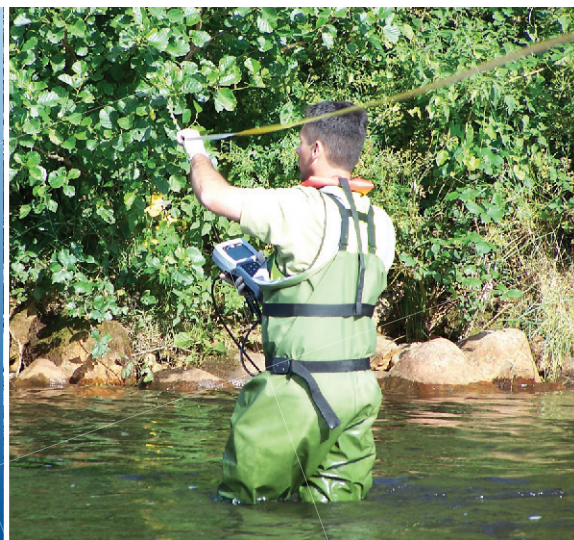


Department of Communications, Energy & Natural Resources



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

**Avoca Monitoring Report
- Round 1 (2014)**

Final



**CDM
Smith**



Document Control Sheet

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Section 1

Introduction

1.1 Objectives and Scope

The Department of Communications, Energy and Natural Resources (the Department) appointed CDM Smith Ireland Ltd (CDM Smith) to undertake a programme of environmental monitoring at the closed mine sites of Silvermines and Avoca for a three year period, commencing in 2013.

The scope of the field investigation activities was defined in the *Environmental Monitoring of Former Mining Areas of Silvermines and Avoca Monitoring Plan*, (Document Ref: 95735/40/DG01, dated 26 February 2013) and sampling activities were performed in accordance with the programme and procedures set out therein.

The Monitoring Report for the Avoca Mining Area presents an evaluation of the results of the field investigations carried out in February and March 2014. This report should be read alongside the Avoca Data Report (Document Ref: 95735/40/DG12, dated May 2014) which contains all field observations and laboratory analytical results collected during the monitoring programme.

1.2 Background of Avoca Mining Area

The Avoca mining area is located in the eastern foothills of the Wicklow Mountains, some 55 kilometres south of Dublin. The site includes the East and West Avoca mining areas and the Shelton Abbey Tailings Management Facility (TMF) which is located approximately 8 km to the south. The Avoca River divides the East and West Avoca mine sites and runs along the base of TMF.

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

1.3 Catchment Description

The Avoca Mines are located within the Avoca River Catchment which includes an area of 650 km². The East and West Avoca Mines are separated by the Avoca River, which flows through the Vale of Avoca, a noted tourist attraction. To the north of the mines, the Avoca River is formed at the "Meeting of the Waters" by the confluence of the Avonbeg and Avonmore Rivers, while 6.5 km to the south, it is joined by the Aughrim River and flows an additional 7.5 km to the sea at the fishing port of Arklow. Several smaller tributaries join the Avoca River close to the mine water discharges, including Sulphur Brook to the south of East Avoca Mines, and the Vale View and Red Road streams to the north and south respectively of West Avoca Mines.

1.4 Geology and Hydrogeology

1.4.1 Geology

The mineralised zone at Avoca is hosted in the Ordovician Avoca Formation that consists of tuffs (consolidated volcanic ash) and felsites (volcanic or extrusive igneous rocks) interbedded with slaty mudstones. The rocks trend northeast/southwest and are generally steeply-dipping to the southeast. Tight folds a few hundred metres wide are also present. The main ore zones, from which copper and pyrite (FeS_2) were extracted, occur as generally stratiform lenses up to a few tens of metres thick at the top of a sequence of tuffs and felsites.

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

There are three main ore types:

- Banded sulphides with more than 95% pyrite (FeS_2) accompanied by chalcopyrite (CuFeS_2), sphalerite (ZnS), and galena (PbS);
- Vein or disseminated ore invariably associated with silicification and containing pyrite and chalcopyrite; and
- Lead-zinc ore (galena and sphalerite) with banded pyrite.

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

The uppermost 30 to 60 m of the deposits have been oxidised. The most important minerals include iron oxides, chalcocite (Cu_2S) and covellite (CuS) together with various copper and iron oxides.

1.4.2 Hydrogeology

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

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

Overall water movement consists of three primary pathways:

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

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

1.5 Description of Adit Discharges

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

The Cronebane Intermediate Adit 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 was partially diverted into a marshy area to the east of the spoils area in February 2014, however very little flow was diverted and the marsh area was mostly dry.

The 850 Adit is also located northwest of Whites Bridge. In 2009 a significant volume of water was observed issuing from the adit for the first time. This was investigated on behalf of the Department by GWP who concluded that the water flow is most likely to be due to a collapse inside the mine, diverting water from the Deep Adit to higher levels. The flow from 850 Adit passes through a culvert under the railway embankment and then joins the Deep Adit discharge channel. Since the initial discharge in 2009, flow has been intermittently observed from the 850 Adit and it was added to the sampling programme in February 2014.

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. Works to the Road Adit channel were underway in June 2014.

The Spa Adit is located in West Avoca on a hillside approximately 150 m northwest of (and approximately 40 m above) the Wicklow County Council recycling centre. The discharge issues 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 24 and 26 February 2014, 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 **Error! Reference source not found.** and the data are contained in Appendix C of the Data Report.

2.1.2 Surface Water Sampling

Twenty-three surface water locations were sampled between 26 February and 2 March 2014, 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. Three new sample locations were added to the programme for this round of sampling, to include the 850 Adit discharge and to monitor the quality and the flow of the Deep Adit and Road Adit before they discharge to the Avoca River (Deep Adit Confluence and Road Adit Confluence). This was to determine if there was any measurable infiltration into the adit ditches between the portals and the confluences. In addition field parameters were also tested in the 850 Adit Confluence prior to it discharging to the Deep Adit ditch.

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.

Table 2 Location of Surface Water Monitoring Points

Site Name	Sample Site Description	Easting	Northing	Flow Measurement Method
Ballinacleish Bridge	Avoca River Location	317197	185010	Flow Meter
Lions Bridge	Avoca River Location	319207	183287	Float Method
Vale View	Tributary of Avoca River	319453	182396	Flow Meter
Site T1	Avoca River Location (Upstream of Whites Br.)	319239	182805	Calculated from Ballinacleish Bridge and Lions Bridge flows
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	Float Method & depth profile calculated based on measurements taken at low flow
Avoca Bridge	Avoca River above Avoca Bridge	320372	179932	Float Method
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
850 Adit*	Adit Discharge (at portal)	319919	182161	Flow Meter
850 Adit Confluence*	Adit Discharge (before entering Deep Adit Discharge)	319845	182122	Not required
Deep Adit	Adit Discharge (at portal)	319850	182123	Flow Meter
Deep Adit Confluence*	Adit Discharge (before entering Avoca River)	319896	181986	Flow Meter
Road Adit	Adit Discharge (at portal)	319858	181512	Measured from permanent flume
Road Adit Confluence*	Adit Discharge (before entering Avoca River)	319934	181443	Flow Meter
Cronebane Intermediate Adit	Adit Discharge	320320	182749	Flume
Cronebane Shallow Adit	Adit Discharge	320268	182646	Flume
Ballygahan Adit	Adit Discharge	319940	181610	Immeasurable as the flow was too low
Spa Adit	Adit Discharge	319637	181747	Bucket and stopwatch
Cronebane Pit Lake	Pit Lake	320933	183402	n/a

* New locations added to the sampling programme in round 3

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 15 locations (see Table 2) using various methods depending upon the quantity of flow to be measured and any safety concerns as detailed in the standard operating procedures in the Monitoring Plan. Surface water flow results are discussed in Section 5.1 and the data and measurement methodologies are contained in Appendix B of the Data Report. Methods included using a portable flume (for small discharges), a Marsh McBirney meter (flow meter) to measure flow velocities and depths at regular intervals across the streams by wading and for very small discrete discharges, a stop watch and calibrated volume container were used.

The Float Method was used when the location of the river was unsafe to wade. It is the least accurate method but provides a reasonable estimate. This method requires the measurement and calculation of the cross-sectional area of the channel as well as the time it takes an object to “float” a designated distance. The water depth was measured from a bridge at regular intervals (approximately 8 locations). The float was released into the channel upstream from the beginning of the section and measured the amount of time it takes the “float” to travel the marked section. This was repeated at least three times and the average time calculated.

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

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
AVGD01.3	GW Duplicate	Duplicate of MWSA2
AVDB01.3	GW Decontamination blank	DI water (Lennox Batch TE130418W) though pump after decon after site MWSA2
AVSD01.3	SW Duplicate	Duplicate of Road Adit Confluence
AVSD02.3	SW Duplicate	Duplicate of Wicklow Co Co Main. Yard GS
AVDB02.3	SW Decontamination blank	DI water (Lennox Batch TE130418W) poured over SW sampling beaker after decon at site Sulphur Brook
AVSR01.3	Standard Reference Material	Water ERA Lot #P222-740B
AVSR02.3	Standard Reference Material	Water ERA Lot #P222-740B
WB01.3	Water blank	Deionised water (Lennox Batch TE130418W)

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 NO₃ and nitrite as NO₂, orthophosphate, sulphate, total alkalinity as CaCO₃, 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.

Analysis of free cyanide for 8 of the 9 groundwater samples could not be performed as the samples were unsuitable. The laboratory attempted 4 times to run the samples and each time the analysis failed. It is believed that this was due to the low level of pH within the samples, which were affecting the instrument. There was insufficient sample provided to the laboratory for Ballygahan Adit due to the low flow, and analysis for the following parameters could not be performed; total silver, acidity, total dissolved solids, conductivity, alkalinity and COD.

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 AVSR01.3 and AVSR02.3) to evaluate laboratory accuracy. The certified SRM was supplied by ERA Certified Reference Materials and was Lot #P222-740B (Metals). The Certificate of Analysis is provided in Appendix G of the Data Report. The use of a blind or unknown SRM is the only method to independently verify the laboratory accuracy; 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 if both the original and duplicate results were less than the detection limit then the RPD was zero.

The majority of RPD values were significantly below 50 %. The RPDs for the key parameters aluminium (1 to 9 %), copper (3 to 4%), manganese (0 to 10 %) and zinc (2 to 2.5 %) are good as they are below 10 %.

There was only one RPD that was above 50 % as highlighted in Table 4, which was dissolved nickel for the Wicklow CoCo Maintenance Yard GS/AVSD02.3 (RPD 81 %) sample pair. The highest reported value of the duplicate pair is selected for interpretive use in Section 4 therefore providing a conservative evaluation.

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

Dissolved Metal	LOD (µg/l)	MWSA2	AVGD01.3	RPD	Road Adit Con.	AVSD01.3	RPD	WCC Main. Yard GS	AVSD023	RPD
Aluminium	<2.9	46900	51700	-9.7	14700	14800	-0.7	188	179	4.9
Antimony	<0.16	<0.16	<0.16	0	<1.6*	<1.6*	0	<0.16	<0.16	0
Arsenic	<0.12	14.2	13.6	4.3	3.31	3.44	-3.9	0.16	0.134	17.7
Barium	<0.03	8.74	8.47	3.1	17.8	18.7	-4.9	5.66	5.48	3.2
Cadmium	<0.1	1.62	1.64	-1.2	7.26	6.79	6.7	0.364	0.359	1.4
Chromium	<0.22	7.45	7.37	1.1	<2.2*	<2.2*	0	0.309	0.397	-24.9
Cobalt	<0.06	151	148	2.0	225	224	0.4	0.631	0.678	-7.2
Copper	<0.85	123	128	-4.0	334	325	2.7	21.1	20.4	3.4
Iron	<19	76400	78600	-2.8	249000	255000	-2.4	87.8	91	-3.6
Lead	<0.02	27.3	28	-2.5	216	218	-0.9	3.26	3.19	2.2
Manganese	<0.04	28100	31100	-10.1	19500	19700	-1.0	48.4	49.2	-1.6
Mercury	<0.01	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01	0
Molybdenum	<0.24	<0.24	<0.24	0	<2.4*	<2.4*	0	<0.24	<0.24	0
Nickel	<0.15	117	117	0	97.3	91.3	6.4	1.35	0.569	81.4
Selenium	<0.39	0.749	0.674	10.5	4	4.46	-10.9	<0.39	<0.39	0
Silver	<1.5	<1.5	<1.5	0	<15*	-	-	<1.5	<1.5	0
Thallium	<0.96	<0.96	<0.96	0	<9.6*	<9.6*	0	<0.96	<0.96	0
Tin	<0.36	<0.36	<0.36	0	<3.6*	<3.6*	0	<0.36	<0.36	0
Uranium	<1.5	5.85	5.89	-0.7	<15*	<15*	0	<1.5	<1.5	0
Vanadium	<0.24	0.816	0.951	-15.3	<2.4*	<2.4*	0	<0.24	<0.24	0
Zinc	<0.41	4250	4170	1.9	19900	20400	-2.5	121	118	2.5

Notes:

Bold indicates an exceedance in the Duplicate RPD acceptance criteria

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

3.2.2 Decontamination Blanks

Two decontamination blanks were created by pumping 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.

Detections were observed for eleven dissolved metals ranging from 0.045 to 17.6 µg/l. Five of the metals (barium, chromium, manganese, nickel and zinc) were also detected in the DI water blank. The levels of detections in the decontamination blanks were similar to those found in the DI water blank. Detections of dissolved antimony, arsenic, cobalt, copper, lead and selenium were also found in the decontamination blanks but not the DI water blank.

In total there were fourteen low level detections of dissolved metals in the decontamination blanks. Only three of these were greater than ten times the detection limit, manganese in SMDB01.3 (1.24 µg/l) and zinc in both AVDB01.3 and AVDB02.3 (5.7 and 17.6 µg/l). The highest detections of dissolved metals in the DI water blank and the two decontamination blanks were for dissolved zinc which ranged from 5.7 to 17.6 µg/l.

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. Two exceptions were the detection of arsenic and chromium in AVDB02.3 which were determined to be 114% and 74.9% of the preceding environmental sample, respectively. Chromium was detected in the DI water blank and dissolved arsenic was only slightly above the detection limit in the decontamination blank and environmental sample 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). It was noted that the parameters detected in the method blanks for both sample batches were similar to those in the decontamination blank samples, as follows:

- Three detections of parameters were present in method blank for Sample Batch 140228-68 that occurred in the decontamination blank from the same batch (see Table 5): manganese 0.042 µg/l, molybdenum 0.241 µg/l and tin 0.498 µg/l.
- Dissolved antimony at 0.271 µg/l was detected in the method blank for Sample Batch 140307-117 and also occurred in the decontamination blank from the same batch (see Table 5).

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)

Dissolved Metal	LOD (µg/l)	Water Blank WB01.3 (µg/l)	Decon blank AVDB01.3 (µg/l)	Laboratory Method Blank (µg/l)	Decon blank AVDB02.3 (µg/l)	Laboratory Method Blank (µg/l)
<i>Sample batch:</i>		<i>140228-68</i>			<i>140307-117</i>	
Aluminium	<2.9	<2.9	<2.9	<2.9	<2.9	<2.9
Antimony	<0.16	<0.16	<0.16	0.859	1.4	<i>0.271</i>
Arsenic	<0.12	<0.12	<0.12	<0.12	0.176	<0.12
Barium	<0.03	0.128	0.066	<0.03	0.045	<0.03
Cadmium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chromium	<0.22	0.437	<0.22	<0.22	0.28	<0.22
Cobalt	<0.06	<0.06	0.092	<0.06	<0.06	<0.06
Copper	<0.85	<0.85	2.47	<0.85	<0.85	<0.85
Iron	<19	<19	<19	<19	<19	<19
Lead	<0.02	<0.02	0.083	<0.02	0.06	<0.02
Manganese	<0.04	0.109	1.24	<i>0.0420</i>	0.336	<0.04
Mercury	<0.01	<0.01	<0.01	NP	<0.01	NP
Molybdenum	<0.24	<0.24	<0.24	0.241	<0.24	<0.24
Nickel	<0.15	0.151	<0.15	<0.15	<0.15	<0.15
Selenium	<0.39	<0.39	<0.39	<0.39	0.631	<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	0.498	<0.36	<0.36
Uranium	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
Vanadium	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
Zinc	<0.41	8.73	17.6	<0.41	5.7	<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 AVSR01.3 and AVSR02.3) 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, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, selenium, thallium, vanadium and zinc are in excellent agreement with the certified value (%R ranged from 90 to 108 %).

One of the reported value for dissolved nickel (ID AVSR02.3) was low at 90 % and 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.

The reported values for dissolved iron were low for both samples at 82 % and 87 % R. The reported values for dissolved silver were low for both samples at 86 % R. The values were just outside the acceptable range indicating that there may be a bias in the results for dissolved iron and silver. Dissolved iron and silver reported values were biased low and any use of these values should be noted with this observation.

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

Dissolved Metal	Certified Value (µg/l)	Acceptance Limits		AVSR01.3 (µg/l)	% R	AVSR02.3 (µg/l)	% R
		Lower (%)	Upper (%)				
Aluminium	420	87.4	114	452	108	419	100
Antimony	429	86.9	111	421	98	393	92
Arsenic	342	87.1	111	354	104	332	97
Barium	702	90.9	109	708	101	681	97
Cadmium	203	88.7	106	200	99	186	92
Chromium	229	90.8	109	233	102	219	96
Cobalt	409	92.9	111	420	103	389	95
Copper	490	90.4	109	486	99	457	93
Iron	836	90.1	111	682	82	729	87
Lead	741	90.1	110	778	105	725	98
Manganese	483	92.3	109	504	104	468	97
Molybdenum	273	89.7	109	267	98	250	92
Nickel	360	91.1	109	348	97	324	90
Selenium	638	87.5	111	641	100	595	93
Silver	572	89.7	110	494	86	493	86
Thallium	342	87.7	111	349	102	330	96
Vanadium	211	91.0	107	216	102	206	98
Zinc	1690	90.5	110	1650	98	1630	96

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's.

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

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

3.4 Summary of Data Checks

3.4.1 Field 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 36 % which is good. The RPDs between laboratory and field pH were also good at less than 21 %. The field pH and conductivity are more representative of actual conditions and are used for interpretive purposes. Overall the %RPDs between the field and laboratory data are considered satisfactory.

Table 7 Field 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	2.79	2.75	1.4	3.910	4.471	-13.4
MWDA2	3.9	3.82	2.1	1.400	1.581	-12.1
MWPF1	5.97	4.83	21.1	0.145	0.149	-2.7
MWET1	3.48	3.38	2.9	1.930	2.093	-8.1
MWET2	6.35	6.37	-0.3	3.160	3.368	-6.4
GW1/05	4.07	4.25	-4.3	2.510	2.693	-7.0
GW2/05	3.68	3.73	-1.3	1.530	1.653	-7.7
SG104	2.97	2.94	1.0	7.910	8.605	-8.4
MWSA2	4.12	3.93	4.7	2.100	2.297	-9.0
Cronebane Inter. Adit	3.05	2.74	10.7	1.230	1.451	-16.5
Cronebane Pit Lake	3.25	2.96	9.3	0.459	0.541	-16.4
Cronebane Shallow Adit	2.9	2.72	6.4	2.500	2.753	-9.6
850 Adit	2.93	2.78	5.3	1.330	1.537	-14.4
850 Adit Confluence	ND	2.82	-	ND	1.485	-
Ballygahan Adit	3	2.99	0.3	ND	2.533	-
Deep Adit	3.37	3.49	-3.5	1.190	1.284	-7.6
Deep Adit Confluence	3.15	3.03	3.9	1.230	1.410	-13.6
Road Adit	4.31	4.4	-2.1	2.380	2.575	-7.9
Road Adit Confluence	4.19	4.49	-6.9	2.360	2.576	-8.8
Spa Adit	2.82	2.74	2.9	1.860	2.094	-11.8
Ballinacleish Bridge	6.7	5.84	13.7	0.056	0.061	-8.9
Lions Bridge	7	6.22	11.8	0.065	0.072	-10.8
Site T1	6.75	6.57	2.7	0.065	0.072	-9.6
Vale View	7.01	6.88	1.9	0.137	0.152	-10.4
Whites Bridge	7.03	6.81	3.2	0.071	0.076	-7.4
Whites Bridge GS	6.84	6.64	3.0	0.070	0.082	-16.4
DS Deep Adit	5.9	5.46	7.7	0.090	0.112	-22.2
Wicklow CO.CO. Main. Yard GS	6.72	5.62	17.8	0.075	0.108	-36.3
Site T5	6.13	5.85	4.7	0.104	0.118	-12.6
Avoca Bridge	6.72	6.2	8.0	0.081	0.091	-11.4
Sulphur Brook	7.37	6.64	10.4	0.141	0.153	-8.2
US Shelton Abbey	6.85	5.8	16.6	0.089	0.091	-2.7
DS Shelton Abbey	6.98	5.83	18.0	0.085	0.093	-8.6

Notes:

Bold indicates an exceedance in acceptance limits

ND Not Determined

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:

$$(\text{TDS-Calcul} - \text{TDS-Measured}) / \text{TDS-Measured} \times 100\%$$

TDS-Calcul 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-Measured) 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 outside the range. The mass balance, in the majority of cases (bolded values) did not meet these criteria. Most values were less than 30 %; which overall is very good considering the low pH, high TDS and complex nature of the high metal concentrations of many of the samples. The fact that the mass balance values are mostly negative suggests that either one or more parameters were under-reported by the analytical laboratory and/or one or more parameters present within the samples were not analysed (e.g. silica).

