

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 September 2014. This report should be read alongside the Avoca Data Report (Document Ref: 95735/40/DG16, dated November 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 (FeS₂) 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 (FeS₂) accompanied by chalcopyrite (CuFeS₂), 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 (Cu₂S) and covellite (CuS) together with various copper and iron oxides.

1.4.2 Hydrogeology

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

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

Overall water movement consists of three primary pathways:

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



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

1.5 Description of Adit Discharges

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

The Cronebane Intermediate Adit (also known as Fathom Stope 43) flows from an opening in the southeast wall of the East Avoca Pit and across the bottom of the pit forming a lake on the southwest end.

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

The Deep Adit is located northeast of Whites Bridge and is the main mine drainage for East Avoca. The water flows from the portal into a ditch that runs semi-parallel to the Avoca River before discharging into the river. In September 2014 the adit discharge was mostly diverted into the Millrace through a marshy area to the east of the spoils area. As a result, the deep adit discharges both to the Avoca River at its normal discharge point (approximately 170 m from the adit portal) and approximately 20 m downstream of the normal discharge point, through a break the side of the Millrace. Both of these discharge points were located upstream of the Downstream of the Deep Adit sampling location on the Avoca River. There was not much flow further downstream in the Millrace itself.

The 850 Adit is also located northeast of Whites Bridge. In 2009 a significant volume of water was observed issuing from the adit for the first time. This was investigated on behalf of the Department by GWP who concluded that the water flow is most likely to be due to a collapse inside the mine, diverting water from the Deep Adit to higher levels. The flow from 850 Adit passes through a culvert (the "northwest culvert") under the railway embankment and then joins the Deep Adit discharge channel. Since the initial discharge in 2009, flow has been intermittently observed from the 850 Adit and it was added to the sampling programme in February 2014, however there was no discharge in September 2014 and so it was not sampled. It is now believe that the flow in the 850 was blocked by a dam and that it only flowed during high flows. This blockage has been removed since September 2014 and it is believed that the flow from the 850 Adit may be continuous.

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 September 2014. The Road Adit will no longer flow along the road and will instead go through a pipe underneath the council yard and discharge directly into the Avoca River above the Wicklow County Council Gauging Station. This diversion was due to take place at the end of September but was not in place at the time of sampling.



The Spa Adit is located in West Avoca on a hillside approximately 150 m northwest of (and approximately 40 m above) the Wicklow County Council recycling centre. The flow discharges from a break in a pipe which was observed soaking into the ground. 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 on 15, 29 and 30 September 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 MP1). The static water level was recorded prior to pumping and measured throughout the purging process to monitor drawdown.

Water quality indicator parameters were monitored in the field during low-flow purging using a flow-through cell to minimise oxidation by the atmosphere. Water quality indicator parameters include temperature, pH, ORP, conductivity and dissolved oxygen (DO). Purging continued until the field parameters had stabilised. The results were recorded approximately every five minutes during the purging process on the Groundwater Purging and Sampling Form. Field sheets are contained in Appendix H and 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 exceptions to the low-flow sampling procedure were for SG104 and GW2/05. Sufficient water was not present in the wells to perform the low flow sampling procedure. The sample was collected after greater than three volumes of the well had been purged (calculated as $\pi r^2 h$ – where r is the inner casing radius and h is the height of the water column) and the field parameters had stabilised.

Groundwater levels were measured at the nine wells using a portable electronic water level recorder. Automatic groundwater recorders have been placed in six wells and the data were downloaded. Groundwater level data are discussed in Section 6 and the data are contained in Appendix C of the Data Report.

2.1.2 Surface Water Sampling

Twenty-three surface water locations were sampled between 15 and 18 September 2014, as listed in Table 2 and shown on Map 1 and 2 in <u>Appendix A</u>.

Surface water sampling was conducted consistent with the Surface Water Sampling Procedure (SOP 1-1) as detailed in the Monitoring Plan. No sample could be obtained from the 850 Adit because it was not discharging water in September 2014. An additional sample was collected from the Millrace just prior to its main discharge into the Avoca River.

The predetermined surface water sampling locations were located in the field using a GPS. Photographs were taken of the surface water sampling locations (Appendix D of the Data Report). The sample location was approached from downstream so that the underlying sediments are not disturbed. Samples were grab samples collected from a well-mixed portion of the water stream where possible. For the samples collected on the Avoca river and at Ballinacleish Bridge and Lions Bridge, the grab sample was taken as a composite sample across the river, whereby a volume of water was collected along a transect in proportion to the river flow. Water was collected from approximately 6 to 10 locations (depending on the width of the channel) along a transect. This was different than previous sampling events when a grab sample was taken from the middle of the stream or river. In the spring sampling events a grab sample from the bank is taken using an extendable rod as the Avoca River is not wadable during high flows. At Shelton Abbey the same method was used as during high flow as the river is not wadable at his location.



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	Flow Meter
Whites Bridge	Avoca River Location (at Whites Br.)	319773	182066	Equal to flow recorded at Whites Bridge GS
Whites Bridge Gauging Station (GS)	Avoca River Location (90m downstream of Whites Br.)	319843	182015	Automatic recorder (Data from EPA)
Downstream (DS) Deep Adit	Avoca River Location (Downstream of Deep Adit confluence on the Avoca River)	319951	181922	Equal to flow recorded at Wicklow Co Co. Maintenance Yard GS
Wicklow Co Co. Maintenance Yard Gauging Station (GS)	Avoca River Location	319939	181445	Automatic Recorder (Data from EPA)
Site T5	Avoca River Location (Abandoned Coal Yard)	319972	181114	Flow Meter
Avoca Bridge	Avoca River above Avoca Bridge	320372	179932	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	No Flow
850 Adit Confluence	Adit Discharge (before entering Deep Adit Discharge)	319845	182122	No Flow
Deep Adit	Adit Discharge (at portal)	319850	182123	Flow Meter
Deep Adit Confluence	Adit Discharge (before entering Avoca River)	319896	181986	Flow Meter
Millrace (additional sample on the Deep Adit)	Adit Discharge (along the Millrace)	319920	181960	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	Bucket and stopwatch
Spa Adit	Adit Discharge	319637	181747	Bucket and stopwatch
Cronebane Pit Lake	Pit Lake	320933	183402	n/a



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

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

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

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 pouring deionised (DI) water over 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. An additional filtration blank was collected in order to try to quantify any contamination caused by the filtration procedure.



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

Table 3 Field QA/ QC Sample IDs and Descriptions

Sample ID	QA/QC Sample Type	Description
AVGD01.4	GW Duplicate	Duplicate of MWSA2
		DI water (VWR Chemicals Product: 102923C, Batch
AVDB01.4	GW Decontamination blank	14D290025) poured over pump after decon after site
		MWSA2
AVSD01.4	SW Duplicate	Duplicate of Road Adit Confluence
AVSD02.4	SW Duplicate	Duplicate of Ballinacleish Bridge
		DI water (VWR Chemicals Product: 102923C, Batch
AVDB02.4	SW Decontamination blank	14D290025) poured over SW composite sample bottle after
		final decon at site Sulphur Brook
AVSR01.4	Standard Reference Material	Water ERA Lot #P230-740A
AVSR02.4	Standard Reference Material	Water ERA Lot #P230-740A
WB01.4	Filtration blank	Deionised water filtered onsite (VWR Chemicals Anala R
VVDU1.4	FIIII ation blank	Normapur Product: 102923C, Batch 14D290025)
WB02.4	Water blank	Deionised water (VWR Chemicals Anala R Normapur
VVDUZ.4	water bialik	Product: 102923C, Batch 14D290025)

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.

No determination was possible for fluoride (anions by ion chromatography) for 8 samples (MWDA1, Cronebane Inter. Adit, Cronebane Shallow Adit, Deep Adit, Deep Adit Confluence, Millrace, Road Adit Confluence, and Spa Adit) as the acidity caused interference with the instrument. Refer to laboratory reports SDG 140918-56 and SDG 141002-49 in Appendix F of the Data Report for further details.



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

D₂ = 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 AVSR01.4 and AVSR02.4) to evaluate laboratory accuracy. The certified SRM was supplied by ERA Certified Reference Materials and was Lot #P230-740A (Metals). The Certificate of Analysis is provided in Appendix G of the Data Report. The use of a blind or unknown SRM is the only method to independently verify the laboratory accuracy; and
- One water blank was collected of the DI water during the sampling event. An additional filtration blank was collected in order to try to quantify any contamination caused by the filtration procedure.



3.2 Results of Field QA/QC Samples

3.2.1 Duplicates

Three duplicate samples (one groundwater sample and two surface water samples) were generated in the field and sent to ALcontrol for analysis. Table 4 provides the results of the 21 metals for the three duplicate samples and the calculated RPD between each pair of samples. Note if both the original and duplicate results were less than the detection limit then the RPD was zero.

The majority of RPD values were below 50 % and the RPDs for the key parameters ranged from 5.5 to 49 % for aluminium, 6 to 21% for copper and 4 to 27 % zinc which was good.

There was five % RPDs that exceeded 50 % as highlighted in Table 4 that ranged from 54 to 126%. Each of the five exceedances were for different parameters including dissolved antimony, selenium, iron, manganese and nickel. Each of these duplicate results were checked and confirmed with ALcontrol and they said they were within their duplicate policy margin. The highest reported value of the duplicate pair is selected for interpretive use in Section 4 therefore providing a conservative evaluation.

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

Dissolved Metal	LOD (µg/l)	MWSA 2	AVGD 01.4	RPD	Road Adit Conf	AVSD 01.4	RPD	Ballina- cleish Bridge	AVSD 02.4	RPD
Aluminium	<2.9	58400	55300	5.5	15000	16400	-8.9	32.8	54.1	-49
Antimony	<0.16	3.72	1.88	65.7	<1.6*	<1.6*	0.0	0.166	<0.16	3.7
Arsenic	<0.12	11.3	11.8	-4.3	7.93	5.56	35.1	0.478	0.603	-23.1
Barium	<0.03	9.16	8.77	4.4	19.6	23.6	-18.5	9.48	6.22	41.5
Cadmium	<0.1	1.87	1.93	-3.2	13.6	12.4	9.2	<0.1	<0.1	0
Chromium	<0.22	6.6	6.7	-1.5	4.88	3.13	43.7	0.502	0.79	-44.6
Cobalt	<0.06	140	140	0	139	146	-4.9	<0.06	<0.06	0
Copper	<0.85	118	111	6.1	299	360	-18.5	<0.85	1.04	-20.1
Iron	<19	107000	100000	6.8	122000	108000	12.2	57.3	109	-62.2
Lead	<0.02	29.7	29.1	2.0	400	413	-3.2	0.996	1.22	-20.2
Manganese	<0.04	30100	28900	4.1	10000	10500	-4.9	6.2	10.8	-54.1
Mercury	<0.01	<0.01	NA	-	<0.01	<0.01	0.0	<0.01	<0.01	0
Molybdenum	<0.24	0.557	0.359	43.2	3.84	<2.4*	0	0.277	<0.24	14.3
Nickel	<0.15	111	114	-2.7	56.4	63.7	-12.2	0.662	<0.15	126.1
Selenium	<0.39	1.09	1.1	-0.9	18.8	4.69	120	<0.39	<0.39	0
Silver	<1.5	<1.5	<1.5	0	<15*	<15*	0	<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	0.413	<0.36	13.7	<3.6*	<3.6*	0	<0.36	<0.36	0
Uranium	<1.5	8.88	5.6	45.3	<15*	<15*	0	<1.5	<1.5	0
Vanadium	<0.24	0.833	0.712	15.7	<2.4*	<2.4*	0	<0.24	0.276	-14.0
Zinc	<0.41	4370	4170	4.7	11700	10800	8.0	19.9	26.1	-27.0

Notes:

Bold indicates an exceedance in the Duplicate RPD acceptance criteria

NA analyte not determined by the laboratory



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

3.2.2 Decontamination Blanks

Two decontamination blanks were created by pouring water over the sampling equipment after decontamination and sent to Alcontrol for analysis. Table 5 provides the results of the 21 metals for the two decontamination blank samples along with the results of the DI water blank and filtration blank also created in the field.

The majority of reported concentrations were below the limits of detection. Most metals were analysed by ICP-MS to achieve the lowest possible detection limits. The limits of detection ranged from 0.01 to 2.9 μ g/l except for iron with a detection limit of 19 μ g/l.

Detections were observed for eleven dissolved metals ranging from 0.043 to 18.4 μ g/l except for one result of 389 μ g/l for iron. Five of the metals (aluminium, barium, chromium, manganese and zinc) were also detected in the DI water blank and the filtration blank. The levels of detections in the decontamination blanks were similar to those found in the DI water blank. Detections of dissolved arsenic, iron, lead, molybdenum and tin were also found in the decontamination blanks but not the DI water blank. Antimony was found in all the decontamination blanks but only the DI water blank and not the filtration blank.

In total there were sixteen detections of dissolved metals in the decontamination blanks. Of the parameters not detected in the DI water blank only two were greater than ten times the detection limit, in AVDB01.4 for antimony (1.75 μ g/I) also detected in the method blank as discussed below and iron (389 μ g/I).

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 some of the parameters detected (not chromium, iron, zinc, aluminium and manganese) in the method blanks for both sample batches were similar to those in the decontamination blank samples, as follows:

- Two detections of parameters were present in method blank for Sample Batch 140919-55 that occurred in the decontamination blank from the same batch (see Table 5): antimony $0.775 \mu g/l$ and tin $0.747 \mu g/l$.
- Three detections of parameters were present in method blank for Sample Batch 141002-75 that occurred in the decontamination blank from the same batch (see Table 5): antimony $1.36 \,\mu\text{g/l}$, arsenic $0.275 \,\mu\text{g/l}$ and lead $0.035 \,\mu\text{g/l}$.

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. In AVDB01.4 antimony was 47% of the preceding sample and iron was less than 0.5 %. The level of antimony is similar to the level detected in the laboratory method blank for that batch. The detection of dissolved iron in AVDB01.4 (the final groundwater pump decontamination sample) was greater than the human health criteria (outlined in Section 4) of 200 μ g/l, however, it was considerably less than the preceding sample (MWSA2 107,000 μ g/l) but is considered to indicate cross-contamination in the field given the elevated dissolved iron result. For the groundwater samples where the groundwater pump was used the results that exceeded the human health criteria for iron ranged from 37,500 to 217,000 μ g/l (see Table B-2 in Appendix B), which were significantly higher than the criteria of 200 μ g/l and therefore this detection of iron is not considered to affect the interpretation of the results.



Overall, the decontamination blank samples do not indicate any cross-contamination in the field. One exception was the dissolved iron result in the groundwater decontamination blank sample, however, the groundwater samples results were not affected by the cross-contamination and therefore all the results are considered acceptable.

