.06	7.9	0.0717	0.079	-9.7
Site T5	6.52	5.84	11.0	0.0854	0.099	-14.8
Avoca Bridge	6.8	6.09	11.0	0.0812	0.089	-9.2
Vale View	7.33	7.25	1.1	0.121	0.14	-14.6
Sulphur Brook	7.39	6.8	8.3	0.161	0.153	5.1
US Shelton Abbey	7.14	6.65	7.1	0.108	0.102	5.7
DS Shelton Abbey	7.01	6.59	6.2	0.113	0.107	5.5

Notes:

**Bold** indicates an exceedance in acceptance limits

ND Not Determined

\* Difficulties stabilising pH readings in the field

### 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 3 samples just 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 values are all 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).

**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
MWDA1	1747	2340	5.7	9.4	<b>-25.3</b>	Missing anions
MWDA2	1331	1700	2.3	5.3	<b>-21.7</b>	Missing anions
MWPF1	82	84	-0.1	-4.0	-2.0	Missing cations
SG104	12387	15700	35.4	8.1	<b>-21.1</b>	Missing anions
GW1/05	2363	2970	-0.4	-0.5	<b>-20.5</b>	Missing cations
GW2/05	1145	1530	0.4	1.2	<b>-25.1</b>	Missing anions
MWET1	2492	3400	3.5	4.3	<b>-26.7</b>	Missing anions
MWET2	3419	3700	3.1	2.9	-7.6	Missing anions
MWSA2	2287	2910	2.2	3.1	<b>-21.4</b>	Missing anions
Ballygahan Adit	1846	2430	-1.2	-2.0	<b>-24.0</b>	Missing cations
Cronebane Inter. Adit	778	1220	-3.0	<b>-12.6</b>	<b>-36.3</b>	Missing cations
Cronebane Pit Lake	204	316	-0.7	<b>-10.5</b>	<b>-35.5</b>	Missing cations
Cronebane Shallow Adit	4472	6090	-7.5	-5.2	<b>-26.6</b>	Missing cations
Deep Adit	1327	1750	1.0	2.3	<b>-24.2</b>	Missing anions
Road Adit	1172	1630	-0.1	-0.2	<b>-28.1</b>	Missing cations
Vale View	74	96.3	-0.1	-6.2	<b>-23.4</b>	Missing cations
Ballinacleish Bridge	21	31	0.1	9.6	<b>-30.7</b>	Missing anions
DS Deep Adit	36	45.6	0.1	5.8	<b>-21.8</b>	Missing anions
Lions Bridge	40	44.4	0.0	1.2	<b>-10.6</b>	Missing anions
Site T1	27	43	0.1	<b>10.8</b>	<b>-37.0</b>	Missing anions
Whites Bridge	35	48.8	0.1	4.5	<b>-28.4</b>	Missing anions
Whites Bridge GS	34	35.6	0.1	5.8	-5.2	Missing anions
Wicklow CO.CO. Main. Yard GS	42	57.8	0.0	3.0	<b>-26.6</b>	Missing anions
Avoca Bridge	48	51.1	0.0	-1.0	-6.7	Missing cations
Site T5	50	40	0.0	-0.3	<b>25.5</b>	Too many anions
Sulphur Brook	96	122	-0.1	-3.0	<b>-21.0</b>	Missing cations
US Shelton Abbey	61	65.6	0.0	-0.8	-6.4	Missing cations
DS Shelton Abbey	64	71.1	-0.1	-2.9	-9.6	Missing cations

Notes:

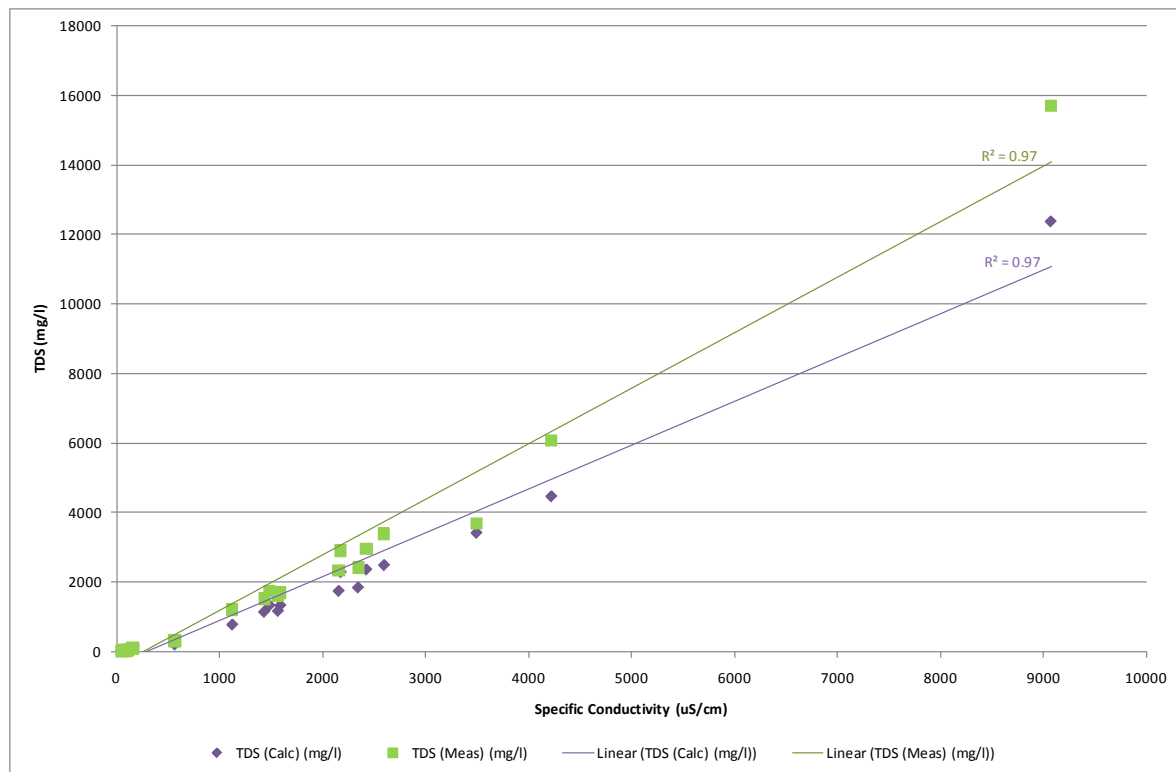
**Bold** indicates an exceedance of the acceptance criteria

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 for 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).

Figure 1 shows the relationship between specific conductivity and TDS. There is a strong positive correlation between SC with both the calculated ( $R^2=0.97$ ) and measured ( $R^2=0.97$ ) TDS.

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

Sample Description	Sample Type	Conductivity @ 20 deg.C	TDS (Calc)	TDS (Meas)	Ratio	
		(uS/cm)	(mg/l)	(mg/l)	SC/ TDS- Calc	SC/ TDS - Meas
MWDA1	GW	2154	1747	2340	1.2	0.9
MWDA2	GW	1588	1331	1700	1.2	0.9
MWPF1	GW	153	82	84	1.9	1.8
SG104	GW	9071	12387	15700	0.7	0.6
GW1/05	GW	2423	2363	2970	1.0	0.8
GW2/05	GW	1430	1145	1530	1.2	0.9
MWET1	GW	2595	2492	3400	1.0	0.8
MWET2	GW	3493	3419	3700	1.0	0.9
MWSA2	GW	2174	2287	2910	1.0	0.7
Ballygahan Adit	Adit	2342	1846	2430	1.3	1.0
Cronebane Inter. Adit	Adit	1121	778	1220	1.4	0.9
Cronebane Pit Lake	Pit Lake	563	204	316	2.8	1.8
Cronebane Shallow Adit	Adit	4220	4472	6090	0.9	0.7
Deep Adit	Adit	1483	1327	1750	1.1	0.8
Road Adit	Adit	1565	1172	1630	1.3	1.0
Vale View	SW	140	74	96.3	1.9	1.5
Ballinacleish Bridge	SW	43	21	31	2.0	1.4
DS Deep Adit	SW	67	36	45.6	1.9	1.5
Lions Bridge	SW	78	40	44.4	2.0	1.8
Site T1	SW	56	27	43	2.1	1.3
Whites Bridge	SW	70	35	48.8	2.0	1.4
Whites Bridge GS	SW	66	34	35.6	2.0	1.9
Wicklow CO.CO. Main. Yard GS	SW	79	42	57.8	1.9	1.4
Avoca Bridge	SW	89	48	51.1	1.9	1.7
Site T5	SW	99	50	40	2.0	2.5
Sulphur Brook	SW	153	96	122	1.6	1.3
US Shelton Abbey	SW	102	61	65.6	1.7	1.6
DS Shelton Abbey	SW	107	64	71.1	1.7	1.5



**Figure 1 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 the key metals aluminium, copper, cadmium, lead and zinc, by calculating the %RPD between the total and dissolved metals to evaluate if the concentrations were indistinguishable. Table B-1 in **Appendix B** shows the full tabulation of results.

The total metals were greater than or equal to the dissolved metals with the exception of 4 out of 140 results, where the RPD was greater than 50%. The reported values were close to the limit of detection and there is therefore greater variability.

The comparison of the total vs. dissolved concentrations in the groundwater and adit samples indicates that many of the parameters are approximately the same for the total and dissolved analyses. Lead was the only parameter where the total metal concentrations were higher than the dissolved for groundwater samples. For the Avoca River and tributaries, the total concentrations are generally significantly higher than the dissolved concentrations particularly for aluminium and cadmium whereas the results for total and dissolved zinc are more similar. Total suspended solids in the surface waters was above detection limit in five samples with concentrations ranging from 2.5 to 11 mg/l. The suspended solid result of 11 mg/l was at Vale View which also had some of the highest differences in total versus dissolved metals especially for aluminium and zinc with RPDs of 179 and 95% respectively.



## 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	8	14.5*	938000	171000	294000
Antimony	<0.16	9	0	0.08	0.8*	-	-
Arsenic	<0.12	9	3	0.06	16.2	2.71	5.49
Barium	<0.03	9	9	0.715	16.7	7.73	5.57
Cadmium	<0.1	9	9	0.525	287	55.6	90.4
Chromium	<0.22	9	9	2.27	37.1	11.4	11
Cobalt	<0.06	9	9	0.768	993	236	295
Copper	<0.85	9	8	4.25	92000	15500	29100
Iron	<19	9	8	9.5	172000	77300	56600
Lead	<0.02	9	9	0.478	1100	136	363
Manganese	<0.04	9	9	30.2	39600	17800	15800
Mercury	<0.01	9	2	0.005	0.049	0.01	0.01
Molybdenum	<0.24	9	2	0.12	1.2	0.55	0.51
Nickel	<0.15	9	9	2.23	365	97.7	108
Selenium	<0.39	9	6	0.195	16.6	3.43	5.39
Silver	<1.5	9	0	0.75	7.5*	-	-
Thallium	<0.96	9	1	0.48	1.88	-	-
Tin	<0.36	9	0	0.18	1.8*	-	-
Uranium	<1.5	9	9	0.75	65.1	12.3	20
Vanadium	<0.24	9	3	0.12	1.33	0.7	0.54
Zinc	<0.41	9	9	68.9	152000	35300	47600

Notes:

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

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

Dissolved aluminium, copper, iron, manganese and zinc were found in significantly high concentrations in the majority of groundwater samples. The shallow well MWPF1 located upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments had the lowest concentrations of dissolved metals. However, it was noted that MWET2 had no detection of dissolved aluminium or copper but was high in dissolved zinc (6,100 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 3 wells with highest concentration at MWSA2 of 16.2 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 6 adit discharge samples and the one pit lake sample and Table 12 provides a summary of the reported results of the 13 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	7	7	11000	387000	117000	136000
Antimony	<0.16	7	0	0.08	0.8*	-	-
Arsenic	<0.12	7	6	0.177	66.8	13.4	24.1
Barium	<0.03	7	7	5.15	13.8	8.84	3.06
Cadmium	<0.1	7	4	13.7	324	89.1	109
Chromium	<0.22	7	4	0.616	8.53	2.71	3.15
Cobalt	<0.06	7	7	22.1	302	139	109
Copper	<0.85	7	7	184	9140	3290	3400
Iron	<19	7	7	836	226000	65700	80000
Lead	<0.02	7	7	101	1990	878	709
Manganese	<0.04	7	7	476	11100	6310	4170
Mercury	<0.01	7	4	0.005	0.0195	0.01	0.01
Molybdenum	<0.24	7	0	0.12	1.2*	-	-
Nickel	<0.15	7	7	6.94	160	58.5	48.7
Selenium	<0.39	7	2	0.195	5.27	2.03	1.58
Silver	<1.5	7	0	0.75	0.75	-	-
Thallium	<0.96	7	0	0.48	4.8*	-	-
Tin	<0.36	7	0	0.18	1.8*	1.57	0.61
Uranium	<1.5	7	2	0.75	33.2	10.2	10.5
Vanadium	<0.24	7	1	0.12	1.2*	-	-
Zinc	<0.41	7	7	4260	133000	36000	44800

Notes:

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

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

Dissolved aluminium, copper, iron, manganese and zinc were found in significantly high concentrations in the majority of the adit discharge and pit samples. The Cronebane Shallow Adit had the highest concentrations of dissolved metals including aluminium (256 µg/l), cadmium (0.931 µg/l) and zinc (355 µg/l). The highest concentration of dissolved copper (9,140 µg/l) was detected in the Spa Adit. The lowest dissolved metals concentrations were found in the Cronbane 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	13	12	1.45	256	115	80.7
Antimony	<0.16	13	9	0.08	2.46	0.57	0.68
Arsenic	<0.12	13	13	0.273	2.09	0.67	0.46
Barium	<0.03	13	13	4.54	8.31	6.59	0.95
Cadmium	<0.1	13	9	0.05	0.931	0.36	0.3
Chromium	<0.22	13	12	0.11	0.953	0.47	0.23
Cobalt	<0.06	13	9	0.03	1.82	0.6	0.63
Copper	<0.85	13	11	0.425	17.1	7.17	5.32
Iron	<19	13	11	9.5	563	130	148
Lead	<0.02	13	13	0.441	6.25	2.56	1.82
Manganese	<0.04	13	13	3.88	126	39.4	43.9
Mercury	<0.01	13	1	0.005	0.659	-	-
Molybdenum	<0.24	13	10	0.12	7.38	1.19	1.94
Nickel	<0.15	13	13	0.534	1.47	0.93	0.28
Selenium	<0.39	13	3	0.195	5.18	0.67	1.38
Silver	<1.5	13	0	0.75	0.75	-	-
Thallium	<0.96	13	2	0.48	3.84	0.84	0.97
Tin	<0.36	13	1	0.18	0.74	-	-
Uranium	<1.5	13	0	0.75	0.75	-	-
Vanadium	<0.24	13	2	0.12	1.36	0.24	0.35
Zinc	<0.41	13	13	6.52	355	131	124

Notes:

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

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

The Vale View tributary discharges to the Avoca River upgradient of the mine site had some of the lowest concentrations of dissolved metals with aluminium at 12.6 µg/l and zinc at 6.52 µg/l. Dissolved metals were detected upgradient of the mining area at Ballinacleish Bridge and Lions Bridge with concentrations of aluminium at 174 and 36.2 µg/l, zinc at 24 and 31.1 µg/l and iron at 106 and 73.5 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 (117 µg/l), copper (<0.85 µg/l) and zinc (23.3 µg/l) slightly lower than the upstream tributaries. 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 (184 µg/l), copper (10 µg/l) and zinc (49.1 µg/l). The dissolved

metals concentrations remain reasonably consistent along the stretch from Whites Bridge to just Downstream (DS) of the Deep Adit confluence on the Avoca River. The only dissolved metal to significantly increase at the DS Deep Adit location on the Avoca River was zinc to a concentration of 92.6 µg/l.

