

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 ICRL 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 The latter were superseded in the 1990s by the Soil Guideline Values (SGVs) produced by the UK's Department of Environment, Food and Rural Affairs (DEFRA). These in turn have been withdrawn pending new values that reflect an updated methodology.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)

Parameter mg/kg	Dutch	Dutch	SGV	SGV	ATSDR	ATSDR
	Target value	Intervention value	Residential / Allotments	Industria l	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 (Fe²⁺, Al³⁺, Zn²⁺, 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 (HCO₃⁻). Acidity is measured by titrating with NaOH until the pH of the solution reaches 8.3. It is expressed as mg/l CaCO₃ equivalent. The acidity of a solution can thus be seen as a measure of the amount of CaCO₃ 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 CaCO₃ (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 (FeS₂).

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.

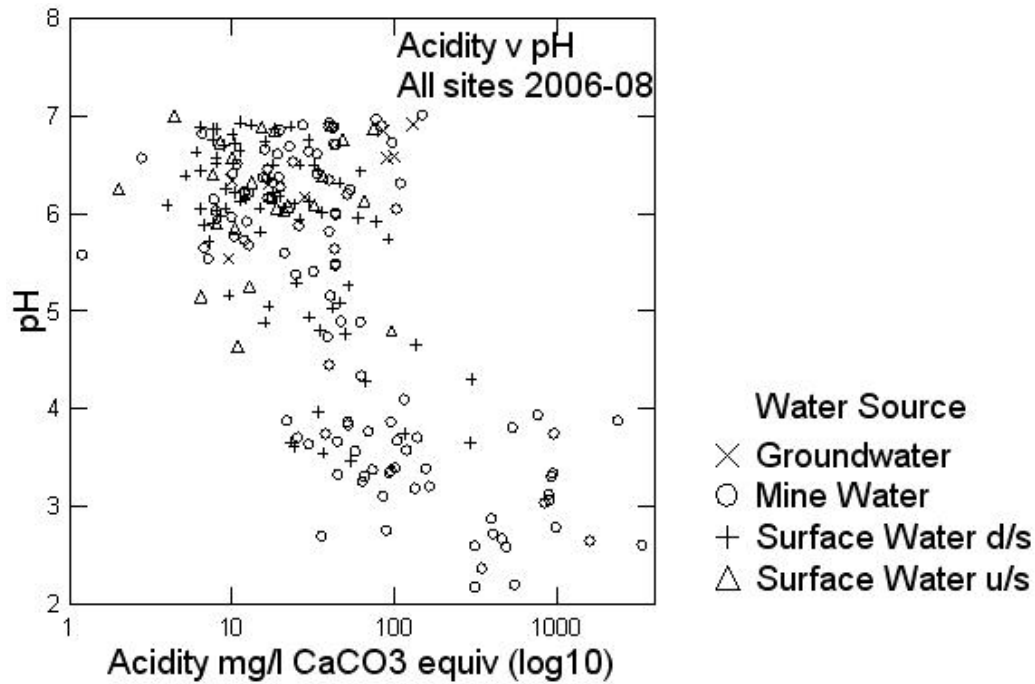


Fig. 1 Acidity v pH for all mine sites sampled, categorized by water source

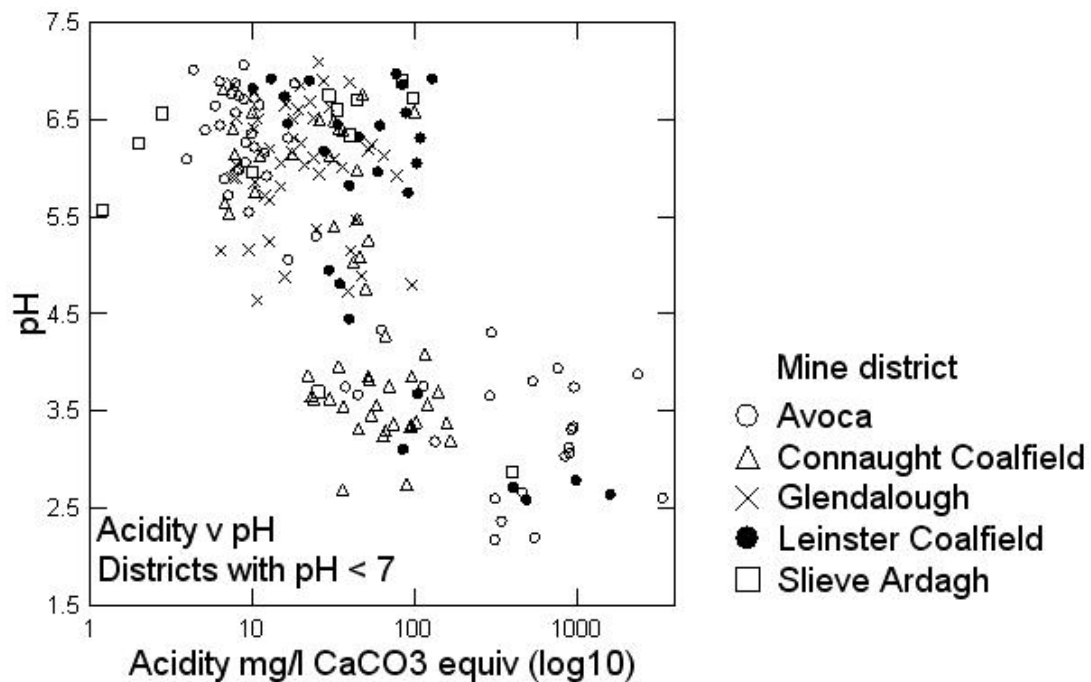


Fig. 2 Acidity v pH for main mine districts where pH < 7

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 CaCO₃).

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% Al₂O₃) (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 Al³⁺, 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/l) (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 summarize 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.

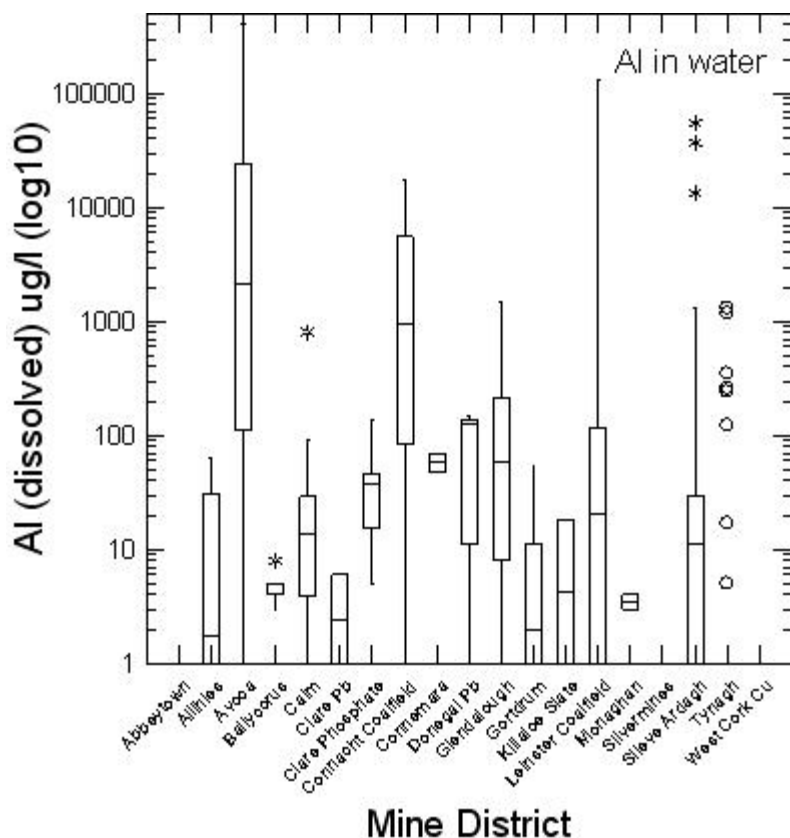


Fig. 3 Al (dissolved) in all water analysed, by mine district (log scale)

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** ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$). 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. Sb₂O₃ 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 Sb₂O₃ 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.

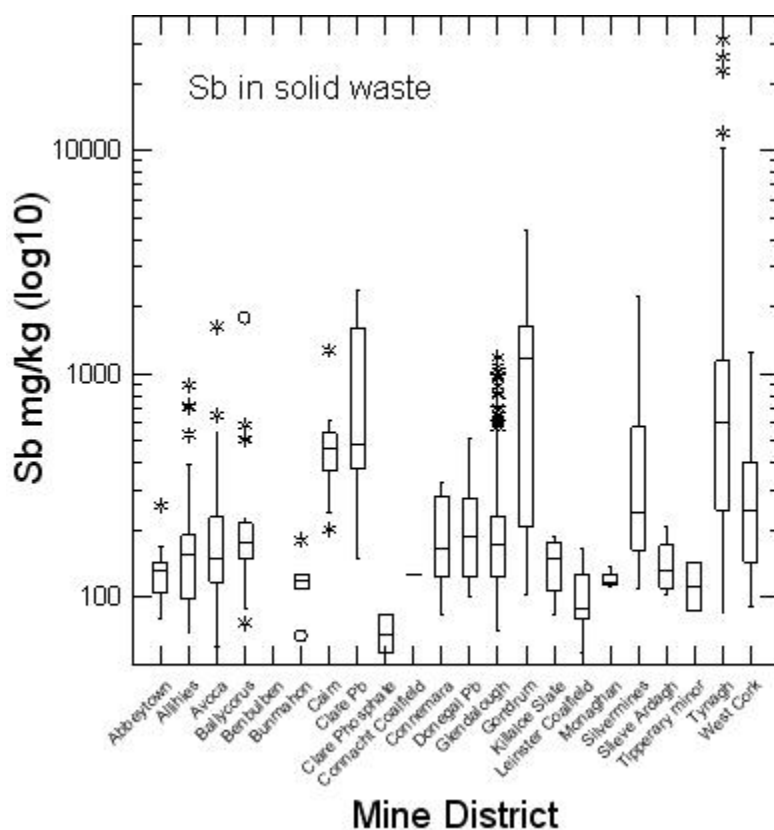


Fig. 4 Boxplots of Sb in solid mine waste for each district investigated

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.