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

Dissolved Metal	LOD (µg/l)	Filtration Blank WB01.4 (µg/l)	Water Blank WB02.4 (μg/l)	Decon blank AVDB02.4 (μg/l)	Laboratory Method Blank (µg/l)	Decon blank AVDB01.4 (μg/l)	Laboratory Method Blank (µg/l)
Sam	ole batch:		140	919-55		14100	02-75
Aluminium	<2.9	5.03	4.64	<2.9	<2.90	18.4	<2.90
Antimony	<0.16	<0.16	0.245	0.264	0.775	1.75	1.36
Arsenic	<0.12	<0.12	<0.12	<0.12	<0.12	0.126	0.275
Barium	<0.03	0.146	0.088	0.173	<0.03	0.099	<0.03
Cadmium	<0.1	<0.1	<0.1	<0.1	NP	<0.1	NP
Chromium	<0.22	0.711	0.365	0.28	<0.22	0.355	<0.22
Cobalt	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Copper	<0.85	<0.85	<0.85	<0.85	<0.85	<0.85	<0.85
Iron	<19	<19	<19	<19	<19	389	<19
Lead	<0.02	<0.02	<0.02	<0.02	<0.02	0.043	0.035
Manganese	<0.04	0.852	0.258	0.322	<0.04	2.68	<0.04
Mercury	<0.01	<0.01	<0.01	<0.01	NP	NP	NP
Molybdenum	<0.24	<0.24	<0.24	<0.24	<0.24	0.371	<0.24
Nickel	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
Selenium	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39
Silver	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
Thallium	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96
Tin	<0.36	<0.36	<0.36	0.362	0.747	<0.36	<0.36
Uranium	<1.5	<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	<0.24
Zinc	<0.41	1.69	1.07	8.79	<0.41	2.99	<0.41

Notes:

Bold indicates a detection

Bold and italics indications 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 AVSR01.4 and AVSR02.4) 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 all of the metals were within the acceptable ranges. Dissolved aluminium, antimony, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, thallium, vanadium and zinc are in excellent agreement with the certified value (%R ranged from 88 to 112 %).



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

Dissolved	Certified Value	Acceptan	ce Limits	AVSR01.4		AVSR02.4	
Metal	(μg/l)	Lower (%)	Upper (%)	(μg/l)	% R	(μg/I)	% R
Aluminium	1120	82.0	116	1200	107	1120	100
Antimony	396	79.5	117	442	112	364	92
Arsenic	210	79.5	120	185	88	196	93
Barium	1720	84.9	115	1710	99	1840	107
Cadmium	822	85.0	115	788	96	771	94
Chromium	402	85.1	115	398	99	395	98
Cobalt	564	84.9	115	551	98	571	101
Copper	563	85.1	115	525	93	538	96
Iron	1710	84.8	115	1550	91	1690	99
Lead	757	84.9	115	741	98	755	100
Manganese	906	85.0	115	913	101	911	101
Molybdenum	455	86.6	112	416	91	431	95
Nickel	410	86.6	114	360	88	434	106
Selenium	198	84.8	115	182	92	183	92
Silver	768	85.0	115	684	89	743	97
Thallium	654	82.9	115	640	98	659	101
Vanadium	1010	85.0	115	979	97	970	96
Zinc	1800	85.0	115	1750	97	1680	93

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 AQCs.

All of the ALcontrol laboratory reports were reviewed to ensure that reported values were ISO17025 certified (where relevant) and for any sample deviations. The sample holding times were exceeded for free cyanide in 15 samples by 2 to 3 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 21 % which is good. The RPDs between laboratory and field pH were very good at less than 13 %. 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

	рН	рН	% RPD	Conductivity @ 20deg.C	Specific Cond. @ 25deg.C	% RPD
	Lab	Field	70 III B	Lab	Field	70 III D
Sample Description	рΗ С	Jnits		mS/	'cm	
Cronebane Inter. Adit	3.13	3.27	-4.4	0.995	1.176	-16.7
Cronebane Pit Lake	3.16	3.08	2.6	0.505	0.607	-18.3
Cronebane Shallow Adit	2.89	2.75	5.0	2.94	3.509	-17.6
Ballygahan Adit	3.07	3.1	-1.0	2.2	2.557	-15.0
Deep Adit	3.4	3.47	-2.0	1.33	1.421	-6.6
Deep Adit Confluence	3.25	3.25	0.0	1.35	1.492	-10.0
Road Adit	3.96	3.93	0.8	1.68	1.924	-13.5
Road Adit Confluence	3.98	3.96	0.5	1.69	1.931	-13.3
Spa Adit	2.75	2.68	2.6	2.3	2.661	-14.6
Ballinacleish Bridge	6.96	6.41	8.2	0.0583	0.062	-6.2
Lions Bridge	7.39	7.07	4.4	0.0838	0.09	-7.1
Site T1	7.28	6.71	8.1	0.0767	0.081	-5.5
Vale View	7.51	6.87	8.9	0.148	0.162	-9.0
Whites Bridge	6.92	6.56	5.3	0.0824	0.093	-12.1
Whites Bridge GS	7.11	6.83	4.0	0.078	0.086	-9.8
DS Deep Adit	6.71	6.86	-2.2	0.0808	0.087	-7.4
Wicklow CO.CO. Main. Yard GS	6.93	6.41	7.8	0.0865	0.098	-12.5
Site T5	6.81	6.21	9.2	0.0939	0.116	-21.1
Avoca Bridge	6.93	6.63	4.4	0.0976	0.11	-11.9
Sulphur Brook	7.34	6.84	7.1	0.142	0.16	-11.9
US Shelton Abbey	7.21	7	3.0	0.106	0.116	-9.0
DS Shelton Abbey	7.08	6.86	3.2	0.109	0.121	-10.4
Millrace	3.3	3.05	7.9	1.18	1.269	-7.3
MWDA1	3.34	2.92	13.4	2.2	2.527	-13.8
MWDA2	3.98	3.89	2.3	1.4	1.568	-11.3
MWPF1	5.3	4.78	10.3	0.151	0.132	13.4
MWET1	3.43	3.23	6.0	2.16	2.411	-11.0
MWET2	6.26	6.26	0.0	3.11	3.476	-11.1
GW1/05	4.24	4.04	4.8	2.26	2.61	-14.4
GW2/05	4.06	3.62	11.5	1.1	1.211	-9.6
SG104	3.03	2.88	5.1	7.26	8.308	-13.5
MWSA2	3.8	4.15	-8.8	2.1	2.322	-10.0

Notes:

Bold indicates an exceedance in acceptance limits



3.4.2 Internal Consistency Analysis

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

The charge balance was calculated as follows:

(Σ(Cations x charge) - Σ(Anions x charge))/ (Σ(Cations x charge) + Σ(Anions x charge)) x 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:

(TDS-Calc – TDS-Meas)/TDS-Meas x 100%

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

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

The general acceptance criteria for internal consistency are ±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 2 samples outside the range. The mass balance, in the majority of cases (bolded values) did not meet these criteria. Most values were less than 30 %; which overall is very good considering the low pH, high TDS and complex nature of the high metal concentrations of many of the samples. The fact that the mass balance values are mostly negative suggests that either one or more parameters were under-reported by the analytical laboratory and/or one or more parameters present within the samples were not analysed (e.g. silica). There were 3 sites (Whites Bridge, Whites Bridge GS and DS Deep Adit) were the mass balance percentage difference was greater than 100%, which also had the lowest measured TDS ranging from <10 to 17.1 mg/l. All of these TDS results were checked using another analytical method by ALcontrol and the results were confirmed. As the SC measurements also indicate that the low TDS results are incorrect it is recommended that these TDS results of <10 mg/l should not be used.



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
Ballygahan Adit	2067	2420	1.6	2.5	-14.6	Missing anions
Cronebane Inter. Adit	797	1340	-4.0	-18.1	-40.5	Missing cations
Cronebane Pit Lake	200	345	-2.1	-40.1	-42.0	Missing cations
Cronebane Shallow Adit	3739	5440	5.6	4.5	-31.3	Missing anions
Deep Adit	1257	1530	2.0	5.0	-17.8	Missing anions
Deep Adit Confluence	1205	1510	0.2	0.5	-20.2	Missing anions
Road Adit	1586	2200	1.3	2.8	-27.9	Missing anions
Road Adit Confluence	1564	2200	2.5	5.1	-28.9	Missing anions
Spa Adit	2292	3020	3.6	4.8	-24.1	Missing anions
Vale View	92	105	0.0	-1.4	-12.7	Missing cations
Avoca Bridge	62	51	0.0	0.3	22.4	Too many cations
DS Deep Adit	48	<10	0.8	0.8	382	Too many anions
Millrace	902	1230	-0.5	-1.6	-26.7	Missing cations
Site T1	42	26	0.0	-1.2	61.5	Too many anions
Site T5	59	57	-0.1	-5.7	2.8	Too many anions
Sulphur Brook	89	92.2	-0.1	-4.7	-3.9	Missing cations
Wicklow CO.CO. Main. Yard GS	53	48	-0.1	-4.7	10.3	Too many anions
Whites Bridge	48	17.1	0.0	-2.5	183	Too many anions
Whites Bridge GS	45	<10	0.8	0.8	348	Too many anions
Ballinacleish Bridge	29	42.2	0.0	-0.5	-30.4	Missing cations
DS Shelton Abbey	63	80	-0.1	-5.9	-20.9	Missing cations
Lions Bridge	45	60	0.0	-2.7	-25.7	Missing cations
US Shelton Abbey	62	80	-0.2	-8.1	-22.2	Missing cations
MWET1	2469	2970	-0.6	-0.7	-16.9	Missing cations
SG104	12238	12800	31.8	7.7	-4.4	Missing anions
GW1/05	2373	2930	-6.4	-9.4	-19.0	Missing cations
GW2/05	942	1100	2.0	6.6	-14.4	Missing anions
MWDA1	2227	2870	5.0	6.8	-22.4	Missing anions
MWDA2	1313	1560	1.5	3.7	-15.8	Missing anions
MWPF1	80	69.4	-0.1	-4.0	15.0	Too many anions
MWET2	3287	3570	0.2	0.2	-7.9	Missing anions
MWSA2 Notes:	2266	2460	0.8	1.1	-7.9	Missing anions

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). There were a few sites with a high SC/TDS-Meas ratio; Site T1 3.1, Whites Bridge 5.4, Whites Bridge GS 8.6 and DS Deep Adit 8.7. These sites also had the lowest measured TDS ranging from <10 to 26 mg/l and at these low levels, the relationships are less accurate. All of these TDS results were checked and confirmed by ALcontrol. However, as discussed above it was determined that the TDS results of <10 mg/l should not be



used. The majority of the ratios in Table 9 are within the range for natural waters and therefore the analyses are considered reliable.

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

	Sample	Specific Conductance	TDS (Calc)	TDS (Meas)	Ra	itio
Sample Description	Type	(uS/cm)	(mg/l)	(mg/l)	SC/ TDS- Calc	SC/ TDS - Meas
Ballygahan Adit	Adit	2560	2067	2420	1.2	1.1
Cronebane Inter. Adit	Adit	1180	797	1340	1.5	0.9
Cronebane Pit Lake	Pit Lake	607	200	345	3.0	1.8
Cronebane Shallow Adit	Adit	3510	3739	5440	0.9	0.6
Deep Adit	Adit	1420	1257	1530	1.1	0.9
Deep Adit Confluence	Adit	1490	1205	1510	1.2	1.0
Road Adit	Adit	1920	1586	2200	1.2	0.9
Road Adit Confluence	Adit	1930	1564	2200	1.2	0.9
Spa Adit	Adit	2660	2292	3020	1.2	0.9
Vale View	SW	162	92	105	1.8	1.5
Avoca Bridge	SW	110	62	51	1.8	2.2
DS Deep Adit	SW	87	48	<10	1.8	8.7
Millrace	SW	1270	902	1230	1.4	1.0
Site T1	SW	81	42	26	1.9	3.1
Site T5	SW	116	59	57	2.0	2.0
Sulphur Brook	SW	160	89	92	1.8	1.7
Wicklow CO.CO. Main. Yard GS	SW	98	53	48	1.9	2.0
Whites Bridge	SW	93	48	17	1.9	5.4
Whites Bridge GS	SW	86	45	<10	1.9	8.6
Ballinacleish Bridge	SW	62	29	42	2.1	1.5
DS Shelton Abbey	SW	121	63	80	1.9	1.5
Lions Bridge	SW	90	45	60	2.0	1.5
US Shelton Abbey	SW	116	62	80	1.9	1.5
MWET1	GW	2410	2469	2970	1.0	0.8
SG104	GW	8310	12238	12800	0.7	0.6
GW1/05	GW	2610	2373	2930	1.1	0.9
GW2/05	GW	1210	942	1100	1.3	1.1
MWDA1	GW	2530	2227	2870	1.1	0.9
MWDA2	GW	1570	1313	1560	1.2	1.0
MWPF1	GW	132	80	69	1.7	1.9
MWET2	GW	3480	3287	3570	1.1	1.0
MWSA2	GW	2320	2266	2460	1.0	0.9

Figure 1 shows the relationship between specific conductivity and TDS. There is a strong positive correlation between SC with both the calculated (R^2 =0.943) and measured (R^2 =0.968) TDS.



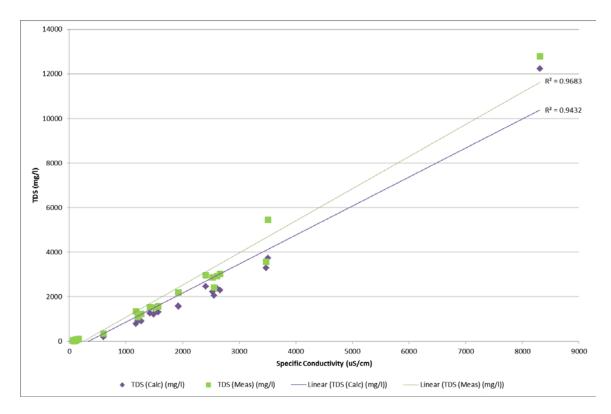


Figure 1 Relationship of Specific Conductivity and Total Dissolved Solids (TDS)

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 $0.45\mu m$ membrane filter. Dissolved metals are more biologically available than total metals.

Normally the dissolved metal concentrations would be less than the total metals because they are a portion of the total concentration. This was checked for some of the key metals aluminium, copper, iron and zinc, by calculating ratio of total and dissolved metals to evaluate if the concentrations were distinguishable. Table B-1 in Appendix B shows the full tabulation of results. The dissolved metals were generally equal to or close to the total metals, indicating that the majority of the aluminium, copper, iron and zinc present were dissolved. For the majority of the river and stream samples however the total aluminium and iron were significantly higher than the dissolved portion. The total suspended solids in the river and stream samples ranged from <1 to 10 mg/l.

The dissolved concentrations were higher than the total concentrations in about 30% of the copper results and 25% of the iron results. Alcontrol repeated the analysis and confirmed the original results. For SG104 Alcontrol noted that the sample was heavily contaminated and they believe the difference between total and dissolved copper and iron was due to interference.