Dissolved iron, manganese and zinc increase between Wicklow Co. Co. Maintenance Yard GS and Avoca Bridge, with the highest concentration at Site T5 which is downstream of the Road Adit Discharge (iron 563 µg/l, manganese 111 µg/l, zinc 355 µg/l). A slight decrease in concentrations was observed at Avoca Bridge (iron 232 µg/l, manganese 88.5 µg/l, zinc 301 µg/l).

Further downstream at the Shelton Abbey location (which is 7 km downstream of Whites Bridge GS) the concentrations are reduced compared to the Avoca River in the main mining area with 33.2 µg/l of dissolved aluminium and 201 µg/l of dissolved zinc.

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 against 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 and zinc hardness-adjusted salmonid-specific preliminary remediation goals were developed with the intention to protect the survival, growth, and reproduction of salmonid fish as part of the previous study for the Department (CDM, 2008). The hardness-adjusted equations were based on studies in which salmonid fish were exposed to dissolved metal at varying hardness. From these studies, a relationship was established between hardness and toxicity. The average hardness was calculated to be approximately 31 mg/l CaCO<sub>3</sub> and preliminary remediation goals for dissolved copper was 11 µg/l and for dissolved zinc was 268 µg/l.

However, the Surface Water Regulations 2009 provide more stringent standards for dissolved copper and zinc also based on hardness and are therefore utilised as the ecological assessment criteria (highlighted in bold in Table 13). Also note that the EU Freshwater Fish Directive (78/659/EEC) which specifies standards for salmonid and cyprinid waters are not utilised because

they will be revoked under the Water Framework Directive (2000/60/EC) on 22 December 2013 and they have been largely replaced by standards in the Surface Water Regulations.

**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	<b>0.14</b>	S.I. No. 272 of 2009	Good status
Ortho-phosphate as P	mg/l	0.035	<b>0.075</b>	S.I. No. 272 of 2009	Good status
pH	pH units		> <b>4.5</b> and < 9.0	S.I. No. 272 of 2009	Within range
Dissolved Oxygen	% Sat		<b>80 to 120</b>	S.I. No. 272 of 2009	Within range. Only relevant to surface water
Free Cyanide	mg/l	<b>0.01</b>	-	S.I. No. 272 of 2009	
Fluoride	mg/l	<b>0.5</b>	-	S.I. No. 272 of 2009	
Arsenic	µg/l	<b>25</b>	-	S.I. No. 272 of 2009	
Cadmium	µg/l	≤0.08 (Class 1) 0.08 (Class 2) 0.09 (Class 3) 0.15 (Class 4) 0.25 (Class 5)	≤ <b>0.45</b> (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)	S.I. No. 327 of 2012	Hardness measured in mg/l CaCO <sub>3</sub> (Class 1: <40 mg CaCO <sub>3</sub> /l, Class 2: 40 to <50 mg CaCO <sub>3</sub> /l, Class 3: 50 to <100 mg CaCO <sub>3</sub> /l, Class 4: 100 to <200 mg CaCO <sub>3</sub> /l and Class5: ≥200 mg CaCO <sub>3</sub> /l)
Chromium	µg/l	<b>3.4</b>	-	S.I. No. 272 of 2009	
Copper	µg/l	<b>5</b> or 30	-	S.I. No. 272 of 2009	5 µg/l applies where the water hardness measured in mg/l CaCO <sub>3</sub> is ≤ 100; the value 30 applies where the water hardness > 100 mg/l CaCO <sub>3</sub> .
Lead	µg/l	<b>7.2</b>	-	S.I. No. 327 of 2012	
Mercury	µg/l	0.05	<b>0.07</b>	S.I. No. 327 of 2012	
Nickel	µg/l	<b>20</b>	-	S.I. No. 327 of 2012	
Zinc	µg/l	8 or <b>50</b> or 100	-	S.I. No. 272 of 2009	8 µg/l for water hardness with annual average values ≤ 10 mg/l CaCO <sub>3</sub> , 50 µg/l for water hardness > 10 mg/l CaCO <sub>3</sub> and ≤ 100 mg/l CaCO <sub>3</sub> and 100 µg/l elsewhere
<b>Supplementary standards:</b>					
Aluminium	µg/l	-	<b>1900</b>	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Barium	µg/l	-	<b>4</b>	Oak Ridge National Laboratory	Invertebrates and Salmon fish
Cobalt	µg/l	-	<b>5.1</b>	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Manganese	µg/l	-	<b>1,100</b>	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Uranium	µg/l	-	<b>2.6</b>	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids

Notes:

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



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 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 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 <sub>3</sub>	mg/l	50
Nitrite as NO <sub>2</sub>	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 all groundwater samples with results ranging from 2.94 to 6.11 (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 specific conductance ranges from 0.153 to 9.071 mS/cm with the lowest conductivity located at MWPF1 and the highest at SG104. The specific conductance only 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 856 to 9560 mg/l. One exception was at MWPF1 where sulphate was below the human health assessment criteria with a value of 33.2 mg/l. Ammonia was detected in 5 of the monitoring wells and both the ecological (0.14 mg/l) and human health (0.3 mg/l) assessment criteria were exceeded in MWDA1, MWET1, GW1/05, SG104 and MWSA2. Fluoride was also present in 6 of the monitoring wells sampled, with 2 of the values exceeding the assessment criteria for ecology (0.5 mg/l) and 4 of the values exceeding 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). Wells MWDA1, MWSA2, MWET2, GW2/05, GW1/05 and MWDA2 also have detections of total arsenic with values of ranging from 6.8 to 85.6 µg/l. There were three detections of dissolved arsenic, only MWSA2 with a result of 16.2 µg/l exceeded only the human health (10 µg/l) criteria.

The dissolved aluminium and copper concentrations at MWET2 (deep) (<29 and <9 µg/l) were significantly lower than at MWET1 (shallow) which had concentrations of 178,000 and 10,600 µg/l, respectively. This could be explained by the apparent confined nature of MWET2 (heads in MWET2 are higher than in MWET1) and also because MWET1 is screened directly beneath the Emergency Tailings deposits.

The bedrock monitoring well GW1/05 showed higher dissolved metal concentrations than its nested, shallow alluvial well GW2/05. For example dissolved copper in GW1/05 µg/l was detected at 12000 and 7010 µg/l in GW2/05. Levels of dissolved lead in GW1/05 exceeded the ecological assessment criteria of 7.2 µg/l, with a value of 1100 µg/l.

SG104 had the highest levels of dissolved copper (938,000 µg/l), mercury (0.049 µg/l), nickel (365 µg/l), uranium (65.1 µg/l) and zinc (152,000 µg/l) compared to the other monitoring wells.

Dissolved selenium in SG104 was detected at 16.6 µg/l which was an exceedance of the human health criteria for selenium of 10 µg/l. Levels of dissolved lead in SG104 exceeded the ecological assessment criteria of 7.2 µg/l, with a value of 77.8 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 which were at concentrations of 146,000 and 12,400 µg/l in MWDA1 and were at concentrations of 66,600 and 7,050 µg/l in MWDA2, respectively. However, both wells still exceeded the criteria for both ecological and human health for aluminium and copper.

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 following assessment criteria were exceeded for human health: dissolved aluminium (200 µg/l) and for ecological assessment criteria: cadmium (0.45 µg/l), copper (5 µg/l) and zinc (50 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 2.6 to 3.72 (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 65.7 mg/l in the Cronbane Pit Lake to 1,940 mg/l in the Cronbane Shallow Adit. The specific conductance ranged from 0.563 to 4.22 mS/cm and only exceeded the human health criteria (2.5 mS/cm) at the Cronebane Shallow Adit and the Spa Adit.

Elevated sulphate, ammonia and fluoride 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 623 to 3,650 mg/l. Ammonia was detected in all of the adit discharges and both the ecological (0.14 mg/l) and human health (0.3 mg/l) criteria were exceeded at all locations, with the highest concentration at Road Adit (9.44 mg/l). Fluoride was also present at all of the adit discharges that were sampled, with 3 of the values exceeding both the assessment criteria for ecological (0.5 mg/l) and human health (1.5 mg/l). The Deep Adit (1.06 mg/l) and the Cronbane Intermediate Adit (1.32 mg/l) only exceeded the criteria for ecological health. Concentrations of sulphate (148 mg/l), ammonia (0.31 mg/l) and fluoride (<0.5 mg/l) were generally lower at Cronbane 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).

The metals concentrations in the Cronebane Shallow Adit discharge were some of the highest observed. The concentrations of dissolved copper only exceeded the ecological assessment criteria (5 µg/l) in the Road and Deep Adits but dissolved copper concentrations exceeded both the ecological and human health (2,000 µg/l) criteria for all of the other adits. The lowest concentrations of metals were found in the Cronebane Pit Lake; however, both the assessment criteria were generally exceeded.

There were six detections of dissolved arsenic, with only Ballygahan Adit (66.8 µg/l) exceeding the criteria for both ecological (25 µg/l) and human health (10 µg/l) and Cronebane Shallow Adit (14.5 µg/l) exceeding only the human health criteria.

### Rivers and Streams

The pH was found to be near neutral in the majority of rivers and streams ranging from 5.5 to 7.28 (field) which are well within acceptable ranges for ecological (4.5 to 9 pH units). However, 5 locations including Ballinacleish Bridge and the stretch between Wicklow Co. Co. Maintenance Yard and Avoca Bridge (inclusive) were below the human health (6.5 to 9.5 pH units) criteria. Acidity was below the limit of detection (<2 mg/l) with the exception of Vale View (36.5 mg/l) and US Shelton Abbey (5.48 mg/l). The specific conductance was well within the criteria for human health of 2.5 mS/cm ranging from 0.07 to 0.153 mS/cm.

Nutrients within the river and stream samples collected were generally below the ecological assessment criteria for ortho-phosphate (0.075 mg/l) and ammonia (0.14 mg/l). Exceptions were Site T5 and US Shelton Abbey which exceeded the criteria for ammonia with values of 0.265 and 0.208 mg/l, respectively.

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 occur. Dissolved copper exceeded the ecological criteria (5 µg/l) at all river and stream locations from Whites Bridge to the Downstream Shelton Abbey location, with results ranging from 5.29 to 17.1 µg/l. Similarly dissolved zinc exceeded the ecological assessment criteria (50 µg/l) from DS Deep Adit on the Avoca River to Downstream Shelton Abbey with results ranging from 92.6 (twice the ecological assessment criteria) to 355 µg/l. Dissolved aluminium exceeded human health criteria (200 µg/l) only at Wicklow Co. Co. Maintenance Yard with a value of 256 µg/l. Dissolved cadmium exceeded ecological assessment criteria (0.45 µg/l) from Wicklow Co. Co. Maintenance Yard to DS Shelton Abbey with values ranging from 0.504 to 0.811 µg/l. Dissolved mercury exceeded the ecological assessment criteria of 0.07 µg/l at Site T5 with a concentration of 0.659 µg/l. However, as noted in Section 3, the field duplicate (AVSD02.2) of this sample was below the detection limit of <0.01 µg/l.

## 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 but just upstream of the Road Adit confluence.

The flow record from 1 April to 31 August 2013 of Whites Bridge GS is reproduced in Figure 2 and for Wicklow County Council Maintenance Yard GS in Figure 3. The figures show the measured flows ranging from  $>20 \text{ m}^3/\text{s}$  following major rainfall events to approximately  $1\text{--}2 \text{ m}^3/\text{s}$  during low-flow. The flashy nature of the river shows a rapid response to rainfall. The median flow for this period was approximately  $4 \text{ m}^3/\text{s}$ , which is relatively low for the Avoca River with this figure being less than half the norm of the long term median of approximately  $10 \text{ m}^3/\text{s}$  (CDM Smith, 2013). Flow in July and August were particularly low with the daily mean flow rarely exceeding  $5 \text{ m}^3/\text{s}$ .

The river appears to respond similarly to rainfall at both gauging stations as can be seen in both figures. The peaks in flow during rainfall events are slightly higher at Whites Bridge GS which is the upstream location by 1 to  $2 \text{ m}^3/\text{s}$ . The recessions in the graph after each rainfall event are shown to be very similar also in the figures.

