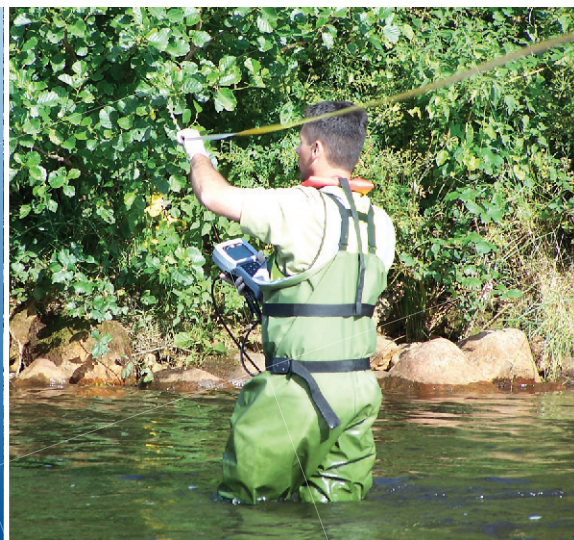


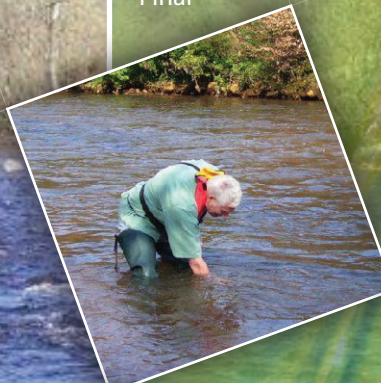
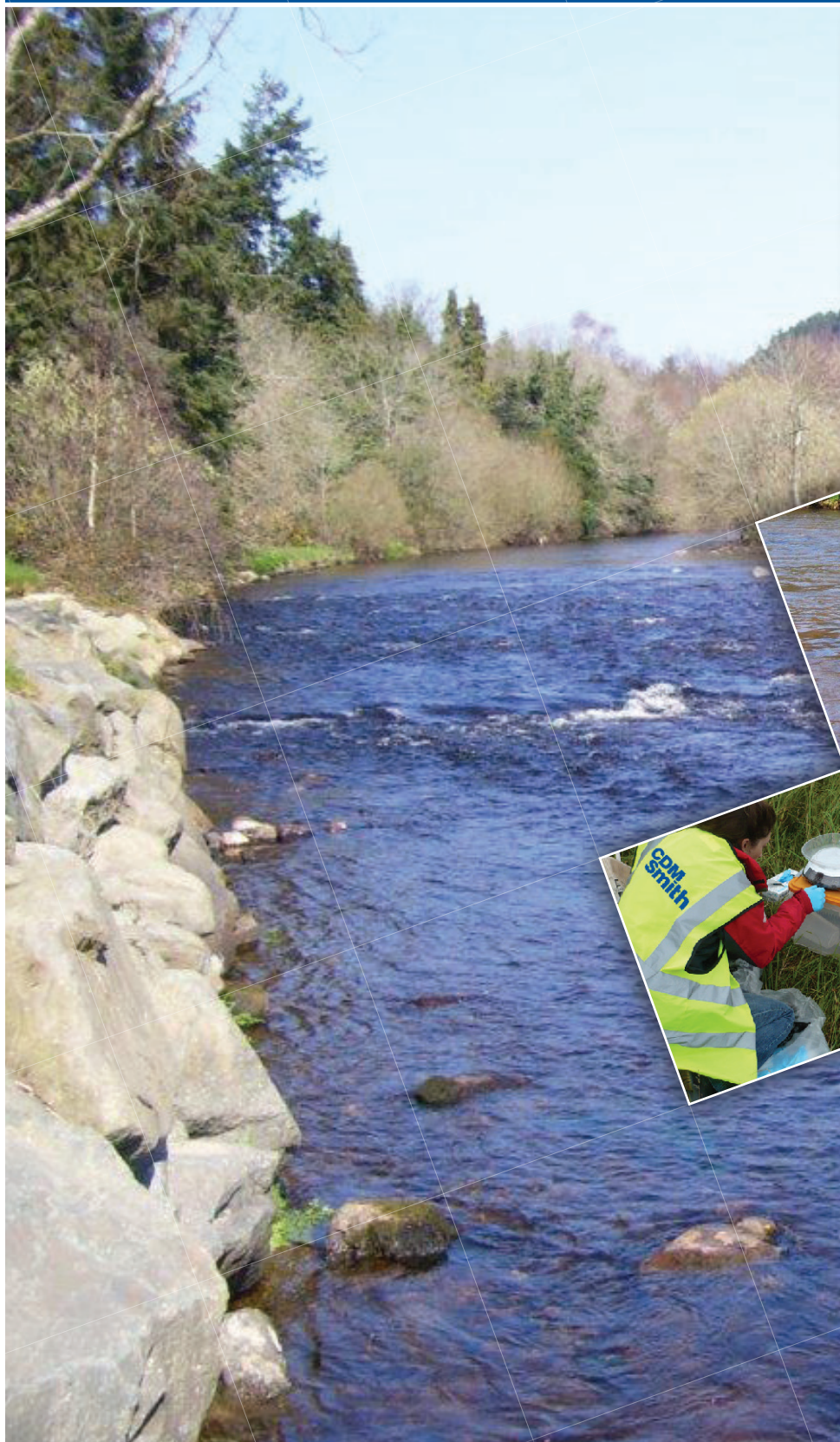
Department of Communications, Energy & Natural Resources



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

Avoca Monitoring Report - Round 1 (2013)

Final



CDM Smith



Document Control Sheet

Client		Department of Communications, Energy and Natural Resources		
Project		Environmental Monitoring of Former Mining Areas of Silvermines and Avoca		
Project No:		95735		
Report		Monitoring Report for the Former Mining Area of Avoca – Round 1		
Document Reference:		95735/40/DG/04		
Version	Author	Checked	Reviewed	Date
1	L Gaston R L Olsen	R O'Carroll	R L Olsen	June 2013
2	L Gaston R L Olsen	R O'Carroll	R L Olsen	September 2013

Distribution	Copy No.

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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 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 March 2013. This report should be read alongside the Avoca Data Report (Document Ref: 95735/40/DG04, dated 2 May 2013) which contains all field observations and laboratory analytical results collected during the monitoring programme.

1.2 Background of Avoca Mining Area

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

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

1.3 Catchment Description

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

1.4 Geology and Hydrogeology

1.4.1 Geology

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

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

There are three main ore types:

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

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

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

1.4.2 Hydrogeology

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

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

Overall water movement consists of three primary pathways:

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

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

1.5 Description of Adit Discharges

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

The Cronebane Intermediate Adit flows from an opening in the southeast wall of the East Avoca Pit and across the bottom of the pit forming a lake on the southwest end.

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

The Deep Adit is located northeast of Whites Bridge and is the main mine drainage for East Avoca. The water flows from the portal into a ditch that runs semi-parallel to the Avoca River for about 60 m before being (recently) diverted into a marsh area east of the spoils area. Previously, the water turned southwest and discharged directly into the river.

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

The Spa Adit is located in West Avoca on a hillside about 150 m northwest of (and about 40 m above) the County Wicklow recycling centre. The discharge exits from a break in a pipe which was observed soaking into the ground, but a gulley formed beneath the pipe suggests that at some time in the past surface flow was present. 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.

Section 2

Methodology

2.1 Field Sampling Methods

2.1.1 Groundwater Sampling

Nine groundwater monitoring wells were sampled between 11 and 14 March 2013, as listed in Table 1 and shown on Map 2 and 3 in **Appendix A**.

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

- Two nested wells in the Emergency Tailings area, downgradient of the West Avoca pit and slightly side-gradient of the Ballymurtagh Landfill (MWET1 - shallow and MWET2 - deep);
- Two nested wells in the Tigroney West spoil area near the Deep Adit (MWDA1 - shallow and MWDA2 - deep);
- One shallow well upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments (MWPF1); and
- One shallow well immediately adjacent to and downgradient of the tailings dam at Shelton Abbey (MWSA2).

The Wicklow County Council monitoring wells follow:

- Three of the wells were installed for Ballymurtagh Landfill monitoring purposes (GW1/05, GW2/05 and SG104), which are located downgradient of the landfill (in West Avoca) and one located at the toe of the landfill (SG104).

Table 1 Location of Avoca Groundwater Monitoring Points

Borehole Identifier	Easting	Northing	Water Level	Field Parameters	Sample for Lab Analysis	Owner	Depth (m bgl)
MWDA1	319877	182043	Yes	Yes	Yes	Dept	12
MWDA2	319879	182039	Yes	Yes	Yes	Dept	24.9
MWET1	319916	181778	Yes	Yes	Yes	Dept	10.9
MWET2	319917	181781	Yes	Yes	Yes	Dept	21
MWPF1	319678	182296	Yes	Yes	Yes	Dept	10
MWSA2	321566	175292	Yes	Yes	Yes	Dept	12.6
GW1/05	319880	181673	Yes	Yes	Yes	WCC	31
GW2/05	319880	181673	Yes	Yes	Yes	WCC	10
SG104	319806	181523	Yes	Yes	Yes	WCC	26.8

Groundwater samples were collected using procedures consistent with the Low Flow Groundwater Sampling Procedure (SOP 1-12) detailed in the Monitoring Plan. Groundwater was collected using

a portable submersible low-flow pump (Grundfos Redi-Flo). The static water level was recorded prior to pumping and measured throughout the purging process to monitor drawdown.

Water quality indicator parameters were monitored in the field during low-flow purging using a flow-through cell to minimise oxidation by the atmosphere. Water quality indicator parameters include temperature, pH, ORP, conductivity and dissolved oxygen (DO). Purging continued until the field parameters had stabilised. The results were recorded approximately every five minutes during the purging process on the Groundwater Purging and Sampling Form. Field sheets are contained in Appendix H and physio-chemical field data are summarised in Appendix A of the Data Report.

After purging the water sample 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 following exceptions to the low-flow sampling procedure applied:

- GW1/05: an obstruction was present in the well at 21.5 m below the top of casing (bTOC) which was 3.5 m above the beginning of the screened interval. Because the pump could not be lowered to the screened interval, the low flow method could not be performed. The sample was collected after three volumes of the well had been purged and the field parameters had stabilised (volume calculated as $\pi r^2 h$ – where r is the inner casing radius and h is the height of the water column); and
- SG104: sufficient water was not present in the well to perform the low flow sampling procedure. The sample was collected after greater than three volumes of the well had been purged 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

Eighteen surface water locations were sampled between 11 and 21 March 2013, as listed in Table 2 and shown on Map 1 and 2 in **Appendix A**.

Surface water sampling was conducted consistent with the Surface Water Sampling Procedure (SOP 1-1) as detailed in the Monitoring Plan. The predetermined surface water sampling locations were located in the field using a GPS. Photographs were taken of the surface water sampling locations (Appendix D of the Data Report). Samples were grab samples collected from a well mixed portion of the water stream where possible. The sample location was approached from downstream so that the underlying sediments are not disturbed.

Samples were placed into new laboratory provided bottles with the correct preservatives. The sample bottles that required no filtering were filled directly in the stream. A container was filled at the same time and transported to the shore for filtering using a 0.45 micron membrane syringe filter before preservation for the trace metal analysis.

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

Flow Measurements

Flow was measured at 13 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 MacBirney 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.

Table 2 Location of Surface Water Monitoring Points

Site Name	Sample Site Description	Easting	Northing	Flow Measurement Method
Ballinacleish Bridge	Avoca River Location	317197	185010	Flow Meter
Lions Bridge	Avoca River Location	319207	183287	Float Method
Vale View	Tributary of Avoca River	319453	182396	Flow Meter
Site T1	Avoca River Location (Upstream of Whites Br.)	319239	182805	Calculated by adding flow from Ballinacleish Bridge and Lions Bridge
Whites Bridge Gauging Station (GS)	Avoca River Location (90m downstream of Whites Br.)	319843	182015	Automatic recorder (Data from EPA)
Wicklow Co Co. Maintenance Yard Gauging Station	Avoca River Location (Abandoned Coal Yard)	319939	181445	Automatic Recorder (Data from EPA)
Site T5	Avoca River Location (Abandoned Coal Yard)	319972	181114	Velocity estimated using Float Method, depth profile to be determined for low flow
Avoca Bridge	Avoca River above Avoca Bridge	320372	179932	Float Method
Upstream of Shelton Abbey	Avoca River Location	320838	175991	Equal to measured flow downstream of Shelton Abbey
Downstream of Shelton Abbey	Avoca River Location	321939	175213	Float Method used at bridge to fertiliser plant
Sulphur Brook	Tributary of Avoca River	320491	180470	Flow Meter
Deep Adit	Adit Discharge	319850	182123	Flow Meter
Road Adit	Adit Discharge	319858	181512	Measured from permanent flume
Cronebane Intermediate Adit	Adit Discharge	320320	182749	Flume
Cronebane Shallow Adit	Adit Discharge	320268	182646	Flume
Ballygahan Adit	Adit Discharge	319940	181610	Bucket and stopwatch
Spa Adit	Adit Discharge	319637	181747	Bucket and stopwatch
Cronebane Pit Lake	Pit Lake	320933	183402	n/a

An additional method for measuring flow was used when the location of the river was unsafe to wade. This method is called the Float Method and is the least accurate method but provides a reasonable estimate. This method requires the measurement and calculation of the cross-

sectional area of the channel as well as the time it takes an object to “float” a designated distance. The water depth was measured from a bridge at regular intervals (approximately 8 locations). The float was released into the channel upstream from the beginning of the section and measured the amount of time it takes the “float” to travel the marked section. This was repeated at least three times and the average time calculated.

Flow rates for two sites could not be determined, as follows:

- Flow at Site T5 could not be directly measured because the river could not be waded on the day of sampling. The velocity was estimated using the Float Method and the depth profile will be obtained during low flow conditions at the next sampling round; and
- No operational automatic recorder was present at Road Adit (EPA station 10041) and the flow rates are not monitored by the EPA or Wicklow County Council. Wicklow County Council took a manual measurement on 25/04/2013. In the future, the flow rate will be determined by manually taking a height reading at the permanently installed flume.

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 samples were collected (also see Table 3):

- Groundwater:
 - One duplicate groundwater sample was collected; and
 - One decontamination blank was collected by pumping deionised (DI) water through the groundwater pump after decontamination.
- Surface Water:
 - Two duplicate surface water samples; and
 - One decontamination blank was collected by pouring DI water over the surface water sampling equipment after decontamination.
- Two certified standard reference material containing known concentrations of the 18 metals was shipped blind to ALcontrol laboratory (the SRM certificate is contained in Appendix G of the Data Report).
- One water blank was collected of the DI water during the sampling event.

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

Table 3 Field QA/ QC Sample IDs and Descriptions

Sample ID	QA/QC Sample Type	Description
AVGD01.1	GW Duplicate	Duplicate of MWPF1
AVDB01.1	GW Decontamination blank	DI water through pump after decon after site MWSA2
AVSD01.1	SW Duplicate	Duplicate of Whites Bridge GS
AVSD02.1	SW Duplicate	Duplicate of Sulphur Brook
AVDB02.1	SW Decontamination blank	DI water over YSI probes after decon after site Sulphur Brook
AVSR01.1	Standard Reference Material	
AVSR02.1	Standard Reference Material	
AVWB01.1	Water blank	Deionised water

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 and time of sample collection. Samples were stored appropriately so they remained representative of the time of sampling. Sufficient ice was added to cool the samples to 4°C.

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, dissolved oxygen, 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.

Section 3

Data Quality and Usability Evaluation

3.1 Introduction

Laboratory data quality and usability were assessed using data quality indicators (DQIs). Data “usability” means that the data are acceptable to use for their intended purpose and associated evaluations. The DQIs for assessing data are expressed in terms of precision and accuracy. These DQIs provide a mechanism to evaluate and measure laboratory data quality throughout the project. The definitions and methods of measurement of precision and accuracy are discussed below. In addition, use of blank samples as a DQI is also discussed.

3.1.1 Accuracy

Accuracy is defined as the degree of agreement of a measurement with an accepted reference or true value. The accepted reference is typically a standard reference material (SRM) provided by an established institute or company. The “true” value has been determined by performing multiple analyses by various methods and laboratories. Accuracy is a measure of the bias in a system (i.e. the laboratory procedures). Each measurement performed on a sample is subject to random and systematic error. Accuracy is related to the systematic error. Attempts to assess systematic error are always complicated by the inherent random error of the measurement. Accuracy is quantitative and usually expressed as percent recovery (%R) of a sample result compared to the SRM.

%R is calculated as follows:

$$\% R = \frac{A}{T} \times 100$$

where: %R	=	Percent recovery
A	=	Measured value of analyte (metal) as reported by the laboratory
T	=	True value of the analyte in the SRM as reported by the certified institute

Acceptable QC limits are typically between 80 to 120 %R for inorganic methods (i.e. metals in this report). The SRMs used for this project are discussed below.