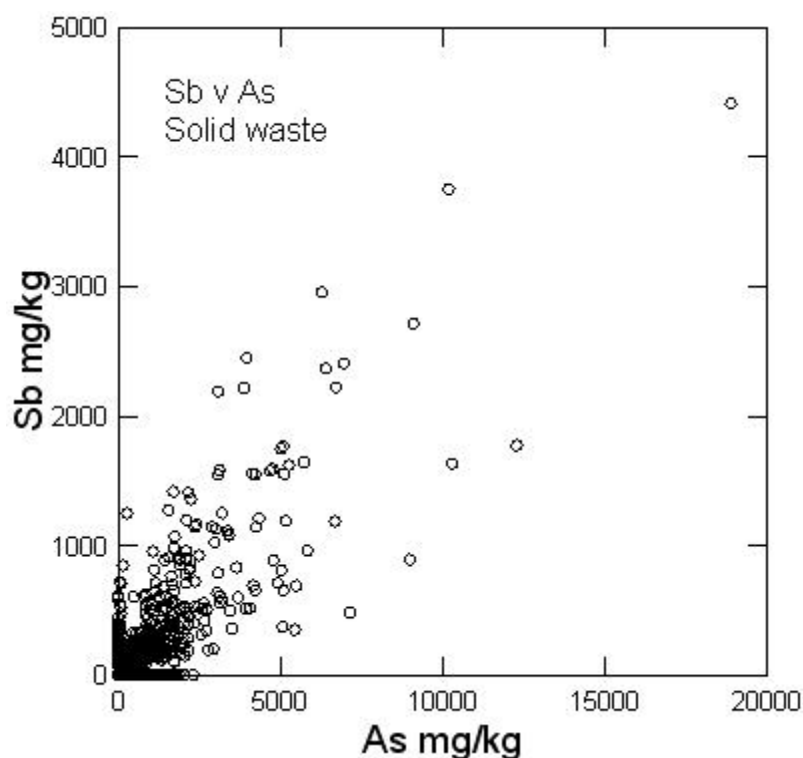


Fig. 5 Sb v As for *in situ* solid waste analyses (limited range)

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).

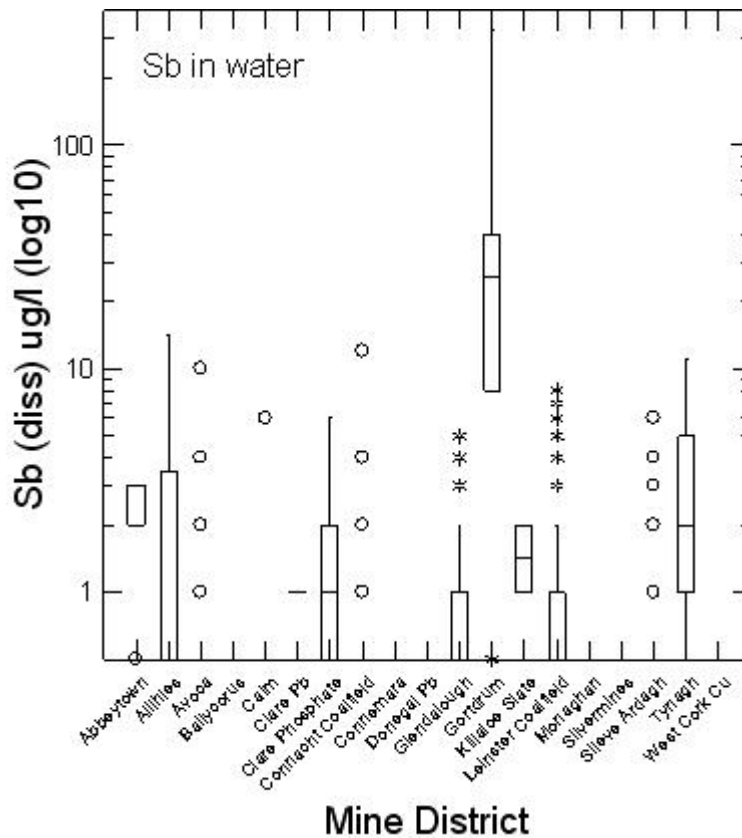


Fig. 6 Dissolved Sb in all waters analysed, by mine district (log scale)

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.

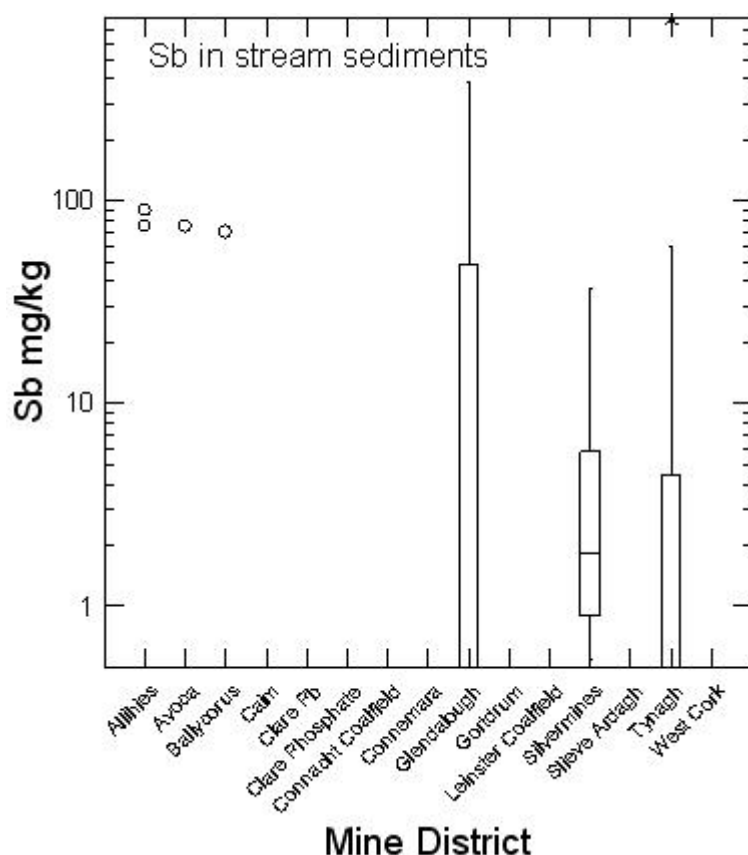


Fig. 7 Sb in stream sediments in mine districts

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 (FeS₂).

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. As³⁺ is found under low-pH, anaerobic conditions, As⁵⁺ under alkaline, oxidizing conditions. As³⁺ 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.

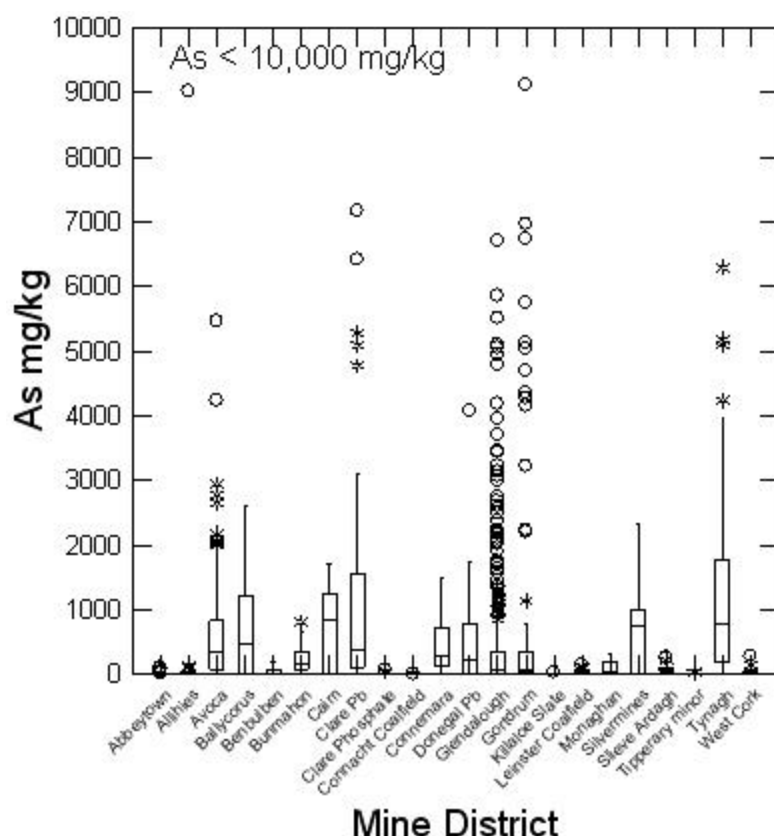


Fig. 8 Boxplots of As in solid mine waste for each district investigated

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.