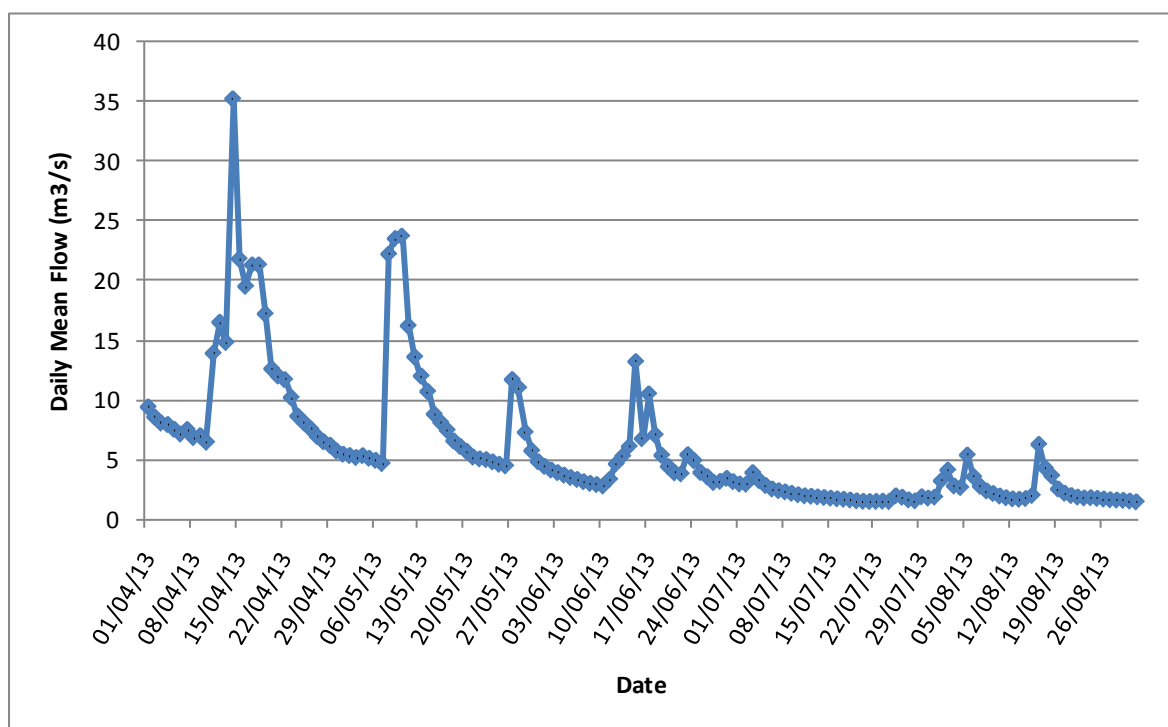
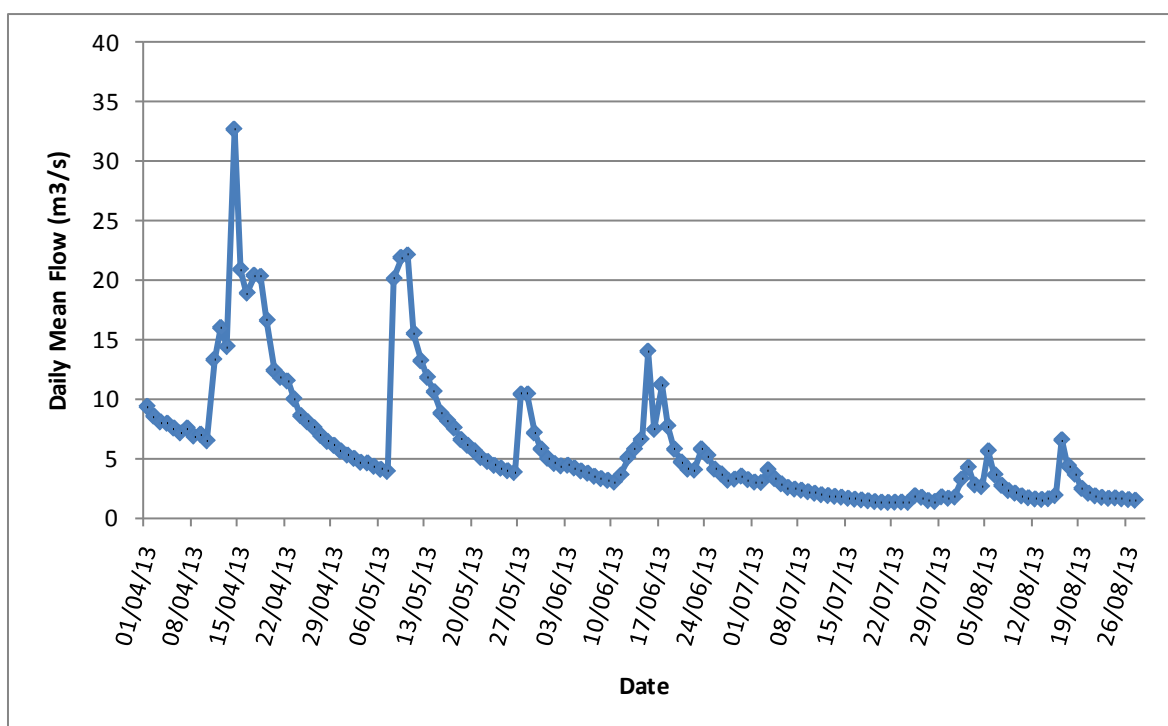


Figure 2 Mean Daily Flow ( $\text{m}^3/\text{s}$ ) at Whites Bridge (Station 10044) from 1 Apr to 31 Aug 2013



**Figure 3 Mean Daily Flow (m<sup>3</sup>/s) at Wicklow County Council Maintenance Yard (Station 10045) from 1 Apr to 27 Aug 2013**

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 15 presents as a summary of the results from the flows measured in August 2013 at the time of sampling. Refer to Appendix B of the Data Report for details of methodologies used per site and associated calculations.

It is noted that some of the flow measurements were carried out on different days and the average flow in the Avoca River varies. The flow measurement at Avoca Bridge is believed to be unrepresentative and likely underestimated. The measurement was probably influenced by the uneven river bed and extreme windy conditions in the shallower waters along the south bank.

The recorded flows at Wicklow Co. Co. Maintenance Yard GS on the 19 and 20 of August were less than the flows recorded at Whites Bridge GS which is further upstream. This suggests that this is a losing stretch of river on those particular days.

The measured flows at the Deep Adit of 13 l/s and Road Adit of 16 l/s are relatively low flows. Past records for the Deep Adit ranged from approximately 10 to 72 l/s and the Road Adit from 6 to 58 l/s (CDM, 2008).



**Table 15 Surface Water Flow Value Measured in August 2013**

Site Name	Flow m <sup>3</sup> /s	Flow l/s	Date	Notes
Ballinacleish Bridge	1.18	1,180	19/08/2013	
Lions Bridge	1.67	1,670	19/08/2013	
Vale View	0.004	4.0	15/08/2013	
Site T1	2.52	2,520	19/08/2013	
White's Bridge	2.54	2,540	19/08/2013	
White's Bridge GS	2.54	2,540	19/08/2013	Mean daily flow on 20/08/2013 was 2.18 m <sup>3</sup> /s
DS Deep Adit	2.45	2,450	19/08/2013	
Wicklow Co Co. Maintenance Yard GS	2.45	2,450	19/08/2013	Mean daily flow on 14/08/13 was 1.58m <sup>3</sup> /s and on 20/08/2013 it was 2.04 m <sup>3</sup> /s
Site T5	2.33	2,330	20/08/2013	
Avoca Bridge	1.94	1,940	20/03/2013	Unrepresentative
Upstream of Shelton Abbey	3.05	3,050	14/08/2013	
Downstream of Shelton Abbey	3.05	3,050	14/08/2013	
Sulphur Brook	0.020	20	14/08/2013	
Deep Adit	0.013	13.1	15/08/2013	
Road Adit	0.016	15.6	15/08/2013	
Cronebane Intermediate Adit	0.001	1.0	15/08/2013	
Cronebane Shallow Adit	0.00002	0.02	15/08/2013	
Ballygahan Adit	0.00006	0.06	15/08/2013	
Spa Adit	Immeasurable		15/08/2013	

## 5.2 Loading Analysis

### 5.2.1 Loading Analysis Methodology

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

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

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

F = the flow rate of the input

### 5.2.2 Loading Results and Discussion

The calculated mass loads in Table 16 aid with the interpretation of the loading of sulphate and dissolved aluminium, copper, iron, lead and zinc to the Avoca River. Background loads upstream of the Avoca Mining Area of sulphate and these metals were present which is evident from the calculated loads at Ballinacleish Bridge, Lions Bridge and Site T1. Sulphate loads at Site T1 were calculated to be 218 kg/day and the dissolved metal loads of aluminium were 25.5 kg/day, copper 0.09 kg/day, iron 19.1 kg/day, lead 0.4 kg/day and zinc 5.07 kg/day.

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

Sample Description	Date Sampled	Flow l/s	pH Units	Sulphate		Aluminium		Copper		Iron		Lead		Zinc	
				µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day
Ballinacleish Bridge	19/08/2013	1180	5.5	1000	102	174	17.7	0.425	0.04	106	10.8	3.26	0.33	24.6	2.51
Lions Bridge	19/08/2013	1670	7.28	5700	822	36.2	5.22	0.897	0.13	73.5	10.6	1.06	0.15	31.1	4.49
Vale View	15/08/2013	4.26	7.25	16200	5.6	12.6	0.004	7.46	0.003	9.5	0.003	0.949	0.0003	6.52	0.002
Site T1	19/08/2013	2520	6.71	1000	218	117	25.5	0.425	0.09	87.5	19.1	1.85	0.4	23.3	5.07
Whites Bridge	19/08/2013	2540	6.84	5000	1100	184	40.4	10	2.19	75.3	16.5	1.6	0.35	49.1	10.8
Whites Bridge GS	19/08/2013	2540	6.97	4200	922	129	28.3	4.18	0.92	78.8	49.7	1.74	0.38	40.5	8.89
DS Deep Adit (Avoca R.)	19/08/2013	2450	6.33	6300	1330	180	38.1	5.29	1.12	121	25.6	2.9	0.61	92.6	19.6
Cronebane Inter. Adit	15/08/2013	0.99	2.89	623000	53.3	44100	3.77	629	0.05	1620	0.14	1290	0.11	27500	2.35
Cronebane Shallow Adit	15/08/2013	0.020	2.52	3650000	6.31	387000	0.67	6290	0.01	4090	0.01	1360	0.002	133000	0.23
Deep Adit	15/08/2013	13	3.52	999000	1130	96700	110	184	0.21	68300	77.4	1990	2.25	44900	50.9
Ballygahan Adit	15/08/2013	0.060	3.1	1350000	7.35	60000	0.33	3730	0.02	89600	0.49	155	0.001	19500	0.11
Wicklow CO.CO. Main. Yard GS	19/08/2013	2450	6.06	13100	2770	256	54.2	17.1	3.62	235	49.7	4.45	0.94	278	58.6
Road Adit	15/08/2013	15.6	3.72	811000	1100	16400	22.1	335	0.45	69500	93.9	374	0.51	7810	10.5
Site T5	20/08/2013	2330	5.84	20600	4150	166	33.4	15.5	3.12	563	113	5.04	1.01	355	71.5
Sulphur Brook	14/08/2013	20.5	6.8	13900	24.6	1.45	0.003	9.19	0.02	9.5	0.02	0.532	0.001	76.2	0.13
Avoca Bridge*	20/08/2013	1940	6.09	17800	2980	161	27	10.8	1.81	232	38.9	3.23	0.54	301	50.5
US Shelton Abbey	14/08/2013	3050	6.65	17000	4480	33.2	8.75	5.76	1.52	47.9	12.6	0.441	0.12	201	53
DS Shelton Abbey	14/08/2013	3050	6.59	20000	5270	47.4	12.5	6.12	1.61	52.6	13.9	6.25	1.65	230	60.6

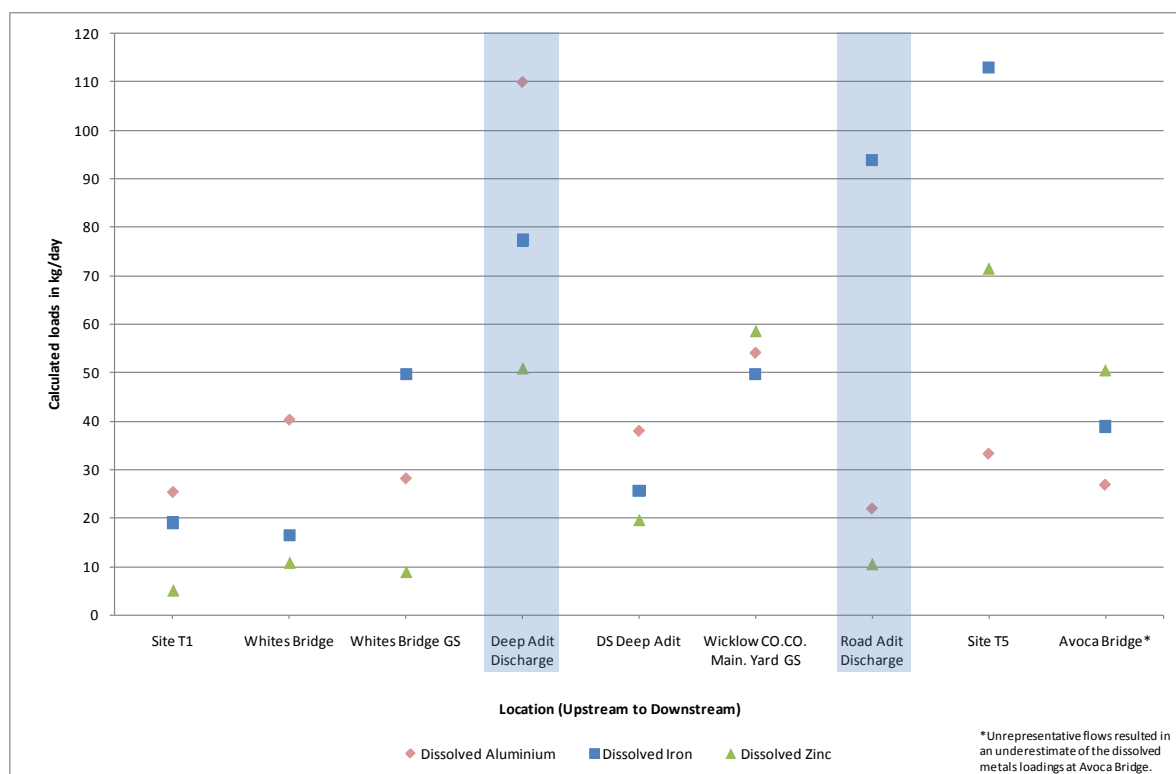
**Notes:**

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

Figure 4 graphically shows the calculated loads of dissolved aluminium, 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**). The loads from the Deep and the Road Adits are also displayed on the graph at their respective locations.

An increase in loads occurs at Whites Bridge with loads of dissolved aluminium at 40.4 kg/day, copper at 2.19 kg/day, and zinc at 10.8 kg/day. There is an apparent slight decrease in dissolved aluminium (28.3 kg/day), copper (0.92 kg/day) and zinc (8.89 kg/day) loads 90 metres downstream at Whites Bridge GS but an increase in dissolved iron to 49.7 kg/day from 16.5 kg/day at Whites Bridge. At DS Deep Adit (downstream of the confluence) on the Avoca River the load for dissolved aluminium increases again to 38.1 kg/day and it significantly increases for dissolved zinc to 19.6 kg/day. However, the dissolved iron load decreases to 25.6 kg/day despite the dissolved iron load from the Deep Adit of 77.4 kg/day. The calculated loads from the adits are discussed further below.

The apparent difference in dissolved metal loads along this stretch of the Avoca River between Whites Bridge and the DS Deep Adit is clearly shown on Figure 4 and is probably due to the complex nature of the infiltration from the Deep Adit discharge ditch and the input of contaminated groundwater through this area, from the Deep Adit spoils.



**Figure 4 Calculated Loads of Dissolved Aluminium, Iron and Zinc in kg/day in Avoca River and the Deep and Road Adits in August 2013**

The Deep Adit and the Road Adit had similar loads of sulphate (1130 and 1100 kg/day), copper (0.21 and 0.45 kg/day) and iron (77.4 and 93.9 kg/day). However, the Deep Adit has much higher loadings of aluminium and zinc with loads of 110 and 50.9 kg/day at the Deep Adit and 22.1 and 10.5 kg/day at the Road Adit. These calculated loads may be an over estimation of the loads

directly discharging directly to the Avoca River because during a previous study for the Department by CDM (2008) there was a large difference in the concentrations between the actual adit discharge and the confluence due to precipitation of iron-aluminium oxyhydroxides with coprecipitation of metals such as copper resulting in significant attenuation occurring within the ditches before discharging into the Avoca River. For the Deep Adit, zinc was the only metal that appeared to be relatively conservative, with only a 9.5% decrease in concentration at the confluence compared to the adit discharge (CDM, 2008).

The calculated loading of dissolved aluminium 28.3 kg/day and zinc was 8.89 kg/day at Whites Bridge GS and at DS Deep Adit the calculated load was 38.1 kg/day of aluminium and 19.6 kg/day of zinc. This location is downstream of the Deep Adit discharge so the loads would be expected to be 138 kg/day for aluminium and 59.8 kg/day for zinc to account for the loading at Whites Bridge GS (28.3 kg/day aluminium and 8.89 kg/day zinc) and the Deep Adit (110 kg/day aluminium and 50.9 kg/day zinc). However, as the loading at Whites Bridge GS likely contains the diffuse loads from the Deep Adit ditch it is likely that the load from the Deep Adit is double counted using this method. Also as previously discussed, precipitation of iron-aluminium oxyhydroxides in the Deep Adit ditch result in a significant decrease in metal loads. It is therefore recommended that an additional sampling point is added to the monitoring programme on the Deep Adit channel just before it enters the Avoca River.