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	4766	6200	-1.0	-0.6	-23.1	Missing cations
MWDA2	1337	1700	1.2	2.7	-21.4	Missing anions
MWPF1	75	94.4	0.0	-0.4	-20.1	Missing cations
GW1/05	2789	3430	0.1	0.1	-18.7	Missing anions
GW2/05	1410	1820	-0.9	-2.1	-22.5	Missing cations
MWET1	1951	2520	0.2	0.3	-22.6	Missing anions
MWET2	3236	3930	-7.4	-7.6	-17.7	Missing cations
SG104	12262	15700	2.9	0.7	-21.9	Missing anions
MWSA2	2151	2600	-2.0	-3.1	-17.3	Missing cations
Cronebane Intermediate Adit	1005	1390	-1.5	-4.8	-27.7	Missing cations
Cronebane Pit Lake	199	241	-1.0	-17.4	-17.4	Missing cations
Cronebane Shallow Adit	2545	3540	-1.5	-1.8	-28.1	Missing cations
850 ADIT	961	1290	-1.5	-5.0	-25.5	Missing cations
Deep Adit	1048	1380	0.6	1.8	-24.1	Missing anions
Deep Adit Confluence	987	1340	-0.6	-2.0	-26.3	Missing cations
Road Adit	2330	2890	2.0	2.8	-19.4	Missing anions
Road Adit Confluence	2377	2860	-0.4	-0.5	-16.9	Missing cations
Spa Adit	1486	2010	-2.3	-4.9	-26.1	Missing cations
Ballinacleish Bridge	26	44	0.0	-5.2	-39.9	Missing cations
DS Deep Adit	51	58.8	-0.1	-5.4	-13.4	Missing cations
Lions Bridge	32	52	0.0	-3.9	-39.4	Missing cations
Site T1	32	46.7	-0.1	-6.9	-32.2	Missing cations
Vale View	80	103	-0.2	-5.9	-22.3	Missing cations
Whites Bridge	35	62.5	-0.1	-10.5	-43.7	Missing cations
Whites Bridge GS	37	54.3	-0.1	-9.4	-32.0	Missing cations
Avoca Bridge	48	41.3	0.0	0.9	17.3	Too many cations
Site T5	73	44.4	0.4	17.6	63.5	Too many cations
Sulphur Brook	86	74.7	-0.1	-2.0	15.2	Too many anions
Wicklow Co.Co. Maintenance Yard GS	44	29.3	0.0	1.2	50.1	Too many cations
DS Shelton Abbey	49	54.7	0.0	0.1	-9.9	Missing anions
US Shelton Abbey	47	47.8	0.0	1.2	-1.8	Missing anions

Notes:

Bold indicates an exceedance of the acceptance criteria

The specific conductivity (SC) of the solutions can be used to further evaluate the internal consistency. The specific conductivity/total dissolved solids (SC/TDS) ratio of natural waters varies, but typically ranges from ranges from 1 to 1.8. An evaluation can be made of these analyses by examining the ratios of SC/TDS (see Table 9). The low ratios of less than 1 are generally due to samples with high TDS and SC. In these samples, there were also high sulphate values, and at high concentrations of sulphate, ion pairing occurs which results in the SC values being lower (i.e. not all the sulphate will provide independent anions). The one exception on the high range (Wicklow Co Co Maintenance Yard GS with ratio of 3.7 for SC/TDS-Meas) had the lowest measured TDS. At these low levels, the relationships are less accurate. The majority of the ratios in Table 9 are within the range for natural waters and therefore the analyses are considered reliable.

Figure 1 shows the relationship between specific conductivity and TDS. There is a strong positive correlation between SC with both the calculated ($R^2=0.95$) and measured ($R^2=0.95$) TDS.

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

Sample Description	Sample Type	Specific Conductance	TDS (Calc)	TDS (Meas)	Ratio	
		(uS/cm)	(mg/l)	(mg/l)	SC/ TDS- Calc	SC/ TDS - Meas
MWDA1	GW	4471	4766	6200	0.9	0.7
MWDA2	GW	1581	1337	1700	1.2	0.9
MWPF1	GW	149	75	94	2.0	1.6
GW1/05	GW	2693	2789	3430	1.0	0.8
GW2/05	GW	1653	1410	1820	1.2	0.9
MWET1	GW	2093	1951	2520	1.1	0.8
MWET2	GW	3368	3236	3930	1.0	0.9
SG104	GW	8605	12262	15700	0.7	0.5
MWSA2	GW	2297	2151	2600	1.1	0.9
Cronebane Inter. Adit	Adit	1451	1005	1390	1.4	1.0
Cronebane Pit Lake	Pit Lake	541	199	241	2.7	2.2
Cronebane Shallow Adit	Adit	2753	2545	3540	1.1	0.8
850 Adit	Adit	1537	961	1290	1.6	1.2
Deep Adit	Adit	1284	1048	1380	1.2	0.9
Deep Adit Confluence	Adit	1410	987	1340	1.4	1.1
Road Adit	Adit	2575	2330	2890	1.1	0.9
Road Adit Confluence	Adit	2576	2377	2860	1.1	0.9
Spa Adit	Adit	2094	1486	2010	1.4	1.0
Ballinacleish Bridge	SW	61	26.4	44.0	2.3	1.4
DS Deep Adit	SW	112	50.9	58.8	2.2	1.9
Lions Bridge	SW	72	31.5	52.0	2.3	1.4
Site T1	SW	72	31.7	46.7	2.3	1.5
Vale View	SW	152	80.1	103	1.9	1.5
Whites Bridge	SW	76	35.2	62.5	2.2	1.2
Whites Bridge GS	SW	82	36.9	54.3	2.2	1.5
Site T5	SW	118	72.6	44.4	1.6	2.7
Sulphur Brook	SW	153	86.1	74.7	1.8	2.0
Wicklow CO.CO. Main. Yard GS	SW	108	44.0	29.3	2.5	3.7
Avoca Bridge	SW	91	48.5	41.3	1.9	2.2
US Shelton Abbey	SW	91	46.9	47.8	1.9	1.9
DS Shelton Abbey	SW	93	49.3	54.7	1.9	1.7

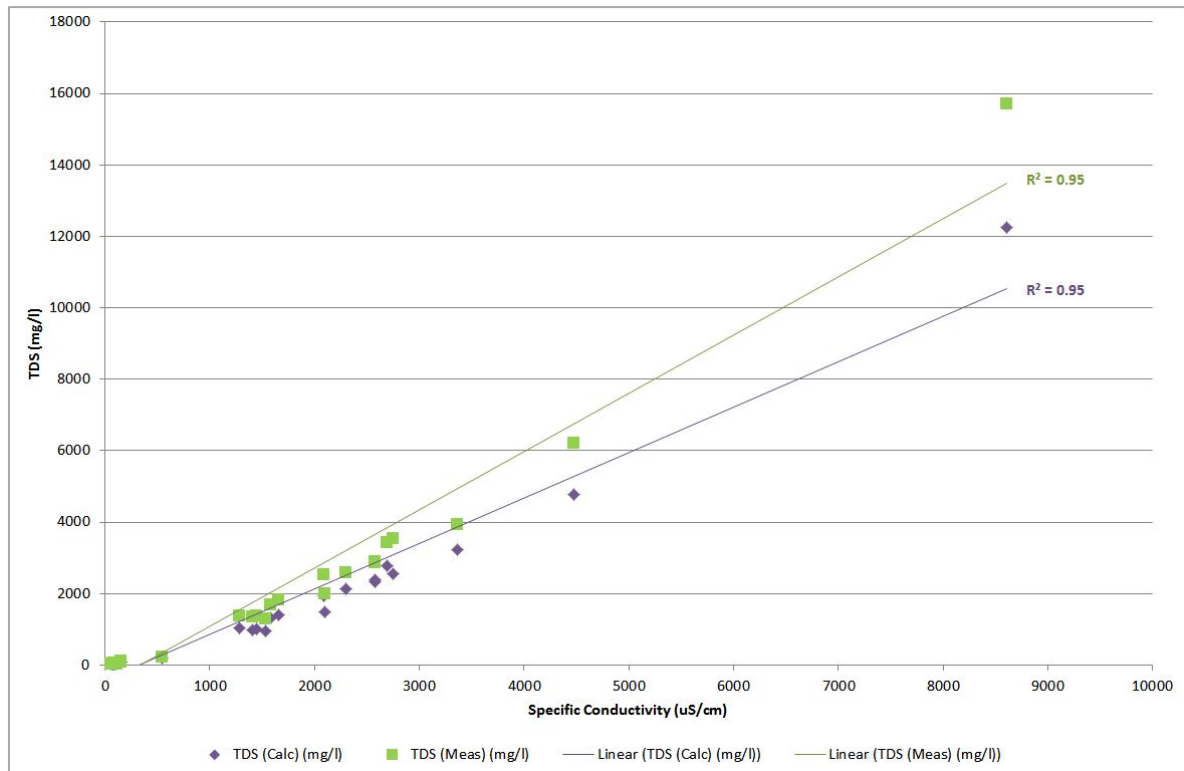


Figure 1 Relationship of Specific Conductivity and Total Dissolved Solids (TDS)

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 some of the key metals aluminium, copper, iron and zinc, by calculating ratio of total and dissolved metals to evaluate if the concentrations were distinguishable. Table B-1 in [Appendix B](#) shows the full tabulation of results. The dissolved metals were generally equal to or close to the total metals, indicating that the majority of the aluminium, copper, iron and zinc present were dissolved.

The dissolved concentrations were higher than the total in about 30% of the zinc results. This was checked with ALcontrol alongside the AQC and blank data and no issues have been found. They confirmed that the majority of the zinc results where the total is lower than the dissolved are within their margin for difference between repeats. There were a couple of exceptions where the concentration was low and the difference may have been induced by the filtration procedure. Zinc contamination is known to be induced by all membrane filter materials and can result in overestimated zinc detections (Hedberg et al., 2011). This effect is already minimised in the field by allowing the first 10 ml of the filtered water to be wasted before the filtered sample is collected. Overall, the results are considered acceptable.

Section 4

Results and Evaluations

This section provides a statistical summary of the analytical results for groundwater and surface water and a comparison of the analytical results against selected assessment criteria. An analysis of loading and time trends is provided in Section 5 and groundwater levels are discussed in Section 6.

All the laboratory reports and analytical data are contained in Appendix F of the Data Report.

4.1 Statistical Summary of Analytical Results

4.1.1 Groundwater Sample Results

Table 10 provides a summary of the reported results of the nine groundwater samples. Included in the table are the minimum, maximum, mean and standard deviation (SDEV). Where the reported values were below the detection limit, the values were substituted with a value of half the limit of detection. The highest reported value of the field duplicate pair was used where applicable.

Table 10 Summary of Dissolved Metal Concentrations in Groundwater

Dissolved Metal	LOD (µg/l)	Number	Number of Detections	Minimum (µg/l)	Maximum (µg/l)	Mean (µg/l)	SDEV
Aluminium	<2.9	9	9	126	886000	187000	287000
Antimony	<0.16	9	1	0.08	8	2.27	3.29
Arsenic	<0.12	9	3	0.06	14.2	3.39	4.79
Barium	<0.03	9	9	2.28	22.9	9.58	6.47
Cadmium	<0.1	9	9	0.599	592	106	189
Chromium	<0.22	9	8	1.1	74.1	19	23.5
Cobalt	<0.06	9	9	2.21	1090	285	324
Copper	<0.85	9	9	8.88	83100	17700	27700
Iron	<19	9	9	23.3	266000	75100	82600
Lead	<0.02	9	9	0.37	1700	199	563
Manganese	<0.04	9	9	98.8	45500	19200	15300
Mercury	<0.01	9	2	0.005	0.0873	0.02	0.03
Molybdenum	<0.24	9	3	0.12	12	2.31	3.72
Nickel	<0.15	9	9	2.41	449	123	133
Selenium	<0.39	9	3	0.195	7.83 (19.5*)	4.06	6.22
Silver	<1.5	9	0	0.75	(75*)	-	-
Thallium	<0.96	9	0	0.48	(48*)	-	-
Tin	<0.36	9	0	0.18	(18*)	-	-
Uranium	<1.5	9	3	0.75	17.3 (75*)	14.7	23.0
Vanadium	<0.24	9	1	0.12	0.951 (12*)	-	-
Zinc	<0.41	9	9	88.3	159000	41000	51900

Notes:

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

* LOD was raised due to a dilution that was carried out on the sample. Where there were detections the maximum reported value given with maximum LOD value in brackets.

Dissolved aluminium, copper, iron, manganese and zinc were found in significantly high concentrations in the majority of groundwater samples. The shallow well MWPF1 located upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments had the lowest concentrations of dissolved metals. However, MWET2 had the lowest concentration of dissolved aluminium (126 µg/l) and copper (8.88 µg/l) but was high in dissolved zinc (6,700 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 14.2 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 9 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	10	10	9260	208000	74600	59100
Antimony	<0.16	10	4	0.08	3.18	0.72	0.92
Arsenic	<0.12	10	10	0.77	34.4	9.06	12.4
Barium	<0.03	10	10	3.85	18.7	8.46	5.4
Cadmium	<0.1	10	10	7.26	104	42.5	32.4
Chromium	<0.22	10	10	0.729	7.77	2.62	2.35
Cobalt	<0.06	10	10	16.4	230	119	70.5
Copper	<0.85	10	10	321	13200	6670	5020
Iron	<19	10	10	5740	265000	91200	94000
Lead	<0.02	10	10	47	1340	569	468
Manganese	<0.04	10	10	314	19800	7070	7240
Mercury	<0.01	10	3	0.005	0.025	0.010	0.010
Molybdenum	<0.24	10	2	0.12	1.2	0.530	0.510
Nickel	<0.15	10	10	7.02	97.3	53.6	30.1
Selenium	<0.39	10	3	0.195	4.46	1.04	1.39
Silver	<1.5	10	0	0.75	(7.5*)	-	-
Thallium	<0.96	10	5	0.48	2.77 (4.8*)	2.47	1.78
Tin	<0.36	10	2	0.18	9.75	1.58	-
Uranium	<1.5	10	7	1.62	19.4	8.3	4.57
Vanadium	<0.24	10	4	0.12	1.35	0.66	0.53
Zinc	<0.41	10	10	3480	62600	25700	16100

Notes:

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

* LOD was raised due to a dilution that was carried out on the sample. Where there were detections the maximum reported value given with maximum LOD value in brackets.

Dissolved aluminium, copper, iron, manganese and zinc were found in significantly high concentrations in the majority of the adit discharges and the pit lake sample. The Cronebane Shallow Adit had the highest concentrations of dissolved metals including aluminium (208,000 µg/l), arsenic (18.8 µg/l), cadmium (104 µg/l), copper (13,200 µg/l) and zinc (62,600 µg/l). 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	13	15.4	976	187	245
Antimony	<0.16	13	7	0.08	4.9	0.76	1.35
Arsenic	<0.12	13	13	0.154	0.562	0.29	0.13
Barium	<0.03	13	13	5.34	7.91	6.05	0.76
Cadmium	<0.1	13	11	0.05	2.16	0.39	0.55
Chromium	<0.22	13	13	0.22	0.706	0.42	0.13
Cobalt	<0.06	13	13	0.195	2.88	0.81	0.83
Copper	<0.85	13	11	0.425	126	18.9	33.1
Iron	<19	13	12	9.5	1750	263	468
Lead	<0.02	13	13	0.217	20.3	4.9	4.84
Manganese	<0.04	13	13	11.6	200	57.1	49.6
Mercury	<0.01	13	12	0.005	0.339	0.03	0.09
Molybdenum	<0.24	13	7	0.12	1.66	0.41	0.43
Nickel	<0.15	13	13	0.741	1.72	1.12	0.3
Selenium	<0.39	13	1	0.195	0.677	-	-
Silver	<1.5	13	0	0.75	0.75	-	-
Thallium	<0.96	13	0	0.48	0.48	-	-
Tin	<0.36	13	5	0.18	2.38	0.52	0.63
Uranium	<1.5	13	0	0.75	0.75	-	-
Vanadium	<0.24	13	11	0.12	0.332	0.15	0.07
Zinc	<0.41	13	13	24.7	669	143	170

Notes:

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

Dissolved metals were detected upgradient of the mining area at Ballinacleish Bridge and Lions Bridge with concentrations of aluminium at 109 and 77.9 µg/l, zinc at 59.5 and 83.5 µg/l and iron at 43.8 and 66.5 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 (90.4 µg/l), copper (<0.85 µg/l) and zinc (24.7 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 (124 µg/l), copper (5.39 µg/l) and zinc (49.5 µg/l).

The dissolved metals highest dissolved metals concentrations on the Avoca River were Downstream (DS) of the Deep Adit confluence on the Avoca River; dissolved aluminium was 976 µg/l, copper was 126 µg/l and zinc was 669 µg/l. The concentrations decreased again further

downstream at Wicklow Co. Co. Maintenance Yard GS where the river is better mixed, to 188 µg/l for aluminium, 21.1 µg/l for copper and 121 µg/l for 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 for both ecological and human health. To assess ecological criteria, the environmental quality standards (EQS) from the European Communities Environmental Objectives (Surface Water) Regulations, 2009 (S.I. 272 of 2009) and amendments were utilised, as shown in Table 13. These include standards for physico-chemical conditions supporting the biological elements general conditions and standards for specific pollutants. In the case of metals the EQS refers to the dissolved concentration. Compliance with the standards in the surface water regulations is either based on an annual average (AA), a maximum allowable concentration (MAC) or a 95 percentile standard. The MAC or 95 percentile (95%ile) was selected where possible as the assessment criteria because it is the most appropriate for assessment of one value; however, the AA was used in the absence of the MAC or 95%ile. To supplement the Irish legislation, screening criteria were selected from Oak Ridge National Laboratory (Suter and Tsao, 1996) for certain metals including aluminium, barium, cobalt, manganese and uranium (Table 13).

For hardness-dependent metals copper, zinc and cadmium, the hardness is taken into account when selecting the appropriate EQS value. The average hardness in the rivers and streams in the Avoca mining area was determined to be 31 mg/l CaCO₃ (CDM, 2008) and the appropriate ecological assessment criteria are highlighted in bold in Table 13.

