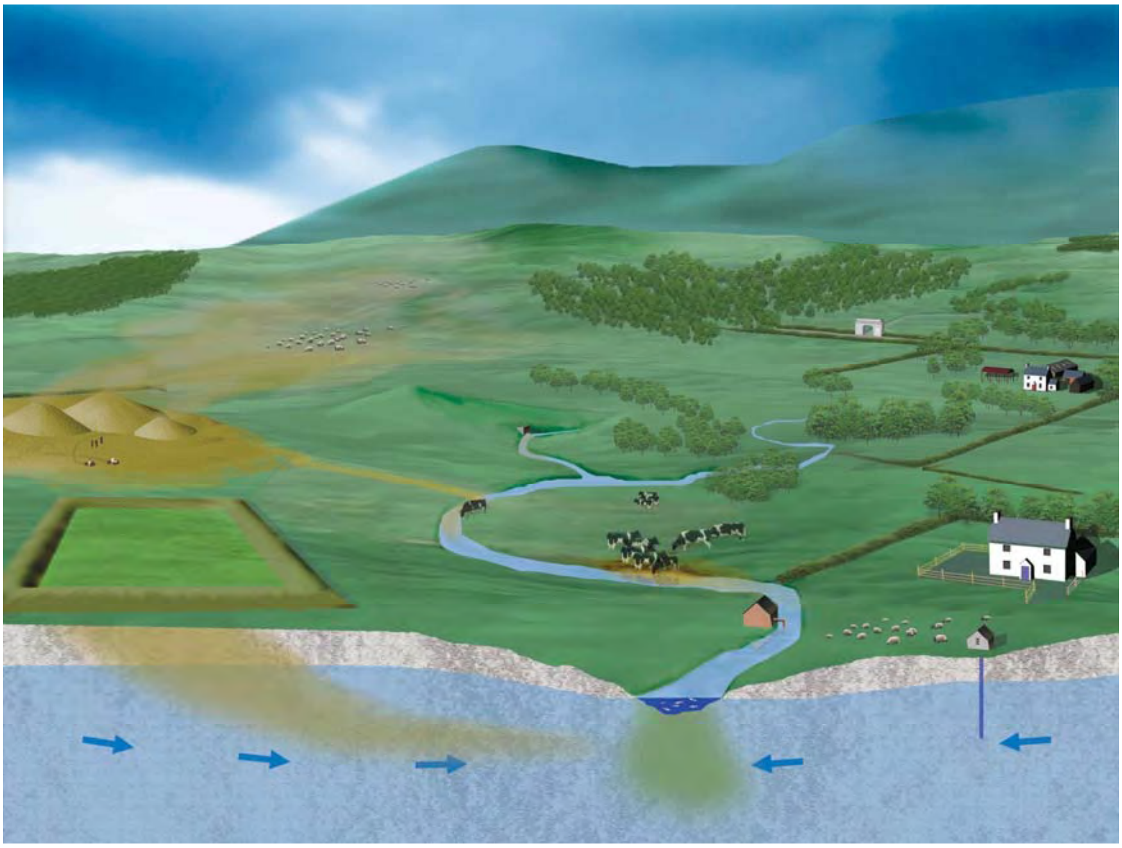
VOLUME I

GEOCHEMICAL CHARACTERISATION AND ENVIRONMENTAL MATTERS

Historic Mine Sites – Inventory and Risk Classification

A joint study carried out by

The Environmental Protection Agency
and
The Geological Survey of Ireland



This Volume should be read in conjunction with Volume II (Site Safety)

July 2009

epa
Office of Environmental Enforcement

Comhshaol, Oidhreacht agus Rialtas Áitiúil
Environment, Heritage and Local Government

GSI
Geological Survey of Ireland
Suirbhéireacht Gheolaíochta Éireann

Department of Communications, Energy and Natural Resources
Roinn Cumarsáide, Fuinnimh agus Acmhainní Nádúrtha

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Preface

Mining is one of the most ancient activities in the world. It has enriched many nations. However, exploration of mineral resources has often been carried out without due recognition of the effects on the environment, especially prior to the 20th century. In the latter part of the 20th century, the environmental impacts of mining became more apparent and regulators responded to this by enhancing legislation and permitting requirements.

In Ireland, environmental effects were recognised primarily at Silvermines, Tynagh and Avoca. Both the Environmental Protection Agency (EPA) and the Geological Survey of Ireland (GSI) asked the question simultaneously 'how many other sites were impacted by previous mining activity?'. At the same time, the European Commission, being aware of the potential of mining operations to impact on the environment through incidents at active mines in Spain at Aznalcóllar and in Romania at Bare Mare, introduced Directive 2006/21/EC on the management of waste from the extractive industries. Article 20 of the Directive requires Member States to produce an inventory of closed mine waste facilities. The combination of these events created the impetus for this project, the Historic Mine Sites – Inventory and Risk Classification.

The GSI, founded in 1845, has extensive data holdings on past mining activity in Ireland, including reports, drawings, maps and diagrams of mining activity. The EPA, established in 1993, has responsibility for environmental assessment, regulation and enforcement.

In this joint study, the EPA contributed financial resources and Ms Jane Brogan dedicated much of her time to the project. The GSI contributed its large databases, Head of Minerals Section, Mr Gerry Stanley, its considerable expertise in digital map compilation, its drilling unit and support staff. The EPA funding permitted the recruitment of Dr Vincent Gallagher and Ms Fionnuala Ní Mhairtín to the geochemical characterisation and investigations and Mr Phelim Lally to site safety investigations. The GSI also contributed funding for the provision of expert advice from international consultants Camp, Dresser and McKee (US) and Geoffrey Walton Practice (UK).

The work has resulted in the most comprehensive inventory of past mining activity in Ireland. All of the major sites have been characterised geochemically and all major chemical site hazards have been identified. Volume I of the report classifies the sites that present the greatest threat to human and animal health and the environment. Volume II will identify the physical hazards associated with the historic mine sites. The two volumes should be read in conjunction with each other. The work provides an important benchmark from which future investigations can be both directed and assessed. An important recommendation from the work is that monitoring of the various sites should be undertaken at varying intervals, depending on the nature of contamination of the site.

The joint project demonstrates the benefits of collaboration between government bodies and provides a template for future actions.

Dr Peadar McArdle
Director, GSI

Dr Mary Kelly
Director General, EPA

Acknowledgements

The authors would like to acknowledge the input and advice of the following individuals to the project. Their input has significantly improved the quality of the output from the project.

From the Environmental Protection Agency: **Dr Matt Crowe, Dr Mícheál Lehane, Ms Fiona O'Rourke** and **Mr George McHugh**. Student workers supported by the EPA: **Mr Philip Colgan** and **Paul Brennan**.

From the Geological Survey of Ireland: **Dr Peadar McArdle**, **Mr Tom McIntyre, Mr Padraig Connaughton, Mr John Dooley, Ms Taly Hunter-Williams.**

From the Exploration and Mining Division: **Dr Wayne Cox**.

Members of the Consultative Committee: **Mr Karl Cashen** (County and City Managers Association, Tipperary County Council), **Trevor Champ** (Central Fisheries Board), **Noel Culleton** (Teagasc), **Dr Jonathan Derham** (Environmental Protection Agency), **Dr Ben Dhonau** (Exploration and Mining Division), **Mr Kieran Fay** (Shannon River Basin District), **Dr Tessa Greally** (Health Services Executive), **Mr Pat Griffen** (Health and Safety Authority), **Mr Jim McGuirk** (County and City Managers Association, Galway County Council), **Mr Jimmy McLaughlin** (Central Veterinary Laboratory, Department of Agriculture and Food), **Mr Kevin Motherway** (Environmental Protection Agency), **Mr John O'Neill** (Department of Environment, Heritage and Local Government), **Mr John Pyne** (Exploration and Mining Division), **Ms Alice Wemaere** (Environmental Protection Agency).

Consultants: **Camp, Dresser and McKee** (USA), **Geoffrey Walton Partnership** (UK), **Land Quality Management** (UK), and **Chemical Hazards and Poisons Division, Health Protection Agency** (UK).

VOLUME I

TABLE OF CONTENTS

Tables

Figures

HISTORIC MINE SITES – INVENTORY AND RISK CLASSIFICATION

SUMMARY

Introduction

The objectives of the Historic Mine Sites – Inventory and Risk Classification (HMS-IRC) project are to carry out site investigations at priority historic mine sites in Ireland and to assess the potential risk posed by these sites to human and animal health and to the wider environment and to consider issues related to safety at each of the sites. The commodities worked at these sites included metals, for example copper or lead, industrial minerals, for example slate or barite, and coal. This volume identifies the geochemical nature of the sites. Volume II, which will be published later in the year, will identify the physical hazards on the historic mine sites. These two volumes should be read together.

One of the drivers for this project is the requirement of Article 20 of the extractive industries waste directive issued in 2006. The full title of the directive is:

> *'Directive 2006/21/EC of the European Parliament and of the Council on the management of waste from extractive industries and amending Directive 2004/35/EC'*

Article 20 requires that an inventory of closed sites be prepared. The text of the Article is as follows:

> *'Member States shall ensure that an inventory of closed waste facilities, including abandoned waste facilities, located on their territory which cause serious negative environmental impacts or have the potential of becoming in the medium or short term a serious threat to human health or the environment is drawn up and periodically updated. Such an inventory, to be made available to the public, shall be carried out by 1 May 2012, taking into account the methodologies as referred to in Article 21, if available.'*

Priority sites

The 27 sites or districts scored in this study are listed in Table 1. Five other sites were assessed but not scored because of the lack of waste material and hence they did not pose any threat to the environment. In addition some individual sites within districts were not scored for the same reason.

No.	Mine / District	No. of Sites
1	Abbeytown	1
2	Allihies	6
3	Avoca	7
4	Ballycorus	1
5	Ballyhickey (Clare Pb)	1
6	Ballyvergin (Clare Pb)	1
7	Benbulben	1
8	Bunmahon	1
9	Caim	1
10	Clements (Connemara Pb)	3
11	Clontibret (Monaghan Pb)	1
12	Connacht Coalfield	7
13	Doolin (Clare Phosphate)	1
14	Glendalough–Glendasan	8
15	Glenmalure	2
16	Glentogher (Donegal Pb)	1
17	Gortdrum	1
18	Hollyford (Tipperary)	1
19	Hope (Monaghan Pb)	1
20	Keeldrum (Donegal Pb)	1
21	Kilbricken (Clare Pb)	1
22	Leinster Coalfield	7
23	Silvermines	6
24	Slieve Ardagh Coalfield	10
25	Tassan (Monaghan Pb)	1
26	Tynagh	4
27	West Cork Cu-Ba	8

Table 1 Site districts and individual sites scored in the HMS-IRC project.

Conceptual model and scoring system

In order to carry out the fieldwork in an efficient manner a systematic methodology was needed, leading to the development of a **Conceptual Model**. This model provided a guide for data collection in the field but was not so rigid as to prevent the recording of features unique to any one site.

The EU Directive on the management of waste from the extractive industries requires that the inventory of closed and/or abandoned waste facilities be addressed using risk assessment procedures. However, it is important to note that this is NOT a risk assessment of the sites. Rather the sites have been ranked on a risk basis so as to determine a relative ranking for possible future actions.

The conceptual model uses the Source–Pathway–Receptor paradigm. This paradigm requires that each of the parameters within the model is documented, estimated, measured or recorded. The model identifies the source of any contamination, who or what is affected (the receptor), and how the source may reach the receptor (pathway).

The overall approach is to apply scores for the hazard (source), the likelihood of release, and the receptors for each waste type along each pathway at each site.

The **Hazard** of a waste pile or mine water discharge is determined by:

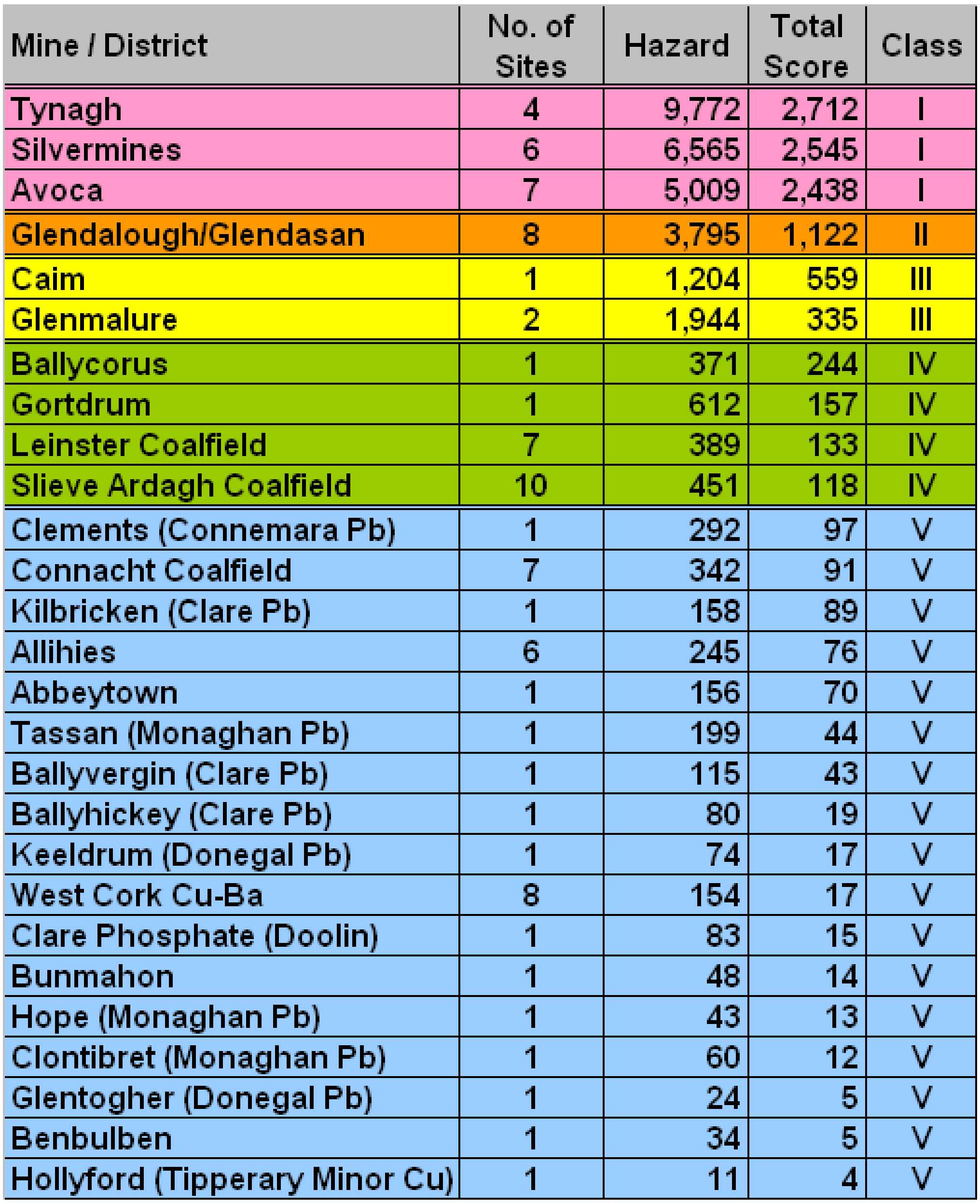
The chemical composition of the waste pile or discharge;
The relative toxicities of the different constituent elements; and
The volume (or area) of the waste pile or discharge.

The **Likelihood of release** of a contaminant from a waste pile or discharge is an assessment of whether or not there have been releases of contaminants to the environment in the past and it takes account of whether the waste pile or discharge is in any way contained in order to minimise or reduce release. In all cases any contaminant must be attributable to the mine site.

The **Receptors** are the people, animals, ecosystems or protected areas that may be affected by a release from the mine site.

Results

Mine districts and sites scored under the HMS-IRC scoring system are assigned to one of five classes, I, II, III, IV or V. Table 2 shows the final score for each district/site investigated. Of the 27 individual districts/sites listed in Table 2, three are classified in the highest class, Class I, one as Class II, two as Class III, five as Class IV and the remaining 16 as Class V.



Mine / District	No. of Sites	Hazard	Total Score	Class
Tynagh	4	9,772	2,712	I
Silvermines	6	6,565	2,545	I
Avoca	7	5,009	2,438	I
Glendalough/Glendasan	8	3,795	1,122	II
Caim	1	1,204	559	III
Glenmalure	2	1,944	335	III
Ballycorus	1	371	244	IV
Gortdrum	1	612	157	IV
Leinster Coalfield	7	389	133	IV
Slieve Ardagh Coalfield	10	451	118	IV
Clements (Connemara Pb)	1	292	97	V
Connacht Coalfield	7	342	91	V
Kilbricken (Clare Pb)	1	158	89	V
Allihies	6	245	76	V
Abbeytown	1	156	70	V
Tassan (Monaghan Pb)	1	199	44	V
Ballyvergin (Clare Pb)	1	115	43	V
Ballyhickey (Clare Pb)	1	80	19	V
Keeldrum (Donegal Pb)	1	74	17	V
West Cork Cu-Ba	8	154	17	V
Clare Phosphate (Doolin)	1	83	15	V
Bunmahon	1	48	14	V
Hope (Monaghan Pb)	1	43	13	V
Clontibret (Monaghan Pb)	1	60	12	V
Glentogher (Donegal Pb)	1	24	5	V
Benbulben	1	34	5	V
Hollyford (Tipperary Minor Cu)	1	11	4	V

Table 2 HMS-IRC scores and classification.

Conclusions

1. Lead (Pb) is the single most important contaminant on Irish mine sites in terms of its toxicity, the concentration in which it is found, the quantity of Pb-enriched material, and its geographical dispersion on and around mine sites. Mine districts and sites most severely contaminated by Pb include Caim, Clare Pb Mines, Glendalough, Silvermines and Tynagh.

2. The sites of the former ore processing plants at Gortdrum, Silvermines and Tynagh are significantly contaminated by heavy metals. In all three cases, the sites are being utilised by new businesses. Contaminants include not only the metals produced from the site, such as lead, zinc (Zn) and copper (Cu),

but also minor constituents of the ore that have become concentrated during processing. These minor constituents include arsenic (As) and mercury (Hg), which have been found in concentrations exceeding 1,000 mg/kg.

3. Concentrations of Cu in stream sediment are very high downstream of some sites, notably Allihies, Avoca and at Glandore and Ballycummisk in West Cork. The potential for impact on the aquatic ecosystem may warrant further investigation. The total Cu in surface waters downstream of mines indicates some impact on water chemistry from mine discharges. However, numerous upstream surface-water samples and even some groundwater samples also contain copper in excess of regulatory levels, suggesting that mine waste is just one of a number of sources of elevated Cu in surface water and groundwater.

4. High concentrations of Zn in solid mine waste pose no threat to human health.

5. High concentrations of Zn in stream sediments and/or downstream surface waters at Avoca, Glendalough, Silvermines and Tynagh pose a risk to livestock and the aquatic environment.

6. Nickel (Ni) is enriched in mine water, downstream surface water and stream sediments at some sites in the three coalfields investigated. It is also found in excess of the Draft EC Surface Water Regulations downstream of mines such as Avoca and Tynagh.

7. Issues of concern have been identified at a number of sites that warrant further investigation or action. These sites include: **Abbeytown** (Pb- and As-rich leachate from the tailings pond); **Avoca** (measured Pb concentrations >1% in solid waste); **Ballycorus** (measured Pb concentrations >1% in solid waste); **Caim** (measured Pb concentrations >5% in solid waste); **Clare Lead District** (measured Pb concentrations >20% in solid waste); **Glendalough** (measured Pb >10% in solid waste); **Gortdrum** (measured concentrations of Hg (>0.5%) and As (>1%) in solid waste); **Silvermines** (measured concentrations of Pb (>2%) and As (>0.1%) were detected in

solid waste); and **Tynagh** (measured concentrations of Pb >2%, As >0.1% and Hg >0.1% in solid waste and a cadmium-rich discharge from a waste heap.

Recommendations

1. The Local Authorities should be advised of all issues of environmental concern falling within their functional area. Other authorities such as the Health Services Executive (HSE), the Health and Safety Authority (HSA) and Teagasc may also need to be informed of specific relevant issues.

2. Sites assigned to Class I should have a full environmental risk assessment carried out, if not already undertaken. Ongoing monitoring should be carried out at these sites.

3. The site assigned to Class II should have general monitoring of most or all waste piles, discharges or stream sediments carried out on an annual basis.

4. Sites assigned to Class III should have specific monitoring of particular waste piles, discharges or stream sediments on a biennial basis.

5. Sites assigned to Class IV should have specific monitoring of particular waste piles, discharges or stream sediments on a five-yearly basis.

6. Sites assigned to Class V do not require any specific monitoring.

7. A scientific-based monitoring scheme should be developed appropriate to each of the site classes, incorporating relevant expertise from the Environmental Protection Agency (EPA) and the Geological Survey of Ireland (GSI). Funding needs to be allocated for this task. The GSI could carry out such a monitoring programme.

8. An inventory of wastes from the quarry sector should be carried out to comply fully with the Directive on the management of waste from the extractive industries.

Historic Mine Sites

Inventory and Risk Classification

Non-technical Summary

Geological Survey of Ireland
Suirbhéireacht Gheolaíochta Éireann

epa
Office of Environmental Enforcement

Department of Communications, Energy and Natural Resources
Roinn Cumarsáide, Fuinnimh agus Acmhainní Nádúrtha

Comhshaol, Oidhreacht agus Rialtas Áitiúil
Environment, Heritage and Local Government

2009

For a complete understanding of the work that was carried out the reader is referred to the full report which is available on the following websites:

www.gsi.ie

www.epa.ie

The Historic Mine Sites – Inventory and Risk Classification is a joint project carried out by the Geological Survey of Ireland and the Environmental Protection Agency.

Preface

Mining is one of the world's most ancient of activities. It has enriched many a nation. However, exploration of mineral resources has often been carried out without due recognition of the effects on the environment, especially prior to the 20th century. In the latter part of the 20th century the environmental impacts of mining became more apparent and regulators responded to this by enhancing legislation and permitting requirements.

In Ireland, environmental effects were recognised primarily at Silvermines, Tynagh and Avoca. Both the Environmental Protection Agency and the Geological Survey of Ireland asked the question simultaneously 'how many other sites were impacted by previous mining activity?' At the same time the European Commission, being aware of the potential of mining operations to impact on the environment through incidents at active mines in Spain at Aznalcóllar and in Romania at Bare Mare, introduced Directive 2006/21/EC on the management of waste from the extractive industries. Article 20 of the Directive requires Member States to produce an inventory of closed mine waste facilities. The combination of these events created the impetus for this project, the Historic Mine Sites – Inventory and Risk Classification.

The work has resulted in the most comprehensive inventory of past mining activity in Ireland. All of the major sites have been characterised geochemically and all major site hazards have been identified. The report classifies the sites which present the greatest threat to human and animal health and the environment. The work provides an important benchmark from which future investigations can be both directed and assessed. An important recommendation from the work is that monitoring of the various sites should be undertaken at varying intervals depending on the nature of contamination of the site.

Dr. Peadar McArdle	Dr. Mary Kelly
Director, GSI	Director General, EPA

CONTENTS

1. What is this project about?

This project sets out to:

- Make a list of the closed mine sites in Ireland.
- Identify the features and structures related to mining at each of the closed mine sites.
- Identify any waste related to mining at each of the closed mine sites.
- Describe the waste at each of the closed mine sites.
- Classify the closed mine sites in terms of the potential threat they pose to humans, animals and the environment.

The EPA (Environmental Protection Agency) and the DCENR (Department of Communications, Energy and Natural Resources) wished to find out how many closed mines there were in the country and what potential threat they posed to human and animal health, and the environment. At the same time that the project was being developed the European Union was drafting a Directive on 'waste from the extractive industries'. This became known as **Directive 2006/21/EC of the European Parliament and of the Council on the management of waste from extractive industries and amending Directive 2004/35/EC.** One of the Articles (number 20) of this Directive concerns the preparation of an **Inventory of closed waste facilities.** The article requires each Member State of the EU to draw up an inventory of closed waste facilities, including abandoned waste facilities which

An abandoned aerial ropeway at Benbulben, Co. Sligo cause serious negative environmental impacts or have the potential of becoming, in the medium or short term, a serious threat to human health or the environment. Therefore the goals of both the EPA/DCENR and the EU would be met at the same time by carrying out this project.

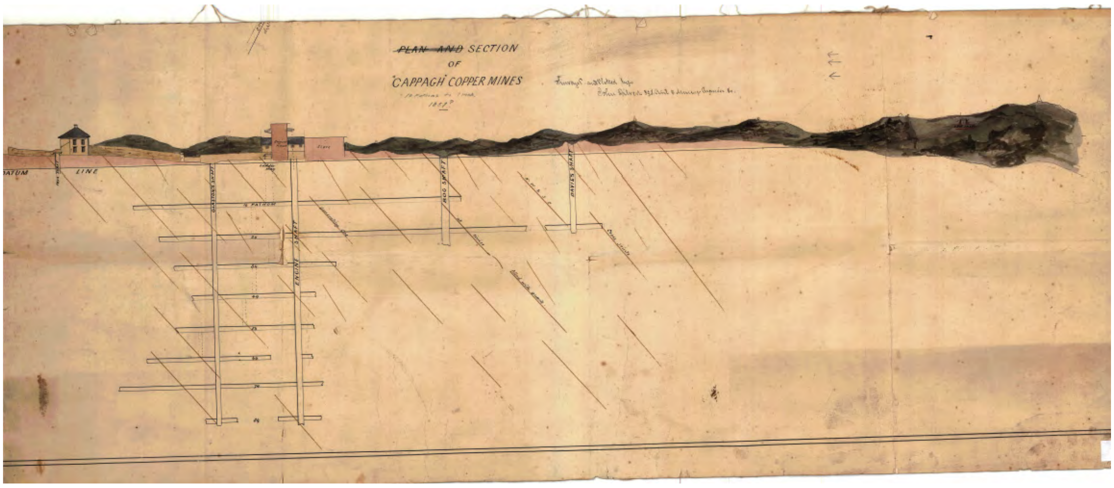
The EU makes the distinction between a site that is closed, meaning that mining has ceased but the person who operated the mine still exists and is known and a site that is abandoned, which means that mining has ceased and that the operator is no longer known. This latter case can easily be envisaged where mining took place in earlier times, for example the Bronze Age (usually dated at 2000BC to 500BC in Ireland).

This project is not a full risk assessment of the closed mine sites. Risk assessment is a process used to assess and manage risk associated with hazardous situations of any sort, not just in mining areas.

2. **Who carried out the project?**

The project was carried over a three year period from 2006 to 2008. It was led by the GSI (Geological Survey of Ireland) with assistance from the EPA (Environmental Protection Agency) and EMD (the Exploration and Mining Division of DCENR). GSI hired specialist geochemists, environmentalists and mining geologists to assist in the carrying out of the work.

GSI is the National Earth Science Agency and is responsible for providing geological advice and information. GSI is the location of records of ancient and modern mines in Ireland. These records are an important data source for information on mining. The EPA has responsibilities for a wide range of licensing, enforcement, monitoring and assessment activities associated with environmental protection. EMD formulates policy for the minerals sector and regulates exploration and mining in Ireland.



An historic mine drawing showing underground workings at Cappagh, Co. Cork.

3. What past mining activity took place in Ireland?

Mine waste at Glenmalure, Co. Wicklow

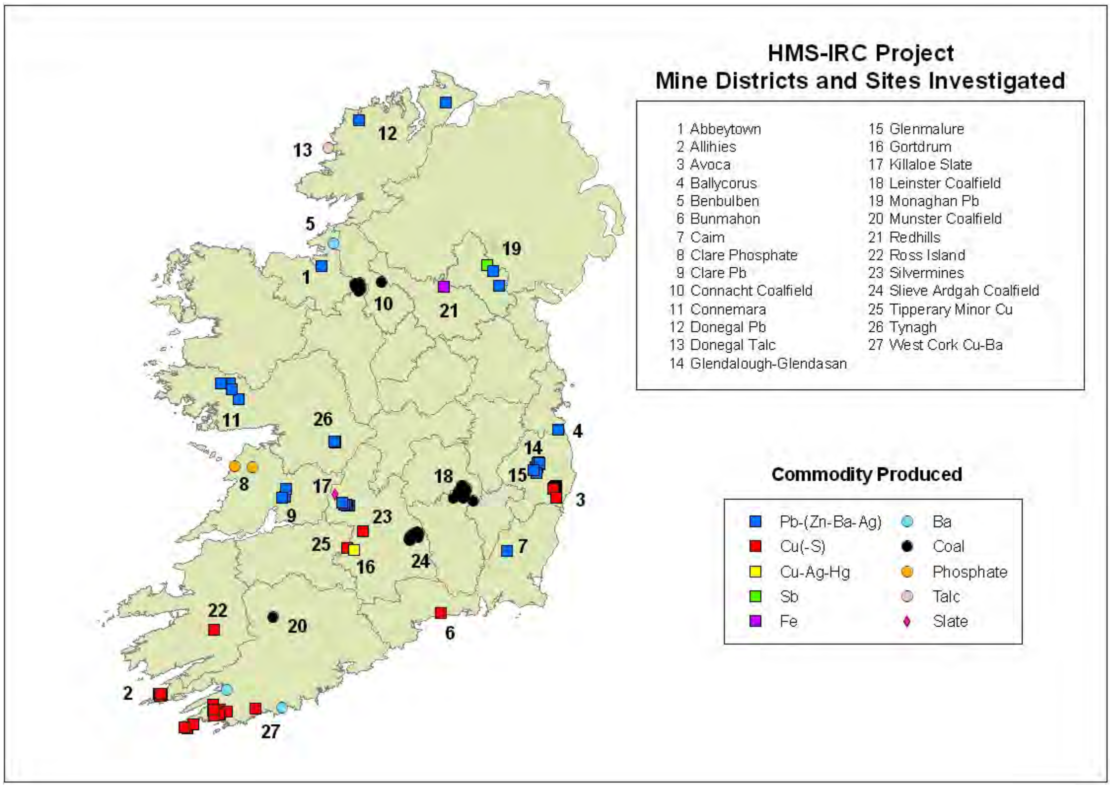
Ireland has a rich mining history dating back to the Bronze Age. GSI's minerals localities database, known as Minlocs, has over 5,000 entries which include both metallic and non-metallic commodities. Of these entries almost 1,500 are for metallic minerals and over 450 are described as mines.

There are numerous types of mineral deposits and Ireland has examples of many of them that have been worked over the years. Of the 450 mines listed in Minlocs some 220 had significant production of metals (for example lead (Pb) or copper (Cu)), non-metals (for example, gypsum used in the manufacture of plaster) and coal. Many of the deposits that are described as mines were often trials – an excavation into the ground exploring for minerals. A map showing the main mineral deposits in Ireland is shown on the next page.

The closed mines can be classified according to the mineral worked and the time in which they operated:

1. Underground and surface mining operations for coal since the 18th century.
2. Workings for non-metals prior to the 1920s.
3. Metal bearing veins worked for the most part prior to the 20th century – but some workings operated into the 1950s.
4. Modern workings for non-metals (latter half of 20th century).

5. Modern metal operations mainly from the latter half of the 20th century.



Map of Ireland showing various mineral deposits

Coal Mines

Coal deposits in Ireland date from the Upper Carboniferous (approximately 320 million years ago) and occur in four areas – the Leinster Coalfield straddling Counties, Kilkenny, Laois and Carlow; the Slieve Ardagh Coalfield on the border of Counties Kilkenny and Tipperary; the Kanturk Coalfield in northwest County Cork and the Connaught Coalfield straddling Counties Leitrim, Roscommon, Sligo and Cavan. Most coal mining operations in Ireland started during the 18th century and were worked intermittently into the 20th century, some up until the 1990s.

Vein Operations

Up until the start of the 20th century most mining operations in Ireland worked veins of minerals containing metal. Most of these were for copper (Cu) or lead (Pb) while a smaller number were worked for either iron (Fe) or zinc (Zn). Silver

(Ag) was commonly recovered from the lead veins. The veins occurred in a number of settings:

1. Lead (and silver) veins associated with granites, e.g. Glendalough District, Co. Wicklow.
2. Copper veins within volcanic rocks, e.g. Bunmahon, Co. Waterford.
3. Copper veins within sandstones, e.g. Allihies, Co. Cork.
4. Lead (and silver) veins in limestones, e.g. Kilbricken, Co. Clare.
5. Iron veins associated with volcanic rocks, e.g. Kilbride, Co. Wicklow.

Modern Mining

Modern mining operations in Ireland commenced in the 1960s with the opening of the Tynagh mine in Co. Galway. Also at this time the historic mine at Avoca commenced large scale production using modern mining techniques. Mining activity at Avoca was intermittent from about 1720 until 1982. Extensive development had occurred at Avoca in the 18th and 19 Centuries using relatively primitive means that focussed on higher grade ore. Other examples of mechanised mining include Silvermines and Gortdrum, both in Co. Tipperary and three metal mines continue to operate today – Navan, Lisheen and Galmoy (although Galmoy is due to close in 2009).

The East Avoca Open Pit, Co. Wicklow

There were or are also a number of modern mining operations for industrial minerals, in particular for barytes and gypsum.

4. What is mine waste?

Mining, like any industry, produces waste. Mineral deposits occur within rock that, for the most part does not contain the valuable minerals. However, the extraction process requires the removal (or mining) of both the valuable mineral (known as ***ore*** in the mining industry) and the non-valuable rock that contains it (known as ***waste*** by the mining industry). It is necessary to separate the two and it is the non-valuable part or waste that is stored at the closed mining sites.

The mining industry produces two principal types of waste. The first has the consistency of a fine powder and in the mining industry is called ***tailings***. For this reason it is usually transported as slurry, that is, it is a mixture of the rock or mineral powder and water. This slurry is pumped, in pipes, to an area where it can not flow.

This photograph shows the two types of waste from the mining industry. In the foreground is a rehabilitated tailings facility. The background is an example of a waste heap. The photograph is from the closed Gortdrum mine in Co. Tipperary.

This is often referred to as a ***tailings management facility*** or ***tailings dam.*** A tailings dam structure is like a reservoir that contains water – only in the case of a tailings dam the contained material is tailings or mine waste. The second waste type from the mining industry consists of lumps of broken rock. The size of the lumps can vary from approximately 2mm to over 2m. Such materials are commonly heaped up forming mounds with shapes varying from pyramids to long berms. They are often referred to as ***spoil tips*** or ***heaps*** in the industry.

There is also waste water which comes from former mine sites. Water may flow from old entrances to mines (called ***adits***) or seeps from heaps. This water may then flow to streams or rivers, or to the sea in coastal areas and cause contamination to those streams or rivers or seas and affect any fish life or other habitat within them.

Above: Road Adit, West Avoca, Co. Wicklow

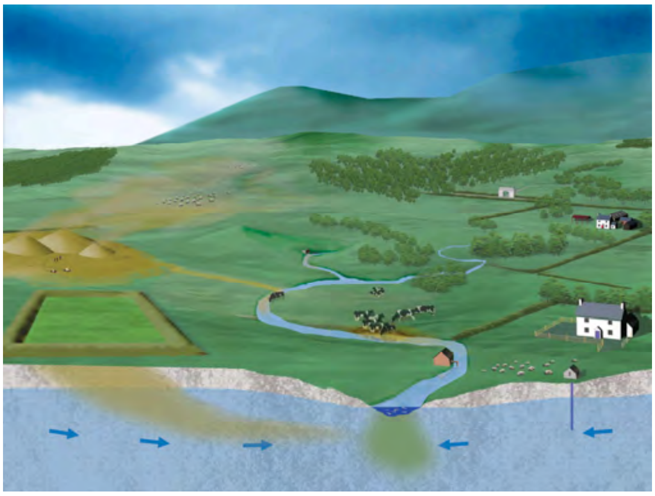
Right: Seep from Abbeytown Tailings, Co. Sligo

5. How was the project carried out?

This review involved an examination of mine records in the GSI, an examination of reported incidents from historic mine sites in Ireland, and a review of available documents on them. This formed the basis for planning the work at each of the sites. It was quickly realised that in order to carry out the field work that a systematic method was needed and the optimum approach would be to develop a **Conceptual Model**. This would guide the data collection in the field but would not be so rigid as to prevent the recording of features unique to any one site.

The Historic Mine Sites – Inventory and Risk Classification Project addresses the EU Directive on Wastes from the Extractive Industries requirement for an inventory of waste facilities and the national need for data at closed and/or abandoned mine sites. Both needs have been addressed on a risk basis. However, it is important to note that this is NOT a risk assessment of the sites. Rather the sites have been ranked so as to determine a relative ranking for future actions.

Conceptual Model

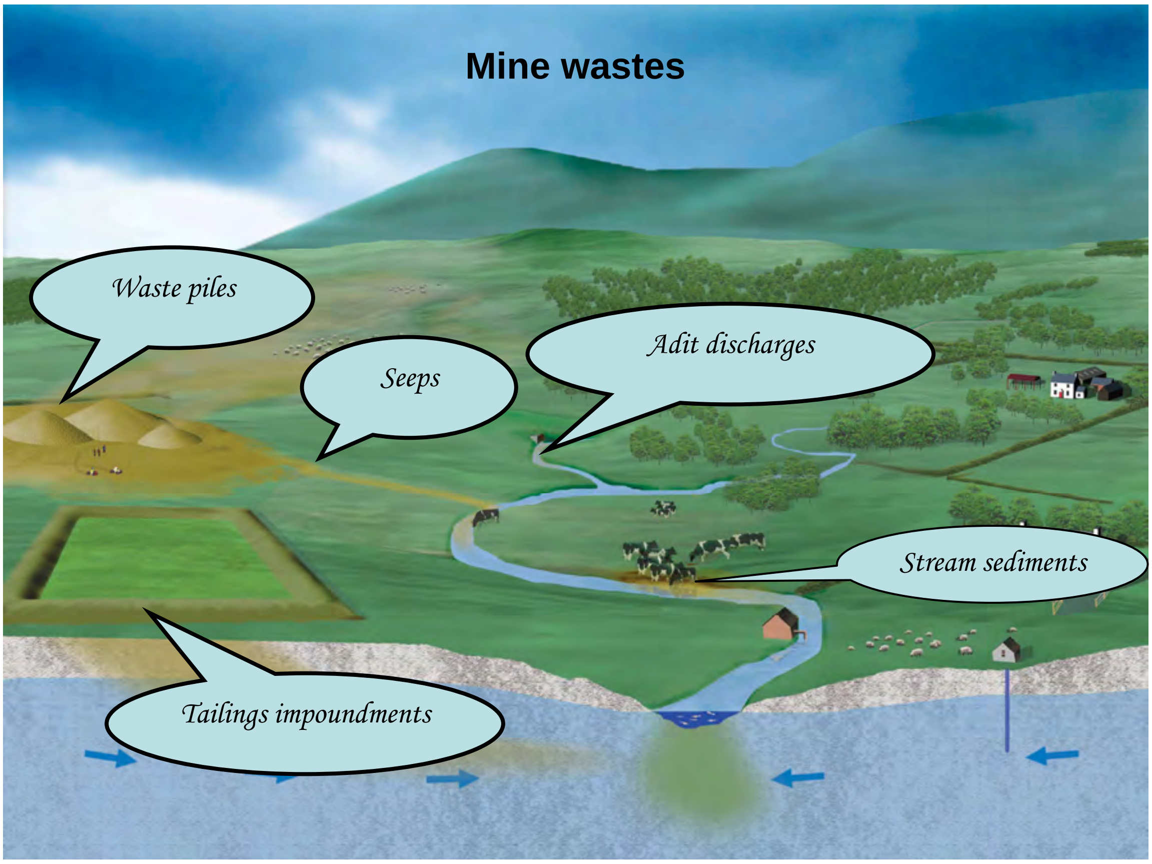


Contaminant risks come from waste facilities on the site. A common approach taken by environmental scientists in assessing hazard at a site is to use what is known as the Source – Pathway – Receptor Paradigm. The paradigm requires that each of the parameters within the model are documented, estimated, measured or recorded. The Conceptual Model to describe this is illustrated pictorially above.

The model identifies the source of any contamination; identifies who or what is affected (the receptor); and identifies how the source may reach the receptor (pathway). A contaminant linkage occurs when a source, pathway and receptor are demonstrated to occur together resulting in the receptor being connected to the source *via* a particular pathway. The conceptual model identifies all the sources, pathways and receptors. The collection of field data, observations and estimates confirms whether a linkage exists between the source and receptor and conclusions are drawn about the potential risks caused by the source of contamination.

Sources of contaminants

Sources are the origin of contaminants that may issue from an historic mine site. The cause or source of the contamination is identified as well as its location. The possible sources of contamination are listed on the next page and illustrated in the diagram below.



Liquid (water)

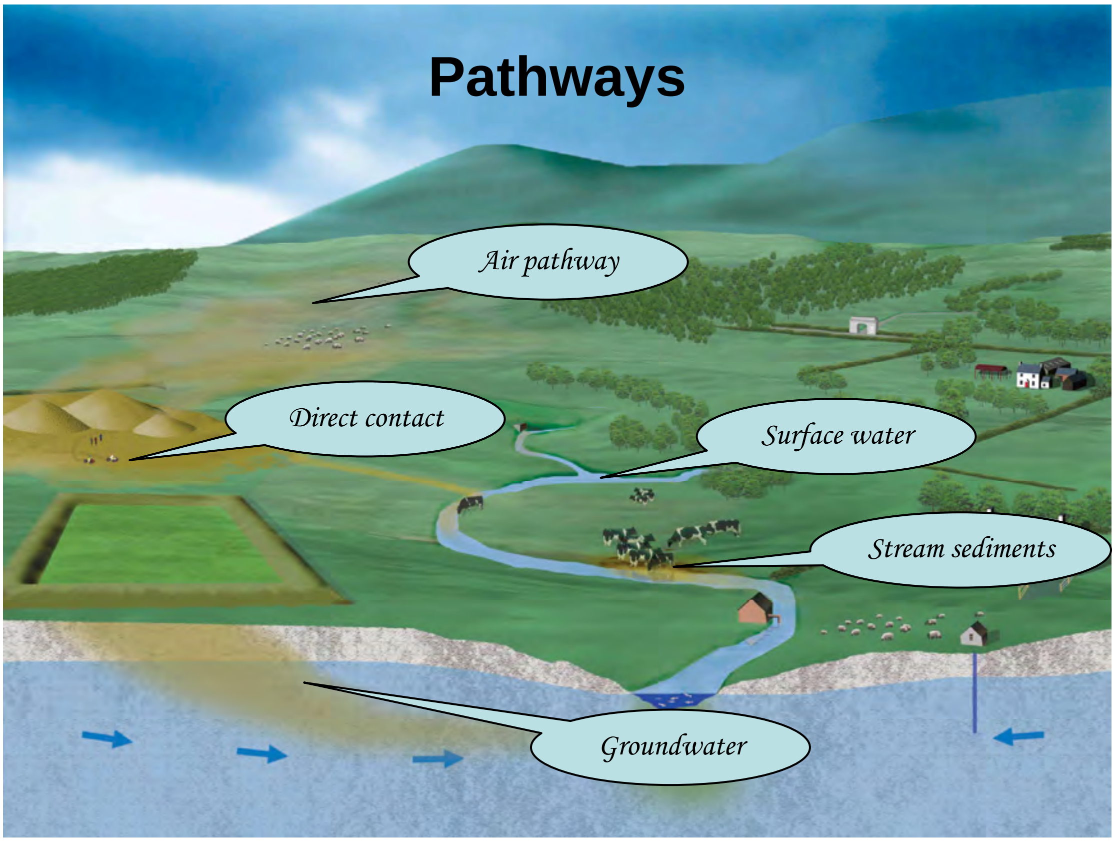
  - Adit discharges
  - Seeps from waste heaps

Solids

  - Waste piles
  - Tailings impoundments
  - Stream sediments

Pathways

The pathway is the route the source takes to reach the receptor. The five pathways for the Conceptual Model are illustrated in the diagram and listed below.



Groundwater

Surface water

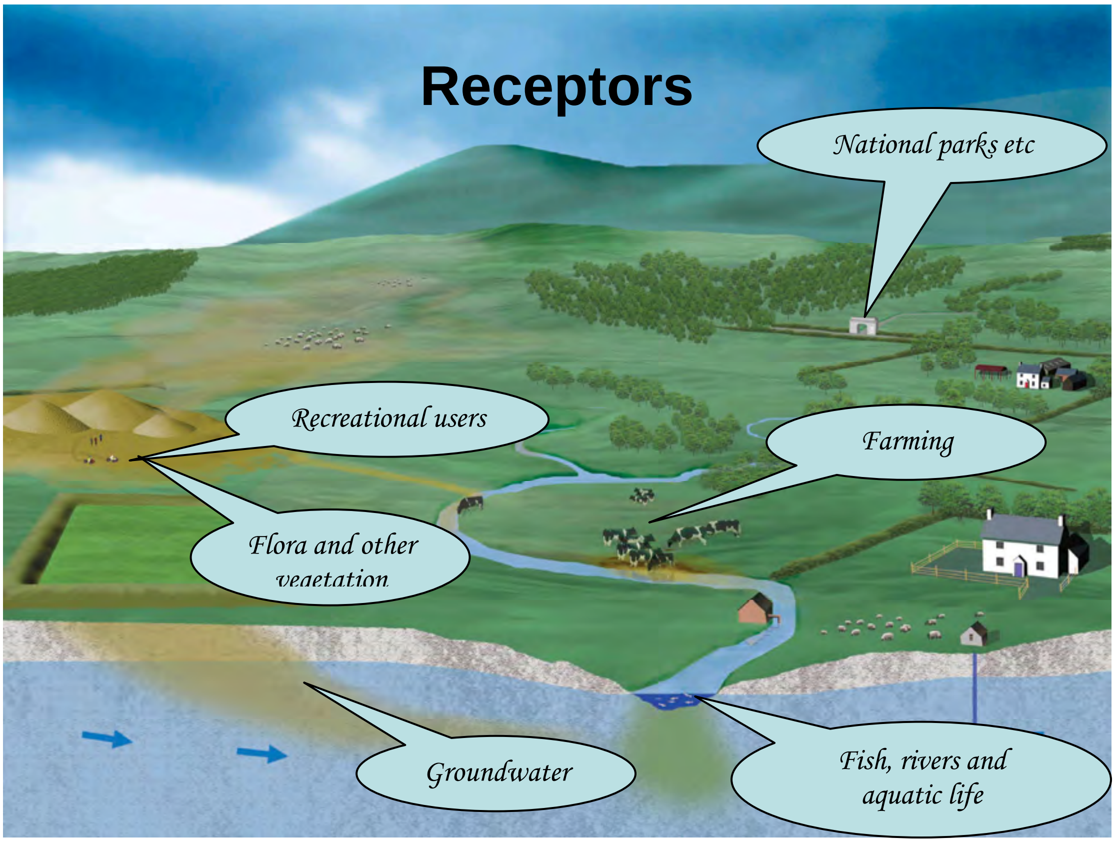
Air pathway

- Direct contact – solid waste piles
- Direct contact – stream sediments

Receptors

Receptors are those elements of the paradigm that are affected by the potential contamination emanating from the various sources via the different pathways. If contamination is to cause harm, it must reach a receptor. A receptor is any person, animal, plant, eco-system, water system, protected site, or property. Receptors, in the context of the Historic Mine Site project include the following which are also illustrated on the diagram on the next page:

- People
  - Local inhabitants
  - Workers
  - Visitors to the site (authorised or otherwise)
- Farm animals
  - Livestock
- Ecosystem / Aquatic
  - Rivers
  - Estuaries
  - Groundwater
- Protected areas
  - National parks
  - National Heritage Areas (NHAs)
  - Special Protection Areas (SPAs)
  - Special Areas of Conservation (SACs)
  - Nature Reserves



Historic Mine Sites – Inventory and Risk Classification Scoring System

Each of the parameters of the model (Source – Pathway – Receptor) is scored according to the observations made in the field and other information available to the project. The scores are added to give a final score which is then assigned a category according to the table below.

Class	Score	Description
I	>2,000	Sites which should have a full risk assessment carried out. Ongoing monitoring should be carried out.
II	1,000 – 2,000	Sites requiring general monitoring of most or all waste piles, discharges or stream sediments on an annual basis.
III	300 – 1,000	Sites requiring general monitoring of most or all waste piles, discharges or stream sediments on a biannual basis.
IV	100 – 300	Sites requiring specific monitoring on particular waste piles, discharges or stream sediments on a five yearly basis.
V	<100	Site not requiring any specific monitoring.

6. What sites were classified?

In all 82 sites were scored resulting in the classification of 27 individual sites or districts. Examples of individual sites include Ballycorus, Co. Dublin and Gortdrum, Co. Tipperary while examples of districts include the Leinster Coalfield and West Cork. The accompanying table provides a list of the sites and the minerals worked at them scored in this project.

Cronebane Open Pit, Avoca, Co. Wicklow.

Mine name	**County**	**Commodity(ies) extracted**
1. Abbeytown	Sligo	Pb, Zn, Ag
2. Allihies	Cork	Cu
3. Avoca	Wicklow	Cu, pyrite
4. Ballycorus	Dublin	Pb, Ag
5. Ballyhickey	Clare	Pb, Ag
6. Ballyvergin	Clare	Pb, Cu, Ag
7. Benbulben	Sligo	Barite
8. Bunmahon	Waterford	Cu
9. Caim	Wexford	Pb, Cu
10. Clements	Galway	Pb
11. Clontibret	Monaghan	Sb
12. Connacht Coalfield	Cavan, Leitrim, & Roscommon	Coal
13. Doolin	Clare	Phosphate
14. Glendalough/Glendasan	Wicklow	Pb
15. Glenmalure	Wicklow	Pb
16. Glentogher	Donegal	Pb
17. Gortdrum	Tipperary	Cu, Hg, Ag
18. Hollyford	Tipperary	Cu
19. Hope	Monaghan	Pb, Ag
20. Keeldrum	Donegal	Pb
21. Kilbricken	Clare	Pb
22. Leinster Coalfield	Carlow, Laois, & Kilkenny	Coal
23. Silvermines	Tipperary	Zn, Pb
24. Slieve Ardagh Coalfield	Kilkenny & Tipperary	Coal
25. Tassan	Monaghan	Pb, Ag
26. Tynagh	Galway	Zn, Pb, Ag, barite
27. West Cork	Cork	Cu, barite

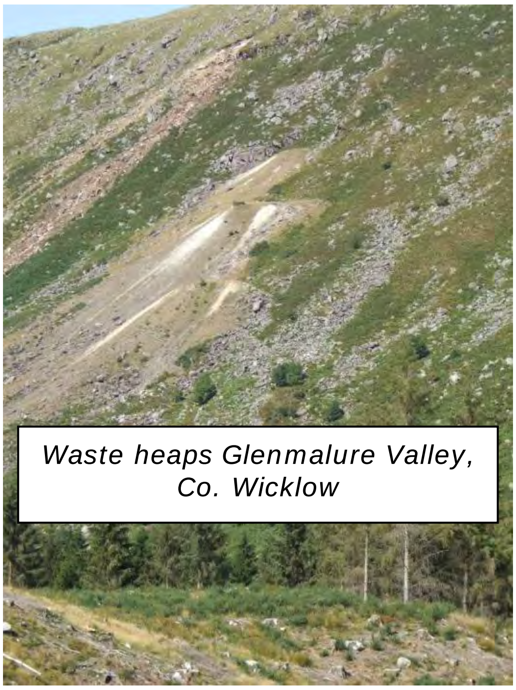
7. How do we know if a site has been impacted?

Mine waste can affect the environment and ultimately human and animal health by contaminating surface water, groundwater, the soil, and stream sediments. These media can become polluted by the release of contaminant elements from the mine waste. Such elements include the metal(s) for which the mining was carried out for in the first instance and minor elements associated with the ore minerals but which were not the goal to recover from the mining operation. Examples of the former would be lead (Pb), copper (Cu), zinc (Zn) and silver (Ag) while examples of the latter would be arsenic (As), cadmium (Cd), antimony (Sb) and mercury (Hg).

Ireland, the European Union and other countries have developed standards or guidelines for the different media that can be affected by these various contaminants. Where Irish standards or guidelines exist we have used these. Where such standards do not exist we have used any European values. We have also drawn upon standards and guidelines from the United Kingdom, Holland, the United States of America and Canada where there were no Irish or European values.

Allihies, Coom engine house.

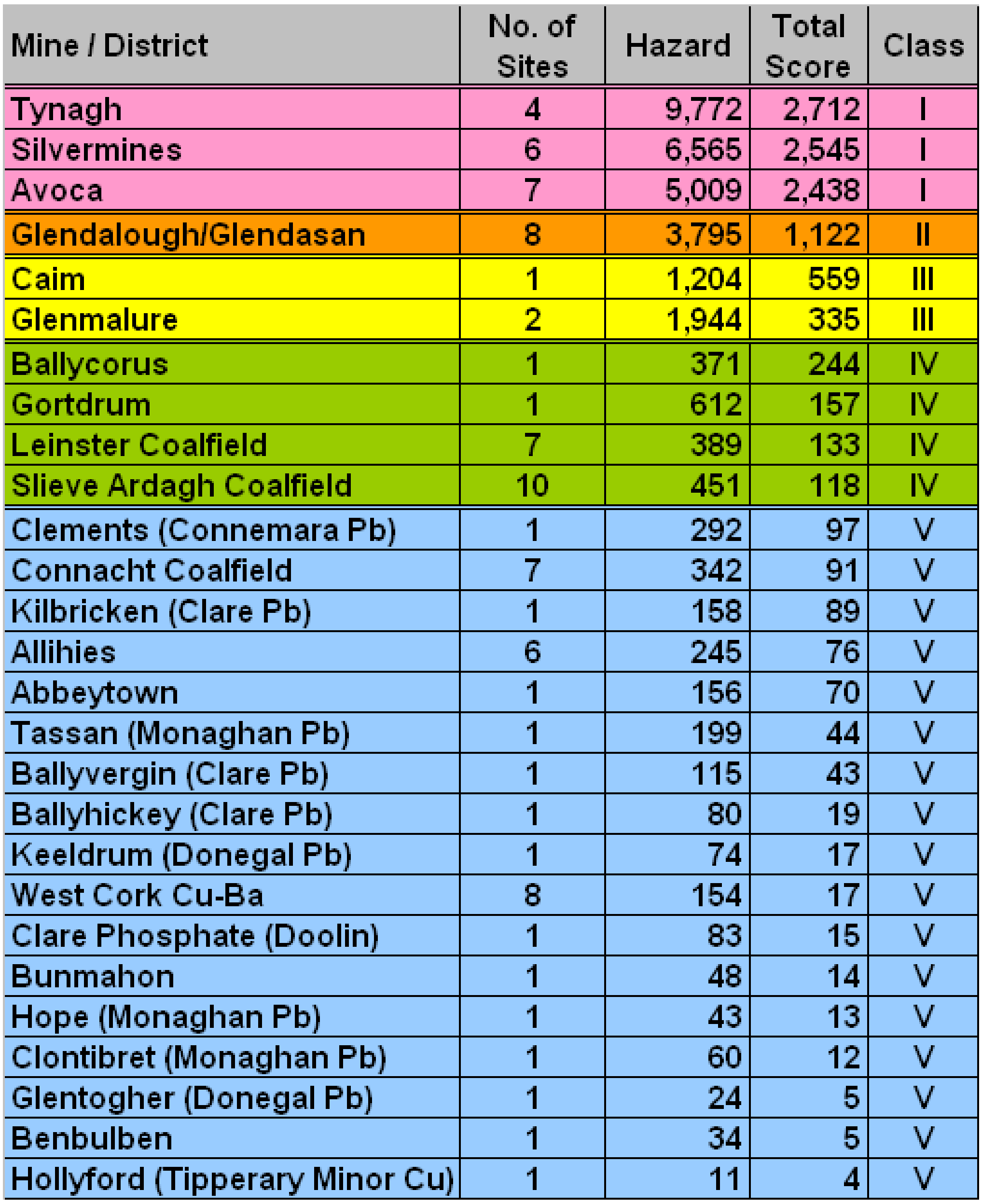
8. What are the results?



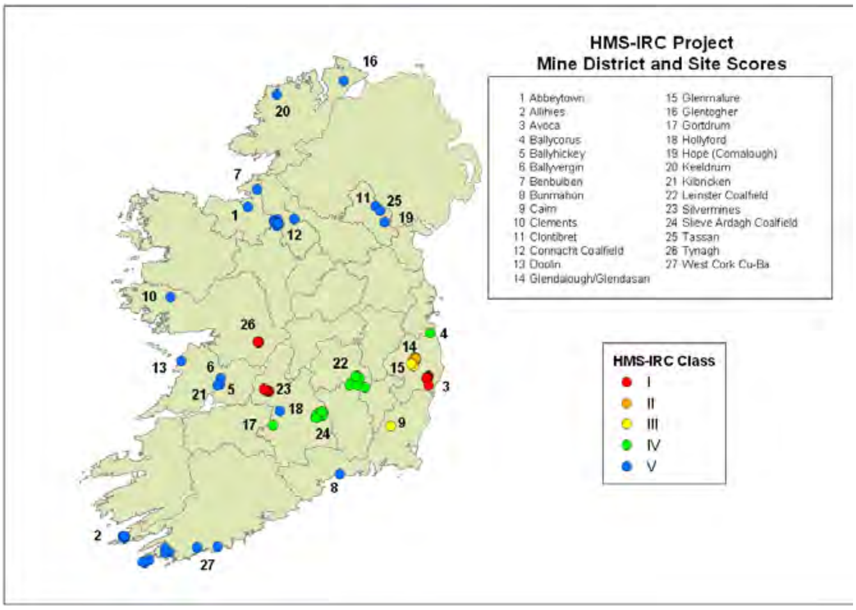
Waste heaps Glenmalure Valley, Co. Wicklow

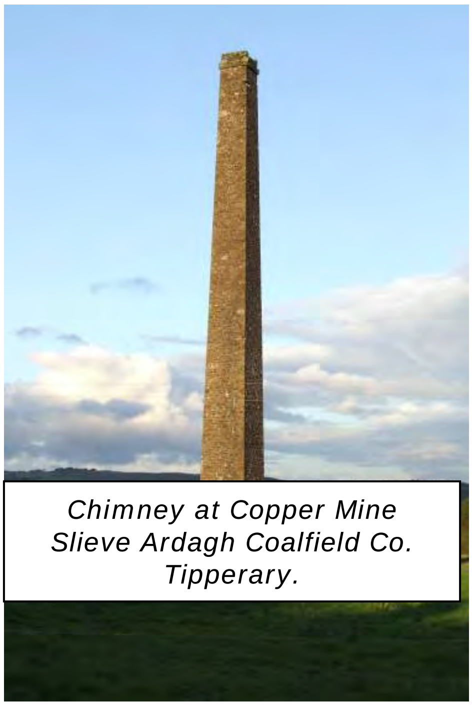
Of the 27 individual districts/sites listed in the Table on the next page, three are classified in the highest Class I, one as Class II, two as Class III, four as Class IV the remaining 17 as Class V. The three Class A mine districts/sites are Silvermines, Tynagh and Avoca. All three districts were operated in the last century as modern, mechanized mines that produced large volumes of ore and waste. Volume and area of waste are important contributors to site scores in the HMS-IRC scoring system. However, large volume and area of waste are not sufficient in themselves to place a mine district or site in the highest category. The waste must also have significant concentration of contaminants with high relative toxicity. In the case of the three Class I sites, high Pb concentrations, in particular, contribute significantly to the total sites scores. In contrast, other mine districts and sites that were operated in the 20th century and that have very large volumes of waste, such as Gortdrum and the three coalfields, have relatively low rankings because none has significant concentrations of high-relative-toxicity contaminants.

Many of the 18th and 19th century sites produced much lower volumes of waste because mining was essentially manual and focused on relatively high-grade, low-volume ore. Thus, although their waste can have very high concentrations of high-relative-toxicity contaminants, especially Pb, these sites generally have relatively low ranking because of their small volumes of waste. The exception is the Glendalough-Glendasan district (Class II) which contains numerous sites spread over an extensive area.



Mine / District	No. of Sites	Hazard	Total Score	Class
Tynagh	4	9,772	2,712	I
Silvermines	6	6,565	2,545	I
Avoca	7	5,009	2,438	I
Glendalough/Glendasan	8	3,795	1,122	II
Caim	1	1,204	559	III
Glenmalure	2	1,944	335	III
Ballycorus	1	371	244	IV
Gortdrum	1	612	157	IV
Leinster Coalfield	7	389	133	IV
Slieve Ardagh Coalfield	10	451	118	IV
Clements (Connemara Pb)	1	292	97	V
Connacht Coalfield	7	342	91	V
Kilbricken (Clare Pb)	1	158	89	V
Allihies	6	245	76	V
Abbeytown	1	156	70	V
Tassan (Monaghan Pb)	1	199	44	V
Ballyvergin (Clare Pb)	1	115	43	V
Ballyhickey (Clare Pb)	1	80	19	V
Keeldrum (Donegal Pb)	1	74	17	V
West Cork Cu-Ba	8	154	17	V
Clare Phosphate (Doolin)	1	83	15	V
Bunmahon	1	48	14	V
Hope (Monaghan Pb)	1	43	13	V
Clontibret (Monaghan Pb)	1	60	12	V
Glentogher (Donegal Pb)	1	24	5	V
Benbulben	1	34	5	V
Hollyford (Tipperary Minor Cu)	1	11	4	V





Chimney at Copper Mine Slieve Ardagh Coalfield Co. Tipperary.

9. What are the conclusions and recommendations?

The main conclusions arising from this work are:

1. Ireland possesses an abundance of historic mine sites dating from the Bronze Age to the late 20th century.
2. The mineral deposits produced a wide range of commodities.
3. The Class I Sites are Silvermines, Tynagh and Avoca.
4. The Class II Sites is Glendalough-Glendasan
5. The Class III Sites are Caim and Glenmalure.
6. The Class IV Sites are Ballycorus, Gortdrum, the Leinster Coalfield and the Slieve Ardagh Coalfield.
7. The Class V Sites are Clements, the Connacht Coalfield, Kilbricken, Allihies, Abbeytown, Tassan, Ballyvergin, Ballyhickey, Keeldrum, West Cork Cu-Ba, Clare Phosphate (Doolin), Bunmahon, Hope, Clontibret, Glentogher, Benbulben and Hollyford.
8. The following sites have specific issues of concern which should be addressed:

   a. Abbeytown

   Pb- and As-rich leachate from the tailings pond enters the estuary at Ballysadare Bay.

   b. Avoca

   Measured Pb concentrations exceed 1% in solid waste at Connary, a site where sheep graze.

c. Ballycorus

Measured Pb concentrations exceed 1% in solid waste at Ballycorus in an area popular with walkers and horse riders.

d. Caim

Measured Pb concentrations exceed 5% in a solid waste heap at Caim, used by quad bikers and others.

e. Ballyvergin

Pb concentrations in excess of 20% were measured in fine-grained mine waste in an area used by cattle for feeding at Ballyvergin.

Old powder house (explosive store) at Earlshill, Slieve Ardagh Coalfield, Co. Tipperary

f. Glendalough - Glendasan

i. Measured Pb concentrations exceed 10% in solid waste at the Hero Processing site, at the head of the Glendasan valley. The site is very popular with tourists.

ii. Measured Pb concentrations exceed 10% in solid waste at Ballinafunshoge, Glenmalure, a site popular with quad bikers.

iii. High concentrations of Pb and Zn were measured in stream sediments in Glendasan and Glenealo Rivers downstream of the mines.

g. Gortdrum

Very high concentrations of Hg (>0.5%) and As (> 1%) were measured in solid waste at the site of former processing plant, now the site of an active business. The contaminated material is, however, contained on the site but may be a risk to on-site workers.

h. Silvermines

High concentrations of Pb (>2%) and As (>0.1%) were measured in solid waste at the site of the former processing plant in Garryard, now the site of an active business.

i. Tynagh

High concentrations of Pb (>2%) and As (>0.1%) were measured in solid waste at the site of the former processing plant, now the site of an active business. A Cd-rich discharge from a waste heap crosses grazing land and seeps underground, potentially affecting groundwater.

Discharge from Deep Adit, East Avoca, Co. Wicklow.

The principal recommendations are:

1. Local Authorities and other relevant agencies, such as the Health Services Executive, Health and Safety Authority and Teagasc should be advised of all issues falling within their specific areas of responsibility.
2. Sites classified as Class I, from a contaminant point of view should have a full environmental risk assessment carried out, if not already undertaken. A full study has been undertaken at the Avoca site and remediation work is currently underway at Silvermines. Ongoing monitoring should be carried out at these sites.

3. Sites classified as Class II, from a contaminant point of view, should have general monitoring of most or all waste piles, discharges or stream sediments carried out on an annual basis.
4. Sites classified as Class III, from a contaminant point of view should have specific monitoring on particular waste piles, discharges or stream sediments on a biennial basis.
5. Sites classified as Class IV, from a contaminant point of view should have specific monitoring on particular waste piles, discharges or stream sediments on a five yearly basis.
6. Sites classified as Class V do not requiring any specific monitoring.
7. A scientific based scheme of monitoring should be developed appropriate to each of the site classes incorporating relevant expertise from the EPA and GSI.
8. In order to comply fully with the Directive an inventory of closed aggregate and stone operations (quarries and pits) should be carried out.

Crookhaven, Co. Cork – magazine.

The Creevelea iron furnace, Creevelea, Co. Leitrim.

Appendix 5 Full Site Reports

The link below brings you to all the detailed site reports for all of those mines visited and scored in this project.
http://gis.epa.ie/ENVisionMines/reports/MinesPg1_app5Index.htm

Appendix 6 HMS-IRC Scoring Sheets

The link below brings you to all the individual scoring sheets for each mine site that was visited and scored.
http://gis.epa.ie/ENVisionMines/reports/MinesPg2_app6Index.htm

CHAPTER 1

Introduction

1.1 Background

The Historic Mine Sites – Inventory and Risk Classification (HMS-IRC) project is a joint project of the Environmental Protection Agency (EPA) and the Department of Communications, Energy and Natural Resources (DCENR) (the Geological Survey of Ireland (GSI) and the Exploration and Mining Division (EMD)). The project, which commenced in February 2006, was managed by the GSI and the work was completed in 2009.

This project identifies waste piles and other features, for example shafts and adits (which are documented in Volume II), associated with closed/abandoned mines in Ireland. It also identifies broader issues of health and safety and the environment linked to closed mine sites. It provides a comprehensive understanding of each mine site/district and scores 27 mine sites/districts (encompassing 82 individual sites) relative to each other. The study assists Ireland to comply with Article 20 of the European Directive 2006/21/EC for the management of waste from the extractive industries. It does not address closed stone, sand and gravel quarries, which also require management under the Directive. It can also be used by Local Authorities to assist in their planning function.

In the past, it was normal practice that mining sites closed with little or no remediation. This practice has left the local environment vulnerable to pollution and site safety is also a common issue. Such historic mine sites may continue to cause ongoing damage to the environment and potential risks to human and animal health in the surrounding areas. There is also the potential that the risks posed by these sites may increase with time as large abandoned tailings impoundments, rock waste piles and underground workings gradually deteriorate. Often no consideration was given to long-term maintenance and aftercare of closed mine sites.

In recent years, detailed investigations have been carried out at a number of the larger abandoned/closed base-metal mine sites, namely Silvermines, Co. Tipperary, Tynagh Mines, Co. Galway, and Avoca Mines, Co. Wicklow. The DCENR with Tipperary North Riding County Council (TNRCC) is currently carrying out large-scale remediation works at Silvermines. A detailed feasibility study for the remediation and long-term management at Avoca managed by the GSI has been completed (Camp, Dresser and McKee (CDM), 2008) and the EPA carried out investigations at Tynagh.

Modern mines operate under proper planning legislation and conditions. Integrated Pollution Prevention Control (IPPC) licensing supports strict environmental standards. Modern mines now implement and fund planned closure, monitored closely by relevant bodies (e.g. EPA, Local Authority).

1.1.1 Definition of historic mine site

Many terms have been used to refer to historic mines including *closed*, *abandoned, derelict* or *orphan.* There is no widely accepted single definition for historic mines. They may be dormant, may or may not have an identifiable owner, and may or may not have been reclaimed. A historic or closed mine site can be defined as one where *minerals are not being worked, the mine site is not in the process of rehabilitation and is not under active management (addressing health and safety, and environmental issues) by a competent person.* A competent person is a person who has the technical knowledge and experience to manage the site.

Some common characteristics of historic mine sites are:

- Ownership of the site is difficult to establish, and can be further complicated by the fact that ownership of minerals can be held separately from the land in which they lie;
- That regular maintenance of the site is not undertaken; and
- Mining ceased without proper rehabilitation.

In this report, the term **historic mine site** will be used to refer to closed mine sites that are not regulated by a current permit(s) under mining, environmental or planning legislation and which encompass infrastructure related to a mine, including, but not limited to, adits, shafts, pits, tailings facilities, waste rock dumps, buildings and mineral processing areas.

1.2 Project objectives and deliverables

1.2.1 Project objectives

The key objective of this study is to establish how many of the sites actually constitute an environmental problem and/or a risk to human and animal health. The specific objectives include:

1. To draw up a list of priority sites for investigation based on existing information;
2. To review existing sampling protocols and to select or develop, as appropriate, a sampling protocol that will be used at each site to ensure reliability and replication at that site for a range of sampling media (e.g. soil, water, sediment, mine wastes, vegetation, etc.);
3. To carry out site investigation and characterisation on the priority sites identified, including an inventory of all extant surface and underground mine workings and associated buildings;
4. To review and document the potential impacts of historic mine sites in Ireland on the environment and human and animal health, and on human safety;
5. To develop a risk classification methodology based on best international practice, i.e. to develop a methodology for risk-ranking historic mine sites that would provide a robust scientific basis for making decisions about actions that need to be taken to minimise or manage risks associated with such sites. To classify the sites investigated according to the system developed; and
6. To present the findings of the work in a two-volume report. Volume I deals with the geochemical and environmental aspects of the sites and Volume II deals with the physical hazards of the site. All information will be compiled and analytical results obtained for each site during this project into a Geographic Information System (GIS) database.

1.2.2 Project deliverables

The key project deliverables for Volume I are:

1. An inventory of historic mine sites in Ireland;
2. Protocols for conducting site investigations and characterisation for historic mine sites;
3. A semi-quantitative risk assessment methodology developed and applied to each site and utilising site-specific analytical and observational information;
4. Site-specific investigation, characterisation and assessment reports for all the mine sites included in the inventory;

5. Identify site-specific issues which may require further action at each site to minimise the actual and/or potential risk posed by each site to human and animal health and the wider environment; and
6. Publication of a final report and the compilation of all relevant information on each site into a GIS format for future use.

1.2.3 Project management

The project team established to undertake the work includes staff from the EPA, the GSI and consultants employed full-time on the project, with the GSI as manager of the project. International experts were employed by the project to provide expertise in the areas of risk assessment and risk ranking and geostability. A steering committee comprising representatives from the GSI, the EPA and the EMD reviewed the performance of the project in meeting its objectives. A consultative committee comprising representatives from the Department of Environment, Heritage and Local Government (DEHLG), the Department of Agriculture, Fisheries and Food, the HSE, the Health and Safety Authority (HSA), Teagasc, the Central Fisheries Board, the Shannon River Basin District and the County and City Managers Association, in conjunction with the steering committee, provided advice and assistance in their relevant areas of expertise.

1.3 Review of potential impacts of historic mine sites

The working of minerals at metal or coal or industrial mineral mines over the centuries in Ireland has caused varying degrees of environmental damage locally, often in remote and sometimes scenic rural areas. Mining, unlike renewable natural resource land uses (e.g. fishing, farming, forestry), is a transient occupier of land while the minerals of economic interest are being extracted.

It is important to note that mining sites by their nature are anomalous accumulations of the constituents of the orebody, e.g. heavy metals, sulphides, etc. However, the disturbance caused by mining and the generation of various waste streams may result in an increased dispersion of these constituents into the wider environment, causing, in some cases, environmental pollution.

The impacts of mining on the environment may be long term and, in some cases, represent a risk to human health, animal health and the environment unless remediation and long-term management are undertaken. The impact of historic mine sites on the environment can be significant and may include:

- Potential loss of alternative land uses, e.g. agriculture, forestry, conservation, amenity, etc.;
- Pollution of surface and groundwaters through, for example, acid mine drainage (AMD) and/or metal leaching or sedimentation in watercourses;
- Dust generation and heavy-metal deposition, resulting in contamination of soils;
- Rock waste storage and disposal;
- Site safety, for example subsidence, slope instability, open shafts and adits;
- Chemical residues from ore processing; and
- Degradation of the visual environment.

The potential risk posed by the resulting contamination will be site specific and will be determined by linkages or connectivity between the sources of contamination and potential receptors – human, livestock and terrestrial and aquatic ecosystems.

1.3.1 Surface and groundwater contamination

Surface and groundwater contamination may occur through AMD, metal leaching and precipitation and sedimentation.

Acid mine drainage and acid rock drainage (ARD) occur when minerals, e.g. pyrite (FeS_2), containing sulphide and iron are exposed to the weathering effects of air and water. This reaction (oxidation) is catalysed and accelerated by sulphophilic bacteria and results in the formation of sulphuric acid and the release of iron hydroxide. The acid leaches metals from exposed underground workings (this is normally referred to as AMD) or from waste rock piles or tailings on the surface (normally referred to as ARD). This process will continue for as long as the sulphide minerals remain exposed to air and water and until the sulphides are completely oxidised. The environmental impact of AMD/ARD will depend on the sulphide minerals, the host geology, the sensitivity of the receiving environment and the degree of neutralisation, dilution and/or natural attenuation. These acidic waters make their way into surface and groundwaters.

Enhanced metal leaching is associated with acidic drainage due to high metal solubility and sulphide weathering rates under acidic conditions. For many rock types and environmental settings, metal leaching will only be significant where the pH drops below 5.5. However, a neutral pH does not necessarily eliminate metal leaching. While the solubility of aluminium (Al), iron (Fe), and copper (Cu) is greatly reduced in neutral pH drainage, elements such as antimony (Sb), arsenic (As), cadmium (Cd), molybdenum (Mo), selenium (Se) and zinc (Zn) remain relatively soluble and therefore can be found in significant concentrations in drainage water (Price and Errington, 1998). These metal-bearing waters may precipitate their metal load onto a river bed. This can also result in a ferricrete developing on the river bed which destroys the nature of the river bed and impacts on the habitat for aquatic macroinvertebrates.

Erosion occurs when bare rock, soils or processing wastes from mining activities are eroded by wind or water. Subsequently, the eroded material may be deposited in either watercourses or on land, causing contamination. During the mining operations, materials may have been deliberately discharged into watercourses. Livestock accessing rivers may come into contact with such contaminated sediments and this may be a cause for concern depending on the composition of the mine-generated sediment.

1.3.2 Dust generation and deposition

Wind erosion can occur when finer particles from mine waste dumps and tailings become airborne under dry weather conditions. They are subsequently deposited onto other parts of the mine site or onto adjoining lands. This process can have environmental impacts on soil through the deposition of elevated metal material.

1.3.3 Waste rock piles

Many waste piles have elevated metal levels (e.g. As, Pb), and in some cases the level of metals may be toxic. Such waste piles are a concern in situations where there is the possibility of direct contact by humans or animals.

1.3.4 Chemical residues

During mining operations, target minerals are separated from waste minerals using mineral processing techniques that involve the use of chemical reagents. Over the operational life of the mine there may have been accidental spillages of some of these reagents. Usually these would have been cleaned up at the time. The reagents commonly adhere to either the recovered minerals, which are transported offsite, or to the waste minerals, which are deposited in the tailings impoundment. Most of these reagents degrade naturally to harmless compounds.

1.3.5 Site safety

Many mine sites have features such as open pits, high cliff walls, waterbodies, shafts, adits, derelict buildings or steep slopes that may cause a safety hazard. Ground instability is another issue that may occur. Unrestricted public access to such sites is a safety issue. These physical hazards are documented in Volume II.

1.4 Legislation relating to historic mine sites

Legislation relating to mining relates to permission to mine (emanating from DCENR) and to how mining is carried out (largely from the DEHLG) and includes the:

- Minerals Development Acts, 1940 to 1999;
- Environmental Protection Agency Acts, 1992 and 2003;
- Waste Management Acts, 1996 to 2003;
- Water Pollution Acts, 1977 to 1990; and the
- Energy (Miscellaneous Provisions) Act 2006 Part 9 – Rehabilitation of Mines.

Directives from the EU are also relevant and the principal ones related to mining are:

- Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Dangerous Substances Directive);
- Directive 2000/60/EC establishing a framework for the Community action in the field of water policy (Water Framework Directive);
- Directive 2006/21/EC on the management of waste from the extractive industries (Mining Waste Directive);
- Directive 2006/118/EC on the protection of groundwater against pollution and deterioration (Groundwater Daughter Directive).

1.4.1 Legislation overview

The Minerals Development Acts, 1940 to 1999, under the aegis of the Minister for Communications, Energy and Natural Resources, govern exploration for and development of all minerals other than ordinary clay, stone, sand and gravel. Minerals can be held either by the State or be privately owned. Of the mineral ownership that has been determined, 60% is in State ownership. All gold (Au) and silver (Ag) are State owned.

Current mining, planning and environmental legislation ensures that mine operators make provision for the funding and proper closure and remediation of sites. This is enforced by the Local Authority, the EPA and the DCENR. These arrangements were not in place for historic mine sites.

The legal obligation to deal with environmental and health and safety issues at historic mine sites rests in the first instance with the owner. It is the responsibility of the Local Authority to enforce compliance with environmental legislation within its functional area. Account must also be taken of other legislation that can be invoked, such as the Derelict Sites Act, 1990, which gives bodies such as Local Authorities powers and responsibilities in relation to historic mine sites.

Under current minerals legislation (Section 32 of the Minerals Development Act, 1940) the Minister for the Department of Communications, Energy and Natural Resources has limited powers to enter lands and erect fencing around, for example, shafts and openings where State minerals have been worked. The Minister has no such powers in relation to sites where private minerals have been worked. Provisions were included in the Energy (Miscellaneous Provisions) Act 2006 to give the Minister powers to prepare and implement a mine rehabilitation plan in respect of the site of a historic mine where such a plan is deemed necessary for the purposes of human or animal health or safety, for the protection of the environment, or is otherwise in the public interest. Provision is made also in the Act for the Minister to appoint a Local Authority as agent to prepare and implement such a plan.

Ireland is obliged under Article 20 of Directive 2006/21/EC on the management of waste from the extractive industries to prepare an inventory of closed/abandoned mine waste facilities that cause serious negative environmental impacts or have the potential of becoming in the medium or short term a serious threat to human health or the environment and to periodically update it. The inventory is to be made available to the public and be completed by 1 May 2012. As the historic mine sites inventory and scoring system deals with those minerals covered by the Minerals Development Acts, 1940 to 1999 (Scheduled Minerals), it only partially fulfils this obligation. However, an inventory for closed stone, sand and gravel quarries is also required under the Directive. There is no obligation under this Directive to take any action at listed sites.

1.4.1.1 Water Framework Directive

The Water Framework Directive (2000/60/EEC) came into force on 22 December 2000 and establishes a strategic framework for managing the water environment of the European Community. The Directive establishes a common approach to protecting and setting environmental objectives for all waters, including groundwaters, rivers, lakes, canals, reservoirs, estuaries and coastal waters. The Directive aims at maintaining and improving water quality within the European Community by setting objectives for all waterbodies requiring at least ‘good status’, ‘no deterioration’ and ‘restoration’ where necessary.

The River Basin District (RBD) will be the main unit for managing the water environment and a single River Basin Management Plan (RBMP) must be produced for each RBD. Identification and analysis of the pressures and impacts on the water environment is required in the preparation of an RBMP, which will determine what measures need to be taken in order to achieve ‘good status’. For surface waters, ‘good status’ includes good chemical and ecological status and, for groundwater, includes good chemical and good quantitative status.

The waters in each area where mine sites are located will ultimately be managed by the relevant competent authority under an RBMP, with the objective of achieving good water status. However, waters in mining areas have generally been influenced by both the natural geological conditions of the area and past mining activities. The Water Framework Directive provides for this by stating *In cases where a body of water is so affected by human activity or its natural condition is such that it may be unfeasible or unreasonably expensive to achieve good status, less stringent environmental objectives may be set on the basis of appropriate, evident and transparent criteria, and all practicable steps should be taken to prevent any further deterioration of the status of waters.*

1.4.1.2 Dangerous Substances Directive

Under the Dangerous Substances Directive (76/464/EEC), Member States are required to take appropriate steps to eliminate pollution of waters by List I substances listed in the Annex and to reduce pollution of waters by List II substances also listed in the Annex. List I includes Cd and its compounds. List II includes metalloids and metals, such as Pb, Zn, As and Cu. The Dangerous Substances Directive will remain in force until 22 December 2013, when it will be repealed by the Water Framework Directive.

The Water Quality (Dangerous Substances) Regulations, 2001 (SI No. 12 of 2001), were enacted on 1 July 2001. The Regulations transpose certain requirements of the

Dangerous Substances Directive into national legislation. They prescribe water quality standards in relation to specified List II substances, including Pb, Zn and As, in surface water, e.g. rivers, streams, etc. The Regulations require that the annual mean concentration of certain substances is not exceeded and the standard specified for fresh waters depends upon hardness of water measured in mg/l $CaCO_3$. Where the existing condition of a waterbody does not meet a specified standard in relation to a substance there should be no disimprovement and compliance with the specified standard should occur no later than 31 December 2010 or by 31 December 2015 for specific cases.

However, in common with the Water Framework Directive, exemptions are provided for in the Regulations. Article (9) (2) states that *a specified standard shall not apply in relation to a water body where the Agency [Environmental Protection Agency] is satisfied that the water body is so permanently affected by naturally occurring conditions or by past human activity that compliance with that standard is not feasible or would be disproportionately expensive*.

1.4.1.3 Groundwater Directive

The purpose of the Groundwater Directive (80/68/EEC) is to prevent the pollution of groundwater by substances belonging to the families and groups of substances in List I or List II in the Annex to the Directive and, where possible, to check or eliminate the consequences of pollution that has already occurred. List I substances include Cd and Hg, while Pb, Zn and As are included as List II substances. The Directive requires that Member States prevent the introduction of List I substances into groundwaters and to limit the introduction of List II substances.

However, in common with the Water Framework Directive, exemptions are provided for in the Directive. Article 4 (2) states *that should prior investigation reveal that the groundwater into which the discharge of substances in List I is envisaged is permanently unsuitable for other uses, especially domestic or agricultural, the Member States may authorise the discharge of these substances provided their presence does not impede exploitation of ground resources. These authorisations may be granted only if all technical precautions have been taken to ensure that these substances cannot reach other aquatic systems or harm other ecosystems*.

It is likely that groundwaters in many of the mining areas have been influenced by both the natural geological conditions of the area and past mining activities.

Information on the status of groundwater in these areas is limited in this study. Groundwater samples have been taken where this has been feasible.

1.5 Overview of the geology and mining history of Ireland

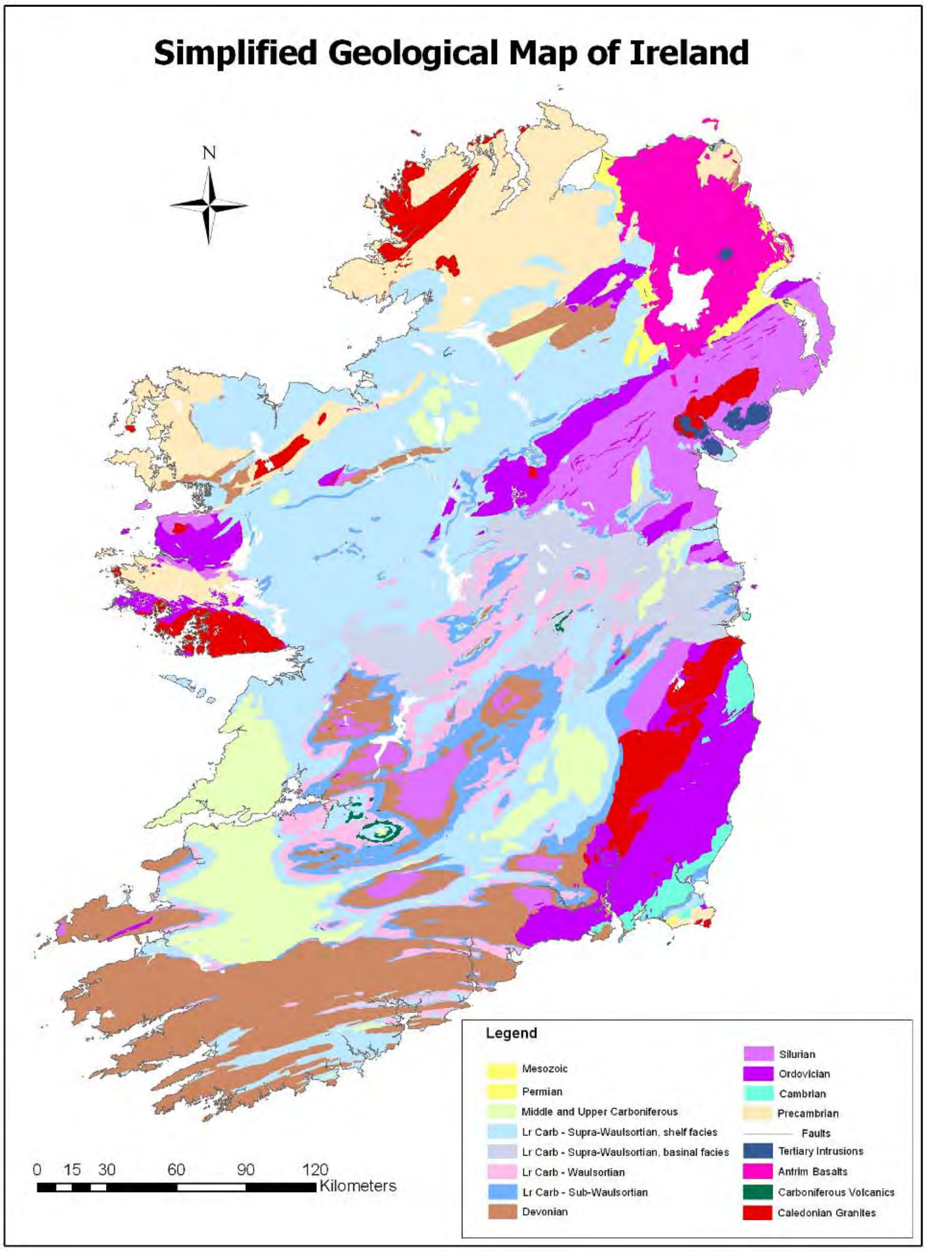
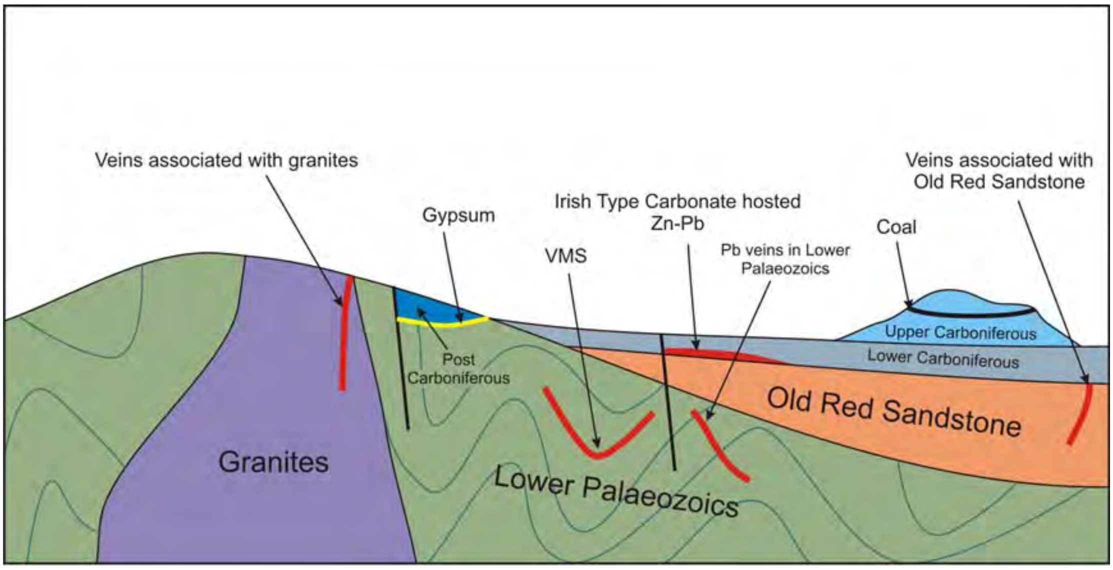


Figure 1.1 Geology map of Ireland.

Figure 1.1 is a simplified geological map of Ireland and shows the disposition of rock largely from an age perspective. Ireland has a diverse geology for its area, with rocks ranging in age from Precambrian (approximately 4.6 billion years to 540 million years) to Quaternary (approximately 2.5 million years to present). However, most rocks are from the Palaeozoic era (approximately 540 to 250 million years ago). This overview relates mineral deposits to the principal geological events in Ireland. Figure

1.2 is a schematic north–south geological section through the country, with typical mineral deposits illustrated in their respective geological units.

Figure 1.2 Schematic north–south geological section of mineral deposits in Ireland.



1.5.1 Precambrian

The oldest rocks in Ireland occur in the north-west (Galway, Mayo and Donegal) and south-east (Rosslare), and originated on separate continents that were brought together during the later Ordovician and Silurian Periods. Most Precambrian rocks occur in the north-west where they are known as the Dalradian. They are composed mainly of metamorphosed marine sedimentary rocks (quartzite) but include volcanic and intrusive rocks, marbles, greywackes, slates, and metamorphosed glacio-marine deposits.

Mineralisation in the Dalradian is relatively minor. It is comprised for the most part of narrow veins of sulphide minerals (galena, chalcopyrite and sphalerite), skarns deposits in Connemara, and rare stratiform sedimentary exhalative (SEDEX) mineralisation in Co. Donegal. Only the veins were worked to any significant extent.

1.5.2 Lower Palaeozoic (Cambrian, Ordovician and Silurian Periods)

The geological evolution of Ireland continued in the Lower Palaeozoic, with the north-west and south-east separated by the Iapetus Ocean and consequently separate geological formations were developed on the different sides of the Ocean.

To the north-west some Dalradian rocks may be of Cambrian age while Ordovician rocks are comprised of slates, greywackes, and mafic and felsic volcanic lithologies in Counties Mayo, Galway and Cavan. Silurian rocks occur in Counties Mayo, Galway, Roscommon, Cavan, Louth and Monaghan and are mainly composed of slates, greywackes and quartzites.

The rocks of the south-east occur primarily in Counties Wicklow, Wexford and Waterford and parts of adjoining counties and are mainly slates, greywackes, quartzites, and mafic and felsic volcanics.

The close of the Iapetus Ocean led to the collision of the two continents and resulted in the Caledonian Orogeny (Grampian Phase), which resulted in mountain building, deformation, metamorphism, and the intrusion of large volumes of granite magma. The Leinster, Galway and Donegal Granites are the principal granitic intrusions and were emplaced at this time.

Mineralisation comprises two main types. One is volcanogenic massive sulphides (VMSs), as at Avoca in Co. Wicklow, where both stratiform and stringer Cu and pyrite mineralisation along with minor Pb and Zn sulphides are associated with felsic volcanic rocks. The other principal style of mineralisation is vein type comprising, for the most part, the sulphides of Cu, Pb and Zn. Some of the veins in Counties Monaghan and Mayo are gold bearing. Veins occur in most rock types but are especially common in greywackes (Co. Monaghan) and in granites (e.g. Glendalough, Co. Wicklow).

1.5.3 Upper Palaeozoic (Devonian, Carboniferous and Permian Periods)

Following the Caledonian Orogeny, there occurred a long period when the rocks forming the Caledonian Mountain Belt were subjected to erosion. The transported sediments were deposited in a fluvial environment forming the Devonian Old Red Sandstones. Devonian rocks crop out as far north as Co. Tyrone but occur mainly across the south in Counties Cork and Kerry. Devonian rocks also occur in the Midlands where they underlie the younger Carboniferous rocks of the Central Plain. They comprise conglomerates, sandstones, siltstones and mudstones.

Mineral deposits in the Devonian are mainly confined to West Cork and consist of vein-type deposits of Cu sulphides (e.g. Allihies) and barite vein deposits (e.g. Lady’s Well). Following the Devonian, a marine transgression from the south led to the development of Carboniferous limestones of various types. From a mineralisation point of view, there are two important limestones, the Navan Beds and the Waulsortian. The Waulsortian Mudbank limestone is a thick mound-like body of mud-sized calcium carbonate. These mounds often coalesce to form thick continuous layers. These Waulsortian rocks occur across the Central Plain from Cork in the south as far northward as Co. Westmeath. The currently operating Navan deposit in Co. Meath is hosted in the Navan Beds.

Carboniferous rocks underlie approximately half of the country. In terms of Irish metal mining, the Lower Carboniferous is by far the most important unit for ore deposits. From the 1950s, when the modern phase of mining commenced, up until today, the Lower Carboniferous continues to provide the greatest amount of metal and the greatest prospects for the future. Six major deposits have been worked since the initial discovery, in 1961, at Tynagh in Co. Galway. The subsequent discoveries were Silvermines, Co. Tipperary (which also had historic production), Gortdrum, also in Co. Tipperary, Navan in Co. Meath (the largest Zn–Pb orebody in Europe and the sixth largest in the world), Galmoy, Co. Kilkenny, and Lisheen, Co. Tipperary. The latter three deposits continue working today and together make Ireland the largest producer of Zn and Pb in Europe. The deposits are commonly known as Irish Type, having features that are intermediate between Mississippi Valley-type and SEDEX-type deposits. They are much sought after on account of their high grades and clean metallurgy. Major barite deposits also occur in this interval with both stratabound (e.g. Silvermines) and vein-type (e.g. Benbulben) deposits occurring.

Following the Lower Carboniferous, deltaic conditions prevailed over much of Ireland, resulting in the deposition of sandstones and coal deposits. There are now three major areas underlain by Middle and Upper Carboniferous rocks – in Leinster (Counties Kilkenny, Laois and Carlow), Slieve Ardagh (Counties Kilkenny and Tipperary) and Connacht (Counties, Leitrim, Roscommon, Sligo and Cavan). There are also smaller deposits in Kanturk (Co. Cork) and at Cratloe (Co. Limerick). The principal deposits of these rocks are thin coal seams, which in Slieve Ardagh and Leinster are anthracite grade and in Connacht are bituminous-grade coals.

Permian rocks occur at Kingscourt in Co. Cavan (and neighbouring parts of Counties Monaghan and Meath). They comprise massive gypsum deposits formed in shallow coastal lagoons subjected to evaporation (sabhkas). At Kingscourt, two main gypsum and anhydrite layers (totalling about 45 m in thickness) are interbedded with red and purple mudstones of uppermost Permian age. In the past, gypsum has been mined from both layers at Kingscourt in several underground operations and is currently extracted from the upper layer in a major opencast pit at Knocknacran in Co. Monaghan.

1.5.4 Post-Palaeozoic

There are very few post-Palaeozoic rocks in onshore Ireland, except for Northern Ireland where there are Jurassic, Cretaceous and Tertiary rocks – the latter which includes the famous Antrim basalts and the Giants Causeway. In the south, there are a few instances where sinkholes in the Carboniferous limestones have preserved younger rocks such as at Killarney where Cretaceous chalk is preserved. No mining activity is known from these rocks although one such sinkhole has been investigated as a potential ball clay source.

1.6 Mining in Ireland

Mining supported the economic welfare of local communities for a decade or more. At some celebrated sites (e.g. Avoca, Silvermines) mining activity spanned hundreds of years and employed thousands of workers and a rich industrial and cultural heritage is now linked to these sites.

1.6.1 Overview

Ireland has a rich mining history dating back to the Bronze Age. Cowman and Morris (2003) provide an overview of mining prior to 1700. Many deposits and deposit types have been worked over the years. The MinLocs database in the GSI has over 5,000 entries, which include both metallic and non-metallic commodities (almost 200 different commodities are recorded). Of these entries, almost 1,500 are for metallic minerals, while some 3,300 are for non-metallic minerals, with the remainder containing both metallic and non-metallic minerals. Of the total 5,000+ locations in the database, just over 450 are described as mines, while some 1,300 are described as quarries. The remainder are either borehole intersections or outcrops (natural or man-made) of one form or another with the occurrence of a mineral or rock.

Within the group of 450 mines, some 350 were worked for metallic commodities while there were approximately equal numbers of non-metallic and coal operations, 49 and 57, respectively. Of the 450+ mines, some 220 had what could be described as significant workings or production.

The former mines can also be classified according to time of working and commodity produced. Using this as a basis the following groupings may be identified:

1. Underground and surface mining operations for coal;
2. Workings for industrial minerals prior to the 1920s;
3. Modern workings for industrial minerals (latter half of the 20th century);
4. Base-metal veins worked for the most part prior to the 20th century – but some workings operated into the 1950s;
5. Modern (industrial) operations mainly from the latter half of the 20th century.

1.6.2 Coal mines

Coal measure rocks, in Ireland, date from the Upper Carboniferous and occur in four areas – the Leinster Coalfield, straddling Counties, Kilkenny, Laois and Carlow; the Slieve Ardagh Coalfield on the border of Counties Kilkenny and Tipperary; the Kanturk Coalfield in north-west Co. Cork; and the Connacht Coalfield, straddling Counties Leitrim, Roscommon, Sligo and Cavan. The type of coal worked varied from anthracite in the southern coalfields to bituminous coal in the Connacht Coalfield. Coal working methods varied over time also, with opencast, bell pits and longwall mining being the principal types. Most coal mining operations in Ireland date from the 18th century and the various coalfields were worked intermittently up until the 1990s.

1.6.3 Vein operations

Up until the start of the 20th century, most mining operations in Ireland worked metalliferous veins. Most of these were for Cu or Pb while a smaller number were worked for either Fe or Zn. Silver was commonly recovered from the Pb veins.

The veins occurred in a number of settings:

1. Pb (and Ag) veins associated with granites, e.g. Glendasan, Co. Wicklow;
2. Cu veins within volcanic rocks with a VMS affinity, e.g. Bunmahon, Co. Waterford;
3. Cu veins within sandstone lithologies, e.g. Allihies, Co. Cork; and
4. Pb (and Ag) veins in limestone lithologies, e.g. East Co. Clare.

1.6.4 Modern mining

Modern mining operations in Ireland commenced in the 1960s with the development of the Tynagh mine. This heralded a new era for mining in Ireland as it focused attention on the prospectivity of the Irish Midlands for carbonate-hosted Zn–Pb deposits. This attention was rewarded with the discovery and eventual development of a further five deposits and the finding of ten other sub-economic deposits. The historic mine at Avoca was intermittently active from about 1720 until 1982. The early workings of this deposit were largely by primitive means (until the latter part of the 19th century). However, in the late 1950s modern mechanised mining methods were applied to this VMS deposit. There were, or are, also a number of modern mining operations for industrial minerals, in particular for barite and gypsum. Figure 1.3 shows the mining sites and districts in Ireland that were investigated for the HMS-IRC project. Not all of these sites contain mine waste and therefore only the relevant ones have been scored and classified.

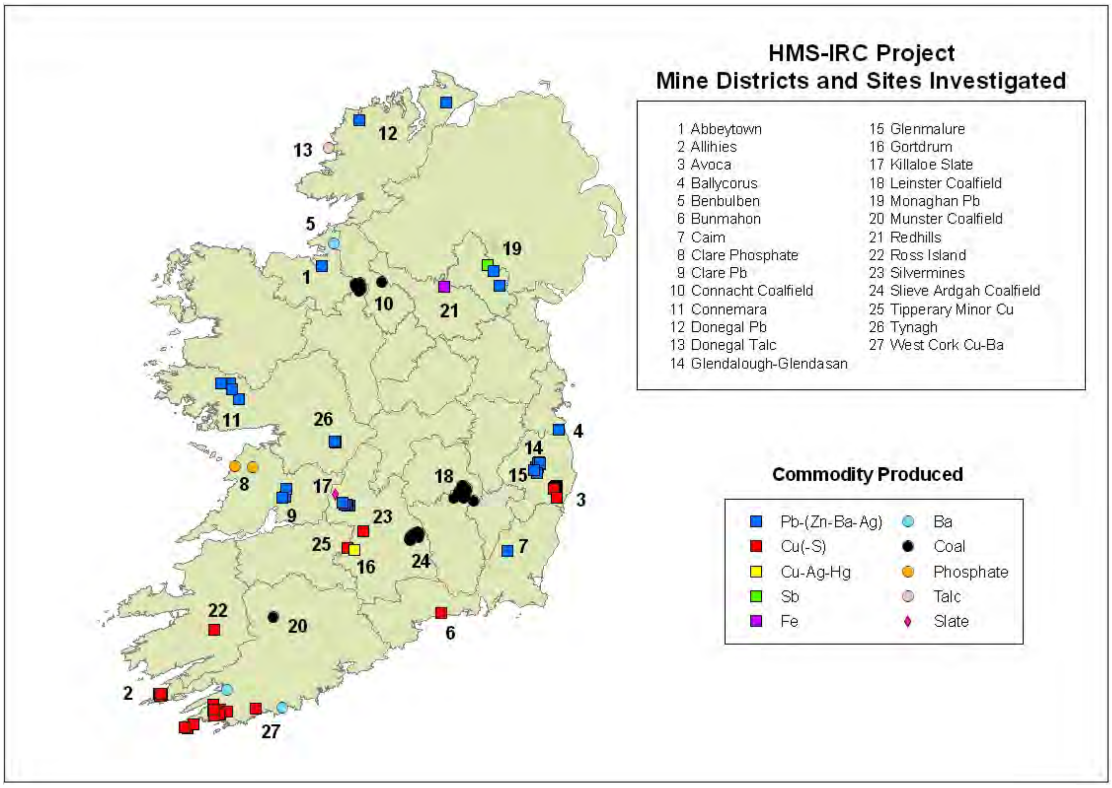


Figure 1.3 Mines and mining districts in Ireland investigated for the HMS-IRC project.

CHAPTER 2

Historic Mine Sites – Inventory and Risk Classification Scoring System

2.1 Methodology overview

The purpose of this chapter is to provide an overview of the methodology used in the project in relation to the following areas of work:

1. Preliminary screening and site selection for the historic mine sites included in this investigation;
2. Conceptual model; and
3. Risk ranking and classification.

A more detailed description of these work areas is given in the Appendices to this report, which are referenced at specific parts of the report.

2.2 Preliminary screening and site selection

Two-hundred and twenty mine sites were located across the country from which there has been extraction of minerals using the GSI databases. Expert judgment was then applied to the existing databases to extract a list of sites that should be included in the risk ranking and classification work. Detailed knowledge on mining history, mining methods, mineral processing, geology and mineralisation, coupled with assessment criteria, such as scale, elements present (Pb, Zn, Cu, Ni, As, Cd, Hg), ARD/AMD potential, principal sources of polluting materials present (tailing impoundments, processing wastes, rock waste dumps, etc.) and environmental setting, was used to carry out a preliminary screening of the sites.

A desk-top study carried out by Eamonn Grennan, Sligo Institute of Technology, in 1996 for the EPA which used a combination of expert judgement and assessment criteria to derive a pollution index potential for 128 mine sites across the country was used in the preliminary screening (Grennan, 1996). This work assigned a potential Pollution Index Number (PIN) from 1 to 9 to the 128 sites. PIN 1 sites included all recently closed large-scale base-metal mines (closed in the 1980s) and major coalfields where significant volumes of waste are present and the ARD/AMD potential is high. Table 2.1 provides a summary of the PIN codes, the number of mines included within a particular code and a general description of the mines included in the code.

Pollution Index No.	**Number of Sites**	**Main Assessment Criteria Used**
1	10	Recently closed, large-scale metal mines and coalfields, processing chemical(s) used, presence of tailing impoundments, high ARD/AMD potential
2	14	Medium sized sites (>100,000 tpa production or 100 persons employed), usually worked prior to 1960 and/or satellite deposits associated with larger mines. They may also contain particularly toxic elements such as Cd and As
3	16	Coalfields and smaller metal mines and industrial mines. AMD thought to be significant. Smaller than PIN 2 sites. Includes sites with a high S content. This is generally the highest class for coalfield sites.
4	20	Non-toxic suspended solids presenting a major problem to surface waters. Highest class for slate, associated metal mines working, generally small scale.
5	14	Older, long-abandoned mines, insufficient information to classify with any degree of certainty, further investigations required.
6	21	Small working scattered over large areas, possible groundwater issues
7	11	Industrial mineral workings that are old and small and include very small metalliferous mines located inland.
8	15	Small coastal metalliferous mines
9	7	Very small and very old, no significant metals, located along cliff edges.

Table 2.1 Assessment criteria and pollution index number for mine sites.

The preliminary screening and site selection process identified 110 individual mine sites for investigation in the HMS-IRC project. Many of these sites can be grouped into mining ***districts*** in which numerous sites share metallogenic and geochemical features. Additionally, sites within mining districts were typically exploited simultaneously and may have shared processing facilities. Their proximity to one another means that they are likely to have an impact on the same environmental receptors, e.g. surface watercourses or groundwater aquifers. Thus, where justified by proximity and shared development history, sites have been grouped into districts and the districts have been treated as individual entities for scoring purposes. Where sites assigned to the same district are physically separate and do not share potential receptors, they have been scored separately. Stand-alone sites, e.g. Tynagh, are considered to be a district in themselves for classification purposes.

The mine sites in the Glendalough–Glendasan–Glenmalure area provide an example of this district classification process. Geologically and geochemically, all the sites in this area can be considered to be part of a single district — the Glendalough District — and they are treated as such for descriptive purposes and in the overall geochemical assessment. However, while the sites in Glendalough and Glendasan were exploited by a single company, used shared processing facilities and are in close proximity to one another, those in Glenmalure are physically separated from the others and were exploited independently. Potential receptors affected by environmental contamination in Glendalough–Glendasan and Glenmalure are entirely different. Thus, instead of grouping all sites into just one district for scoring purposes, the individual sites in both Glendalough–Glendasan and in Glenmalure are grouped into two districts, according to the logic outlined above. Similarly, Ballyvergin, Ballyhickey and Kilbricken have been grouped into the Clare Lead District but, because they are physically separate sites, they have been scored individually.

All sites in the country have been assigned to a mine district in a similar way. Table 2.2 lists those districts and sites that have been investigated for the HMS-IRC project. Not all districts or sites visited and investigated were subjected to geochemical assessment and subsequent classification using the HMS-IRC scoring system (geochemistry). Of the 32 districts or sites listed in Table 2.2, five were not scored: Crohy Head, Kanturk, Killaloe, Redhills and Ross Island. The nine sites in the Killaloe slate quarries district have large volumes of waste but analysis indicates that it contained no elements of concern from an environmental perspective. Crohy Head is a talc mine and, as such, had no waste of chemical concern. Kanturk and Redhills both lacked significant exposed waste. Ross Island is now a managed heritage site and contains only very minor amounts of solid waste. Both Killaloe and Kanturk have significant geotechnical features and are included in the HMS-IRC geotechnical assessment. In addition to the above five, seven sites in the West Cork Copper–Barium District (Ardagh, Ballydehob, Cappagh, Derreennamolane, Derryginagh, Roaring Water and Scart), one site in the Clare Phosphate District (Noughaval), and two in Connemara (Tiernakill and Doorus) were not scored because they lacked mine waste. The 27 districts or sites scored listed in Table 2.2 include a total of 82 individual mine sites that were geochemically assessed and scored using the HMS-IRC scoring system.

Name	**Mine District**	**No. of Sites**	**Sites Classified**	**Commodity(ies) Extracted**
Abbeytown	Abbeytown	1	✓	Pb, Zn
Allihies	Allihies	6	✓	Cu
Avoca	Avoca	7	✓	Cu, pyrite
Ballycorus	Ballycorus	1	✓	Pb
Ballyhickey	Clare Pb	1	✓	Pb
Ballyvergin	Clare Pb	1	✓	Pb
Benbulben	Benbulben	1	✓	Barite
Bunmahon	Bunmahon	1	✓	Cu
Caim	Caim	1	✓	Pb
Connemara	Connemara	3	✓	Pb
Clontibret	Monaghan	1	✓	Pb
Connacht Coalfield	Connacht Coalfield	7	✓	Coal
Crohy Head	Donegal Talc	1		Talc
Clare Phosphate	Clare Phosphate	2	✓	Phosphate
Glendalough–Glendasan	Glendalough	8	✓	Pb, Zn
Glenmalure	Glendalough	2	✓	Pb
Glentogher	Donegal Pb	1	✓	Pb
Gortdrum	Gortdrum	1	✓	Cu, Hg
Hollyford	Tipperary Minor Cu	1	✓	Pb
Hope (Cornalough)	Monaghan	1	✓	Pb
Kanturk	Munster Coalfield	6		Coal
Keeldrum	Donegal Pb	1	✓	Pb
Kilbricken	Clare Pb	1	✓	Pb
Killaloe	Killaloe Slate	9		Slate
Leinster Coalfield	Leinster Coalfield	7	✓	Coal
Redhills	Redhills	1		Fe
Ross Island	Ross Island	1		Cu
Silvermines	Silvermines	6	✓	Cu, Zn, Pb, barite
Slieve Ardagh Coalfield	Slieve Ardagh Coalfield	10	✓	Coal
Tassan	Monaghan	1	✓	Pb
Tynagh	Tynagh	4	✓	Zn, Pb, Cu, barite
West Cork	West Cork	15	✓	Cu, barite

Table 2.2 Summary of mines and mine districts included in the HMS-IRC project.

2.3 Conceptual model

2.3.1 Introduction

In order to address the project a careful review of the issues that may be associated with historic mine sites was undertaken. This review involved an examination of mine records in the GSI, an examination of reported incidents from historic mine sites in Ireland, a review of available literature on the topic and discussions with CDM and Geoffrey Walton Practice (GWP) (UK) (consultants employed to provide advice specifically on the task of preparing the inventory).

It was quickly realised that in order to carry out the fieldwork that a systematic method was needed and the optimum approach would be to develop a **Conceptual Model**. This would therefore guide the data collection in the field but would not be so rigid as to prevent the recording of features unique to any one site.

The HMS-IRC project addresses the requirement of the EU Directive on wastes from the extractive industries for an inventory of waste facilities and the national need for data on physical hazards at closed and/or abandoned mine sites. Both needs have been addressed on a risk basis. However, it is important to note that this is NOT a risk assessment of the sites. Rather the sites have been ranked on a risk basis so as to determine a relative ranking for future actions.

As indicated in the previous paragraph, each site is assessed for waste facilities and for physical hazards. The former assessment looks primarily at hazards from a chemical or geochemical point of view while the latter assesses the geotechnical and site safety aspects of a site.

This section will briefly provide an overview of the conceptual model developed for contaminant risks. The scoring system for the conceptual model is described in the appendices to this report.

2.3.2 Contaminant conceptual model

Contaminant risks emanate from waste facilities on the site. In order to identify and assess these, the Source–Pathway–Receptor Paradigm has been used. The paradigm requires that each of the parameters within the model are documented, estimated, measured or recorded. The conceptual model to describe this is illustrated pictorially in Figure 2.1. The model identifies the source of any contamination, who or what is affected (the receptor), and how the source may reach the receptor (pathway). The conceptual model identifies all the sources, pathways and receptors. The collection of field data, observations and estimates confirms whether a linkage exists between the source and receptor and conclusions are drawn about the potential risks caused by the source of contamination. Conceptual models are used to inform and drive site investigations. Later a conceptual model may assist with the identification of remedial strategies.

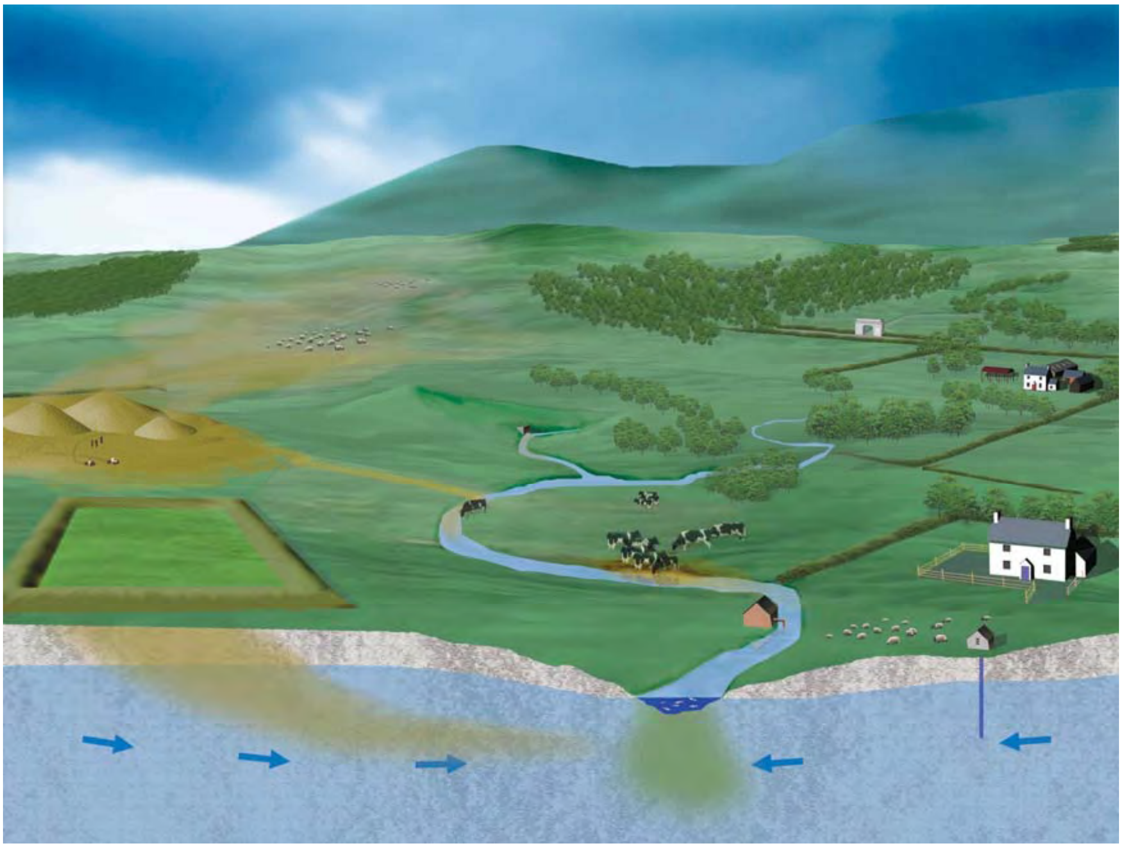


Figure 2.1 Conceptual model for a potential historic mine contaminating the environment.

2.3.3 Sources of contaminants

Sources are the origin of contaminants that may issue from a historic mine site. The cause or source of the contamination is identified as well as its location. The possible sources of contamination are listed below and illustrated in Figure 2.2:

- Liquid (water)
  - Adit discharges
  - Seeps
- Solids
  - Waste piles
  - Tailings impoundments
  - Stream sediments

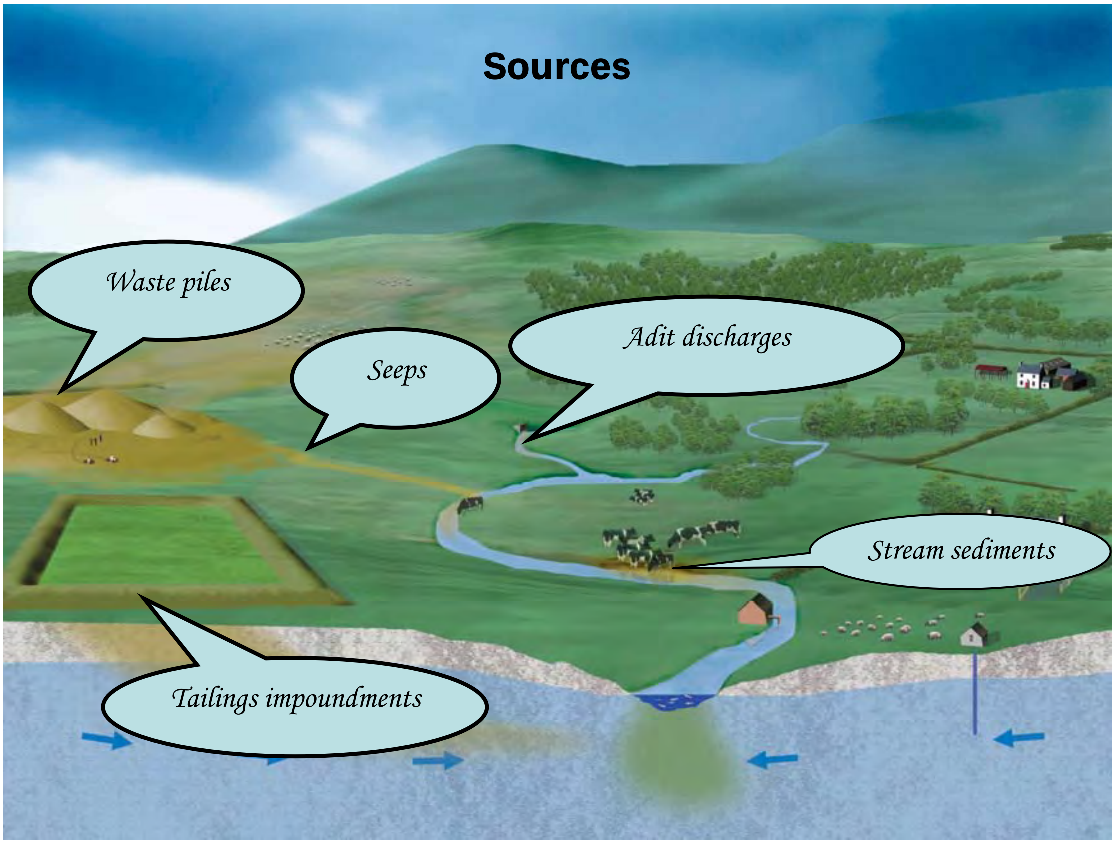


Figure 2.2 Possible sources of contamination at historic mine sites.

2.3.4 Pathways

The pathway is the route the source takes to reach the receptor. Evidence for the movement of the potential contaminants is noted for each pathway at the site. Pathways that are considered for the movement of contaminants at historic mine sites are (numbers refer to elements shown in Figure 2.3):

Groundwater

Surface water

Air

Direct contact – solid waste piles

Direct contact – stream sediments

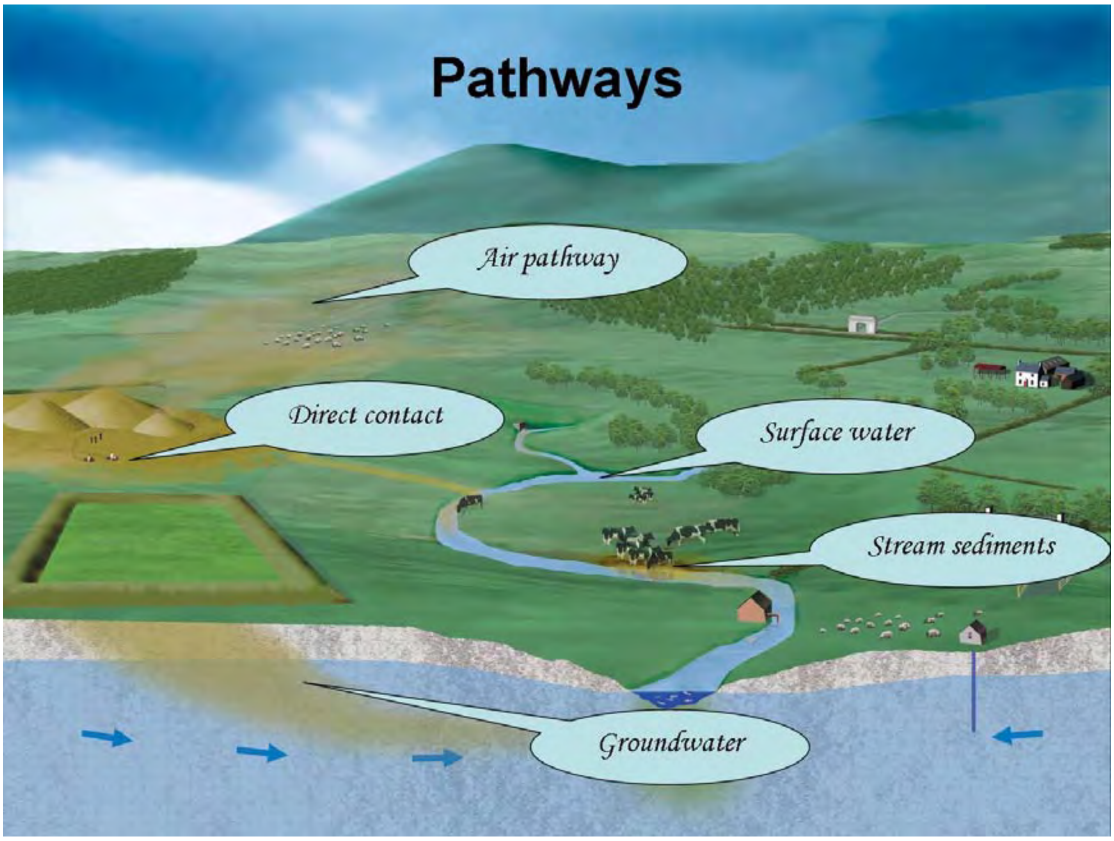


Figure 2.3 Pathways by which potential contaminants may reach receptors.