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	31.6	876000	145000	279000
Antimony	<0.16	9	6	0.08	10.4	3.65	3.85
Arsenic	<0.12	9	7	0.06	11.8	3.36	4.17
Barium	<0.03	9	9	1.09	31	8.66	9.07
Cadmium	<0.1	9	9	0.422	343	61.3	109
Chromium	<0.22	9	9	1.34	77.7	15.6	24.4
Cobalt	<0.06	9	9	0.668	894	216	268
Copper	<0.85	9	9	1.06	79000	13700	25000
Iron	<19	9	9	36.9	217000	81200	69200
Lead	<0.02	9	9	0.459	1260	150	417
Manganese	<0.04	9	9	24.6	42600	15400	16000
Mercury	<0.01	9	0	0.005	0.005	-	-
Molybdenum	<0.24	9	6	0.12 (12*)	1.68	2.03	3.78
Nickel	<0.15	9	9	1.5	385	93.6	115
Selenium	<0.39	9	7	0.195	24.2	5.84	9.18
Silver	<1.5	9	0	0.75	0.75	-	-
Thallium	<0.96	9	2	0.48 (48*)	1.72	6.49	15.6
Tin	<0.36	9	4	0.18 (18*)	1.65	2.68	5.78
Uranium	<1.5	9	7	0.75 (75*)	12.4	13.6	23.3
Vanadium	<0.24	9	5	0.12 (12*)	0.833	1.74	3.86
Zinc	<0.41	9	9	44	150000	28500	47900

Notes:

^{*} LOD was raised due to a dilution that was carried out on the sample. Where there were detections the maximum reported value was presented as the maximum value.



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

Dissolved aluminium, copper, iron, manganese and zinc were found in significantly high concentrations in the majority of groundwater samples. The shallow well MWPF1 located upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments had the lowest concentrations of dissolved metals. However, MWET2 had the lowest concentration of dissolved aluminium (31.6 μ g/l) and copper (1.06 μ g/l) but was high in dissolved zinc (5,740 μ g/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 7 wells with highest concentration at MWSA2 of 11.8 μ g/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	1700	306000	81600	95200
Antimony	<0.16	10	1	0.08 (0.8*)	0.22	-	-
Arsenic	<0.12	10	9	0.06	42.4	9.8	13.8
Barium	<0.03	10	10	5.24	23.6	11.1	6.23
Cadmium	<0.1	10	10	12.8	282	68	79.7
Chromium	<0.22	10	10	0.619	11.8	5.45	3.7
Cobalt	<0.06	10	10	23.6	291	139	92.4
Copper	<0.85	10	10	69.4	9280	2340	3380
Iron	<19	10	10	2010	202000	91100	58300
Lead	<0.02	10	10	127	1910	828	699
Manganese	<0.04	10	10	267	12000	6050	4340
Mercury	<0.01	10	0	0.005	0.005	-	-
Molybdenum	<0.24	10	2	0.12	3.84	1.050	1.110
Nickel	<0.15	10	10	5.03	136	54.6	37.3
Selenium	<0.39	10	7	0.195	21.4	8.11	8.73
Silver	<1.5	10	0	0.75 (7.5*)	7.5*	-	-
Thallium	<0.96	10	2	0.48 (4.8*)	2.29	3.38	1.91
Tin	<0.36	10	1	0.18 (1.8*)	0.732	-	-
Uranium	<1.5	10	5	2.21 (7.5*)	29.8	9.37	7.47
Vanadium	<0.24	10	1	0.12 (1.2*)	0.835	-	-
Zinc	<0.41	10	10	550	103000	27900	30200

Notes:

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

^{*} LOD was raised due to a dilution that was carried out on the sample. Where there were detections the maximum reported value was presented as the maximum value.



Dissolved aluminium, copper, iron, manganese and zinc were found in significantly high concentrations in the majority of the adit discharges and the pit lake sample. The Cronebane Shallow Adit had the highest concentrations of dissolved metals including aluminium (306,000 μ g/l), cadmium (282 μ g/l) and zinc (103,000 μ g/l). Ballygahan Adit had the highest concentrations of arsenic (42.4 μ g/l) and copper (6,260 μ g/l). The lowest dissolved metals concentrations were found in the Cronebane Pit Lake, indicating that there is likely to be a significant rainwater input diluting the concentrations of metals.

Rivers and Streams

Table 12 Summary of Dissolved Metal Concentrations in Surface Water

Dissolved Metal	LOD (µg/l)	Number	Number of Detections	Minimum (μg/l)	Maximum (μg/l)	Mean (μg/l)	SDEV
Aluminium	<2.9	13	13	28	139	80.6	38.7
Antimony	<0.16	13	12	0.08	4.65	0.79	1.23
Arsenic	<0.12	13	13	0.321	0.983	0.49	0.17
Barium	<0.03	13	13	5.3	9.48	7.13	1.35
Cadmium	<0.1	13	9	0.05	0.616	0.4	0.16
Chromium	<0.22	13	13	0.37	0.79	0.49	0.11
Cobalt	<0.06	13	13	0.03	1.71	0.67	0.6
Copper	<0.85	13	11	0.885	23.6	10.4	7.87
Iron	<19	13	12	9.5	377	97.7	95.4
Lead	<0.02	13	12	0.001	4.66	1.84	1.16
Manganese	<0.04	13	13	4.86	99.5	40	35.6
Mercury	<0.01	13	0	0.005	0.005	-	-
Molybdenum	<0.24	13	5	0.12	1.57	0.3	0.4
Nickel	<0.15	13	12	0.075	1.49	0.9	0.39
Selenium	<0.39	13	3	0.195	1	0.3	0.24
Silver	<1.5	13	0	0.75	0.75	-	-
Thallium	<0.96	13	0	0.48	0.48	-	-
Tin	<0.36	13	6	0.18	2.74	0.58	0.72
Uranium	<1.5	13	0	0.75	0.75	-	-
Vanadium	<0.24	13	2	0.12	0.283	0.14	0.06
Zinc	<0.41	13	13	9.74	335	145	115

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 54.1 and 40.9 μ g/l, zinc at 26.1 and 24.8 μ g/l and iron at 109 and 62.9 μ g/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 (36.2 μ g/l), copper (0.924 μ g/l) and zinc (31 μ g/l). Whites Bridge (at the bridge) is the first sampling location along the Avoca River within the mining area where increases in metals concentrations are observed namely; aluminium (123 μ g/l), copper (23.6 μ g/l) and zinc (133 μ g/l).

Along the Avoca River the concentrations of dissolved metals were variable; the highest dissolved aluminium was $139 \,\mu\text{g/l}$ at Downstream (DS) of the Deep Adit confluence, the highest dissolved



copper was 16.4 μ g/l at WCC Maintenance Yard and the highest dissolved zinc was 335 μ g/l at Site T5.

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

4.2 Assessment Criteria

4.2.1 Groundwater and Surface Water Assessment Criteria

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

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

To assess the potential human health risks, the Drinking Water Regulations, 2007 (S.I. No. 106 of 2007) and amendments were utilised and are listed in Table 14. These values are the maximum permissible values for a drinking water source. In the case of metals the standards are for total metals. However, they apply post treatment (including filtration) and therefore the dissolved portion is used in the assessment in Section 4.

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

The two main receptors to groundwater in the Avoca mining area are surface water bodies and the groundwater resource as a drinking water supply. Therefore to assess the potential impact of the groundwater quality on relevant groundwater receptors, the same standards and guidelines as discussed for surface water were utilised for screening purposes for groundwater (Table 13 and Table 14).



Table 13 Surface Water and Groundwater Assessment Criteria for Biological Elements

Parameter	Unit	AA	MAC (or 95%ile)	Source	Description
Ammonia as N	mg/l	0.065	0.14	S.I. No. 272 of 2009	Good status
Ortho-phosphate as P	mg/l	0.035	0.075	S.I. No. 272 of 2009	Good status
рН	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 CaCO3 (Class 1: <40 mg CaCO3/l, Class 2: 40 to <50 mg CaCO3/l, Class 3: 50 to <100 mg CaCO3/l, Class 4: 100 to <200 mg CaCO3/l and Class 5: ≥200 mg CaCO3/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 CaCO3 is ≤ 100; 30 μg/l applies where the water hardness > 100 mg/l CaCO3.
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 CaCO3; 50 μg/l for water hardness > 10 mg/l CaCO3 and ≤ 100 mg/l CaCO3; and 100 μg/l elsewhere.
Supplementary sta	ındards:				
Aluminium	μg/l	-	1900	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Barium	μg/l	-	4	Oak Ridge National Laboratory	Invertebrates and Salmon fish
Cobalt	μg/l	-	5.1	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Manganese	μg/l	-	1,100	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Uranium	μg/l	-	2.6	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids

Notes:

Bold indicates the selected assessment criteria for ecological health



Table 14 Surface Water and Groundwater Assessment Criteria for Drinking Water

Parameter	Unit	Parametric value
рН	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 NO3	mg/l	50
Nitrite as NO2	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 <u>Appendix B</u> 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 2.88 to 6.26 (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 4.78 pH and MWET2 with 6.26 pH which only exceeded the criteria for human health. The specific conductance ranged from 0.132 to 8.308 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 653 to 9,170 mg/l. One exception was at MWPF1 where sulphate was below the human health assessment criteria with a value of 31.9 mg/l. Ammonia was detected in 7 of the monitoring wells and both the ecological (0.14 mg/l) and human health (0.3 mg/l) assessment criteria were exceeded in all but 3 monitoring wells MWPF1, MWET2 and GW2/05. Fluoride was also present in 6 of the monitoring wells sampled, with all values exceeding the assessment criteria for ecology (0.5 mg/l) and human health criteria (1.5 mg/l).

The dissolved metal concentrations were elevated in the majority of the monitoring wells with numerous exceedances of ecological, human health criteria or both, particularly for aluminium, cadmium, copper, iron, manganese, nickel and zinc (Table B-2 in Appendix B includes the full listing). There were seven detections of dissolved arsenic, only MWSA2 with a result of 11.8 μ g/l exceeded only the human health (10 μ g/l) criteria.

The dissolved aluminium and copper concentrations at MWET2 (deep) (31.6 and 1.06 μ g/l) were significantly lower than at MWET1 (shallow) which had concentrations of 118,000 and 8,180 μ g/l, respectively. MWET1 exceeded both the ecological and human health criteria for aluminium (1,900 and 200 μ g/l) and copper (5 and 2000 μ g/l). This could be explained by the apparent confined nature of MWET2 (heads in MWET2 are higher than in MWET1) and also because MWET1 is screened directly beneath the Emergency Tailings deposits.

The bedrock monitoring well GW1/05 showed higher dissolved metal concentrations than its nested, shallow alluvial well GW2/05. For example dissolved copper was 8,880 μ g/l in GW1/05 and 6,230 μ g/l in GW2/05, both exceeded the ecological and human health criteria for copper (5 and 2000 μ g/l). Levels of dissolved lead in GW1/05 exceeded the ecological assessment criteria of 7.2 μ g/l and the human heath criteria of 10 μ g/l, with a value of 1,260 μ g/l.



SG104 had the highest levels (compared to the other monitoring wells) of dissolved copper (876,000 μ g/I), cadmium (343 μ g/I) and nickel (385 μ g/I) exceeding the ecological and human health criteria. Dissolved cobalt (894 μ g/I) and zinc (150,000 μ g/I) 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 μ g/I and the human heath criteria of 10 μ g/I, with a value of 44.4 μ g/I.

The groundwater in the shallow well at the Deep Adit area MWDA1 showed higher metal concentrations than at MWDA2 (deep). This was especially the case for dissolved aluminium and copper with concentrations of 154,000 and 16,400 μ g/l in MWDA1 and concentrations of 49,700 and 4,810 μ g/l in MWDA2, respectively. However, both wells still exceeded the criteria for both ecological and human health for aluminium and copper. Both monitoring wells exceeded the assessment criteria for ecology (3.4 μ g/l) and human health (50 μ g/l) for chromium with concentrations of 25.3 and 5.93 μ g/l.

The well located upgradient of the Deep Adit area and at the eastern margin of the alluvial aquifer, MWPF1, had significantly lower metal concentrations than the other wells. However, the human health assessment criteria for dissolved aluminium (200 μ g/l) was exceeded with a value of 313 μ g/l and the ecological assessment criteria for dissolved copper (5 μ g/l) was exceeded with a value of 39.6 μ g/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 2.68 to 3.96 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 115 mg/l in the Cronebane Pit Lake to 1,720 mg/l in the Cronebane Shallow Adit. The specific conductance ranged from 0.607 to 3.509 mS/cm. There were three exceedances of the human health criteria (2.5 mS/cm) at the Cronebane Shallow Adit, Ballygahan Adit and Spa Adit.

Elevated sulphate and ammonia were found at all of the adit discharge locations. Sulphate levels greatly exceeded the criteria for human health of 250 mg/l in all of the adit discharges with values ranging from 165 to 2,820 mg/l. Ammonia was detected in all of the adit discharges and the ecological criteria (0.14 mg/l) and the human health criteria for ammonia (0.3 mg/l) were exceeded at all locations, with values ranging from 0.239 to 11 mg/l. One exception was for the Millrace sample where ammonia was less than the detection limit. Concentrations of sulphate (165 mg/l) and ammonia (0.239 mg/l) were generally lower at Cronebane Pit Lake than the adit discharges.

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

Dissolved zinc ranged from 550 to 103,000 μ g/l which exceeded the ecological assessment criteria of 50 μ g/l. Dissolved aluminium ranged from 1,700 to 306,000 μ g/l which exceeded both the ecological (1,900 μ g/l) and human health (200 μ g/l) criteria. The concentrations of dissolved copper only exceeded the ecological assessment criteria (5 μ g/l) in all of the adit discharges and



also the human health (2,000 μ g/l) criteria in the Cronebane Shallow Adit, Ballygahan Adit, and Spa Adit where concentrations ranged from 5,550 and 9,280 μ g/l.

Dissolved cadmium ranged from 12.8 to 282 μ g/l which exceeded both the ecological (0.45 μ g/l) and human health (5 μ g/l) criteria. Dissolved cobalt ranged from 23.6 to 291 μ g/l which exceeded the ecological criteria (5.1 μ g/l). Dissolved lead ranged from 127 to 1,910 μ g/l which exceeded both the ecological (7.2 μ g/l) and human health (10 μ g/l) criteria. Dissolved nickel ranged from 24.4 to 136 μ g/l which exceeded both the ecological and human health criteria of 20 μ g/l.

Dissolved arsenic was detected in all of the adit discharges, with Ballygahan Adit (42.4 μ g/l) and Cronebane Shallow Adit (25.9 μ g/l) exceeding the criteria for both ecological (25 μ g/l) and human health (10 μ g/l). Dissolved chromium was detected and exceeded the ecological assessment criteria of 3.4 μ g/l in all the adit discharges ranging from a concentration of 3.69 to 11.8 μ g/l. One exception was Cronebane Intermediate Adit that only had a concentration of 1.47 μ g/l.

Dissolved iron and manganese were also high in all adit discharges. Iron ranged from 15,700 to 202,000 μ g/I, exceeding the human health assessment criteria of 200 μ g/I. Manganese ranged from 267 to 12,000 μ g/I which exceeded the criteria for human health (50 μ g/I) and the ecological assessment criteria (1,100 μ g/I) in all but one adit discharge. Note that iron and manganese are not important criteria for human health (see Section 4.2.1).

Rivers and StreamsTable 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 6.21 to 7.07 (field) which were within acceptable ranges for ecological criteria (4.5 to 9 pH units). Three locations including Ballinacleish Bridge, Downstream of the Deep Adit and Wicklow County Council Maintenance Yard were below the human health (6.5 to 9.5 pH units) criteria. Acidity was below the limit of detection (<2 mg/l) at most locations with the exception of Site T5, Whites Bridge GS and Avoca Bridge ranging from 5.48 to 9.13 mg/l. The specific conductance was well within the criteria for human health of 2.5 mS/cm ranging from 0.062 to 0.162 mS/cm. Nutrients in the river and stream samples collected were below the limit of detection for ortho-phosphate and ammonia.