Table 13 Surface Water and Groundwater Assessment Criteria for Biological Elements

Parameter	Unit	AA	MAC (or 95%ile)	Source	Description
Ammonia as N	mg/l	0.065	0.14	S.I. No. 272 of 2009	Good status
Ortho-phosphate as P	mg/l	0.035	0.075	S.I. No. 272 of 2009	Good status
pH	pH units		> 4.5 and < 9.0	S.I. No. 272 of 2009	Within range
Dissolved Oxygen	% Sat		80 to 120	S.I. No. 272 of 2009	Within range. Only relevant to surface water
Free Cyanide	mg/l	0.01	-	S.I. No. 272 of 2009	
Fluoride	mg/l	0.5	-	S.I. No. 272 of 2009	
Arsenic	µg/l	25	-	S.I. No. 272 of 2009	
Cadmium	µg/l	≤0.08 (Class 1) 0.08 (Class 2) 0.09 (Class 3) 0.15 (Class 4) 0.25 (Class 5)	≤ 0.45 (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)	S.I. No. 327 of 2012	Hardness measured in mg/l CaCO ₃ (Class 1: <40 mg CaCO ₃ /l, Class 2: 40 to <50 mg CaCO ₃ /l, Class 3: 50 to <100 mg CaCO ₃ /l, Class 4: 100 to <200 mg CaCO ₃ /l and Class 5: ≥200 mg CaCO ₃ /l)
Chromium	µg/l	3.4	-	S.I. No. 272 of 2009	
Copper	µg/l	5 or 30	-	S.I. No. 272 of 2009	5 µg/l applies where the water hardness measured in mg/l CaCO ₃ is ≤ 100; 30 µg/l applies where the water hardness > 100 mg/l CaCO ₃ .
Lead	µg/l	7.2	-	S.I. No. 327 of 2012	
Mercury	µg/l	0.05	0.07	S.I. No. 327 of 2012	
Nickel	µg/l	20	-	S.I. No. 327 of 2012	
Zinc	µg/l	8 or 50 or 100	-	S.I. No. 272 of 2009	8 µg/l for water hardness with annual average values ≤ 10 mg/l CaCO ₃ ; 50 µg/l for water hardness > 10 mg/l CaCO ₃ and ≤ 100 mg/l CaCO ₃ ; and 100 µg/l elsewhere.
Supplementary standards:					
Aluminium	µg/l	-	1900	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Barium	µg/l	-	4	Oak Ridge National Laboratory	Invertebrates and Salmon fish
Cobalt	µg/l	-	5.1	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Manganese	µg/l	-	1,100	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Uranium	µg/l	-	2.6	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids

Notes:

Bold indicates the selected assessment criteria for ecological health

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 ₃	mg/l	50
Nitrite as NO ₂	mg/l	0.5
Sulphate	mg/l	250
Sodium	mg/l	200
Aluminium	µg/l	200
Antimony	µg/l	5
Arsenic	µg/l	10
Cadmium	µg/l	5
Chromium	µg/l	50
Copper	µg/l	2,000
Iron	µg/l	200
Lead	µg/l	10
Manganese	µg/l	50
Mercury	µg/l	1
Nickel	µg/l	20
Selenium	µg/l	10

4.3 Comparison to Assessment Criteria

A comparison of the groundwater and surface water analytical results was made against the relevant assessment criteria for ecological and human health as described in Section 4.2. The dissolved metal concentrations are assessed as they are more biologically available than total metals and non-dissolved metals are generally removed from drinking water by filtration.

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

4.3.1 Groundwater Assessment

The pH was found to be acidic in the majority of groundwater samples with results ranging from 2.75 to 6.37 (field). All exceeded the acceptable ranges for ecological (4.5 to 9 pH units) and human health (6.5 to 9.5 pH units) criteria, except the two locations with highest pH at MWPF1 with 4.83 pH and MWET2 with 6.37 pH which only exceeded the criteria for human health. The specific conductance ranged from 0.149 to 8.605 mS/cm with the lowest conductivity located at MWPF1 and the highest at SG104. The specific conductance exceeded the human health criteria (2.5 mS/cm) at MWDA1, MWET2, GW1/05 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 989 to 9770 mg/l. One exception was at MWPF1 where sulphate was below the human health assessment criteria with a value of 26.3 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 7 of the monitoring wells sampled, with 2 of the values exceeding the assessment criteria for ecology (0.5 mg/l) and 5 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 3.84 to 32.8 µg/l. There were three detections of dissolved arsenic, only MWSA2 with a result of 17.2 µg/l exceeded only the human health (10 µg/l) criteria.

The dissolved aluminium and copper concentrations at MWET2 (deep) (126 and 8.88 µg/l) were significantly lower than at MWET1 (shallow) which had concentrations of 136,000 and 8,710 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 was detected at 11,000 and 8,800 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 1700 µg/l.

SG104 had the highest levels compared to the other monitoring wells, of dissolved copper (83,100 µg/l), cadmium (592 µg/l) and nickel (449 µg/l) exceeding the ecological and human health criteria. Dissolved mercury (0.087 µg/l), cobalt (1,090 µg/l) and zinc (159,000 µg/l) were also highest in SG104 and exceeded the ecological health criteria. Levels of dissolved lead in SG104 exceeded the ecological assessment criteria of 7.2 µg/l, with a value of 51.7 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 392,000 and 41,500 µg/l in MWDA1 and were at concentrations of 72,300 and 5,600 µg/l in MWDA2, respectively. However, both wells still exceeded the criteria for both ecological and human health for aluminium and copper. MWDA1 chromium exceeded the assessment criteria for ecology (3.4 µg/l) and human health (50 µg/l) with a concentration of 74.1 µg/l and had a detection of dissolved mercury of 0.0706 µg/l, that exceeded the ecological health criteria (0.07 µg/l).

The well located upgradient of the Deep Adit area and at the eastern margin of the alluvial aquifer, MWPF1, had significantly lower metal concentrations than the other wells. However, the 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 2.72 to 4.49 pH (field) which exceeded the acceptable ranges for ecological (4.5 to 9 pH units) and human health (6.5 to 9.5 pH units) criteria. The acidity as HCl ranged from 74.8 mg/l in the Cronbane Pit Lake to 2,000 mg/l in the Cronbane Shallow Adit. The specific conductance ranged from 0.541 to 2.753 mS/cm. There were four exceedances of the human health criteria (2.5 mS/cm) at the Cronbane Shallow Adit, Road Adit, Road Adit Confluence and Ballygahan 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 758 to 1990 mg/l. Ammonia was detected in all of the adit discharges and the ecological criteria (0.14 mg/l) was exceeded at all locations. The human health criteria for ammonia (0.3 mg/l) was also exceeded at 6 locations with the highest concentrations at Ballygahan Adit (5.14 mg/l) and the Road Adit (4.79 mg/l). Fluoride was also present at all of the adit discharges that were sampled, with 8 of the values exceeding both the assessment criteria for ecological (0.5 mg/l) and human health (1.5 mg/l). The Deep Adit (1.24 mg/l) only exceeded the criteria for ecological health. Concentrations of sulphate (143 mg/l), ammonia (<0.02 mg/l) and fluoride (1.14 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).

Dissolved zinc ranged from 9,850 to 62,600 µg/l which exceeded the ecological assessment criteria of 50 µg/l. Dissolved aluminium ranged from 14,800 to 208,000 µg/l which exceeded both the ecological (1,900 µg/l) and human health (200 µg/l) criteria. 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, where concentrations ranged from 6,240 and 13,200 µg/l. The concentration of dissolved copper was significantly higher in the 850 Adit with a concentration of 10,900 µg/l, when compared to the Deep Adit at 1,500 µg/l.

Dissolved cadmium ranged from 7.26 to 104 µg/l which exceeded both the ecological (0.45 µg/l) and human health (5 µg/l) criteria. Dissolved cobalt ranged from 67.9 to 230 µg/l which exceeded the ecological (5.1 µg/l). Dissolved lead ranged from 47 to 1340 µg/l which exceeded both the ecological (7.2 µg/l) and human health (10 µg/l) criteria. Dissolved nickel ranged from 23 to 97.3 µg/l which exceeded both the ecological and human health criteria of 20 µg/l.

Dissolved arsenic was detected in all of the adit discharges, with Ballygahan Adit (25.2 µg/l) and Cronebane Shallow Adit (34.4 µg/l) exceeded the criteria for both ecological (25 µg/l) and human health (10 µg/l). Cronebane Intermediate Adit (18.8 µg/l) exceeded only the human health criteria. Dissolved chromium was detected and exceeded the ecological assessment criteria of 3.4 µg/l at Cronebane Shallow Adit (7.77 µg/l), Ballygahan Adit (3.59 µg/l) and the Spa Adit (5.49 µg/l).

Dissolved iron and manganese were also high in all adit discharges. Iron ranged from 12,200 to 265,000 µg/l, exceeding the human health assessment criteria of 200 µg/l. Manganese ranged from 2,070 to 19,800 µg/l which exceeded the criteria for both ecological (1,100 µg/l) and human health (50 µg/l).

Rivers and Streams

Table 15 provides a summary of the reported values for rivers and streams in the Avoca Mining area that exceeded the relevant ecological and human health assessment criteria. The pH was found to be near neutral in the majority of rivers and streams ranging from 5.46 to 6.88 (field) which were within acceptable ranges for ecological (4.5 to 9 pH units). However, 8 locations including Ballinacleish Bridge and Lions Bridge and the stretch from Downstream of the Deep Adit to Downstream of Shelton Abbey (inclusive) were below the human health (6.5 to 9.5 pH units) criteria. Acidity was below the limit of detection (<2 mg/l). The specific conductance was well within the criteria for human health of 2.5 mS/cm ranging from 0.061 to 0.153 mS/cm.

Nutrients in the river and stream samples collected were below the limit of detection for ortho-phosphate and ammonia. One exception was US Shelton Abbey which exceeded the ecological assessment criteria for ammonia (0.14 mg/l) with value of 0.233 mg/l.

The dissolved metal concentrations in the rivers and streams were low in comparison to the groundwater and the adit discharges; however, several exceedances of both ecological and human health criteria 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 5.39 to 126 µg/l. Similarly dissolved zinc exceeded the ecological assessment criteria (50 µg/l) from Whites Bridge GS on the Avoca River to Downstream Shelton Abbey with results ranging from 99.7 (twice the ecological assessment criteria) to 669 µg/l. Dissolved zinc was also detected at concentrations above the ecological assessment criteria upstream of the Avoca Mines at Lions Bridge and Ballinacleish Bridge and in the two tributaries at concentrations ranging from 59.5 to 83.5 µg/l.

Dissolved aluminium exceeded human health criteria (200 µg/l) only at Whites Bridge GS and DS of the Deep Adit with concentrations of 236 µg/l and 976 µg/l, respectively. Dissolved cadmium exceeded the ecological assessment criteria (0.45 µg/l) at the DS Deep Adit location on the Avoca River with 2.16 µg/l. Dissolved lead exceeded the ecological (7.2 µg/l) and human health (10 µg/l) criteria at the DS Deep Adit location on the Avoca River with 20.3 µg/l. Dissolved mercury exceeded the ecological assessment criteria of 0.07 µg/l at Site T5 with a concentration of 0.339 µg/l.

From DS of the Deep Adit location on the Avoca River to Shelton Abbey, dissolved iron ranged from 204 to 1750 µg/l, exceeding the human health assessment criteria of 200 µg/l. Dissolved manganese ranged from 57.4 to 200 µg/l which exceeded the criteria for both ecological (1,100 µg/l) and human health (50 µg/l).

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

Sample Description	Date Sampled Units	Ammoniacal Nitrogen asN mg/l	pH (field) pH Units	Aluminium µg/l	Cadmium µg/l	Copper µg/l	Iron µg/l	Lead µg/l	Manganese µg/l	Mercury µg/l	Zinc µg/l
Ecological Criteria		0.14	4.5 to 9	1,900	0.45	5	-	7.2	1100	0.07	50
Human Health Criteria		0.3	6.5 to 9.5	200	5	2000	200	10	50	1	-
Vale View	03/03/2014	<0.2	6.88	15.4	<0.1	1.7	24.1	0.217	11.6	<0.01	63.1
Sulphur Brook	04/03/2014	<0.2	6.64	29	0.236	18	<19	5.92	21.5	<0.01	59.6
Ballinacleish Bridge	03/03/2014	<0.2	5.84	109	0.114	<0.85	43.8	4.53	35	<0.01	59.5
Lions Bridge	03/03/2014	<0.2	6.22	77.9	0.156	1.08	66.5	5.05	25	<0.01	83.5
Site T1	03/03/2014	<0.2	6.57	90.4	<0.1	<0.85	47.2	4.03	27.8	<0.01	24.7
Whites Bridge	03/03/2014	<0.2	6.81	124	0.222	5.39	60.4	4.43	29.4	<0.01	49.5
Whites Bridge GS	03/03/2014	<0.2	6.64	236	0.34	12.8	77.1	4.2	39.7	<0.01	99.7
DS Deep Adit	03/03/2014	<0.2	5.46	976	2.16	126	347	20.3	95.1	<0.01	669
Wicklow CO.CO. Main. Yard GS	04/03/2014	<0.2	5.62	188	0.364	21.1	91	3.26	49.2	<0.01	121
Site T5	04/03/2014	<0.2	5.85	123	0.444	19.8	1750	3.46	200	0.339	273
Avoca Bridge	04/03/2014	<0.2	6.2	152	0.388	18.5	485	3.3	84.4	<0.01	161
US Shelton Abbey	26/02/2014	0.233	5.8	155	0.27	10.4	211	2.62	57.4	<0.01	90.4
DS Shelton Abbey	26/02/2014	<0.2	5.83	151	0.233	10.1	204	2.39	65.9	<0.01	105

Notes

xx Exceeds Ecological Assessment Criteria

xx Exceeds Human Health Assessment Criteria

xx Exceeds both Ecological and Human Health Criteria

Metals are dissolved

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 September 2013 to 19 March 2014 of Whites Bridge GS is reproduced in Figure 2 and for Wicklow County Council Maintenance Yard GS from 1 September 2013 to 19 March 2014 in Figure 3. The figures show the measured flows ranged from $>40 \text{ m}^3/\text{s}$ 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 of approximately $16 \text{ m}^3/\text{s}$ is higher than the long term median of approximately $10 \text{ m}^3/\text{s}$ (CDM Smith, 2013), which reflects the high levels of rainfall during the monitoring period. Flow in January and February were particularly high with the daily mean flow exceeding $50 \text{ m}^3/\text{s}$ on numerous occasions.

The river appears to respond similarly to rainfall at both gauging stations as can be observed in both figures. In general, the rate of flow at Whites Bridge GS which is the upstream location is slightly higher than Wicklow County Council Maintenance Yard GS throughout the monitoring period. This trend is exaggerated during high rainfall events where the peaks at Whites Bridge GS are higher by 6 to $7 \text{ m}^3/\text{s}$. The recessions in the graph after each rainfall event appear to be similar.

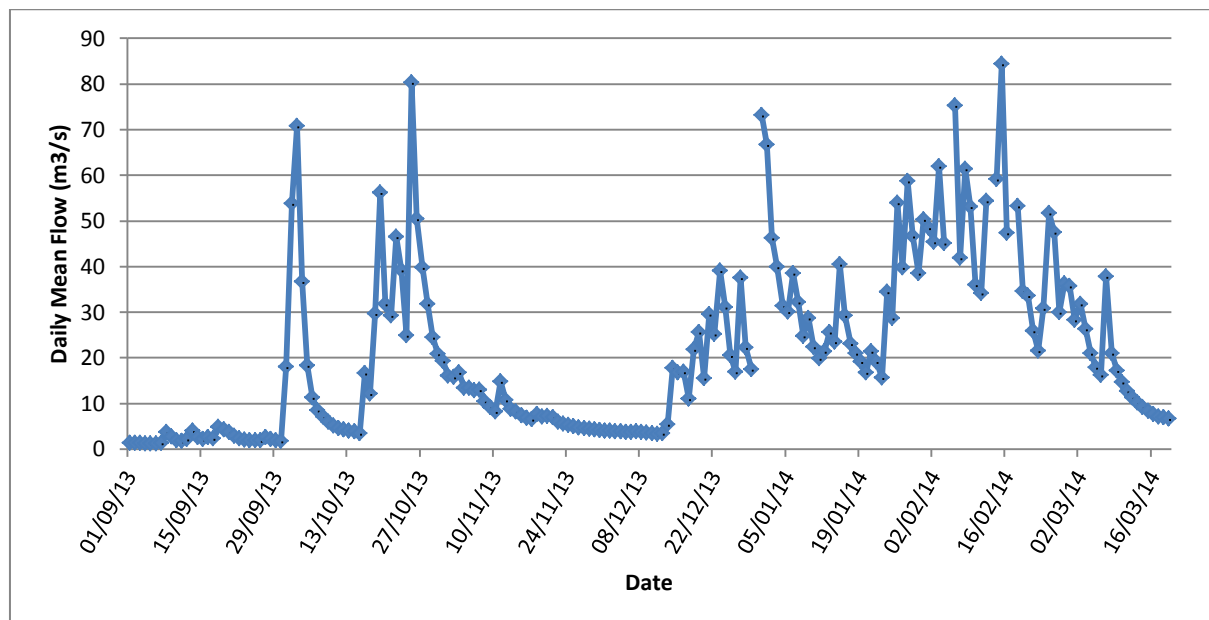


Figure 2 Mean Daily Flow (m^3/s) at Whites Bridge (Station 10044) from 1 Sept 2013 to 19 Mar 2014

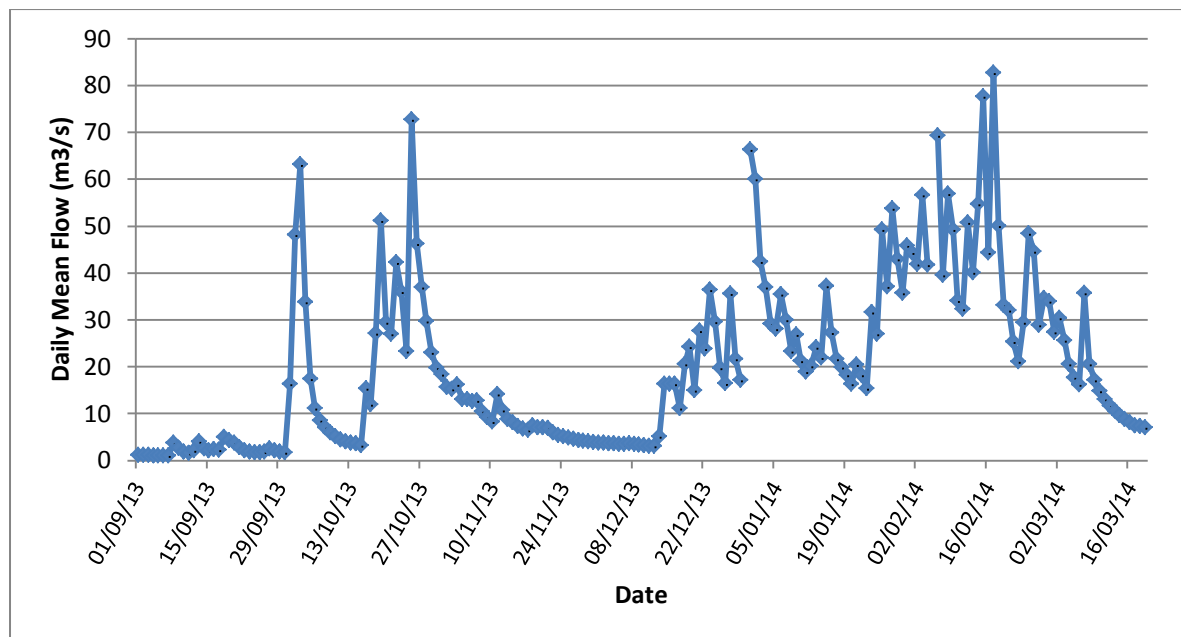


Figure 3 Mean Daily Flow (m3/s) at Wicklow County Council Maintenance Yard (Station 10045) from 1 Sept 2013 to 19 Mar 2014

Flow was measured directly in the field using different methodologies depending upon the quantity of flow to be measured and any safety concerns, as described in Section 2.1.2 Surface Water Sampling. Table 16 presents as a summary of the results from the flows measured in February and March 2014 at the time of sampling. It is noted that some of the flow measurements were carried out on different days and the average flow in the Avoca River varies. Refer to Appendix B of the Data Report for details of methodologies used per site and associated calculations.