3.1.2 Precision

Precision is the measurement of the ability to obtain the same value on re-analysis of a sample (i.e. the reproducibility of the data). The closer the results of the measurements are together, the greater is the precision. Precision is not related to accuracy or the true values in the sample; instead precision is focused upon the random errors inherent in the analysis that result from the measurement process and are compounded by the sample vagaries. Precision is measured by analysing two portions of the sample (sample and duplicate) and then comparing the results. This comparison can be expressed in terms of relative percent difference (RPD). RPD is calculated as the difference between the two measurements divided by the average of the two measurements.

RPD is calculated as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2) \times 0.5} \times 100$$

where: RPD = Relative percent difference
 D_1 = First sample value
 D_2 = Second sample value (duplicate)

Acceptable RPD values for duplicates generated in the laboratory are usually 65 % to 135 %. Acceptable RPD values for field duplicates are usually 50 % to 150 %. The higher values for field duplicates reflects the difficulty in generating homogeneous duplicates in the field. Both field and laboratory duplicates were generated for this project and are discussed below.

3.1.3 Blanks

Several different types of “blank” samples may be generated to assist in evaluating general data usability. Periodic analysis of laboratory method blanks ensures there is no carryover of contaminants between samples because of residual contamination on the instrument or from contaminants introduced in the laboratory. Laboratory method blanks are typically laboratory pure water, acids or sand that have been processed through all of the procedures, materials, reagents, and labware used for sample preparation and analysis. In addition to the laboratory blanks, decontamination blanks were generated in the field to evaluate the sampling equipment decontamination process. The DI water used in the decontamination was also analysed. Each of these types of blanks is discussed below.

3.1.4 Field QA/QC Samples

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

- Duplicate Samples: Duplicate groundwater and surface water samples were created in the field and submitted blind to the laboratory (see Table 3 for sample IDs). The results are used to evaluate the combined reproducibility of both the laboratory analyses and field sampling;
- Decontamination Blanks: After the sampling equipment was cleaned, DI water was poured over or pumped through the sampling equipment and collected for laboratory analysis. Analyses of these samples were used to evaluate the adequacy of the sampling equipment cleaning or decontamination procedure;
- Standard Reference Material (SRM): Two certified water SRMs were sent blind to the laboratory (Sample IDs AVSR01.1 and AVSR02.1) to evaluate laboratory accuracy. The certified SRM was supplied by Phenova Certified Reference Materials and was Lot #8128-04 (Metals). The Certificate of Analysis is provided in Appendix G of the Data Report. The use of a blind or unknown SRM is the only method to independently verify the laboratory accuracy; and
- Water Blank: To ensure that the DI water used for equipment decontamination is analyte free, one water blank sample was collected of the DI water during the sampling event.

3.2 Results of Field QA/QC Samples

3.2.1 Duplicates

Three duplicate samples (one groundwater sample and two surface water samples) were generated in the field and sent to ALcontrol for analysis. Table 4 provides the results of the 21 metals for the three duplicate samples and the calculated RPD between each pair of samples.

The majority of RPD values are below 50 %. The RPDs for the key parameters aluminium (1 to 2 %), copper (0 to 3 %), manganese (0 to 5 %) and zinc (0 to 4 %) are excellent as they are below 5 %. The RPDs that are above 50 % are selenium for all sample pairs with the RPD values of ranging from 55 to 112 %, antimony and arsenic for one sample pair MWPF1/AVGD01.1, molybdenum for samples pairs MWPF1/AVGD01.1 and Sulphur Brook/AVSD02.1 and tin for the Sulphur Brook/AVSD02.1 sample pair.

Low concentrations near the detection limits typically have higher variability and in all of these examples, the reported values were less than 5 times the detection limit. Considering this, the elevated RPD identified are not considered to significantly impact the integrity of the results or preclude their use for evaluation. The highest reported value of the duplicate pair is selected for interpretive use.

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

Sample Description Dissolved Metal	LOD (µg/l)	MWPF1 (µg/l)	AVGD01.1 (µg/l)	% RPD	WHITES-BRIDGE (µg/l)	AVSD01.1 (µg/l)	% RPD	SULPHUR BROOK (µg/l)	AVSD02.1 (µg/l)	% RPD
Aluminium	<2.9	374	378	-1.06	242	233	3.79	22.5	22.9	-1.76
Antimony	<0.16	0.389	0.691	-55.9	<0.16	<0.16	-	0.276	0.257	7.13
Arsenic	<0.12	0.444	0.255	54.1	0.375	0.502	-30.0	0.444	0.643	-36.61
Barium	<0.03	9.26	9.1	1.7	3.82	3.93	-2.84	7.53	7.66	-1.71
Cadmium	<0.1	0.623	0.674	-7.9	0.537	0.58	-7.70	0.439	0.432	1.61
Chromium	<0.22	0.602	0.6	0.3	<0.22	0.283	-25.1	0.283	<0.22	25.1
Cobalt	<0.06	1.5	1.44	4.08	0.865	0.952	-9.58	0.254	0.26	-2.33
Copper	<0.85	52.5	50.8	3.29	19.5	19.5	0	26.3	26.5	-0.76
Iron	<19	<19	<19	-	115	111	3.54	24.1	<19	23.7
Lead	<0.02	0.399	0.379	5.14	1.35	1.35	0	4.32	4.27	1.16
Manganese	<0.04	74.6	74.5	0.13	44.6	45.4	-1.78	27.7	29	-4.59
Mercury	<0.01	<0.01	<0.01	-	<0.01	<0.01	-	<0.01	<0.01	-
Molybdenum	<0.24	0.446	0.266	50.6	<0.24	<0.24	-	0.258	0.814	-103.7
Nickel	<0.15	1.95	1.5	26.1	0.871	0.893	-2.49	0.878	0.749	15.9
Selenium	<0.39	1.38	<0.39	112	0.685	<0.39	54.9	0.623	1.66	-90.9
Silver	<1.5	<15*	<15*	-	<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	-	<0.36	<0.36	-	1.57	<0.36	159
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	62.9	60.4	4.06	207	207	0	95.5	97.2	-1.76

Notes:

Bold indicates an exceedance in the Duplicate RPD acceptance criteria

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

3.2.2 Decontamination Blanks

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

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

Low level detections were observed for seven metals. Four of the metals (barium, lead, manganese and zinc) were also detected in the DI water blank but at slightly lower concentrations than the decontamination blanks. Detections of aluminium, copper and tin were also found in the decontamination blanks but not the DI water blank. In total there were ten low level detections of dissolved metals in the decontamination blanks. Only two of these were greater than ten times the detection limit, manganese in AVDB01.1 and lead in AVDB02.1. All of the detections including manganese and lead were significantly less than the assessment criteria outlined in Section 4; therefore, these low concentrations in the blanks do not affect interpretation of results.

To assess the level of cross-contamination between samples in the field, the concentrations in the decontamination blanks were compared with the concentration in the preceding environmental samples. The concentrations in the blanks were less than 10% of the concentration in the preceding environmental samples. One exception was the detection of tin in AVDB02.1 which was determined to be 38% of the preceding environmental sample.

The results from the laboratory instrumentation blank were obtained from ALcontrol to determine if any contamination occurred within the laboratory. Two detections were present in Sample Batch 130322-60 and none in 130316-35. There was a detection of 0.412 µg/l of tin and 0.052 µg/l lead which could account for the elevated concentrations in the water blank and one of the decontamination blanks (AVDB02.1) shown in Table 5.

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

Sample Description	LOD (µg/l)	Water Blank AVWB01.1 (µg/l)	Decon blank AVDB01.1 (µg/l)	Decon blank AVDB02.1 (µg/l)
Dissolved Metal	Sample batch:	130322-60	130316-35	130322-60
Aluminium	<2.9	<2.9	3.88	<2.9
Antimony	<0.16	<0.16	<0.16	<0.16
Arsenic	<0.12	<0.12	<0.12	<0.12
Barium	<0.03	0.045	0.112	0.17
Cadmium	<0.1	<0.1	<0.1	<0.1
Chromium	<0.22	<0.22	<0.22	<0.22
Cobalt	<0.06	<0.06	<0.06	<0.06
Copper	<0.85	<0.85	2.12	<0.85
Iron	<19	<19	<19	<19
Lead	<0.02	0.172	0.063	0.332
Manganese	<0.04	0.084	1.9	0.126
Mercury	<0.01	<0.01	<0.01	<0.01
Molybdenum	<0.24	<0.24	<0.24	<0.24
Nickel	<0.15	<0.15	<0.15	<0.15
Selenium	<0.39	<0.39	<0.39	<0.39
Silver	<1.5	<1.5	<15	<1.5
Thallium	<0.96	<0.96	<0.96	<0.96
Tin	<0.36	<0.36	<0.36	0.599
Uranium	<1.5	<1.5	<1.5	<1.5
Vanadium	<0.24	<0.24	<0.24	<0.24
Zinc	<0.41	0.568	3.2	0.941

Notes:

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

3.2.3 Standard Reference Materials

As previously discussed, two certified water SRMs were sent blind to the laboratory (Sample IDs AVSR01.1 and AVSR02.1) 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 aluminium, antimony, arsenic, barium, cadmium, chromium, cobalt, copper, iron, manganese, molybdenum, nickel, selenium, thallium, vanadium and zinc are in excellent agreement with the certified value (%R ranged from 90 to 107 %). The reported values for silver are within 20% of the certified value and are acceptable. One of the reported values for lead (ID AVSR02.1) is low at 84 % and just falls out of the acceptable range; however, the second reported value is within the acceptable range and therefore it is considered that the reported values for lead overall are usable.

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

Sample Description Dissolved Metal	Certified Value (µg/l)	Acceptance Limits (%)	AVSR01.1 (µg/l)	% R	AVSR02.1 (µg/l)	% R
Aluminium	2640	82.6 -116	2510	95	2510	95
Antimony	605	70.2 -120	560	93	647	107
Arsenic	672	84.1 -117	655	97	678	101
Barium	1710	86.5 -113	1660	97	1640	96
Cadmium	423	85.1 -113	400	95	382	90
Chromium	765	87.2 -113	717	94	746	98
Cobalt	346	87.6 -112	316	91	319	92
Copper	637	90.0 -110	614	96	615	97
Iron	1560	88.5 -113	1490	96	1410	90
Lead	245	85.3 -114	213	87	205	84
Manganese	805	89.8 -111	770	96	764	95
Molybdenum	337	84.3 -115	321	95	312	93
Nickel	644	89.9 -112	581	90	606	94
Selenium	1820	79.7 -116	1650	91	1760	97
Silver	399	86.0 -115	347	87	358	90
Thallium	466	79.8 -121	427	92	426	91
Vanadium	1480	87.8 -112	1380	93	1380	93
Zinc	1980	86.4 -115	1830	92	1860	94

Notes:

Bold indicates an exceedance in acceptance limits

3.3 Laboratory QA/QC Samples

3.3.1 ALcontrol

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

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

- Replicate samples (samples tested more than once using the same method) were included at the same frequency as the AQC's.

All of the ALcontrol laboratory reports were reviewed to ensure that reported values were ISO17025 certified (where relevant) and for any sample deviations. The sample holding times were occasionally exceeded for dissolved oxygen and total dissolved solids. Sample holding times were exceeded in the laboratory for free cyanide which is seven days with preservative. The holding times were exceeded by one to seven days. Small exceedances are typically considered acceptable from a technical perspective given the preservation and conservative nature of holding times. Note that all the reported values for free cyanide were below the detection limit of 0.05 mg/l. We will work with the laboratory to prevent the free cyanide holding times being exceeded in the future.

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, conductivity and Dissolved Oxygen (DO) and provides the calculated %RPD values. Note that DO and 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).

DO measurements for the groundwater and adits were generally lower in the field than the readings in the laboratory and field results are considered more representative of actual dissolved oxygen conditions. In some instances the pH reading in the field were lower than the laboratory, all had a RPD of less than 50 % except for Cronbane Pit Lake which had an RPD of 51.6%. These differences can be attributed to the use of the field pH backup probe which was utilised when the main pH probe on the multi-parameter field probe was damaged in the field (as highlighted in Table 7). The backup field pH probe had difficulties stabilising readings on occasion and is therefore considered (as highlighted in Table 7) less reliable than the main field probe or the laboratory results, therefore on this occasion the laboratory pH values were selected for interpretive use. One exception was the laboratory result for the Road Adit with a pH of 5.02 which is considered too high and the field reading of 3.7 is likely more accurate. Overall the RPDs between the field and lab data are considered satisfactory.

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

Sample Description	pH Lab	pH Field	% RPD	Cond. Lab	Sp. Cond. Field	% RPD	DO Lab	DO Field	% RPD
	pH Units			(mS/cm)			(mg/l O ₂)		
AVOCA BRIDGE	6.97	6.63*	5.00	0.0743	0.079	-6.13	10.2	12.13	-17.29
BALLINACLEISH BRIDGE	7	6.92*	1.15	0.0566	0.061	-7.48	10.5	13.49	-24.93
DS SHELTON ABBEY	7.3	6.61*	9.92	0.0892	0.099	-10.4	11.1	12.2	-9.44
LIONS BRIDGE	7.09	7.29*	-2.78	0.0696	0.071	-1.99	10.5	14.07	-29.06
SITE T1	7.09	7.14*	-0.70	0.0693	0.071	-2.42	10.2	13.59	-28.50
SITE T5	7.08	6.43*	9.62	0.083	0.088	-5.85	9.87	12.32	-22.08
SULPHUR BROOK	7.46	7.34*	1.62	0.15	0.163	-8.31	10.3	12.04	-15.58
US SHELTON ABBEY	7.18	7.02*	2.25	0.0938	0.096	-2.32	11	12.95	-16.28
VALE VIEW	7.08	7	1.14	0.148	0.16	-7.79	12.2	13	-6.35
WHITES BRIDGE GS	7.55	6.34*	17.42	0.0726	0.077	-5.88	10.2	11.95	-15.80
WICKLOW MAIN YARD	6.99	5.51*	23.68	0.0748	0.081	-7.96	9.93	12.37	-21.88
MWDA1	2.68	2.61	2.65	4.04	4.931	-19.9	5.13	0.55	161
MWDA2	3.8	3.91	-2.85	1.48	1.614	-8.66	4.17	0.32	172
MWET1	3.39	3.46	-2.04	2.53	2.8	-10.1	5.55	0.2	186
MWET2	6.08	6.2	-1.95	3.01	3.446	-13.5	4.74	0.15	188
MWPF1	5.28	4.71**	11.41	0.161	0.158	1.88	10.6	9.63	9.59
MWSA2	4.01	4.04*	-0.75	2.17	2.505	-14.3	4.06	0.17	184
SG104	2.97	2.36*	22.89	8.38	8.99	-7.02	8.63	5.66	41.57
GW1/05	3.76	3.41*	9.76	1.72	1.912	-10.6	5.15	1.53	108
GW2/05	3.8	3.36*	12.29	1.22	1.349	-10.0	8.44	6.29	29.19
BALLYGAHAN ADIT	3.19	2.66**	18.12	2.43	2.81	-14.5	0.93	1.49	-46.28
CRANBANE INTER ADIT	3.02	2.87*	5.09	1.23	1.354	-9.60	0.69	0.42	48.65
CRONBANE PIT LAKE	5.05	2.98**	51.6	0.399	0.444	-10.7	9.76	11.28	-14.45
CRONBANE SHALLOW ADIT	2.89	2.44*	16.89	3.18	3.587	-12.0	8.65	4.16	70.1
DEEP ADIT	3.96	3.27*	19.09	1.45	1.581	-8.64	5.69	0.42	173
ROAD ADIT	5.02	3.7*	30.28	1.37	1.529	-11.0	7.25	3.23	76.7
SPA ADIT	2.84	2.36*	18.46	2.02	2.463	-19.8	11.2	9.43	17.2

Notes:

Bold indicates an exceedance in acceptance limits

* Backup pH probe utilised (Model Hanna HI 98129)

** Difficulties stabilising pH readings in the field

3.4.2 Internal Consistency Analysis

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

The charge balance was calculated as follows:

$$(\Sigma(\text{Cations} \times \text{charge}) - \Sigma(\text{Anions} \times \text{charge})) / (\Sigma(\text{Cations} \times \text{charge}) + \Sigma(\text{Anions} \times \text{charge})) \times 100\%$$

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

The mass balance was calculated using the following relationship:

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

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

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

The general acceptance criteria for internal consistency is $\pm 10\%$ for both the charge balance and the mass balance. The mass balance, in the majority of cases (bolded values) did not meet these criteria. Most values were less than 20 to 30 %; which overall is very good considering the low pH, high TDS and complex nature of the high metal concentrations of many of the samples. The fact that the values are all negative suggests that either one or more parameters were under-reported by the analytical laboratory and/or one or more parameters present within the samples were not analysed (e.g. silica). The charge balance was consistently positive, which suggests that anions were missing from the analysis and/or were under-reported. Again most values were less than 20 to 30 %; which overall is very good considering the low pH and complex nature of the high metal concentrations of many of the samples. Note that Site T5 had the highest imbalances (both charge and mass) which is believed to be due to the reported alkalinity result of 326 mg/l which is an outlier in the data probably due to laboratory error. Note: the laboratory checked the value and found no transcription error; no sample was available for reanalysis.