The dissolved metal concentrations in the rivers and streams were low in comparison to the groundwater and the adit discharges; however, several exceedances of both ecological and human health criteria occurred. Dissolved copper exceeded the ecological criteria (5 μ g/l) at all river and stream locations from Whites Bridge to the Downstream Shelton Abbey location, with results ranging from 8.57 to 23.6 μ g/l. Similarly dissolved zinc exceeded the ecological assessment criteria (50 μ g/l) from Whites Bridge on the Avoca River to Downstream Shelton Abbey with results ranging from 76.5 to 335 μ g/l. Dissolved cadmium exceeded the ecological assessment criteria (0.45 μ g/l) from WCC Maintenance Yard to Avoca Bridge with concentrations ranging from 0.56 to 0.616 μ g/l.

Dissolved iron only exceeded the human health assessment criteria of 200 μ g/l at Site T5 with a concentration of 377 μ g/l. Dissolved manganese ranged from 55.7 to 99.5 μ g/l at Site T5 to DS Shelton Abbey, which exceeded the criteria for human health (50 μ g/l). Note that iron and manganese are not important criteria for human health (see Section 4.2.1).



Dissolved aluminium did not exceed the human health criteria (200 $\mu g/I$) at any of the river sampling locations. Dissolved lead also did not exceed the ecological (7.2 $\mu g/I$) and human health (10 $\mu g/I$) at any of the river sampling locations.

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

Sample Description	Date Sampled Units	pH (field) pH Units	Cadmium (diss.filt) µg/l	Copper (diss.filt) µg/l	lron (diss.filt) μg/l	Manganese (diss.filt) μg/l	Zinc (diss.filt) μg/l
Ecological Cr		4.5 to 9	0.45	5	-	1100	50
Human Health		6.5 to 9.5	5	2000	200	50	-
Ballinacleish Bridge	18/09/2014	6.41	<0.1	1.04	109	10.8	26.1
Lions Bridge	18/09/2014	7.07	< 0.1	0.885	62.9	5.23	24.8
Site T1	17/09/2014	6.71	< 0.1	0.924	58.7	4.86	31
Vale View	16/09/2014	6.87	< 0.1	2.48	<19	6.3	9.74
Whites Bridge	17/09/2014	6.56	0.258	23.6	45.3	33.6	133
Whites Bridge GS	17/09/2014	6.83	0.112	9.34	52.4	19.2	76.5
DS Deep Adit	17/09/2014	6.86	0.27	8.57	66.7	26.8	174
WCC Main. Yard GS	17/09/2014	6.41	0.56	16.4	76.7	49.1	280
Site T5	17/09/2014	6.21	0.57	15.6	377	94.3	335
Avoca Bridge	17/09/2014	6.63	0.616	14.5	182	94.1	314
Sulphur Brook	17/09/2014	6.84	0.247	22.7	26.2	20.3	81.6
US Shelton Abbey	18/09/2014	7	0.273	9.38	95.7	55.7	186
DS Shelton Abbey	18/09/2014	6.86	0.357	9.43	118	99.5	209

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 new discharge location for the Road Adit will be upstream of the Wicklow County Council Maintenance Yard GS.

The flow record from 1 April 2014 to 30 September 2014 of Whites Bridge GS is reproduced in Figure 2 and for Wicklow County Council Maintenance Yard GS from 1 April 2014 to 30 September 2014 in Figure 3. The figures show the measured flows ranged from >30 m³/s following rainfall events to approximately 1-2 m³/s during low-flow. The flashy nature of the river shows a rapid response to rainfall. The median flows for this period of approximately 5.59 m³/s at Whites Bridge GS and 5.52 m³/s at Wicklow County Council Maintenance Yard GS are lower than the long term median of approximately 10 m³/s at Whites Bridge GS (CDM Smith, 2013), which reflects the relatively low levels of rainfall during the monitoring period. Flow in June, July and September was particularly low with a baseline flow of 1.7 m³/s at Whites bridge GS and 1.6 m³/s at Wicklow County Council Maintenance Yard GS which is below the 95%-ile flow (low flow) of approximately 2 m³/s at both stations.

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

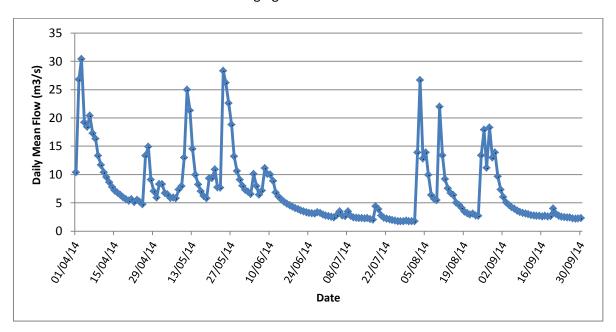


Figure 2 Mean Daily Flow (m3/s) at Whites Bridge (Station 10044) from 1 April to 30 Sept 2014



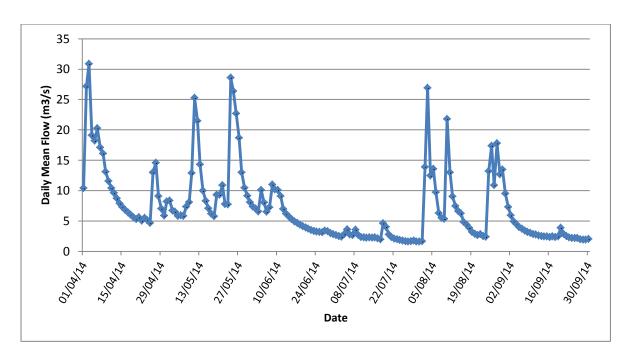


Figure 3 Mean Daily Flow (m3/s) at Wicklow County Council Maintenance Yard (Station 10045) from 1 April to 30 Sept 2014

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 September 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 17.5 l/s is considered a moderate flow as past records for the Deep Adit ranged from approximately to 10 to 37.5 l/s. The flow was also measured at the Deep Adit Confluence prior to it discharging to the river and the measured flow was less than 1 l/s as most of the flow was diverted through the Millrace. The flow in the Millrace was measured just after it was diverted from the Deep Adit channel where the flow was still channalised and therefore measureable, the measured flow was 11.4 l/s. This indicates that there is a loss of flow which is likely due to the dispersed flow along the channel and infiltration into the channel bed. Note that the Millrace sample was collected further downstream and the flow was unable to be measured at this location as the flow was too dispersed.

The measured flow at the Road Adit of 18 l/s and past records for the Road Adit ranged from approximately 6 to 58 l/s (CDM, 2008). The flow was also measured at the Road Adit Confluence prior to the adit discharging to the river and the measured flow was 12.7 l/s which is less than at the adit portal. There was some flow that was seeping into the newly installed culvert under the road and it is possible that there was some infiltration along the ditch.



Table 16 Surface Water Flow Value Measured in September 2014

Site Name	Flow m³/s	Flow I/s	Date	Notes
Ballinacleish Bridge	1.52	1520	18/09/2014	Flow meter was having difficulty
				providing stable readings
Lions Bridge	2.0	2028	18/09/2014	
Vale View	0.010	9.96	16/09/2014	
Site T1	2.8	2793	17/09/2014	
White's Bridge GS	2.7	2690	17/09/2014	Note that flow on 18/9/2014 was 2.6 m ³ /s
Wicklow Co Co. Maintenance Yard GS	2.5	2480	17/09/2014	Note that flow on 18/9/2014 was 2.3 m ³ /s
Site T5	2.6	2633	17/09/2014	
Avoca Bridge	3.2	3242	17/09/2014	
Upstream of Shelton Abbey	4.7	4736	18/09/2014	
Downstream of Shelton Abbey	4.7	4736	18/09/2014	
Sulphur Brook	0.10	103	19/09/2014	
850 Adit	-	-	16/09/2014	No Flow
Deep Adit	0.018	17.5	16/09/2014	
Deep Adit Confluence	0.0001	0.125	16/09/2014	
Millrace (Deep Adit)	0.011	11.4	16/09/2014	
Road Adit	0.018	18.0	16/09/2014	
Road Adit Confluence	0.013	12.7	16/09/2014	
Cronebane Intermediate Adit	0.004	3.96	16/09/2014	
Cronebane Shallow Adit	0.0004	0.357	16/09/2014	
Ballygahan Adit	0.00005	0.049	16/09/2014	
Spa Adit	0.00001	0.012	16/09/2014	

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:

Load (kg/day) =[C (μ g/L) * F (L/day)] / 1,000,000,000 μ 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

				Sulph	nate	Alum	inium	Со	pper	Iro	on	L	ead	Zi	nc
Sample Description	Date Sampled	Flow I/s	pH Units	μg/l	kg/day	μg/l	kg/day	μg/l	kg/day	μg/l	kg/day	μg/l	kg/day	μg/l	kg/day
Cronebane Inter. Adit	16/09/2014	3.96	3.27	606000	207	5340	1.83	972	0.330	88700	30.3	146	0.050	3000	1.03
Cronebane Shallow Adit	16/09/2014	0.36	2.75	2820000	87	306000	9.44	5550	0.170	202000	6.23	1420	0.040	103000	3.18
Ballygahan Adit	16/09/2014	0.05	3.1	1480000	6.27	68900	0.290	6260	0.030	70200	0.300	158	0.0000	20500	0.090
Deep Adit	16/09/2014	17.5	3.47	917000	1390	80200	121	130	0.20	98100	148	1910	2.89	39900	60.3
Deep Adit Confluence	16/09/2014	0.13	3.25	910000	9.83	77300	0.830	131	0.00	61000	0.660	1740	0.020	37700	0.410
Millrace (Deep Adit)	17/09/2014	11.4	3.05	688000	678	63200	62.2	69.4	0.070	15700	15.5	1330	1.31	39000	38.4
Road Adit	16/09/2014	18.0	3.93	1090000	1700	15600	24.3	294	0.460	126000	196	403	0.630	9810	15.3
Road Adit Confluence	16/09/2014	12.7	3.96	1060000	1160	16400	18.0	360	0.400	122000	134	413	0.450	11700	12.8
Spa Adit	16/09/2014	0.0	2.68	1720000	1.78	181000	0.19	9280	0.010	125000	0.130	127	0.000	13400	0.010
Ballinacleish Bridge	18/09/2014	1520	6.41	1000	131	54.1	7.1	1.04	0.140	109	14.3	1.22	0.160	26.1	3.43
Lions Bridge	18/09/2014	2030	7.07	3700	648	40.9	7.17	0.885	0.160	62.9	11.0	1.18	0.210	24.8	4.35
Site T1	17/09/2014	2790	6.71	3100	748	36.2	8.74	0.924	0.220	58.7	14.2	1.17	0.280	31	7.48
Vale View	16/09/2014	10	6.87	19900	17.10	31.6	0.030	2.48	0.000	0.095	0.000	0.001	0.000	9.74	0.010
Whites Bridge	17/09/2014	2690	6.56	9600	2230	123	28.6	23.6	5.49	45.3	10.5	1.08	0.250	133	30.9
Whites Bridge GS	17/09/2014	2690	6.83	6800	1580	94.9	22.1	9.34	2.17	52.4	12.2	0.977	0.230	76.5	17.8
DS Deep Adit	17/09/2014	2480	6.86	10100	2160	139	29.8	8.57	1.84	66.7	14.3	2.48	0.530	174	37.3
WCC Main. Yard GS	17/09/2014	2480	6.41	14400	3090	131	28.1	16.4	3.51	76.7	16.4	2.76	0.590	280	60.0
Site T5	17/09/2014	2630	6.21	19800	4500	94.8	21.6	15.6	3.55	377	85.8	2.62	0.600	335	76.2
Avoca Bridge	17/09/2014	3240	6.63	19900	5570	93.1	26.1	14.5	4.06	182	51.0	2.36	0.660	314	88.0
Sulphur Brook	17/09/2014	103	6.84	12500	111.0	28	0.250	22.7	0.200	26.2	0.230	4.66	0.040	81.6	0.730
US Shelton Abbey	18/09/2014	4740	7	16400	6710	95.3	39.0	9.38	3.84	95.7	39.2	1.87	0.770	186	76.1
DS Shelton Abbey	18/09/2014	4740	6.86	17400	7120	86.1	35.2	9.43	3.86	118	48.3	1.54	0.630	209	85.5

Loading from Adit Discharges

The Deep Adit had aluminium, copper and zinc loads of 121, 0.2 and 60.3 kg/day and the Road Adit had loads of 24.3, 0.460 and 15.3 kg/day, respectively. The Road Adit had a higher load of sulphate with 1,700 kg/day and dissolved iron with 196 kg/day and the Deep Adit had 1,390 kg/day sulphate and 148 kg/day of iron.

To determine if there was any apparent loss of sulphate or metals loading along the Deep Adit ditch closer to where it discharges into the Avoca River, the flow and loading results were evaluated between the portal and confluence samples (Table 17). Flow were measured at two locations further along the Deep Adit ditch at the Deep Adit Confluence and on the Millrace where it was still channelised. The recorded flow was lower further downstream which is likely due to the difficulties in measuring the flows as the discharge was dispersed and flowing several different directions. There is likely infiltration occurring in the channel also. The concentrations of sulphate and the dissolved metals were similar in the Deep Adit portal and the confluence samples. The loading of aluminium and iron in particular were significantly lower at the Deep Adit Confluence and on the Millrace (total aluminium 63 kg/day and iron 16.6 kg/day) when compared with the Deep Adit portal (aluminium 121 kg/day and iron 148 kg/day). The sulphate load also decreased downstream of the portal from 1,390 to 687 kg/day. The decreases in loads are likely due to the loss of flow which can be attributed to the difficulties in measuring the flows or from infiltration.

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 evaluated 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 lower at the confluence location but this was likely due to the lower flow measurement at the confluence.

The Cronebane Intermediate Adit had dissolved metals loads of $1.83 \, \text{kg/day}$ for aluminium, $30.3 \, \text{kg/day}$ iron and $1.03 \, \text{kg/day}$ zinc. The Cronebane Shallow Adit, Spa Adit and Ballygahan were of minor importance in terms of dissolved metals loads to the Avoca, either because of absence of surface flow to the river or due to low loads (either low concentrations or low flows). Loads from these adits range from $0.19 \, \text{to} \, 9.44 \, \text{kg/day}$ for aluminium, $0.01 \, \text{to} \, 0.33 \, \text{kg/day}$ for copper and $0.01 \, \text{to} \, 1.03 \, \text{kg/day}$ for zinc.

Avoca River Loadings

Background loads upstream of the Avoca Mining Area of metals were present which is evident from the calculated loads at Ballinacleish Bridge, Lions Bridge and Site T1. The dissolved metal loads at Site T1 were 8.74 kg/day for aluminium, 0.22 kg/day for copper, 14.2 kg/day for iron, 0.28 kg/day for lead and 7.48 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). Figure 4 shows how the dissolved zinc load increases considerably downstream, however the there is a slight decrease at Whites Bridge GS.

An increase in loads occurs at Whites Bridge with loads of dissolved aluminium at 28.6 kg/day, copper at 5.49 kg/day, and zinc at 30.9 kg/day. There was a slight decrease in dissolved aluminium 22.1 kg/day, copper 2.17 kg/day and zinc 17.8 kg/day loads, 90 metres downstream at Whites Bridge GS.