2.3.5 Receptors

Receptors are those elements of the paradigm that are affected by the potential contamination emanating from the various sources via the different pathways. If contamination is to cause harm, it must reach a receptor. A receptor is any person, animal, plant, ecosystem, protected site, or property. Receptors, in the context of the HMS-IRC project include the following, which are illustrated in Figure 2.4:

- People
  - Local inhabitants
  - Workers
  - Visitors to the site (legal or otherwise)
- Farm animals
  - Livestock
- Ecosystem/Aquatic
  - Rivers
  - Estuaries
  - Groundwater
- Protected areas
  - National Parks
  - National Heritage Areas (NHAs)

Special Protection Areas (SPAs)
Special Areas of Conservation (SACs)
Nature Reserves

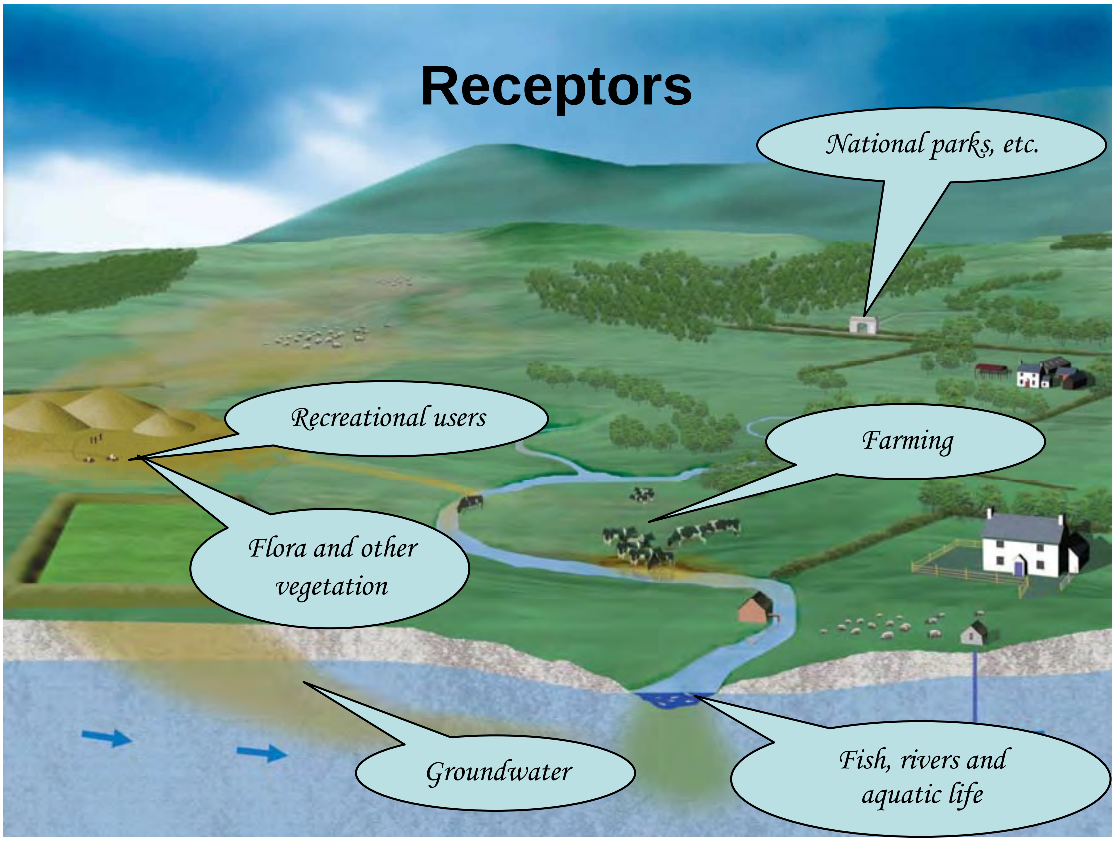


Figure 2.4 Possible receptors that may be exposed to contamination originating from historic mine sites.

2.4 Overview of scoring system

2.4.1 Overall philosophy

The scoring system for the historic mine sites was developed from the Abandoned and Inactive Mines Scoring System (AIMSS), which itself was devised to produce a ranking of abandoned mine sites in the State of Montana (USA) and is itself a development of the US EPA Hazard Ranking System. This is a summary of the system developed by the Project Team to score the Irish historic mine sites with assistance from international consultants CDM (USA) and Land Quality Management (LQM) Limited (UK) to take account of particular issues specific to Ireland.

The overall approach to the scoring is illustrated in Figure 2.5. The system comprises five steps. This section of the report provides a summary of Steps 4 and 5 of this process.

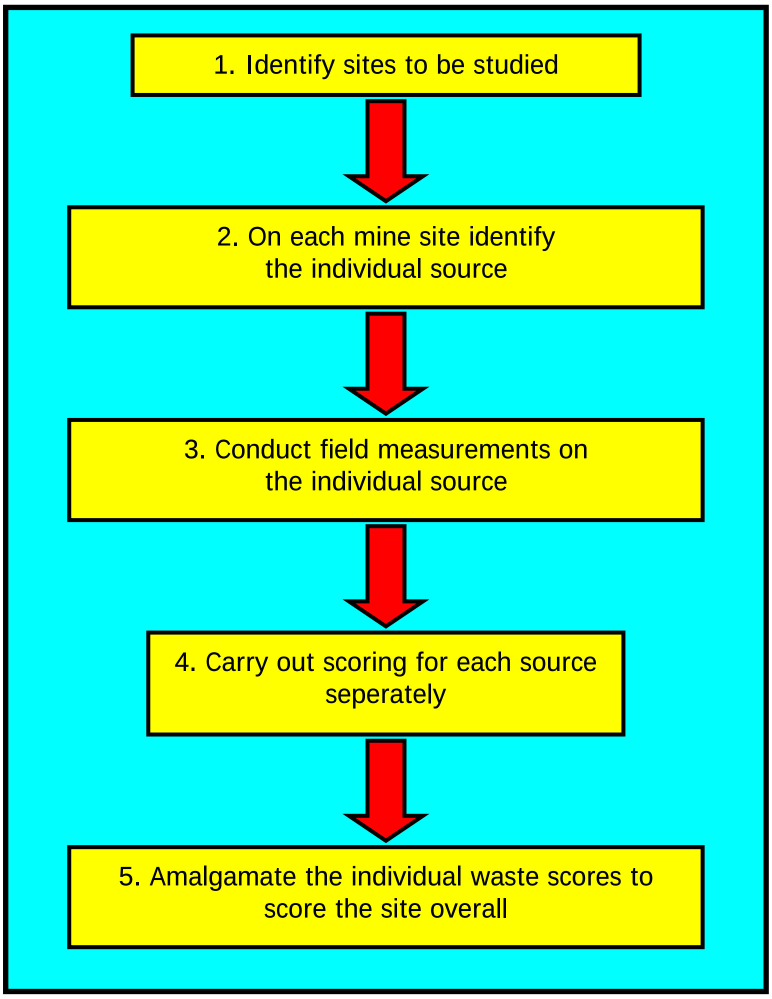


Figure 2.5 The five steps to scoring a historic mine site for contamination hazards.

As indicated above, each waste pile or discharge is assessed and scored separately. Five pathways are evaluated:

Groundwater pathway
Surface water pathway
Air pathway
Direct contact pathway (waste piles)
Direct contact pathway (stream sediments)

Each pathway may have a greater or lesser influence on the overall score depending upon the individual circumstances at each site.

The overall approach to scoring for each pathway is to assess and score the following three factors: hazard; likelihood of release; and receptors.

The **Hazard** of a waste pile or discharge is determined by:

The chemical composition of the waste pile or discharge;

The relative toxicities of the different constituent elements; and
The volume (or area) of the waste pile or discharge.

The **Likelihood of release** of a contaminant from a waste pile or discharge is an assessment of whether there have been releases of contaminants to the environment in the past and it addresses whether the waste pile or discharge is in any way contained. The former determines whether there have been releases of the contaminants from the mine site in the past while the latter addresses the possibility of releases from the source in the future. In all cases any contaminant must be attributable to the mine site.

The **Receptors** are the people, animals, ecosystems or protected areas that may be affected by a release from the mine site.

Each waste pile or discharge is mapped, measurements taken and other data collected on each mine site. The individual waste facilities are characterised so that the **Hazard** associated with each is known. The factors for **Likelihood of release** and the **Receptors** are recorded for each pathway at every waste pile or discharge.

The scoring process is automated with the use of an Excel workbook. There are eight worksheets in the workbook:

1. Waste hazard
2. Groundwater
3. Surface water
4. Air pathway
5. Direct contact (waste piles)
6. Direct contact (stream sediments)
7. Score
8. Lookup tables

The first worksheet scores individual waste sources that have been identified, measured, sampled and examined during this study. The next five worksheets (numbers 2 to 6 inclusive) score the named pathway. The seventh worksheet gives the overall score for the particular waste pile. The final worksheet contains the lookup tables servicing the input to the other tables. The remainder of this section outlines the criteria used in scoring the different factors for each pathway.

2.4.2 Hazard scoring

Within the scoring system there are three potential types of contamination hazard from one or other of the following:

1. Waste piles
2. Discharges
3. Stream sediments

As mentioned above the Hazard score is determined from the amount of contaminants, the relative toxicity of these contaminants and the volume (or area) within each source.

2.4.2.1 Waste piles

For waste piles the following elemental data are entered:

Sb (median value in mg/kg)
As (median value in mg/kg)
Ba (median value in mg/kg)
Cd (median value in mg/kg)
Cr (median value in mg/kg)
Cu (median value in mg/kg)
Fe (median value in mg/kg)
Pb (median value in mg/kg)
Mn (median value in mg/kg)
Hg (median value in mg/kg)
Ni (median value in mg/kg)
Se (median value in mg/kg)
Ag (median value in mg/kg)
Th (median value in mg/kg)
U (median value in mg/kg)
V (median value in mg/kg)
Zn (median value in mg/kg)

For each pile there may be up to 50 separate analyses. The median value has been chosen as the measure of ‘central tendency’ as it eliminates, to some degree, the influence of extreme outliers in the data.

The volume of the waste pile is required for the groundwater and surface water pathways while the area of the waste pile is required for the air and direct contact (waste piles) pathways. So the following are required:

1. Volume of solid waste pile (value in m^3)
2. Area of solid waste pile (value in m^2)

Not all elements pose the same threat to humans or animals. For example, Pb and Cd are known to pose a greater threat to humans than, say, Cu or Fe. Also, there are different threats to different animal or human receptors. However, there are no universally accepted values of absolute toxicities for the different elements and how they affect different receptors. There is some, but not total, agreement on the basis of relative toxicities. Table 2.3 presents the relative toxicities used in this study for human and livestock receptors. It was generated from the US EPA relative toxicity table and updated with expert advice for additional elements and receptors from CDM, LQM and the Department of Agriculture, Fisheries and Food (DAFF), Ireland. The table essentially represents, on a relative basis, the threat of the indicated element to either humans or livestock if ingested or inhaled from either soil or sediment.

Soil and Sediment		
Element	**Human Ingestion & Inhalation**	**Livestock**
Sb	10.00	0.10
As	10.00	0.10
Ba	0.01	0.01
Cd	10.00	10.00
Cr	10.00	0.10
Cu	0.00	0.10
Fe	0.001	0.01
Pb	10.00	1.00
Mn	0.10	0.001
Hg	10.00	1.00
Ni	10.00	0.10
Se	0.10	1.00
Ag	0.10	0.01
Th	10.00	0.01
U	10.00	0.01
V	0.10	0.10
Zn	0.01	0.01

Table 2.3 Relative toxicities for the elements indicated as used in this study if taken up from soil or sediment.

In addition to the expert input of those listed above, expert advice was also received late in the project from the Chemical Hazards and Poisons Division of the UK Health Protection Agency (UKHPA). The UKHPA agreed with 13 of the designations arrived at by our expert advisors. However, it made alternative suggestions for the following elements (Table 2.4).

Element	**CDM and LQM**	**UKHPA**
Mn	0.10	1.00
Se	0.01	1.00
Tl	0.00	1.00
Fe	0.001	0.01
Cu	0.00	0.01
Al	0.00	0.01
Co	0.00	0.01

Table 2.4 Comparison between CDM/LQM and UKHPA designations.

For thallium field-portable X-ray florescence (FP XRF) analysis is unreliable and was therefore not used in the scoring system. For Co and Se the amounts of elements were generally low and close to the detection limit (DL) and would not make any difference to the calculations. In the case of aluminium, the FP XRF does not allow for its detection (atomic number too low) and therefore Al would not contribute to the score in any case.

In order to assess the suggested changes to the relative toxicity numbers of the other elements (Cu, Fe and Mn) a number of test re-scorings were carried out. There was no material difference in the final scores.

Therefore it was decided not to use the relative toxicity numbers as suggested by the UKHPA as there was no effect on the conclusions reached in this test.

This additional expert input supported the relative toxicity numbers that had already been determined.

2.4.2.2 Discharges

Chemical analysis of water was undertaken during the summer and winter months at each of the measured discharges. The value entered was the one that gave the maximum load (that is, the maximum value of flow times analysis of either the summer flow or the winter flow). For discharges the following elemental data are entered:

Al (maximum measured value, µg/l)
Sb (maximum measured value, µg/l)
As (maximum measured value, µg/l)
Ba (maximum measured value, µg/l)
Cd (maximum measured value, µg/l)
Cr (maximum measured value, µg/l)
Cu (maximum measured value, µg/l)
Fe (maximum measured value, µg/l)
Pb (maximum measured value, µg/l)
Mn (maximum measured value, µg/l)
Hg (maximum measured value, µg/l)
Ni (maximum measured value, µg/l)
Se (maximum measured value, µg/l)
U (maximum measured value, µg/l)
V (maximum measured value, µg/l)
Zn (maximum measured value, µg/l)

The volume of the discharge is measured and entered into the spreadsheet:

1. Volume of liquid waste discharge ('Observed but not measurable' OR a value in l/day).

Not all elements pose the same threat to humans, animals or different ecosystems. For example, Pb and Cd are known to pose a greater threat to humans than, say, Cu or Fe. Also, there are different threats to different animal or human receptors. However, there are no universally accepted values of absolute toxicities for different elements and how they affect different receptors. There is some, but not total, agreement on the basis of relative toxicities. Table 2.5 presents the relative toxicities used in this study for human and livestock receptors. It was generated from the US EPA relative toxicity table and updated with expert advice for additional elements and receptors from CDM, LQM and DAFF. The table essentially shows, on a relative basis, the threat of the indicated element to humans, livestock and to two different ecosystems – a freshwater aquatic system and a marine water ecosystem – if taken up from either surface or groundwater. See also discussion on input from the UKHPA on relative toxicities for humans in Section 2.4.2.1.

Surface Water and Groundwater				
Element	**Human Ingestion**	**Eco Aquatic**	**Eco Salt – Aquatic**	**Livestock**
Al	0.00	0.10	0.10	0.001
Sb	10.00	0.10	0.10	0.10
As	10.00	0.01	0.10	0.10
Ba	0.01	0.001	0.001	0.01
Cd	10.00	10.00	1.00	10.00
Cr	10.00	0.10	0.10	0.10
Cu	0.00	1.00	1.00	0.10
Fe	0.001	0.01	0.01	0.01
Pb	10.00	1.00	1.00	1.00
Mn	0.10	0.00	0.00	0.001
Hg	10.00	10.00	10.00	1.00
Ni	10.00	0.10	1.00	0.10
Se	0.10	1.00	0.10	1.00
U	10.00	0.01	0.01	0.01
V	0.10	0.00	0.00	0.10
Zn	0.01	0.01	0.10	0.01

Table 2.5 Relative toxicities for the elements indicated as used in this study if taken up from surface or groundwater.

2.4.2.3 Stream sediments

For stream sediments the following elemental data are entered:

Sb (maximum value in mg/kg)
As (maximum value in mg/kg)
Ba (maximum value in mg/kg)
Cd (maximum value in mg/kg)
Cr (maximum value in mg/kg)
Cu (maximum value in mg/kg)
Fe (maximum value in mg/kg)
Pb (maximum value in mg/kg)
Mn (maximum value in mg/kg)
Hg (maximum value in mg/kg)
Ni (maximum value in mg/kg)
Se (maximum value in mg/kg)
Ag (maximum value in mg/kg)
Th (maximum value in mg/kg)
U (maximum value in mg/kg)
V (maximum value in mg/kg)
Zn (maximum value in mg/kg)

The length of stream or river contaminated is recorded and entered into the spreadsheet. ‘Contaminated’ is defined as values of mine-related elements greater than three times the upstream value for that element.

2.4.2.4 Contaminated stream sediments (value in metres)

As in the other hazard sources not all elements pose the same threat to livestock in stream sediments. However, there are no universally accepted values of absolute toxicities for different elements and how they affect livestock if ingested from stream sediments. There is some, but not total, agreement on the basis of relative toxicities. Table 2.6 shows the relative toxicities used in this study for human and livestock receptors. It was generated from the US EPA relative toxicity table and updated with expert advice for additional elements and receptors from CDM, LQM and DAFF. The table essentially represents, on a relative basis, the threat of the indicated element to livestock if taken up from stream sediments.

Soil and Sediment	
Element	**Livestock**
Sb	0.10
As	0.10
Ba	0.01
Cd	10.00
Cr	0.10
Cu	0.10
Fe	0.01
Pb	1.00
Mn	0.001
Hg	1.00
Ni	0.10
Se	1.00
Ag	0.01
Th	0.01
U	0.01
V	0.10
Zn	0.01

Table 2.6 Relative toxicities for the elements indicated as used in this study if taken up from stream sediments by livestock.

Having entered all relevant data, a **Hazard** score is generated for each pathway within the spreadsheet and used in the overall calculation of the score for that pathway (for further detail see Appendix 1).

2.4.3 Likelihood of release score

The following inputs were used for each of the pathways.

2.4.3.1 Groundwater pathway

Criterion	Options
Observed release	YES or NO
Exceedances of water standards	YES or NO
Potential to release	
Containment at site (select from list)	1. No containment 2. Presence of ONE of the following: berm, liner, run-on diversions or vegetated cover 3. Presence of TWO of the following: berm, liner, run-on diversions or vegetated cover 4. Presence of THREE of the following: berm, liner, run-on diversions or vegetated cover 5. Completely contained – presence of ALL FOUR of the following: berm, liner, run-on diversions or vegetated cover
Depth to water table	Enter value in metres

2.4.3.2 Surface water pathway

Criterion	Options
Observed release	YES or NO
Exceedances of water standards	YES or NO
Potential to release	
Containment at site (select from list)	1. No containment 2. Presence of ONE of the following: dams, diversions, pit lakes and sediment basins or traps 3. Presence of TWO of the following: dams, diversions, pit lakes and sediment basins or traps 4. Presence of all THREE of the following: dams, diversions, pit lakes and sediment basins or traps
Distance from waste pile or discharge to nearest surface water drainage (select from list)	1. <10 m 2. 10–30 m 3. >30 m

2.4.3.3 Air pathway

Criterion	Options
Observed release (select from list)	1. Yes (dust blow observed, evidence of waste blown from a pile, reliable eyewitness accounts) 2. No
Potential to release – containment at the site (select from list)	1. High dust potential (<50% cover or screening) 2. Moderate dust potential (50–75% cover or screening) 3. Low dust potential (75–95% cover or screening) 4. No dust potential (>95% cover or screening)

2.4.3.4 Direct contact pathway (waste piles)

Criterion	Options
Observed exposure	
Residence within 250 m of the waste pile	YES or NO
Recreational activities taking place at the site (direct observation or evidence)	YES or NO
Potential to release	
Site accessibility (select from list)	1. Easily accessible (no fences, gates or signs) 2. Moderately accessible (barbed wire fences, road gated, signage) 3. Difficult access (chain link fence, road gated and locked) 4. Not accessible (site completely fenced, access road gated and locked, on-site security within 250 m of the waste piles)
Condition of restrictions (select from list)	1. Well maintained, no breaches 2. Small animals can access with ease, humans and animals can access with difficulty. Vehicles cannot gain entry. Less than three breaches. 3. Small animals, human and livestock can access with ease. Vehicles can enter. Less than five breaches. 4. Small animals, human and livestock can access with ease. Vehicles can enter or more than five breaches
Distance to nearest residence	Enter value in metres

2.4.3.5 Direct contact pathway (stream sediments)

Criterion	Options
Observed exposure	
Farm within 250 m of the waste pile	YES or NO

Having entered all relevant data, a **Likelihood of release** score is generated within the spreadsheet and used in the overall calculation of the score for that pathway.

2.4.4 Receptor score

The following is input for each of the pathways.

2.4.4.1 Groundwater pathway

Criterion	Options*
Aquifer category (select from list). The aquifer classification has been developed by the GSI/EPA and the GSI has maps for the country indicating the type of aquifer. This information was used for the groundwater pathway.	1. Rk – Karstified 2. Rkc – Karstified, dominated by conduit flow 3. Rg – Extensive sand/gravel 4. Rkd – Karstified, dominated by diffuse flow 5. Rf – Fissured bedrock 6. Lm – Generally moderately productive 7. Ll – Moderately productive only in local zones 8. Lk – Locally important karstified aquifer 9. Lg – Local sand/gravel 10. Pl – Generally unproductive except for local zones 11. Pu – Generally unproductive
Number of wells within 1 km	Number of wells from CSO statistics adjusted for area from a GIS.
Vulnerability of groundwater adjustment (select from list as determined from groundwater vulnerability map (GSI))	1. Extreme (rock near surface or karst) 2. Extreme 3. High 4. High to low 5. Moderate 6. Low 7. No data

*Note R = Regional and L = Local.

2.4.4.2 Surface water pathway

Criterion	Options
Total number of persons using surface water for drinking from all abstractions within a 10-km radius	Enter number from CSO statistics
Is there a local stream/drainage within 100 m?	YES or NO
Other users	
Fishery class (select from list)	1. Salmonid 2. No classification
Recreational use (select from list)	1. Observed (fishing or boating or

	swimming, etc.) 2. Not observed
Protected area status (select from list)	1. Yes (National Park, SAC, SPA, NHA) 2. No designation
Livestock watering (select from list)	1. Yes 2. Unknown

2.4.4.3 Air pathway

Criterion	Options
Population within 1 km of the waste	Enter value from CSO statistics
Distance to the nearest residence	Enter value in metres
Protected areas (NHAs, SPAs, SACs, Nature Reserves or National Parks)	YES or NO

2.4.4.4 Direct contact pathway (waste piles)

Criterion	Options
Population within 2 km of the site	Enter number from CSO statistics
Distance to the nearest residence	Enter value in metres
On-site workers (select from list)	1. Predominantly working outside 2. Farmers 3. Predominantly working inside 4. No workers
Attractiveness of the site for recreational use (select from list)	1. Highly attractive 2. Moderately attractive 3. Low attractiveness 4. Not attractive

2.4.4.5 Direct contact pathway (stream sediments)

Criterion	Options
Livestock accessing the stream (select from list)	1. Livestock observed in stream or other signs, e.g. hoof marks 2. Unknown

Having entered all relevant data a **Receptor** score is generated within the spreadsheet and used in the overall calculation of the score for that pathway.

2.4.5 Total site score for human and animal health

The total score has been set up in the spreadsheet to be automatically generated for an individual waste pile or discharge or stream sediment section by first multiplying the **Hazard** score by the **Likelihood to release** score by the **Receptor** score and then summing the relevant pathways. For a waste pile or discharge source, the groundwater, surface water, air and direct contact pathways are summed. For the stream sediment source just the stream sediment pathway is used.

2.4.6 Total mine site score

For an individual mine site all the individual scores for waste piles, discharges and stream sediments are summed. This is the final score for the site.

2.5 Classification Once the final score for the mine site is obtained it is assigned to one of the following classes:

Class	Score	Description	Response
I	>2,000	Relates to large complex sites that have a number of issues, the sites contain large volumes of metal-rich waste that potentially pose risks to human and animal health and safety as well as to the environment.	These sites should have a full risk assessment carried out. These sites should be monitored on an ongoing basis.
II	1,000 – 2,000	A district consisting of several sites, containing numerous small spoil piles with high concentrations of metals and are visited regularly by the public. Accordingly these sites potentially pose risks to human and animal health and safety as well as to the environment.	These sites require general monitoring of most or all waste piles, discharges or stream sediments on an annual basis.
III	300 – 1,000	Sites containing fewer and smaller spoil piles that have high concentrations of metals. The sites are used by the public and potentially pose risks to human and animal health and safety as well as to the environment.	These sites require general monitoring of most or all waste piles, discharges or stream sediments on a biennial basis.
IV	100 – 300	Sites that generally have large volumes of waste with low concentrations of those metals that potentially pose risks to human and animal health and safety as well as to the environment. Any high metal spoil piles are very small in volume.	These sites require specific monitoring of particular waste piles, discharges or stream sediments on a five-yearly basis.
V	<100	These sites pose little threat to humans, animals or the environment, although there may be minor site-specific issues which need to be addressed	These sites generally do not require monitoring except where there are minor specific issues.

CHAPTER 3

Geochemical Methodology

3.1 Aims and scope of geochemical site investigations

The aims of the geochemical site investigations undertaken for the HMS-IRC project were:

(1) To provide a basic chemical characterisation of each site, with the added aim of identifying issues of concern for human and animal health and the environment, and

(2) To provide sufficient data to allow scoring of each site using the HMS-IRC scoring system.

Initially, the scope of the site investigations included **solid waste**, **surface water**, **groundwater**, **stream sediments** and **soil**. Later, **leachate** testing was incorporated into the geochemical programme while soil was excluded. A geochemical soil survey around each of the sites would be a substantial undertaking and would require significant resources and would be time consuming. For this reason, the soil geochemical survey is more appropriate to site-specific investigations of individual sites rather than to a national survey of the kind conducted under the HMS-IRC project.

3.2 Solid waste analyses

3.2.1 Types of solid mine waste

For the purpose of the HMS-IRC project, solid waste means any solid matter on mine sites that is a by-product of mining or of the processing of mined material. This includes spoil, whether in deliberately created spoil heaps or in casually dumped material, tailings, processing waste and stripping waste. It also includes a thin layer of fines or dust that is dispersed at most mine sites as a consequence of action on partially or fully processed material. This dispersal may occur as a result of human or mechanical activity, wind or rain. This is largely confined to former processing areas and a short distance from them. On some of the older sites, revegetation has taken place leaving a thin layer of **soil** on top of mine waste. This soil is generally a mixture of organic material, mine waste and introduced soil. It can be heavily contaminated by heavy metals and it constitutes a particular type of soil in the context of Irish mine sites, not to be confused with soil on land surrounding but never a part of a mine site.

Spoil *sensu stricto* is mined ore that has become diluted in the course of mining by its largely unmineralised host rock or gangue. In consequence, its concentration of ore material is diluted to the point of making it uneconomic to process further. In Ireland, extensive spoil heaps are characteristic of 18th and 19th century mine sites, e.g. Avoca and Glendasan. Before the large-scale, mechanised mining of the 20th century and the efficient extraction techniques that accompanied it, miners focused on high-grade zones within relatively narrow ore zones or *lodes*. Blasting of such zones caused dilution by the host rock. The mined material was usually tipped close to the entrance to shafts or adits and picked over by hand to extract the best ore. This inefficient winnowing process has created many spoil heaps with significant metal contents.

In contrast to the relatively inefficient mining of high-grade ore in the 19th century, mining in the 20th and 21st centuries has involved mechanical mining of large volumes of ore material and relatively efficient extraction of the ore material using sophisticated techniques in purpose-built processing plants. Ore is generally crushed in the mine itself and then passed to the processing plant for grinding, typically to sand- or silt-sized particles. Froth flotation has been employed in most modern Irish metal mines to separate the ore minerals from the gangue material and it is particularly useful because it can be used to process polymetallic ores. Surfactants are added to the slurry that binds preferentially to specific metals to make them hydrophobic. When air is passed through, a froth forms to which the hydrophobic metals bind. This froth or scum is removed from the surface of the slurry. The waste slurry left after completion of this process is called tailings. The tailings material is commonly disposed of in purpose-built lagoons called tailings ponds. Tailings are also placed underground as backfill providing storage for the tailings and support for the underground workings. Backfilling of underground workings is commonplace in modern operating underground mines in Ireland but was not extensively employed as a disposal method in the closed mines studied in the HMS-IRC project, with the exception of Avoca.

The four abandoned large-scale 20th century mines in Ireland (Tynagh, Gortdrum, Silvermines and Avoca) are, therefore, characterised by large tailings ponds. Smaller-scale deposits of similar material are found on 19th century sites also but these tailings are generally by-products of gravity separation methods. In addition to tailings ponds, the large 20th century mines studied also have waste heaps created from low-grade material stripped from the surface during excavation of open pits. These waste heaps, not spoil heaps in the narrow meaning of the term, are generally very large-scale accumulations that typically contain a high proportion of very coarse blocks.

Siltation ponds are used on mine sites to separate material from process water. Solid siltation wastes are found, for example, at Gortdrum and Tynagh in the remains of dried-out ponds. Other waste found on the sites of processing plants is generally a product of a specific process.

On 19th century sites such processes including cobbing or hand-dressing of ore with hammers, coarse crushing, stamping, i.e. fine crushing and gravity separation into buddles.

In the case of 20th century sites, the processing equipment and buildings have, in general, been dismantled and removed after mine closure. Remains of processed or concentrated ore are therefore not widespread or voluminous. Nevertheless, most of the sites have some examples of processing waste. Such waste, because of its nature, can contain very high levels of metals or other elements.

3.2.2 General overview of solid waste analyses

Solid waste analyses were carried out using an FP-XRF analyser. The analyser allowed semi-quantitative *in-situ* analysis of mine waste and quantitative laboratory-based analysis of prepared samples. The field analytical method is outlined in Appendix 2. Approximately 10% of sites analysed in the field were sampled for follow-up analysis by XRF in the GSI laboratory. Most of these samples were also sent to a certified commercial laboratory where they were analysed by inductively coupled plasma – atomic emission spectrometry (ICP-AES) after multi-acid digestion. Comparison of these samples with those analysed by XRF has allowed a detailed assessment of the XRF analyser's performance to be carried out (Appendix 4). The FP-XRF has proved to be an extremely useful tool that has enabled completion of many more analyses than would have been possible using traditional laboratory-based methods. As described in Appendix 4, the analyser's performance, both *in situ* and in the laboratory, has more than met the project's requirements.

Table 3.1 provides a breakdown of the numbers of solid waste analyses completed for the HMS-IRC project, excluding check samples sent to the external laboratory.

The 1,432 *in-situ* analyses form the basis for the scores assigned to waste heaps in the HMS-IRC scoring system and comprise over 87% of all solid waste analyses. The bulk of these analyses were on spoil. Of the 208 samples analysed by XRF in the GSI laboratory, 37 were not previously analysed in the field. These were mostly siltation pond samples from Gortdrum that were too wet for *in-situ* analysis. The remaining 171 samples were from the 1,432 sites analysed in the field and, of these, 165 were sent to OMAC Laboratories for comparative analysis by ICP-AES. These 165 samples constitute 11.5% of the 1,432 *in-situ* analyses.

Waste Type	**Field**	**Lab**	**Totals**
Spoil	906	94	1,000
Tailings	341	55	396
Processing Waste	148	49	197
Soil	25	3	28
Other	12	7	19
Totals	**1,432**	**208**	**1,640**

Table 3.1 Numbers of solid analyses carried out during the HMS-IRC project.

3.2.3 XRF analysis

X-ray fluorescence (XRF) analysis is a long-established and well-understood analytical technique. The analyser used for the HMS-IRC project (right) uses a battery-powered cathode tube to generate a beam of X-rays. This beam is focused through a 20-mm diameter aperture onto the sample. The X-rays then collide with atoms of elements within the sample. The excitation of, or transfer of energy to, an atom results in the emission of X-rays by that atom. The emitted X-rays each have an energy that is characteristic of the atom that emits it. Thus, iron emits two principal X-rays, called Kα and Kβ, with characteristic energies of 6.40 and 7.06 KeV, respectively (Fig. 3.1). The X-rays emitted from the sample are in turn detected by the XRF analyser. The relative concentration of any element in a sample is proportional to the number of its characteristic X-rays emitted.

The XRF analyser is equipped with two filters, one for detection of elements of atomic number ≥23 (vanadium) and one for elements with atomic number between

15 (phosphorus) and 22 (titanium). Each filter allows better detection and resolution of elements within the ranges specified.

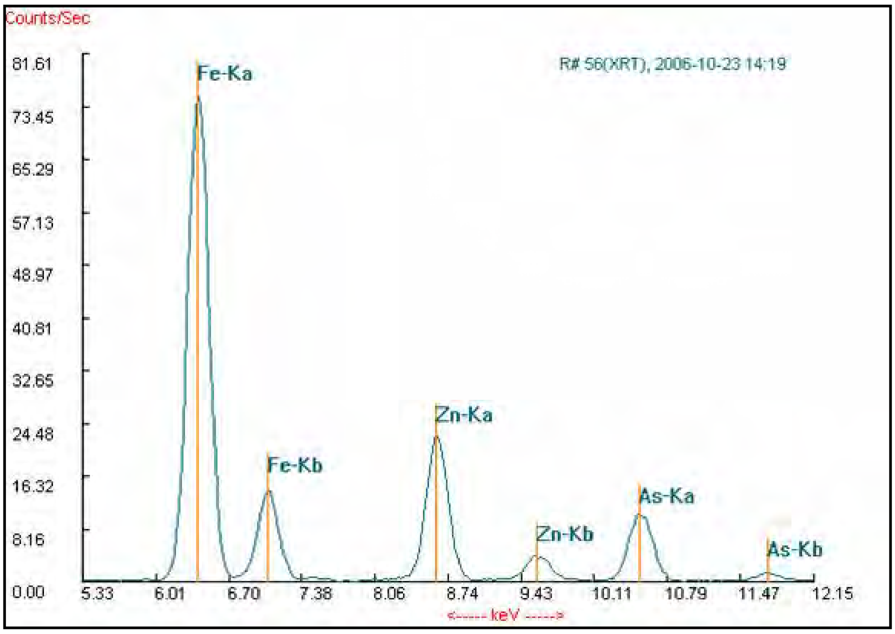


Figure 3.1 Typical X-ray spectrum for portable XRF analyser.

As the analysis is carried out, the X-ray count data are processed by the analyser using an in-built programme that utilises standard correction factors and calibration data for each element. The analyser is calibrated at the factory prior to delivery. Different calibrations can be used depending on the nature of the material to be analysed. In the case of the HMS-IRC instrument, an 'environmental' calibration was selected as most appropriate as it allowed for a wide range of sample types. The calibration was carried out using well-characterised soil and sediment standards containing variable amounts of metals and other elements of interest. Further details are contained in Appendix 4.

The analyser is calibrated to analyse 30 elements (Table 3.2). Inter-element interference and peak overlap can make accurate calibration of some element combinations difficult. The elements were selected for calibration on the basis of what were considered to be the most useful in the context of Irish mine sites.

The detection limits listed in Table 3.2 are those supplied by the manufacturer of the analyser, NITON, for prepared samples analysed under optimum conditions. Detection limits have not been determined for all elements, especially relatively rare elements such as (Bi) and (Tl). The standards used in determining the detection limits were soils and sediments.

Where sample preparation and analytical conditions are consistent, variation in detection limit for any given element will depend primarily on sample matrix composition. For example, in a sample with a high concentration of heavy elements such as iron and lead, X-rays emitted by various elements in the sample, and especially the lighter elements, will not easily escape the sample matrix owing to interference by atoms of the heavy elements. Thus the detection limit for any element will be higher than in a sample with a low or lower concentration of heavy elements.

Trials conducted by the US EPA on the NITON portable XRF analyser (US EPA 2006) gave detection limits of 1 to 20 mg/kg for As, Pb, Hg, Se and V, 20 to 50 mg/kg for Cu, Ag and Zn, 50 to 100 mg/kg for Cr and Ni and >100 mg/kg for Sb and Cd. The detection limits for Sb and Cd may have been biased toward high values as a consequence of high concentrations of other metals in the matrices of the standards analysed. Otherwise, the US EPA tests are in good agreement with the detection limits reported by NITON.

Accuracy in XRF analyses depends upon the correction programme used and, principally, the calibration. Correction programmes take account of the physics of X-ray excitation and emission and are relatively standard. Calibration is the greatest influence on accuracy. The greater the difference in composition between the sample being analysed and the standards used in the calibration the greater the potential inaccuracy in the results. The HMS-IRC analyser was calibrated using soil and sediment standards. The matrix in such standards comprises mainly silicates.

The matrix in mine waste samples will have, in addition to silicates, high concentrations of metal sulphides, oxides and hydroxides that will influence X-ray behaviour during analysis. Such influences will not necessarily be accounted for by the correction programme and the result can be a significant departure from accuracy. Comparison of the certified composition of the National Institute of Standards and Technology (NIST) mine waste standard (NIST 2780) with the results of analyses by the HMS-IRC analyser (Appendix 4) show a consistent bias towards lower measured element concentrations than those certified by NIST.

	NIST Standard Reference Material (Soil matrix)	
Element	**60 s**	**120 s**
P	2.5%	
S	1.5%	
K	500	
Ca	400	
Sc	200	
Ti	200	
V	175	
Cr	60	
Ag		50
As		15
Ba	1,000	
Cd		65
Co		150
Cu		60
Fe		175
Hg		12
Mn		175
Ni		90
Pb		20
Rb		15
Sb		175
Se		150
Sn		150
Sr		30
Zn		40

Table 3.2 Elements calibrated for XRF analysis with detection limits (mg/kg).

The analysis time is controlled by the user. For HMS-IRC analyses, analysis time was 90 s for *in-situ* analyses and 180 s for laboratory analyses. In each case, two-thirds of the analysis time (60 and 120 s, respectively) were apportioned to the heavy-element filter and one-third (30 and 60 s, respectively) to the light-element filter. All HMS-IRC samples analysed in the laboratory were run at least twice and the average of the two results was taken as the final result.

Quality control (QC)/quality assurance (QA) procedures for XRF analysis included:

1. Routine calibration of the X-ray beam at 1- to 2-h intervals;
2. Regular analyses of a range of standard material during laboratory-based analyses of prepared samples;
3. Re-analysis of prepared samples by a certified external laboratory using ICP-AES and other standard analytical techniques.

Appendix 4 contains a detailed account of the performance of the XRF analyser, based on analysis of standards and comparison of results for samples analysed both by XRF and ICP-AES in an external laboratory.

3.2.4 Spoil analyses

Most solid waste analysed in the course of the project was spoil. The analysis method followed the sampling protocol in Appendix 2. In general, the aim of the *in-situ* analyses was to provide an estimate of minimum, maximum and median concentrations in any given spoil heap and on mine sites. The median value has been adopted in the HMS-IRC scoring system. Typically, five-, six- or nine-point grids with 5- to 10-m spacings were employed. However, modifications to this ideal approach were made depending on heap shape, size and chemical variability.

Chemical variability can be implied by visible colour or mineralogical variation. The real-time analysis afforded by the portable XRF analyser also allowed judgements to be made in the field regarding changes to sampling plans. Such modifications included reducing the number of analyses where low levels of elements of interest were detected and increasing the number where 'hot spots', i.e. zones with unusually high concentrations of elements of interest, were detected. While the inclusion of hot-spot analyses may serve to bias the median value towards higher concentrations, recognition and analysis of such zones are important aspects of the characterisation of mine sites and the determination of issues of concern.

The general approach to *in-situ* analysis is to mark out a 20 x 20 cm area in which the top 5 cm approximately of spoil are raked over and larger clasts removed. The spoil is then compressed and smoothed to form a suitable flat, compacted surface with minimal pore space, thus reducing the influence of air on the analysis (right). Three separate spots within the 20 x 20 cm area were covered within the 90 s of XRF analysis in order to counteract the effects of the chemical variability inherent in many samples of mine spoil. High moisture contents also posed some difficulties for *in-situ* analyses at some sites. Moisture is a potential problem because, like air, it dilutes the proportion of solid material in any given sample and it also interferes with and attenuates the X-rays. The result is a lower apparent concentration of elements of interest in a sample. However, analyses of fine or compacted material, such as tailings or siltation deposits, are more likely to be affected by moisture than those of spoil which is typically relatively coarse-grained and less retentive of water than fine waste.

3.2.5 Tailings analyses

The 20th century mines studied for the HMS-IRC project all have large tailings impoundments that store the waste material following mineral processing. Some 19th century mines also have tailings deposits, though they are much smaller in scale and typically less well impounded.

The general approach to tailings analysis was similar to that adopted for spoil analysis. The aim was to obtain an estimate of the minimum, maximum and median concentrations of elements of interest in the tailings. A grid was defined for each deposit. Because of the typically much greater surface area, grids on tailings deposits tended to be much larger than those on individual spoil heaps, with the number of individual sites exceeding 30 in some cases. In addition to the composition at the surface of the deposit, vertical compositional variation was also assessed. At Avoca and Gortdrum, a trailer-mounted mechanical drill was used to retrieve samples up to 6 m below the surface of the tailings pond. At other sites (Tynagh, Abbeytown, Glendalough), a combination of manual digging and augering was used to analyse samples at depths of up to 1.5 m below the surface.

Tailings analysed for the HMS-IRC project are typically sand to silt grade. On the surface of deposits they are relatively dry and easily analysed *in situ* by portable XRF. At depth, however, owing to the effects of retained water and the pressure of overlying tailings, they become increasingly plastic and less viscous (right). Below approximately 1 m at Gortdrum and Avoca, the tailings have the consistency of wet mud. This material was placed in plastic bags prior to analysis through the bag.

3.2.6 Processing waste

On 19th century mine sites scored for HMS-IRC, processing waste includes waste from crushers, stamps batteries, gravity-separation equipment, such as buddles, and furnaces. Processing waste observed on 20th century mine sites included siltation pond sediment, furnace residue and thickener waste. Apart from waste derived from specific processes, a thin layer of waste typically covers the sites of former processing plants. This is material that has been spread around the vicinity of the processing plant by human and mechanical activity, as well as by wind and rain and it is relatively thin.

With the exception of siltation pond residue and the thin coating referred to above, processing waste tends to occur in very localised areas on the sites of former processing plants, e.g. in and around particular buildings and structures. Analysis of such waste for the HMS-IRC project was typically opportunistic and directed towards ascertaining the range of elements and their concentrations present in the waste. It followed no preconceived pattern of analysis, e.g. a grid.

3.2.7 Soil and other waste

Soil in this context refers to soil overlying mine sites, particularly 19th century sites that have undergone revegetation over a long period of time. On such sites the establishment of a soil cover appears to follow from a gradual colonisation of the mine surface by invading species from the immediate surrounding land and the establishment of an organic substrate on top of the residual mine waste. On some sites, grassland has been established, presumably through intensive amelioration efforts by landowners. Where grass is established, the base of the root zone is typically at or just above the buried mine waste. The soil is inevitably mixed to some degree with residual mine waste from the surface of the mine site. Analysis of this soil was generally accomplished by turning over the sod and analysing the soil at the base of the root zone, with a grid-based approach similar to that adopted for spoil.

Other waste analysed included granite blocks and mortar in a smelter chimney in Ballycorus and mortar in the remains of an engine house in Ballyhickey. Aggregate derived from waste piles at Gortdrum was also analysed. Again, these were opportunistic analyses and followed no specified pattern.

3.3 Water analyses

Surface water analyses were carried out on and around mine sites to assess the potential for downstream contamination of local watercourses by mine water discharges via adits or shafts, by leachate generated within solid waste heaps or by surface run-off from the site. In general, water from rivers and streams was sampled upstream and downstream of the mine site. Mine discharges and leachate were also sampled. Active surface run-off was sampled in only one instance but ponding of run-off is common on mine sites and this water can give an indication of the chemistry of run-off.

Groundwater was sampled from field wells and springs where available. Wells bored for water supply to private homes were not sampled because the time required to locate wells, secure permission and sample them was considered excessive. In addition, many such wells are equipped with treatment cells that inevitably alter the chemistry of the water.

Water was sampled in both summer and winter in order to determine the effect on water chemistry as a result of the variation in flow rates of water in rivers, streams and mine discharges. Winter sampling took place between November 2006 and early March 2007, summer sampling between June and September 2007. Not all sites were sampled in both periods – smaller sites with only minor or even no mine water discharges were sampled only once. Flow rates were measured using a portable cut-throat flume. This was suitable for small-channelled discharges less than 1 m wide, i.e. adit discharges and small streams. Some flows too large to be measured with the flume were estimated by measuring the depth of water at intervals across the stream and measuring the speed of flow with a float. Table 3.3 provides a summary of the number and type of samples collected for the project.

A description of the sampling methodology is contained in Appendix 2. Samples were analysed by Alcontrol Ltd. Table 3.4 lists the parameters analysed and the analytical method employed. Some parameters analysed in the first period, winter 2006–2007, were not analysed in summer 2007. These included biological oxygen demand (BOD) and chemical oxygen demand (COD). The exclusion of these parameters reflected the fact that they are largely indicative of contamination of water by organic sources and not mine waste. Moreover, the requirement that BOD and COD analyses be carried out within 48 h of sampling placed significant constraints on the sampling programme, particularly in remote areas where it was not always possible to arrange rapid delivery of samples to the laboratory.

Sample Type	**Winter 2006–2007**	**Summer 2007**
Upstream of Mine Site	33	28
Downstream of Mine Site	86	80
Adit/Shaft Discharge	54	38
Ponding/Surface Run-off/Seepage	53	26
Open Pit Lake	9	10
Spring/Well	15	12
Total	**250**	**194**

Table 3.3 Water samples by source and season, HMS-IRC project.

Analysis	**Method**	**Elements**
Total Metals	ICP MS	Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, U, V, Zn (Detection limits: <1–2 µg/l)
Dissolved Metals	ICP MS	Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, U, V, Zn (Detection limits: 1–2 µg/l)
Total Mercury (Hg)	ICP IRIS	Hg (Detection limit: 50 µg/l)
Dissolved Mercury (Hg)	CV AA	Hg (Detection limit: 0.05 µg/l)
Major Cations (Total)	ICP-MS	Ca (Detection limit: 120 µg/l) Mg (Detection limit: 100 µg/l)
Major Cations (Total)	Flame Photo	Na, K (Detection limit: 200 µg/l)
Anions	KONE	PO_4 (Detection limit: 30 µg/l) SO_4 (Detection limit: 3,000 µg/l)
Oxygen Demand	5-day ATU	BOD (Detection limit: 2,000 µg/l)
Oxygen Demand	Photometry	COD (Detection limit: 15,000 µg/l)
Solids	Meter	TDS (Detection limit: 5,000 µg/l)
Solids	Gravimetric	TSS (Detection limit: 10,000 µg/l)

Table 3.4 HMS-IRC water analyses: parameters and methods.

3.4 Stream sediment analysis

Stream sediments upstream and downstream of mine sites were sampled to assess the degree of contamination, if any, arising from mine water discharges and transport of solid waste into watercourses. Elements in mine water discharges are either in the dissolved state or in solid matter in suspension. Precipitation of dissolved chemical elements from mine discharges onto the stream bed occurs when the solubility of these elements decreases as the mine water mixes with stream water. Elements in suspension can be deposited on the stream bed in response to changes in flow velocity or other physical parameters.

A total of 107 samples were collected at 16 mine sites. At each site, sediment was collected from a number of sub-sites over a stream length of 5–10 m where feasible. Not all mine sites are in proximity to streams and not all streams near mine sites contained sufficient sediment for sampling. Each sample was passed through a 2-mm and then a 150-µm polypropylene mesh sieve in the field and the fine fraction was stored in a sealed bucket. After drying in the GSI laboratory, the samples were analysed by XRF. Analysis procedure was the same as that for laboratory-analysed solid waste samples: 120 s for the heavy-element filter, 60 s for the light-element filter, each sample analysed at least twice with the average concentrations taken as the result. Appendix 2 contains a full description of the sampling methodology and analytical procedure employed.

Sampling of the 150-µm fraction as opposed to, say, the total sediment fraction has a number of advantages. Metals tend to partition into the finer fraction in stream sediments and as a consequence detection of metal contamination of stream sediments is more likely using the 150-µm fraction than a coarser or total fraction. Aquatic organisms that feed on the river or stream bed may more readily ingest the finer than the coarser sediment fraction so that the former is a more relevant measure of environmental impact. Finally, analysis of the fine fraction allows comparison of HMS-IRC data with those of the GSI’s Regional Geochemistry Programme and the use of the latter to augment the data for selected areas.

3.5 Leachate analyses

Leachate analyses were carried out on solid waste samples to provide a proxy analysis for contaminated groundwater in the vicinity of waste heaps. The HMS-IRC scoring system requires an indication of the potential of any waste heap to contaminate groundwater. In the absence of specific groundwater data around sites, the leachate analysis was used to model the extreme case where groundwater is contaminated to the extent that its composition is essentially that of leachate.

Leachate testing is described in detail in Appendix 2. Analyses of dissolved elements were carried out by Alcontrol Ltd. using ICP-MS, as outlined for water analyses (Section 3.3). Samples were selected as far as possible from among those already collected as part of the solid waste analysis programme. A total of 64 samples, covering 23 mine districts or sites, were analysed. For most sites, composite samples were created from several individual samples in an attempt to make the leachate sample as ‘representative’ as possible and the results were applied to all waste heaps in that site.

CHAPTER 4

Geochemical Assessment

4.1 Introduction

A detailed review of the geochemistry of each mine site studied for the HMS-IRC project is contained in each site report. This section summarises the findings of the detailed geochemical assessment contained in Appendix 3. It summarises the main findings in respect of measured parameters and considers those findings in the context of human, animal or environmental impacts that may arise as a consequence of exposure to these parameters.

Table 4.1 provides a full listing of all parameters measured for the project, according to sample type. Not all parameters measured are discussed in this assessment, which focuses on those that are included in the HMS-IRC scoring system.

4.2 Standards

In assessing the environmental impact of mine waste, reference is made to national and European standards or guidelines where appropriate. In addition reference was also made to standards from the following countries, Canada, Holland, the UK and the USA. Standards define maximum permitted levels of various parameters in specified media. Guidelines on the other hand provide maximum levels above which adverse affects may be expected. Where there are no national or European standards then guidelines or standards from the most relevant international sources were used.

4.2.1 Soils

As yet there are no uniform European standards for soil. Various guidelines have been developed over the years including the Dutch Intervention values for ‘standard’ soil (Table 4.2) and the UK’s Inter-Departmental Committee on the Redevelopment of Contaminated Land (ICRCL) threshold values. The latter were superseded in the 1990s by the soil guideline values (SGVs) produced by the UK’s Department of Environment, Food and Rural Affairs (DEFRA). These in turn have been withdrawn pending new values that reflect an updated methodology. The SGVs are based on modelled exposure of humans in occupational and non-occupational settings to the relevant element. They can be viewed as trigger values above which there may be cause for concern for human health that warrants further assessment. Because they are exposure or dose related, the SGVs differ for different soil categories or land uses. SGVs are similar in concept to the comparison values (CVs) defined by the US Agency for Toxic Substances and Disease Registry (ATSDR). These are also reproduced in Table 4.2.

Parameter	**Solid Waste/Stream Sediment Analyses**	**Water Analyses**	**Leachate Analyses**
Temperature		✓	✓
pH		✓	✓
EC		✓	✓
DO		✓	
Alkalinity/Acidity		✓	✓
BOD/COD		✓	
TDS/TSS		✓	
Al		✓	✓
As	✓	✓	✓
Ba	✓	✓	✓
Bi*	✓		
Ca*	✓	✓	✓
Cd	✓	✓	✓
Co**	✓	✓	✓
Cr	✓	✓	✓
Cu	✓	✓	✓
Fe	✓	✓	✓
Hg	✓	✓	✓
K*	✓	✓	✓
Mg		✓	✓
Mn	✓	✓	✓
Mo		✓	✓
Na*		✓	✓
Ni	✓	✓	✓
P/PO_4*	✓	✓	
Pb	✓	✓	✓
Rb*	✓		
S/SO_4	✓	✓	
Sb	✓	✓	✓
Se	✓	✓	✓
Sn*	✓	✓	✓
Sr*	✓		
Th	✓		
Tl**	✓		
U	✓	✓	✓
V	✓	✓	✓
W*	✓		
Zn	✓	✓	✓

* No relative toxicity value, not included in HMS-IRC scoring system.

** XRF analysis unreliable, not included in HMS-IRC scoring system.

Table 4.1 Parameters analysed for the HMS-IRC project, various media.

4.2.2 Water

Water standards are available for drinking water (European Communities Drinking Water Standards, SI 278, 2007) and surface water (Draft European Communities

Environmental Objectives (Surface Waters) Regulations, 2008). Neither of these standards includes all parameters of interest but in combination they cover the main ones. Table 4.3 summarises the standard data used in the HMS-IRC scoring system.

In the HMS-IRC project, water standards are used to determine if any parameter in groundwater or surface water downstream of a mine waste source exceeds the standard. This information is incorporated into the HMS-IRC scoring system and it is also used in the context of individual site descriptions to identify watercourses at risk of mine-related contamination.

	Dutch		**SGV**		**ATSDR**	
Parameter mg/kg	**Target Value**	**Intervention Value**	**Residential /Allotments**	**Industrial**	**Child**	**Adult**
As	29	55	20	500	20	200
Ba	200	625			4,000	50,000
Cd	0.8	12	1–8	1,400	10	100
Cr VI			130	5,000	200	2,000
Cr	100	380				
Cu	36	190			2,000	20,000
Hg	0.3	10	8	480		
Mn					3,000	40,000
Mo	10	200			300	4,000
Ni	35	210	50	5,000	1,000	10,000
Pb	85	530	450	750		
Sb					20	300
Se			35	8,000	300	4,000
U (soluble)					100	1,000
V					200	2,000
Zn	140	720			20,000	200,000

Table 4.2 Soil reference values (Dutch Intervention, DEFRA SGV and pre-2004 ATSDR CV). All values in mg/kg.

Parameter	Unit	Standard	Source
pH		≥ 6.5–≤ 9.5	SI 278 (2007)
EC	mS/cm	≤ 2.5	SI 278 (2007)
Al	µg/l	200	SI 278 (2007)
As*	µg/l	25	Draft EC (2008)
Ba	µg/l	2,000	US EPA
Cd	µg/l	0.25	Draft EC (2008)
Cr	µg/l	50	SI 278 (2007)
Cr III*	µg/l	4.7	Draft EC (2008)
Cr IV	µg/l	3.4	Draft EC (2008)
Cu* [hardness < 100 mg/l CaCO$_3$]	µg/l	5	Draft EC (2008)
Cu* [hardness > 100 mg/l CaCO$_3$]	µg/l	30	Draft EC (2008)
Hg	µg/l	0.05	Draft EC (2008)
Fe	µg/l	200	SI 278 (2007)
Mn	µg/l	50	SI 278 (2007)
Na	µg/l	200,000	SI 278 (2007)
Ni	µg/l	20	Draft EC (2008)
Pb	µg/l	7.2	Draft EC (2008)
Sb	µg/l	5	SI 278 (2007)
Se	µg/l	10	SI 278 (2007)
SO$_4$	µg/l	250,000	SI 278 (2007)
Zn* [hardness < 10 mg/l CaCO$_3$]	µg/l	8	Draft EC (2008)
Zn* [hardness 10–100 mg/l CaCO$_3$]	µg/l	50	Draft EC (2008)
Zn* [hardness > 100 mg/l CaCO$_3$]	µg/l	100	Draft EC (2008)

***Note: values for As, CrIII, Cu and Zn are to be added to background values.**

Table 4.3 Water standards used for the HMS-IRC project.

4.2.3 Stream sediments

Stream sediment data are included in the scoring system since contaminated stream sediments are a potential hazard to livestock that use streams as a source of drinking water. Reference values (Table 4.4) have been provided by the Central Veterinary Research Laboratory (CVRL) (Ireland), compiled from published sources, in the form of an estimated dry matter ingestion limit. These limits relate to the total stream sediment size fraction. Stream sediments analysed for the HMS-IRC project are typically from the <150-µm fraction. Metals tend to be concentrated in the finer fractions in stream sediments so that the 150-µm fraction generally has higher metal concentrations than the total fraction. An example of this is provided by stream sediments from Caim, Co. Wexford, where both the <150-µm and the much coarser <2-mm fractions were analysed. Lead concentrations in the <150-µm fraction in three samples were 557, 894 and 2,583 mg/kg, respectively, while in the <2-mm fraction in the same samples the concentrations were less than half as much, i.e. 234, 350 and 926 mg/kg, respectively. Although most stream sediment data for the HMS-IRC project are for the <150-µm fraction, nevertheless the standards in

Table 4.4 provide a useful indication of potential hazards to livestock arising from stream sediment contamination around mine sites.

Parameter	Unit	Guideline Value	Source
Ag	mg/kg (dry matter)	1,000	CVRL
As	mg/kg (dry matter)	300	CVRL
Ba	mg/kg (dry matter)	1,000	CVRL
Cd	mg/kg (dry matter)	100	CVRL
Cr III	mg/kg (dry matter)	1,000	CVRL
Cu	mg/kg (dry matter)	100	CVRL
Fe	mg/kg (dry matter)	10,000	CVRL
Hg	mg/kg (dry matter)	5	CVRL
Mn	mg/kg (dry matter)	5,000	CVRL
Ni	mg/kg (dry matter)	1,000	CVRL
Pb	mg/kg (dry matter)	1,000	CVRL
Sb	mg/kg (dry matter)	1,000	CVRL
Se	mg/kg (dry matter)	12	CVRL
Sn	mg/kg (dry matter)	1,000	CVRL
V	mg/kg (dry matter)	500	CVRL
Zn	mg/kg (dry matter)	5,000	CVRL

Note: values assume sediment is 10% of diet with no consumable herbage growth and that metals are bioavailable.

Table 4.4 Stream sediment guidelines used for the HMS-IRC project.

4.3 Summary of findings for measured parameters

4.3.1 Acidity, alkalinity and pH

Low pH and high acidity are features of mine water in the three Irish coalfields as well as in the Avoca mine. Some low-volume seepages draining coal waste can have very high acidity but only at Avoca are there high-volume discharges of mine water that are also highly acidic. Low pH and high acidity are of particular concern for aquatic ecosystems.

4.3.2 Aluminium – Al

Some mine waters have very high concentrations of both total and dissolved Al. There is an inverse relationship between pH and Al concentration, with those mine districts with low-pH water, such as Avoca and the three coalfields, having the highest concentrations of Al in mine water and downstream surface waters. There is no clear evidence that Al is toxic to humans but excess Al can have a significant impact on aquatic ecosystems. Concentrations of total Al measured in most downstream surface water samples at Irish mine sites are typically in excess of both drinking water standards and Canadian guidelines for the protection of the aquatic environment.

4.3.3 Antimony – Sb

Antimony is a significant component of solid waste on some Irish mine sites, notably Gortdrum, Glendalough, Silvermines, Tynagh and the minor Pb deposits in east Clare. Sb is probably chemically associated in sulphides with As. Gortdrum is the only mine with a reported Sb enrichment and this is reflected in the composition of mine water sampled on the site. With the exception of Gortdrum, Sb did not exceed 11 µg/l in water analysed for the HMS-IRC project. However, samples of seepage from tailings and spoil at Gortdrum had Sb concentrations in excess of 240 µg/l. In stream sediments, Sb was not detected at most sites investigated. Where it was detected, it was well below animal health guidelines.

4.3.4 Arsenic – As

Arsenic is a significant component of solid mine waste on some mine sites in Ireland, notably Avoca, Tynagh, Gortdrum, Silvermines and some small sites in east Clare. Typically, concentrations are less than 1,000 mg/kg but higher concentrations do occur, especially on the sites of former processing plants. Concentrations of As in stream sediments are generally below 100 mg/kg although a few samples on some sites exceed this. Among water samples, only mine waters, including adit/shaft discharges and waste seepages, have arsenic concentrations exceeding the standard of 25 µg/l for surface water (Draft European Communities Environmental Objectives (Surface Waters) Regulations, 2008). The total As concentrations measured in stream water samples, including those taken downstream of mine sites, are all ≤25 µg/l. In the context of Irish mine sites, arsenic is thus likely to be a concern where humans come in contact with solid waste containing high As concentrations or are likely to inhale As-bearing dust.

4.3.5 Barium – Ba

High concentrations of Ba have been found in solid waste on mine sites where barite is known to have been a significant component of the mineralisation. Concentrations exceed the ATSDR CVs in some cases, notably at Tynagh, Silvermines and Ballycorus, but are generally lower. Ba can be toxic to humans when present in drinking water in concentrations above 2,000 µg/l, the US EPA maximum concentration limit (MCL) for drinking water. All of the water samples collected for HMS-IRC project had barium concentrations well below this limit. However, Ba exceeded the guidelines for animal health in stream sediments at Silvermines.

4.3.6 Cadmium – Cd

Cadmium concentrations in excess of standard limits have been detected in solid waste and stream sediments in the Glendalough District, Silvermines and Tynagh. Solid waste at Kilbricken in east Clare also has high Cd concentrations. Concentrations in some solid waste, in particular, are significantly above the ATSDR adult CV of 100 mg/kg. A few adit discharges, waste seeps and surface run-off samples at Avoca, Glendalough and Caim were found to have total Cd concentrations in excess of 10 or even 100 µg/l. These have potential implications for aquatic ecosystems where they discharge to streams.

4.3.7 Chromium – Cr

The analytical data available for Cr in both solid waste and stream sediments at Irish mine sites are somewhat limited in terms of quality. Moreover, they refer to total Cr and do not distinguish between different species. However, there is little evidence to suggest that Cr is a significant component of solid waste or stream sediments on Irish mine sites. The same is true for Cr concentrations in water discharging from and downstream of mine sites. The exception appears to be the Leinster Coalfield where elevated Cr concentrations were detected in seepages and run-off from coal-rich solid waste. The volumes of these discharges are very low, however, and are unlikely to represent a significant environmental risk.

4.3.8 Copper – Cu

Copper is a common component of ore deposits in Ireland and is present in significant concentrations in solid mine waste even on mine sites where it was not produced as a commodity. Sites with particularly high Cu in solid waste (median >1,000 mg/kg) include Allihies, Bunmahon, Gortdrum, the West Cork Cu–Ba District, Caim and Tynagh. However, standards or guideline limits for Cu are relatively high for solid matter and only those sites with concentrated processing waste, in which copper may be present at levels exceeding 20%, i.e. Gortdrum and Tynagh, can be considered a significant concern. Concentrations of Cu in stream sediment are very high downstream of some sites, notably Allihies, Avoca and, in West Cork, Glandore and Ballycummisk, and the potential impact of this on the aquatic ecosystem at these sites may warrant further investigation. The total Cu concentration in surface waters downstream of mines indicates some impact on water chemistry from mine discharges. However, numerous upstream surface water samples and even some groundwater samples also had Cu in excess of standard limits, suggesting that mine waste is just one of a number of sources of elevated Cu in surface water and groundwater around the mine sites.

4.3.9 Iron – Fe

Mine sites in Ireland are associated with high concentrations of Fe in solid waste, water and stream sediments. The main risk associated with high Fe is the potential impact on the aquatic environment. Discharge of Fe-rich mine water to streams and rivers causes Fe to come out of solution as hydroxide minerals. These form colloids or flocs that then blanket the stream bed, having a severe impact on biota. Such discharges have been noted in particular at Avoca and in the Leinster, Slieve Ardagh and Connacht Coalfields.

4.3.10 Lead – Pb

Out of 27 mine districts examined for the HMS-IRC project, 13 have high concentrations of Pb in solid waste (median >1,000 mg/kg or 0.1%), namely Avoca, Ballycorus, Caim, the Clare Pb mines (3), Clements in Connemara, Glendalough–Glendasan, Glenmalure, Keeldrum in Donegal, Tassan in Monaghan, Silvermines and Tynagh. The UK guideline limit for soils (SGV) on industrial sites is 750 mg/kg Pb (Table 4.2). Concentrations of Pb in stream sediment exceed the 1,000 mg/kg guideline limit for livestock downstream of most of these sites, though only at Glendalough–Glendasan and Silvermines are such high concentrations known to be sustained over a significant length of stream bed. The Pb concentration in surface waters downstream of mines indicates a significant impact on water chemistry from mine discharges at three sites, Avoca, Glendalough and Silvermines, where significant volumes of mine water with high Pb concentrations discharge into local rivers and streams.

4.3.11 Manganese – Mn

High concentrations of Mn occur in solid waste on some sites but only a small proportion of samples (5%) exceeds the relatively modest child CV (Table 4.2) of 3,000 mg/kg. Mine water with low pH tends to have relatively high Mn concentrations and sites such as Avoca and the coalfields can exhibit high concentrations of manganese (>1,000 µg/l). However, most water analysed around mine sites has a Mn concentration below the Irish Drinking Water standard of 50 µg/l. There are examples of localised extreme Mn concentrations in stream sediments downstream of some mines but, in general, Mn concentrations in stream sediments in Irish mine districts are consistent with those measured in regional surveys at sites unaffected by mining.

4.3.12 Mercury – Hg

High Hg concentrations measured by XRF in solid waste from the processing areas at Gortdrum and Tynagh have been confirmed by analysis in an external laboratory. Both of these sites are work places where there is potential for human exposure to the waste. Some samples of solid waste in the Glendalough District may also contain significant Hg concentrations, although this has not been confirmed by external analysis. Other sites investigated for the HMS-IRC project do not appear to contain concentrations of Hg in solid waste that are detectable by XRF. Hg was detected in mine water and downstream surface water at a number of sites, principally Avoca, where the concentration of dissolved mercury ranged up to 0.38 µg/l, well above the Draft EC value (0.05 µg/l).

4.3.13 Nickel – Ni

Nickel was below the detection limit in most solid mine waste samples analysed for HMS-IRC. Exceptions were samples at Tynagh mine, where Ni–Cd-rich zones were known to occur in the ore, slag waste at Ballycorus and Allihies and phosphatic shales in Clare. Both water and stream sediment samples reveal an association between Ni and coalfields – samples from all three Irish coalfields have elevated Ni in one or both of these media. Other than in mine water, Ni does not generally exceed reference values in surface waters with the exception of some waters downstream of coalfield sites and the sulphide mines, such as Avoca and Tynagh.

4.3.14 Selenium – Se

Selenium has been detected at very low concentrations in solid waste and stream sediments in several mine districts, notably Allihies and Doolin (Clare Phosphate). Water samples generally have Se concentrations below the detection limit or at least below the Drinking Water standard. Although there appears to be no indication of Se toxicity on farms in the north Clare area, nevertheless care is needed when interpreting the solid waste data, particularly with reference to the Clare Phosphate District. Phosphate mines, in particular, are associated with downstream Se contamination as a result of leaching of relatively small concentrations of Se from solid waste. The concentration selenium measured in solid waste in the Clare Phosphate District (18–30 mg/kg) are similar to the median concentration of Se in phosphate rock and waste rock in phosphate mines in the US that have been associated with excess Se in downstream environments. Se concentrations in soils in north-west Clare, where the phosphate deposits are located, are in the upper 25th percentile of the range for soils in Ireland (Fay *et al.*, 2007).

4.3.15 Silver – Ag

Silver was detected in solid waste at most mines investigated for the HMS-IRC project, usually in concentrations well below 100 mg/kg. Several Pb mines had relatively high concentrations of Ag, especially in solid waste on former processing areas or in processing waste itself. Most stream sediments samples analysed had silver concentrations below the detection limit, estimated to be 10–20 mg/kg. Ag has a very low toxicity to humans and is generally not included under regulations that set statutory limits for water or other media.

4.3.16 Thorium – Th

Thorium was detected in a small number of samples of solid waste and stream sediments at a limited number of mine districts investigated for the HMS-IRC project, usually in concentrations below 50 mg/kg. It is not known if Th is directly associated with ore minerals in sulphide mines in Ireland – at Avoca, at least, it is known to occur in relatively high concentrations in host volcanic rocks. In the Clare Phosphate deposits, it is probably associated with U in apatite, the main ore of phosphate. The lack of any reference values make it difficult to assess any potential risks associated with the occurrence of Th on Irish mine sites. However, comparison of concentrations measured for this study with the range of concentrations in Irish rock types suggest that, for the most part, Th is not enriched in mine sites relative to normal background levels.

4.3.17 Uranium – U

Uranium was detected in a small number of samples of solid waste, mainly at Avoca, Doolin, Gortdrum and the Leinster Coalfield. Very few samples had a U concentration exceeding any published standards. At least some of the U in solid waste is in soluble form and, as a consequence, has been remobilised into mine water which, on some sites, has relatively high concentrations of total U. However, only one of the samples analysed (from Avoca) had in excess of 30µg/l U, the US EPA MCL for drinking water. Levels of U in stream sediments are typically very low.

4.3.18 Vanadium – V

Vanadium was detected in only a limited number of solid mine waste samples in the mine districts investigated for HMS-IRC, to a large extent as a consequence of the unfavourable detection limit for V in the XRF analyser used for *in-situ* analyses. The Clare Phosphate deposit at Doolin had the highest concentrations of V. V was also detected in the Leinster and Slieve Ardagh coalfields. The presence of V in these mine districts may reflect the occurrence of shales with a high content of organic carbon. The concentration of V in water analysed for HMS-IRC did not exceed 5 µg/l. In the absence of standards for V in water, it is difficult to assess the potential relevance of these results. Stream sediments in Doolin and the Connacht Coalfield had high V contents both upstream and downstream of the mines, suggesting that V is enriched in the country rock in both districts.

4.3.19 Zinc – Zn

Solid mine waste at Caim, Glendalough, Tassan mine in Monaghan, Silvermines and Tynagh is significantly enriched in Zn. Published reference values for soil vary significantly but Zn concentrations measured in mine waste on Irish mine sites do not appear to pose a risk to human health. Concentrations of Zn exceed 5,000 mg/kg in stream sediments downstream of Glendalough, Silvermines and Tynagh and may represent a risk to livestock. High concentrations of Zn in stream sediments also pose a potential threat to aquatic organisms. The Zn concentration in surface waters downstream of mines indicates a significant impact on water chemistry from mine discharges at Avoca, Glendalough, Silvermines and Tynagh.

4.4 Geochemical assessment: overview

4.4.1 Lead

Lead is the most important single contaminant on Irish mine sites in terms of the quantity of Pb-enriched material, the concentration in which it is found, its toxicity and its geographical dispersion on and around mine sites. It is present in high concentrations in 11 out of 23 districts investigated, not only in solid waste but also in mine waters and in surface waters and stream sediments downstream of mines. Mine districts and sites most severely contaminated by lead include Caim, Clare Pb Mines, Glendalough, Silvermines and Tynagh.

4.4.2 Acid mine drainage

Acid mine drainage is characterised by low pH and high acidity, and when generated in metal or coal mines is typically rich in metals such as Fe, Mn, Al, Cu, Pb, Ni and Zn, and therefore potentially toxic to aquatic organisms. At Avoca mine, AMD has had a major impact on the Avoca River. Low pH and high acidity are also found in some mine waters at the Slieve Ardagh, Leinster and Connacht Coalfields. However, only in the Connacht Coalfield are there volumetrically significant discharges of AMD. Relatively high concentrations of Al, Ba, Cd, Fe, Mn and Ni are present in water in these mine districts.

4.4.3 Former processing plant sites

The sites of the former ore processing plants at Gortdrum, Silvermines and Tynagh are significantly contaminated by heavy metals. In all three cases, the sites are being utilised by new businesses. Contaminants include not only the metals produced from the site, such as Pb, Zn and Cu, but also minor constituents of the ore that have become concentrated during processing. These minor constituents include As and Hg, which have been found in concentrations exceeding 1,000 mg/kg. Arsenic is also present in high concentrations in solid waste outside of processing areas at both Avoca and the Clare Pb Mines. Despite its occurrence at high concentrations in solid waste, As has not been detected in surface waters downstream of mine sites at concentrations in excess of the Draft EC Surface Water Regulations.

4.4.4 Aquatic ecosystems

Draft EC Surface Water Regulations (Table 4.3) set low limits for some metals that occur in significant concentrations in surface water downstream of Irish mine sites. These metals include Cd, Cu, Pb and Zn. They pose risks to aquatic ecosystems even at low concentrations and may require inclusion in surface water monitoring programmes.

4.4.5 Copper

Concentrations of Cu in stream sediment are very high downstream of some sites, notably Allihies, Avoca and, in West Cork Glandore and Ballycummisk. The potential impact on the aquatic ecosystem may warrant further investigation. The total Cu concentration in surface waters downstream of mines indicates some impact on water chemistry from mine discharges. However, numerous upstream surface water samples and even some groundwater samples also have Cu in excess of regulatory levels, suggesting that mine waste is just one of a number of sources of elevated Cu in surface water and groundwater in Ireland.

4.4.6 Zinc

High concentrations of Zn in solid mine waste pose no threat to human health. However, high concentrations of Zn in stream sediments and/or downstream surface waters at Avoca, Glendalough, Silvermines and Tynagh pose a risk to livestock and the aquatic environment.

4.4.7 Selenium

Selenium is a common component of phosphate rock and the shales that typically host it. Leaching of Se from solid waste heaps at phosphate mines in the USA has led to significant downstream Se contamination of aquatic organisms, mammals, birdlife and grazing animals. The concentration of Se in solid waste from the Clare Phosphate deposits (18–30 mg/kg) falls within the range of concentrations reported for US phosphate mine waste. While there is no evidence for leaching of Se into the aquatic environment, a large part of the former mine site is now grazing land and may pose a risk of Se toxicity to grazing animals.

4.4.8 Aluminium

Some mine waters have very high concentrations of both total and dissolved Al. There is an inverse relationship between pH and Al concentration, with those mine districts with low-pH water, such as Avoca and the three coalfields, having the highest concentrations of Al in mine water and downstream surface waters. Concentrations of total Al measured in surface water downstream of these sites are typically in excess of both Irish drinking water standards and the Canadian guidelines for the protection of the aquatic environment.

4.4.9 Nickel

Nickel is enriched in mine water, downstream surface water and stream sediments at some sites in the Irish coalfields. It is also found in excess of the Draft EC Surface Water Regulations downstream of mines such as Avoca and Tynagh.

4.5 Geochemical assessment: site-specific issues identified in the HMS-IRC investigation

4.5.1 Abbeytown

Pb- and As-rich leachate from the tailings pond enters the estuary at Ballysadare Bay.

4.5.2 Avoca

Measured Pb concentrations exceed 1% in solid waste at Connary, a site where sheep graze.

4.5.3 Ballycorus

Measured Pb concentrations exceed 1% in solid waste at Ballycorus in an area popular with walkers and horse riders.

4.5.4 Caim

Measured Pb concentrations exceed 5% in a solid waste heap at Caim, used by quad bikers and others.

4.5.5 Clare Pb District – Ballyvergin

Pb concentrations in excess of 20% were measured in fine-grained mine waste in an area used by cattle for feeding at Ballyvergin.

4.5.6 Glendalough–Glendasan

Measured Pb concentrations exceed 10% in solid waste at the Hero Processing site, at the head of the Glendasan Valley. The site is very popular with tourists. High concentrations of Pb and Zn are present in stream sediments in Glendasan River downstream of the mines.

4.5.7 Glenmalure

Measured Pb concentrations exceed 10% in solid waste at Ballinafunshoge, Glenmalure, a site popular with quad bikers.

4.5.8 Gortdrum

Very high concentrations of Hg and As (both >1%) were measured in solid waste at the site of the former processing plant, now the site of an active business.

4.5.9 Silvermines

Very high concentrations of Pb (>2%) and As (>0.1%) were measured in solid waste at the site of the former processing plant in Garryard, now the site of an active business.

4.5.10 Tynagh

Very high concentrations of Pb (>2%) and As (>0.1%) were measured in solid waste at the site of the former processing plant, now the site of an active business. A Cd-rich discharge from a waste heap crosses grazing land and seeps underground, potentially affecting groundwater.

CHAPTER 5

HMS-IRC Summary Site Descriptions

The following one-page summaries review the principal geochemical findings at each of the sites studied. The headings used for the summaries are the same for each and a brief description of each is presented below.

Mine District: *This is the name of the mine district or the area within which the individual mine occurs.*

Mine Name: *This is the name of the individual mine.*

Minerals Worked: *These are the commodities worked or recovered at the mine. For metal mines the elemental signature is given while for industrial minerals the mineral name is provided.*

County: *The county name is given here.*
Townland: *The name(s) of the townland(s) within which the mine is situated.*
Grid Reference: *The easting is given first followed by the northing.*

Site Score: *This is the score for each site or district.*
Site Class: *This is the Site Class – for the site in the case of single sites or the district in the case of sites that are part of a district.*

Class	Score	Description
I	>2,000	Sites that should have a full risk assessment carried out. Ongoing monitoring should be carried out.
II	1,000–2,000	Sites requiring general monitoring of most or all waste piles, discharges or stream sediments on an annual basis.
III	300–1,000	Sites requiring general monitoring of most or all waste piles, discharges or stream sediments on a biennial basis.
IV	100–300	Sites requiring specific monitoring on particular waste piles, discharges or stream sediments on a five-yearly basis.
V	<100	Site not requiring any specific monitoring.

Elements of Interest: *These are the elements at the site that may be of concern from a contamination point of view.*
Media of Concern: *This provides a list of the media that are contaminated at the site.*

Geochemical Overview: *This section provides a brief summary of the main issues at the site from a geochemical standpoint.*

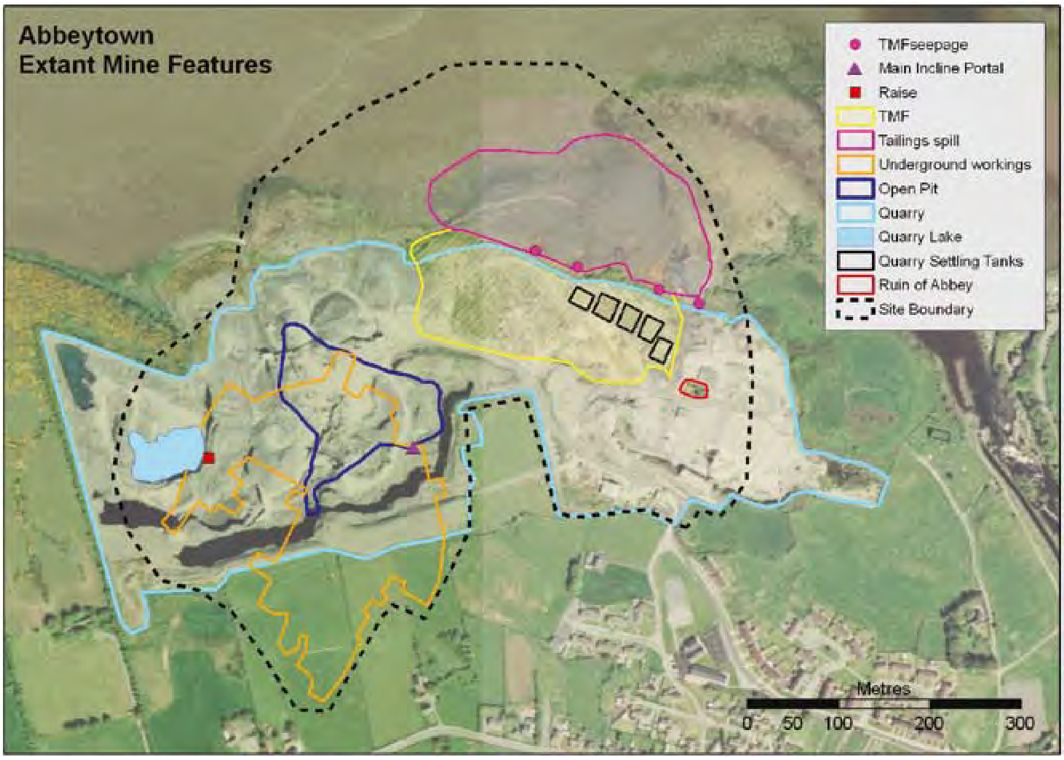
In addition, there is a map of the site using the Ordnance Survey orthophotographs as a backdrop.

5.1 Abbeytown Mine

Mine District:	Abbeytown
Mine Name:	Abbeytown
Minerals Worked:	Pb, Zn, Ag
County:	Sligo
Townland:	Abbeytown
Grid Reference:	E165991, N329711
Site Score:	74
Site Class:	V
Elements of Interest:	Pb, Zn, Ag, Cu, As, Ni, Hg
Media of Concern:	Solid waste, mine water discharge

Geochemical Overview

Abbeytown mine is now an active quarry and most mine features have been subsumed by surface excavations in the years since closure. However, the tailings pond remains intact although lined concrete settling ponds have now been built in shallow excavations on its surface. A previous tailings spill, apparently during the 1950s' mining period, has caused significant contamination of the foreshore by Pb, Zn and Cu in an area 300 m wide, with measured concentrations of Pb up to 1,800 mg/kg. The action of tides has increased the dispersion of the contamination further west along the shore. Discharge from several seepages at the base of the tailings pond contains high levels of Pb (≤24,210 µg/l), Zn (≤4,580 µg/l), Ni (≤208 µg/l) and As (≤106 µg/l). These seepages drain directly into the waters of the bay. The tailings spill on the foreshore and the discharge of seepage from the tailings pond into Ballysadare Bay represent specific environmental threats to the estuary.



5.2 Allihies District

Mine District: Allihies

Mine Name: Various
Minerals Worked: Cu

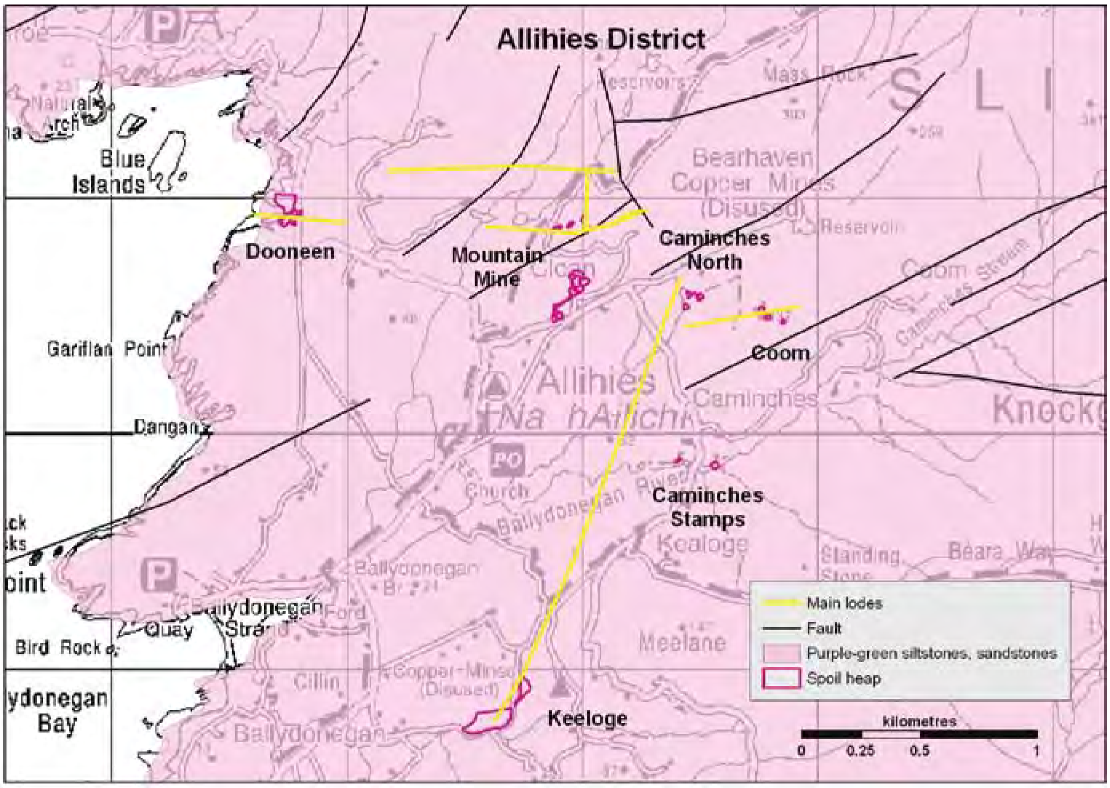
County: Cork
Townland: Various
Grid Reference: E59000, N45000

Site Score: 76
Site Class: V

Elements of Interest: Cu
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

Mine discharge and run-off in the Allihies District has a near-neutral pH and poses no risk of AMD. Concentrations of metals in water samples reflect the relatively simple mineralogy of the ore in that only Cu is consistently measured at elevated concentrations in both mine water (45–465 µg/l, median 245 µg/l) and stream waters (31–132 µg/l, median 52 µg/l). Leachate extracted from a number of solid waste samples contained high concentrations of Cu, indicating the potential for contamination of groundwater in the vicinity of mine sites in the district. Stream sediments downstream of mine sites generally contained elevated Cu concentrations. The highest copper concentrations (>1%) were found directly downstream of Mountain Mine in a drain that carries most of the mine water discharge from the site. Sediments in streams draining other mines in the district generally have significantly lower if still elevated Cu. In solid waste, the only element that is consistently measured at high concentrations is Cu (median 2,888 mg/kg; range: <DL–75,520 mg/kg).



5.2.1 Caminches

Mine District: Allihies

Mine Name: Caminches
Minerals Worked: Cu

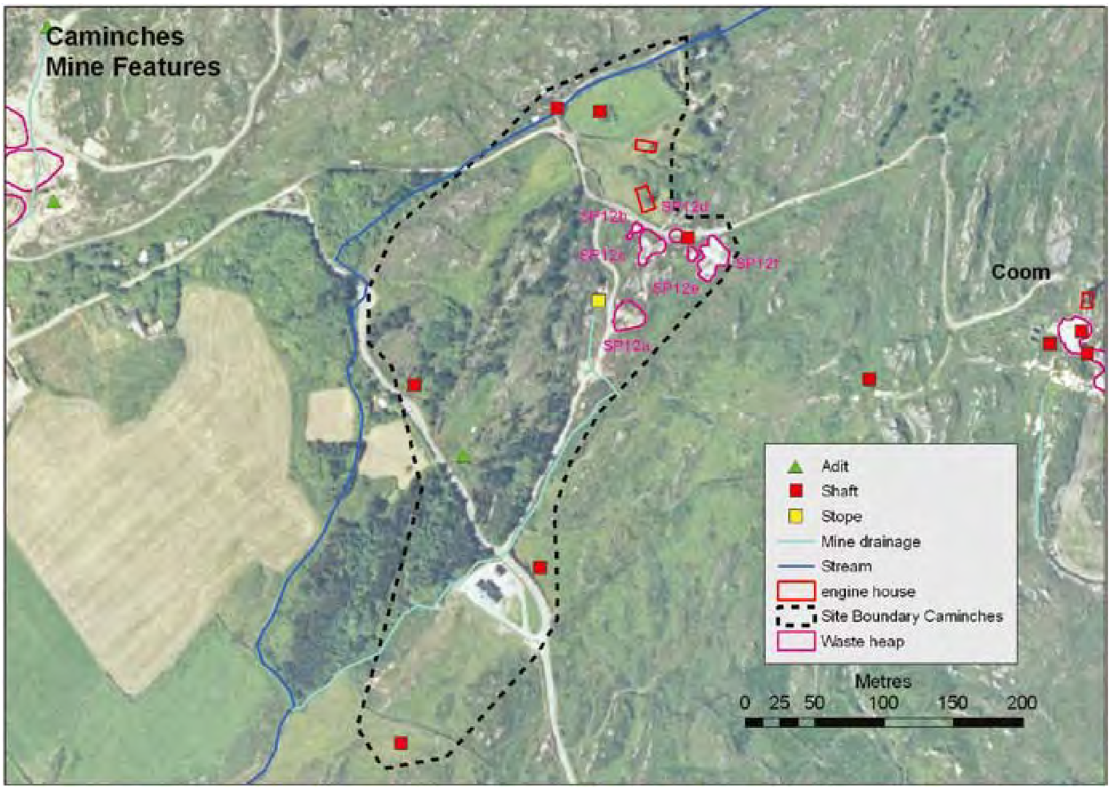
County: Cork
Townland: Caminches
Grid Reference: E59360, N45497

Site Score: 4
Site Class: V (Allihies District)

Elements of Interest: Cu
Media of Concern: Solid waste, stream sediments

Geochemical Overview

The Caminches site has relatively low volumes of solid mine waste, most of which has moderately elevated Cu concentrations, with a median of 5,973 mg/kg Cu. Very small volumes of fine processing waste have in excess of 1% Cu. Stream sediments immediately downstream of the site are enriched in Cu. The stope discharge on the site does not have the characteristics of a mine water discharge in that metal concentrations are low. These low waste volumes and metal concentrations give rise to a very low site score. Direct drainage of Cu-rich leachate to local streams appears to represent the most significant potential environmental risk on the site.

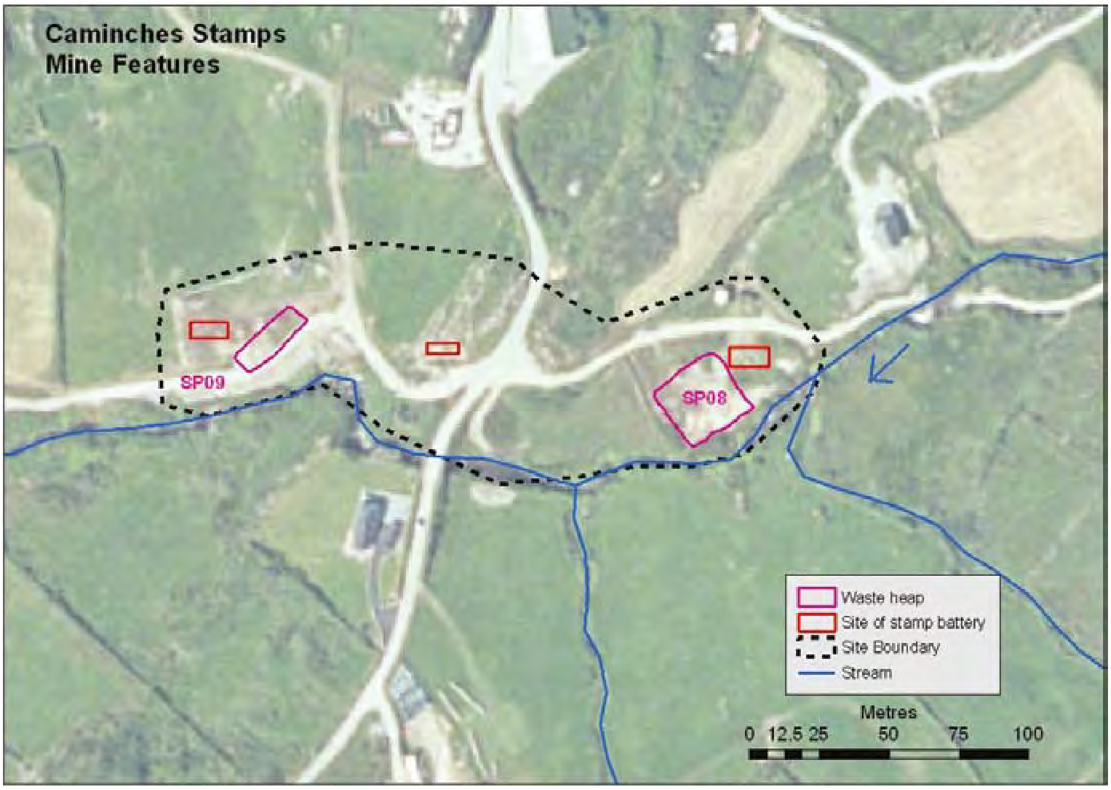


5.2.2 Caminches Stamps

Mine District:	Allihies
Mine Name:	Caminches
Minerals Worked:	Cu
County:	Cork
Townland:	Caminches
Grid Reference:	E59485, N44880
Site Score:	10
Site Class:	V (Allihies District)
Elements of Interest:	Cu
Media of Concern:	Solid waste, stream sediments

Geochemical Overview

The Caminches Stamps site contains two solid waste heaps with some of the highest measured Cu concentrations in the Allihies District, ranging from 2,289 to 75,520 mg/kg, i.e. up to 7.5% Cu. Only Cu is significantly enriched. Stream sediments downstream of the site have elevated Cu concentrations, apparently as a consequence of the stamps operations. However, surface water in the Ballydonegan River appears to be unaffected by the waste lying along the river bank. Despite the high measured Cu concentrations in some of the stamps waste, the low volume of the waste and the absence of high concentrations of elements of high relative toxicity give rise to a relatively low site score. Direct drainage of Cu-rich leachate to local streams appears to represent the most significant potential environmental risk on the site.



5.2.3 Coom

Mine District: Allihies

Mine Name: Coom
Minerals Worked: Cu

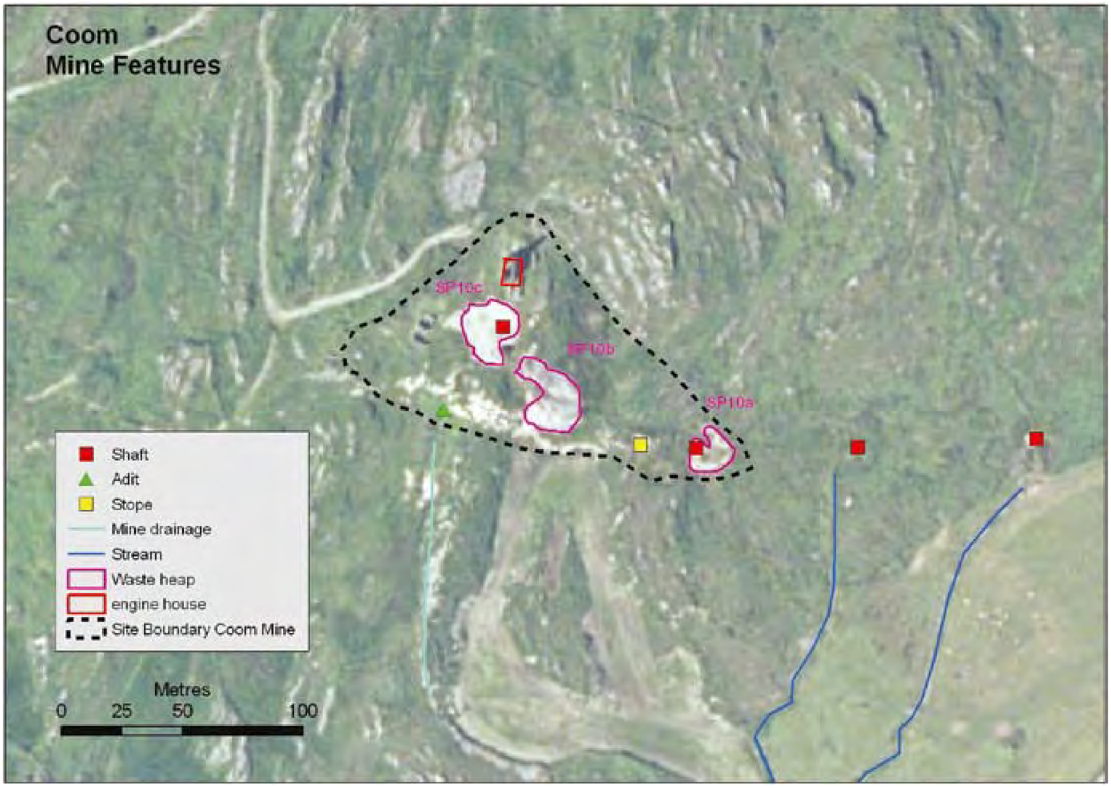
County: Cork
Townland: Coom
Grid Reference: E59780, N45512

Site Score: 4
Site Class: V (Allihies District)

Elements of Interest: Cu, Sb
Media of Concern: Solid waste

Geochemical Overview

Solid mine waste at Coom has lower median concentrations of Cu than waste on most sites elsewhere in the Allihies District. Moreover, the volume of waste on this small mine site is relatively low. The concentration of Cu in stream sediment down-gradient of the site is also relatively low, suggesting limited movement off-site of solid waste over the years. Only the leachate sample (673 µg/l) suggests any potential for contamination but the very modest Cu concentration in the adit discharge (44 µg/l) suggests that, at present, the mine is unlikely to contaminate either surface or groundwater directly. Again, as elsewhere in the district, the low volume of the waste and the absence of high concentrations of elements of high relative toxicity give rise to a low site score. Direct drainage of Cu-rich leachate to groundwater appears to represent the most significant potential environmental risk on the site.



5.2.4 Dooneen

Mine District: Allihies

Mine Name: Dooneen
Minerals Worked: Cu

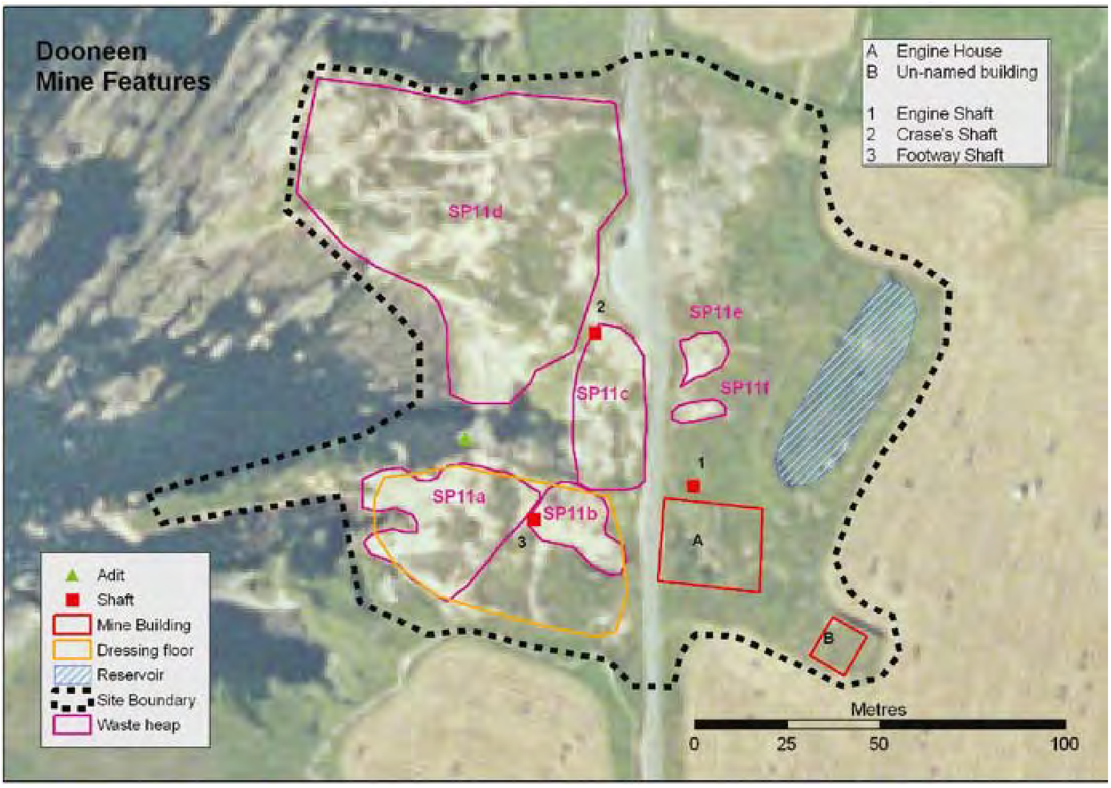
County: Cork
Townland: Allihies
Grid Reference: E57776, N45942

Site Score: 1
Site Class: V (Allihies District)

Elements of Interest: Cu, Sb
Media of Concern: Solid waste

Geochemical Overview

Limited field-XRF analysis suggests that the solid waste has lower metal concentrations at Dooneen than elsewhere in the Allihies District, with the exception of Sb. Only Cu is present in solid waste in significant concentrations but the levels are well below those recorded at Mountain Mine. In contrast, Sb concentrations, though not especially high in the context of Irish mine sites examined for the HMS-IRC project, do appear to exceed those found elsewhere in the Allihies District. Again, as elsewhere in the district, the absence of high concentrations of elements of high relative toxicity is the main reason for the very low site score. The location of the site on a cliff edge, where its potential influence on the wider environment is limited, also contributes to this.



5.2.5 Keeloge

Mine District: Allihies

Mine Name: Keeloge
Minerals Worked: Cu

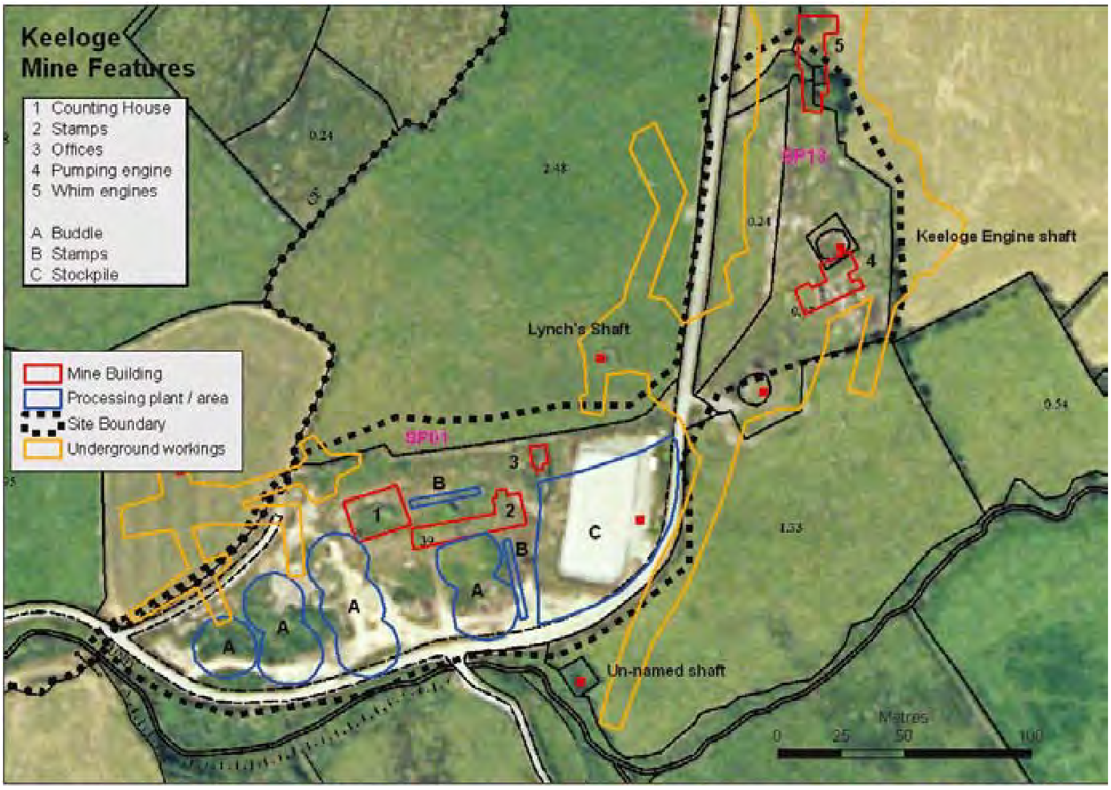
County: Cork
Townland: Cahermeeleboe
Grid Reference: E58648, N43822

Site Score: 6
Site Class: V (Allihies District)

Elements of Interest: Cu
Media of Concern: Solid waste, stream sediments

Geochemical Overview

Solid mine waste on the Keeloge site contains some very high concentrations of Cu (up to 6.7%) but median concentrations are lower than those for the Allihies District as a whole. Other elements are present in relatively low concentrations. The considerable quantities of material, including soil and builders' rubble, imported onto the site subsequent to mining have obscured much of the original waste and possibly diluted its chemistry. The Cu concentration of water in the Keeloge River immediately downstream of the site exceeds the Draft EC Surface Water Regulation limit. Cu is significantly elevated in stream sediments for at least 650 m downstream of the site. The total site score for Keeloge is just 6, a relatively low score for a former processing site. The main reason for the low score is the absence of high concentrations of elements of high relative toxicity, such as lead or arsenic. Direct drainage of Cu-rich leachate to local streams appears to represent the most significant potential environmental risk on the site.



5.2.6 Mountain Mine

Mine District: Allihies

Mine Name: Mountain Mine
Minerals Worked: Cu, Mo

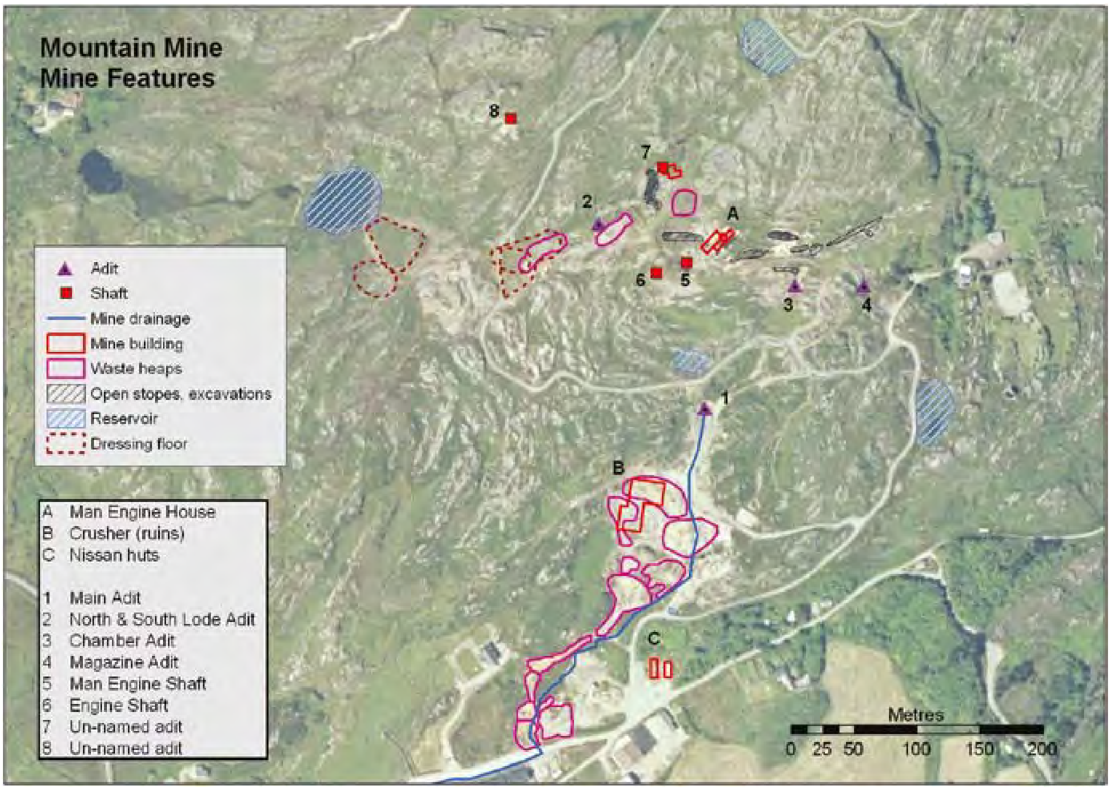
County: Cork
Townland: Cloan
Grid Reference: E58987, N45774

Site Score: 29
Site Class: V (Allihies District)

Elements of Interest: Cu, Sb
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

Mountain Mine is the largest mine site and has the most significant environmental impact in the Allihies District. High concentrations of Cu in solid waste and in mine water discharging from Mountain Mine have given rise to significantly elevated Cu concentrations in stream sediment and stream water downstream of the site. Concentrations of Cu above 100 µg/l, well in excess of the limit for Cu in the Draft EC (Surface Water) Regulations, have been measured in some stream water samples. Combined with stream sediment concentrations exceeding 1,000 mg/kg, these Cu concentrations could potentially have a significant impact on the freshwater ecosystem and freshwater aquatic species. Mountain Mine contributes 38% of the total HMS-IRC score of 76 for the Allihies District, a reflection of the relatively high concentrations of Cu measured in mine waste on the site and in mine water draining from the site. Direct drainage of Cu-rich leachate to local streams appears to represent the most significant potential environmental risk on the site.

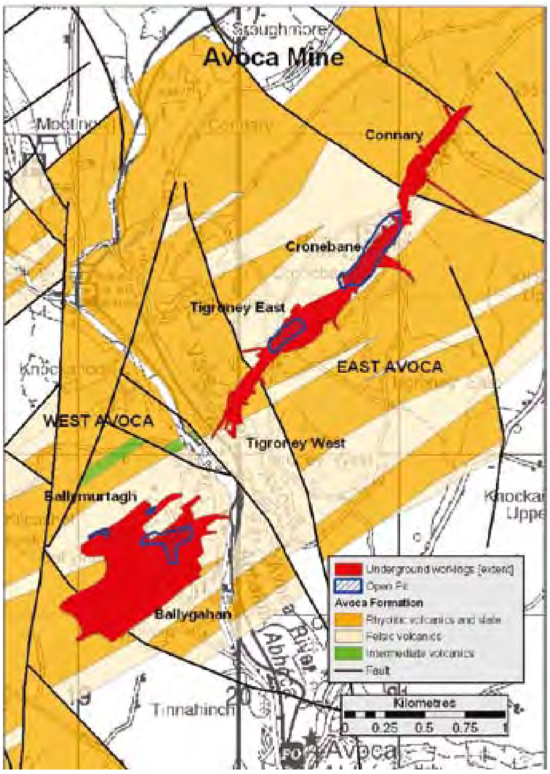


5.3 Avoca District

Mine District:	Avoca
Mine:	Various
Minerals Worked:	Cu, S, Ag
County:	Wicklow
Townland:	Various
Grid Reference:	E319800, N182000
Site Score:	2,439
Site Class:	I
Elements of Interest:	Pb, As, Sb, Cu, Zn, Cd, Cr, Ni
Media of Concern:	Solid waste, surface water, stream sediments

Geochemical Overview

Avoca has a history of mining extending back over 250 years. A large volume of AMD continues to drain from underground mine workings, causing extensive ongoing pollution of the Avoca River. High metal concentrations are apparent at adit discharges on the mine site and can be observed in the river adjacent to the mine. A gradual decline in metal concentrations in river water is apparent with increasing distance from the mine site. Groundwater in the immediate vicinity of the mine is also contaminated as a consequence of interaction with solid mine waste. Large volumes of this waste remain on the site and the waste can contain in excess of 1% Pb, Cu or Zn. Concentrations of As are also high. Though not major components of the ore, Pb and As are the main elements of concern in solid waste. The median Pb concentration for spoil in the district is 2,846 mg/kg. Stream sediments downstream of the site have high concentrations of Cu, Pb and Zn and contamination is apparent up to 10 km from the site, where 177 mg/kg copper was recorded.



Summary reports for the individual sites in the Avoca District follow below.

5.3.1 Ballygahan

Mine District: Avoca

Mine Name: Ballygahan
Minerals Worked: Cu, S

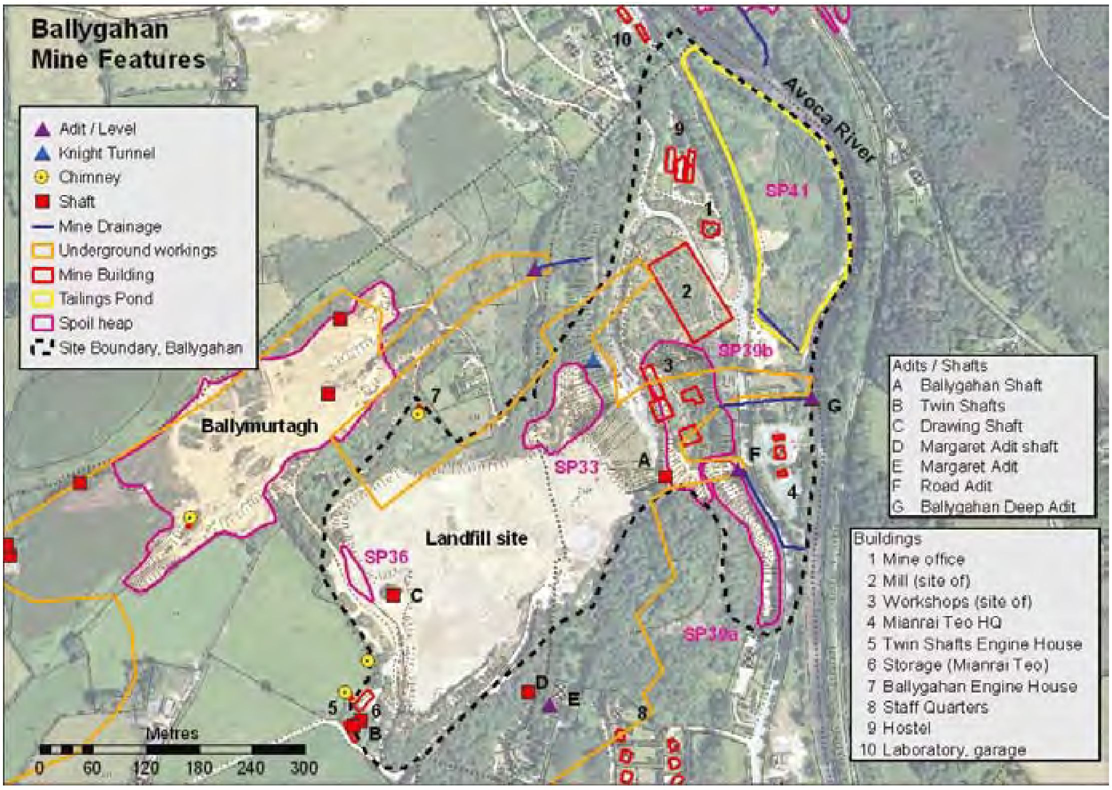
County: Wicklow
Townland: Ballygahan
Grid Reference: E319719, N181573

Site Score: 399
Site Class: I (Avoca District)

Elements of Interest: Pb, As, Cu, Zn, Cd, Ni
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

The Road Adit in Ballygahan has very high concentrations of Cu, Pb, Zn and high Ni, Cd and Cr, as well as low pH and high acidity. Metal discharge rates ranged up to 0.75 kg/day Pb, 21.04 kg/day Zn, 0.74 kg/day Cu, 232 kg/day Fe and 0.02 kg/day Cd, indicating an ongoing and significant input of metals to the Avoca River ecosystem. As a consequence, the Road Adit is by far the most important contributor (360) to the total Ballygahan score in the HMS-IRC scoring system. Although there has been extensive rehabilitation of parts of the site, involving vegetation of imported topsoil, large heaps of bare waste remain. Groundwater from several monitoring wells on the site have very high measured concentrations of Cu, Zn, Pb and Ni, emphasising the potential for extreme groundwater contamination in the areas around the site.



5.3.2 Ballymurtagh

Mine District: Avoca

Mine Name: Ballymurtagh
Minerals Worked: Cu, S

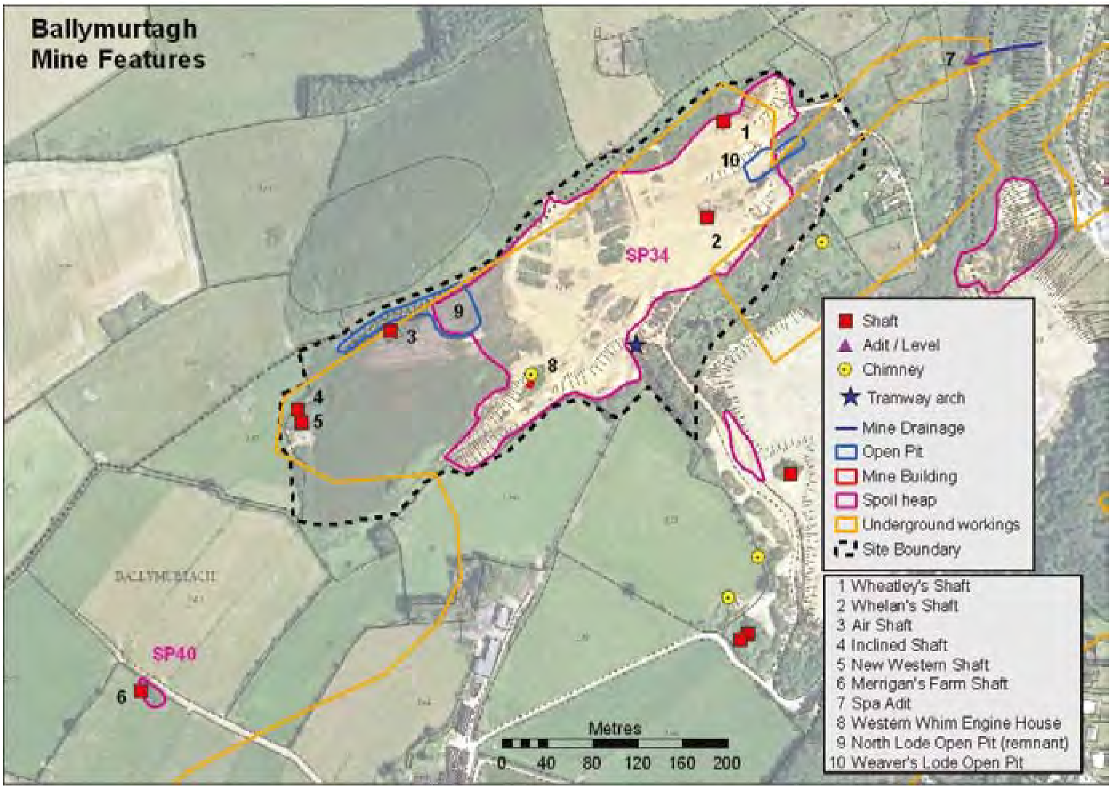
County: Wicklow
Townland: Ballymurtagh
Grid Reference: E319276, N181526

Site Score: 47
Site Class: I (Avoca District)

Elements of Interest: Pb, As, Cu, Zn
Media of Concern: Solid waste

Geochemical Overview

Concentrations of elements of interest are relatively low in spoil at Ballymurtagh compared to spoil in East Avoca. Median concentrations of Pb (1,056 mg/kg), Cu (342 mg/kg) and Zn (< DL) are considerably lower than those for other spoil heaps in the district. The one exception is As (median 987 mg/kg) which is relatively enriched in the Ballymurtagh spoil, possibly reflecting a changed mineralogy relative to spoil from other parts of the Avoca site. A leachate test on a composite sample of spoil suggests the potential to contaminate groundwater in the vicinity of the site. Water from a monitoring well downhill and east of the site had high measured concentrations of Cu and Zn.

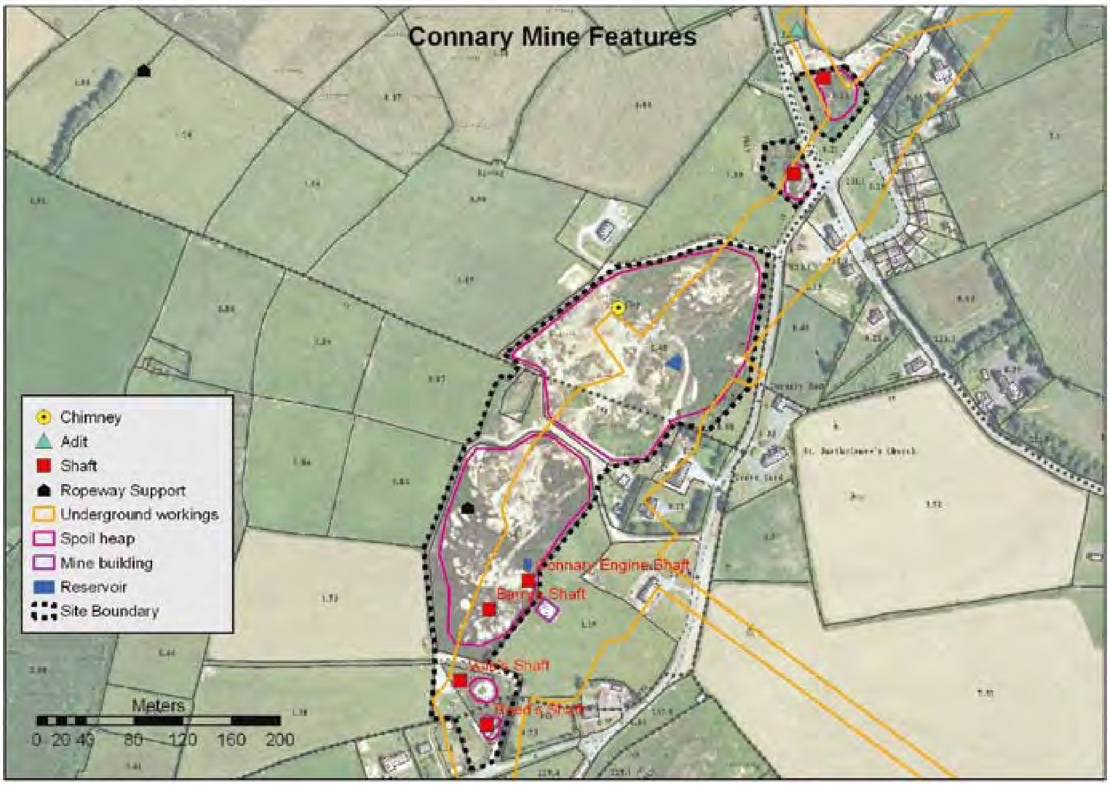


5.3.3 Connary

Mine District:	Avoca
Mine Name:	Connary
Minerals Worked:	Cu, S
County:	Wicklow
Townland:	Connary Upper; Sroughmore
Grid Reference:	E321110, N183830
Site Score:	174
Site Class:	I (Avoca District)
Elements of Interest:	Pb, As, Cu, Zn
Media of Concern:	Solid waste

Geochemical Overview

The solid mine waste at Connary has relatively high levels of Pb (median 10,432 mg/kg), As (589 mg/kg), Cu (741 mg/kg) and Zn (173 mg/kg). Largely intact, if breached, fencing on the site limits the possibility for direct contact while extensive natural vegetation and the coarse grain size of spoil have reduced the scope for dust blows. Use of spoil by local people as an aggregate for concrete mixes is apparently continuing, despite its high sulphide content. A seasonal adit discharge has significant metal concentrations and low pH but minimal acidity and very low flow rates. A stream fed by this adit discharge has high metal concentrations at least 1 km downstream of the site.



5.3.4 Cronebane

Mine District: Avoca

Mine Name: Cronebane
Minerals Worked: Cu, S

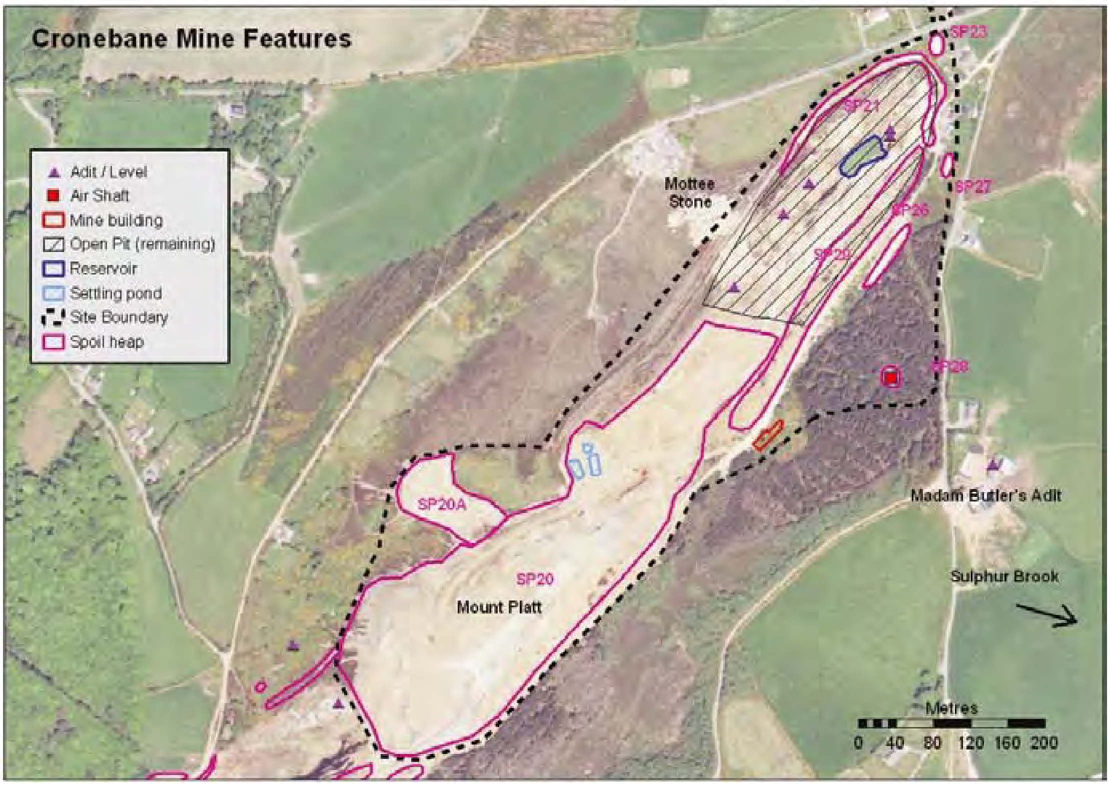
County: Wicklow
Townland: Cronebane
Grid Reference: E320735, N183142

Site Score: 410
Site Class: I (Avoca District)

Elements of Interest: Pb, As, Cu, Zn
Media of Concern: Solid waste, stream sediments

Geochemical Overview

The solid mine waste at Cronebane has concentrations of Pb (median 2,707 mg/kg), As (377 mg/kg), Cu (290 mg/kg) and Zn (125 mg/kg) that are typical of or somewhat lower than those measured elsewhere in Avoca. There is no evidence of any processing waste on-site. There are numerous breaches in the fencing on this site, which has become popular with quad bikers. In consequence there is potential for direct contact with and/or inhalation of mine waste. Although their metal concentrations and acidity can be extremely high, the largely seasonal spoil seepages have very low flow rates and seep into the ground around the site. Evidence from stream sediment collected from the Sulphur Brook suggests that Madam Butler's Adit was a significant source of metal-rich mine water in the past. However, no trace of this discharge has been found on the farmland south of the original discharge point.