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
AVOCA BRIDGE	39.3	59.8	-0.16	-12.9	-34.3	Missing cations
BALLINACLEISH BRIDGE	29.4	22	-0.15	-16.4	33.5	Too many anions
BALLYGAHAN ADIT	2181.5	2790	-15.70	-26.2	-21.8	Missing cations
CRONBANE INTER ADIT	876.8	1010	-11.04	-52.8	-13.2	Missing cations
CRONBANE PIT LAKE	155.0	194	-0.98	-22.1	-20.1	Missing cations
CRONBANE SHALLOW ADIT	3953.0	5100	-13.83	-11.4	-22.5	Missing cations
DEEP ADIT	1405.8	1780	-6.98	-17.1	-21.0	Missing cations
DS SHELTON ABBEY	49.5	52	-0.26	-17.8	-4.88	Missing cations
GW1/05	1656.4	2040	-8.34	-17.6	-18.8	Missing cations
GW2/05	1041.0	1270	-4.75	-15.8	-18.0	Missing cations
LIONS BRIDGE	33.0	49	-0.08	-7.10	-32.7	Missing cations
MWDA1	4428.0	6100	-25.20	-19.3	-27.4	Missing cations
MWDA2	1313.3	1810	-6.26	-16.3	-27.4	Missing cations
MWET1	2727.2	3550	-7.48	-8.87	-23.2	Missing cations
MWET2	2926.7	3750	-15.69	-19.7	-22.0	Missing cations
MWPF1	87.6	62.2	-0.17	-6.82	40.9	Too many anions
MWSA2	2191.4	2780	-9.89	-15.8	-21.2	Missing cations
ROAD ADIT	1128.0	1370	-6.27	-20.5	-17.7	Missing cations
SG104	12450.2	16000	-86.86	-23.9	-22.2	Missing cations
SITE T1	34.0	54.8	-0.11	-9.86	-37.9	Missing cations
SITE T5	233.3	53	-6.59	-86.2	340	Too many anions
SPA ADIT	2006.6	2630	1.05	1.54	-23.7	Missing anions
SULPHUR BROOK	93.2	94	-0.42	-15.2	-0.82	Missing cations
US SHELTON ABBEY	47.8	60	-0.31	-21.9	-20.4	Missing cations
VALE VIEW	81.6	102	-0.45	-18.3	-20.0	Missing cations
WHITES BRIDGE GS	40.5	52	-0.29	-23.4	-22.1	Missing cations
WICKLOW MAIN YARD	40.8	49	-0.28	-22.3	-16.7	Missing cations

Notes:

Bold indicates an exceedance of the acceptance criteria

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

Figure 1 shows the relationship between specific conductivity and TDS. There is a strong positive correlation between SC with both the calculated ($R^2=0.96$) and measured ($R^2=0.97$) TDS. Site T5 which had the highest mass imbalances plots at the lower end of the graph near zero and does not affect the correlation.

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

Sample Description	Sample Type	Conductivity	TDS (Calc)	TDS (Meas)	Ratio	
		(uS/cm)	(mg/l)	(mg/l)	SC/ TDS- Calc	SC/ TDS - Meas
AVOCA BRIDGE	SW	74.3	39.3	59.8	1.9	1.2
BALLINACLEISH BRIDGE	SW	56.6	29.4	22	1.9	2.6
BALLYGAHAN ADIT	Adit	2430	2180	2790	1.1	0.9
CRANBANE INTER ADIT	Adit	1230	877	1010	1.4	1.2
CRONBANE PIT LAKE	Pit Lake	399	155	194	2.6	2.1
CRONBANE SHALLOW ADIT	Adit	3180	3950	5100	0.8	0.6
DEEP ADIT	Adit	1450	1410	1780	1.0	0.8
DS SHELTON ABBEY	SW	89.2	49.5	52	1.8	1.7
GW1/05	GW	1720	1660	2040	1.0	0.8
GW2/05	GW	1220	1040	1270	1.2	1.0
LIONS BRIDGE	SW	69.6	33.0	49	2.1	1.4
MWDA1	GW	4040	4430	6100	0.9	0.7
MWDA2	GW	1480	1310	1810	1.1	0.8
MWET1	GW	2530	2730	3550	0.9	0.7
MWET2	GW	3010	2930	3750	1.0	0.8
MWPF1	GW	161	87.6	62.2	1.8	2.6
MWSA2	GW	2170	2190	2780	1.0	0.8
ROAD ADIT	Adit	1370	1130	1370	1.2	1.0
SG104	GW	8380	12500	16000	0.7	0.5
SITE T1	SW	69.3	34.0	54.8	2.0	1.3
SITE T5	SW	83.0	233	53	0.4	1.6
SPA ADIT	Adit	2020	2010	2630	1.0	0.8
SULPHUR BROOK	SW	150	93.2	94	1.6	1.6
US SHELTON ABBEY	SW	93.8	47.8	60	2.0	1.6
VALE VIEW	SW	148	81.6	102	1.8	1.5
WHITES BRIDGE GS	SW	72.6	40.5	52	1.8	1.4
WICKLOW MAIN YARD	SW	74.8	40.8	49	1.8	1.5

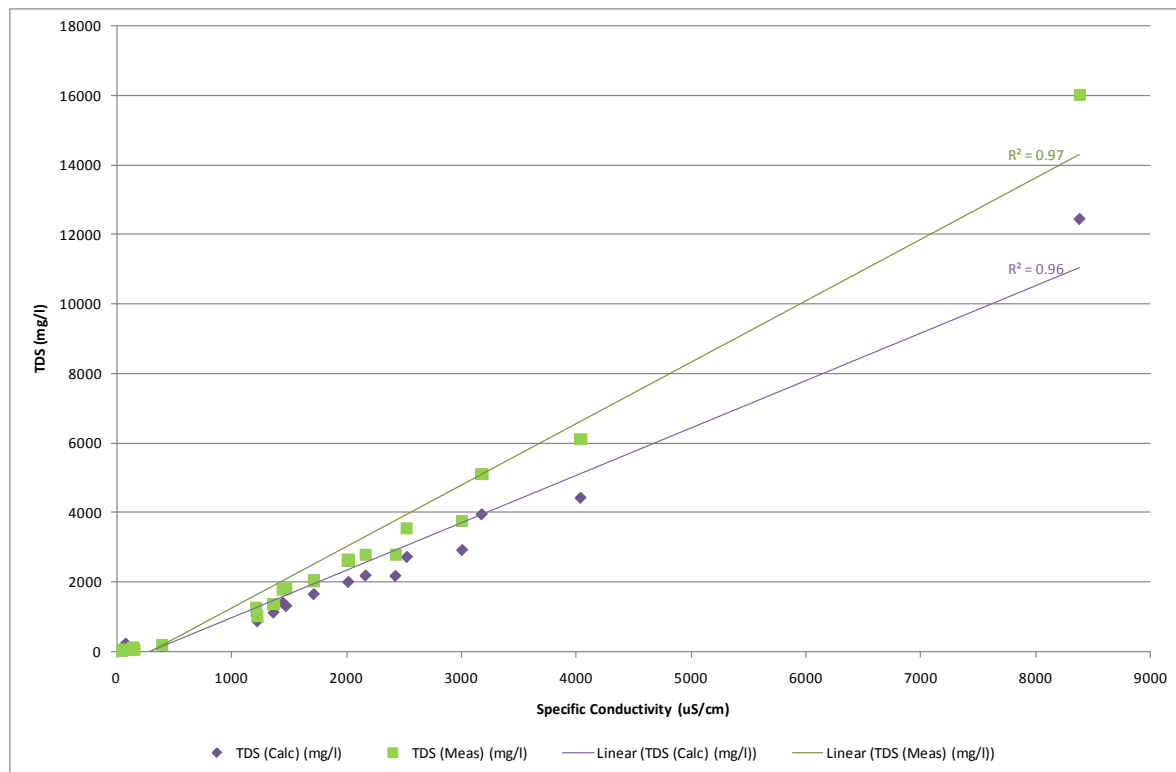


Figure 1 Relationship of Specific Conductivity and Total Dissolved Solids (TDS)

3.4.3 Comparison of Total and Dissolved Metals

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

Normally the dissolved metal concentrations would be less than the total metals because they are a portion of the total concentration. This was checked for the key metals aluminium, copper, cadmium, lead and zinc, by calculating the RPD between the total and dissolved metals to evaluate if the concentrations were indistinguishable. Table B-1 in **Appendix B** shows the full tabulation of results.

The total metals were greater than or equal to the dissolved metals with the exception of five results in groundwater where the RPD was greater than 50%. The comparison of the total vs. dissolved concentrations in the groundwater and adit samples indicates that many of the parameters are approximately the same for the total and dissolved analyses. For the Avoca River and tributaries, the total concentrations are generally significantly higher than the dissolved concentrations particularly for aluminium and cadmium whereas the results for total and dissolved zinc are more similar. Total suspended solids in the surface waters were above detection limits with only three detections with concentrations ranging from 2 to 6.5 mg/l. The suspended solid result of 6.5 mg/l was at Vale View which also had some of the highest differences in total versus dissolved metals with RPDs generally between 180 to 190 %.

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 average, minimum, maximum 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	378	996000	206000	319000
Antimony	<0.16	9	5	0.08	63.8	8.74	20.8
Arsenic	<0.12	9	4	0.06	27.6	4.26	9.08
Barium	<0.03	9	9	0.97	67.8	14.2	20.61
Cadmium	<0.1	9	9	0.67	553	92.6	178
Chromium	<0.22	9	8	0.60	90.2	15.7	28.8
Cobalt	<0.06	9	9	1.50	1030	248	303
Copper	<0.85	9	9	20.7	94700	18300	31100
Iron	<19	9	8	9.50	163000	58400	55700
Lead	<0.02	9	9	0.40	436	56.0	143
Manganese	<0.04	9	8	74.6	45600	15400	15700
Mercury	<0.01	9	6	0.01	1.21	0.19	0.39
Molybdenum	<0.24	9	3	0.45	44	6.11	14.2
Nickel	<0.15	9	9	1.95	384	109	116
Selenium	<0.39	9	6	0.20	21.5	5.35	6.79
Silver	<1.5	9	0	0.75	75.0**	-	-
Thallium	<0.96	1*	0	4.80	4.8	-	-
Tin	<0.36	9	2	1.80	88.4	11.8	28.7
Uranium	<1.5	9	3	0.75	77.7	14.2	24.9
Vanadium	<0.24	9	0	0.12	1.20**	-	-
Zinc	<0.41	9	9	62.9	151000	32500	48400

Notes:

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

* There is only one result for dissolved thallium (TI) because the laboratory incorrectly analysed dissolved titanium (Ti) instead. This error will be corrected for the next round of sampling and analysis.

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

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 concentration of metals. SG104 is located immediately downgradient of Ballymurtagh Landfill had the highest concentrations of metals especially aluminium, barium, cadmium and zinc, and included detections of tin and uranium. Arsenic was only detected in 4 wells with highest concentration at MWSA2 of 27.6 µg/l.

4.1.2 Surface Water Sample Results

Surface water samples were collected for two major categories: the first includes mine adit discharges and the pit lake and the second includes the Avoca River and tributaries. Table 11 provides a summary of the reported results of the 6 adit discharge samples and the one pit lake sample and Table 12 provides a summary of the reported results of the 11 river and stream samples. Included in the tables are the average, minimum, maximum and standard deviation (SDEV). Where the reported values were below the detection limit the values were substituted with a value of half the limit of detection. The highest reported value of the field duplicate pair was used where applicable.

Adit Discharges and Pit Lake

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

Dissolved Metal	LOD (µg/l)	Number	Number of Detections	Minimum (µg/l)	Maximum (µg/l)	Mean (µg/l)	SDEV
Aluminium	<2.9	7	7	7610	377000	122000	143000
Antimony	<0.16	7	3	0.80	1.93	1.27	0.58
Arsenic	<0.12	7	7	1.04	82.3	18.9	30.9
Barium	<0.03	7	7	3.92	16.6	8.44	4.21
Cadmium	<0.1	7	7	8.11	277	80.0	93.6
Chromium	<0.22	7	4	0.10	9.69	2.76	3.97
Cobalt	<0.06	7	7	13.7	262.00	126	81.7
Copper	<0.85	7	7	366	12700	4840	4510
Iron	<19	7	7	3190	183000	86400	52500
Lead	<0.02	7	7	62.5	1770	688	663
Manganese	<0.04	7	7	301	14500	6280	4640
Mercury	<0.02	7	5	0.01	0.20	0.06	0.07
Molybdenum	<0.24	7	1	0.12	1.20*	0.71	0.56
Nickel	<0.15	7	7	5.40	138.00	56.8	41.7
Selenium	<0.39	7	5	0.20	5.85	2.89	2.35
Silver	<1.5	7	0	7.50*	7.50*	7.50	-
Thallium	<0.96	6	1	1.21	4.80	4.20	1.47
Tin	<0.36	7	2	0.18	62.20	10.3	23.0
Uranium	<1.5	7	3	6.32	28.9	10.55	8.12
Vanadium	<0.24	7	1	0.12	1.20*	0.80	-
Zinc	<0.41	7	7	2550	99500	28500	34900

Notes:

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

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

Aluminium, copper, iron, manganese and zinc were found in significantly high concentrations in the majority of the adit discharge and pit samples. The Cronebane Shallow Adit had the highest concentrations of metals including aluminium, copper and zinc. The lowest concentrations were found in the Cronbane Pit Lake, indicating that there is likely to be a significant rainwater input diluting the concentrations of metals.

Rivers and Streams

Table 12 Summary of Dissolved Metal Concentrations in Surface Water

Dissolved Metal	LOD (µg/l)	Number	Number of Detections	Minimum (µg/l)	Maximum (µg/l)	Mean (µg/l)	SDEV
Aluminium	<2.9	11	11	11.7	242	108	75.5
Antimony	<0.16	11	2	0.08	0.28	0.11	0.08
Arsenic	<0.12	11	11	0.22	0.64	0.37	0.12
Barium	<0.03	11	11	3.93	7.66	5.16	1.36
Cadmium	<0.1	11	8	0.05	0.58	0.29	0.20
Chromium	<0.22	11	2	0.11	0.45	0.16	0.11
Cobalt	<0.06	11	11	0.09	1.17	0.48	0.36
Copper	<0.85	11	9	0.43	26.50	9.28	8.73
Iron	<19	11	11	2.80	339	99.6	91.0
Lead	<0.02	11	11	0.09	4.32	2.21	1.10
Manganese	<0.04	11	11	14.6	66.2	34.11	15.32
Mercury	<0.01	11	0	0.01	0.01	-	-
Molybdenum	<0.24	11	2	0.12	0.81	0.21	0.22
Nickel	<0.15	11	11	0.42	1.28	0.79	0.26
Selenium	<0.39	11	2	0.20	1.66	0.37	0.45
Silver	<1.5	11	0	0.75	7.50*	-	-
Thallium	<0.96	7	0	0.48	0.48	-	-
Tin	<0.36	11	2	0.18	1.57	0.37	0.45
Uranium	<1.5	11	0	0.75	0.75	-	-
Vanadium	<0.24	11	0	0.12	0.12	-	-
Zinc	<0.41	11	11	8.56	207	96.2	70.7

Notes:

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

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

Some metals were detected upgradient of the mining area at Ballinacleish Bridge and Lions Bridge with concentrations of aluminium at 56.7 and 58 µg/l, zinc at 20.1 and 27.6 µg/l and iron at 35.6 and 69.3 µg/l at the respective locations. The Vale View tributary discharges to the Avoca River upgradient of the mine site had the lowest concentrations of metals with aluminium at 11.7 µg/l and zinc 8.56 µg/l.

Whites Bridge GS is 90 metres downstream of the bridge and is the first sampling location along the Avoca River within the mining area where significant increases in metals concentrations are observed namely; aluminium (242 µg/l), copper (19.5 µg/l) and zinc (207 µg/l). This probably reflects infiltration from the Deep Adit discharge ditch and the input of groundwater through this area.

The concentrations of these metals are reduced at Avoca Bridge compared with the concentrations found at the Whites Bridge GS location (approximately by a quarter). Further

downstream at the Shelton Abbey location (which is 7 km downstream of Whites Bridge GS) the concentrations are reduced further to approximately half that found at Whites Bridge GS.