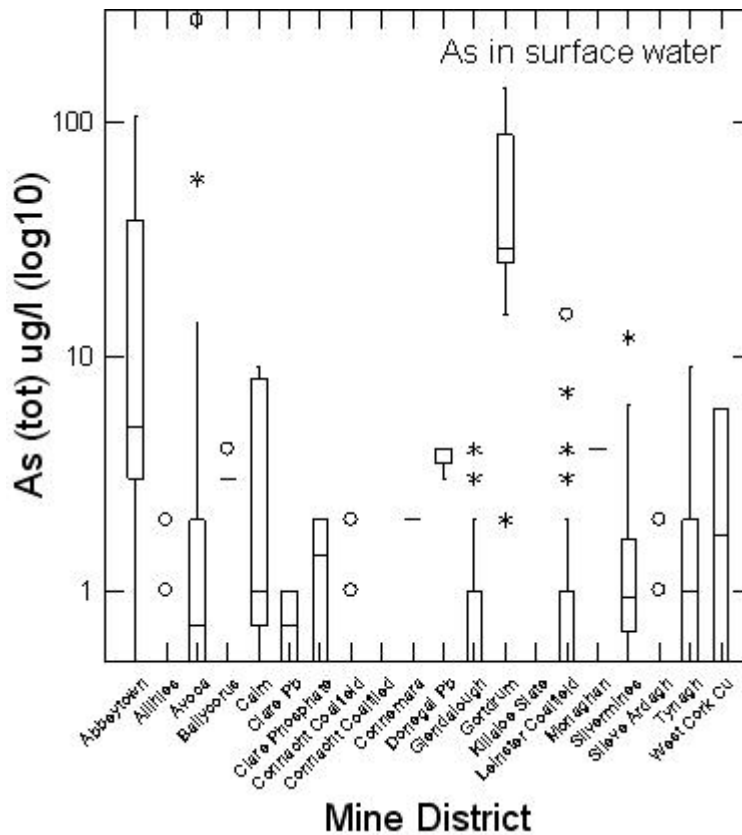


Fig. 9 Total As in all waters analysed, by mine district (log scale)

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).

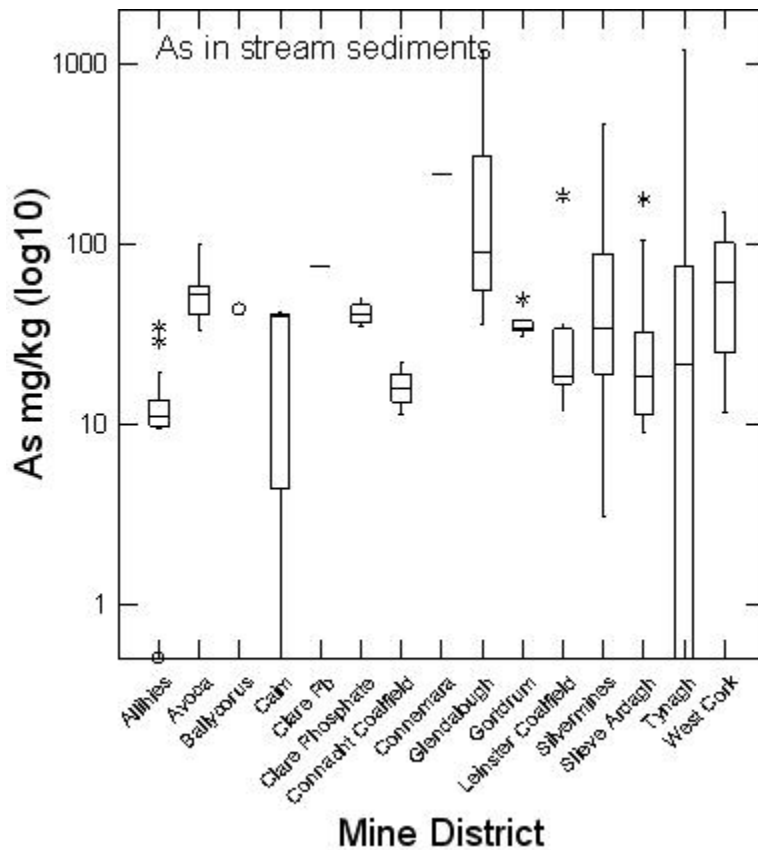


Fig. 10 As in stream sediments in mine districts

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** (BaSO₄) and **witherite** (BaCO₃). Ba²⁺ has the largest ionic radius of the divalent cations apart from Ra²⁺. It substitutes isostructurally for other large cations such as K⁺, Ca²⁺, Pb²⁺, Sr²⁺. 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** (BaAl₂Si₂O₈) 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 Benbulbin, 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.

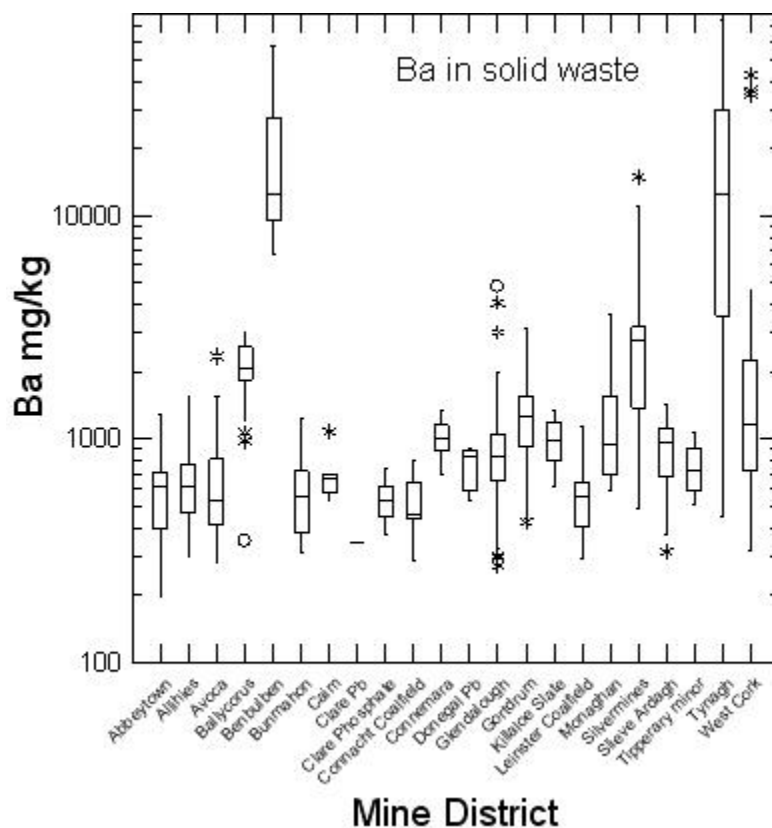


Fig. 11 Boxplots of Ba (log scale) in solid mine waste v mine district

Table 15 Summary statistics for Ba in several mine districts (*in-situ* analyses)

mg/kg Ba	All sites	Ballycorus	Benbulbin	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

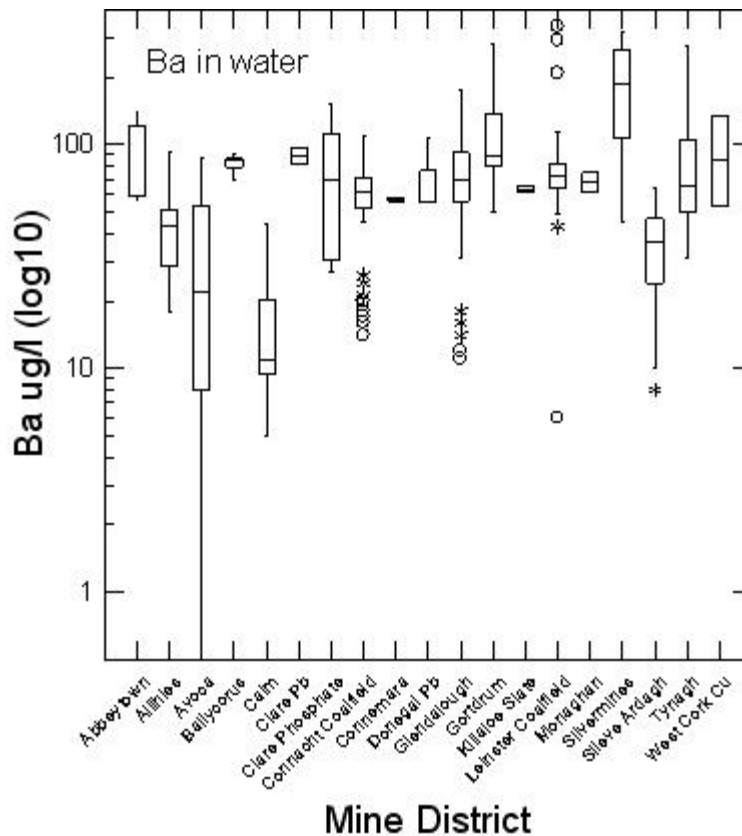


Fig. 12 Total Ba in all waters analysed, by mine district (log scale)

Stream sediments were collected in most mining districts and the fine fraction ($<150 \mu\text{m}$) 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 $1,000 \text{ mg/kg}$ (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 $<150 \mu\text{m}$ fraction analysed for HMS-IRC may be expected to have somewhat higher metal concentration.