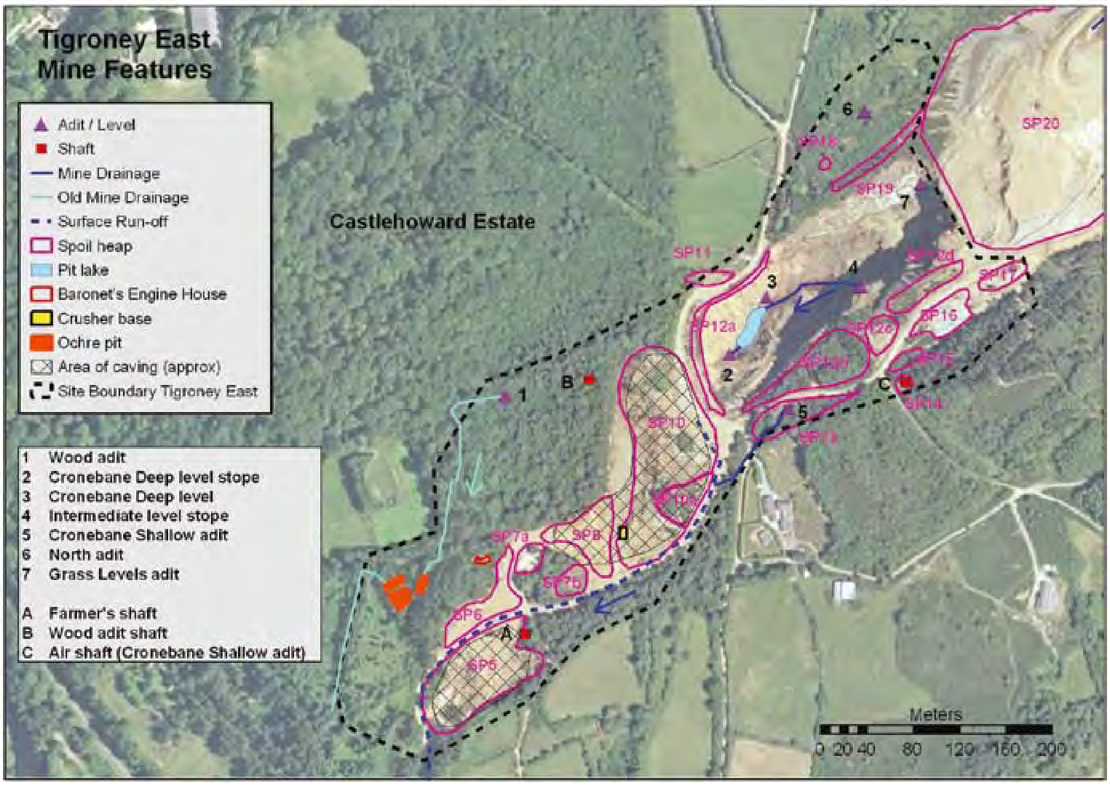


5.3.5 Tigroney East

Mine District:	Avoca
Mine Name:	Tigroney East
Minerals Worked:	Cu, S
County:	Wicklow
Townland:	Tigroney West; Cronebane
Grid Reference:	E320165, N182625
Site Score:	366
Site Class:	I (Avoca District)
Elements of Interest:	Pb, As, Cu, Zn
Media of Concern:	Solid waste, surface water

Geochemical Overview

Concentrations of Pb (median 2,384 mg/kg), As (441 mg/kg) and Zn (73 mg/kg) in solid waste at Tigroney East are similar or a little lower than those elsewhere on the Avoca site while copper concentrations (median 739 mg/kg) are higher. The latter reflects a cluster of high Cu values in the vicinity of Baronet's engine house where ore was raised in the 19th century. One part of one heap (SP16) is enriched in lead (>10%). Tigroney East is a significant source of ARD that is generated by run-off of rainwater during periods of heavy rain. This run-off eventually meets the discharge from the Deep Adit before entering the Avoca River. The discharge from the Cronebane Shallow Adit is very acidic and very metal-rich. However, the flow is small and drains back into the ground in the area of caving. A much larger flow within the open pit has created a low-pH, metal-rich pond in the base of the open pit.

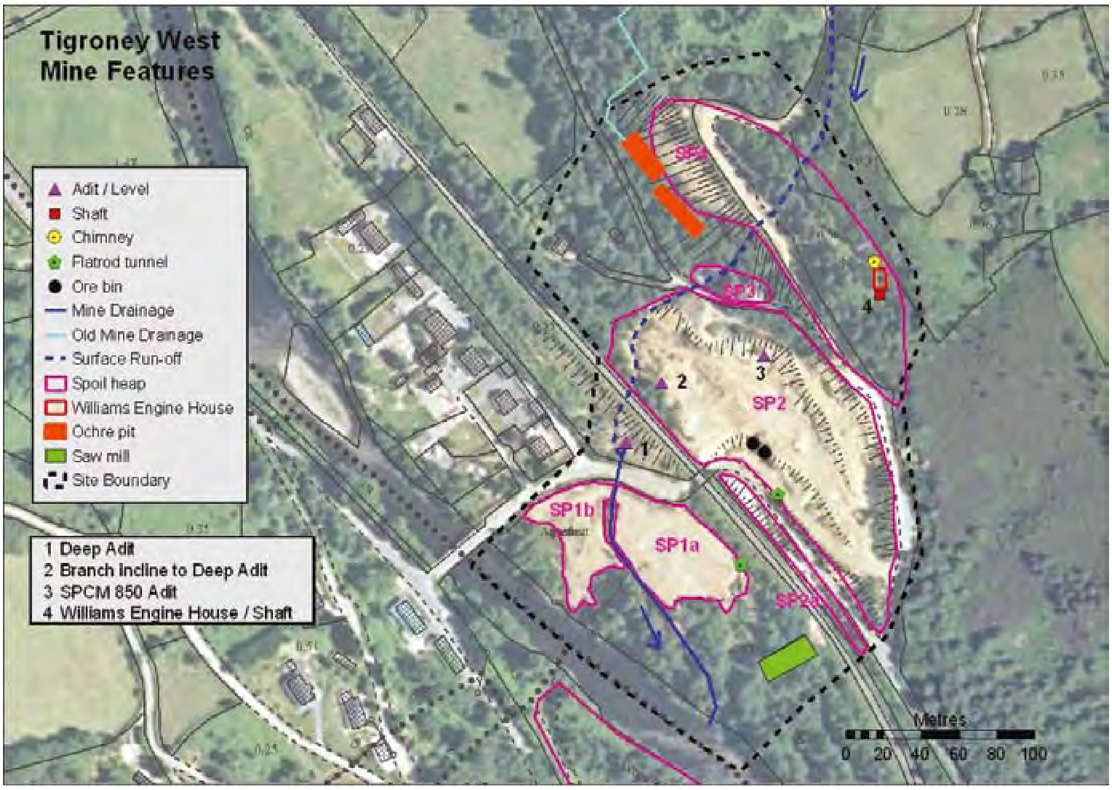


5.3.6 Tigroney West

Mine District:	Avoca
Mine Name:	Tigroney West
Minerals Worked:	Cu, S
County:	Wicklow
Townland:	Tigroney West
Grid Reference:	E319899, N182135
Site Score:	935
Site Class:	I (Avoca District)
Elements of Interest:	Pb, As, Cu, Zn, Cd
Media of Concern:	Solid waste, surface water, stream sediments

Geochemical Overview

Concentrations of Pb (median 8,240 mg/kg), As (835 mg/kg), Cu (826 mg/kg) and Zn (214 mg/kg) in solid waste are significantly higher in Tigroney West than elsewhere on the Avoca site. Most of the waste is benched on sloping ground and run-off from it drains to the Avoca River. The Tigroney Deep Adit drains much of the underground workings in East Avoca; the mine water it discharges has very high concentrations of Cu, Pb, Zn and elevated Cd and Cr, as well as low pH and high acidity. Dilution by the Avoca River is rapid when water levels are high; at times of low river flow, river water can contain concentrations of Cu, Pb and Zn in excess of Surface Water Regulatory limits. Metal discharge rates measured during the course of the HMS-IRC project ranged up to 3.1 kg/day Pb, 79 kg/day Zn, 2.9 kg/day Cu and 0.3 kg/day Cd, indicating an ongoing and significant input of metals to the Avoca River ecosystem. Stream sediments in the Avoca River have high concentrations of Cu, Pb and Zn adjacent to and downstream of the Tigroney West site.

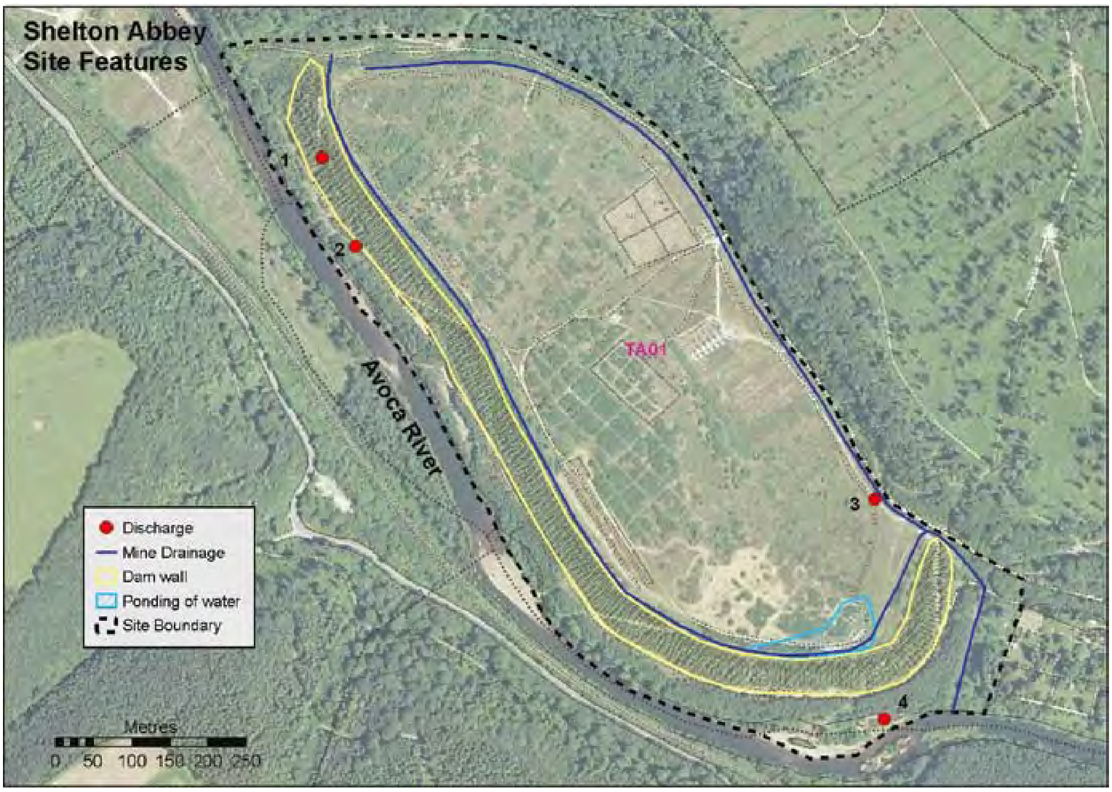


5.3.7 Shelton Abbey

Mine District:	Avoca
Mine Name:	Tailings Pond
Minerals Worked:	
County:	Wicklow
Townland:	Shelton Abbey
Grid Reference:	E321289, N175686
Site Score:	64
Site Class:	I (Avoca District)
Elements of Interest:	Pb, As, Cu, Zn
Media of Concern:	Solid waste, surface water, stream sediments

Geochemical Overview

Concentrations of elements of interest, including Pb (median, 175 mg/kg), As (75 mg/kg), Cu (197 mg/kg) and Zn (87 mg/kg), are relatively low in the tailings pond at Shelton Abbey compared to the composition of solid waste elsewhere on the Avoca mine site. However, a leachate test, data from well monitoring and analysis of surface water that is apparently contaminated by seepage suggest that the tailings have the potential for significant groundwater contamination. Analysis of surface water, both the Avoca River and drainage from the surface of the tailings pond, suggests a very limited impact from the tailings pond, chiefly from seepages. The site scores for Shelton Abbey reflect these results with the groundwater pathway contributing over 50% of the total site score.



5.4 Ballycorus

Mine District: Ballycorus

Mine Name: Ballycorus
Minerals Worked: Pb, Ag

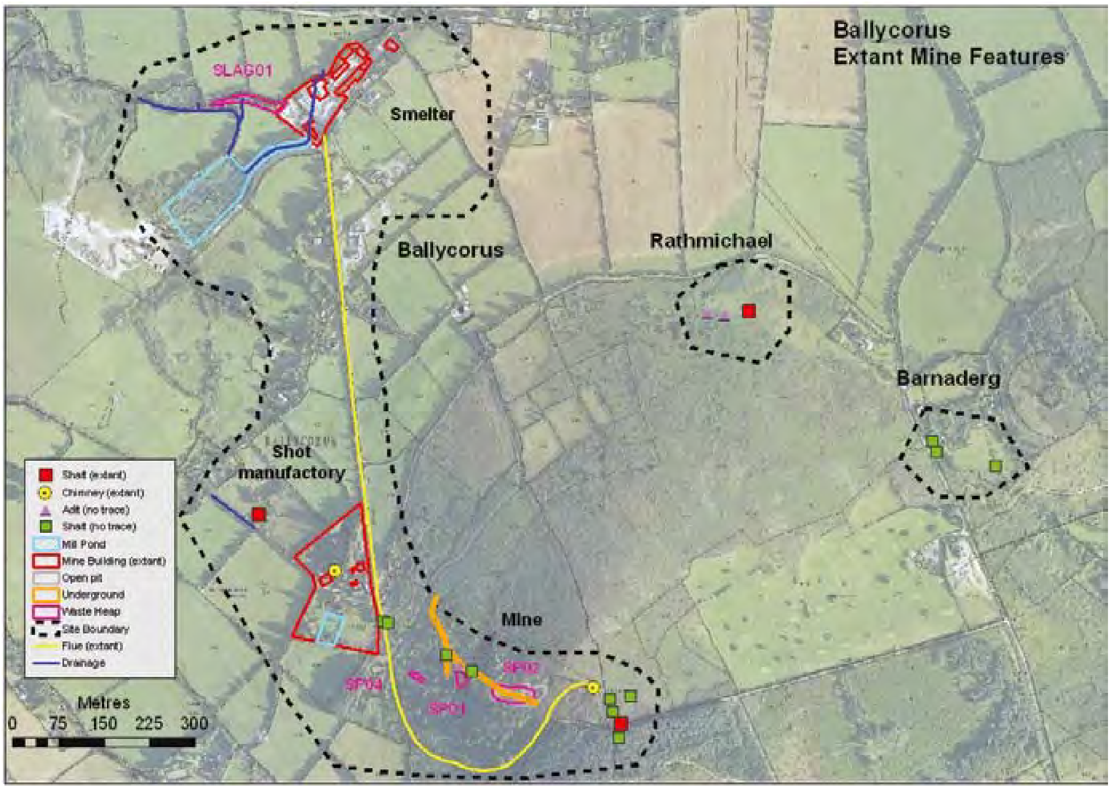
County: Dublin
Townland: Ballycorus
Grid Reference: E322283, N221384

Site Score: 244
Site Class: IV

Elements of Interest: Pb, Zn, Ag
Media of Concern: Solid waste, stream sediments

Geochemical Overview

Solid waste at Ballycorus has high concentrations of Pb, with median values exceeding 1.5% in both spoil and slag waste. The spoil is well exposed in an area popular with walkers and horse riders. These concentrations are in excess of guideline values for soil. The inner walls of the flue chimney are partly covered with Pb-rich coatings. Surface water analyses indicate a modest impact by the smelter/mine site on the chemistry of the Loughlinstown River, with elevated downstream concentrations of Pb and Ni, both in excess of current Draft EC Regulations for Surface Water. Stream sediment analyses also indicate a significant downstream impact on the aquatic ecosystem, with concentrations of Pb in the fine fraction of stream sediments ranging up to 2,024 mg/kg. The site score of 244 is relatively high for a site with only limited quantities of solid waste and no discharge of mine water.

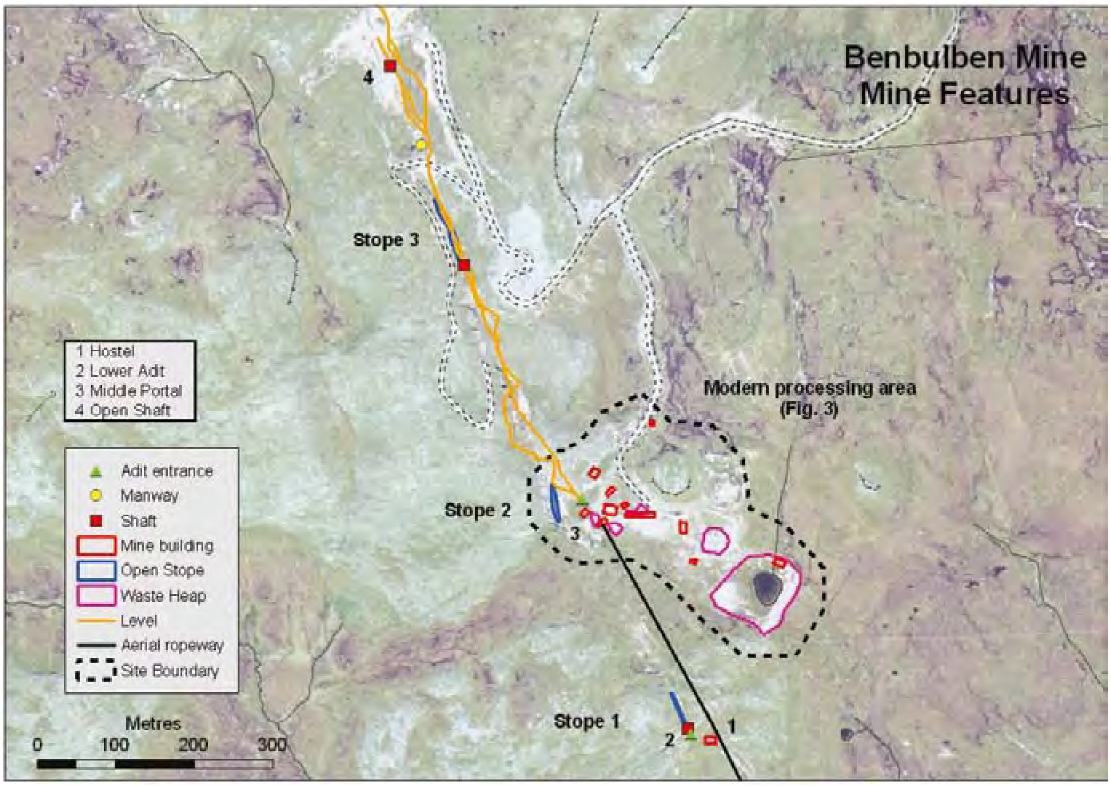


5.5 Benbulben

Mine District:	Benbulben
Mine Name:	Benbulben
Minerals Worked:	Barite
County:	Sligo
Townland:	Glencarbury
Grid Reference:	E173217, N345263
Site Score:	5
Site Class:	V
Elements of Interest:	Ba, Cu
Media of Concern:	Solid waste

Geochemical Overview

The Benbulben mine is chiefly remarkable for the number of extant mine features on the site, including some deep openings that could present a risk to the unwary. Despite production of up to 50,000 tons per year in the 1970s, the volume of solid waste remaining on the site is relatively small. The waste contains percentage levels of Ba but concentrations of other elements such as Pb, As and Cu are typically low, less than a few hundred milligrams per kilogram. There are no discharges of mine water from the underground workings. The lack of a significant chemical hazard as well as the remoteness of the site combine to give a very low HMS-IRC score of just 5, placing it in Class V with the second lowest site score of all mines investigated.



5.6 Bunmahon District

Mine District: Bunmahon

Mine Name: Bunmahon
Minerals Worked: Cu, Ag

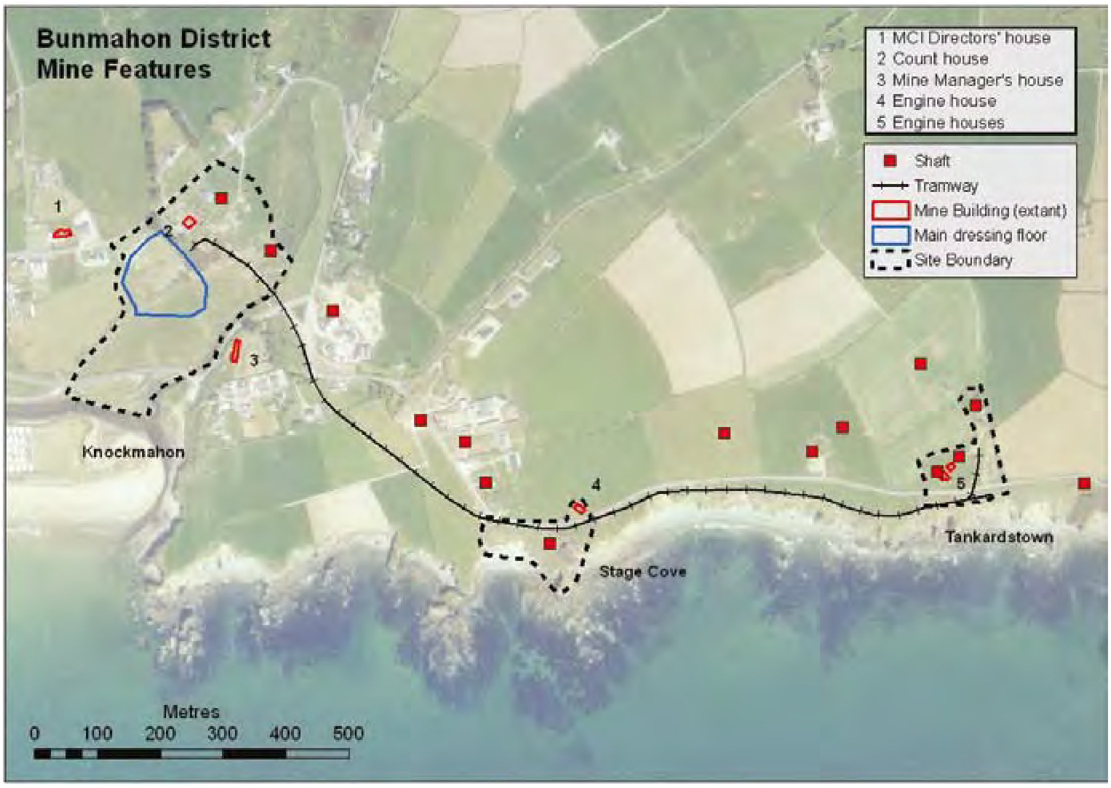
County: Waterford
Townland: Knockmahon
Grid Reference: E243962, N98996

Site Score: 14
Site Class: V

Elements of Interest: Cu
Media of Concern: Solid waste

Geochemical Overview

Bunmahon was a highly productive and profitable mine district in the 19th century. Only limited mine waste remains on the three sites investigated for the HMS-IRC project, with most found on the old processing area at Knockmahon. High concentrations of Cu, in excess of guideline values for soil, were measured in both processing waste (109–4,737 mg/kg, median 1,943 mg/kg) and in stream sediment (4,909 mg/kg) downstream of the mine. Among other elements measured, only As is present in significant concentrations.



5.7 Caim

Mine District:	Caim
Mine Name:	Caim
Minerals Worked:	Pb, Cu
County:	Wexford
Townland:	Ballyhighland
Grid Reference:	E288549, N140967
Site Score:	559
Site Class:	III
Elements of Interest:	Pb, Zn, Cu, S, Sb, Mn
Media of Concern:	Solid waste, surface water, stream sediments

Geochemical Overview

Solid mine waste at Caim has very high concentrations of Pb (5,674–85,213 mg/kg; median 56,028 mg/kg) as well as high concentrations of Zn, Cu, S and Mn. The fine processing waste that forms the waste heap on the southern part of the site is uncovered and potentially a source of airborne contamination and direct-contact contamination. Evidence on-site suggests that quad biking has taken place, increasing the potential for dust release. The high Pb concentrations measured in run-off and seepage from the solid waste heaps do not appear to persist for any significant length downstream of the site once the surface water has been diluted by stream water. However, stream sediments are contaminated for at least 1 km downstream of the site where the measured Pb concentration was 2,582 mg/kg.

5.8 Clare Lead Mines – Ballyhickey

Mine District: Clare Lead Mines

Mine Name: Ballyhickey
Minerals Worked: Pb, Ag

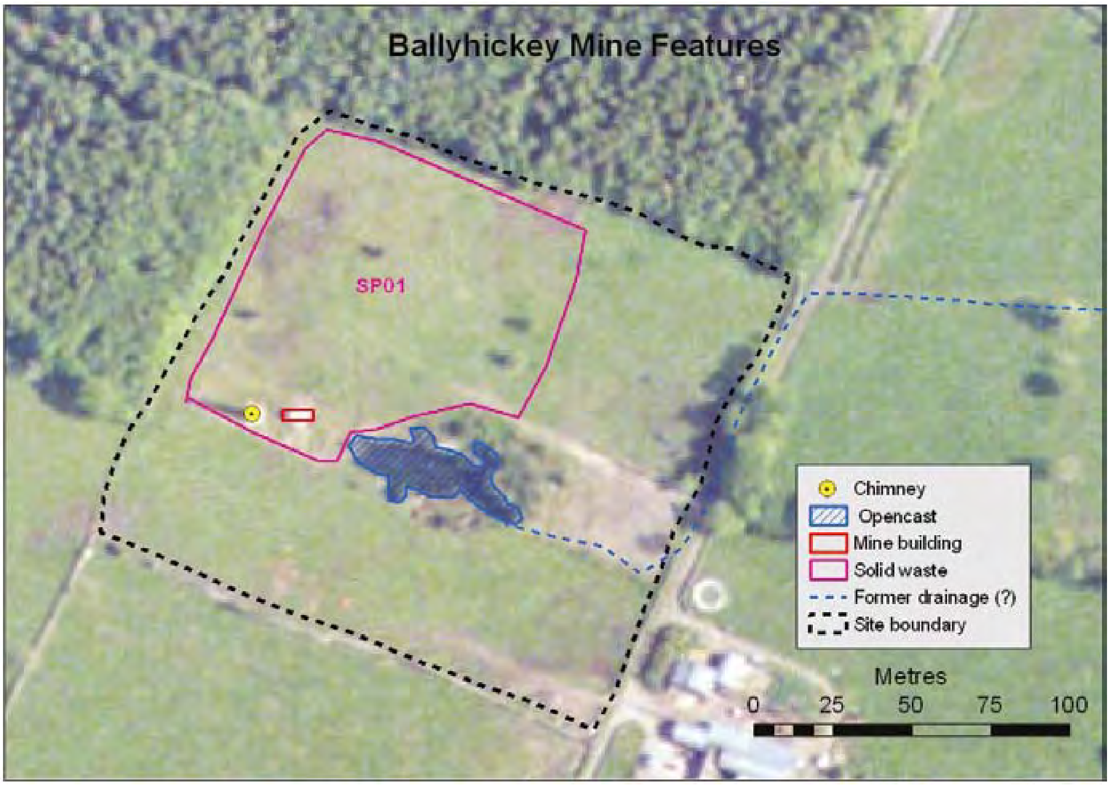
County: Clare
Townland: Ballyhickey
Grid Reference: E141735, N176868

Site Score: 19
Site Class: V

Elements of Interest: Pb, Zn, Cu, Sb, As, Ag, S
Media of Concern: Solid waste

Geochemical Overview

The solid waste at Ballyhickey is covered by grass and soil in a field that has been in use, at least in the past, for pasture. Both the waste and the soil that covers it have very high measured concentrations of Pb (up to 26%) and high concentrations of Zn, Cu and As. Small amounts of solid waste around the remains of the engine house are also enriched in Pb and other elements of interest. The lack of nearby surface watercourses limits the potential impact of the site on the surrounding environment and gives it a relatively low HMS-IRC score of 19. The clearest potential risk is to livestock that might use the site for grazing. The composition of water in the open pit is unknown. Ballyhickey is underlain by Waulsortian limestone that is known to be karstified in the vicinity of the mine site. There is therefore the potential for contamination of groundwater from contact with water in the open pit lake.



5.9 Clare Lead Mines – Ballyvergin

Mine District: Clare Lead Mines

Mine Name: Ballyvergin
Minerals Worked: Pb, Ag, Cu

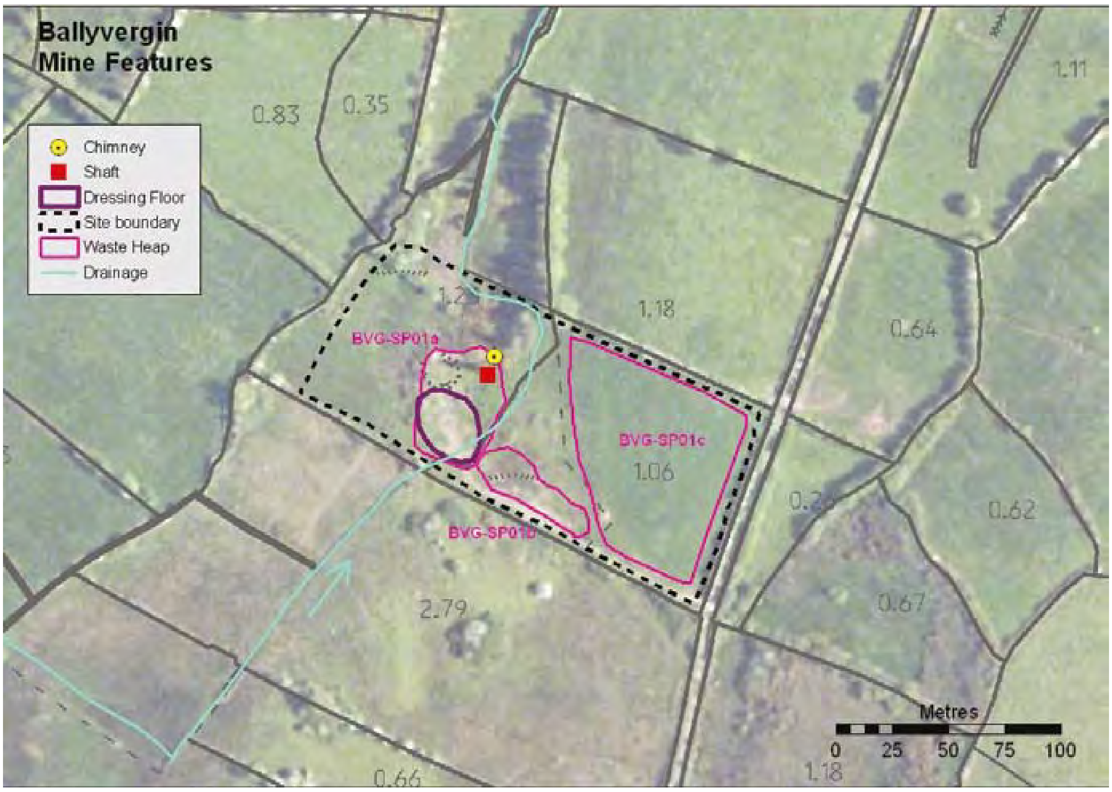
County: Clare
Townland: Ballyvergin
Grid Reference: E142143, N181731

Site Score: 39
Site Class: V

Elements of Interest: Pb, Cu, Ag, S, Z
Media of Concern: Solid waste

Geochemical Overview

Solid waste at Ballyvergin has very high levels of Pb and elevated levels of Cu, As, Zn and S. Pb levels are of particular concern as the site appears to be used for grazing cattle. Up to 14% Pb was recorded by *in-situ* XRF analysis (31% lead by laboratory assay) in an unvegetated area of fine-grained mine waste that was heavily marked by cattle hooves at the time of site visits in 2007 and 2008. There is, therefore, potential for ingestion of metal-rich waste by feeding cattle or other grazing animals. Surface water analyses suggest that the mine may have a small impact on stream water quality but further analyses are required to assess this properly.

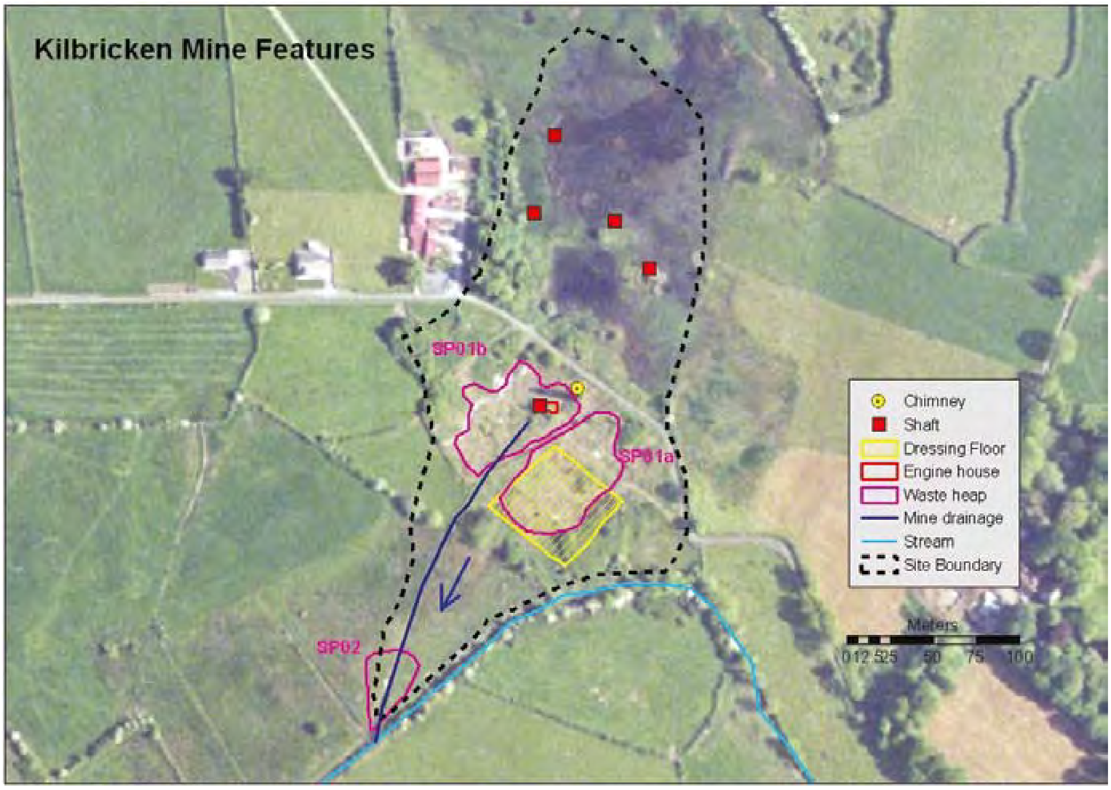


5.10 Clare Lead Mines – Kilbricken

Mine District:	Clare Pb Mines
Mine Name:	Kilbricken
Minerals Worked:	Pb, Ag
County:	Clare
Townland:	Monanoe
Grid Reference:	E141735, N176868
Site Score:	89
Site Class:	V
Elements of Interest:	Pb, As, Cu, Zn, Sb
Media of Concern:	Solid waste

Geochemical Overview

Kilbricken has some of the highest concentrations of Pb and Zn recorded in solid waste on Irish mine sites. Measured concentrations of Pb and Zn in the dressing floor waste reached almost 4% and 5%, respectively. Most of the solid waste is grassed over. A leachate test indicates that there is potential for groundwater contamination in the vicinity of this waste. Surface water draining the site had low concentrations of Pb, Zn and As, with the Pb concentration marginally in excess of surface water regulatory limits. The concentrations of Pb and Zn in stream sediment downstream of the mine were well below guideline limits for the protection of livestock.



5.11 Clare Phosphate – Doolin

Mine District: Clare Phosphate

Mine Name: Doolin
Minerals Worked: Phosphate

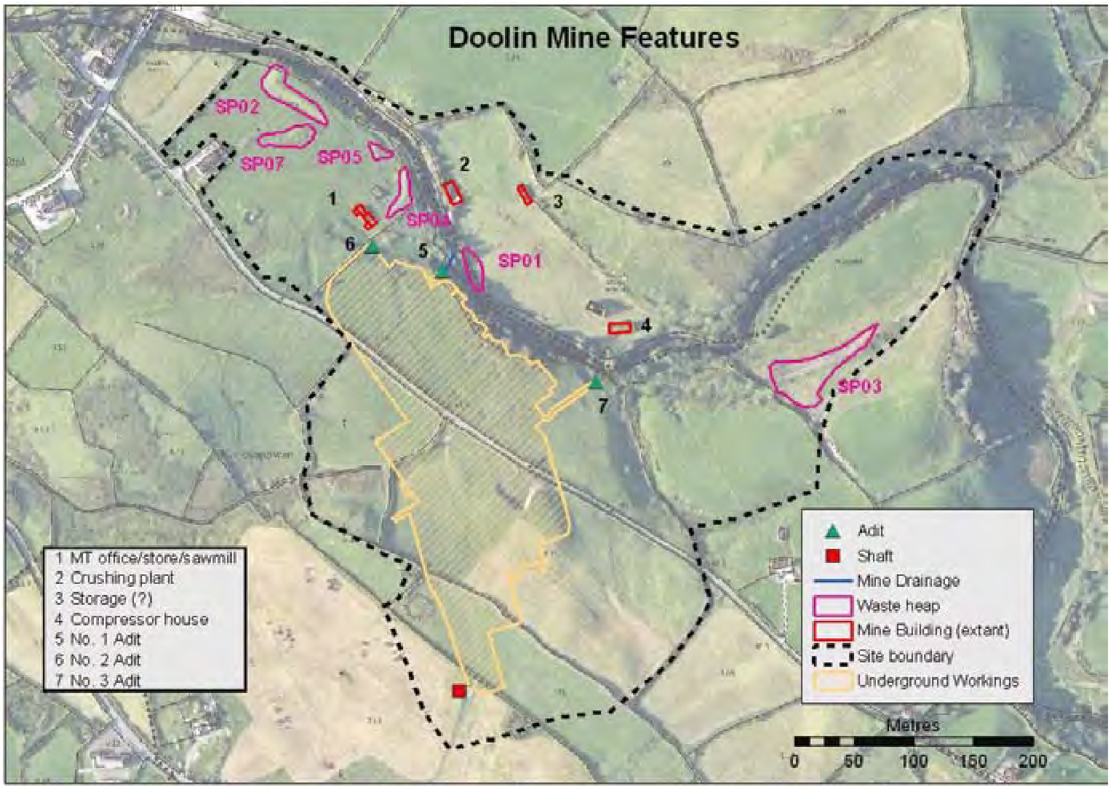
County: Clare
Townland: Teergonean; Toormullin
Grid Reference: E108345, N196999

Site Score: 15
Site Class: V

Elements of Interest: U, Ni, V, Se
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

Solid waste at Doolin contains elevated concentrations of U, Ni, V and Se, and both U and Ni are slightly elevated in the No. 1 Adit discharge that flows into the Aille River. However, the volume of the waste and the absolute concentrations of the elements are too low to cause contamination of either river water or stream sediments and the site has a relatively low HMS-IRC score of 15. Se occurs in low concentrations in the phosphate waste but similarly low concentrations of Se have been associated with Se toxicity in livestock and aquatic ecosystems downstream of phosphate mines in the USA.

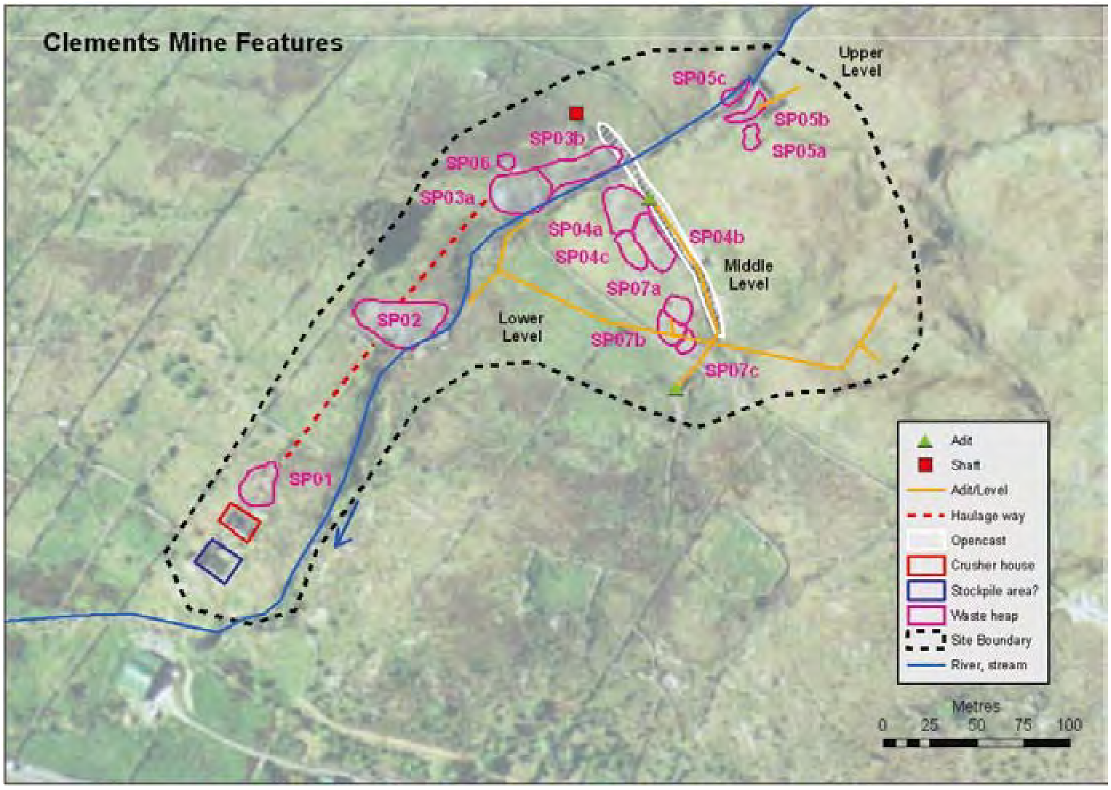


5.12 Clements

Mine District:	Connemara
Mine Name:	Clements
Minerals Worked:	Pb, Ag
County:	Galway
Townland:	Carrowgarrif
Grid Reference:	E99410, N251843
Site Score:	97
Site Class:	V
Elements of Interest:	Pb, Zn, Ag, As, Ni
Media of Concern:	Solid waste, stream sediments

Geochemical Overview

Solid waste heaps at Clements comprise both oxidised, metal-rich waste and relatively fresh waste with a high concentration of unmineralised material. All waste has relatively high concentrations of Pb, with the maximum concentration (5.4%) recorded in crushing waste. The median Pb value of all the solid waste analysed was 5,621 mg/kg (0.56%). A surface water sample taken downstream of the mine had 161 µg/l Zn and 13 µg/l Pb (total metal), in excess of the Draft EC Surface Water Regulation standard (100 µg/l and 7.2 µg/l, respectively). Upstream concentrations were 41 and 8 µg/l, respectively. These values suggest some impact from the mine waste. However, caution is required as dissolved metal concentrations show no similar pattern. One stream sediment sample downstream of the mine had high concentrations of Pb (1,971 mg/kg), Zn (1,755 mg/kg), As (245 mg/kg) and Ni (557 mg/kg).



5.13 Connacht Coalfield

Mine District: Connacht Coalfield

Mine Name: Various
Minerals Worked: Coal (Bituminous)

County: Leitrim, Roscommon, Sligo
Townland: Various

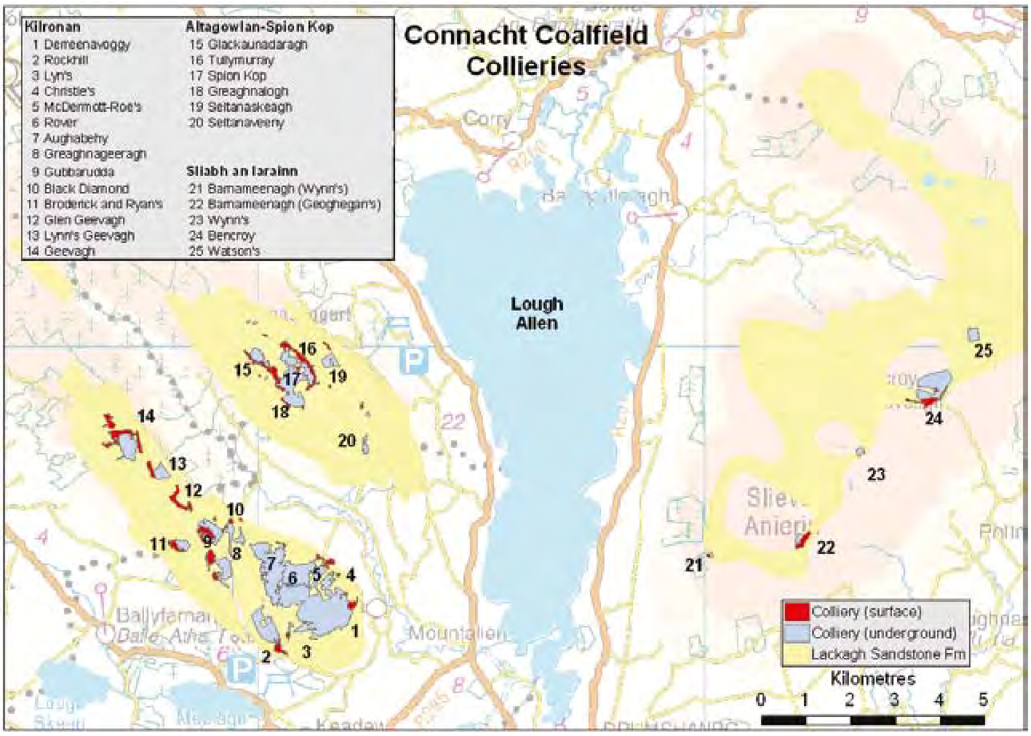
Grid Reference: E193000, N314000

Site Score: 91
Site Class: V

Elements of Interest: Ni, Zn, sulphate, acidity
Media of Concern: Solid waste, surface water

Geochemical Overview

Large waste heaps, open pit lakes and active drainage adits remain and are the main potential sources of environmental impacts in the Connacht Coalfield District. Water draining from mine adits in the district has relatively high concentrations of elements such as Al, Ni, Zn and SO_4 as well as low pH and high EC and acidity. Stream water downstream of such discharges also displays elevated concentrations of some of these elements, notably Ni and SO_4. Concentrations of Zn, Ni and SO_4 in mine water and in surface water immediately downstream of mines are generally above standard limits. Most surface water samples from the Connacht Coalfield exceed the standard (drinking water) concentration for aluminium of 200 µg/l. Samples of stream water taken further downstream of mine sites and adit discharges show only very limited and localised chemical impact from mining. Solid waste analysis at one site revealed no significantly elevated metal concentrations. Metal concentrations in stream sediments were below guideline limits for the protection of livestock.



5.14 Donegal Lead Mines – Glentogher

Mine District: Donegal Pb

Mine Name: Glentogher
Minerals Worked: Pb, Ag

County: Donegal
Townland: Stranagappoge Demesne
Grid Reference: E247847, N437881

Site Score: 5
Site Class: V

Elements of Interest: Pb, Zn, As, Sb
Media of Concern: Stream sediments

Geochemical Overview

Glentogher mine was a small mine that produced a limited quantity of lead ore. There is no clear evidence that it has had or continues to have any major impact on its surroundings. Water analyses do not indicate contamination of the downstream surface water by the adit discharge, which has low metal concentrations. Pb and Zn concentrations in stream sediments in the Glentogher area are higher than those found in Inishowen as a whole and Pb concentrations downstream of the mine are higher than those upstream. This suggests some downstream impact from mining. Median concentrations of other metals, such as Cu and As, in stream sediments downstream of the mine are not readily distinguishable from those recorded for the rest of Glentogher as a whole.

5.15 Donegal Lead Mines – Keeldrum

Mine District: Donegal Pb

Mine Name: Keeldrum
Minerals Worked: Pb, Ag

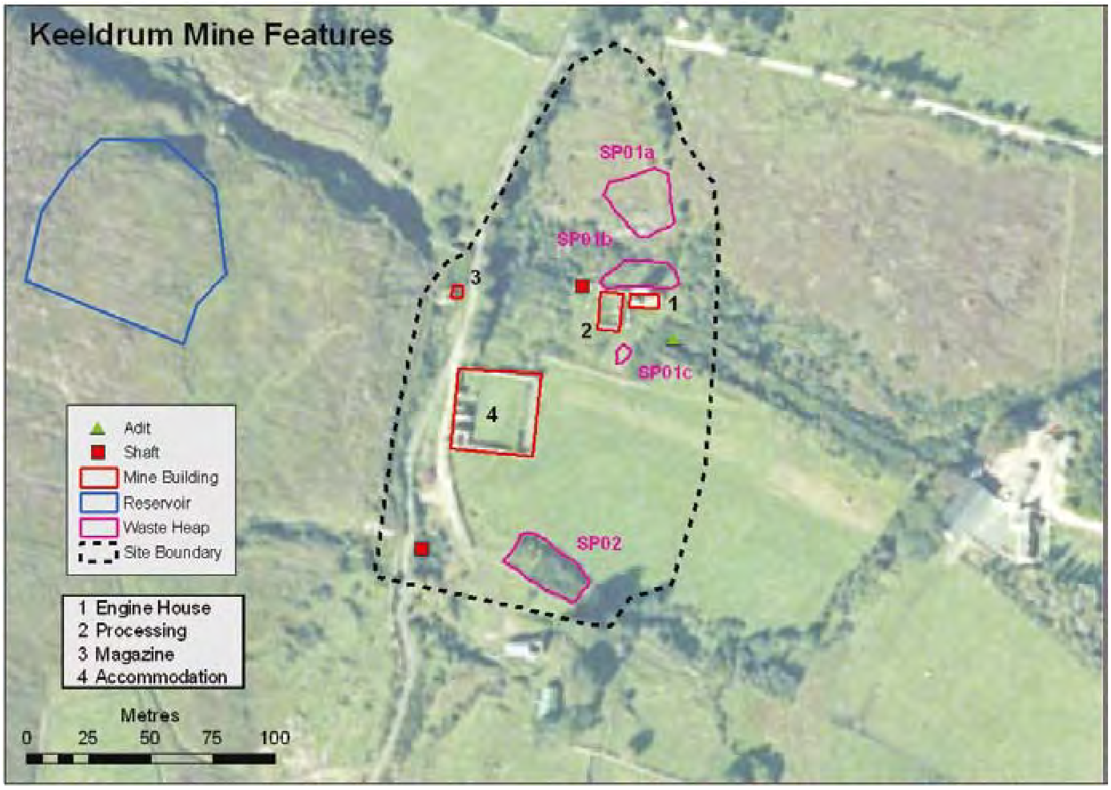
County: Donegal
Townland: Keeldrum
Grid Reference: E190346, N426239

Site Score: 17
Site Class: V

Elements of Interest: Pb, Zn, Cu
Media of Concern: Solid waste

Geochemical Overview

Keeldrum operated as a lead mine for a total of around 10 years in the 19th century, producing less than 2,000 tons of ore. The site is largely grassed over but small amounts of solid waste remain on the site. There are no mine water discharges or evidence of downstream contamination of surface water. Solid waste contains high concentrations of Pb (median 7,146 mg/kg) with the highest concentrations (up to 13.5%) found in processing waste. A leachate test on the solid waste yielded an extremely high concentration of Pb (19,860 µg/l) and suggests the potential for groundwater contamination in the vicinity of the site.



5.16 Glenmalure District
5.16.1 Ballinafunshoge

Mine District: Glenmalure

Mine Name: Ballinafunshoge
Minerals Worked: Pb

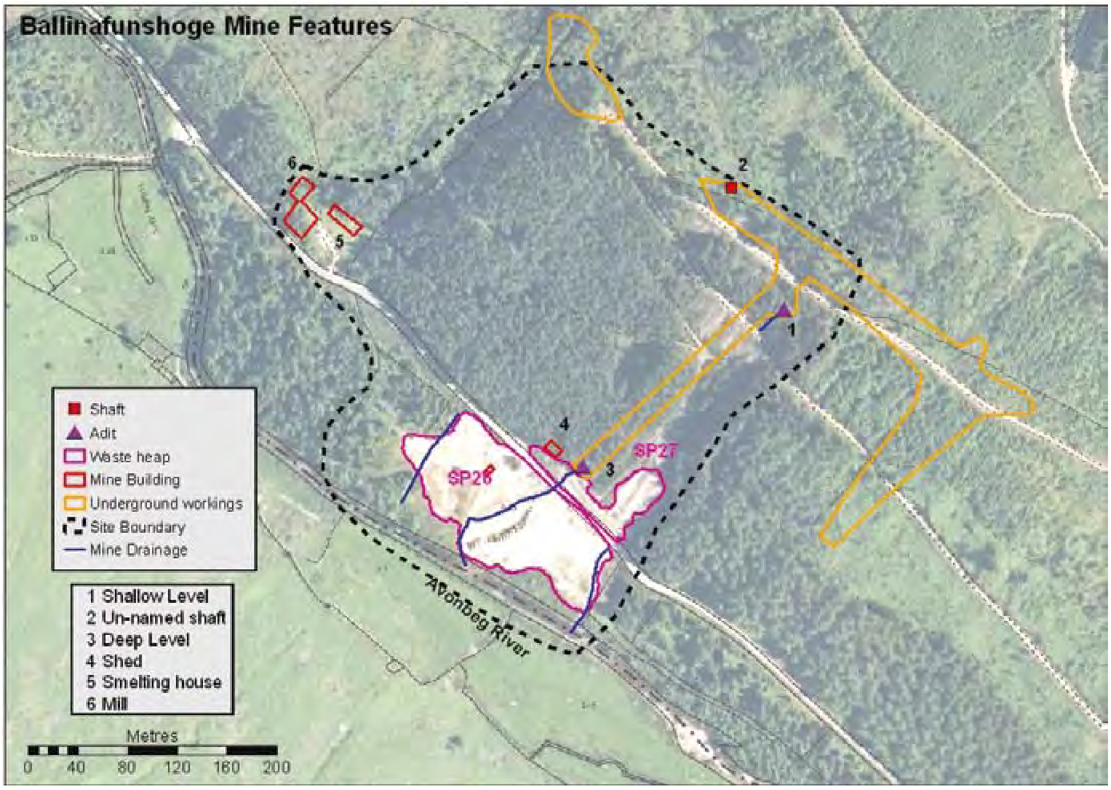
County: Wicklow
Townland: Ballinafunshoge
Grid Reference: E308265, N192695

Site Score: 305
Site Class: III (Glenmalure District)

Elements of Interest: Pb, Zn, Cu, Cd
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

The Ballinafunshoge site is notable for an adit discharge with very high Pb (≤6,512 µg/l) and Zn (≤15,860 µg/l) concentrations as well as an extensive area of processing waste with some very high measured concentrations of Pb (>19%). The adit discharge drains directly to the Avonbeg River and, combined with run-off from the solid waste heaps, has significant potential to contaminate the aquatic ecosystem. However, the acidity of the mine water is very low and there is no risk of AMD at the site. As is the case for most sites in the district, Cd is generally present in significant concentrations in both solid (≤238 mg/kg) and liquid (≤70 µg/l) waste. There is significant contamination of stream sediments, with high Pb (1,226 mg/kg) and Zn (475 mg/kg) concentrations recorded 200 m downstream of the mine site.



5.16.2 Barravore–Ballinagoneen

Mine District: Glenmalure

Mine Name: Barravore–Ballinagoneen
Minerals Worked: Pb

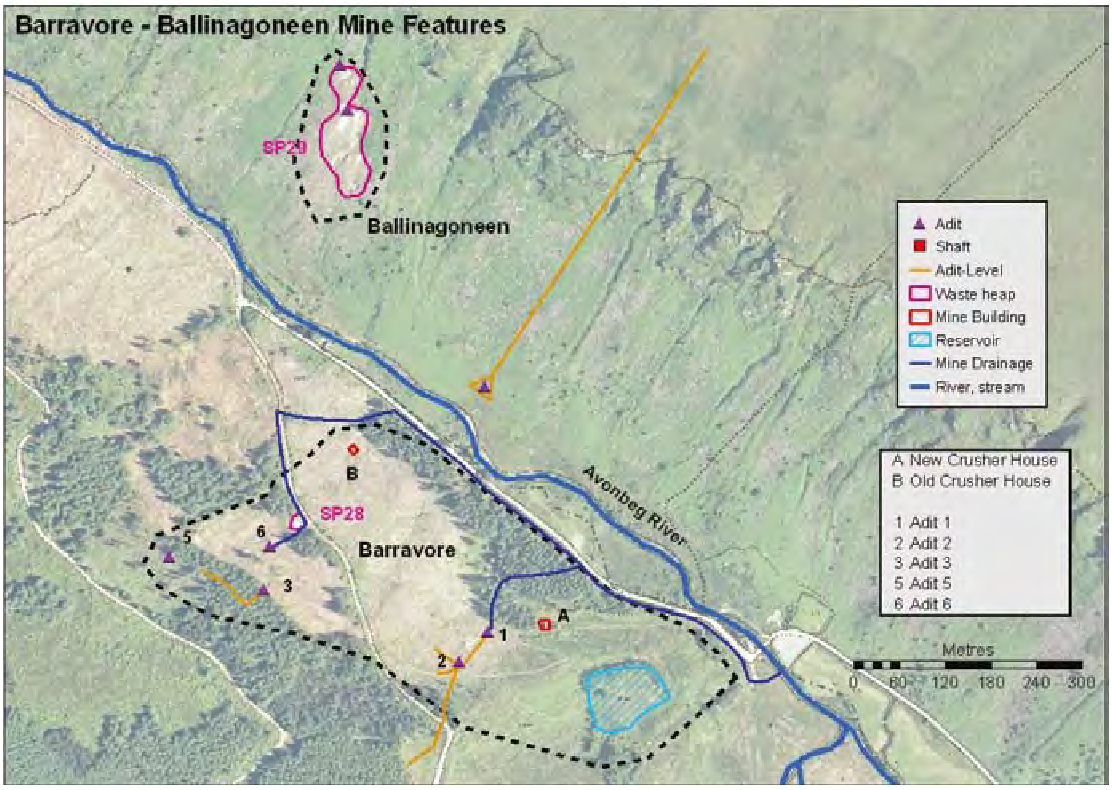
County: Wicklow
Townland: Barravore; Ballinagoneen
Grid Reference: E306180, N194231;
E306041, N194835

Site Score: 6
Site Class: III (Glenmalure District)

Elements of Interest: Pb, Zn, Cu, Cd
Media of Concern: Solid waste, stream sediments

Geochemical Overview

Stream sediment analyses indicate a significant impact on the Avonbeg River by mining activities, with the Pb concentration immediately downstream of the site in excess of 1,000 mg/kg, the guideline limit for the protection of livestock. Very limited volumes of solid waste remain on the site. One adit (Adit 6) discharges a low flow of mine water with elevated Pb (65 µg/l) and Zn (446 µg/l) but these concentrations are not particularly high. Thus, the existing waste sources on the site appear to pose only limited risk to the environment.

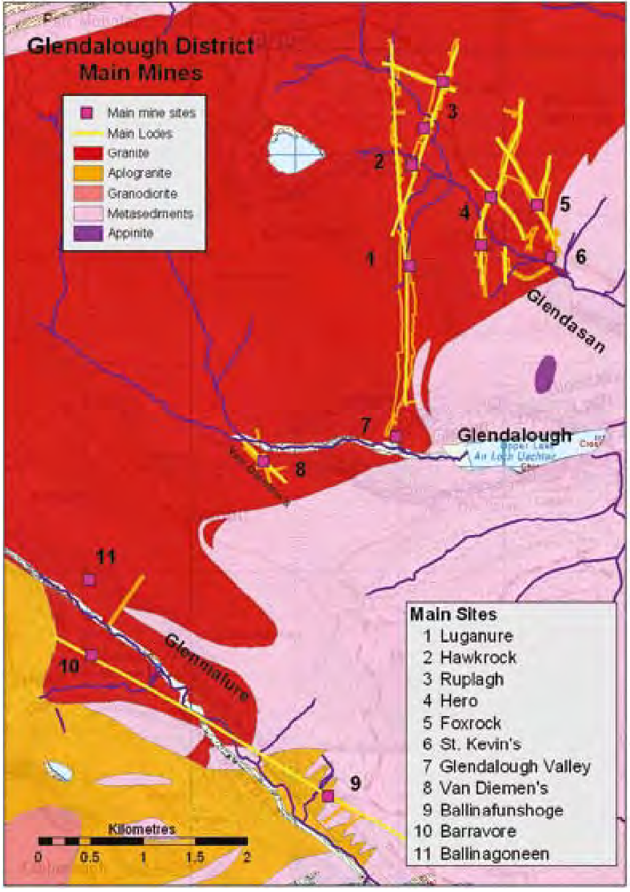


5.17 Glendalough–Glendasan District

Mine District:	Glendalough
Mine Name:	Various
Minerals Worked:	Pb
County:	Wicklow
Townland:	Various
Grid Reference:	E308265, N192695
Site Score:	1,457
Site Class:	III (Glenmalure District) II (Glendasan–Glendalough)
Elements of Interest:	Pb, Zn, Cu, Cd
Media of Concern:	Solid waste, surface water, stream sediments

Geochemical Overview

The Glendalough District has an extensive history of 19th-century lead and silver mining that has left a striking physical legacy in the three valleys that comprise it: Glendasan, Glendalough and Glenmalure. In addition to numerous ruined mine buildings, white quartz-rich solid waste heaps are a feature of the district. All of these contain significant measured concentrations of Pb and Zn and some, notably those on old ore processing sites, have very high concentrations, with maximum recorded values of Pb of almost 20%. Several significant adit discharges drain to the Glendasan, Glenealo and Avonbeg Rivers. These discharges contain significant concentrations of contaminants, chiefly Pb and Zn, but including Cu and Cd, and have a measurable impact on the water quality in the rivers downstream of the mine sites, albeit over short distances. Stream sediments, in contrast, are contaminated over very extensive lengths of the rivers downstream of the mines. The worst affected is the Glendasan River, with concentrations of up to 7.2% Pb measured in stream sediments downstream of the mines. Contamination of stream sediments has been measured at least 4 km downstream of the Glendasan sites. The total HMS-IRC score for the Glendalough District is 1,457 but this has been split into two sub-groups for the purpose of national ranking of the sites: the Glendasan–Glendalough Valley group has a HMS-IRC score of 1,122, while the Glenmalure sites have a total score of 335.



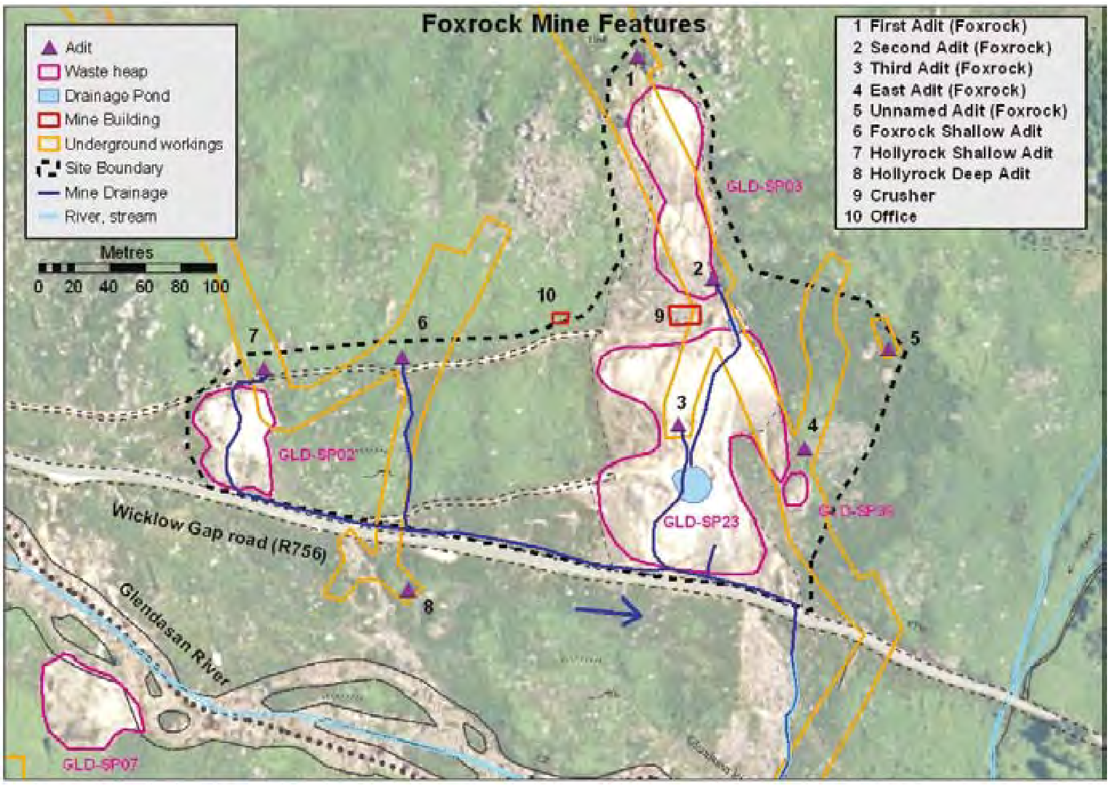
Reports for the individual mine sites in the district follow below.

5.17.1 Foxrock

Mine District:	Glendalough–Glendasan
Mine Name:	Foxrock
Minerals Worked:	Pb
County:	Wicklow
Townland:	Brockagh
Grid Reference:	E310367, N198209
Site Score:	197
Site Class:	II (District)
Elements of Interest:	Pb, Cu, Zn, Cd
Media of Concern:	Solid waste, surface water

Geochemical Overview

The Foxrock site contains two adits that discharge a significant quantity of mine water to the Glendasan River. Part of the discharge flows through the largest waste heap on the site, contributing to potential undermining of the heap. The 2nd and 3rd Adits have near-neutral pH, low acidity, and metal concentrations are of the order of 700–1,800 µg/l Pb and 1,800–2,800 µg/l Zn. The solid waste chemistry is typical of the quartz-rich mine waste found in the district, with Pb concentrations typically of the order of 500–4,000 mg/kg with a maximum in excess of 1%. Zn is also present in high concentrations but apart from Cd, which is typically present in concentrations below 50 mg/kg, other elements of interest are not present in significant concentrations.



5.17.2 Glendalough Valley

Mine District: Glendalough–Glendasan

Mine Name: Glendalough Valley
Minerals Worked: Pb

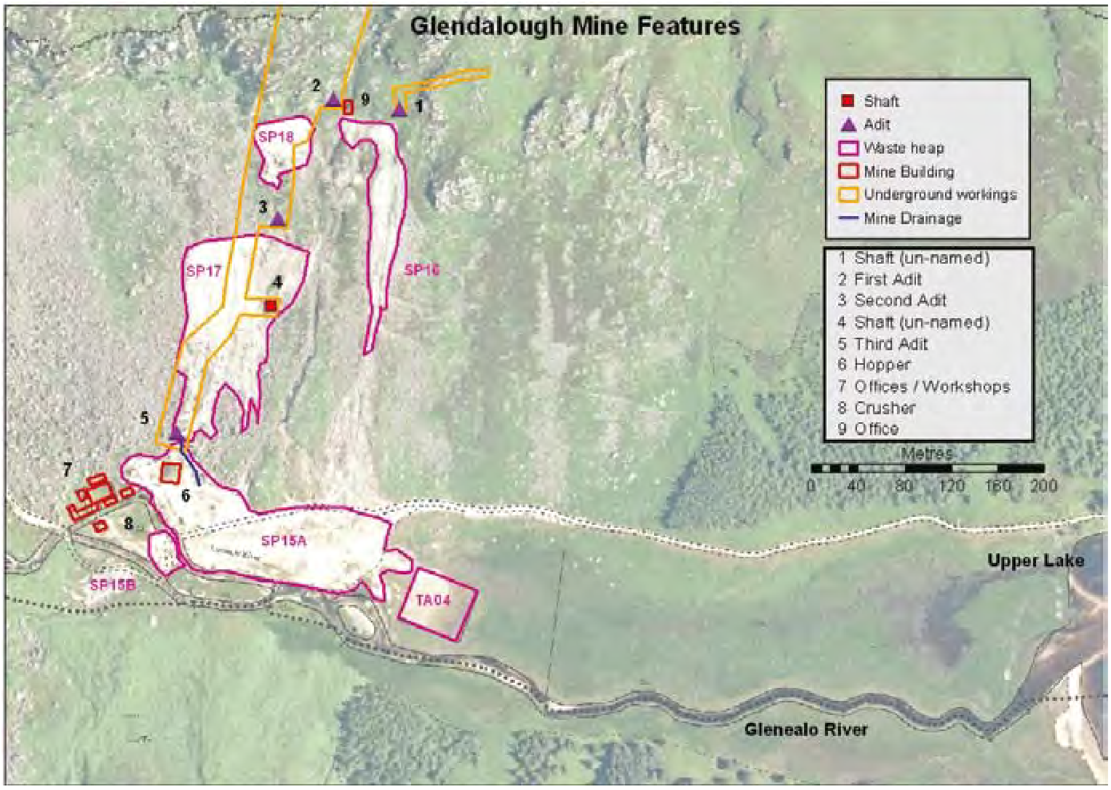
County: Wicklow
Townland: Camaderry; Lugduff
Grid Reference: E308964, N196346
E307695, N196116

Site Score: 331
Site Class: II (District)

Elements of Interest: Pb, Cu, Zn, Cd
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

The Glendalough Valley site contains a large volume of solid waste. Most of the solid waste chemistry is typical of quartz-rich mine waste found in the district, with Pb concentrations typically of the order of 5,000 mg/kg. However, Pb concentrations in processing waste can exceed 4%. Water seeping from the largest solid waste heap has high Pb (812 µg/l) and Zn (5,037 µg/l) concentrations. Discharge of this water to the Glenealo River contributes directly to contamination of the river water, although it recovers quickly downstream through dilution. Stream sediments in the river are seriously contaminated, however, with concentrations of Pb in excess of 6,000 mg/kg at the point of discharge to the Upper Lake.



5.17.3 Hero

Mine District: Glendalough–Glendasan

Mine Name: Hero
Minerals Worked: Pb

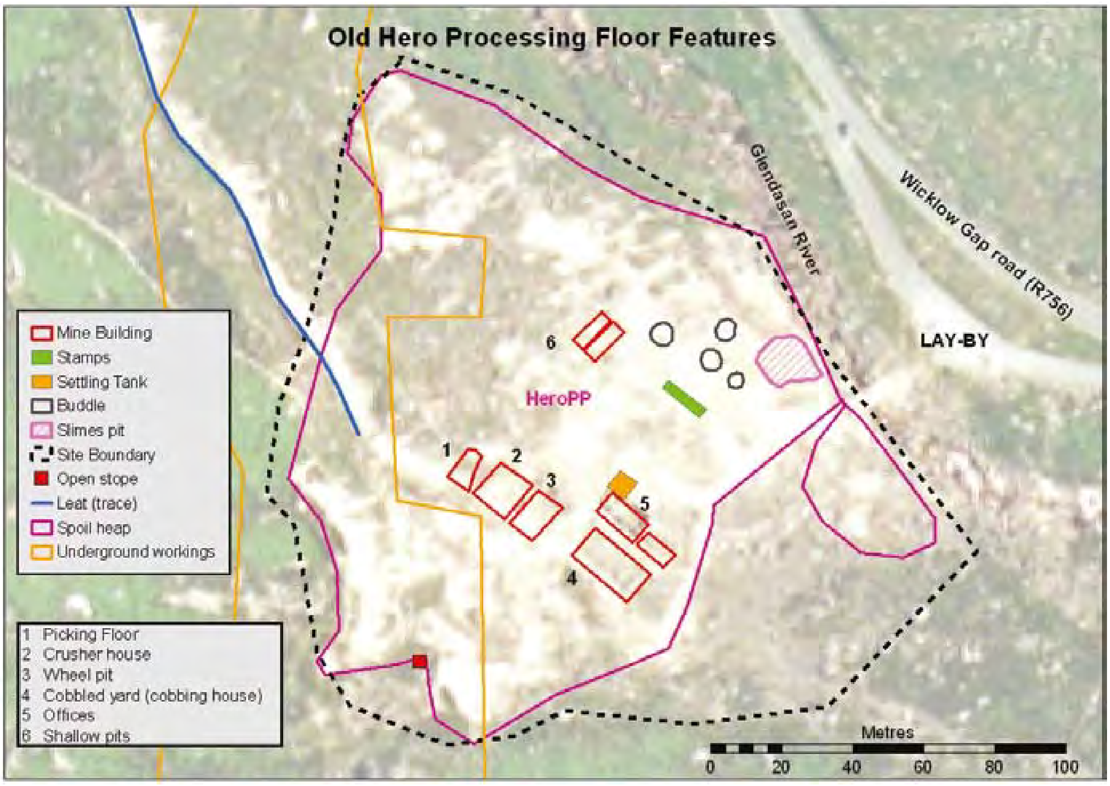
County: Wicklow
Townland: Camaderry
Grid Reference: E309848, N198158

Site Score: 183
Site Class: II (District)

Elements of Interest: Pb, Cu, Zn, Cd
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

This site includes the Old Hero and North Hero sites. Solid waste at the Old Hero processing site includes significant volumes of fine material with exceptionally high concentrations of Pb (≤14.5%) and Zn (≤19.3%). Cd has also been measured in relatively high concentrations (≤658 mg/kg). The site is a common stop-off point for visitors in the area. There are potential risks to humans as a result of direct contact with metal-rich waste and, additionally, to animals as a result of ingestion of same. The presence of fine waste such as slimes and the prevalence of westerly winds blowing through the Wicklow Gap raise the possibility that wind-blown metal-rich dust might be an inhalation issue in dry periods. The site is on the side of the valley and during wet weather run-off drains directly into the Glendasan River. Leachate testing indicates that the dissolved metal content of run-off is likely to be high. Stream sediment samples downstream of the site have very high concentrations of Pb and Zn, though other sites in Glendasan have also contributed to this.

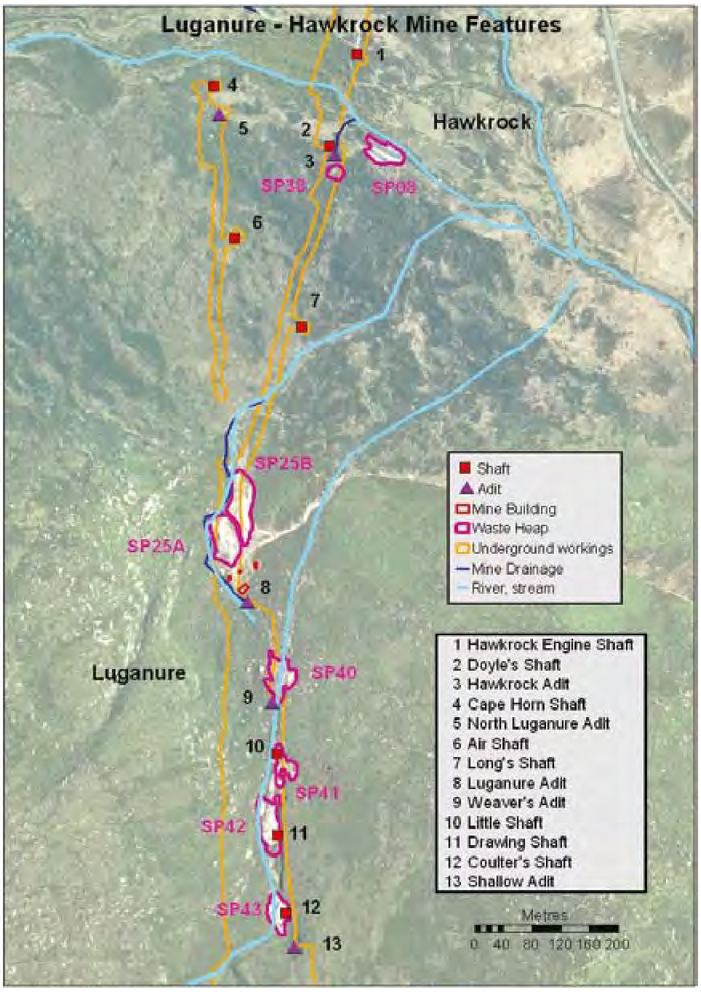


5.17.4 Luganure – Hawkrock

Mine District:	Glendalough–Glendasan
Mine Name:	Luganure – Hawkrock
Minerals Worked:	Pb
County:	Wicklow
Townland:	Camaderry
Grid Reference:	E309055, N198177 (Luganure) E309195, N198887 (Hawkrock)
Site Score:	48
Site Class:	II (District)
Elements of Interest:	Pb, Cu, Zn, Cd
Media of Concern:	Solid waste, surface water, stream sediments

Geochemical Overview

High concentrations of Pb, Zn and Cd were measured in the Hawkrock Adit discharge, and stream water downstream of the mine site had relatively high concentrations of Pb (32 µg/l) and Zn (414 µg/l), at least in winter. As is the case for all mine water discharges in the Glendasan area, pH is close to neutral in the Hawkrock Adit discharge. The Luganure–Hawkrock site contains several solid waste heaps scattered along the line of the Luganure lode. The largest are found on the main Luganure mine site, in front of the Luganure Adit. These have the highest HMS-IRC scores of any waste in Luganure–Hawkrock. Nevertheless, the total score for Luganure–Hawkrock (48) is among the lowest recorded in the district.

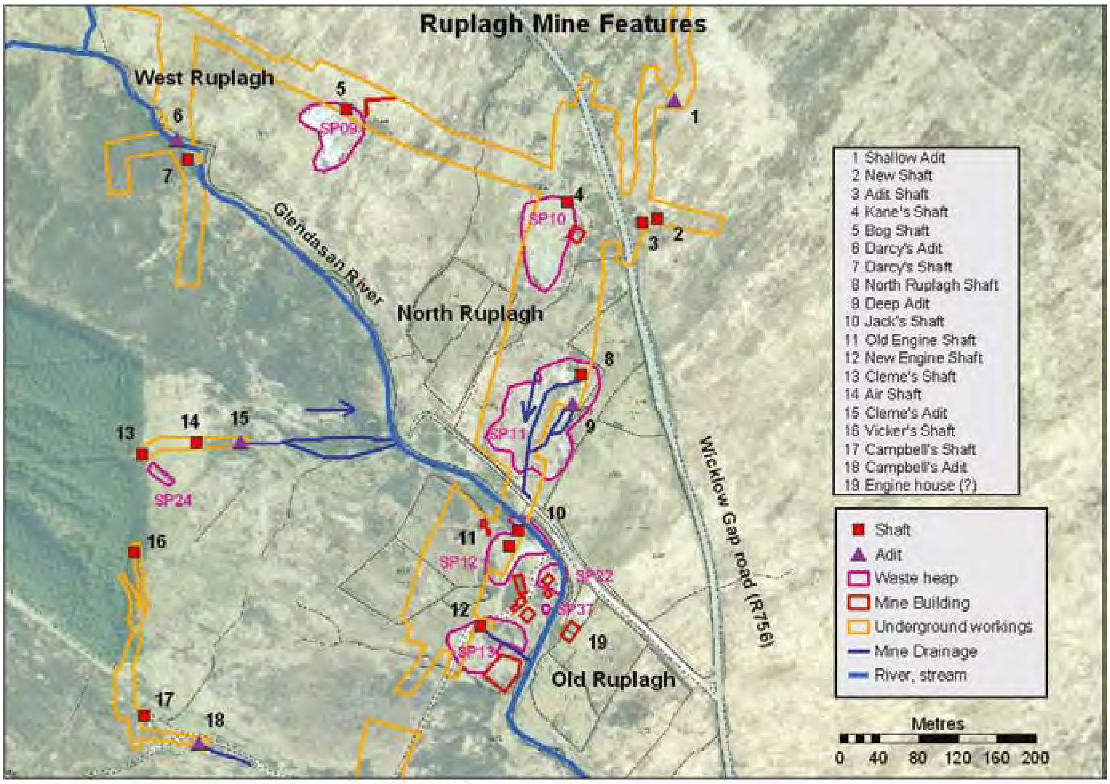


5.17.5 Ruplagh

Mine District:	Glendalough–Glendasan
Mine Name:	Ruplagh
Minerals Worked:	Pb
County:	Wicklow
Townland:	Brockagh
Grid Reference:	E309295, N199494
Site Score:	45
Site Class:	II (District)
Elements of Interest:	Pb, Cu, Zn, Cd
Media of Concern:	Solid waste, surface water, stream sediments

Geochemical Overview

Two discharges from flooded shafts at Ruplagh have elevated concentrations of Pb (≤72 µg/l) and Zn (≤994 µg/l). The maximum downstream concentration of Pb was 11 µg/l and of Zn 166 µg/l, lower than those measured in the Glendasan River downstream of the sites in Lower Glendasan (Hero, Foxrock and St. Kevin's), but still above the limits set by EC Surface Water Regulations. A stream sediment sample taken immediately downstream of the site had 6,874 mg/kg Pb and 4,876 mg/kg Zn, indicating significant contamination of stream sediments as a result of mining at Ruplagh. Concentrations of Pb and Zn in solid waste exceed 1% in some samples but median concentrations (3,301 and 5,433 mg/kg, respectively) are similar to those found in quartz- and granite-rich solid waste elsewhere in the district.



5.17.6 St. Kevin's

Mine District: Glendalough–Glendasan

Mine Name: St. Kevin's
Minerals Worked: Pb

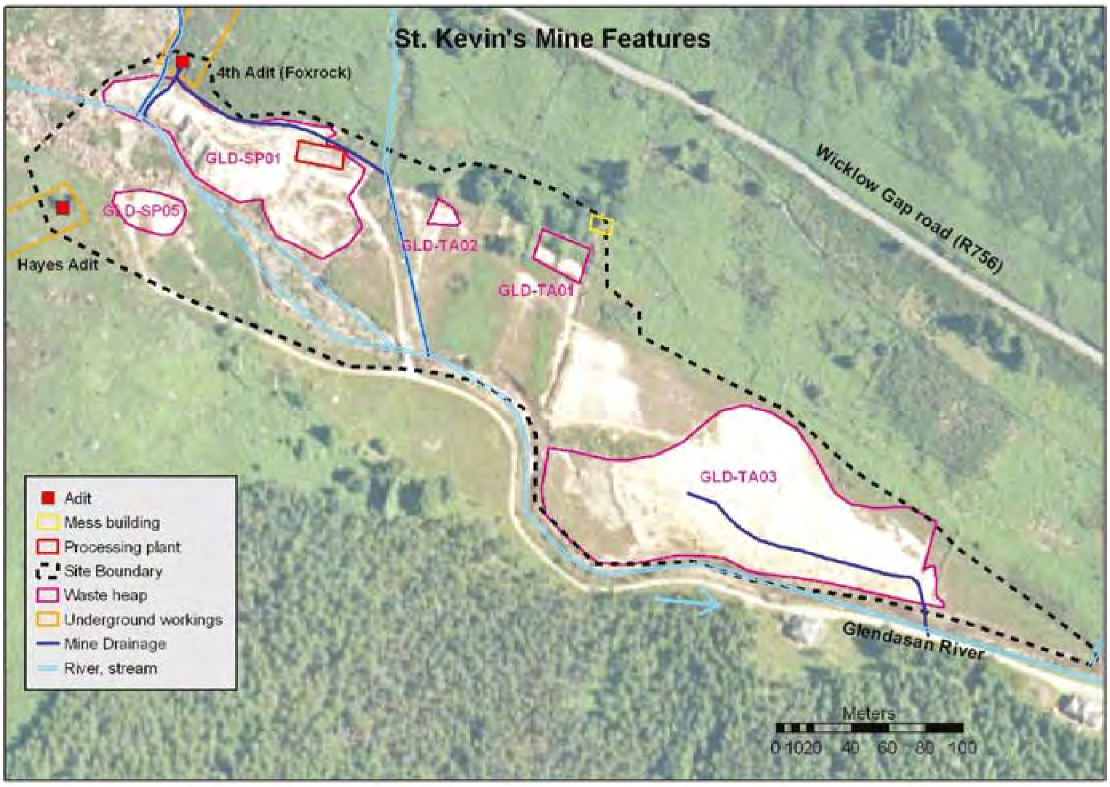
County: Wicklow
Townland: Camaderry; Sevenchurches
Grid Reference: E310646, N197839

Site Score: 129
Site Class: II (District)

Elements of Interest: Pb, Cu, Zn, Cd
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

The St. Kevin's site contains one of the largest spoil heaps in the district as well as its only significant accumulation of tailings. The spoil chemistry is typical of quartz-rich mine waste found in the district, with Pb concentrations typically of the order of 500–4,000 mg/kg with a maximum in excess of 2%. The tailings material generally has higher concentrations of Pb; Cd was recorded at levels of 102–660 mg/kg. The Foxrock 4th Adit discharges constantly into the Glendasan River; metal concentrations are of the order of 200–300 µg/l Pb and 1,500–2,000 µg/l Zn. In wet weather, the tailings is a source of metal-rich run-off to the river. The Glendasan River has consistently elevated Pb and Zn concentrations downstream of the site, although the 4th Adit is unlikely to be the sole source of this contamination given that other adits in Foxrock drain into the river nearby. Stream sediments immediately downstream of the tailings deposit have extremely high concentrations of Pb (7.2%), Zn (5.1%) and Cd (179 mg/kg).



5.18 Gortdrum

Mine District: Gortdrum

Mine Name: Gortdrum
Minerals Worked: Cu, Hg, Ag

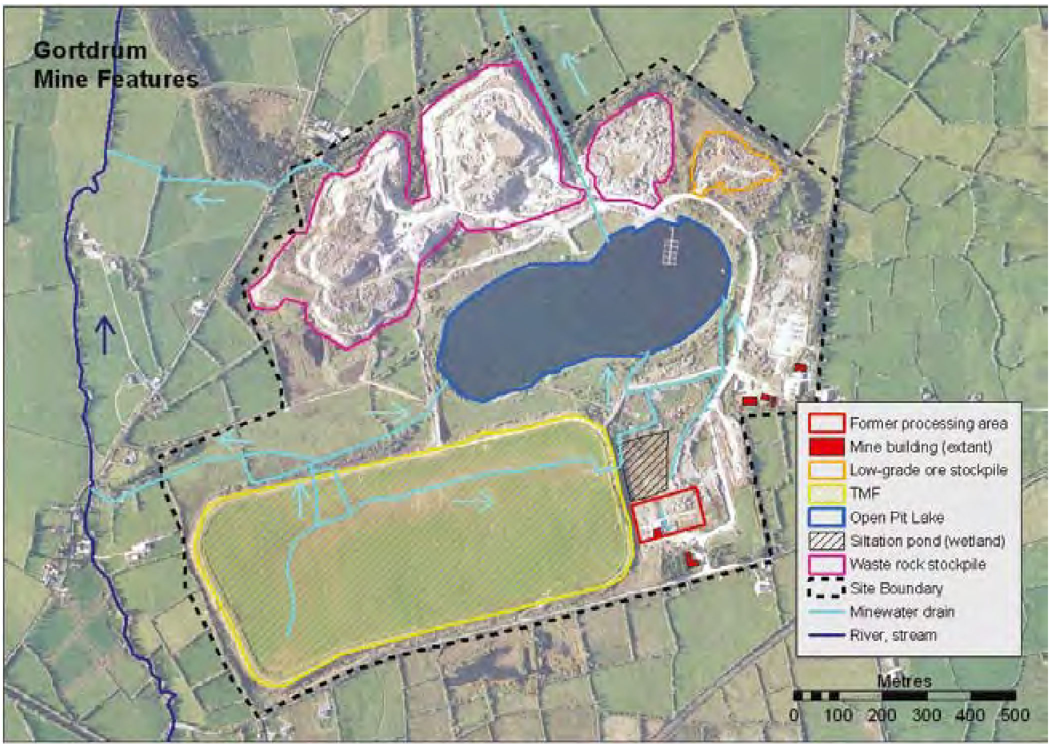
County: Tipperary
Townland: Gortdrum; Ballyryan East; Kyleagarry
Grid Reference: E187111, N141012

Site Score: 157
Site Class: IV

Elements of Interest: Cu, Sb, As, Hg, Ag
Media of Concern: Solid waste, surface water

Geochemical Overview

Gortdrum mine is one of the most extensive abandoned mine sites in the country with very large volumes of solid waste remaining on the site. The ground cover in the old processing area has high concentrations of Cu, As and Hg. The tailings management facility (TMF) has been successfully revegetated and is in general use as a cattle pasture. Cu and As concentrations in the tailings are low and Hg is typically below detection limit. The former Hg plant siltation pond is now a wetland; metal concentrations are low. The stockpile/waste heaps north of the open pit are now part of an aggregate extraction operation but significant levels of metals, including As and Hg, are contained in the aggregate. Very little water appears to flow off the site, instead draining into the flooded open pit lake. Leachate draining from waste heaps on the north-western end of the site has high concentrations of Cu, Sb, As and Hg, as does the open pit lake water. There is potential for some impact on groundwater downgradient of the site but stream sediments appear to be unaffected by mining.



5.19 Hollyford

Mine District: Tipperary

Mine Name: Hollyford
Minerals Worked: Cu

County: Tipperary
Townland: Reafadda; Lackenacree

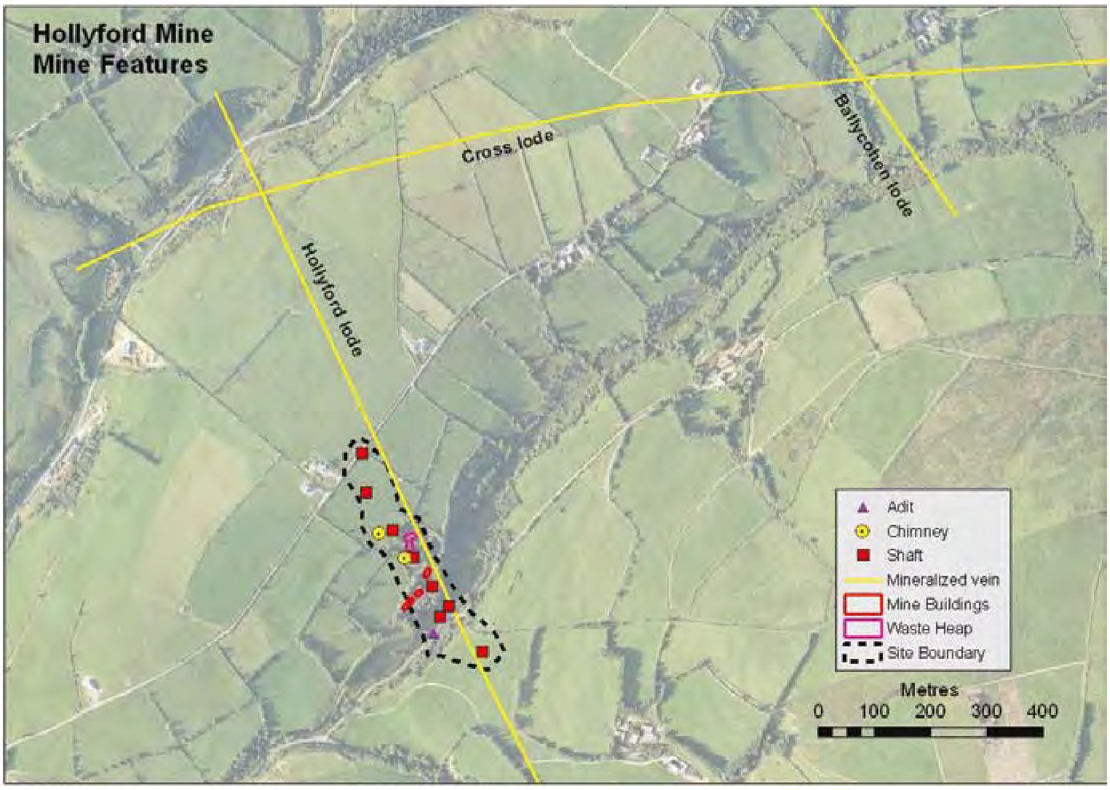
Grid Reference: E193361, N154077

Site Score: 4
Site Class: V

Elements of Interest: Cu
Media of Concern: Solid waste

Geochemical Overview

Hollyford mine was a small operation that produced several thousand tons of Cu ore over a period of 20 years in the mid-19th century. It had a correspondingly limited impact on its surroundings and today only minor amounts of solid waste remain. This waste has, by comparison with solid mine waste elsewhere in the country, relatively low levels of Cu, Pb and As. The low site score reflects the small volume of waste remaining and the low measured concentrations of metals within it. It also reflects the absence of observed mine water discharge and, perhaps, the lack of stream sediment analyses.

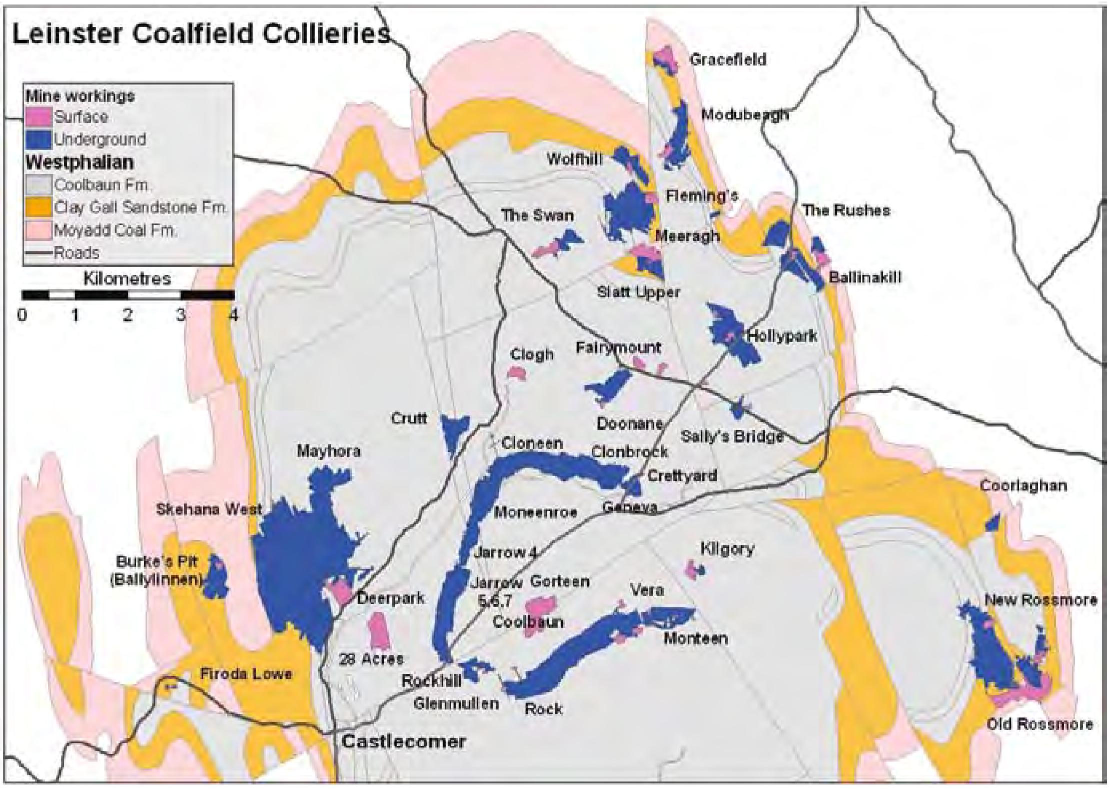


5.20 Leinster Coalfield

Mine District:	Leinster Coalfield
Mine Name:	Various
Minerals Worked:	Coal (Anthracite)
County:	Carlow, Kilkenny, Laois
Townland:	Various
Grid Reference:	E257000, N179000
Site Score:	133
Site Class:	IV
Elements of Interest:	As, Cu, Ni, Pb, Zn, SO_4, acidity
Media of Concern:	Solid waste, surface water, stream sediments

Geochemical Overview

Many of the numerous individual collieries in the Leinster Coalfield have been partly or fully rehabilitated since closure but large waste heaps, open pit lakes and active drainage adits remain. Stream water has low concentrations of most parameters measured and shows only very limited and localised chemical impact from mining. Adit discharges in general have similar compositions to stream water. In contrast, surface run-off from solid waste has relatively high concentrations of elements such as Al, Cd, Cu, Ni, Zn and SO_4 as well as low pH and high EC. Some solid waste in the Leinster Coalfield has elevated metal concentrations, with As, Zn, Cu and Pb exceeding regional background levels for soil but the absolute concentrations measured were low. Stream sediments show some impact from mining but measured metal concentrations were below the guideline limits for the protection of livestock.



5.21 Monaghan Lead Mines – Clontibret

Mine District: Monaghan

Mine Name: Clontibret
Minerals Worked: Sb

County: Monaghan
Townland: Lisglassan; Tullybuck

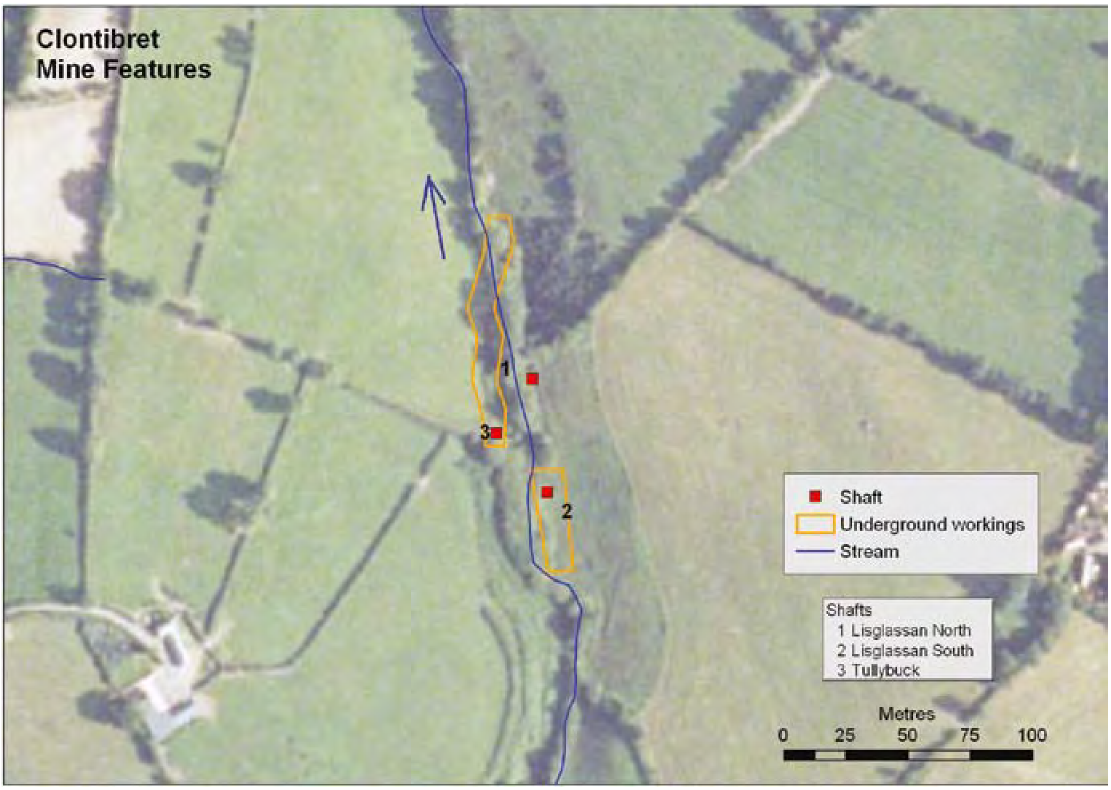
Grid Reference: E275550, N330110

Site Score: 12
Site Class: V

Elements of Interest: Sb, As, Au, Pb, Zn
Media of Concern: Stream sediments

Geochemical Overview

Mining at Clontibret was short-lived and there is now little physical trace of any former activity on the site. There are no discharges of mine water on-site and surface water samples show no evidence of any mine-related impact. Stream sediments have very elevated concentrations of Sb, As and Au that can be attributed to the mineralisation at the site. It can be assumed that mining has contributed directly to the observed stream sediment concentrations although natural erosion of mineralised veins cropping out in the Clontibret stream may have contributed also. The stream sediment contamination accounts for the entire Clontibret site score of 12.



5.22 Monaghan Lead Mines – Hope (Cornalough)

Mine District: Monaghan

Mine Name: Hope (Cornalough)
Minerals Worked: Pb, Ag

County: Monaghan
Townland: Cornalough

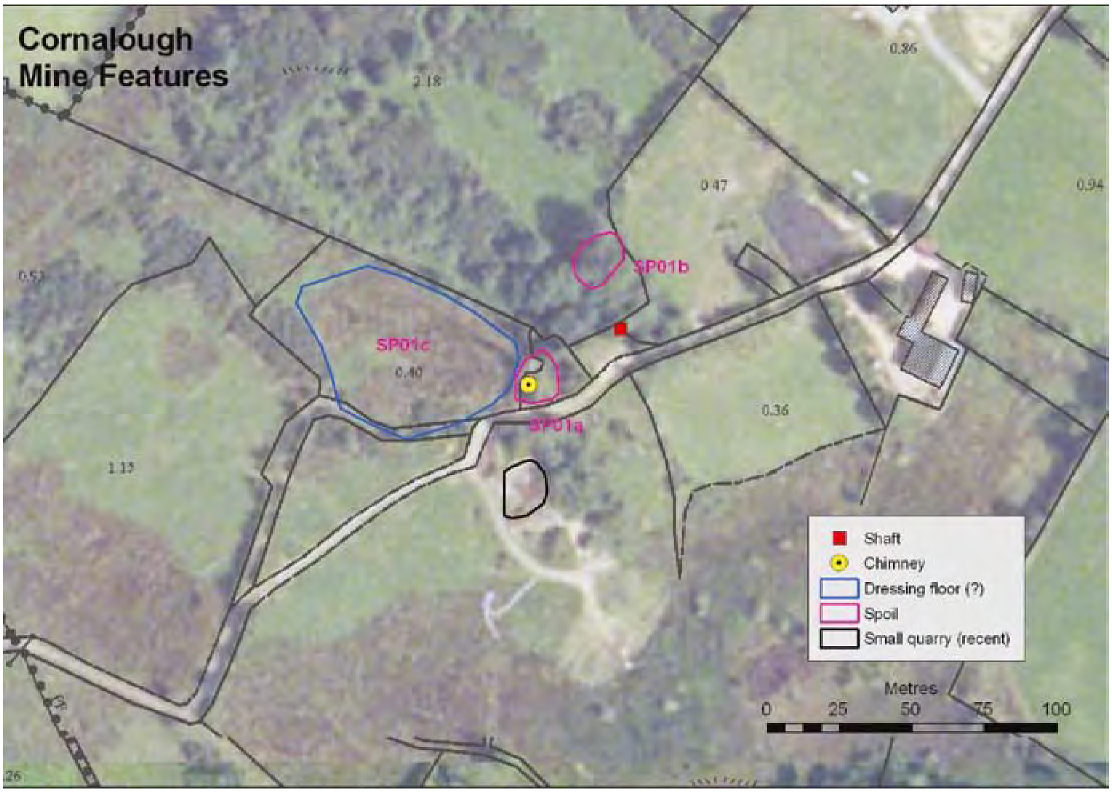
Grid Reference: E283126, N316125

Site Score: 13
Site Class: V

Elements of Interest: Pb, Zn, Ag
Media of Concern: Solid waste

Geochemical Overview

Hope mine was a small mine that produced a limited quantity of Pb ore over the course of a decade. It had a correspondingly limited impact on its surroundings and today only minor amounts of solid waste remain. This waste has, by comparison with solid mine waste elsewhere in the country, relatively low levels of Pb (2,833–3,818 mg/kg) and Zn (77–1,019 mg/kg) and very minor As levels. The low site score reflects the small volume of waste remaining and the low measured concentrations of elements.



5.23 Monaghan Lead Mines – Tassan

Mine District: Monaghan

Mine Name: Tassan
Minerals Worked: Pb, Ag

County: Monaghan
Townland: Tassan

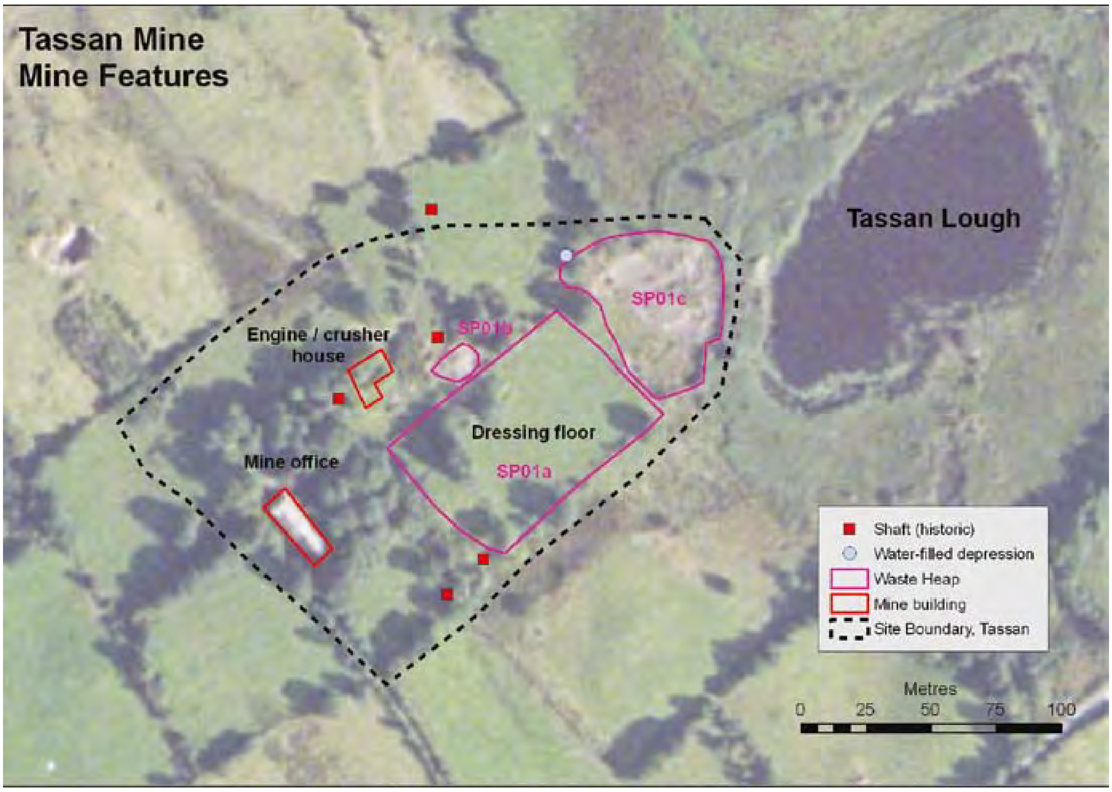
Grid Reference: E279228, N326112

Site Score: 44
Site Class: V

Elements of Interest: Pb, Zn, As
Media of Concern: Solid waste, stream sediments

Geochemical Overview

Tassan mine was the largest and most productive of the Monaghan District mines. Concentrations of Pb and Zn in the sediments of streams draining the site are much higher than regional medians and suggest a direct input from mining. However, sediments elsewhere in the area, in streams not directly draining the mine site, also have Pb and Zn concentrations well above regional median values, though they are considerably lower than those downstream of the mine. Very high (2.5%) concentrations of Pb have been measured in solid waste on the surface of the site as well as in soil on top of the former dressing floor. Concentrations of other elements are generally moderate, except perhaps for As, which has been measured at concentrations exceeding 300 mg/kg. A leachate test on the spoil at Tassan suggests very limited potential for groundwater contamination.



5.24 Silvermines

Mine District: Silvermines

Mine Name: Various
Minerals Worked: Pb, Zn, Cu, Ba, Ag

County: Tipperary
Townland: Various

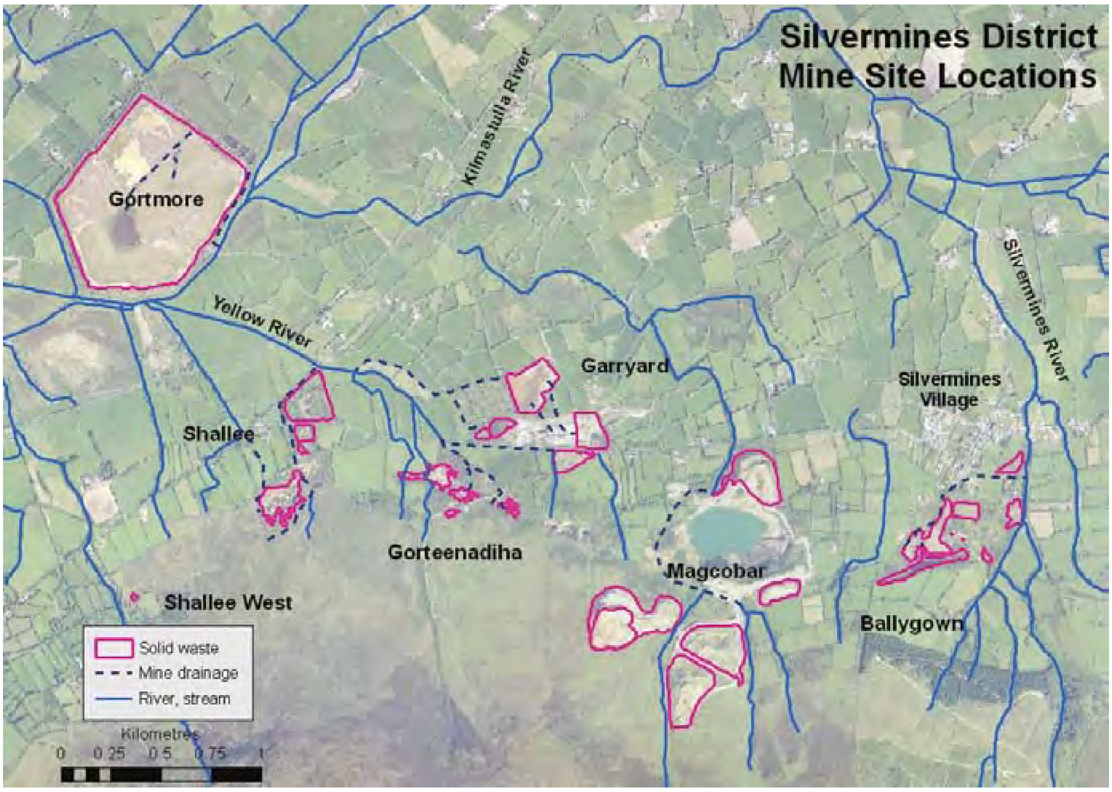
Grid Reference: E182343, N171560

Site Score: 2,545
Site Class: I

Elements of Interest: Pb, Zn, Cu, Ag, Ba
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

The Silvermines District is a very extensive Pb–Zn–Ag–Ba mining area located on the northern flank of Silvermines Mountain. Six individual mine sites (Ballygown, Magcobar, Garryard, Gorteenadiha, Shallee and Gortmore) have been defined, most of them abandoned in the 20th century, although some were also worked in the 19th century or even earlier. The sites are drained by a network of streams flowing north to the valley of the Kilmastulla River.



In general, surface water sampled downstream of mine sites in Silvermines contain elevated concentrations of mine-related metals such as Pb, Zn, and Cd. The median values for Pb, Zn and Cd in surface water downstream of mine sites all exceed the Draft EC Regulations for surface water. The highest concentrations of metals were found in water standing on solid waste, such as at the tailings lagoon in Garryard. The high concentrations of metals in surface water immediately downstream of solid waste heaps at Garryard, Gorteenadiha and Shallee suggest that surface run-off and seepage have a significant impact on surface water quality in the district. Water samples taken from the Yellow River and its tributaries that drain the mine sites at Garryard, Gorteenadiha and Shallee typically had elevated Pb and Zn concentrations: upstream of its confluence with the Kilmastulla River, the measured concentrations in the Yellow River were 307 µg/l Pb and 1,298 µg/l Zn. Metal concentrations in the Kilmastulla River were generally much lower than those in the Yellow River and were only significantly elevated downstream of the tailings pond at Gortmore and downstream of the confluence with the Yellow River.

Stream sediments taken downstream of mine sites in the district typically have high concentrations of Pb and Zn. The data tend to mirror those for surface water with sediment from the Yellow River showing the highest metal concentrations (3,271–12,332 mg/kg Pb, 743–208,233 mg/kg Zn, 61–468 mg/kg As, 421–733 mg/kg Cu and 0.35–218 mg/kg Cd). The highest concentrations were measured in the sample taken immediately downstream of the Garryard tailings lagoon discharge.

Solid waste in the district is notable for its typically high concentration of Pb and Zn, with percentage levels of both common across most sites. In addition to Pb and Zn, some individual waste heaps have very high concentrations of elements of concern such as As and Cd. In combination with high volumes of material on some sites, these high metal concentrations are largely responsible for the high total HMS-IRC score of 2,545 recorded for the Silvermines District.

5.25 Slieve Ardagh Coalfield

Mine District: Slieve Ardagh

Mine Name: Various
Minerals Worked: Coal (Anthracite)

County: Tipperary
Townland: Various

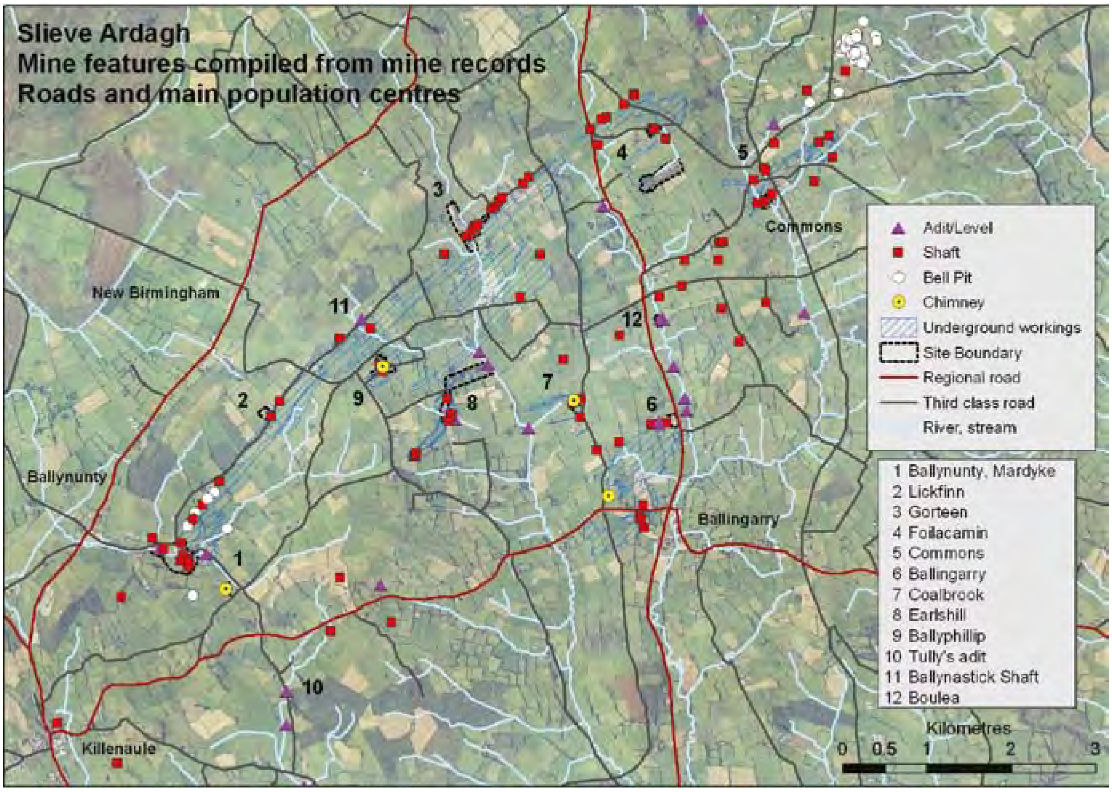
Grid Reference: E228000, N150000

Site Score: 118
Site Class: IV

Elements of Interest: As, Cu, Ni, Pb, Zn, acidity
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

The Slieve Ardagh District is a very extensive area with numerous abandoned mine operations. Large waste heaps, open pit lakes and active drainage adits are the main potential sources of environmental impacts in the district. Stream water generally has low concentrations of most parameters measured. Adit discharges in general have similar compositions to stream water. In contrast, surface run-off from solid waste has relatively high concentrations of elements such as Al, Cu, Ni, Zn and SO_4 as well as low pH and high EC. Surface water samples taken immediately downstream of such run-off, in open pit lakes and streams, can show raised element concentrations and reduced pH. Some coal waste in Slieve Ardagh has measured concentrations of As, Zn, Cu, Ni and Pb exceeding regional background soil levels. Stream sediments gave somewhat similar results.



5.26 Tynagh Mine

Mine District: Tynagh

Mine Name: Tynagh
Minerals Worked: Pb, Zn, Ag, Ba

County: Galway
Townland: Derryfrench; Garraunnameetagh

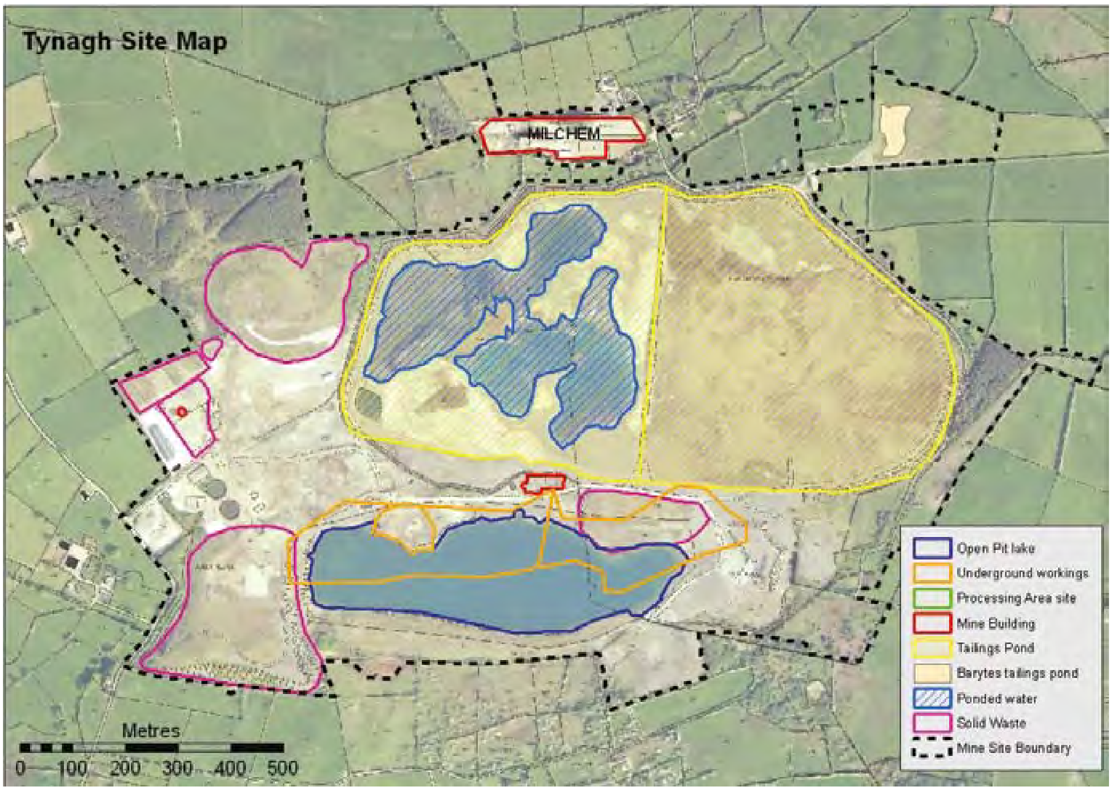
Grid Reference: E174935, N213024

Site Score: 2,712
Site Class: I

Elements of Interest: Pb, Zn, Cu, As, Hg, Ni, Cd, Sb, Ba
Media of Concern: Solid waste, surface water, stream sediments

Geochemical Overview

Tynagh Mine contains large volumes of solid mine waste with high concentrations of Pb and other heavy metals. Part of the site is occupied by two companies and, in the case of one of these, part of the work site is heavily contaminated by Pb, Zn, As, Hg and Cd. Several seepages from spoil and tailings introduce Zn, Cd and Ni to local streams and groundwater although the volume of these discharges is generally low. None of these discharges poses a threat of AMD on or around the site. Leachate testing indicates that the waste at Tynagh has the potential to contaminate groundwater; analysis of water in one well east of the site revealed a high concentration of As. Stream sediments are severely contaminated by Pb and other metals close to the site, mainly in the Barnacullia stream on the northern boundary of the tailings pond. High concentrations of mine-related metals have been detected almost 3 km downstream of the site.

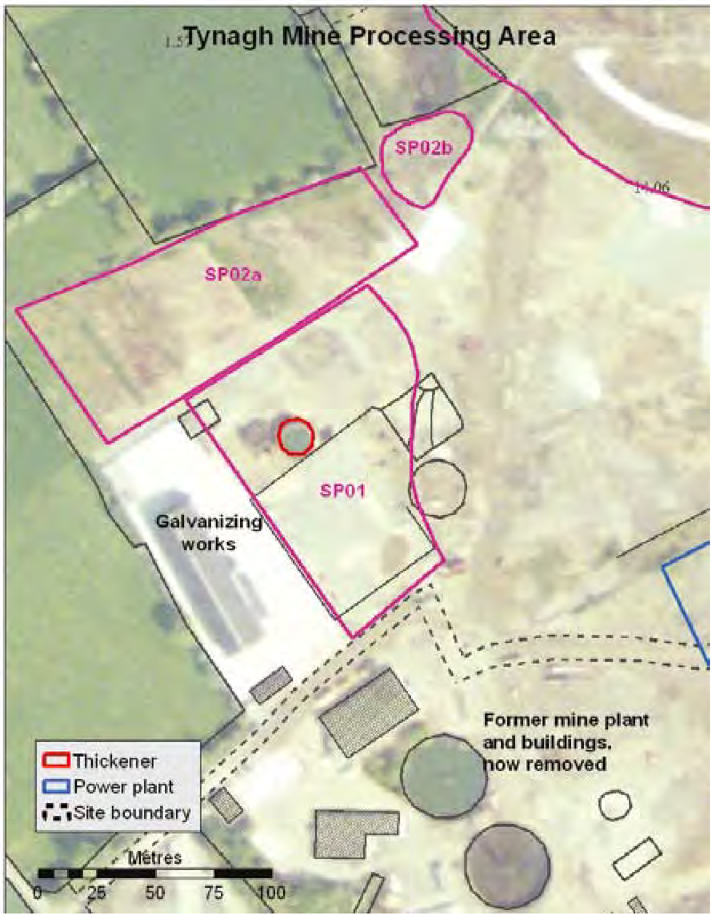


5.26.1 Tynagh – Processing Area

Mine District:	Tynagh
Mine Name:	Processing area
Minerals Worked:	Pb, Zn, Ag, Ba
County:	Galway
Townland:	Derryfrench
Grid Reference:	E174262, N213016
Site Score:	40
Site Class:	I (District)
Elements of Interest:	Pb, As, Hg, Cd, Cu, Sb, Zn, Ba
Media of Concern:	Solid waste

Geochemical Overview

Very high concentrations of Pb (>10%), Zn, Cu, As (>3%), Hg (287 mg/kg), Cd (573 mg/kg) and Sb have been measured in process waste on the site of the former processing plant at Tynagh. The thin cover of sand–clay-grade material on the surface of the ground around the remaining structures is also metal rich. Some of the process waste is relatively inert, e.g. the Pb-rich coatings on concrete walls, but most is in the form of loose sand–silt-grade material that is either lying on the ground around the thickener or packed in open barrels. This is an active work site: fabricated iron structures are stored here prior to and after galvanising. The hardcore layer has not made any obvious difference to the chemistry of the surface material, at least around the thickener. The very high concentrations of Pb, As, Cd and Hg represent a potential health risk to workers in this area, although access is restricted to the area around the thickeners where the highest metal concentrations were measured. The settlement ponds, outside the area used by the galvanising company, also have high Pb, Zn, Cu, As, Hg, Cd and Sb, albeit in lower concentrations than found around the thickener. There is some risk of dust blow from this material during dry weather.