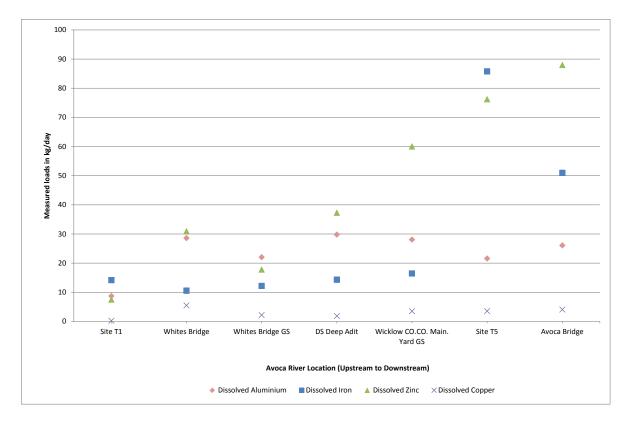


Figure 4 Calculated Loads of Dissolved Aluminium, Iron, Zinc and Copper in kg/day in Avoca River in September 2014

The DS Deep Adit location is on the Avoca River downstream of the Deep Adit discharge (Deep Adit Confluence and Millrace sample) so the loads would be expected to be 85.1 kg/day for aluminium, 28.4 kg/day for iron and 56.6 kg/day for zinc to account for the loading at Whites Bridge GS (22.1 kg/day aluminium, 12.2 kg/day iron and 17.8 kg/day zinc) and the Deep Adit discharges (Deep Adit Confluence and Millrace - 63.0 kg/day aluminium, 16.2 kg/day iron and 38.1 kg/day zinc). However, the loadings were determined to be significantly lower at DS Deep Adit with 29.8 kg/day aluminium, 14.3 kg/day iron and 37.3 kg/day zinc. The discharges from the Deep Adit and Millrace are unlikely to be fully mixed with the Avoca River at this point, however a representative sample was collected along a transect. As a result this indicates that there was an overestimation in the Millrace flow rate as it was measured at a channelised section upstream of the main discharge point itself. There was further dispersion of flow and infiltration in the Millrace itself prior to discharging to the Avoca River.

Further downstream on the Avoca River at the Wicklow Co. Co. Maintenance Yard GS the measured loads are similar to DS Deep Adit with 28.1 kg/day for aluminium and 16.4 kg/day for iron; however zinc is higher and closer to the expected load with 60.0 kg/day. At Wicklow Co. Co. Maintenance Yard GS location the Deep Adit discharge is better mixed with the Avoca River.

Site T5 was downstream of the Road Adit discharge so the loads would be expected to be 46.1 kg/day for aluminium, 150 kg/day for iron and 72.8 kg/day for zinc to account for the loading at Wicklow Co. Co. Maintenance Yard GS (28.1 kg/day aluminium, 16.4 kg/day iron and 60.0 kg/day zinc) and the Road Adit Confluence (18.0 kg/day aluminium, 134 kg/day iron and 12.8 kg/day zinc). However, the loadings were determined to be lower at Site T5 with 21.6 kg/day aluminium, 85.8 kg/day for iron and for zinc the loading was similar with 76.2 kg/day. At Site T5



there is a significant increase in dissolved iron loads compared with the upstream location which can be attributed to the Road Adit Discharge.

There was an apparent increase in the dissolved iron and zinc loads from 39.2 kg/day for iron and 76.1 kg/day for zinc Upstream of Shelton Abbey to 48.3 kg/day for iron and 85.5 kg/day for zinc Downstream of Shelton Abbey. The calculated loads for dissolved aluminium, copper and lead were similar at the upstream and downstream locations of Shelton Abbey.

Two tributaries to the Avoca River were sampled: Vale View and Sulphur Brook. Both tributaries had insignificant loads relative to the adit discharges, with the highest loading of 0.730 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 Sept 2014), Figure 6 (Road Adit from Oct 2001 to Sept 2014) and Figure 7 (Avoca River at Avoca Bridge from Oct 2001 to Sept 2014).

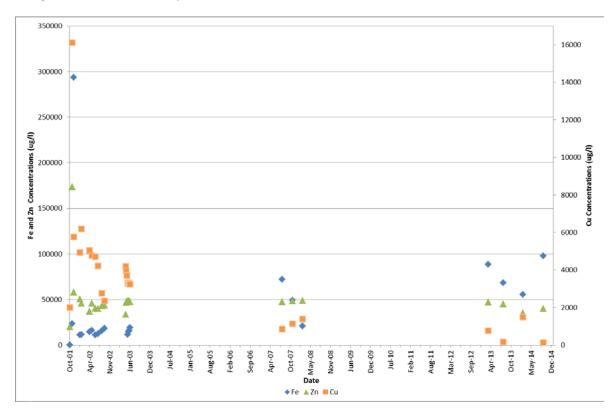


Figure 5 Concentration trends for dissolved copper, zinc and iron within the Deep Adit Discharge (Oct 2001 to Sept 2014)



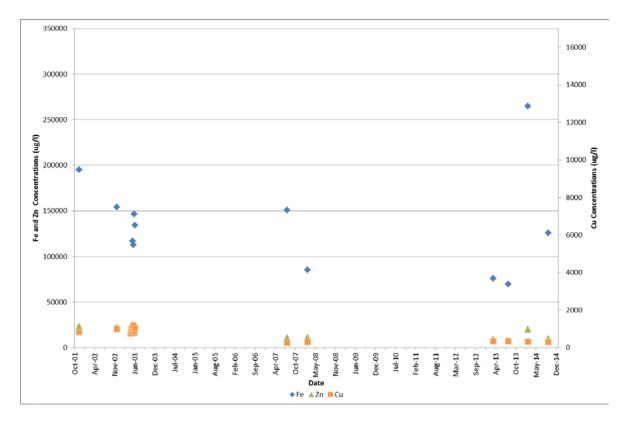


Figure 6 Concentration trends for dissolved copper, zinc and iron within the Road Adit Discharge (Oct 2001 to Sept 2014)

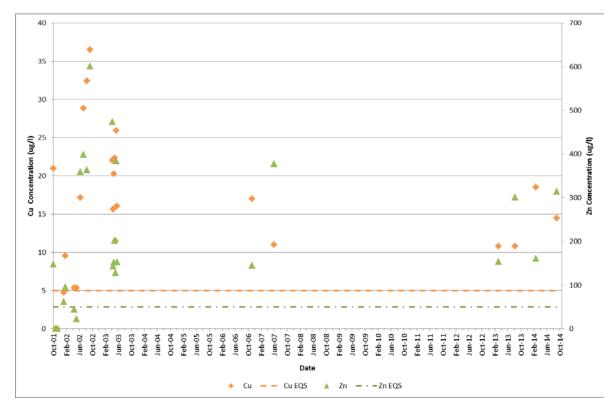


Figure 7 Concentration trends for dissolved copper and zinc at Avoca Bridge compared with the environmental quality objective (EQS) (Oct 2001 to Sept 2014)



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
	0 <= p < 0.05	Decreasing
Decreasing	0.05 <= p < 0.1	Likely Decreasing
	p >= 0.1	No Trend
	0 <= p < 0.05	Increasing
Increasing	0.05 <= p < 0.1	Likely Increasing
	p >= 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

Comple lesstion	Parameter	October	2001 to S	eptember 2014	June 2007 to September 2014			
Sample location	Parameter	P value	S value	Trend	P value	S value	Trend	
Deep Adit	Copper	0.0000	-216	Decreasing	0.274	-5	No Trend	
	Zinc	0.472	-4	No Trend	0.0358	-13	Decreasing	
	Iron	0.0005	117	Increasing	0.274	5	No Trend	
	Copper	0.0374	-37	Decreasing	0.5	1	No Trend	
Road Adit	Zinc	0.0037	-55	Decreasing	0.5	-1	No Trend	
Noad Adit	Iron	0.0963	-20	Likely decreasing	0.5	-1	No Trend	
	Copper	0.466	-4	No Trend	0.307	3	No Trend	
Avoca Bridge	Zinc	0.0879	49	Likely Increasing	0	n/a	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 and dissolved copper were



decreasing in the Road Adit and iron was 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 decreasing in the Deep Adit and that 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. Dissolved zinc at Avoca Bridge however has a trend that is likely increasing from 2001 but there was no statistically significant trend was present for dissolved copper for either time period analysed or dissolved zinc from 2007 to 2014. The ecological assessment criteria (or EQS) are also shown on the graph for reference. At Avoca Bridge the dissolved copper has been above the ecological assessment criteria of 50 μ g/l and dissolved zinc ecological assessment criteria of 50 μ g/l since mid-2002.

5.3.2 Seasonal Trends

Table 20 shows the seasonal variation between the concentrations of dissolved metals and the calculated loads observed between the high flow sampling events in March 2013 (R1) and February 2014 (R3) and the low flow sampling events in August 2013 (R2) and September 2014 (R4). 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 and September 2014 compared with the high flow sampling. The concentration of dissolved iron at Avoca Bridge is quite variable and dissolved zinc is higher in concentration during the low flow sampling events in August 2013 and September 2014.

Table 20 also shows that the calculated loads of dissolved aluminium, copper, iron and zinc were all significantly lower in August 2013 and September 2014 due to the low flow conditions.

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

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

Notes:



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

Section 6

Groundwater Levels and Groundwater-Surface Water Interaction

6.1 Groundwater Levels

Groundwater levels were measured at the nine wells using a portable electronic water level recorder prior to purging. Table 21 provides the measured depth to groundwater and calculated groundwater elevations. All groundwater level data are contained in Appendix C of the Data Report. The groundwater elevations varied between 25.6 to 33.1 m Ordnance Datum (OD) in the Avoca Mining Area. These groundwater elevations were between 1.1 to 1.5 metres lower than the elevations measured in the winter season (February 2014) with the exception of SG104 which was 0.2m higher. 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 September 2014

Borehole Identifier	Date	Time	Depth to Groundwater (m bTOC)	Depth to Groundwater (m bgs)	Groundwater Elevation (m OD)
MWDA1	29/9/2014	15:50	6.39	5.79	26.4
MWDA2	29/9/2014	15:45	6.46	5.73	26.16
MWPF1	29/9/2014	13:20	4.74	4.15	26.75
MWET1	15/9/2014	10:05	7.40	6.83	25.99*
MWET2	15/9/2014	10:15	7.26	6.56	26.11*
GW1/05	29/9/2014	10:20	5.21	4.57	25.59*
GW2/05	29/9/2014	11:40	5.33	4.5	25.62*
SG104	15/9/2014	14:45	25.04	unknown	33.13*
MWSA2	30/9/2014	9:20	8.74	8.46	1.43

Notes:

m is metres

OD is Ordnance Datum

bTOC is below top of casing

bgs is below ground surface

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 1 April 2014 to 30 September 2014. Figure 9 shows the groundwater elevation at MWSA2 at Shelton Abbey Tailings Facility between 1 April 2014 and 30 September 2014. Due to data logger malfunctions data are missing for MWPF1 and MWET1 for the periods 26 July to 30 September and 1 April to 26 July respectively. Data are missing for MWSA2 from 1 July to 26 July due to batteries dying.



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

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.

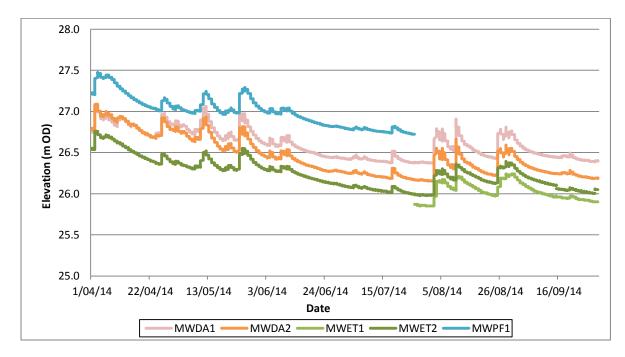


Figure 8 Groundwater Elevations in the Avoca Mining Area from 1 April to 30 Sept 2014

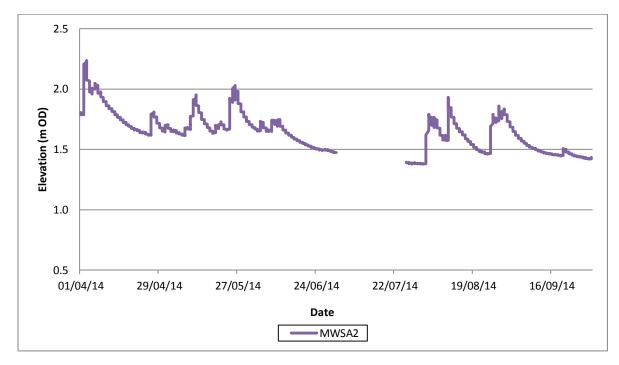


Figure 9 Groundwater Elevation at Shelton Abbey from 1 April to 30 Sept 2014



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 marginal 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 April 2014 to 30 September 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. Streambed characteristics and the elevations both influence the flow rates and help define any apparent losses or gains in river flow.

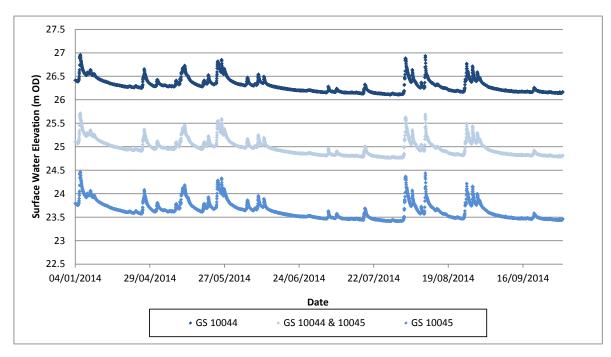


Figure 10 Elevation of the Avoca River at GS 10044 and GS 10045 at the Deep Adit Area from 1 April to 30 September 2014

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 at the time of sample collection in September 2014.

Table 22 Calculated Groundwater Gradients for September 2014

Borehole Identifier	Date	Time	Groundwater Elevation (m OD)	Water Elevation at Perpendicular Stream Point (m OD)	Distance to Perpendicu Iar Stream Point (m)	Gradient
MWDA1	29/9/2014	15:50	26.4	26.14	40	0.006
MWDA2	29/9/2014	15:45	26.2	26.14	40	0.0005
MWPF1	29/9/2014	13:20	26.8	26.14	44	0.014
MWET1	15/9/2014	10:05	26.0*	24.82**	72	0.016
MWET2	15/9/2014	10:15	26.1*	24.82**	72	0.018
GW1/05	29/9/2014	10:20	25.6*	24.79**	74	0.011
GW2/05	29/9/2014	11:40	25.6*	24.79**	74	0.011
SG104	15/9/2014	14:45	33.1	23.47	142	0.068
MWSA2	30/9/2014	9:20	1.4	Not available	45	Not available

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

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.