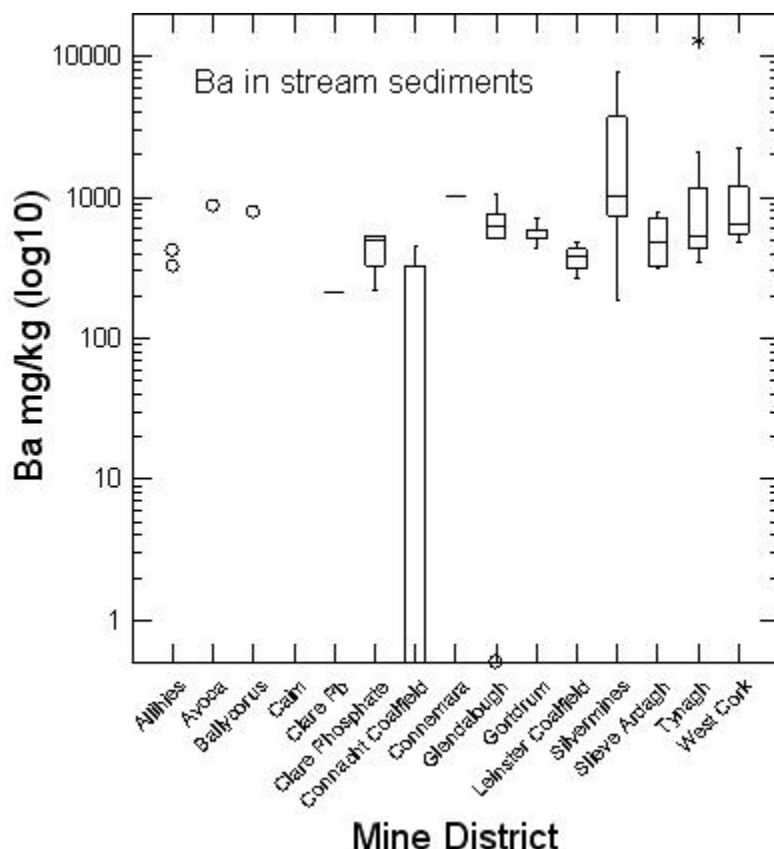


Fig. 13 Ba in stream sediments in mine districts

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 isotopic 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** (CdCO₃) 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.

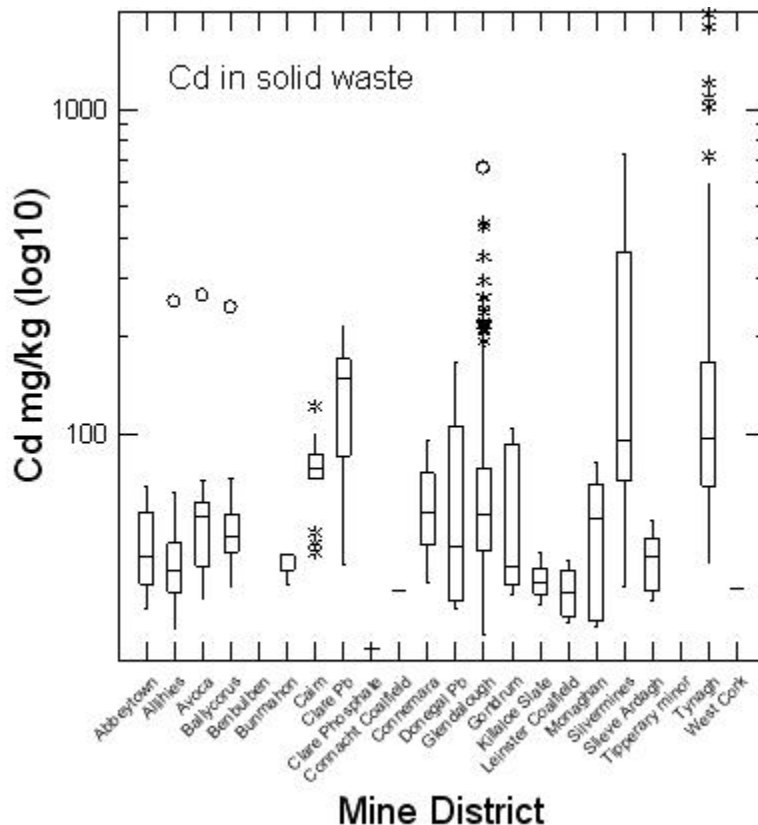


Fig. 14 Cd in solid waste, by district

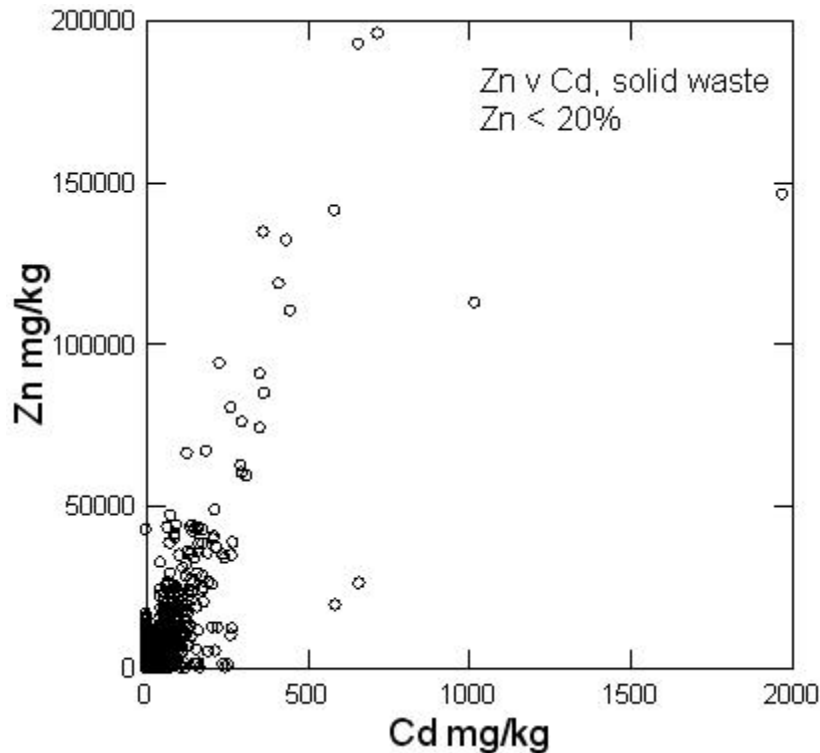


Fig. 15 Cd v Zn in solid waste (Zn < 20%)

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

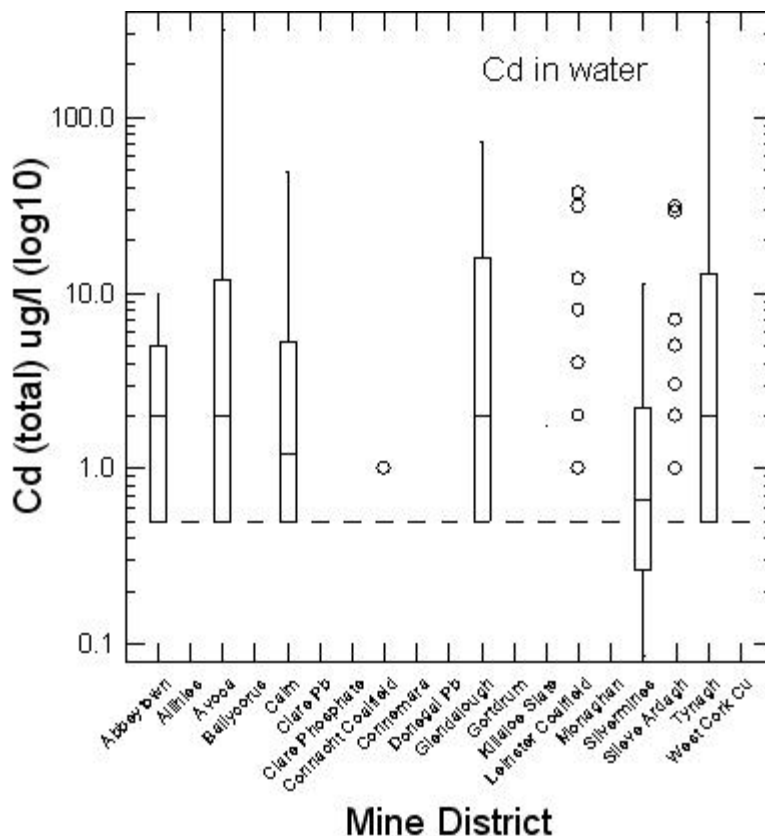


Fig. 16 Total Cd in all waters analysed, by mine district (log scale)

The highest Cd concentration in waters analysed for HMS-IRC (350 $\mu\text{g/l}$ 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 $\mu\text{g/l}$), adit discharges in Glendalough district (up to 73 $\mu\text{g/l}$) and seeps and run-off from processing waste at Caim (up to 49 $\mu\text{g/l}$). Also notable are a few isolated high concentrations (up to 37 $\mu\text{g/l}$) 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.