Further downstream at Wicklow Co. Co. Maintenance Yard GS the aluminium load was calculated to be 54.2 kg/day and the zinc load was calculated to be 58.6 kg/day. As shown on Figure 4 this is a significant increase from the calculated loads at DS Deep Adit. At Wicklow Co. Co. Maintenance Yard GS location the Deep Adit discharge is better mixed with the Avoca River and there could also be further groundwater discharge and seepage from the Road Adit ditch, and contaminated groundwater from the emergency tailings area. However, the aluminium load is still less than what is expected, which also indicates there is precipitation of aluminium and zinc in the deep adit ditch, attenuation in the aquifer material or that some of the loads are deposited as ferricrete cement on the bank of the river and in the mixing zone in the river.

Similarly the estimated loads of dissolved iron in the both the Deep and Road adits are not an accurate representation of the direct loads to the Avoca River. The calculated load at Wicklow County Council Maintenance Yard GS is 128 kg/day (Whites Bridge GS 49.7 kg/day + Deep Adit 77.4 kg/day + Ballygahan Adit 0.49 kg/day) whereas the actual iron load at that location was calculated to be 49.7 kg/day. As mentioned above however this method may double count the load from the Deep Adit and does not account for the large decrease in load due to precipitation of iron-aluminum oxyhydroxides and other metals in the Deep Adit ditch. The loading of iron from the Road Adit was estimated to be 93.9 kg/day. When added to the Wicklow County Council Maintenance Yard GS of 49.7 kg/day, the total is 144 kg/day which is slightly higher than the downstream location of Site T5 which had a calculated load of zinc of 113 kg/day. This further indicates the precipitation of iron-aluminium oxyhydroxides and loads being deposited as ferricrete cement. However, at Site T5 there is a significant increase in dissolved iron loads compared with the upstream location (see Figure 4).

The Cronebane Intermediate Adit has significantly less loads of dissolved aluminium (3.77 kg/day), iron (0.14 kg/day) and zinc (2.35 kg/day) compared with the Road and Deep Adits. The Cronebane Shallow and Ballygahan adits are 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. Loads from these

adits range from 0.33 to 0.67 kg/day for aluminium, 0.1 to 0.2 kg/day for copper and 0.11 to 0.23 kg/day for zinc. Loads from the Spa Adit could not be calculated because the flow was too low to measure; however, it does not discharge to the Avoca River.

Two tributaries to the Avoca River were sampled: Vale View and Sulphur Brook. Both tributaries had insignificant loads, with the highest loading of 0.13 kg/day for zinc.

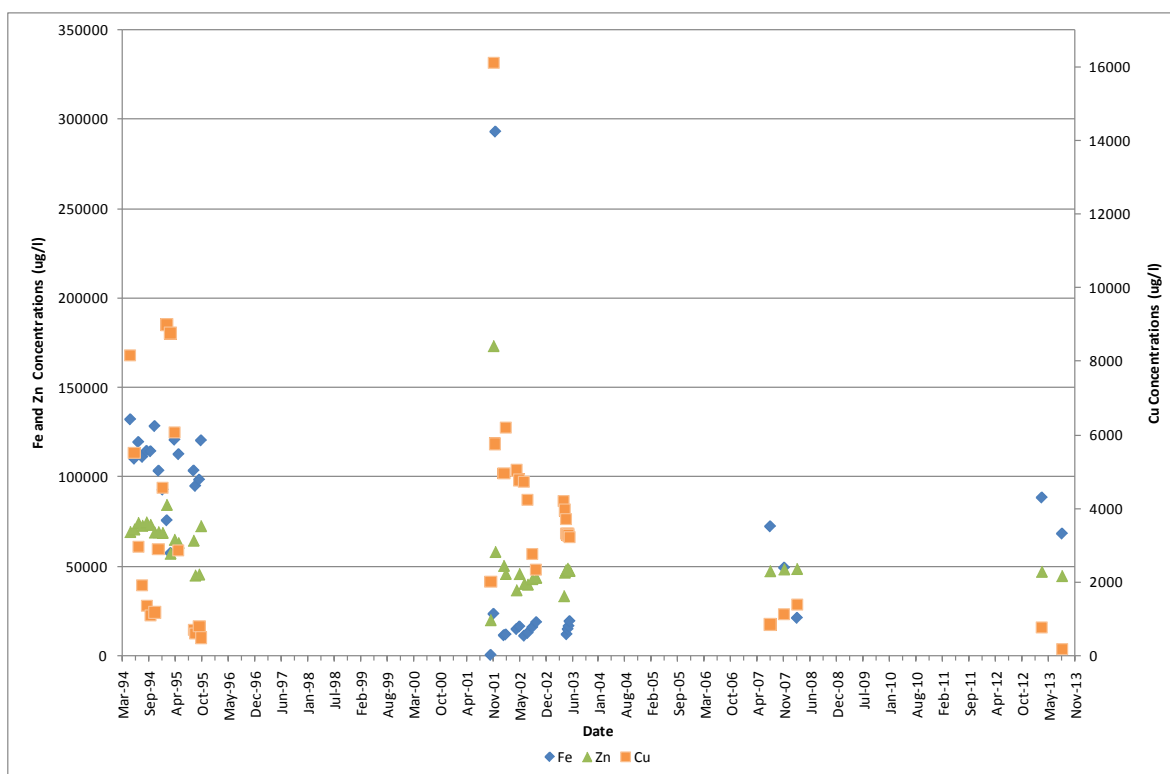
There is an apparent increase in the loads of dissolved metals evident Downstream of Shelton Abbey compared to the upstream location; for example, dissolved aluminium increases from 8.75 to 12.5 kg/day and dissolved zinc from 53 to 60.6 kg/day.

## 5.3 Trend Analysis

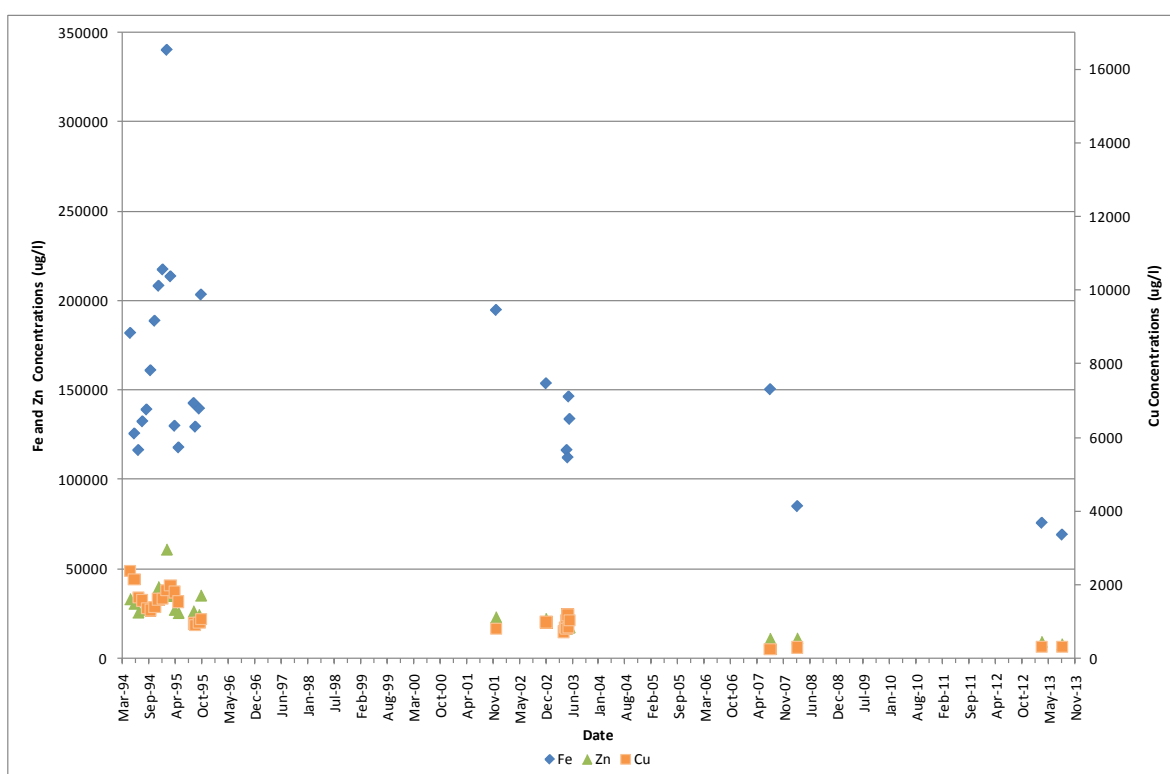
This section discusses concentration time trends for select locations including the Deep Adit, the Road Adit and one location on the Avoca River for selected parameters including dissolved copper, zinc and iron. The trends are shown graphically in Figure 5 (Deep Adit from Dec 1993 to Aug 2013), Figure 6 (Road Adit from May 1993 to Aug 2013) and Figure 7 (Avoca River at Avoca Bridge from May 2001 to Aug 2013).

A general declining trend in metal concentrations for both the Deep and Road adits can be inferred from Figure 5 and 6; however, a seasonal trend exists with some peaks in concentration that can mask this overall trend.

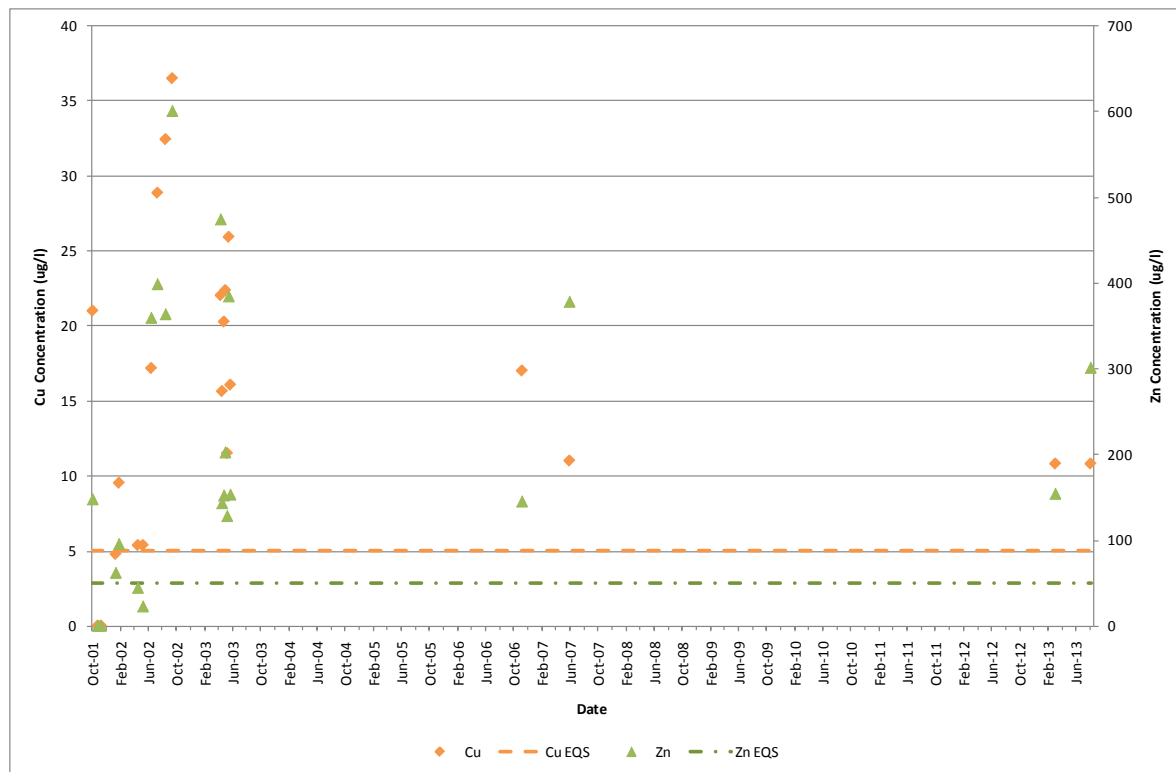
Figure 7 displays the results for dissolved copper and zinc in the Avoca River at Avoca Bridge which is downstream of the main Avoca Mining Area, from 2001 to present. The ecological assessment criteria (or EQS) are also shown on the graph for reference. The results also appear to be trending downwards but further analysis on seasonal trends will be required as more data becomes available.



**Figure 5 Concentration trends for dissolved copper, zinc and iron within the Deep Adit Discharge (Dec 1993 to Aug 2013)**



**Figure 6 Concentration trends for dissolved copper, zinc and iron within the Road Adit Discharge (May 1993 to Aug 2013)**



**Figure 7 Concentration trends for dissolved copper and zinc at Avoca Bridge compared with the environmental quality objective (EQS) (May 2001 to Aug 2013)**

Table 17 shows the seasonal variation between the concentrations of dissolved metals and the calculated loads observed between the high flow sampling event in March 2013 (R1) and the low flow sampling event in August 2013 (R2). As can be seen from Table 17 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 compared with March. There was a significant increase in the concentration of dissolved iron and zinc at the Avoca Bridge sampling location on the Avoca River in August compared with March. Table 17 also shows that the calculated loads of dissolved aluminium, copper, iron and zinc were all significantly lower in August due to the low flow conditions.