^{**} Estimated elevations based on two surface water gauges

Both figures show that in the recorded data several significant hydrological (rainfall) events occurred in April, May and August which resulted in groundwater levels rising. For example groundwater levels rose by approximately 0.4 metres between 2 August and 3 August and again on 10 August. These peaks were in response to river levels which rose by up to 0.7 metres during both events. High groundwater levels were recorded at the beginning of the monitoring period due to sustained high rainfall in the preceding months. However, relatively low levels of rainfall in July and September resulted in an overall decrease in groundwater levels at the deep adit area and the emergency tailings area.

Figure 12 and Figure 14 show the calculated gradient to the Avoca River at the deep adit area (MWDA1, MWDA2) and the emergency tailings area (MWET1, MWET2) from 1 April to 30 September 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.

On 2 and 3 August a significant hydrological (rainfall) event resulted in groundwater levels rising in MWDA1 and MWDA2 by approximately 0.4 metres. A negative gradient can be observed during this period between the river and both wells, as shown in Figure 12. During the 2 and 3 August period the river water level also rose (approximately 0.7 metres) but more rapidly which resulted in water moving into the monitoring well area, apparent from the rise in groundwater levels. It is likely the river water moved into an unsaturated zone, which could result in mobilising new metals if they were not exposed before. A similar hydrological event occurred on 10 August and again between the 25 to 28 August. MWDA2 appears to respond less to the river than MWDA1 and may be more seasonally influenced (e.g. aquifer storage). A positive gradient existed for over 95% of the monitoring period for MWDA2 with a minimum gradient of minus 0.012 and an average gradient of 0.004.

For MWET1 and MWET2 only positive gradients were observed with a minimum gradient of 0.004 (MWET1) and a maximum of 0.021 (MWET2) 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.



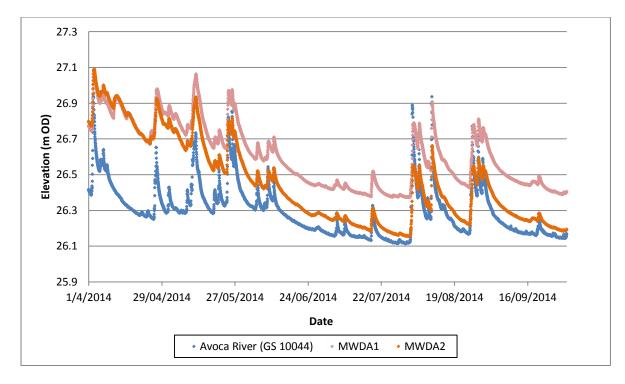


Figure 11 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044) at the Deep Adit Area from 1 April to 30 Sept 2014

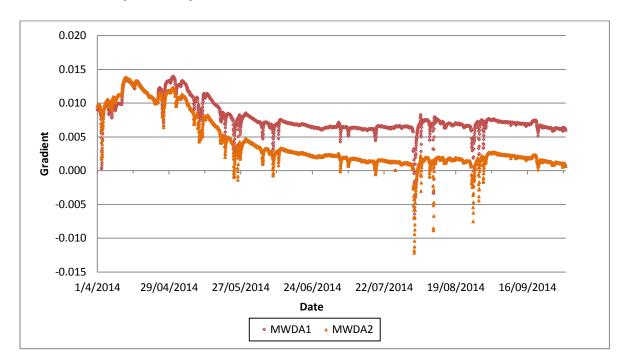


Figure 12 Calculated Groundwater Gradient to the Avoca River at the Deep Adit Area from 1 April to 30 Sept 2014



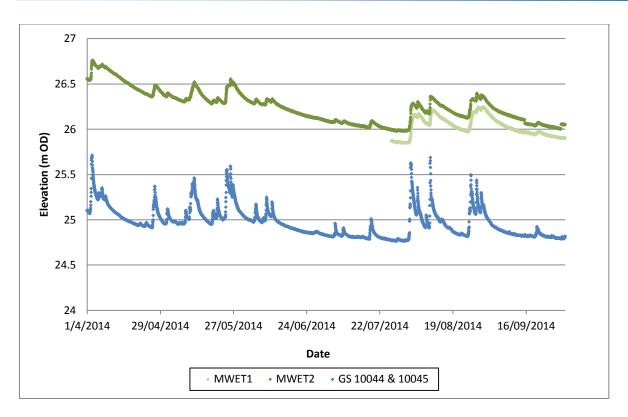


Figure 13 Comparison of Groundwater Elevation and Elevation of the Avoca River (GS 10044 & 10045) at the Emergency Tailings Area from 1 April to 30 Sept 2014

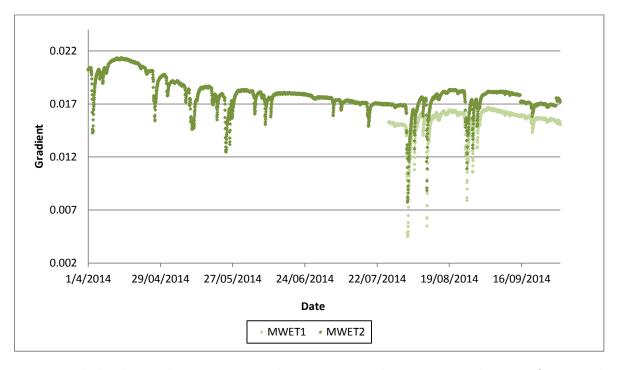


Figure 14 Calculated Groundwater Gradient to the Avoca River at the Emergency Tailings Area from 1 April to 30 Sept 2014



6.4 Summary of Diffuse Loading

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

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

6.4.1 Point Source and Diffuse Loading

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

- Between Site T1 to Whites Bridge, zinc load increased from 7.48 to 30.9 kg/day which is a 76 % increase. The only surface water input in this segment is from Vale View which contributes very little load (0.01 kg/day). This indicates that the increase in loading is primarily due to diffuse load;
- Between Whites Bridge and Whites Bridge GS, zinc load decreases from 30.9 to 17.8 kg/day which is a 74 % decrease. This shows that the concentrations are very variable along the stretch of river between Whites Bridge and Whites Bridge GS with a greater diffuse load contributing at the bridge location;
- Between Whites Bridge GS and DS Deep Adit on the Avoca River, the zinc load increases from 17.8 to 37.3 kg/day which is a 52 % increase. The Deep Adit discharge (confluence sample) and the Millrace contributes 38.8 kg/day which is less than would be expected at this location given the background load at Whites Bridge GS. The discharges from the Deep Adit and Milrace are unlikely to be fully mixed with the Avoca River at this point, however a representative sample was collected along a transect. As a result this indicates that there was an overestimation in the Millrace flow rate as it was measured at a channelised section upstream of the main discharge point itself. There was further dispersion of flow and infiltration in the Millrace itself prior to discharging to the Avoca river;
- Between DS Deep Adit and WCC Maintenance Yard GS on the Avoca River, zinc load increases from 37.3 to 60 kg/day which is a 38 % increase and the only discharge in this stretch is from Ballygahan Adit which only contributes an extra load of approximately 0.09 kg/day. At Wicklow Co. Co. Maintenance Yard GS location the Deep Adit discharge is better mixed with the Avoca River and is therefore likely a more accurate representation of the loads or it could indicate that there is some contribution of diffuse flow along this stretch. It should also be noted that the flow is not measured at DS Deep Adit location and the losing and gaining nature of this stretch of river is discussed further below; and
- Between WCC Maintenance Yard GS and Site T5, zinc load increases from 60 to 76.2 kg/day. The Road Adit (confluence sample) contributed 12.8 kg/day of the load so there is little evidence of diffuse flow in this stretch.



6.4.2 Groundwater Gradients

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

6.4.3 Surface Water Flow Data at the EPA Gauging Stations

In order to examine whether the Avoca River was a losing or gaining river between Whites Bridge GS and WCC Maintenance Yard GS (see Map 3 in <u>Appendix A</u> for locations) the flow records were examined for the monitoring period. Figure 15 displays the mean daily flow at Whites Bridge (Station 10044) and Wicklow County Council Maintenance Yard (Station 10045) from 1 April to 30 Sept 2014 and plotted below is the percentage difference of the flow at the two gauges.

Discharge measurements in open channel cross-sections are all subject to some level of error. It is not possible to predict the error but an indication can be taken from the deviation plots. The deviation plots compare the measured flow against the rating curve flow. The deviation plots were obtained from the EPA for the Whites Bridge GS and the Council Yard GS. The total number of gauging's at Whites Bridge GS was 26 and the difference between the measured flow and the flow rating curve ranged from 0.010 to 1.22 m³/s (or 0.1 to 6.7 %). The total number of gauging's at Council Yard GS was 20 and the difference between the measured flow and the flow rating curve ranged from 0.010 to 0.418 m³/s (or 0.4 to 12.7 %).

Figure 15 shows that the mean daily flow at the two stations is very similar with the percentage difference being under 5% which is likely within the margin of error. In August and September however the percentage increases and reaches minus 12 %. This could indicate that the flow is reduced further downstream and that the stretch of river is likely a losing stream during this time. This could be related to riverbed seepage and riverbank storage after the period of dry weather and low flow during June and July. Overall the current and past studies have shown that the Avoca River/groundwater interaction is dynamic.

During the September 2014 sampling event there is a 9 % decrease in flow between the two gauging stations. This result indicates that the river is likely losing along this stretch, however there is some evidence of diffuse flow along this stretch given the increase in zinc load between DS Deep Adit and WCC Maintenance Yard GS but no large adit discharges along this stretch.



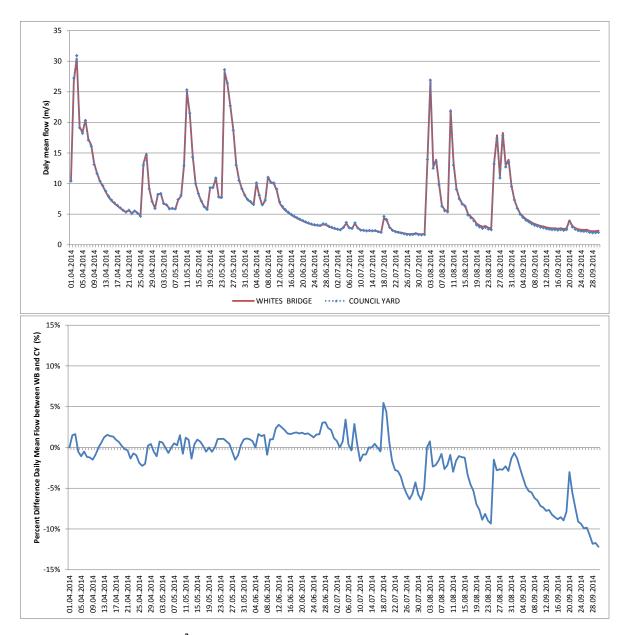


Figure 15 Mean Daily Flow (m³/s) at Whites Bridge (Station 10044) and Wicklow County Council Maintenance Yard (Station 10045) and the Percent Difference between them from 1 April to 30 Sept 2014

6.4.4 Diffuse Loading Conclusion

Overall it has been shown that the Avoca River and its interaction groundwater is very dynamic. The quantity of diffuse loading varies along each river stretch with the greatest evidence of diffuse loading just above Whites Bridge and some indication of diffuse loading between DS Deep Adit and the WCC Maintenance Yard GS.

The groundwater gradients are predominantly positive which also suggests that the Avoca River is a net gaining river from the alluvium in the Deep Adit area and the Emergency Tailings area during the monitoring period. This indicates that the stretch between Whites Bridge GS and DS Deep Adit is also likely contributing diffuse load to the river however it is difficult to quantify given the problems with measuring dispersed flow within the Deep Adit and Millrace areas.



The mean daily flow at the two GS stations has been shown to be very similar with the percentage difference being under 5% which is likely within the margin of error for the flow measurements. In August and September however the percentage difference increases and reaches minus 12 %, which could indicate that the flow is reduced further downstream and that the stretch of river is likely a losing stream during this time. This could be related to riverbed seepage and riverbank storage after the period of dry weather and low flow during June and July.

The implication of the diffuse loading is that the spoil and the alluvial areas on both sides of the river contribute contaminant load to the river. For example, prior to Whites Bridge there is greater evidence of diffuse flow as it accounts for approximately 100 % of the increased dissolved zinc load. Dissolved zinc exceeded the ecological assessment criteria (50 μ g/l) from Whites Bridge on the Avoca River to Downstream Shelton Abbey with results ranging from 76.5 to 335 μ g/l. The dissolved zinc result at Whites Bridge was 133 μ g/l and the primary source was from diffuse flow upstream of the Deep Adit discharge into the Avoca River.



Section 7

Summary and Recommendations

7.1 Summary of Findings

Nine groundwater monitoring wells were sampled and analysed in September 2014 and water levels were measured. Twenty-three surface water locations were sampled and analysed in September 2014 with flows measured at 17 of the locations. The field QA/QC sample results were reviewed for accuracy and precision. The laboratory QC/QC samples and laboratory reports were also reviewed. Overall, the data quality is considered acceptable and the data can be used to compare to the assessment criteria and perform trend and loading evaluations.

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

The overall conclusions are as follows:

- The dissolved metal concentrations were elevated in the majority of the monitoring wells and adit discharges with numerous exceedances of ecological criteria, human health criteria or both, particularly for dissolved aluminium, cadmium, copper, iron, manganese, nickel and zinc. Sulphate levels greatly exceeded the criteria for human health in the majority of monitoring wells.
- The shallow well MWPF1 located upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments had the lowest concentration of dissolved metals. SG104 located immediately downgradient of Ballymurtagh Landfill had the highest concentrations of dissolved metals especially aluminium, cadmium, nickel and zinc.
- The Cronebane Shallow Adit was the adit discharge with the highest concentrations of metals including aluminium, cadmium and zinc. The Cronebane Shallow, Ballygahan and Spa adits are of minor importance in terms of metals loads to the Avoca, either because of absence of direct flow to the river or due to low concentrations and/ or flows.
- In the Avoca River and tributaries, dissolved metal concentrations were low in comparison to the groundwater and the adit discharges; however, 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 8.57 to 23.6 μg/l. Similarly dissolved zinc exceeded the ecological assessment criteria (50 μg/l) from Whites Bridge on the Avoca River to Downstream Shelton Abbey with results ranging from 81.6 to 335 μg/l. Dissolved cadmium exceeded ecological assessment criteria (0.45 μg/l) from WCC Maintenance Yard GS to Avoca Bridge with a concentrations of 0.56 to 0.616 μg/l.
- There was an apparent loss of sulphate, dissolved iron and aluminium load from the Deep Adit and Millrace samples when compared to the Deep Adit portal sample. This is likely due



to the precipitation of iron and other metals along the ditch. The decreases in loads are likely due to the loss of flow which can be attributed to the difficulties in measuring the flows or from infiltration.

- 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 lower at the confluence
 location but this was likely due to the lower flow measurement at the confluence.
- 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 and dissolved copper were decreasing in the Road Adit and iron was likely decreasing. Dissolved zinc at Avoca Bridge however has a trend that is likely increasing from 2001 but there was no statistically significant trend was present for dissolved copper for either time period analysed or dissolved zinc from 2007 to 2014. At Avoca Bridge the dissolved copper has been above the ecological assessment criteria of 5 μg/l and dissolved zinc ecological assessment criteria of 50 μg/l since mid-2002.
- As river stages change hydraulic gradients to or from the river also change. Gradients are predominantly positive which suggests that the Avoca River is a net gaining river from the alluvium during the monitoring period. The implication is that the spoil and the alluvial areas either side of the river contribute contaminant load to the river. This is especially evident in the measured zinc load results, in the stretches of river between Site T1 and Whites Bridge where the diffuse load accounts for a large portion of the zinc loading to the Avoca River. There is also some indication of diffuse loading between the DS Deep Adit location and the WCC Maintenance Yard GS.