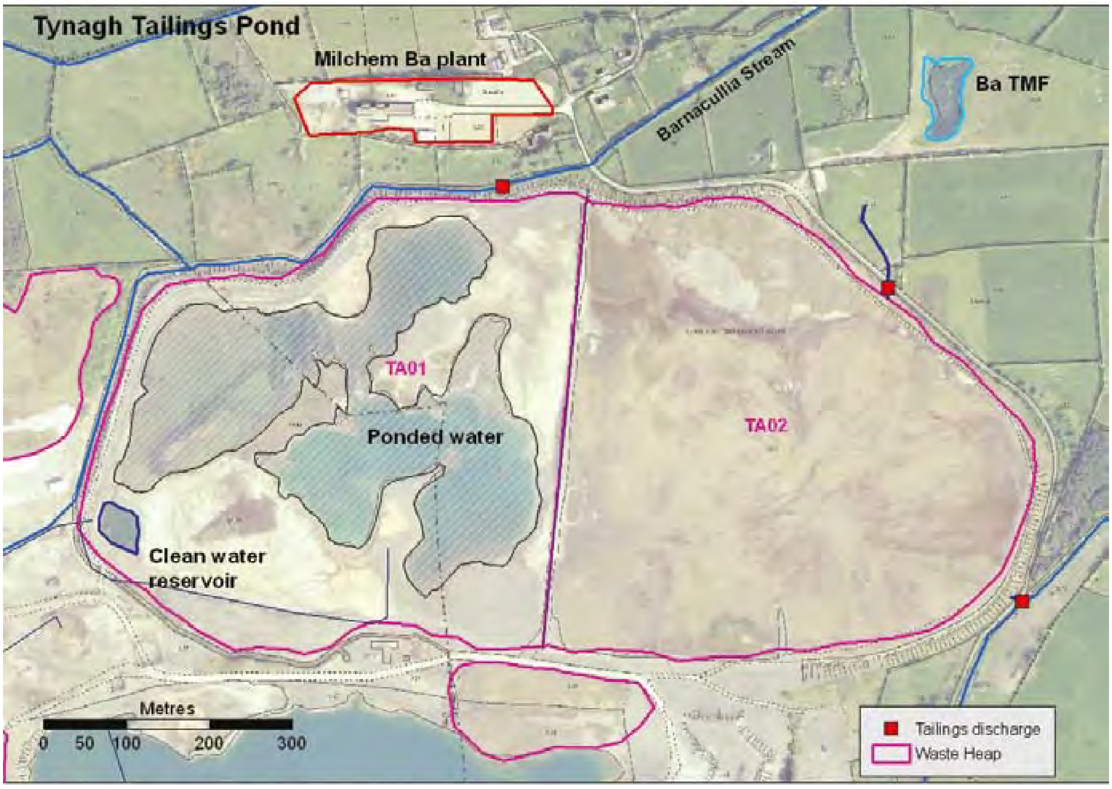


5.26.2 Tynagh – Tailings Pond

Mine District:	Tynagh
Mine Name:	Tailings Pond
Minerals Worked:	Pb, Zn, Ag, Ba
County:	Galway
Townland:	Derryfrench; Garraunnameetagh
Grid Reference:	E175142, N213129
Site Score:	1,246
Site Class:	I (District)
Elements of Interest:	Zn, Pb, Cu, As, Ni, Cd, Ba
Media of Concern:	Solid waste, surface water, stream sediments

Geochemical Overview

The TMF at Tynagh has an estimated volume of more than 2.2 million m^3. Three discharges from the TMF enter local streams and, in one case, the groundwater system via a sinkhole. The discharges have high concentrations of Zn, Ni and SO_4 and elevated Cd and As levels. As expected for a limestone-hosted ore deposit, the pH of the discharges is high and there is no risk of AMD at Tynagh. Leachate analyses of tailings samples confirm the potential for groundwater contamination below the unlined tailings pond. The tailings in the western cell have very high concentrations of Pb (≤5.3%), Zn, Cu, As, Ni, Cd, Sb and Ba. Those in the revegetated eastern cell have much lower measured metal concentrations. The high site score reflects these high metal concentrations and the very large volume of the TMF.

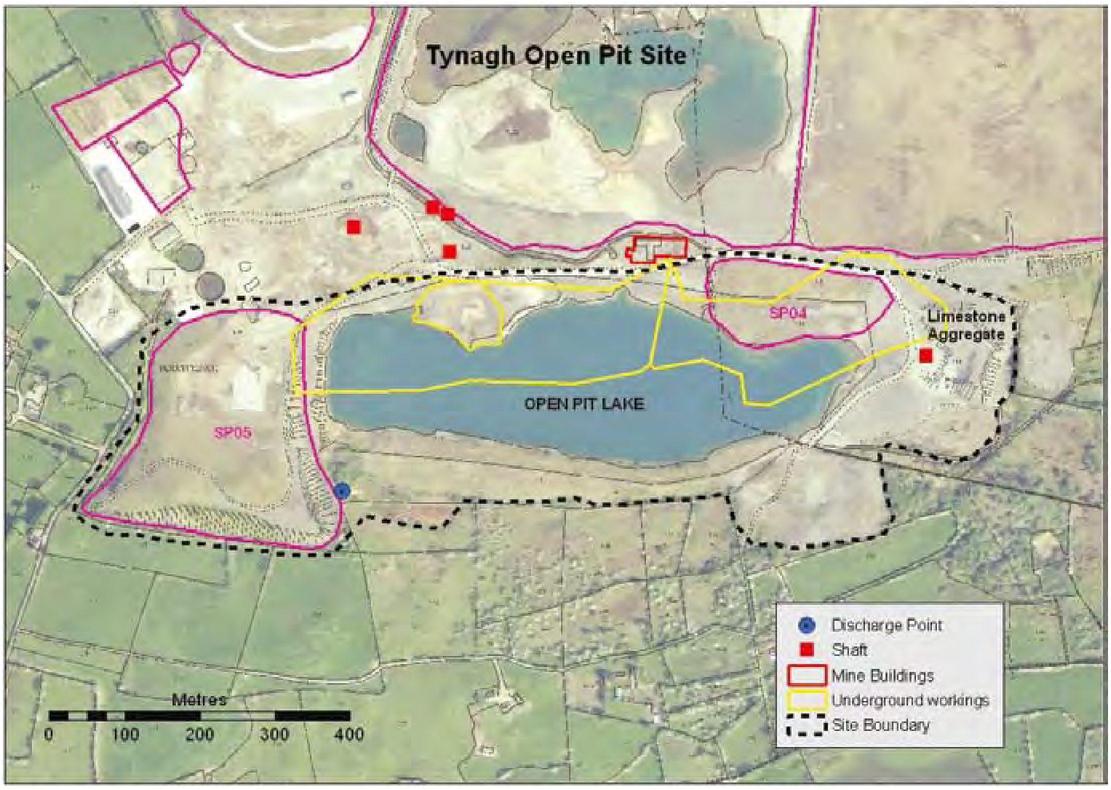


5.26.3 Tynagh – Open Pit Area

Mine District:	Tynagh
Mine Name:	Open Pit area
Minerals Worked:	Pb, Zn, Ag, Ba
County:	Galway
Townland:	Derryfrench; Garraunnameetagh
Grid Reference:	E174807, N212730
Site Score:	1,292
Site Class:	I (District)
Elements of Interest:	Pb, As, Cd, Cu, Zn, Sb
Media of Concern:	Solid waste, surface water

Geochemical Overview

The high concentrations of Cd, Ni and Zn in the seepage at the south-eastern end of SP05, first noted by the EPA, were confirmed in this study. This seepage drains into a nearby field where it seeps into the ground. The solid waste heap from which the seepage discharges (SP05) has significant Cd content (≤366 mg/kg), as well as consistently high measured concentrations of Pb (≤3.8%, median 1.4%) and Zn (≤8.5%, median 2.5%). The other waste heap on the site, SP04, on the northern side of the open pit, is a low-grade deposit, with concentrations recorded *in situ* by XRF much lower than elsewhere on the site. Nevertheless, a lab analysis of one sample yielded a Pb concentration in excess of 1%. The water in the open pit lake was not analysed – it is used by the power plant for cooling purposes.

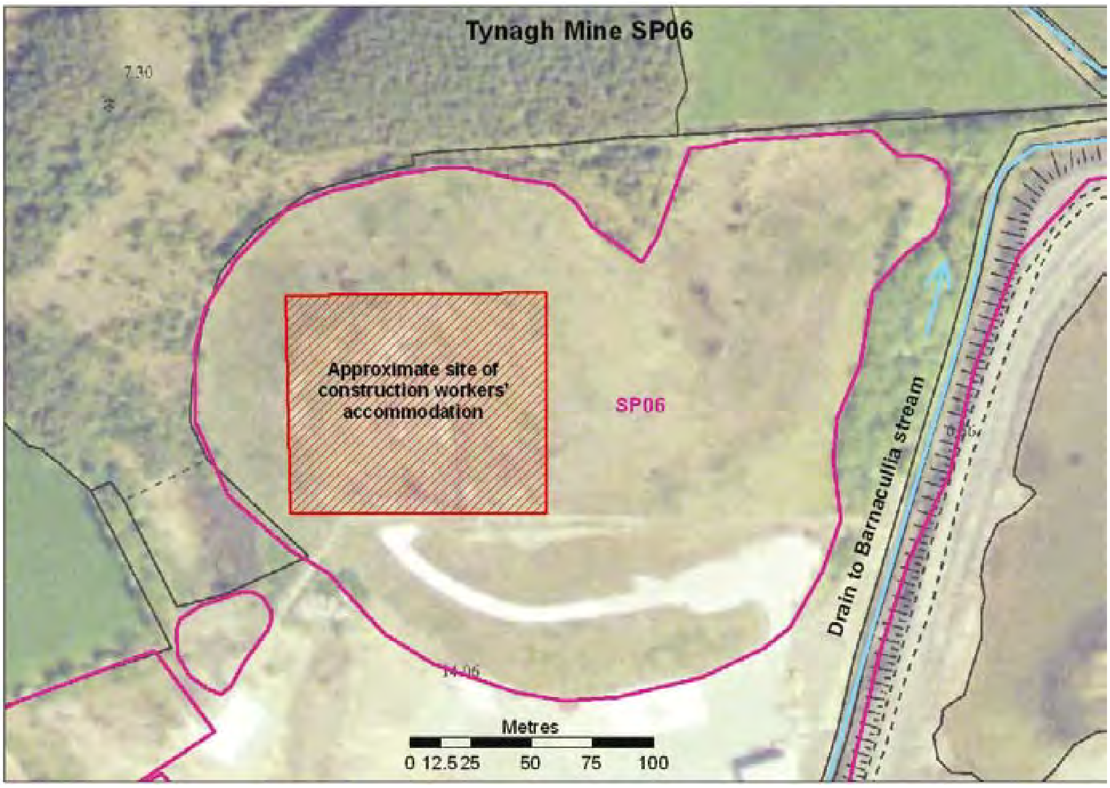


5.26.4 Tynagh – SP06

Mine District:	Tynagh
Mine Name:	SP06
Minerals Worked:	Pb, Zn, Ag, Ba
County:	Galway
Townland:	Derryfrench
Grid Reference:	E174442, N213227
Site Score:	97
Site Class:	I (District)
Elements of Interest:	Pb, As, Ni, Cd, Cu, Cr, Zn
Media of Concern:	Solid waste

Geochemical Overview

SP06 is a waste heap that evidently contains some low-grade ore, with concentrations of almost 6% Zn and 2% Pb measured at one location. Overall, however, concentrations of elements of interest are typically lower in the samples analysed than in other sub-sites at Tynagh mine. The heap may contribute or may have contributed in the past to metal contents of surface water or stream sediments in the Barnacullia stream.



5.27 West Cork Copper–Barium Mines
5.27.1 West Cork Cu-Ba Mines – Ballycummisk

Mine District: West Cork Cu-Ba

Mine Name: Ballycummisk
Minerals Worked: Cu

County: Cork
Townland: Ballycummisk

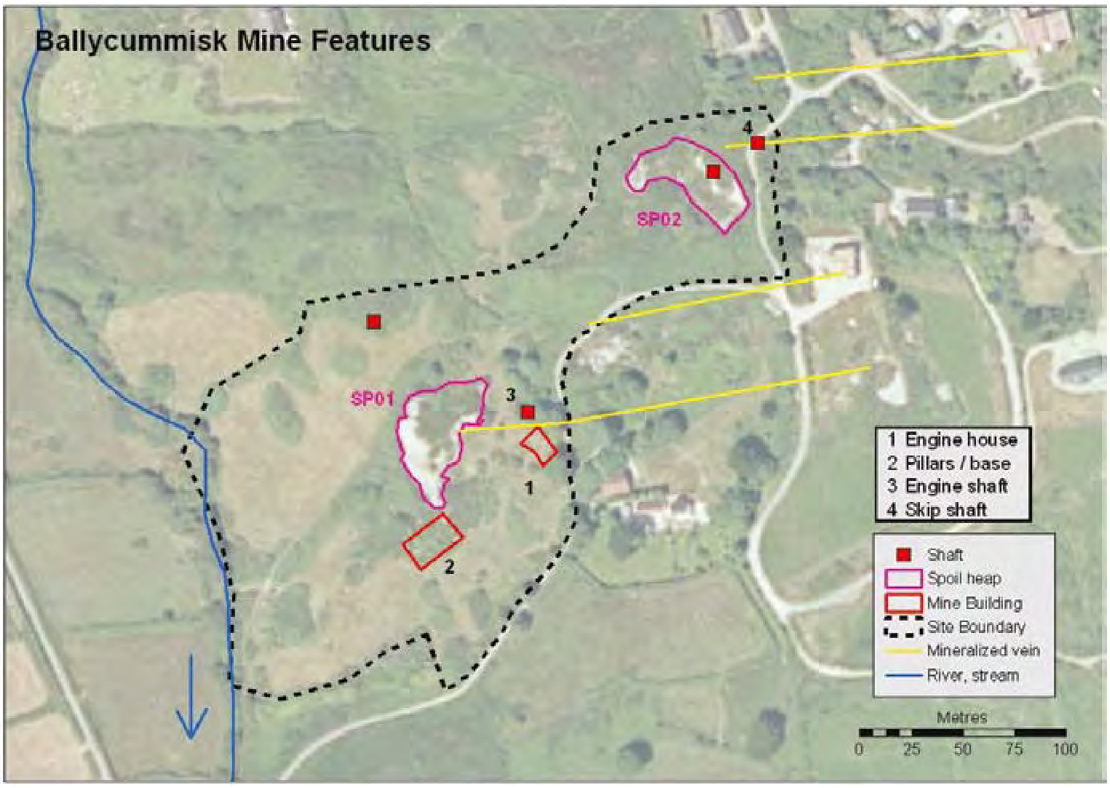
Grid Reference: E97657, N32197

Site Score: 4
Site Class: V (District)

Elements of Interest: Cu, Ba, Pb, Zn, As, Sb
Media of Concern: Solid waste, stream sediments

Geochemical Overview

Solid waste at Ballycummisk has relatively high concentrations of Cu (≤1.06%) and Ba (≤4,608 mg/kg) and above-background concentrations of As, Sb, Pb and Zn. A leachate sample derived from the waste reflected this composition, containing modest if nonetheless elevated concentrations of Ba, Cu and Sb. The most significant impact of the mine site on the environment was observed in stream sediments in which high concentrations of Cu and Ba were recorded downstream of the mine. The HMS-IRC score is 4, placing Ballycummisk at the lower end of the Class V sites.

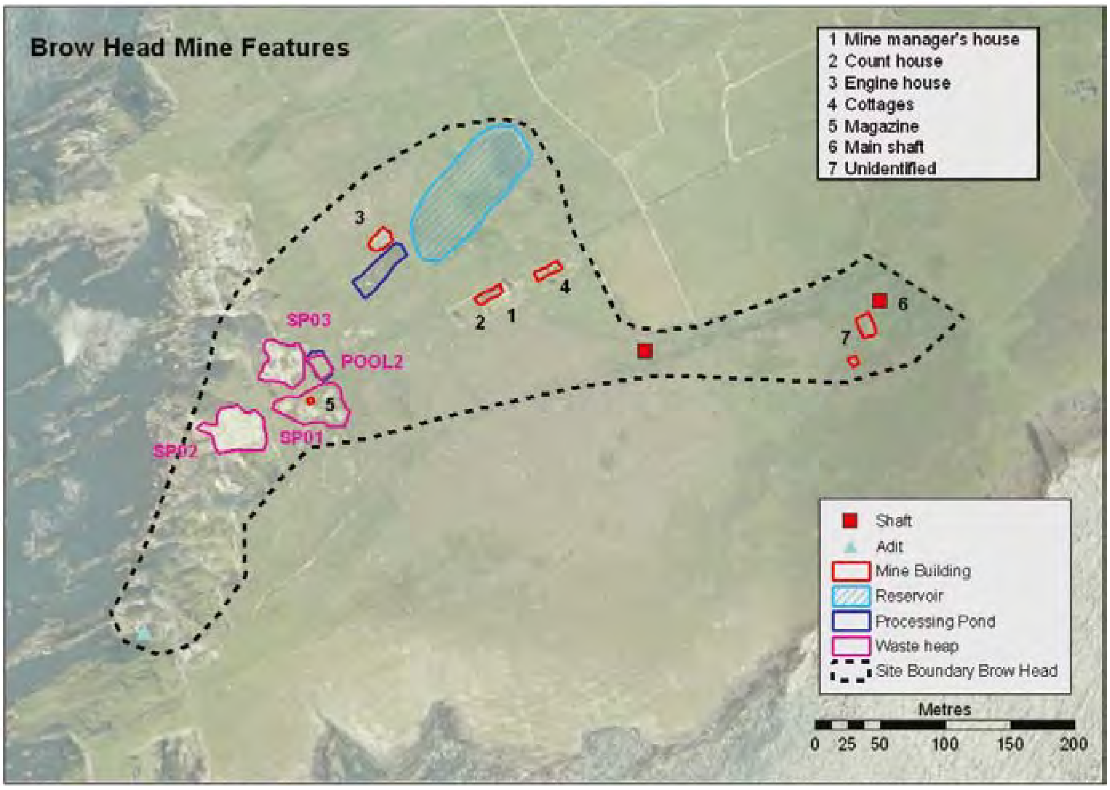


5.27.2 West Cork Cu-Ba Mines – Brow Head

Mine District:	West Cork Cu-Ba
Mine Name:	Brow Head
Minerals Worked:	Cu
County:	Cork
Townland:	Mallavoge
Grid Reference:	E77247, N23592
Site Score:	1
Site Class:	V (District)
Elements of Interest:	Cu
Media of Concern:	Solid waste

Geochemical Overview

Brow Head mine was exploited for a short period in the mid-19th century and again in the early 20th century. Although the underground workings are reputedly extensive, production was low and this is reflected in the modest amounts of solid waste remaining on the site. Only Cu is found in significant concentrations in the solid waste (≤2,580 mg/kg). The absence of high relative toxicity elements in the waste and the remoteness of the site, in a location where little impact on human health can be expected, give rise to a very low HMS-IRC score.



5.27.3 West Cork Cu-Ba Mines – Coosheen

Mine District: West Cork Cu-Ba

Mine Name: Coosheen
Minerals Worked: Cu

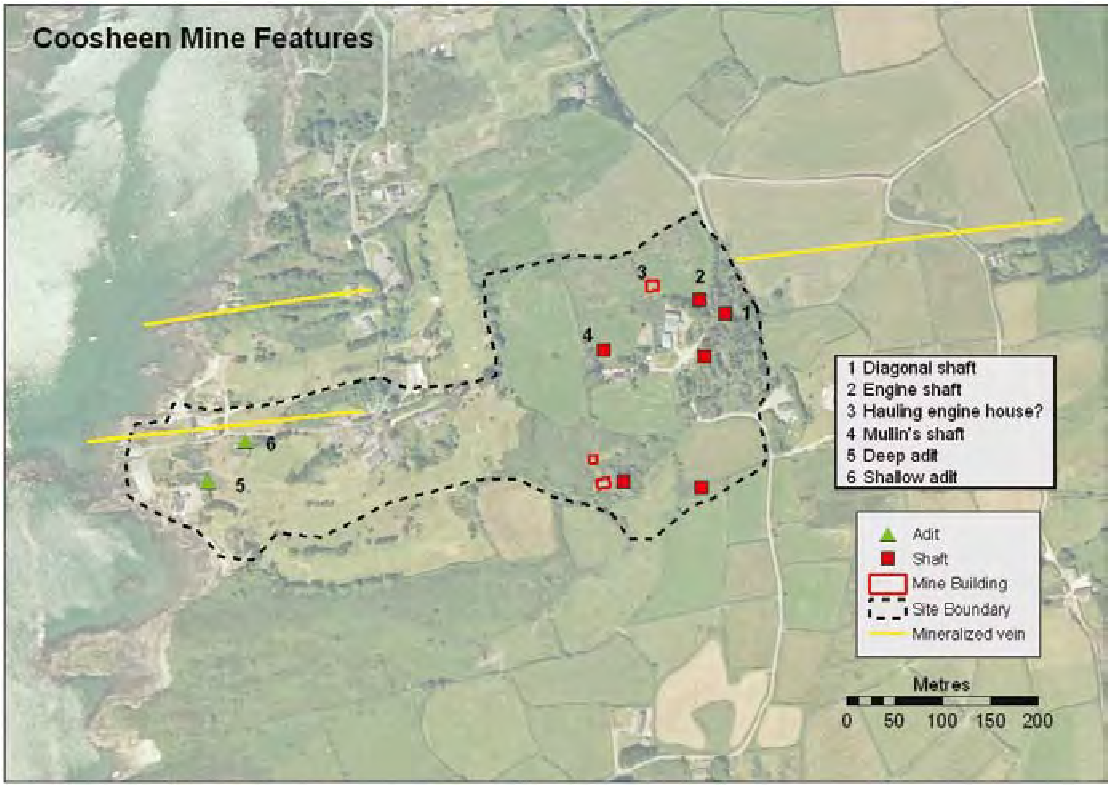
County: Cork
Townland: Coosheen

Grid Reference: E94118, N31226

Site Score: 1
Site Class: V (District)

Elements of Interest: Cu
Media of Concern: Surface water

Geochemical Overview
Much of the site of Coosheen mine is now a landscaped area surrounding residences and holiday homes on the shore of Schull Harbour. There is little mine waste on the site except for mineralised beach pebbles on the shore, at the site of what was the lower dressing floor. Only the shallow adit discharge was sampled and it has only modestly elevated concentrations of Cu (323 µg/l) and Al (459 µg/l).



5.27.4 West Cork Cu-Ba Mines – Crookhaven

Mine District: West Cork Cu-Ba

Mine Name: Crookhaven
Minerals Worked: Cu

County: Cork
Townland: Crookhaven

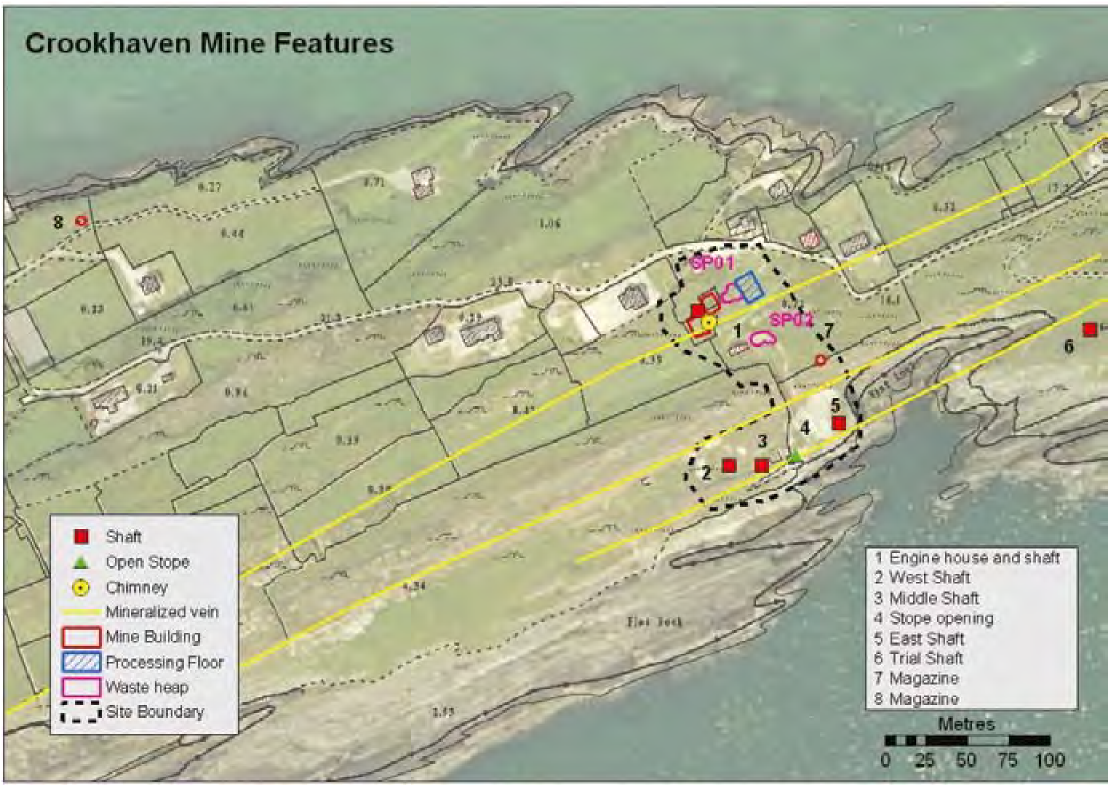
Grid Reference: E81094, N25454

Site Score: 1
Site Class: V (District)

Elements of Interest: Cu
Media of Concern: Solid waste

Geochemical Overview

The Crookhaven mine produced very little ore over almost a decade of endeavour when most of the extensive underground workings were excavated in search of mineralisation rather than in extracting it. Some small volumes of solid waste lie about the site and concentrations of Cu as high as 1.4% have been measured. However, their generally low metal content, and in particular the absence of high relative toxicity elements, combined with a paucity of potential receptors give rise to a very low HMS-IRC score for this site.



5.27.5 West Cork Cu-Ba Mines – Glandore

Mine District: West Cork Cu-Ba

Mine Name: Glandore
Minerals Worked: Cu

County: Cork
Townland: Aghatubrid Beg

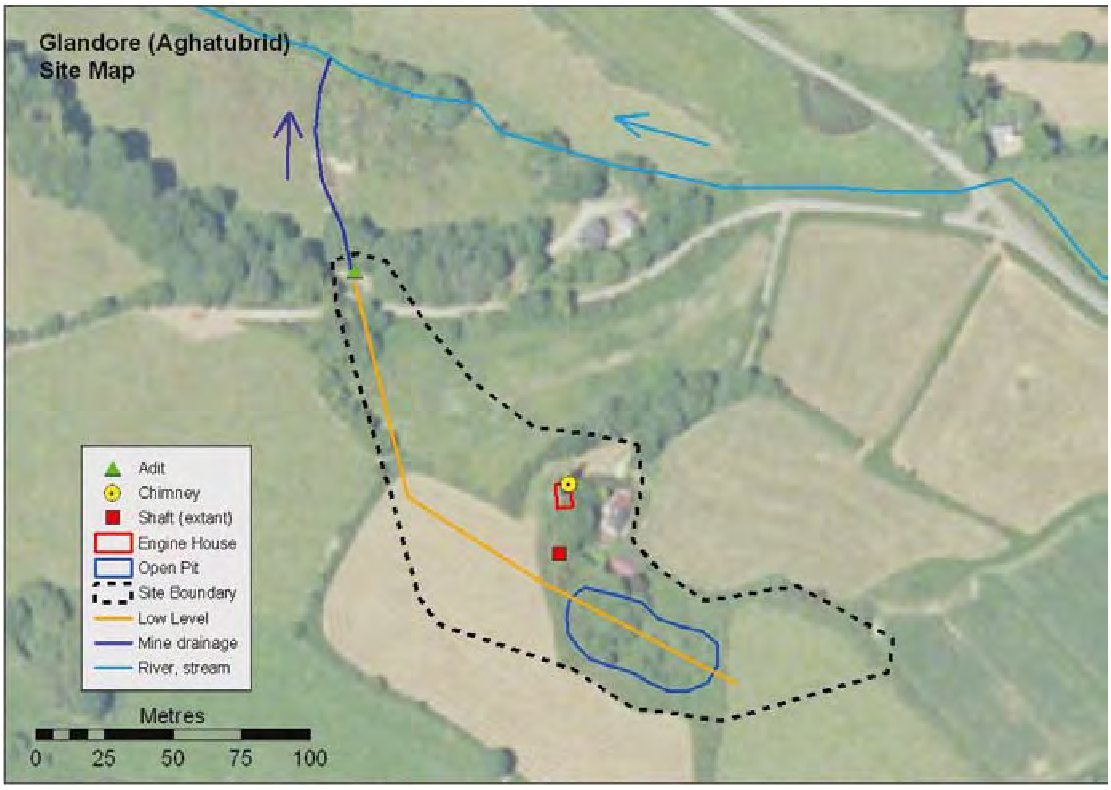
Grid Reference: E122216, N36243

Site Score: 6
Site Class: V (District)

Elements of Interest: Mn, Cu
Media of Concern: Surface water, stream sediments

Geochemical Overview

Glandore was a significant producer of Mn in the 19th century and also produced a limited amount of Cu. The workings were mainly carried on by opencast mining but exploratory underground workings were undertaken and the mine is now drained by a deep ('Low') level. The opencast is densely overgrown and no solid waste was identified on the site. The adit discharges around 1 l/s of mine water with elevated Cu concentration (215 µg/l). Stream sediments in the adjacent river have high concentrations of both Mn and Cu, in excess of guideline limits for the protection of livestock, which are most likely a consequence of mining.



5.27.6 West Cork Cu-Ba Mines – Lady's Well

Mine District:	West Cork Cu-Ba
Mine Name:	Lady's Well
Minerals Worked:	Ba
County:	Cork
Townland:	Dunmore
Grid Reference:	E139626, N37092
Site Score:	1
Site Class:	V (District)
Elements of Interest:	Ba
Media of Concern:	Solid waste

Geochemical Overview

Lady's Well barite mine contains a significant concentration of Ba-rich waste but concentrations of elements of concern within it are low. A previous history of subsidence and evidence of collapse of waste represent more immediate issues of concern than the geochemistry of the waste.

5.27.7 West Cork Cu-Ba Mines – Letter

Mine District: West Cork Cu-Ba

Mine Name: Letter
Minerals Worked: Ba, Cu

County: Cork
Townland: Letter

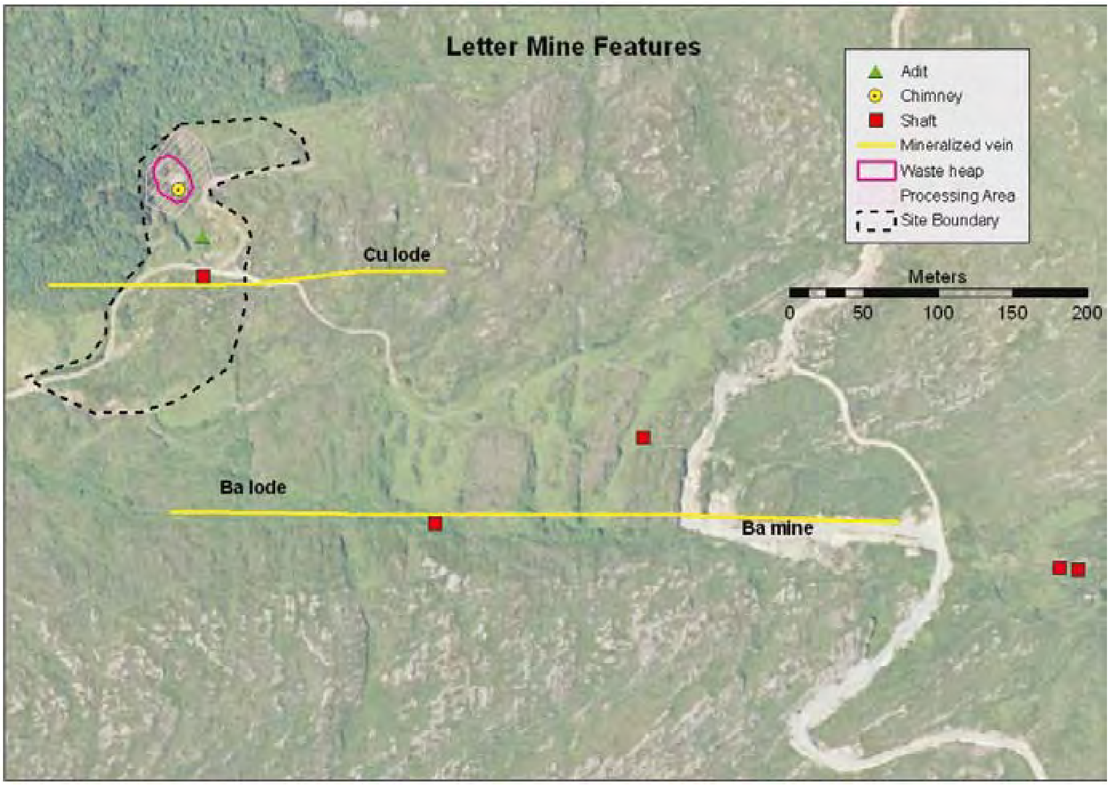
Grid Reference: E94723, N35338

Site Score: 1
Site Class: V (District)

Elements of Interest: Ba, Cu
Media of Concern: Solid waste

Geochemical Overview

Letter mine was a very minor producer of copper and barite in the 19th century. A small volume of solid waste around the processing floor of the copper mine had modest measured concentrations of Cu (6,821 mg/kg) and Ba (7,147 mg/kg). A leachate test on the waste yielded concentrations of dissolved Cu (183 µg/l) and Ba (168 µg/l) that were elevated but below limits set by the drinking water standards. The HMS-IRC score for Letter (1) is very low, reflecting the absence of major volumes of waste on-site as well as the low concentrations of high relative toxicity elements.



5.27.8 West Cork Cu-Ba Mines – Mizen Head

Mine District: West Cork Cu-Ba

Mine Name: Mizen Head
Minerals Worked: Cu

County: Cork
Townland: Cloghane

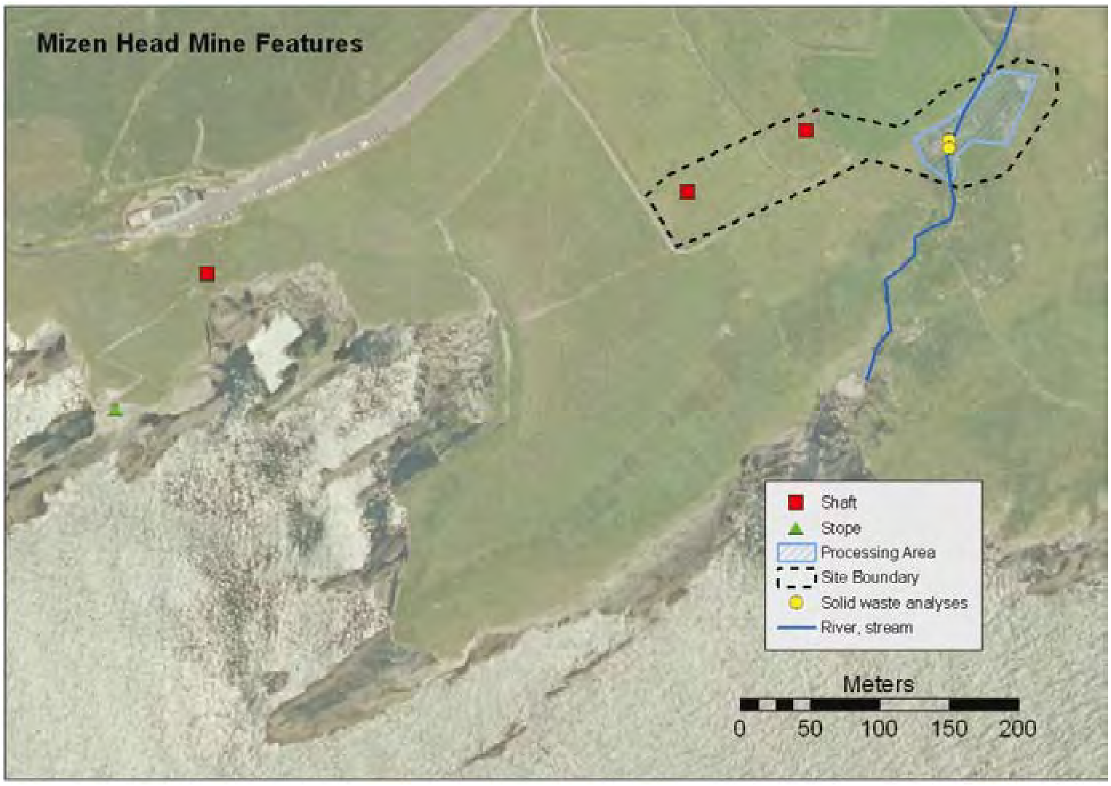
Grid Reference: E74636, N23620

Site Score: 2
Site Class: V (District)

Elements of Interest: Ba, Cu
Media of Concern: Solid waste

Geochemical Overview

The very small amount of solid waste exposed at Mizen Head has low concentrations of most elements except for Cu (≤1,979 mg/kg). None appear to represent any significant risk to human or animal health. The proximity of the site to a stream indicates the possibility of some contamination of the aquatic ecosystem. However, the site is close to the cliff edge where the stream terminates so the scope for contamination is limited.



CHAPTER 6

Site Scores

6.1 Classification system

The classification system devised from the HMS-IRC scoring system is based on an analysis of the scores of all the sites. Natural breaks analysis was performed within ArcGIS on the total site score for all 27 sites and districts. The number of classes chosen was five. The actual numbers chosen for the break points between classes was adjusted to the nearest 100. This did not change the classification of any site. The natural breaks out of the values are 100, 300, 1,000 and 2,000 resulting in five classes, as follows:

<100
100–300
300–1,000
1,000–2,000
>2,000

Descriptions of the various classes are given in Table 6.1.

Class	**Score**	**Description**
I	>2,000	Sites that should have a full risk assessment carried out. These sites should be monitored on an ongoing basis.
II	1,000–2,000	Sites requiring general monitoring of most or all waste piles, discharges or stream sediments on an annual basis.
III	300–1,000	Sites requiring general monitoring of most or all waste piles, discharges or stream sediments on a biennial basis.
IV	100–300	Sites requiring specific monitoring on particular waste piles, discharges or stream sediments on a five-yearly basis.
V	<100	Sites generally not requiring any specific monitoring.

Table 6.1 HMS-IRC scoring system – site score classes.

6.2 Classification of sites

Table 6.2 shows the classification of the sites scored in the HMS-IRC project. Of the 27 sites scored, three are assigned to Class I (11%), one to Class II (4%), two to Class III (7%), four to Class IV (15%) and 17 to Class V (63%). Figure 6.1 shows the distribution of the classified sites.

6.2.1 Class I sites

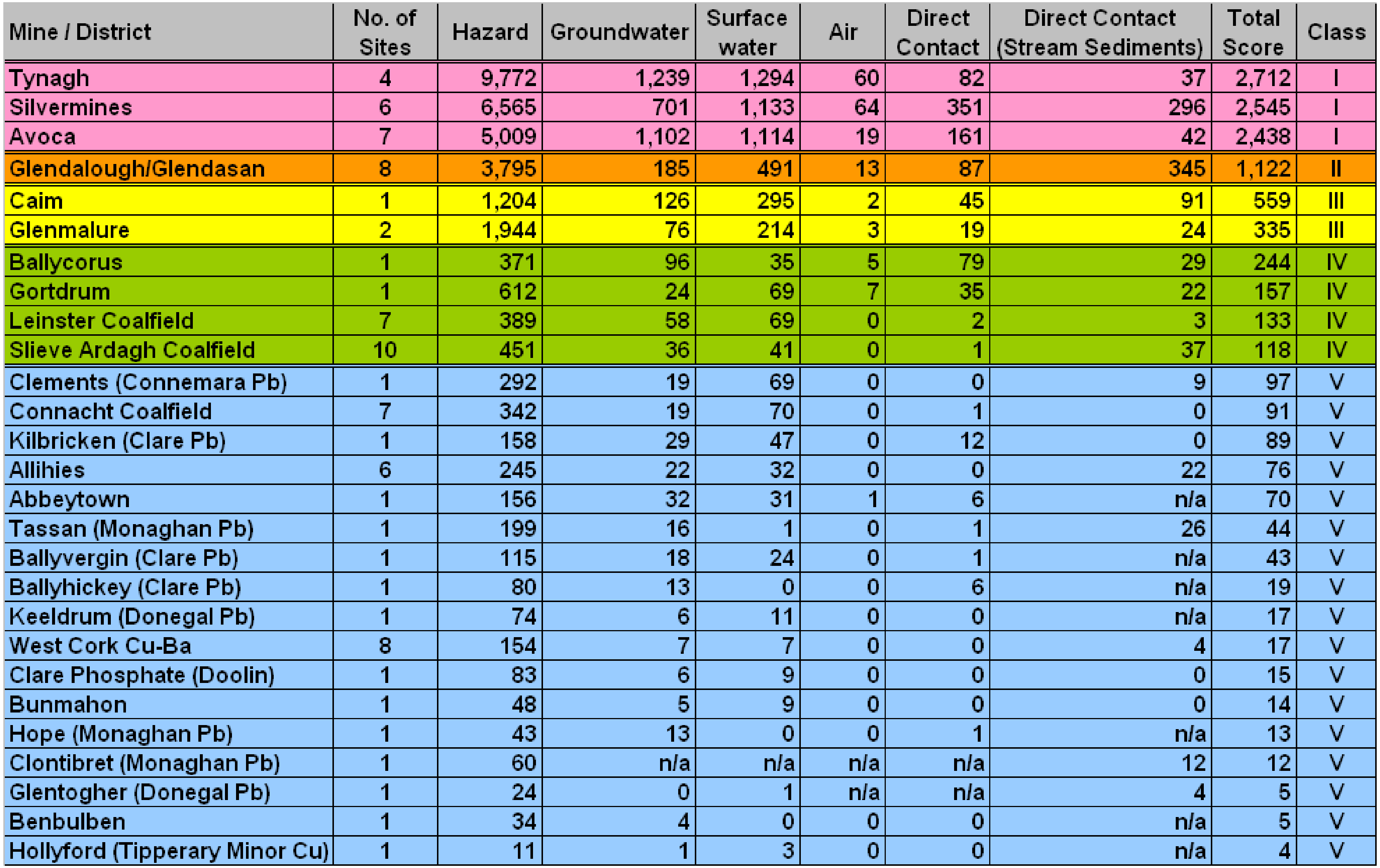
The three sites assigned to Class I are Tynagh, Silvermines and Avoca. The final scores for each of the three sites are similar (Tynagh – 2,712; Silvermines – 2,545; and Avoca – 2,439). All three mines operated as mechanised mines in the latter part of the 20th century, although both Silvermines and Avoca have a long history of production. All three mines have large tailings impoundments and significant waste rock piles. Both Tynagh and Silvermines produced Zn and Pb sulphides from Carboniferous limestones while Cu and pyrite was produced from the Avoca deposit, which was hosted primarily in volcanic rocks.

6.2.2 Class II sites

Glendalough–Glendasan is the single site assigned to Class II. The score for the site is 1,122 – significantly different than the scores in Class I sites – less than half their scores – and Class III sites – approximately double the top scoring site in Class III. Glendalough–Glendasan was primarily worked in the 19th century but operations did continue intermittently into the 20th century when the mine finally closed in 1957. The mine mainly worked Pb sulphide and tailings were generated in the 20th century operation and deposited in a non-engineering pile beside the Glendasan River.

6.2.3 Class III sites

The two sites assigned to Class III are Caim and Glenmalure. The score for Caim is 559 while that for Glenmalure is 335. Both were Pb veins, with the Glenmalure site similar to the Class II Glendalough–Glendasan site. At Glenmalure, Pb was worked from a Pb vein associated with the Leinster Granite. There are significant waste piles at each site which do not support vegetation and which contain elevated levels of lead. At Caim there is a large unvegetated waste pile with elevated Pb levels.



Mine / District	No. of Sites	Hazard	Groundwater	Surface water	Air	Direct Contact	Direct Contact (Stream Sediments)	Total Score	Class
Tynagh	4	9,772	1,239	1,294	60	82	37	2,712	I
Silvermines	6	6,565	701	1,133	64	351	296	2,545	I
Avoca	7	5,009	1,102	1,114	19	161	42	2,438	I
Glendalough/Glendasan	8	3,795	185	491	13	87	345	1,122	II
Caim	1	1,204	126	295	2	45	91	559	III
Glenmalure	2	1,944	76	214	3	19	24	335	III
Ballycorus	1	371	96	35	5	79	29	244	IV
Gortdrum	1	612	24	69	7	35	22	157	IV
Leinster Coalfield	7	389	58	69	0	2	3	133	IV
Slieve Ardagh Coalfield	10	451	36	41	0	1	37	118	IV
Clements (Connemara Pb)	1	292	19	69	0	0	9	97	V
Connacht Coalfield	7	342	19	70	0	1	0	91	V
Kilbricken (Clare Pb)	1	158	29	47	0	12	0	89	V
Allihies	6	245	22	32	0	0	22	76	V
Abbeytown	1	156	32	31	1	6	n/a	70	V
Tassan (Monaghan Pb)	1	199	16	1	0	1	26	44	V
Ballyvergin (Clare Pb)	1	115	18	24	0	1	n/a	43	V
Ballyhickey (Clare Pb)	1	80	13	0	0	6	n/a	19	V
Keeldrum (Donegal Pb)	1	74	6	11	0	0	n/a	17	V
West Cork Cu-Ba	8	154	7	7	0	0	4	17	V
Clare Phosphate (Doolin)	1	83	6	9	0	0	0	15	V
Bunmahon	1	48	5	9	0	0	0	14	V
Hope (Monaghan Pb)	1	43	13	0	0	1	n/a	13	V
Clontibret (Monaghan Pb)	1	60	n/a	n/a	n/a	n/a	12	12	V
Glentogher (Donegal Pb)	1	24	0	1	n/a	n/a	4	5	V
Benbulben	1	34	4	0	0	0	n/a	5	V
Hollyford (Tipperary Minor Cu)	1	11	1	3	0	0	n/a	4	V

Table 6.2 Site score for Historic Mine Sites in Ireland.

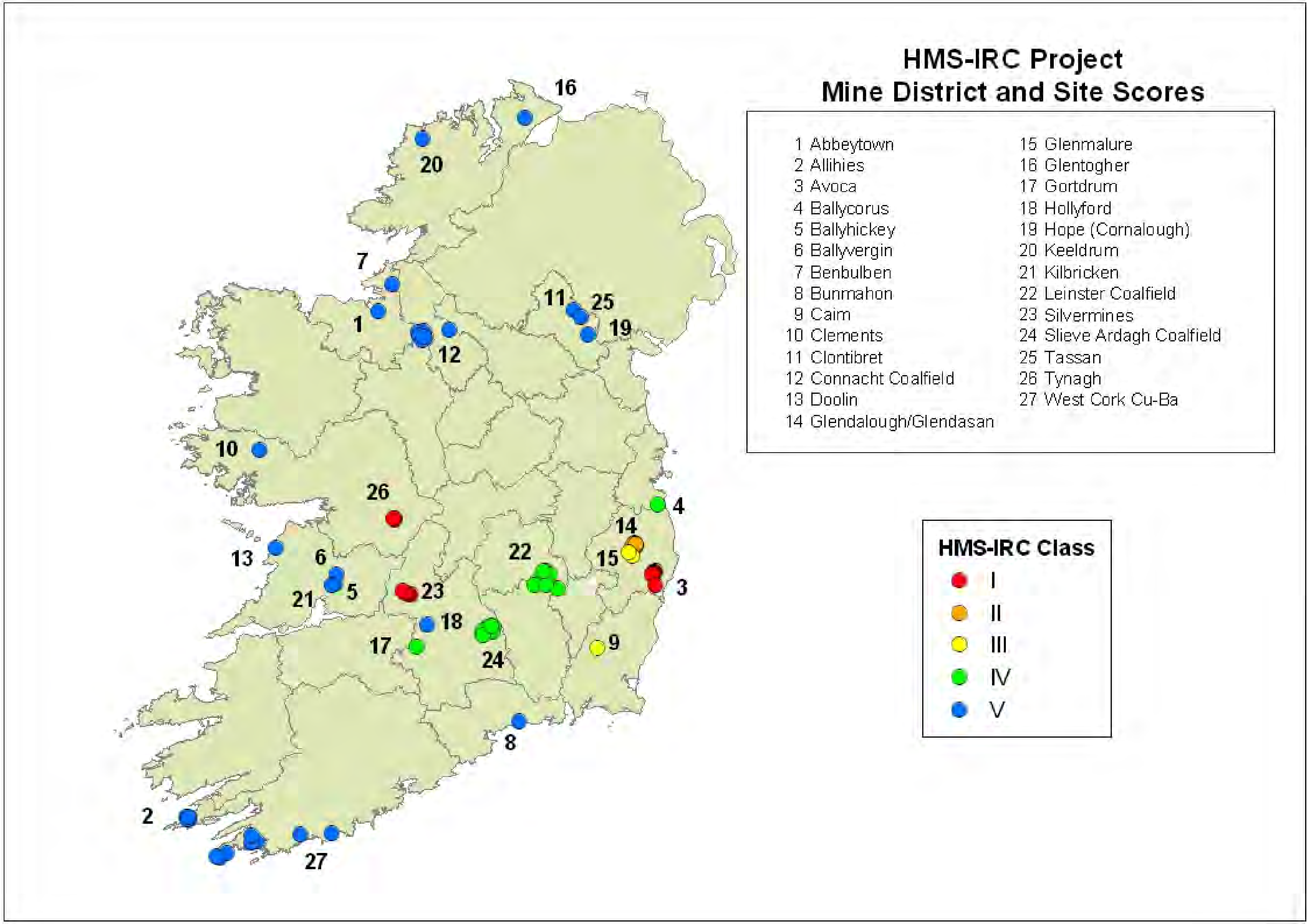


Figure 6.1 Map showing sites colour coded by historic mine site scoring system class.

6.2.4 Class IV sites

Four sites are assigned to Class IV – Ballycorus with a score of 244, Gortdrum 157, the Leinster Coalfield with an aggregate score of 133 and the Slieve Ardagh Coalfield with an aggregate score of 118. The two lower scores are for coalfields, while Ballycorus is a site similar to Glendalough–Glendasan and Glenmalure – it is a Pb vein associated with the Leinster Granite. The Ballycorus vein however was much smaller than the others but a significant feature of the Ballycorus is that a smelter operated at the site which acted as a smelter for almost all of the Pb concentrate produced in Ireland in the 19th century. A specially constructed flue was built to take the fumes from the smelting process up to a chimney on an adjacent hill. This flue may be accessed at several points and deposits of Pb-rich material occur along its interior.

In the 1960s and 1970s, the Gortdrum deposit worked Cu from the basal part of the Carboniferous succession. Although there are significant waste rock piles and a large tailings impoundment (which has been rehabilitated), the absence of high relatively toxic elements results in the site receiving a low score. Nevertheless there are some site-specific issues that need to be addressed on the site.

Two of the three coalfields scored in this exercise are assigned to Class IV. The third coalfield (Connacht) scored 91 and is close to the cut-off point between Class IV and Class V sites. Although the sites contain large amounts of waste they are relatively benign and hence have low scores.

6.2.5 Class V sites

The remaining 17 sites are assigned to Class V. Their scores range from a high of 97 (Clements (Pb), Connemara) to a low of 4 (Hollyford (Cu), Tipperary). The commodities produced at these sites were as follows:

Deposit Type	No.	Site Names
Pb Veins in Precambrian Rocks	3	Clements, Glentogher, Keeldrum
Pb Veins in Carboniferous Rocks	3	Ballyhickey, Ballyvergin, Kilbricken
Pb Veins in Lower Palaeozoic Rocks	3	Clontibret, Hope, Tassan
Copper (Ba) Veins in Devonian Rocks	3	Allihies, Hollyford, West Cork
Coalfield	1	Connacht
Industrial Minerals	2	Benbulben (Ba), Doolin (phosphate)

With the exception of the Connacht Coalfield and to a lesser extent the Abbeytown Pb–Zn deposit, the deposits worked in this class were all small. Nevertheless, there are some features at some of the sites that require further investigation or action.

6.3 Discussion

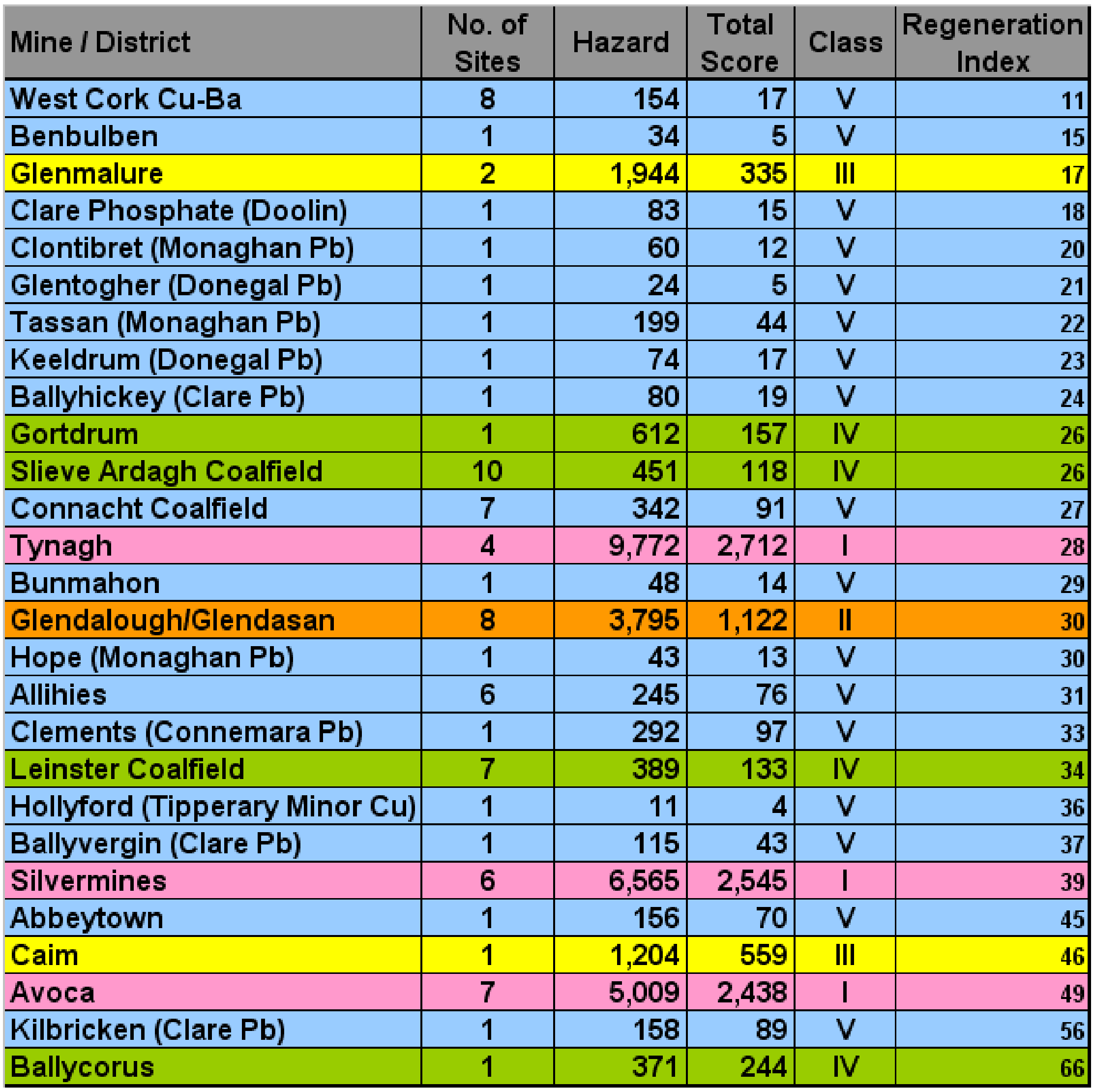
6.3.1 Hazard score

The hazard score for each site is the threat to the environment from solid waste and mine discharges. These have been added together to give an accumulated total for each site and they are shown in Table 6.2. The hazard is a combination of the volume of waste, the amount of a particular contaminant and the relative toxicity of the contaminant to different human and environmental receptors.

The highest hazard score is 9,772 and occurs at Tynagh followed by Silvermines (6,565) and Avoca (5,009). These three sites maintain this order when the full HMS-IRC score is developed for each although the three final scores are much closer together, indicating that there are mitigating factors at work, particularly at Tynagh. If the final score is represented as a percentage of the hazard score we get an indication of how well the hazard at each site has been remediated or managed – lower percentages indicate better management or natural regeneration while higher percentages indicate poorer management or natural regeneration (Table 6.3). We refer to this as the **Regeneration Index (RI)**. The original colour coding for classes has been retained in Table 6.3.

The range of values for RI is from 11 (West Cork Cu–Ba District) to 66 (Ballycorus) with an overall average of 31. Within Class I sites, Avoca ranks as the least regenerated site with an RI of 49, followed by Silvermines at 39 and Tynagh at 28. With the exception of Tynagh both the other Class I sites are well above the RI average. Overall sites in Table 6.3 with an RI less than or equal to the average number 17 (from the West Cork Cu–Ba District to Allihies) possibly indicate a level of regeneration that is acceptable. The sites with RI values greater than the average are:

Clements (Connemara Pb)
Leinster Coalfield
Hollyford (Tipperary Minor Cu)
Ballyvergin (Clare Pb)
Silvermines
Abbeytown
Caim
Avoca
Kilbricken (Clare Pb)
Ballycorus

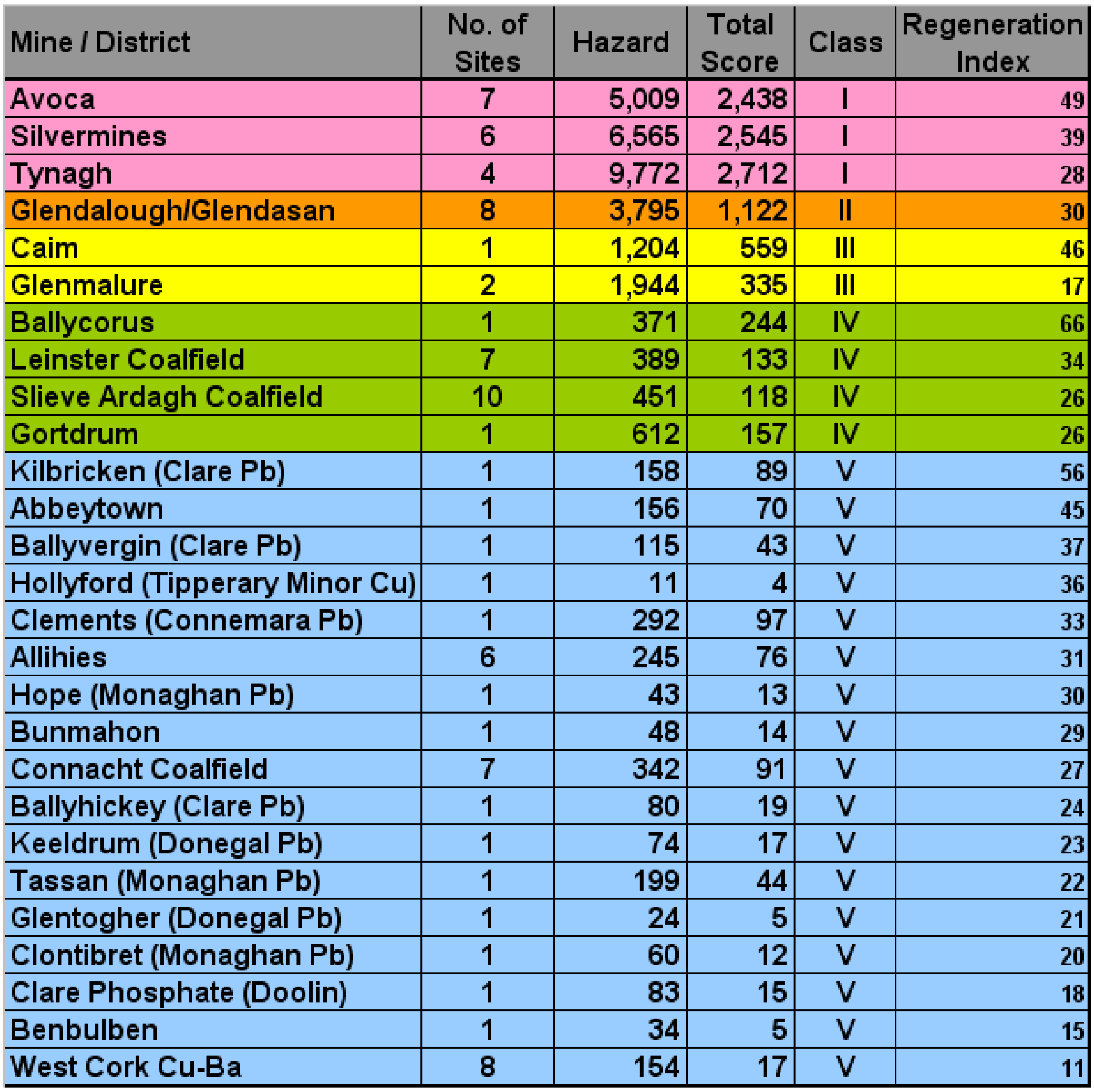


Mine / District	No. of Sites	Hazard	Total Score	Class	Regeneration Index
West Cork Cu-Ba	8	154	17	V	11
Benbulben	1	34	5	V	15
Glenmalure	2	1,944	335	III	17
Clare Phosphate (Doolin)	1	83	15	V	18
Clontibret (Monaghan Pb)	1	60	12	V	20
Glentogher (Donegal Pb)	1	24	5	V	21
Tassan (Monaghan Pb)	1	199	44	V	22
Keeldrum (Donegal Pb)	1	74	17	V	23
Ballyhickey (Clare Pb)	1	80	19	V	24
Gortdrum	1	612	157	IV	26
Slieve Ardagh Coalfield	10	451	118	IV	26
Connacht Coalfield	7	342	91	V	27
Tynagh	4	9,772	2,712	I	28
Bunmahon	1	48	14	V	29
Glendalough/Glendasan	8	3,795	1,122	II	30
Hope (Monaghan Pb)	1	43	13	V	30
Allihies	6	245	76	V	31
Clements (Connemara Pb)	1	292	97	V	33
Leinster Coalfield	7	389	133	IV	34
Hollyford (Tipperary Minor Cu)	1	11	4	V	36
Ballyvergin (Clare Pb)	1	115	43	V	37
Silvermines	6	6,565	2,545	I	39
Abbeytown	1	156	70	V	45
Caim	1	1,204	559	III	46
Avoca	7	5,009	2,438	I	49
Kilbricken (Clare Pb)	1	158	89	V	56
Ballycorus	1	371	244	IV	66

Table 6.3 Regeneration index for sites scored in the HMS-IRC project.

It should be remembered that these are aggregate values for the site as a whole and there could still be issues with individual waste piles, contamination or mine discharges.

The RI could be used in conjunction with the Class designation to assist in prioritising sites for further study or action. Table 6.4 presents a possible prioritisation. On this basis within the Class I sites, Avoca is prioritised followed by Silvermines and Tynagh. Within Class II sites there is only Glendalough–Glendasan. Within Class III sites, the order is the same as the initial ranking – Caim followed by Glenmalure. For Class IV sites, Ballycorus remains on top but Gortdrum drops to the last place in this class with the two included coalfields jumping above Gortdrum and staying in the same order (Gortdrum is classed lower as there rounding without decimal places has been carried out). Within Class V sites the priority sites are Kilbricken, Abbeytown, Ballyvergin, Hollyford and Clements.



Mine / District	No. of Sites	Hazard	Total Score	Class	Regeneration Index
Avoca	7	5,009	2,438	I	49
Silvermines	6	6,565	2,545	I	39
Tynagh	4	9,772	2,712	I	28
Glendalough/Glendasan	8	3,795	1,122	II	30
Caim	1	1,204	559	III	46
Glenmalure	2	1,944	335	III	17
Ballycorus	1	371	244	IV	66
Leinster Coalfield	7	389	133	IV	34
Slieve Ardagh Coalfield	10	451	118	IV	26
Gortdrum	1	612	157	IV	26
Kilbricken (Clare Pb)	1	158	89	V	56
Abbeytown	1	156	70	V	45
Ballyvergin (Clare Pb)	1	115	43	V	37
Hollyford (Tipperary Minor Cu)	1	11	4	V	36
Clements (Connemara Pb)	1	292	97	V	33
Allihies	6	245	76	V	31
Hope (Monaghan Pb)	1	43	13	V	30
Bunmahon	1	48	14	V	29
Connacht Coalfield	7	342	91	V	27
Ballyhickey (Clare Pb)	1	80	19	V	24
Keeldrum (Donegal Pb)	1	74	17	V	23
Tassan (Monaghan Pb)	1	199	44	V	22
Glentogher (Donegal Pb)	1	24	5	V	21
Clontibret (Monaghan Pb)	1	60	12	V	20
Clare Phosphate (Doolin)	1	83	15	V	18
Benbulben	1	34	5	V	15
West Cork Cu-Ba	8	154	17	V	11

Table 6.4 Possible prioritisation for further study or action at the HMS-IRC sites.

6.3.2 Pathways

Each pathway contributes differently for each site depending on the individual conditions at the site. The highest individual score for the groundwater pathway is at Tynagh (1,239), for the surface water pathway Tynagh (1,293), for the air pathway Silvermines (64), for the direct contact, waste piles pathway Silvermines (351) and for the direct contact, stream sediments pathway Glendalough–Glendasan (345).

At each site the relative proportion varies. The percentage contribution of each pathway to the final site score is presented in Figure 6.2. The predominant contribution comes from either the groundwater or surface water pathways. Table 6.5 provides a summary of the dominant pathway for each of the sites scored.

Pathway	No. of Sites where the Given Pathway is Dominant	Sites
Groundwater	6	Ballycorus, Abbeytown, Ballyhickey, West Cork Cu-Ba, Hope, Benbulben
Surface Water	18	Tynagh, Silvermines, Avoca, Glendalough–Glendasan, Caim, Glenmalure, Gortdrum, Leinster Coalfield, Slieve Ardagh Coalfield, Clements, Connacht Coalfield, Kilbricken, Allihies, Ballyvergin, Keeldrum, Clare Phosphate (Doolin), Bunmahon, Hollyford
Air	0	
Direct Contact (waste piles)	0	
Direct Contact (stream sediments)	3	Tassan, Clontibret, Glentogher

Table 6.5 List of sites with their relevant dominant pathway.

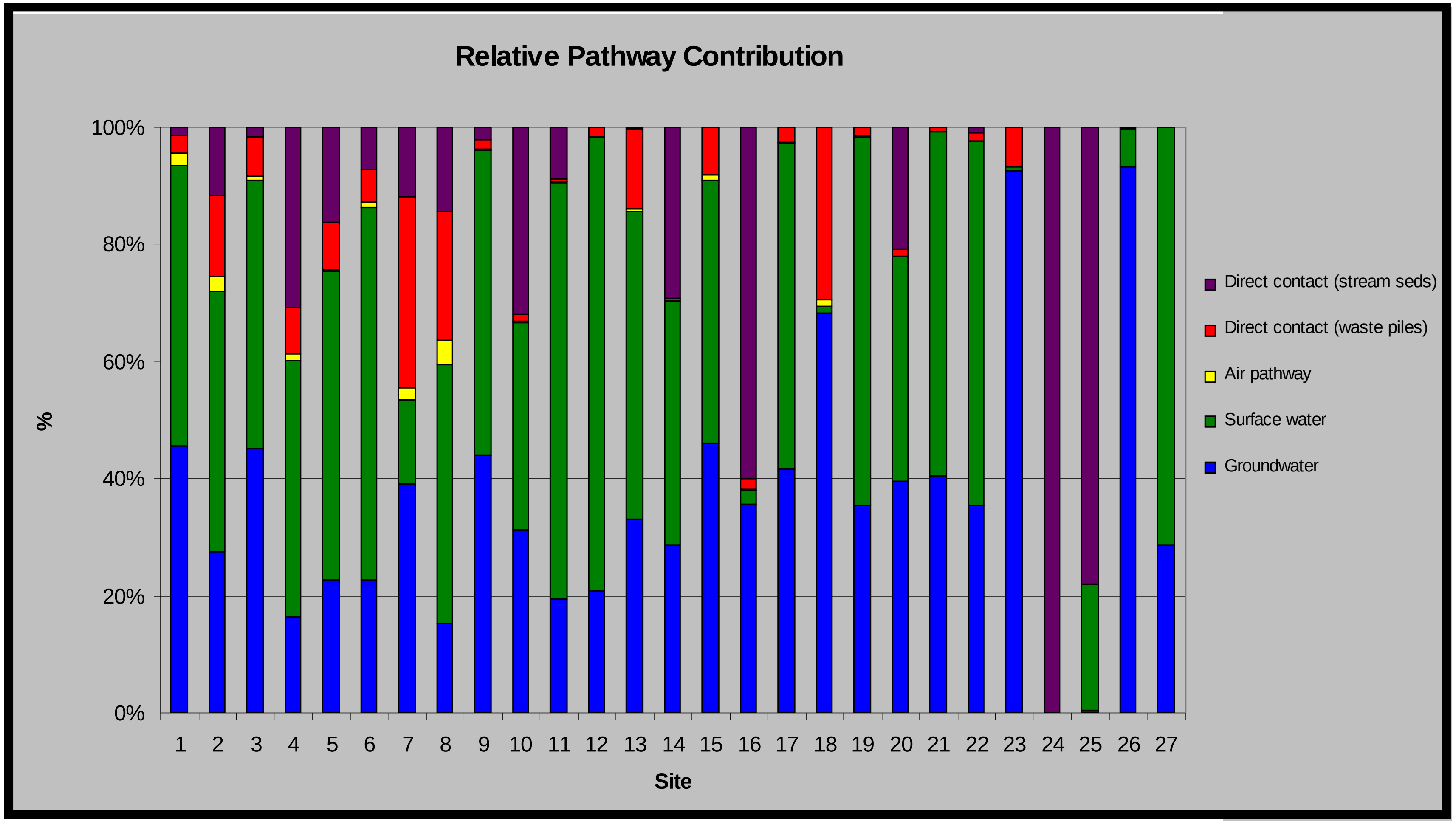
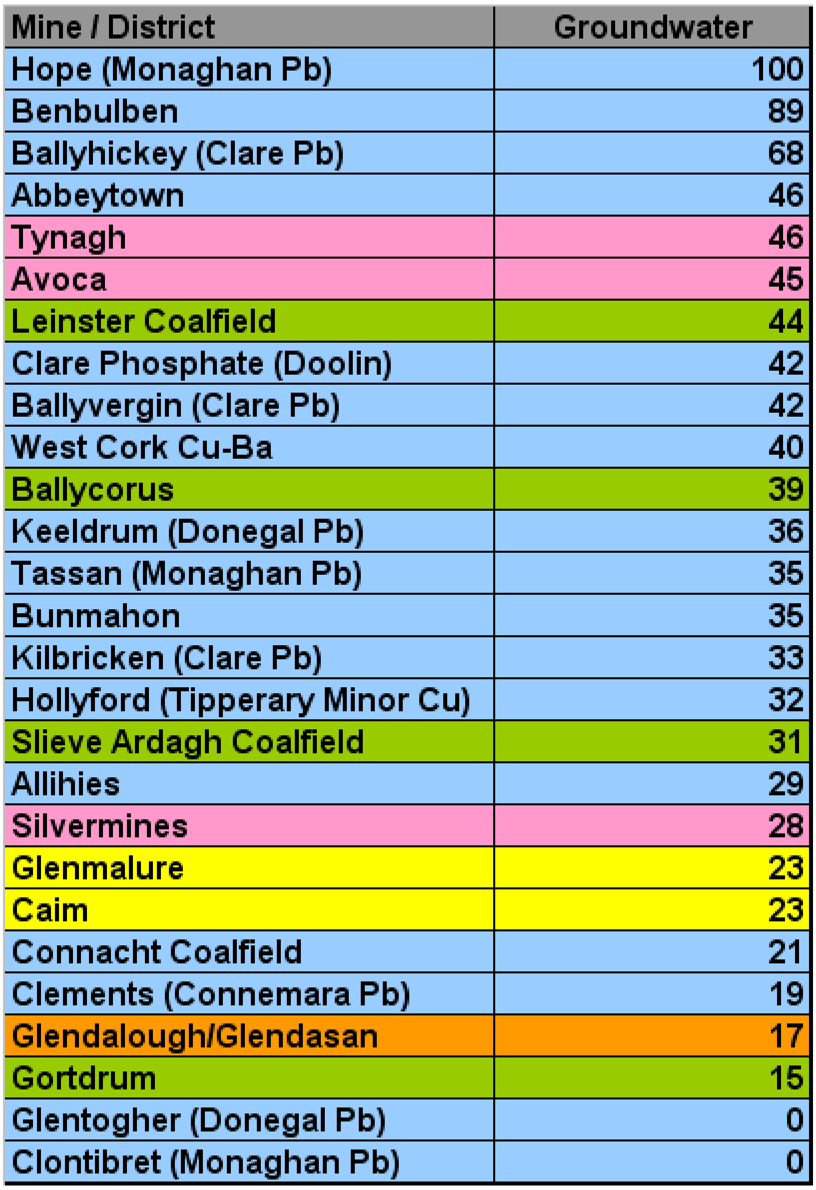


Figure 6.2 Relative contributions by pathway to the final score at each site. 1. Tynagh, 2. Silvermines, 3. Avoca, 4. Glendalough–Glendasan, 5. Caim, 6. Glenmalure, 7. Ballycorus, 8. Gortdrum, 9. Leinster Coalfield, 10. Slieve Ardagh Coalfield, 11. Clements (Connemara Pb), 12. Connacht Coalfield, 13. Kilbricken (Clare Pb), 14. Allihies, 15. Abbeytown, 16. Tassan (Monaghan Pb), 17. Ballyvergin (Clare Pb), 18. Ballyhickey (Clare Pb), 19. Keeldrum (Donegal Pb), 20. West Cork Cu-Ba, 21. Clare Phosphate (Doolin), 22. Bunmahon, 23. Hope (Monaghan Pb), 24. Clontibret (Monaghan Pb), 25. Glentogher (Donegal Pb), 26. Benbulben, 27. Hollyford (Tipperary Minor Cu).

The dominant pathway for all Class I, II and III sites is the surface water pathway. In addition, the surface water pathway is the dominant pathway for 18 (67%) of the sites. The groundwater pathway is the next most dominant being the principal contributor to six sites (22%) and direct contact (stream sediments) is the dominant contributor in three sites (11%). Neither the air pathway nor the direct contact (waste piles) pathway is a dominant contributor to scores. Overall the air pathway contributes little to the scores while the direct contact (waste piles) is a significant contributor to only two sites – Ballycorus and Ballyhickey.

Table 6.6 provides a list of the percentage contribution of the groundwater pathway to the overall site score for each of the sites scored. At Hope all of the final score is contributed

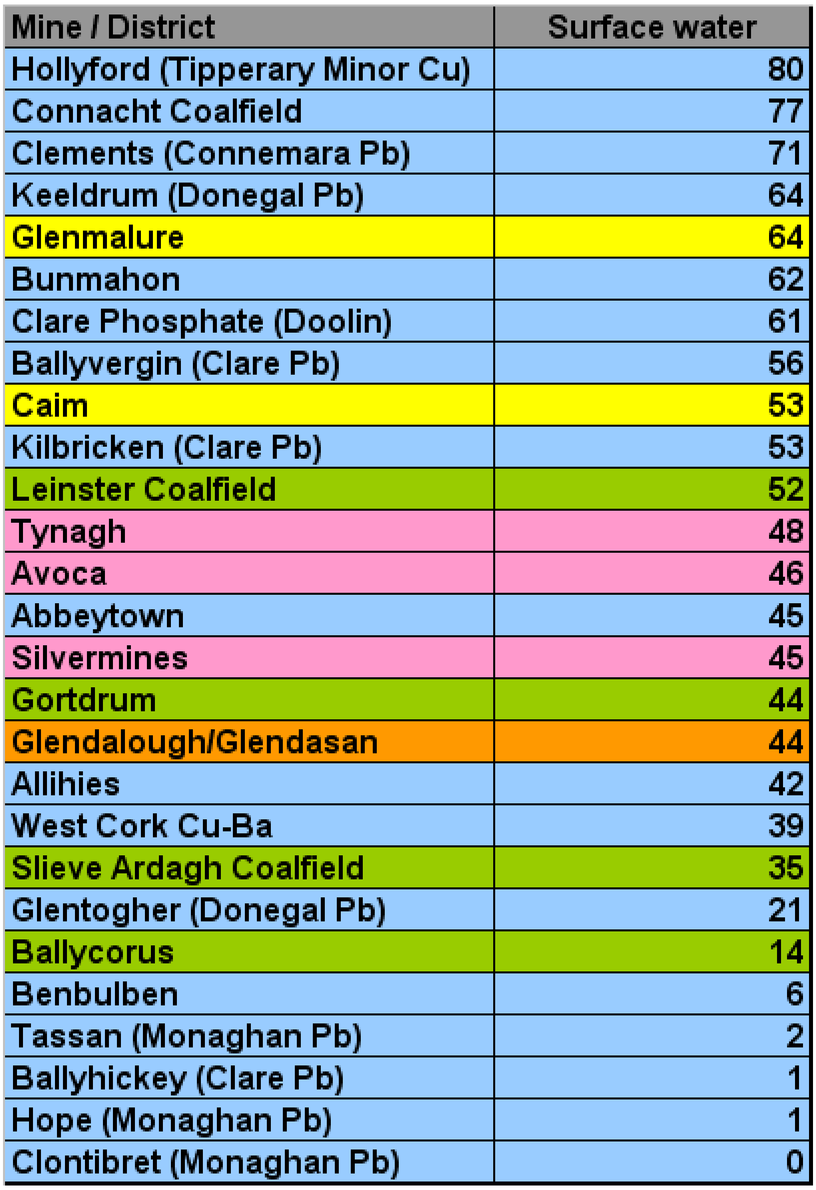


Mine / District	Groundwater
Hope (Monaghan Pb)	100
Benbulben	89
Ballyhickey (Clare Pb)	68
Abbeytown	46
Tynagh	46
Avoca	45
Leinster Coalfield	44
Clare Phosphate (Doolin)	42
Ballyvergin (Clare Pb)	42
West Cork Cu-Ba	40
Ballycorus	39
Keeldrum (Donegal Pb)	36
Tassan (Monaghan Pb)	35
Bunmahon	35
Kilbricken (Clare Pb)	33
Hollyford (Tipperary Minor Cu)	32
Slieve Ardagh Coalfield	31
Allihies	29
Silvermines	28
Glenmalure	23
Caim	23
Connacht Coalfield	21
Clements (Connemara Pb)	19
Glendalough/Glendasan	17
Gortdrum	15
Glentogher (Donegal Pb)	0
Clontibret (Monaghan Pb)	0

Table 6.6 Percentage contribution of the groundwater pathway to the overall site score.

by the groundwater pathway while this pathway also contributes significantly (>40%) to the final scores for Benbulben, Ballyhickey (Clare Pb), Abbeytown, Tynagh, Avoca, the Leinster Coalfield, Clare Phosphate (Doolin), Ballyvergin (Clare Pb), and the West Cork Cu–Ba District. At the opposite end of the spectrum the groundwater pathway does not contribute to the final score for either Clontibret or Glentogher.

Table 6.7 provides a list of the percentage contribution of the surface water pathway to the overall site score for each of the sites scored. Hollyford is at the top of the list with an overall contribution of 80% from the surface water pathway. Other sites to which the

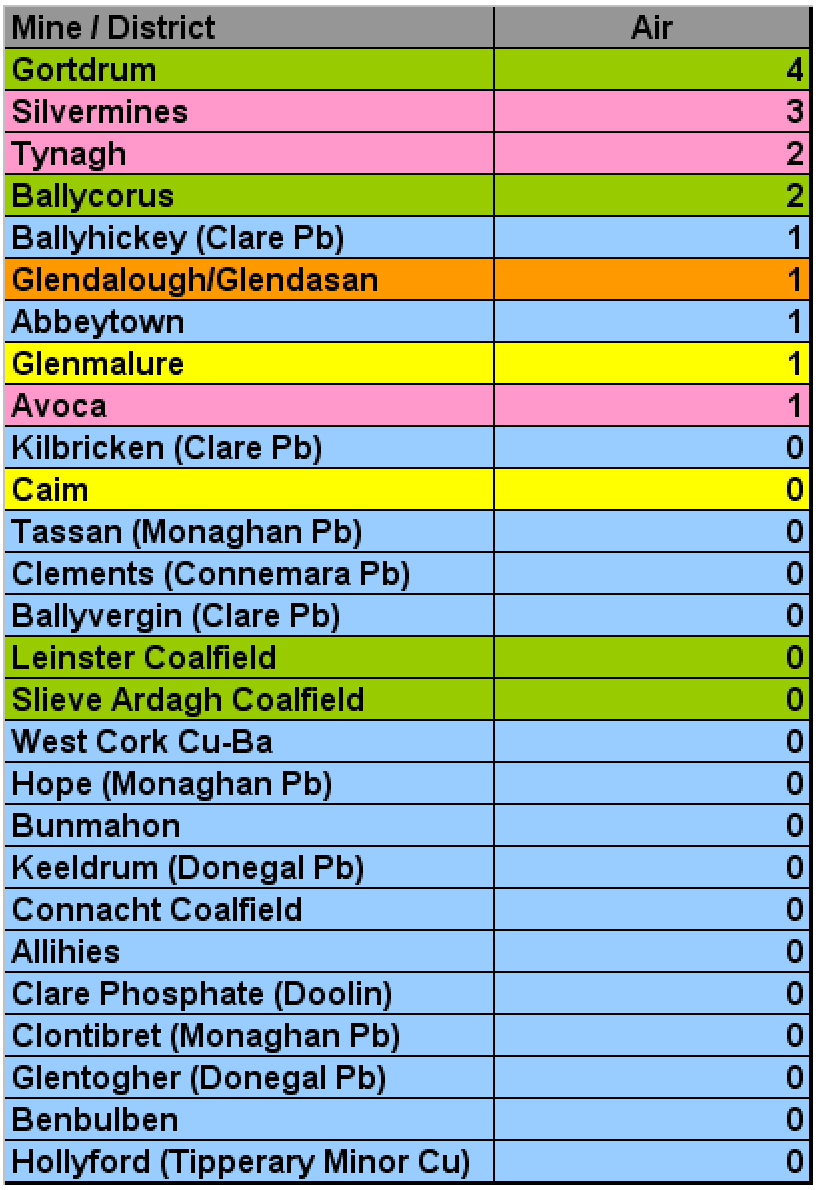


Mine / District	Surface water
Hollyford (Tipperary Minor Cu)	80
Connacht Coalfield	77
Clements (Connemara Pb)	71
Keeldrum (Donegal Pb)	64
Glenmalure	64
Bunmahon	62
Clare Phosphate (Doolin)	61
Ballyvergin (Clare Pb)	56
Caim	53
Kilbricken (Clare Pb)	53
Leinster Coalfield	52
Tynagh	48
Avoca	46
Abbeytown	45
Silvermines	45
Gortdrum	44
Glendalough/Glendasan	44
Allihies	42
West Cork Cu-Ba	39
Slieve Ardagh Coalfield	35
Glentogher (Donegal Pb)	21
Ballycorus	14
Benbulben	6
Tassan (Monaghan Pb)	2
Ballyhickey (Clare Pb)	1
Hope (Monaghan Pb)	1
Clontibret (Monaghan Pb)	0

Table 6.7 Percentage contribution of the surface water pathway to the overall site score.

surface water pathway is a significant (>40%) contributor to the final score are: the Connacht Coalfield, Clements, Keeldrum, Glenmalure, Bunmahon, Clare Phosphate (Doolin), Ballyvergin, Caim, Kilbricken, the Leinster Coalfield, Tynagh, Avoca, Abbeytown, Silvermines, Gortdrum, Glendalough–Glendasan, and Allihies. The surface water pathway does not contribute significantly to the total score for Benbulben, Tassan, Ballyhickey, Hope, and Clontibret.

Table 6.8 provides a list of the percentage contribution of the air pathway to the overall site score for each of the sites scored. The air pathway is the least significant pathway and

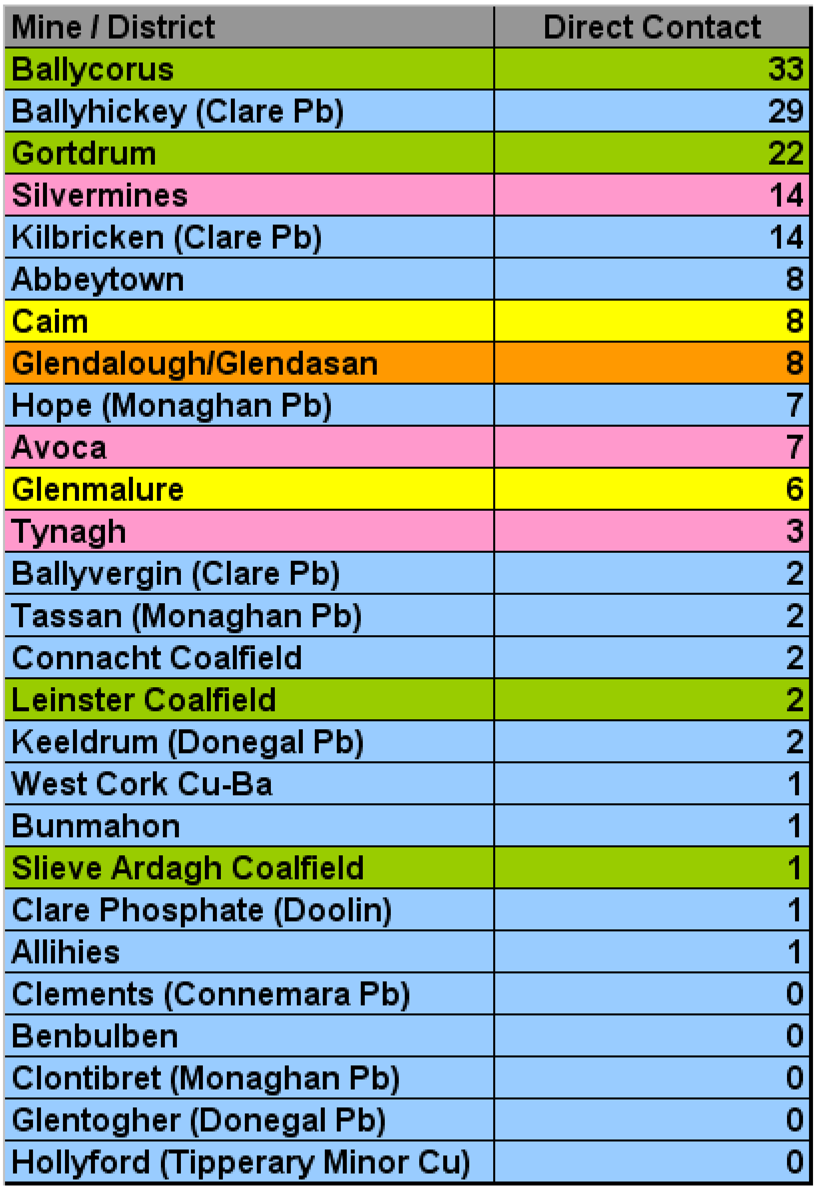


Mine / District	Air
Gortdrum	4
Silvermines	3
Tynagh	2
Ballycorus	2
Ballyhickey (Clare Pb)	1
Glendalough/Glendasan	1
Abbeytown	1
Glenmalure	1
Avoca	1
Kilbricken (Clare Pb)	0
Caim	0
Tassan (Monaghan Pb)	0
Clements (Connemara Pb)	0
Ballyvergin (Clare Pb)	0
Leinster Coalfield	0
Slieve Ardagh Coalfield	0
West Cork Cu-Ba	0
Hope (Monaghan Pb)	0
Bunmahon	0
Keeldrum (Donegal Pb)	0
Connacht Coalfield	0
Allihies	0
Clare Phosphate (Doolin)	0
Clontibret (Monaghan Pb)	0
Glentogher (Donegal Pb)	0
Benbulben	0
Hollyford (Tipperary Minor Cu)	0

Table 6.8 Percentage contribution of the air pathway to the overall site score.

does not contribute significantly to any site score. For most sites the contribution is nil. Only nine sites registered a score (within the bounds of rounding errors), namely, Gortdrum, Silvermines, Tynagh, Ballycorus, Ballyhickey (Clare Pb), Glendalough–Glendasan, Abbeytown, Glenmalure and Avoca.

Table 6.9 provides a list of the percentage contribution of the direct contact (waste piles) pathway to the overall site score for each of the sites scored. The site that had the greatest contribution from the direct contact pathway is Ballycorus, with 33%. Only two other sites had a significant contribution from this pathway – Ballyhickey and Gortdrum.



Mine / District	Direct Contact
Ballycorus	33
Ballyhickey (Clare Pb)	29
Gortdrum	22
Silvermines	14
Kilbricken (Clare Pb)	14
Abbeytown	8
Caim	8
Glendalough/Glendasan	8
Hope (Monaghan Pb)	7
Avoca	7
Glenmalure	6
Tynagh	3
Ballyvergin (Clare Pb)	2
Tassan (Monaghan Pb)	2
Connacht Coalfield	2
Leinster Coalfield	2
Keeldrum (Donegal Pb)	2
West Cork Cu-Ba	1
Bunmahon	1
Slieve Ardagh Coalfield	1
Clare Phosphate (Doolin)	1
Allihies	1
Clements (Connemara Pb)	0
Benbulben	0
Clontibret (Monaghan Pb)	0
Glentogher (Donegal Pb)	0
Hollyford (Tipperary Minor Cu)	0

Table 6.9 Percentage contribution of the direct contact (waste piles) pathway to the overall site score.

Table 6.10 provides a list of the percentage contribution of the direct contact (stream sediments) pathway to the overall site score for each of the sites scored. Three sites have a percentage contribution greater than 50% – Clontibret, Glentogher and Tassan. All three sites are small. Other sites with a significant contribution include the Slieve Ardagh Coalfield, Glendalough–Glendasan, Allihies and the West Cork Cu–Ba District. For most sites, this is not a significant pathway. The principal impact from direct contact (stream sediments) is for watering livestock and wildlife.

Mine / District	Direct Contact (Stream Sediments)
Clontibret (Monaghan Pb)	99
Glentogher (Donegal Pb)	77
Tassan (Monaghan Pb)	59
Slieve Ardagh Coalfield	32
Glendalough/Glendasan	31
Allihies	29
West Cork Cu-Ba	21
Caim	16
Gortdrum	14
Ballycorus	12
Silvermines	12
Clements (Connemara Pb)	9
Glenmalure	7
Leinster Coalfield	2
Avoca	2
Tynagh	1
Bunmahon	1
Kilbricken (Clare Pb)	0
Connacht Coalfield	0
Abbeytown	0
Ballyvergin (Clare Pb)	0
Ballyhickey (Clare Pb)	0
Keeldrum (Donegal Pb)	0
Clare Phosphate (Doolin)	0
Hope (Monaghan Pb)	0
Benbulben	0
Hollyford (Tipperary Minor Cu)	0

Table 6.10 Percentage contribution of the direct contact (stream sediments) pathway to the overall site score.

6.3.3 Specific risks

The HMS-IRC scoring system provides an effective ranking of mine sites investigated in terms of their potential to affect human or animal health or to have a negative impact on the environment. One effect of the ranking system, however, is that, by focusing attention on a few Class I, II or III sites, it can draw attention away from specific problems on smaller, low-ranking sites. Ranking is a relative concept and a low ranking does not mean that any given site is free of significant health or environmental risks that may need to be addressed. For example at Ballyvergin, a Class V site, Pb concentrations in excess of 20% were measured in fine-grained mine waste in an area used by cattle for feeding. These and other instances are detailed in the individual site reports.

CHAPTER 7

Conclusions

7.1 Environmental conclusions

The conclusions in this section incorporate the work that was carried out to examine the chemical characteristics of each of the mine sites and their impact on human and animal health and the environment.

Conclusion 1

Ireland possesses an abundance of historic mine sites dating from the Bronze Age to the late 20th century.

Conclusion 2

The HMS-IRC scoring system provides an effective ranking of mine sites in terms of their potential to affect human or animal health or to have an impact on the environment. Based on their scores, sites are assigned to one of five classes ranging from I (high priority) to V (low priority).

Conclusion 3

The three Class I sites are Silvermines, Tynagh and Avoca.

Conclusion 4

The Class II site is Glendalough–Glendasan.

Conclusion 5

The two Class III sites are Caim and Glenmalure.

Conclusion 6

The four Class IV sites are Ballycorus, Gortdrum, the Leinster Coalfield and the Slieve Ardagh Coalfield.

Conclusion 7

The seventeen Class V sites are Clements, the Connacht Coalfield, Kilbricken, Allihies, Abbeytown, Tassan, Ballyvergin, Ballyhickey, Keeldrum, West Cork Copper–Barium District, Clare Phosphate (Doolin), Bunmahon, Hope, Clontibret, Glentogher, Benbulben and Hollyford.

Conclusion 8

Lead is the single most important contaminant on Irish mine sites in terms of its toxicity, the concentration in which it is found, the quantity of Pb-enriched material, and its geographical dispersion on and around mine sites. It is present in high concentrations in 13 out of 27 districts investigated, not only in solid waste but also in mine waters and in surface waters and stream sediments downstream of mines. Mine districts and sites most severely contaminated by Pb include Caim, Clare Lead Mines, Glendalough, Silvermines and Tynagh.

Conclusion 9

The routes that have the dominant effect on the final scores are the surface water and groundwater pathways.

Conclusion 10

Acid mine drainage is characterised by low pH and high acidity, and when generated in metal or coal mines is typically rich in metals such as Fe, Mn, Al, Cu, Pb, Ni and Zn, and therefore potentially toxic to aquatic organisms. At Avoca mine, AMD has had a major impact on the Avoca River. Low pH and high acidity are also found in some mine waters at the Slieve Ardagh, Leinster and Connacht Coalfields. However, only in the Connacht Coalfield is there volumetrically significant discharges of AMD. Relatively high concentrations of Al, Ba, Cd, Fe, Mn and Ni are present in water in these mine districts.

Conclusion 11

The sites of the former ore processing plants at Gortdrum, Silvermines and Tynagh are significantly contaminated by heavy metals. In all three cases, the sites are being utilised by new businesses. Contaminants include not only the metals produced from the site, such as Pb, Zn and Cu, but also minor constituents of the ore that have become concentrated during processing. These minor constituents include As and Hg, which have been found in concentrations exceeding 1,000 mg/kg. Arsenic is also present in high concentrations in solid waste outside of processing areas at both Avoca and the Clare Pb Mines. Despite its occurrence at high concentrations in solid waste, As has not been detected in surface waters downstream of mine sites at concentrations in excess of the Draft EC Surface Water Regulations.

Conclusion 12

Draft EC Surface Water Regulations set low limits for some metals that occur in significant concentrations in surface water downstream of Irish mine sites. These metals include Cd, Cu, Pb and Zn. They pose risks to aquatic ecosystems even at low concentrations and may require inclusion in surface water monitoring programmes.

Conclusion 13

Concentrations of Cu in stream sediment are very high downstream of some sites, notably Allihies, Avoca and, in West Cork, at Glandore and Ballycummisk. The potential for impact on the aquatic ecosystem may warrant further investigation. The total Cu concentration in surface waters downstream of mines indicates significant impact on water chemistry from mine discharges at some sites. However, numerous upstream surface water samples and even some groundwater samples also contain Cu in excess of regulatory levels, indicating that mine waste is one of a number of sources of elevated Cu in surface water and groundwater.

Conclusion 14

High concentrations of Zn in solid mine waste pose no threat to human health. However, high concentrations of Zn in stream sediments and/or downstream surface waters at Avoca, Glendalough, Silvermines and Tynagh pose a risk to livestock and the aquatic environment.

Conclusion 15

Selenium is a common component of phosphate rock and the shales that typically host it. Leaching of Se from solid waste heaps at phosphate mines in the USA has led to significant downstream Se contamination of aquatic organisms, mammals, birdlife and grazing animals. The concentration of Se in solid waste from the Clare Phosphate deposits (18–30 mg/kg) falls within the range of concentrations reported for US phosphate mine waste. While there is no evidence for leaching of Se into the aquatic environment, a large part of the former mine site is now used as grazing land and may pose a risk of Se toxicity to grazing animals.

Conclusion 16

Some mine waters have very high concentrations of both total and dissolved Al. There is an inverse relationship between pH and Al concentration, with those mine districts with low-pH water, such as Avoca and the three coalfields, having the highest concentrations of Al in mine water and downstream surface waters. Concentrations of total Al measured in surface water downstream of these sites are typically in excess of both drinking water standards and Canadian guidelines for the protection of the aquatic environment.

Conclusion 17

Nickel is enriched in mine water, downstream surface water and stream sediments at some sites in the Irish coalfields. It is also found in excess of the Draft EC Surface Water Regulations downstream of mines such as Avoca and Tynagh.

Conclusion 18

The following site-specific issues were identified during the course of the project

Abbeytown

- Pb- and As-rich leachate from the tailings pond enters the estuary at Ballysadare Bay.

Avoca

- Measured Pb concentrations exceed 1% in solid waste at Connary, a site where sheep graze.

Ballycorus

- Pb concentrations exceed 1% in solid waste at Ballycorus in an area popular with walkers and horse riders.

Caim

- Pb concentrations exceed 5% in a solid waste heap at Caim, used by quad bikers and others.

Clare Pb District – Ballyvergin

- Pb concentrations in excess of 20% were measured in fine-grained mine waste in an area used by cattle for feeding at Ballyvergin.

Glendalough

- Measured Pb concentrations exceed 10% in solid waste at the Hero Processing site, at the head of the Glendasan Valley. The site is very popular with tourists.
- High concentrations of Pb and Zn were measured in stream sediments in Glendasan River downstream of the mines.

Glenmalure

- Measured Pb concentrations exceed 10% in solid waste at Ballinafunshoge, Glenmalure, a site popular with quad bikers.

Gortdrum

- Very high concentrations of Hg (>0.5%) and As (> 1%) were measured in solid waste at the site of the former processing plant, now the site of an active business.

Silvermines

- Very high concentrations of Pb (>2%) and As (>0.1%) were measured in solid waste at the site of the former processing plant in Garryard, now the site of an active business.

Tynagh

- Very high concentrations of Pb (>2%) and As (>0.1%) were measured in solid waste at the site of the former processing plant, now the site of an active business.
- A Cd-rich discharge from a waste heap crosses grazing land and seeps underground, potentially affecting groundwater.

CHAPTER 8

Recommendations

8.1 Environmental recommendations

The recommendations in this section arise from the findings of the work that was carried out to examine the chemical characteristics of each of the mine sites and their impact on human and animal health and the environment.

Recommendation 1

The Local Authorities should be advised of all issues of environmental concern falling within their functional area. Other authorities such as the HSE, the HSA and Teagasc may also need to be informed of specific relevant issues.

Recommendation 2

Sites assigned to Class I should have a full environmental risk assessment carried out, if not already undertaken. Ongoing monitoring should be carried out at these sites.

Recommendation 3

The site assigned to Class II should have general monitoring of most or all waste piles, discharges or stream sediments carried out on an annual basis.

Recommendation 4

Sites assigned to Class III should have specific monitoring on particular waste piles, discharges or stream sediments on a biennial basis.

Recommendation 5

Sites assigned to Class IV should have specific monitoring on particular waste piles, discharges or stream sediments on a five-yearly basis.

Recommendation 6

Sites assigned to Class V generally do not require any specific monitoring.

Recommendation 7

In order to comply fully with the Directive an inventory of closed aggregate and stone operations (quarries and pits) should be carried out.

Recommendation 8

A scientific-based scheme of monitoring should be developed appropriate to each of the site classes incorporating relevant expertise from the EPA and the GSI.

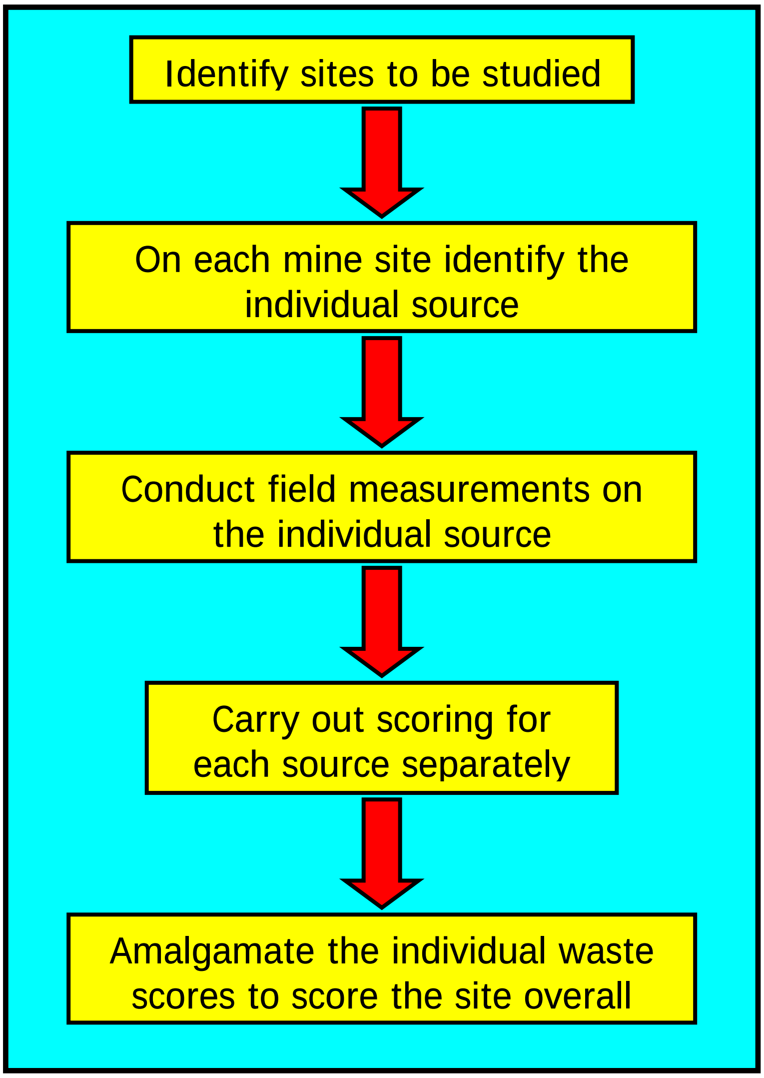
APPENDIX 1

HISTORIC MINE SITES

SCORING SYSTEM

(HMS – SS)

A project to categorize contamination sources from mine waste at Historic Mine Sites



GEOLOGICAL SURVEY OF IRELAND AND THE ENVIRONMENTAL PROTECTION AGENCY

FOREWORD

The Historic Mine Sites – Inventory and Risk Categorization Project addresses the EU Directive on Wastes from the Extractive Industries requirement for an inventory of waste facilities and the National need for data on physical hazards at closed and/or abandoned mine sites. In order to categorize and rank these relatively the Source – Pathway – Receptor Paradigm was utilized. Contaminant risks at mine sites come from potential contaminated mine waste source found on a site. The paradigm requires that each of the parameters within the model are documented, estimated, measured or recorded. The model identifies the source of any contamination; identifies who or what is affected (the receptor); and identifies how the source may reach the receptor (pathway). A contaminant linkage occurs when a source, pathway and receptor are demonstrated to occur together. The collection of field data, observations and estimates confirms whether a linkage exists between the source and receptor.

The scheme developed to risk categorise the sites is described in this Appendix. The overall scheme seeks to score various parameters in order to develop an overall score for an individual waste pile, mine discharge or contaminated stream sediments. The individual waste scores are then added to develop an overall score for the site in question.

TABLE OF CONTENTS

APPENDICES

1. INTRODUCTION

EU Directive 2006/21/EC, the Management of Waste from the Extractive Industries, requires each Member State to compile an inventory of closed waste facilities, including abandoned waste facilities, within their jurisdiction by 1st May 2012 and to update the inventory periodically thereafter (Article 20). Article 21 states that the inventory should be complied on a risk basis. The Geological Survey of Ireland, the Environmental protection Agency and the Exploration and Mining Division of the Department of Communications, Energy and Natural Resources (the partners) are conducting the inventory of closed waste facilities for Ireland.

This document describes the risk assessment method developed by the partners and known as the Historic Mine Sites Scoring System (HMS-SS). The system was developed to prioritise the historic mine sites from a human and animal health perspective as well as the general environment. The system is based on the Abandoned and Inactive Mines Scoring System (AIMSS) which was developed to carry out a similar exercise in the State of Montana, United States of America.

The system requires information from many sources including:

Geological Survey of Ireland data
Environmental Protection Agency data
Exploration and Mining Division data
Central Statistics Office data
Teagasc subsoils data
Local Authority data

Data from several sources needed to be compiled from documented sources in a GIS environment. This was then validated by field visits to each of the sites.

In addition, data has been collected in the field to be used in the scoring system. This included:

1. Surface water sampling and analysis (both summer and winter)
2. Stream sediment sampling and analysis
3. Tailings sampling and analysis
4. Waste pile sampling and analysis

Site safety and stability is assessed and described in a separate document associated with this project.

HMS-SS is not a detailed quantitative risk assessment. The scoring is designed to rank differing and disparate sites using existing or easily obtained new information on a common foundation on the basis of threats to human health, animal health and the environment.

2. OVERALL PHILOSOPHY

The overall approach to the scoring of the sites is illustrated in Figure 2.1.

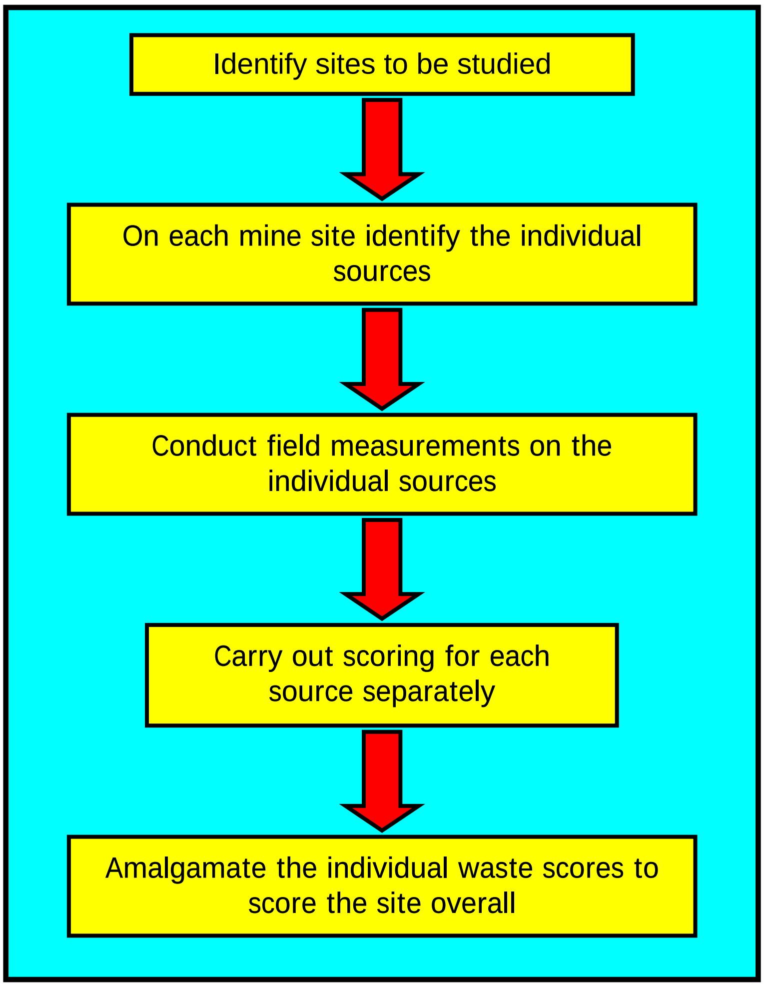


Figure 2.1. Overall approach to ranking contamination at mine sites.

First, the closed mine sites to be studied are identified, as described in Section 2.2 (Preliminary screening and site selection) of the Main Report. Next, within these sites individual contamination sources are identified. These sources are mapped and measurements and other data collected in and around each. The individual source types are characterised so that the hazard associated with each is known. In effect, the volume and chemical composition of each facility is determined and combined to produce a hazard score for each. The individual sources are assessed for the potential risk they pose to human health, animal health, and the environment. The scoring for human health, animal health and the environment within HMS-SS follows the source – pathway – receptor paradigm. Finally, the scores for the individual source types are combined to produce a site score whereby all the selected sites from around the country can be compared and a ranking categorization developed.

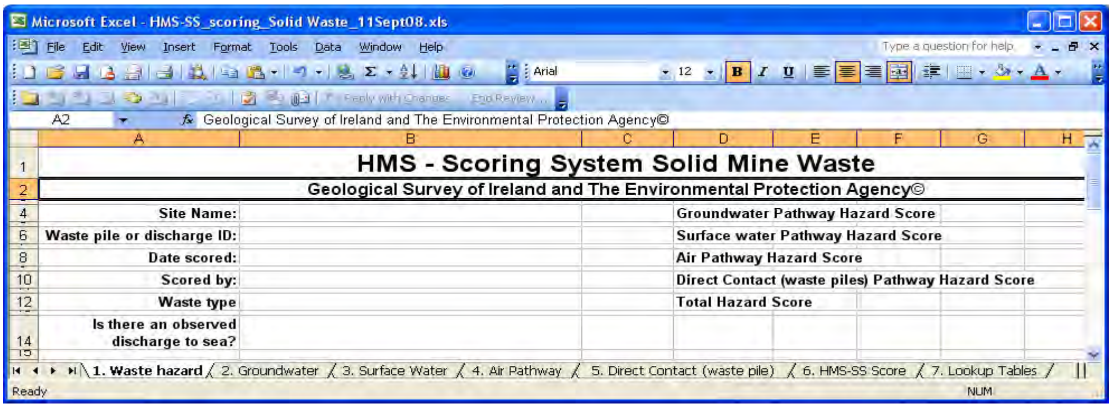
The sources, pathways and receptors that are considered in the HMS-SS system and pose a risk to human health, animal health and the wider environment are described in the following three sub-sections (Sections 2.1, 2.2 and 2.3 respectively).

The scoring process is automated with the use of an EXCEL workbook (HMS-SS_scoring.xls) for each source type. There are three workbooks with up to seven different worksheets within each. The table below displays the different combinations of worksheets for each source type.

Solid Sources	Liquid Sources	Stream Sediments
1. Waste Hazard 2. Groundwater 3. Surface water 4. Air Pathway 5. Direct Contact (waste piles) 6. HMS-SS Score 7. Lookup Tables	1. Waste Hazard 2. Groundwater 3. Surface water 4. HMS-SS Score 5. Lookup Tables	1. Waste Hazard 2. Direct Contact (stream sediments) 3. HMS-SS Score 4. Lookup Tables

Table 2.1. The HMS-SS EXCEL workbooks.

The first worksheet (Waste Hazard) is common to all three workbooks. This sheet scores individual sources that have been investigated during this study. The next worksheets, the number depends on the source type, score the named and relevant pathways. Solid sources contain four of these pathways (Fig 2.2). Liquid sources have only two pathways sheets, groundwater and surface water. One pathway worksheet is present in the Stream Sediment workbook. The overall score for each source type is calculated on the HMS-SS worksheet. The final worksheet contains the lookup tables servicing the input to the other tables.



Geological Survey of Ireland and The Environmental Protection Agency©

HMS - Scoring System Solid Mine Waste

Geological Survey of Ireland and The Environmental Protection Agency©

4	Site Name:	Groundwater Pathway Hazard Score
6	Waste pile or discharge ID:	Surface water Pathway Hazard Score
8	Date scored:	Air Pathway Hazard Score
10	Scored by:	Direct Contact (waste piles) Pathway Hazard Score
12	Waste type	Total Hazard Score
14	Is there an observed discharge to sea?	

Figure 2.2. An example of a Solid Waste workbook.

2.1 Sources

The potential sources of contamination at mine sites include:

1. Tailings
2. Waste piles
3. In situ mineralization
4. Contaminated runoff
5. Adit and other discharges and seeps
6. Standing water on waste facilities and other ground within mine sites
7. Stream sediments

These can also be subdivided into solids sources, liquid sources and stream sediment contamination.

2.1.1 Solid sources

The solid mine waste scored using the HMS-SS system are:

1. Waste heaps or tips – natural rock extracted in the mining process but not processed for mineral extraction.
2. Tailings – the non-valuable end product of mineral processing having the consistency of fine to coarse flour.
3. Unprocessed ore – ore that has been taken out of the ground but has not been processed for any one of a number of reasons.
4. Processed or part processed waste – ore material which has been processed but is not tailings; often this is a waste from earlier more primitive processing methods.
5. A mixture of any of the above.

However, not all sources are equally a threat to humans, animals or the environment. The factors determining the threat posed for each source include:

1. Volume of waste material.
2. Surface area of the site.
3. Surface area of the particles (grain size).
4. Physical state of the source.
5. Chemical composition of the waste material.
6. Linkage to pathway and / or receptors.

2.1.2 Liquid sources

The liquid waste scored using the HMS-SS system are:

1. Contaminated surface water, streams, rivers and lakes.
2. Contaminated point source discharges to surface waters, for example, adit discharges and seeps.
3. Contaminated diffuse discharges to groundwater or surface waters.
4. Standing water in ponds.

However, not all sources are equally a threat to humans, animals or the environment. The factors determining the threat posed for each source include:

1. Volume of contaminated water.
2. Chemical composition of contaminated water.
3. Linkage to pathway and / or receptors.

2.1.3 Stream sediment contamination

Stream sediments are scored separately using the HMS-SS system.

However, not all sources are equally a threat to humans, animals or the environment.

The factors determining the threat posed for each source include:

1. Length of stream or river containing contaminated stream sediments.
2. Chemical composition of contaminated stream sediments.
3. Linkage to pathway and / or receptors.

2.2 Pathways

The potential pathways for contamination to reach receptors that are used in the HMS-SS are:

1. Groundwater
2. Surface water
3. Air
4. Direct contact involving waste piles
5. Direct contact involving stream sediments

2.3 Receptors

The potential receptors are:

1. Humans
2. Groundwater
3. Surface water
4. Fresh water ecosystems
5. Land based ecosystems
6. Marine (estuarine ecosystems)
7. Livestock

2.4 Scoring

The overall approach to the scoring system is to take for each source type, each relevant pathway in turn, groundwater, surface water, air and direct contact (with waste heaps or stream sediments). For each pathway three **primary factors** are evaluated:

- **Likelihood of release** of a contaminant to humans or the environment.
- Waste **hazard** characteristics, including chemical composition, quantity and relative toxicity.
- Potential **receptors** of exposure (human, animal and environmental)

There are several items within each factor and these are combined (either added or multiplied) to give an overall score. Once each factor within a pathway has been scored the total score is calculated and is the designated Site Score for the site under consideration.

For **Solid Waste**, the HMS Score is:

{[Groundwater Score (likelihood of release)*(hazard)*(receptors)] +
[Surface water Score (likelihood of release)*(hazard)*(receptors)] +
[Air pathway Score (likelihood of release)*(hazard)*(receptors)] +
[Direct contact (Waste piles) Score (likelihood of release)*
(hazard)*(receptors)]} ÷ 100,000

For **liquid Waste**, the HMS Score is:

{[Groundwater Score (likelihood of release)*(hazard)*(receptors)] +
[Surface water Score (likelihood of release)*(hazard)*(receptors)]} ÷
100,000

For **Stream Sediments**, the HMS Score is:

{[Direct contact (Stream Sediments) Score (likelihood of release)*
(hazard)*(receptors)]} ÷ 100,000

The three primary factors are multiplied together to derive each of the pathway scores. This equalises the relative effect of each primary factor. Hence, a greater likelihood of release, higher constituent concentrations, or more potential receptors all affect the pathway score similarly – as should be the case when assessing relative risk.

The associated pathways for each source type are summed and the result divided by 100,000 – simply to reduce the order of magnitude of the scores. Within the system the groundwater and surface water pathway are given greater relevance as they have the potential to affect more receptors than either the air or direct contact pathways.

There are inevitable uncertainties for some parameters. Those parameters which have the greatest uncertainties have been intervalised, i.e., ranges of values have been identified within which the score is the same. An examples of these parameters is population statistics.

Once each source type has been assessed, all the scores for each of the waste types for each mine site are added together to give an overall score for the mine site.

2.5 Some overarching topics

At the outset some of the overarching concepts, parameters and definitions need to be described.

2.5.1 Site boundary

The site boundary is often identified for a measure, for example the nearest residence. Where this is the case the site boundary is from the nearest waste feature – waste heap, tailings facility, adit discharge etc. see Figure 2.2.

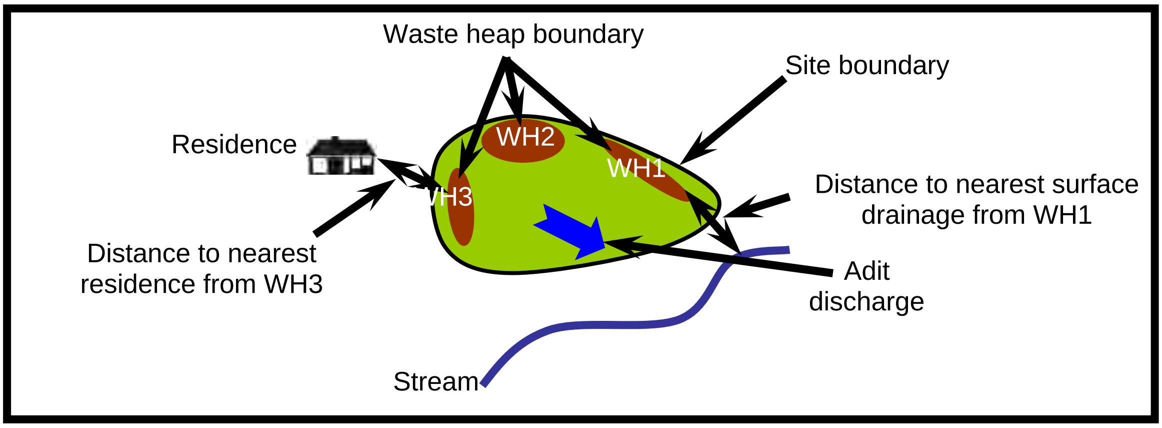


Figure 2.3. Illustration of nearest distances measurements from waste heaps to stream or residence. WH = waste heap.

2.5.2 Measure of central tendency of chemical composition for waste heaps

Large bodies of mine waste are typically heterogeneous and require up to several tens of samples to be collected and analysed to provide a realistic assessment of the likely overall composition of that facility. Different numbers of samples were taken at sites depending on its size and complexity. Also, smaller numbers of samples tend to provide a greater tendency for outliers (unusually small or large values) to occur. For this reason the decision was made to use the median value as a measure of central tendency. The median value limits the influence of outliers and provides a more robust estimate value for average composition.

2.5.3 Measure of central tendency of chemical composition for stream sediments

Stream sediment sampling involved sampling a number of sub-sites downstream of each mine. Stream Sediments in a river are typically heterogeneous and require up to several tens of samples to obtain a realistic representation of the stream. For this reason the median statistic was used as a measure of central tendency. The median value limits the influence of outliers and provides a more robust estimate value for average composition.

2.5.4 Measure of chemical composition for water samples

Flow rates and concentrations of discharges and seepages vary seasonally. For this reason water samples were taken during both winter and summer seasons. The more conservative value was used when scoring these liquid wastes in the HMS-SS workbooks.

2.5.5 Relative toxicities

The relative toxicity of elements is taken into account in the scoring by modifying the hazard score throughout the system. This is achieved by multiplying the amount of the element by the relative toxicity number. However, the relative toxicities are different for different environments or habitats. For this study six relative toxicities categories are recognised:

Soil and sediment

- Human ingestion and inhalation
- Livestock

Surface water and groundwater

- Human ingestion
- Fresh water aquatic environment
- Marine water aquatic environment
- Livestock

The relative toxicities are given in Table 2.2.

Throughout the study the total quantity of the element is used. This is far simpler than having to carry out speciation studies, which are often complex and controversial, for elements in order to determine bio-availability. The approach of using total concentrations is also conservative.

In addition, not every pathway is relevant to each environmental situation or habitat. The relevant pathways for each environmental situation or habitat are illustrated in Table 2.3.

Relative Toxicity Values						
	Soil and sediment		Surface water and groundwater			
Metal	**Human ingestion & inhalation**	**Livestock**	**Human ingestion**	**Eco Aquatic**	**Eco Salt - Aquatic**	**Livestock**
Aluminium*	N/A	N/A	0	0.1	0.1	0.01
Antimony	10	0.1	10	0.1	0.1	0.1
Arsenic	10	0.1	10	0.01	0.1	0.01
Barium	0.01	0.01	0.01	0.001	0.001	0.1
Cadmium	10	10	10	10	1	10
Chromium	10	0.1	10	0.1	0.1	0.1
Copper	0	0.1	0	1	1	0.1
Iron	0.001	0.01	0.001	0.01	0.01	0.01
Lead	10	1	10	1	1	1
Manganese	0.1	0.001	0.1	0	0	0.001
Mercury	10	1	10	10	10	1
Nickel	10	0.1	10	0.1	1	0.1
Selenium	0.1	1	0.1	1	0.1	1
Silver	0.1	0.01	0.1	10	10	0.01
Thorium	10	0.01	10	0.01	0.01	0.01
Uranium	10	0.01	10	0.01	0.01	0.01
Vanadium	0.1	0.1	0.1	0	0	0.1
Zinc	0.01	0.01	0.01	0.01	0.1	0.01

Table 2.2. Relative toxicity values for different environmental and habitat situations.