**Table 17 Seasonal Variation of Concentrations and Calculated Loads of Dissolved Metals in the Adits and at Avoca Bridge in 2013**

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 15/03/13	29.2	98800	249	770	1.9	88500	223	47300	119
	R2 15/08/13	13	96700	110	184	0.21	68300	77.4	44900	50.9
Road Adit	R1 15/03/13	28.9	14900	37.2	366	0.9	76100	190	9140	22.8
	R2 15/08/13	15.6	16400	22.1	335	0.45	69500	93.9	7810	10.5
Avoca Bridge	R1 20/03/13	12000	162	168	10.8	11.2	153	158	154	159
	R2 20/08/13	1940*	161	27	10.8	1.81	232	38.9	301	50.5

**Notes:**

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



## Section 6

# Groundwater Levels

## 6.1 Groundwater Levels

Groundwater levels were measured at the nine wells using a portable electronic water level recorder prior to purging. Table 18 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 25.4 to 32.5 m Ordnance Datum (OD) in the Avoca Mining Area which 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 18 Measured Groundwater Levels and Calculated Elevation August 2013**

Borehole Identifier	Date	Time	Depth to Groundwater (m bTOC)	Groundwater Elevation (m OD)
MWDA1	12/08/2013	11:10	6.51	26.3
MWDA2	12/08/2013	11:05	6.62	26.0
MWPF1	12/08/2013	14:30	4.74	26.8
MWET1	13/08/2013	09:55	7.545	25.8*
MWET2	13/08/2013	09:55	7.445	25.9*
GW1/05	13/08/2013	12:50	5.45	25.4*
GW2/05	13/08/2013	12:50	5.59	25.4*
SG104	12/08/2013	16:00	25.63	32.5*
MWSA2	14/08/2013	10:20	8.78	1.39

Notes:

m is metres

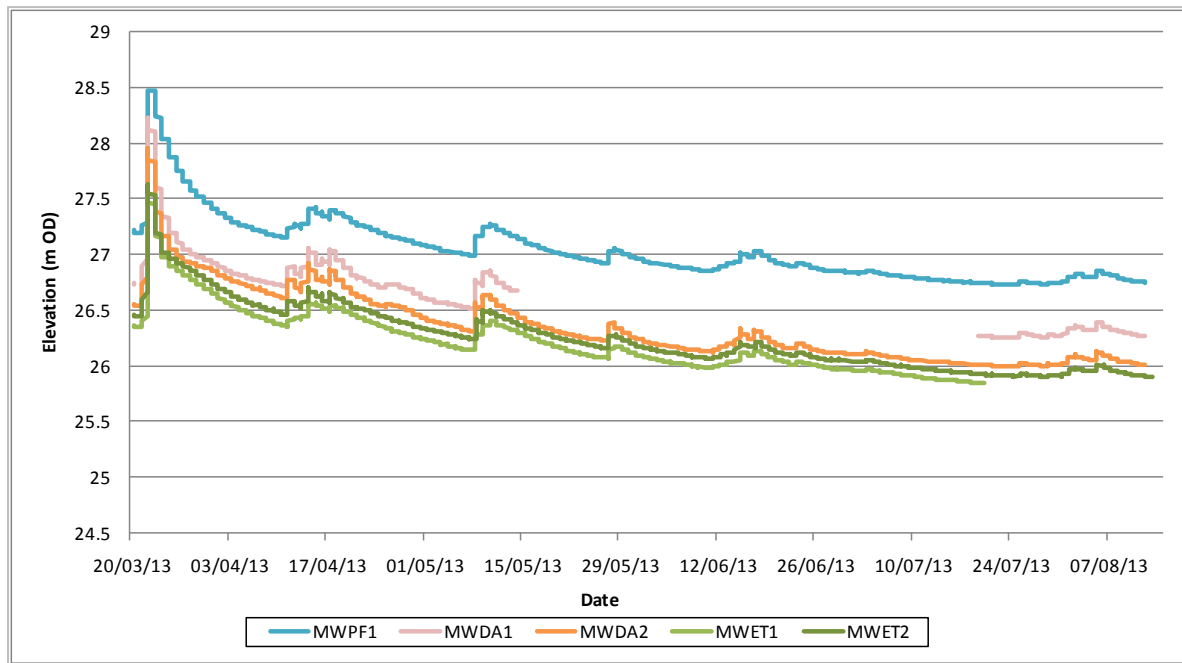
OD is Ordnance Datum

bTOC is below top of casing

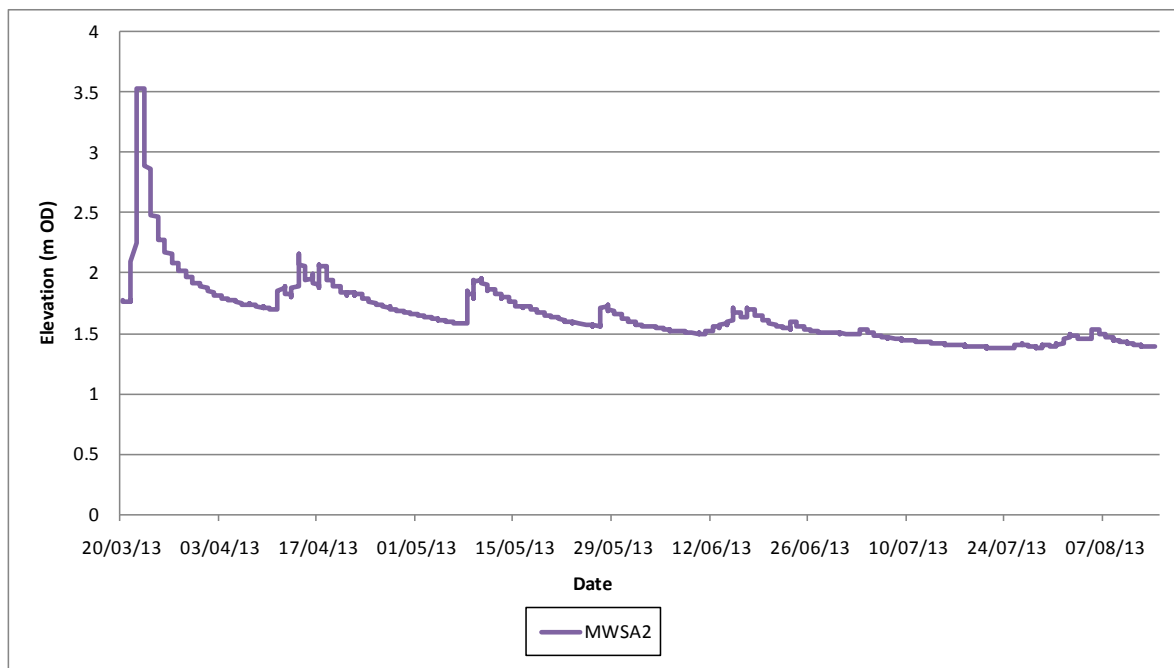
\* Borehole elevations were based on a GPS survey and therefore may be less accurate

Automatic pressure transducers and loggers have been installed in the six wells owned by the Department. Figure 8 shows the groundwater elevations from the 5 wells located in the Avoca Mining Area from 20 March 13 August to 2013. Data are missing for MWDA2 from 14 May to 19 July due to a fault with the batteries, which were replaced on 19 July. Figure 9 shows the groundwater elevation at MWSA2 at Shelton Abbey Tailings Facility between 20 March and 14 August 2013.

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.



**Figure 8 Groundwater Elevations in the Avoca Mining Area from 20 March to 13 August 2013**



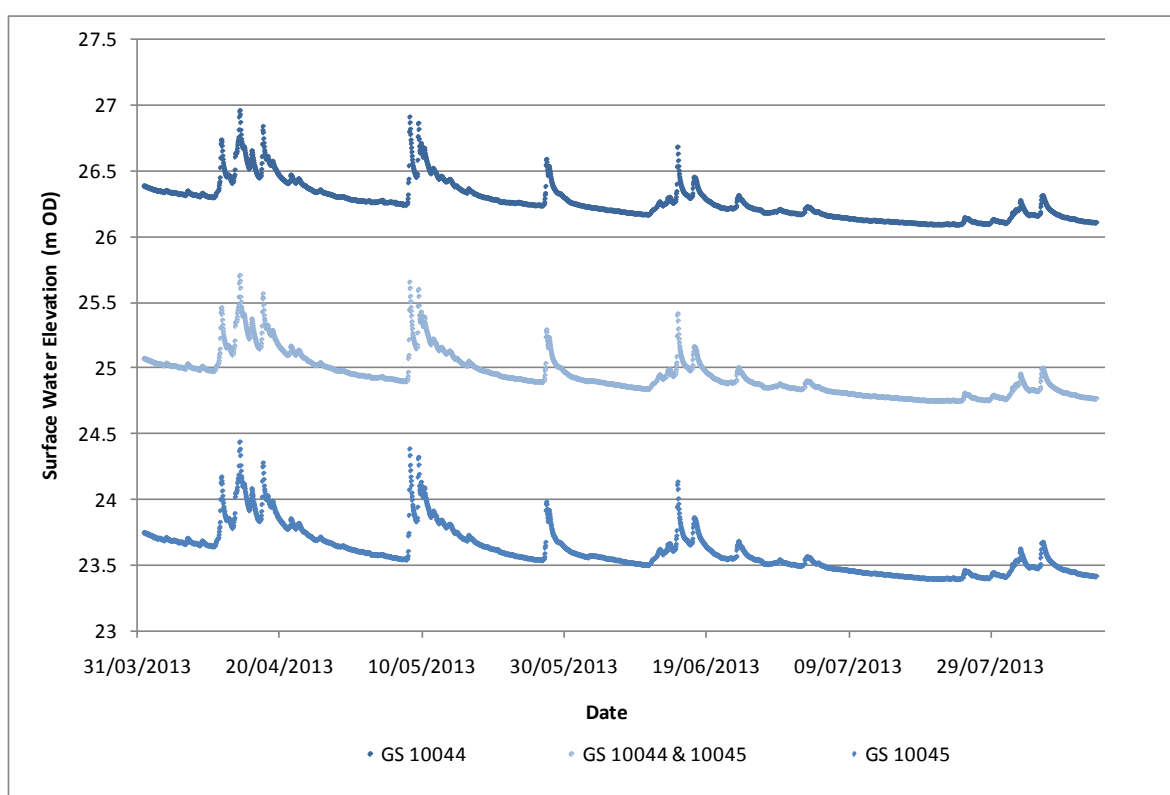
**Figure 9 Groundwater Elevation in the at Shelton Abbey from 20 March to 14 August 2013**

For MWET1 and MWET2 pair the reverse is true with the head slightly greater in the deep well MWET2. 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 no measurable hydraulic gradient between the alluvial well GW2/05 and top of bedrock (GW1/05) at this location (Table 18).

## 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 April to 31 August 2013 of 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. Combined with streambed characteristics and the elevations, they both influence the velocities and help define any apparent losses or gains in river flow.



**Figure 10 Elevation of the Avoca River at GS 10044 and GS 10045 at the Deep Adit Area from 1 April to 12 August 2013**

## 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 day 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 19 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 in August 2013.

**Table 19 Calculated Groundwater Gradients for August 2013**

Borehole Identifier	Date	Time	Groundwater Elevation (m OD)	Water Elevation at Perpendicular Stream Point (m OD)	Distance to Perpendicular Stream Point (m)	Gradient
MWDA1	12/08/2013	11:10	26.3	26.11	40	0.005
MWDA2	12/08/2013	11:05	26	26.11	40	-0.003
MWPF1	12/08/2013	14:30	26.8	26.11	44	0.016
MWET1	13/08/2013	09:55	25.8*	24.76**	72	0.014
MWET2	13/08/2013	09:55	25.9*	24.76**	72	0.016
GW1/05	13/08/2013	12:50	25.4*	24.76**	74	0.009
GW2/05	13/08/2013	12:50	25.4*	24.76**	74	0.009
SG104	12/08/2013	16:00	32.5*	23.42	142	0.064
MWSA2	14/08/2013	10:20	1.4	Not available	45	Not available

\* Borehole 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 for the emergency tailings area. Both figures demonstrate that there is a direct relationship between the river stage and the groundwater levels in both areas. Rises in river levels are accompanied by rises in groundwater levels.

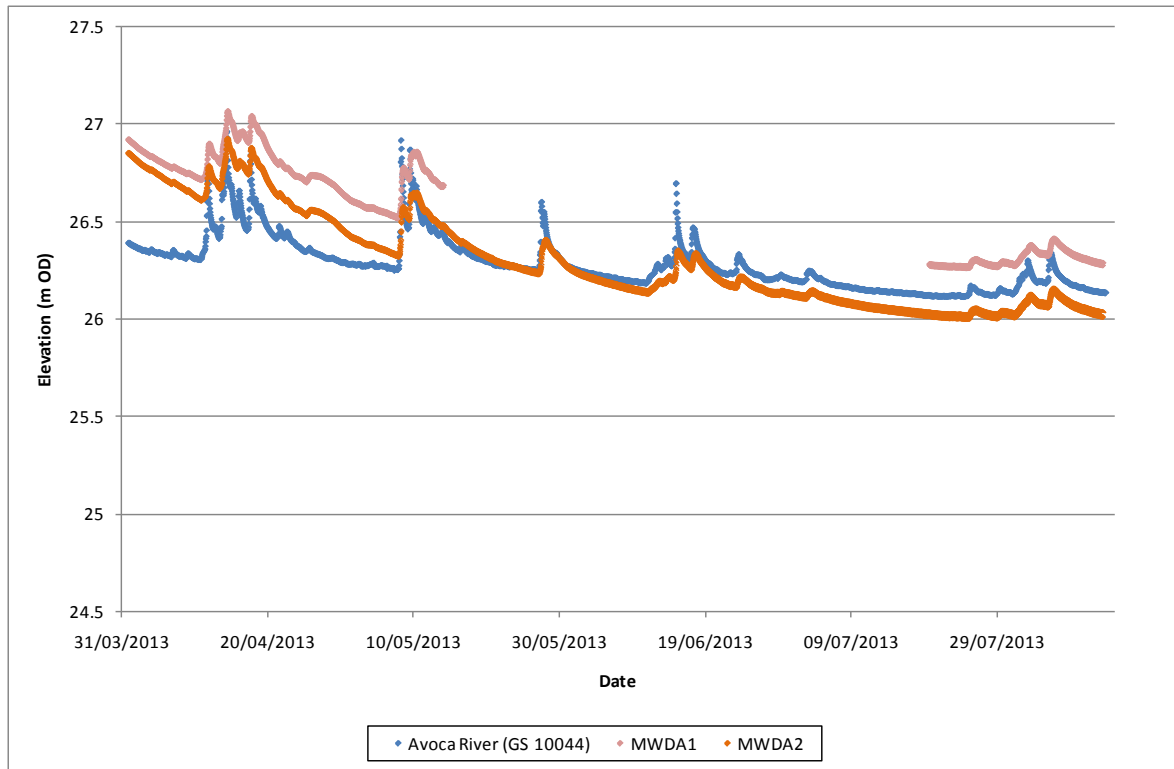
Both figures show that in the recorded data there are two significant hydrological (rainfall) events which resulted in groundwater levels rising. The first between 14 to 18 April and the second between 8 and 9 May, where the groundwater levels rose by up to 0.3 metres on both occasions in response to river levels which rose by up to 0.5 metres in the April event and 0.7 metres in the May event. The hydraulic response to rainfall and river stage is more muted in MWET1 than in MWET2, which is possibly due to the fact that the two wells are separated by a fine silt/clay layer at approximately 16 metres depth, which could act as a confining layer to MWET2.

Figure 12 and Figure 14 show the calculated gradient to the Avoca River over the same period at the deep adit area (MWDA1, MWDA2) and the emergency tailings area (MWET1, MWET2) based on hourly elevation data. Both figures show that as river stages change 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.