4.2 Assessment Criteria

4.2.1 Groundwater and Surface Water Assessment Criteria

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

For hardness-dependent metals, copper and zinc hardness-adjusted salmonid-specific preliminary remediation goals were developed with the intention to protect the survival, growth, and reproduction of salmonid fish as part of the previous study for the Department (CDM, 2008). The hardness-adjusted equations were based on studies in which salmonid fish were exposed to dissolved metal at varying hardness. From these studies, a relationship was established between hardness and toxicity. The average hardness was calculated to be approximately 31 mg/l CaCO_3 and preliminary remediation goals for dissolved copper was 11 µg/l and for dissolved zinc was 268 µg/l.

However the Surface Water Regulations 2009 provide more stringent standards for dissolved copper and zinc also based on hardness and are therefore utilised as the ecological assessment criteria (highlighted in bold in Table 13). Also note that the EU Freshwater Fish Directive (78/659/EEC) which specifies standards for salmonid and cyprinid waters are not utilised as they will be revoked under the Water Framework Directive (2000/60/EC) on 22 December 2013 and they have been largely replaced by standards in the Surface Water Regulations.

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.

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

Table 13 Surface Water and Groundwater Assessment Criteria for Biological Elements

Parameter	Unit	AA	MAC (or 95%ile)	Source	Description
Ammonia as N	mg/l	0.065	0.14	S.I. No. 272 of 2009	Good status
Ortho-phosphate as P	mg/l	0.035	0.075	S.I. No. 272 of 2009	Good status
pH	pH units		> 4.5 and < 9.0	S.I. No. 272 of 2009	Within range
Free Cyanide	mg/l	0.01	-	S.I. No. 272 of 2009	
Fluoride	mg/l	0.5	-	S.I. No. 272 of 2009	
Arsenic	µg/l	25	-	S.I. No. 272 of 2009	
Cadmium	µg/l	≤0.08 (Class 1) 0.08 (Class 2) 0.09 (Class 3) 0.15 (Class 4) 0.25 (Class 5)	≤ 0.45 (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)	S.I. No. 327 of 2012	Hardness measured in mg/l CaCO ₃ (Class 1: <40 mg CaCO ₃ /l, Class 2: 40 to <50 mg CaCO ₃ /l, Class 3: 50 to <100 mg CaCO ₃ /l, Class 4: 100 to <200 mg CaCO ₃ /l and Class5: ≥200 mg CaCO ₃ /l)
Chromium	µg/l	3.4	-	S.I. No. 272 of 2009	
Copper	µg/l	5 or 30	-	S.I. No. 272 of 2009	5 µg/l applies where the water hardness measured in mg/l CaCO ₃ is ≤ 100; the value 30 applies where the water hardness > 100 mg/l CaCO ₃ .
Lead	µg/l	7.2	-	S.I. No. 327 of 2012	
Mercury	µg/l	0.05	0.07	S.I. No. 327 of 2012	
Nickel	µg/l	20	-	S.I. No. 327 of 2012	
Zinc	µg/l	8 or 50 or 100	-	S.I. No. 272 of 2009	8 µg/l for water hardness with annual average values ≤ 10 mg/l CaCO ₃ , 50 µg/l for water hardness > 10 mg/l CaCO ₃ and ≤ 100 mg/l CaCO ₃ and 100 µg/l elsewhere
Supplementary standards:					
Aluminium	µg/l	-	1900	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Barium	µg/l	-	4	Oak Ridge National Laboratory	Invertebrates and Salmon fish
Cobalt	µg/l	-	5.1	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Manganese	µg/l	-	1,100	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids
Uranium	µg/l	-	2.6	Oak Ridge National Laboratory	Invertebrates only - Lowest Chronic Value for Daphnids

Notes:

Bold indicates the selected assessment criteria for ecological health

Table 14 Surface Water and Groundwater Assessment Criteria for Drinking Water

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

4.3 Comparison to Assessment Criteria

A comparison of the groundwater and surface water analytical results was made against the relevant assessment criteria for ecological and human health as described in Section 4.2. Table B-2 in **Appendix B** highlights the exceedances of the assessment criteria. Where there was an exceedance of the ecological assessment criteria, the result is highlighted in purple, for an exceedance of the human health criteria the result is highlight in blue. In some cases the reported values exceeded both the ecological and human health criteria and these results are highlighted in pink. The results and exceedances are discussed in this section.

4.3.1 Groundwater Assessment

The pH was found to be acidic in all groundwater samples with results within the range of 2.68 to 6.08 (laboratory) which exceeded the acceptable ranged for ecological (4.5 to 9 pH units) and human health (6.5 to 9.5 pH units) criteria. The electrical conductivity ranged from 0.161 to 8.380 mS/cm with the lowest conductivity located at MWPF1 and the highest at SG104. The conductivity only exceeded the human health criteria (2.5 mS/cm) at MWDA1, MWET1 and MWET2 and SG104.

Sulphate levels greatly exceeded the criteria for human health of 250 mg/l in all of the monitoring wells with values ranging from 811 to 10,800 mg/l. One exception was at MWPF1 where sulphate was below the human health assessment criteria with a value of 30.1 mg/l. Ammonia was detected in 6 of the monitoring wells and both the ecological (0.14 mg/l) and human health

(0.3 mg/l) criteria are exceeded in MWDA1, MWET1, MWET2, GW1/05, SG104 and MWSA2. Fluoride was also present in 7 of the monitoring wells sampled, with 5 of the values exceeding both the assessment criteria for ecological (0.5 mg/l) and human health (1.5 mg/l). MWDA2 (1.32 mg/l) only exceeded the criteria for ecological health and MWET1 was below both the assessment criteria.

The dissolved metal concentrations were elevated in the majority of the monitoring wells with numerous exceedances of ecological, human health criteria or both, particularly for aluminium, cadmium, copper, iron, manganese, nickel and zinc (Table B-2 in **Appendix B** includes the full listing). Wells MWSA2 and SG104 also had detections of total arsenic with values of 30.8 and 18 µg/l respectively. There were four detections of dissolved arsenic, only MWSA2 with a result of 27.6 µg/l exceeded both the ecological (25 µg/l) and human health (10 µg/l) criteria.

The dissolved aluminium and copper concentrations at MWET2 (deep) (613 and 20.7 µg/l) were significantly lower than at MWET1 (shallow) which had concentrations of 225,000 and 8,260 µg/l, respectively. This could be explained by the apparent confined nature of MWET2 (heads in MWET2 are higher than in MWET1) and also because MWET1 is screened directly beneath the Emergency Tailings deposits.

The bedrock monitoring well GW1/05 showed higher metal concentrations than its nested, shallow alluvial well GW2/05. Levels of dissolved lead and mercury in GW1/05 exceeded the ecological assessment criteria of 7.2 and 0.07 µg/l, respectively, with values of 436 and 0.08 µg/l. SG104 has the highest levels of dissolved copper, mercury, nickel, uranium and zinc compared with all of the other monitoring wells.

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, copper and zinc which were at concentrations of 364,000; 39,100 and 60,700 µg/l in MWDA1 and were at concentrations of 85,200; 7,050 and 34,800 µg/l in MWDA2, respectively. Levels of dissolved lead and mercury in MWDA1 exceeded the ecological assessment criteria of 7.2 and 0.07 µg/l, respectively, with values of 8.81 and 0.294 µg/l.

The well located upgradient of the Deep Adit area and at the eastern margin of the alluvial aquifer, MWPF1, had significantly lower metal concentrations than the other wells. However the ecological assessment criteria (but not the human health criteria) were exceeded for dissolved barium (4 µg/l), cadmium (0.45 µg/l), copper (5 µg/l) and zinc (50 µg/l).

4.3.2 Surface Water Assessment

Adit Discharges and Pit Lake

The pH was found to be acidic in all adit discharges and the pit lake with results within the range of 2.84 to 5.05 (laboratory) 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 ranged from 67.5 mg/l in the Cronbane Pit Lake to 1,890 mg/l in the Cronbane Shallow Adit. The electrical conductivity ranged from 0.399 to 3.180 mS/cm and only exceeded the human health criteria at the Cronebane Shallow Adit.

Elevated sulphate, ammonia and fluoride were found at all of the adit discharge locations. Sulphate levels greatly exceeded the criteria for human health of 250 mg/l in all of the adit discharges with values ranging from 748 to 3,230 mg/l. Ammonia was detected in all of the adit discharges and both the ecological (0.14 mg/l) and human health (0.3 mg/l) criteria were exceeded

in at all locations, with the highest concentration at Road Adit (7.32 mg/l). Fluoride was also present at all of the adit discharges that were sampled, with 4 of the values exceeding both the assessment criteria for ecological (0.5 mg/l) and human health (1.5 mg/l). The Deep Adit (1.41 mg/l) only exceeded the criteria for ecological health and Spa Adit was below both the assessment criteria. Concentrations of sulphate (113 mg/l), ammonia (0.248 mg/l) and fluoride (0.674 mg/l) were generally lower at Cronbane Pit Lake than the adit discharges.

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

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

Rivers and Streams

The pH was found to be near neutral in all the rivers and streams within the range of 6.97 to 7.46 (laboratory), which were well within acceptable ranges for ecological (4.5 to 9 pH units) and human health (6.5 to 9.5 pH units) criteria and acidity was below the limit of detection. The electrical conductivity was well within the criteria for human health of 2.5 ms/cm and ranged from 0.057 to 0.150 mS/cm.

Nutrients within the river and stream samples collected were generally below the ecological assessment criteria for ortho-phosphate (0.075 mg/l) and ammonia (0.14 mg/l). One exception was Sulphur Brook which exceeded the criteria for ammonia with a value of 0.213 mg/l and also had elevated chloride (14.9 mg/l) and nitrate (21.8 mg/l) results; indicating some local source of contamination such as onsite wastewater treatment system. Elevated chloride (12.7 mg/l) and nitrate (16.4 mg/l) results were also found in the Vale View tributary. The elevated chloride and nitrate results were still below the assessment criteria for human health which are 250 and 50 mg/l, respectively.

The dissolved metal concentrations were low in comparison to the groundwater and the adit discharges; however several exceedances of both ecological and human health criteria occurred. Dissolved copper exceeded the ecological criteria (5 µg/l) at all river and stream locations from Whites Bridge GS and to the Downstream Shelton Abbey location, with results ranging from 6.46 to 26.5 µg/l. Similarly dissolved zinc exceeded the ecological assessment criteria (50 µg/l) from Whites Bridge GS to Downstream Shelton Abbey with results ranging from 99.6 (twice the ecological assessment criteria) to 207 µg/l. Aluminium exceeded human health criteria (200 µg/l) at Whites Bridge GS with a value of 242 µg/l. Cadmium exceeded ecological assessment criteria (0.45 µg/l) at Whites Bridge GS with 0.58 µg/l and Site T5 with 0.496 µg/l.

Section 5

Flows, Loads and Trend Analysis

5.1 Surface Water Flows

Two EPA stream flow gauges exist on the Avoca River near the mine site: Whites Bridge GS (EPA station 10044) and the Wicklow County Council Maintenance Yard (EPA Station 10045). The Whites Bridge GS is located 90 m downstream of the bridge and just upstream of the former location of the Deep Adit confluence which was recently diverted to discharge into the marsh east of the spoil area. The Wicklow County Council Maintenance Yard Gauge is downstream of the Deep Adit but just upstream of the Road Adit confluence.

The flow record of Station 10044 for the period from December 2009 to April 2013 is reproduced in Figure 2 and flow record of Station 10045 from September 2010 to April 2013 is shown in Figure 3. The figures show the measured flows ranging from $>40 \text{ m}^3/\text{s}$ following major rainfall events to approximately $1\text{--}2 \text{ m}^3/\text{s}$ during low-flow, with a median flow of about $10 \text{ m}^3/\text{s}$. The flashy nature of the rivers within the Avoca catchment reflects a rapid response to rainfall.

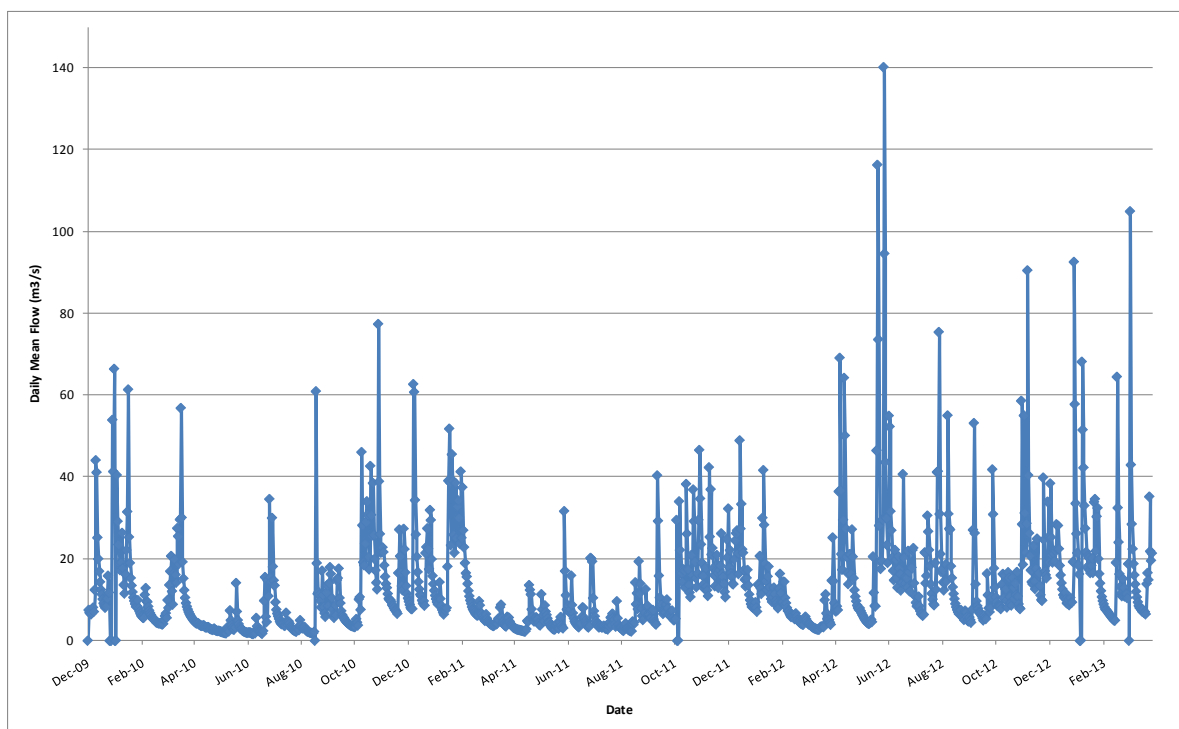


Figure 2 Mean Daily Flow (m^3/s) at Whites Bridge (Station 10044) from Dec 09 to Apr 13

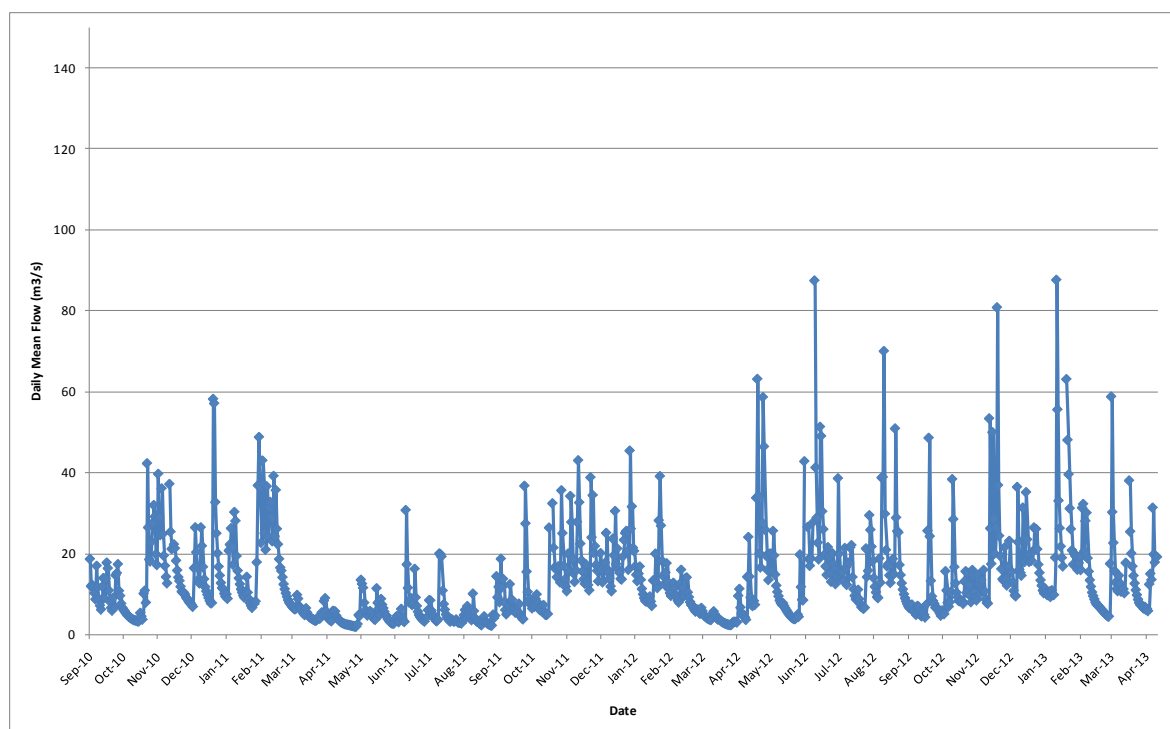


Figure 3 Mean Daily Flow (m^3/s) at Wicklow County Council Maintenance Yard (Station 10045) from Sep 10 to Apr 13

Flow was measured directly in the field using different methodologies depending upon the quantity of flow to be measured and any safety concerns, as described in Section 2.1.2 Surface Water Sampling. Table 15 presents a summary of the results from the flow measured taken in March 2013 at the time of sampling. Refer to Appendix B of the Data Report for details of methodologies used per site and associated calculations.