The measured flow at the Deep Adit of 22 l/s is considered a moderate flow as past records for the Deep Adit ranged from approximately 10 to 37.5 l/s. Based on the past records and the period of high flow it would be expected that the flow from the Deep Adit would have been higher. There was significant flow issuing from the 850 Adit at 19 l/s, which is likely to be some of the Deep Adit flow which has been redirected due collapse deep inside the mine, diverting water from the Deep Adit to higher levels. The combined flow of the Deep Adit and the 850 Adit was calculated to be 41.3 l/s. The flow was also measured at the Deep Adit Confluence (Deep Adit + 850 Adit) prior to it discharging to the river and the measured flow was 41.9 l/s which was similar to the combined flow of the two adits. Note this location is not ideal for measuring flow as it is not properly channelised and the measurement should be considered an estimate. Any loss of flow along the Deep Adit channel either due to the millrace diversion or infiltration was not apparent in the measured flow at the Deep Adit Confluence, and it is likely that these flow quantities fall within the margin of error in the flow measurements.

The measured flow at the Road Adit of 56.2 l/s is a high flow as past records for the Road Adit ranged from approximately 6 to 58 l/s (CDM, 2008). It was observed that the flow may been higher prior to the visit as sand bags were in place to prevent the discharge from overflowing onto the road. The flow was also measured at the Road Adit Confluence prior to the adit discharging to the river and the measured flow was 69 l/s which is a lot higher than at the adit portal. This would

indicate that there could be a small stream or road runoff contributing flow to the Road Adit discharge. It is unlikely that any infiltration (i.e. flow loss) in the Road Adit ditch would be apparent in the flow measurements given the margin of error in the flow measurements and other contributing surface water runoff.

Table 16 Surface Water Flow Value Measured in Feb/Mar 2014

Site Name	Flow m ³ /s	Flow l/s	Date	Notes
Ballinacleish Bridge	7.85	7850	03/03/2014	
Lions Bridge	16.9	16800	03/03/2014	
Vale View	0.089	89	03/03/2014	
Site T1	24.7	24700	03/03/2014	
White's Bridge GS	26.4	26400	03/03/2014	Mean daily flow on 4/03/2014 was 21 m ³ /s
Wicklow Co Co. Main. Yard GS	25.6	25600	03/03/2014	Mean daily flow on 4/03/2014 was 20.6 m ³ /s
Site T5	20.6	20600	04/03/2014	
Avoca Bridge	24.0	24000	04/03/2014	
Upstream of Shelton Abbey	42.5	42500	26/02/2014	
Downstream of Shelton Abbey	42.5	42500	26/02/2014	
Sulphur Brook	0.646	646	04/03/2013	
850 Adit	0.019	19	27/02/2014	
Deep Adit	0.022	22	27/02/2014	
Deep Adit Confluence	0.042	42	27/02/2014	Deep Adit + 850 Adit
Road Adit	0.056	56.2	27/02/2014	
Road Adit Confluence	0.069	69.0	27/02/2014	
Cronebane Intermediate Adit	0.025	25.4	26/02/2014	
Cronebane Shallow Adit	0.0005	0.499	26/02/2014	
Ballygahan Adit	-	-	26/02/2014	
Spa Adit	0.0003	0.300	27/02/2014	
Cronebane Pit Lake	n/a	n/a		

5.2 Loading Analysis

5.2.1 Loading Analysis Methodology

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

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

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

F = the flow rate of the input

5.2.2 Loading Results and Discussion

The calculated mass loads in Table 17 aid with the interpretation of the loading of sulphate and dissolved aluminium, copper, iron, lead and zinc to the Avoca River.

Table 17 Summary of Measured Flows and Concentrations and Calculated Loads of Sulphate and Dissolved Metals in kg/day in the Adits and Avoca River

Sample Description	Date Sampled	Flow l/s	pH Units	Sulphate		Aluminium		Copper		Iron		Lead		Zinc	
				µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day
Cronebane Inter. Adit	26/02/14	25.4	2.74	767000	1690	67100	147	11300	24.8	59100	130	929	2.04	29900	65.7
Cronebane Shallow Adit	26/02/14	0.50	2.72	1990000	85.8	208000	8.97	13200	0.6	115000	4.96	859	0.04	62600	2.70
850 Adit (portal)	27/02/14	19.1	2.78	758000	1250	74300	122	10900	18.0	12200	20	838	1.38	25800	42.5
Deep Adit (portal)	27/02/14	22.2	3.49	781000	1500	71600	138	1500	2.9	55800	107	1340	2.57	35500	68.2
850 Adit (portal) + Deep Adit (portal)		41.3	-	-	2750	-	260	-	20.9	-	127	-	3.95	-	111
Deep Adit Confluence	27/02/14	41.9	3.03	759000	2750	71600	259	6240	22.6	29900	108	986	3.57	29500	107
Road Adit (portal)	27/02/14	56.2	4.4	1610000	7820	15000	72.8	321	1.6	265000	1290	219	1.06	20100	97.6
Road Adit Confluence	27/02/14	69.0	4.49	1680000	10000	14800	88.3	334	2.0	255000	1520	218	1.30	20400	122
Spa Adit	27/02/14	0.3	2.74	1180000	30.6	111000	2.9	7650	0.2	64200	1.66	52.1	0.00	9850	0.260
Vale View	03/03/14	88.6	6.88	14000	107	15.4	0.12	1.7	0.0	24.1	0.18	0.217	0.00	63.1	0.480
Sulphur Brook	04/03/14	646.0	6.64	11600	647	29.0	1.62	18	1.00	9.5	0.53	5.92	0.33	59.6	3.330
Ballinacleish Bridge	03/03/14	7850	5.84	1000	678	109	73.9	0.425	0.29	43.8	29.7	4.53	3.07	59.5	40.3
Lions Bridge	03/03/14	15100	6.22	1000	1300	77.9	102	1.08	1.41	66.5	86.7	5.05	6.58	83.5	109
Site T1	03/03/14	22900	6.57	1000	1980	90.4	179	0.425	0.84	47.2	93.5	4.03	7.99	24.7	48.9
Whites Bridge	03/03/14	26400	6.81	4100	9350	124	283	5.39	12.3	60.4	138	4.43	10.1	49.5	113
Whites Bridge GS	03/03/14	26400	6.64	5400	12300	236	538	12.8	29.2	77.1	176	4.2	9.6	99.7	227
DS Deep Adit	03/03/14	25600	5.46	20500	45300	976	2160	126	279	347	768	20.3	44.9	669	1480
WCC Main. Yard GS	04/03/14	25600	5.62	8700	19200	188	416	21.1	46.7	91	201	3.26	7.21	121	268
Site T5	04/03/14	20600	5.85	26000	46200	123	219	19.8	35.2	1750	3110	3.46	6.15	273	485
Avoca Bridge	04/03/14	24000	6.2	13100	27200	152	315	18.5	38.4	485	1010	3.3	6.85	161	334
US Shelton Abbey	26/02/14	42500	5.8	7600	27900	155	569	10.4	38.2	211	774	2.62	9.61	90.4	332
DS Shelton Abbey	26/02/14	42500	5.83	9000	33000	151	554	10.1	37.1	204	748	2.39	8.77	105	385

Loading from Adit Discharges

The Deep Adit had an aluminium, copper and zinc load of 138, 2.9 and 68.2 kg/day and the Road Adit had a loading of 72.8, 1.9 and 97.6 kg/day. The Road Adit had a significantly higher loading of sulphate with 7,820 kg/day and dissolved iron with 1,290 kg/day whereas the Deep Adit only had 107 kg/day sulphate and 1,500 kg/day of iron.

The Deep Adit and 850 Adit showed similar loadings for sulphate (1,250 kg/day and 1,500 kg/day), dissolved aluminium (122 kg/day and 138 kg/day) and zinc (42.5 kg/day and 68.5 kg/day). However the 850 Adit had significantly higher loading of dissolved copper with 18 kg/day and the Deep Adit had 2.9 kg/day. The reverse was true for dissolved iron as the 850 Adit had a load of 20 kg/day and the Deep Adit had a load of 107 kg/day.

To determine if there was any apparent loss of sulphate or metals loading along the Deep Adit ditch before it discharges into the Avoca River the flow and loading results were summed for the Deep Adit and the 850 Adit portal samples and compared with the measured loads at the Deep Adit Confluence (Table 17). The flows are similar and do not show any evidence of loss due to the millrace diversion or infiltration and it is likely that these flow quantities fall within the margin of error in the flow measurements. Despite this there was a slight apparent loss of dissolved iron load from the portals to the confluence as it decreased from 127 to 108 kg/day and the rest of the loadings were similar at both locations. This is likely due to the precipitation of iron along the ditch however there was no evidence of coprecipitation of metals such as copper.

To determine if there was any apparent loss of sulphate or metals loading along the Road Adit ditch before it discharges into the Avoca River the flow and loading results were between the portal and confluence samples (Table 17). The concentrations of sulphate and the dissolved metals were similar in the portal and the confluence samples. The loadings appeared to be slightly higher at the confluence location but this was likely due to the higher flow measurement at the confluence.

The Cronebane Intermediate Adit had dissolved metals loads of 147 kg/day for aluminium, 130 kg/day iron and 65.7 kg/day zinc. The Cronebane Shallow Adit and Spa Adit were of minor importance in terms of dissolved metals loads to the Avoca, either because of absence of surface flow to the river or due to low loads. Loads from these adits range from 2.9 to 8.97 kg/day for aluminium, 0.2 to 0.6 kg/day for copper and 0.26 to 2.7 kg/day for zinc. Loads from the Ballygahan Adits could not be calculated because the flow was too low to measure.

Avoca River Loadings

Background loads upstream of the Avoca Mining Area of these metals were present which is evident from the calculated loads at Ballinacleish Bridge, Lions Bridge and Site T1. The dissolved metal loads at Site T1 were 179 kg/day for aluminium, 0.84 kg/day for copper, 93.5 kg/day for iron, 7.99 kg/day for lead and 48.9 kg/day for zinc. Figure 4 graphically shows the calculated loads of dissolved aluminium, copper, iron and zinc at each location along the Avoca River from Site T1 upstream of the mining area to Avoca Bridge (see also Map 1 and 3 in [Appendix A](#)). Note that the samples were collected and flows recorded on different dates.

An increase in loads occurs at Whites Bridge with loads of dissolved aluminium at 283 kg/day, copper at 12.3 kg/day, and zinc at 113 kg/day. There is a further increase in dissolved aluminium 538 kg/day, copper 29.2 kg/day, iron 176 kg/day and zinc 227 kg/day, loads 90 metres downstream at Whites Bridge GS.

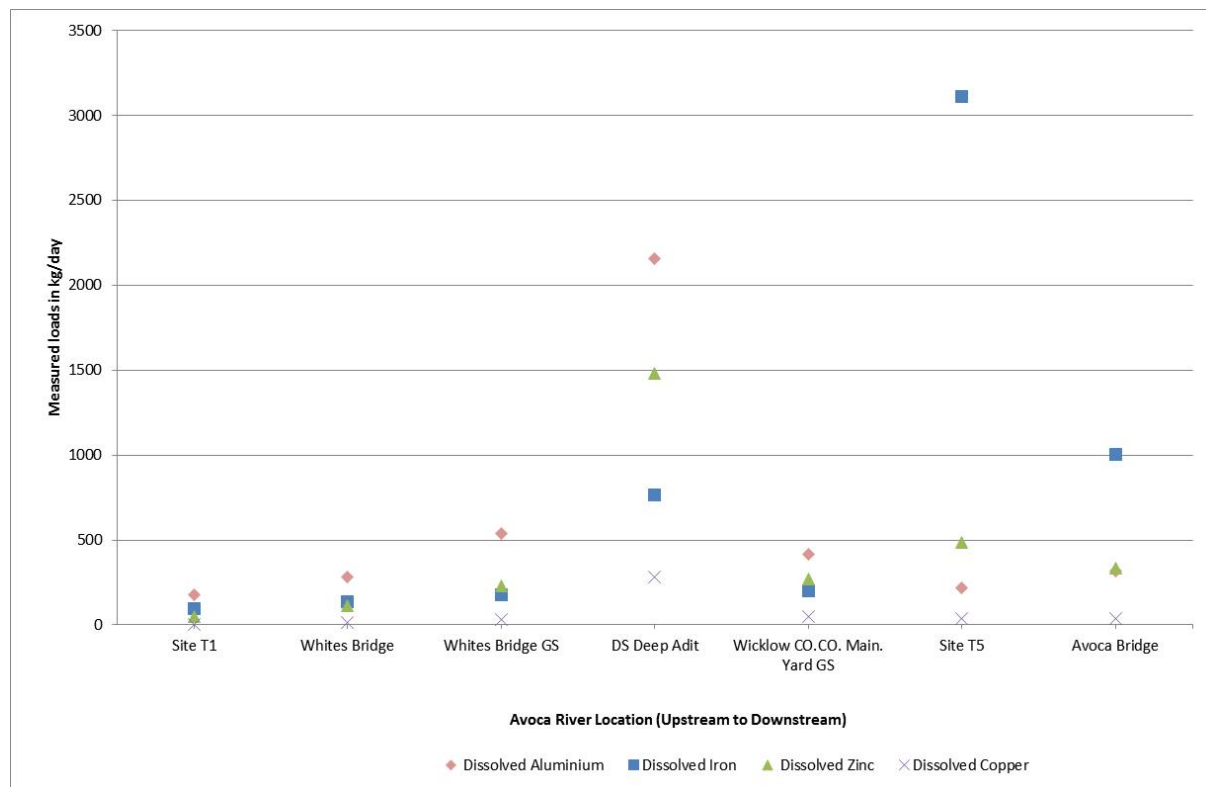


Figure 4 Calculated Loads of Dissolved Aluminium, Iron and Zinc in kg/day in Avoca River in March 2014

The DS Deep Adit location is on the Avoca River downstream of the Deep Adit discharge so the loads would be expected to be 797 kg/day for aluminium, 284 kg/day iron and 334 kg/day for zinc to account for the loading at Whites Bridge GS (538 kg/day aluminium, 108 kg/day iron and 227 kg/day zinc) and the Deep Adit Confluence (259 kg/day aluminium, 176 kg/day iron and 107 kg/day zinc). However, the loadings were determined to be significantly higher at DS Deep Adit with 2,160 kg/day, 768 kg/day iron and 1,480 kg/day. The DS Deep Adit sample was collected from the river bank and so the discharge is unlikely to be fully mixed with the Avoca River therefore the loadings are an overestimation of the actual loads. Further downstream on the Avoca River at the Wicklow Co. Co. Maintenance Yard GS the measured loads are closer to expected loads with 416 kg/day for aluminium 201 kg/day iron and 268 kg/day for zinc. At Wicklow Co. Co. Maintenance Yard GS location the Deep Adit discharge is better mixed with the Avoca River, as shown on Figure 4 this is a significant decrease from the calculated loads at DS Deep Adit. These loads at Wicklow Co. Co. Maintenance Yard GS are slightly lower than the expected loads but this is likely due to the elevated results along the bank at Whites Bridge GS which likely results from the diffuse contaminated groundwater flow and the fact that the samples (and flow measurements) were collected on separate days.

Site T5 was downstream of the Road Adit discharge so the loads would be expected to be 504 kg/day for aluminium 1,740 kg/day and 390 kg/day for zinc to account for the loading at Wicklow Co. Co. Maintenance Yard GS (416 kg/day aluminium, 201 kg/day iron and 268 kg/day zinc) and the Road Adit Confluence (88.3 kg/day aluminium, 1,520 kg/day iron and 122 kg/day zinc). However, the loadings were determined to be higher at Site T5 with 3,110 kg/day for iron and 485 kg/day for zinc. At Site T5 there is a significant increase in dissolved iron loads compared

with the upstream location and it cannot all be attributed to the Road Adit Discharge and could indicate diffuse loading from contaminated groundwater. Dissolved aluminium load was less half the expected with 219 kg/day.

There was an apparent increase in the dissolved zinc loads from 332 kg/day Upstream of Shelton Abbey to 385 kg/day Downstream of Shelton Abbey. The calculated loads for dissolved aluminium, copper, lead and iron were similar at the upstream and downstream locations of Shelton Abbey.

Two tributaries to the Avoca River were sampled: Vale View and Sulphur Brook. Both tributaries had insignificant loads relative to the adit discharges, with the highest loading of 3.3 kg/day for zinc.

5.3 Trend Analysis

5.3.1 Historical Trends

This section discusses concentration time trends for select locations including the Deep Adit, the Road Adit and one location on the Avoca River for selected parameters including dissolved copper, zinc and iron. The trends are shown graphically in Figure 5 (Deep Adit from Oct 2001 to Mar 2014), Figure 6 (Road Adit from Oct 2001 to Mar 2014) and Figure 7 (Avoca River at Avoca Bridge from Oct 2001 to Mar 2014).

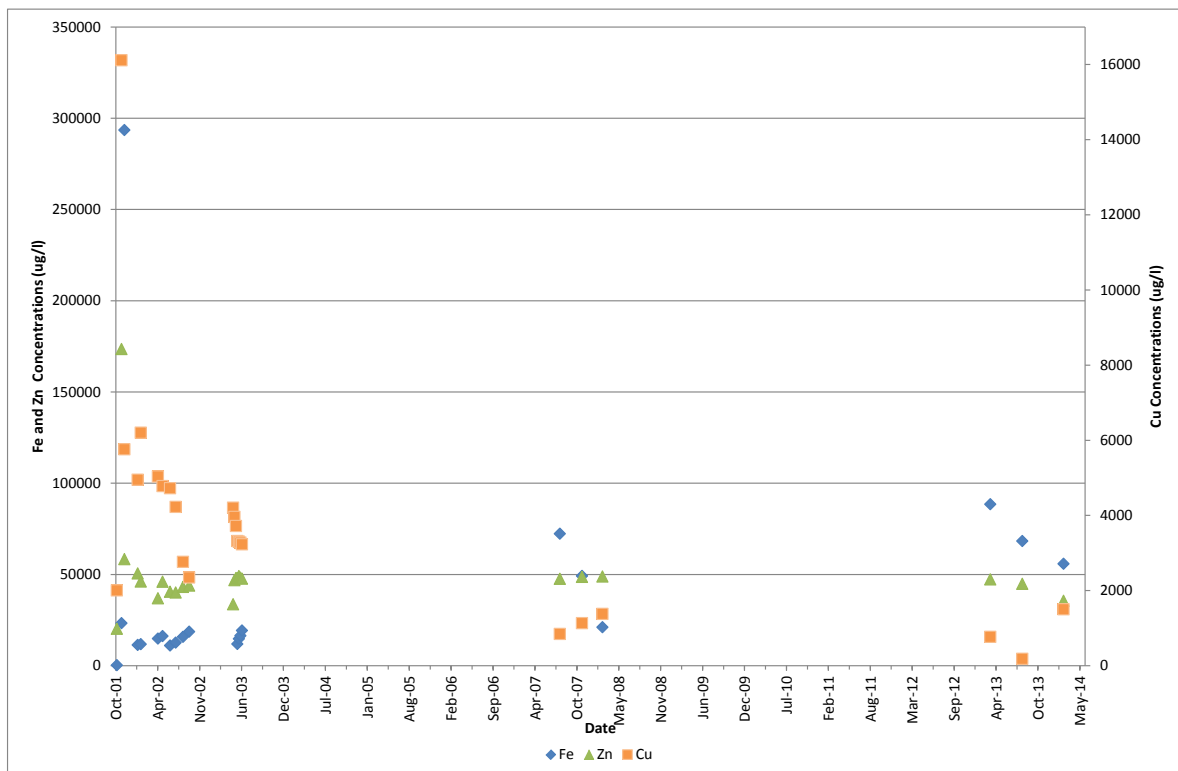


Figure 5 Concentration trends for dissolved copper, zinc and iron within the Deep Adit Discharge (Oct 2001 to Mar 2014)