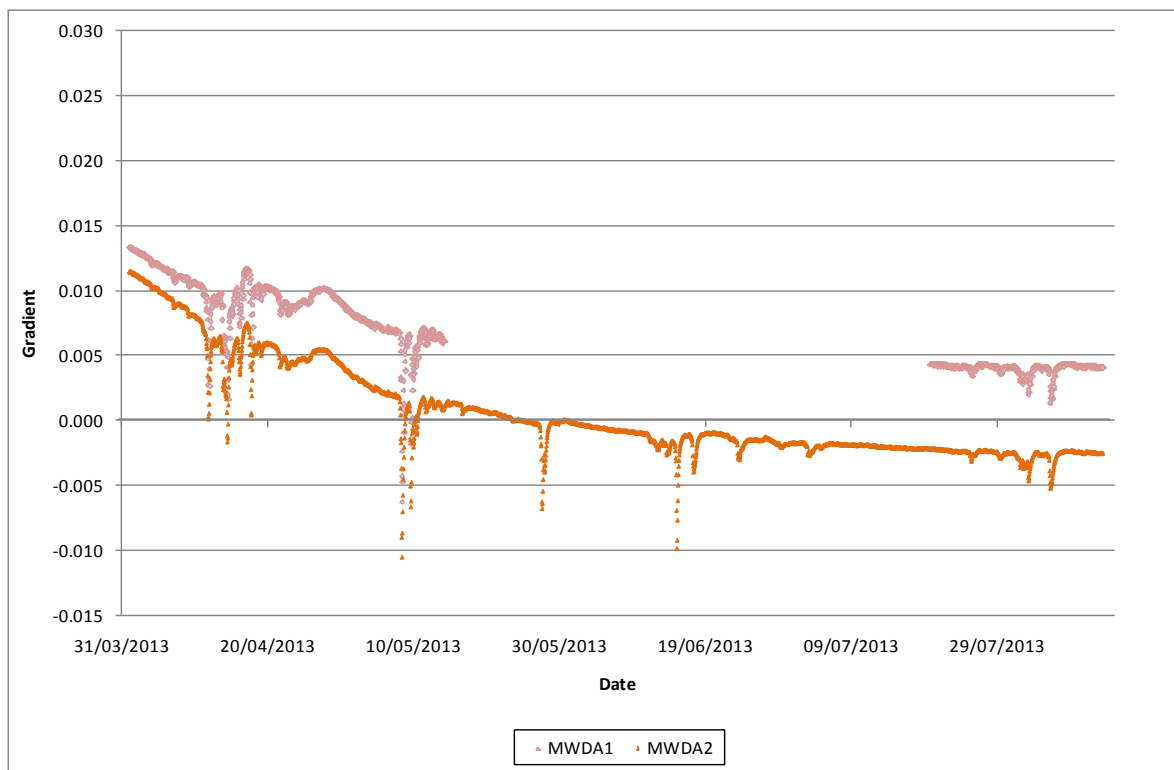
However, MWDA2 appears to respond less to the river than MWDA1 and may be more seasonally influenced (e.g. aquifer storage). Figure 11 and Figure 12 shows that the gradient is net positive until approximately 30 May and after this date the gradient is net losing. The minimum gradient was minus 0.011 while the average was 0.001. MWDA2 is located in the deeper alluvium and is 24.9 m (bgl) deep and therefore suggests that the deeper groundwater in the deep adit area does not discharge directly to the Avoca River throughout the entire monitoring period. As more data become available, further analysis of the gradients will be carried out to explore the apparent seasonal trends.

On 8 and 9 May a significant hydrological (rainfall) event which resulted in groundwater levels rising in MWDA1 and MWDA2 by approximately 0.3 metres. There were occasions over this period where a negative gradient can be observed between the river and MWDA1, as shown in Figure 12. During 8 and 9 May period the river water level also rose 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.

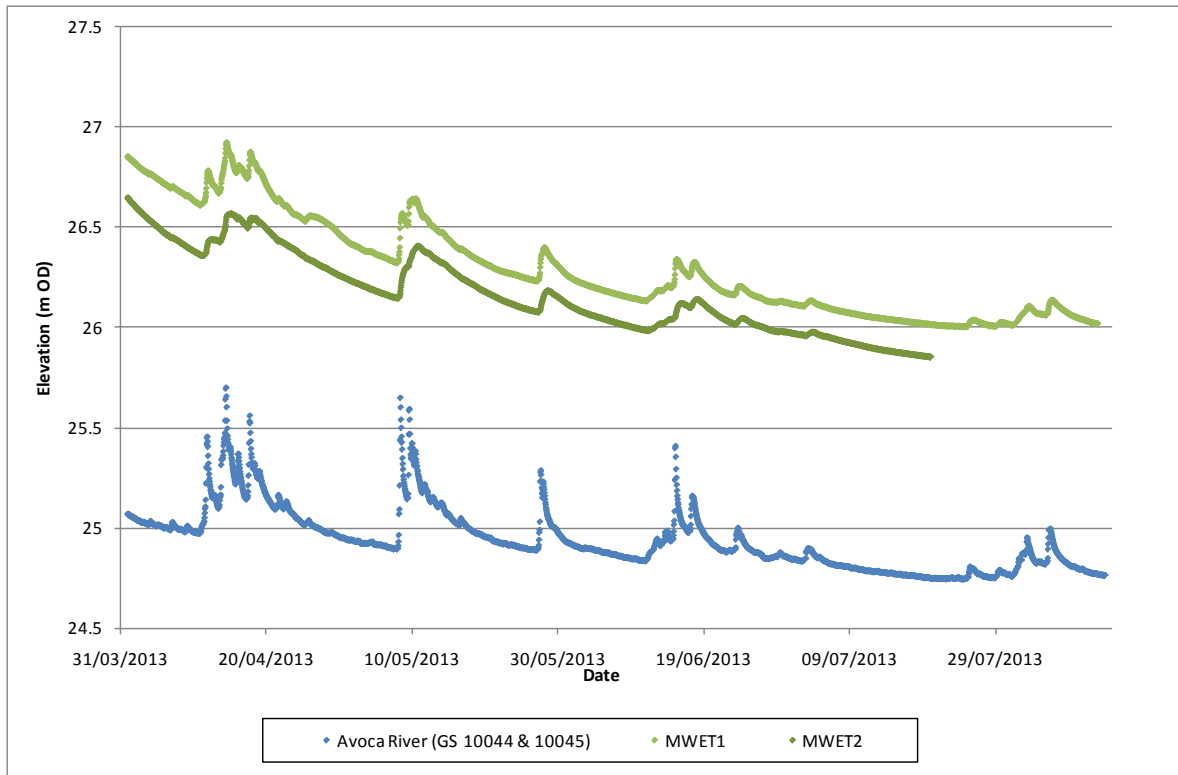
For MWET1 and MWET2 only positive gradients were observed with a minimum gradient of 0.017 (MWET2) and a maximum of 0.025 (MWET1) during the monitoring period. Note that the elevations are based on a GPS survey of the boreholes and the river water elevations was estimated using both the Whites Bridge GS elevation and the Wicklow Maintenance Yard County Council gauges because they are located equidistance between the gauges.



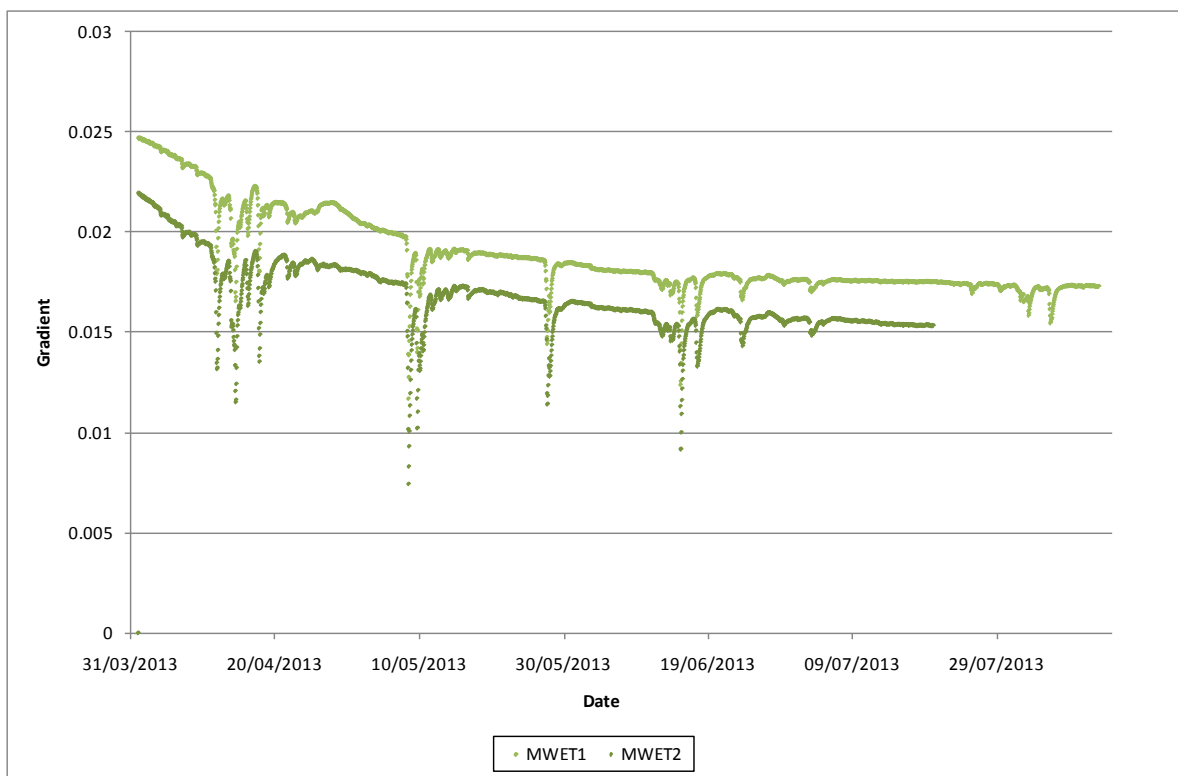
**Figure 11 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044) at the Deep Adit Area from 1 Apr to 12 August 2013**



**Figure 12 Calculated Groundwater Gradient to the Avoca River at the Deep Adit Area from 1 Apr to 12 August 2013**



**Figure 13 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044 & 10045) at the Emergency Tailings Area from 1 Apr to 13 August 2013**



**Figure 14 Calculated Groundwater Gradient to the Avoca River at the Emergency Tailings Area from 1 Apr to 13 August 2013**



## Section 7

# Summary and Recommendations

### 7.1 Summary of Findings

Nine groundwater monitoring wells were sampled and analysed in August 2013 and water levels were measured. Twenty surface water locations were sampled and analysed in August 2013 with flows measured at 14 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 sulphate and dissolved metals. SG104 located immediately downgradient of Ballymurtagh Landfill had the highest concentrations of dissolved metals especially aluminium, barium, cadmium and zinc, and included detections of tin and uranium.
- The Cronebane Shallow Adit was the adit discharge with the highest concentrations of metals including aluminium, copper 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 loads.
- In the Avoca River and tributaries, dissolved metal concentrations were low in comparison to the groundwater and the adit discharges; however, several exceedances of both the ecological and human health criteria occurred, namely for dissolved copper and zinc. Some dissolved metals including aluminium, zinc and iron were detected upgradient of the mining area at Ballinacleish Bridge and Lions Bridge which contribute background loads to the Avoca River.
- Whites Bridge (at the bridge) is the first sampling location along the Avoca River within the mining area where increases in dissolved metals concentrations are observed namely for; aluminium, copper and zinc. The dissolved metals concentrations remain reasonably consistent along the stretch from Whites Bridge to just DS of the Deep Adit. The only dissolved metal to significantly increase at the DS Deep Adit location was dissolved zinc.

- The Deep Adit and the Road Adit had similar loads of sulphate, dissolved copper and iron. However, the Deep Adit had much higher loadings of dissolved aluminium and zinc than the Road Adit. The calculated loads may be an over estimation of the direct loads discharging to the Avoca River due to precipitation of metals resulting in attenuation occurring within the ditches before discharging or infiltrating into the Avoca River. However the infiltration from the Deep Adit discharge ditch ultimately discharges as groundwater baseflow to the Avoca River as discussed in Section 6.
- The concentration time trends for Deep and Road adits and the Avoca Bridge location for dissolved copper and zinc, revealed a general declining trend in metal concentrations since 2001. The concentrations of dissolved aluminium, copper, iron and zinc are very similar in R1 and R2 for both the Deep and Road adits. However, dissolved copper in the Deep Adit was significantly lower in concentration in August (low-flow) 2013 compared with March (high-flow) 2013.
- As river stages change hydraulic gradients to or from the river also change. Gradients are predominantly positive which suggests that the Avoca River is a net gaining river from the alluvium during the monitoring period. The implication is that the spoil and the alluvial areas either side of the river contribute contaminant load to the river. However, MWDA2 appears to respond less to the river and may be more seasonally influenced (e.g. aquifer storage) and therefore suggests that the deeper groundwater in the deep adit area does not discharge directly to the Avoca River throughout the entire monitoring period.

## 7.2 Recommendations for the Monitoring Programme

Based on the data analysis and above conclusions the following recommendations are made:

- There were significant differences in the calculated loads of dissolved metals for the Deep Adit and the Road Adit to what was actually calculated for the Avoca River at the locations downstream of the respective discharges. This is due to the precipitation of metals resulting in attenuation occurring within the ditches before discharging or infiltrating into the Avoca River, as discussed in Section 5. In order to understand the direct loads that are actually discharging to the Avoca River from both adits, consideration should be given to collecting extra representative samples from both adits just before they discharge to the river. This will also allow for an estimate of the contaminant loads discharging to the Avoca River as diffuse flow between Whites Bridge and the Deep Adit confluence to be estimated; and
- It is noted that the DS Deep Adit sampling location was accessed by wading the Avoca River in August 2013 and as such access may not be feasible during high flow sampling rounds.

## Section 8

### References

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

CDM Smith (2013). Monitoring Report for the Avoca Mining Area Round 1 2013. June 2013. Document Reference: 95735/ DG 06.