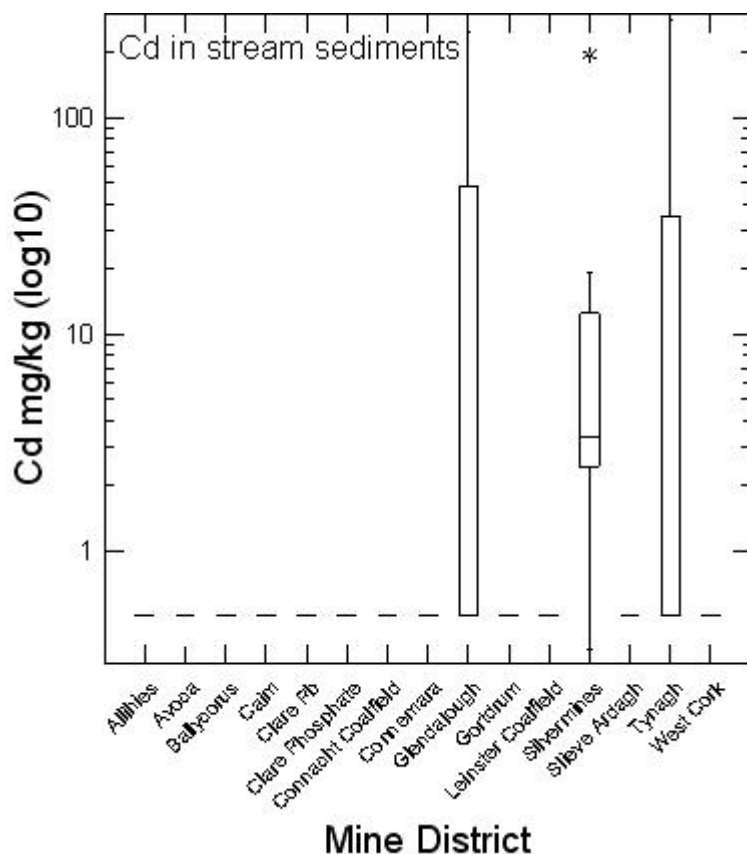


Fig. 17 Cd in stream sediments in mine districts (log scale)

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** (FeCr₂O₄), characterized by considerable replacement of Cr by Al. Natural Cr sulphides, such as **daubréelite** (FeCr₂S₄), 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 Cr⁰, Cr³⁺ (CrIII) and Cr⁶⁺ (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 Cr⁶⁺ 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 Benbulbin 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 Cr³⁺ and Cr⁶⁺ species rather than total Cr. The reference value for Cr³⁺ 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 Cr³⁺ 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

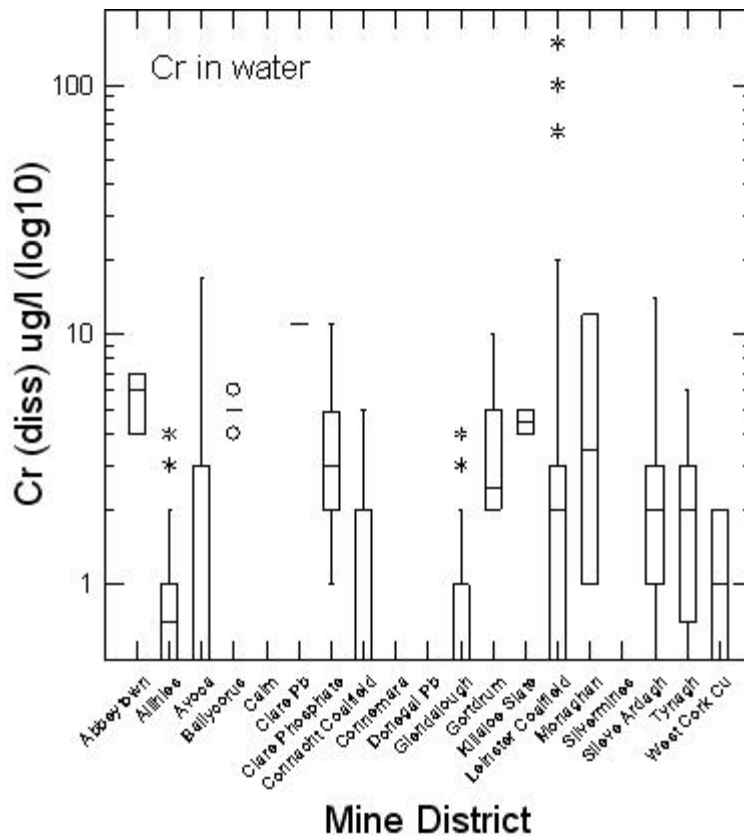


Fig. 18 Dissolved Cr in all waters analysed, by mine district (log scale)

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 Cr³⁺ 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** ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) and **malachite** ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) and numerous sulphates, arsenates, phosphates and silicates.

Copper is used in the manufacture of electrical equipment, including wiring, plumbing pipes, alloys such as bronze, algacides, 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 $\mu\text{g/l}$ (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 $\mu\text{g/l}$ (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.

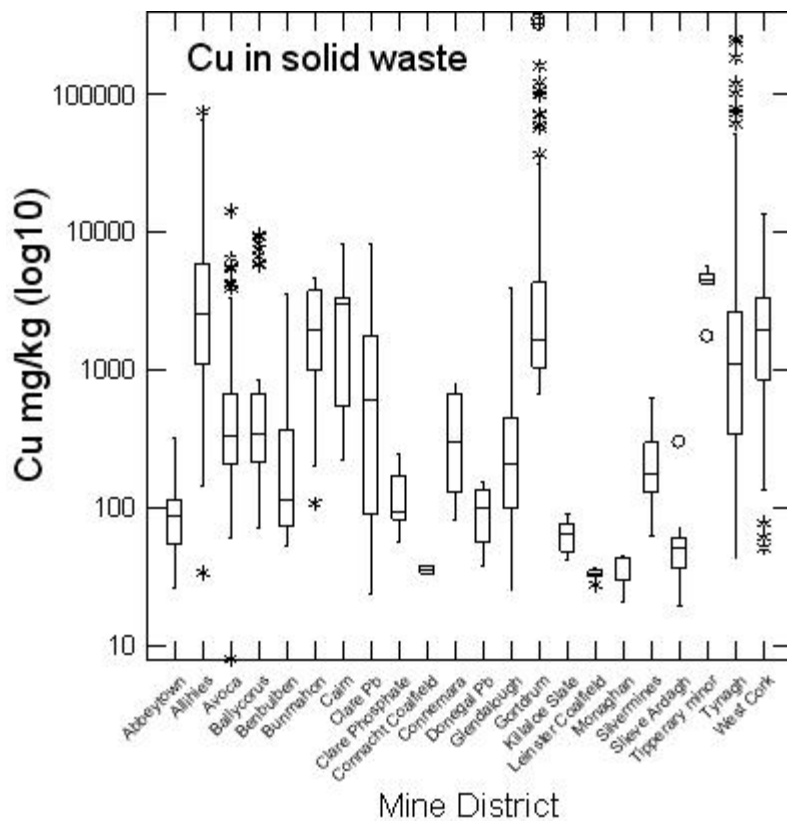


Fig. 19 Boxplots of Cu (log scale) in solid mine waste v mine district

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).

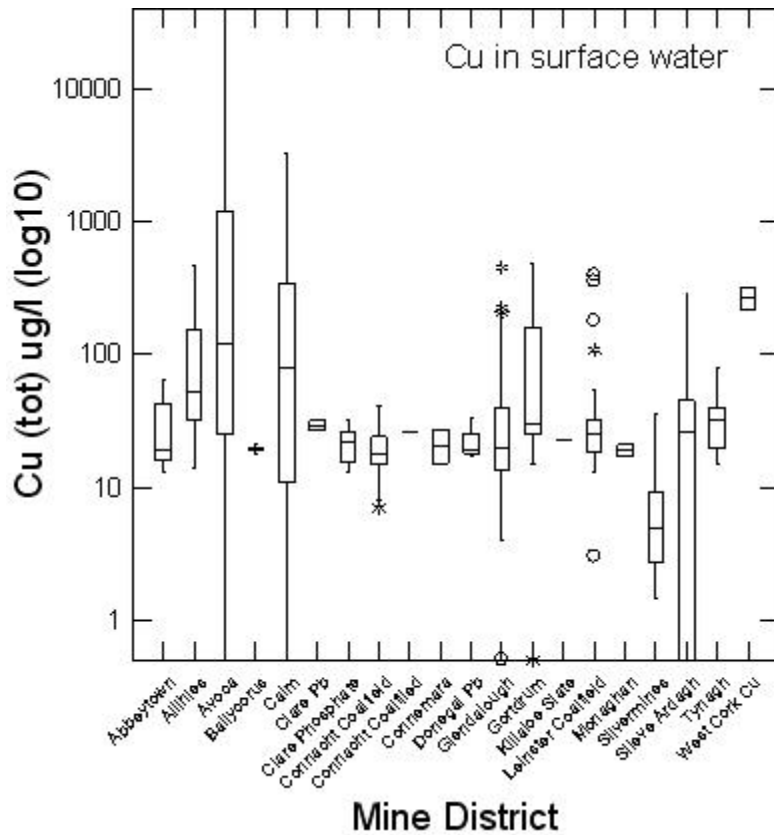


Fig. 20 Total Cu in all waters analysed, by mine district (log scale)

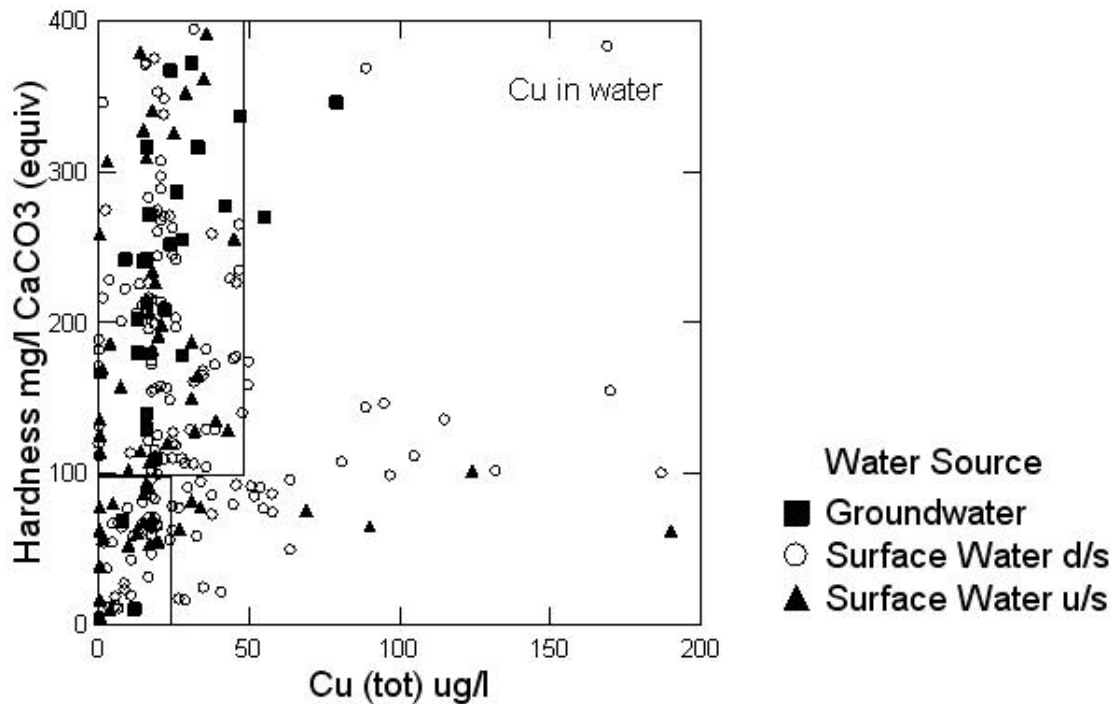


Fig. 21 Total Cu v hardness in surface water and groundwater (Boxes enclose concentrations below the standard concentrations)

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.