***Aluminium is only measured in water samples.**

	Pathway				
				Direct contact	
Receptors	**Groundwater**	**Surface water**	**Air**	**Waste pile**	**Stream sediment**
Human					
ingestion	●	●		●	
inhalation			●		
Fresh water aquatic		●			
Marine water aquatic		●			
Livestock	●	●		●	●

Table 2.3. Cross tabulation of which pathway affects which environmental situation or habitat.

The table should be interpreted as follows. For each receptor the pathways indicated are the means by which the particular receptor is exposed to the hazard (mine waste). Therefore, human receptors are exposed to the hazard through coming into contact with groundwater (by drinking groundwater), by surface water (by drinking it), by the air pathway (by inhaling dust) and by direct contact (by walking over or being otherwise on a site). Fresh water aquatic ecosystems are exposed to mine wastes via the surface water pathway (that is where they live). Marine water aquatic ecosystems are exposed to mine wastes via the surface water pathway (these water enter the marine environment and therefore pose a risk to marine organisms). Livestock are exposed to the hazard posed by mine wastes via the groundwater pathway (some livestock may get their drinking water from this source), via the surface water pathway (most livestock receive their water from surface water), via the direct contact pathway (livestock may enter onto mine waste facilities, either intentionally or by accident) and livestock my ingest mine waste by having access to contaminated stream sediments when drinking from surface drainages.

2.5.6 Constituents attributable to the site

In scoring the different pathways elements must be attributable to the site. For example, if a surface water sample is contaminated with lead but there is no lead at the site then the element is not attributable to the site. The source of the contamination must be other than the mine site. On the other hand, if the mine site does contain lead and there is lead contamination in the stream then the presumption is that the source of the lead is from the site is reasonable – even though there could be other sources.

3. APPLYING A HAZARD SCORE TO A MINE WASTE

As discussed above each waste facility is scored for the hazard that it presents to the environment separately. Once this score has been calculated the actual state of the facility and the receptors that are likely to be affected by the facility are then scored. Refer to Worksheet No. 1 Hazard Score in the workbook.

The hazard score is determined by two factors:

- the 'quantity' of waste, and
- the contamination hazard represented by the waste.

3.1 Quantity of waste

Waste can be either solid or liquid and each type is reported differently.

3.1.1 Solid waste quantity

In the case of a solid waste for the groundwater and surface water pathways the 'quantity' measure is a volume and is reported in cubic metres (m^3). In the case of a solid waste for the air and direct contact pathways the 'quantity' measure is an area and is reported in square metres (m^2).

Information requirements and sources:

The information required to score this sub-factor is:

- Solid wastes volumes – a measure of the volume of waste within each accumulation. This is obtained from field measurements, use of aerial photographs and the use of GIS software. The volume should be reported in m^3.
- Solid wastes areas – a measure of the area of waste within each accumulation. This is obtained from field measurements, use of aerial photographs and the use of GIS software. The area should be reported in m^2.

SCORING

Once the 'quantity' has been determined a score is applied as follows in Tables 3.1 and 3.2.:

For volumes:

Solid waste volume (m^3)	**Score**
<1,000	1
1,000 – 1,000,000	1 + Vol*/10,000
1,000,000	100

Table 3.1. Scores to be assigned for volumes of solid waste estimated for sites.

*Vol = volume of waste in m^3.

For areas:

Solid waste area (m^2)	Score
<100	0.001
100 – 1,000	0.01
1,000 – 10,000	0.1
10,000 – 100,000	1
100,000 – 1,000,000	10
1,000,000 – 10,000,000	100
>10,000,000	1,000

Table 3.2. Scores to be assigned for areas of solid waste estimated for sites.

3.1.2 Liquid waste quantity

For liquid wastes the measurement is in litres/day (l/d) for the groundwater and surface water pathways. In the HMS-SS system liquid wastes do not contribute to the air or direct contact pathways, so a 'quantity' measurement is not required for these pathways.

Information requirements and sources:

For liquid wastes – a measure of the flow of liquid waste in the field by use of the 'cut-throat' measuring device. The flow should be reported in l/day.

SCORING

Liquid waste volume (l/day)	Score
No seepage observed	0
Observed but not measureable	3
<10,000	10
10,000 – 100,000	30
100,000 – 1,000,000	100
>1,000,000	300

Table 3.3. Scores to be assigned for liquid wastes issuing from adits or other seeps at mine sites.

3.1.3 Contaminated Stream Sediments

For stream sediments the length of stream with contaminated stream sediments is the relevant 'quantity' and is reported in metres (m).

Information requirements and sources:

The information required to score this sub-factor is:

- A measure of the length of stream sediments contaminated by discharges from the mine site. This is obtained from identifying which parts of the stream sediment are contaminated through an examination of stream sediment analyses carried out and by measuring the distance along the stream or river, usually by using GIS software. The length should be reported in metres. The contaminating substance must be attributable to the mine site.

SCORING

Length of stream containing contaminated stream sediments (m)	Score
<10	0.001
10 – 50	0.01
50 – 100	0.1
100 – 150	1
150 – 250	10
250 – 500	100
>500	1,000

Table 3.4. Scores to be assigned for the length of contaminated stream sediments identified along drainages emanating from sites.

3.2 Contamination hazard

The contamination hazard of the waste is assessed by reference to:

- Chemical composition of the waste, and
- The relative toxicity of the particular element with reference to the receptor under consideration.

Therefore each receptor represents a different hazard to different receptors by virtue of the fact that different receptors are more or less sensitive to the same elements.

The chemical nature of each waste is assessed by carrying out a chemical analysis of the waste. Typically there will be a number of analyses. The median composition is calculated for both solid sources and stream sediments. A more conservative view is used with liquid sources, taking the higher values with the associated flow. These are described in Sections 2.5.2 – 2.5.4.

Each element (Cu, Pb, Zn etc) is assessed on its own. No account is made for ‘original’ background values as these are for the most part unknown or unknowable. The relative toxicity for each element is taken into account with the ‘average’ value (AV) of the element multiplied by the relative toxicity number (for the appropriate habitat under consideration). These numbers are given in Table 2.2 above. This is the ‘**hazard value’** for each site. Once the ‘hazard value’ for each element is calculated they are summed together to obtain the ‘**total hazard value’**.

SCORING

Because each receptor has a different relative toxicity number there are two potential hazard scores for each solid waste facility; four hazard scores for liquid waste sources and one additional one for stream sediments (Table 3.5).

Waste type	Receptor	Pathway(s)	Exposure mechanism
Solid	Human	Air	Inhalation
Solid	Human	Direct contact	Ingestion
Solid	Livestock	Direct contact	Ingestion
Liquid	Human	Groundwater OR surface water	Ingestion
Liquid	Fresh water ecosystem	Surface water	Ingestion
Liquid	Marine ecosystem	Surface water	Ingestion
Liquid	Livestock	Groundwater OR surface water	Ingestion
Contaminated stream sediment	Livestock	Direct contact	Ingestion

Table 3.5. The different hazard numbers generated when carrying out a full evaluation under HMS-SS.

Another way of looking at this is to consider each pathway and examine which receptors are affected (Table 3.6).

Pathway	Receptors affected
Groundwater	Human, livestock
Surface water	Human, fresh water ecosystems, marine ecosystems, livestock
Air	Human
Direct contact (waste pile)	Human, livestock
Direct contact (contaminated stream sediments)	Livestock

Table 3.6. Tabulation of receptors potentially at risk by the different pathways.

The same basic procedure is used to score each of the hazard scores for each receptor (Table 3.7).

Element no.	Average value (AV)	Relevant* toxicity no. (RT)	Hazard value (HV)
1	Element$_1$ conc (AV$_1$)	RT$_1$	AV$_1$ * RT$_1$
2	Element$_2$ conc (AV$_2$)	RT$_2$	AV$_2$ * RT$_2$
⋮	⋮	⋮	⋮
n	Element$_n$ conc (AV$_n$)	RT$_n$	AV$_n$ * RT$_n$

TOTAL	$= \sum_{i=1}^{n} (AV_i * RT_i)$

Table 3.7. Computation of Hazard Scores

*** The relevant toxicity number could be the human toxicity by ingestion/inhalation due to either solid or liquid wastes, the fresh water aquatic environment due to liquid waste, the marine water aquatic environment due to liquid waste or livestock toxicity due to either solid or liquid waste – all values obtained from Table 2.2.**

Information requirements and sources:
The information required to score this sub-factor is:

- Concentrations of contaminants measured for each waste source, liquid or solid. Chemical analysis comes from field measurements with a field portable XRF in case of solids and from laboratory analysis for liquids.

TOTAL Hazard SCORE

The total score for HAZARD (waste characteristics) is obtained by calculating the product of the quantity of waste score and the total hazard score for each receptor for each pathway for each waste source and dividing the result by 10,000, i.e.,

$$\textbf{Total Score} = \left(\sum_{i=1}^{n} (AV_i * RT_i) * Q\right) / 10{,}000$$

4. SCORING THE GROUNDWATER PATHWAY

In this section both the information sources used for the scoring and the scoring for each of the 'Likelihood of Release' and 'Receptor' factors for the groundwater pathway are described. Refer to Worksheet No. 2 in both the solid source and liquid source workbooks.

4.1 Likelihood of Release

The likelihood of release score evaluates three sub-factors:

- Potential for observed releases to groundwater;
- Exceedances of water standards; and
- Potential to release.

4.1.1 Potential for observed releases to groundwater

An observed release is when the analytical results from a leach test (HMS-IRC Project Report, Appendix 2, *Geochemical Sampling protocols*) carried out on a sample of waste from the site for any constituent is THREE times the upgradient concentration of groundwater or surface water for that constituent that is attributable to the site. Surface water analysis is used as a substitute for groundwater analysis where no upgradient groundwater analysis exists. In the event that no groundwater or surface water was sampled during the project then the nearest analogous water sample, either surface water or groundwater, for which analytical results exist, may be used. Concentrations do not have to exceed any standards.

Wastes that could be sampled are:

- Waste rock heaps
- Tailings
- Ore concentrate
- Discharges

Scoring for Potential for observed release to groundwater is as per Table 4.1.

SCORING

Observed release	Score
YES	200
NO	0

Table 4.1. Scoring the 'Potential for observed releases to groundwater' sub-factor.

Information requirements and sources:

The information required to score this sub-factor is:

- Analytical results of groundwater or surface water upgradient of the site from work carried out during this project.

OR

- Analytical results for the nearest surface water or groundwater from work carried out previously and possibly for another organisation.

AND

- Analytical results for leach test carried out on waste from the site from work carried out during this project.
- Evidence that the element is attributable to the site.

4.1.2 Exceedances of water standards

For a solid waste source, an exceedance occurs when the analytical results from either a leach test carried out on a sample of solid waste from the site or an analysis of seepage from a solid waste heap for any constituent exceeds the **Surface water** or **Drinking Water Standard** for that constituent. For a liquid waste source, an exceedance occurs when an analysis of a mine water discharge for any constituent exceeds the **Surface water** or **Drinking Water Standard** for that constituent. The relevant standards are contained in the Draft European Communities Environmental Objectives (Surface Waters) Regulations, 2008 and the European Communities (Drinking Water) (No.2) Regulations 2007, **S.I. No. 278 of 2007.** The Drinking Water Standard came into operation in June 2007 (Appendix 1.1). The exceedance score applies whether a release has occurred or not. The score is applied for any one exceedance. Exceedances of water standards is scored as per Table 4.2.

SCORING

Exceedance	Score
YES	200
NO	0

Table 4.2. Scoring for the 'exceedances of water standards' sub-factor.

Information requirements and sources:

The information required to score this sub-factor is:

- Analytical results for leach test carried out on waste from the site. Work carried out during this project.
- Analytical results for a discharge at the site. Work carried out during this project.
- Current surface water and drinking water standards.

4.1.3 Potential to release

The potential to release is evaluated by:

- The extent to which waste at the site is contained; and
- The estimated depth to the water table.

Site containment

The extent to which a waste heap or discharge is contained by engineered structures designed to prevent releases is evaluated by reference to any as-built engineering drawings and by a visual inspection of the facility. Structures include berms, liners, covers and surface water run-on diversions. Any of these structures must be intact, functioning, and monitored / maintained regularly. Containment is scored as per Table 4.3.

SCORING

Containment	Score
No containment	20
Presence of ONE of the following: berm, liner, run-on diversions or vegetated cover	15
Presence of TWO of the following: berm, liner, run-on diversions or vegetated cover	10
Presence of THREE of the following: berm, liner, run-on diversions or vegetated cover	5
Completely contained - presence of ALL FOUR of the following: berm, liner, run-on diversions or vegetated cover	1

Table 4.3. Scoring the 'containment' element of the 'potential to release' sub-factor.

<u>Depth to the water table</u>
Virtually no bedrock in Ireland has primary porosity or permeability remaining; secondary porosity and permeability have been created through processes of fracturing, weathering and karstification. Although fractures/karst conduits within a bedrock unit may occupy only a small fraction of the total volume (typically 1-2%), the permeabilities of the individual fractures/conduits are typically high. Fractures and some conduits are typically sub-vertical.

In general, little attenuation of contaminants occurs in the bedrock. Because of the high permeability and orientation of the fractures, once any contaminated water comes in contact with bedrock it can pass rapidly to the water table, regardless of how far below the top of the bedrock the water table is. Therefore, in Ireland, depth to bedrock rather than depth to water table is used when assessing groundwater vulnerability to contamination, as it is the subsoils overlying the bedrock that are considered to be the single most important natural feature influencing groundwater vulnerability and groundwater contamination prevention. The exception is where the subsoil is itself an aquifer, i.e. sand and gravel deposits.

The depth to bedrock is estimated from existing boreholes and wells and subsoil maps that show where rock is at or close to the surface. As far as is known, there are no mine sites in Ireland underlain by sand and gravel aquifers but should this be the case then a detailed examination of depth to water table is warranted. In general, however, depth to bedrock is used instead of depth to water table. The depth to the water table is scored as per Table 4.4.

SCORING

Depth to the water table	Score
<10m	20
10 – 30m	10
>30m	2

Table 4.4. Scoring the 'depth to the water table' part of the 'potential to release' sub-factor.

Potential to Release Score

The total score for potential to release to obtained as the product of the Containment and Depth to the water table scores.

Containment score X Depth to the water table score

Information requirements and sources:

The information required to score this sub-factor is:

- Containment: visual inspection at the site into the presence, functioning and maintenance / monitoring of liners, covers and run-on diversions.
- Depth to water table: depth-to-bedrock maps (GSI Bedrock and Groundwater Section; Teagasc Subsoil map), borehole and well logs, field observations of depth to bedrock.

TOTAL Likelihood of Release SCORE

The total score for LIKELIHOOD TO RELEASE is obtained by summing the three sub-factors:

Observed releases to groundwater + Exceedances of water standards + Potential to release

The score will range from a low 2 of to a high of 800.

4.2 Receptors

The receptor sub-factor is evaluated by assessing the following:

- The aquifer category.
- No. of wells within certain radii of the site.
- Distance to nearest well.
- Groundwater vulnerability.

4.2.1 Aquifer category

Under the Water Framework Directive a national aquifer categorization has been developed. The classification recognizes the following two gravel aquifer categories plus nine bedrock aquifer categories as shown in Table 4.5.

	Regionally Important	**Locally Important**	**Poor**
Bedrock aquifers	**Rk** – Karstified	**Lm** – Generally moderately productive	**Pl** – Generally unproductive except for local zones
	Rkc – Karstified, dominated by conduit flow	**Ll** – Moderately productive only in local zones	**Pu** – Generally unproductive
	Rkd – Karstified, dominated by diffuse flow	**Lk** – Locally important karstified aquifer	
	Rf – Fissured bedrock		
Sand/gravel aquifers	**Rg** – Extensive sand/gravel	**Lg** – sand/gravel	

Table 4.5. Aquifer classification used in Ireland.

SCORING

Each aquifer category receives a score. Those aquifers that are more productive receive a greater score than the less productive aquifers (Table 4.6).

Aquifer Class	**Score**
Rk – Regionally Important Karstified	20
Rkc – Regionally Important Karstified, dominated by conduit flow	18
Rg – Regionally Important Extensive sand/gravel	15
Rkd – Regionally Important Karstified, dominated by diffuse flow	15
Rf – Regionally Important Fissured bedrock	10
Lm – Locally Important Generally moderately productive	8
Ll – Locally Important Moderately productive only in local zones	5
Lk – Locally important karstified aquifer	5
Lg – Locally Important sand/gravel	5
Pl – Generally unproductive except for local zones	2
Pu – Generally unproductive	1

Table 4.6. Scores for the different aquifer classes.

Information requirements and sources:

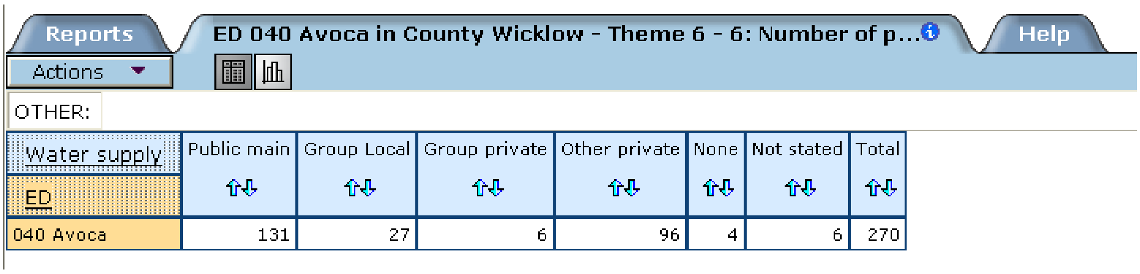
The aquifer category is obtained from the National Aquifer Map produced by the Groundwater Section of the Geological Survey of Ireland (Appendix 1.2). This is available in digital form.

4.2.2 Number of wells within 1km

The 2006 National Census is the basis for scoring under this heading published by the Central Statistics Office (CSO). The data is obtained from the CSO website (www.cso.ie).

The data from the National Census are categorized as follows:

- Public main
- Group local
- Group private
- Other private
- None
- Not stated
- Total



Water supply ED	Public main	Group Local	Group private	Other private	None	Not stated	Total
040 Avoca	131	27	6	96	4	6	270

Figure 4.1. Screen dump from the CSO Small Area Population Statistics.

SCORING

The National Census reports information on an Electoral Division basis. There are 3409 Electoral Divisions in the country (Appendix 1.3). It is necessary to identify the Electoral Division or Electoral Divisions relevant to the site under consideration. This is achieved through GIS. Obviously a 1km buffer around a facility will not coincide with an Electoral Division. The area intersected by the 1km buffer should be expressed as a percentage of the total area of the Electoral Division (adjusted area) and this percentage is used to calculate the number of wells within 1km.

The adjusted number of wells is multiplied by 3 which is the national average of the number of persons per household (actually 2.81 but rounded up to 3).

Therefore, the score for the number of wells within 1km of the site boundary is the number of wells in the District Electoral Division(s) adjusted for area and population centres multiplied by 3:

$$(\textbf{Group local}_{aa} + \textbf{Group private}_{aa} + \textbf{Other private}_{aa} + \textbf{Not stated}_{aa})\ \textbf{X 3}$$

Where aa = adjusted area.

Information requirements and sources:

The number of wells is obtained from the CSO website (www.cso.ie).

4.2.3 Basic groundwater receptor score

The above two scores are added together.

Score for aquifer category + Score for no. of wells within 1km

GROUNDWATER receptor SCORE

The above takes no account of the vulnerability of the aquifer. Groundwater vulnerability maps have been prepared for the Water Framework Directive. The vulnerability map is reproduced in Appendix 1.4 and is available in ArcGIS digital format.

Seven vulnerability classes are recognized:

- Extreme (rock near surface or karst)
- Extreme
- High
- High to low
- Moderate
- Low
- No data

The total score is adjusted by multiplying by a factor determined by the vulnerability classification. This takes into account the protection provided by the composition of the overlying materials, their thickness, etc. Those areas that are less vulnerable have their scores reduced while those areas that are vulnerable are not adjusted as much.

TOTAL Receptor SCORE

The Groundwater receptor score is determined by multiplying the Basic Groundwater Score by a factor (Table 4.8).

Description	Factor
Extreme (rock near surface or karst)	1.00
Extreme	1.00
High	0.80
High to low	0.50
Moderate	0.40
Low	0.25
No data	0.50

Table 4.8. Adjustment factors for receptor score.

(Score for aquifer category + Score for no. of wells within 1km)* X *vulnerability factor

4.3 Groundwater Pathway Score

TOTAL GROUNDWATER SCORE

The total Groundwater pathway score for the waste under consideration is obtained by multiplying the three main factors together:

[Likelihood of Release] X [Hazard (waste characteristics)] X [Receptors]

5. SCORING THE SURFACE WATER PATHWAY

In this section both the information sources used for the scoring and the scoring for each of the 'Likelihood of Release' and 'Receptor' factors for the surface water pathway are described. Refer to Worksheet No. 3 in both the Solid source and Liquid source workbooks.

5.1 Likelihood of Release

The likelihood of release score evaluates three sub-factors:

- Potential for observed releases to surface water;
- Exceedances of water standards; and
- Potential to release.

5.1.1 Potential for observed releases to surface water

An observed release is recorded when the analytical results of a water sampled down stream of a mining facility is THREE times the upgradient concentration of surface water for that constituent OR the analytical results of a stream sediment sampled down stream of a mining facility is THREE times the upgradient concentration of stream sediment for that constituent. The constituent must be one that is attributable to the mine site. A constituent is considered attributable to the site if that constituent exists in any waste material at the site at a concentration more than three times the background concentration of the constituent. The background concentrations are obtained from the National Soil Database, 2007 (Fay et al. 2007) (Appendix 1.5). Concentrations do not have to exceed any standards. In the absence of chemical data OR where there is a visible discharge to a local drainage (discolouration) without a chemical exceedance then the visible discharge should be scored.

SCORING

Observed release	Score
YES	200
Visible discharge	50
NO	0

Table 5.1. Scores to be assigned to the 'potential for observed releases to surface water' sub-factor.

Information requirements and sources:

The information required to score this sub-factor is:

- Analytical results for surface water upstream AND downstream of the site from work carried out during this project.

OR

- Analytical results for stream sediments upstream AND downstream of the site from work carried out during this project.
- Evidence that the element is attributable to the site.
- National Soil Database.

5.1.2 Exceedances of water standards

An exceedance occurs when the analytical results from a downstream surface water for any constituent exceeds the **Draft Surface Water Standards** or the **Drinking Water Standard** for that constituent, which can be attributed to the site. The relevant standards are contained in the Draft European Communities Environmental Objectives (Surface Waters) Regulations, 2008 and the Drinking Water Standard **S.I.**

No. 278 of 2007. The Drinking Water Standard came into operation in June 2007 (Appendix 1.1). The standard applied will be the more stringent of the standards in either legislation in the case where there is a difference between the two standards. The exceedance score applies whether a release has occurred or not. The score is applied for any one exceedance.

SCORING

Exceedance	Score
YES	200
NO	0

Table 5.2. Scores assigned to the 'exceedances of water standards' sub-factor.

Information requirements and sources:

The information required to score this sub-factor is:

- Analytical results for surface water upstream AND downstream of the site from work carried out during this project.
- Evidence that the element is attributable to the site.

5.1.3 Potential to release

The potential to release is evaluated by:

- The extent to which waste at the site are contained; and
- The distance from waste to surface water.

<u>Site containment</u>

Containment of the waste pile is assessed by reference to any as-built engineering drawings and by a visual inspection of the facility. Surface water from a waste pile may be contained by engineered features designed to mitigate releases to surface waters. Engineered features include dams, diversions and sediment basins or traps. Surface water run-off can also be contained by bodies of standing water, such as open-pit lakes. Any of these structures must be intact, functioning, and monitored / maintained regularly.

SCORING

Containment	Score
No containment	40
Presence of ONE of the following: dams, diversions, pit lakes and sediment basins or traps	20
Presence of TWO of the following: dams, diversions, pit lakes and sediment basins or traps	10
Presence of all THREE of the following: dams, pit lakes, diversions and sediment basins or traps	1

Table 5.3. Scores assigned to the 'containment' of the waste pile under consideration.

Distance to nearest surface water drainage

The distance to the nearest surface water drainage, including intermittent drainages, is measured during the field work at the site, in metres.

SCORING

Distance to nearest surface drainage	Score
<10m	10
10 – 30m	5
>30m	1

Table 5.4. Scores assigned to the 'distance to the nearest surface water drainage' from the waste pile under consideration.

Potential to Release Score

The total score for potential to release to obtained as the product of ***Containment*** and ***Distance to the nearest surface water drainage***.

Containment score X Distance to the nearest surface water drainage score

Information requirements and sources:

The information required to score this sub-factor is:

- Containment: visual inspection at the site into the presence, functioning and maintenance / monitoring of dams, diversions, pit lakes and sediment basins or traps.
- Distances of waste pile(s) to nearest surface water drainage: measured either in the field or within the GIS program.

TOTAL Likelihood of Release SCORE

The total score for LIKELIHOOD TO RELEASE is obtained by summing the three sub-factors:

Observed releases to surface water score + Exceedances of water standards score + Potential to release score

The score will range from a low 1 of to a high of 800.

5.2 Receptors

The receptor sub-factor is evaluated by assessing the following:

- The number of persons using surface water for drinking.
- Impacted drainages.
- Other water users.

5.2.1 The number of persons using surface water for drinking

The number of persons using surface water for drinking is obtained from the compilation of Abstractions of Ground and Surface Water in Ireland prepared for the Water framework Directive and published in 2007 within 10km downstream of the site. Each and every abstraction is counted and the sum calculated.

SCORING

Abstraction no.	Score
1	No. of people serviced by abstraction no. 1
2	No. of people serviced by abstraction no. 2
⋮	⋮
n	No. of people serviced by abstraction no. n

TOTAL	$\sum_{n=1}^{n}(no.\_of\_people\_served\_by\_abstraction\_n)$

Table 5.5. Scoring the 'number of persons using surface water for drinking' sub-factor.

Information requirements and sources:

The information for this sub-factor is obtained from Abstractions of Ground and Surface Water in Ireland prepared for the Water Framework Directive and published in 2007. The 10km radius is obtained from the GIS project.

5.2.2 Impacted drainage

Impacted drainage is approached differently for both Solid and Liquid sources.

5.2.2.1 Solid Waste

An impacted drainage score is applied to solid waste heaps if the waste heap is within 100m of a drainage system. The presence of a drain within 100m of the waste heap that links the heap with a drainage system also results in an impacted drainage score for the waste heap. Drainage refers to small streams, rivers or constructed channels that can facilitate the transfer of any surface water to the local river network.

SCORING

Presence	Score
YES	200
NO	0

Table 5.6. Scoring the 'drainage system' sub-factor.

Information requirements and sources:

The information required for this sub-factor is:

- The presence of a drainage system gathered during field work at the site.
- The distance within 100m is measured using the ArcGIS system.

5.2.2.2 Liquid Waste

This is the cumulative total length of a river or stream impacted downstream by discharges issuing from the mine. The length of an impacted river or stream is estimated from the chemical composition of water or stream sediment samples. A stream is impacted if the analytical results of water sampled or stream sediments sampled down stream of a mining facility is THREE times the upgradient concentration of surface water for that constituent. The stream length, in metres, is the figure used in scoring. This value is divided by 100 to obtain the score.

SCORING

= Measured impacted drainage length (m) / 100

Information requirements and sources:

The information required to score this sub-factor is:

- Analytical results for surface water upstream AND downstream of the site from work carried out during this project.

OR

- Analytical results for stream sediments upstream AND downstream of the site from work carried out during this project.

AND

- Evidence that the element is attributable to the site.
- The length is measured using the GIS system.

5.2.3 Other users

Other uses are:

- Fishery class.
- Recreational use.
- Protected area status (SACs, SPA, NHA, and National Parks).
- Livestock watering.

These are assessed within a 10km radius downstream of the site. They are assessed from observations on the site visit and data available from other agencies.

SCORING

Use	Class or Category	Score
Fishery class	Salmonid	20
	No classification	0

Recreational use	Observed	5
	Not observed	0

Protected area status	YES	20
	NO	0

Livestock watering	YES	20
	Unknown	10

Information requirements and sources:

- Fishery classification data are obtained from the Central Fisheries Board and the EPA.
- Recreational use is observed while in the field.
- Protected areas designations are obtained from the classifications prepared by the National Parks and Wildlife Service and are available online at www.npws.ie
- Livestock watering is observed while in the field.

TOTAL Receptor SCORE

The Total Receptor Score is the sum of the above six sub-factors.

(No. of persons using surface water for drinking) + ***(Impacted drainage)*** + (***Fishery class***) + (***Recreational use***) + (***Protected area status***) + (***Livestock watering***)

TOTAL SURFACE WATER SCORE

The total Surface Water pathway score is obtained by multiplying the three main factors together:

[Likelihood of Release] X [Hazard (waste characteristics)] X [Receptors]

6. SCORING THE AIR PATHWAY

In this section both the information sources used for the scoring and the scoring for each of the 'Likelihood of Release' and 'Receptor' factors for the air pathway are described. Refer to Worksheet No. 4 in the Solid source workbook.

6.1 Likelihood of Release

The likelihood of release score evaluates two sub-factors:

- Observed release to the air pathway.
- Potential to release.

6.1.1 Observed release to the air pathway

An observed release to the air pathway is defined in three ways:

- Material (dust) observed blowing off the site during any site visit.
- Evidence of wind deposited waste away from the waste source.
- Anecdotal evidence from other investigators, local residences or other reliable sources attributable to the site.

One or more of the constituents in the source must be more than THREE times the background concentration of that constituent.

SCORING

Observed release	Score
YES	300
NO	0

Table 6.1. Scores assigned to the 'observed release to the air pathway' sub-factor.

Information requirements and sources:

The information required for this sub-factor is derived by:

- Observation while on the site visit;
- Discussions with local residents;
- Research carried out by others and recorded in reports and documents;
- Concentrations of constituents in soils in and around the site; and
- The National Soils Database.

6.1.2 Potential to release

The potential to release to the air pathway is evaluated by the criterion:

- Containment of the waste at the site.

The containment of waste with respect to the air pathway is facilitated by the presence of topsoil, vegetative cover or perennially wet cover. The percentage of any of these three is estimated and used as the basis for scoring.

SCORING

Description	% cover	Score
High dust potential	<50% or screening	300
Moderate dust potential	50 – 75%	200
Low dust potential	75 – 95%	100
No dust potential	>95%	10

Table 6.2. Scores assigned to the 'potential to release' sub-factor.

Information requirements and sources:

The information required for this sub-factor is obtained by observation during the site visit.

Potential to Release Score

The potential to release score is given by the ***Containment of the waste at the site*** score*.*

TOTAL Likelihood of release SCORE

The total score for LIKELIHOOD TO RELEASE is obtained by summing the two sub-factors:

Observed release score + Potential to release score

The score will range from a low 10 of to a high of 600.

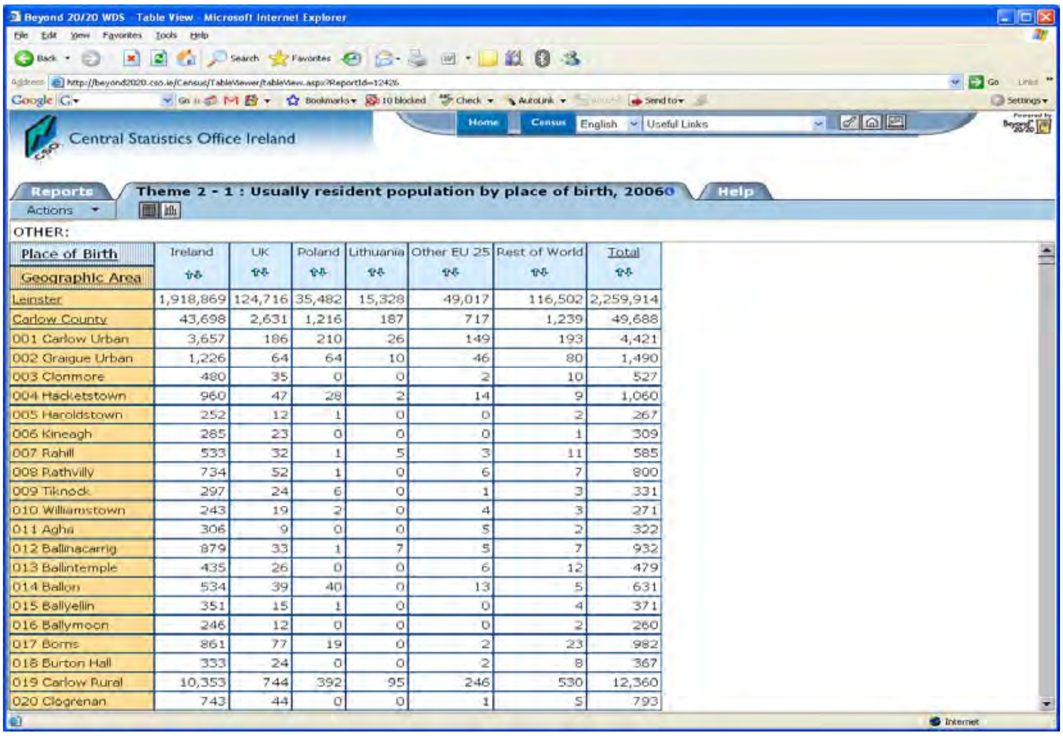
6.2 Receptors

The air pathway receptor sub-factor is evaluated by assessing the following:

- Population within 1km of a waste pile at the site.
- Distance to the nearest residence.
- Sensitive environments.

6.2.1 Population within 1km of the site.

The number of persons within 1km of the site is obtained from the 2006 National Census. The data is obtained from the CSO website (www.cso.ie). The statistics are broken down by nationality and include a total population figure for each Electoral Division area (Figure 6.1).



Theme 2 - 1 : Usually resident population by place of birth, 2006

OTHER:

Place of Birth Geographic Area	Ireland	UK	Poland	Lithuania	Other EU 25	Rest of World	Total
Leinster	1,918,869	124,716	35,482	15,328	49,017	116,502	2,259,914
Carlow County	43,698	2,631	1,216	187	717	1,239	49,688
001 Carlow Urban	3,657	186	210	26	149	193	4,421
002 Graigue Urban	1,226	64	64	10	46	80	1,490
003 Clonmore	480	35	0	0	2	10	527
004 Hacketstown	960	47	28	2	14	9	1,060
005 Haroldstown	252	12	1	0	0	2	267
006 Kineagh	285	23	0	0	0	1	309
007 Rahill	533	32	1	5	3	11	585
008 Rathvilly	734	52	1	0	6	7	800
009 Tiknock	297	24	6	0	1	3	331
010 Williamstown	243	19	2	0	4	3	271
011 Agha	306	9	0	0	5	2	322
012 Ballinacarrig	879	33	1	7	5	7	932
013 Ballintemple	435	26	0	0	6	12	479
014 Ballon	534	39	40	0	13	5	631
015 Ballyellin	351	15	1	0	0	4	371
016 Ballymoon	246	12	0	0	0	2	260
017 Borris	861	77	19	0	2	23	982
018 Burton Hall	333	24	0	0	2	8	367
019 Carlow Rural	10,353	744	392	95	246	530	12,360
020 Clogrenan	743	44	0	0	1	5	793

Figure 6.1. Screen dump from the CSO website showing the figures used in the 'population within 1km of the site sub-factor'.

SCORING

The National Census reports information on an Electoral Division basis. There are 3409 Electoral Divisions in the country (Appendix 1.3). It is necessary to identify the Electoral Division or Electoral Divisions relevant to the site under consideration. This is achieved through GIS. Obviously a buffer of 1km around a facility will not coincide with an Electoral Division. The area intersected by the 1km buffer should be expressed as a percentage of the total area of the Electoral Division (adjusted area) and this percentage is used to calculate the population within 1km of the site.

Once the population within 1km of the site has been determined the following Table is used to assign the score.

Population range	Score
0	0
1 – 10	1
10 – 30	10
30 – 100	30
100 – 300	100
300 – 1,000	300
1,000 – 3,000	1,000
3,000 – 10,000	3,000
>10,000	10,000

Table 6.3. Scores assigned to the 'population within 1km of the site' sub-factor.

Information requirements and sources:
The population statistics is obtained from the CSO website (www.cso.ie).

6.2.2 Distance to nearest residence
The distance to the nearest residence is measured in metres. It is obtained from the site survey or by assuming the nearest building to the site is a residence on air photographs.

SCORING

Distance (m)	**Score**
<100	20
100 – 200	15
200 – 300	10
>300 or unknown	5

Table 6.4. Scores assigned to the 'distance to the nearest residence' sub-factor.

Information requirements and sources:
The distance to the nearest residence is obtained during the field survey or from air photographs.

6.2.2 Sensitive environments
Sensitive environments are designated sites, such as:

- Natural Heritage Area (NHA)
- Special Protection Area (SPA)
- Special Area of Conservation (SAC)
- Statutory Nature Reserve
- National Park

SCORING

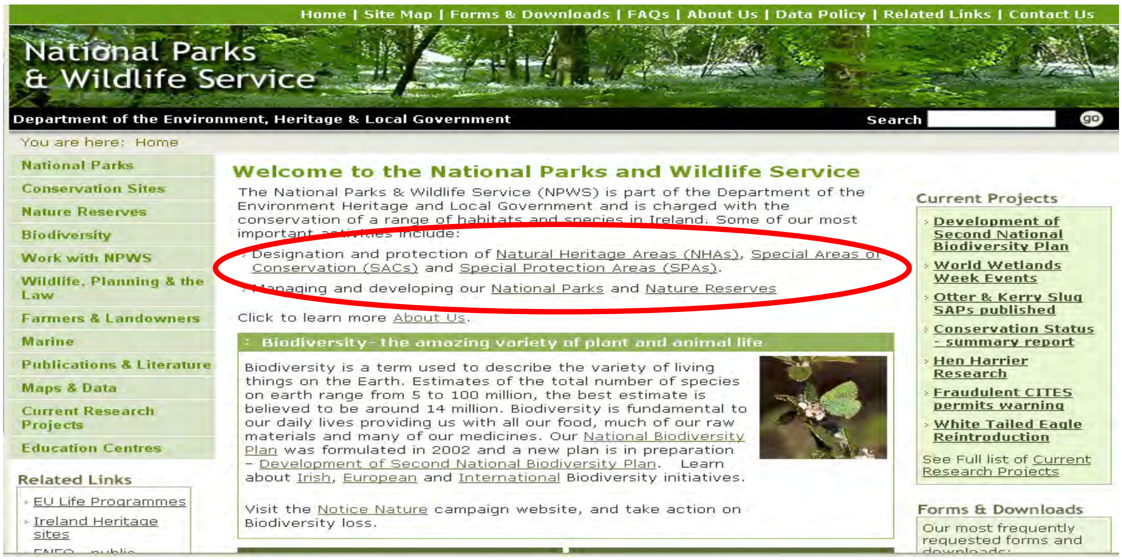
If any of **Natural Heritage Area** (NHA), **Special Protection Area** (SPA), **Special Area of Conservation** (SAC), **Statutory Nature Reserve** or **National Park** are within 1km of a mine waste site then the following scores should be applied. If more than one area is within the 1km radius then the presence score is multiplied by the number of designated areas present.

Designated area	**Score**
Present	20
Absent	0

Table 6.5. Scores assigned to the 'sensitive environment' sub-factor.

Information requirements and sources:

These sites are published on the National Parks and Wildlife Service website in GIS format. This is imported to our GIS project and the presence or absence within 1km of a mine waste site of these special areas determined. The NPWS website is www.npws.ie (see Figure 6.2 for a view of the home page).



Welcome to the National Parks and Wildlife Service

The National Parks & Wildlife Service (NPWS) is part of the Department of the Environment Heritage and Local Government and is charged with the conservation of a range of habitats and species in Ireland. Some of our most important activities include:

- Designation and protection of Natural Heritage Areas (NHAs), Special Areas of Conservation (SACs) and Special Protection Areas (SPAs).
- Managing and developing our National Parks and Nature Reserves

Click to learn more About Us.

Biodiversity - the amazing variety of plant and animal life

Biodiversity is a term used to describe the variety of living things on the Earth. Estimates of the total number of species on earth range from 5 to 100 million, the best estimate is believed to be around 14 million. Biodiversity is fundamental to our daily lives providing us with all our food, much of our raw materials and many of our medicines. Our National Biodiversity Plan was formulated in 2002 and a new plan is in preparation – Development of Second National Biodiversity Plan. Learn about Irish, European and International Biodiversity initiatives.

Visit the Notice Nature campaign website, and take action on Biodiversity loss.

See Full list of Current Research Projects

Our most frequently requested forms and

Figure 6.2. Screen dump of the NPWS home page.

TOTAL Receptor SCORE

The total score for the Air pathway is the sum of the above three:

Population score + ***Distance to nearest residence score*** + ***Sensitive environments score***

TOTAL AIR PATHWAY SCORE

The total Air pathway score is obtained by multiplying the three main factors together:

[Likelihood of Release] X [Hazard (waste characteristics)] X [Receptors]

7. SCORING THE DIRECT CONTACT (WASTE PILES) PATHWAY

In this section both the information sources used for the scoring and the scoring for each of the 'Likelihood of Release' and 'Receptor' factors for the direct contact (waste piles) are described. Refer to Worksheet No. 5 in the Solid sources workbook.

In this section both the information sources used for the scoring and the scoring for each primary factor for the direct contact pathway are described.

7.1 Likelihood of Release

The likelihood of release score evaluates two sub-factors:

- Observed exposure.
- Potential exposure.

7.1.1 Observed exposure

An observed exposure is defined in two ways:

- Residence within 250m of the mine waste.
- Used for recreational purposes – either permitted or not permitted. Examples of recreational activity include quad biking, pony trekking, clay pigeon shooting. These may be direct observation or evidence of such activities taking place, e.g., quad bike tracks.

One or more of the constituents in the source must be more than THREE times the background concentration of that constituent and attributable to the site.

Residence within 250m of a mine waste

Information requirements and sources:

Residences can be observed either on the site visit or through the examination of air photographs.

SCORING

The score for the direct contact pathway is allocated as follows:

Criterion	Score
Residence within 250m of the site	200
No residence within 250m of the site	0

Table 7.1. Score assigned to 'residence within 250m of the site' sub-factor.

Used for recreational purposes

Information requirements and sources:

Whether the site is used for recreational use or not may be observed while on the site or through the observation of on-site evidence for such activities.

Criterion	Score
Used for recreational use	200
Not used for recreational use	0

Table 7.2. Score assigned to 'used for recreational use' sub-factor.

Observed Exposure Score

The Observed Exposure score is the sum of Residence within 250m of a mine waste and Used for recreational purposes sub-factors.

Residence within 250m of a mine waste score + Used for recreational purposes

7.1.2 Potential exposure

This is assessed by determining the accessibility of the mine waste site and the distance to the nearest residence.

Accessibility is evaluated with respect to fencing, signs and other physical barriers or deterrents present at the site which restrict access to the site. These access restrictions must be intact and partially effective at limiting access to people.

Site accessibility is scored by evaluating both, the type of access restrictions employed and the condition /maintenance of the access restrictions.

Access restrictions

The type of access restrictions are scored as in Table 7.3.

SCORING

Access restrictions	Score
Easily accessible (no fences, gates or signs)	20
Moderately accessible (barbed wire fences, road gated, signage)	10
Difficult access (chain link fence, road gated and locked)	5
Not accessible (site completely fenced, access road gated and locked, on site security within 250m of the waste pile)	1

Table 7.3. Scores assigned to the type of access restrictions employed at a site.

Information requirements and sources:

Site observation is required to evaluate this accessibility.

Maintenance of the site restrictions

The condition of the fencing and other restriction are scored according to Table 7.4.

SCORING

Condition of restrictions	Score
Well maintained, no breaches	0.1
Small animals can access with ease. Humans and animals can access with difficulty. Vehicles cannot gain entry. Less than three breaches.	0.7
Small animals, human and livestock can access with ease. Vehicles* can enter. Less than five breaches.	1.0
Small animals, human and livestock can access with ease. Vehicles* can enter. More than five breaches.	2.0

Table 7.4. Scores assigned to the 'condition of restrictions' sub-factor.
*** A vehicle can be a motor cycle, quad bike or car.**

Information requirements and sources:
Site observation is required to evaluate maintenance of the site restrictions.

Distance to the nearest residence
The distance to the nearest residence is measured in metres. It is obtained from the site survey or by assuming the nearest building to the site is a residence on air photographs.

SCORING

Distance (m)	Score
<500	20
500 – 1,000	10
>1,000	5

Table 7.5. Scores assigned to the 'distance to the nearest residence' sub-factor.

Information requirements and sources:
The distance to the nearest residence is obtained during the field survey or from air photographs.

Potential Exposure Score

The score for the Potential Exposure factor is the product of the site restrictions score, the condition of the site restrictions score and the distance to the nearest residence score.

***Site restrictions score* X *condition of the site restrictions score* X *distance to the nearest residence score*.**

TOTAL Likelihood of release SCORE

The total score for LIKELIHOOD TO RELEASE is obtained by summing the two sub-factors Observed exposure + Potential Exposure:

Observed exposure + ***Potential Exposure***

The score will range from a low of 0.5 to a high of 1,200.

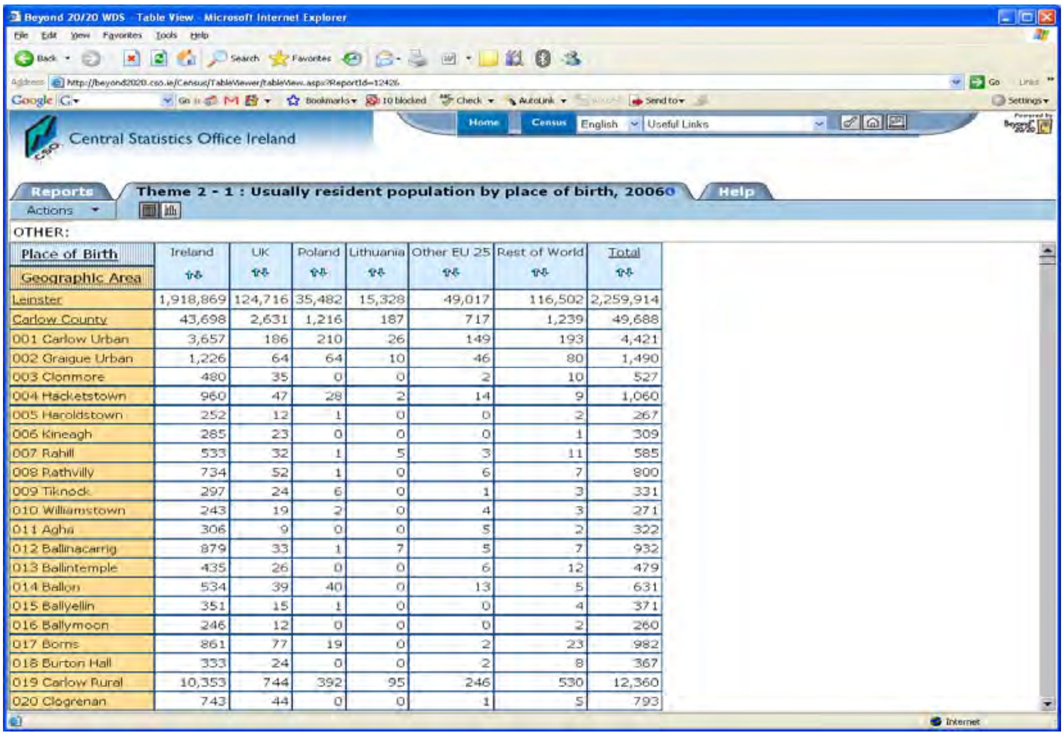
7.2 Receptors

The direct contact pathway receptor sub-factor is evaluated by assessing the following:

- Population within 2km of a waste pile at the site.
- Distance to the nearest residence.
- On site workers.
- Attractiveness of the site for recreational use.

7.2.1 Population within 2km

The number of persons within 2km of the site is obtained from the 2006 National Census. The data is obtained from the CSO website (www.cso.ie). The statistics are broken down by nationality and include a total population figure for each Electoral Division area (Figure 7.1).



Theme 2 - 1 : Usually resident population by place of birth, 2006

OTHER:

Place of Birth / Geographic Area	Ireland	UK	Poland	Lithuania	Other EU 25	Rest of World	Total
Leinster	1,918,869	124,716	35,482	15,328	49,017	116,502	2,259,914
Carlow County	43,698	2,631	1,216	187	717	1,239	49,688
001 Carlow Urban	3,657	186	210	26	149	193	4,421
002 Graigue Urban	1,226	64	64	10	46	80	1,490
003 Clonmore	480	35	0	0	2	10	527
004 Hacketstown	960	47	28	2	14	9	1,060
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017 Borris	861	77	19	0	2	23	982
018 Burton Hall	333	24	0	0	2	8	367
019 Carlow Rural	10,353	744	392	95	246	530	12,360
020 Clogrenan	743	44	0	0	1	5	793

Figure 7.1. Screen dump of page from the CSO website showing population statistics.

SCORING

The National Census reports information on an Electoral Division basis. There are 3409 Electoral Divisions in the country (Appendix 1.3). It is necessary to identify the Electoral Division or Electoral Divisions relevant to the site under consideration. This is achieved through GIS. Obviously a buffer of 2km around a facility will not coincide with an Electoral Division. The area intersected by the 2km buffer should be expressed as a percentage of the total area of the Electoral Division (adjusted area) and this percentage is used to calculate the population within 2km of the site

Population range	Score
0	0
1 – 10	1
10 – 30	10
30 – 100	30
100 – 300	100
300 – 1,000	300
1,000 – 3,000	1,000
3,000 – 10,000	3,000
>10,000	10,000

Table 7.6. Scores assigned for the 'population within 2km of the site' sub-factor.

Information requirements and sources:
The number of wells is obtained from the CSO website (www.cso.ie).

7.2.2 Distance to nearest residence

The distance to the nearest residence is measured in metres. It is obtained from the site survey or by assuming the nearest building to the site is a residence as displayed on air photographs.

SCORING

Distance (m)	Score
<500	10
500 – 1,000	5
>1,000 or unknown	0

Table 7.7. Scores assigned to the 'distance to the nearest residence' sub-factor.

Information requirements and sources:
The distance to the nearest residence is obtained during the field survey or from air photographs.

7.2.3 On-site workers

At a number of sites post mining activities were taking place. This involved workers being in contact with the waste piles to a greater or lesser extent depending on the nature of the post mining activity.

SCORING

On-site workers	Score
Predominantly working outside	200
Farmers	100
Predominantly working inside	50
No workers	0

Table 7.8. Scores assigned to the 'on-site workers' sub-factor.

Information requirements and sources:
The information required to score on-site workers is made by direct observation during the site visit.

7.2.4 Attractiveness of the site for recreational use

Recreational use is evaluated to take into account those people who live outside the 2km radius. Some sites may be more attractive than others for such use and may be influenced by criteria such as:

- Proximity to heavily populated areas.
- Proximity to roads.
- Uncommon feature attracting visitors to the site.
- Proximity to other attractions.
- Evidence of the use of the site for recreational use.
- Mining heritage.

SCORING

The attractiveness of the site for recreational use is scored as in Table 7.9.

Observation	Score
Highly attractive for recreational use	100
Moderately attractive for recreational use	50
Low attractiveness for recreational use	25
Not attractive for recreational use	0

Table 7.9. Scores assigned to the 'attractiveness of the site for recreational use' sub-factor.

TOTAL Receptor SCORE

The total score for RECEPTOR is the sum of the four sub-factors – Population score, Distance to the nearest residence score, On-site workers score and Attractiveness of the site for recreational use score.

Population score + ***Distance to the nearest residence score*** + ***On-site workers score*** + ***Attractiveness of the site for recreational use score***

TOTAL DIRECT CONTACT PATHWAY (waste piles) SCORE

The total **DIRECT CONTACT** (Waste Pile) pathway score is obtained by multiplying the three main factors together:

[Likelihood of Release] X [Hazard (waste characteristics)] X [Receptors]

8. SCORING THE DIRECT CONTACT (STREAM SEDIMENTS) PATHWAY

In this section both the information sources used for the scoring and the scoring for each of the 'Likelihood of Release' and 'Receptor' factors for the direct contact (stream sediments) are described. Refer to Worksheet No. 2 in the Stream Sediments score workbook.

8.1 Likelihood of Release

The likelihood of release score evaluates a single sub-factor:

- Observed exposure.

8.1.1 Observed exposure

One or more of the constituents in the stream sediments must be at a concentration level that is more than THREE times the upstream concentration levels and that the constituent is attributable to the site. It is assumed that livestock will have access to any length of stream section.

An observed exposure is defined as:

- A farm within 250m of the stream or drainage section.

Information requirements and sources:

Farms can be observed either on the site visit or through the examination of air photographs.

SCORING

Criterion	Score
Farm within 250m of the stream or drainage	200
No farm within 250m of the stream or drainage	0

Table 8.1. Score assigned to 'residence within 250m of the site' sub-factor.

TOTAL Likelihood of release SCORE

The total score for LIKELIHOOD TO RELEASE is obtained from the Observed Exposure score.

Observed exposure score

The score will range from a low 0 of to a high of 200.

8.2 Receptors

The direct contact (stream sediments) pathway receptor sub-factor is evaluated by assessing:

- Livestock accessing the stream.

When livestock access a stream for watering they will, more than likely ingest some of the bottom sediment. Evidence therefore for cattle using any particular stream can be by direct observation or through indirect evidence such as hoof prints in the stream.

SCORING

Livestock using stream for watering	Score
Livestock observed in stream or other signs, e.g., hoof marks	200
Unknown	100

Table 8.2. Scores assigned to the 'livestock using stream for watering' sub-factor.

Information requirements and sources:

Evidence for assessing whether livestock use a stream for watering is obtained during the field survey or from air photographs.

TOTAL Receptor SCORE

The total score for RECEPTOR is the Livestock using stream for watering score.

Livestock using stream for watering score

TOTAL DIRECT CONTACT PATHWAY (stream sediments) SCORE

The total **DIRECT CONTACT** (Stream Sediments) pathway score is obtained by multiplying the three main factors together:

[Likelihood of Release] X [Hazard (waste characteristics)] X [Receptors]

9. TOTAL SITE SCORE FOR HUMAN AND ANIMAL HEALTH

9.1 Total Waste Score

The total waste score for each waste or contamination type (solid waste, liquid waste and stream sediment contamination) is determined as described in the following sub-sections.

9.1.1 Solid Waste

The total score for solid waste is obtained by summing the total for each of the relevant pathways – Groundwater, Surface water, Air and Direct Contact (waste piles) pathways and dividing by 100,000. The subscript **sw** indicates a solid waste score.

(**GROUNDWATER**$_{sw}$ Score + **SURFACE WATER**$_{sw}$ Score + **AIR PATHWAY**$_{sw}$ Score + **DIRECT CONTACT (Waste Piles)**$_{sw}$ Score) / 100,000

9.1.2 Liquid Waste

The total score for liquid waste is the summation of the Groundwater pathway score and Surface water pathway score. This total is then divided by 100,000 to give the total Liquid waste score. The subscript **lw** indicates a liquid waste score.

(**GROUNDWATER**$_{lw}$ Score + **SURFACE WATER**$_{lw}$ Score) / 100,000

9.1.3 Stream Sediments

The total stream sediments score is the total of Direct Contact (Stream sediment) pathway divided by 100,000. The subscript **ss** indicates stream sediment contamination.

(**DIRECT CONTACT (Stream Sediments)**$_{ss}$ Score) / 100,000

9.2 Final Mine Site Score

The final score for a mine site is the sum of all the individual waste scores, i.e., for all waste piles, mine discharges and stream sediments.

FINAL Mine Site Score

Total **Solid** Waste score + Total **Liquid** Waste score + Total **Stream Sediments** score

9.3 Classification

All sites are then classified as follows:

Class	**Score**	**Description**	**Response**
I	>2,000	Relates to large complex sites which have a number of issues, the sites contain large volumes of metal-rich waste that potentially pose risks to human and animal health and safety as well as the environment.	These sites should have a full risk assessment carried out. These sites should be monitored on an ongoing basis.
II	1,000 – 2,000	A district consisting of several sites, containing numerous small spoil piles with high concentrations of metals and are visited regularly by the public. Accordingly these sites potentially pose risks to human and animal health and safety as well as the environment.	These sites require general monitoring of most or all waste piles, discharges or stream sediments on an annual basis.
III	300 – 1,000	Sites containing fewer and smaller spoil piles which have high concentrations of metals. The sites are used by the public and potentially pose risks to human and animal health and safety as well as to the environment.	These sites require general monitoring of most or all waste piles, discharges or stream sediments on a biennial basis.
IV	100 – 300	Sites which generally have large volumes of waste with low concentrations of those metals that potentially pose risks to human and animal health and safety as well as to the environment. Any high metal spoil piles are very small in volume.	These sites require specific monitoring of particular waste piles, discharges or stream sediments on a five-yearly basis.
V	<100	These sites pose little threat to humans, animals or the environment, although there may be minor site specific issues which need to be addressed	These site generally do not require monitoring except where there are minor specific issues.

APPENDIX 1.1

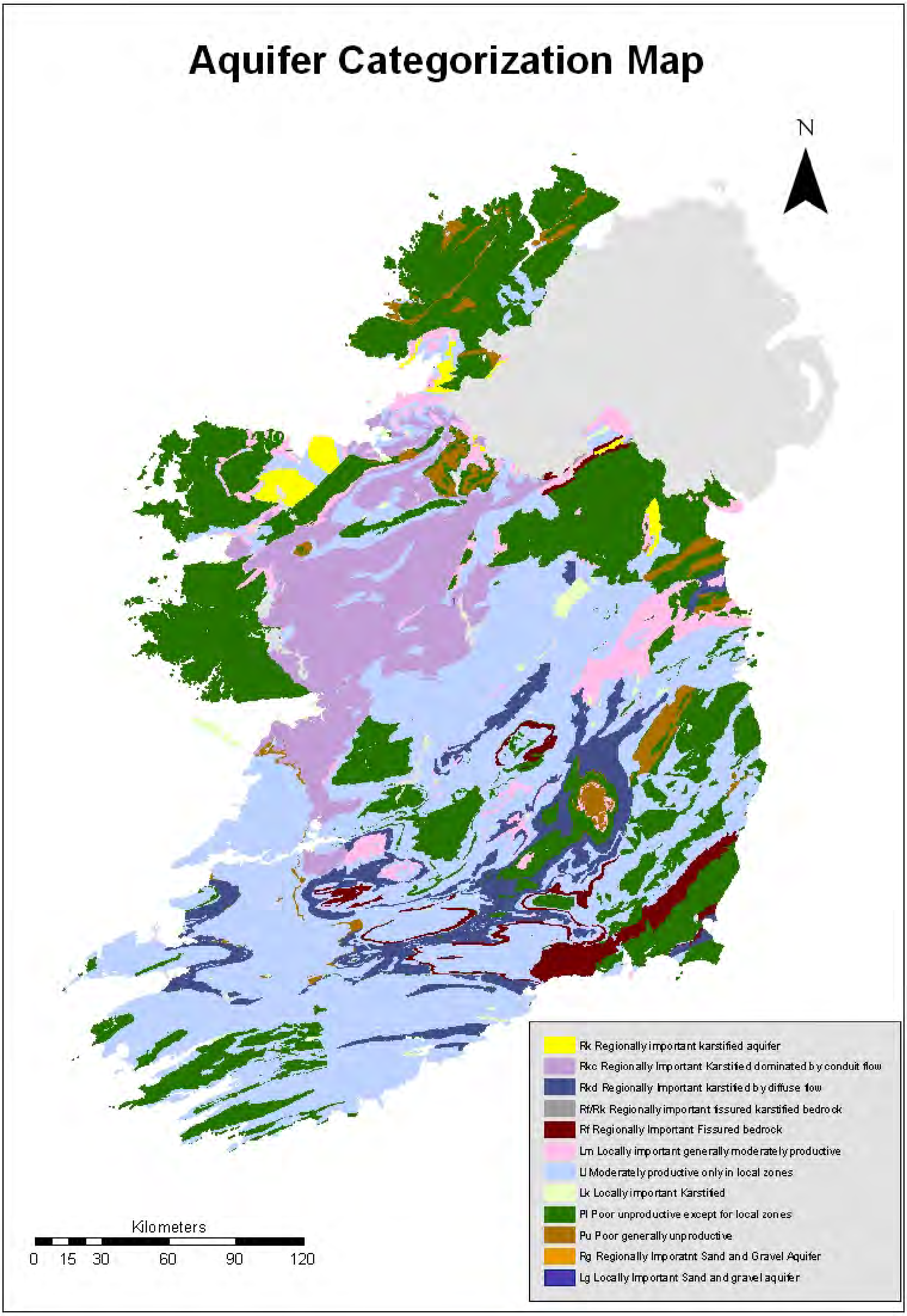
Water standards used for the HMS-IRC project.

Parameter	Unit	Standard	Source
pH		≥ 6.5–≤ 9.5	SI 278 (2007)
EC	mS/cm	≤ 2.5	SI 278 (2007)
Al	µg/l	200	SI 278 (2007)
As	µg/l	25	Draft EC (2008)
Cd	µg/l	0.25	Draft EC (2008)
Cr	µg/l	50	SI 278 (2007)
Cr III	µg/l	4.7	Draft EC (2008)
Cr IV	µg/l	3.4	Draft EC (2008)
Cu [hardness < 100 mg/l $CaCO_3$]	µg/l	5	Draft EC (2008)
Cu [hardness > 100 mg/l $CaCO_3$]	µg/l	30	Draft EC (2008)
Hg	µg/l	0.05	Draft EC (2008)
Fe	µg/l	200	SI 278 (2007)
Mn	µg/l	50	SI 278 (2007)
Na	µg/l	200,000	SI 278 (2007)
Ni	µg/l	20	Draft EC (2008)
Pb	µg/l	7.2	Draft EC (2008)
Sb	µg/l	5	SI 278 (2007)
Se	µg/l	10	SI 278 (2007)
SO_4	µg/l	250,000	SI 278 (2007)
Zn [hardness < 10 mg/l $CaCO_3$]	µg/l	8	Draft EC (2008)
Zn [hardness 10-100 mg/l $CaCO_3$]	µg/l	50	Draft EC (2008)
Zn [hardness > 100 mg/l $CaCO_3$]	µg/l	100	Draft EC (2008)

APPENDIX 1.2

Aquifer Categorization

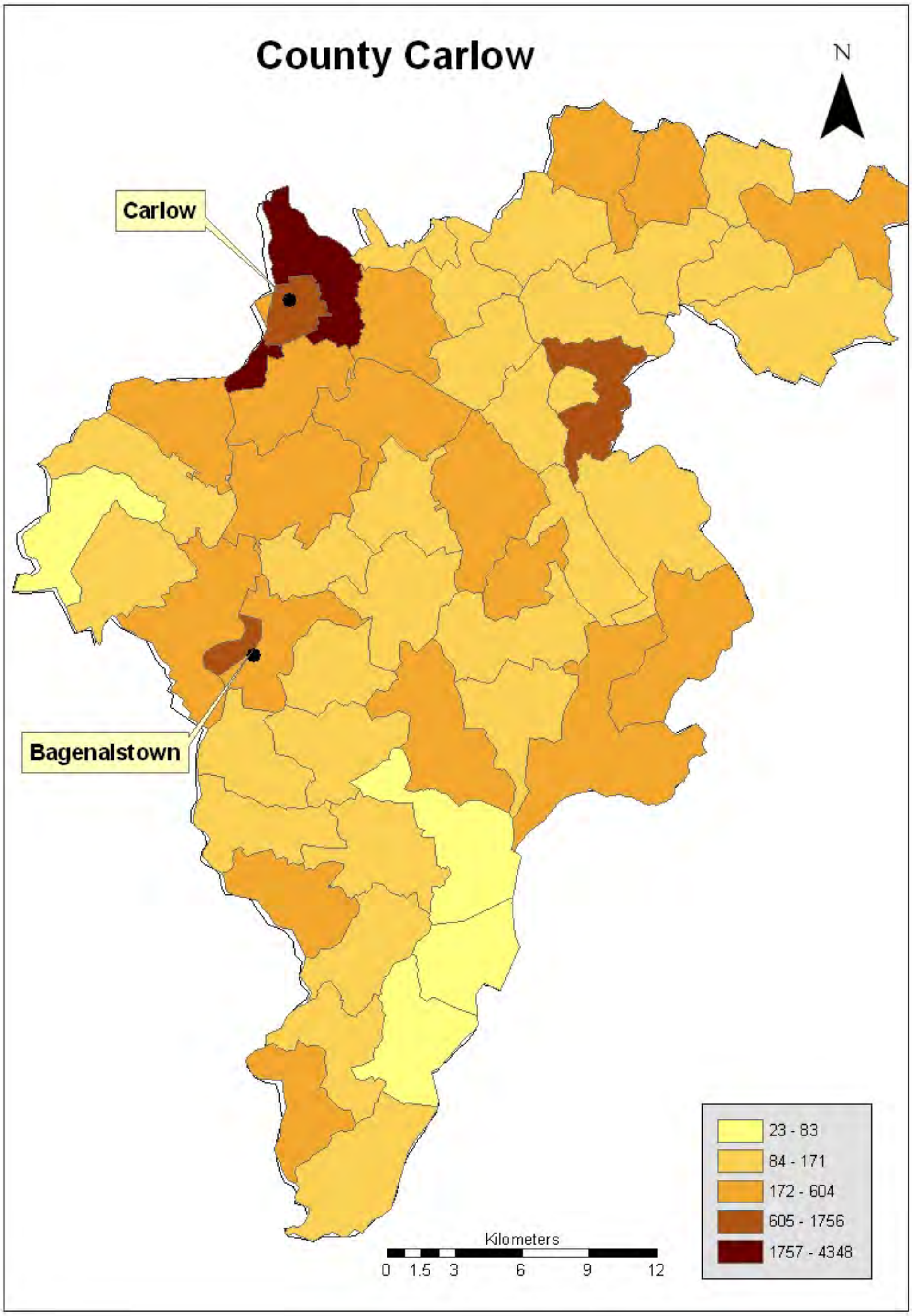
(Water Framework Directive)



APPENDIX 1.3

District Electoral Divisions

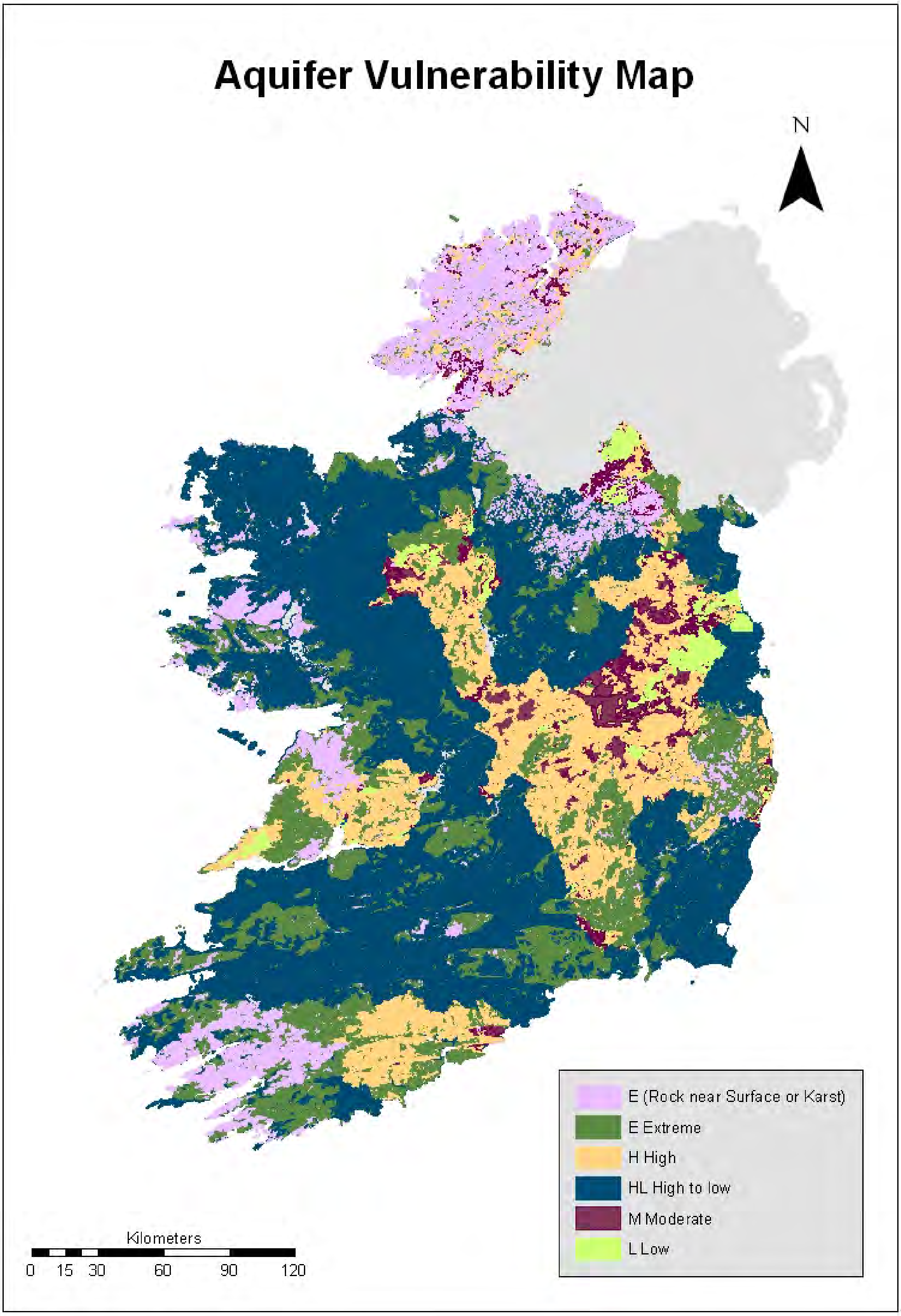
There are 3409 DED in the 26 counties in Ireland. The map below displays County Carlow. This contains 54 different DED within its area of 90,018ha.



APPENDIX 1.4

Groundwater vulnerability map

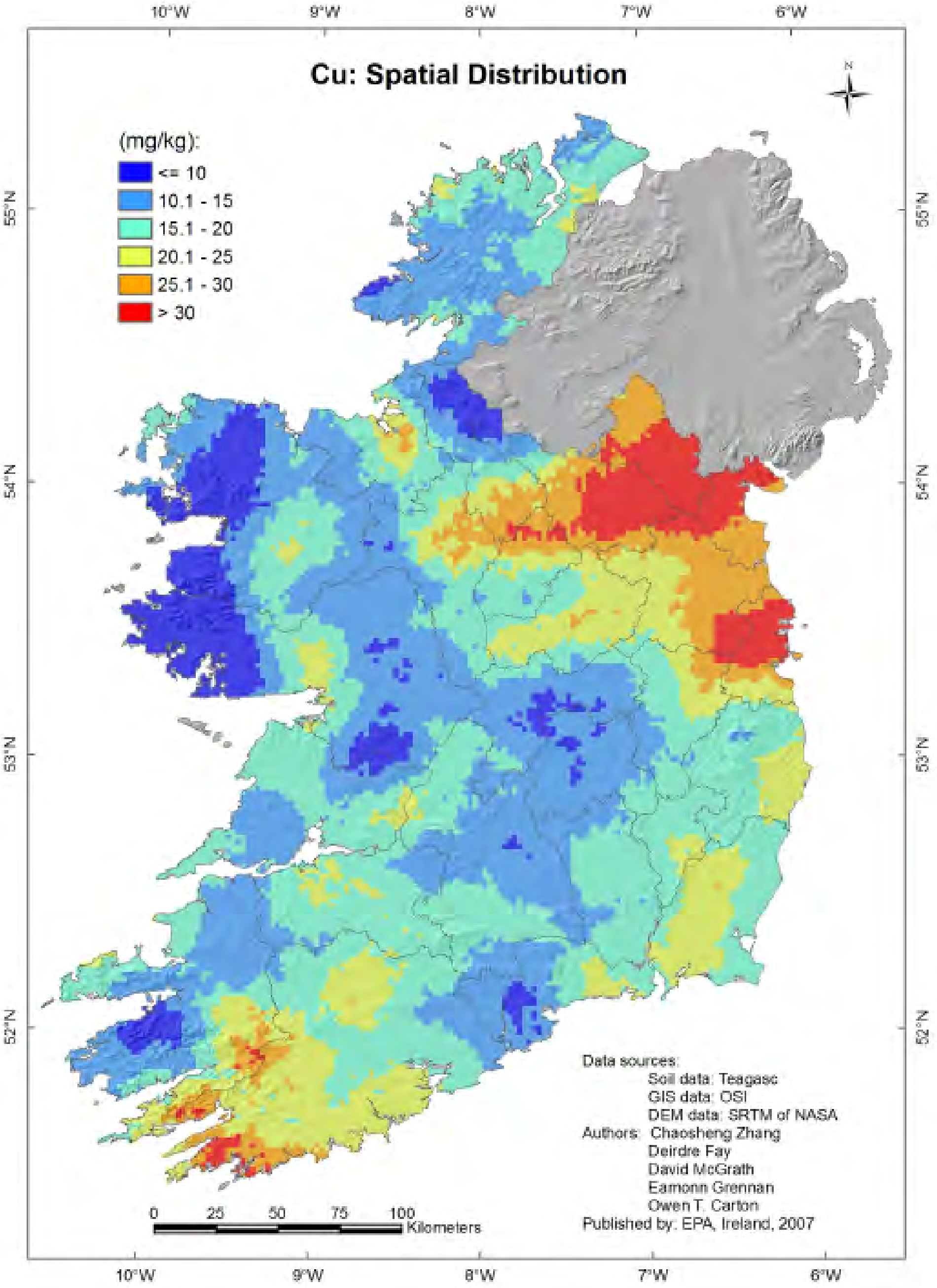
(Water Framework Directive)



APPENDIX 1.5

Soils Geochemical Atlas of Ireland

The National Soils Database was used as a guideline to natural background levels present in soils in Ireland. **The Soils Geochemical Atlas of Ireland**, Fay *et al.*, (**2007**) provided a baseline of soil geochemistry. It was used as a point of reference for both stream sediments and direct contact (waste piles). Mine waste, obviously does contain higher and more localised concentrations of elements attributed to the specific mine conditions. The atlas is good statistical indication of the distribution of elements around Ireland. The atlas is available from the EPA website (http://erc.epa.ie/safer/iso19115/displayISO19115.jsp?isoID=105). Below is an example of krigged Cu data. Krigging is an interpolation technique used to estimate value at regular intervals from originally more widely spaced data.



Appendix 2
Geochemical Sampling Protocol

1. Stream sediment sampling and analysis

General Information

Sampling protocols will *essentially* follow those described for the FOREGS programme (www.gsf.fi/**foregs**/geochem/fieldman.pdf). However, this programme is designed for regional geochemical studies rather than contamination studies so some modifications will be required in respect of the number and location of sub-samples collected. The <150µm size fraction is particularly useful for regional geochemistry sampling, especially where common ore metals are of interest, but other size fractions may also be considered for contamination studies.

Regional geochemical studies sample the active stream sediment, i.e. the fine- to medium-grained bed-load material (silty-clayey-sandy) that is transported by running water. Studies into the distribution of trace elements in relation to the size fraction of stream sediments generally show that several elements including Mo, Cu, Zn, Mn and Fe are concentrated in the finest fractions of the sediment. Typically, the <150µm size fraction is analysed, as this is fine enough to include only the very fine sand, silt, clay and colloidal fractions, but is coarse enough to yield sufficient fine material in the majority of situations. However, the possibility that some elements of interest may be preferentially bound to coarser, sandy material in the vicinity of the mine site could also be considered. The potentially complex physico-chemical conditions prevailing in streams around mine sites may warrant a more detailed sampling and analytical approach than that adopted for FOREGS. However, as GSI has already completed regional studies in southeast Ireland, Longford-Down and Inishowen in which the <150 µm fraction was collected, it would be desirable, in order to allow comparison with and/or use of this data, that samples of this size fraction be collected for the HMS-IRC project. This does not preclude collection of coarser samples if desired or necessary in some instances.

The emphasis in FOREGS protocols on collecting enough sediment to produce at least 0.5kg of <150µm sample is less relevant in contamination studies as there is no requirement to collect a sample that is representative of a much larger area.

It is important to avoid metal contamination at every stage of the sampling process:

- No hand jewellery or medical dressings should be worn during sampling. Heavy duty rubber gloves should be worn at all times to avoid contamination of the samples.
- Metal-free polyethylene scoops will be used.
- Metal-free nylon or polypropylene sieve-mesh housed in inert wooden frames will be used.
- Metal free funnels and sample collection containers (Kraft bags, plastic bags or bottles) will be used.

Site selection

Whereas regional stream sediment samples comprise material taken from 5-10 points over a stream stretch of 250 - 500 m, sampling of streams around mine sites will, for obvious reasons of scale, be more focused. The aim will be to demonstrate the spatial extent of any stream sediment contamination around the mine site and, depending on the scale of the site, sampling sites may be relatively closely spaced. Individual samples should still aggregated from a number of sub-sites but the sub-sites will ideally be chosen to ensure the width of the stream is sampled over a limited length. A decision about the length of the stream over which sub-samples are collected will be made for each site separately on the basis of detailed mapping. *Accessibility will play a significant part in determining sample locations.* Because sampling points used for regional geochemical studies are relatively widely spaced, sub-sites can be spread over a wide area. In contrast, sub-sites for contamination studies will be tightly constrained thereby limiting site selection opportunities. If water is being collected simultaneously from the same stream, then stream sediment sampling should start from the water sampling point and the other sub-samples should be collected up stream. A composite sample should not be made from samples taken from beds of different nature.

Vertical profiling of stream sediment should be considered in those cases where initial sampling has indicated that contamination has occurred. A suitable vertical sampling device would have to be acquired for this purpose.

Standard Equipment

Not all of the equipment listed will necessarily be employed.

1. Kraft paper bags
2. Polythene bags
3. Heavy duty elbow length rubber gloves
4. Plastic wash bottle
5. Sieve set with wooden frames, nylon or PPP 2.0 mm and 0.150 mm mesh screens
6. Metal-free gold pan
7. Metal free plastic buckets or containers with lids
8. Trenching tool - metal free, polyethylene (PE) or polypropylene (PP)
9. Permanent drawing ink marker (preferably black or blue)
10. Permanent ink pen
11. Maps (OS maps, site map, aerial photo)
12. Field observation recording sheet
13. GPS
14. Camera

Sampling procedure

This procedure assumes that samples are being sieved through a very fine (<0.150 mm) mesh. This may not always be the case in the course of this project.

Mark the sample identifier on the outside of the plastic bucket using permanent ink marker. Mark the exact site location of the first (downstream) sub-sample on the field map and note distance upstream over which other sub-samples were collected. Record GPS reading. Complete the details of the field observation sheet (below).

Samples will be sieved using wet sieving whenever it is possible. Rubber gloves are recommended for protection throughout sampling. Following collection of any water samples, prepare the equipment for stream sediment sampling:

- wash all stream sediment sampling equipment (buckets, sieves, gold pans, gloves and scoop) with stream water downstream of the sampling point;
- set-up the gold pan in a stable position;

- if using two sieves, place the sieve with the finer mesh in a stable position resting on the gold pan;
- place the sieve with the coarser mesh over the first sieve;
- because fine sediment can lodge in spaces between holding rings and mesh used in GSI sieves, it is desirable to pre-contaminate the sieves - load some sediment into the top sieve and work it through both sieves before washing again in stream water downstream of the sampling point;
- load sediment into the top sieve with the scoop;
- rub the material through the top sieve wearing rubber gloves for protection;
- take care to remove large stones from the sediment by hand;
- once the bottom sieve contains a reasonable quantity of sediment, remove the top sieve and discard the material in it;
- fill wash bottle with stream water;
- the finer sediment in the bottom sieve is washed and rubbed through the sieve with the aid of stream water;
- it is very important at this stage that coarse material that would bias the sample does not enter the collection pan – ensure no such material is adhering to bottom sieve or is introduced to the finer material during the collection process;
- the sample should be repeatedly washed until all the fine material has passed through the sieve;
- transfer the contents of the pan to the plastic bucket, using water from the wash bottle if necessary, a replace lid on bucket;
- the whole sieving process should be repeated until the bucket contains sufficient fine-grained sediment;
- seal bucket with lid and store in vehicle;
- the sediment should be allowed to stand until all the suspended material has settled and clear water sits on top of the sediment – this may be at end of the day or following day in field base or GSI laboratory;
- once the suspended material has settled, excess water on the surface of the sediment should be carefully decanted - care should be taken to remove only water and not sediment at this stage;
- the remaining sediment should be thoroughly homogenised and mixed using the plastic stirring rod before being transferred into Kraft bags;
- write the sample identifier on enough 10 x 22 cm Kraft paper bags to hold all the sample volume - this size of Kraft bag allows ease of drying the samples;
- if sample is bagged in field or at field base, the number of bags for each sample site should be recorded on the field sheet and on a sample check-list sheet.
- once the sample has been homogenized, carefully transfer the sample into the Kraft bags using a clean plastic funnel;
- the Kraft bags should be air-dried for as long as required;
- if moving the samples from field base place each Kraft bag in a 15 x 40 cm polythene bag and secure the top of the bag with a knot to prevent loss or cross contamination of samples during transport;
- the samples should be secured upright in a plastic crate or box and transported carefully to the next location or to the GSI laboratory base for further drying;
- at the GSI laboratory, the samples should be completely dried at < 40°C. Freeze drying is a recommended as this helps to disaggregate the samples;
- all sampling equipment must be thoroughly cleaned between each site to avoid cross contamination.

In dry conditions where there is no flow in the stream bed, samples will have to be dry-sieved. Since water is not available to wet sieve the stream sediment to the required <0.150 mm fraction, collect a bulk composite sample from the 5-10 sampling points. Collect material of finer grain size or if possible only the top thin layer of silt on the sand bar, from the centre of the stream. Care should be taken to sample stream sediment with as little as possible organic matter, and to avoid the reduced material, identifiable by its typically dark colour and bad odour, that occurs at greater depths. Also, in the case of narrow channels take care not to collect material that has fallen from the banks.

The removal of stones and other coarse-grained material could be achieved by sieving through a 5 mm nylon sieve and collecting the material in a plastic bowl. Collect equal amounts of material from the 5-10 sub-sites. The use of the 2 mm nylon sieve is not recommended for dry sieving, because it is too small for clay agglomerates and slightly moist samples.

Transfer the fine-grained sample to the Kraft paper bag and seal. Place the sealed Kraft envelope within a polythene bag, and tie a loose knot in the polythene bag to prevent loss or cross contamination during transportation.

Air dry the sample, disaggregate if necessary in porcelain bowl and sieve it through a 2 mm (or other) aperture nylon sieve.

At each stream sediment/water sample site take two photographs, the first to show general upstream topography from the lowermost sub-site and the second the nature of the stream bed at the best sub-site.

Sample processing

Samples will be dried in Kraft bags either in air or at 30°C in the oven. If caking occurs during drying, grinding with a pestle and mortar may be required. Samples will be placed in plastic bottles for storage prior to analysis.

Quality assurance and control

The likely heterogeneous nature of contaminant dispersion in stream sediments around mine sites presents particular issues for QA / QC protocols. Potentially large differences in composition between samples emphasize the need to take measures to avoid inter-sample contamination. Inherently large variations in composition also cast doubt on the value of collecting field duplicates. Other areas that need to be addressed in respect of QA / QC are:

- homogenization of samples prior to analysis and
- analytical accuracy / precision for samples with anomalously high concentrations of metals and other elements.

Specific QA / QC measures proposed for stream sediment sampling and analysis are:

1. adherence to FOREGS sampling protocols, particularly those relevant to contamination of samples by sampling equipment;
2. pre-contamination of sieves with sample followed by washing in stream water to reduce risk of inter-sample contamination;
3. analysis of replicate samples (splits taken from final prepared sample) to monitor sample homogenization and preparation;
4. analysis of standard sample to monitor analytical accuracy and precision.

Analysis

- Analysis will routinely be carried out by portable XRF, using a bench-top docking station;
- Approximately 5 - 10% of all samples will be analysed in a commercial laboratory by ICP techniques to provide a check on the XRF results.

2. Surface water sampling and analysis

General Information

Surface water will include streams, adit discharges, run-off from solid waste and ponded water on mine sites. Water sampling should be repeated at different times of the year to assess the effects of variations in flow rates.

A number of parameters will be measured in the field rather than the lab. These will include:

- temperature
- EC
- pH
- dissolved oxygen
- flow rate (where relevant / possible)

Field-based measurements allow an initial, rapid assessment of water quality and can be used as part of a reconnaissance study to help identify sites for laboratory-based water analysis.

In addition to the parameters listed above, acidity / alkalinity will be measured using a Hach titrator kit either *in situ* or at the field base at the end of the day. In the latter case, samples should be kept in a fridge / cool box after sampling.

The sampling protocol will essentially follow that of FOREGS ("Stream Water"). Filtering of water samples will be done *in situ*, using disposable syringe filters, rather than subsequently in the lab, given the limitations of GSI's lab facilities.

Water samples to be collected

Both filtered and unfiltered samples will be collected, as follows:

- 1 x 1000 ml PE bottle of unfiltered water for major ion and trace element analysis;
- 1 x 100 ml Nalgene trace element-free bottle (or equivalent as supplied by the laboratory) of filtered water, preserved with conc. HNO_3, for dissolved ion and trace element analysis;
- 1 x 500ml PE bottle of unfiltered water for alkalinity / acidity testing.

Sample bottles will be supplied by the laboratory for both total and dissolved element analyses. Bottles will have to be purchased for storing samples for alkalinity / acidity testing.

Equipment to be used

Sample bottles for total major and trace element analyses of unfiltered water and analysis of dissolved elements in filtered water will be provided by the laboratory. Other recommended equipment includes:

- 500 ml new polyethylene bottles (for non-filtered water samples for alkalinity / acidity analysis);
- disposable gloves (vinyl gloves, powder free);
- disposable syringes;
- disposable cellulose syringe filters 0.45 µm (pyrogen free);
- deionized water;
- HPLC water for preparation of lab / travel blanks;
- washing bottles;
- permanent drawing ink markers;
- cool boxes / fridges and ice packs / batteries for them;
- rubbish bags for discarded filters, etc.;
- pH-meter;
- buffer solutions for calibration of pH-meters;
- EC-meter;
- buffer solutions for calibration of EC meters;
- two polyethylene (500 ml) beakers for sample water to measure pH and EC;
- alkalinity / acidity measurement kit (Hach or equivalent);
- dissolved oxygen meter and calibration material.

Water sampling procedures

Where stream sediment is also being collected then the water sample should be taken first, from the lowermost stream sediment sampling point, as stream sediment sampling will cause sediment to enter into suspension.

The sampling procedure closely follows that of FOREGS, with some modifications. GSI's temperature, pH and EC meters are integrated in one device and thus field measurements of these parameters are carried out simultaneously. The procedure is:

1. write the sample number on sample bottles;
2. complete sample card and mark location and sample number on the map;
3. rinse temp / pH / EC meter thoroughly in stream / adit, etc., to be sampled to remove any trace of previous sample or storage solution;
4. rinse twice and fill the polyethylene beaker with stream water, place the temp / pH / EC meter in water and measure the temperature, pH and conductivity – record on field data sheet;
5. alternatively, the measurement can be made directly in the stream / adit, etc., if flow and /or chemical homogeneity allow stable reading to be achieved;
6. wearing vinyl gloves rinse a disposable syringe with sample water and fill it up with water;
7. put filter on syringe;
8. discard the first 10 ml of filtered water from each new filter unit used;
9. take a 100 ml marked sample bottle for acidified sample fill the bottle up to its neck with filtered water (change filter if needed) and close it tightly; note that the filtered sample water should go straight into the bottle without contact with hands;

10. rinse the marked 1000 ml sample bottle with sample water twice and fill it up so that the bottle is completely submerged in the water and no air bubbles are left in the bottle. Fill the bottle as full as possible and close it tightly below water level;
11. rinse the 500ml alkalinity / acidity sample bottle twice and fill to brim before replacing cap;
12. after recording the temp / pH / EC readings on field data sheet, rinse the meter and beaker with deionized water and keep the meter in its cap with storage solution;
13. the filled sample bottles are placed in the cool box / fridge;
14. alkalinity / acidity measurements should be carried out either in field or at field base at end of day as per instructions in Hach kit – samples to be stored in cool box prior to analysis;
15. record alkalinity / acidity titration results and computed alkalinity / acidity (mg/l $CaCO_3$) on field sheets;
16. a lab blank (HPLC water) should be enclosed with each batch returned to the lab – sample is prepared in lab using same techniques as in field.

Treatment of water samples

1. After return from field, place the bottles in a cool unit, e.g. refrigerator;
2. Complete Chain-of-Custody forms;
3. Place water samples in cool box and send to the laboratory.

Quality control and assurance

1. Duplicate water samples should be taken at regular intervals.
2. Lab blanks, made up using HPLC water should be included with each sample batch.
3. Trip blanks, containing HPLC water, can also be included.

3. Solid Mine Waste

General Information

Solid mine waste can be analysed either by portable XRF or by standard wet chemical methods in a certified commercial laboratory. The portable XRF offers rapid *in situ* semi-quantitative analysis and, in a laboratory environment, quantitative analysis of prepared samples; wet chemical analysis offers potentially greater accuracy but is a relatively slow process. The high initial cost of the XRF will be offset to a degree by the savings on laboratory analyses.

There are two issues in relation to mine spoil, particularly, that are directly relevant to the choice of analytical technique. Firstly, the typically very heterogeneous nature of mine spoil, both compositionally and in terms of grain size, poses significant problems for analysis since it is virtually impossible to obtain a truly “representative” sample. Secondly, even if a representative sample were found, achieving true homogenization of the sample would be very difficult. Standard laboratory analytical techniques rely on analysis of a small sub-sample of a homogenized sample. Tailings are generally much less heterogeneous and have a finer grain size and would not, therefore, pose so severe a problem.

The difficulties posed by sample heterogeneity apply to whatever analytical technique is employed. Since these difficulties make truly accurate analyses of mine spoil at least problematic, it is suggested that the semi-quantitative portable XRF method is preferable as the rapid *in situ* analysis will allow detailed mapping of contamination “hot-spots” on and around mine sites – the perceived relative lack of absolute accuracy of the method would be outweighed by the large number and wide range of samples analysed. A number of wet chemical analyses of spoil could also be carried out on selected material to establish concentration ranges for elements of interest. Such samples would be selected on the basis of initial XRF analysis.

Portable XRF analysis

EPA/GSI acquired a Niton XLt 792Y for use in the HMS-IRC project. An account of the analyser’s analytical performance is provided in Appendix 4. The XRF’s portability means it can be used to analyse most solid material provided it can be positioned so that the X-ray window lies flat against the surface being analysed. Material should be raked over to disaggregate it and then smoothed and compacted for *in situ* analysis. The window of the Niton XLt has a diameter of 20mm so for coarse material it is desirable to analyse a number of points on the surface to achieve a representative analysis. Given the inherent compositional variation in solid mine waste, such an approach, i.e. analysing several spots at each sample site, is desirable in any case, regardless of grain size. Approximately 10% of sites should be sampled for laboratory analysis both by XRF on prepared samples in the GSI lab and by wet chemical methods in a certified commercial laboratory.

Spoil Sampling protocol

For single spoil heaps of relatively homogeneous appearance, where the aim is to obtain an estimate of the range and median element concentrations in the heap, a minimum of 5 points should be analysed, one at each corner of the grid, the other in the centre. The more spots analysed the better so the grid can be modified to include 6, 9 or more spots in a regular array. The general approach to analysis is:

- mark the outlines of a grid, the size of which will depend to some extent on the areal extent of the spoil heap - a 10m x 10m area can be considered a standard area but larger or smaller areas may apply depending on size and time available for analysis;
- use a trowel to mark out a 20 x 20cm spot, turn over and rake the top 5cm of material, smooth and compress it to form a flat surface;
- analyse for 90 seconds using the “soil” mode, 60 seconds on the main filter and 30 seconds on the light-element filter;
- during the 60 seconds on the main filter, move the XRF twice to a different point in the sample site so that three spots are analysed, each for 20 seconds – the movement should be swift to avoid analysis of “air” for any significant length of time;
- do the same when using the light-element filter except reduce the interval to 10 seconds;
- record all observations for each sample analysed on appropriate field sheets – data to be transferred to digital file at earliest opportunity;
- for every 5 to 10 sample spots, and ideally at least once for each spoil heap, collect a 0.5 – 1kg sample of material from the 20cm spot analysed, place in plastic bag, seal and return to GSI lab for processing;
- samples returned to the lab should be passed through a 2mm nylon sieve before quartering, if required, and grinding in an agate or equivalent contaminant-free mill;

- milled samples should be placed in labelled bottles for storage;
- quartered remains of sample material not milled should be stored for potential future use.

Where the spoil is heterogeneous in appearance, distinctive parts of the spoil heap should be analysed, with the number of spots in each distinctive part reflecting its relative size. Apart from attempting to determine the range and median composition of heaps, the portable XRF should be used to help identify “hot spots” or parts of waste heaps with anomalously high element concentrations.

Tailings sampling protocol

A similar approach to that for spoil heaps can be applied to tailings although grain size variation, at least, will be smaller than for spoil. In order to sample at depth, a pit should be dug to the required depth using a stainless steel spade. Alternatively, a sample can be cored using a manual coring device. The sample can then be analysed either *in situ* or in the lab / field base on the XRF stand.

4. Leachate testing

General Information

The protocol for leachate testing follows that of the U.S Geological Survey’s field leach test for mine wastes and other materials (Hageman 2007). This rapid test was originally devised specifically for mine wastes and compares favourably to the US EPA’s 18-hour leaching procedure (Method 1312) (Hageman 2007). It uses a 20:1 leachate:solid extraction ratio, the same as the US EPA method, which ensures the readily soluble components of a sample can be taken into solution without exceeding leachate saturation limits. Use of this ratio also allows direct comparison with results obtained using the US EPA test and it ensures that there is sufficient leachate to allow complete geochemical analysis and characterization.

Laboratory equipment required

1. 2mm-mesh nylon sieve;
2. laboratory or field balance capable of weighing 50g of sample;
3. 1000 ml wide-neck PE bottles;
4. 500ml or 1000 ml graduated cylinder;
5. deionized water;
6. pH, EC meter;
7. beaker for pH, EC tests;
8. alkalinity / acidity kit (Hach);
9. 50-60ml plastic syringe;
10. disposable cellulose 0.45µm capsule syringe filter;
11. 100ml plastic bottles with 10% nitric (laboratory-supplied) for sample storage.

Procedure for extracting leachate

Once a representative sample is available, the procedure below is used to extract the leachate for analysis. Collection of a “representative” sample entails collecting a series of samples from sub-sites within a waste heap, using a grid or other non-biased method of sampling. The recommended number of sub-sites (Hageman 2007) is 30 where the aim is to collect a truly representative sample. The final composite sample should weigh at least 1kg. Mixing and homogenization of sub-samples can be carried out using large buckets.

1. Samples should be air-dried in the laboratory;
2. dry samples are passed through a 2mm-mesh nylon sieve;
3. 50g of the composite sample is added to a wide-necked 1000ml PE bottle;
4. 1000ml of deionized water is added to the PE bottle which is then capped;
5. the PE bottle is then clamped to a laboratory shaker along with other bottles if more than one sample is being processed;
6. the shaker is run for 5 minutes at highest speed possible;
7. after shaking, the sample is allowed to settle for 10 minutes;
8. after settling, the syringe and filter are used to fill the acidified bottle with supernatant liquid from PE bottle;
9. part of the remaining supernatant liquid is poured carefully into a beaker for pH, EC and temperature measurement;
10. remaining supernatant liquid can be used for alkalinity / acidity test either immediately or later after storing in 250ml plastic bottle in fridge;
11. the filtered leachate sample should be stored under refrigeration until returned to the laboratory for analysis.

References

Hageman, P.L. (2007) U.S Geological Survey field leach test for assessing water reactivity and leaching potential of mine wastes, soils and other geologic and environmental materials. U.S. Geological Survey Techniques and Methods, book 5, chapter D3, 14p.

Appendix 3

General Geochemical Assessment

1. Introduction

A detailed review of the geochemistry of each mine site studied for the HMS-IRC project is contained in each site report. The aim of this general assessment is to outline the main findings in respect of measured parameters and to place those findings in the context of human, animal or environmental impacts that may arise as a consequence of exposure to these parameters.

Table 1 provides a full listing of all parameters measured for the project, according to sample type. Not all parameters listed in Table 1 are discussed further in this section. Some of those analysed by XRF, because of peak overlap and/or lack of adequate calibration, yielded consistently unreliable results when compared to check analyses carried out by an external laboratory using MA-ES. These include cobalt (Co) and thallium (Tl). Other elements, for which there are no relatively toxicity values, do not feature in the HMS-IRC Site Scoring System (Table 1). For the most part these are elements that are not considered to represent significant toxicity risks.

2. Standards

In assessing the environmental impact of mine waste reference is made to national and European standards or guidelines where appropriate. Such standards or guidelines define maximum permitted levels of various parameters in specified media.

As yet there are no uniform European standards for soil. Various guidelines have been developed over the years including the Dutch Intervention values for “standard” soil (Table 2) and the UK’s ICRCL threshold values. The latter were superseded in the 1990s by the Soil Guideline Values (SGVs) produced by the UK’s Department of Environment, Food and Rural Affairs (DEFRA). These in turn have been withdrawn pending new values that reflect an updated methodology. The SGVs are based on modelled exposure of humans in occupational and non-occupational settings to the relevant chemical. They can be viewed as trigger values above which there may be a cause of concern for human health that warrants further assessment. Because they are exposure- or dose-related, the SGVs differ for different soil categories or land uses. They are reproduced in Table 2. SGVs are similar in concept to the Comparison Values (CVs) defined by the US Agency for Toxic Substances and Disease Registry (ATSDR). These are also reproduced in Table 2.

Water standards include those for Drinking Water (Irish Drinking Water Standards, SI 278, 2007) and Surface Water (Draft European Communities Environmental Objectives (Surface Waters) Regulations, 2008). Neither of these standards includes all parameters of interest but in combination they cover the main ones. Table 3 summarizes the standard data used in HMS-IRC.

In the HMS-IRC project the water standards are used to determine if any parameter in groundwater or surface water downstream of a mine waste source exceeds the standard. This information is incorporated into the HMS-IRC Site Scoring System and it is also used in the context of individual site descriptions to identify water courses at risk of mine-related contamination.

Table 1 Parameters analysed for HMS-IRC project, various media

Parameter	Solid Waste / stream sediment analyses	Water analyses	Leachate analyses
Temperature		✓	✓
pH		✓	✓
EC		✓	✓
Dissolved oxygen		✓	
Alkalinity / acidity		✓	✓
BOD / COD		✓	
TDS / TSS		✓	
Al		✓	✓
As	✓	✓	✓
Ba	✓	✓	✓
Bi*	✓		
Ca*	✓	✓	✓
Cd	✓	✓	✓
Co**	✓	✓	✓
Cr	✓	✓	✓
Cu	✓	✓	✓
Fe	✓	✓	✓
Hg	✓	✓	✓
K*	✓	✓	✓
Mg		✓	✓
Mn	✓	✓	✓
Mo		✓	✓
Na*		✓	✓
Ni	✓	✓	✓
P / PO_4*	✓	✓	
Pb	✓	✓	✓
Rb*	✓		
S / SO_4	✓	✓	
Sb	✓	✓	✓
Se	✓	✓	✓
Sn*	✓	✓	✓
Sr*	✓		
Th	✓		
Tl**	✓		
U	✓	✓	✓
W*	✓		
Zn	✓	✓	✓

* No relative toxicity value, not included in HMS-IRC Site Scoring System

** XRF analysis unreliable, not included in HMS-IRC Site Scoring System

Table 2 Soil reference values (Dutch Intervention, DEFRA SGV and pre-2004 ATSDR CV)

	Dutch	Dutch	SGV	SGV	ATSDR	ATSDR
Parameter mg/kg	**Target value**	**Intervention value**	**Residential / Allotments**	**Industrial**	**Child**	**Adult**
As	29	55	20	500	20	200
Ba	200	625			4000	50000
Cd	0.8	12	1-8	1400	10	100
Cr VI			130	5000	200	2000
Cr	100	380				
Cu	36	190			2000	20000
Hg	0.3	10	8	480		
Mn					3000	40000
Mo	10	200			300	4000
Ni	35	210	50	5000	1000	10000
Pb	85	530	450	750		
Sb					20	300
Se			35	8000	300	4000
U (soluble)					100	1000
V					200	2000
Zn	140	720			20000	200000

Table 3 Water Standards used for HMS-IRC project

Parameter	Unit	Standard	Source
pH		≥ 6.5–≤ 9.5	SI 278 (2007)
EC	mS/cm	≤ 2.5	SI 278 (2007)
Al	μg/l	200	SI 278 (2007)
As	μg/l	25	Draft EC (2008)
Cd	μg/l	0.25	Draft EC (2008)
Cr	μg/l	50	SI 278 (2007)
Cr III	μg/l	4.7	Draft EC (2008)
Cr IV	μg/l	3.4	Draft EC (2008)
Cu [hardness < 100 mg/l $CaCO_3$]	μg/l	5	Draft EC (2008)
Cu [hardness > 100 mg/l $CaCO_3$]	μg/l	30	Draft EC (2008)
Hg	μg/l	0.05	Draft EC (2008)
Fe	μg/l	200	SI 278 (2007)
Mn	μg/l	50	SI 278 (2007)
Na	μg/l	200,000	SI 278 (2007)
Ni	μg/l	20	Draft EC (2008)
Pb	μg/l	7.2	Draft EC (2008)
Sb	μg/l	5	SI 278 (2007)
Se	μg/l	10	SI 278 (2007)
SO_4	μg/l	250,000	SI 278 (2007)
Zn [hardness < 10 mg/l $CaCO_3$]	μg/l	8	Draft EC (2008)
Zn [hardness 10-100 mg/l $CaCO_3$]	μg/l	50	Draft EC (2008)
Zn [hardness > 100 mg/l $CaCO_3$]	μg/l	100	Draft EC (2008)

Note: values for As, CrIII, Cu and Zn are to be added to background values

Stream sediment data are included in the scoring system since contaminated stream sediments are a potential hazard to livestock that use streams as a source of drinking water. Reference values (Table 4) have been provided by the Central Veterinary Research Laboratory, compiled from published sources, in the form of an estimated dry matter ingestion limit. These limits relate to the total stream sediment size fraction. Stream sediments analysed for the HMS-IRC project are typically from the <150 μm fraction. Metals tend to be concentrated in the finer fractions in stream sediments so that the 150 μm fraction generally has higher metal concentrations than the total fraction. An example of this is provided by stream sediments from Caim, Co. Wexford, where both the <150 μm and the much coarser <2mm fractions were analysed. Pb concentrations in the <150 μm fraction in three samples were 557, 894 and 2583 mg/kg; in the <2 mm fraction in the same samples the concentrations were less than half as much, i.e. 234, 350 and 926 mg/kg, respectively. Although most stream sediment data for HMS-IRC are for the <150 μm fraction, nevertheless the standards in Table 4 provide a useful indication of potential hazards to livestock arising from stream sediment contamination around mine sites.

Table 4 Stream Sediment Standards used for HMS-IRC project

Parameter	Unit	Standard	Source
Ag	mg/kg (dry matter)	1,000	Irish Veterinary Laboratory
As	mg/kg (dry matter)	300	Irish Veterinary Laboratory
Ba	mg/kg (dry matter)	1,000	Irish Veterinary Laboratory
Cd	mg/kg (dry matter)	100	Irish Veterinary Laboratory
Cr III	mg/kg (dry matter)	1,000	Irish Veterinary Laboratory
Cu	mg/kg (dry matter)	100	Irish Veterinary Laboratory
Fe	mg/kg (dry matter)	10,000	Irish Veterinary Laboratory
Hg	mg/kg (dry matter)	5	Irish Veterinary Laboratory
Mn	mg/kg (dry matter)	5,000	Irish Veterinary Laboratory
Ni	mg/kg (dry matter)	1,000	Irish Veterinary Laboratory
Pb	mg/kg (dry matter)	1,000	Irish Veterinary Laboratory
Sb	mg/kg (dry matter)	1,000	Irish Veterinary Laboratory
Se	mg/kg (dry matter)	12	Irish Veterinary Laboratory
Sn	mg/kg (dry matter)	1,000	Irish Veterinary Laboratory
V	mg/kg (dry matter)	500	Irish Veterinary Laboratory
Zn	mg/kg (dry matter)	5,000	Irish Veterinary Laboratory

Note: values assume sediment is 10% of diet and that metals are bioavailable.

3. Summary of data for individual parameters

3.1 Acidity, alkalinity and pH

The **pH** of a solution is a measure of the hydrogen ion concentration of a solution and, as such, determines whether a liquid is acid or alkaline. It is governed by the dissolution of the water molecule into H^+ and OH^- ions. Although the lower the pH the more acid a solution is, **acidity** is not entirely accounted for by pH since acidity is also governed by the concentration of metals (Fe^{2+}, Al^{3+}, Zn^{2+}, etc.) in solution that can release H^+ and/or neutralize OH^- ions. Thus solutions with low pH are not always strongly acidic. Likewise, high-pH solutions are not always strongly alkaline as **alkalinity** is a measure of the concentration of anions in solution, chiefly bicarbonate anion (HCO_3^-). Acidity is measured by titrating with NaOH until the pH of the solution reaches 8.3. It is expressed as mg/l $CaCO_3$ equivalent. The acidity of a solution can thus be seen as a measure of the amount of $CaCO_3$ required to neutralize it. If pH is a measure of the degree of acidity of a solution, the acidity is a measure of how strongly it resists neutralization. Such measurements are important in the context of remediation of acid mine wastes.

There are no guideline or standard values for acidity or alkalinity. The Irish Drinking Water Standards (2007) limit pH within the range 6.5 to 9.5, EU Salmonid Water Quality Regulations (1988) between 6.0 to 9.0 and EU Shellfish Water Quality Regulations (2006) between 7.0 and 9.0. In Ireland, pH in fresh waters ranges naturally between 4.0 and 10 or more. Low pH is found in acid waters formed in upland peat areas and in water draining commercial forestry plantations. In areas underlain by granite bedrock, the pH of surface water and groundwater is typically around 6 to 6.5, whereas in areas of carbonate bedrock, i.e. around 40% of the island of Ireland, the range is normally between 7 and 8. Acidity measurements are not widely available; alkalinity of Irish surface and ground waters ranges up to approximately 400 mg/l $CaCO_3$ (equiv).

For fish and other aquatic organisms the optimum pH range of water is around 6.5 to 8.0. Acid mine drainage (AMD) or acid rock drainage (ARD) are characterized by low pH and high acidity that can be toxic to aquatic species. Low pH (<5) can increase the permeability of cells in fish gill membranes, causing loss of electrolytes such as Na^+ and K^+. Moreover, at low pH the solubility of metals, and therefore their toxicity, increases. AMD generated in metal or coal mines is typically rich in metals such as Fe, Mn, Al, Cu, Pb, Ni and Zn, and therefore potentially highly toxic to aquatic organisms. AMD and ARD are particularly associated with ore deposits rich in pyrite (FeS_2).

Table 5 pH, acidity and alkalinity at Irish mine sites

Water Source	**pH**	**Acidity**	**Alkalinity**
Upstream			
n	63	21	33
Range	4.64 – 8.46	2 – 96	4.4 – 318
Median (Mean)	7.1 (6.98)	15 (25)	115 (124)
Mine water*			
n	195	114	76
Range	2.17 – 8.70	1 - 3400	2 - 248
Median (Mean)	6.45 (5.96)	44 (202)	105 (102)
Downstream			
n	164	69	86
Range	3.46 – 8.51	4 – 300	3 - 385
Median (Mean)	7.08 (6.82)	18 (34)	110 (123)

***Mine water includes adit/shaft discharges, waste seepages, ponded water and pit lake water**

The pH, acidity and alkalinity were measured in most water samples taken for the HMS-IRC project. Acidity was measured where the pH was less than 7, alkalinity where it exceeded 7. Table 5 summarizes the data and Fig. 1 illustrates the relationship between pH, acidity and water source.

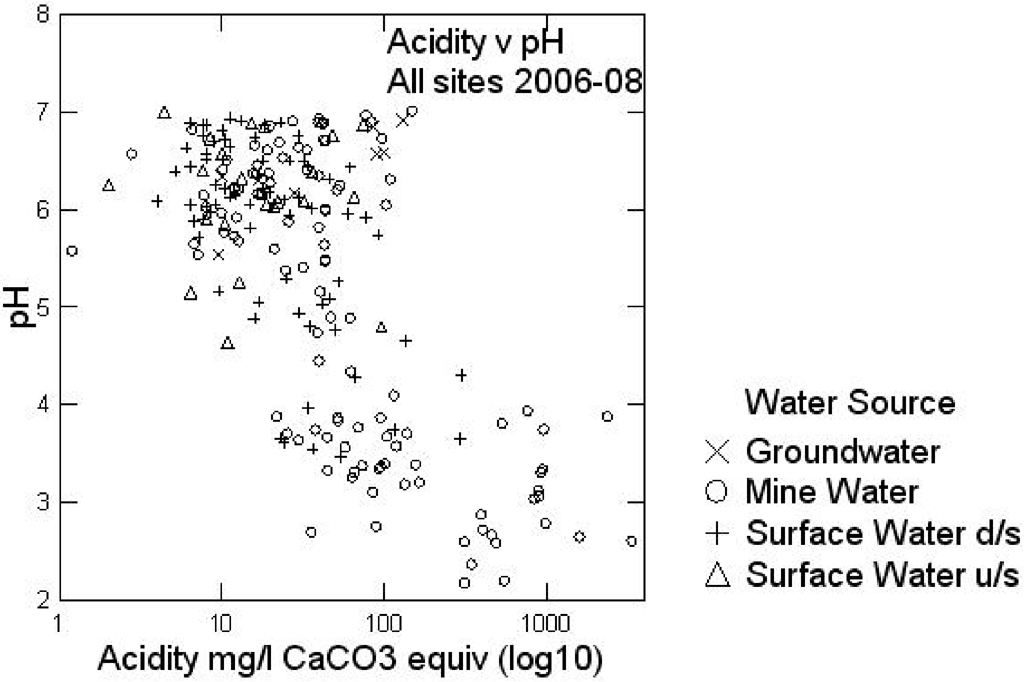


Fig. 1 Acidity v pH for all mine sites sampled, categorized by water source

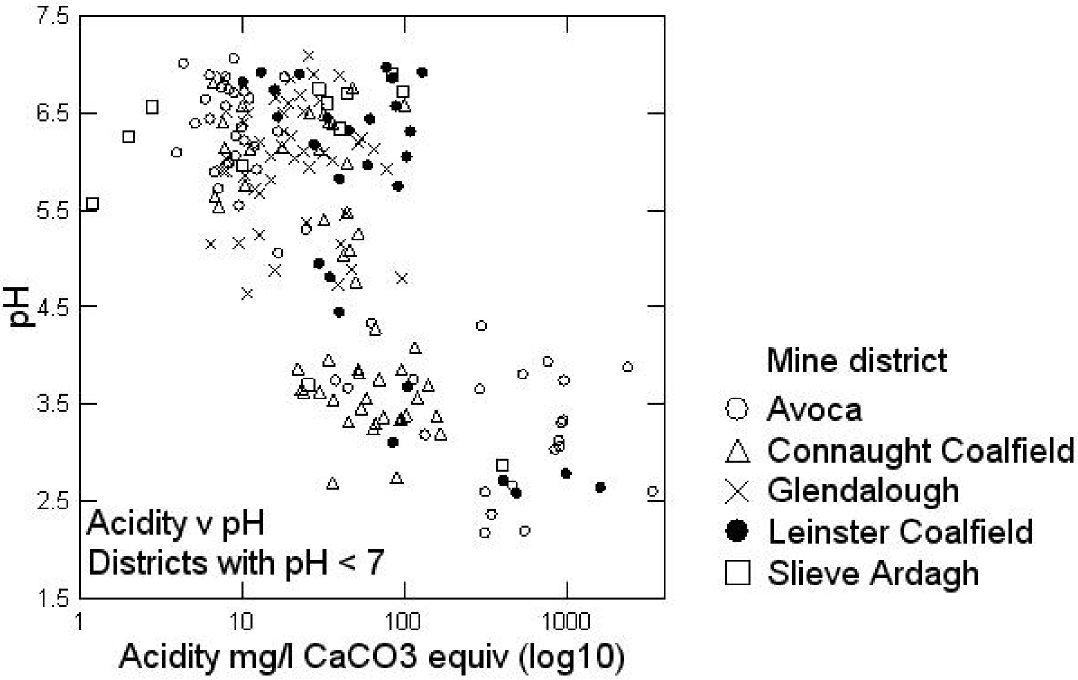


Fig. 2 Acidity v pH for main mine districts where pH < 7

Both Table 5 and Fig. 1 demonstrate that low pH (< 6) and high acidity are most likely to be found in mine waters themselves and in the surface water downstream of the mine sites. Fig. 2 shows the relationship between pH and acidity for the main mine districts where pH is typically below 7. The problem with AMD at Avoca is well known and the AMD is primarily a product of the pyrite-rich nature of the ore. The pH of mine waters and surface waters in the Glendalough District is as low as 4.6 and acidity is modestly elevated (maximum 96 mg/l) but this appears to reflect drainage from upland areas covered in blanket bog and commercial forests since both mine water and surface water have a similar range of pH and acidity. Coal deposits typically contain significant pyrite as well, disseminated throughout the coal seams and their host rocks, and AMD is thus a common feature of coal mines. All three Irish coalfields examined have low-pH, high-acidity mine water discharges and some, notably those in the Leinster Coalfield, are comparable in these respects to those at Avoca (Fig. 2). However, their metal contents are generally much lower. Moreover, the coalfield mine waters with lowest pH and highest acidity are small-scale seepages generated from direct contact between surface run-off and exposed coal waste. Only in the Connacht Coalfield are there volumetrically significant adit discharges with low pH (2.75 – 4) and relatively high acidity (up to 166 mg/l $CaCO_3$).

In summary, low pH and high acidity are features of mine water in the three Irish coalfields as well as Avoca mine. Some low-volume seepages draining coal waste can have very high acidity but only at Avoca are there high-volume discharges of mine water that are also highly acidic.

3.2 Aluminium - Al

3.2.1 Introduction to Al

Al is the most abundant metal in the earth's crust, with an estimated upper crustal abundance of 8% (15.2% Al_2O_3) (Taylor and McLennan 1986). It is found in combination with other elements, chiefly Na, K, Ca, Si, O, Fe and Mg, in the major rock-forming minerals, principally silicates such as feldspars, micas and pyroxenes.

Al is one of the most commonly used metals, both in industrial and domestic environments. It is also extensively used in food products, such as antacids, food additives and antiperspirants. Alum (hydrated aluminium sulphate) is a flocculant used in water treatment to remove colour and non-filterable matter. Al compounds are toxic to most plants and slightly toxic to animals (Fay *et al.* 2007) but exposure to Al is usually not harmful to humans (ATSDR 2006). Some studies have suggested a link between Al and Alzheimer's disease but others have not.

Most Al compounds are insoluble at pH levels between 6 and 8. Solubility of Al increases as pH decreases and high concentrations of dissolved Al, mainly in the form of Al^{3+}, can be found in waters with pH below 5 (Solomon 2007). Speciation of Al in the environment is complex; apart from pH, the concentration of dissolved organic carbon (DOC), i.e. mainly humic acids, can have a major impact on the availability and toxicity of Al (Canadian Council of Ministers of the Environment 2003). Thus the levels at which Al becomes toxic to aquatic life, including plants, are likely to be very variable. Interim Canadian water quality guidelines for the protection of aquatic life suggest a limit of 84 µg/l total Al for pH < 5.2 and DOC concentration < 0.5 mg/l (Canadian Council of Ministers of the Environment 2003). As the DOC concentration rises, the guideline value increases, reaching 201 µg/l for DOC = 10 mg/l.

In general, the total Al concentration of water at pH levels >5.5 is <100 µg/l; raw surface waters in the US analysed in the 1960s had a mean Al concentration of 74 µg/l (range: 1 – 2760 µg/) (ATSDR 2006). Al concentrations in drinking water have been found to be higher in water subjected to alum-based coagulation treatment than in water not subjected to such treatment. Of 8,450 water supply zone samples analysed in 2006-2007 in Ireland, 607, or 7.2%, exceeded the Drinking Water Standard for Al of 200 µg/l (EPA 2007). This is generally a consequence of problems at treatment plants and in distribution networks rather than water sources with high Al concentrations.

3.2.2 Aluminium on Irish mine sites

Al has been measured in water for the HMS-IRC project but not in any other media. The current drinking water standard for Al is 200 µg/l (Table 3). Both dissolved and total Al were measured in most samples. Based on results for lab blanks, the total Al analyses are not reliable for some batches of samples analysed in which very high Al concentrations were measured, apparently as a consequence of cross-contamination. Nevertheless, the data is included below for comparison as the median values give an indication of the relative concentrations of dissolved and total Al in waters analysed.

Tables 6 and 7 summarizes the results for all analyses of dissolved and total Al in water collected for the HMS-IRC project, both in winter and summer sampling campaigns. Data for Silvermines are included only in Table 7 as only total Al was analysed there (EPA 2000). What is immediately apparent from both tables is that the range of Al in mine water and in surface water downstream of mines is much greater than that for upstream surface water or groundwater, with very high maximum Al concentrations measured in both mine water and surface water downstream of mines.

Table 6 Dissolved Al concentrations in waters around mine sites, by source

µg/l Al	All	Groundwater	Mine Water	Upstream	Downstream
n	445	27	194	60	163
Minimum	<2	<2	<2	<2	<2
Maximum	407700	229	407700	1337	24970
Median	30	3	23.5	39.5	40
Mean	6189	121	13577	136	666

Table 7 Total Al concentrations in waters around mine sites, by source

µg/l Al	All	Groundwater	Mine Water	Upstream	Downstream
n	466	27	197	67	174
Minimum	10	29	10	25	10
Maximum	371800	776	371800	8754	32310
Median	504	395	551	435	538
Mean	5762	341	12175	763	1297

Fig. 3 shows the distribution of Al (dissolved) in the various mine districts investigated. Almost all the analyses for which Al (dissolved) exceeded 100 µg/l were for samples from Avoca and the three coalfields, Connacht, Leinster and Slieve Ardagh. These are the only mine districts where mine waters typically have low pH. Given that Al is relatively insoluble at pH > 6, it is not surprising that high Al concentrations are found only in these districts. When *total* Al is plotted the same mine districts display the highest relative concentrations.

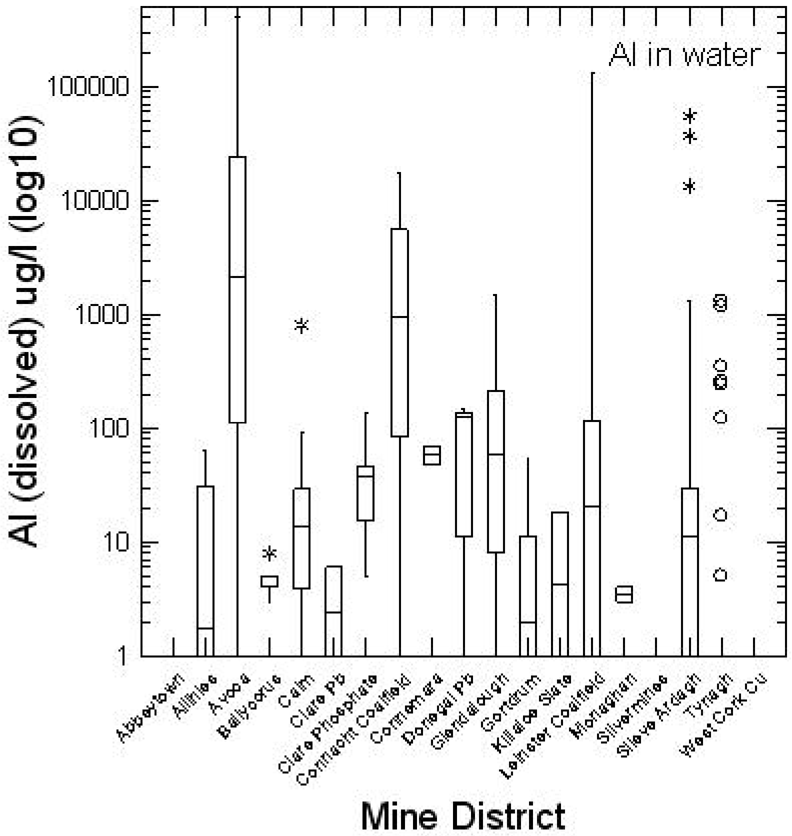


Fig. 3 Al (dissolved) in all water analysed, by mine district (log scale)

In summary, some mine waters have very high concentrations of both total and dissolved Al. There is an inverse relationship between pH and Al concentration, with those mine districts with low-pH water, such as Avoca and the three coalfields, having the highest concentrations of Al in mine water and downstream surface waters. Concentrations of total Al measured in most downstream surface water samples at Irish mine sites are typically in excess of both drinking water standards and Canadian guidelines for the protection of the aquatic environment.

3.3 Antimony - Sb

3.3.1 Introduction to Sb

Antimony is a metal found at relatively low levels in the earth's crust. It occurs naturally as native Sb, in alloys, antimonides and in sulphides such as **stibnite** (Sb_2S_3) and **tetrahedrite** ($Cu_{12}Sb_4S_{13}$). Sb is isostructural with As and Bi and all three occur in the same column of the Periodic Table. Sb is completely miscible with As in alloys; stibnite forms a solid solution with **bismuthinite** (Bi_2S_3) (Wedepohl 1978). Sb can probably substitute for Fe and is therefore likely to be contained mainly within the ferromagnesian minerals in rocks (Wedepohl 1978). In sulphide mineralization, Sb can be present in large amounts in galena (PbS) (up to 10000 mg/kg), sphalerite (ZnS) (up to 5000 mg/kg), pyrite and arsenopyrite (FeAsS) (up to 1000 mg/kg) (Wedepohl 1978). Its concentration in the upper continental crust is estimated to be 0.2 mg/kg (Taylor and McLennan 1986).

Sb metal is used in alloys with lead and other metals to increase their hardness, strength, corrosion resistance and electrochemical stability (ATSDR 1992a). It has mostly been used in antimonial lead in lead acid storage batteries. Sb_2O_3 is typically used in a suitable organic solvent as a flame retardant for plastics, rubber, pigments and paper (ATSDR 1992a). Sb has in recent years received attention because of the use of Sb_2O_3 as a catalyst in the manufacture of the plastic PET, widely used as containers for bottled water and soft drinks. Shotyk *et al.* (2006) have shown that bottled waters in PET containers can be contaminated with Sb.