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

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

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

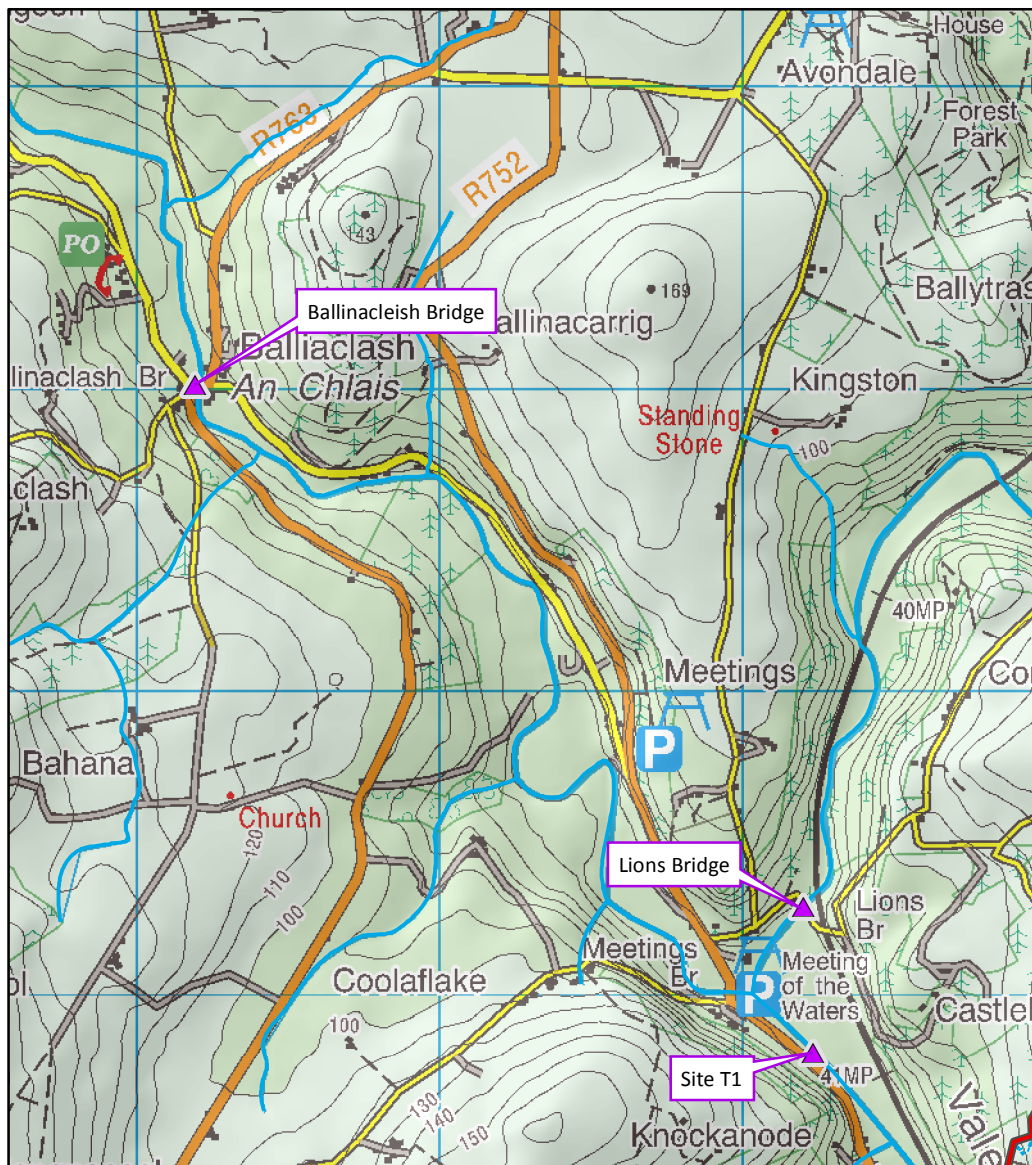
# Appendix A

## Figures

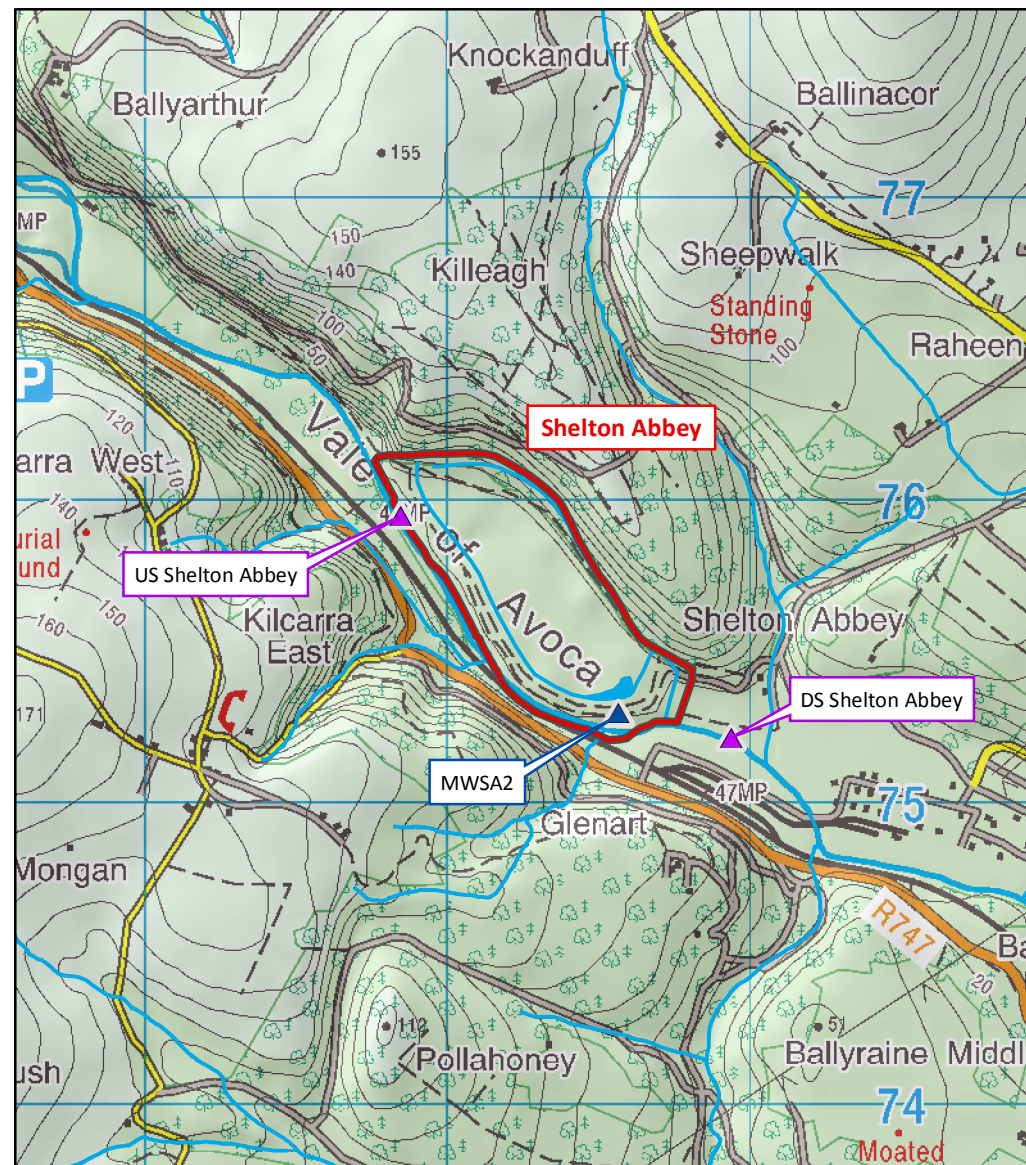








## Ballinacleish



## Shelton Abbey

### Map 2 - Avoca - Ballinacleish and Shelton Abbey

Drawn by: OC Date: 28/11/2013

Internal Project Reference: S:\CURRENT\_PROJECTS\95735\_Avoca\_Silver\02\_GIS\_Tasks\05\_MonRptR2\MXD\02\_AvocaMon2.mxd



Source: © Ordnance Survey Ireland.  
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### Legend

#### Sampling Locations

- ▲ Surface water
- ▲ Groundwater (Shelton Abbey)
- Rivers

#### Mines

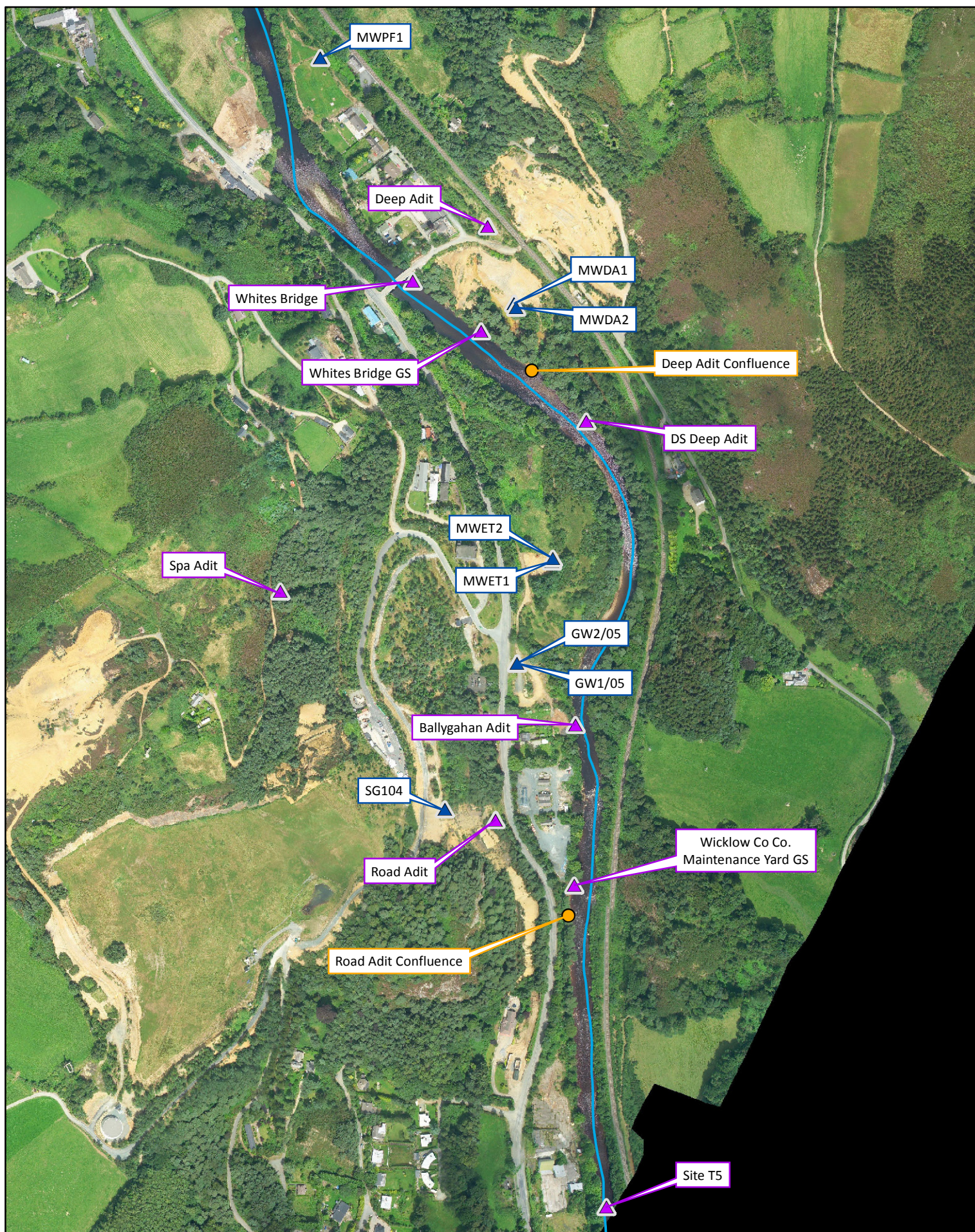
- Mining Areas

Scale is 1:25,000

0 125 250 500 750 1,000 m







### Map 3 - Avoca - Main Area - Groundwater (& Surface Water)

Drawn by: OC Date: 28/11/2013

Internal Project Reference: S:\CURRENT\_PROJECTS\95735\_Avoca\_Silver\  
02\_GIS\_Tasks\05\_MonRptR2\MXD\03\_AvocaMonGW.mxd



Source: © DCENR Lidar Survey

#### Legend

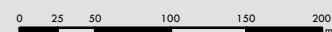
##### Sampling Locations

▲ Surface water

▲ Groundwater

— Rivers

Scale is 1:5,000







## Appendix B

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### Analytical Data Tables and Assessment Criteria



Table B-1 Comparison of Total Versus Dissolved Metals  
Concentrations in groundwater adits and surface water

SDG	Sample Description	Date Sampled	Suspended solids, Total	Aluminium (tot.unfilt)	Aluminium (diss.filt)	%RPD	Cadmium (tot.unfilt)	Cadmium (diss.filt)	%RPD	Copper (tot.unfilt)	Copper (diss.filt)	%RPD	Lead (tot.unfilt)	Lead (diss.filt)	%RPD	Zinc (tot.unfilt)	Zinc (diss.filt)	%RPD
			Units mg/l	µg/l	µg/l		µg/l	µg/l		µg/l	µg/l		µg/l	µg/l		µg/l	µg/l	
130814-44	MWDA1	12/08/2013	-	149000	146000	-2.03	70.7	64	-9.9	13600	12400	-9.2	13.4	3.25	-121.9	48100	42300	-12.8
130814-44	MWDA2	12/08/2013	-	94900	66600	-35.05	146	40.1	-113.8	7770	5380	-36.3	113	1.21	-195.8	46300	42300	-9.0
130814-44	MWPF1	12/08/2013	-	448	364	-20.69	0.551	0.525	-4.8	57.5	51.5	-11.0	1	0.702	-35.0	69.3	68.9	-0.6
130814-44	SG104	12/08/2013	-	1410000	938000	-40.20	908	287	-103.9	157000	92000	-52.2	439	77.8	-139.8	220000	152000	-36.6
130815-53	GW1/05	13/08/2013	-	94700	82300	-14.01	101	66.1	-41.8	14000	12000	-15.4	1570	1100	-35.2	64200	48600	-27.7
130815-53	GW2/05	13/08/2013	-	63500	56600	-11.49	20	16	-22.2	8090	7010	-14.3	4.55	0.478	-162.0	10400	8430	-20.9
130815-53	MWET1	13/08/2013	-	215000	178000	-18.83	23.9	20.4	-15.8	14500	10600	-31.1	8.85	5.72	-43.0	17600	13000	-30.1
130815-53	MWET2	13/08/2013	-	67.4	14.5	-129.18	1.97	3.84	64.4	9.74	4.25	-78.5	4.83	0.772	-144.9	4560	6100	28.9
130816-44	MWSA2	14/08/2013	-	84900	69500	-19.95	2.14	2.09	-2.4	161	141	-13.2	29	30.1	3.7	3800	4690	21.0
130817-28	Ballygahan Adit	15/08/2013	27.5	68000	60000	-12.50	71.7	41.2	-54.0	5890	3730	-44.9	280	155	-57.5	26200	19500	-29.3
130817-28	Cronebane Inter. Adit	15/08/2013	12	44700	44100	-1.35	109	96.1	-12.6	792	629	-22.9	1710	1290	-28.0	32700	27500	-17.3
130817-28	Cronebane Pit Lake	15/08/2013	<2	11700	11000	-6.17	14.8	13.7	-7.7	3390	2710	-22.3	1260	879	-35.6	4990	4260	-15.8
130817-28	Cronebane Shallow Adit	15/08/2013	9.5	440000	387000	-12.82	349	324	-7.4	6420	6290	-2.0	1360	1360	0.0	155000	133000	-15.3
130817-31	Deep Adit	15/08/2013	7.5	97800	94500	-3.43	132	89.7	-38.2	344	184	-60.6	2760	1990	-32.4	53700	44100	-19.6
130817-31	Road Adit	15/08/2013	2.5	15500	16400	5.64	14.7	13.7	-7.0	404	335	-18.7	516	374	-31.9	>5000	7810	43.3
130817-31	Vale View	15/08/2013	11	227	12.6	-178.96	0.25	0.05	-	2	7.46	115.4	2.78	0.949	-98.2	18.2	6.52	-94.5
130821-35	Ballinaclesh Bridge	19/08/2013	<4	212	174	-19.69	0.25	0.05	-	2	0.425	-	4.64	3.26	-34.9	26.3	24.6	-6.7
130821-37	DS Deep Adit	19/08/2013	<4	320	180	-56.00	0.25	0.229	-8.8	5.27	5.29	0.4	5.15	2.9	-55.9	109	92.6	-16.3
130821-35	Lions Bridge	19/08/2013	<4	66.2	36.2	-58.59	0.25	0.05	-	2	0.897	-76.1	1.82	1.06	-52.8	33.8	31.1	-8.3
130821-35	Site T1	19/08/2013	<4	152	117	-26.02	0.25	0.05	-	2	0.425	-	2.85	1.85	-42.6	24.9	23.3	-6.6
130821-37	Whites Bridge	19/08/2013	<4	226	184	-20.49	0.25	0.131	-62.5	9.46	10	5.5	2.72	1.6	-51.9	54.5	49.1	-10.4
130821-37	Whites Bridge GS	19/08/2013	<2	186	129	-36.19	0.25	0.349	33.1	2	4.18	70.6	2.51	1.74	-36.2	46.5	40.5	-13.8
130821-37	Wicklow CO.CO. Main. Yar	19/08/2013	3.5	837	256	-106.31	0.849	0.654	-25.9	26.4	17.1	-42.8	12.7	4.45	-96.2	311	278	-11.2
130821-36	Avoca Bridge	20/08/2013	4.44	920	161	-140.43	0.874	0.811	-7.5	22.5	10.8	-70.3	12.2	3.23	-116.3	394	301	-26.8
130821-36	Site T5	20/08/2013	6.5	1110	134	-156.91	0.837	0.915	8.9	30.2	14.7	-69.0	16.2	4.17	-118.1	454	350	-25.9
130816-44	Sulphur Brook	14/08/2013	<2	25	1.45	-	0.25	0.322	25.2	10.2	9.19	-10.4	1.29	0.532	-83.2	82.2	76.2	-7.6
130816-44	US Shelton Abbey	14/08/2013	2.5	252	33.2	-153.44	0.598	0.509	-16.1	9.88	5.76	-52.7	4.6	0.441	-165.0	266	201	-27.8
130816-44	DS Shelton Abbey	14/08/2013	<2	271	47.4	-140.45	0.579	0.504	-13.9	10.1	6.12	-49.1	3.52	6.25	55.9	281	230	-20.0