Table 15 Surface Water Flow Value Measured in March/ April 2013

Site Name	Flow m^3/s	Flow l/s	Date
Ballinacleish Bridge	2.03	2030	19/03/2013
Lions Bridge	9.07	9070	19/03/2013
Vale View	0.04	36	12/03/2013
Site T1	11.7	11700	20/03/2013
Whites Bridge Gauging Station	10.4	10422	20/03/2013
Wicklow Co Co. Maintenance Yard Gauging Station	10.4	10400	20/03/2013
Site T5	-	-	20/03/2013
Avoca Bridge	11.97	12000	20/03/2013
Upstream of Shelton Abbey	16.3	16300	14/03/2013
Downstream of Shelton Abbey	16.3	16300	14/03/2013
Sulphur Brook	0.17	169	21/03/2013
Deep Adit	0.029	29	15/03/2013
Road Adit	0.029	28.9	25/04/2013
Cronebane Intermediate Adit	0.007	7.2	19/03/2013
Cronebane Shallow Adit	0.0003	0.3	15/03/2012
Ballygahan Adit	0.00015	0.15	15/03/2012
Spa Adit	0.00005	0.05	14/03/2013

Notes:

- means there is presently no flow value. The depth profile could not be measured during high flow. The velocity was estimate and height of the water measured on 20/03/2013. The flow for this period will be calculated after the depth profile is determined this fall.

Note that the flow was calculated at Site T1 by adding the measured flow from Ballinacleish Bridge (Flow Meter) and Lions Bridge (Float Method) and is likely overestimated for that date because the measured flow at both EPA gauging stations was 10.4 m³/s. The measured flows at the Deep Adit and Road Adit of 29 l/s are relatively high flows. Past records for the Deep Adit ranged from approximately 10 to 72 l/s and the Road Adit from 6 to 58 l/s (CDM, 2008).

5.2 Loading Analysis

5.2.1 Loading Analysis Methodology

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

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

where, C = the concentration of the parameter in the water
F = the flow rate of the input

5.2.2 Loading Results and Discussion

The calculated mass loads in Table 16 aid with the interpretation of the loading of sulphate and dissolved aluminium, copper, iron, lead and zinc to the Avoca River. Background loads upstream of the Avoca Mining Area of sulphate and these metals were present based on the calculated loads at Ballinacleish Bridge, Lions Bridge and Site T1. Sulphate loads at Site T1 were calculated to be 2,841 kg/day and the dissolved metal loads were aluminium 53.7 kg/day, copper 0.4 kg/day, iron 52.7 kg/day, lead 2.1 kg/day and zinc 19.6 kg/day.

A significant increase in loads exists at Whites Bridge GS (90 metres downstream of the bridge and is the first sampling location along the Avoca River within the mining area) with loads of dissolved aluminium at 217 kg/day, copper 17.6 kg/day, and zinc 186 kg/day. This probably reflects infiltration from the Deep Adit discharge ditch and the input of groundwater through this area. There was a decrease in lead loads to 1.2 kg/day from the upstream location at Site T1.

Two tributaries to the Avoca River were sampled: Vale View and Sulphur Brook. Vale View had insignificant loads whereas Sulphur Brook displayed small loads of dissolved metals such as 0.3 kg/day of aluminium and 1.4 kg/day of zinc.

The Deep Adit and the Road Adit have similar loads of sulphate (2849 and 2092 kg/day), copper (1.9 and 0.9 kg/day) and iron (223 and 190 kg/day). However, the Deep Adit has much higher loadings of aluminium and zinc with loads of 249 and 119 kg/day at the Deep Adit and 37.2 and 22.8 kg/day at the Road Adit. These calculated loads may be an over estimation of the loads discharging to the Avoca River because during a previous study for the Department by CDM (2008) there was a large difference in the concentrations between the actual adit discharge and the confluence due to precipitation of iron-aluminium oxyhydroxides with coprecipitation of metals such as copper resulting in significant attenuation occurring within the ditches before discharging into the Avoca River. For the Deep Adit, zinc was the only metal that appeared to be relatively conservative, with only a 9.5% decrease in concentration at the confluence compared to the adit discharge (CDM, 2008).

However, the calculated loading of zinc is 186 kg/day at Whites Bridge GS which is likely comprised of diffuse loading from infiltration from the Deep Adit ditch and groundwater discharging through the area. Wicklow County Council Maintenance Yard GS is the next location downstream on the Avoca River with 120 kg/day of zinc. This location is downstream of the Deep Adit ditch and marsh area so the load would be expected to be 305 kg/day to account for the loading at Whites Bridge GS (186 kg/day) and the Deep Adit (119 kg/day), however it was calculated to be 120 kg/day which is in fact lower than the upstream location. This result also indicates there is precipitation of zinc in the deep adit ditch, attenuation in the aquifer material or that some of the loads are deposited as ferricrete cement on the bank of the river.

Similarly the estimated loads of dissolved iron in the both the Deep and Road adits are not an accurate representation of the loads to the Avoca River. The calculated load at Wicklow County Council Maintenance Yard GS is 328 kg/day (Whites Bridge 103.6 kg/day + Deep Adit 223 kg/day + Ballygahan Adit 1.1 kg/day) whereas the actual iron load at that location was estimated to be 89 kg/day. The loading of iron from the Road Adit was estimated to be 190 kg/day. When added to the Wicklow County Council Maintenance Yard GS of 89 kg/day, the total is 279 kg/day which is significantly higher than the estimation at the downstream location of Avoca Bridge (no flow available for Site T5) which had an estimate load of zinc of 158 kg/day. This further indicates the precipitation of iron-aluminium oxyhydroxides and loads being deposited as ferricrete cement.

The Cronebane Shallow, Ballygahan and Spa adits are of minor importance in terms of metals loads to the Avoca, either because of absence of surface flow to the river or due to low loads. Loads from these adits range from 1.1 to 9.8 kg/day for aluminium, 0 to 0.3 kg/day for copper and 0.1 to 2.6 kg/day for zinc.

A slight increase in the loads of metals is present Downstream of Shelton Abbey compared to the upstream location, for example dissolved aluminium increases from 144 to 159 kg/day.

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

Sample Description	Date Sampled	Flow l/s	pH Units	Sulphate		Aluminium		Copper		Iron		Lead		Zinc	
				µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day	µg/l	kg/day
Ballinacleish Bridge	19/03/2013	2030	7	2200	386.1	56.7	10.0	0.425	0.1	35.6	6.2	2.69	0.5	20.1	3.5
Lions Bridge	19/03/2013	9070	7.09	1000	783.8	58	45.5	0.986	0.8	69.3	54.3	3.05	2.4	27.6	21.6
Site T1	19/03/2013	11700	7.09	2800	2840.9	52.9	53.7	0.425	0.4	51.9	52.7	2.11	2.1	19.3	19.6
Vale View	11/03/2013	36.0	7.08	15400	47.9	11.7	0.0	1.21	0.0	2.8	0.0	0.089	0.0	8.56	0.0
White's Bridge GS	20/03/2013	10422	7.55	8200	7383.8	242	217.9	19.5	17.6	115	103.6	1.35	1.2	207	186.4
Deep Adit	15/03/2013	29.2	3.96	1130000	2848.9	98800	249.1	770	1.9	88500	223.1	1770	4.5	47300	119.3
Ballygahan Adit	15/03/2013	0.1	3.19	1750000	22.2	87900	1.1	7020	0.1	87300	1.1	147	0.0	24500	0.3
Wicklow Co Co. Main. Yard GS	20/03/2013	10400	6.99	8200	7368.2	198	177.9	13.6	12.2	99.2	89.1	2.38	2.1	133	119.5
Road Adit	15/03/2013	28.9	3.7	838000	2091.7	14900	37.2	366	0.9	76100	190.0	334	0.8	9140	22.8
Sulphur Brook	21/03/2013	169	7.46	14600	213.3	22.9	0.3	26.5	0.4	24.1	0.4	4.32	0.1	97.2	1.4
Avoca Bridge	20/03/2013	12000	6.97	9500	9826.9	162	167.6	10.8	11.2	153	158.3	2.52	2.6	154	159.3
Upstream of Shelton Abbey	14/03/2013	16300	7.18	9900	13950.9	102	143.7	6.87	9.7	96.2	135.6	1.51	2.1	99.6	140.4
Downstream of Shelton Abbey	14/03/2013	16300	7.3	10400	14655.5	113	159.2	6.46	9.1	109	153.6	1.46	2.1	102	143.7
Cronebane Intermediate Adit	19/03/2013	7.2	3.02	748000	464.8	7610	4.7	3020	1.9	75500	46.9	1210	0.8	4010	2.5
Cronebane Shallow Adit	15/03/2013	0.3	2.89	3230000	83.7	377000	9.8	12700	0.3	183000	4.7	1080	0.0	99500	2.6
Spa Adit	14/03/2013	0.1	2.84	1590000	7.0	259000	1.1	7820	0.0	91500	0.4	62.5	0.0	12400	0.1

5.3 Trend Analysis

This section discusses concentration time trends for select locations including the Deep Adit, the Road Adit and one location on the Avoca River for selected parameters including dissolved copper, zinc and iron. The trends are shown graphically in Figure 4 (Deep Adit from Dec 1993 to Mar 2013), Figure 5 (Road Adit from May 1993 to Mar 2013) and Figure 6 (Avoca River at Avoca Bridge from May 2001 to Mar 2013).

A general declining trend in metal concentrations for both the Deep and Road adits can be inferred from Figure 4 and 5; however, a strong seasonal trend exists with some peaks in concentration that can mask this overall trend.

Figure 6 displays the results for dissolved copper and zinc in the Avoca River at Avoca Bridge which is downstream of the main Avoca Mining Area, from 2001 to present. The ecological assessment criteria (or EQS) are also shown on the graph for reference. The results also appear to be trending downwards but further analysis on seasonal trends will be required as more data becomes available.

More complete trend evaluations will be carried out as additional data are collected throughout the monitoring programme using an appropriate statistical package.

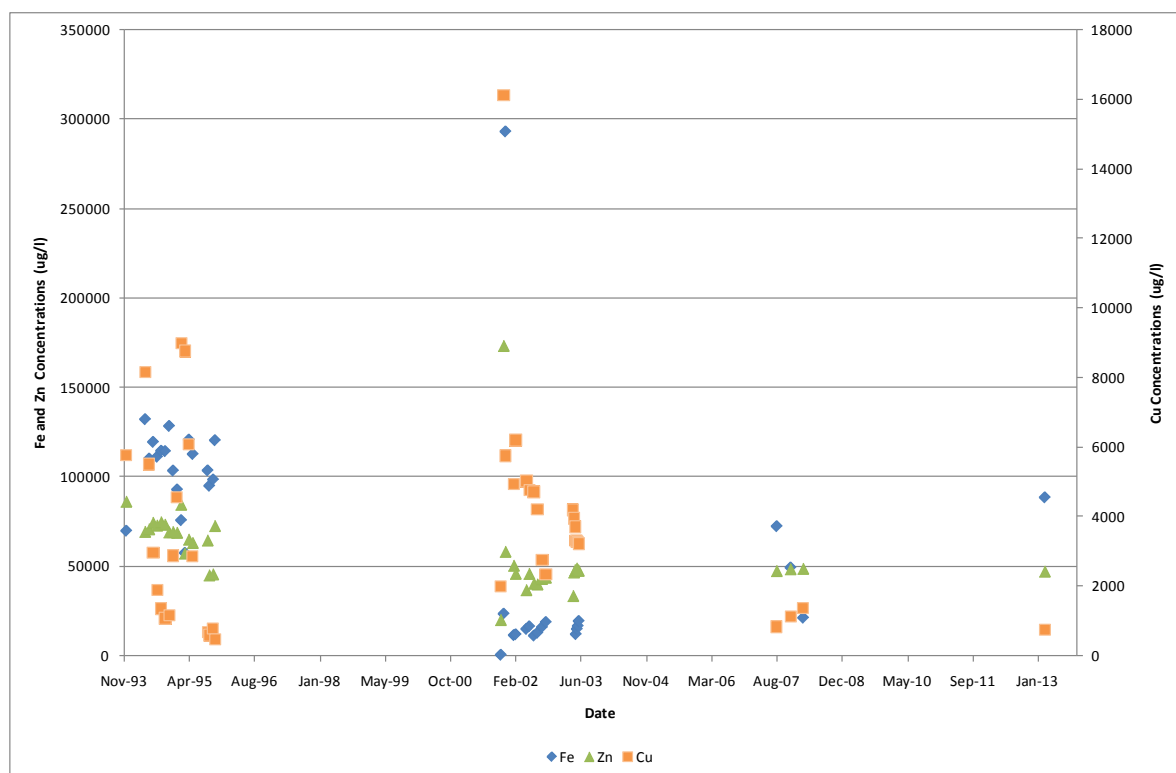


Figure 4 Concentration trends for dissolved copper, zinc and iron within the Deep Adit Discharge (Dec 1993 to Mar 2013)

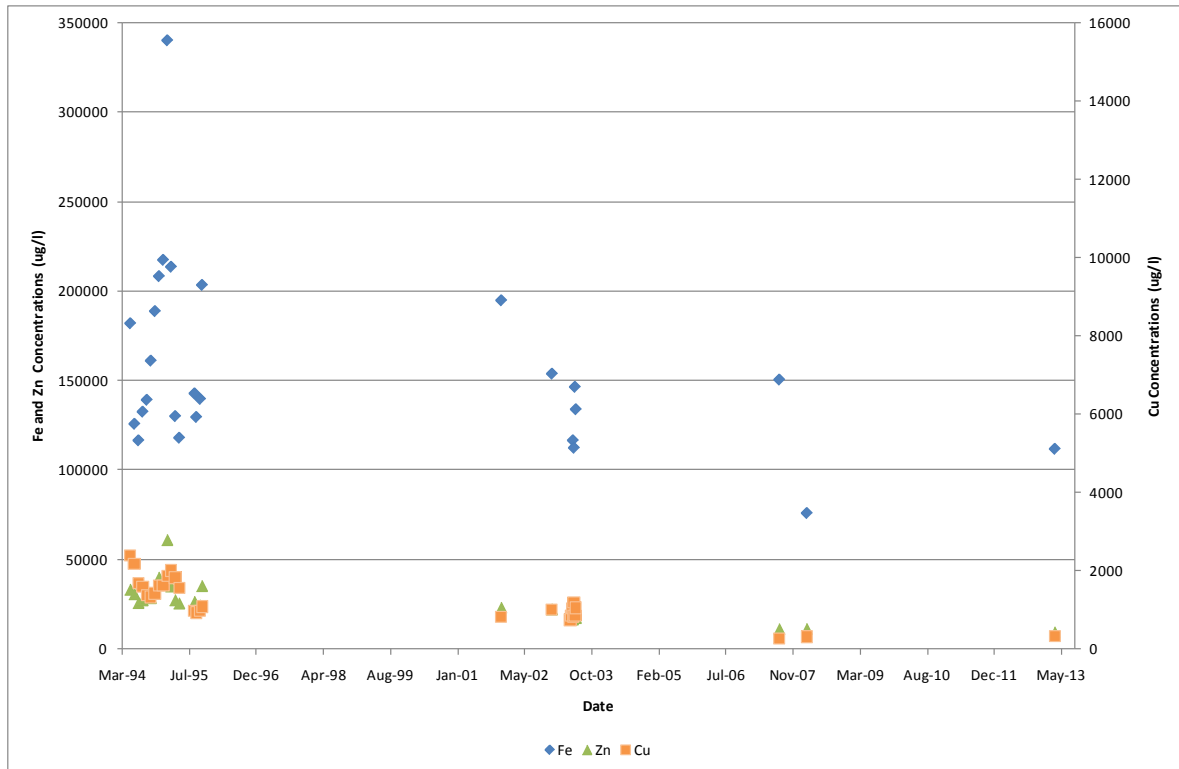


Figure 5 Concentration trends for dissolved copper, zinc and iron within the Road Adit Discharge (May 1993 to Mar 2013)