Table 8 Concentration of Sb in some Irish soils, sediments and rocks

Sb	**Range (mg/kg)**	**Median (mg/kg)**
National Soils Database (n=1310)[1]	<0.05 – 5.29	0.53
Stream sediments SE Ireland (n=1884)[2]	<0.1 – 88.4	0.9
Stream sediments Inishowen (n=128)[3]	<0.1 – 4.1	0.5
Stream sediments NE Ireland (n=386)[2]	<0.1 - 186	1.1
Leinster Granite SE Ireland (n=26)[2]	<0.1 – 2	<0.1
Sedimentary rocks SE Ireland (n=222)[2]	<0.1 – 84.3	0.7
Volcanic rocks SE Ireland (n=123)[2]	<0.1 - 280	1.6

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

Table 8 summarizes the range of concentrations of Sb found in Irish soils, sediments and rocks. The concentrations are similar to those reported worldwide. For example, the range of Sb reported for U.S. soils by the US Geological Survey was 1 – 8.8 mg/kg, with a mean of 0.48 mg/kg (ATSDR 1992a). Mean concentrations of Sb in gabbros and granites range between 0.1 and 0.3 mg/kg; only shales, with a mean of 1 mg/kg, have significantly higher Sb concentrations (Wedepohl 1978). A survey of dissolved Sb in 1077 ambient water samples by the US Geological Survey in the 1980s showed only 6% in excess of the detection limit of 5 µg/l. Groundwater concentrations appear to be similarly low or even lower – Shotyk *et al.* (2006) report pristine groundwaters in Canada with Sb concentrations of only 0.0022 µg/l (2.2 ng/l). The current Drinking Water Standard in Ireland is 5 µg/l. In 2006-2007, only two drinking water samples, among 1,084 samples taken from 1,020 water source zones, exceeded this limit (EPA 2007).

Exposure to large amounts of Sb through inhalation or ingestion can have significant health effects in humans, including heart and lung problems, vomiting and stomach ulcers (ATSDR 1995). There is evidence of carcinogenicity of some Sb compounds by inhalation but insufficient evidence by ingestion.

3.3.2 Antimony on Irish mine sites

Sb is present in apparently significant concentrations in solid waste on most Irish mine sites, especially sulphide mines such as the minor Clare Pb deposits, Glendalough district, Gortdrum, Silvermines and Tynagh where measured *in situ* concentrations exceed 1000 mg/kg (Fig. 4). It is only a minor component in the coalfields and the phosphate mine in Clare.

Analyses of Sb by the portable XRF analyser can give rise to somewhat exaggerated results, particularly at higher concentrations (Appendix 4). The manufacturer's quoted detection limit is 175 mg/kg and under the conditions of *in situ* analyses the limit may be higher. The highest concentrations of Sb recorded were in processing waste at Gortdrum and Tynagh that had extremely high measured concentrations (>10%) of other elements such as As, Pb and Cu. Tennanite at Gortdrum was enriched in Sb so the high concentrations recorded for this mine are not surprising. Table 9 summarizes the Sb data for selected mine districts.

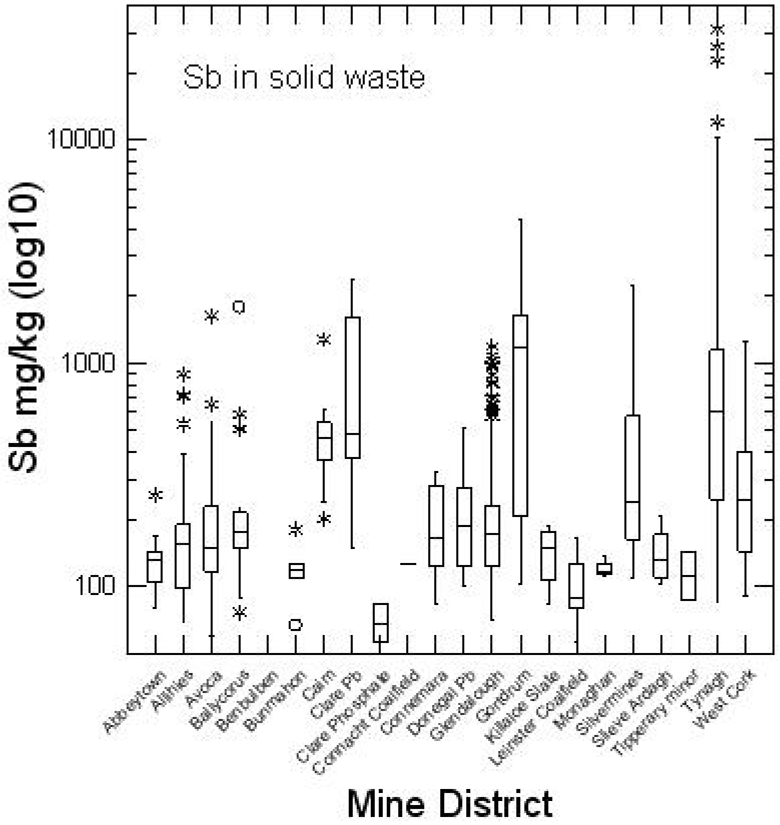


Fig. 4 Boxplots of Sb in solid mine waste for each district investigated

Table 9 Summary statistics for Sb in several mine districts (*in-situ* analyses)

mg/kg Sb	Avoca	Caim	Clare Pb	Glendalough	Gortdrum	Silvermines	Tynagh
n	347	20	33	381	79	24	134
Minimum	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Maximum	1629	1272	2364	1188	4410	2210	31335
Median	0.0	387	0.0	143	0.0	152	287
Mean	52	370	313	177	341	287	1418

Note: A value of 0.0 indicates result < detection limit

The high concentrations recorded for Sb on some sites reflects its common occurrence in sulphide ores. Fig. 5 plots Sb v As, where Sb < 5,000 mg/kg and As < 20,000 mg/kg. Although there is considerable dispersion of the data there is a degree of correlation (correlation coefficient r = 0.65) between the two elements as might be expected given that they are isostructural. This suggests that Sb is likely to be contained in those minerals that also contain As. The only available reference values for Sb in soil are the pre-2004 ATSDR Comparison Values (Table 2) of 20 mg/kg (child) and 300 mg/kg (adult). Clearly some mine sites have at least some solid waste with concentrations well in excess of these concentrations.

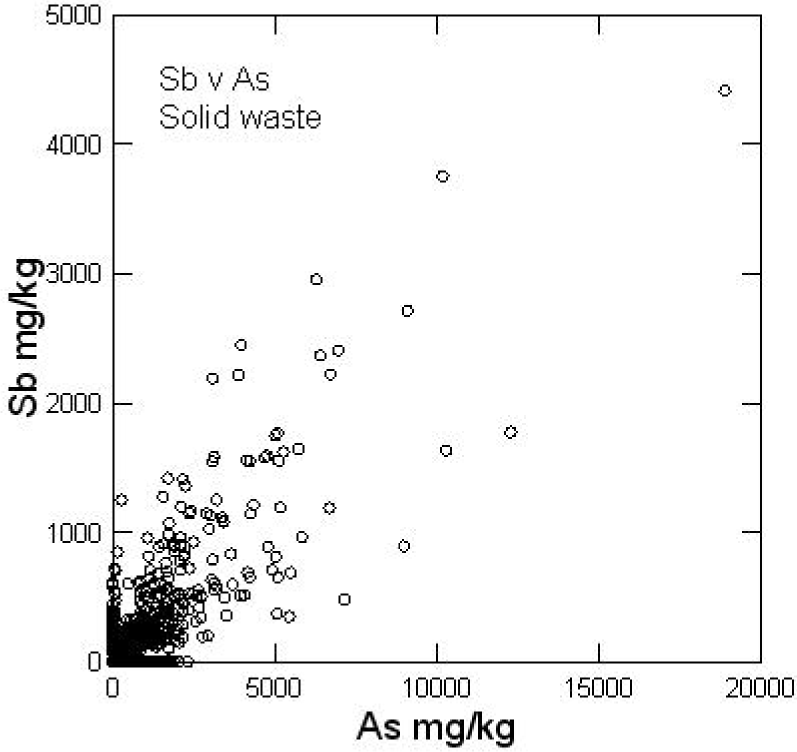


Fig. 5 Sb v As for *in situ* solid waste analyses (limited range)

The concentrations of both total and dissolved Sb in surface and groundwater at Irish mine sites investigated for HMS-IRC are generally low. Most samples analysed had Sb concentrations below the detection limit of 1 µg/l (Table 10). Fig. 6 shows that for most mine districts, the maximum measured dissolved Sb concentrations in all waters analysed did not exceed 10 µg/l. Only at Gortdrum did water samples contain dissolved Sb significantly in excess of 10 µg/l. The concentration of dissolved Sb in the TMF drainage at Gortdrum was 241 µg/l; in seepage from spoil the measured concentration was 328 µg/l. Significant concentrations (28 – 30 µg/l) were also measured in the Open Pit lake. High concentrations of Sb are not unexpected at Gortdrum where it was enriched in one of the main ore minerals, tennanite. Some elevated total Sb concentrations (24 – 40 µg/l) were measured in surface run-off at Caim. Corresponding measured dissolved Sb concentrations were low, suggesting that the Sb in the total Sb analyses was in suspended particles.

Table 10 Sb (dissolved) in water on and around Irish mine sites, by source

µg/l Sb	All samples	Groundwater	Mine Water	Upstream	Downstream
n	445	27	194	60	163
Minimum	<1	<1	<1	<1	<1
Maximum	328	10	328	22	11
Median	<1	<1	<1	<1	<1
Mean	3.2	1.1	5.6	1.2	1.4

The current standard for Sb is 5 µg/l (Table 3), based upon the Irish Drinking Water standard. Only samples from Gortdrum and Tynagh consistently have measured Sb concentrations in excess of this level and most Tynagh samples had concentrations below 10 µg/l. The median dissolved Sb concentration for Gortdrum samples is 25 µg/l. A few samples from other sites, including the coalfields and Avoca, have Sb concentrations exceeding the standard (Fig. 6). Most of these samples were of mine water, i.e. adit discharges or run-off / seepages from solid waste. A few samples of stream water taken downstream of mines also had Sb concentrations above 5 µg/l, mainly at Tynagh (up to 11 µg/l), but including one case in the Leinster Coalfield (7 µg/l) and downstream of the phosphate mine in Doolin (6 µg/l).

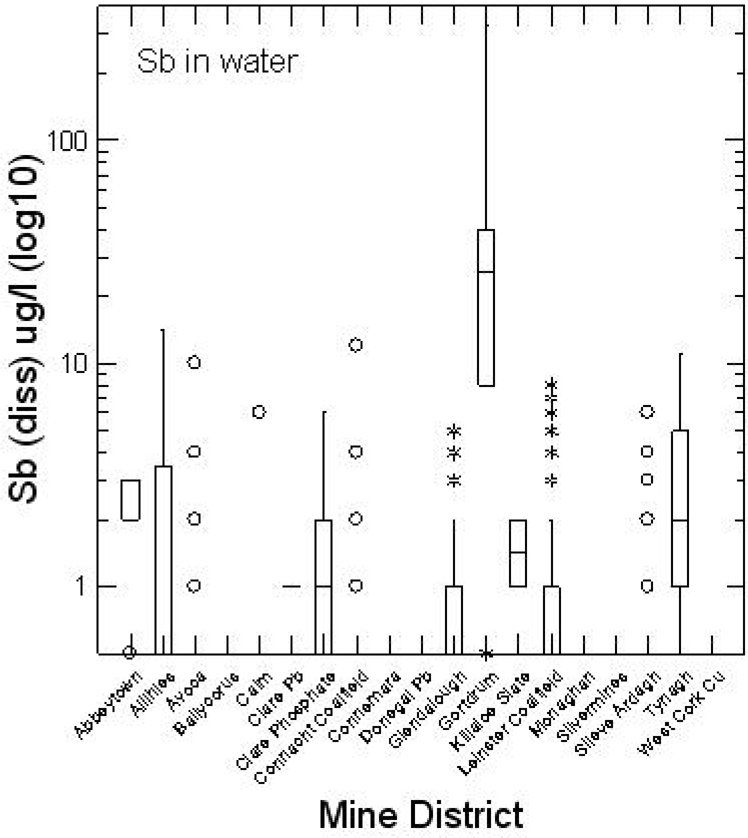


Fig. 6 Dissolved Sb in all waters analysed, by mine district (log scale)

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). As illustrated in Fig. 7 the concentration of Sb is typically below the detection limit in stream sediments around most mine sites investigated. It was apparently detected in one or two samples from Allihies, Avoca and Ballycorus and more generally at Glendalough, Silvermines and Tynagh (Fig. 7), but at concentrations below the portable XRF manufacturer's quoted detection limit (175 mg/kg). The latter three sites also have significant As in stream sediments (section 3.4, below) and the Sb data may reflect the general association of As and Sb. The standard for As in stream sediments is 1,000 mg/kg (Table 4). This is considered the maximum concentration of Sb from the perspective of animal health. None of the analyses carried out for HMS-IRC had Sb in excess of 1000 mg/kg – the maximum measured concentration was 775 mg/kg in a fine (< 150 µm) fraction from the Barnacullia stream adjacent the tailings pond. This sediment was apparently contaminated with tailings material, giving rise to much higher Sb concentrations, as well as Pb and other elements, than would otherwise be expected. All other samples analysed for the HMS-IRC project had Sb concentrations below 400 mg/kg. Since these data pertain to the fine fraction, and the total sediment fraction typically has lower metal concentrations, it is therefore unlikely that Sb exceeds standard concentrations in stream sediments around any mine site investigated for HMS-IRC project.

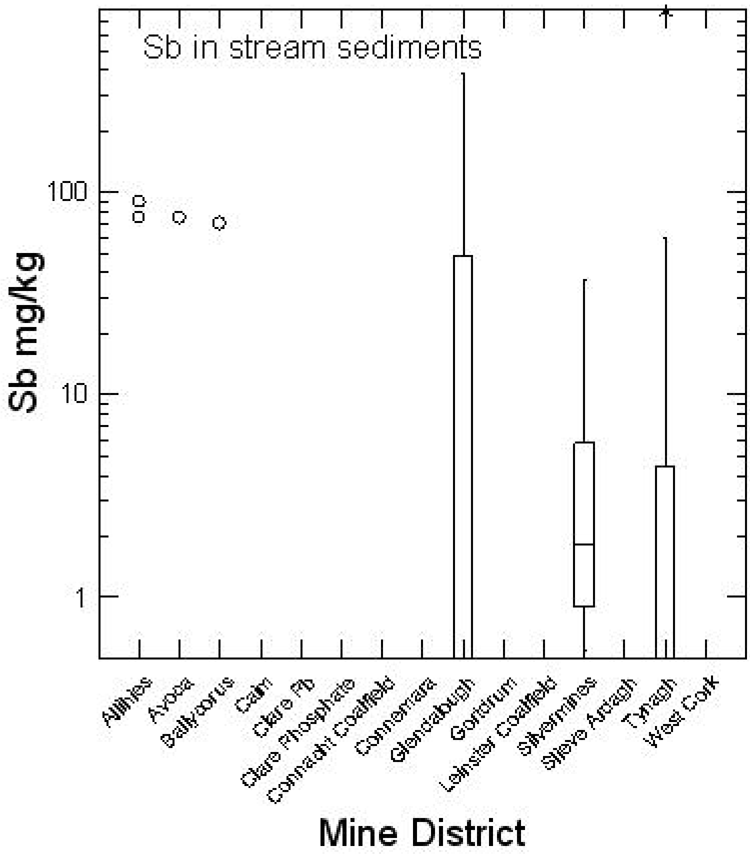


Fig. 7 Sb in stream sediments in mine districts

In summary, Sb is a significant component of solid waste on some Irish mine sites, notably Gortdrum, Glendalough, Silvermines, Tynagh and the minor Pb deposits in east Clare. Sb is probably chemically associated in sulphides with As. Gortdrum is the only mine with a reported Sb enrichment and this is reflected in the composition of mine water sampled on the site. With the exception of Gortdrum, Sb did not exceed 11 µg/l in water analysed for the HMS-IRC project. However, samples of seepage from tailings and spoil at Gortdrum had Sb concentrations in excess of 240 µg/l. In stream sediments, Sb was not detected at most sites investigated. Where it was detected, it was well below animal health standards.

3.4 Arsenic - As

3.4.1 Introduction to As

Arsenic is a *metalloid*, forming compounds in which it has the properties of a cation (As^{3+}, As^{5+}) and anion (As^{3-}). It is widely distributed in low concentrations in soils and rocks. It is an essential element for humans and animals at very low levels (Fay *et al.* 2007). The most important group of As compounds are arsenides in which As is covalently bonded to metals. Arsenides are analogous to sulphides and are common constituents of sulphide ores, especially those of Cu and Pb. The most common arsenide found in Irish mineral deposits is **arsenopyrite** (FeAsS). Arsenic can also be present in high concentrations (up to 10,000 mg/kg) in sulphides such as galena (PbS), sphalerite (ZnS) and pyrite (FeS_2).

Table 11 Concentration of As in some Irish soils, sediments and rocks

As	**Range (mg/kg)**	**Median (mg/kg)**
National Soils Database (n=1310)[1]	<0.2 - 123	7.3
Stream sediments SE Ireland (n=1884)[2]	1.4 - 779	23
Stream sediments Inishowen (n=128)[3]	2.6 - 272	17
Stream sediments NE Ireland (n=386)[2]	3.2 - 271	12
Leinster Granite SE Ireland (n=26)[2]	0.25 – 6.7	1.5
Sedimentary rocks SE Ireland (n=222)[2]	0.5 - 332	11
Volcanic rocks SE Ireland (n=123)[2]	0.25 - 5250	20

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

Table 11 summarizes the range of concentrations of As found in Irish soils, sediments and rocks. The concentrations are similar to those reported worldwide. Wedepohl (1978) reports a global average of 5–10 mg/kg As for soils, 13 mg/kg As for shales (sedimentary clay rock) and 3 mg/kg As for granite, with the upper continental crust having about 1.5 – 2.0 mg/kg As.

Globally, the concentration of As in rivers and lakes is generally below 10 µg/l, although individual samples may range up to 5000 µg/l near anthropogenic sources. Arsenic levels in groundwater have a mean of about 1 – 2 µg/l (WHO 2001).

Arsenic is used in alloys in solders and ammunition and as an anti-friction additive to metals used in bearings. Historically it has been used in the wood preservative CCA (copper chromated arsenate), now phased out for all but some specific construction products, and in arsenical weedkillers. It is used in pesticides, insecticides, batteries, semi-conductors and LEDs (Fay *et al.* 2007). Non-occupational exposure of humans to arsenic is generally through food. The daily intake of total arsenic from food and beverages is generally between 20 and 300 µg/day (WHO 2001).

Inorganic arsenic is a carcinogen. Inhalation and / or ingestion of inorganic arsenic increase the risk of lung, skin and bladder cancer, in addition to causing cardiovascular, dermal and neurological effects (ATSDR 2007). However, the toxicity of As depends on its bioavailability and this in turn depends on As speciation. As^{3+} is found under low-pH, anaerobic conditions, As^{5+} under alkaline, oxidizing conditions. As^{3+} is the more soluble and thus more toxic species. Low pH increases the bioavailability of As but this is counteracted in some surface waters by adsorption of As onto Fe- and clay-mineral particulates, particularly at low pH (Plumlee *et al.* 1999).

3.4.2 Arsenic on Irish mine sites

Arsenic is widely distributed in solid waste on Irish mine sites. Measured *in-situ* As concentrations range from below the detection limit to in excess of 1% (Table 12). Caution is needed in relation of XRF analyses of As, however, particularly for apparent high concentrations. In samples with high Pb concentrations, peak overlap between As and Pb (Appendix 4) can generate false high concentrations of As. Check samples analysed by MA-ES help identify where such false As concentrations occur.

Table 12 Summary statistics for As in solid waste in some mine districts (*in-situ* analyses)

mg/kg As	All sites	Tynagh	Avoca	Gortdrum	Silvermines	Clare Pb
n	1432	134	347	79	24	47
Minimum	0.0	0.0	0.0	14	0.0	0.0
Maximum	86734	86734	10316	18924	20934	17293
Median	95	896	361	64	757	578
Mean	861	4061	575	1150	1532	1709

Note: A value of 0.0 indicates result < detection limit

Fig. 8 shows the range and median concentrations of As for each mine district investigated for HMS-IRC. The range shown is restricted to As concentrations below 10,000 mg/kg (1%) for illustrative purposes. Given that the maximum concentration of As in analysed soils, sediments and rocks in Ireland is generally well below 1000 mg/kg, and median concentrations below 25 mg/kg (Table 11), a concentration of As in excess of 500 mg/kg may certainly be considered high. This value is also equivalent to the SGV for As in industrial soils (Table 2). On this basis, mine districts with apparently high As concentrations in solid mine waste include Avoca, Ballycorus, Caim , Clare Lead mines, Donegal Lead mines, Glendalough, Gortdrum, Silvermines and Tynagh. However, comparison of samples analysed by both XRF and MA-ES suggest that the high measured As in samples from Ballycorus, Caim, Donegal Lead mines and Glendalough are most likely a consequence of high concentrations of Pb leading to false high measured As concentration in XRF analyses. In the case of Tynagh and Silvermines, the extreme measured As concentrations mostly reflect analysis of Pb-rich processed waste. Spoil or tailings in both districts typically has much lower but still relatively high As concentrations. In Gortdrum, spoil and tailings generally have low As concentrations but high As concentrations have been verified in samples from the old processing site. Table 12 summarizes the data for those sites where the measured concentration of As in solid mine waste consistently exceeds 500 mg/kg.

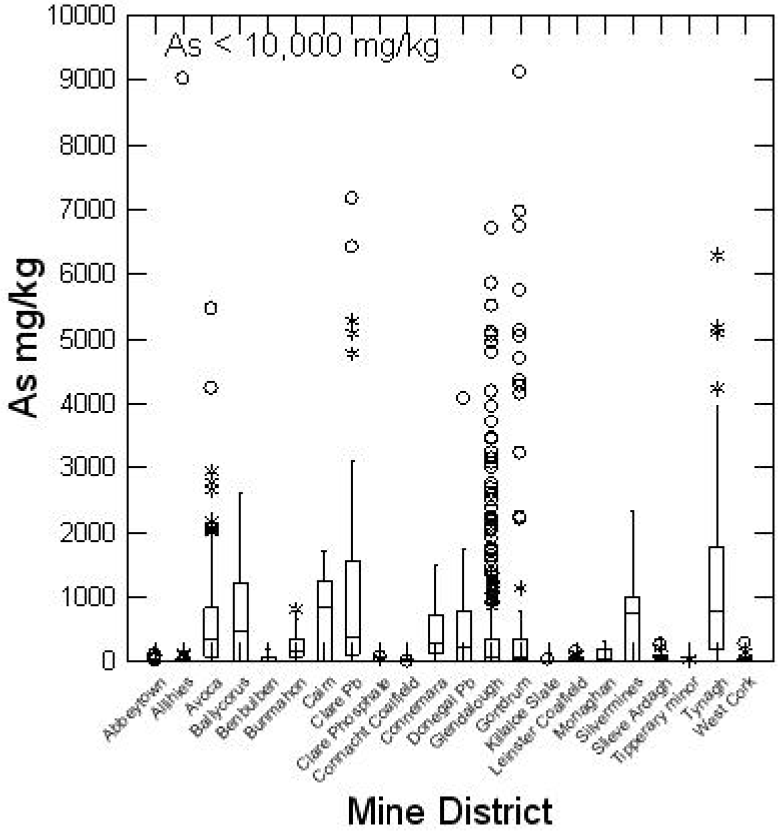


Fig. 8 Boxplots of As in solid mine waste for each district investigated

Levels of total As in surface and groundwater at Irish mine sites investigated for HMS-IRC are generally low. Only mine waters have significantly elevated concentrations of As. Table 13 summarizes the data for total As in all samples analysed for the HMS-IRC project as well as 21 samples collected at Silvermines (Inter-Agency Group 2000). Fig. 9 shows the variation in total As across the various mine districts. Total As is used since analyses of laboratory blanks indicate that there was no apparent analytical problems for As.

The current standard for As is 25 µg/l (Table 3) and, among those analysed, only mine waters exceed this, specifically some samples from Abbeytown (tailings drainage), Avoca (surface run-off) and Gortdrum (tailings drainage, open pit lake and spoil seepage). The Abbeytown water drains into the estuary of Ballysadare Bay while the Gortdrum spoil seepage drains underground.

Table 13 As (total) in water on and around Irish mine sites, by source

µg/l As	All samples	Groundwater	Mine Water	Upstream	Downstream
n	466	27	197	67	174
Minimum	<1	<1	<1	<1	<1
Maximum	271	1	271	25	15
Median	<1	<1	<1	<1	<1
Mean	3.8	<1	7.3	1.5	1.1

A preliminary groundwater study (Henry 2008), carried out on behalf of concerned residents in the area, examined four wells around the site, three to the east and one to the west. Samples from the wells east of the mine showed As concentrations ≤ 299 µg/l, Ni ≤ 35 µg/l and Pb ≤ 20 µg/l. These concentrations of As and Ni exceed the current drinking water standards (European Communities 2007) of 10 µg/l and 20 µg/l, respectively.

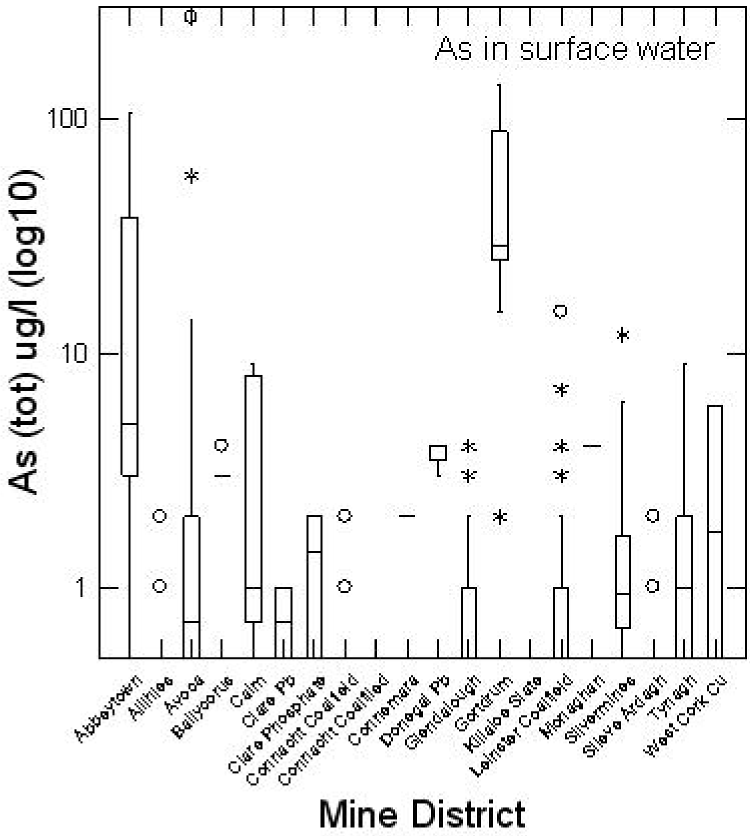


Fig. 9 Total As in all waters analysed, by mine district (log scale)

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). As illustrated in Fig. 10, the concentration of As in stream sediments around mine sites is typically below 100 mg/kg. The standard for As in stream sediments is 300 mg/kg (Table 4). The median value of all samples analysed is 33 mg/kg (range: <DL – 1183 mg/kg). This includes samples from Glendalough (median: 60 mg/kg) where the As concentration is somewhat exaggerated owing to high Pb concentrations. Apart from Glendalough, Tynagh (median: 18 mg/kg) and Silvermines (median: 44 mg/kg) are the districts where high As has been consistently detected in stream sediments. In both districts, however, only a few samples relatively close to mine sites have As concentrations exceeding 100 mg/kg, as indicated by their low median concentrations. Isolated high As concentrations have also been measured in the Leinster Coalfield, Slieve Ardagh coalfield, West Cork (Ballycummisk and Glandore) and Clements mine in Connemara (Fig. 10).

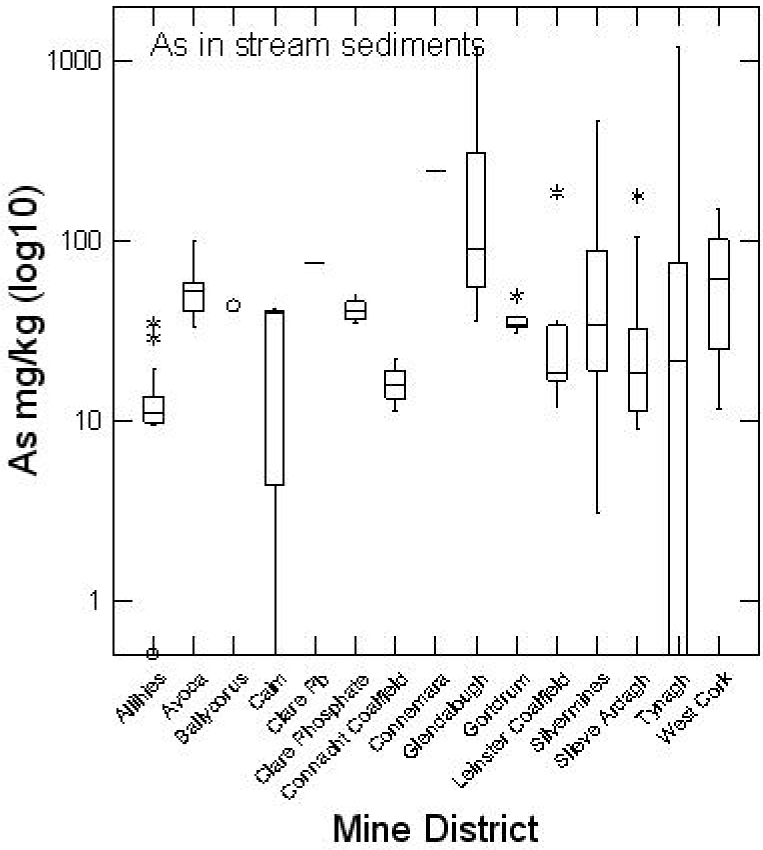


Fig. 10 As in stream sediments in mine districts

In summary, As is a significant component of solid mine waste on some mine sites in Ireland, notably Avoca, Tynagh, Gortdrum, Silvermines and some small sites in east Clare. Typically, concentrations are less than 1000 mg/kg but higher concentrations do occur, especially on the sites of former processing plants. Concentrations of As in stream sediment are generally below 100 mg/kg although a few samples on some sites exceed this. Among water samples, only mine waters, including adit/shaft discharges and waste seepages, have As concentrations exceeding the standard of 25 µg/l (Surface Water (Draft European Communities Environmental Objectives (Surface Waters) Regulations, 2008). The total As concentrations measured in stream water samples, including those taken downstream of mine sites, are all ≤25 µg/l.

3.5 – Barium - Ba

3.5.1 Introduction to Ba

Barium is a common metal found mostly in polymetallic ore deposits. Barium compounds are used to make paint, bricks, ceramics, glass, rubber and even rat poison. It is used as a drilling mud by the oil and gas industry. The search for new supplies of Ba for the exploration industry led to an upsurge in Ba mining in Ireland in the 1960s and 1970s. Ba sulphate is the main component of the barium meal used for X-rays of the gastrointestinal tract. Ba is introduced to the environment by mining and refining of Ba compounds and by the burning of coal and oil. Ba compounds that are soluble, such as chlorides and nitrates, do not last long in solution as they combine with sulphate and carbonate to form the insoluble sulphate and carbonate.

Ba forms compounds with sulphate and carbonate, such as **barite** ($BaSO_4$) and **witherite** ($BaCO_3$). Ba^{2+} has the largest ionic radius of the divalent cations apart from Ra^{2+}. It substitutes isostructurally for other large cations such as K^+, Ca^{2+}, Pb^{2+}, Sr^{2+}. In igneous rocks, Ba is usually distributed among silicates, mainly K feldspars and micas in which it substitutes for K (Wedepohl 1978). Ca is substituted in plagioclase, pyroxene and amphibole. BaO rarely exceeds 2% (20,000 mg/kg) in K feldspar, and is typically present in amounts less than 1000 mg/kg. However, forms a solid solution with orthoclase and in this series up to 9.5 % Ba may be present. The most important Ba minerals are K feldspar with a **celsian** ($BaAl_2Si_2O_8$) component in igneous rocks, in which Ba may reach 9.5%, and barite in sedimentary rocks and hydrothermal ore deposits. The average Ba content of the upper continental crust is 550 mg/kg (Taylor and McLennan 1986).

Table 14 Concentration of Ba in some Irish soils, sediments and rocks

Ba	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	6.6 – 1297	230
Stream sediments SE Ireland (n=1884)[2]	<50 – 4000	420
Stream sediments Inishowen (n=128)[3]	<340 – 1300	650
Stream sediments NE Ireland (n=386)[2]	280 - 3900	590
Leinster Granite SE Ireland (n=26)[2]	25 – 680	435
Sedimentary rocks SE Ireland (n=222)[2]	25 – 1300	550
Volcanic rocks SE Ireland (n=123)[2]	25 - 8740	330

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

Table 14 summarizes the range of concentrations of Ba found in Irish soils, sediments and rocks. The mean concentration of Ba in US soils is reported to be 420 mg/kg (ATSDR 2007), with distinctly lower concentrations found in areas not affected by industrial activity. Concentrations of Ba in igneous, sedimentary and metamorphic rocks worldwide are broadly similar and range from around 300 to 600 mg/kg (Wedepohl 1978). Ba in raw surface waters and drinking water in the US was found to range from <5 to 15,000 µg/l, with mean concentrations of the order of 10 – 60 µg/l (ATSDR 2007). Most drinking water had Ba < 200 µg/l. Groundwater in the US has been found to contain high Ba concentrations in places, with leaching of sediments the likely cause. Concentrations of up to 10,000 µg/l have been measured (ATSDR 2007).

Ba is not included in either the current Drinking Water Standard in Ireland or the Surface Water (Draft European Communities Environmental Objectives (Surface Waters) Regulations, 2008). The US EPA has set a drinking water maximum contaminant level of 2,000 µg/l Ba (2 mg/l). Ba can cause gastrointestinal problems and muscular weakness when people drink water with Ba levels above this limit, even for short periods of time. Prolonged exposure to Ba in water or food has been shown to cause kidney damage and even death in animals.

3.5.2 Ba on Irish mine sites

Reference values for Ba in soils (Table 2) vary significantly. Thus the Dutch Intervention value for “standard” soil is 625 mg/kg whereas ATSDR Comparison Values of 4,000 mg/kg Ba (0.4%) for a child and 50,000 mg/kg Ba (5%) for an adult, are much higher. Given that the concentration of Ba occurring apparently naturally in Irish soils ranges up to 1297 mg/kg (Table 14), the Dutch value appears to be too low to be used as a reference.

Fig. 11 shows the distribution of Ba in solid mine waste in the various mine districts in Ireland. Median values for the various districts are typically between 500 and 1000 mg/kg with the median of all analyses carried out for the HMS-IRC project 600 mg/kg (Table 15). Not surprisingly, high concentrations of Ba have been recorded in mine districts where barite ($BaSO_4$) was a significant component of the mineralization, such as Benbulben, Silvermines, Tynagh and West Cork. Only in these districts or sites does Ba exceed the ATSDR Comparison Values (Fig. 11). Since barite is relatively insoluble, high concentrations of Ba held in this form are not necessarily of immediate concern unless the conditions are such as to promote leaching of Ba from the solid waste. Such conditions would include low pH and high acidity, neither of which are features of the districts listed.

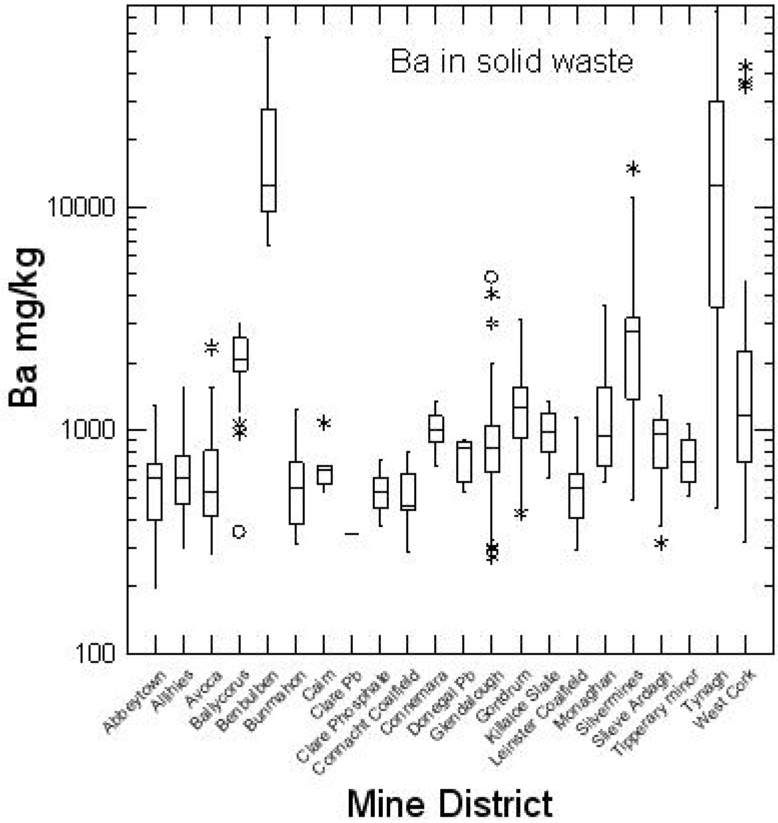


Fig. 11 Boxplots of Ba (log scale) in solid mine waste v mine district

Table 15 Summary statistics for Ba in several mine districts (*in-situ* analyses)

mg/kg Ba	All sites	Ballycorus	Benbulben	Gortdrum	Silvermines	Tynagh	W Cork
n	1432	40	8	79	24	134	28
Minimum	0.0	0.0	6761	0.0	0.0	0.0	0.0
Maximum	75032	2978	57354	3114	14952	75032	42590
Median	598	666	12690	1175	2210	12375	1111
Mean	2565	1066	20893	1184	2972	19478	5112

Note: A value of 0.0 indicates result < detection limit

Table 16 summarizes the data for total Ba in surface and groundwater at Irish mine sites investigated for HMS-IRC and at Silvermines (Inter-Agency Group 2000) and Fig. 12 shows the range and median across the districts. Given that there are no Irish or EU reference values for Ba, the US EPA's 2000 µg/l maximum value for drinking water can be used as a proxy. All samples of water analysed for HMS-IRC project had a total Ba concentrations well below 2000 µg/l. Median concentration of all samples analysed is 61 µg/l and there is little variation in median concentration when source is taken into account (Table 16). The highest Ba concentration measured for HMS-IRC was in water from a spring in the Leinster Coalfield, in use as a drinking water source, where winter and summer concentrations were 293 and 337 µg/l, respectively. When the US EPA's drinking water limit of 2,000 µg/l is applied, it can be concluded that concentrations of Ba in water around mine sites in Ireland are below levels of concern.

Table 16 Ba (total) in water on and around Irish mine sites, by source

µg/l Ba	All samples	Groundwater	Mine Water	Upstream	Downstream
n	466	27	197	67	174
Minimum	<1	<1	2	5	6
Maximum	337	337	280	316	321
Median	61	55	60	55	63
Mean	67	78	64	64	70

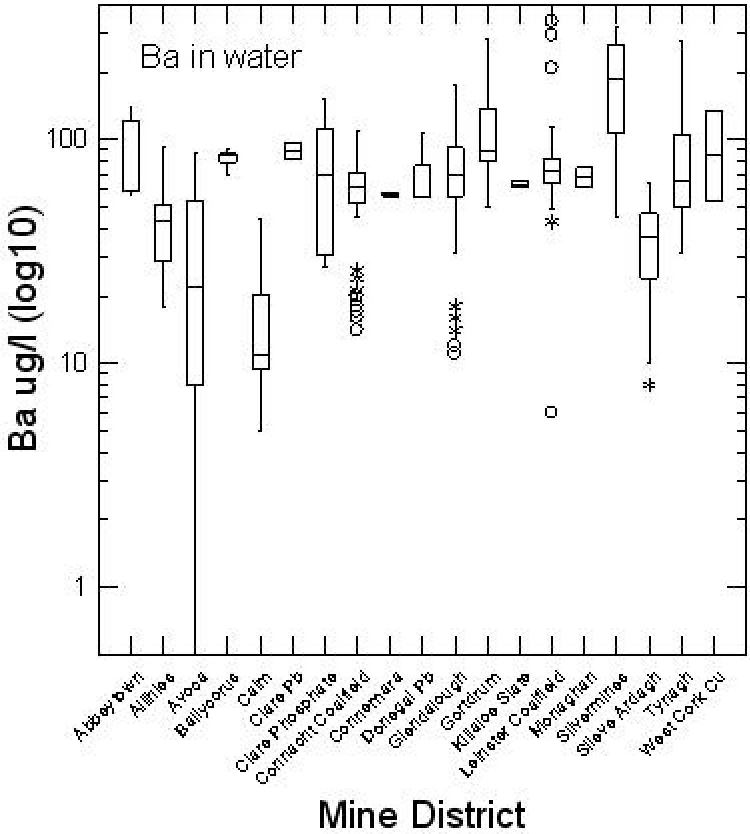


Fig. 12 Total Ba in all waters analysed, by mine district (log scale

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples, taken in 1999 by the EPA, have been added for the Silvermines district (Inter-Agency Group 2000). Fig. 13 illustrates the variation in Ba concentration in stream sediments across the various districts sampled. The standard for Ba in stream sediments employed for the HMS-IRC project is 1,000 mg/kg (Table 4). Only samples at Silvermines are consistently in excess of this level (Fig. 13). Moreover, the standard is for the total stream sediment size fraction and the <150 µm fraction analysed for HMS-IRC may be expected to have somewhat higher metal concentration.

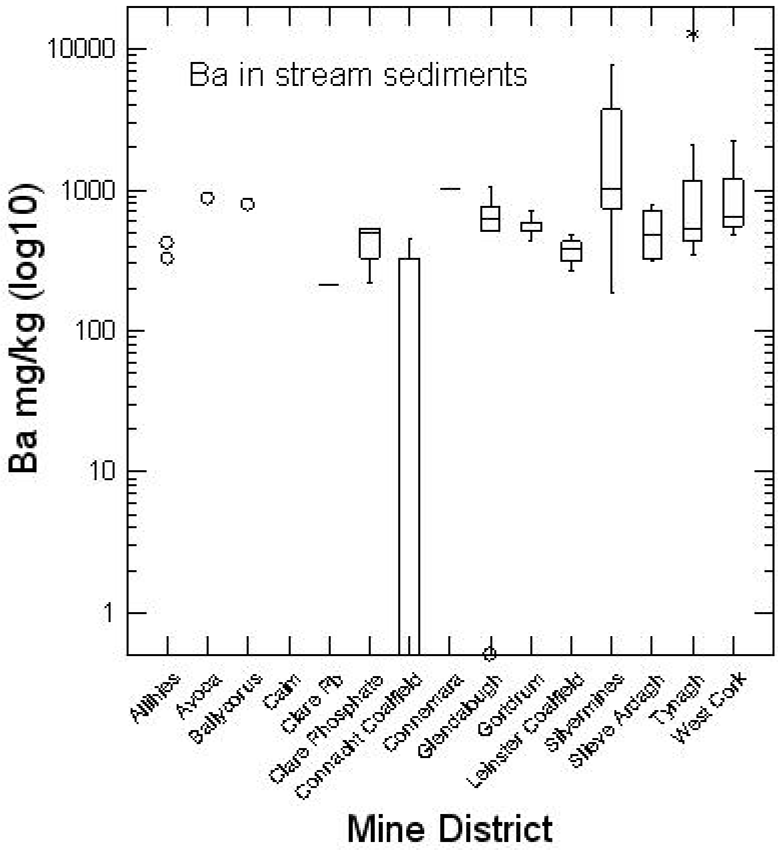


Fig. 13 Ba in stream sediments in mine districts

In summary, high concentrations of Ba have been found in solid waste on mine sites where barite is known to have been a significant component of the mineralization. Concentrations exceed the ATSDR Comparison Values in some cases, notably at Tynagh, Silvermines and Ballycorus, but are generally lower. Barium can be toxic to humans when present in drinking water in concentrations above 2000 µg/l, the US EPA MCL for drinking water. All of the water samples collected for HMS-IRC project had Ba concentrations well below this limit. However, Ba exceeded the standard limits set for animal health in stream sediments at Silvermines.

3.6 – Cadmium - Cd

3.6.1 Introduction to Cd

Cd is a naturally occurring element in the earth's crust. It occurs exclusively in compounds with oxygen, chlorine or sulphur. These are often isotypic with compounds of Zn, Mg, Fe, Co, Ni and Ca. The average abundance of Cd is higher in ferromagnesian minerals such as olivine and pyroxene (c. 0.05-0.10 mg/kg) and magnetite (0.20-3.0 mg/kg) than in feldspar (≤ 0.10 mg/kg). Biotite is an important host for Cd, e.g. in biotites from Nigerian biotite granites an average of 1.50 mg/kg Cd has been found (Wedepohl 1978). In ore minerals, the Zn minerals sphalerite and smithsonite are the main hosts, typically containing 1.0-5.0 mg/kg Cd. The Zn:Cd ratio in sphalerite at Tynagh mine was 200:1. The common Cd minerals are **greenockite** (CdS), **octavite** ($CdCO_3$) and **cadmium oxide** (CdO). Greenockite and cadmium oxide occur as coatings on sphalerite and smithsonite, respectively.

The average Cd abundance in granites and intermediate igneous rocks is < 0.10 mg/kg; in basalts and gabbros is c. 0.10 ppb (Heinrichs *et al.* 1981). The abundance of Cd is the same in the *bulk*, the *upper* and the *lower* continental crust and is estimated to be 0.10 mg/kg (Heinrichs *et al.* 1981). The average content of Cd in normal shales is 0.1100-0.20 mg/kg and in limestones 0.07-0.16 mg/kg (Heinrichs *et al.* 1981). Higher values are found for black shales (e.g. 1.45 mg/kg) and manganese nodules. Soils not contaminated by anthropogenic sources have Cd concentrations between 0.06 and 1.10 mg/kg (ATSDR 2008). The generally low concentration of Cd in common rocks and soils, as well as high detection limit of technique employed (NAA), mean that it has been detected in only a limited number of samples analysed as part of stream sediment and rock geochemistry programmes in Ireland (Table 17). The concentration of Cd in groundwater and natural surface waters is generally <1µg/l (ATSDR 2008).

Table 17 Concentration of Cd in some Irish soils, sediments and rocks

Cd	**Range (mg/kg)**	**Median (mg/kg)**
National Soils Database (n=1310)[1]	<0.02 – 15.15	0.33
Stream sediments SE Ireland (n=1884)[2]	<5 – 350	<5
Stream sediments Inishowen (n=128)[3]	<5 – 12	<5
Stream sediments NE Ireland (n=386)[2]	<5 - 55	<5
Leinster Granite SE Ireland (n=26)[2]	<5 - <5	<5
Sedimentary rocks SE Ireland (n=222)[2]	<5 – 77	<5
Volcanic rocks SE Ireland (n=123)[2]	<5 - 20	<5

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

Cd is used in Ni-Cd batteries, in pigments and in plating and coating (Fay *et al.* 2007). It is released to the environment through smelting, mining and production of phosphatic fertilizers. It has no known biological role and both it and its compounds are toxic (Fay *et al.* 2007). Humans are exposed to Cd through food, which contains low concentrations of Cd, cigarette smoke and contaminated air and water downstream of industrial sites, including mines. Long-term exposure can have serious health effects on humans, particularly lung damage, liver damage, kidney damage and bone loss (ATSDR 2008; Solomon 2007). Cd is a carcinogen. Its long half-life of 30 years means that it is impossible for humans to clear it from their bodies once it has accumulated. Cd has significant potential impacts on aquatic ecosystems where it can impair plant growth. In fish Cd can damage renal function and cause skeletal deformities by replacing Ca in bones (Solomon 2007). Standard concentrations for Cd are among the lowest of any element (Tables 2 and 3).

3.6.2 Cadmium on Irish mine sites

Reference values for Cd in soils range from 12 mg/kg (Dutch Intervention value) to a SGV of 1400 mg/kg for "industrial" sites (Table 2). ATSDR Comparison Values are 10 mg/kg for a child and 100 mg/kg for an adult. The latter is a useful threshold value for HMS-IRC since it is above the quoted detection limit but low enough to provide discrimination among sites investigated.

Cadmium's typically low abundance in most minerals and rocks, combined with a relatively high detection limit in the portable XRF (around 65 mg/kg for prepared samples, higher for *in*-situ samples), means that it was recorded in just under 40% of all *in-situ* XRF analyses of solid mine waste. Comparison of samples analysed in the external laboratory by MA-ES and in the field by portable XRF indicates that the field analyses tend to give lower concentrations than the lab analyses. Where high Cd concentrations, i.e. in excess of 100 mg/kg, were measured by MA-ES, high concentrations were also generally measured by portable XRF. Fig. 14 shows the distribution of Cd in solid mine waste across the districts and sites investigated. Only four districts or sites show consistently high measured Cd concentrations: minor Pb deposits in Kilbricken and Ballyhickey in East Clare, Glendalough, Silvermines and Tynagh. In the Glendalough district, the high Cd concentrations were measured mainly in processing waste; in Silvermines and Tynagh, high Cd concentrations were measured in processing waste, spoil and tailings. In Kilbricken, only spoil was analysed while high Cd concentrations were also detected in mortar in the ruins of the engine house in Ballyhickey. Table 18 summarizes the data for these deposits.

Table 18 Summary statistics for Cd in several mine districts (*in-situ* analyses)

mg/kg Cd	All sites	Clare Pb	Glendalough	Silvermines	Tynagh
n	1432	47	381	24	134
Minimum	0.0	0.0	0.0	0.0	0.0
Maximum	1969	505	660	728	1969
Median	0.0	0.0	51	89	57
Mean	39	59	63	198	129

Note: A value of 0.0 indicates result < detection limit

As discussed above, Cd generally substitutes for Zn in sulphide deposits. At Tynagh, sphalerite (ZnS) was known to be enriched in Cd with a Zn:Cd ratio of 200:1. Fig. 15 shows the relationship between Zn and Cd for all samples analysed for the HMS-IRC project. A general linear relationship is apparent.

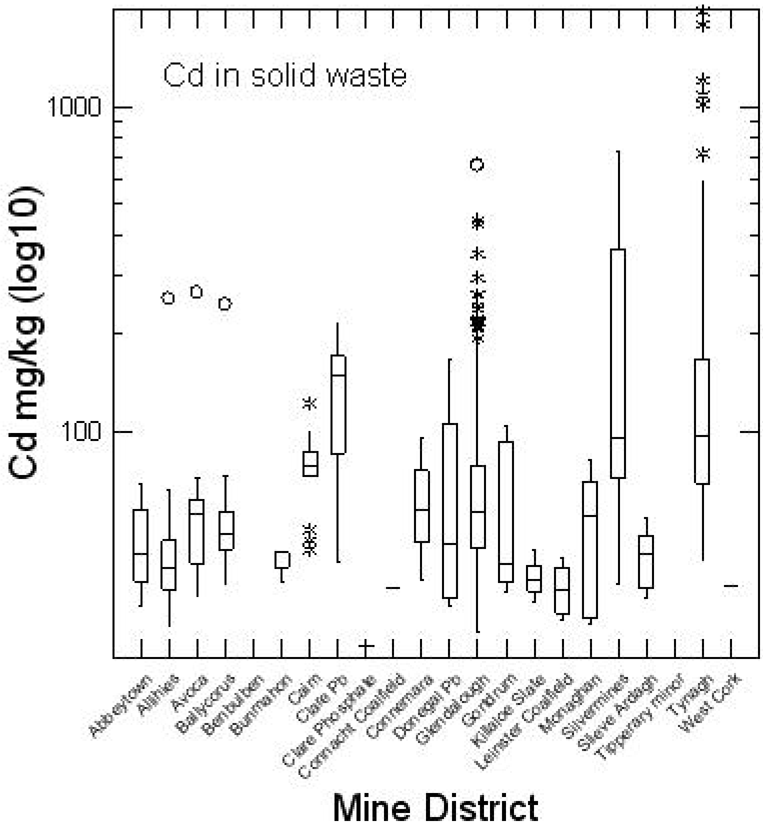


Fig. 14 Cd in solid waste, by district

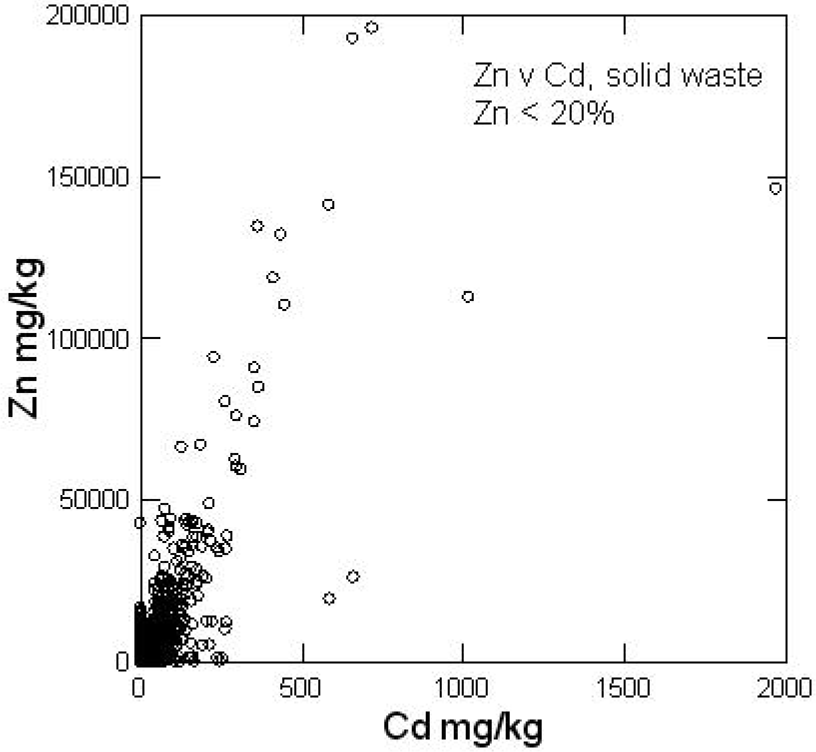


Fig. 15 Cd v Zn in solid waste (Zn < 20%)

Table 19 summarizes the data for total Cd in surface and groundwater at Irish mine sites investigated for HMS-IRC and at Silvermines (Inter-Agency Group 2000) and Fig. 16 shows the range and median across the districts. The Draft EC surface water standard is 0.25 µg/l. The detection limit for total Cd during the period of analysis was 1 µg/l for samples analysed for the HMS-IRC project; a detection limit of less than 0.1 µg/l applied for the Silvermines analyses carried out for the Inter-Agency Report. In the 466 samples analysed, Cd (total) was detected in 143, i.e. about 30% of samples. Of these 143 samples, 93, or 65% , were mine water samples.

Table 19 Cd (total) in water on and around Irish mine sites, by source

µg/l Cd	All samples	Groundwater	Mine Water	Upstream	Downstream
n	466	27	197	67	174
Minimum	0.1	<1	<1	0.1	0.21
Maximum	350	7	350	25	22
Median	<1	<1	<1	<1	<1
Mean	8.9	1.0	19.3	0.8	1.5

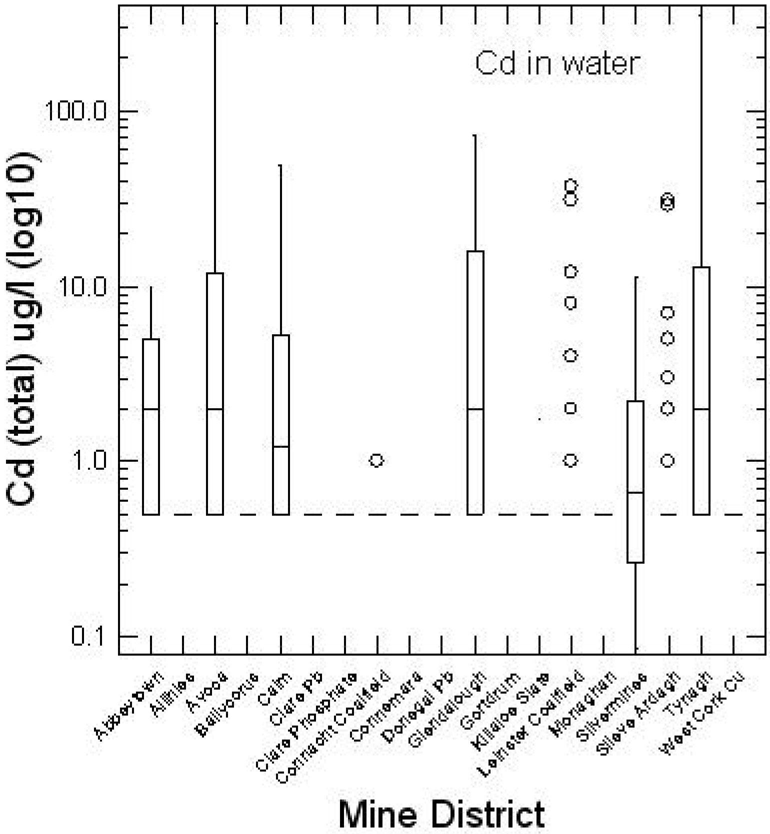


Fig. 16 Total Cd in all waters analysed, by mine district (log scale)

The highest Cd concentration in waters analysed for HMS-IRC (350 µg/l total Cd) was measured in a seepage from a large spoil heap at Tynagh mine. This had previously been identified by the EPA in its investigation at Tynagh (EPA 2003). High Cd concentrations in mine water at Tynagh are not unexpected given the high Cd concentration in sphalerite. Other mine waters with high Cd concentrations include adit discharges at Avoca (up to 317 µg/l), adit discharges in Glendalough district (up to 73 µg/l) and seeps and run-off from processing waste at Caim (up to 49 µg/l). Also notable are a few isolated high concentrations (up to 37 µg/l) in surface run-off from coal waste in the Leinster and Slieve Ardagh coalfields. In both the Avoca and coalfield samples, low pH and high acidity may play a role in bringing Cd into solution.

Cd was detected in stream sediments at only three districts or sites: Glendalough, Silvermines and Tynagh. In the case of Silvermines, analysis was by wet chemical technique and correspondingly low detection limits applied. The standard for Cd in stream sediments, based on protection of animal health, is 100 mg/kg (Table 4). This was exceeded in one stream sediment sample at Silvermines, immediately downstream of the Garryard processing site, at Tynagh in a stream highly contaminated by tailings and in a few sites at Glendasan, downstream of the mines. Some caution is required when interpreting XRF data for stream sediments since there is a tendency for Cd concentrations in dried and prepared samples analysed by XRF in the GSI laboratory to be somewhat exaggerated (Appendix 4). However, the presence of relatively high Cd in these samples is consistent with the measured high Cd concentrations in processing waste upstream of the sediment sampling locations.

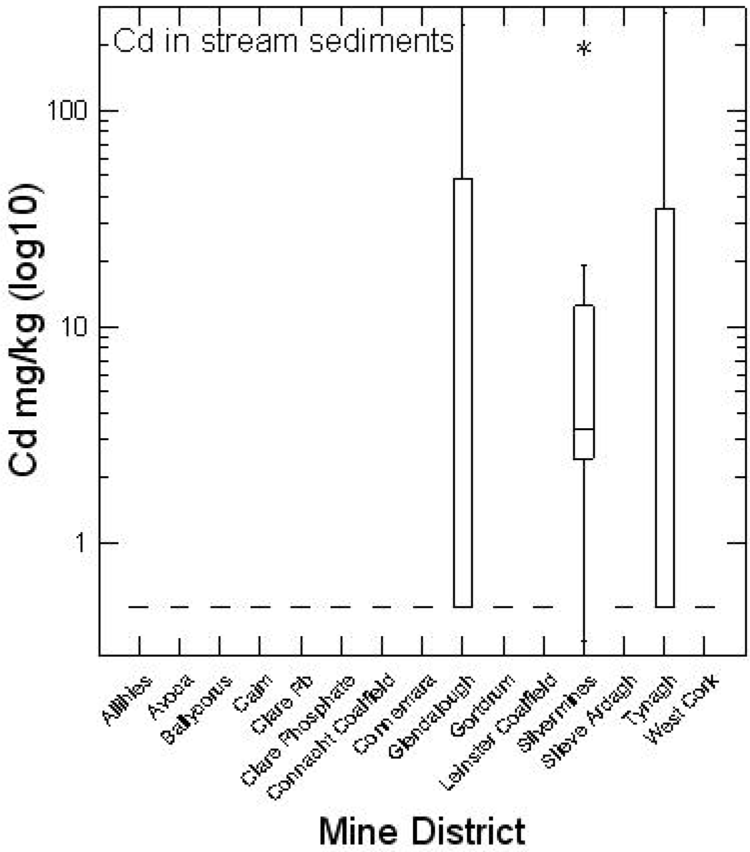


Fig. 17 Cd in stream sediments in mine districts (log scale)

In summary, Cd concentrations in excess of standards have been detected in solid waste and stream sediments in the Glendalough district, Silvermines and Tynagh. Solid waste at Kilbricken and Ballyhickey in east Clare also has high Cd concentrations. Concentrations in some solid waste, in particular, are significantly above the ATSDR Adult Comparison Value of 100 mg/kg. A few adit discharges, waste seeps and surface run-off samples at Avoca, Glendalough and Caim were found to have total Cd concentrations in excess of 10 or even 100 µg/l. These have potential implications for aquatic ecosystems where they discharge to streams. However, in 70% of water samples Cd was found to be below the detection limit. It should be noted that the detection limit for the HMS-IRC project, using ICP-MS for total Cd, was 1 µg/l, well above the draft EC level of 0.25 µg/l (Table 2).

3.7 – Chromium - Cr

3.7.1 Introduction to Cr

Cr occurs widely in rocks and minerals, in which it replaces Al, Fe and Mg. The most important mineral in which Cr is a major component is the spinel **chromite** ($FeCr_2O_4$), characterized by considerable replacement of Cr by Al. Natural Cr sulphides, such as **daubréelite** ($FeCr_2S_4$), have been described only from meteorites. The estimated concentration of Cr in the upper crust is 35 mg/kg (Taylor and McLennan 1986). Cr partitions into the mafic phase of crystallizing magmas and is thus relatively enriched in mafic and ultramafic igneous rocks (250 – 2300 mg/kg) relative to granite (10 mg/kg). The Cr content of sediments reflects their source and can range up to 100 mg/kg or more, with sandstones and limestones having considerably lower concentrations than shales and greywackes. Soil concentrations in one study the US ranged from 1 to 2,000 mg/kg (mean 37 mg/kg); in Canada the range was 5 to 1,500 mg/kg with a mean of 43 mg/kg (ATSDR 2008b). The median values in both cases are very close to that obtained for Irish soils (Table 20).

Table 20 Concentration of Cr in some Irish soils, sediments and rocks

Cr	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	<2 – 222	43
Stream sediments SE Ireland (n=1884)[2]	9 – 1100	69
Stream sediments Inishowen (n=128)[3]	43 – 156	89
Stream sediments NE Ireland (n=386)[2]	51 - 825	137
Leinster Granite SE Ireland (n=26)[2]	7 – 32	17
Sedimentary rocks SE Ireland (n=222)[2]	22 – 708	83
Volcanic rocks SE Ireland (n=123)[2]	100 - 483	88

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

Concentrations of Cr in US river water ranges from <1 µg/l to 30 µg/l with a median of 10 µg/l (ATSDR 2008b). The Irish Drinking Water standard for Cr is 50 µg/l. None of the samples of drinking water sources analysed in 2006-2007 exceeded this level (EPA 2007).

Cr occurs in nine valence states of which the most important are Cr^0, Cr^{3+} (CrIII)and Cr^{6+} (CrVI). CrVI is a carcinogen and regarded as highly toxic to humans by ingestion and inhalation. It is normally released to the environment only as a consequence of industrial activity (Fay *et al.* 2007). CrIII, by contrast, the most common form, is an essential nutrient for humans in small amounts (Fay *et al.* 2007). Cr is used in the manufacture of corrosion-resistant alloys, chrome-plating, dyes and pigments and in leather tanning. It was formerly used as a wood preservative, particularly for outdoor furniture and decking, in the form of the now-restricted CCA (chromated copper arsenate). CCA was a significant source of CrVI released to the environment. Cr is released to the environment through industrial activity, chiefly manufacturing. Humans are exposed to Cr through food (CrIII), and workplace exposure and contaminated air and water downstream of industrial sites. Ingestion of CrVI can cause ulcers of the digestive tract, nasal tract irritation and damage, kidney damage, deformation of the spine, low white blood cell counts, miscarriages, and lung and stomach cancer (Solomon 2007). In aquatic systems, CrVI reduces algal growth at concentrations above 60 µg/l but it can inhibit fish growth at concentrations as low as 15 µg/l (Solomon 2007). Growth reduction may make species more vulnerable to predators and thus this sub-lethal effect becomes a lethal effect.

3.7.2 Chromium on Irish mine sites

Published reference values for Cr in soils typically refer to the Cr^{6+} valence state since this is a known carcinogen. There is a Dutch Intervention value of 380 mg/kg for "total" Cr in "normal" soil (Table 2) and this value is referred to here.

Comparison of total Cr concentrations in prepared samples measured by portable XRF in the GSI laboratory and by MA-ES in a commercial laboratory suggests that the detection limit for Cr in XRF analyses is at least 50 mg/kg and that concentrations measured by XRF are in many cases exaggerated or otherwise unreliable (Appendix

4). There are several possible reasons for this exaggeration, including interference from Ba, Mn and V peaks in the XRF spectrum. In samples with high Ba, apparently high Cr concentrations have been measured, e.g. at Benbulben barite deposit and at Tynagh, where barite is an important component of the ore. Detailed assessment of the XRF spectra for these analyses as well as consideration of samples analysed by MA-ES in the external laboratory suggest that these samples are unlikely to contain significant concentrations of Cr and that the apparent high Cr concentrations reflect overlap of the Cr X-ray peak by Ba and Mn peaks. In the Clare Phosphate deposits, high V concentrations in the black shale host give rise to apparent high Cr concentrations because of overlap of Cr by V in the XRF spectrum. In 221 analyses of solid waste samples by MA-ES in the external laboratory, Cr had a maximum concentration of 157 mg/kg and a median concentration of 34 mg/kg. In the light of these results and the lack of certain evidence in the XRF analyses of solid waste for high Cr concentrations, it is concluded that there is no firm evidence that Cr is present in solid waste on Irish mine sites in excess of the reference value of 380 mg/kg.

Table 21 summarizes the data for dissolved Cr in surface and groundwater at Irish mine sites investigated for HMS-IRC and Fig. 18 shows the range and median across the districts. Dissolved Cr is quoted here because data for laboratory blanks suggest that total Cr analyses are insufficiently reliable in a number of cases, with evidence for cross-contamination during analysis giving rise to false high total Cr concentrations. The Irish Drinking Water standard for Cr is 50 µg/l, well in excess of the concentrations measured in most samples (Table 21). The Draft EC Surface Water standards refer to the individual Cr^{3+} and Cr^{6+} species rather than total Cr. The reference value for Cr^{3+} in the EC Draft standards, 4.7 µg/l, is to be added to the background level. If it is assumed that Cr as analysed is equivalent to Cr^{3+} then the highest concentration measured in an upstream sample, 11 µg/l, when added to 4.7 µg/l gives a standard of 15.7 µg/l for dissolved Cr in waters around Irish mine sites. One sample of waste run-off at Avoca had a concentration of 17 µg/l Cr. Five samples from the Leinster Coalfield, mostly run-off and seepage from coal-rich waste at Fleming’s mine site, accounted for all other samples with Cr in excess of the standard.

Table 21 Cr (dissolved) in water on and around Irish mine sites, by source

µg/l Cr	All samples	Groundwater	Mine Water	Upstream	Downstream
n	445	27	194	60	163
Minimum	<1	<1	<1	<1	<1
Maximum	148	7	100	11	148
Median	1	3	1	1	1
Mean	2.7	3.0	3.1	2.0	2.5

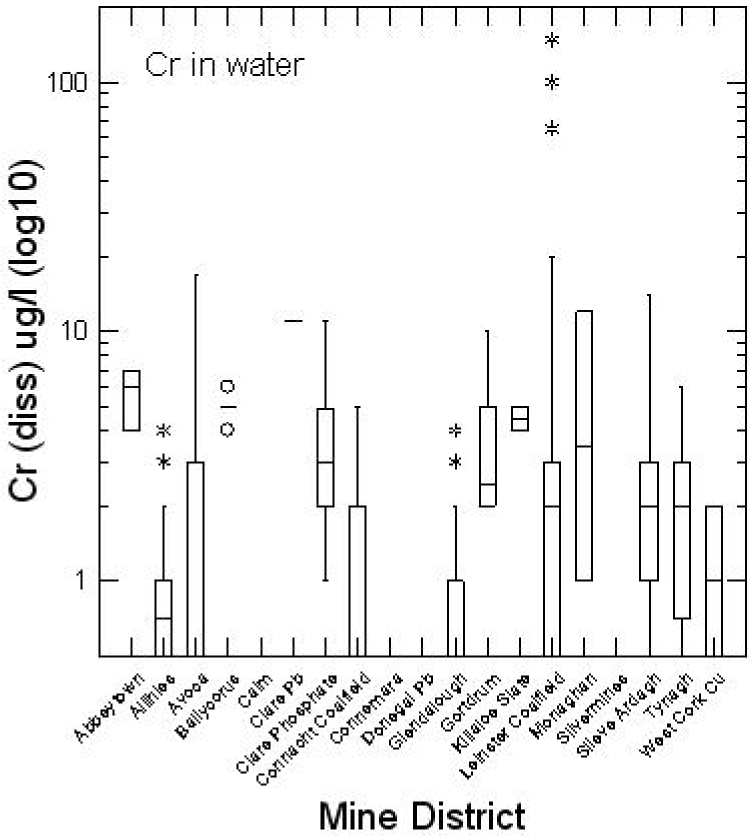


Fig. 18 Dissolved Cr in all waters analysed, by mine district (log scale)

Cr was detected in a limited number of stream sediment samples analysed for HMS-IRC. The analytical concerns identified in respect of XRF analyses of solid waste also apply to stream sediment analyses. Only the data for Silvermines, where the analysis was carried out in a commercial laboratory using a wet chemical method, can be considered reliable. The range in Cr concentration was 9 to 27 mg/kg with a median concentration of 18 mg/kg. The highest Cr concentration measured by XRF was 220 mg/kg. Given the tendency in XRF analyses toward excessively high measured concentrations and the fact that the fine fraction analysed tends to concentrate metals, it is unlikely that the Cr concentration of the total size fraction of stream sediments downstream of any mine site investigated exceeds 200 mg/kg. The animal health standard for Cr^{3+} in stream sediments is 1,000 mg/kg so there does not appear to be any risk to livestock of exposure to excessive concentrations of Cr in stream sediments around Irish mine sites.

In summary, the analytical data available for Cr in both solid waste and stream sediments at Irish mine sites are somewhat limited in terms of quality. However, there is little evidence to suggest that Cr is a significant component of solid waste or stream sediments on Irish mine sites. The same is true for Cr concentrations in water discharging from and downstream of mine sites. The exception appears to be the Leinster Coalfield where elevated Cr concentrations were detected in seepages and run-off from coal-rich solid waste. The volumes of these discharges are very low, however, and unlikely to represent a significant environmental risk.

3.8 – Copper - Cu

3.8.1 Introduction to Cu

Copper occurs naturally in rocks, soils, air, water, plants and animals. It is an essential element for all plants and animals, including humans. Copper is a metal, occurring in three valence states, Cu^0, Cu^+ and Cu^{2+}. The main Cu minerals are the native metal, Cu; sulphides such as **chalcopyrite** ($CuFeS_2$); oxides, e.g. **cuprite** (Cu_2O); carbonates such as **azurite** ($Cu_3(CO_3)_2(OH)_2$) and **malachite** ($Cu_2(CO_3)(OH)_2$) and numerous sulphates, arsenates, phosphates and silicates.

Copper is used in the manufacture of electrical equipment, including wiring, plumbing pipes, alloys such as bronze, algaecides, molluscicides and fungicides. It is widely used in feed additives for farm animals (Fay *et al.* 2007). It is introduced to the environment through activities such as mining, manufacturing and the spreading of sewage sludge and pig slurry, as well as natural phenomena including volcanic eruptions, dust blows, decaying vegetation and forest fires.

Table 22 summarizes the range of concentrations of Cu found in Irish soils, sediments and rocks. The range for stream sediments and volcanic rocks in southeast Ireland is high, reflecting the presence of major Cu mineralization at Avoca and Bunmahon. Median values range from 16 to 41 mg/kg. These median concentrations are similar to average concentrations reported elsewhere for Cu. For example, Wedepohl (1978) reports a global average of 25 mg/kg Cu for soils, 45 mg/kg for shales and 12 mg/kg for granite. The average Cu concentration of the earth's upper crust is 25 mg/kg (Taylor and McLennan 1985).

Table 22 Concentration of Cu in some Irish soils, sediments and rocks

Cu	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	1.1 - 272	16
Stream sediments SE Ireland (n=1884)[2]	4 - 1115	25
Stream sediments Inishowen (n=128)[3]	14 - 119	41
Stream sediments NE Ireland (n=386)[2]	16 - 524	38
Leinster Granite SE Ireland (n=26)[2]	3 – 50	16
Sedimentary rocks SE Ireland (n=222)[2]	3 - 93	22
Volcanic rocks SE Ireland (n=123)[2]	3 - 15500	24

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

The concentration of Cu in unpolluted freshwater is generally below 1 µg/l (Wright and Wellborn 2002). Cu binds to sediments and organic compounds, decreasing its bioavailability, but as pH decreases the bioavailability of Cu increases because the concentration of free Cu^{2+} increases. Cu is highly toxic to aquatic organisms, including algae, crustaceans and fish but much less so to humans and other mammals who can detoxify Cu in the liver. Cu can affect aquatic ecosystems and organisms at levels as low as 1 µg/l (Solomon 2007).

Although Cu is essential for human and animal health at low concentrations (5 – 20 mg/kg), higher levels can be harmful. Inhalation and / or ingestion of high levels of Cu can cause irritation of nose and throat, nausea, vomiting and diarrhoea in humans (ATSDR 2004). Very high doses can cause liver or kidney damage and even death. High doses are particularly harmful to sheep and young calves (Fay *et al.* 2007).

3.8.2 Copper on Irish mine sites

Copper is widely distributed at levels in excess of 100 mg/kg in solid waste in Irish mine districts investigated for HMS-IRC (Fig. 19). Unsurprisingly, Cu mines generally have the highest Cu concentrations. Those with median Cu concentrations exceeding 1000 mg/kg (0.1%) include Allihies, Bunmahon, Gortdrum and the West Cork district (Table 23). Two Pb mines, Caim and Tynagh, also have relatively high Cu concentrations. Avoca, the only significant Cu producer in the 20th century, has distinctly lower Cu concentrations in solid waste. While the relatively low median for Avoca, 341 mg/kg Cu, reflects to some extent the inclusion of a high proportion of low-Cu tailings analyses in the calculation, the median for Avoca spoil samples alone is still only 443 mg/kg Cu. Low average Cu content of the ore (0.6-0.7% or 6000-7000 mg/kg) and efficient removal of Cu during processing are likely causes of the low median concentration in solid waste. At both Tynagh and Caim, Cu was a significant if minor component of the ore. At Tynagh, the Cu grade (0.6-1.3%) even exceeded that of Avoca. The relatively high Cu in solid waste at both Tynagh and Caim reflects the fact that much of the solid waste analysed at these sites included material processed to remove Pb rather than Cu, as well as the presence of process concentrate in the Tynagh waste.

Table 23 Summary statistics for Cu in several mine districts (*in-situ* analyses)

mg/kg Cu	All sites	Allihies	Avoca	Bunmahon	Caim	Gortdrum	Tynagh	West Cork
n	1432	103	347	23	20	79	134	28
Minimum	0.0	0.0	8	109	224	683	0.0	0.0
Maximum	348978	75520	14358	4737	8354	348978	256276	13652
Median	311	2588	341	1943	3090	1652	1099	1784
Mean	3143	6094	645	2229	2511	22352	10573	2424

Note: A value of 0.0 indicates result < detection limit

Reference values for Cu in soils are limited. Comparison Values (CV) of 2,000 mg/kg (child) and 20,000 mg/kg (adult) were suggested by ATSDR (Table 2). The Comparison Value is generated from estimated minimum dosage levels (MRLs) that are used to trigger further assessment of a contaminated site. A CV of 20,000 mg/kg would suggest that Cu in solid waste on Irish mine sites is not likely to be a cause for concern except in extreme cases such as process waste around old plant sites at Gortdrum and Tynagh (Fig. 19). Even the lower child level of 2,000 mg/kg exceeds the measured Cu concentration in around 85% of all analysed samples.

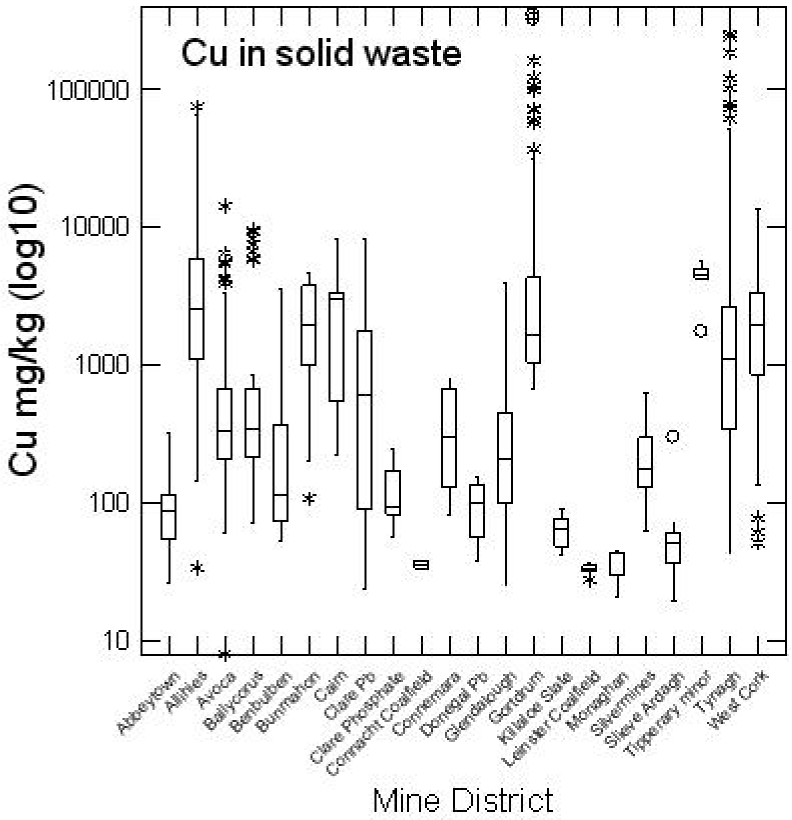


Fig. 19 Boxplots of Cu (log scale) in solid mine waste v mine district

Table 24 summarizes the data for total Cu in surface and groundwater at Irish mine sites investigated for HMS-IRC and at Silvermines (Inter-Agency Group 2000) and Fig. 20 shows the range and median across the districts. The Draft EC surface water standards are 5 µg/l (hardness < 100 mg/l) and 30 µg/l (hardness > 100 mg/l). These are intended as values to be added to the background levels for a given site. A sample taken upstream of a contamination source can be considered a background sample. For the HMS-IRC samples, the median upstream total Cu concentration is 17 µg/l (Table 24). If this is taken as an estimate of the national background level, then this implies actual standards of 22 µg/l Cu (hardness < 100 mg/l) and 47 µg/l Cu (hardness < 100 mg/l). Table 24 shows that maximum values in all water types exceed the uppermost Draft EC level of 47 µg/l. Fig. 21 shows the relationship between hardness and total Cu for non-mine water – when hardness is allowed for, a significant proportion of upstream (c. 10%) and downstream (c. 24%) water samples exceed the standards.

Table 24 Cu (total) in water on and around Irish mine sites, by source

µg/l Cu	All samples	Groundwater	Mine Water	Upstream	Downstream
n	466	27	197	70	174
Minimum	<1	8	<1	<1	<1
Maximum	30830	79	30830	190	323
Median	25	19	34	17	22
Mean	251	25	554	22	33

There is clearly some degree of impact from mine sites on the Cu concentration of downstream surface waters - the median Cu concentration is higher than in upstream surface waters and a higher proportion of downstream waters exceed the standards. However, these impacts must be seen in the context of exceedance of the standards in upstream waters and even in some groundwaters (Fig. 21).

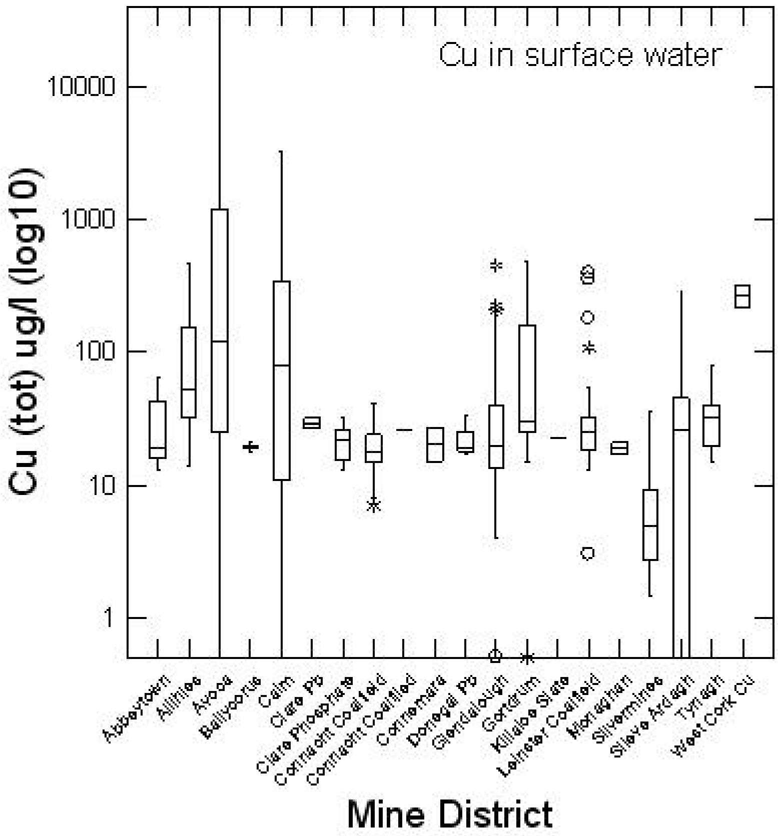


Fig. 20 Total Cu in all waters analysed, by mine district (log scale)

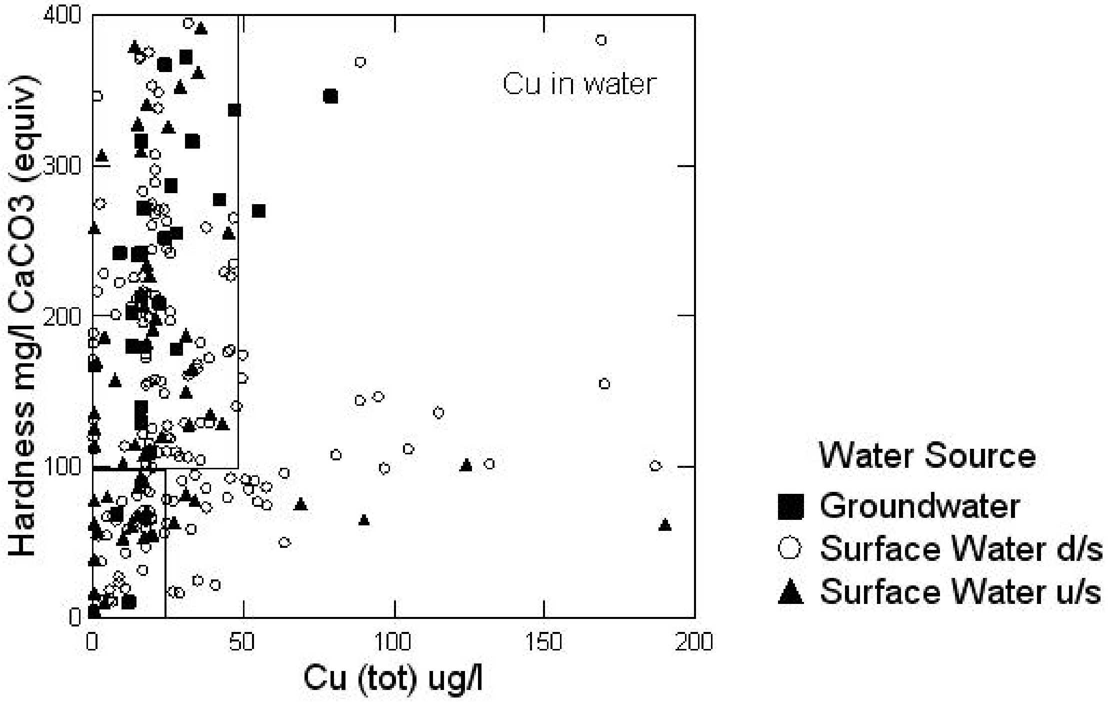


Fig. 21 Total Cu v hardness in surface water and groundwater
(Boxes enclose concentrations below the standard concentrations)

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples, taken in 1999 by the EPA, have been added for the Silvermines district (Inter-Agency Group 2000). Fig. 22 illustrates the variation in Cu concentration in stream sediments across the various districts sampled. The median Cu concentration for all samples analysed is 57 mg/kg (range: <DL – 11,430 mg/kg). The standard for Cu in stream sediments (Table 4) is 100 mg/kg. The median Cu concentration exceeds 100 mg/kg in Allihies (median 1247 mg/kg, range 26 – 11,430 mg/kg), Avoca (median 257 mg/kg, range 34 – 2183 mg/kg) and West Cork (median 2181 mg/kg, range 37 – 2689 mg/kg). Sampling was limited in the latter district with only one downstream sample taken at each of two sites. Even allowing for the fact that the standard quoted is for the total size fraction of stream sediments, rather than the <150 µm fraction, the concentrations measured in these three districts are striking, even if some of the streams sampled are little more than minor drainages.

Bioavailability of Cu in sediments has not been assessed for the HMS-IRC project. Nevertheless, given a stream sediment standard of 100 mg/kg and the sensitivity of aquatic ecosystems and organisms to Cu toxicity, streams and rivers with sediment Cu concentrations exceeding 1000 mg/kg in places represent a potentially significant environmental impact.

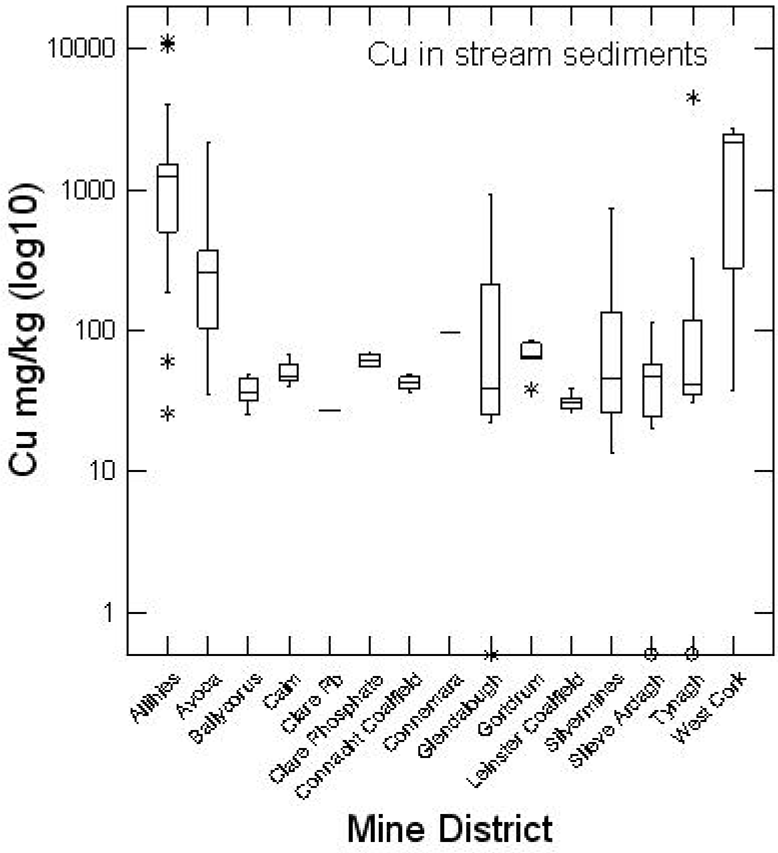


Fig. 22 Cu in stream sediments in mine districts

In summary, Cu is a common component of ore deposits in Ireland and is present in significant concentrations in solid mine waste even on mine sites where it was not produced as a commodity. Sites with particularly high Cu in solid waste (median >

1000 mg/kg) include Allihies, Bunmahon, Gortdrum, West Cork district, Caim and Tynagh. However, standards or guideline limits for Cu are relatively high for solid matter and only those sites with concentrated processing waste, in which Cu may be present at levels exceeding 20%, i.e. Gortdrum and Tynagh, can be considered a significant concern. Concentrations of Cu in stream sediment are very high downstream of some sites, notably Allihies, Avoca and, in West Cork, Glandore and Ballycummisk, and the potential impact of this on the aquatic ecosystem at these sites may warrant further investigation. The total Cu concentration in surface waters downstream of mines indicates some impact on water chemistry from mine discharges. However, numerous upstream surface water samples and even some groundwater samples also had Cu in excess of standard limits, suggesting that mine waste is just one of a number of sources of elevated Cu in surface water and groundwater in Ireland.

3.9 – Iron - Fe

3.9.1 Introduction to Fe

The geochemistry of Fe is largely determined by the ease with which its valence state changes in response to prevailing physicochemical conditions. By far the greatest amount of Fe in igneous rocks occurs as FeO and Fe_2O_3 in oxides, e.g. **magnetite** (Fe_3O_4), and silicates such as **pyroxene** ($(Fe,Mg)_2Si_2O_6$), **amphibole** (e.g. hornblende: $Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$) and **biotite** ($K(Mg, Fe)_3AlSi_3O_{10}(F, OH)_2$). Accessory sulphides, e.g. **pyrite** (FeS_2), also account for some of it. Low-temperature sedimentary minerals include **haematite** (Fe_2O_3), **goethite** (FeO(OH)), **glauconite** ($K_2(Fe,Al,Mg)_4(Si_7AlO_{20})(OH)_4\bullet n(H_2O)$), **siderite** ($FeCO_3$), **marcasite** ($FeS_2$), **pyrrhotite** ($FeS_{1-x}$), etc. (Wedepohl 1978).

The behaviour of Fe in the surface geochemical environment is intimately linked to that of oxygen, sulphur and carbon (Wedepohl 1978). These four elements and Mg are the most abundant crustal elements that exhibit variable valence states. Important redox reactions involve Fe. Fe^{2+} minerals react with O_2 to form Fe^{3+} oxides during weathering. In sediments, bacteria use organic carbon to reduce Fe^{3+} oxides to Fe^{2+} compounds and dissolved SO_4^{2-} to sulphide. If the amount of dissolved sulphide is sufficient, Fe sulphide may be formed. If sulphide is low, oxidized carbon in CO_3^{2-} may react with Fe to form siderite. If sulphur and carbon contents are low, Si may react with Fe to form glauconite (Wedepohl 1978). During weathering, Fe^{2+} is oxidized to Fe^{3+} and forms ferric oxides, e.g. goethite. Ferric oxide compounds are very fine-grained and can be carried by rivers as colloids or adsorbed on coatings on detrital particles such as clays. Fe silicates and oxides, such as magnetite, that are not completely destroyed by weathering, can be transported as detrital particles. Fe sulphides do not usually survive weathering and are almost never found as detrital grains (Wedepohl 1978). The great fractionation of Fe that occurs during weathering, erosion, sedimentation and diagenesis means that the total Fe content of sediments and sedimentary rocks is very variable. The ability of clays to carry adsorbed Fe means that shales and other fine-grained sedimentary rocks are richer in Fe than sandstones. Overall, the Fe content ranges from 0% in some quartz sandstones to > 50% in sedimentary haematite iron ore deposits. Shales have an average of 4% FeO and 2.5% Fe_2O_3, sandstones 1.7% FeO and 1.5% Fe_2O_3, carbonates 0.5% Fe_2O_{3tot} and pelagic clays 9.3% Fe_2O_{3tot} (Wedepohl 1978). In metamorphic rocks, Fe is present in silicates as FeO in solid solution with MgO. Fe_2O_3 is present as a substitution for Al_2O_3

in silicates or occurs in separate oxides such as magnetite and haematite. Fe is also present in sulphides (Wedepohl 1978).

Table 25 summarizes the range of concentrations of Fe found in some Irish soils, sediments and rocks. Median values range from 0.87 to 7.40%. These median concentrations are similar to average concentrations reported elsewhere for Fe. Taylor and McLennan (1986) give the upper crustal abundance of Fe as 3.5%.

Table 25 Concentration of Fe in some Irish soils, sediments and rocks

Fe	Range (%)	Median (%)
National Soils Database (n=1310)[1]	0.05 – 19.43	1.87
Stream sediments SE Ireland (n=1884)[2]	0.30 – 12.44	3.30
Stream sediments Inishowen (n=128)[3]	3.10 – 24.0	7.40
Stream sediments NE Ireland (n=386)[2]	1.97 – 12.49	4.93
Leinster Granite SE Ireland (n=26)[2]	0.36 – 1.97	0.87
Sedimentary rocks SE Ireland (n=222)[2]	0.41 – 8.40	3.03
Volcanic rocks SE Ireland (n=123)[2]	0.22 – 25.7	3.69

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

The Irish Drinking Water standard for Fe is 200 µg/l. This is set on grounds of appearance and taste, especially the former, rather than health considerations. Previously, iron deficiency, anaemia, has been seen as a greater risk to humans than excess Fe. In recent years, however, iron toxicity has been recognized as a significant health issue for some at-risk individuals, although toxicity typically arises from sources other than diet or environmental exposure, such as blood transfusions, alcoholism and hereditary conditions such as haemochromatosis. High concentrations of Fe in freshwater can cause major problems to aquatic systems where the Fe becomes insoluble and precipitates onto the stream bed or forms suspended particles. Precipitates can damage plant life and thus alter the food chain. They can also damage delicate tissues such as gills. Blanketing of stream beds can eliminate salmonid populations by destruction of suitable spawning grounds (Gray and Sullivan 1995).

3.9.2 Iron on Irish mine sites

The Fe content of solid mine waste varies widely, with most sites showing a considerable range in concentration (Fig. 23). On most sites, the bulk of the samples have Fe concentration between 1 and 10% (10,000 – 100,000 mg/kg). Exceptions are Abbeytown and Benbulben where the original host rock was limestone. At the other end of the spectrum, a significant proportion of the solid waste at Avoca and, especially, Silvermines has Fe concentration in excess of 10% (Fig. 23). Table 26 summarizes the data for selected mine districts and sites. As with all XRF analyses, caution should be exercised when considering the data. Comparison of results for samples analysed by both XRF in the GSI laboratory and by MA-ES in an external laboratory suggest that the XRF analyses can overstate the composition at high apparent concentrations (>10% Fe). There is, however, good agreement between both techniques for Fe < 5%.

Table 26 Summary statistics for Fe in several mine districts (*in-situ* analyses)

% Fe	All sites	Abbeytown	Avoca	Glendalough	Slieve Ardagh	Silvermines	Tynagh
n	1432	41	347	381	29	24	134
Minimum	0.07	0.36	0.08	0.33	1.17	0.13	0.07
Maximum	58.28	1.58	58.28	7.23	13.47	35.97	35.69
Median	2.53	0.74	5.65	1.28	4.03	22.43	3.87
Mean	5.29	0.76	11.65	1.42	4.58	18.93	5.42

Note: A value of 0.0 indicates result < detection limit

There are no reference values for Fe in soils. While excess Fe levels in humans can have serious health consequences, most human Fe intake is dietary and soil or solid mine waste concentrations are unlikely to have a major impact on human health.

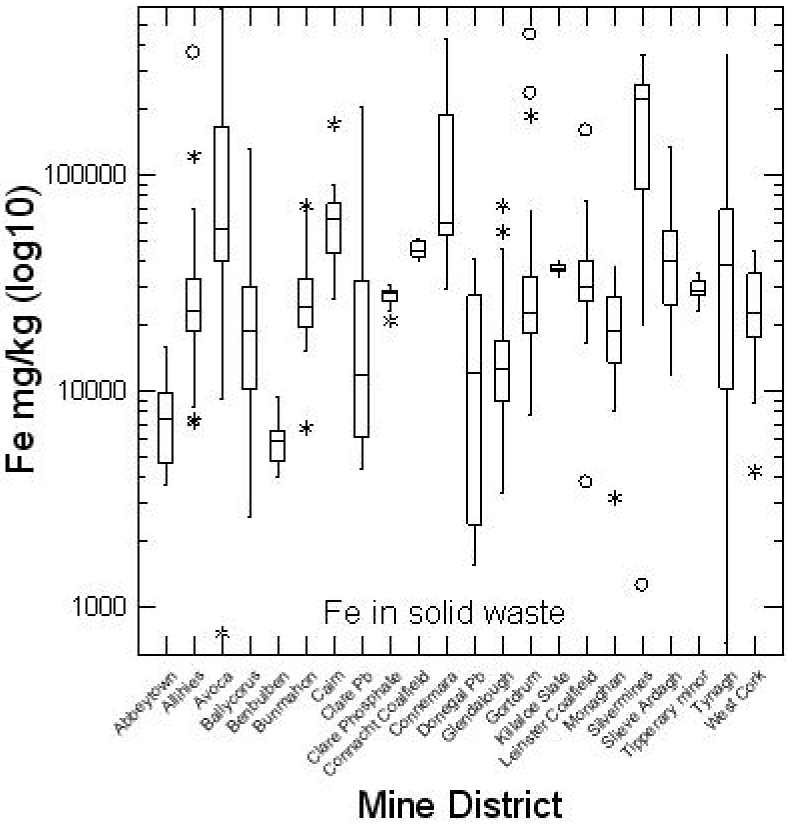


Fig. 23 Boxplots of Fe (log scale) in solid mine waste v mine district

Table 27 summarizes the data for total Fe in surface and groundwater at Irish mine sites investigated for HMS-IRC and at Silvermines (Inter-Agency Group 2000) and Fig. 24 shows the range and median across the districts. The Irish Drinking Water standard (Table 3) sets a limit of 200 µg/l for Fe, although this mainly reflects appearance and taste considerations. Most samples analysed for HMS-IRC had total Fe concentration in excess of 200 µg/l. The highest concentrations were recorded in mine water and in surface waters downstream of mines. However, median concentrations of total Fe for all water types analysed were broadly similar (Table 27).

Table 27 Fe (total) in water on and around Irish mine sites, by source

µg/l Fe	All samples	Groundwater	Mine Water	Upstream	Downstream
n	466	27	197	67	174
Minimum	21	78	21	55	34
Maximum	303600	1983	303600	4537	40930
Median	563	420	594	525	579
Mean	4034	501	8152	737	1209

For Fe concentrations below 1000 µg/l, total Fe is generally much higher than dissolved Fe concentration, i.e. Fe occurs predominantly in suspension rather than solution (Fig. 25). Such samples generally have high pH (>7). As pH falls, Fe becomes more soluble and the proportion of Fe in solution increases until total Fe is equivalent to dissolved Fe (Fig. 26). The overall concentration of Fe increases as well. Mine sites with low-pH water, such as Avoca and the coalfields, have the highest Fe concentrations (Fig. 24).

High dietary intake of Fe can contribute to Fe toxicity in humans. However, there are no specific guidelines as to what constitutes excess Fe in drinking water from the perspective of human health. The existing Drinking Water Standards relate to colour and taste but are sufficiently low to safeguard human health. Fe can be quite toxic to aquatic life, particularly when it comes out of solution and forms flocs that can have a severe direct or indirect effect on biota (Gray and Sullivan 1995). Precipitation of such kind has been observed in some mine districts, principally Avoca and the Leinster and Connacht Coalfields.

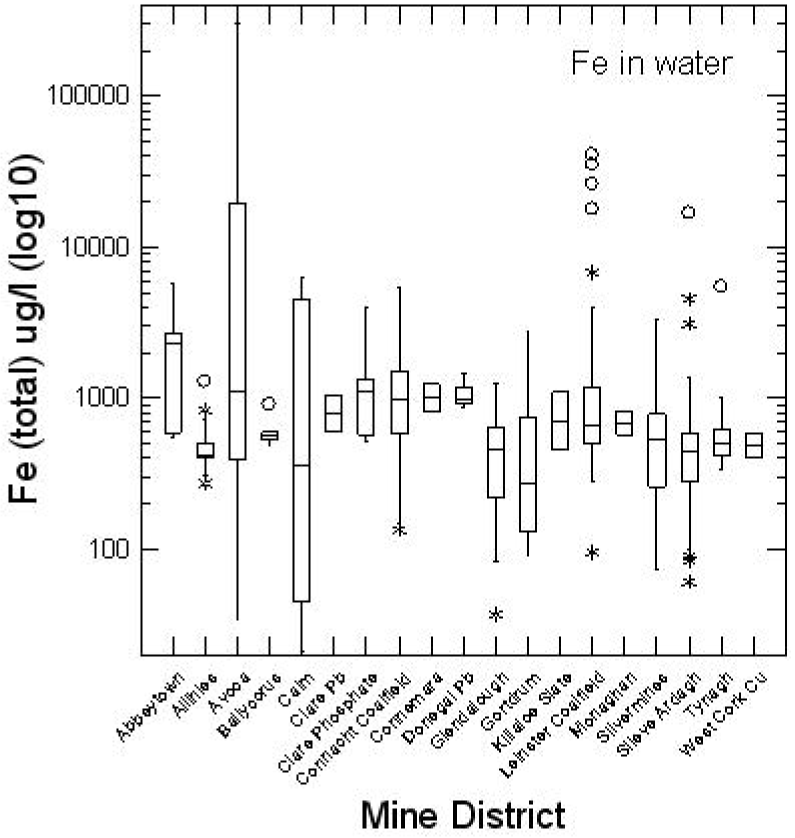


Fig. 24 Total Fe in all waters analysed, by mine district (log scale)

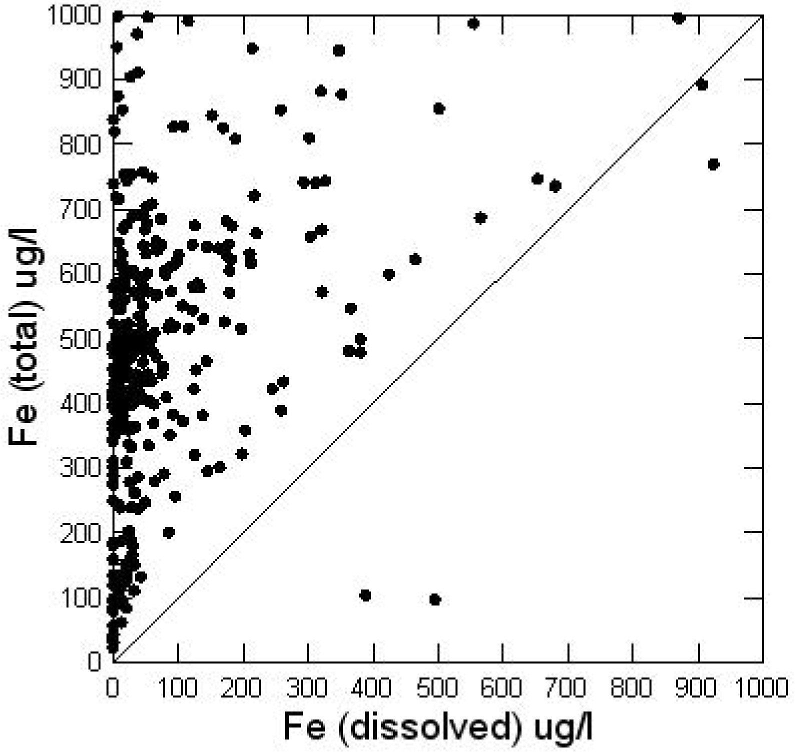


Fig. 25 Total v dissolved Fe, for concentrations < 1000 µg/l

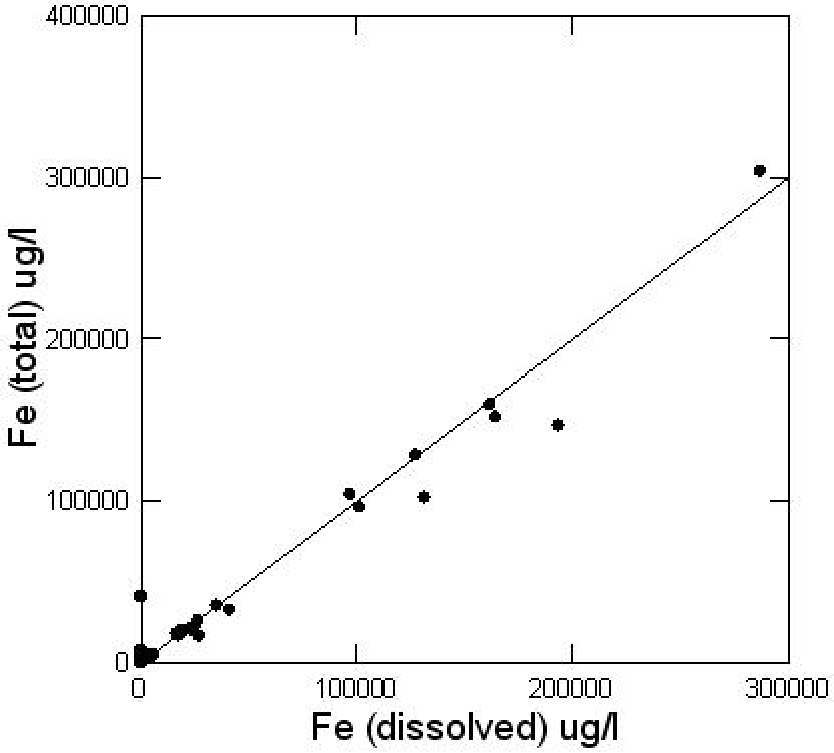


Fig. 26 Total v dissolved Fe, all samples

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for the HMS-IRC project; a further 19 samples, taken in 1999 by the EPA, have been added for the Silvermines district (Inter-Agency Group 2000). Fig. 27 illustrates the variation in Fe concentration in stream sediments across the various districts sampled. The median Fe concentration for all samples analysed is 4.03% (range: 0.26 – 29.77%). The standard for Fe in stream sediments (Table 4) is 1%. However, regional stream sediment surveys suggest that this level is typically exceeded by most natural sediments (Table 25), with the median concentration of Fe in sediments typically above 3%. Nevertheless, there is a clear correlation between high Fe concentrations in stream sediments and mine sites. Although the median concentrations of Fe in sediments collected upstream and downstream of mine sites are both around 4%, downstream sediments show a much greater range with several extreme concentrations in excess of 10% Fe (Fig. 28). Mine districts with the highest concentration of Fe in stream sediments include Avoca, Silvermines and the three coalfields, Connacht, Leinster and Slieve Ardagh.

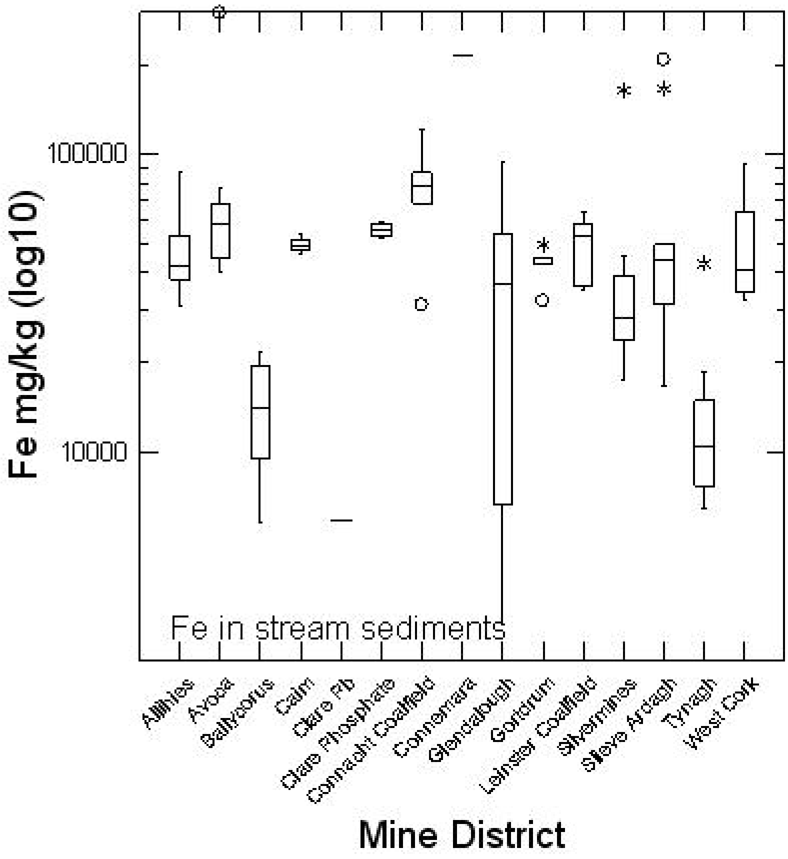


Fig. 27 Fe in stream sediments in mine districts

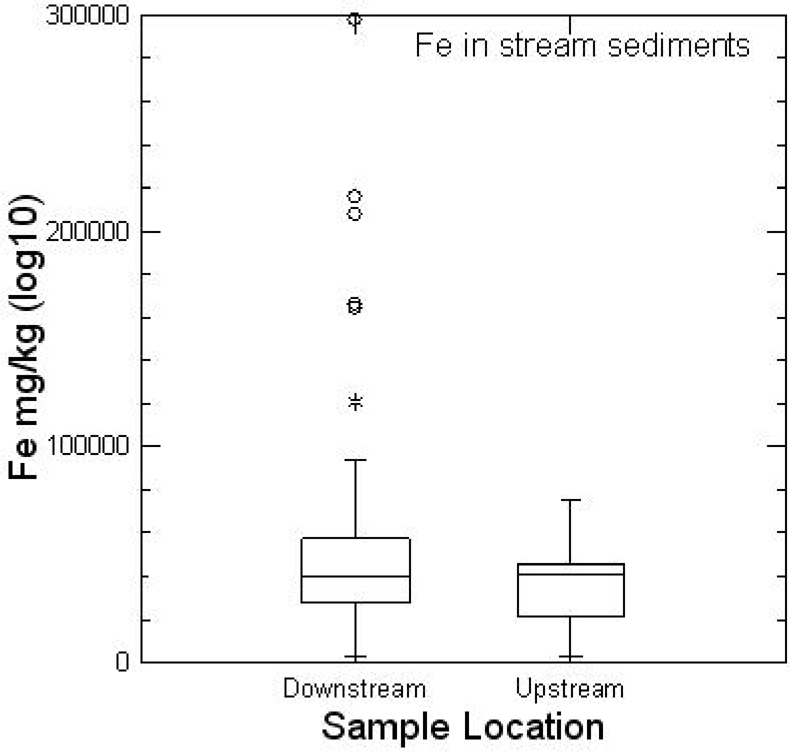


Fig. 28 Fe in stream sediments: upstream v downstream samples

In summary, mine sites in Ireland are associated with high concentrations of Fe in solid waste, water and stream sediments. The main risk associated with high Fe is the potential impact on the aquatic environment. Discharge of Fe-rich mine water to streams and rivers causes Fe to come out of solution as hydroxide minerals. These form colloids or flocs that then blanket the stream bed, having a severe impact on plants and animals. Such discharges have been noted in particular at Avoca and in the Leinster, Slieve Ardagh and Connacht coalfields.

3.10 – Lead - Pb

3.10.1 Introduction to Pb

Pb occurs naturally in rocks and soils derived from them, generally in low concentrations. Unlike other metals such as copper, it is not an essential element for life. Pb is found in ore deposits around the world, predominantly as the sulphide **galena** (PbS) but also as sulphosalts, oxides and carbonates. Because of its large ionic radius, Pb tends to be incorporated in silicates in the structural position of large monovalent or divalent metals such as K^+ and Ca^{2+}. Thus, K-feldspar in granites contains on average about 50 mg/kg Pb (Wedepohl 1978). Other minerals tend to have much lower concentrations of Pb, which is why granites and their volcanic equivalents have higher average Pb contents than other rock types.

Pb has been mined for over 5,000 years. It resists discolouration and corrosion and was therefore used to manufacture pipes and vessels for transporting and storing water. It has also been extensively used in paint manufacture as it imparts brightness to the colour (Solomon 2007). Although Pb has been banned as a paint additive in developed countries for many years it is still used extensively in developing countries. In recent years toys exported from China have been found to contain Pb-based paint. Its former use as an additive to petrol has given rise to elevated Pb concentrations in soils close to roadways, particularly in urban areas. Pb is also used in ammunition, rechargeable batteries, glass, solder and in computer and television screens (Fay *et al.* 2007).

Table 28 summarizes the range of concentrations of Pb found in Irish soils, sediments and rocks. The median concentration in Irish soils of 25 mg/kg (Fay *et al.* 2007) is typical of soils worldwide. It is very similar to the median value of sedimentary rocks in southeast Ireland (24 mg/kg) and also similar to the estimated upper crust composition of 20 mg/kg (Taylor and McLennan). Median stream sediment concentrations (50 – 55 mg/kg) are similar for the three areas for which data is available and are significantly higher than the soil median. Both granitic and volcanic rocks in southeast Ireland have similar median concentrations to those of stream sediments.

Table 28 Concentration of Pb in some Irish soils, sediments and rocks

Pb	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	1.1 - 2635	25
Stream sediments SE Ireland (n=1884)[2]	1 - 12070	53
Stream sediments Inishowen (n=128)[3]	26 - 221	50
Stream sediments NE Ireland (n=386)[2]	10 - 1218	55
Leinster Granite SE Ireland (n=26)[2]	29 – 66	49
Sedimentary rocks SE Ireland (n=222)[2]	3 - 6325	24
Volcanic rocks SE Ireland (n=123)[2]	1 - 4080	51

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

Pb in surface water and groundwater in the U.S. ranges between 5 and 30 µg/l (ATSDR 2007). Solomon (2007) quotes "background" Pb levels in freshwater of 0.5 µg/l. Pb concentrations in water increase with decreasing pH. Aquatic organisms bioconcentrate Pb, i.e. the concentration of Pb in these organisms will be higher than the concentration of Pb in water or sediments in which they live (Solomon 2007). Pb is not very soluble in water but adsorbs onto sediments. It tends to remain in the mineral form in which it entered the water. Because it tends to be found in sediments rather than dissolved in water, organisms that feed in sediments are more likely to suffer from Pb toxicity. Pb affects algal growth at water concentrations above 500 µg/l and thus interferes with the aquatic food chain (Solomon 2007). Levels in excess of 50 µg/l can have an adverse effect on gill function in fish.

Pb accumulates in bones and teeth from where it is released into the bloodstream. Health impacts in humans include neurological effects such as hyperactivity and low IQ, especially in children (Solomon 2007) and psychological effects in adults (ATSDR 2007), gastrointestinal problems, anaemia, high blood pressure and kidney damage. Pb toxicity is most acute in children under the age of six (Solomon 2007). As with all elements, bioavailability is a key issue in assessing the risks of Pb to humans and animals. Pb-rich solid mine waste is typically a relatively coarse-grained material in which the Pb is contained in non-reactive minerals such as galena that, even if ingested in significant quantities, may have little or no impact on human health because they do not break down in the gut (Krieger *et al.* 1999).

3.10.2 Lead on Irish mine sites

Of the 22 mines or mine districts on which solid waste was analysed, 10 were Pb producers. Pb is therefore present in relatively high concentrations in a high proportion of the sites investigated for the HMS-IRC project (Fig. 29). Those with median Pb concentrations exceeding 1000 mg/kg (0.1%) include Avoca, which did not produce Pb, Ballycorus, Caim, the Clare Pb mines, Clements in Connemara, Glendalough, Keeldrum in Donegal, Tassan in Monaghan, Silvermines and Tynagh. Only Abbeytown among the Pb mines does not have solid waste with similarly high Pb concentration, in part because it is an active quarry with no exposed solid waste on site. The material analysed at Abbeytown is tailings that spilled onto the foreshore during the last mining phase in the 1950s.

Table 29 summarizes the data for Pb in solid waste for selected sites. Medians at the sites tabulated range from 1288 mg/kg to 56028 mg/kg (5.6%), with maximum concentrations exceeding 50%. Of particular note are spoil at Silvermines, in which Pb concentrations of several % are common, various wastes at Tynagh and a single large heap of process waste at Caim in county Wexford. The very maximum high Pb concentration (>91%) recorded at Tynagh was in a Pb concentrate and the measured concentration is likely to be exaggerated because of the limits of calibration in the XRF analyser.

Table 29 Summary statistics for Pb in several mine districts (*in-situ* analyses)

mg/kg Pb	All sites	Avoca	Caim	Clare	Glendalough	Silvermines	Tynagh
n	1432	347	20	47	381	24	134
Minimum	0.0	41	5674	40	99	45	72
Maximum	913892	200512	85213	259168	194677	373999	912892
Median	2208	1288	56028	7771	7912	24769	11243
Mean	14133	4561	51103	17528	22440	38251	35371

Note: A value of 0.0 indicates result < detection limit

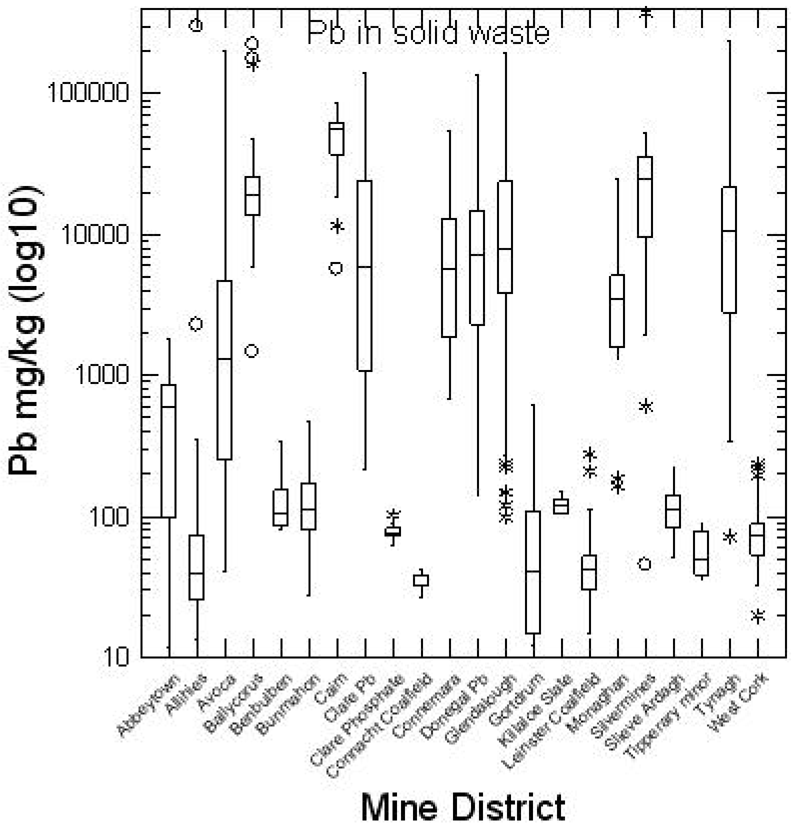


Fig. 29 Boxplots of Pb (log scale) in solid mine waste v mine district

As discussed in Appendix 4, the XRF analyser is not calibrated to analyse material with metal concentrations exceeding 2%. This does not automatically mean that high measured concentrations of Pb are inaccurate but with increasing Pb concentration, measured values become increasingly semi-quantitative or even qualitative. In the cases of three concentrate samples at Tynagh with measured Pb exceeding 50%, it is possible to conclude only that the samples had very high Pb concentrations. Extreme measured values such as these do not materially affect the calculated median concentrations. Of more direct concern is the accuracy of Pb analyses in samples where the measured Pb ranges between 2% and 20%. A selection of samples containing a range of measured Pb concentrations were analysed by assay at OMAC laboratories. Measured assay concentrations ranged up to 30%. Comparison with GSI *in-situ* XRF data suggests that, if anything, the XRF analyses tend to understate the amount of Pb in the samples (Appendix 4).

Table 2 gives a Soil Guideline Value of 750 mg/kg Pb on industrial sites. As noted above, the median value of Pb in solid waste on mine sites in Ireland in which Pb was a component of the ore typically exceeds this value.

Table 30 summarizes the data for *dissolved* Pb in surface and groundwater at Irish mine sites investigated for HMS-IRC. Dissolved Pb is used here because of apparent inaccuracies in a number of batches of total Pb analyses as indicated by very high concentrations of total Pb in lab blanks. For Silvermines (Inter-Agency Group 2000) only total Pb data are available – these are not directly comparable to dissolved Pb data as total Pb can be significantly higher in areas of Pb mineralization. Fig. 30 shows the range and median across the districts. The standard for total Pb in surface waters is 7.2 µg/l (Table 3). This standard is exceeded in waters of all categories except groundwater on and around some Irish mine sites. Mine water at

Avoca, Caim, Glendalough and Tynagh typically has high Pb concentrations but only at Avoca, Glendalough and Silvermines, where there is significant discharge of Pb-rich mine water into streams and rivers, is surface water downstream of the mine sites consistently in excess of the standard. Downstream surface water dissolved Pb concentration ranges from <1 to 239 µg/l at Avoca (median 2 µg/l) and from <1 – 132 µg/l at Glendalough (median 35 µg/l). Total Pb concentrations in downstream surface water range from 3 to 313 µg/l at Silvermines (median 81 µg/l). Except in a few isolated cases (Fig. 30), other mine sites generally do not show elevated Pb concentrations.