xx RPD greater than 50% i.e. dissolved metal result is greater that total metal

xx RPD less than 50% i.e. total metal result is greater that dissolved

Values less than the Limit of Detection (LOD) - Value taken to be 0.5 of the LOD

- Not analysed

RPD - Relative percent difference



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

Sample Description	Type	Date Sampled	Units	Specific Conductance @ deg.C (field) mS/cm																	pH (field) pH Units	Phosphate (ortho) as P mg/l	Sulphate mg/l	Sodium (diss.filt) mg/l	Suspended solids, Total mg/l	Aluminium (diss.filt) µg/l
				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											
Ecological Criteria				-	-	-	0.14	-	-	-	0.01	-	0.5	-	-	80 to 120*	4.5 to 9	0.075	-	-	-	-	1,900			
Human Health Criteria				-	-	-	0.3	250	-	2.5	0.05	-	1.5	50	0.5	-	6.5 to 9.5	-	250	200	-	200				
MWDA1	GW	12/08/2013	-		1	2.44	0.683	13.8	-	2.154	0.025	2340	0.015	0.15	0.025	1.8	2.94	0.01	1290	8.22	-		146000			
MWDA2	GW	12/08/2013	-		1	2.44	0.1	14.3	-	1.588	0.025	1700	1.43	0.377	0.025	1.2	3.66	0.0212	962	11.9	-		66600			
MWPF1	GW	12/08/2013	-		2.5	3.05	0.1	13.8	-	0.153	0.025	84	0.25	10.2	0.025	66.8	4.66	0.01	33.2	8.12	-		364			
SG104	GW	12/08/2013	-		1	2.44	2.97	15.4	-	9.071	0.025	15700	12.9	0.75	0.025	85	3.03	0.0202	9560	6.39	-		938000			
GW1/05	GW	13/08/2013	-		1	2.44	0.311	14.1	-	2.423	0.025	2970	1.55	0.676	0.025	1.2	3.82	0.023	1740	12.1	-		82300			
GW2/05	GW	13/08/2013	-		1	2.44	0.1	14.5	-	1.43	0.025	1530	1.45	6.49	0.025	60.2	3.56	0.023	856	10.2	-		56600			
MWET1	GW	13/08/2013	-		1	2.44	0.58	20.9	-	2.595	0.025	3400	0.015	0.02	0.025	4	3.31	0.023	1860	14.7	-		178000			
MWET2	GW	13/08/2013	-		70	85.4	0.1	15.2	-	3.493	0.025	3700	25.5	0.15	0.025	1.8	6.11	0.01	2400	25.3	-		14.5			
MWSA2	GW	14/08/2013	-		1	2.44	1.1	13.6	-	2.174	0.025	2910	4.13	0.02	0.025	1.6	3.94	0.023	1640	9.55	-		69500			
Ballygahan Adit	Adit	15/08/2013	-	412	1	2.44	11.3	43.8	24.3	2.342	0.025	2430	1.5	3.56	0.025	16.8	3.1	0.023	1350	32.1	27.5		60000			
Cronebane Inter. Adit	Adit	15/08/2013	-	318	1	2.44	0.361	13.3	14.9	1.121	0.025	1220	1.32	0.0809	0.025	6.4	2.89	0.023	623	8.82	12		44100			
Cronebane Pit Lake	Pit Lake	15/08/2013	-	65.7	1	2.44	0.31	11.1	3.5	0.563	0.025	316	0.25	2.55	0.025	86.8	3.11	0.01	148	6.58	1		11000			
Cronebane Shallow Adit	Adit	15/08/2013	-	1940	1	2.44	0.668	12	31.6	4.22	0.025	6090	2.73	2.8	0.025	38.7	2.52	0.023	3650	6.09	9.5		387000			
Deep Adit	Adit	15/08/2013	-	465	1	2.44	0.393	12.9	13	1.483	0.025	1750	1.06	0.096	0.025	8.2	3.52	0.023	999	7.61	7.5		96700			
Road Adit	Adit	15/08/2013	-	188	1	2.44	9.44	37.4	20.8	1.565	0.025	1630	2.34	3.93	0.108	34.8	3.72	0.01	811	26.2	2.5		16400			
Spa Adit	Adit	15/08/2013	-	-	-	-	-	-	-	2.882	-	-	-	-	-	98.4	2.6	-	-	-	-	-	203000			
Vale View	SW	15/08/2013	-	36.5	25	30.5	0.1	9.7	13.6	0.14	0.025	96.3	0.25	10.6	0.025	92.1	7.25	0.0206	16.2	5.34	11		12.6			
Sulphur Brook	SW	14/08/2013	-	2	26	31.72	0.1	16.1	3.5	0.153	0.025	122	0.25	21.8	0.025	100.1	6.8	0.0232	13.9	9.87	1		1.45			
Ballinacleish Bridge	SW	19/08/2013	-	2	5	6.1	0.1	6	19.6	0.043	0.025	31	0.25	1.98	0.025	103.1	5.5	0.01	1	4.03	2		174			
Lions Bridge	SW	19/08/2013	-	2	11.5	14.03	0.1	9.9	10	0.078	0.025	44.4	0.25	3.03	0.025	108	7.28	0.01	5.7	7.4	2		36.2			
Site T1	SW	19/08/2013	-	2	7.5	9.15	0.1	7.2	17.1	0.056	0.025	43	0.25	2.44	0.025	107.3	6.71	0.01	1	5.24	2		117			
Whites Bridge	SW	19/08/2013	-	2	9.5	11.59	0.1	8.6	14.8	0.07	0.025	48.8	0.25	2.8	0.025	104.3	6.84	0.01	5	6.36	2		184			
Whites Bridge GS	SW	19/08/2013	-	2	9	10.98	0.1	8.4	13.8	0.066	0.025	35.6	0.25	3.11	0.025	108.2	6.97	0.01	4.2	6.34	1		129			
DS Deep Adit	SW	19/08/2013	-	2	8	9.76	0.1	8.5	13.8	0.067	0.025	45.6	0.25	2.98	0.025	108.2	6.33	0.01	6.3	6.39	2		180			
Wicklow CO.CO. Main. Yard GS	SW	19/08/2013	-	2	5.5	6.71	0.1	8.6	14.6	0.079	0.025	57.8	0.25	3.23	0.025	104.4	6.06	0.01	13.1	6.55	3.5		256			
Site T5	SW	20/08/2013	-	2	4	4.88	0.265	8.9	17.4	0.099	0.025	40	0.25	2.73	0.025	103.5	5.84	0.01	20.6	6.24	6.5		166			
Avoca Bridge	SW	20/08/2013	-	2	5.5	6.71	0.1	8.8	11.9	0.089	0.025	51.1	0.25	2.99	0.025	107.1	6.09	0.01	17.8	6.18	4.44		161			
US Shelton Abbey	SW	14/08/2013	-	5.48	12.5	15.25	0.208	10.8	3.5	0.102	0.025	65.6	0.25	6.73	0.088	106.9	6.65	0.01	17	7.79	2.5		33.2			
DS Shelton Abbey	SW	14/08/2013	-	2	12.5	15.25	0.1	10.7	3.5	0.107	0.025	71.1	0.25	6.6	0.058	107.5	6.59	0.01	20	7.46	1		47.4			

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

Sample Description	Type	Date Sampled	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			-	25	4	0.45	3.4	5.1	5	-	7.2	1100	0.07	-	20	-	-	-	-	2.6	-	50
Human Health Criteria			5	10	-	5	50	-	2000	200	10	50	1	-	20	10	-	-	-	-	-	-
MWDA1	GW	12/08/2013	0.08	0.06	1.99	64	17.2	102	12400	78000	3.25	8000	0.005	0.12	56.8	0.195	0.75	0.48	0.18	6.49	0.254	42300
MWDA2	GW	12/08/2013	0.08	0.06	4.33	40.1	5.26	136	5380	74800	1.21	9680	0.005	0.12	72.4	1.05	0.75	0.48	0.18	4.81	0.12	42300
MWPF1	GW	12/08/2013	0.08	0.129	9.48	0.525	2.27	0.768	51.5	9.5	0.702	30.2	0.005	0.555	2.23	0.195	0.75	0.48	0.18	0.75	0.12	68.9
SG104	GW	12/08/2013	0.8	0.6	16.7	287	37.1	993	92000	46100	77.8	39600	0.0487	1.2	365	16.6	0.75	4.8	1.8	65.1	1.2	152000
GW1/05	GW	13/08/2013	0.8	0.6	9.83	66.1	8.34	274	12000	172000	1100	13300	0.005	1.2	81.1	6.53	7.5	4.8	1.8	7.5	1.2	48600
GW2/05	GW	13/08/2013	0.08	0.06	0.715	16	5.58	83.3	7010	165	0.478	4180	0.005	0.12	42.1	0.675	0.75	0.48	0.18	2.85	0.12	8430
MWET1	GW	13/08/2013	0.08	0.06	2.48	20.6	15.5	219	10600	131000	5.72	10200	0.005	0.12	93.9	0.195	0.75	1.88	0.18	9.86	0.781	13000
MWET2	GW	13/08/2013	0.8	6.6	13.1	3.84	2.65	134	4.25	103000	0.772	37800	0.005	1.2	24.8	4.12	0.75	4.8	1.8	7.5	1.2	6100
MWSA2	GW	14/08/2013	0.08	16.2	10.9	2.09	8.53	182	141	90400	30.1	37300	0.0111	0.295	141	1.31	0.75	0.48	0.18	5.88	1.33	4690
Ballygahan Adit	Adit	15/08/2013	0.8	66.8	9.1	41.2	1.1	127	3730	89600	155	11100	0.017	1.2	58.3	5.27	0.75	4.8	1.8	7.5	1.2	19500
Cronebane Inter. Adit	Adit	15/08/2013	0.8	7.34	9.16	96.1	1.1	64.7	629	1620	1290	2370	0.005	1.2	37.4	1.95	0.75	4.8	1.8	7.5	1.2	27500
Cronebane Pit Lake	Pit Lake	15/08/2013	0.08	0.177	11.5	13.7	0.616	22.1	2710	836	879	476	0.0102	0.12	6.94	0.195	0.75	0.48	0.18	0.75	0.12	4260
Cronebane Shallow Adit	Adit	15/08/2013	0.8	14.5	7.13	324	8.53	302	6290	4090	1360	10100	0.019	1.2	160	1.95	0.75	4.8	1.8	33.2	1.2	133000
Deep Adit	Adit	15/08/2013	0.8	1.29	6.07	89.7	0.703	99.7	184	68300	1990	4000	0.005	1.2	41.6	0.947	0.75	4.8	1.8	7.23	0.365	44900
Road Adit	Adit	15/08/2013	0.8	3.18	13.8	13.7	1.1	79.3	335	69500	374	6380	0.005	1.2	37.8	1.95	0.75	4.8	1.8	7.5	1.2	7810
Spa Adit	Adit	15/08/2013	0.8	0.6	5.15	45.1	5.8	280	9140	226000	101	9760	0.0195	1.2	67.6	1.95	0.75	4.8	1.8	7.5	1.2	15200
Vale View	SW	15/08/2013	0.08	0.381	6.74	0.05	0.868	0.03	7.46	9.5	0.949	4.28	0.0103	0.12	0.534	0.195	0.75	0.48	0.18	0.75	0.494	6.52
Sulphur Brook	SW	14/08/2013	0.194	0.502	7.8	0.322	0.568	0.03	9.19	9.5	0.532	6.78	0.005	0.308	0.642	0.195	0.75	0.48	0.18	0.75	0.12	76.2
Ballinacleish Bridge	SW	19/08/2013	0.507	0.655	8.31	0.05	0.405	0.101	0.425	106	3.26	12.2	0.005	0.549	0.834	0.195	0.75	0.48	0.18	0.75	0.12	24.6
Lions Bridge	SW	19/08/2013	0.534	0.748	4.54	0.05	0.365	0.03	0.897	73.5	1.06	3.88	0.005	0.993	0.663	0.195	0.75	0.48	0.18	0.75	0.12	31.1
Site T1	SW	19/08/2013	0.299	0.659	7.1	0.05	0.403	0.03	0.425	87.5	1.85	5.41	0.005	0.592	0.742	0.195	0.75	0.48	0.18	0.75	0.12	23.3
Whites Bridge	SW	19/08/2013	0.768	0.736	6.07	0.131	0.319	0.249	10	75.3	1.6	14.3	0.005	0.932	0.773	0.195	0.75	0.48	0.18	0.75	0.12	49.1
Whites Bridge GS	SW	19/08/2013	2.46	2.09	7.28	0.349	0.953	0.387	4.18	78.8	1.74	10.6	0.005	7.38	1.1	5.18	0.75	3.84	0.18	0.75	1.36	40.5
DS Deep Adit	SW	19/08/2013	0.785	0.754	6.09	0.229	0.332	0.357	5.29	121	2.9	16	0.005	1.05	0.801	0.423	0.75	0.48	0.18	0.75	0.12	92.6
Wicklow CO.CO. Main. Yard GS	SW	19/08/2013	1.33	0.751	6.25	0.654	0.381	1.18	17.1	235	4.45	53	0.005	2.09	1.14	1.2	0.75	1.83	0.18	0.75	0.12	278
Site T5	SW	20/08/2013	0.08	0.273	6.93	0.931	0.312	1.82	15.5	563	5.04	111	0.659	0.12	1.33	0.195	0.75	0.48	0.18	0.75	0.12	355
Avoca Bridge	SW	20/08/2013	0.08	0.288	6.43	0.811	0.11	1.43	10.8	232	3.23	88.5	0.005	0.12	1.13	0.195	0.75	0.48	0.18	0.75	0.12	301
US Shelton Abbey	SW	14/08/2013	0.08	0.465	5.97	0.509	0.543	0.916	5.76	47.9	0.441	60.2	0.005	0.715	0.995	0.195	0.75	0.48	0.18	0.75	0.12	201
DS Shelton Abbey	SW	14/08/2013	0.245	0.402	6.13	0.504	0.521	1.25	6.12	52.6	6.25	126	0.005	0.454	1.47	0.195	0.75	0.48	0.74	0.75	0.12	230

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