7.2 Recommendations for the Monitoring Programme

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

- The Road Adit channel was being upgraded by Wicklow County Council in September 2014 and it is likely that the WCC Maintenance Yard GS sampling location will need to be moved or an additional point added. It is recommended that an additional sampling location be added between the DS Deep Adit and the new Road Adit discharge location and that the location of the WCC Maintenance Yard GS sampling point remains the same. The exact location of the new sampling point will have to be determined during the next sampling road as it will depend of the safe access to the river;
- The 850 Adit was not discharging during the September 2014 sampling round. A blockage
 within the 850 Adit has been removed and it is believed that it may flow all year round and
 it should therefore remain on the sampling programme; and
- An adhoc sample was taken from the Millrace in September 2014. It is recommended that a sample is taken from the main Millrace discharge point to the Avoca River in each sampling round if the flow is diverted through the Millrace. The flow should also be measured at a suitable location along the Millrace (where it is channalised) to provide an estimate of the flow and also measured at the discharge point of the main Millrace discharge to the Avoca River if it is feasible (i.e. if the flow is not too dispersed); and



It is recommended that consideration is given to installing two permanent continuous flow measuring devices, one at the 850 Adit discharge and one at the Deep Adit inside the new box culvert. A continuous water level recorder is also required on the new monitoring well R3-04.



Section 8

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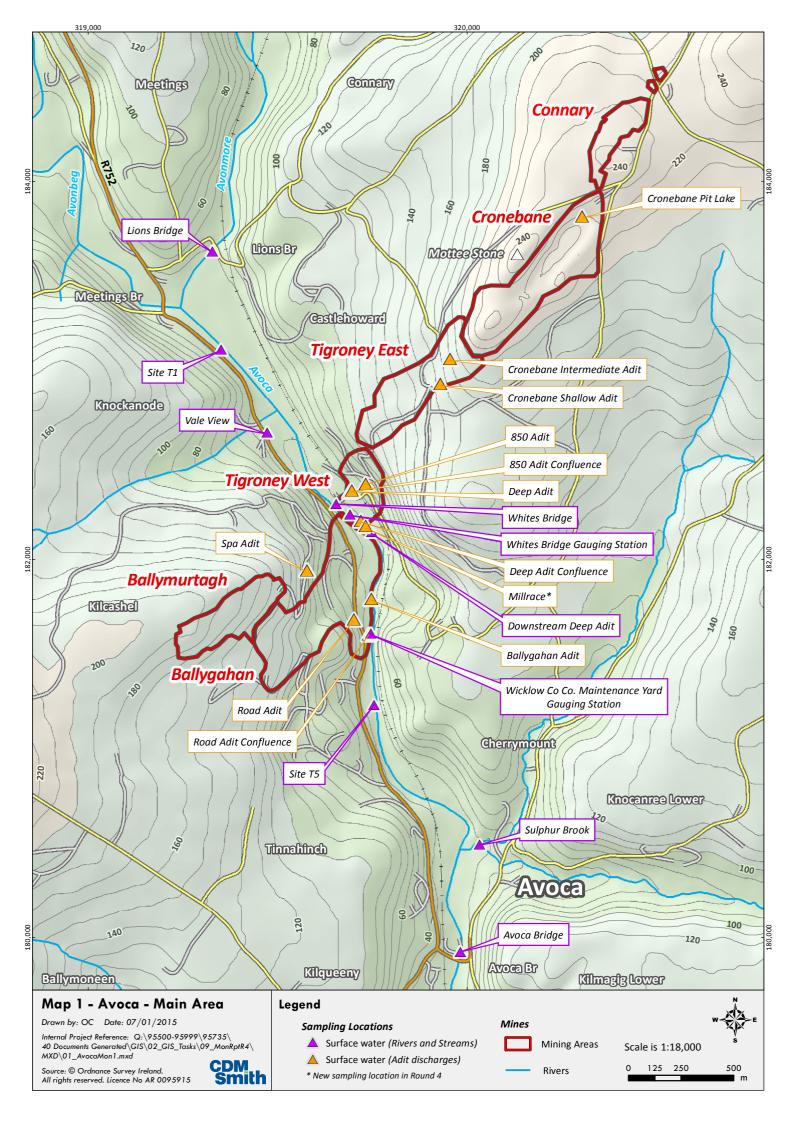
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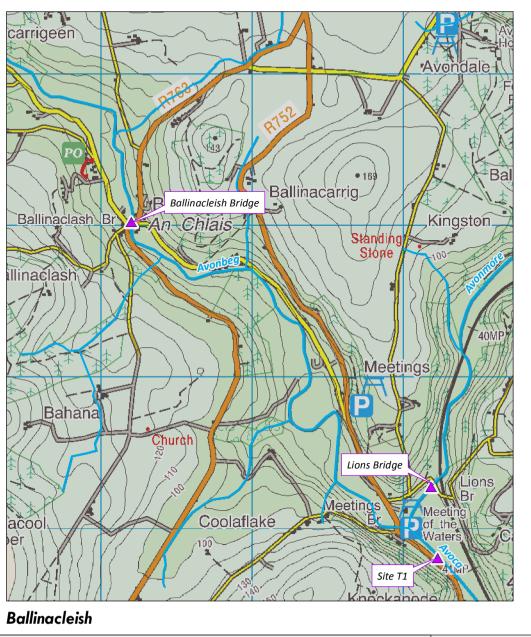


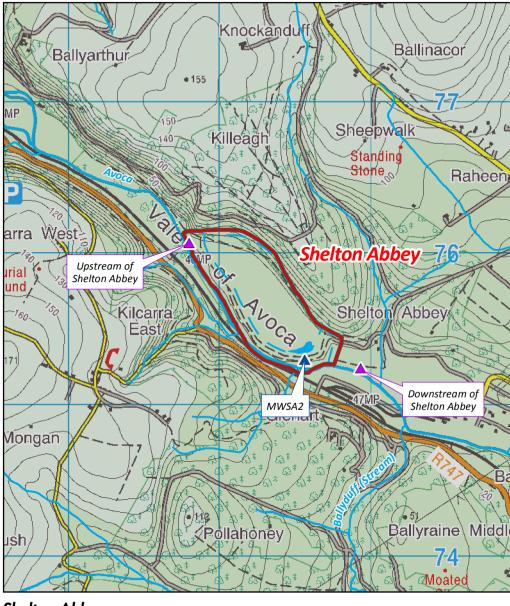
Appendix A

Figures









Map 2 - Avoca - Ballinacleish and Shelton Abbey

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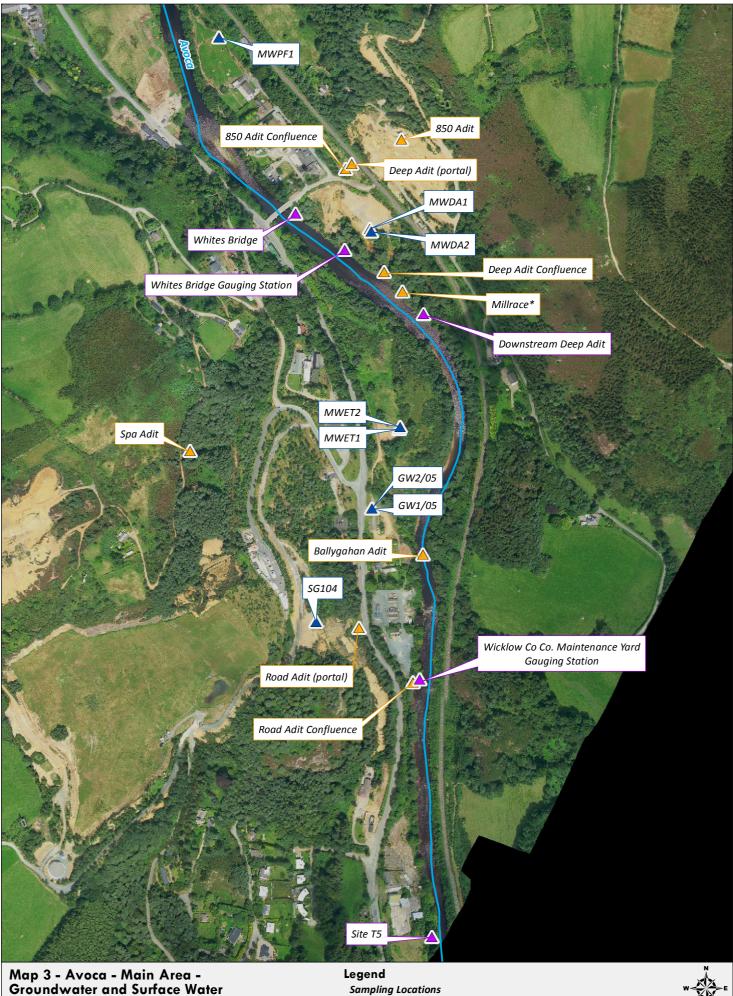
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Shelton Abbey

Legend Sampling Locations △ Surface water (Rivers and Streams) Mines △ Surface water (Adit discharges) Mining Area Groundwater (Shelton Abbey) Mining Area



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Source: © DCENR Lidar Survey (2007)

▲ Groundwater

Surface water (Rivers and Streams) Surface water (Adit discharge)

* New sampling location in Round 4



Scale is 1:5,000

Rivers

50 100

Appendix B

Analytical Data Tables and Assessment Criteria



Table B-1 Comparison of Total versus Dissolved Metals R4

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	
MWET 1	15/09/2014		169000	118000	0.70	12000	8180	0.68	139000	139000	1.00	14700	9310	0.63
SG 104	15/09/2014		823000	876000	1.06	35400	79000	2.23	52100	37500	0.72	70600	150000	2.12
BALLYGAHAN ADIT	16/09/2014	4.5	97000	68900	0.71	3930	6260	1.59	62100	70200	1.13	3 24100	20500	0.85
CRONEBANE INTER AD	16/09/2014	20.5	59300	5340	0.09	1120	972	0.87	7 86100	88700	1.03	33200	3000	0.09
CRONEBANE PIT LAKE	16/09/2014	1	15400	1700	0.11	3830	338	0.09	2040	2010	0.99	6690	550	0.08
CRONEBANE SHOLLOV	16/09/2014	8.5	379000	306000	0.81	3650	5550	1.52	138000	202000	1.46	104000	103000	0.99
DEEP ADIT	16/09/2014	2	98000	80200	0.82	80.2	130	1.62	59500	98100	1.65	44100	39900	0.90
DEEP ADIT CONF.	16/09/2014	3.5	109000	77300	0.71	86.6	131	1.51	50400	61000	1.21	1 48600	37700	0.78
ROAD ADIT	16/09/2014	2.5	18700	15600	0.83	220	294	1.34	96700	126000	1.30	11900	9810	0.82
ROAD ADIT CONF	16/09/2014	2.5	18600	15000	0.81	210	299	1.42	81700	122000	1.49	12100	11700	0.97
SPA ADIT	16/09/2014	1	217000	181000	0.83	5000	9280	1.86	94500	125000	1.32	14600	13400	0.92
VALE VIEW	16/09/2014	1	209	31.6	0.15	4.95	2.48	0.50	81.7	, (0.00	16.8	9.74	0.58
AVOCA BRIDGE	17/09/2014	4.5	833	93.1	0.11	29.2	14.5	0.50	697	182	0.26	329	314	0.95
DS DEEP ADIT	17/09/2014	5	539	139	0.26	11.2	8.57	0.77	7 203	67	0.33	3 208	3 174	0.84
MILLRACE	17/09/2014	10	67700	63200	0.93	67.7	69.4	1.03	19500	15700	0.81	1 34000	39000	1.15
SITE T1	17/09/2014	7	50.7	36.2	0.71	. 2	0.924	0.46	129	59	0.46	5 21.5	31	1.44
SITE T5	17/09/2014	3.5	799	94.8	0.12	25	15.6	0.62	2 821	. 377	0.46	357	335	0.94
SULPHUR BROOK	17/09/2014	1	63.9	28	0.44	27.7	22.7	0.82	2 44.3	26	0.59	83.8	81.6	0.97
WCC MAIN YARD GS	17/09/2014	6	868	131	0.15	28.9	16.4	0.57	262	. 77	0.29	315	280	0.89
WHITES BRIDGE	17/09/2014	3	452	123	0.27	28.2	23.6	0.84	138	45	0.33	3 127	133	1.05
WHITES BRIDGE GAUG	17/09/2014	2	2 267	94.9	0.36	11.2	9.34	0.83	3 146	5 52	0.36	5 73.8	76.5	1.04
BALLINACLEISH BRIDG	18/09/2014	1	25	32.8	1.31	. 2	0.405	0.20	144	57	0.40	20.1	19.9	0.99
DS SHELTON ABBEY	18/09/2014	3	403	86.1	0.21	11.7	9.43	0.81	474	118	0.25	5 219	209	0.95
LIONS BRIDGE	18/09/2014	1	63.8	40.9	0.64	. 2	0.885	0.44	149	63	0.42	2 27	24.8	0.92
US SHELTON ABBEY	18/09/2014	5.5	365	95.3	0.26	10.5	9.38	0.89	381	. 96	0.25	5 190	186	0.98
GW1/05	29/09/2014		76400	7180	0.09	11100	8880	0.80) -	217000)	67600	5640	0.08
GW2/05	29/09/2014		44400	39300	0.89	7850	6230	0.79	45200	165	0.00	7600	6080	0.80
MWDA1	29/09/2014		176000	154000	0.88	18800	16400	0.87	7 80500	63200	0.79	47400	29200	0.62
MWDA2	29/09/2014		47600	49700	1.04	3850	4810	1.25	92400	68400	0.74	53000	46100	0.87
MWPF1	29/09/2014		374	313	0.84	60.5	39.6	0.65	133	37	0.28	3 103	3 44	0.43
MWET 2	30/10/2014		- 25	31.6	1.26	6.28	1.06	0.17	7 .	98300)	4750	5740	1.21
MWSA 2	30/10/2014		- 58600	58400	1.00	155	118	0.76	76500	107000	1.40	3760	4370	1.16

Table B-2 Comparison of Groundwater and Surface Water Results to Assessment Criteria R4