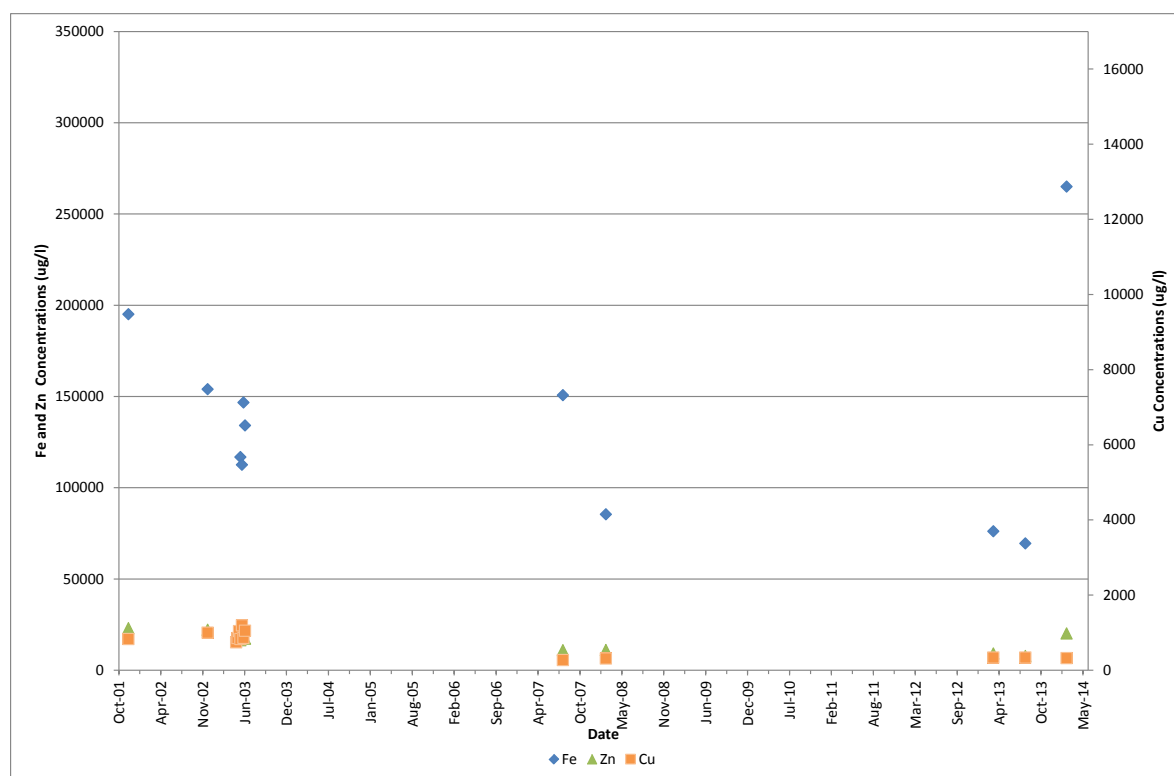


Figure 6 Concentration trends for dissolved copper, zinc and iron within the Road Adit Discharge (Oct 2001 to Mar 2014)

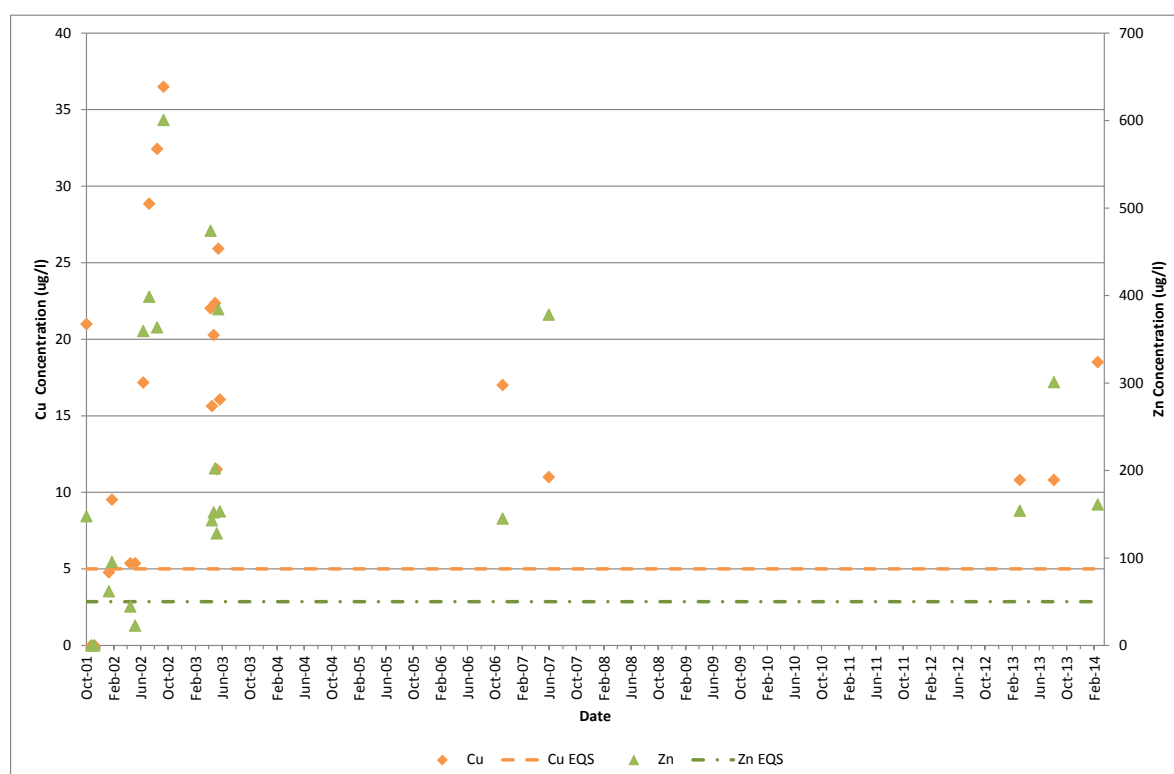


Figure 7 Concentration trends for dissolved copper and zinc at Avoca Bridge compared with the environmental quality objective (EQS) (Oct 2001 to Mar 2014)

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

The Mann-Kendall test results in the identification of a trend (if one exists) and the probability of that trend being real. Table 18 shows the possible outcomes of the Mann-Kendall trend analysis as applied to the water quality data.

Table 18 Reporting the Mann-Kendall Results

Trend	P value	Trend reported as
Decreasing	$0 \leq p < 0.05$	Decreasing
	$0.05 \leq p < 0.1$	Likely Decreasing
	$p \geq 0.1$	No Trend
Increasing	$0 \leq p < 0.05$	Increasing
	$0.05 \leq p < 0.1$	Likely Increasing
	$p \geq 0.1$	No Trend
No Trend	$p = 1$	No Trend

Notes:

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

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

The confidence coefficient is 0.95.

Trend analysis was conducted for all data since the October 2001 as data was available for all of the sample locations from that date onwards. Analysis on data since June 2007 was also carried out to determine if there were any trends in more recent data, which also eliminated the high results in 2001/2002. The Mann-Kendall test results for both time periods are presented in Table 19 and facilitate general observations about trends in the water quality of the two main adit discharges and the downstream location of Avoca Bridge.

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

Sample location	Parameter	October 2001 to March 2014			June 2007 to March 2014		
		P value	S value	Trend	P value	S value	Trend
Deep Adit	Copper	0.0000	-198	Decreasing	0.5	1	No Trend
	Zinc	0.392	12	No Trend	0.068	-9	Likely Decreasing
	Iron	0.0017	98	Increasing	0.5	-1	No Trend
Road Adit	Copper	0.0944	-25	Likely decreasing	0.242	4	No Trend
	Zinc	0.0080	-45	Decreasing	0.592	0	No Trend
	Iron	0.0806	-19	Likely decreasing	0.408	-2	No Trend
Avoca Bridge	Copper	0.5000	1	No Trend	0.625	1	No Trend
	Zinc	0.1080	42	No Trend	0.375	-2	No Trend

Notes:

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

The confidence coefficient is 0.95.

The results of the Mann-Kendall analysis for October 2001 to March 2014, show that dissolved copper concentrations are decreasing in the Deep Adit and there is no trend for dissolved zinc. Dissolved iron however is increasing in the Deep Adit. Dissolved zinc is decreasing in the Road Adit

and dissolved copper and iron are likely decreasing. These trends can also be inferred from Figure 5 and 6.

The results of the Mann-Kendall analysis for June 2007 to March 2014, show that dissolved zinc is likely decreasing and that there were no other trends for dissolved zinc, iron or copper for this time period in the adit discharges.

Figure 7 displays the results for dissolved copper and zinc in the Avoca River at Avoca Bridge which is downstream of the main Avoca Mining Area, from 2001 to present. The ecological assessment criteria (or EQS) are also shown on the graph for reference. The results also appear to be trending downwards but the Mann-Kendall results show that no statistically significant trend was present for dissolved copper or zinc for either time period analysed.

5.3.2 Seasonal Trends

Table 20 shows the seasonal variation between the concentrations of dissolved metals and the calculated loads observed between the high flow sampling events in March 2014 (R1) and February 2014 (R3) and the low flow sampling event in August 2013 (R2). As can be seen from Table 20 the concentrations of dissolved aluminium, copper, iron and zinc were very similar in each sampling event with a few exceptions. Dissolved copper in the Deep Adit was significantly lower in concentration in August 2013 compared with the high flow sampling in March 2013 and February 2014. 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 2013 compared with the high flow sampling in March 2013 and 2014. Table 20 also shows that the calculated loads of dissolved aluminium, copper, iron and zinc were all significantly lower in August 2013 due to the low flow conditions.

Table 20 Seasonal Variation of Concentrations and Calculated Loads of Dissolved Metals in the Adits and at Avoca Bridge in 2013/2014

Sample Description	Date Sampled	Flow l/s	Aluminium		Copper		Iron		Zinc	
			µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day
Deep Adit	R1 15/03/2013	29.2	98800	249.1	770	1.9	88500	223.1	47300	119.3
	R2 15/08/2013	13	96700	110	184	0.21	68300	77.4	44900	50.9
	R3 27/02/2014	22.2	71600	138	1500	2.9	55800	107	35500	68.2
Road Adit	R1 15/03/2013	28.9	14900	37.2	366	0.9	76100	190	9140	22.8
	R2 15/08/2013	15.6	16400	22.1	335	0.45	69500	93.9	7810	10.5
	R3 27/02/2014	56.2	15000	72.8	321	1.6	265000	1290	20100	97.6
Avoca Bridge	R1 20/03/2013	12000	162	167.6	10.8	11.2	153	158.3	154	159.3
	R2 20/08/2013	1940*	161	27	10.8	1.81	232	38.9	301	50.5
	R3 04/03/2014	24000	152	315	18.5	38.4	485	1010	161	334

Notes:

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

Section 6

Groundwater Levels and Groundwater-Surface Water Interaction

6.1 Groundwater Levels

Groundwater levels were measured at the nine wells using a portable electronic water level recorder prior to purging. Table 21 provides the measured depth to groundwater and calculated groundwater elevations. All groundwater level data are contained in Appendix C of the Data Report. The groundwater elevations varied between 27.1 to 32.9 m Ordnance Datum (OD) in the Avoca Mining Area. These groundwater elevations were between 0.4 to 1.8 metres higher than the elevations measured in the summer season (12 to 14 August 2013). The groundwater elevations were consistent with the hydraulic gradient towards the Avoca River. MWSA2 is located downgradient of Shelton Abbey Tailings which is in a different part of the catchment and the groundwater elevation is much lower than that of the West and East Avoca.

Table 21 Measured Groundwater Levels and Calculated Elevation February 2014

Borehole Identifier	Date	Time	Depth to Groundwater (m bTOC)	Groundwater Elevation (m OD)
MWDA1	2/24/2014	11:30	5.34	27.5
MWDA2	2/24/2014	11:20	5.21	27.4
MWPF1	2/24/2014	15:45	3.56	27.9
MWET1	2/25/2014	10:15	6.15	27.2*
MWET2	2/25/2014	10:20	6.04	27.3*
GW1/05	2/25/2014	13:45	3.68	27.1*
GW2/05	2/25/2014	12:45	3.75	27.2*
SG104	2/25/2014	16:00	25.26	32.9*
MWSA2	2/26/2014	9:15	7.83	2.3

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 14 August 2013 to 23 February 2014. Figure 9 shows the groundwater elevation at MWSA2 at Shelton Abbey Tailings Facility between 14 August and 25 February 2014. Data are missing for MWPF1 from 22 Nov 2013 to 24 February 2014 due to a fault with the batteries, which were replaced on 24 February. Data are missing for MWET1 for the majority of the monitoring period due to a fault in the data logger which was removed for repair on 25 February.

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.

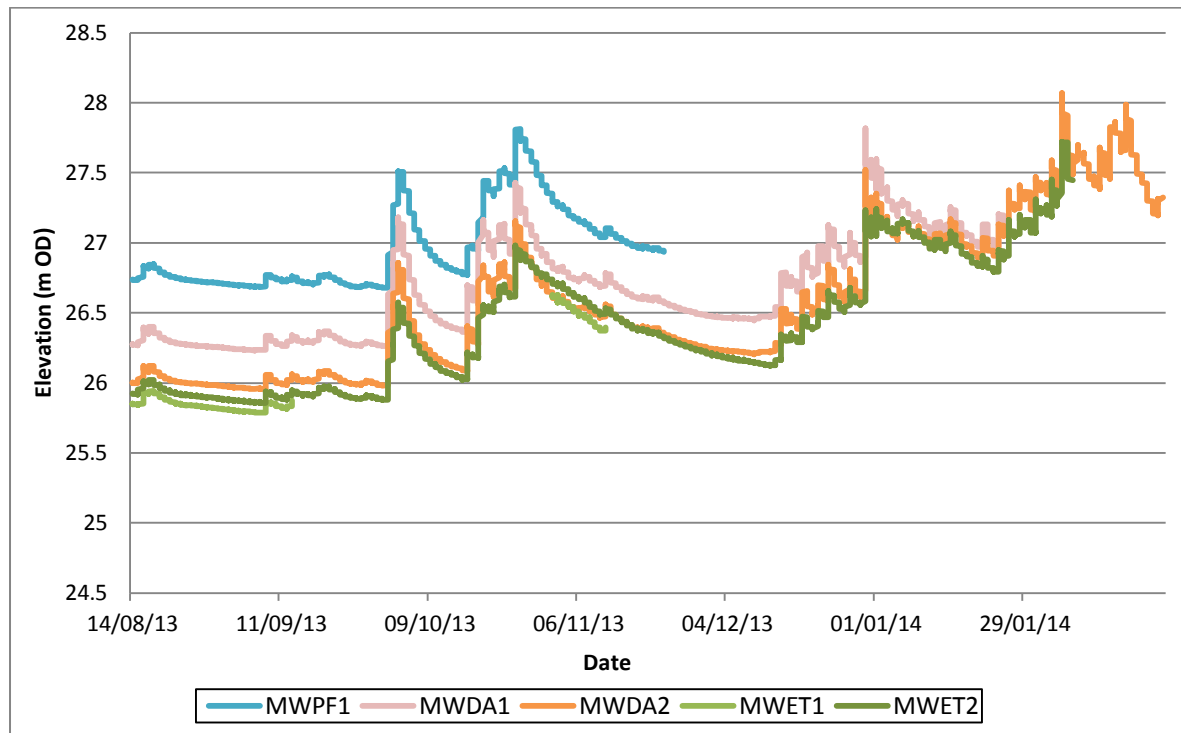


Figure 8 Groundwater Elevations in the Avoca Mining Area from 14 Aug 2013 to 23 Feb 2014

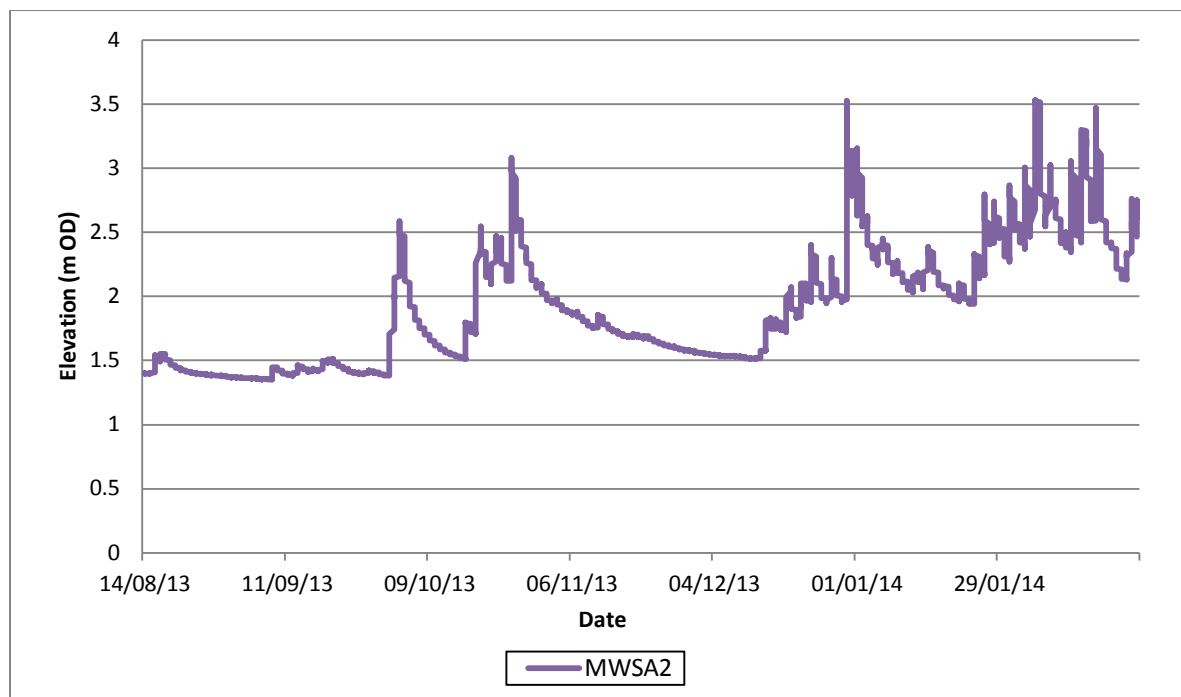


Figure 9 Groundwater Elevation in the at Shelton Abbey from 14 Aug 2013 to 25 Feb 2014

Using the limited data available, the reverse is shown to be true for MWET1 and MWET2 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 a slight downward gradient between the alluvial well GW2/05 and top of bedrock (GW1/05) at this location (Table 21).

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 September 2013 to 24 March 2014 for Whites Bridge GS and Wicklow County Council Maintenance Yard GS are reproduced in Figure 10. The figure demonstrates that the river appears to respond similarly to rainfall at both gauging stations.

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

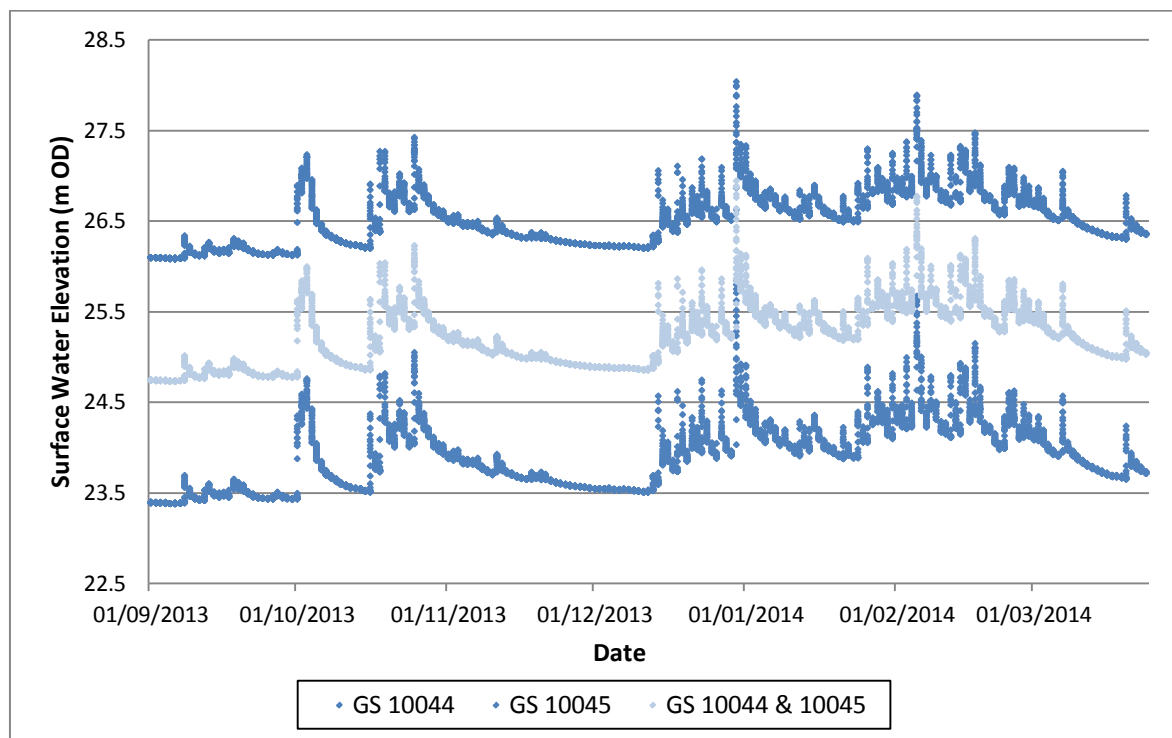


Figure 10 Elevation of the Avoca River at GS 10044 and GS 10045 at the Deep Adit Area from 1 Sept 2013 to 24 Mar 2014

6.3 Groundwater-Surface Water Interaction

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

- For MWDA1, MWDA2 and MWPF1 the river water elevation was taken from the EPA gauge located at Whites Bridge GS (GS 10044);
- MWET1, MWET2, GW1/05 and GW2/05 are located approximately equidistance between the two gauges. To take account of the gradient between the two gauges, the river water elevation was estimated using both the Whites Bridge GS (GS 10044) and the Wicklow Maintenance Yard County Council GS (GS 10045) by selecting a midpoint water level. The estimated surface water elevations for the emergency tailing area are also displayed on Figure 10 (GS 10044 & GS 10045);
- For SG104 the water elevation from Wicklow Maintenance Yard County Council was used (GS 10045); and
- The river water level at MWSA2 was unable to be determined because there are no gauges available at a nearby location.