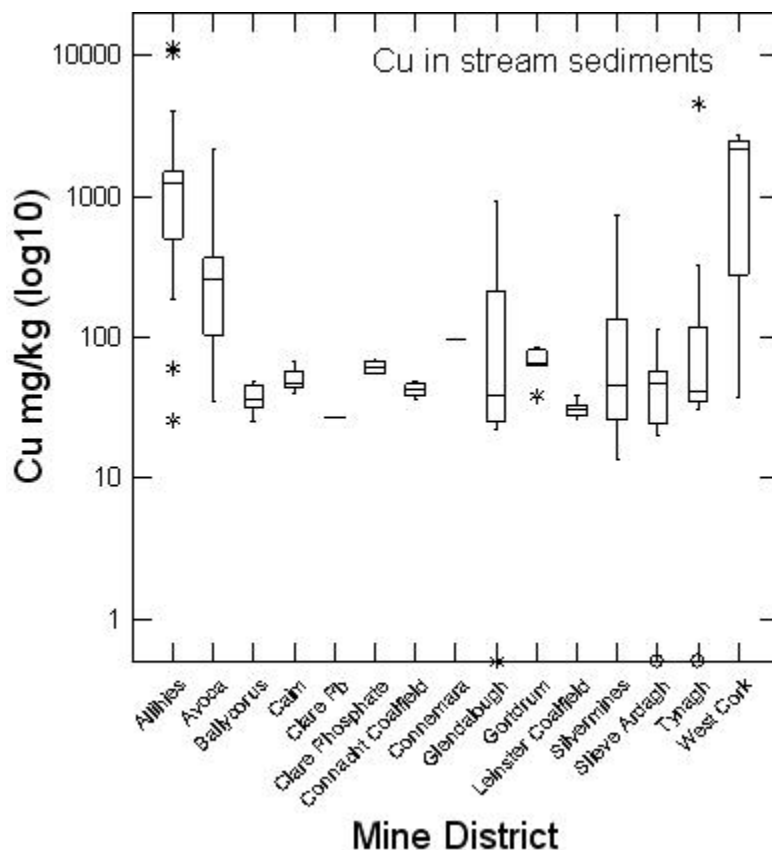


Fig. 22 Cu in stream sediments in mine districts

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 Fe₂O₃ in oxides, e.g. **magnetite** (Fe₃O₄), and silicates such as **pyroxene** ((Fe,Mg)₂Si₂O₆), **amphibole** (e.g. hornblende: Ca₂(Mg,Fe,Al)₅(Al,Si)₈O₂₂(OH)₂) and **biotite** (K(Mg, Fe)₃AlSi₃O₁₀(F, OH)₂). Accessory sulphides, e.g. **pyrite** (FeS₂), also account for some of it. Low-temperature sedimentary minerals include **haematite** (Fe₂O₃), **goethite** (FeO(OH)), **glauconite** (K₂(Fe,Al,Mg)₄(Si₇AlO₂₀)(OH)₄•*n*(H₂O)), **siderite** (FeCO₃), **marcasite** (FeS₂), **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. Fe²⁺ minerals react with O₂ to form Fe³⁺ oxides during weathering. In sediments, bacteria use organic carbon to reduce Fe³⁺ oxides to Fe²⁺ compounds and dissolved SO₄²⁻ to sulphide. If the amount of dissolved sulphide is sufficient, Fe sulphide may be formed. If sulphide is low, oxidized carbon in CO₃²⁻ 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, Fe²⁺ is oxidized to Fe³⁺ 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% Fe₂O₃, sandstones 1.7% FeO and 1.5% Fe₂O₃, carbonates 0.5% Fe₂O_{3tot} and pelagic clays 9.3% Fe₂O_{3tot} (Wedepohl 1978). In metamorphic rocks, Fe is present in silicates as FeO in solid solution with MgO. Fe₂O₃ is present as a substitution for Al₂O₃

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 Abbeystown and Benbulbin 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.

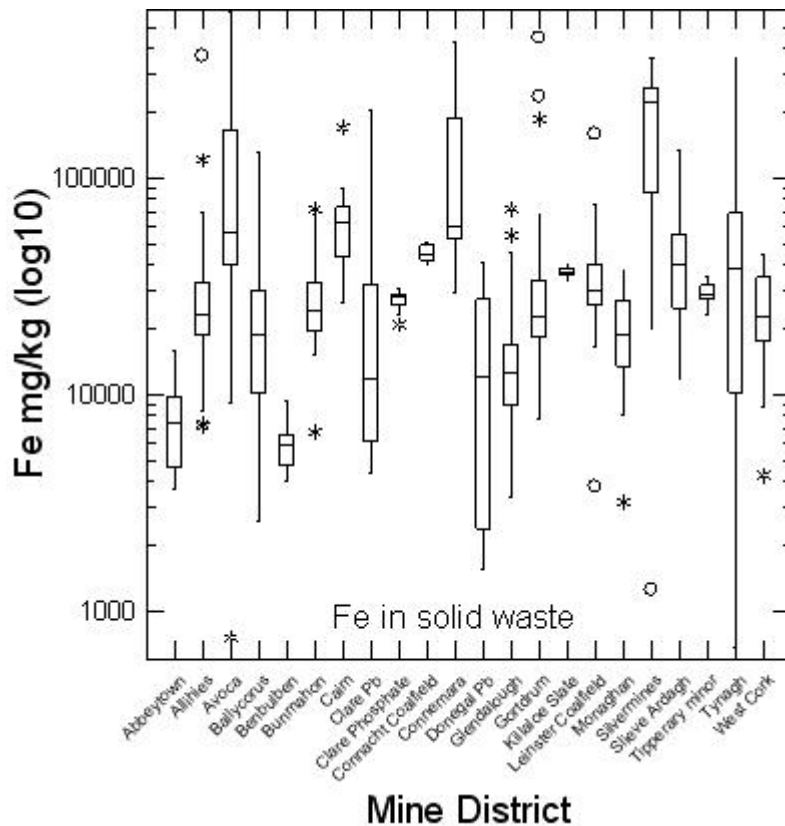


Fig. 23 Boxplots of Fe (log scale) in solid mine waste v mine district

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

$\mu\text{g/l Fe}$	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 $\mu\text{g/l}$, 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.

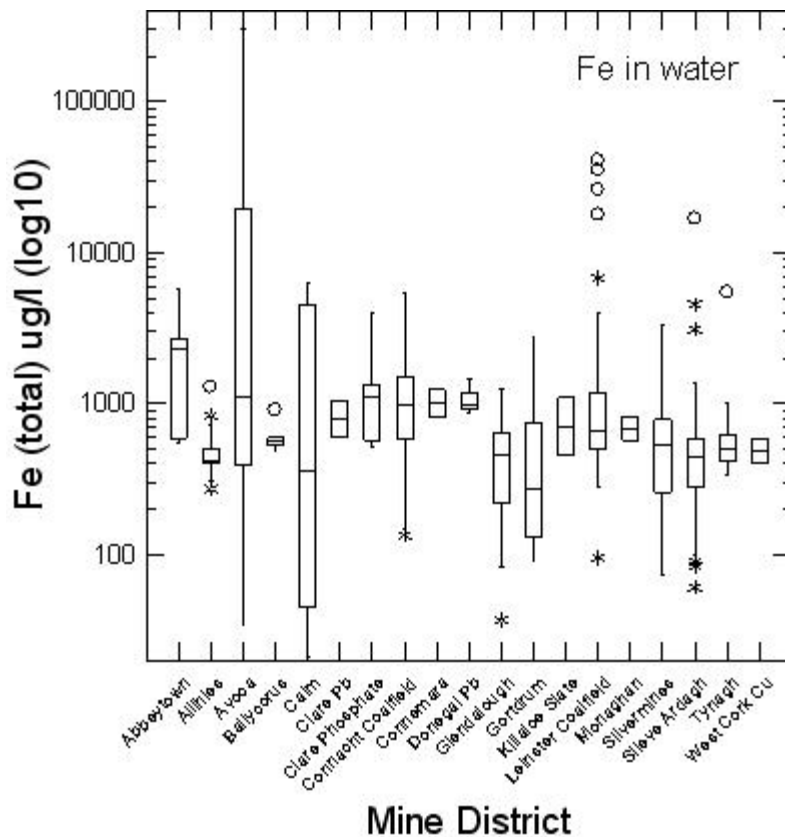


Fig. 24 Total Fe in all waters analysed, by mine district (log scale)