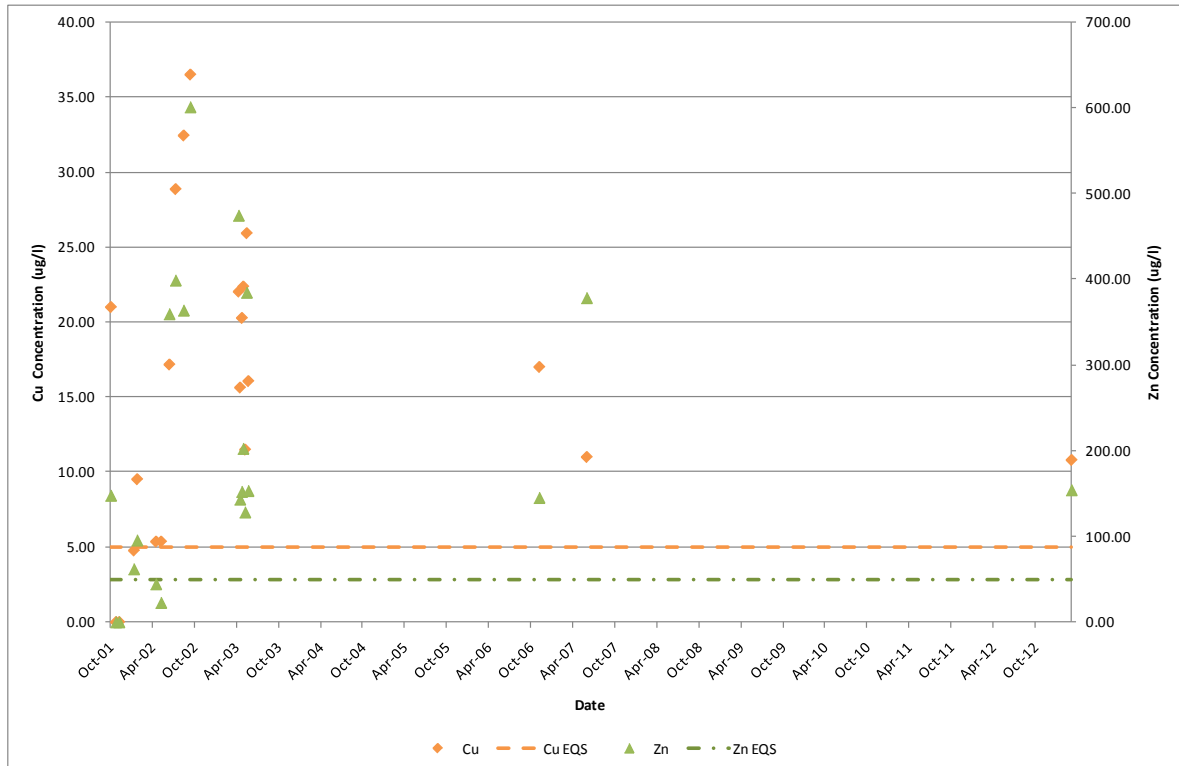


Figure 6 Concentration trends for dissolved copper and zinc at Avoca Bridge compared with the environmental quality objective (EQS) (May 2001 to Mar 2013)

Section 6

Groundwater Levels

Groundwater levels were measured at the nine wells using a portable electronic water level recorder prior to purging. Table 17 provides the measured depth to groundwater and calculated groundwater elevations. All groundwater level data are contained in Appendix C of the Data Report. The groundwater elevations varied between 26.08 to 32.85 m Ordnance Datum (OD) in the Avoca Mining Area which were consistent with the hydraulic gradient towards the Avoca River. MWSA2 is located downgradient of Shelton Abbey Tailings which is in a different part of the catchment and the groundwater elevation is much lower than that of the West and East Avoca.

Table 17 Measures Groundwater Levels March 2013

Borehole Identifier	Date	Time	Depth to Groundwater (m bTOC)	Groundwater Elevation (m OD)
MWDA1	11/03/2013	11:00	5.87	26.92
MWDA2	12/03/2013	10:00	5.96	26.66
MWPF1	13/03/2013	15:30	4.20	27.29
MWET1	12/03/2013	12:30	6.90	26.49
MWET2	12/03/2013	14:00	6.80	26.57
GW1/05	13/03/2013	10:00	4.72	26.08
GW2/05	13/03/2013	11:00	4.83	26.12
SG104	13/03/2013	12:45	25.32	32.85
MWSA2	14/03/2013	14:30	8.35	1.82

Notes:
m is metres
OD is Ordnance Datum
bTOC is below top of casing

The six wells owned by the department have been fitted with automatic pressure transducers and loggers. All the data loggers were confirmed to be working on 15 March 2013 and their date/time were reset where necessary and battery voltage checked. Figure 7 shows the groundwater elevations from the 5 wells located in the Avoca Mining Area 15-20 March 2013. Over this short period the groundwater levels showed little fluctuation.

Figure 7 and Table 17 shows the head is higher in the shallow alluvium monitoring well MWDA1 with respect to its nested well pair in the deeper alluvium MWDA2 which suggests a downward hydraulic gradient between the pair. For MWET1 and MWET2 pair the reverse is true with the head 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 northeast of the MWET1/ET2 well cluster. There is a slight downward gradient between the alluvial well GW2/05 and top of bedrock (GW1/05) at this location (Table 17). Figure 8 shows the groundwater elevation at MWSA2 at Shelton Abbey Tailings Facility between 15 and 20 March 2013.

Groundwater gradients to the Avoca River were calculated using the measured groundwater elevations and corresponding river water elevations for the same day. For the river elevations, the EPA gauges were used where possible. For MWDA1, MWDA2 and MWPF1 the river water

elevation was taken from the EPA gauge located at Whites Bridge GS. The river water elevation was estimated for MWET1, MWET2, GW1/05 and GW2/05 using both the Whites Bridge GS elevation and the Wicklow Maintenance Yard County Council gauges because they are located equidistance between the gauges. For SG104 the water elevation from Wicklow Maintenance Yard County Council was used. The river water level at MWSA2 was unable to be determined because there are no gauges or detailed mapping available.

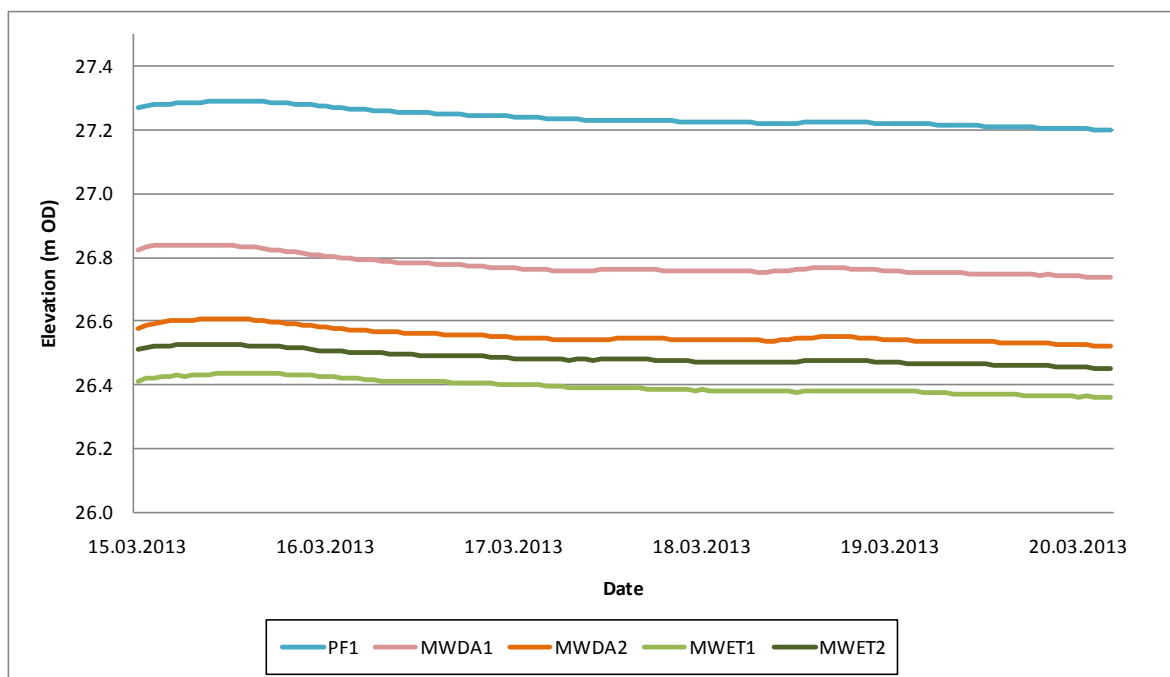


Figure 7 Groundwater Elevations in the Avoca Mining Area from 15-20th March 2013

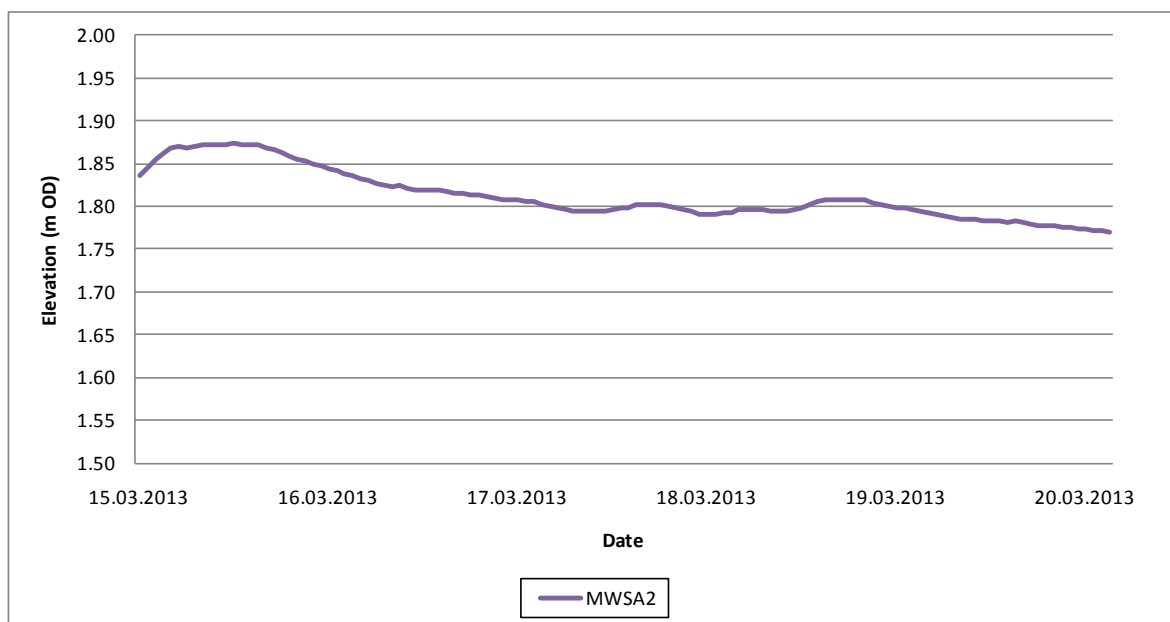


Figure 8 Groundwater Elevation in the at Shelton Abbey from 15-20th March 2013

Table 18 summarises resulting hydraulic gradient data between the monitoring well clusters and the Avoca River, and shows an estimated net positive gradient from the wells to the river in March 2013.

Table 18 Calculated Groundwater Gradients for March 2013

Borehole Identifier	Date	Groundwater Elevation (m OD)	Water Elevation at Perpendicular Stream Point (m OD)	Distance to Perpendicular Stream Point (m)	Gradient
MWDA1	15/03/2013	26.823	26.49	40	0.008
MWDA2	15/03/2013	26.574	26.49	40	0.002
MWPF1	15/03/2013	27.271	26.49	44	0.018
MWET1	15/03/2013	26.411	25.18	72	0.017
MWET2	15/03/2013	26.511	25.18	72	0.018
GW1/05	13/03/2013	26.08	25.12	74	0.013
GW2/05	13/03/2013	26.12	25.12	74	0.014
SG104	13/03/2013	32.85	23.81	142	0.064
MWSA2	15/03/2013	1.836	unknown	45	unknown

Data from the MWDA1 was able to be recovered from the end of 2009 onwards and was plotted against the measured elevation of the Avoca River at the Whites Bridge GS as shown in Figure 9. The figure shows a very strong relationship between the levels of the river and the groundwater levels in MWDA1 whereby rises in levels in the river are accompanied by a measured response in the well. The Avoca River has an immediate and measurable impact on groundwater levels in the alluvial sediments in the mines area.

Figure 9 also shows the average daily hydraulic gradients between MWDA1 and the Avoca River (at Whites Bridge GS) calculated for the period December 2009 to April 2013. 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 predominates (i.e., the head in the aquifer is higher than in the river), the Avoca River is a net gaining river. The average gradient was 0.009 (standard deviation 0.004) and the minimum gradient was -0.006 and the maximum gradient was 0.069. There were only four days when a negative gradient was calculated. All of these negative gradient values were when the river water levels were high, however the gradients were still found to be positive during high flow and so the negative gradients are considered exceptions to the norm.

Figure 9 also shows that even during periods of very high river stage, surface-water levels never really exceeded groundwater levels and in fact increases can be observed in the hydraulic gradient. Therefore the Avoca River is a net gaining river from the alluvium at the Deep Adit location and diffuse groundwater contaminants will contribute to the contaminant loads in the river. As more data becomes available, further analysis of the gradients will be carried out for the other monitoring wells with data loggers installed.

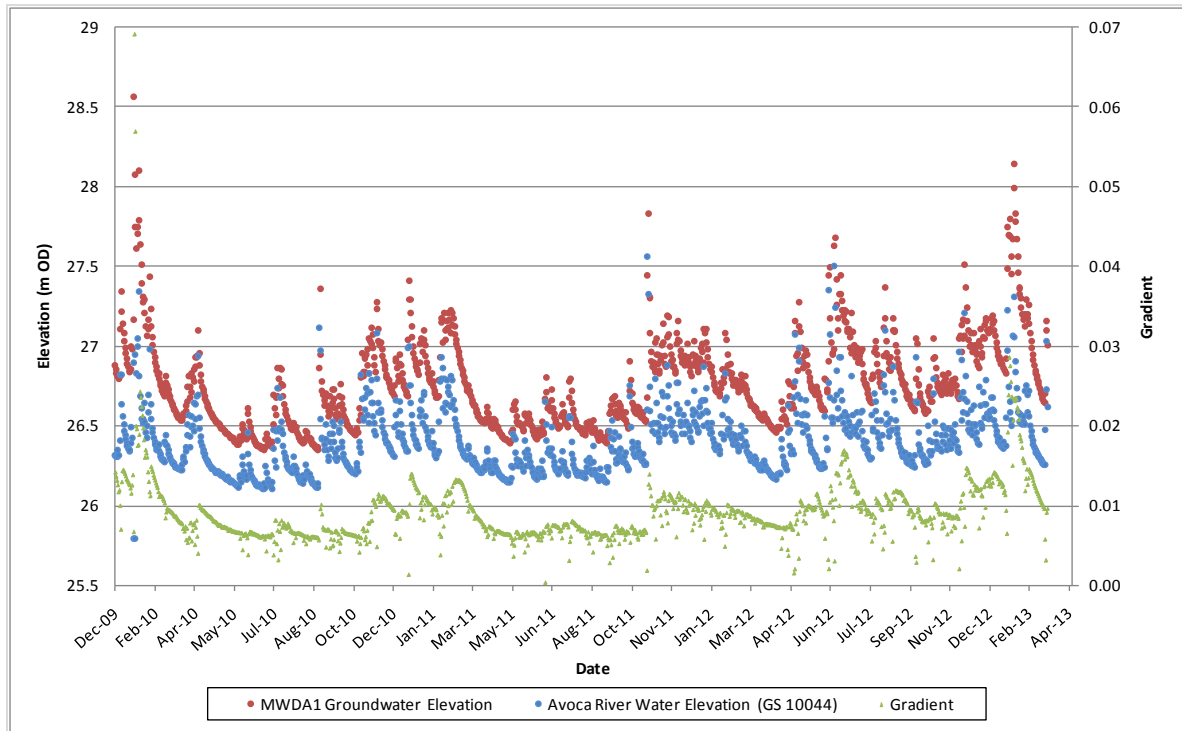


Figure 9 Comparison of Groundwater Elevation and Elevation of the Avoca River and Associated Gradient at the Deep Adit Area from Dec 2009 to Apr 2013

Section 7

Summary and Recommendations

7.1 Summary of Findings

Nine groundwater monitoring wells were sampled and analysed in March 2013 and water levels were measured. Eighteen surface water locations were sampled and analysed between in March 2013 with flows measured at 13 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 acceptable and the data can be used to compare to the assessment criteria.