									Specific											
				Alkalinity,					Conductance						Oxygen,					
		Date	Acidity as	Total as	Hardness as	Ammoniacal		COD,	@ deg.C		Dissolved		Nitrate as		dissolved		Phosphate		Sodium	Suspended
Sample Description	Type	Sampled	HCL	CaCO3	CaCO3	Nitrogen as N	Chloride	unfiltered	(field)	Cyanide, Free	solids, Total	Fluoride	NO3	Nitrite as NO2	(field)	pH (field)	(ortho) as P	Sulphate	(diss.filt)	solids, Total
		Units	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mS/cm	mg/l	mg/I	mg/l	mg/l	mg/I	% Sat	pH Units	mg/l	mg/l	mg/l	mg/l
	Eco	logical 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	29/09/2014	-	1	1.22		13.8	-	2.527		2870	-	0.15		2.2			1630	8.27	
MWDA2	GW	29/09/2014	-	1	1.22	-	14.2	-	1.568	0.025	1560	1.68	0.15		1.9	3.89		934	12.3	
MWPF1	GW	29/09/2014		2.5			15.6	-	0.132	0.025	69.4	0.25	7.6	0.025	87.4	4.78	0.01	31.9	7.77	
MWET1	GW	15/09/2014	-	1	1.22	0.645	25.1		2.411	0.025	2970	1.65	0.15	0.025	1.5	3.23		1830	16.7	
MWET2	GW	30/10/2014		65	79.3		15.6	-	3.476	0.025	3570	32.5	0.15		1.4	6.26	0.01	2340	23.8	
GW1/05	GW	29/09/2014	-	1	1.22	0.747	15.7	-	2.61	0.025	2930	2.02	0.75	0.025	1.6	4.04	0.01	1760	13.1	
GW2/05	GW	29/09/2014	-	1	1.22	0.1	16.8		1.211	0.025	1100	0.25	7.88	0.025	62.2	3.62	0.0222	653	10.6	
SG104	GW	15/09/2014	-	1	1.22	2.7	15.7	-	8.308	0.025	12800	5.3	0.075	0.025	41.8	2.88	0.01	9170	8.05	
MWSA2	GW	30/10/2014	-	1	1.22	0.798	16	-	2.322	0.025	2460	4.19	0.04	0.025	2.2	4.15	0.01	1630	10.2	
Cronebane Inter. Adit	Adit	16/09/2014	347	1	1.22	0.397	14.8	8.09	1.176	0.025	1340	-	0.15	0.025	14.4	3.27	0.01	606	9.01	20.5
Cronebane Pit Lake	Pit Lake	16/09/2014	115	1	1.22	0.239	7.7	4.5	0.607	0.025	345	0.25	1.1	0.025	85.2	3.08	0.01	165	4.01	. 1
Cronebane Shallow Adit	Adit	16/09/2014	1720	1	1.22	0.552	16.1	21	3.509	0.025	5440	-	0.15	0.025	13.5	2.75	0.01	2820	7.48	8.5
Ballygahan Adit	Adit	16/09/2014	469	1	1.22	11	43	26.9	2.557	0.025	2420	5.26	6.2	0.025	26.2	3.1	0.01	1480	31.9	4.5
Deep Adit	Adit	16/09/2014	475	1	1.22	0.372	13.7	16.7	1.421	0.025	1530	-	0.15	0.025	5	3.47	0.01	917	8.43	3
Deep Adit Confluence	Adit	16/09/2014	471	1	1.22	0.328	14.2	12.6	1.492	0.025	1510	-	0.15	0.025	82.2	3.25	0.01	910	8.11	3.5
Millrace	Adit	17/09/2014	354	1	1.22	0.1	14.6	8.34	1.269	0.025	1230	-	3.3	0.025	40.5	3.05	0.01	688	8.33	3 10
Road Adit	Adit	16/09/2014	270	1	1.22	8.94	34.3	29.4	1.924	0.025	2200	0.975	1.9	0.051	34.6	3.93	0.01	1090	24.5	2.5
Road Adit Confluence	Adit	16/09/2014	265	1	1.22	8.87	33.6	27.4	1.931	0.025	2200	-	1.9	0.064	86	3.96	0.01	1060	24.8	3.5
Spa Adit	Adit	16/09/2014	1130	1	1.22	0.973	11.1	23.4	2.661	0.025	3020	-	0.15	0.025	103.1	2.68	0.01	1720	5.88	. 1
Ballinacleish Bridge	River	18/09/2014	2	11	13.42	0.1	8.3	4.5	0.062	0.025	42.2	0.25	3.1	0.025	98.4	6.41	0.01	1	4.98	. 1
Lions Bridge	River	18/09/2014	2	18.5	22.57	0.1	10.3	9.22	0.09	0.025	60	0.25	4.10	0.025	100.4	7.07	0.01	3.7	8.62	. 1
Site T1	River	17/09/2014	5.48	17	20.74	0.1	9.7	7.33	0.081	0.025	26**	0.25	4.3	0.025	98.5	6.71	0.01	3.1	7.6	,
Vale View	River	16/09/2014	2	27	32.94	0.1	14	7.12	0.162	0.025	105	0.25	12.4	0.025	102.1	6.87	0.01	19.9	7.28	. 1
Whites Bridge	River	17/09/2014	2	14.5	17.69	0.1	9.9	11.3	0.093	0.025	17.1**	0.25	4.3	0.025	103.5	6.56	0.01	9.6	7.81	
Whites Bridge GS	River	17/09/2014	5.48	15	18.3	0.1	9.7	9.98	0.086	0.025	5**	0.25	4.2	0.025	103.2	6.83	0.01	6.8	7.53	,
DS Deep Adit	River	17/09/2014	2	14	17.08	0.1	9.9	11.1	0.087	0.025	5**	0.25	4.2	0.025	106.3	6.86	0.01	10.1	7.76	, !
Wicklow CO.CO. Main. Yard GS	River	17/09/2014	2	13.5	16.47	0.1	9.9	4.5	0.098	0.025	8	0.25	4.2	0.025	106.9	6.41	0.01	14.4	7.94	, (
Site T5	River	17/09/2014	2	12	14.64	0.1	10.1	7.24	0.116	0.025	57	0.25	4.12	0.025	103.1	6.21	0.01	19.8	7.76	3.
Avoca Bridge	River	17/09/2014	9.13	11.5	14.03	0.1	10	8.43	0.11	0.025	51	0.25	5.0	0.025	106	6.63	0.01	19.9	9.45	4.
Sulphur Brook	River	17/09/2014	2	23.5	28.67	0.1	15.4	4.5	0.16	0.025	92.2	0.25	20.0	0.025	100.7	6.84	0.01	12.5	9.29	
US Shelton Abbey	River	18/09/2014	2	16.5	20.13	0.1	11	10.5	0.116	0.025	80	0.25	7.13	0.025	102.4	7	0.01	16.4	7.47	5.!
DS Shelton Abbey	River	18/09/2014	2	15.5	18.91	0.1	10.9	8.27	0.121	0.025	80	0.25	7.1	0.025	88.4	6.86	0.01	17.4	7.51	. 3

xx Exceeds Ecological Assessment Criteria

xx Exceeds Human Health Assessment Criteria
xx Exceeds both Ecological and Human Health Criteria

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

- Not analysed or no assessment criteria
* Only applies to rivers or streams (i.e. not discharges or groundwater)

** Qualifier - result should be used with caution

Table B-2 Comparison of Groundwater and Surface Water Results to Assessment Criteria R4

	_	Date	Aluminium	Antimony	Arsenic	Barium	Cadmium	Chromium	Cobalt	Copper	. (1: 61.)		Manganese	Mercury	Molybdenum	Nickel	Selenium	Silver	Thallium	/ I: CII)	Uranium	Vanadium	Zinc
Sample Description	Туре	Sampled Units	(diss.filt) µg/l	(diss.filt) µg/l	(diss.filt) μg/l	(diss.filt) μg/l	(diss.filt) μg/l	(diss.filt) μg/l	(diss.filt) μg/l	(diss.filt) μg/l	Iron (diss.filt) μg/l	Lead (diss.filt) μg/l	(diss.filt) µg/l	(diss.filt) μg/l	(diss.filt) μg/l	(diss.filt) μg/l	(diss.filt) µg/l	(diss.filt) μg/l	(diss.filt) μg/l	Tin (diss.filt) μg/l	(diss.filt) μg/l	(diss.filt) μg/l	(diss.filt) μg/l
	Eco	logical 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	29/09/2014	154000	0.563	0.06	2.57	56.1	25.3	114	16400	63200	3.54	9350	0.005	0.538	70.5	0.195	0.75	0.48	0.18	6.82	0.434	29200
MWDA2	GW	29/09/2014	49700	10.4	0.402	4.27	44	5.93	142	4810	68400	1.7	9590	0.005	1.39	67.6	2	0.75	1.47	1.06	4.91	0.12	46100
MWPF1	GW	29/09/2014	313	1.48	0.216	8.95	0.422	1.34	0.668	39.6	36.9	0.459	24.6	0.005	0.44	1.5	0.476	0.75	0.48	0.666	0.75	0.12	44
MWET1	GW	15/09/2014	118000	0.08	0.308	2.27	21.5	9.97	183	8180	139000	6.93	7260	0.005	0.12	75.1	1.54	0.75	1.72	0.18	12.4	0.32	9310
MWET2	GW	30/10/2014	31.6	0.822	4.39	7.92	1.55	1.94	105	1.06	98300	0.683	35100	0.005	0.339	16.9	2.79	0.75	0.48	0.18	1.98	0.368	5740
GW1/05	GW	29/09/2014	7180	0.8	6.75	10.7	69.8	8.71	307	8880	217000	1260	1460	0.005	1.2	79.7	24.2	0.75	4.8	1.8	9.08	1.2	5640
GW2/05	GW	29/09/2014	39300	6.97	0.287	1.09	13.5	2.58	58.5	6230	165	0.585	3280	0.005	1.68	32.5	0.786	0.75	0.48	1.65	2.86	0.28	6080
SG104	GW	15/09/2014	876000	8_	6	31	343	77.7	894	79000	37500	44.4	42600	0.005	12	385	19.5	0.75	48	18	<i>75</i>	12	150000
MWSA2	GW	30/10/2014	58400	3.72	11.8	9.16	1.93	6.6	140	118	107000	29.7	30100	0.005	0.557	114	1.1	0.75	0.48	0.413	8.88	0.833	4370
Cronebane Inter. Adit	Adit	16/09/2014	5340	0.22	6.46	6.03	59.8	1.47	55	972	88700	146	267	0.005	0.12	33	4.41	0.75	2.29	0.18	10	0.835	3000
Cronebane Pit Lake	Pit Lake	16/09/2014	1700	0.08	0.333	7.61	14.7	2.46	23.6	338	2010	635	503	0.005	0.12	5.03	0.195	0.75	0.48	0.18	2.21	0.12	550
Cronebane Shallow Adit	Adit	16/09/2014	306000	0.8	25.9	10.9	282	11.8	285	5550	202000	1420	8720	0.005	1.2	136	20.1	7.5	4.8	1.8	29.8	1.2	103000
Ballygahan Adit	Adit	16/09/2014	68900	0.8	42.4	14.4	54.2	4.97	192	6260	70200	158	12000	0.005	1.2	88	9.29	7.5	4.8	1.8	7.5	1.2	20500
Deep Adit	Adit	16/09/2014	80200	0.8	3.22	9.15	86.4	10.2	106	130	98100	1910	3810	0.005	1.2	38.5	4.29	7.5	4.8	1.8	7.5	1.2	39900
Deep Adit Confluence	Adit	16/09/2014	77300	0.8	2.37	8.76	81	6.08	101	131	61000	1740	3520	0.005	1.2	35.8	1.95	7.5	4.8	1.8	7.5	1.2	37700
Millrace	Adit	17/09/2014	63200	0.08	0.06	5.82	36.2	0.619	58.2	69.4	15700	1330	2780	0.005	0.12	24.4	0.475	0.75	0.48	0.18	5.55	0.12	39000
Road Adit	Adit	16/09/2014	15600	0.8	8.76	19.6	12.8	3.69	132	294	126000	403	9940	0.005	1.2	52.1	21.4	7.5	4.8	1.8	7.5	1.2	9810
Road Adit Confluence	Adit	16/09/2014	16400	0.8	7.93	23.6	13.6	4.88	146	360	122000	413	10500	0.005	3.84	63.7	18.8	7.5	4.8	1.8	7.5	1.2	11700
Spa Adit	Adit	16/09/2014	181000	0.08	0.525	5.24	39.4	8.3	291	9280	125000	127	8470	0.005	0.282	69.4	0.195	0.75	1.75	0.732	8.64	0.12	13400
Ballinacleish Bridge	River	18/09/2014	54.1	0.166	0.603	9.48	0.05	0.79	0.03	1.04	109	1.22	10.8	0.005	0.277	0.662	0.195	0.75	0.48	0.18	0.75	0.276	26.1
Lions Bridge	River	18/09/2014	40.9	0.231	0.602	5.3	0.05	0.433	0.03	0.885	62.9	1.18	5.23	0.005	0.12	0.562	0.195	0.75	0.48	0.18	0.75	0.12	24.8
Site T1	River	17/09/2014	36.2	4.65	0.983	7.44	0.05	0.589	0.216	0.924	58.7	1.17	4.86	0.005	1.57	0.774	1	0.75	0.48	2.74	0.75	0.283	31
Vale View	River	16/09/2014	31.6	0.08	0.368	9.31	0.05	0.57	0.063	2.48	9.5	0.001	6.3	0.005	0.12	0.075	0.423	0.75	0.48	0.18	0.75	0.12	9.74
Whites Bridge	River	17/09/2014	123	0.269	0.416	6.89	0.258	0.4	0.661	23.6	45.3	1.08	33.6	0.005	0.12	0.932	0.195	0.75	0.48	0.18	0.75	0.12	133
Whites Bridge GS	River	17/09/2014	94.9	0.557	0.575	6.7	0.112	0.48	0.359	9.34	52.4	0.977	19.2	0.005	0.12	0.716	0.195	0.75	0.48	0.516	0.75	0.12	76.5
DS Deep Adit	River	17/09/2014	139	0.275	0.444	6.61	0.27	0.446	0.569	8.57	66.7	2.48	26.8	0.005	0.12	0.857	0.195	0.75	0.48	0.18	0.75	0.12	174
Wicklow CO.CO. Main. Yard GS	River	17/09/2014	131	0.647	0.376	6.65	0.56	0.455	1.11	16.4	76.7	2.76	49.1	0.005	0.12	1.12	0.195	0.75	0.48	0.579	0.75	0.12	280
Site T5	River	17/09/2014	94.8	0.457	0.321	5.94	0.57	0.508	1.68	15.6	377	2.62	94.3	0.005	0.12	1.35	0.195	0.75	0.48	0.41	0.75	0.12	335
Avoca Bridge	River	17/09/2014	93.1	0.941	0.371	6.02	0.616	0.37	1.71	14.5	182	2.36	94.1	0.005	0.338	1.41	0.195	0.75	0.48	0.792	0.75	0.12	314
Sulphur Brook	River	17/09/2014	28	1.58	0.45	9.15	0.247	0.412	0.192	22.7	26.2	4.66	20.3	0.005	0.553	0.797	0.567	0.75	0.48	1.24	0.75	0.12	81.6
US Shelton Abbey	River	18/09/2014	95.3	0.227	0.454	6.34	0.273	0.444	0.929	9.38	95.7	1.87	55.7	0.005	0.253	0.993	0.195	0.75	0.48	0.18	0.75	0.12	186
DS Shelton Abbey	River	18/09/2014	86.1	0.181	0.389	6.91	0.357	0.495	1.21	9.43	118	1.54	99.5	0.005	0.12	1.49	0.195	0.75	0.48	0.18	0.75	0.12	209

xx Exceeds Ecological Assessment Criteria

xx Exceeds Human Health Assessment Criteria
xx Exceeds both Ecological and Human Health Criteria

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

- Not analysed or no assessment criteria
* Only applies to rivers or streams (i.e. not discharges or groundwater)

** Qualifier - result should be used with caution