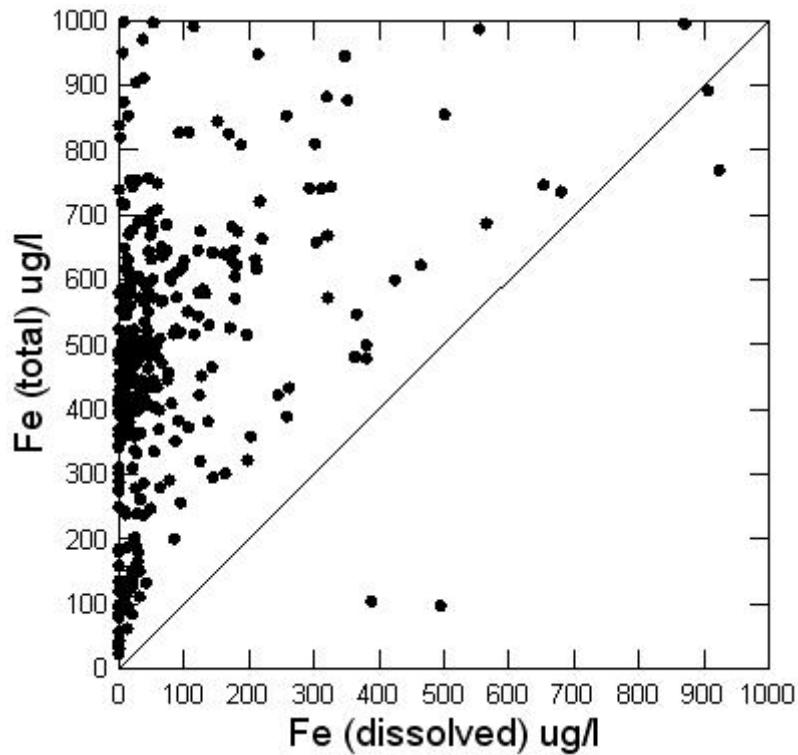


Fig. 25 Total v dissolved Fe, for concentrations < 1000 µg/l

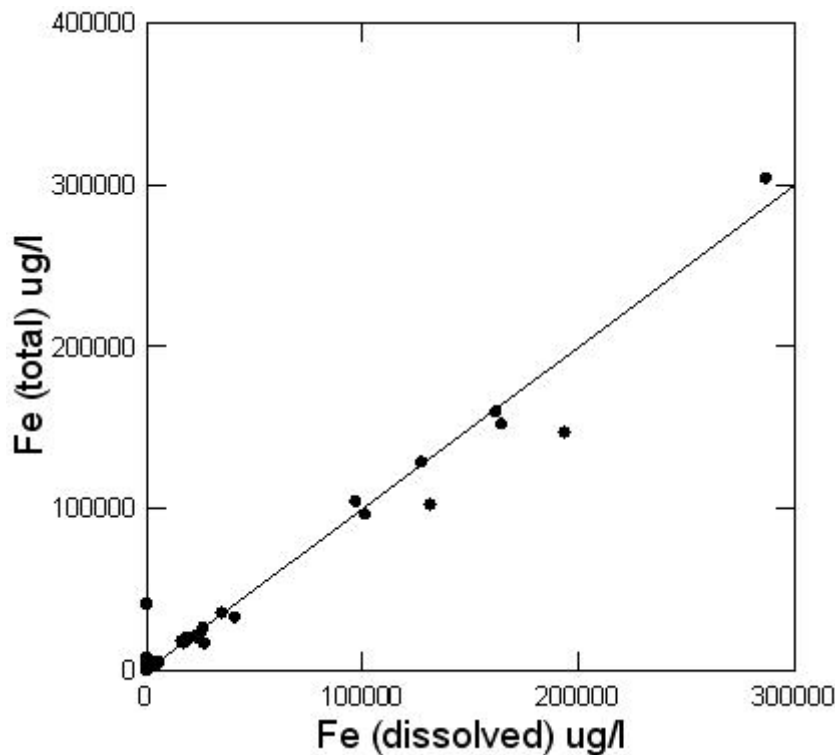


Fig. 26 Total v dissolved Fe, all samples

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.