Table 22 summarises resulting hydraulic gradient data between the monitoring well clusters and the Avoca River during the sampling event, and shows an estimated gradient from the wells to the river in February 2014.

Table 22 Calculated Groundwater Gradients for February 2014

Borehole Identifier	Date	Time	Groundwater Elevation (m OD)	Water Elevation at Perpendicular Stream Point (m OD)	Distance to Perpendicular Stream Point (m)	Gradient
MWDA1	24/2/2014	11:30	27.5	26.91	40	0.015
MWDA2	24/2/2014	11:20	27.4	26.91	40	0.012
MWPF1	24/2/2014	15:45	27.9	26.81	44	0.025
MWET1	25/2/2014	10:15	27.2*	25.59**	72	0.022
MWET2	25/2/2014	10:20	27.3*	25.59**	72	0.024
GW1/05	25/2/2014	13:45	27.1*	25.58**	74	0.021
GW2/05	25/2/2014	12:45	27.2*	25.58**	74	0.022
SG104	25/2/2014	16:00	32.9	24.33	142	0.060
MWSA2	26/2/2014	9:15	2.3	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 the emergency tailings area. Both figures demonstrate that there is a direct relationship between the

river stage and the groundwater levels in both areas. Rises in river levels are accompanied by rises in groundwater levels.

Rainfall totals were significantly higher than the Long-Term-Average (LTA) during the monitoring period (Met Éireann, 2014). This resulted in several hydrological events which caused groundwater levels to rise, both figures show that significant peaks in groundwater levels occurred in October, December and February. For example groundwater levels rose by approximately 0.9 metres between 30 September and 3 October and again between 29 and 30 December. These peaks were in response to river levels which rose by up to 1.2 metres in the October event and 1.5 metres in the December event. Extensive rainfall in January and February 2014 resulted in an overall increase in groundwater levels at the deep adit area and emergency tailings area. River levels also rose by up to 1.4 metres between January and February 2014.

Figure 12 and Figure 14 show the calculated gradient to the Avoca River at the deep adit area (MWDA1, MWDA2) from 1 September 2013 to 24 February 2014 and the emergency tailings area (MWET1, MWET2) from 1 September 2013 to 7 February 2014 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 a negative gradient occurs during periods of high flow, particularly when there is a rapid rise in water level. However, following a sustained period of high rainfall in January and February the gradient at MWDA2 becomes net positive which is due to rising water levels from extensive aquifer recharge. A positive gradient existed for over 60% of the monitoring period. The minimum gradient was minus 0.016 while the average was 0.003. 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 when groundwater levels are low in periods of dryer weather, which was the case for the majority of last monitoring period (March to August 2013).

On 29 and 30 December a significant hydrological (rainfall) event resulted in groundwater levels rising in MWDA1 and MWDA2 by approximately 0.9 metres. A negative gradient can be observed during this period between the river and both wells, as shown in Figure 12. During 29 and 30 December period the river water level also rose (approximately 1.5 metres) but more rapidly which resulted in water moving into the monitoring well area, apparent from the rise in groundwater levels. It is likely the river water moved into an unsaturated zone, which could result in mobilising new metals if they were not exposed before.

For MWET1 and MWET2 only positive gradients were observed with a minimum gradient of 0.003 (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.

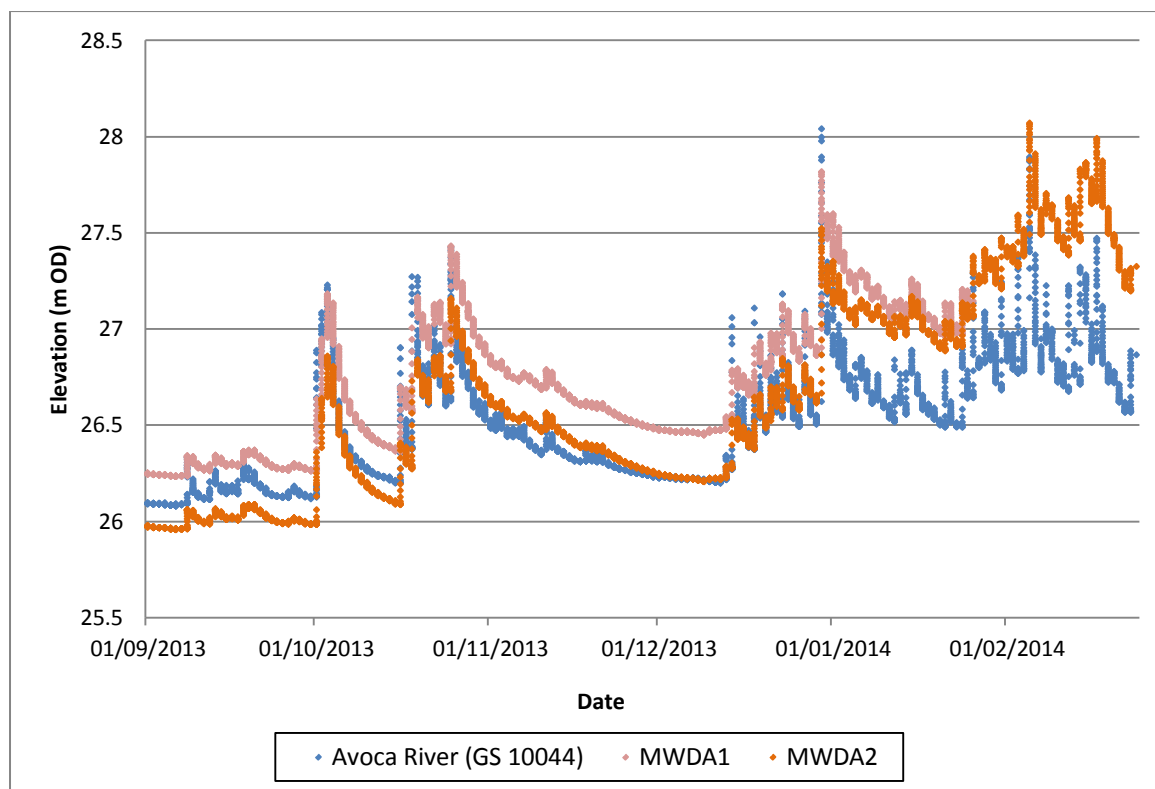


Figure 11 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044) at the Deep Adit Area from 1 Sep 2013 to 24 Feb 2014

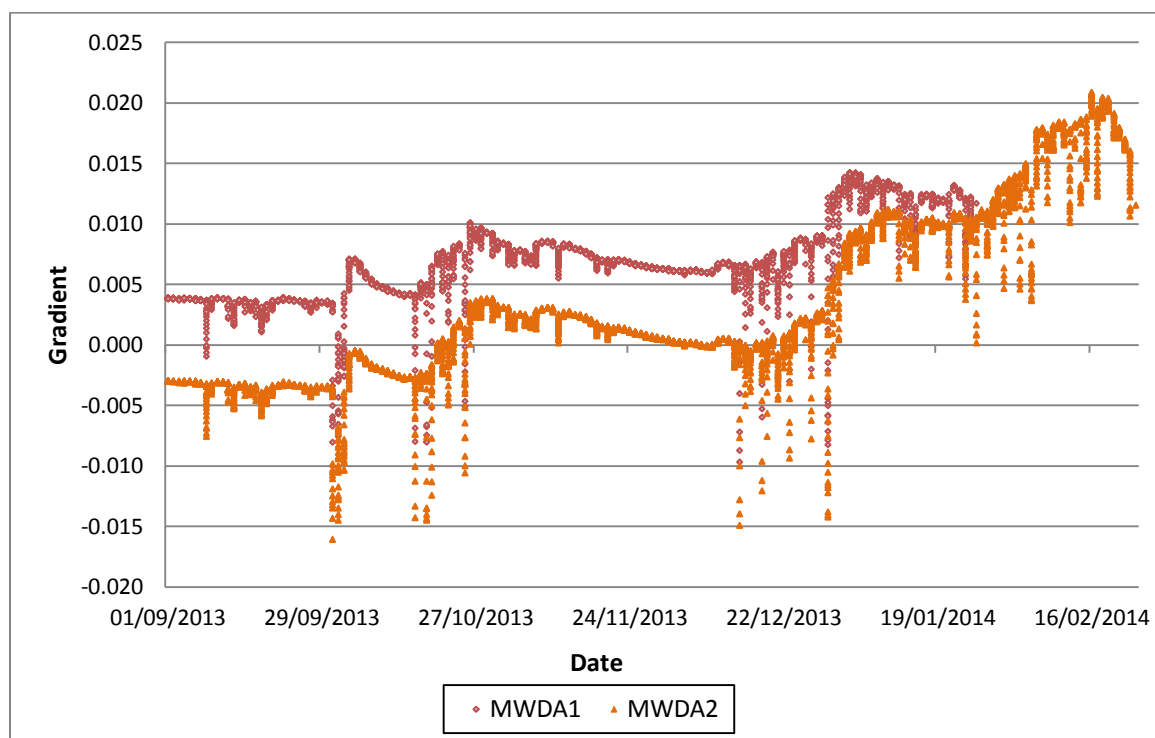


Figure 12 Calculated Groundwater Gradient to the Avoca River at the Deep Adit Area from 1 Sep 2013 to 24 Feb 2014

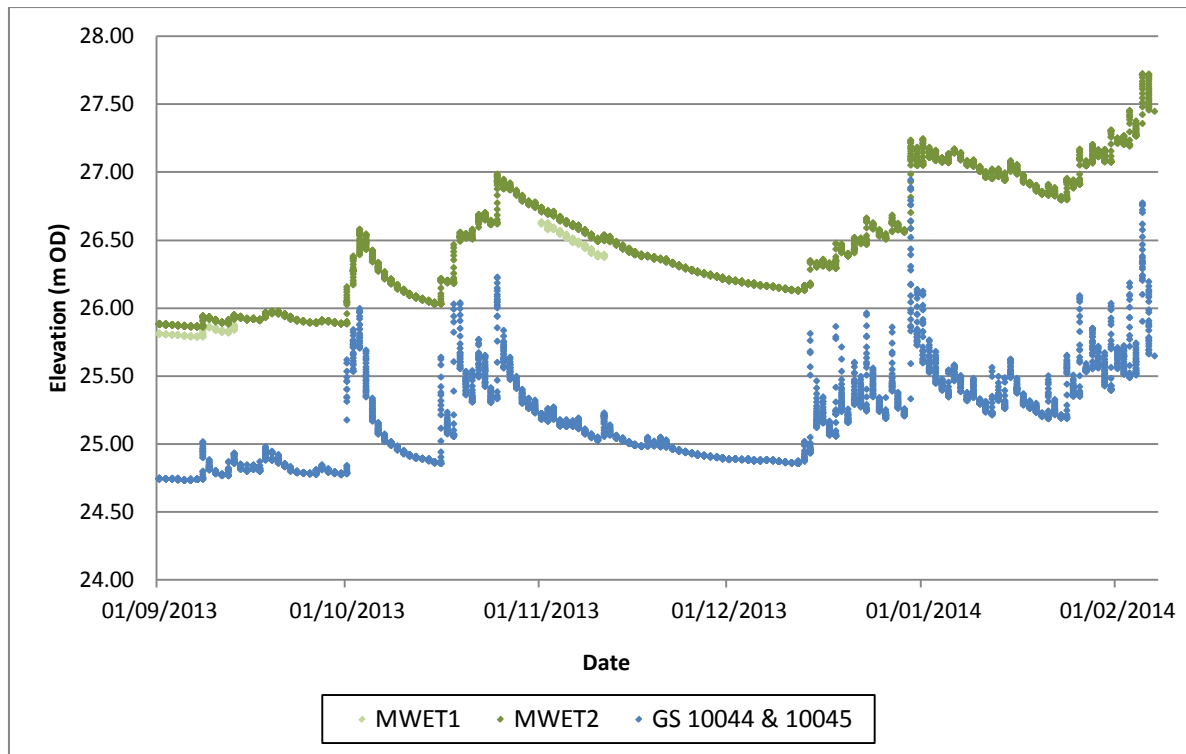


Figure 13 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044 & 10045) at the Emergency Tailings Area from 1 Sep 2013 to 7 Feb 2014

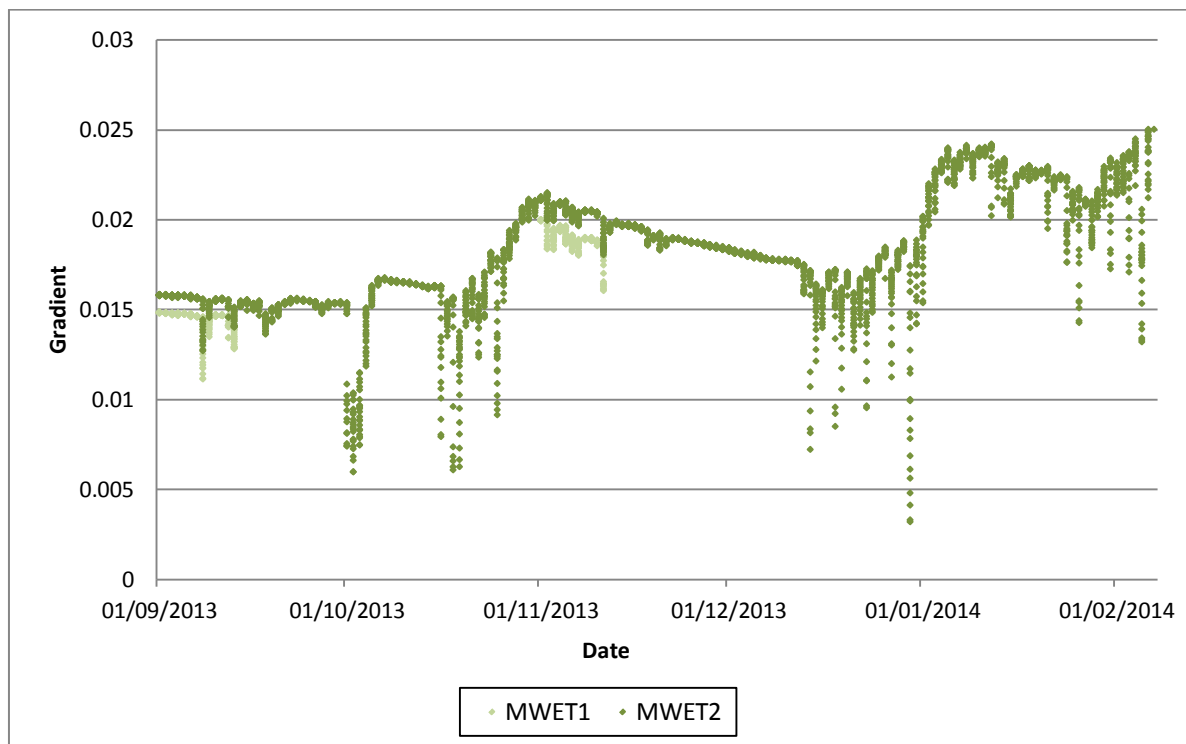


Figure 14 Calculated Groundwater Gradient to the Avoca River at the Emergency Tailings Area from 1 Sep 2013 to 7 Feb 2014

6.4 Summary of Diffuse Loading

In the Avoca mining area diffuse flow load discharges to the Avoca River from a combination of sources including groundwater, ditch infiltration and infiltration on spoil piles. The analysis of loading to the Avoca River is discussed in Section 5.2.2 Loading Results and Discussion and can be summarised as follows using the zinc loading as an example:

- Between Site T1 to Whites Bridge, zinc load increased from 48.9 to 113 kg/day which is a 57 % increase. The only surface water input in this segment is from Vale View which contributes very little load (0.48 kg/day). This indicates that the increase in loading is primarily due to diffuse load;
- Between Whites Bridge and Whites Bridge GS, zinc load increases from 113 to 227 kg/day which is a 50 % increase. There are no direct discharges in this segment which again indicates that the increase in loading is primarily due to diffuse load;
- Between Whites Bridge GS and WCC Maintenance Yard GS, zinc load increases from 227 to 268 kg/day which is a 15 % increase. The Deep Adit discharge (confluence sample) contributes 107 kg/day and Ballygahan Adit contributes extra load in this segment however the load was not measureable. Overall there is an apparent loss of 25 % in zinc load in this segment, which is likely due to the fact that the samples (and flow measurements) were collected on separate days or precipitation of iron/metals occurred in the river at Deep Adit confluence; and
- Between WCC Maintenance Yard GS and Site T5, zinc load increases from 268 to 485 kg/day. The Road Adit (confluence sample) contributed 112 kg/day of the load. This indicates that 95 kg/day which indicates that the diffuse loading contributes almost as much as the Road Adit in this segment (despite the decrease in flow in this segment).

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

This is especially evident in the measured zinc load results from the March 2014 sampling, in the stretches of river between Site T1 and Whites Bridge GS and between WCC Maintenance Yard GS and Site T5, where the diffuse load accounts for a large portion of the zinc loading to the Avoca River. Dissolved zinc exceeded the ecological assessment criteria (50 µg/l) from Whites Bridge GS on the Avoca River to Downstream Shelton Abbey with results ranging from 99.7 to 669 µg/l. The dissolved zinc result at Whites Bridge GS was 99.7 µg/l which is almost twice the ecological assessment criteria and primarily from diffuse flow upstream of the Deep Adit discharge into the Avoca River.

Section 7

Summary and Recommendations

7.1 Summary of Findings

Nine groundwater monitoring wells were sampled and analysed in February 2014 and water levels were measured. Twenty-three surface water locations were sampled and analysed in February/March 2014 with flows measured at 15 of the locations. The field QA/QC sample results were reviewed for accuracy and precision. The laboratory QC/QC samples and laboratory reports were also reviewed. Overall, the data quality is considered acceptable and the data can be used to compare to the assessment criteria and perform trend and loading evaluations.