Table 30 Pb (dissolved) in water on and around Irish mine sites, by source

µg/l Pb	**All samples**	**Groundwater**	**Mine Water**	**Upstream**	**Downstream**
n	465	27	194	60	163
Minimum	<1	<1	<1	<1	<1
Maximum	8637	3	8637	114	239
Median	<1	<1	1	<1	<1
Mean	245	0.6	551	5.2	9.9

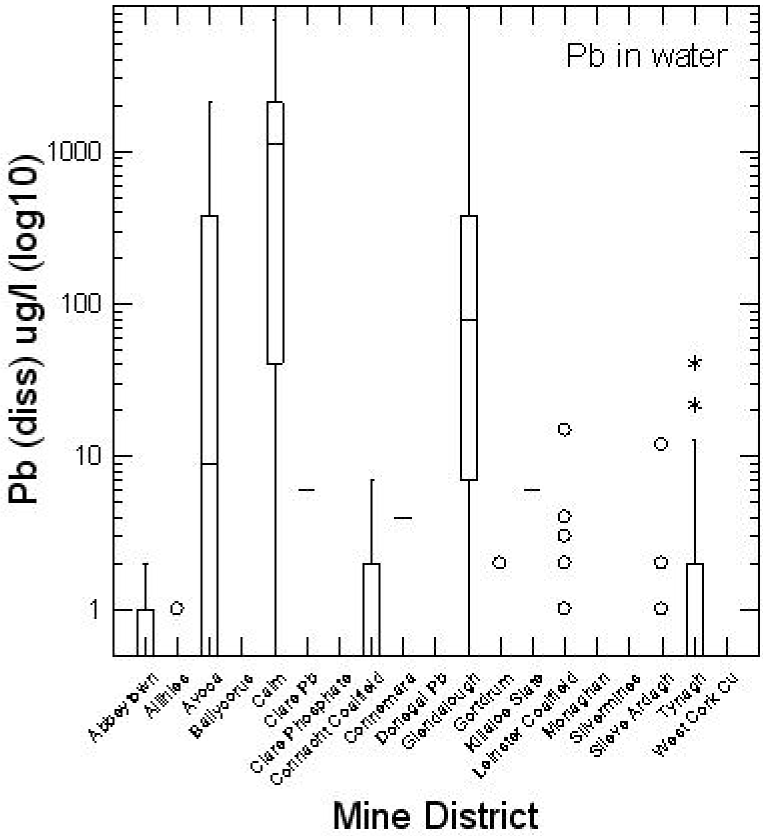


Fig. 30 Dissolved Pb in all waters analysed, by mine district (log scale)

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). Fig. 31 illustrates the variation in Pb concentration in stream sediments across the various districts sampled. The median Pb concentration for all samples analysed is 223 mg/kg (range: 15 – 72,031 mg/kg). The standard for Pb in stream sediments (total size fraction) is 1,000 mg/kg (Table

4). Pb concentration exceeded 1000 mg/kg in at least one sample in streams at Glendalough, Ballycorus, Caim, Clements in Connemara, Tynagh and Silvermines. However, concentrations measured in the fine (<150 µm) fraction of stream sediments tend to be significantly higher than those in the total fraction. For example, at Caim, Co. Wexford, Pb concentrations in the <2 mm size fraction were less than half those measured in the <150 µm fraction. The applicable standard for Pb in the <150 µm fraction of stream sediments may be thus closer to 2,000 mg/kg than 1,000 mg/kg. On this basis, stream sediments at Glendalough-Glendasan (median 1130 mg/kg, range 41 – 72031 mg/kg) and Silvermines (median 1780 mg/kg, range 57 – 12332 mg/kg), in particular, are potentially significant in the context of animal health.

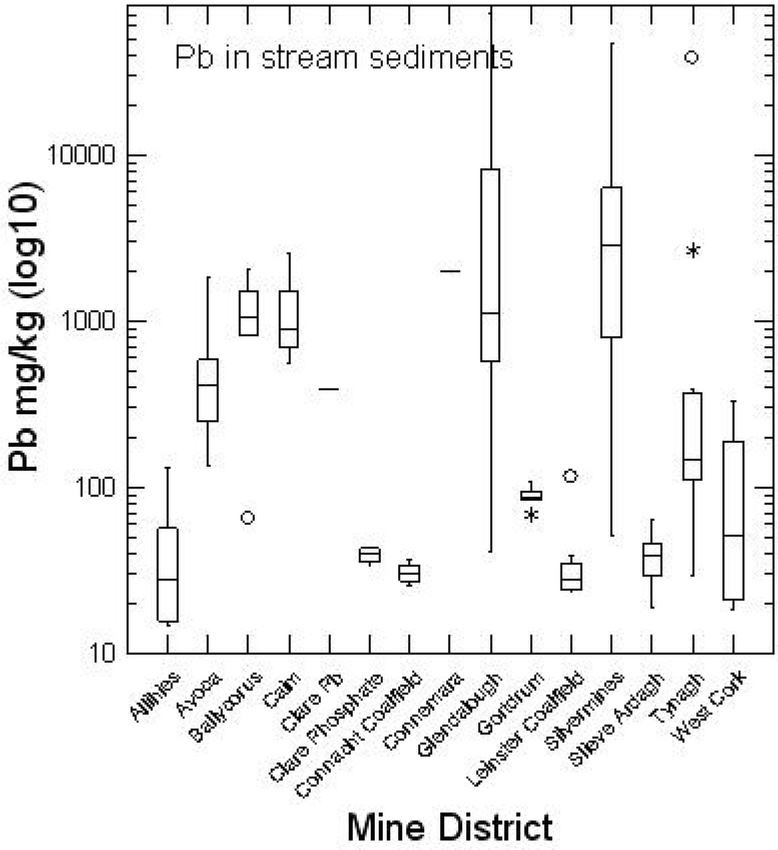


Fig. 31 Pb in stream sediments in mine districts

In summary, out of 22 mine districts examined for the HMS-IRC project, 10 have high concentrations of Pb in solid waste (median > 1000 mg/kg), namely Avoca, Ballycorus, Caim, the Clare Pb mines, Clements in Connemara, Glendalough, Keeldrum in Donegal, Tassan in Monaghan, Silvermines and Tynagh. Concentrations of Pb in stream sediment exceed 1000 mg/kg downstream of most of these sites, though only at Glendalough-Glendasan and Silvermines are such high concentrations known to be sustained over a significant length of stream bed. The Pb concentration in surface waters downstream of mines indicates significant impact on water chemistry from mine discharges at three sites, Avoca, Glendalough and Silvermines, where significant volumes of mine water with high Pb concentration discharge into local rivers and streams.

3.11 - Manganese

3.11.1 Introduction to Mn

Mn is essential for all organisms and is toxic only at very high concentrations. It is released into the environment through weathering of rocks, agriculture and smelting. Mn, along with Fe, helps to fix nutrient elements in soils and thus enhances soil fertility. Mn deficiency in soils, e.g. on acidic soils rendered alkaline by addition of lime, can cause Mn deficiency in ruminants (Fay *et al.* 2007).

Mn occurs in nature mainly as Mn^{2+} but also as Mn^{3+} and Mn^{4+}. Mn^{2+} can form normal spinels such as **hausmannite** (Mn_3O_4). Mn^{4+} occurs as **pyrolusite** (MnO_2) which is isotypic with rutile (TiO_2). Hydroxides include **manganite** (MnO(OH)) and **psilomelane** ($Ba_3Mn_8O_{16}(OH)_6$). In rock-forming minerals, Mn, in the form of Mn^{2+}, substitutes for Fe, Mg, Al and Ca. It forms secondary Mn minerals during weathering and oxidation but separate Mn minerals are rare in igneous rocks and uncommon in metamorphic rocks (spessartine garnet, containing up to 30% Mn, is an example). Minerals such as olivine, pyroxene and hornblende can contain several thousand mg/kg Mn (Wedepohl 1978). Over 8000 mg/kg Mn has been recorded in biotite in pegmatite. Mn contents are generally low in carbonate rocks such as limestone because of the low Mn content of solutions that precipitate carbonates. **Rhodochrosite** ($MnCO_3$) is crystallographically related to siderite ($FeCO_3$) with which it forms a solid solution series. Mn sulphides are uncommon because of the widespread presence of carbonate in mineralizing environments, thus favouring rhodochrosite over Mn sulphide. Only sphalerite and pyrrhotite incorporate Mn easily, typically at levels of 500-5000 mg/kg (Wedepohl 1978).

Mn^{2+} is partly oxidized during weathering and much of it is mobilized and precipitated as Mn^{4+} within the profile of decomposition. Only a minor proportion is lost to surface run-off. Mn decreases with increasing distance from source. Thus relatively immature greywackes have an average of 700 mg/kg Mn, more mature sandstones 170 mg/kg (Wedepohl 1978). Shales have an average of 600 mg/kg Mn. Most limestones have Mn values below 100 mg/kg but there are Mn-rich varieties with 1700+ mg/kg Mn. Mn concentrations in sediments are derived from diagenetic remobilization of Mn under reducing conditions. Deep sea clays can have in excess of 10,000 mg/kg Mn. In metamorphic rocks, parentage governs Mn content. Gneisses and mica schists have average Mn contents of around 600 mg/kg but metamorphosed basic igneous rocks have mean Mn contents of 1500 mg/kg. The upper crust has an estimated Mn concentration of 600 mg/kg (Taylor and McLennan 1986). Average background levels of Mn in soils ranges from 40 to 900 mg/kg with an estimated mean background composition of 330 mg/kg (ATSDR 2008c).

Table 31 Concentration of Mn in some Irish soils, sediments and rocks

Mn	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	7 - 21077	462
Stream sediments SE Ireland (n=1884)[2]	160 - 99900	1403
Stream sediments Inishowen (n=128)[3]	300 - 37000	2500
Stream sediments NE Ireland (n=386)[2]	142 - 22100	1760
Leinster Granite SE Ireland (n=26)[2]	72 – 1273	220
Sedimentary rocks SE Ireland (n=222)[2]	45 - 5521	331
Volcanic rocks SE Ireland (n=123)[2]	16 - 4800	370

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

Mn in surface water in various studies undertaken in the U.S. ranged from between 0.3 and 3230 µg/l; median concentrations for different studies ranged from 16 to 24 µg/l (ATSDR 2008c). The median groundwater concentrations reported for 20 watersheds and 16 drainage basins in the US was 5 µg/l, although the maximum concentration exceeded 5,000 µg/l (ATSDR 2008c). A median of 10 µg/l Mn was reported for 4,000 US public water supplies (ATSDR 2008c). The Irish Drinking Water standard for Mn is 50 µg/l. Analyses of 4,826 samples in 1,653 water source zones in Ireland in 2006-2007 indicated exceedance of the standard in 168 (10.2%) of zones and 241 (5%) of samples. Almost 8% of private group schemes exceeded the standard as opposed to 3.6% of public group schemes and 3% of public water supplies.

Excessive levels of Mn in humans can compromise the nervous system, affecting movements that can become slow and clumsy ("manganism") (ATSDR 2008c). The use of Mn in the octane enhancer MMT in the US, Canada, Australia, India and elsewhere led to controversy and it was banned in the US for many years.

3.11.2 Manganese on Irish mine sites

Compared to Mn concentrations that are typical of rocks and soils in Ireland (Table 31), Mn concentrations are significantly enriched on some mine sites in Ireland (Fig. 32). Mine districts or mines where the median Mn concentration in solid waste exceeds 1000 mg/kg include Caim, Clements in Connemara, Gortdrum, Silvermines and the slate quarry at Killaloe. Caim has the most significant concentration of Mn-rich mine waste in Ireland, contained mainly within a single heap of processing waste that is also rich in Pb. Table 32 summarizes the data for selected districts.

The reference values for soils (Table 2) are the ATSDR Comparison Values for children (3,000 mg/kg) and adults (40,000 mg/kg). The adult reference value was exceeded only in one analysis at Caim. The child reference value is relatively low and is exceeded in approximately 5% of analyses carried out for the HMS-IRC project at Allihies, Caim, Clements, Glendalough, Gortdrum, Silvermines, Tynagh, West Cork and Killaloe. Comparison of Mn concentrations in prepared mine waste samples analysed by MA-ES in an external laboratory and by XRF in the GSI laboratory indicate generally good agreement between the two methods, with a slight bias towards lower Mn concentrations in the XRF for samples with Mn concentrations below approximately 5000 mg/kg (Appendix 4). In samples with very high Mn concentrations, the XRF tended to give significantly higher measured concentrations than those obtained using MA-ES.

Table 32 Summary statistics for Mn in some mine districts (*in-situ* analyses)

mg/kg Mn	All sites	Caim	Connemara	Gortdrum	Silvermines	Killaloe Slate
n	1432	20	15	79	24	5
Minimum	0.0	1044	777	0.0	0.0	866
Maximum	51170	51170	10089	3750	38313	3564
Median	398	20112	2993	1231	2224	1075
Mean	960	16140	3334	1353	5503	1532

Note: A value of 0.0 indicates result < detection limit

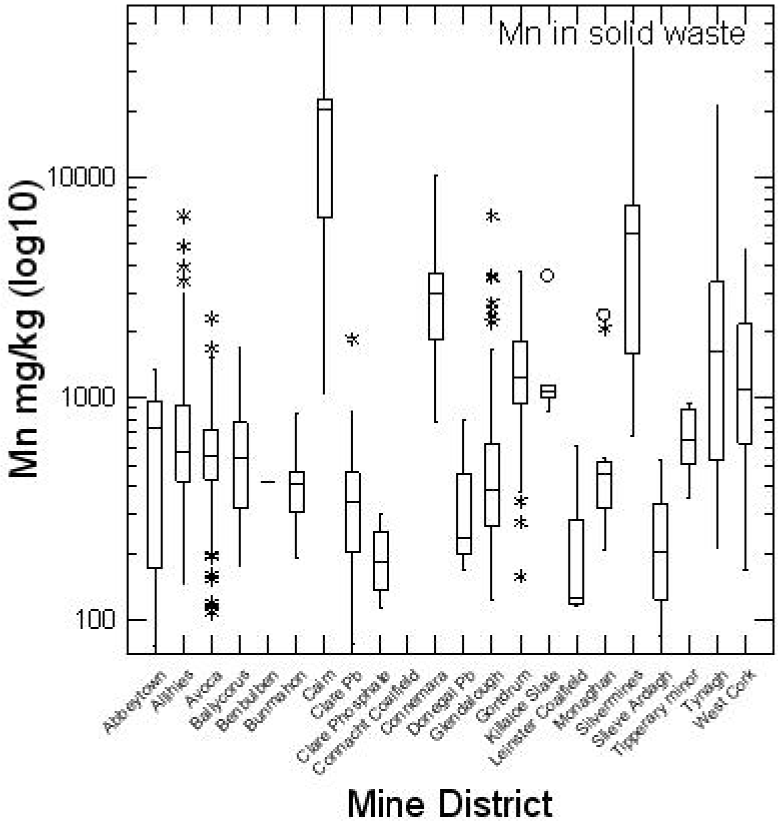


Fig. 32 Boxplots of Mn (log scale) in solid mine waste v mine district

Table 33 summarizes the data for *dissolved* Mn in surface and groundwater at Irish mine sites investigated for HMS-IRC. Dissolved Mn is used here because of apparent inaccuracies in a number of batches of total Mn analyses as indicated by high concentrations of total Mn in lab blanks. In practice, however, the difference between dissolved and total concentrations is not great over the full range of values measured. There is a strong, almost 1:1 relationship between dissolved and total Mn (Fig. 33), implying most Mn measured is in solution. Differences are apparent mainly at concentrations below 50 µg/l.

Table 33 Mn (dissolved) in water on and around Irish mine sites, by source

µg/l Pb	All samples	Groundwater	Mine Water	Upstream	Downstream
n	445	27	194	60	163
Minimum	<1	<1	<1	<1	<1
Maximum	15840	334	15300	910	15840
Median	26	<1	77	7	28
Mean	776	36	1425	48	399

The reference value for Mn is 50 µg/l, the Irish Drinking Water standard. This relatively stringent value reflects the effect Mn has on appearance and taste of water, rather than toxicity. Like Fe, it can cause significant staining of clothes and other material.

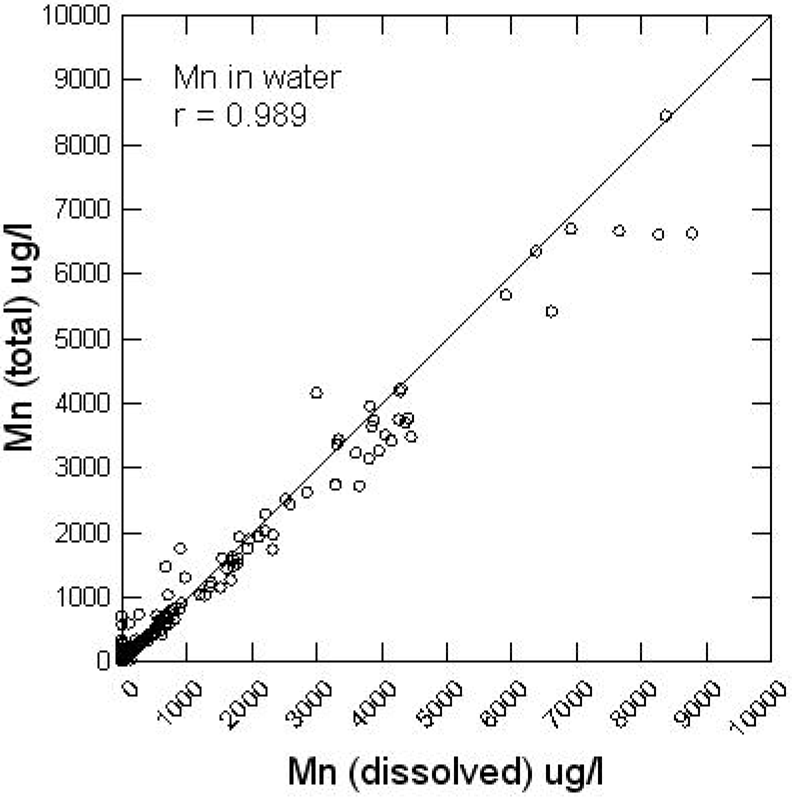


Fig. 33 Total v dissolved Mn, all samples (<10,000 µg/l)

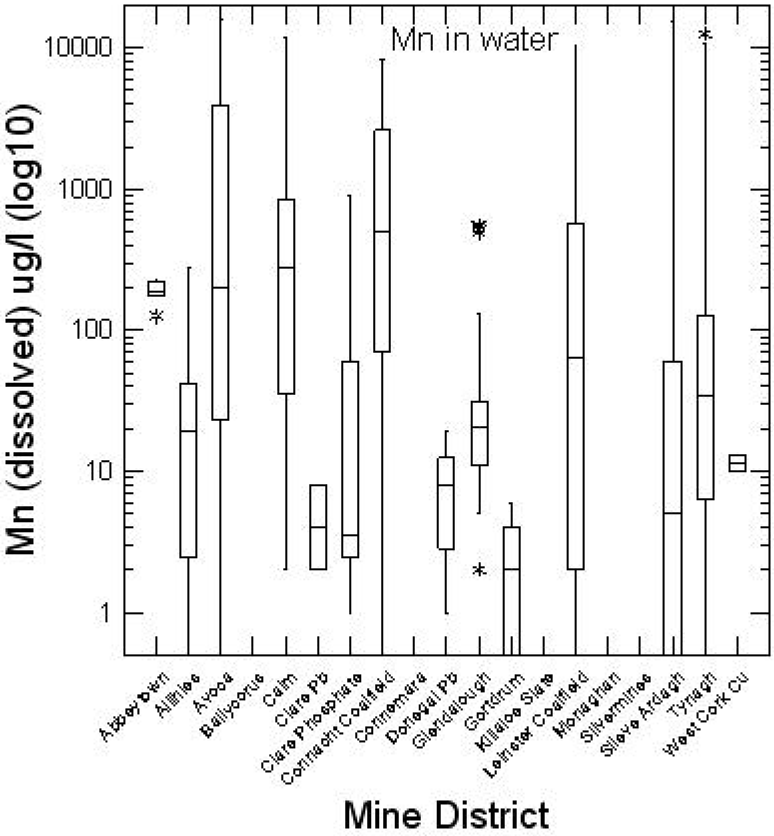


Fig. 34 Mn (dissolved) in all waters analysed, by mine district (log scale)

Mine waters have significantly higher Mn concentrations than groundwater or water upstream of mine sites (Table 33). Mine districts where water has low pH and high acidity, such as Avoca and the coalfields, have a greater range of Mn concentrations with more extreme high values (> 1000 µg/l) than elsewhere (Fig. 34). In most other districts or sites, with the exception of Caim and Tynagh, most water has a dissolved Mn concentration below 50 µg/l. At Caim, the high Mn content of solid waste run-off and leachate reflects the high concentration of Mn in the solid waste.

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). Fig. 35 illustrates the variation in Mn concentration in stream sediments across the various districts sampled. The median Mn concentration for all samples analysed is 2,764 mg/kg (range: 118 – 70,066 mg/kg) and most sediments sampled for HMS-IRC have a Mn concentration between 1,000 and 10,000 mg/kg (Fig. 35). The median concentration and range of Mn in samples collected for HMS-IRC are consistent with results of regional stream sediment programmes (Table 31).

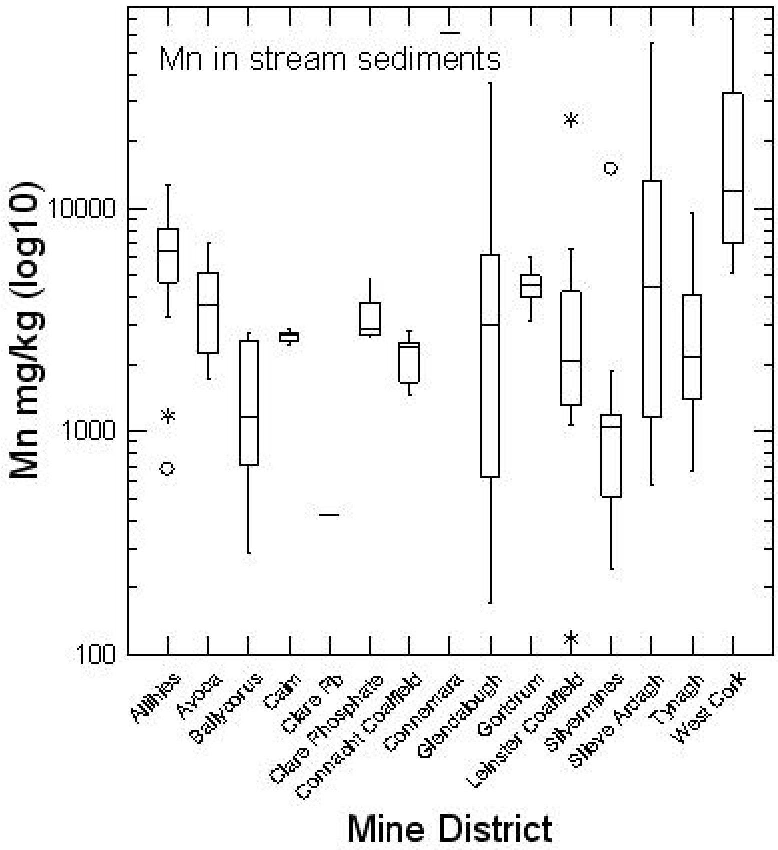


Fig. 35 Mn in stream sediments in mine districts

The impact of mining on the stream sediment composition is localized. The median concentration of Mn in samples collected upstream of mine sites is 2510 mg/kg, with a range of 244 to 9338 mg/kg. Downstream samples have a median of 2802 mg/kg and a range of 118 to 70,066 mg/kg. The main difference between upstream and downstream samples is that extreme high concentrations (> 10,000 mg/kg) are only found in the latter. Out of 126 samples analysed, 14 had Mn concentration > 10,000 mg/kg. Examples include Glendalough, Slieve Ardagh and Leinster coalfields, Allihies, Silvermines and Glandore in West Cork. Thus mining gives rise to localized cases of very high Mn concentration in stream sediments but, overall, its impact is not very pronounced. The standard for Mn in sediments is 5,000 mg/kg. This is clearly exceeded at many of the mine sites investigated but is also exceeded at many sites in Ireland that are unrelated to mining (Table 31). It is therefore not possible to conclude that mining, in particular, increases the risk of Mn toxicity in animals that have access to stream sediments.

In summary, high concentrations of Mn occur in solid waste on some sites but only a small proportion of samples (5%) exceed the relatively modest child Comparison Value of 3,000 mg/kg. Mine water with low pH tends to have relatively high Mn concentrations and sites such as Avoca and the coalfields can exhibit extreme high concentrations of Mn (> 1000 µg/l). However, most water analysed around mine sites has Mn concentration below the Irish Drinking Water standard of 50 µg/l. There are examples of localized extreme Mn concentrations in stream sediments downstream of some mines but, in general, Mn concentrations in stream sediments in Irish mine districts are consistent with those measured in regional surveys at sites unaffected by mining.

3.12 – Mercury - Hg

3.12.1 Introduction to Hg

Hg occurs naturally in rocks and soils derived from them, generally in very low concentrations. Unlike other metals such as copper, it is not an essential element for life but is widespread in most food chains (Fay *et al.* 2007). Hg occurs in combination with chlorine, sulphur or oxygen to form salts, or with carbon to form organic mercury compounds. The most common organic compound is methylmercury which is produced by microscopic organisms in water and soil (ATSDR 1999). Inorganic Hg (metallic Hg and its compounds) enters the environment from mining activity, including artisanal gold mining in which it is used to trap Au by amalgamation, smelting of Hg, Cu and Pb ores, coal burning, manufacturing plants and waste disposal. Human exposure to Hg comes through consumption of fish contaminated with methylmercury, inhalation of Hg vapour in the workplace, ingestion of dental fillings or application of skin creams containing Hg.

Hg has been used extensively in industrial and consumer applications because of its ability to form alloys with other metals, its fluidity, its surface tension and its uniform volume expansion when heated. However, the use of Hg has been declining steadily as alternative, less toxic materials have been developed. Hg is or has been used in the manufacture of alkaline batteries, the manufacture of caustic soda, switching devices, fluorescent lights, dental amalgams, thermometers and pharmaceutical products.

The main ore of Hg is the stable, insoluble sulphide **cinnabar** (HgS). Hg is present in very low concentrations in most rocks and soils, in many cases below the detection limit of the analytical methods routinely employed in their analysis. The average crustal content is 0.5 mg/kg (ATSDR 1999). The median Hg content of Irish soils is 0.09 mg/kg (Table 28), within the range (0.02 – 0.625 mg/kg) quoted for natural, uncontaminated soils in the US and elsewhere (ATSDR 1999).

Table 28 Concentration of Hg in Irish soils

Hg	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	<0.02 – 3.45	0.09

[1] Fay *et al.* 2007

Hg concentration in rainwater and fresh snow is generally below 0.20 µg/l (ATSDR 1999). Hg in freshwater without known sources of Hg contamination is generally < 0.005 µg/l. Water from rivers and lakes in Ontario has Hg concentrations ranging from 3.5 to 11.4 µg/l (ATSDR 1999). Organic Hg is formed in aquatic ecosystems by methylation of inorganic Hg at the sediment-water interface. Monomethylmercury is the most toxic, persistent form of Hg – it bioaccumulates in fish muscle and persists in fatty tissues of organisms (Solomon 2007). Hg is bioconcentrated in organisms from water and sediment and then biomagnifies up the food chain, i.e. increases in concentration from sediment to invertebrates, invertebrates to fish, fish to mammals, etc. Fish are relatively insensitive to the toxic effects of methylmercury and can tolerate 10 times as much of it as humans (Solomon 2007). However, very high concentrations of methylmercury can lead to decreased hatching rate of fish and bird eggs, impaired growth and development and even death (Solomon 2007).

The human nervous system is sensitive to all forms of Hg (ATSDR 1999). Methylmercury and metallic Hg vapours are the most harmful forms of Hg because they can reach the brain more effectively. Hg causes structural damage to the brain leading to memory and speech loss, poor hand-eye coordination, poor vision or even blindness and poor performance on intelligence tests (Solomon 2007). It can give rise to brain damage and birth defects in babies. At concentrations higher than those that cause neurological symptoms it can cause kidney damage (Solomon 2007). Methylmercury is classed as a possible human carcinogen.

3.12.2 Mercury on Irish mine sites

Obtaining useful analyses of Hg in solid waste using the portable XRF analyser presents several challenges (Appendix 4). Hg generally occurs in very low concentrations in most geological materials (see section 3.12.1, above), at levels below the detection limit of the XRF. For well prepared soil samples analysed in ideal conditions in the laboratory, the XRF detection limit is estimated to be around 12 mg/kg (Table 2.4.2). This assumes no other major contaminants are present. In practice, the presence of other metals, especially Pb and Zn, has a significant impact on the analysis of Hg. High concentrations of both these metals increase the count data in the region of the Hg X-ray peak, potentially producing spuriously high measured Hg. Detailed analysis of the spectra of such samples is required to identify spurious Hg concentrations.

Fig. 36 shows the data for Hg as measured *in situ* on mine sites. Hg was apparently detected in eight districts or sites: Allihies, Ballycorus, Kilbricken and Ballyhickey in Clare, Doolin phosphate mine in Clare, Glendalough, Gortdrum, Silvermines and Tynagh. No Hg peaks are visible for the Allihies (8 – 10 mg/kg) or Doolin (12 mg/kg) samples and the measured concentrations apparently reflect noise in the samples. The measured Hg concentration in a slag sample from Ballycorus was 138 mg/kg but the spectrum lacks any clear Hg peak and the measured concentration appears to be an artifact of the very high Pb and Zn in the sample. Samples from the Glendalough district typically have relatively high concentrations of Pb and Zn, particularly in areas of processing waste. Nevertheless, at least some of the samples in which Hg was detected do have a small Hg X-ray peak. Hg was a component of the ore at Gortdrum and high measured Hg concentrations (59 – 5468 mg/kg) in solid waste from the old processing area at this site have been confirmed by MA-ES analysis in an external laboratory. The same is true of samples of processing waste at Tynagh (max 2496 mg/kg Hg). However, measured Hg concentrations in other waste samples at Tynagh, ranging up to around 100 mg/kg, are probably spurious, reflecting the high Pb and Zn contents of this waste. The same is true of waste at Silvermines.

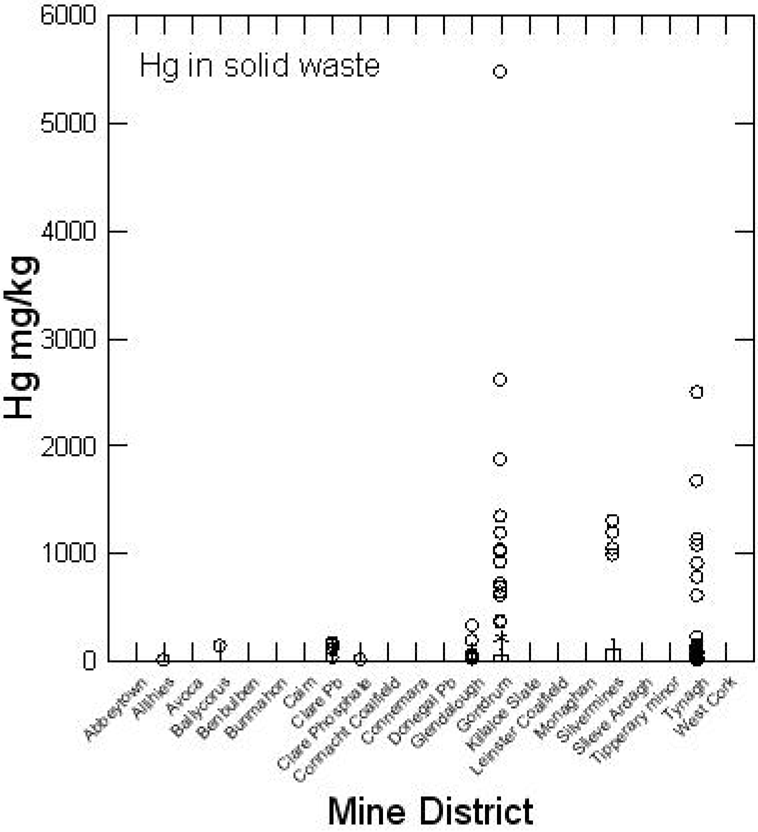


Fig. 36 Measured Hg in solid waste v mine district

Table 2 gives a Soil Guideline Value of 480 mg/kg Hg on industrial sites. Reference values for normal or garden soils are around 10 mg/kg. Some samples of waste from the processing areas at Gortdrum and Tynagh have Hg concentrations well in excess of 480 mg/kg. Solid waste in most other districts and sites examined do not appear to have significant concentrations of Hg, as far as can be determined from XRF analyses.

Both dissolved and total Hg were analysed in surface water and groundwater in mine districts investigated for the HMS-IRC project. The detection limit for dissolved Hg was 0.05 µg/l; for total Hg it was 50 µg/l. The latter limit, in particular, is very high and of limited use given the low concentration of Hg in most water. The 0.05 µg/l detection limit for dissolved Hg is equivalent to the Draft EC Surface Water standard (Table 3).

In only a limited number of samples did dissolved Hg exceed the detection limit of 0.05 µg/l. At Avoca, in the 9 samples in which it was detected, dissolved Hg ranged from 0.05 to 0.38 µg/l, with the highest concentrations measured in surface run-off and an adit discharge. One river water sample downstream of the mine had dissolved Hg of 0.29 µg/l. Dissolved Hg in 10 Gortdrum samples ranged from 0.05 to 0.38 µg/l. Several samples, including downstream samples, from Doolin (Clare Phosphate), the Leinster Coalfield, Slieve Ardagh, the Connacht Coalfield and Tynagh has dissolved Hg at or just above the detection limit of 0.05 µg/l.

Very few analyses of total Hg yielded concentrations in excess of the detection limit of 50 µg/l. Three samples from Avoca that yielded the highest dissolved Hg concentrations of 0.14, 0.38 and 0.19 µg/l had measured total Hg of 120, 120 and

230 μg/l, respectively. A few samples at Abbeytown, Glendalough, Tynagh and the Connacht Coalfield had total Hg concentrations of 50 – 60 μg/l, i.e. at or very close to the detection limit.

The disparities between measured dissolved Hg and total Hg for the same Avoca samples cited above are striking. Whether these reflect inaccuracies in the total Hg analyses or the presence of Hg-rich particulate matter in the total sample is not known.

Stream sediments were collected in most mining districts and the fine fraction (<150 μm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). Hg was below the limit of detection in all samples analysed for HMS-IRC. It was not included in the analysis of the Silvermines samples. Canadian sediment quality guidelines suggests a limit of 0.13 mg/kg Hg (Solomon 2007) and the HMS-IRC limit for livestock is 5 mg/kg (Table 4). Both limits are below the detection limit of the XRF. Consequently, the failure to detect Hg in sediments around Irish mine sites should not be taken as evidence that the sediments have Hg concentrations below those that could potentially pose a risk to aquatic species of livestock.

In summary, high Hg concentrations measured by XRF in solid waste from the processing areas at Gortdrum and Tynagh have been confirmed by analysis in an external laboratory. X-ray spectral analysis suggests some samples in the Glendalough district may also contain significant Hg concentrations. However, other sites investigated for HMS-IRC do not appear to contain Hg in solid waste in concentrations detectable by XRF. Mercury was detected in mine water and downstream surface water at a number of sites, principally Avoca, where the concentration of dissolved Hg ranged up to 0.38 μg/l.

3.13 Nickel - Ni

3.13.1 Introduction to Ni

Ni is a relatively abundant metal that is widespread in nature, occurring in most rocks, soil, water and food. It is classed as a carcinogen. Ni is particularly abundant in ultramafic and mafic (Fe-Mg-rich) volcanic rocks such as basalt and its geochemical equivalents and occurs in much lower concentrations in granite and its chemical equivalents. The crystallochemistry of Ni is dominated by its strong tendency to form metal-metal bonds and its preference, in compounds, for octahedral co-ordination (Wedepohl 1978). Native Ni is rare - it occurs as an alloy with Fe in meteorites. Ni forms metallic bonds in sulphides and arsenides such as **niccolite** (NiAs) and **pentlandite** ($(Fe,Ni)_9S_8$), the commonest Ni sulphide, in sulphide deposits hosted by ultramafic and mafic rocks.

Ni is released into the environment primarily by volcanic eruptions and emissions from Ni smelters, Ni industries, oil- and coal-fired power plants. It is generally used in combination with other metals such as iron, copper, chromium and zinc to form alloys for use in coins, jewellery, valves and heat exchangers (ATSDR 2005A). Most Ni is used in the manufacture of stainless steel. Compounds of Ni and other elements such as chlorine, sulphur and oxygen are readily soluble in water and are used for nickel plating, colouring ceramics, in rechargeable batteries and as catalysts.

Table 29 summarizes the range of concentrations of Ni found in Irish soils, sediments and rocks. The median concentration in Irish soils of 18 mg/kg (Fay *et al.* 2007) is typical of soils worldwide and very similar to the estimated upper crust composition of 20 mg/kg (Taylor and McLennan 1986). Median stream sediment concentrations (36 – 91 mg/kg) vary considerably for the three areas for which data is available - all are significantly higher than the soil median. The high median stream sediment concentration for northeast Ireland may reflect the abundance of volcanic rocks within the Lower Palaeozoic succession. A similar explanation has been advanced to explain relatively high Ni concentrations in soils in this region (Fay *et al.* 2007). The low median (4 mg/kg) for granitic rocks in southeast Ireland is almost identical to the estimated average of 5 mg/kg for granites worldwide (Wedepohl 1978).

Table 29 Concentration of Ni in some Irish soils, sediments and rocks

Ni	**Range (mg/kg)**	**Median (mg/kg)**
National Soils Database (n=1310)[1]	0.8 - 176	18
Stream sediments SE Ireland (n=1884)[2]	2 - 179	36
Stream sediments Inishowen (n=128)[3]	13 - 102	43
Stream sediments NE Ireland (n=386)[2]	16 - 459	91
Leinster Granite SE Ireland (n=26)[2]	<1 - 25	4
Sedimentary rocks SE Ireland (n=222)[2]	5 - 367	33
Volcanic rocks SE Ireland (n=123)[2]	<1 - 234	46

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

Median Ni concentrations in river and lake water are low, ranging from 0.5 to 6 µg/l (ATSDR 2007). Solomon (2007) quotes background Ni levels in "pristine" freshwater of 0.2 - 10 µg/l. Aquatic plant and animal species vary in their sensitivity to Ni (Solomon 2007). Algae have reduced growth rates when exposed to levels of 500-2000 µg/l in water and excess Ni can lead to increased embryo mortality and decreased growth in fish. Certain molluscs and crustaceans are sensitive to Ni and can be entirely suppressed in Ni-contaminated sites.

Food is the main source of Ni exposure for most people. Some people are sensitive to Ni and may experience reaction after contact with the metal or ingestion or inhalation of Ni. Only in Ni-producing industries is human exposure likely to reach levels that might cause serious harm to health. Chronic bronchitis, asthma and reduced lung function are three effects observed in workers in Ni refineries and processing plants. Ni reacts directly with DNA and may cause lung cancer and nasal passage cancer (Solomon 2007).

3.13.2 Nickel on Irish mine sites

Nickel has never been mined in Ireland. None of the mines investigated for HMS-IRC have Ni as a major component of the ore although Tynagh and Silvermines, in common with some other Carboniferous limestone-hosted Zn-Pb deposits in Ireland, e.g. the working Lisheen mine, have some ore zones that are relatively enriched in Ni.

Table 30 summarizes the data for Ni in solid waste for selected sites and Fig. 37 shows the variation in measured Ni across the mine districts. Ni was detected in solid waste in only 10 out of 22 districts. Even then, in most of those districts, in the majority of analyses it was still below the detection limit. This can be seen in Table 30 where the median value for most districts is below the detection limit, implying that Ni was detected in fewer than 50% of samples. At Ballycorus, Ni was detected in slag waste beside the old smelter site – the median for this waste alone is 337 mg/kg – but not at all in spoil. A single sample of slag in Allihies also had a high Ni concentration of 536 mg/kg. Ni was detected in only two samples of spoil in both Caim and Silvermines. It was detected in most samples of phosphatic shale waste at Doolin in Clare, along with V and Cr. This association of elements, Cr-Ni-V is common in black shales formed in relatively deep marine environments. At Tynagh, Ni was detected in most waste types with the highest concentrations measured in waste on the processing plant site.

Table 30 Summary statistics for Ni in several mine districts (*in-situ* analyses)

mg/kg Ni	All sites	Ballycorus	Caim	Clare Phosphate	Silvermines	Tynagh
n	1432	40	20	9	24	134
Minimum	0.0	0.0	0.0	0.0	0.0	0.0
Maximum	2395	1178	418	257	547	2395
Median	0.0	0.0	0.0	91	0.0	0.0
Mean	12	91	26	117	39	65

Note: A value of 0.0 indicates result < detection limit

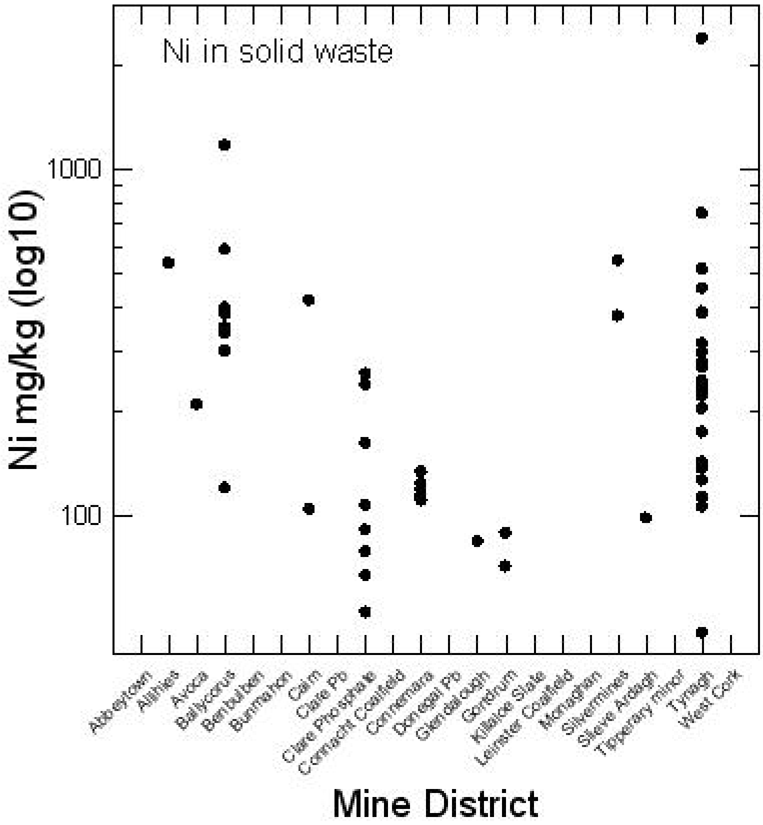


Fig. 37 Scatterplot of Ni v. mine district for HMS-IRC solid waste analyses

The standards for Ni in soil are relatively high (Table 2). ATSDR's comparison values for Ni are 1,000 mg/kg (child) and 10,000 mg/kg (adult). The soil guideline value for industrial land is 5,000 mg/kg, that for residential soil or allotments 50 mg/kg. The latter is exceeded by many “uncontaminated” soils in Ireland (Fay *et al.* 2007). The maximum Ni concentration detected on Irish mine sites is 2395 mg/kg and most measured values are much lower. In consequence, Ni in solid mine waste in Ireland is unlikely, in the context of published standard concentrations, to pose a major risk to humans or animals.

Table 31 Ni (total) in water on and around Irish mine sites, by source

µg/l Ni	All samples	Groundwater	Mine Water	Upstream	Downstream
n	466	27	197	67	174
Minimum	<1	<1	<1	<1	<1
Maximum	1069	16	1069	58	192
Median	8	3	12	5	7
Mean	33	5	59	7	18

Table 31 summarizes the data for total Ni concentration in water samples analysed for HMS-IRC as well as samples from Silvermines (Inter-Agency Group 2000). The reference value for Ni in surface water is 20 µg/l (Table 3). Of the 466 samples analysed in summer and winter periods, 118 had total Ni concentration exceeding the reference value. Of these 118, 76 were mine water samples, 39 were taken downstream of a mine and 3 upstream. No groundwater sample exceeded the standard. Thus, mine water samples and samples taken downstream of mines account for over 97% of samples that exceed the standard.

Fig. 38 shows the variation in total Ni in water samples across all districts investigated for HMS-IRC. The highest Ni concentrations (>100 µg/l) were measured in the tailings seepage at Abbeytown, spoil and tailings seepage at Tynagh, in adit and spoil discharges at Avoca and in adit discharges and waste seepages in the three coalfields, Connacht, Leinster and Slieve Ardagh (Fig. 38, Table 32). The presence of elevated Ni in some waters at sulphide mines is not surprising, particularly at Tynagh which has Ni-Cd-rich zones. However, the high Ni concentrations measured at the coalfields are striking, not least because these sites are typically not metal-rich.

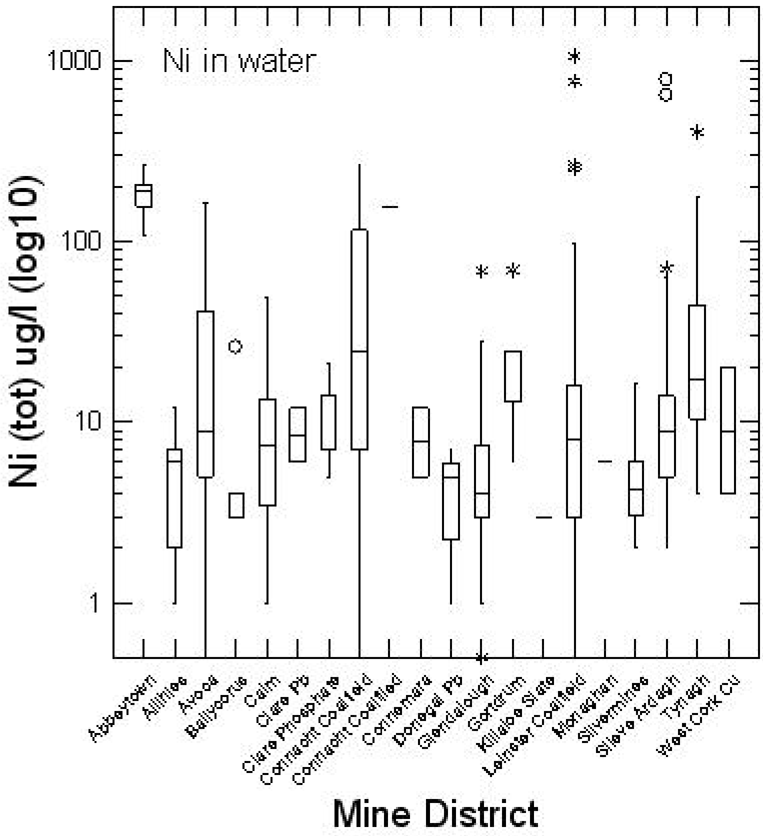


Fig. 38 Total Ni in all waters analysed, by mine district (log scale)

The concentration of Ni in bulk coal is generally less than 20 mg/kg but Ni is associated with the sulphide component in coal. As a consequence, Ni is a significant component of stack emissions from coal-burning power plants, especially where no flue gas desulphurization system is fitted (ATSDR 2007). This association with coal helps explain the high Ni concentrations observed in waters sampled in the Irish coalfields.

Table 32 Ni (total) in water on and around Irish coalfield sites

µg/l Ni	All samples	Connacht	Leinster	Slieve Ardagh
n	466	53	75	61
Minimum	<1	<1	<1	2
Maximum	1069	264	1069	785
Median	8	25	8	9
Mean	33	71	45	39

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). Fig. 39 illustrates the variation of Ni concentration in stream sediments across the various districts sampled.

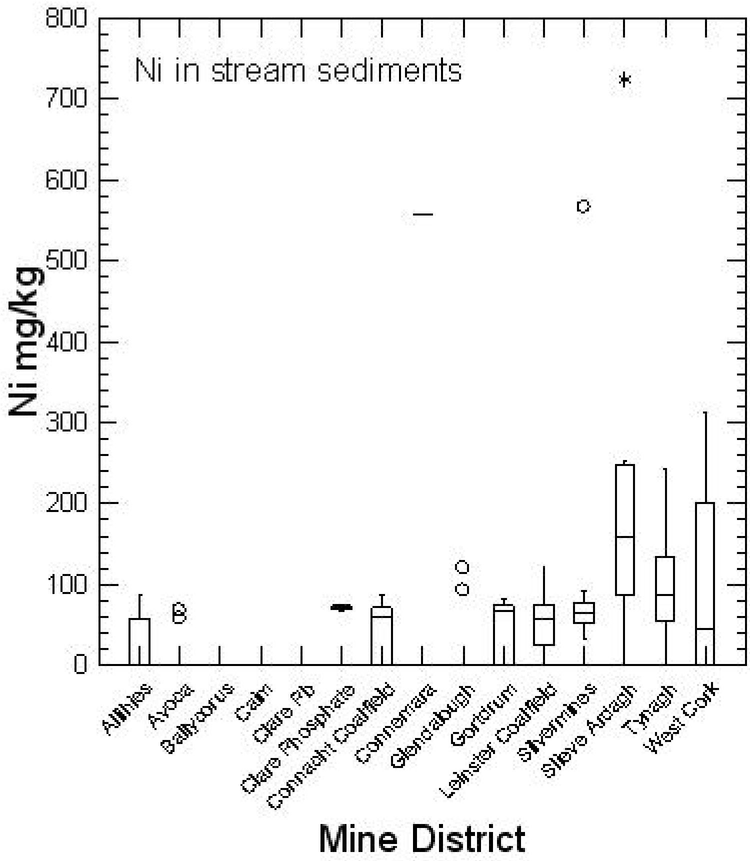


Fig. 39 Boxplot of Ni in stream sediments across all districts

With the exception of a single stream sediment sample at Clements mine in Connemara, containing almost 560 mg/kg Ni, only stream sediments from Slieve Ardagh (median 158 mg/kg, range <DL – 724 mg/kg), Tynagh (median 87 mg/kg, range <DL - 247 mg/kg) and Glandore in West Cork (one analysis with 313 mg/kg) have measured Ni concentrations exceeding 100 mg/kg. The high median Ni concentration at Slieve Ardagh confirms the association of coal sites with Ni. That Ni is detected in stream sediments at Slieve Ardagh but hardly at all in solid mine waste may reflect the fractionation of metals into the finer size fraction sample of stream sediments.

In summary, Ni was below the detection limit in most solid mine waste samples analysed for HMS-IRC. Exceptions were samples at Tynagh mine, where Ni-Cd-rich zones were known to occur in the ore, slag waste at Ballycorus and Allihies and phosphatic shales in Clare. Both water and stream sediment samples reveal an association between Ni and coalfields – samples from all three Irish coalfields have elevated Ni in one or both of these media. Other than in mine water, Ni does not generally exceed reference values in surface waters with the exception of some streams downstream of coalfield sites and the sulphides mines such as Avoca and Tynagh.

3.14 Selenium - Se

3.14.1 Introduction to Se

Selenium is a metalloid that occurs naturally as the native element Se^0, in sulphide minerals and in ores of Ag, Cu, Pb and Ni (Solomon 2007). It occupies the same column in the periodic table as sulphur and its chemical behaviour mimics that of S – it forms compounds in valence states Se^{2-} (selenides), Se^{4+} (selenites) and Se^{6+} (selenates).

Se occurs naturally in rocks and soils but is also released into the environment by burning coal and oil, phosphate mining, agricultural activities (application of phosphatic fertilizers on farms, addition of Se to animal feeds) and various industrial activities involving the production of electronics, glass, paints, rubber and shampoo. Human exposure to Se comes mainly through very low levels in food and drinking water.

Se is an essential element for all animals at low doses. Chronic oral exposure to high concentrations can cause selenosis in humans, leading to hair loss, brittle nails and neurological abnormalities (numbness in arms and legs), as well as damage to DNA (ATSDR 2003; Solomon 2007). Se can have significant effects on aquatic ecosystems at relatively low concentrations (Solomon 2007). Fish can suffer DNA damage and reduced survival after hatching where adult fish are exposed to concentrations of 10 µg/l Se. The Canadian water quality guideline for protection of aquatic life is 1 µg/l (Solomon 2007); the Irish Drinking Water standard is 10 µg/l.

Se toxicity in livestock is known to occur at a few localities in Ireland, particularly in horses, and has been linked to leaching of Se from Namurian black shales (Rogers *et al.* 1990). Soil concentrations of Se in Se-toxic fields range from 3.2 to 132 mg/kg with a mean of 21 mg/kg (Rogers *et al.* 1990). This compares to the median soil concentration for Irish soils of 0.74 mg/kg (Table 33). Se toxicity in grazing animals can give rise to lameness, cracked hooves, hair loss and even death.

Se generally occurs in rocks in concentrations up to 2 mg/kg and has an average crustal abundance between 0.05 and 0.09 mg/kg (ATSDR 2002). Concentrations of Se measured in Irish rocks and stream sediments (GSI unpublished data) were generally below the limit of detection of 5 mg/kg (Table 33). Phosphate rock and shales that host it can have much higher concentrations of Se. Mean concentrations for stockpiles and waste rock piles from phosphate mines in Idaho and elsewhere in the US (Moyle and Causey 2001) have Se concentrations ranging from 1.3 to 285 mg/kg (median 23.2 mg/kg) (Moyle and Causey 2001). Groundwater, surface water, stream sediment, soils and vegetation downstream of phosphate mines in Idaho are known to have concentrations of Se in excess of regulatory limits.

Concentrations of Se in surface waters in the US are typically below 1 µg/l; higher concentrations are more likely to be found in irrigation waters that drain Se-bearing soils (ATSDR 2002).

Table 33 Concentration of Se in some Irish soils, sediments and rocks

Se	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	0.08 – 17.44	0.74
Stream sediments SE Ireland (n=1884)[2]	<5 - 6	<5
Stream sediments Inishowen (n=128)[3]	<5 - <5	<5
Stream sediments NE Ireland (n=386)[2]	<5 - <5	<5
Leinster Granite SE Ireland (n=22)[2]	<5 - <5	<5
Sedimentary rocks SE Ireland (n=233)[2]	<5 - <5	<5
Volcanic rocks SE Ireland (n=130)[2]	<5 - 5	<5

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

3.14.2 Selenium on Irish mine sites

Although Se is found in very low concentrations in most rocks and soils, its similarity to sulphur means that it can be concentrated in sulphides, including those most commonly found on Irish mine sites. It is also associated with phosphate mines where it occurs both in phosphatic rock and host shales. Nevertheless, out of 1432 *in-situ* analyses of solid waste completed for the HMS-IRC project, Se was detected in at most 69. Almost half of these (32) were in Allihies where the measured Se concentration ranged from <DL to 13 mg/kg. These concentrations are very low and are close to or even below the detection limit that might be expected for the XRF. Yet peak analysis shows clearly defined Se peaks in these samples and analysis of four prepared samples by MA-ES in an external laboratory gave good agreement with analyses carried out by the GSI XRF. Nine samples from the Clare Phosphate at Doolin had *in-situ* Se concentrations of 18 - 30 mg/kg, again with good X-ray peak definition. These data have not been confirmed by external analysis. Se was also detected in five samples of mixed shale and coal waste at Slieve Ardagh, at concentrations ranging from 8 to 14 mg/kg. Most of the remaining samples with detected Se came from Tynagh (14), where measured Se ranged from 17 to 546 mg/kg, and Silvermines (4) where apparently high Se concentrations (188 – 282 mg/kg) were detected in processing waste. However, peak analysis for the Tynagh and Silvermines samples was inconclusive as the Se peak appears to be partly overlapped by a small Au peak. Several analyses of processing waste at Silvermines, carried out for the Inter-Agency Group study, yielded Se concentrations of up to 19 mg/kg (Inter-Agency Group 2000). Two samples at Kilbricken in East Clare and one each at Ballycorus, Glendalough and West Cork also appear to contain small amounts of Se. Fig. 40 summarizes the data for samples in which Se was apparently detected.

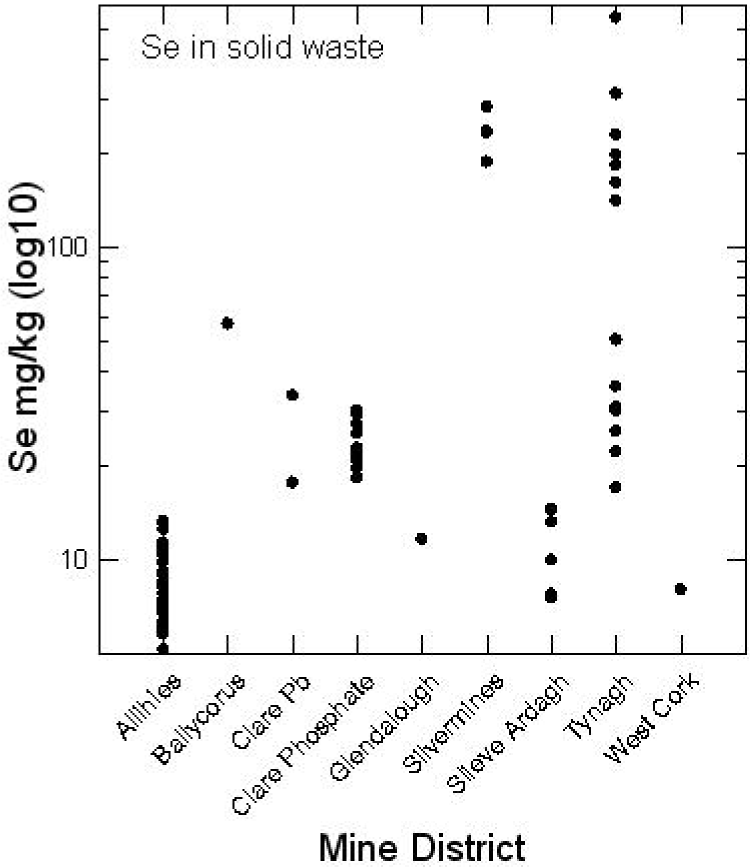


Fig. 40 Scatterplot of Se in solid waste, by district (log scale)

SGV values for Se in soils vary from 35 mg/kg for residential land to 8000 mg/kg for industrial land; ATSDR Comparison Values are 300 mg/kg for a child and 4,000 mg/kg for an adult (Table 2). However, as noted in section 3.14.1 (above), much lower concentrations of Se (means of 30 mg/kg or less) in phosphate mine waste have been associated with significant environmental problems in the USA, particularly where Se can be leached from solid waste into water courses. Therefore, while Irish mine sites do not appear to contain sufficient Se to cause problems to human health, the levels measured on some sites may be of concern in a broader environmental context.

Table 34 Se (total) in water on and around Irish mine sites, by source

µg/l Se	All samples	Groundwater	Mine Water	Upstream	Downstream
n	466	27	197	67	174
Minimum	<1	<1	<1	<1	<1
Maximum	110	3	110	8	11
Median	<1	<1	<1	<1	<1
Mean	1.5	0.8	2.1	1.4	1.1

Table 34 summarizes the data for total Se concentration in water samples analysed for HMS-IRC as well as samples from Silvermines (Inter-Agency Group 2000). The reference value for Se is 10 µg/l, the Irish Drinking Water standard (Table 3). Of the 466 samples analysed in summer and winter periods, only two samples had measured total Se exceeding the standard. One was drainage from the tailings pond at Gortdrum in which the measured total Se was 110 µg/l. This is an unusually very high concentration for which no obvious explanation exists. Dissolved Se in this sample was 3 µg/l. The other sample with total Se > 10 µg/l was a downstream sample at Glentogher, one of the Donegal Pb mines, in which measured Se was 11 μg/l. This sample came from an analytical batch in which laboratory blank water had high total Se, among other elements, indicating cross-contamination in the analysis. The dissolved Se for this sample was below the 1 μg/l detection limit. However, the adit discharging to the stream had *dissolved* Se content of 3 μg/l, so there is some suggestion that this small mine may give rise to raised Se concentrations in surface water, if not at concentrations significantly in excess of the standards.

Stream sediments were collected in most mining districts and the fine fraction (<150 μm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). Se was apparently detected at very low concentrations (4 – 9 mg/kg) in only four mine districts for which sediments were analysed by XRF: Allihies, Bunmahon, Doolin (Clare Phosphate) and Tynagh. The lower detection limit (1.1 mg/kg) obtained with the laboratory-based method used for the Silvermines samples allowed detection of Se in 5 out of the 19 samples analysed. Peak analysis of the X-ray spectra for stream sediments analysed by XRF suggest that the result for the Bunmahon sample is unreliable – at 4 mg/kg this is just too low to allow any confidence that Se was detected. Peak analysis for the Tynagh samples is inconclusive but the X-ray spectra for the Allihies and Doolin samples appear to have defined Se peaks. The highest Se concentration measured at Doolin was 7 mg/kg; at Allihies the maximum was 9 mg/kg. In the Silvermines samples, measured Se ranged up to 7 mg/kg.

Allihies, Doolin and Silvermines are three sites where Se was consistently detected in solid waste analyses so the presence of small concentrations of Se in stream sediments is not surprising. The reference concentration for Se in stream sediments (Table 4) is 12 mg/kg – none of the samples in which Se was detected exceed this. Indeed, since the standard is set for the total fraction, and the measured concentration of most elements is higher in the fine fraction, as collected for the HMS-IRC project, it is likely that the Se concentration in the total sediment fraction at these sites is even lower than the concentrations reported above.

In summary, Se has been detected at very low concentrations in solid waste and stream sediments in several mine districts, notably Allihies and Doolin (Clare Phosphate). Water samples generally have Se concentrations below the detection limit or at least below the Drinking Water standard. Although there appears to be no indication of Se toxicity on farms in the north Clare area (Rogers *et al.* 1990) nevertheless care is needed interpreting the solid waste data, particularly with reference to the Clare Phosphate district. Phosphate mines, in particular, are associated with downstream Se contamination as a result of leaching of relatively small concentrations of Se from solid waste. The concentration of Se measured in solid waste in the Clare Phosphate (18 – 30 mg/kg) are similar to the median concentration of Se in phosphate rock and waste rock in phosphate mines in the US (Moyle and Causey 2001) that have been associated with excess Se in downstream environments. Se concentrations in soils in northwest Clare, where the phosphate deposits are located, are in the upper 25% of the range for soils in Ireland (Fay *et al.* 2007).

3.15 Silver - Ag

3.15.1 Introduction to Ag

Silver occurs naturally in the environment in rocks, soils and ore deposits, usually in combination with other elements in compounds such as alloys and sulphides. It is used to make silverware and jewellery, electronic equipment, dental fillings, photographic chemicals and as a disinfectant. It is released into the environment through ore processing and industrial activities.

Silver is in the same group of the Periodic Table as Au and Cu. It occurs most commonly in nature as sulphides or sulphosalts, in alloys with Au or as a minor component in sulphides. Ag minerals include native Ag, alloys such as **electrum** (Au-Ag), **silver amalgam** (Ag-Hg), sulphides such as **argentite** (Ag_2S), **argentopyrite** ($AgFe_2S_3$), and various antimonides, arsenides and tellurides. Sulphosalts include **proustite** (Ag_3AsS_3) and **tetrahedrite-tennantite** ($((Cu,Fe,Ag)_{12}(Sb,As)_4S_{13})$ (Wedepohl 1978). The concentration of Ag in silicates rarely exceeds 0.5 mg/kg. High but very variable amounts of Ag occur in sulphides and arsenides, e.g. argentiferous galena, pyrite (1 - 500 mg/kg), sphalerite (3 - 3500 mg/kg), chalcopyrite (5 - 3300 mg/kg) (Wedepohl 1978). The Ag content of oxides such as magnetite and chromite is typically 1 - 5 mg/kg. Among carbonate minerals, only metal carbonates such as cerussite and malachite contain significant Ag.

In general, there is no strong relationship between Ag contents and rock composition except that Ag, as a chalcophile element, may be higher in rocks containing minor sulphides, chiefly the more mafic rocks (Wedepohl 1978). The Ag concentration in rocks ranges from around 0.01 mg/kg in limestones, to 0.05 mg/kg in granite to 0.1 mg/kg in gabbros and basalts. The mean upper crustal concentration is 0.05 mg/kg (Taylor and McLennan 1986). The average Ag content of soils is probably < 1 mg/kg. A study of Canadian soils suggested a mean of 0.3 mg/kg with elevated Ag concentrations related to the application of sewage sludge. Ag was below the limit of detection in most rocks and stream sediments analysed for GSI's regional geochemical programmes (Table 35), even where the detection limit was as low as 0.1 mg/kg.

Table 35 Concentration of Ag in some Irish soils, sediments and rocks

Ag	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	not analysed	not analysed
Stream sediments SE Ireland (n=1884)[2]	<2 - 25	<2
Stream sediments Inishowen (n=128)[3]	< 0.1	< 0.1
Stream sediments NE Ireland (n=386)[2]	<2	<2
Leinster Granite SE Ireland (n=26)[2]	<2	<2
Sedimentary rocks SE Ireland (n=222)[2]	<2 - 3	<2
Volcanic rocks SE Ireland (n=123)[2]	<2 - 12	<2

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

Various concentrations of Ag have been reported for surface water in the US, with mean concentrations in various studies in the 1960s and 1970s ranging from 0.2 to 9 µg/l (ATSDR 1990a). Concentrations in areas close to Ag mines were much higher.

Exposure of humans to high Ag levels over long periods of time can result in a condition called arygria. This blue-grey discolouration of the skin is not known to be harmful but is a permanent, cosmetic effect (ATSDR 1990a).

3.15.2 Silver on Irish mine sites

Silver has been mined at numerous locations in Ireland, typically in lead mines where it occurs in association with galena (PbS) (Cole 1922). Table 36 summarizes the data for Ag in solid waste for selected sites and Fig. 41 shows the variation in measured Ag across the mine districts. XRF analyses of Ag are generally free of significant problems because the Ag X-ray peak is rarely overlapped by that of any other element (Appendix 4).

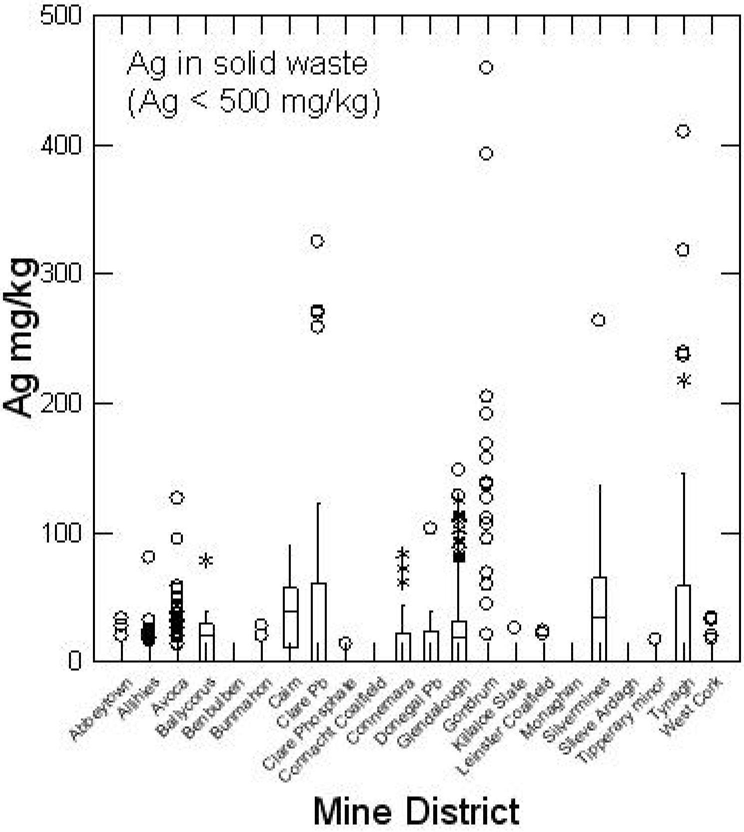


Fig. 41 Boxplots of Ag in solid waste, by district (log scale)

Table 36 Summary statistics for Ag in several mine districts (*in-situ* analyses)

mg/kg Ag	All sites	Avoca	Clare Pb	Glendalough	Gortdrum	Silvermines	Tynagh
n	1432	347	47	381	79	24	134
Minimum	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Maximum	1599	126	325	148	459	264	1599
Median	0.0	0.0	0.0	19	0.0	35	0.0
Mean	20.4	3.8	48.9	21.0	31.4	49.6	84.7

Note: A value of 0.0 indicates result < detection limit

Ag was detected in solid waste in 18 out of 22 districts, with only the Connacht and Slieve Ardagh coalfields, Benbulben barite mine and the Monaghan Pb mines failing to show any Ag in *in-situ* analyses. The latter is somewhat surprising since Ag was apparently produced along with Pb at the Hope mine in Monaghan. Almost 50% of the sites where Ag was detected were in the Glendalough district, although it accounts for just over a quarter of the total sites. Ag was detected at 54% of *in-situ* analyses made in Glendalough. Ag was also detected in a high proportion of the *in-situ* analyses at Silvermines (70%), Caim (75%), Ballycorus (52%), Tynagh (44%) and the Clare Pb mines (38%).

The highest concentration of Ag measured was at Tynagh in the area of the former processing plant, where *in-situ* measured Ag concentrations exceeded 1,000 mg/kg. Processing waste or waste in former processing areas also yielded the highest Ag concentrations measured at Gortdrum, Glendalough and Caim.

There are no available standard concentrations for Ag in soil. It is generally present in very low concentrations in most natural materials (Table 35). Its low toxicity to humans and relatively scarcity mean that it is not always included in analytical programmes.

Ag was not analysed in water samples collected for HMS-IRC. It is not included in Irish or European water quality standards. The concentration of Ag in 19 water samples taken at Silvermines (Inter-Agency Group 2000) was below the detection limit of 0.5 µg/l in all cases.

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). Ag was detected in very few samples analysed by XRF. Three samples from Glendalough had concentrations of Ag between 31 and 52 mg/kg. A sediment sample at Tynagh, containing almost 4% Pb and considered to be contaminated by tailings or other solid waste, had a measured Ag concentration of 57 mg/kg. Ten samples from Silvermines, analysed in a commercial laboratory using more sensitive techniques than the XRF, had Ag concentrations ranging up to 13 mg/kg.

In summary, Ag was detected in solid waste at most mines investigated for the HMS-IRC project, usually in concentrations well below 100 mg/kg. Several Pb mines had relatively high concentrations of Ag, especially in solid waste on former processing areas or in processing waste itself. Most stream sediments samples analysed had Ag concentrations below the detection limit, estimated to be 10 – 20 mg/kg.

3.16 Thorium - Th

3.16.1 Introduction to Th

Thorium is a naturally occurring radioactive element, found in rocks, soils, water, plants and animals. It has no known biological role and is toxic and carcinogenic. Th is used in the manufacture of ceramics, in metals used in the aerospace industry and in gas mantles. It can also be used as a nuclear fuel. Humans are exposed to small amounts of Th in food, water and air. Working in or living close to industries that use Th or to Th, U, Sn or phosphate mines can also increase exposure to Th.

Thorium occurs as the Th^{4+} ion with an ionic radius comparable to U^{4+} and Ce^{4+}. A considerable number of isostructural compounds of Th, Ce, U and Zr exist (Wedepohl 1978). Pure Th minerals such as **thorianite** (ThO_2) or **thorite** ($ThSiO_4$) are rare but Th occurs as a minor constituent of a large number of minerals containing U and the rare earth elements, e.g. **monazite** ($(Ce,La,Nd,Th)(PO_4,SiO_4)$). ThO_2 and UO_2 form a solid solution series and Th is usually present in CeO_2. Unlike UO_2, ThO_2 is very stable. Th in quartz and feldspar in rocks ranges from 0.5 to 10 mg/kg and up to 50 mg/kg in biotite and hornblende. Magnetite has a relatively low content of Th (up to 20 mg/kg) but other common accessory minerals can have much higher contents, e.g. allanite (up to 20,000 mg/kg), zircon (up to 1,000 mg/kg) and monazite (up to 125,000 mg/kg) (Wedepohl 1978). Apatite (up to 250 mg/kg) and sphene (up to 1000 mg/kg) can also be relatively enriched in Th. Th minerals are uncommon because Th itself is scarce, it easily substitutes into other minerals and because it is not concentrated into secondary oxides by, for example, precipitation from surface and near-surface waters. Th is thus, unlike U, widely dispersed (Wedepohl 1978).

Table 37 summarizes the range of concentrations of Th found in Irish soils, sediments and rocks. The median concentration in Irish soils of 4.65 mg/kg (Fay *et al.* 2007) is within the typical range for soils of 2 – 12 mg/kg (mean 6 mg/kg) (ATSDR 1990b). The estimated upper crust composition is 10.7 mg/kg (Taylor and McLennan 1986). Granitic rocks generally have much higher mean Th concentrations (around 15 mg/kg) than basic igneous rocks (2 mg/kg), with sediments in between. Most of the median concentrations for Irish sediments and rocks are close to these values (Table 37). The relatively high median concentration of Th in volcanic rocks in southeast Ireland reflects the number of samples from the Avoca Formation, which is relatively enriched in Th compared to other rocks in the region.

Table 37 Concentration of Th in some Irish soils, sediments and rocks

Th	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	<0.1 – 11.15	4.65
Stream sediments SE Ireland (n=1884)[2]	<0.2 - 126	11
Stream sediments Inishowen (n=128)[3]	6 - 14	11
Stream sediments NE Ireland (n=386)[2]	4.6 - 16	9.1
Leinster Granite SE Ireland (n=26)[2]	1.3 – 22.1	9.5
Sedimentary rocks SE Ireland (n=222)[2]	<0.2 – 46.7	12
Volcanic rocks SE Ireland (n=123)[2]	<0.2 – 69.5	16

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

The concentrations of Th in surface waters are of the order of 1 – 5 µg/l. There are, however, no reference values for Th in either drinking waters or surface waters.

Th decays slowly and its alpha radiation does not penetrate human skin (Fay *et al.* 2007). However, ingestion of aerosolized Th is potentially carcinogenic because the alpha particles can penetrate the walls of internal organs. Studies have shown that workers who have inhaled high concentrations of Th dust have increased risk of lung disease and cancer (ATSDR 1990b).

3.16.2 Thorium on Irish mine sites

Thorium was detected in solid waste at a limited number of mine districts in concentrations generally below 50 mg/kg. Most waste analysed had Th below the limit of detection but Th was detected in 34 out of the 1432 samples analysed. Solid waste in the Avoca district had the highest measured Th concentration of 171 mg/kg. The volcanic rocks that host the Avoca ore are generally somewhat enriched in Th and U (Gallagher *et al.* 1994) relative to other rocks in the region. Other sites where Th was consistently detected included Allihies and the Leinster coalfield. Its presence in one sample from the Clare Phosphate deposit is unsurprising as the phosphatic rock also contains U-bearing apatite. There is no standard for Th concentration in soils or solid waste. As most Th in rocks is generally bound in stable minerals such as monazite and apatite it is unlikely to present a significant risk at the levels detected in mine waste analysed for HMS-IRC.

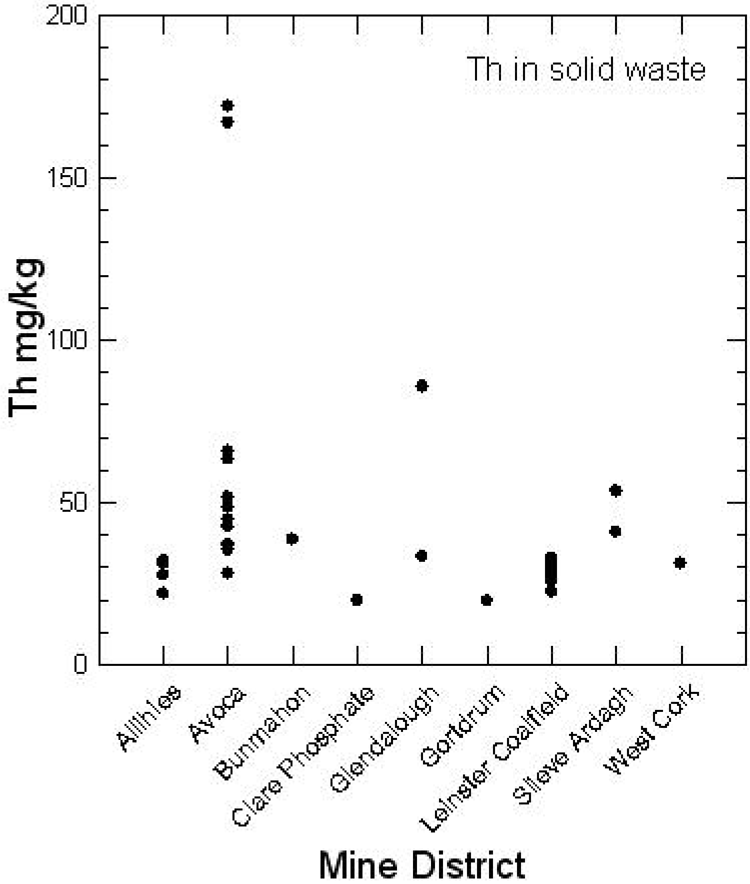


Fig. 42 Scatter plot of Th in solid waste, by district (log scale)

Th was not analysed in water samples collected for HMS-IRC. It is not included in Irish or European water quality standards. The concentration of Th in 19 water samples taken at Silvermines (Inter-Agency Group 2000) was below the detection limit of 0.5 µg/l in all cases.

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). Th was detected in 34 out of these 126 samples. Half of these detections were in samples from Silvermines, analysed using more sensitive technique with a detection limit of 0.5 mg/kg. The concentration of Th in Silvermines samples ranged from <0.5 to 23 mg/kg, with a median of 0.55 mg/kg. Concentrations measured by the XRF in the remaining samples ranged up to 55 mg/kg. Th was detected in samples from Allihies, Avoca, Caim, Glendalough, Gortdrum, the Leinster coalfield and the Slieve Ardagh coalfield. There is no reference concentration for Th in sediments. Exposure levels for Th are generally measured in terms of radioactivity, rather than element concentration.

In summary, Th was detected in a small number of samples of solid waste and stream sediments at a limited number of mine districts investigated for the HMS-IRC project, usually in concentrations below 50 mg/kg. It is not known if Th is directly associated with ore minerals in sulphide mines in Ireland – at Avoca, at least, it is known to occur in relatively high concentrations in host volcanic rocks. In the Clare Phosphate deposits, it is probably associated with U in apatite, the main ore of phosphate. The lack of any reference values make it difficult to assess any potential risks associated with the occurrence of Th on Irish mine sites. However, comparison of concentrations measured for this study with the range of concentrations in Irish rock types (Table 37) suggest that, for the most part, Th is not enriched in mine sites relatively to normal background levels.

3.17 Uranium - U

3.17.1 Introduction to U

Uranium is a naturally occurring radioactive element, found in rocks, soils, water, plants and animals. It has no known biological role and is toxic and carcinogenic. It is chemically similar to Th but is readily soluble in water. Leaching of U from rocks and soils gives rise to enrichment of U in groundwater and in secondary deposits of U oxides. U is used as a fuel in nuclear power plants and in armaments. Humans are exposed to small amounts of U in water and air in areas with high background levels of U, working in factories that process U or working with phosphate fertilizers. Coal-fired power plants also emit small amounts of U.

In minerals only the U^{4+}, U^{5+} and U^{6+} valence states are known. U occurs in a variety of minerals but characteristically is concentrated in a few species of minor abundance (Wedepohl 1978). In silicates, it is highest in micas and hornblende (ranging up to 60 mg/kg, average 2-8 mg/kg) and lowest in olivine (average 0.05 mg/kg). Concentrations in quartz and feldspar are typically 1 to 3 mg/kg. Accessory minerals contain more, e.g. allanite (30-1000 mg/kg), apatite (10-100 mg/kg), monazite (500-3000 mg/kg), sphene (10-700 mg/kg), xenotime (300-40,000 mg/kg) and zircon (100-6000 mg/kg) (Wedepohl 1978). The most abundant U mineral is

uraninite/pitchblende (UO_2 - U_3O_8 - the variation reflects oxidation after deposition). Uraninite oxidizes easily to UO_2^{2+} that, in turn, is easily mobilized in surface and near-surface waters, reacting to form a variety of carbonates, phosphates, vanadates, silicates and sulphates. These include the common phosphates **autunite** ($Ca(UO_2)_2(PO_4)_2 \bullet 8\text{-}12H_2O$) and **torbernite** ($Cu(UO_2)_2(PO_4)_2 \bullet 12H_2O$) (Wedepohl 1978).

Table 38 summarizes the range of concentrations of U found in Irish soils, sediments and rocks. The median concentration in Irish soils of 2.0 mg/kg is within the typical range for soils of 1 – 4 mg/kg (Fay *et al.* 2007). The estimated upper crust composition is 2.8 mg/kg (Taylor and McLennan 1986). Granitic rocks generally have much higher mean U concentrations (around 4 mg/kg) than basic igneous rocks (<1 mg/kg), with sediments in between. Most of the median concentrations for Irish sediments and rocks are close to these values (Table 38).

Table 38 Concentration of U in some Irish soils, sediments and rocks

U	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	<0.1 – 64.2	2.0
Stream sediments SE Ireland (n=1884)[2]	1.3 - 818	3.4
Stream sediments Inishowen (n=128)[3]	1.0 – 8.5	2.9
Stream sediments NE Ireland (n=386)[2]	1.9 - 13	3.0
Leinster Granite SE Ireland (n=26)[2]	2.2 – 7.3	3.4
Sedimentary rocks SE Ireland (n=222)[2]	<0.2 – 19	2.5
Volcanic rocks SE Ireland (n=123)[2]	<0.2 – 58.8	4.7

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

A 1980s US EPA study of 35,000 surface water samples gave a mean U concentration of 1.1 pCi/l (1.65 µg/l); 55,000 groundwater samples for the same study gave a mean of 3.1 pCi/l (4.8 µg/l) (ATSDR 1999). However, levels can be much higher in areas with high background concentrations of U in bedrock.

Exposure to high concentrations of U can lead to kidney damage but the associated radiation does not cause cancer. However, U decays into other radioactive substances that have been associated with increased cancer risk, notably radon.

3.17.2 Uranium on Irish mine sites

Uranium was detected in solid waste at a limited number of mine districts in concentrations generally below 100 mg/kg. Out of 1432 samples analysed *in-situ* by XRF, U was detected in 57. Fig. 43 shows the distribution of U for these samples. The detection limit for U in the XRF analyses is unknown. Comparison of standard analyses and of the results for prepared samples analysed by XRF in the GSI laboratory and by MA-ES in an external laboratory (Appendix 4) suggests that the XRF can detect U in concentrations as low as 20 mg/kg or even lower in some cases. However, accuracy at such concentrations is likely to be poor.

Most samples with measured U came from three mine districts or sites: Avoca, the Clare Phosphate and Gortdrum. U is known to be present in relatively high background levels in the host rocks to the Avoca ores. Thus, 59 samples of rocks from the Avoca Formation, measured by neutron activation, had a median U concentration of 7.4 mg/kg (range: 0.3 – 59 mg/kg), significantly higher than the median for volcanic rocks in the southeast Ireland region as a whole (4.7 mg/kg)

(GSI unpublished data). The maximum U concentration measured at Avoca for HMS-IRC was 78 mg/kg. Although this is consistent with the concentration of U measured in the host volcanic rocks, there is no evidence available as to the form in which U occurs in the Avoca mine waste.

U is commonly found in phosphates, including apatite. It was detected in all 9 *in-situ* analyses made on phosphate mine waste at Doolin in Co. Clare. Measured concentrations ranged from 59 to 129 mg/kg with a median of 98 mg/kg. Analyses of 118 phosphate samples and host rocks carried out by GSI in the late 1970s (GSI Mine Records) gave a median U concentration of 69 mg/kg (range: 3 – 376 mg/kg). U was detected in a proportion of samples at Gortdrum, both in waste at the former processing area (85 – 157 mg/kg in three samples) and in tailings (25 – 38 mg/kg in eight samples). U was also detected at low concentrations in a few samples from Allihies, Ballycorus, the Glendalough district and the Leinster and Slieve Ardagh coalfields. In the latter it is presumably contained in the shale host rock.

The only standard for U in soils or solid waste is the ATSDR Comparison Value which is based on “soluble” U, i.e. U in a form that can be readily taken up and absorbed by humans. The standards are 100 mg/kg for a child and 1000 mg/kg for an adult (Table 2). There is no evidence as to whether any of the U detected in mine waste at Avoca and the coalfields is in soluble or insoluble form. In the Clare Phosphate, U is apparently hosted by apatite, an insoluble, resistant mineral. Zircon, an insoluble resistant mineral that typically contains U, is a common constituent of some lithologies in the Avoca Formation that hosts the Avoca deposit. The form of U at Gortdrum, Allihies and Ballycorus is unknown but even if it is in soluble form the concentrations fall below the reference values in most cases, apart from two processing area samples at Gortdrum, where the measured U concentration exceeded 100 mg/kg.

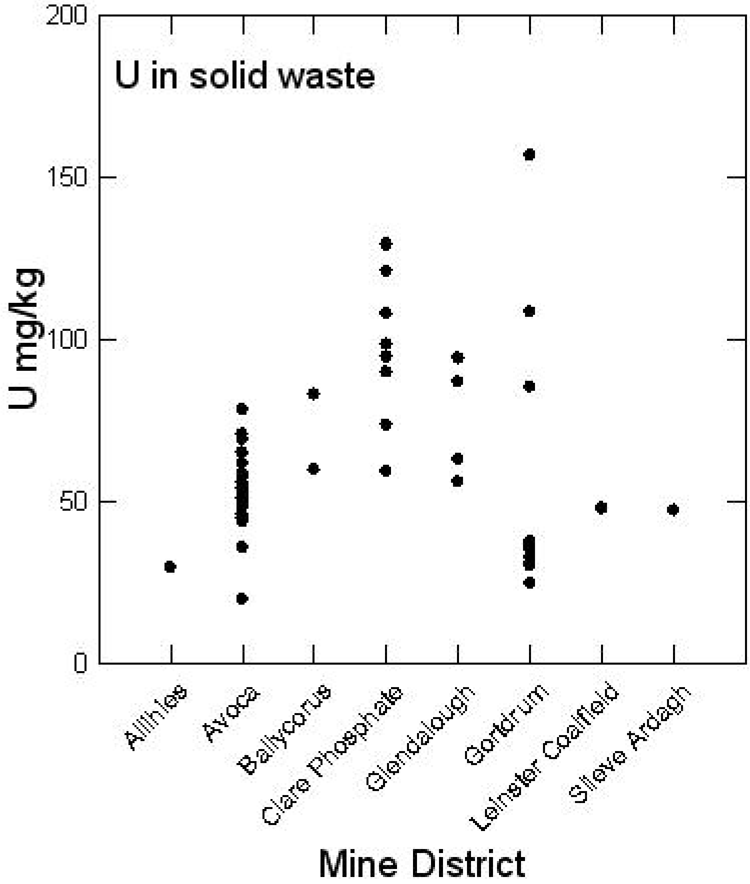


Fig. 43 Scatter plot of U in solid waste, by district (log scale)

Fig. 44 shows the distribution of total U in water samples analysed for HMS-IRC as well as in samples from Silvermines (Inter-Agency Group 2000). There is no Irish or European reference value for U in drinking or surface water but the US EPA's MCL for drinking water is 30 µg/l. Only one sample analysed, from Avoca, exceeds this level. Total U was detected in 375 out of 447 samples. Samples from most mine districts had U concentration below 10 µg/l. Exceptions were Avoca, the Clare Phosphate deposit at Doolin, Gortdrum and the Leinster and Slieve Ardagh coalfields. U was also detected in solid waste in each of these districts.

Fig. 45 is a scatterplot of total U against dissolved U in samples analysed for HMS-IRC. There is a strong correlation between dissolved and total U (r = 0.93), with a slight bias toward higher concentration in total U analyses. Fig. 45 demonstrates that where the U concentration in water exceeds around 5 µg/l, dissolved U concentration is essentially the same as the total U concentration, i.e. most or all of the U is in dissolved form. This in turn indicates that at least a proportion of the U detected in solid waste in the mine districts shown is in a soluble form.

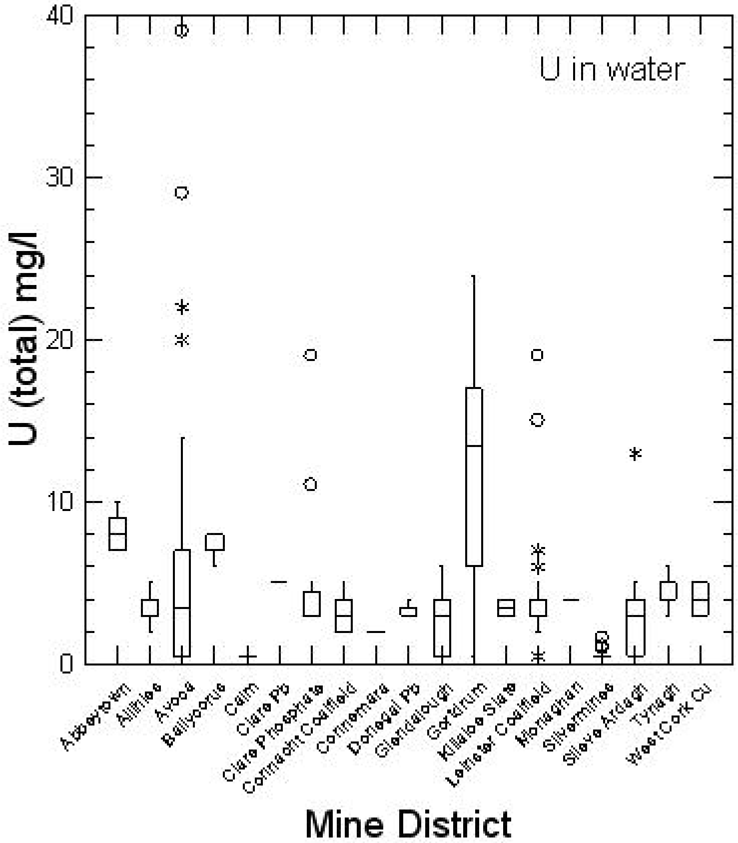


Fig. 44 Boxplots of U (total) in all water samples analysed, by district

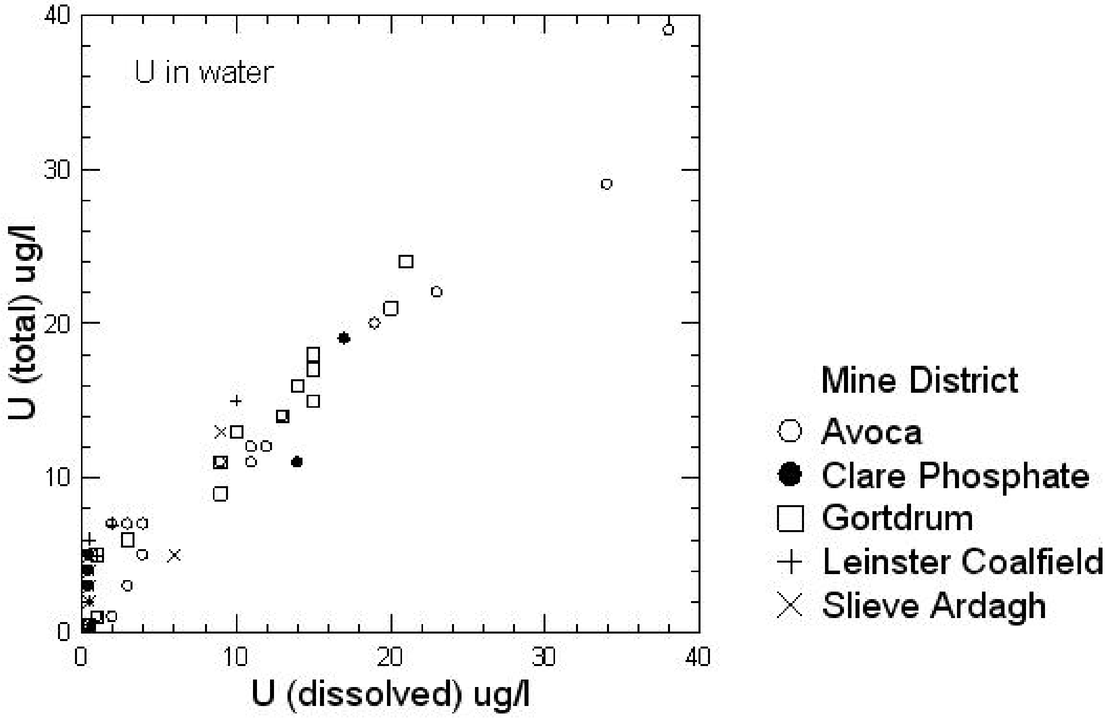


Fig. 45 Scatterplot of U (total) v U (dissolved) for selected mine districts

Fig. 46 shows the distribution of total U in the different water sources. Clearly mine water, including adit discharges, waste seepages and run-off, have the highest U concentrations. Water from all other sources, except one downstream sample at Gortdrum, has measured U concentration below 10 µg/l. From this and Fig. 45, it is apparent that U in solid mine waste has been remobilized into mine waters in at least some mine districts, albeit in concentrations below those likely to be of concern.

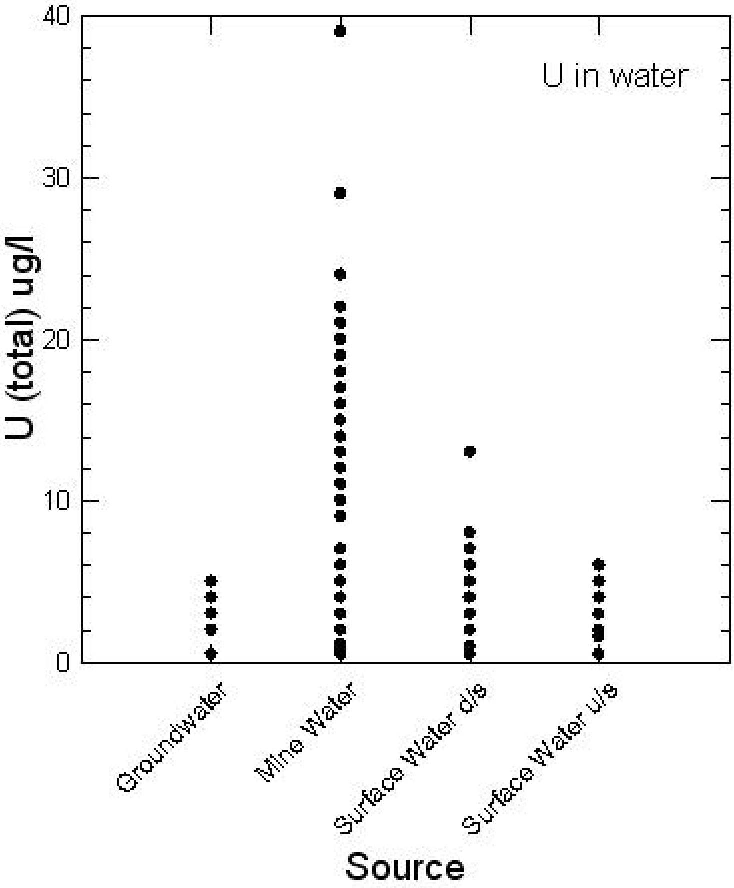


Fig. 46 Scatterplot of U (total) v water source

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). U was detected in only one sample analysed by XRF, a sample from the Glendalough district with measured U of 33 mg/kg. The detection limit for samples from Silvermines was around 1 – 1.2 mg/kg, significantly lower than possible with the XRF. Six samples from Silvermines had U above the limit of detection, with the highest concentration 19 mg/kg U (Inter-Agency Report 2000).

In summary, U was detected in a small number of samples of solid waste, mainly at Avoca, Doolin, Gortdrum and the Leinster Coalfield. Very few samples had U concentration exceeding any published standards. At least some of the U in solid waste is in soluble form and, as a consequence, has been remobilized into mine water which, on some sites, has relatively high concentrations of total U. However, only one of the samples analysed had U in excess of the US EPA MCL for drinking water. Levels of U in stream sediments are typically very low.

3.18 Vanadium – V

3.18.1 Introduction to V

Vanadium is a naturally occurring element, found in relatively abundant amounts in rocks, soils, water, plants and animals. It is an essential element for some organisms but toxic for others in excess. V is mostly used in the form of V_2O_3 to make a special form of steel for use in car parts and ball bearings (ATSDR 1995). It enters the environment from natural sources and from the burning of oil and coal. V is not easily soluble in water and tends to become fixed in soils and sediments. It is not readily taken up by the body and does not build up in the tissues of animals.

V is a transition element with a varied chemistry. It resembles P somewhat in its chemical behaviour. It occurs mainly in the V^{3+} state with an ionic radius close to that of Fe^{3+} (Wedepohl 1978). Hence it tends to follow Fe and is a minor constituent of magnetite, pyroxene, amphibole and biotite. V can be found concentrated in four distinct chemical environments: sulphide deposits, oxidized sulphide ores, silicates (micas) and oxide deposits in sandstones with or without uranium enrichment (Wedepohl 1978).

Average concentrations of V in limestones and sandstones are typically 15 to 20 mg/kg, in granites around 70 mg/kg, in greywackes around 100 mg/kg and in gabbros and basalts 250 mg/kg or more. Table 39 summarizes the range of concentrations of V found in Irish soils, sediments and rocks. The median concentration in Irish soils of 52 mg/kg (Fay *et al.* 2007) is very similar to the estimated upper crust composition of 60 mg/kg (Taylor and McLennan 1986). Median stream sediment concentrations (87 – 144 mg/kg) vary considerably for the three areas for which data is available - all are significantly higher than the soil median but reflect the variable bedrock composition.

Table 39 Concentration of V in some Irish soils, sediments and rocks

V	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	<2 - 240	52
Stream sediments SE Ireland (n=1884)[2]	10 - 380	87
Stream sediments Inishowen (n=128)[3]	62 - 307	144
Stream sediments NE Ireland (n=386)[2]	29 - 257	132
Leinster Granite SE Ireland (n=26)[2]	2 - 51	26.5
Sedimentary rocks SE Ireland (n=222)[2]	14 - 279	70
Volcanic rocks SE Ireland (n=123)[2]	2 - 477	46

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

V concentrations in freshwater in the US have been found to range between 0.3 µg/l and 220 µg/l (ATSDR 1992b). There are, however, no reference values for V in either drinking waters or surface waters.

The main effect of V on human health comes from breathing high concentrations of it, particularly in a work environment (ATSDR 1992b). Effects include lung irritation, chest pain, coughing and throat irritation. These effects generally disappear after stopping breathing the contaminated air. In some animal studies, ingestion of high concentrations of V has caused minor kidney and liver changes, minor birth defects and death. The concentrations of V ingested in these studies are far higher than any likely to be encountered in the natural environment (ATSDR 1992b).

3.18.2 Vanadium on Irish mine sites

The detection limit in the portable XRF analyser used for *in-situ* analyses of solid waste on mine sites is particularly high for V, in part a reflection of almost complete overlap of the main V X-ray peak by that of Ti, a common constituent of many rocks and soils. The manufacturer's estimate is in excess of 100 mg/kg. Out of 221 prepared samples analysed both by XRF in the GSI laboratory and then by MA-ES in an external laboratory, V was detected by the XRF in only 13 samples, as opposed to 217 analysed by MA-ES for which the detection limit was 2 mg/kg. The lowest concentration measured by MA-ES for which a corresponding detection was made by XRF was 81 mg/kg. All other samples in which the XRF detected V had measured MA-ES concentrations above 100 mg/kg. In this context it is perhaps not surprising that V was detected in only 36 out of 1432 *in-situ* analyses carried out for HMS-IRC. Fig. 47 shows the distribution of V for the samples in which it was detected.

The Clare Phosphate deposit at Doolin has the highest V concentrations measured for HMS-IRC. This appears to reflect the presence of black shales in the succession since V is often associated with organic-rich sediments. The same observation may account for the V detected in both the Leinster and Slieve Ardagh coalfields. There is no clear pattern to the occurrence of V on other mine sites where it was detected in one or two samples (Fig. 47).

The only reference values for V are the ATSDR Comparison Values for children (200 mg/kg) and adults (2,000 mg/kg). Samples at several sites exceed the lower reference value, notably Doolin, Avoca, the Clare Phosphate, Gortdrum and the two coalfields.

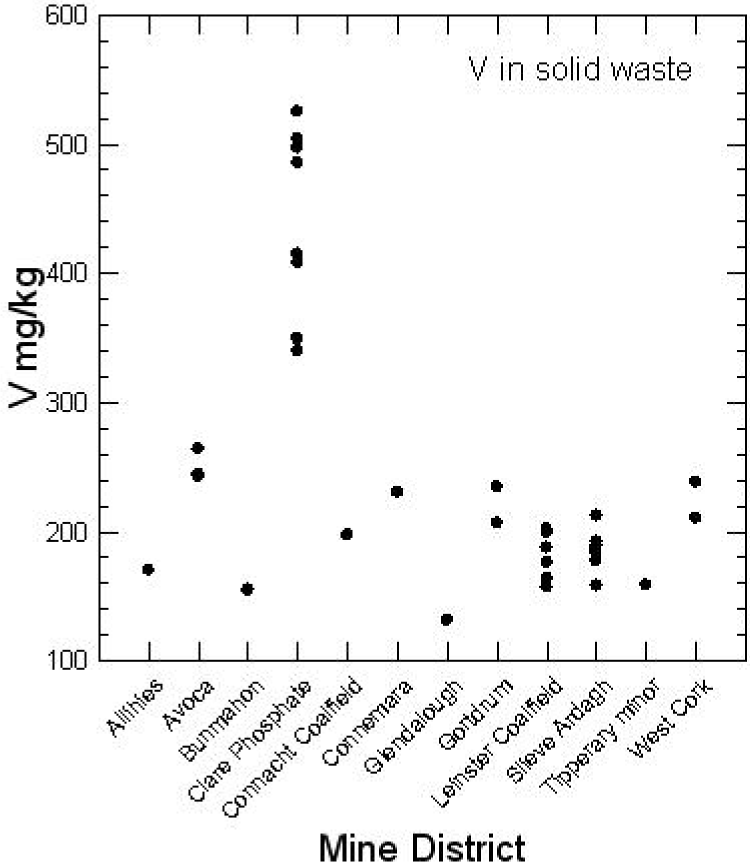


Fig. 47 Scatterplot of V in solid waste samples (> detection limit)

Dissolved V was detected in only 112 out of 445 analyses. Of these, one sample from Doolin, an adit discharge, had a V concentration of 5 µg/l; the rest had a concentration of 3 µg/l or less. Fig. 48 shows the mine districts where V was detected. They include Glendalough (33 samples), the Leinster Coalfield (18), Slieve Ardagh (13), Connacht Coalfield (15) and Doolin (7). There are no reference values in Ireland, Europe or the USA for V in water.

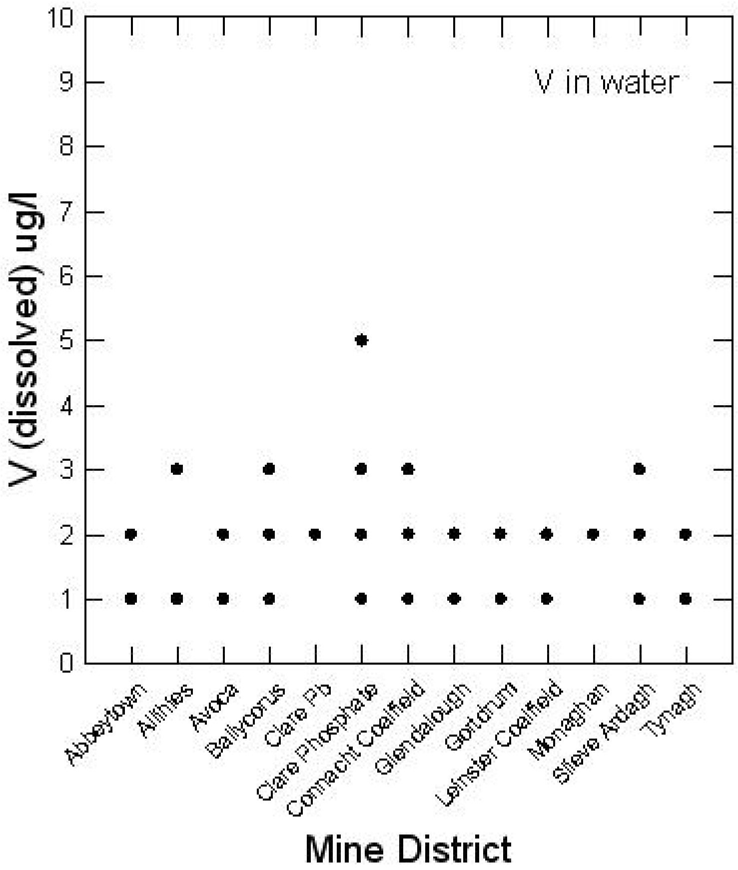


Fig. 48 Scatterplot of V (dissolved) in water, by district

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). V was detected in only 8 of the samples analysed by XRF for HMS-IRC, at Doolin (4 sites: 182 – 231 mg/kg), in the Connacht Coalfield (3 sites: 181 - 222) and in Slieve Ardagh (1 site: 179 mg/kg). In both Doolin and the Connacht Coalfield, V was detected in stream sediment samples taken upstream of the mines, in concentrations similar to those measured downstream. Consequently, it is not possible to conclude that V was introduced to the streams by mining activity. V was detected in each of the Silvermines samples, in concentrations ranging from 9 to 28 mg/kg. The rate of detection reflects the low detection limit employed in the analyses.

In conclusion, V was detected in only a limited number of solid mine waste samples in the mine districts investigated for HMS-IRC, in large part as a consequence of the unfavourable detection limit for V in the XRF analyser used for *in-situ* analyses. The Clare Phosphate deposit at Doolin had the highest concentrations of V. Vanadium was also detected in the Leinster and Slieve Ardagh coalfields. The presence of V in these mine districts may reflect the occurrence of shales with a high content of organic carbon. The concentration of V in water analysed for HMS-IRC was very low, 5 µg/l or less. In the absence of standards for V in water it is difficult to assess the potential relevance of these results. Stream sediments in Doolin and the Connacht Coalfield had high V contents both upstream and downstream of the mines, suggesting that V is enriched in the country rock in both districts.

3.19 – Zinc - Zn

3.19.1 Introduction to Zn

Zinc is a widely dispersed element, present in air, soils, water and in all foods. It is an essential trace element for plants and animals and a common component of diet supplements. It helps maintain a healthy immune system, normal functioning of cell membranes, normal growth and development. It is a cofactor in enzymes associated with DNA and protein synthesis (Solomon 2007). In high concentrations it is toxic to humans but there is a wide margin between normal dietary intake and toxic levels. Harmful effects generally begin at levels 10 – 15 times higher than those needed for good health (ATSDR 2005B). Zn is released by weathering of rocks and volcanic eruptions but most Zn in the environment comes from human activities like mining, steel production, coal burning and the spreading of fertilizers and sewage sludge. Zn is one of the most widely used metals. It is used for galvanizing steel, in batteries, antiseptics and ointments (e.g. infant barrier cream), paints and varnishes, fertilizer and electronic equipment.

Zn occurs in nature as the native metal, in **sphalerite** (ZnS), sulphosalts such as **tetrahedrite-tennantite** ($(CuAg)_{10}(FeZnSn)_2(As,SbBi)_4S_{13}$), oxides including **zincite** (ZnO); carbonates, e.g. **smithsonite** ($ZnCO_3$) and many hydroxides, tellurites, phosphates, sulphates and silicates. In silicates, it substitutes for Fe and Mg and pyroxenes, amphiboles and biotite can contain 10-20% ZnO (Wedepohl 1978). Zn can occur in magnetite and chromite in amounts up to 5000 mg/kg. The occurrence of Zn in such Fe-Mg-rich silicates and oxides accounts for much of the crustal abundance of Zn.

Zn has very low solubility in water at near-neutral pH but solubility increases as pH decreases. It adsorbs onto sediments and is transported after weathering mainly in detrital Fe-bearing material. Thus greywackes contain 70-100 mg/kg Zn, similar to the upper crustal abundance of 71 mg/kg (Taylor and McLennan 1986), but sandstones contain around 30 mg/kg. Shales and clays have an average of 100 mg/kg Zn and those high in organic matter some 200 mg/kg (Wedepohl 1978). Basic igneous rocks like gabbro and basalt have higher average Zn concentrations (c. 100 mg/kg) than granites (50 mg/kg). Soils have quite variable Zn concentrations – averages in several studies in the US (ATSDR 2005B) range from 36 to 60 mg/kg. Wedepohl (1978) cites a global average of 70 mg/kg.

Table 40 summarizes the range of concentrations of Zn found in Irish soils, sediments and rocks. The median concentration in Irish soils of 63 mg/kg (Fay *et al.* 2007) is similar to that of soils worldwide. It is similar to the median value of sedimentary rocks in southeast Ireland (52 mg/kg) and also similar to the estimated upper crust composition of 71 mg/kg (Taylor and McLennan 1986). Median stream sediment concentrations for GSI regional geochemical programmes (126– 213 mg/kg) compare to an average of 110 mg/kg for sediments in the US collected as part of the National Water Quality Assessment Programme (ATSDR 2005B). The GSI data are for <150 µm size fraction in which metal concentrations tend to be higher than in the total size fraction.

Table 40 Concentration of Zn in some Irish soils, sediments and rocks

Zn	Range (mg/kg)	Median (mg/kg)
National Soils Database (n=1310)[1]	3.6 - 1384	63
Stream sediments SE Ireland (n=1884)[2]	23 - 99262	126
Stream sediments Inishowen (n=128)[3]	48 - 1388	184
Stream sediments NE Ireland (n=386)[2]	39 - 2998	213
Leinster Granite SE Ireland (n=26)[2]	22 – 162	65.5
Sedimentary rocks SE Ireland (n=222)[2]	9 - 23647	52
Volcanic rocks SE Ireland (n=123)[2]	12 - 11005	80

[1] Fay *et al.* 2007; [2] Unpublished GSI data; [3] O'Connor *et al.* 1988

Zn concentrations in unpolluted surface water in the U.S. are typically below 50 µg/l (ATSDR 2005B). Solomon (2007) quotes an average Zn concentration of 15 µg/l for freshwater. Higher concentrations have been reported in streams downstream of mining operations. Zn bioaccumulates readily in aquatic organisms, especially invertebrate filter feeders. Concentrations of Zn in freshwater invertebrates may be 40,000 times higher than in water or sediment; in fish the factor is around 1,000 (Solomon 2007). High Zn concentrations alter benthic communities with consequent effects for the entire freshwater ecosystem. Zn does not accumulate in the muscle (flesh) of fish but in their gills, liver and kidneys. It causes structural damage to these organs. Elevated Zn causes a stress response in rainbow trout of fish (Solomon 2007). In Canada, the federal drinking water standard for Zn is 5,000 µg/l and is based on taste rather than health considerations. There is no Irish Drinking Water standard for Zn. For protection of aquatic life in freshwater, the Canadian federal guideline value is only 30 µg/l. Draft EC Surface Water regulations range between 8 and 100 µg/l depending on water hardness.

3.19.2 Zinc on Irish mine sites

Ten of the 22 mines or mine districts investigated for HMS-IRC were Pb producers and most Pb mines in the country contain significant Zn concentrations, sometimes in excess of their Pb content. Moreover, in the 19th century Zn was not mined as a commodity so that solid waste on such sites is often rich in Zn (Fig. 49). Those with median Zn concentrations exceeding 1,000 mg/kg (0.1%) include Caim, Clare Pb, Glendalough, Tassan mine in Monaghan, Silvermines and Tynagh. Table 41 summarizes the data for Zn in solid waste for selected sites. Medians at the sites tabulated range from 906 mg/kg to 41,298 mg/kg (4.1%), with maximum measured concentrations exceeding 30%. Of particular note are spoil at Silvermines, in which Zn concentrations of several % are common, various wastes at Tynagh and a single large heap of process waste at Caim in county Wexford.

Table 41 Summary statistics for Zn in several mine districts (*in-situ* analyses)

mg/kg Zn	All sites	Bally-corus	Caim	Clare Pb	Glenda lough	Silver-mines	Tynagh	Monaghan
n	1432	40	20	47	381	24	134	13
Minimum	0.0	100	170	0.0	64	106	68	77
Maximum	348143	42824	12837	48893	192785	348144	334808	8889
Median	425	906	2022	1594	4891	41298	7701	1109
Mean	6855	3646	2283	9805	8783	77015	28025	3144

Note: A value of 0.0 indicates result < detection limit

The XRF analyser is not calibrated to analyse material with metal concentrations exceeding 2%. This does not automatically mean that high measured concentrations of Zn are inaccurate but with increasing Zn concentration, measured values become increasingly semi-quantitative or even qualitative. Evidence from a limited number of high-Zn samples analysed by assay in an external laboratory suggest that there is reasonable agreement between XRF Zn concentrations and assay values up to 1 or 2% but that above this measured Zn concentrations can be significantly overestimated by the XRF (Appendix 4).

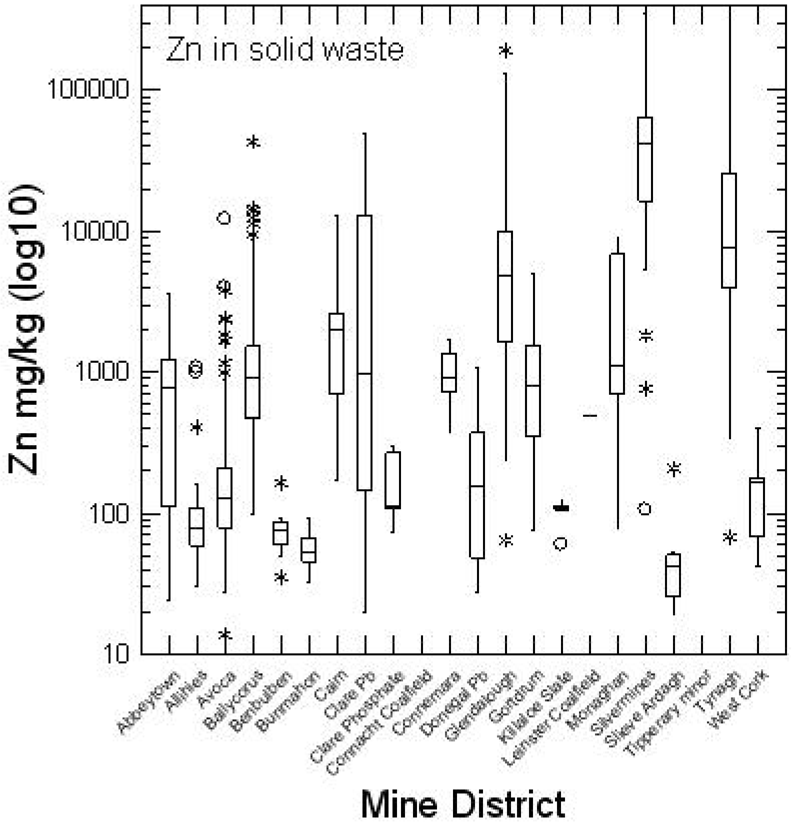


Fig. 49 Boxplots of Zn (log scale) in solid mine waste v mine district

There are contrasting reference values for Zn in soils. The Dutch Intervention value for Zn in "normal" soils is 720 mg/kg. The ATSDR Comparison Values for a child are 20,000 mg/kg Zn (2%) and for an adult 200,000 mg/kg Zn (20%). The Sewage Sludge Directive sets an upper limit of 300 mg/kg Zn for receiving soils. Clearly, the appropriate reference value for Zn will depend on the particular circumstances at any given site. In the context of human health, relatively few samples (98 out of 1432 or 6.8%) analysed for HMS-IRC exceeded the ATSDR Comparison Value of 20,000 mg/kg for a child. Around 52% of samples analysed (746) had Zn concentration exceeding the Sewage Sludge limit of 300 mg/kg, while 45% (653) exceeded the Dutch Intervention value of 720 mg/kg.

Table 42 summarizes the data for *dissolved* Zn in surface and groundwater at Irish mine sites investigated for HMS-IRC. Dissolved Zn is used here because of apparent inaccuracies in a number of batches of total Zn analyses as indicated by high concentrations of total Zn in lab blanks. There is a good 1:1 relationship between dissolved and total Zn for most of the measured concentration range so using dissolved Zn makes little overall difference. For Silvermines (Inter-Agency Group 2000) only total Zn data are available – total Zn concentrations in water from Silvermines were similar to or a little lower than total Zn concentrations in water from Glendalough and Tynagh.

Fig. 50 shows the range and median across the districts. The standard for total Zn in surface waters is from the Draft EC Surface Water Regulations and is not an absolute value. Rather it is a value to be added to the background concentration for a given water source in order to derive the standard for that source. For Zn, the reference value varies with the hardness of the water (Table 3), from 8 µg/l (hardness < 10 mg/l $CaCO_3$) to 100 µg/l (hardness > 100 mg/l $CaCO_3$). Upstream waters analysed for HMS-IRC had a median concentration of 15 µg/l dissolved Zn. The maximum concentration measured was 1143 µg/l (Table 42) for a sample from the Connacht Coalfield but this appears to be a rogue analysis since the total Zn measured for the same samples was 54 µg/l. The two next highest upstream measured dissolved Zn concentrations were 229 and 110 µg/l. Both of these were for a sample immediately upstream of St. Kevin's mine site on the Glendasan River in Glendalough. This site is itself downstream of the Hero Processing site so the samples taken are not entirely true representatives of upstream waters. If these are excluded, the range in dissolved Zn for upstream waters is <1 to 72 µg/l. On this basis, a value of 100 µg/l would appear to represent a reasonable upper limit for a general background dissolved Zn concentration in upstream surface waters. Specific backgrounds will vary from site to site. Since over 75% of samples analysed for HMS-IRC had a hardness in excess of 100 mg/l $CaCO_3$, a standard of 200 µg/l dissolved Zn (background of 100 µg/l plus reference level of 100 µg/l) would embrace most waters studied for HMS-IRC.

Table 42 Zn (dissolved) in water on and around Irish mine sites, by source

µg/l Zn	All samples	Groundwater	Mine Water	Upstream	Downstream
n	445	27	194	59	164
Minimum	<1	<1	<1	<1	<1
Maximum	110500	115	110500	1143	9167
Median	31	14	101	15	32
Mean	2485.4	20.2	5341.9	42.0	406.3

The concentration of dissolved Zn exceeds the 200 µg/l in mine waters at Abbeytown, Avoca, Caim, Glendalough and Tynagh (Fig. 50). Concentrations of total Zn at Silvermines are also higher than this level in the few mine water samples analysed. The concentration of dissolved Zn exceeds the 200 µg/l standard in some downstream surface waters at Avoca, Glendalough and Tynagh; total Zn exceeds 200 µg/l in several downstream samples at Silvermines.

The 200 µg/l standard is substantially higher than levels proposed elsewhere for the protection of aquatic life in freshwater. For example, Canadian guideline values for freshwater are 7.5 µg/l (hardness ≤ 90 mg/l $CaCO_3$), 15 µg/l (hardness = 100 mg/l $CaCO_3$), 90 µg/l (hardness = 200 mg/l $CaCO_3$), 165 µg/l (hardness = 300 mg/l $CaCO_3$) and 240 µg/l (hardness = 400 mg/l $CaCO_3$). On this basis, over 80% of surface water samples analysed for HMS-IRC, with hardness < 300 mg/l $CaCO_3$, would have a guideline value of <165 µg/l and over 60% of samples <90 µg/l. However, even applying these values does not increase the number of districts that have downstream Zn concentrations in excess of guideline values, although it does increase the number of downstream sites within the relevant districts.

Zn concentrations in excess of 200 µg/l were also measured in some samples of mine water and downstream surface water from the three coalfields, particularly the Leinster Coalfield.

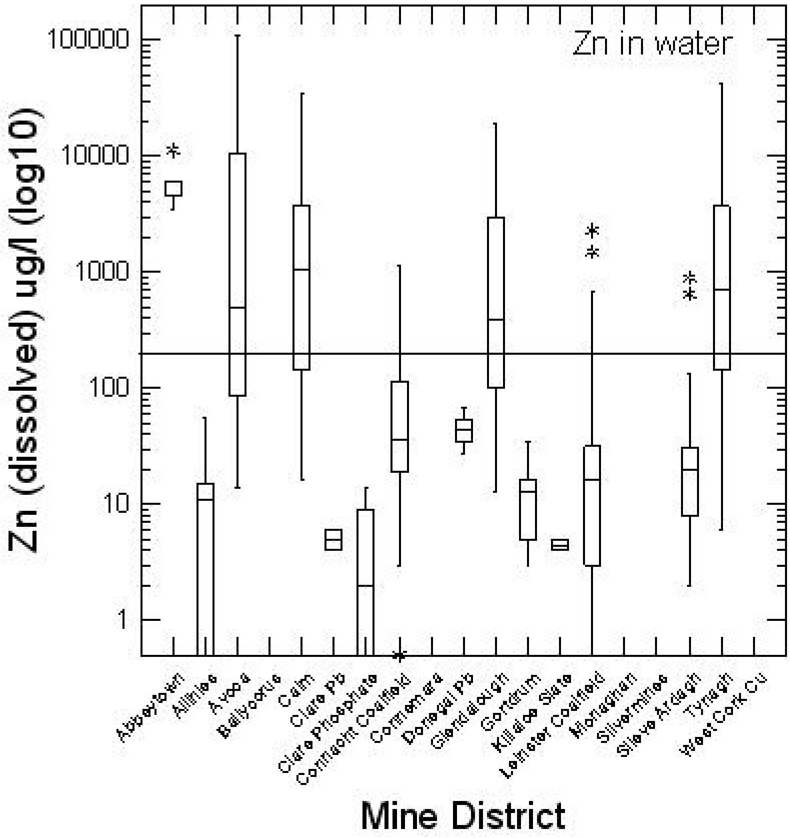


Fig. 50 Dissolved Zn in all waters analysed, by mine district (log scale)

Stream sediments were collected in most mining districts and the fine fraction (<150 µm) analysed by XRF. A total of 107 were collected and analysed for HMS-IRC project; a further 19 samples collected by the EPA in 1999 have been added for the Silvermines district (Inter-Agency Group 2000). Fig. 51 illustrates the variation in Zn concentration in stream sediments across the various districts sampled. The median Zn concentration for all samples analysed is 258 mg/kg (range: <DL – 208,233 mg/kg). On an individual district or site basis, downstream samples generally show significant enrichment in Zn relative to upstream samples. For example, the ranges of Zn concentration for Glendalough samples are 48 – 156 mg/kg (upstream) and 63 – 68,915 mg/kg (downstream). However, relatively few stream sediment samples exceed the standard for Zn in stream sediments (total size fraction) of 5,000 mg/kg (Table 4). This standard relates specifically to livestock that might ingest sediment when using streams for watering. The limits do not apply to aquatic ecosystems or species. Zn concentration exceeded 5,000 mg/kg in some downstream samples only at Glendalough, Silvermines and Tynagh. However, concentrations measured in the fine (<150 µm) fraction of stream sediments tend to be significantly higher than those in the total fraction, in some samples more than twice as high. The applicable standard for Zn in the <150 µm fraction of stream sediments is probably significantly higher than the 5,000 mg/kg level for the total fraction. Even on this basis, some downstream sediments at Glendalough, Silvermines and Tynagh pose a potential risk to animal health.

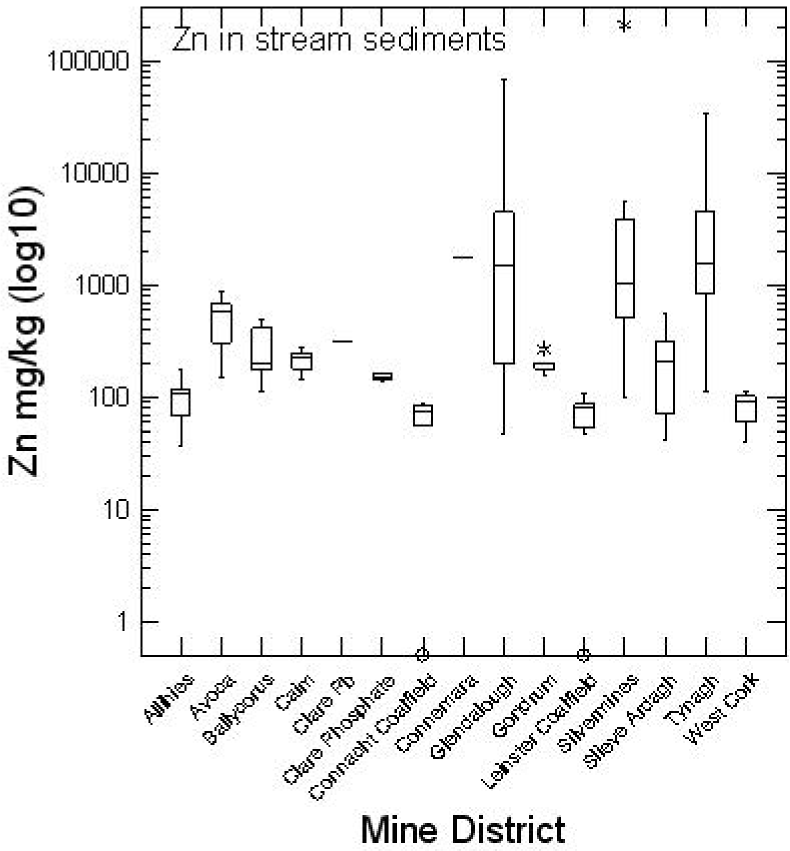


Fig. 51 Zn in stream sediments in mine districts

In summary, solid mine waste at Caim, Glendalough, Tassan mine in Monaghan, Silvermines and Tynagh is significantly enriched in Zn. Published reference values for soil vary significantly but Zn concentrations measured in mine waste on Irish mine sites do not appear to pose a risk to human health. Concentrations of Zn exceed 5,000 mg/kg in stream sediments downstream of Glendalough, Silvermines and Tynagh and may represent a risk to livestock. High concentrations of Zn in stream sediments also pose a potential threat to aquatic organisms. The Zn concentration in surface waters downstream of mines indicates significant impact on water chemistry from mine discharges at Avoca, Glendalough, Silvermines and Tynagh.