A statistical summary of the analytical results for groundwater and surface water was prepared and results were compared to assessment criteria. An analysis of loading, concentration time trends and groundwater levels was 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, human health criteria or both, particularly for dissolved aluminium, cadmium, copper, iron, manganese, nickel and zinc. Sulphate levels greatly exceeded the criteria for human health in the majority of monitoring wells.
- The shallow well MWPF1 located upgradient of the Deep Adit area, near the eastern margin of the alluvial sediments had the lowest concentration of sulphate and dissolved metals. SG104 located immediately downgradient of Ballymurtagh Landfill had the highest concentrations of dissolved metals especially aluminium, barium, cadmium and zinc, and included detections of tin and uranium.
- The Cronebane Shallow Adit was the adit discharge with the highest concentrations of dissolved metals including aluminium, copper and zinc. The Cronebane Shallow, Ballygahan and Spa adits are of minor importance in terms of metals loads to the Avoca, either because of absence of surface flow to the river or due to low concentrations and loads.
- In the Avoca River and tributaries, dissolved metal concentrations were low in comparison to the groundwater and the adit discharges; however, several exceedances of both ecological and human health criteria occurred, namely for dissolved copper and zinc. Some dissolved metals including aluminium, zinc and iron were detected upgradient of the mining area at Ballinacleish Bridge and Lions Bridge which contribute background loads to the Avoca River.
- Whites Bridge GS is 90 metres downstream of the bridge and is the first sampling location along the Avoca River within the mining area where significant increases in dissolved metals concentrations and loads are observed namely for; aluminium, copper and zinc. This reflects infiltration from the Deep Adit discharge ditch and the input of groundwater through this area.

- The Deep Adit and the Road Adit had similar loads of sulphate, dissolved copper and iron. However, the Deep Adit had much higher loadings of dissolved aluminium and zinc. The calculated loads may be an over estimation of the direct loads discharging to the Avoca River due to precipitation of metals resulting in attenuation occurring within the ditches before discharging or infiltrating into the Avoca River. However the infiltration from the Deep Adit discharge ditch ultimately discharges as groundwater baseflow to the Avoca River as discussed in Section 6.
- The concentration time trends for Deep and Road adits and the Avoca Bridge location for dissolved copper and zinc, revealed a general declining trend in metal concentrations; however, a strong seasonal variation is also observed.
- There was a net positive gradient from all of the monitoring wells to the Avoca River in March 2013. A positive hydraulic gradient indicates that contaminated groundwater discharges to the Avoca River. A very strong relationship exists between the levels of the Avoca River and the groundwater levels in MWDA1 whereby rises in levels in the river are accompanied by a measured response in the well.

7.2 Recommendations for the Monitoring Programme

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

- Dissolved Oxygen is currently being analysed in the field and by the laboratory. However, the field measurements are more representative of actual DO of the groundwater and surface water than the results in the laboratory. Consideration should be given to eliminating the laboratory analyses of DO.
- Due to the significant concentrations and loads determined at the Whites Bridge GS location (90 m downstream of the bridge), the diffuse load between the bridge and downstream of the current Deep Adit infiltration areas should be investigated further. Samples could be collected in the Avoca River both upstream of the actual Deep adit discharge (e.g. at Whites Bridge) and downstream of the current marsh infiltration area.

Section 8

References

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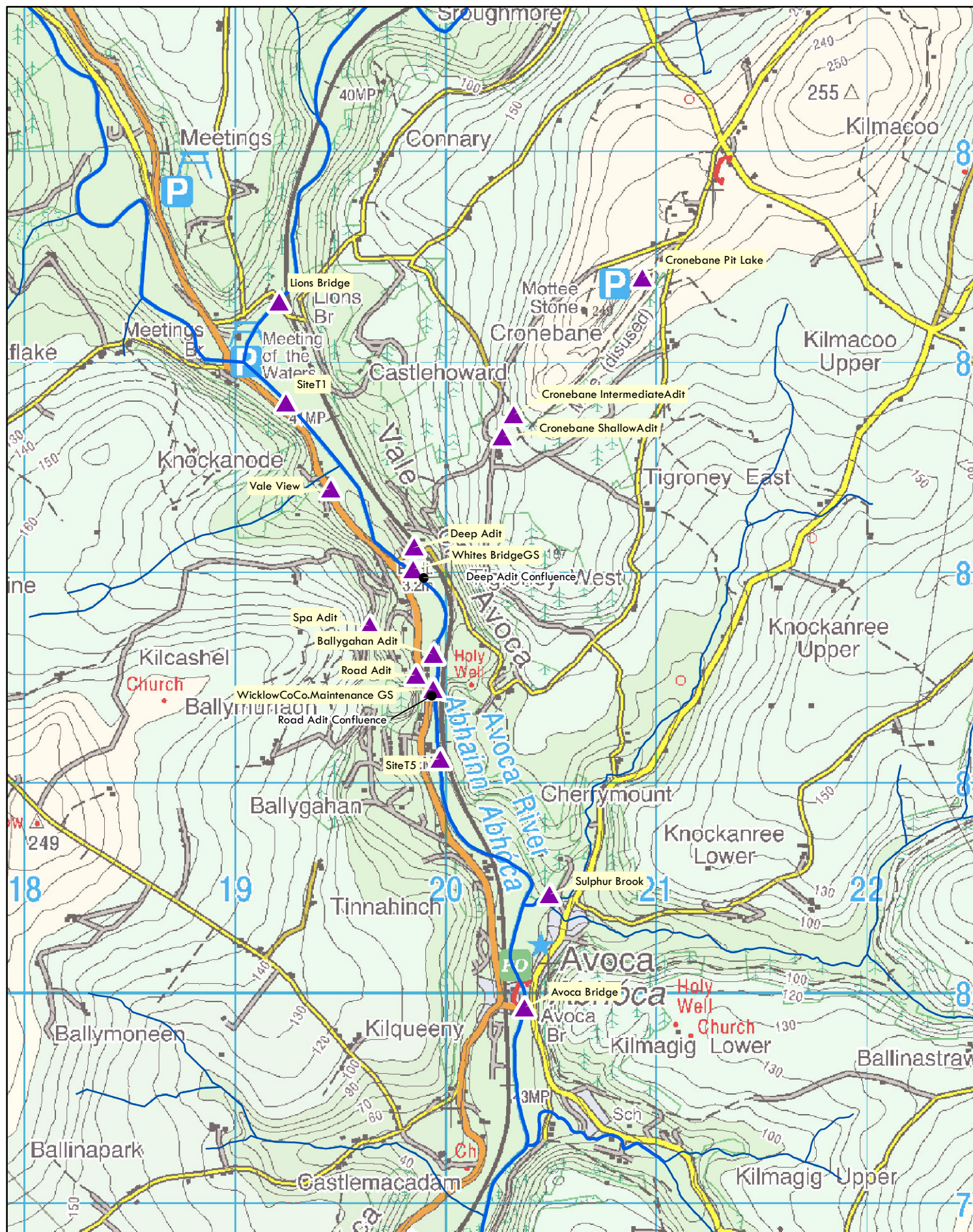
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Appendix A

Figures



Map 1 - Avoca - Main Area

Drawn by: LG Date: 10/06/2013

Internal Project Reference: S:\CURRENT_PROJECTS\95735_Avoca_Silver\02_GIS_Tasks\03_MonRpt\MXD\01_AvocaMon1.mxd

**CDM
Smith**

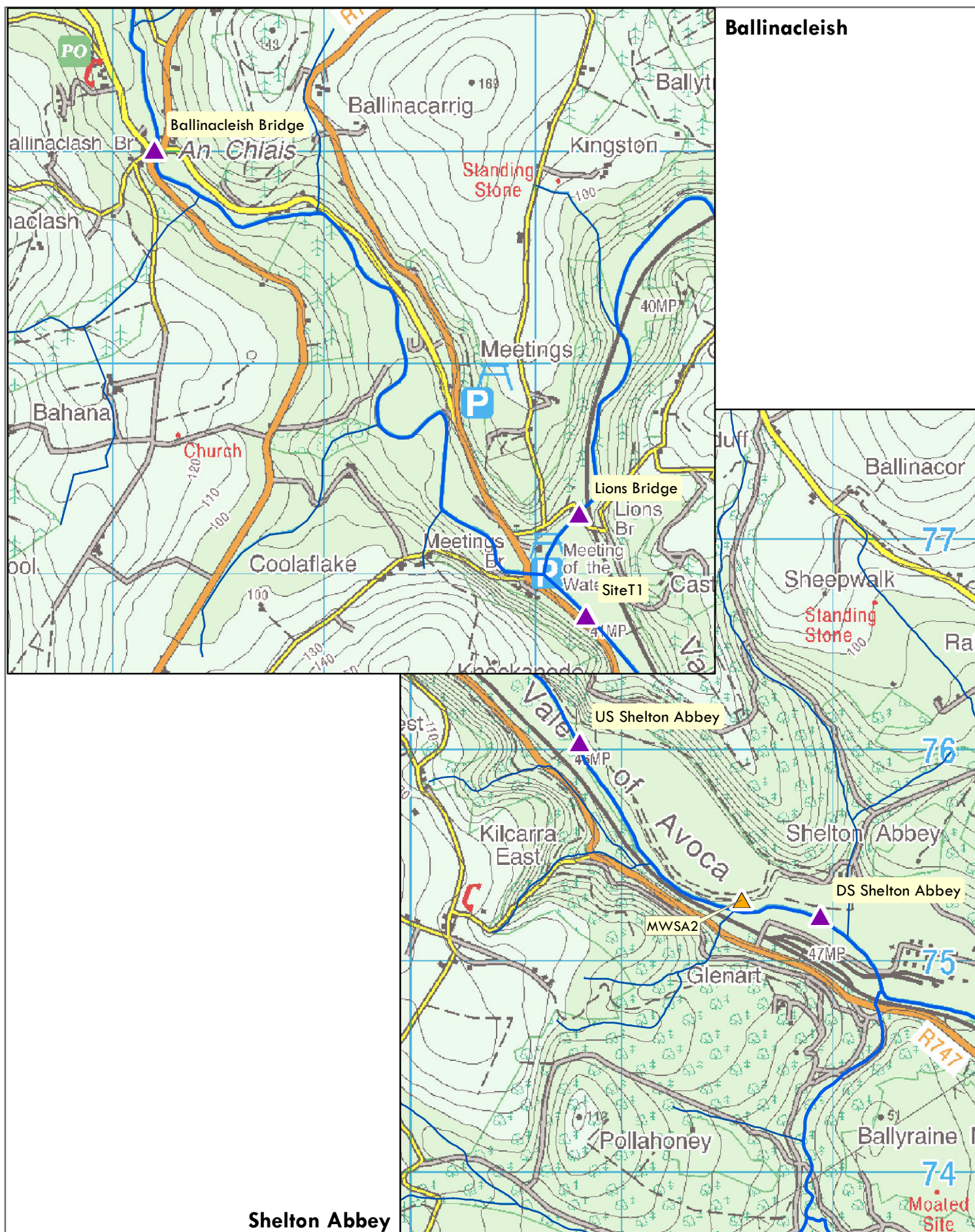
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Legend

- ▲ Surface Water Sampling Locations
- Rivers



0 125 250 500
Meters



Map 2 - Avoca - Ballinacleish and Shelton Abbey

Drawn by: LG Date: 03/06/2013

Internal Project Reference: S:\CURRENT_PROJECTS\95735_Avoca_Silver\02_GIS_Tasks\03_MonRpt\MXD\02_AvocaMon2.mxd



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Legend

- Surface Water Sampling Locations
- Groundwater Sampling Location (Shelton Abbey)
- Rivers



0 125 250 500
Meters



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

Drawn by: LG Date: 04/06/2013

Internal Project Reference: S:\CURRENT_PROJECTS\97535_Avoca_Silver\02_GIS_Tasks\03_MonRpt\MXD\03_AvocaMonGW.mxd



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Legend

- ▲ Groundwater Sampling Locations
- ▲ Surface Water Sampling Locations
- Rivers



0 125 250 Meters

Appendix B

Analytical Data Tables and Assessment Criteria

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

Sample Description	Sample Type	Date Sampled	Suspended solids, Total mg/l	Aluminium (tot.unfilt) µg/l	Aluminium (diss.filt) µg/l	%RPD	Cadmium (tot.unfilt) µg/l	Cadmium (diss.filt) µg/l	%RPD	Copper (tot.unfilt) µg/l	Copper (diss.filt) µg/l	%RPD	Lead (tot.unfilt) µg/l
GW1/05	GW	13/03/2013	-	82200	73400	-11.31	22.9	42.1	59.08	11600	9310	-21.90	341
GW2/05	GW	13/03/2013	-	51200	44000	-15.13	17.7	14.2	-21.94	7970	5790	-31.69	1.16
MWDA1	GW	11/03/2013	-	389000	364000	-6.64	174	140	-21.66	41700	39100	-6.44	11.1
MWDA2	GW	12/03/2013	-	84500	85200	0.82	71.4	61.7	-14.58	7640	7050	-8.03	2.5
MWET1	GW	12/03/2013	-	212000	225000	5.95	31.6	14.9	-71.83	14300	8260	-53.55	10.5
MWET2	GW	12/03/2013	-	165	613	115.17	2.69	3.68	31.08	15.8	20.7	26.85	16.6
MWPF1	GW	13/03/2013	-	463	374	-21.27	0.544	0.623	13.54	65.6	52.5	-22.18	0.2
MWSA2	GW	14/03/2013	-	67800	63400	-6.71	1.47	3.17	73.28	200	153	-26.63	27.7
SG104	GW	13/03/2013	-	1210000	996000	-19.40	124	553	126.74	124000	94700	-26.79	233
BALLYGAHAN ADIT	ADIT	15/03/2013	<0.2	92700	87900	-5.32	49.5	50.1	1.20	8350	7020	-17.31	148
CRANBANE INTER ADIT	ADIT	19/03/2013	9	62700	7610	-156.71	81.6	80.2	-1.73	2250	3020	29.22	1110
CRONBANE SHALLOW ADIT	ADIT	15/03/2013	8.5	355000	377000	6.01	390	277	-33.88	14500	12700	-13.24	1140
DEEP ADIT	ADIT	15/03/2013	4	105000	98800	-6.08	113	104	-8.29	936	770	-19.46	1920
ROAD ADIT	ADIT	15/03/2013	5.5	14100	14900	5.52	14.4	16.3	12.38	419	366	-13.50	327
SPA ADIT	ADIT	14/03/2013	<0.2	167000	259000	43.19	27.2	24.4	-10.85	9740	7820	-21.87	82.3
CRONBANE PIT LAKE	PIT	15/03/2013	<0.2	8590	8250	-4.04	7.51	8.11	7.68	2480	2200	-11.97	240
AVOCA BRIDGE	SW	20/03/2013	2	500	162	-102.11	2.5	0.449	-139.10	20	10.8	-59.74	7.08
BALLINACLEISH BRIDGE	SW	19/03/2013	<0.2	76.2	56.7	-29.35	0.25	0.05	-133.33	2	0.425	-129.90	3.15
DS SHELTON ABBEY	SW	14/03/2013	<0.2	303	113	-91.35	0.25	0.263	5.07	9.98	6.46	-42.82	3.55
LIONS BRIDGE	SW	19/03/2013	<0.2	109	58	-61.08	0.25	0.113	-75.48	2	0.986	-67.92	4.33
SITE T1	SW	19/03/2013	<0.2	68.7	52.9	-25.99	0.25	0.05	-133.33	2	0.425	-129.90	2.44
SITE T5	SW	20/03/2013	2.5	586	165	-112.12	2.5	0.496	-133.78	20	15.3	-26.63	8.68
SULPHUR BROOK	SW	21/03/2013	<0.2	500	22.9	-182.48	2.5	0.439	-140.25	20	26.5	27.96	10.3
US SHELTON ABBEY	SW	14/03/2013	<0.2	303	102	-99.26	0.25	0.346	32.21	10.2	6.87	-39.02	3.87
VALE VIEW	SW	11/03/2013	6.5	500	11.7	-190.85	2.5	0.05	-192.16	20	1.21	-177.18	2.5
WHITESBRIDGE	SW	20/03/2013	<0.2	500	242	-69.54	2.5	0.58	-124.68	20	19.5	-2.53	2.5
WICKLOW MAIN YARD	SW	20/03/2013	<0.2	500	198	-86.53	2.5	0.361	-149.53	20	13.6	-38.10	5.12

Notes:

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

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

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

- Not analysed

RPD - Relative percent difference

GW - Groundwater

SW - Surface Water

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

Sample Description	Sample Type	Date Sampled	Lead (diss.filt) µg/l	%RPD	Zinc (tot.unfilt) µg/l	Zinc (diss.filt) µg/l	%RPD
GW1/05	GW	13/03/2013	436	24.45	21200	20000	-5.83
GW2/05	GW	13/03/2013	0.395	-98.39	9800	7240	-30.05
MWDA1	GW	11/03/2013	8.81	-23.00	73000	60700	-18.40
MWDA2	GW	12/03/2013	2.16	-14.59	40400	34800	-14.89
MWET1	GW	12/03/2013	7.89	-28.38	12700	7630	-49.88
MWET2	GW	12/03/2013	1.59	-165.04	4640	6150	27.99
MWPF1	GW	13/03/2013	0.399	66.44	83.4	62.9	-28.02
MWSA2	GW	14/03/2013	30.8	10.60	3850	4850	22.99
SG104	GW	13/03/2013	18.9	-169.99	199000	151000	-27.43
BALLYGAHAN ADIT	ADIT	15/03/2013	147	-0.68	27200	24500	-10.44
CRANBANE INTER ADIT	ADIT	19/03/2013	1210	8.62	32600	4010	-156.19
CRONBANE SHALLOW ADIT	ADIT	15/03/2013	1080	-5.41	114000	99500	-13.58
DEEP ADIT	ADIT	15/03/2013	1770	-8.13	55400	47300	-15.77
ROAD ADIT	ADIT	15/03/2013	334	2.12	9730	9140	-6.25
SPA ADIT	ADIT	14/03/2013	62.5	-27.35	15100	12400	-19.64
CRONBANE PIT LAKE	PIT	15/03/2013	207	-14.77	2810	2550	-9.70
AVOCA BRIDGE	SW	20/03/2013	2.52	-95.00	202	154	-26.97
BALLINACLEISH BRIDGE	SW	19/03/2013	2.69	-15.75	24	20.1	-17.69
DS SHELTON ABBEY	SW	14/03/2013	1.46	-83.43	126	102	-21.05
LIONS BRIDGE	SW	19/03/2013	3.05	-34.69	56.3	27.6	-68.41
SITE T1	SW	19/03/2013	2.11	-14.51	25.8	19.3	-28.82
SITE T5	SW	20/03/2013	2.78	-102.97	342	190	-57.14
SULPHUR BROOK	SW	21/03/2013	4.32	-81.81	137	97.2	-33.99
US SHELTON ABBEY	SW	14/03/2013	1.51	-87.73	122	99.6	-20.22
VALE VIEW	SW	11/03/2013	0.089	-186.25	15	8.56	-54.67
WHITESBRIDGE	SW	20/03/2013	1.35	-59.74	188	207	9.62
WICKLOW MAIN YARD	SW	20/03/2013	2.38	-73.07	180	133	-30.03

Notes:

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

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

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

- Not analysed

RPD - Relative percent difference

GW - Groundwater

SW - Surface Water

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

Sample Description	Type	Date Sampled Units	Alkalinity, Total as CaCO3, Hardness as CaCO3, Ammoniacal Nitrogen as N, Chloride, COD, unfiltered mg/l, Conductivity @ 20 deg.C mS/cm, Cyanide, Free mg/l, Dissolved solids, Total mg/l, Fluoride mg/l, Nitrate as NO3 mg/l, Nitrite as NO2 mg/l, Oxygen, dissolved mg/l, pH (lab) pH Units, Phosphate (ortho) as P mg/l, Sulphate mg/l, Sodium (diss.filt) mg/l, Suspended solids, Total mg/l																	
			Acidity as HCL mg/l	Total as CaCO3 mg/l	Hardness as CaCO3 mg/l	Ammoniacal Nitrogen as N mg/l	Chloride mg/l	COD, unfiltered mg/l	Conductivity @ 20 deg.C mS/cm	Cyanide, Free mg/l	Dissolved solids, Total mg/l	Fluoride mg/l	Nitrate as NO3 mg/l	Nitrite as NO2 mg/l	Oxygen, dissolved mg/l	pH (lab) pH Units	Phosphate (ortho) as P mg/l	Sulphate mg/l	Sodium (diss.filt) mg/l	Suspended solids, Total mg/l
Ecological Criteria			-	-	-	0.14	-	-	-	0.01	-	0.5	-	-	-	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	11/03/2013	-	1	1.22	1.26	11.5	-	4.040	0.025	6100	25.2	0.15	0.025	5.13	2.68	0.01	3730	5.89	-
MWDA2	GW	12/03/2013	-	1	1.22	0.1	14.3	-	1.480	0.025	1810	1.32	1.06	0.367	4.17	3.8	0.01	1050	10.8	-
MWET1	GW	12/03/2013	-	1	1.22	0.697	25.9	-	2.530	0.025	3550	0.174	0.15	0.025	5.55	3.39	0.01	2170	18.7	-
MWET2	GW	12/03/2013	-	50	61.00	0.242	14.1	-	3.010	0.025	3750	21.6	0.15	0.025	4.74	6.08	0.01	2220	24.9	-
GW1/05	GW	13/03/2013	-	1	1.22	0.269	16.1	-	1.720	0.025	2040	1.61	4.87	0.073	5.15	3.76	0.01	1310	16.6	-
GW2/05	GW	13/03/2013	-	1	1.22	0.1	15.7	-	1.220	0.025	1270	0.25	6.6	0.025	8.44	3.8	0.01	811	13	-
MWPF1	GW	13/03/2013	-	3	3.66	0.1	14.7	-	0.161	0.025	62.2	0.25	15.9	0.025	10.6	5.28	0.01	30.1	9.62	-
SG104	GW	13/03/2013	-	1	1.22	2.95	15.1	-	8.380	0.025	16000	12.2	0.15	0.025	8.63	2.97	0.01	10800	16	-
MWSA2	GW	14/03/2013	-	1	1.22	1.16	14.9	-	2.170	0.025	2780	6.64	0.15	0.025	4.06	4.01	0.01	1720	10.3	-
VALE VIEW	SW	11/03/2013	2	26	31.72	0.1	12.7	3.5	0.148	0.025	102	0.25	16.4	0.025	12.2	7.08	0.01	15.4	5.39	6.5
BALLINACLEISH BRIDGE	SW	19/03/2013	2	9.5	11.59	0.1	8.1	8.47	0.057	0.025	22	0.25	4.56	0.025	10.5	7	0.01	2.2	4.48	0.1
LIONS BRIDGE	SW	19/03/2013	2	9.95	12.14	0.1	10.2	13.6	0.070	0.025	49	0.25	4.44	0.025	10.5	7.09	0.01	<2	6.17	0.1
SITE T1	SW	19/03/2013	2	9.24	11.27	0.1	9.4	10.1	0.069	0.025	66	0.25	5.26	0.025	10.2	7.09	0.01	2.8	5.7	0.1
WHITESBRIDGE GS	SW	20/03/2013	2	14.2	17.32	0.1	8.9	11.3	0.073	0.025	52	0.25	4.2	0.025	10.2	7.55	0.01	8.2	5.38	0.1
WICKLOW MAIN YARD	SW	20/03/2013	2	14.1	17.20	0.1	8.8	10.2	0.075	0.025	49	0.25	4.42	0.025	9.93	6.99	0.01	8.2	5.62	0.1
SITE T5	SW	20/03/2013	2	326	397.72	0.1	8.7	12.3	0.083	0.025	53	0.25	4.41	0.025	9.87	7.08	0.01	13.5	5.63	2.5
SULPHUR BROOK	SW	21/03/2013	2	25.5	31.11	0.213	14.9	3.5	0.150	0.025	94	0.25	21.8	0.025	10.3	7.46	0.01	14.6	12.3	0.1
AVOCA BRIDGE	SW	20/03/2013	2	7.46	9.10	0.1	9.1	8.91	0.074	0.025	59.8	0.25	4.52	0.025	10.2	6.97	0.01	9.5	6.12	2
US SHELTON ABBEY	SW	14/03/2013	2	13	15.86	0.1	9.9	7.47	0.094	0.025	60	0.25	7.77	0.025	11	7.18	0.01	9.9	5.84	0.1
DS SHELTON ABBEY	SW	14/03/2013	2	13	15.86	0.1	9.8	10.5	0.089	0.025	52	0.25	7.87	0.025	11.1	7.3	0.01	10.4	6.15	0.1
SPA ADIT	Adit	14/03/2013	843	1	1.22	0.933	10.6	18.1	2.020	0.025	2630	0.103	1.26	0.025	11.2	2.84	0.01	1590	5.41	0.1
BALLYGAHAN ADIT	Adit	15/03/2013	588	1	1.22	10.6	42.1	34.9	2.430	0.025	2790	1.8	12.8	0.1	0.93	3.19	0.01	1750	33.8	0.1
CRONBANE SHALLOW ADIT	Adit	15/03/2013	1890	1	1.22	0.795	14.4	26.3	3.180	0.025	5100	23	0.631	0.025	8.65	2.89	0.01	3230	6.15	8.5
DEEP ADIT	Adit	15/03/2013	577	1	1.22	0.399	13.3	12.7	1.450	0.025	1780	1.41	0.15	0.025	5.69	3.96	0.01	1130	7.75	4
ROAD ADIT	Adit	15/03/2013	181	1	1.22	7.32	31.4	21.4	1.370	0.025	1370	20.4	3.14	0.171	7.25	3.7	0.01	838	22.6	5.5
CRANBANE INTER ADIT	Adit	19/03/2013	434	1	1.22	0.364	13.6	12.2	1.230	0.025	1410	1.8	0.15	0.025	0.69	3.02	0.01	748	8.18	9
CRONBANE PIT LAKE	Pit Lake	15/03/2013	67.5	1	1.22	0.248	9.6	3.5	0.399	0.025	194	0.674	3.79	0.025	9.76	5.05	0.01	113	5.33	0.1

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

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

Sample Description	Type	Date Sampled Units	Aluminium (diss.filt) µg/l	Antimony (diss.filt) µg/l	Arsenic (diss.filt) µg/l	Barium (diss.filt) µg/l	Cadmium (diss.filt) µg/l	Chromium (diss.filt) µg/l	Cobalt (diss.filt) µg/l	Copper (diss.filt) µg/l	Iron (diss.filt) µg/l	Lead (diss.filt) µg/l	Manganese (diss.filt) µg/l	Mercury (diss.filt) µg/l	Molybdenum (diss.filt) µg/l	Nickel (diss.filt) µg/l	Selenium (diss.filt) µg/l	Silver (diss.filt) µg/l	Thallium (diss.filt) µg/l	Tin (diss.filt) µg/l	Uranium (diss.filt) µg/l	Vanadium (diss.filt) µg/l	Zinc (diss.filt) µg/l
Ecological Criteria			1,900	-	25	4	0.45	3.4	5.1	5	-	7.2	1100	0.07	-	20	-	-	-	-	2.6	-	50
Human Health Criteria			200	5	10	-	5	50	-	2000	200	10	50	1	-	20	10	-	-	-	-	-	-
MWDA1	GW	11/03/2013	364000	1.69	0.6	3.99	140	90.2	252	39100	163000	8.81	13900	0.294	1.2	137	1.95	0.75	-	1.8	7.5	1.2	60700
MWDA2	GW	12/03/2013	85200	7.31	0.6	7.29	61.7	7.06	150	7050	56300	2.16	9110	0.0633	3.32	92.1	4.39	0.75	-	1.8	7.5	1.2	34800
MWET1	GW	12/03/2013	225000	0.08	0.124	2.79	14.9	13.3	208	8260	112000	7.89	9200	0.0568	1.2	80.5	0.999	0.75	-	1.8	10.1	0.12	7630
MWET2	GW	12/03/2013	613	3.42	7.74	12.2	3.68	1.1	140	20.7	96600	1.59	38500	0.005	1.2	22.7	10.1	0.75	-	1.8	7.5	0.12	6150
GW1/05	GW	13/03/2013	73400	0.8	0.6	8.11	42.1	2.49	167	9310	42800	436	7760	0.0809	1.2	65	5.66	7.5	-	5.39	7.5	0.12	20000
GW2/05	GW	13/03/2013	44000	0.08	0.06	0.972	14.2	1.45	70.3	5790	84.8	0.395	4000	0.0256	1.2	33	0.195	7.5	-	1.8	2.08	0.12	7240
MWPF1	GW	13/03/2013	374	0.389	0.444	9.26	0.623	0.602	1.5	52.5	9.5	0.399	74.6	0.005	0.446	1.95	1.38	7.5	-	1.8	0.75	0.12	62.9
SG104	GW	13/03/2013	996000	63.8	0.6	67.8	553	21.3	1030	94700	43800	18.9	45600	1.21	44	384	21.5	75	-	88.4	77.7	1.2	151000
MWSA2	GW	14/03/2013	63400	0.8	27.6	15.4	3.17	4.06	217	153	10900	30.8	10000	0.005	1.2	161	1.95	7.5	4.8	1.8	7.5	1.2	4850
VALE VIEW	SW	11/03/2013	11.7	0.259	0.365	6.83	0.05	0.449	0.092	1.21	2.8	0.089	23.8	0.005	0.12	0.42	0.195	0.75	-	0.875	0.75	0.12	8.56
BALLINACLEISH BRIDGE	SW	19/03/2013	56.7	0.08	0.324	6.8	0.05	0.11	0.218	0.425	35.6	2.69	22	0.005	0.469	0.505	0.195	7.5	-	0.18	0.75	0.12	20.1
LIONS BRIDGE	SW	19/03/2013	58	0.08	0.463	4.81	0.113	0.11	0.086	0.986	69.3	3.05	14.6	0.005	0.12	0.488	0.195	7.5	-	0.18	0.75	0.12	27.6
SITE T1	SW	19/03/2013	52.9	0.08	0.35	5.66	0.05	0.11	0.152	0.425	51.9	2.11	17.1	0.005	0.12	0.641	0.195	7.5	-	0.18	0.75	0.12	19.3
WHITESBRIDGE GS	SW	20/03/2013	242	0.08	0.502	3.93	0.58	0.11	0.952	19.5	115	1.35	45.4	0.005	0.12	0.893	0.685	0.75	0.48	0.18	0.75	0.12	207
WICKLOW MAIN YARD	SW	20/03/2013	198	0.08	0.379	3.97	0.361	0.11	0.618	13.6	99.2	2.38	36.2	0.005	0.12	0.902	0.195	0.75	0.48	0.18	0.75	0.12	133
SITE T5	SW	20/03/2013	165	0.08	0.263	4.04	0.496	0.11	1.17	15.3	339	2.78	66.2	0.005	0.12	1.28	0.195	0.75	0.48	0.18	0.75	0.12	190
SULPHUR BROOK	SW	21/03/2013	22.9	0.276	0.643	7.66	0.439	0.283	0.26	26.5	24.1	4.32	29	0.005	0.814	0.878	1.66	0.75	0.48	1.57	0.75	0.12	97.2
AVOCA BRIDGE	SW	20/03/2013	162	0.08	0.28	4.1	0.449	0.11	0.739	10.8	153	2.52	40.9	0.005	0.12	1.07	0.195	0.75	0.48	0.18	0.75	0.12	154
US SHELTON ABBEY	SW	14/03/2013	102	0.08	0.216	4.48	0.346	0.11	0.507	6.87	96.2	1.51	32.2	0.005	0.12	0.754	0.195	7.5	0.48	0.18	0.75	0.12	99.6
DS SHELTON ABBEY	SW	14/03/2013	113	0.08	0.289	4.46	0.263	0.11	0.527	6.46	109	1.46	47.8	0.005	0.12	0.862	0.195	7.5	0.48	0.18	0.75	0.12	102
SPA ADIT	Adit	14/03/2013	259000	0.8	1.04	3.92	24.4	7.15	173	7820	91500	62.5	7150	0.0451	0.12	60.8	0.195	7.5	1.21	0.18	6.32	0.12	12400
BALLYGAHAN ADIT	Adit	15/03/2013	87900	1.92	82.3	11.1	50.1	0.1	168	7020	87300	147	14500	0.0576	0.12	74	5.72	7.5	4.8	1.8	7.5	1.2	24500
CRONBANE SHALLOW ADIT	Adit	15/03/2013	377000	0.8	37.6	8	277	9.69	262	12700	183000	1080	8630	0.005	1.2	138	5.85	7.5	4.8	62.2	28.9	1.2	99500
DEEP ADIT	Adit	15/03/2013	98800	1.82	2.51	6.85	104	0.1	104	770	88500	1770	3690	0.197	1.2	36.8	4.3	7.5	4.8	5.99	7.5	1.2	47300
ROAD ADIT	Adit	15/03/2013	14900	0.8	3.28	16.6	16.3	0.1	84.4	366	76100	334	6950	0.005	1.2	42.7	1.95	7.5	4.8	1.8	7.5	1.2	9140
CRANBANE INTER ADIT	Adit	19/03/2013	7610	0.8	4.61	6.68	80.2	1.61	73.1	3020	75500	1210	2790	0.0814	0.12	40.2	1.16	7.5	-	0.18	8.62	0.574	4010
CRONBANE PIT LAKE	Pit Lake	15/03/2013	8250	1.93	1.04	5.93	8.11	0.596	13.7	2200	3190	207	301	0.013	1.02	5.4	1.08	7.5	4.8	0.18	7.5	0.12	2550

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