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

The overall conclusions are as follows:

- The dissolved metal concentrations were elevated in the majority of the monitoring wells and adit discharges with numerous exceedances of ecological criteria, human health criteria or both, particularly for dissolved aluminium, cadmium, copper, iron, manganese, nickel and zinc. Sulphate levels greatly exceeded the criteria for human health in the majority of monitoring wells.
- The shallow well MWPF1 located upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments had the lowest concentration of dissolved metals. SG104 located immediately downgradient of Ballymurtagh Landfill had the highest concentrations of dissolved metals especially aluminium, cadmium, nickel and zinc.
- The Cronebane Shallow Adit was the adit discharge with the highest concentrations of metals including aluminium, 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. 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 5.39 to 126 µg/l. Similarly dissolved zinc exceeded the ecological assessment criteria (50 µg/l) from Whites Bridge GS on the Avoca River to Downstream Shelton Abbey with results ranging from 99.7 to 669 µg/l. Dissolved zinc was also detected at concentrations above the ecological assessment criteria upstream of the Avoca Mines at Lions Bridge and Ballinacleish Bridge and in the two tributaries at concentrations ranging from 59.5 to 83.5 µg/l. Dissolved aluminium exceeded human health criteria (200 µg/l) only at Whites Bridge GS and DS of the Deep Adit with a concentrations of 236 µg/l and 976 µg/l, respectively.

- The Deep Adit and 850 Adit showed similar loadings for sulphate (1,250 kg/day and 1,500 kg/day), dissolved aluminium (122 kg/day and 138 kg/day) and zinc (42.5 kg/day and 68.5 kg/day). However the 850 Adit had significantly higher loading of dissolved copper with 18 kg/day and the Deep Adit had 2.9 kg/day.
- There was a slight apparent loss of dissolved iron load from the Deep Adit and 850 portal samples when compared to the Deep Adit confluence sample, as it decreased from 127 to 108 kg/day and the rest of the loadings were similar at both locations. This is likely due to the precipitation of iron along the ditch.
- The concentrations of sulphate and the dissolved metals were similar in the Road Adit portal and the confluence samples. The loadings appeared to be slightly higher at the confluence location but this was likely due to the higher flow measurement at the confluence.
- The results of the Mann-Kendall analysis show that dissolved copper concentrations are decreasing and dissolved iron is increasing in the Deep Adit since 2001. Dissolved zinc is decreasing in the Road Adit and dissolved copper and iron are likely decreasing since 2001. There is no statistically significant trend for dissolved copper or zinc at Avoca Bridge.
- As river stages change hydraulic gradients to or from the river also change. Gradients are predominantly positive which suggests that the Avoca River is a net gaining river from the alluvium during the monitoring period. The implication is that the spoil and the alluvial areas either side of the river contribute contaminant load to the river. This is especially evident in the measured zinc load results, in the stretches of river between Site T1 and Whites Bridge GS and between WCC Maintenance Yard GS and Site T5, where the diffuse load accounts for a large portion of the zinc loading to the Avoca River.

7.2 Recommendations for the Monitoring Programme

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

- The new sampling locations at the 850 adit, Deep Adit Confluence and the Road Adit Confluence should continue to be monitored in order to compare the loadings at the adits portals and the confluences before they discharge to the river;
- It is recommended that the reconfiguration of the Deep Adit during the Avoca Priority Works Project is utilised to install a permanent flow measuring device; and
- The Road Adit channel is currently being upgraded by Wicklow County Council. Whether this has an impact on the sampling locations will be assessed during the next round of sampling.

Section 8

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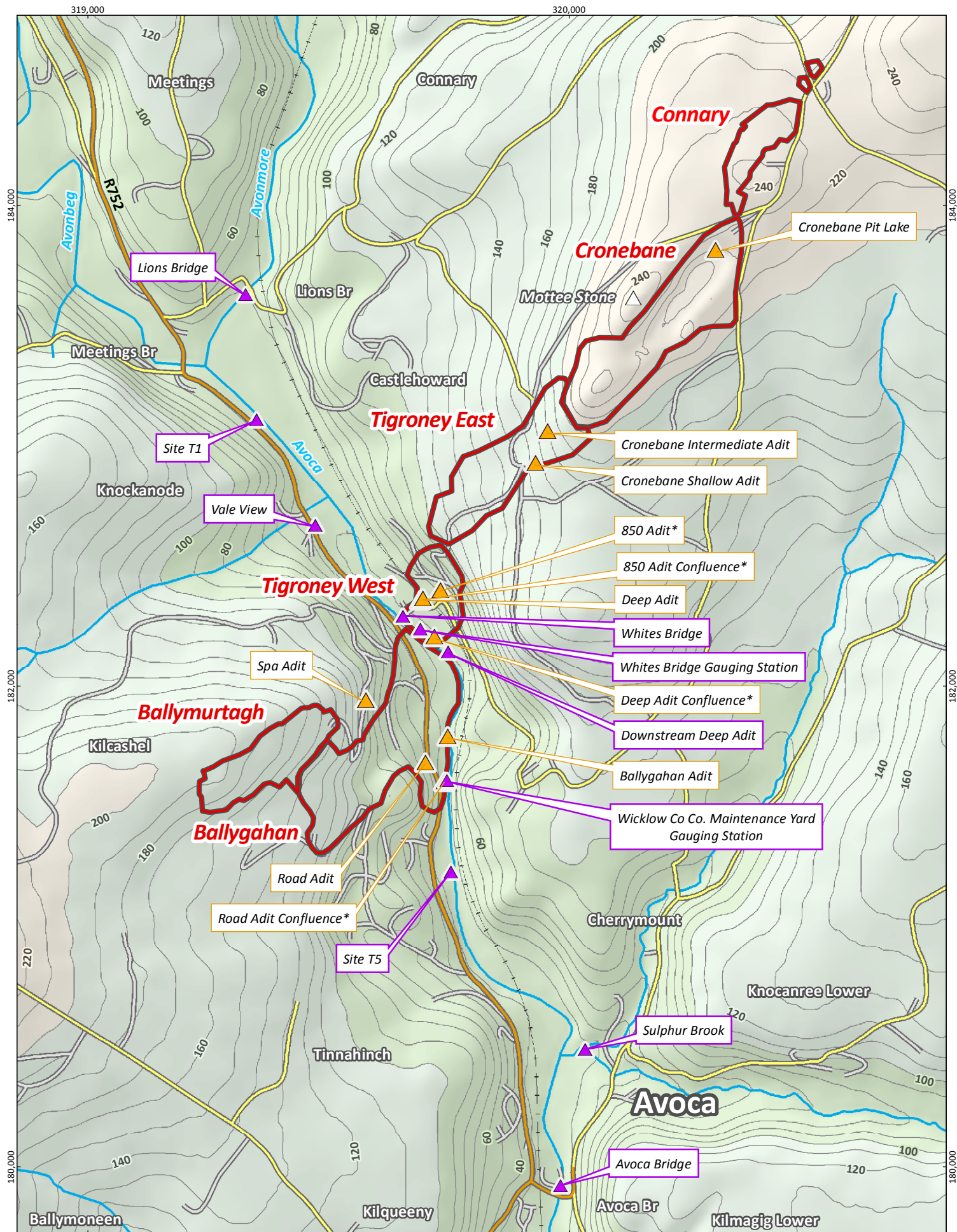
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Appendix A

Figures



Map 1 - Avoca - Main Area

Drawn by: OC Date: 31/03/2014

Internal Project Reference: S:\CURRENT_PROJECTS\95735_Avoca_Silver\02_GIS_Tasks\07_MonRptR3\MXD\01_AvocaMon1.mxd

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Legend

Sampling Locations

- Surface water (Rivers and Streams)
- Surface water (Adit discharges)
- * New sampling locations in Round 3

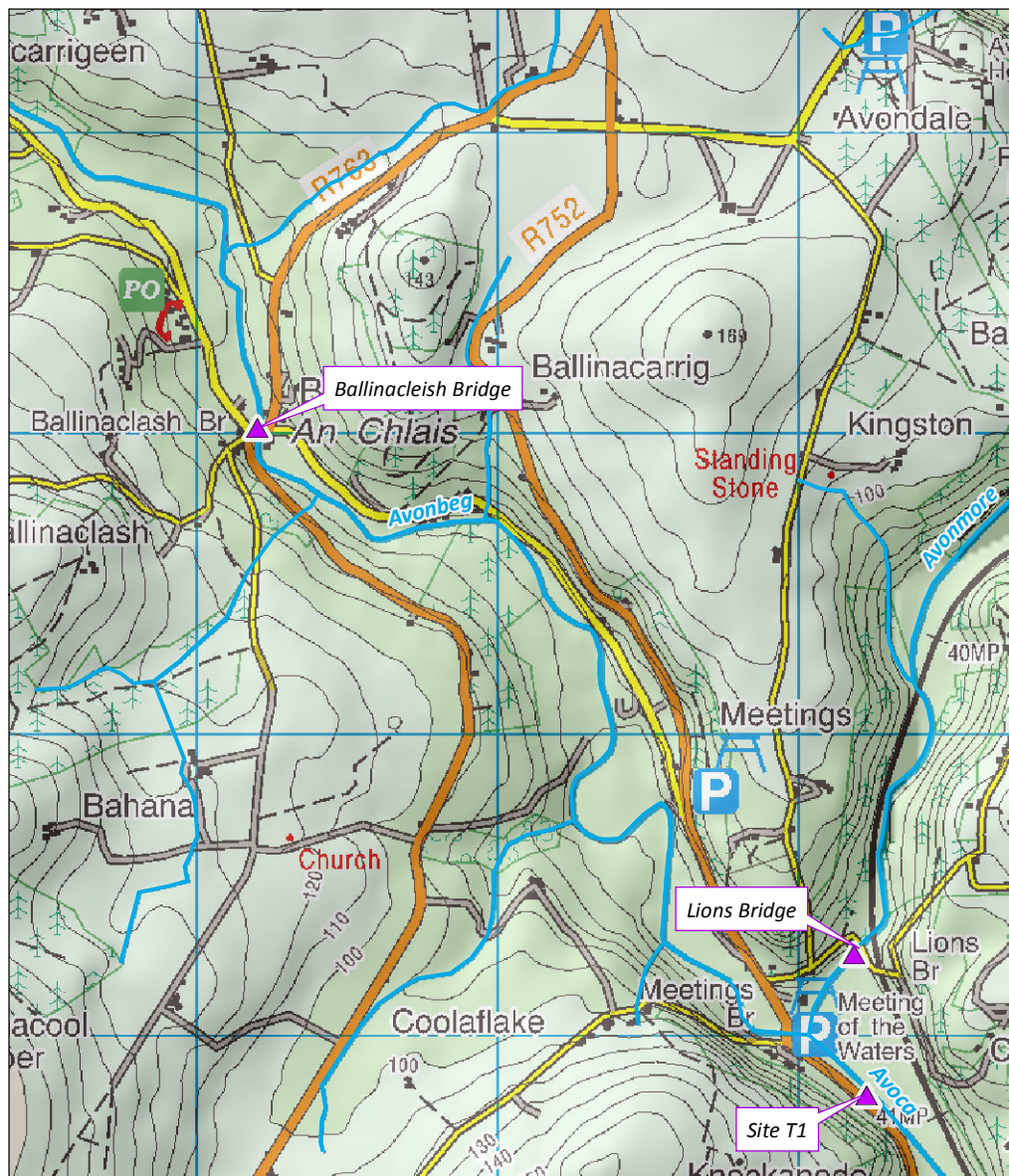
Mines

- Mining Areas
- Rivers

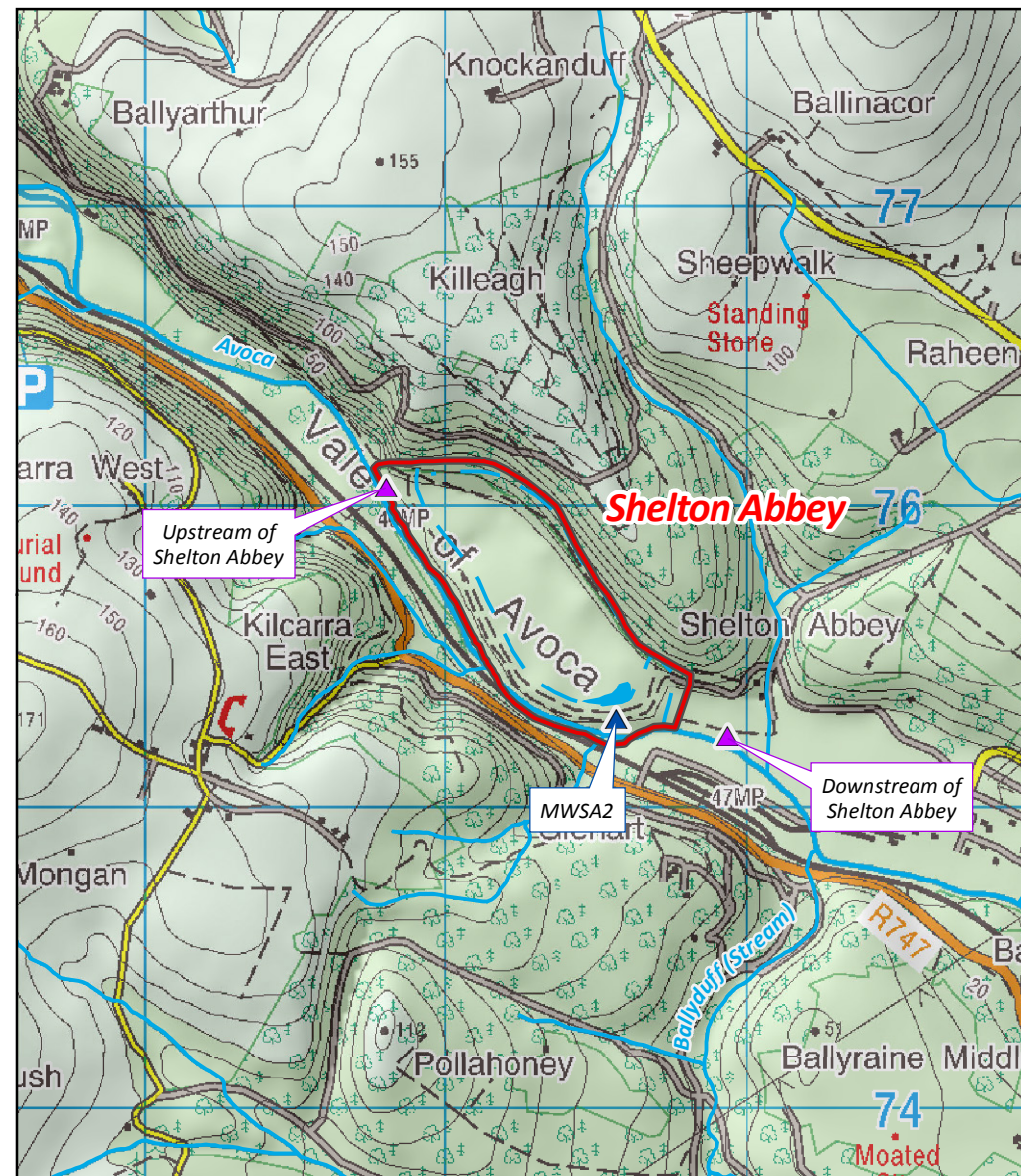


Scale is 1:18,000

0 125 250 500 m



Ballinacleish



Shelton Abbey

Map 2 - Avoca - Ballinacleish and Shelton Abbey

Drawn by: OC Date: 31/03/2014

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Legend

Sampling Locations

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

Mines

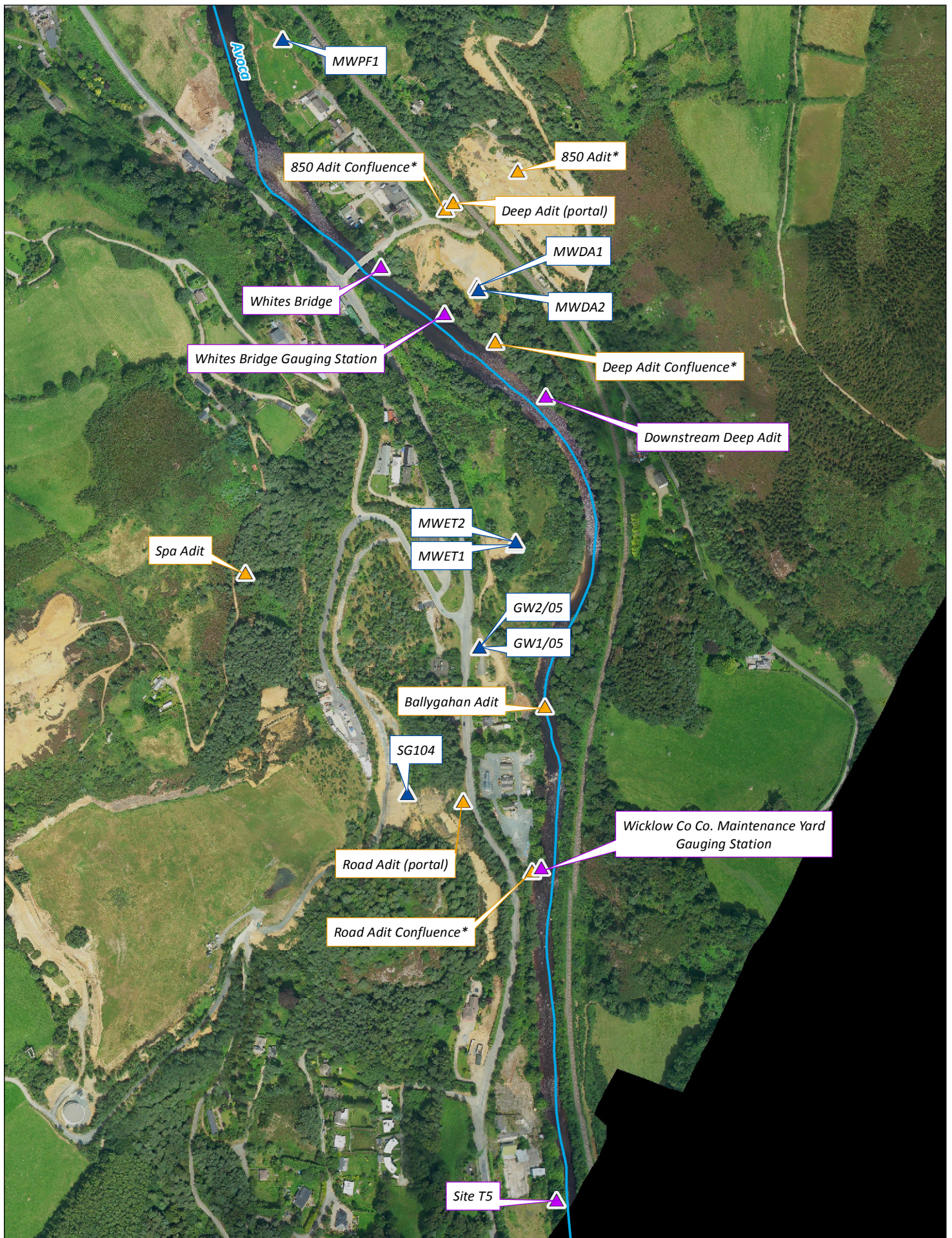
- Mining Area

— Rivers

Scale is 1:25,000

0 250 500 1,000 m





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

Drawn by: OC/LG Date: 26/05/2014

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Source: © DCENR Lidar Survey (2007)