References

ATSDR 1990a Toxicological Profile for Silver. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

ATSDR 1990b Toxicological Profile for Thorium. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

ATSDR 1992a Toxicological Profile for Antimony. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry

ATSDR 1992b Toxicological Profile for Vanadium. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry

ATSDR 1999a Toxicological Profile for Mercury. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

ATSDR 1999b Toxicological Profile for Uranium. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

ATSDR 2002 Toxicological Profile for Selenium. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

ATSDR 2004 Toxicological Profile for Copper. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry

ATSDR 2005a Toxicological Profile for Nickel. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry

ATSDR 2005b Toxicological Profile for Zinc. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

ATSDR 2007 ToxGuide for Arsenic. Agency for Toxic Substances and Disease Registry. CAS 7440-38-2.

ATSDR 2008a Draft Toxicological Profile for Cadmium. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

ATSDR 2008b Draft Toxicological Profile for Chromium. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

ATSDR 2008c Draft Toxicological Profile for Manganese. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

Canadian Council of Ministers of the Environment (2003) Canadian Water Quality Guidelines for the Protection of Aquatic Life – Aluminium. Canadian Environmental Quality Guidelines, Canadian Council of Ministers of the Environment.

European Communities (2007) European Communities (Drinking Water) (No. 2) Regulation 2007. SI 278, Government Publications, Dublin.

Fay, D., Kramers, G., Zhang, C., McGrath, D. and Grennan, E. (2007) Soil Geochemical Atlas of Ireland. Published by Teagasc and the Environmental Protection Agency.

Gallagher, V., O'Connor, P.J. and Aftalion, M. (1994) Intra-Ordovician deformation in southeast Ireland: evidence from the geological setting, geochemical affinities and U-Pb zircon age of the Croghan Kinshelagh granite. Geological Magazine, 131, 669-684.

Heinrichs, H, Schulz-Dobrick, B. and Wedepohl, K.H. (1981) Terrestrial geochemistry of Cd, Bi, Tl, Pb, Zn and Rb. Geochimica et Cosmochimica Acta, 44, 1519-1533.

Henry, T., (2008). Preliminary Groundwater Assessment at Tynagh, Co. Galway. Department of Earth & Ocean Sciences, National University of Ireland, Galway.

Inter-Agency Group (2000) Report of the investigation into the presence and influence of lead in the Silvermines area of County Tipperary. Department of Agriculture, Food and Rural Development, Dublin.

Krieger, G.R., Hattermer-Frey, H.A. and Kester, J.E. (1999) Bioavailability of metals in the environment: implications for health risk assessment. Reviews in Economic Geology, Vol 6B: The environmental geochemistry of mineral deposits, Society of Economic Geologists Inc., 357-361.

Moyle, P.R. and Causey, J.D. (2001) Chemical composition of samples collected from waste rock dumps and other mining-related features at selected phosphate mines in Southeastern Idaho, Western Wyoming, and Northern Utah. USGS Open-File Report 01-411.

O'Connor, P.J., Reimann, C. and Kurzl, H. (1988) A geochemical survey of Inishowen, Co. Donegal. Geological Survey of Ireland Report Series, RS 88/1.

Plumlee, G.S., Smith, K.S., Montour, M.R., Ficklin, W.H. and Mosier, E.L. (1999). Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types. Reviews in Economic Geology, Vol 6B: The environmental geochemistry of mineral deposits, Society of Economic Geologists Inc., 373-407.

Rogers, P.A.M., Arora, S.P., Fleming, G.A., Crinion, R.A.P. and McLaughlin, J.G. (1990) Selenium toxicity in farm animals: treatment and prevention. Irish Veterinary Journal, 43, 151-153.

Solomon, F. (2007) Impacts of metals on aquatic systems and human health. Edumine Professional Development Course.

Taylor, S.R. and McLennan, S.M. (1985) The Continental Crust: its composition and evolution. Blackwell Scientific Publications.

Wedepohl, K.H. (ed.) Handbook of Geochemistry (Springer-Verlag, Berlin etc., 1969 - 1978).

WHO (2001) Environmental health criteria 224: Arsenic and Arsenic Compounds (2nd Edition), Geneva.

Appendix 4

XRF Analyser

Assessment of analytical performance of Niton XLt 792Y field-portable XRF analyser

In order to provide independent assessment of the quality of analyses carried out using the field-portable XRF analyser, 221 samples, or approximately 15% of the total of material analysed *in situ* for the project, were reanalysed by both the Niton XRF in the GSI laboratory and by Emission Spectrography (ES) at OMAC Laboratories in Loughrea, Co. Galway. Prior to laboratory analysis, the samples were air-dried and ground in an agate mill to a nominal grain size of <150 µm. Direct comparison of the results obtained for these 221 samples by XRF and ES allows an assessment of the accuracy of the laboratory-based XRF analyses if it is assumed that the ES analyses are essentially accurate and that samples are completely homogenized. In addition, the results of analyses of several standards, completed during the course of laboratory-based XRF analyses, provide further control on the accuracy of the XRF data.

A limitation to this approach is that the upper calibration limit for both the XRF and ES is around 2% for elements of interest such as Cu, Pb and Zn. *In-situ* XRF analyses indicated that many mine waste samples have metal concentrations well in excess of this limit and this was supported by laboratory-based XRF analysis and ES. In order to assess the performance of the XRF at high (>2%) metal concentrations, a limited number of prepared samples were subjected to assay analysis at OMAC Laboratories. .

The results of all of these comparative analyses are outlined below for the following elements: Ag, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Th, U, V, W, Zn. Other elements analysed routinely by XRF have not been included in the comparative analysis either because they are not of particular importance in mine waste samples (e.g. Rb and Sr) or because very high XRF detection limits prevented detection in most cases (e.g. sulphur and phosphorus).

1. Ag - silver

Table 1.1 Ag statistics (mg/kg)

Ag, n=221	**OMAC**	**GSI**
Min	0.3	<DL
Max	200	649
Median	3.3	<DL

Most GSI analyses of samples recorded Ag values below the limit of detection (Table 1.1). In 53 out of the 60 cases where it was detected in GSI, the measured Ag was higher in the GSI analysis than in the OMAC analysis, indicating a clear relative bias to higher values for the XRF analyser (Figure 1.1). Ag is reported for three standards analysed in GSI: NIST 2710 (35 mg/kg), NIST 2780 (27 mg/kg) and RCRA (500 mg/kg). Mean values for XRF analyses of these standards were, respectively, 29 mg/kg, 21 mg/kg and 432 mg/kg. OMAC ran two lab standards, SY-4 (<0.5 mg/kg) and ICP-4 (28 mg/kg): measured values for the latter were within 0.2 of 28 and below the limit of detection for the former. The upper calibration limit for Ag on the OMAC ES is 500 mg/kg. Data for GSI standard analyses do not suggest significant problems with XRF analyses for Ag at high, or indeed low, concentrations and there are no peak overlaps in the XRF spectrum that could give rise to falsely high Ag results.

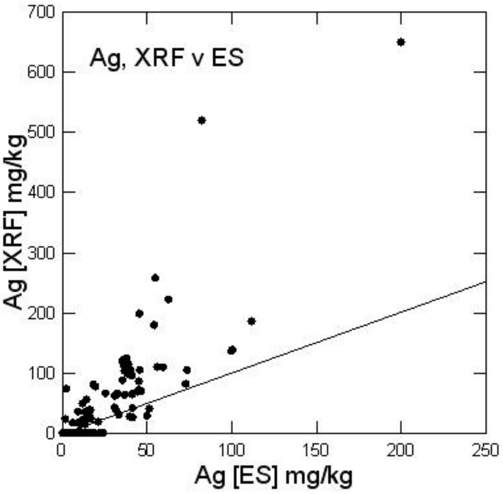


Figure 1.1 Ag XRF (GSI) v ES (OMAC)

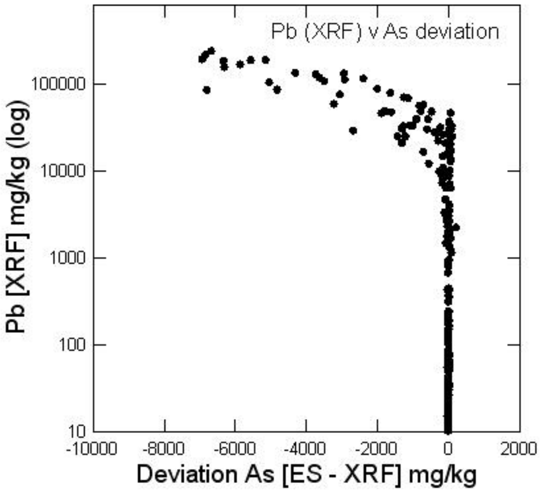
2. As - arsenic

Table 2.1 As statistics (mg/kg)

As, n=221	OMAC	GSI
Min	<5	<DL
Max	6605	55277
Median	58	70

The As results reveal that the GSI analyser shows a similar and even more pronounced bias towards higher values compared to the OMAC analyses. In this case, the OMAC ES system has an upper calibration limit of 20,000 mg/kg, the same as the GSI XRF so this should not be a factor. Moreover, the deviation between GSI and OMAC results can be very high even at low measured OMAC values. Sample heterogeneity does not explain the differences as one would expect a range of high and low values for both instruments rather than a bias for one.

The most obvious potential analytical problem in respect of As lies with the XRF because of almost complete overlap in the XRF spectrum between the main As and Pb peaks. The K_α peak for As is 10.53 keV while the main (L_α) peak for Pb is 10.55 keV. Where there is significant Pb in the sample, as is the case for many of the mine waste samples analysed, the subsidiary peaks, K_β for As (11.73 keV) and L_β for Pb (12.61 keV), provide some discrimination. The K_β peak for As has much lower intensity than the K_α peak and this may have an impact on precision and accuracy levels, especially at low concentrations. However, the most dramatic differences between the GSI XRF data and the OMAC data generally involve high measured XRF concentrations of As and low measured ES concentrations, coinciding with high Pb values as measured by both methods. This is particularly notable in samples from Glendalough and other Pb mines, such as Keeldrum. A plot of the difference in As concentrations as measured by each method and total Pb concentrations, as measured by XRF, shows good agreement between OMAC and GSI As concentrations where Pb concentration does not exceed 1%. Above this level, the measured OMAC and GSI As concentrations diverge sharply. A partial spectrum of one Keeldrum sample (KLD-07-SP01.4 bot) is reproduced below. Measured As values for this sample are 67 mg/kg (OMAC) and 6734 mg/kg (GSI). The Pb values are > 20,000 mg/kg (OMAC) and 233,568 mg/kg (GSI). Despite such a high apparent As value for the XRF analysis, there is no obvious peak for the As K_β line. A similar situation can be observed for other samples with very high Pb concentrations where the As XRF value far exceeds the ES value. It would appear, therefore, that the correction routines for the XRF analyser cannot deal adequately with very high concentrations of Pb and generate falsely high As results.



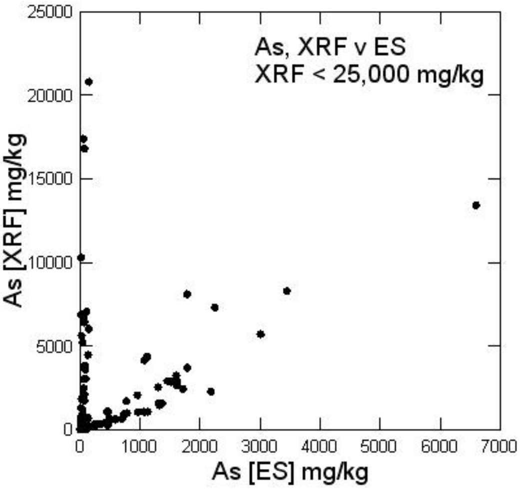


Figure 2.1 AS OMAC v GSI **Figure 2.2 Pb v As deviation**

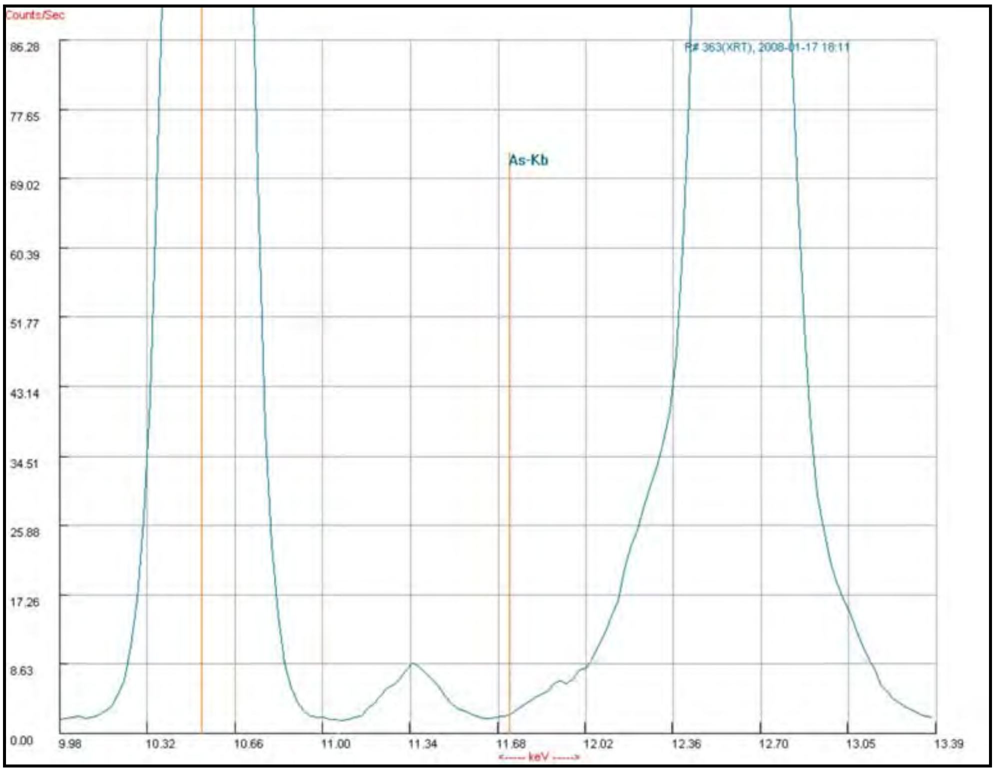


Figure 2.3 As spectrum, GSI XRF (measured As = 233,568 mg/kg)

3. Ba - barium

Table 3.1 Ba statistics (mg/kg)

Ba, n=221	OMAC	GSI
Min	21	<DL
Max	7901	98484
Median	421	646

Ba results again show a bias toward higher data for the GSI XRF analyses relative to the OMAC ES analyses (Table 1.1). This is most pronounced for measured GSI values above 1% (10,000 mg/kg) (Figure 3.1) but is also apparent even at lower values, e.g. below 2000 mg/kg (Figure 3.2). Thus, excluding both ES and XRF data above 2000 mg/kg as well as XRF data below the detection limit, the median value for the GSI XRF is 610 mg/kg, that for OMAC ES analyses 374 mg/kg. Despite the bias toward higher Ba in the GSI analyses, the data below 2000 mg/kg do show a reasonable spread across the 1:1 line (Figure 3.2). When data <10,000 mg/kg are plotted, it is clear that at least some of the ES data are also biased toward higher values, with a distinct grouping of values between 3000 and 8000 mg/kg corresponding to XRF values below 3000 mg/kg (Figure 3.3). Most of these analyses are from Gortdrum and Ballycorus mines. There is also a distinct group of points for which GSI XRF results range up to c. 10% (100,000 mg/kg) and for which OMAC ES results are around 3000 mg/kg or less. These samples are all from Tynagh mine, the one site sampled where barite was a major component of the ore.

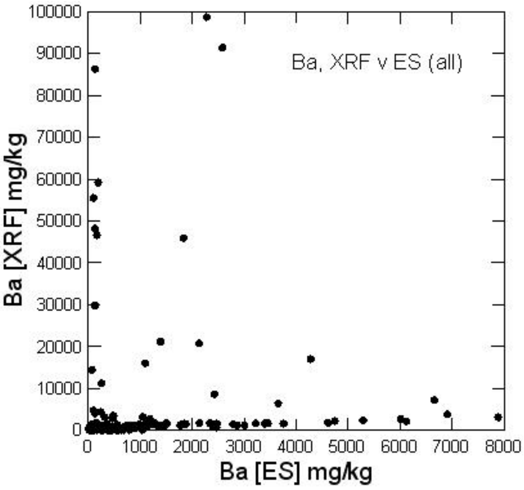


Fig. 3.1 Ba, OMAC v GSI (all)

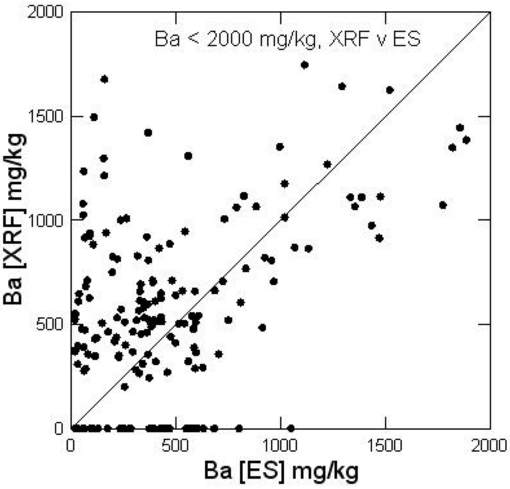


Fig. 3.2 Ba OMAC v GSI, < 2000mg/kg

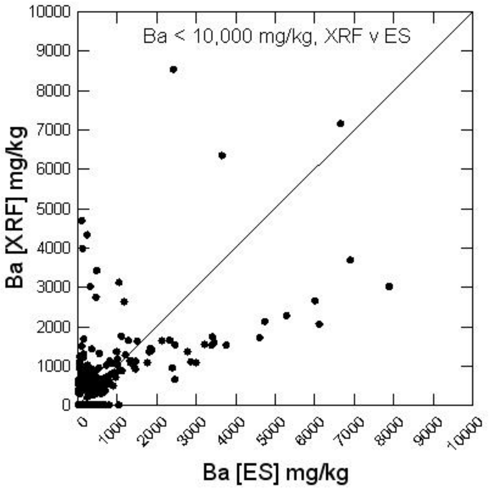


Figure 3.3 Ba, OMAC v GSI, <10,000 mg/kg

Standard analyses (Table 3.2) tend to confirm that there is a general bias toward high values for the GSI XRF. OMAC standard data are too limited to allow firm conclusions but results reported were within ranges defined for the standards employed. The upper calibration limit for the OMAC ES is 5000 mg/kg. In the absence of standards with concentrations of Ba exceeding 1000 mg/kg it is difficult to draw firm conclusions about the overall performance of the XRF given that so many mine waste samples return analyses well in excess of 5000 mg/kg. As with all elements, XRF analyses exceeding 1 – 2% Ba must be considered semi-quantitative.

Table 3.2 Ba XRF standard analyses

Instrument	Standard	n	Analysis χ	Accepted values
GSI XRF	NIST 2710	77	819	707
GSI XRF	NIST 2780	47	638	993
GSI XRF	NCS 73308	42	529	42
GSI XRF	CCRMP TILL-4	5	792	395
OMAC ES	SY-4	3	304 -336	340
OMAC ES	ICP-4	4	224 - 526	250 - 600

The Ba peaks in the XRF spectrum are K_α (32.19 keV), K_β (36.38), L_α (4.47) and L_β (4.83). Both K peaks are at the high-energy end of the spectrum where background counts are high. The Ba L peaks are substantially overlapped by Ti K_α (4.51) and Ti K_β (4.93). At relatively low concentrations of Ba (< 5-800 mg/kg depending on sample type), analysis appears to depend on the L peaks as the K peaks do not exceed background at this level.

4. Bi - bismuth

Table 4.1 Bi statistics, mg/kg

Bi, n=221	OMAC	GSI
Min	<5	<DL
Max	221	10982
Median	<5	<DL

The median values for both GSI XRF and OMAC ES analyses are below the limit of detection (5 mg/kg for ES analyses, set at 2.5 mg/kg), indicating that Bi was not detected by either method in most samples analysed (Table 4.1). Samples where Bi was detected fall mainly into two quite distinct groups: those detected at relatively high levels by both instruments and those detected at high levels by the GSI XRF and at low levels or not detected at all by the ES technique (Figure 4.1 & 4.2). The first group includes Avoca spoil and tailings and the second group includes spoil from Ballyvergin and Glendalough.

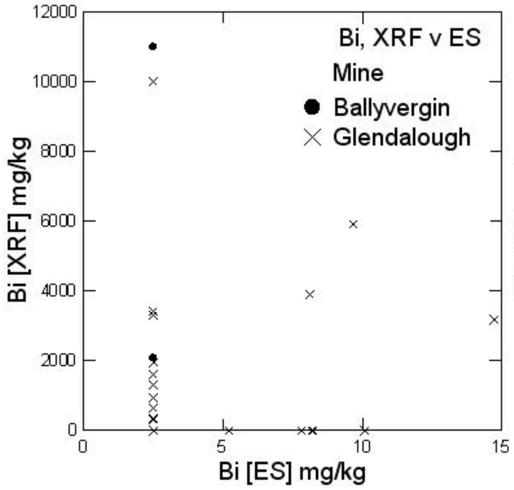


Fig. 4.1 Bi, XRF v ES (all)

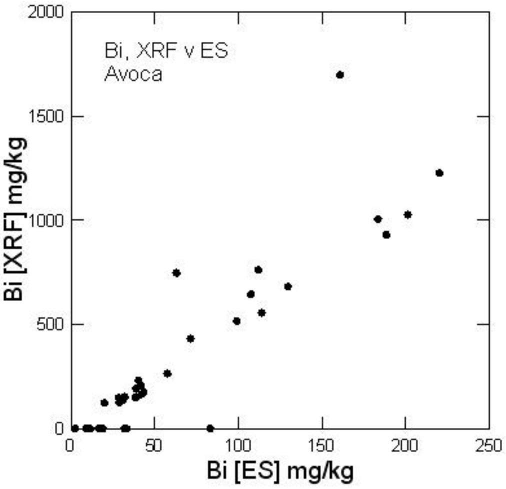


Fig. 4.2 Bi, XRF (high) v ES (low)

The crustal abundance of Bi is < 0.02 mg/kg and consequently it does not occur in significant quantities outside of ore deposits. Some of the values (1000s mg/kg) recorded for Bi by the GSI XRF are greatly in excess of what might be expected for Bi even in Bi-enriched deposits and are suggestive of analytical artefacts. The most obvious source of such artefacts is the overlap between Bi and Pb peaks on the X-ray spectrum. A plot of Bi v Pb shows a broad linear relationship between these elements for GSI analyses but no such relationship for OMAC analyses (Figure 4.3 & 4.4). Nevertheless, some Bi enrichment may be expected in Pb-rich ores because the main Bi species, Bi^{3+}, is isoelectronic with Pb^{2+} and Bi substitutes for Pb, notably in galena.

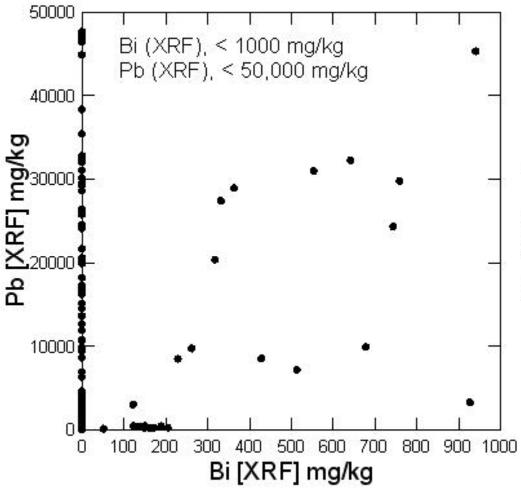


Figure 4.3 Bi v Pb GSI

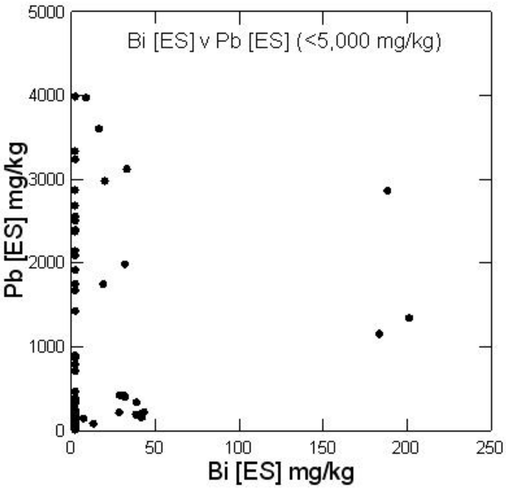


Figure 4.4 Bi v Pb OMAC

Most standards available in GSI do not have recorded Bi values. Exceptions are RCRA (0.88 mg/kg – too low for detection by GSI XRF) and CCRMP TILL-4 (40 mg/kg). The mean Bi value of analyses performed on CCRMP TILL-4 by the GSI XRF was 188 mg/kg, suggesting significant positive bias for Bi XRF analyses. The TILL-4 sample has only 50 mg/kg Pb yet its spectrum suggests that measured Bi concentration may be influenced by overlap from both Pb L_α and Rb K_α peaks. The difference in count data for the Pb L_α and Bi L_α suggests that measured concentration of Bi (= 187 mg/kg in this analysis) should be much less than that of Pb (= 65 mg/kg), yet the reverse is the case. Overlap alone does not seem to explain the very high Bi value returned for the TILL-4 standard and poor calibration is another possibility. One OMAC standard (ICP-4) has 30 mg/kg Bi and results during the ES analysis of GSI samples were,24, 24, 27 and 30 mg/kg.

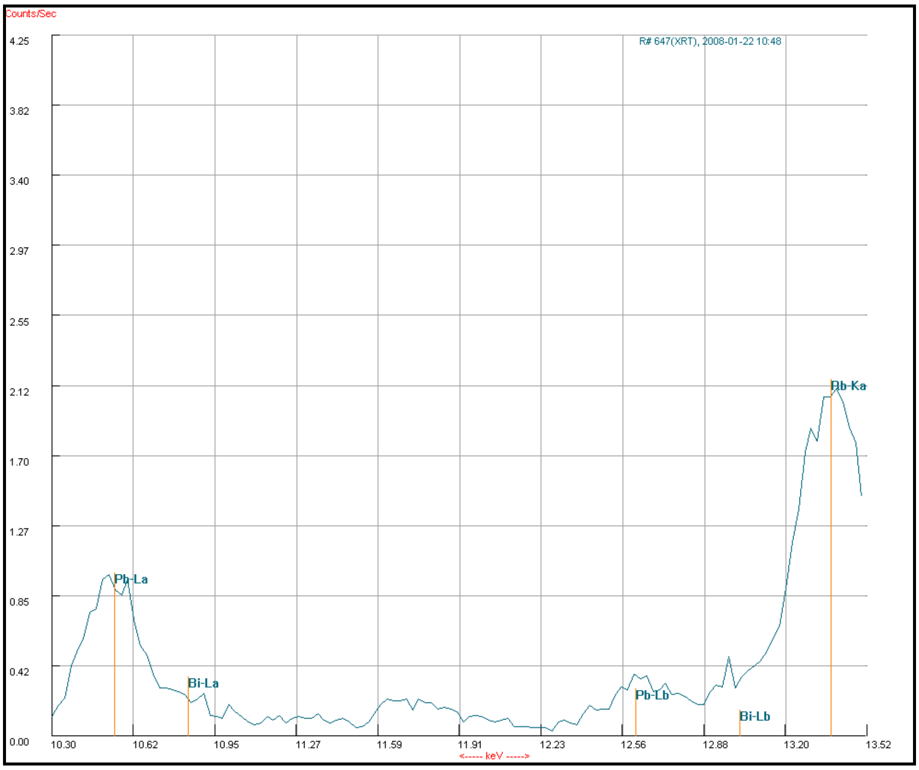


Figure 4.5 Bi spectrum for CCRMP TILL-4 standard

In the case of mine waste samples with high levels of Pb, it appears that overlap between the Pb and Bi peaks has led to false high values for Bi. One of the highest Bi values recorded by the GSI XRF was for a Ballyvergin spoil sample, with measured Bi of 2072 +/- 914 (1σ) mg/kg and over 15% Pb. The OMAC analysis indicated Bi was below the detection limit. In the spectrum extract below the Bi peaks appear to be completely overlapped by the tails of the Pb peaks which have very high counts owing to the high Pb concentration. Additionally, the error on the Bi analysis is very high. For 95% certainty that the element has been detected the measured value should exceed 3σ, so in this case and, indeed all other similar cases of very high Bi XRF values, the analysis cannot be relied upon.

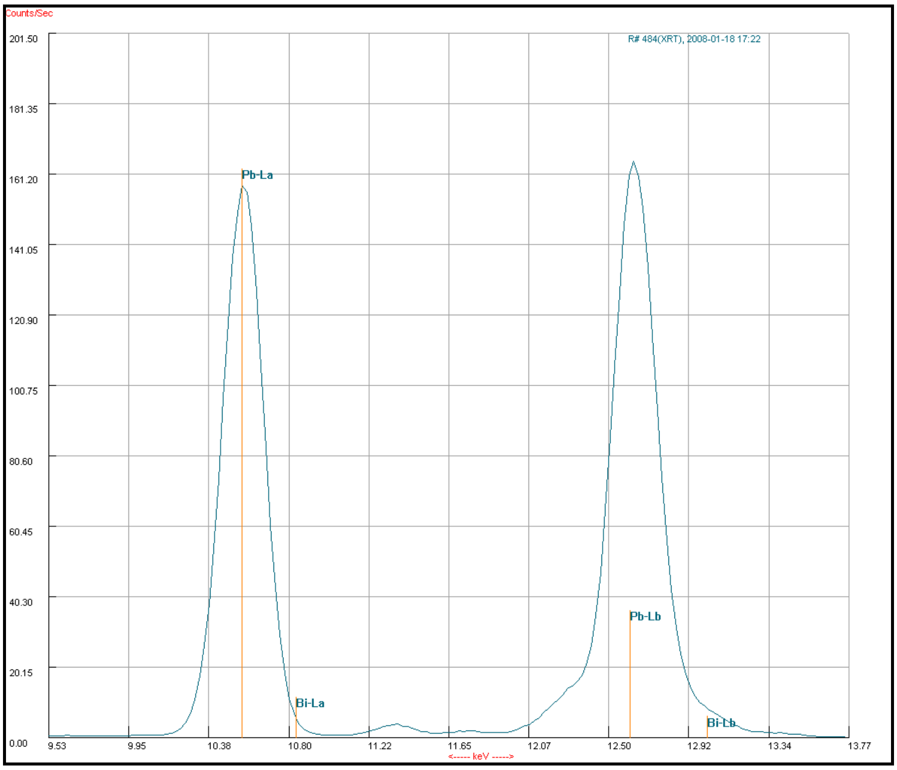


Figure 4.6 Bi spectrum for BVG-07-SP01.9

In summary, Bi XRF analyses are not generally reliable. Where samples have high Pb concentrations, false high Bi values may be recorded. Even where Bi is present in quite significant concentrations up to 200 mg/kg or more, as measured by OMAC ES analysis, the XRF values are generally overstated. Poor or limited XRF calibration as well as high Pb values may be a factor.

5. Ca - calcium

Table 5.1 Ca statistics (mg/kg)

Ca, n=221	**OMAC**	**GSI**
Min	50	<DL
Max	277104	342883
Median	2810	1966

Median values of Ca for ES and XRF data suggest a bias towards higher values among the ES analyses and this is borne out by the scatterplot for values below 100,000 mg/kg (10%) (Figure 5.1). Above 100,000 mg/kg (Figure 5.2), however, most GSI XRF analyses show a strong bias towards higher values compared to the ES data. Ca is one of the lighter elements analysed by XRF and, without a vacuum, detection limits, accuracy and precision are not expected to be as good as for heavier elements. Mean values for GSI XRF analyses of standards are 9837 mg/kg for NIST 2710 (certified value = 12500 mg/kg), 1795 mg/kg for NIST 2780 (1950 mg/kg), 4083 mg/kg for NCS 73308 (2800 mg/kg) and 6987 mg/kg for TILL-4 (8925 mg/kg). The low concentration of Ca in these standards prevents any realistic conclusions being drawn from the standard data other than that reasonable Ca results have been attained at relatively low element concentrations. The upper limit for the OMAC ES calibration is 12.5% and standard analyses showed very good agreement with accepted values (5.75% for SY-4 and 15.5% for ICP-4).

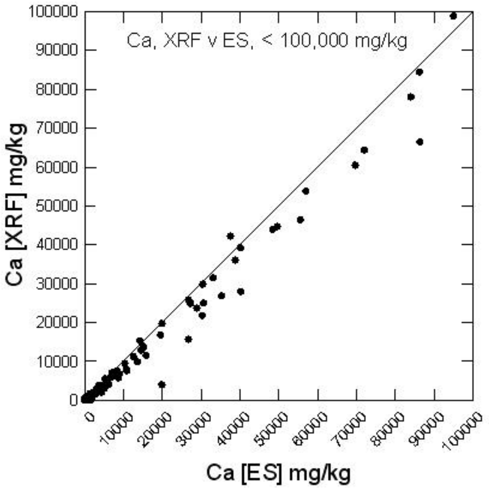


Figure 5.1 Ca, OMAC v GSI [< 10%]

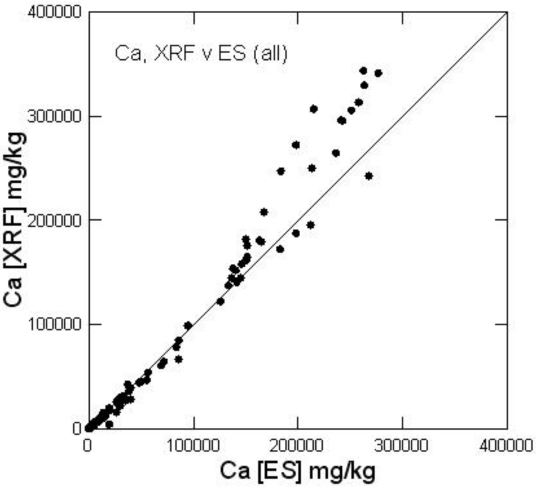


Figure 5.2 Ca, OMAC v GSI [all]

There is no overlap between Ca and any other likely major peak so the variable quality of the analytical performance of the XRF could reflect the calibration, the lightness of the element or matrix effects. The latter may play a significant role, particularly in combination with the lightness of the element, since samples with high concentrations of heavy elements will have a matrix that will impede lower-energy X-rays such as those emitted by lighter elements. This might help explain the general bias to lower values for GSI XRF analyses among samples with < 10% Ca. Those samples with Ca exceeding 10% generally have low concentrations of metals such as Pb and Zn (Figure 5.3 & 5.4).

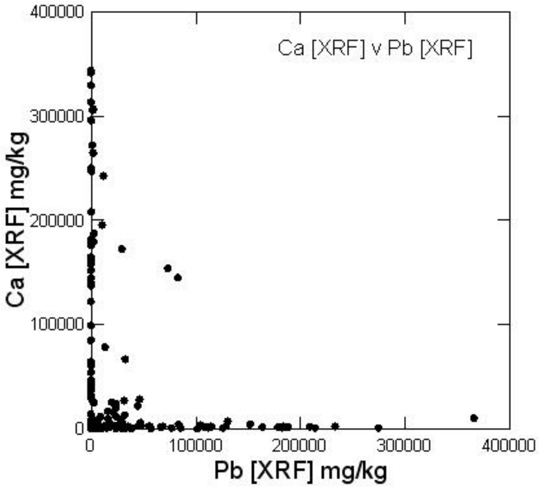


Figure 5.3 Ca v Pb [GSI]

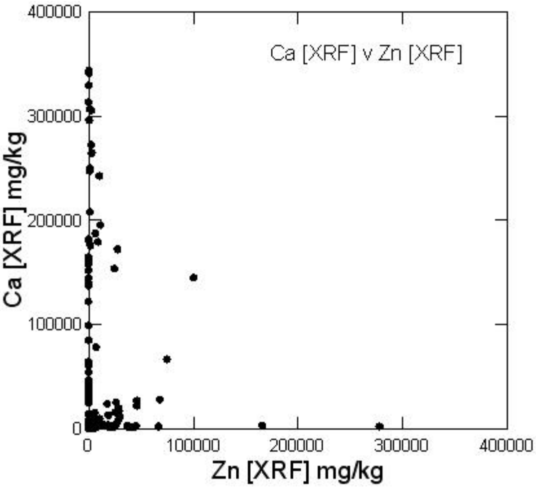


Figure 5.4 Ca v Zn [GSI]

6. Cd - cadmium

Table 6.1 Cd statistics (mg/kg)

Cd, n=221	OMAC	GSI
Min	<1	<DL
Max	648	1215
Median	1.5	<DL

Two thirds of Cd XRF analyses (146 out of 221) were below the limit of detection, giving a median value of 0.0. The minimum measured detected value was 22.5 mg/kg. Most OMAC results (118 out of 221) were ≤ 2mg/kg, close to the limit of detection of 1 mg/kg. For those samples in which the XRF detected Cd (Fig 6.1, 6.2), there is a clear bias towards higher values in the XRF results when compared to the ES results.

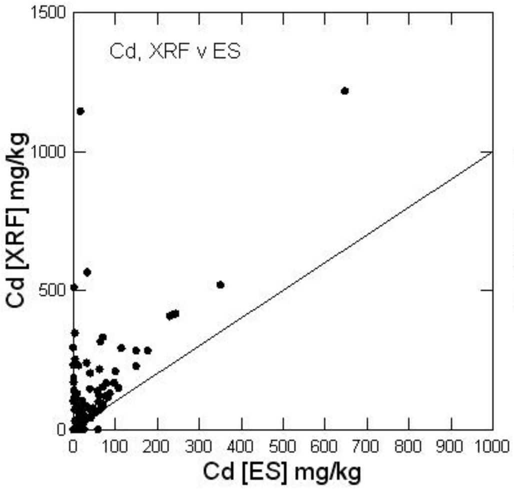


Figure 6.1 Cd, OMAC v GSI

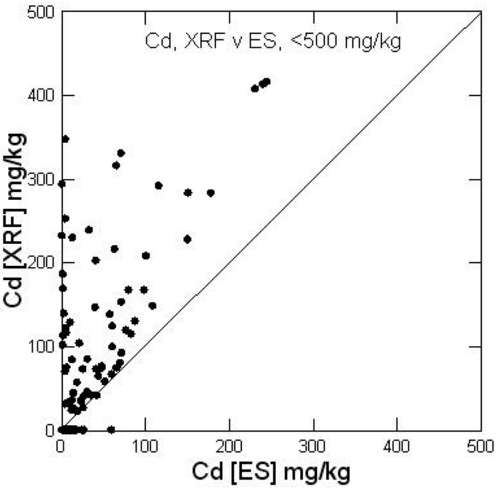


Figure 6.2 Cd, OMAC v GSI < 500ppm

Examples of this bias include spoil from Ballyvergin and Keeldrum, where measured XRF values of 1142 and 294 mg/kg contrast with ES values of 18 and 1 mg/kg, respectively. Comparison of the XRF spectra for the Ballyvergin sample, BVG-07-SP01.9, and the standard RCRA, analysed in the same run, provides striking evidence of this bias toward high values (Fig 6.3). The RCRA standard is a spiked soil with c. 500 mg/kg Cd and 500 mg/kg Ag. Its spectrum shows two strong Kα peaks for Ag and Cd and measured values were 456 and 464 mg/kg, respectively, close to the accepted values. The Ballyvergin sample analysis, with measured Ag and Cd concentrations of 519 and 1142 mg/kg, respectively, shows much smaller peaks for these elements than the standard. Errors on the count data are low and there are no peak overlaps that could explain high measured XRF values for the Ballyvergin sample. Similar spectra can be observed for other samples where measured XRF values greatly exceed those of the ES analyses.

Only the RCRA (500 mg/kg) and NIST HIGH 2710 (21.8 mg/kg) standards have Cd at levels detectable by XRF. Mean Cd value for the RCRA standard (n = 13) was 496 mg/kg (range 466 – 524 mg/kg); for NIST 2710 (n = 77) the mean was 15 mg/kg (range 0.0 – 39 mg/kg). Neither is indicative of major problems with XRF Cd analyses. A possible reason for the bias in analysed samples is that the main Cd X-ray peaks lie at the high-energy end of the X-ray spectrum (Kα = 23.11 keV), where background count data are relatively high. One may speculate that poor correlation of background count data in samples and the standards used to calibrate the XRF contributes to the discrepancies observed.

The preliminary conclusion is that XRF CD analyses are generally unreliable and show bias to higher values compared to those obtained by ES analysis. Deviations from values obtained by ES analysis increase as apparent concentrations increase. Unsatisfactory calibration of the XRF at the high-energy end of the spectrum may contribute to this but the reason for the bias is not know with any certainty.

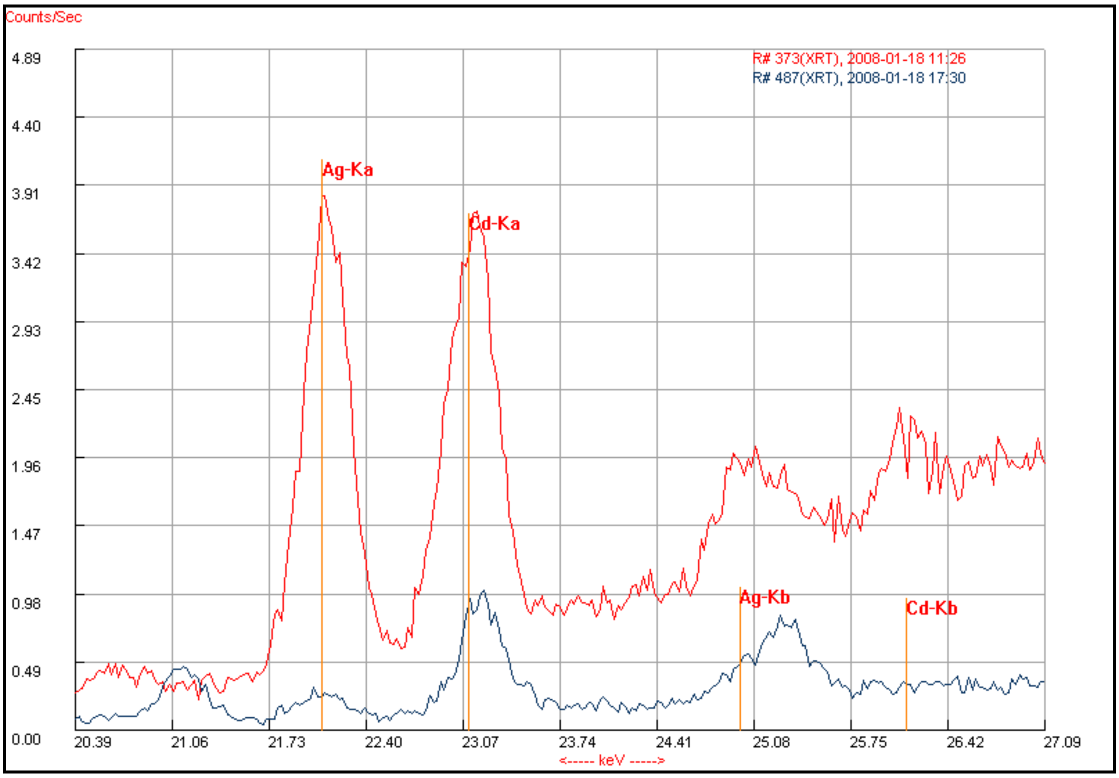


Figure 6.3 RCRA Standard spectrum (red) and Ballyvergin spoil sample spectrum (blue) for Ag and Cd Kα lines

7. Co - cobalt

Table 7.1 Co statistics (mg/kg)

Co, n=221	**OMAC**	**GSI**
Min	<1	<DL
Max	156	2062
Median	10	<DL

Comparison of XRF and ES analyses for Co reveal similar trends as for Cd. Only 40 XRF analyses detected Co and of these 39 had values ≥ 180 mg/kg. Figure 7.1 shows extreme bias toward higher values among XRF analyses compared to ES analyses. This bias is confirmed by standard analyses (Table 7.2).

The Kα and Kβ XRF peaks for Co have energies of 6.93 and 7.65 keV, respectively. The Kβ peak for Fe is very close to the Kα peak for Co and, where Fe is present in high concentrations, its Kβ peak may overlap the Co Kα peak. This overlap appears to provide a reasonable explanation for the behaviour of Co in XRF analyses and can be illustrated by comparison of two samples, AVO-07-SP01.2 and TYN-07-SP01.7, from Avoca and Tynagh, respectively (Figure 7.2).

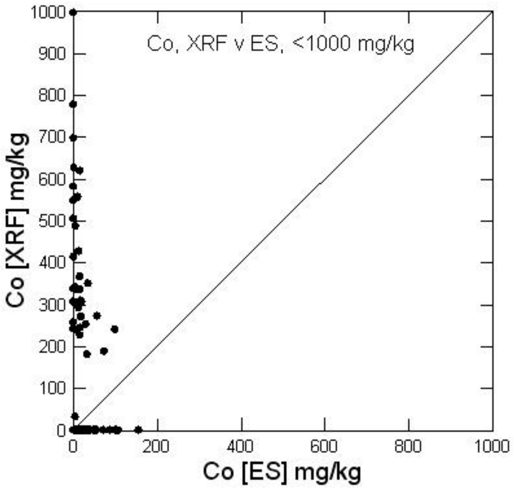


Figure 7.1 Co, OMAC v GSI (<1000 mg/kg)

Table 7.2 Co XRF standard analyses

Standard	n	Range	*x*	Accepted values
NIST 2710	77	0 - 0	0	10
NIST 2780	47	0 - 379	88	2.2
NCS 73308	42	0 - 287	94	15
CCRMP TILL-4	5	0 - 261	198	8

The Avoca sample has measured XRF values of 2061 mg/kg Co and 31.7% Fe. The Tynagh sample has measured XRF values of 0 mg/kg Co and 46.9% Fe. The Tynagh sample has high Cu and Pb and the metal-rich matrix probably accounts for the relatively small size of the Fe peaks when compared to the Avoca sample which has much lower concentrations of other metals. The smaller Fe Kβ peak for the Tynagh sample only partly overlaps the Co Kα peak energy. In contrast, the Avoca sample Kβ peak has a much greater overlap with the Co Kα peak. This could explain why the Avoca sample has a measured XRF Co value of 2061 mg/kg, while Co for the Tynagh sample is below the detection limit, i.e. the large Fe Kβ peak has raised the count rate in the region of the Co Kα peak, giving rise to a false Co measurement.

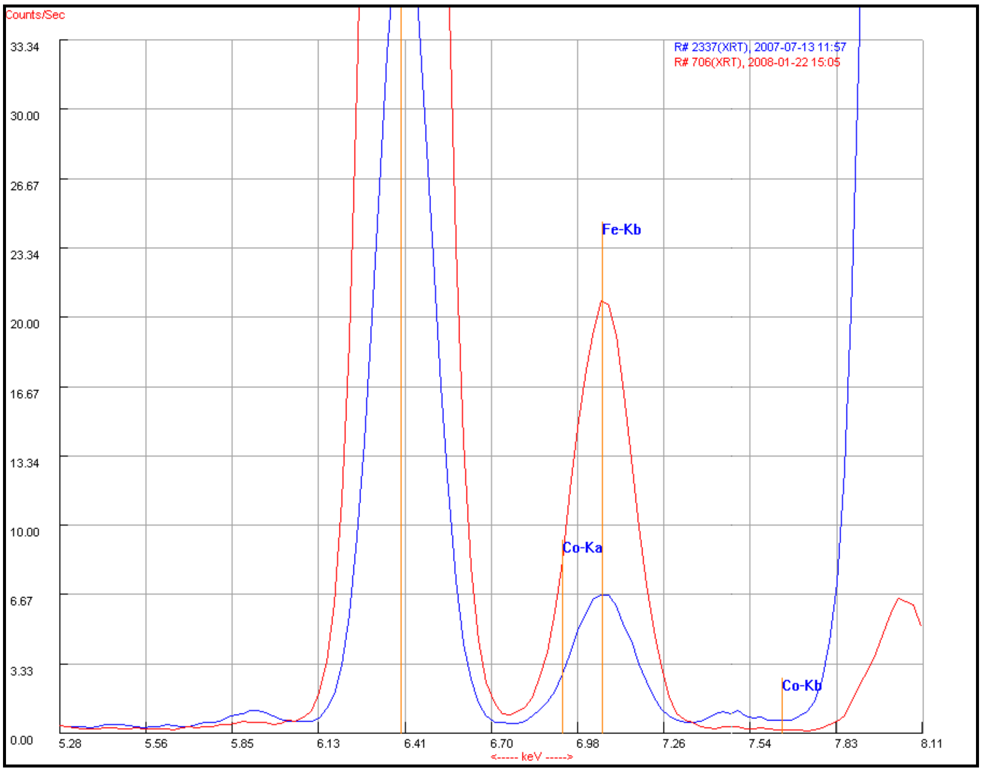


Figure 7.2 Partial spectra for Avoca (red) and Tynagh (blue) samples showing relationship between Co and Fe peaks

8. Cr - chromium

Table 8.1 Cr statistics (mg/kg)

Cr, n=221	**OMAC**	**GSI**
Min	1.0	<DL
Max	157	667
Median	34	0

Analyses of Cr reveal a similar relationship between XRF and ES analyses as observed for Cd and Co: high detection limits and an apparent bias towards higher values for XRF analyses compared to ES analyses (Figure 8.1). Of 221 analyses in the comparison study, Cr was below the detection limit in 139 of the XRF analyses. The lowest recorded measured value for XRF was 26 mg/kg. Table 8.2 summarizes the standard data for the XRF and they suggest a detection limit in excess of 50 mg/kg is more realistic. Analyses of two standards with 136 and 500 mg/kg Cr, respectively, yielded generally good results.

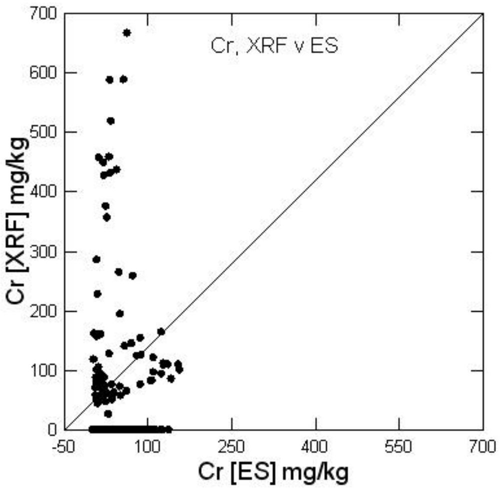


Figure 8.1 Cr, OMAC v GSI

Table 8.2 Cr XRF standard analyses

Standard	**n**	**Range**	***x***	**Accepted values**
NIST 2710	77	0 - 0	0	39
NIST 2780	47	0 - 69	3	44
RCRA	13	432 - 538	461	500
NCS 73308	42	107 - 195	146	136
CCRMP TILL-4	5	0 - 0	0	53

As with other elements that show a bias toward higher values in the XRF analyses, an obvious potential source of spurious high Cr values may be overlap of X-ray peaks. Figure 8.2 shows spectra for the RCRA standard (measured Cr = 454 mg/kg) and a sample of spoil from Letter mine in West Cork (measured Cr = 258 mg/kg). The RCRA standard shows an identifiable Cr Kα peak but there is no clear peak for the Letter mine sample, although apparent background count levels at this point are higher than those in the standard analysis, possibly as a result of interference from the Lα peak of Nd and the Lβ peak of Ce. The Cr Kβ peak location is overlapped by the Mn Kα peak. Whether the latter has any influence on computed XRF values for Cr is unclear. It may be that the relatively high background level of the count data at the Cr Kα peak is sufficient to give rise to measured Cr. The lack of any identifiable peak at this point for the Letter sample suggests that the 258 mg/kg recorded may be spurious. Examination of the spectra for other samples with high Cr in XRF analyses relative to ES analyses indicates a similar situation.

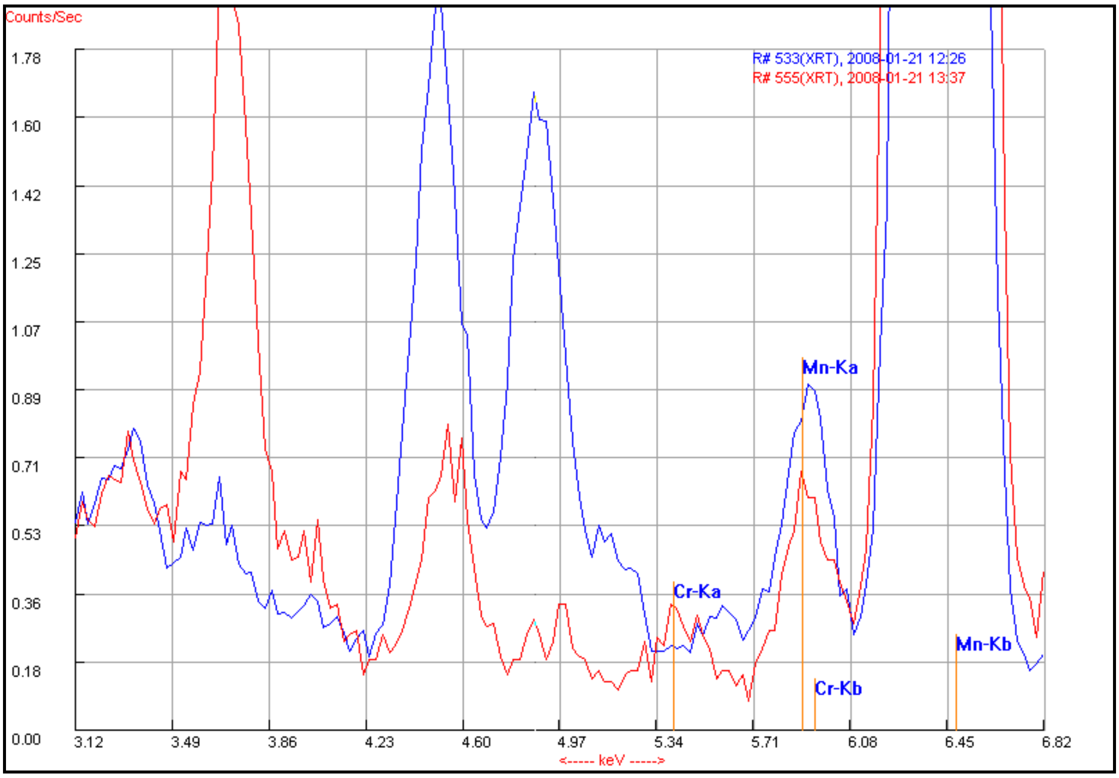


Figure 8.2 Partial spectra for RCRA standard (red) and Letter sample (blue) showing relationship between Cr and Mn peaks

9. Cu - copper

Table 9.1 Cu statistics (mg/kg)

Cu, n=221	**OMAC**	**GSI**
Min	6.1	<DL
Max	73531	102361
Median	453	405

Cu values for XRF and ES analyses show broad agreement across the range of data (Figure 9.1 - 9.3). For values below 10,000 mg/kg the correlation coefficient, r, is 0.85 and for those below 1000 it is 0.95. Below 1000 mg/kg there is a bias towards higher values among ES analyses; between 1000 and 5000 mg/kg, XRF values tend to be higher than ES analyses. These biases reflect different sample compositions: samples from Pb-Zn mines such as Glendalough, Ballycorus, Tynagh, Ballyhickey and Caim tend to give higher Cu results for XRF analyses while samples from Cu mines such as Allihies, Gortdrum and Avoca tend to have higher Cu in ES analyses. In general, however, the biases observed are proportionately much less than those seen for some other elements.

Table 9.2 Cu XRF standard analyses

Standard	n	Range	*x*	Accepted values
NIST 2710	77	2836 - 3100	2993	2950
NIST 2780	47	144 - 206	175	215
NCS 73308	42	0 - 36	23	23
CCRMP TILL-4	5	226 - 242	234	237

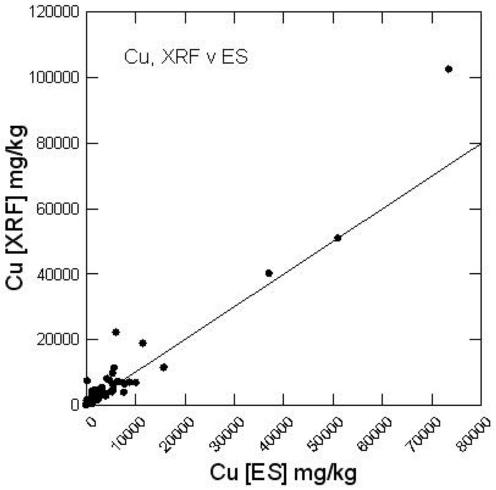


Fig. 9.1 Cr, OMAC v GSI

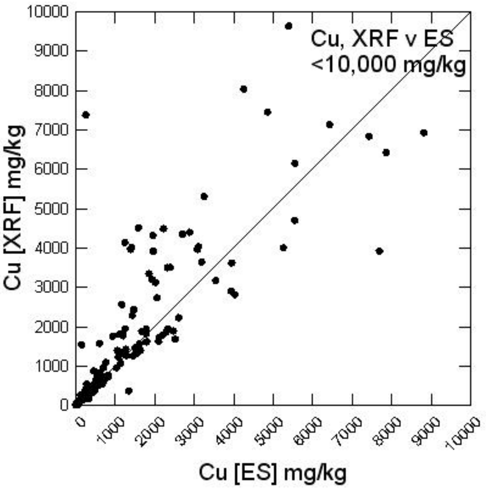


Fig. 9.2 Cr, OMAC v GSI, <10,000 mg/kg

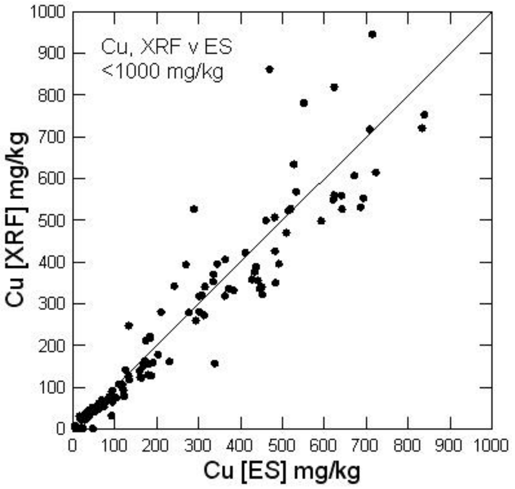


Figure 9.3 Cu, OMAC v GSI, < 1000 mg/kg

Cu was detected in all but 13 samples out of the 221 analysed in the comparison study. The median values for both ES and XRF analyses are in reasonable agreement, as expected from scatterplot distributions. Data for standards (Table 9.2) indicate very good accuracy for XRF data across a range of values. Detection limit for Cu appears to be around 20 mg/kg. An exception to the generally good accuracy obtained for standard analyses is the NIST 2780 mine waste standard. XRF analyses of this standard generally return lower values than expected for a range of metallic elements. This may be interpreted as a reflection of the difference in matrix composition between the mine waste standard and the soil standards used to calibrate the XRF. One might expect similar effects to be observed in the mine waste samples analysed, i.e. a systematic bias towards low values in XRF analyses. If one assumes the ES analyses are accurate, then no such bias is apparent.

10. Fe - iron

Table 10.1 Fe statistics (mg/kg)

Fe, n=221	**OMAC**	**GSI**
Min	1477	2335
Max	490,947	1,851,542
Median	35885	32169

XRF analyses of Fe show a significant bias towards higher values when compared to ES analyses, especially at high concentrations (> 10,000 mg/kg) (Fig 10.1). Below 10,000 mg/kg there is much better agreement between OMAC ES and GSI XRF analyses, with a bias in many cases toward higher values among ES analyses. As with other elements, the XRF is calibrated to 2% (20,000 mg/kg) Fe for a soil matrix, whereas the ES analyses are calibrated to 12.5%.

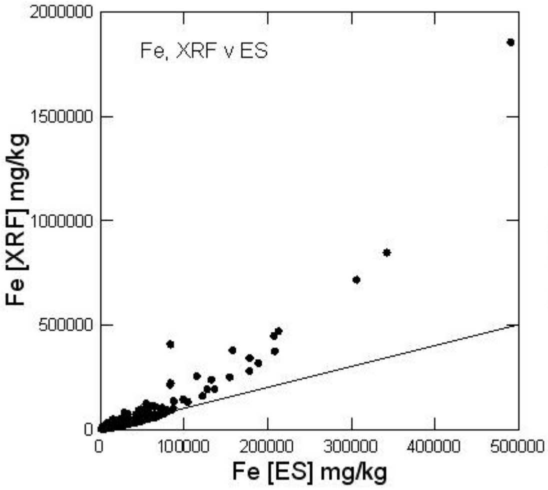


Figure 10.1 Fe, OMAC v GSI

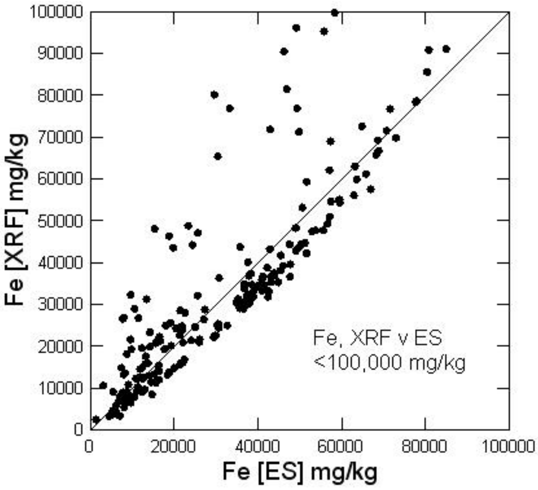


Figure 10.2 Fe, OMAC v GSI, <100,000 mg/kg

Table 10.2 Fe XRF standard analyses

Standard	n	Range	*x*	Accepted values
NIST 2710	77	32694 - 35644	34136	33800
NIST 2780	47	22374 - 23924	23130	27840
NCS 73308	39	18846 - 20304	19660	27000
CCRMP TILL-4	5	32614 - 33813	33008	39700

The two standards (Fe = 5.3% and 4.3%) analysed by ES during sample runs gave acceptable results. Standards (2.7 – 3.97 % Fe) analysed by XRF gave less satisfactory results (Table 10.2), with most returning significantly *lower* values than expected. This is consistent with observed results for most samples in the comparison study below 40,000 mg/kg (4%) Fe (OMAC): at this level, most samples gave higher values in ES analyses compared to XRF analyses (Fig. 10.2, 10.3). Exceptions are samples from, mainly, Glendalough which are significantly biased toward higher Fe values in this range. At higher Fe concentrations, samples from other mines such as Avoca, Caim, Ballyvergin and Tynagh also show bias toward higher XRF values compared to ES analyses (Fig 10.4).

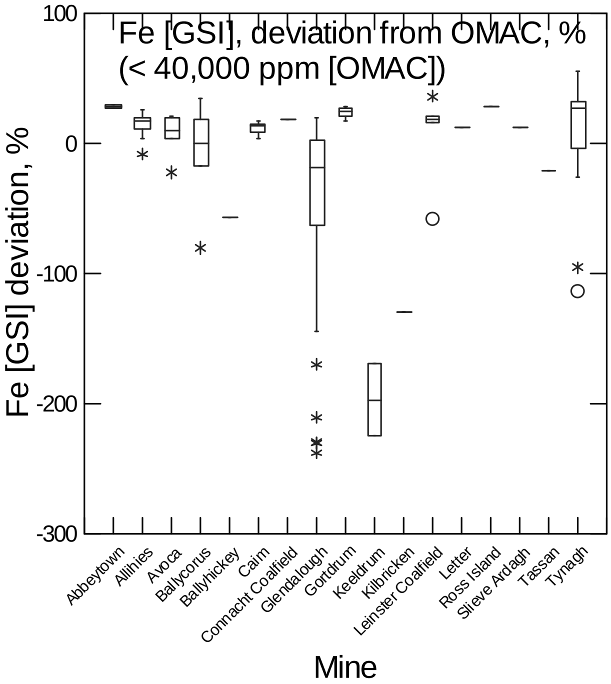


Figure 10.3 Fe deviation, %, < 40,000 mg/kg

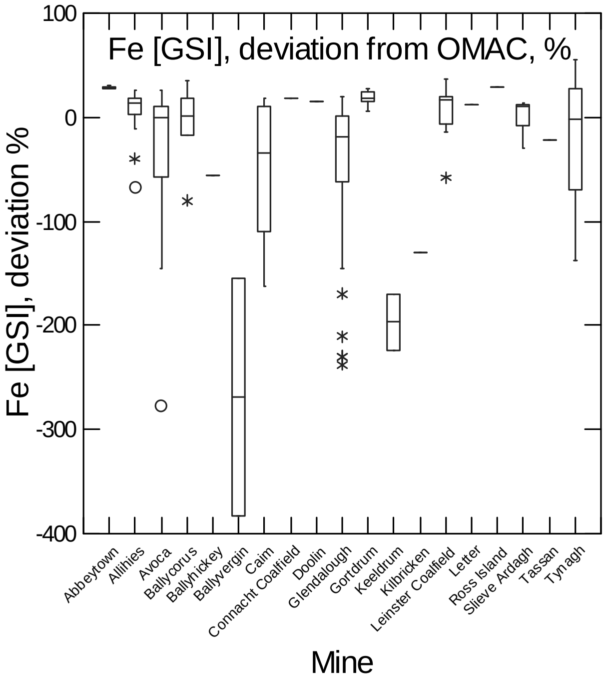


Figure 10.4 Fe deviation %, all

Because Fe is typically present in samples in relatively high (%) concentrations, the main Kα XRF peak (6.40 keV) is generally very well defined and not overlapped by any other peak. Consequently inaccuracies in analysis are likely to reflect uncertainties in either the XRF calibration or correction programme. The XRF is calibrated for soils with metal concentrations below 2% and the complex, metal-rich matrices presented by mine waste will inevitably affect the accuracy of analyses. Fig 10.3 and 10.4 show that the deviations of XRF analyses from those of OMAC ES analyses vary in a coherent way according to mine site, i.e. waste from the same mine site, with a broadly similar composition, tends to produce analyses with similar inaccuracies.

In conclusion, XRF analyses show a bias toward higher Fe compared to ES analyses at high Fe concentrations. At lower concentrations, i.e. below approximately 5%, most XRF Fe analyses are quite close to or even lower than those of ES. Exceptions are samples from specific mines that have much higher XRF values. The correlation of high values with specific mine sites suggests that the deviations observed can best be explained by uncertainties in calibration and correction factors arising from the particular composition of waste on those sites.

11. Hg - mercury

Table 11.1 Hg statistics (mg/kg)

Hg, n=221	OMAC	GSI
Min	0.5	0
Max	3.8	391
Median	0.5	0

Hg was detected by XRF in only 23 samples and by ES in 7. Only in 4 samples, all from Gortdrum, was Hg detected by both methods. In these samples the XRF returned values between 10 and 20 whereas the ES analyses yielded values between 1 and 4. These ES analysis involved multi-acid digestion and this is detrimental to Hg analysis as it causes volatilization and loss of the metal at the preparation stage. The effect of this can be seen in Fig 11.1, where results for samples from Tynagh, Gortdrum and Silvermines, prepared using both multi-acid digestion (MA-ES) and aqua regia (AR-ES), are compared. It is clear that the multi-acid digestion technique causes severe loss of Hg from samples prior to analysis. Comparison of the aqua regia-based analyses with XRF analyses of the same samples show reasonable agreement for most samples across the range of values (Fig 11.2), though there are clearly large deviations in two cases where Hg was measured at very low concentrations in the AR-ES analysis. As all Hg analyses in this comparison study were done by MA-ES it is therefore not possible to make valid comparisons between the GSI XRF and OMAC ES analyses.

Hg occurs in very low concentrations in most soils and for the most part even in mine waste. Only one XRF standard, NIST 2710, contains Hg at a level (33 mg/kg) measurable by XRF. The XRF detected Hg in 32 out of 77 analyses of NIST 2710. For the analyses where it detected Hg, the range was 23 to 44 mg/kg (mean 28.9). The analytical errors are large and 33 mg/kg is clearly very close to the limit of detection for the XRF in this standard. Nonetheless, when the XRF detected Hg the measured value was close to the certified value.

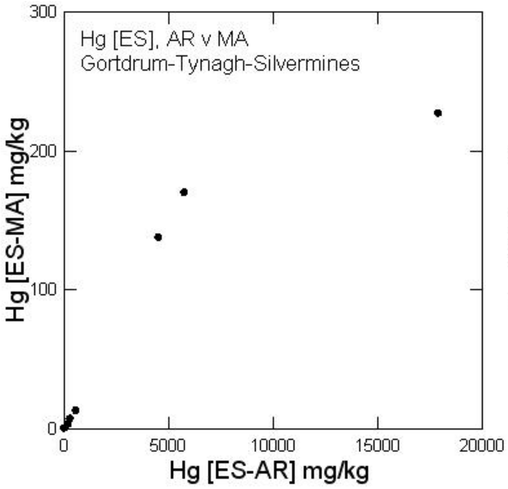


Figure 11.1 Hg, OMAC (AR v MA)

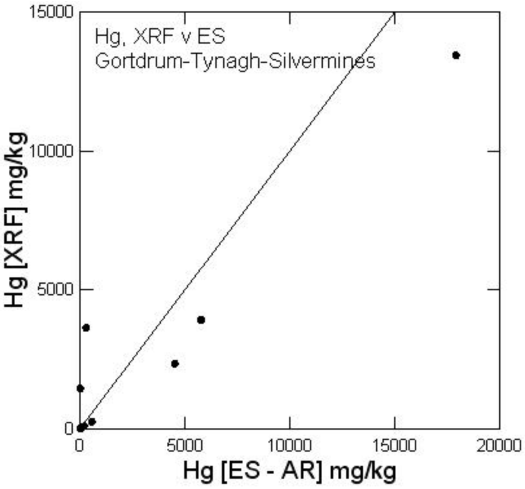


Figure 11.2 Hg, OMAC v GSI

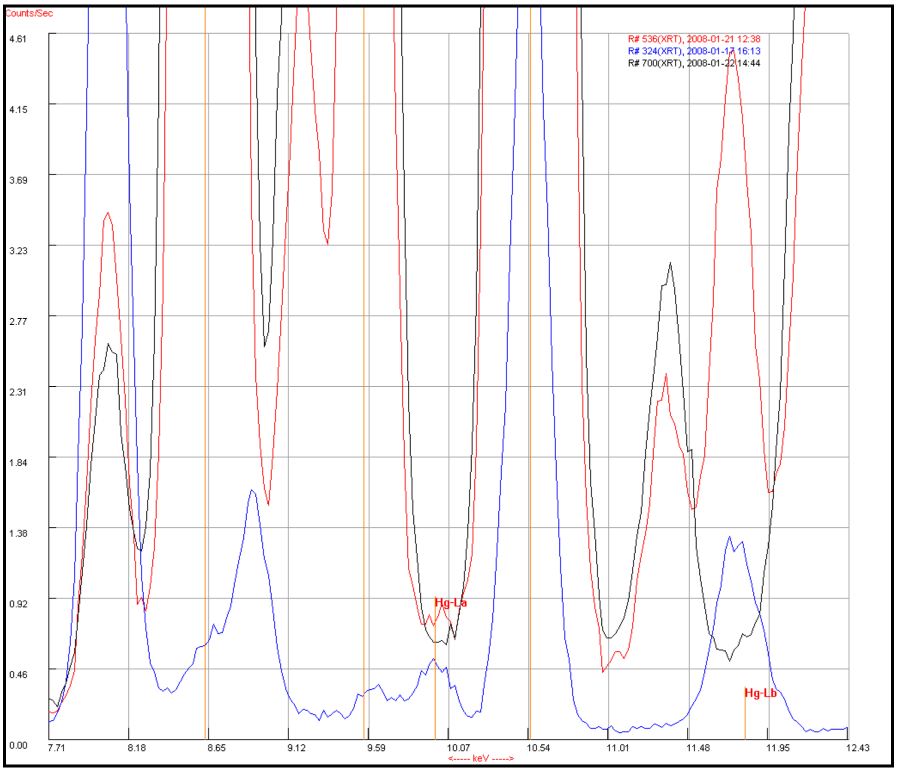


Figure 11.3 Partial spectra for samples from Gortdrum (blue), Kilbricken (red) and Glendalough (black). The peaks to either side of Hg Lα are Zn Kβ (left) and Pb Kα.

Peak overlap must be considered in assessing XRF results for Hg. The Hg Lα peak has energy 9.99 keV and is located between the Kβ peak of Zn and the Kα peak of Pb. In Zn-Pb mines these two peaks can be very strong, raising the background count levels in the vicinity of the Hg peak and potentially giving rise to spurious Hg results. Fig 11.3 show partial spectra for three samples with apparently detected Hg, from Gortdrum (72 mg/kg), Kilbricken (348 mg/kg) and Glendalough (390 mg/kg). The Gortdrum sample has a well-defined peak for Hg but the Glendalough sample does not. The Kilbricken sample, despite having Zn and Pb peaks to either side similar in size to the Glendalough sample, also has a well-defined Hg peak. It is possible therefore that the Glendalough Hg analysis gives a spurious result. The peak close to the Hg Lβ line is that of As Kβ.

Peak analysis of all 23 samples in which Hg was apparently detected by XRF suggests that in most cases a peak is present. Where high concentrations of Pb and Zn are recorded, as in Tynagh and Kilbricken samples, and some Glendalough samples, no peak can be distinguished and the measured Hg value is more likely spurious. In the case of samples of aggregate from Gortdrum with measured XRF values of 14 to 19 mg/kg Hg, a peak is observed (Fig. 11.4) and the ability of the XRF to detect Hg at such low apparent concentrations reflects the lack of any significant Zn and Pb in these samples.

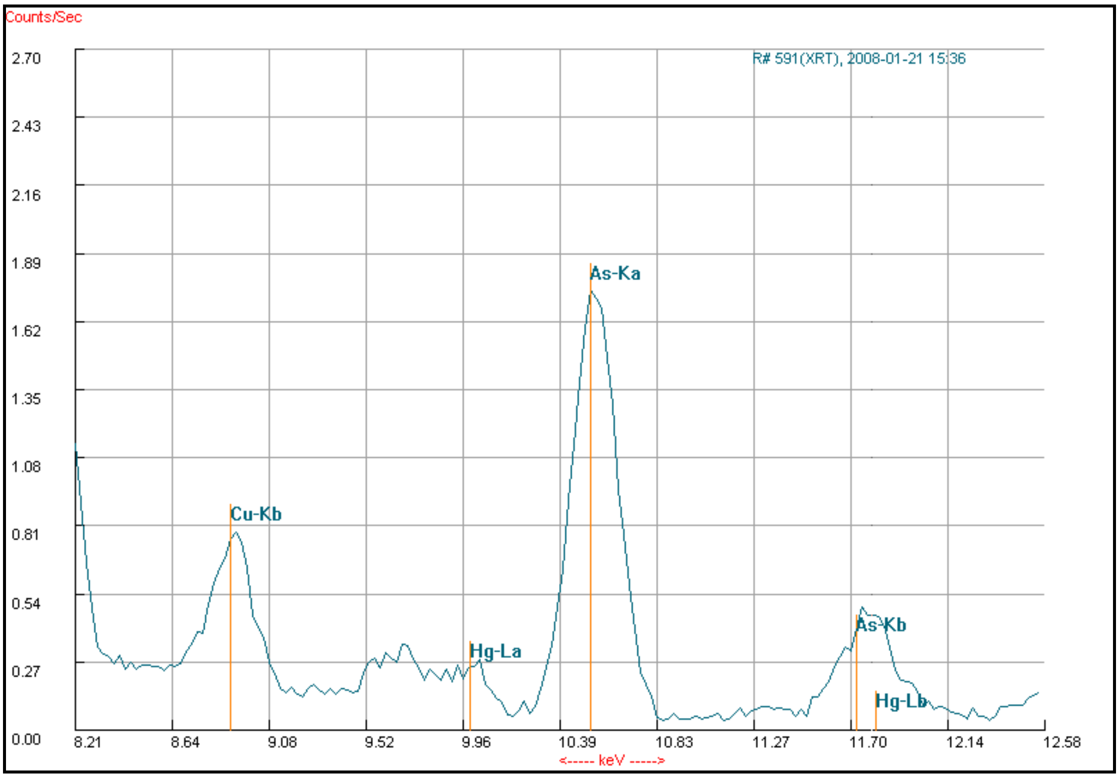


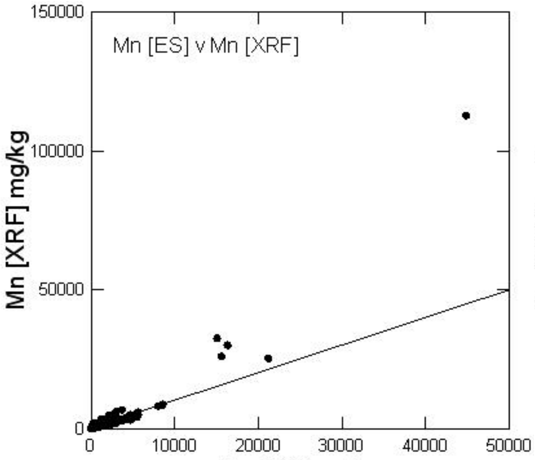
Figure 11.4 Partial spectra for aggregate sample from Gortdrum (measured Hg = 18 mg/kg) showing Hg peaks and adjacent As and Cu peaks.

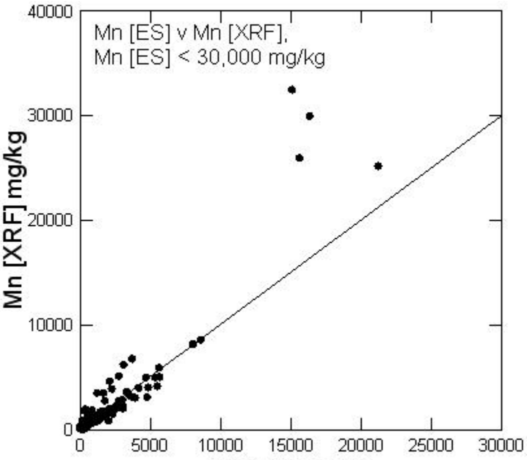
12. Mn - manganese

Table 12.1 Mn statistics (mg/kg)

Mn, n=221	**OMAC**	**GSI**
Min	<5	<DL
Max	44927	112526
Median	825	803

The median concentrations of Mn, measured by XRF and ES in the 221 samples analysed for the comparative study, are very similar (Table 12.1) and suggest good overall agreement between both techniques. For the five samples for which the measured concentration exceeds 10,000 mg/kg or 1%, there is considerable divergence, with measured XRF concentrations significantly higher than corresponding ES concentrations (Fig. 12.1). However, for the 216 samples with measured concentration below 10,000 mg/kg, the correlation coefficient (r) for the two techniques is 0.91 (Fig. 12.1). However, this strong correlation is accompanied by considerable scatter about the 1:1 line. This is particularly apparent above 3000 mg/kg Mn but is also present at lower concentrations (Fig. 12.1). Below 3000 mg/kg, measured ES concentrations tend to exceed measured XRF concentrations. For the 197 samples for which the Mn concentration measured by ES was <3000 mg/kg, the measured ES concentration exceeded the measured XRF concentration in 145 samples. For these 145 samples, the median deviation between the measured XRF and ES concentration was 182 mg/kg (range: 3 – 1257 mg/kg). For the 52 samples for which the measured XRF concentration exceeded that measured by ES, the median deviation was 253 mg/kg (range: 9 – 2443 mg/kg). Thus, although there is a generally strong correlation between Mn concentrations measured by ES and XRF, there are in many cases quite large deviations between results obtained by the two techniques for the same sample.





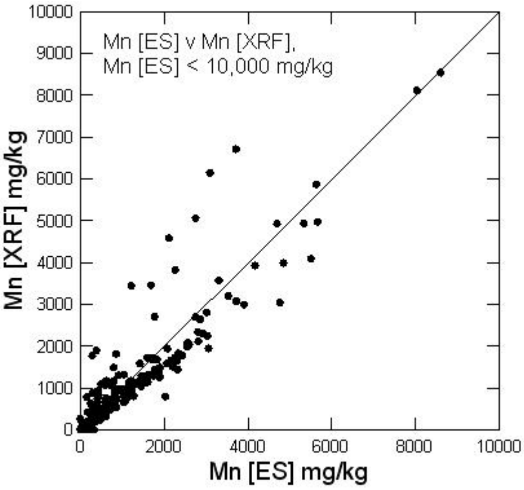


Fig. 12.1 Mn (XRF) v Mn (ES) for various concentration ranges

Certified Mn concentrations, ranging from 323 to 8530 mg/kg, are reported for four standards analysed during the course of the project (Table 12.1). XRF analyses of these standards demonstrate a general bias towards concentrations lower than those certified, with the exception of NIST 2710 for which the certified Mn concentration is relatively high (Table 12.2). These results are consistent with the deviations observed between XRF and ES analyses and confirm that the XRF analyser tends to underestimate the concentration of Mn, particularly for those samples in which the Mn concentration is blow 3000 mg/kg.

Table 12.2 Mn XRF standard analyses

Standard	n	Range	*x*	Accepted values
NIST 2710	77	9762 - 10633	10199	8530
NIST 2780	47	279 - 446	358	462
NCS 73308	39	647 - 768	706	1010
CCRMP TILL-4	5	283 - 367	323	490

13. Ni - nickel

Table 13.1 Ni statistics (mg/kg)

Ni, n=221	OMAC	GSI
Min	<1	<DL
Max	187	399
Median	17	<DL

Nickel was detected in only 29 of the 221 samples analysed by XRF for the comparative study. Comparison of XRF and ES data suggest that the XRF detection limit for these laboratory-prepared samples was typically around 40 to 60 mg/kg. Detection limits for *in-situ* analyses are likely to be significantly higher.

For those samples in which Ni was detected by XRF, there is a rough correlation (correlation coefficient r = 0.51) between concentrations measured by XRF and ES (Fig. 13.1). In 20 out of 29 analyses, the measured XRF concentration exceeds the measured ES concentration.

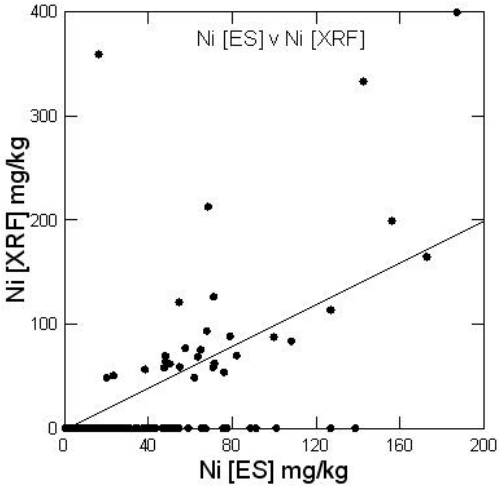


Fig. 13.1 Ni (XRF) v Ni (ES), all samples

A certified Ni concentration is reported for four of the five standards analysed over the course of the project, NIST 2710 (14 mg/kg), NIST 2780 (12 mg/kg), NCS 73308 (30 mg/kg) and CCRMP TILL-4 (17 mg/kg). Ni was detected in only two out of 39 analyses of NCS 73308 (51 and 59 mg/kg) and not at all in the other three standards. These results are generally consistent with the conclusions drawn from the comparative study regarding detection limits for Ni, clearly indication that these limits are typically above 30 mg/kg.

In summary, XRF detection limits for Ni are typically around 40 – 60 mg/kg. There is a broad correlation between Ni concentrations measured by XRF and ES with a tendency for measured XRF concentrations to exceed those of ES.

14. Pb - lead

Table 14.1 Pb statistics (mg/kg)

Pb, n=221	**OMAC**	**GSI**	**Pb, n=162**	**OMAC**	**GSI**
Min	1.5	10	**Min**	2	10
Max	20000	773192	**Max**	19482	32774
Median	1745	1661	**Median**	171	169

The concentration of Pb in the 221 prepared samples measured in the laboratory by portable XRF ranged from 10 to 773,192 mg/kg (Table 14.1). The upper calibration limit for ES analyses was 20,000 mg/kg Pb and 59 of the samples analysed by ES had measured Pb concentrations in excess of this limit. Nevertheless, the similar median concentrations for each method (1661 and 1745 mg/kg, Table 14.1) indicate good agreement between the techniques. For the 162 samples with measured ES concentration below 20,000 mg/kg, the ES and XRF results are strongly correlated (r = 0.94) (Fig. 14.1), with the exception of a few samples for which the XRF results were much higher. For the 144 samples for which the measured ES concentration was below 10,000 mg/kg (1%), the correlation between XRF and ES data is almost identical (r = 0.92) (Fig. 14.1). The upper calibration limit for the XRF is 20,000 mg/kg (2 %) and these data suggest that, for the most part, XRF Pb analyses are generally quite accurate up to this limit.

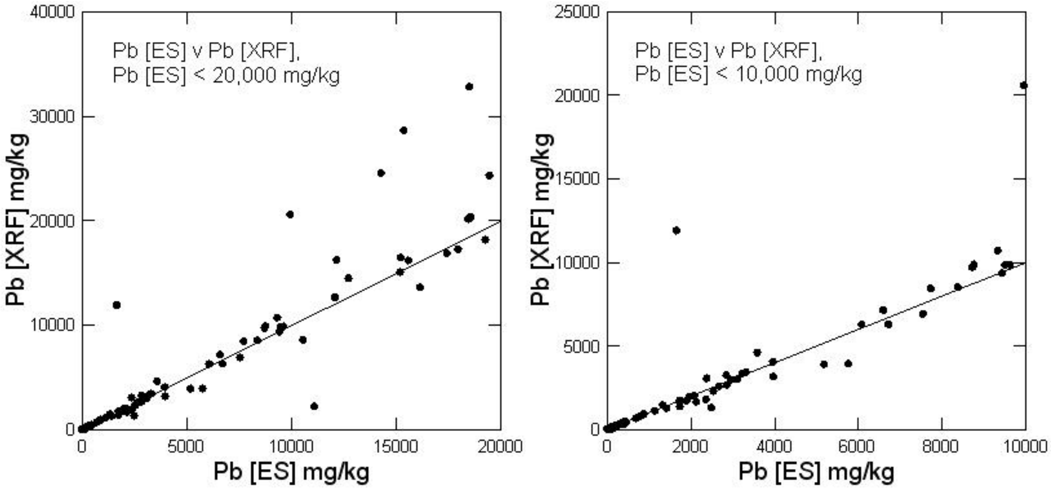


Fig. 14.1 Pb (XRF) v Pb (ES), various concentration ranges

The upper calibration limit for both the ES and XRF analyses is 20,000 mg/kg Pb (2%). Measured XRF concentrations exceeding this limit must be considered semi-quantitative. An attempt was made to assess the accuracy of XRF analyses of samples with very high measured metal concentrations by carrying out assays of the samples at OMAC laboratories. The assay analysis included As, Cd, Cu, Fe, Pb and Zn. Comparison of results of Pb analyses for the 13 samples analysed by assay with those previously obtained by ES analysis at OMAC (Table 14.2) indicates good agreement for the most part between the two methods for concentrations below 20,000 mg/kg. Table 14.2 also compares the summary data for the assay and GSI analyses carried out in the laboratory and the field. In general, GSI XRF results for laboratory-analysed samples are somewhat higher than those obtained by assay, indicating a bias toward high measured values in samples with high concentrations (> 20,000 mg/kg) of Pb (Fig. 14.2). For samples analysed by XRF in the field, measured Pb concentrations tend to be lower than the corresponding assay value. Examples of high XRF results for Pb include (OMAC assay results in brackets) 9343 mg/kg (9149 mg/kg), 2.43 % (1.97%), 4.64% (3.54%), 10.19% (6.74%), 15.24% (9.77%) and 23.36% (15.79%).

Table 14.2 Pb assays

Pb, n=13	OMAC (ES)	OMAC (assay)	GSI XRF (lab)	GSI XRF (field)
Minimum	7744	7599	8427	4796
Maximum	>20000	309890	773192	142067
Median	>20000	67439	83294	39912
Mean	17604	78130	138960	53760

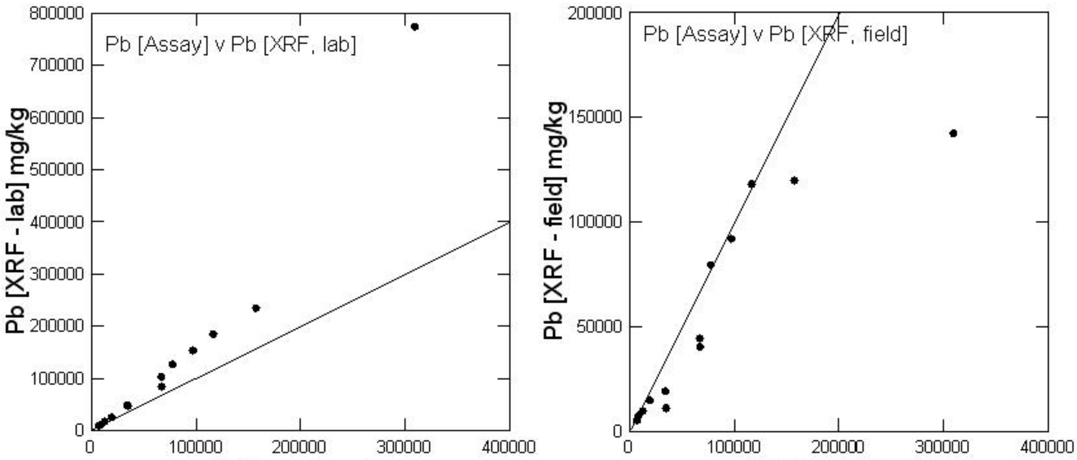


Fig. 14.2 Pb: assays v XRF analyses

Lead is reported for five standards analysed in GSI, NIST 2710 (5532 mg/kg), NIST 2780 (5770 mg/kg), RCRA (500 mg/kg), NCS 73308 (27 mg/kg) and CCRMP Till-4 (50 mg/kg). Mean values for XRF analyses of these standards were, respectively, 5609 mg/kg, 5078 mg/kg, 518 mg/kg, 29 mg/kg and 52 mg/kg. The results for the ICP-4 standard run by OMAC in December 2008 were 6327mg/kg and 6378mg/kg against an accepted value of 6350mg/kg. The SY-4 standard (accepted concentration: 93 mg/kg) gave results of 119 mg/kg and 107 mg/kg. The standard data suggest that the GSI XRF analyses give acceptable results at relatively high concentrations such as those in NIST

2710, a soil standard. The low mean recorded for NIST 2780, a mine waste standard, is typical of metal concentrations measured in this standard by XRF (compare data for other elements such as Zn and Cu). The metal-rich matrix present in this sample is quite different to that of the matrix in the soil samples used to calibrate the instrument and this difference is considered the likely reason for the consistently low metal concentrations measured by XRF in this sample, compared to the published accepted concentrations. In the case of the other three standards, the results are very good, suggesting accuracy in the XRF analyses at both low and high concentrations. Thus, data for GSI standard analyses do not suggest significant problems with XRF analyses for Pb at relatively high or low concentrations. There are no peak overlaps in the XRF spectrum that could, in a typical sample, give rise to falsely high Pb results. The exception is the peak overlap with As but this would represent a potential problem only in the unusual instance of a sample with high As concentration and low Pb concentration..

15. Sb – Antimony

Table 15.1 Sb Statistics

Sb, n=221	**OMAC**	**GSI**
Min	<5	<DL
Max	3504	5075
Median	20	<DL

Antimony was not detected in most GSI XRF analyses, giving a median concentration below the detection limit (Table 15.1). There is a broad correlation between XRF and OMAC ES analyses, with high concentrations measured by ES generally corresponding to high concentrations measured by XRF (Fig. 15.1). However, Sb concentrations measured by XRF tend to be significantly higher than those measured by ES analysis. Samples with low concentrations as measured by ES can have relatively high measured XRF concentrations. Peak overlap is not a factor in Sb XRF analyses. However, the Kα peak for Sb lies at the high-energy end of the X-Ray spectrum (26.36 keV) where background count data are relatively high. This may contribute to spuriously high measured concentrations if there is a significant difference between count data for the sample background and that for the standards used to calibrate the XRF. The Kα peak for Cd (23.11 keV) is also at the high-energy end of the spectrum and Cd concentrations measured by XRF are also biased toward high values relative to ES analyses.

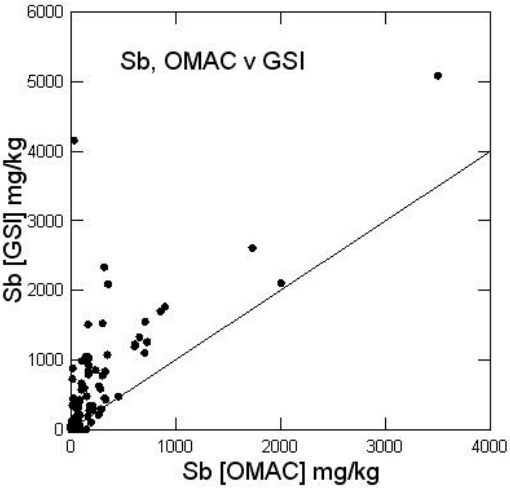


Figure 15.1 Sb OMAC v GSI

Analyses of standards by XRF also show a bias toward higher-than-certified concentrations. Antimony was consistently detected in two standards, NIST 2710 (certified concentration, 38 mg/kg) and NIST MW 2780 (160 mg/kg). The mean concentrations determined by XRF were 84 mg/kg and 216 mg/kg, respectively. Thus, analyses of standards confirm a bias toward high concentrations for analysis of Sb by the GSI XRF

16. Se – Selenium

Table 16.1 Se Statistics

Se, n=221	OMAC	GSI
Min	<10	<DL
Max	27	71
Median	<10	<DL

Selenium was detected in very few samples, whether analysed by ES (detected in six samples) or XRF (13 samples), and in consequence the median concentration of Se for both techniques was below the limit of detection (Table 16.1). The detection limit for Se by ES analysis was 10 mg/kg. In five cases where Se was detected by ES analysis, it was also detected by XRF analysis. There was good agreement between the results for four of these samples (Table 16.2), clearly indicating that the XRF is capable of detecting Se at relatively low concentrations, at least in laboratory-prepared samples. This largely reflects the position of the Kα peak (11.21 keV) which is not overlapped by the peak of any other element commonly detected in mine waste samples. For seven of the eight samples in which Se was detected by XRF but not by ES, the measured XRF Se concentration was below 10 mg/kg. In all these cases the error on the count data was high, indicating considerable uncertainty as to whether the element was detected or not.

Table 16.2 Measured Se concentrations in six samples: ES v XRF

Se mg/kg						
OMAC ES	27	24	23	15	11	9
GSI XRF	31	23	29	71	10	<DL

Selenium is reported only for one standard analysed by XRF in the GSI laboratory, RCRA, a spiked soil sample with a reported Se concentration of 500 mg/kg. The mean Se concentration for 13 XRF analyses was 422 mg/kg, a reasonable result that nevertheless suggests that the XRF is not particularly well calibrated for high Se concentrations. One of the two in-house standards run by OMAC, ICP-4, had a reported Se concentration of 15 mg/kg and four analyses gave concentrations of 13, 14, 16 and 18 mg/kg. This suggests that the ES analyses are accurate. The good agreement between XRF and ES analyses for the five samples in Table 16.2 suggests that the XRF is capable of measuring Se accurately at relatively low concentrations (down to 10 mg/kg).

17. Th – Thorium

Table 17.1 Th Statistics

Th, n=221	OMAC	GSI
Min	>5	<DL
Max	59	68
Median	6	<DL

Thorium was detected by the GSI XRF in only 20 out of the 221 samples analysed and its median concentration is, consequently, below the limit of detection (Table 17.1). The detection limit for the OMAC ES analyses was 5 mg/kg and the median for the 221 analyses was 6.4 mg/kg, with 168 analyses returning a value of 10 mg/kg or less. The concentration of Th in most of the samples analysed was, therefore, only slightly in excess of the 5 mg/kg detection limit. The generally low concentration of Th in most mine waste samples, as evidenced by the ES results, accounts for the low number of XRF detections. In the 20 samples in which Th was detected by the XRF, it was measured at concentrations that were typically around twice those of the corresponding OMAC ES analyses (Fig. 17.1; Table 17.2). Thus concentrations of Th measured by XRF appear to be exaggerated relative to ES analyses. One reason for this may be partial overlap of the main Lα Th peak (12.97 keV) by the Lβ peak of Pb (12.61 keV) (Fig. 17.2).

Table 17.2 Samples in which Th detected by XRF

Th (n = 20)	OMAC ES	GSI XRF
Min	5	18
Max	25	68
Median	12	27

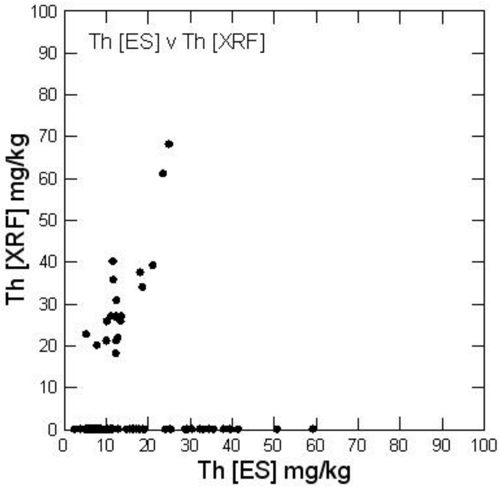


Figure 17.1 Th, OMAC v GSI

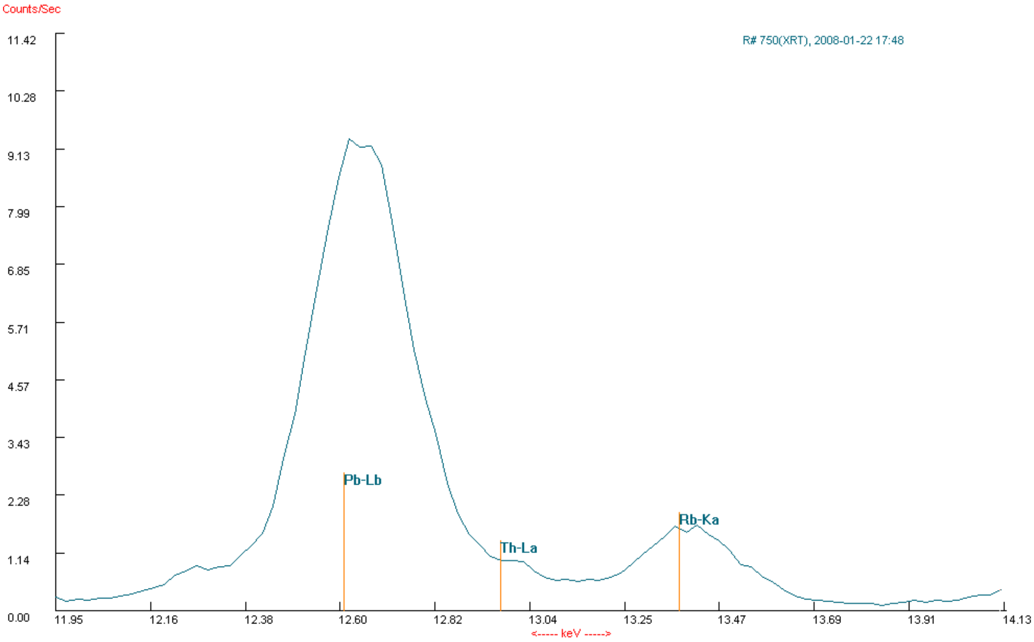


Fig. 17.2 Th Lα peak showing partial overlap by Pb Lβ peak

Of the five standards analysed by the GSI XRF, four have certified Th concentrations: NIST 2710 (13 mg/kg), NIST 2780 (12 mg/kg), NCS 73308 (5 mg/kg) and CCRMP TILL-4 (17.4 mg/kg). The XRF analyses did not detect Th in any of the 77 analyses of NIST 2710. For NIST 2780, only two XRF analyses returned concentrations above the detection limit but both were much higher (92 and 94 mg/kg) than the certified value. Similarly, only three out of 39 XRF analyses of NCS 73308 yielded measured concentrations above the detection limit (all between 15 and 16 mg/kg) and all three were well in excess of the certified concentration. Two out of five XRF analyses of CCRMP TILL-4 detected Th, giving concentrations of 32 and 37 mg/kg, approximately twice the certified concentration. Therefore, analysis of standards suggests that the GSI XRF detected Th at concentrations around 17 mg/kg but that measured concentrations were significantly exaggerated. This is consistent with the results of the analyses of the 221 samples by XRF and ES.

18. U-Uranium

Table 18.1 U Statistics

U, n=221	OMAC	GSI
Minimum	<5	<DL
Maximum	170	124
Median	<5	<DL

The GSI XRF detected U in only seven of the 221 samples analysed, with measured concentrations ranging from 23 to 124 mg/kg. Only in two samples did the measured U exceed 100 mg/kg. There was poor correlation with the corresponding OMAC ES analyses. For the remaining 214 samples in which the XRF did not detect U, the concentrations measured by OMAC ES ranged from <5 to 170 mg/kg, suggesting a relatively high detection limit for the XRF or else poor X-ray peak resolution owing to overlap by adjacent peaks. The most likely peak overlap is that of the U Lα peak with that of the Rb Kα peak.

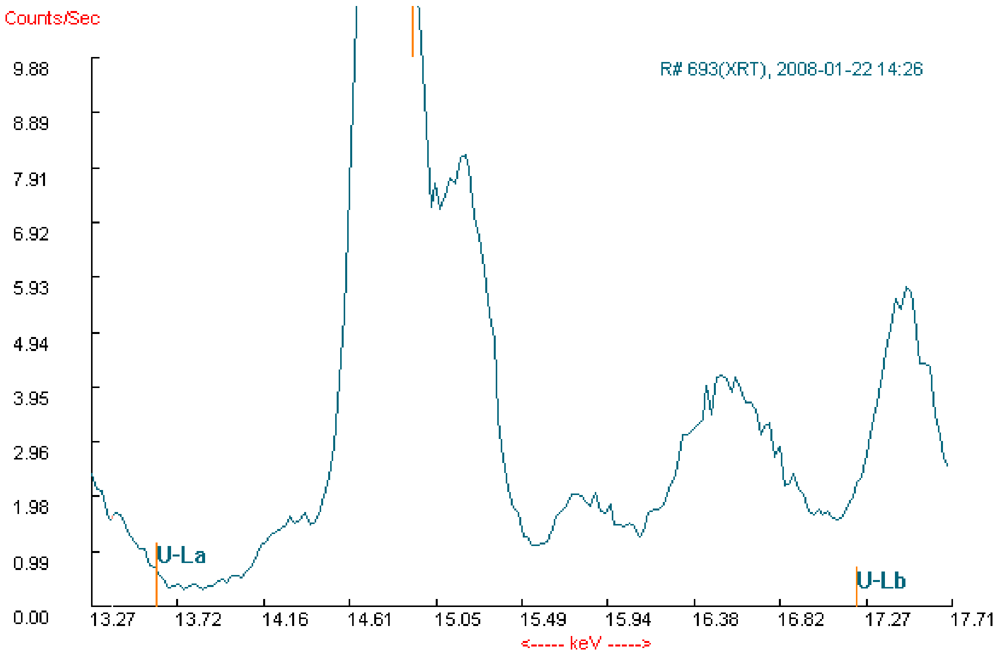


Figure 18.1 GLD-07-HEROPP8.2

Values for U are reported for several standards analysed for the HMS-IRC project but in most cases the reported concentration is 5 mg/kg or less, too low for detection by the XRF. An exception is NIST 2710, for which the accepted concentration is 25 mg/kg. The XRF detected U in 63 out of 77 analyses of this standard, returning a mean of 41 mg/kg. The Rb concentration of NIST 2710 is relatively low (120 mg/kg), indicating minimal potential for peak interference, and this may help explain the relatively successful results for XRF analysis of this standard.

19. V- Vanadium

Table 19.1 V Statistics

Zn, n=221	OMAC	GSI
Minimum	<2	0.0
Maximum	320	381
Median	49	0.0

Vanadium is one of the lighter elements analysed by the XRF and its detection limit is relatively high. Niton, the manufacturer of the XRF, has reported a detection limit in excess of 100 mg/kg V in soil matrix. The GSI XRF detected V in only 13 samples at concentrations ranging from 106 to 381 mg/kg. For the remaining 208 samples, the concentrations measured by OMAC using ES ranged from <2 to 156 mg/kg, with 10 samples exceeding 100 mg/kg. Fig. 19.1 shows the relationship between the OMAC and GSI measurements. For those analyses where V was detected by both techniques, there is a broad linear trend with a tendency for GSI XRF concentrations to exceed the corresponding OMAC ES concentrations.

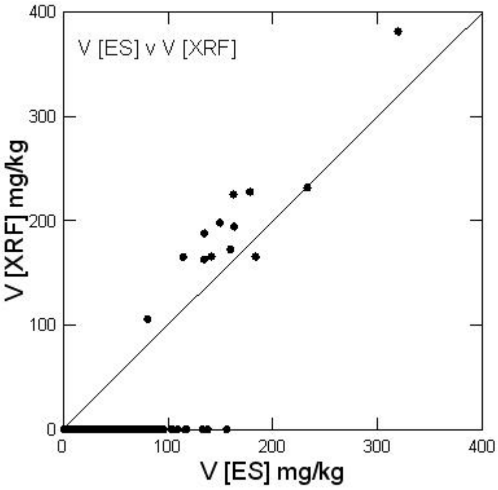


Fig. 19.1 V (ES v XRF)

The concentration of V is reported for four standards analysed in GSI, NIST 2710 (77 mg/kg), NIST 2780 (268 mg/kg), NCS 73308 (107 mg/kg) and CCRMP Till-4 (67 mg/kg). Mean values for GSI XRF analyses of these standards were, respectively, <DL (65 analyses), 277 mg/kg (48 analyses), 113 mg/kg (33 analyses) and <DL (5 analyses). Thus for the two standards in which V exceeds 100 mg/kg, the GSI XRF gave very good overall results.

20. W – Tungsten

Table 20.1 W Statistics

W, n=221	OMAC	GSI
Minimum	<5	<DL
Maximum	28.6	<DL
Median	<5	<DL

The GSI XRF did not detect W in any of the 221 samples analysed for the comparative study. It is recorded as present in only one standard analysed, the CCRMP TILL-4, at a concentration of 204 mg/kg. The XRF gave a mean of 254 mg/kg for five analyses. Tungsten was below the detection limit of 5 mg/kg in 191 samples analysed by ES and the maximum concentration recorded in the remaining 30 samples was 29 mg/kg, suggesting a minimum detection limit for the XRF of around 30 mg/kg. In practice, the XRF detection limit for W in samples of typical mine waste is likely to be much higher in many cases, at least where the sample contains significant Zn. This is because the X-ray peaks for W that fall in the energy spectrum covered by the XRF are the Lα and Lβ peaks with energies of 8.40 keV and 9.67 keV, respectively. These are very close to the two main Zn peaks, Kα (8.63 keV) and Kβ (9.57 keV). Thus W may only be detected unambiguously by the XRF where its concentration exceeds that of Zn, as in the standard CCRMP Till-4, in which the accepted W concentration is 204 mg/kg as opposed to 70 mg/kg for Zn. Fig. 20.1 shows the spectrum for this standard. In samples of mine waste from typical sulphide mines in Ireland, where Zn is one of the most abundant elements, the XRF is likely to detect W only in exceptional circumstances where it is present in very high concentrations or Zn is present in very low concentrations.

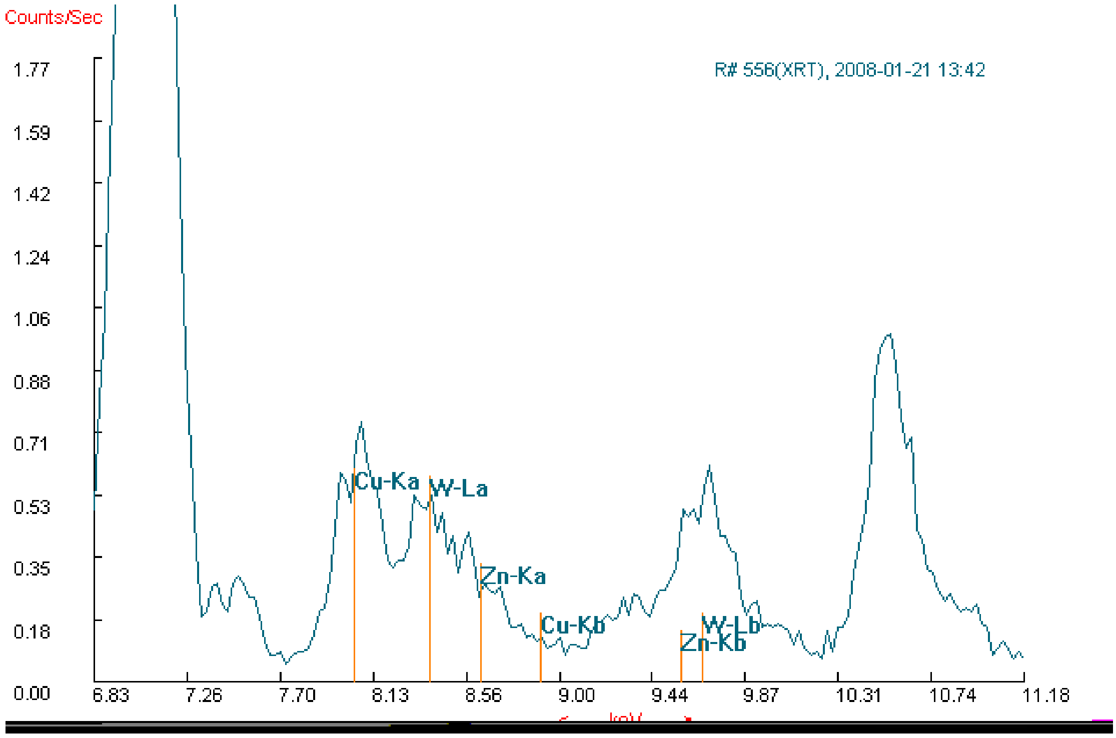


Fig. 20.1 Partial XRF spectrum for CCRMP Till-4, showing W and Zn peaks

21. Zn-Zinc

Table 21.1 Zn Statistics

Zn, n=221	OMAC	GSI
Minimum	3	0.0
Maximum	104,549	278,319
Median	424	386

The measured Zn concentration in GSI XRF analyses exceeded that of the OMAC ES analyses in 77 out of 221 cases. For these 77 samples, the median Zn concentrations were 8578 mg/kg (GSI) and 5961 mg/kg (OMAC). For the 144 samples in which the measured OMAC concentrations exceeded those of

GSI, the median Zn concentrations were 119 mg/kg (GSI) and 168 mg/kg (OMAC). Of these 144 GSI analyses, 38 were below the detection limit. Thus, measured Zn concentrations in GSI analyses tend to be lower than those measured by OMAC ES for samples with relatively low Zn concentrations. Where the Zn concentration is high, i.e. > 1000 mg/kg in most cases, the GSI analyses tend to give higher measured Zn concentration than those of OMAC ES (Fig. 21.1). Overall, there is good agreement between GSI XRF and OMAC ES analyses, with similar median concentrations for all 221 analyses (386 and 424 mg/kg, respectively) (Table 21.1).

Zinc is reported for four standards analysed in GSI, NIST 2710 (6952 mg/kg), NIST 2780 (2570 mg/kg), NCS 73308 (46 mg/kg) and CCRMP Till-4 (70 mg/kg). Mean values for XRF analyses of these standards were, respectively, 6967 mg/kg, 1943 mg/kg, 29 mg/kg and 42 mg/kg. The results for the ICP-4 standard run by OMAC in December 2008 were 6327mg/kg and 6378mg/kg against an accepted value of 6350mg/kg. The SY-4 standard (accepted concentration: 93 mg/kg) gave results of 119 mg/kg and 107 mg/kg. The standard data suggest that the GSI XRF analyses are acceptable at relatively high concentrations such as those in NIST 2710, a soil standard. The low mean recorded for NIST 2780, a mine waste standard, is typical of metal concentrations measured in this standard by XRF (compare data for other elements such as Pb and Cu). The metal-rich matrix present in this sample is quite different to that of the matrix in the soil samples used to calibrate the instrument and this difference is considered the likely reason for the consistently low metal concentrations measured by XRF in this sample, compared to the published accepted concentrations. In the case of the other two standards, the results are reasonable, especially in the case of NCS 73308 where the accepted Zn concentration is not much greater than the expected detection limit for the XRF. Thus, data for GSI standard analyses do not suggest significant problems with XRF analyses for Zn at relatively high or low concentrations and there are no peak overlaps in the XRF spectrum that could give rise to falsely high Zn results.

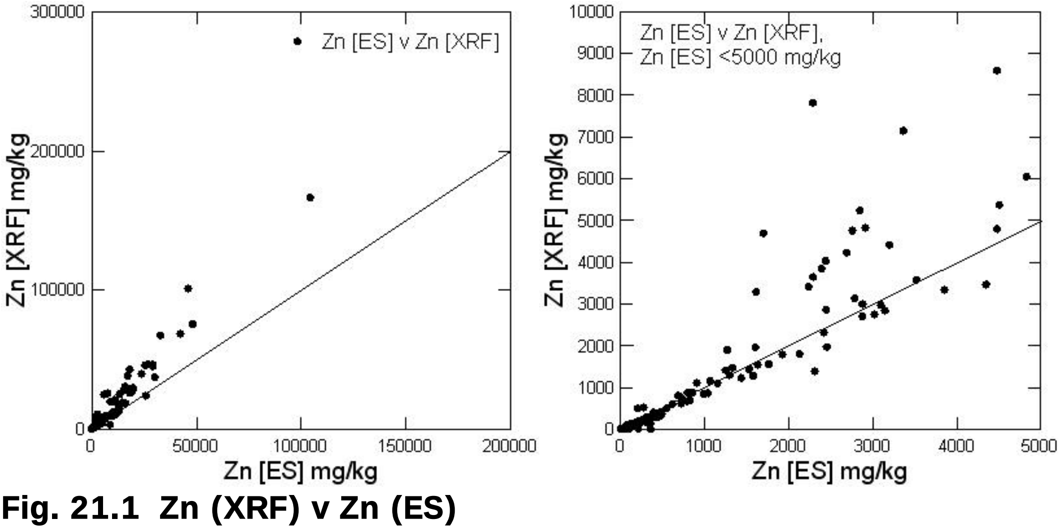
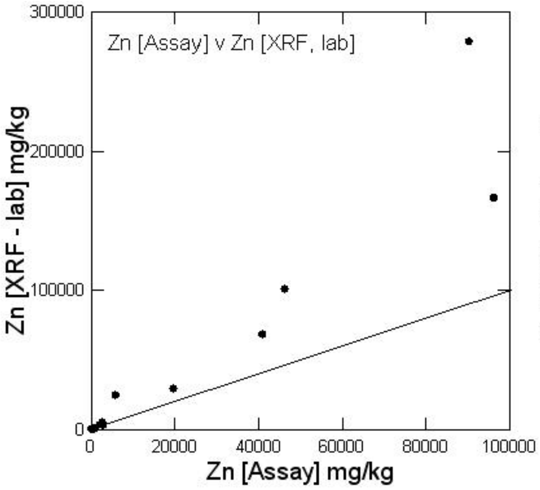


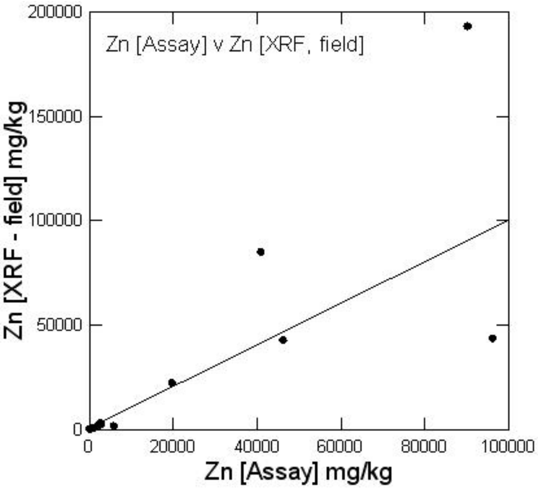
Fig. 21.1 Zn (XRF) v Zn (ES)

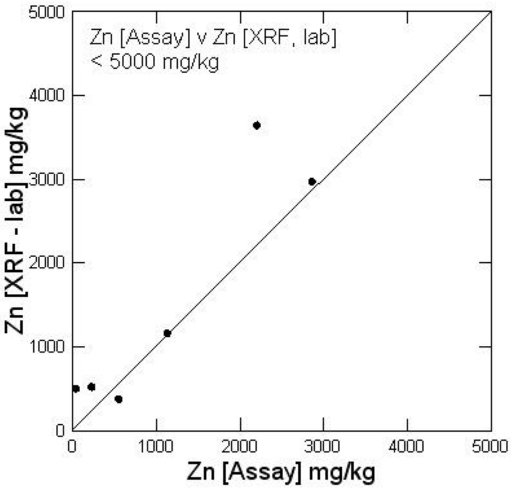
The upper calibration limit for the XRF is 20,000 mg/kg Zn (2%) and measured concentrations exceeding this must be considered semi-quantitative. An attempt was made to assess the accuracy of XRF analyses of samples with very high measured metal concentrations by carrying out assays of the samples at OMAC laboratories. The assay analysis included As, Cd, Cu, Fe, Pb and Zn. Comparison of results for the 13 samples analysed by assay with those previously obtained by ES analysis at OMAC indicates good agreement for the most part between the two methods. Table XX compares the summary data for the assay and GSI analyses. In general, GSI XRF results are significantly higher than those obtained by assay, indicating a bias toward high measured values in samples with high concentrations of Zn. Examples of high XRF results for Zn include (OMAC assay results in brackets) 2964 mg/kg (2866 mg/kg), 6.8% (4.1 %), 10.1% (4.6%) and 16.6% (9.6%).

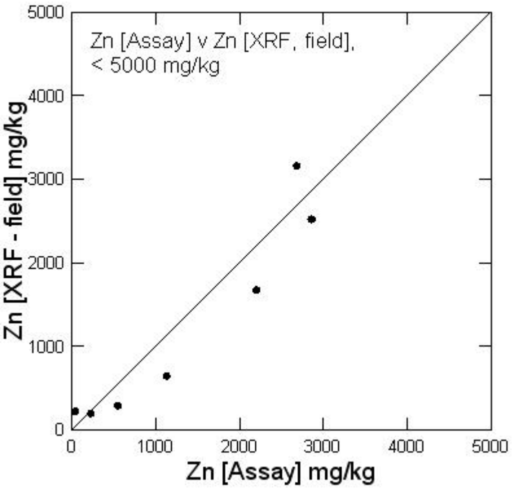
Table 21.2 Zn assays

Zn, n=13	OMAC (ES)	OMAC (assay)	GSI XRF (lab)	GSI XRF (field)
Minimum	209	50	366	191
Maximum	104549	96294	278319	192785
Mean	25216	23790	52457	30494
Median	3102	2866	5230	2515






Zn [Assay] v Zn [XRF, lab]
< 5000 mg/kg
Zn [XRF - lab] mg/kg
Zn [Assay] mg/kg
0
1000
2000
3000
4000
5000
0
1000
2000
3000
4000
5000


Zn [Assay] v Zn [XRF, field],
< 5000 mg/kg
Zn [XRF - field] mg/kg
Zn [Assay] mg/kg
0
1000
2000
3000
4000
5000
0
1000
2000
3000
4000
5000

References

CDM (2008) Feasibility Study for the management and remediation of the Avoca Mining Site. Camp, Dresser and McKee, Cambridge, MA, USA.

Cowman, D. and Morris, J.H. (2003) A history of mining and quarrying in Ireland up to 1700. The Journal of the Mining Heritage Trust of Ireland, 3, 25–32.

Draft European Communities Environmental Objectives (Surface Waters) Regulations, 2008).

European Communities (2007) European Communities (Drinking Water) (No. 2) Regulation 2007. SI 278, Government Publications, Dublin.

Fay, D., Kramers, G., Zhang, C., McGrath, D. and Grennan, E. (2007) Soil Geochemical Atlas of Ireland. Published by Teagasc and the Environmental Protection Agency.

Grennan, E. (1996) EPA Small Scale Study – EPA register of former mine sites. Sligo RTC.

Price, W.A. and Errington, J. C. (1998) Guidelines for Metal Leaching and Acid Rock Drainage at Minesites in British Columbia. BC Ministry of Energy and Mines, Canada.

US EPA (2006) Innovative Technology Verification Report. XRF Technologies for Measuring Trace Elements in Soil and Sediment, Niton XLt 700 Series XRF Analyzer. EPA/540/R-06/004, February 2006.

Glossary of Abbreviations

EPA	Environmental Protection Agency
GSI	Geological Survey of Ireland
EMD	Exploration and Mining Division
ATSDR	Agency for Toxic Substances and Disease Registry
MA-ES	Multi-Acid Emission Spectrography
HMS-IRC	Historic Mine Sites – Inventory and Risk Classification
DOC	Dissolved Organic Carbon
TMF	Tailing Management Facility
XRF	X-Ray Fluorescence
WHO	World Health Organisation
ICP-MS	Inductively Coupled Plasma – Mass Spectrography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
<DL	Below the Detection Limit
EC	Electric Conductivity
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
TDS	Total Dissolved Solids
TSS	Total Suspended Solids

Elements of the Periodic Table

Al	Aluminium
As	Arsenic
Ba	Barium
Bi	Bismuth
Ca	Calcium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
Hg	Mercury
K	Potassium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Na	Sodium
Ni	Nickel
P/PO_4	Phosphorous/Phosphate
Pb	Lead
Rb	Rubidium
S/SO4	Sulphur/Sulphate
Sb	Antimony
Se	Selenium
Sn	Tin
Sr	Strontium
Th	Thorium
Tl	Thallium
U	Uranium
V	Vanadium
W	Tungsten
Zn	Zinc