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Legend

Sampling Locations

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

— Rivers

* New sampling locations in Round 3



Scale is 1:5,000

0 50 100
m

Appendix B

Analytical Data Tables and Assessment Criteria

Table B-1 Total versus Dissolved Metals Comparison R3

Sample Description	Date Sampled	Suspended solids, Total	Aluminium (tot.unfilt)	Aluminium (diss.filt)	Ratio diss to total Aluminium	Copper (tot.unfilt)	Copper (diss.filt)	Ratio diss to total Copper	Iron (tot.unfilt)	Iron (diss.filt)	Ratio diss to total Iron	Zinc (tot.unfilt)	Zinc (diss.filt)	Ratio diss to total Lead
		Units mg/l	µg/l	µg/l		µg/l	µg/l		µg/l	µg/l		µg/l	µg/l	
MWDA1	24/02/2014	-	333000	392000	1.2	41800	41500	1.0	168000	133000	0.8	78700	61700	0.8
MWDA2	24/02/2014	-	48000	72300	1.5	3190	5600	1.8	91600	53700	0.6	62400	44700	0.7
MWPF1	24/02/2014	-	478	377	0.8	75.7	50.5	0.7	26.9	23	0.9	117	88.3	0.8
GW1/05	25/02/2014	-	79800	78000	1.0	12300	11000	0.9	36300	266000	7.3	99100	73300	0.7
GW2/05	25/02/2014	-	68700	64900	0.9	11200	8800	0.8	1910	122	0.1	13000	10100	0.8
MWET 1	25/02/2014	-	136000	136000	1.0	12200	8710	0.7	61000	39700	0.7	12200	9280	0.8
MWET 2	25/02/2014	-	66.4	126	1.9	11.9	8.88	0.7	123000	72500	0.6	4540	6700	1.5
SG104	25/02/2014	-	1040000	886000	0.9	118000	83100	0.7	43400	32200	0.7	216000	159000	0.7
Cronebane Inter. Adit	26/02/2014	1	47000	67100	1.4	12900	11300	0.9	73900	59100	0.8	29100	29900	1.0
Cronebane Pit Lake	26/02/2014	2	11500	9260	0.8	4440	3470	0.8	7100	5740	0.8	4110	3480	0.8
Cronebane Shallow Adit	26/02/2014	2	219000	208000	0.9	15200	13200	0.9	136000	115000	0.8	79000	62600	0.8
MWSA2	26/02/2014	-	53500	46900	0.9	191	123	0.6	92600	76400	0.8	4460	4250	1.0
Shelton Abbey DS	26/02/2014	2	250	151	0.6	20	10.1	0.5	367	204	0.6	95.8	105	1.1
Shelton Abbey US	26/02/2014	5.26	250	155	0.6	20	10.4	0.5	479	211	0.4	95.7	90.4	0.9
850 Adit	27/02/2014	1	53900	74300	1.4	13800	10900	0.8	13600	12200	0.9	28400	25800	0.9
Deep Adit	27/02/2014	2	74900	71600	1.0	1670	1500	0.9	59000	55800	0.9	37400	35500	0.9
Deep Adit Confluence	27/02/2014	1	78700	71600	0.9	7980	6240	0.8	31000	29900	1.0	31300	29500	0.9
Road Adit	27/02/2014	3	16300	15000	0.9	383	321	0.8	275000	265000	1.0	16600	20100	1.2
Road Adit Confluence	27/02/2014	5	17700	14700	0.8	425	334	0.8	280000	249000	0.9	17600	19900	1.1
Spa Adit	27/02/2014	1	93000	111000	1.2	9650	7650	0.8	64800	64200	1.0	11300	9850	0.9
Ballinaclesh Bridge	02/03/2014	1	109	109	1.0	2	0.425	0.2	88.5	44	0.5	22.1	59.5	2.7
DS Deep adit	02/03/2014	9.47	1690	976	0.6	133	126	0.9	656	347	0.5	658	669	1.0
Lions Bridge	02/03/2014	1	96.1	77.9	0.8	2	1.08	0.5	131	67	0.5	37.1	83.5	2.3
Site T1	02/03/2014	1	96.7	90.4	0.9	2	0.425	0.2	106	47	0.4	26.7	24.7	0.9
Vale View	02/03/2014	1	25	15.4	0.6	2	1.7	0.9	87.5	24	0.3	11	63.1	5.7
Whitesbridge	02/03/2014	1	153	124	0.8	7.03	5.39	0.8	107	60	0.6	60.6	49.5	0.8
Whitesbridge GS	02/03/2014	1	279	236	0.8	13.4	12.8	1.0	147	77	0.5	102	99.7	1.0
Avoca Bridge	04/03/2014	3.5	467	152	0.3	24.5	18.5	0.8	720	485	0.7	190	161	0.8
Site T5	04/03/2014	10	649	123	0.2	33.4	19.8	0.6	2310	1750	0.8	350	273	0.8
Sulphur Brook	04/03/2014	6	88.3	29	0.3	20	18	0.9	108	10	0.1	68.4	59.6	0.9
Wicklow CoCo Main. Yard GS	04/03/2014	1	438	188	0.4	24.7	21.1	0.9	191	88	0.5	129	121	0.9

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

Table B-2 Comparison of Groundwater and Surface Water Results to Assessment Criteria R3

Sample Description	Type	Date Sampled Units	Specific Conductance													Oxygen,	pH (field) pH Units	Phosphate (ortho) as P mg/l	Sulphate mg/l	Sodium (diss.filt) mg/l	Suspended solids, Total mg/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	@ deg.C (field) mS/cm	Cyanide, Free mg/l	Dissolved solids, Total mg/l	Fluoride mg/l	Nitrate as NO3 mg/l	Nitrite as NO2 mg/l	dissolved (field) % Sat						
Ecological Criteria			-	-	-	0.14	-	-	-	0.01	-	0.5	-	-	80 to 120*	4.5 to 9	0.075	-	-	-	
Human Health Criteria			-	-	-	0.3	250	-	2.5	0.05	-	1.5	50	0.5	-	6.5 to 9.5	-	250	200	-	
MWDA1	GW	24/02/2014	-	1	1.22	1.03	12	-	4.471	-	6200	15	0.455	0.025	1.8	2.75	0.01	3780	6.01	-	
MWDA2	GW	24/02/2014	-	1	1.22	0.1	13.9	-	1.581	-	1700	2.1	0.75	0.2	5	3.82	0.01	989	11.2	-	
MWPF1	GW	24/02/2014	-	2.5	3.05	0.1	14.8	-	0.149	0.025	94.4	0.25	10.2	0.025	93.6	4.83	0.01	26.3	7.3	-	
MWET1	GW	25/02/2014	-	1	1.22	0.43	35.2	-	2.093	-	2520	1.43	1.65	0.151	2.6	3.38	0.01	1480	22.5	-	
MWET2	GW	25/02/2014	-	70	85.4	0.1	13.4	-	3.368	-	3930	0.809	0.1	0.025	3.2	6.37	0.01	2420	22.6	-	
GW1/05	GW	25/02/2014	-	1	1.22	0.362	15.5	-	2.693	-	3430	2.41	0.15	0.025	2.6	4.25	0.01	2020	13.5	-	
GW2/05	GW	25/02/2014	-	1	1.22	0.1	14.1	-	1.653	-	1820	0.25	8.28	0.025	39.8	3.73	0.01	1070	9.39	-	
SG104	GW	25/02/2014	-	1	1.22	2.72	14.5	-	8.605	-	15700	8.81	0.75	0.025	55.4	2.94	0.01	9770	6.11	-	
MWSA2	GW	26/02/2014	-	1	1.22	1.03	14.7	-	2.297	0.025	2600	6.34	0.15	0.025	3.4	3.93	0.01	1580	8.37	-	
Cronebane Pit Lake	Pit Lake	26/02/2014	74.8	1	1.22	0.1	13.1	3.5	0.541	0.025	241	1.14	3.74	0.025	91.3	2.96	0.01	143	6.2	2	
Cronebane Inter. Adit	Adit	26/02/2014	438	1	1.22	0.351	12.9	7.73	1.451	0.025	1390	8.65	0.499	0.025	9.4	2.74	0.01	767	6.94	1	
Cronebane Shallow Adit	Adit	26/02/2014	1200	1	1.22	0.683	15.6	20.7	2.753	0.025	3540	15.7	0.855	0.025	61.5	2.72	0.01	1990	7.29	2	
850 Adit	Adit	27/02/2014	411	1	1.22	0.274	12.7	7.3	1.537	0.025	1290	3.72	1.65	0.025	85.8	2.78	0.01	758	6.45	1	
Deep Adit	Adit	27/02/2014	392	1	1.22	0.271	13.1	12.7	1.284	0.025	1380	1.24	3	0.025	15.6	3.49	0.01	781	7.89	2	
Deep Adit Confluence	Adit	27/02/2014	389	1	1.22	0.263	12.8	3.5	1.41	0.025	1340	3.75	2.45	0.025	92.4	3.03	0.01	759	7.48	1	
Road Adit	Adit	27/02/2014	469	1	1.22	4.79	27.1	64.2	2.575	0.025	2890	2.8	4.41	0.025	22.6	4.4	0.01	1610	16.7	3	
Road Adit Confluence	Adit	27/02/2014	469	1	1.22	4.78	26.7	65.4	2.576	0.025	2860	2.4	4.11	0.025	76.1	4.49	0.01	1680	16.5	5	
Ballygahan Adit	Adit	27/02/2014	-	-	-	5.14	28.6	-	2.533	0.025	-	8.11	14.1	0.025	73.9	2.99	0.01	1540	18.9	60	
Spa Adit	Adit	27/02/2014	675	1	1.22	0.697	9.7	12.4	2.094	0.025	2010	9.97	3.69	0.025	84.9	2.74	0.01	1180	4.72	1	
Vale View	SW	03/03/2014	2	22	26.84	0.1	14.9	3.5	0.152	0.025	103	0.25	14.1	0.025	95	6.88	0.01	14	5.3	1	
Sulphur Brook	SW	04/03/2014	2	19	23.18	0.1	15.3	3.5	0.153	0.025	74.7	0.25	21.8	0.025	97.5	6.64	0.01	11.6	8.97	6	
Ballinacleish Bridge	SW	03/03/2014	2	7	8.54	0.1	9.2	3.5	0.061	0.025	44	0.25	3.65	0.025	95.5	5.84	0.01	1	3.96	1	
Lions Bridge	SW	03/03/2014	2	9	10.98	0.1	10.4	3.5	0.072	0.025	52	0.25	4.46	0.025	99.2	6.22	0.01	1	5.16	1	
Site T1	SW	03/03/2014	2	9.5	11.59	0.1	10.2	3.5	0.072	0.025	46.7	0.25	4.99	0.025	97	6.57	0.01	1	4.51	1	
Whites Bridge	SW	03/03/2014	2	9	10.98	0.1	10.9	3.5	0.076	0.025	62.5	0.25	4.63	0.025	94.2	6.81	0.01	4.1	4.86	1	
Whites Bridge GS	SW	03/03/2014	2	9	10.98	0.1	10.9	11.3	0.082	0.025	54.3	0.25	4.6	0.025	94.1	6.64	0.01	5.4	4.93	1	
DS Deep Adit	SW	03/03/2014	2	3	3.66	0.1	10.6	3.5	0.112	0.025	58.8	0.25	4.44	0.025	94.3	5.46	0.01	20.5	4.93	9.47	
Wicklow CO.CO. Main. Yard GS	SW	04/03/2014	2	8	9.76	0.1	10.8	8.79	0.108	0.025	29.3	0.25	5.1	0.025	98.3	5.62	0.01	8.7	6.93	1	
Site T5	SW	04/03/2014	2	3	3.66	0.1	10.7	3.5	0.118	0.025	44.4	0.25	5.03	0.025	99	5.85	0.01	26	13.6	10	
Avoca Bridge	SW	04/03/2014	2	6.5	7.93	0.1	10.5	9.19	0.091	0.025	41.3	0.25	5.35	0.025	98.8	6.2	0.01	13.1	6.7	3.5	
US Shelton Abbey	SW	26/02/2014	2	10	12.2	0.233	10.9	9.73	0.091	0.025	47.8	0.25	7.1	0.025	100.1	5.8	0.01	7.6	6.32	5.26	
DS Shelton Abbey	SW	26/02/2014	2	10	12.2	0.1	11	7.42	0.093	0.025	54.7	0.25	7.53	0.025	95.2	5.83	0.01	9	6.45	2	

xx Exceeds Ecological Assessment Criteria

xx Exceeds Human Health Assessment Criteria

xx Exceeds both Ecological and Human Health Criteria

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

- Not analysed or no assessment criteria

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

Table B-2 Comparison of Groundwater and Surface Water Results to Assessment Criteria R3

Sample Description	Type	Date Sampled Units	Aluminium (diss.filt) µg/l	Antimony (diss.filt) µg/l	Arsenic (diss.filt) µg/l	Barium (diss.filt) µg/l	Cadmium (diss.filt) µg/l	Chromium (diss.filt) µg/l	Cobalt (diss.filt) µg/l	Copper (diss.filt) µg/l	Iron (diss.filt) µg/l	Lead (diss.filt) µg/l	Manganese (diss.filt) µg/l	Mercury (diss.filt) µg/l	Molybdenum (diss.filt) µg/l	Nickel (diss.filt) µg/l	Selenium (diss.filt) µg/l	Silver (diss.filt) µg/l	Thallium (diss.filt) µg/l	Tin (diss.filt) µg/l	Uranium (diss.filt) µg/l	Vanadium (diss.filt) µg/l	Zinc (diss.filt) µg/l
Ecological Criteria			1,900	-	25	4	0.45	3.4	5.1	5	-	7.2	1100	0.07	-	20	-	-	-	-	2.6	-	50
Human Health Criteria			200	5	10	-	5	50	-	2000	200	10	50	1	-	20	10	-	-	-	-	-	-
MWDA1	GW	24/02/2014	392000	8	0.6	4.36	137	74.1	271	41500	133000	6.05	19500	0.0706	1.2	173	1.95	7.5	4.8	1.8	17.3	12	61700
MWDA2	GW	24/02/2014	72300	0.8	0.6	7.53	80.8	6.3	173	5600	53700	0.714	9480	0.005	1.2	94.3	1.95	7.5	4.8	1.8	7.5	1.2	44700
MWPF1	GW	24/02/2014	377	0.08	0.06	9.4	0.599	1.92	2.21	50.5	23.3	0.7	98.8	0.005	0.314	2.41	0.195	0.75	48	0.18	0.75	0.12	88.3
MWET1	GW	25/02/2014	136000	0.8	0.6	3.54	26.9	15.8	200	8710	39700	4.52	8530	0.005	1.2	93.8	1.95	0.75	4.8	1.8	7.5	1.2	9280
MWET2	GW	25/02/2014	126	1.8	6.75	14.2	4.52	1.1	157	8.88	72500	0.37	35900	0.005	2.94	26.4	1.95	7.5	4.8	1.8	7.5	1.2	6700
GW1/05	GW	25/02/2014	78000	0.8	1.66	13.3	92.3	24.4	428	11000	266000	1700	17200	0.005	1.2	107	7.83	75	4.8	1.8	7.5	1.2	73300
GW2/05	GW	25/02/2014	64900	0.08	0.06	2.28	17.6	5.67	93.4	8800	122	0.926	5890	0.005	0.63	42.5	0.461	0.75	0.48	0.18	3.51	0.12	10100
SG104	GW	25/02/2014	886000	8	6	22.9	592	34.7	1090	83100	32200	51.7	45500	0.0873	12	449	19.5	75	48	18	75	12	159000
MWSA2	GW	26/02/2014	51700	0.08	14.2	8.74	1.64	7.45	151	128	78600	28	31100	0.005	0.12	117	0.749	0.75	0.48	0.18	5.89	0.951	4250
Cronebane Pit Lake	Pit Lake	26/02/2014	9260	0.08	1.38	6.58	10	0.729	16.4	3470	5740	206	314	0.005	0.12	7.02	0.195	0.75	0.48	0.18	1.62	0.12	3480
Cronebane Inter. Adit	Adit	26/02/2014	67100	0.554	18.8	5.38	80.5	2.66	72.3	11300	59100	929	2070	0.0251	0.266	49.1	0.195	0.75	2.77	0.18	10.9	1.35	29900
Cronebane Shallow Adit	Adit	26/02/2014	208000	0.564	34.4	3.85	104	7.77	148	13200	115000	859	5080	0.02	0.12	73	0.195	7.5	1.37	0.18	19.4	0.701	62600
850 Adit	Adit	27/02/2014	74300	3.18	0.77	6.87	57.6	1.69	78.6	10900	12200	838	2380	0.0152	0.804	35	0.518	0.75	2.68	1.35	8.73	0.12	25800
Deep Adit	Adit	27/02/2014	71600	0.08	1.23	6.7	44	0.863	67.9	1500	55800	1340	2900	0.005	0.12	23	0.547	7.5	1.14	0.18	6.82	0.325	35500
Deep Adit Confluence	Adit	27/02/2014	71600	0.08	0.838	6.44	50.8	1.2	72.5	6240	29900	986	2590	0.005	0.12	29.4	0.195	0.75	1.42	0.18	7.68	0.12	29500
Road Adit	Adit	27/02/2014	15000	0.8	3.35	18.2	7.87	1.1	230	321	265000	219	19800	0.005	1.2	92.1	1.95	7.5	4.8	1.8	7.5	1.2	20100
Road Adit Confluence	Adit	27/02/2014	14800	0.8	3.44	18.7	7.26	1.1	225	334	255000	218	19700	0.005	1.2	97.3	4.46	7.5	4.8	1.8	7.5	1.2	20400
Ballygahan Adit	Adit	27/02/2014	103000	0.8	25.2	7.77	39.9	3.59	151	11800	50500	47	10600	0.005	1.2	70.6	1.95	7.5	4.8	9.75	7.5	1.2	19500
Spa Adit	Adit	27/02/2014	111000	0.239	1.22	4.15	22.6	5.49	133	7650	64200	52.1	5240	0.005	0.12	59.3	0.195	7.5	0.48	0.18	5.36	0.276	9850
Vale View	SW	03/03/2014	15.4	4.9	0.562	7.91	0.05	0.67	0.206	1.7	24.1	0.217	11.6	0.005	1.66	0.741	0.677	0.75	0.48	2.38	0.75	0.332	63.1
Sulphur Brook	SW	04/03/2014	29	0.08	0.154	6.9	0.236	0.374	0.195	18	9.5	5.92	21.5	0.005	0.12	0.935	0.195	0.75	0.48	0.18	0.75	0.12	59.6
Ballinacleish Bridge	SW	03/03/2014	109	0.983	0.303	6.85	0.114	0.365	0.397	0.425	43.8	4.53	35	0.005	0.385	1.1	0.195	0.75	0.48	0.75	0.75	0.12	59.5
Lions Bridge	SW	03/03/2014	77.9	1.85	0.452	5.41	0.156	0.429	0.207	1.08	66.5	5.05	25	0.005	0.553	0.869	0.195	0.75	0.48	1.11	0.75	0.12	83.5
Site T1	SW	03/03/2014	90.4	0.727	0.271	6.26	0.05	0.327	0.263	0.425	47.2	4.03	27.8	0.005	0.354	0.782	0.195	0.75	0.48	0.623	0.75	0.12	24.7
Whites Bridge	SW	03/03/2014	124	0.417	0.391	5.67	0.222	0.434	0.252	5.39	60.4	4.43	29.4	0.005	0.754	1.12	0.195	0.75	0.48	0.451	0.75	0.251	49.5
Whites Bridge GS	SW	03/03/2014	236	0.264	0.322	5.52	0.34	0.408	0.443	12.8	77.1	4.2	39.7	0.005	0.379	0.96	0.195	0.75	0.48	0.18	0.75	0.12	99.7
DS Deep Adit	SW	03/03/2014	976	0.286	0.197	5.6	2.16	0.309	2.16	126	347	20.3	95.1	0.005	0.486	1.57	0.195	0.75	0.48	0.18	0.75	0.12	669
Wicklow CO.CO. Main. Yard GS	SW	04/03/2014	188	0.08	0.16	5.66	0.364	0.397	0.678	21.1	91	3.26	49.2	0.005	0.12	1.35	0.195	0.75	0.48	0.18	0.75	0.12	121
Site T5	SW	04/03/2014	123	0.08	0.156	5.34	0.444	0.22	2.88	19.8	1750	3.46	200	0.339	0.12	1.72	0.195	0.75	0.48	0.18	0.75	0.12	273
Avoca Bridge	SW	04/03/2014	152	0.08	0.161	5.41	0.388	0.431	1.18	18.5	485	3.3	84.4	0.005	0.12	0.95	0.195	0.75	0.48	0.18	0.75	0.12	161
US Shelton Abbey	SW	26/02/2014	155	0.08	0.364	6.04	0.27	0.418	0.827	10.4	211	2.62	57.4	0.005	0.12	1.2	0.195	0.75	0.48	0.18	0.75	0.12	90.4
DS Shelton Abbey	SW	26/02/2014	151	0.08	0.299	6.06	0.233	0.706	0.782	10.1	204	2.39	65.9	0.005	0.12	1.25	0.195	0.75	0.48	0.18	0.75	0.12	105

xx Exceeds Ecological Assessment Criteria

xx Exceeds Human Health Assessment Criteria

xx Exceeds both Ecological and Human Health Criteria

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

- Not analysed or no assessment criteria

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