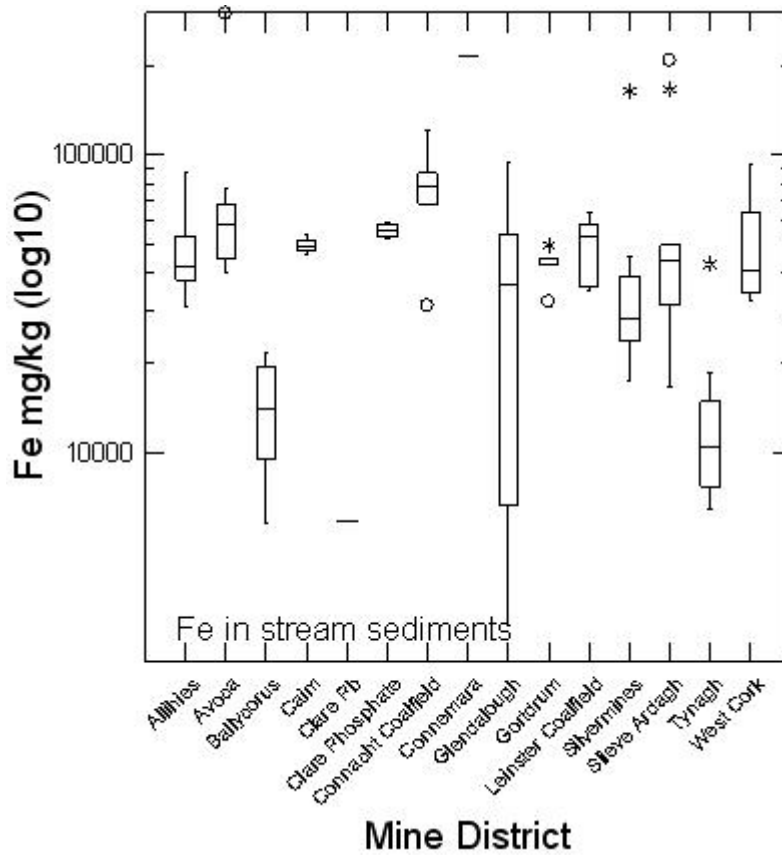


Fig. 27 Fe in stream sediments in mine districts

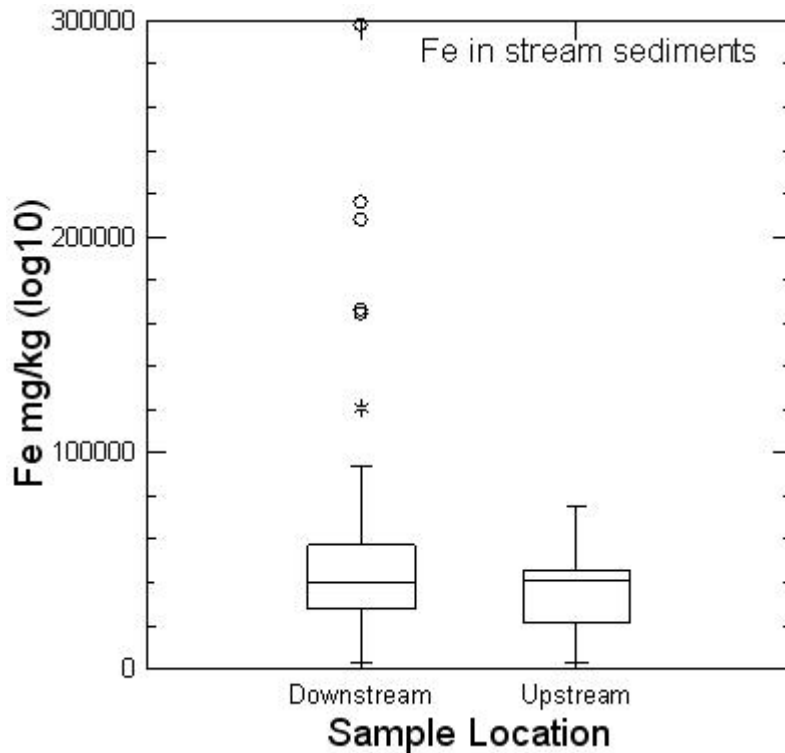


Fig. 28 Fe in stream sediments: upstream v downstream samples

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

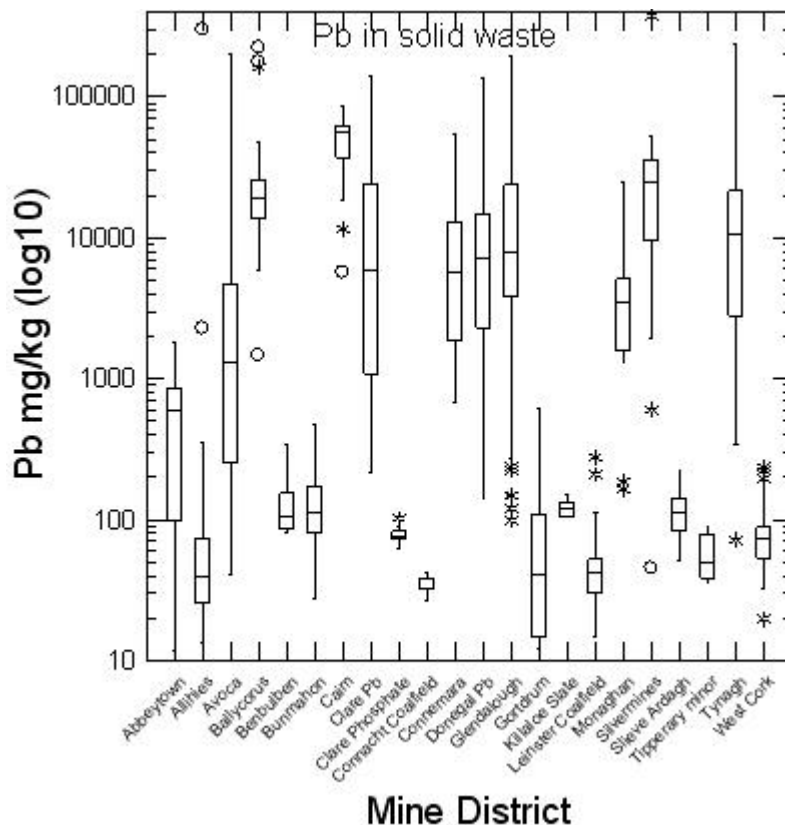


Fig. 29 Boxplots of Pb (log scale) in solid mine waste v mine district

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

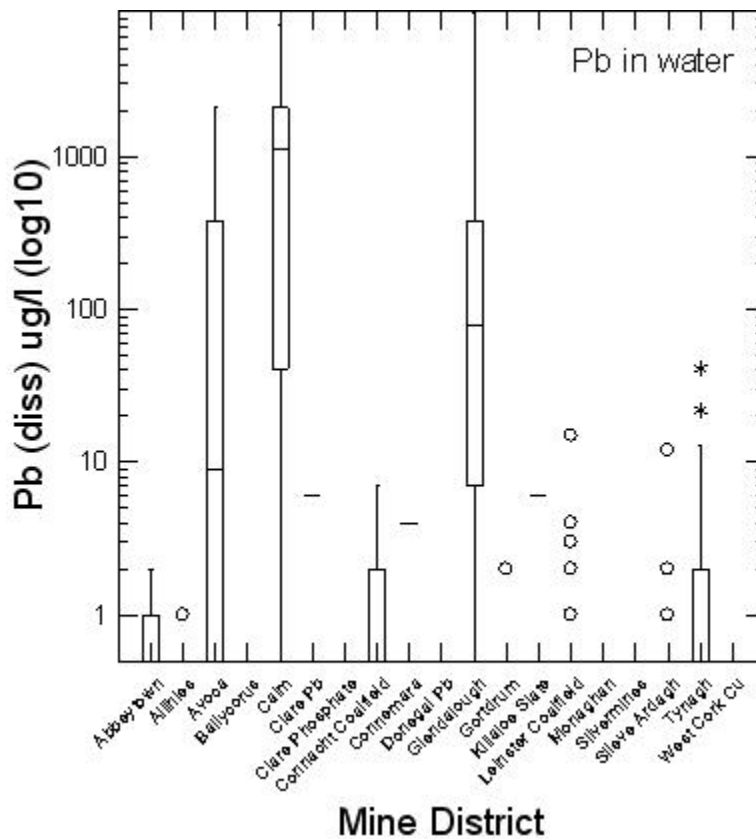


Fig. 30 Dissolved Pb in all waters analysed, by mine district (log scale)

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.

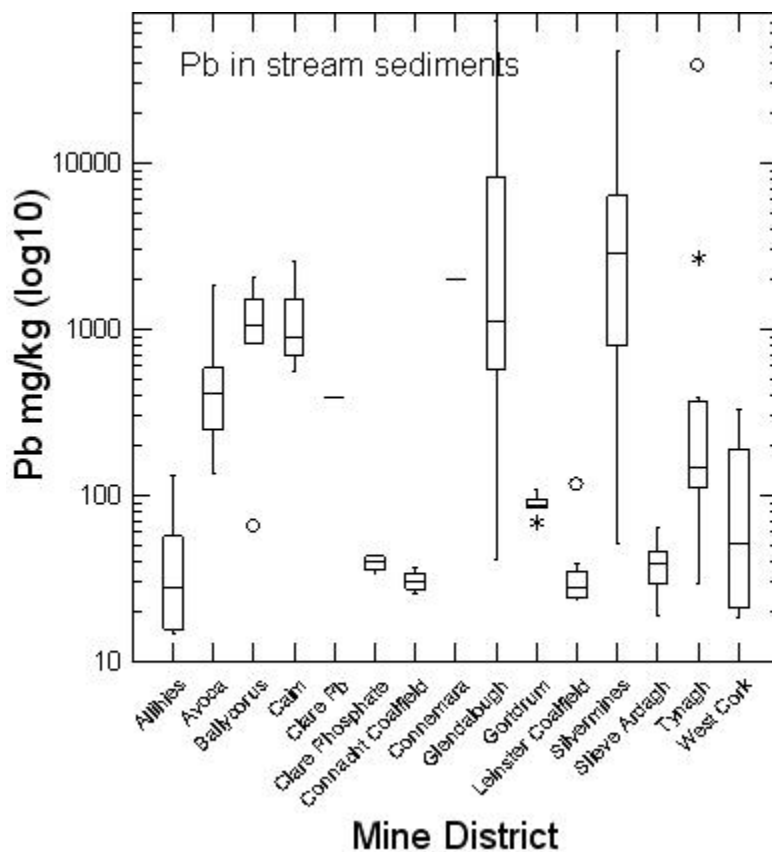


Fig. 31 Pb in stream sediments in mine districts

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 isotopic 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

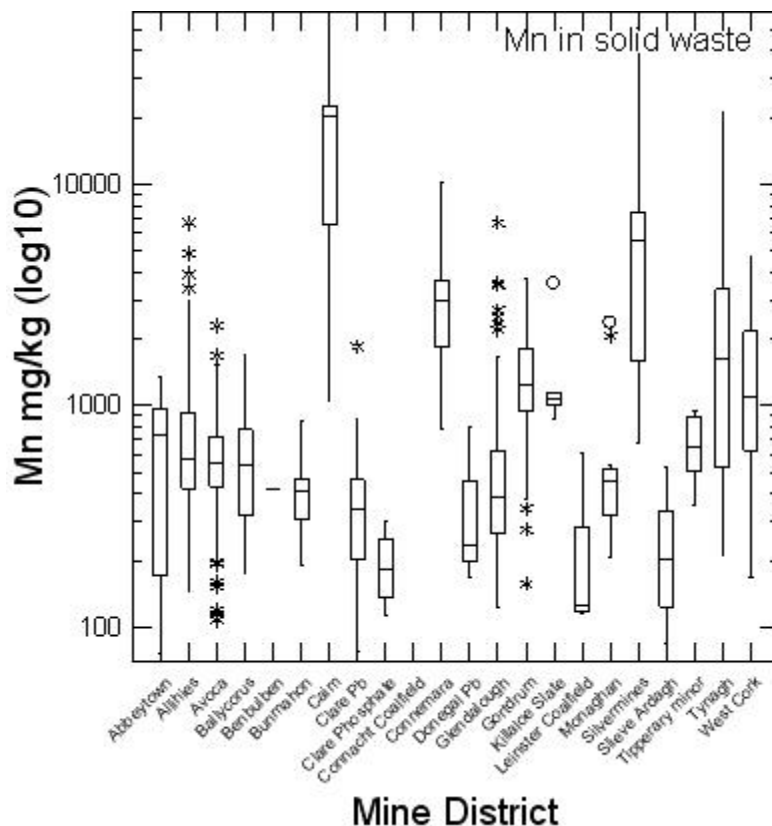


Fig. 32 Boxplots of Mn (log scale) in solid mine waste v mine district

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

$\mu\text{g/l Pb}$	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 $\mu\text{g/l}$, 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.

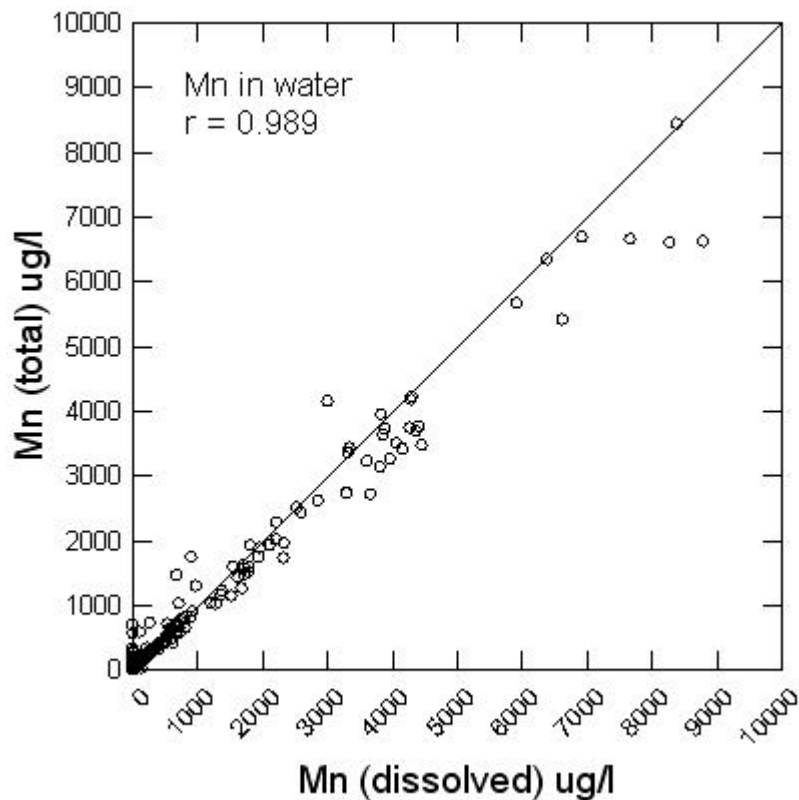


Fig. 33 Total v dissolved Mn, all samples (<10,000 $\mu\text{g/l}$)

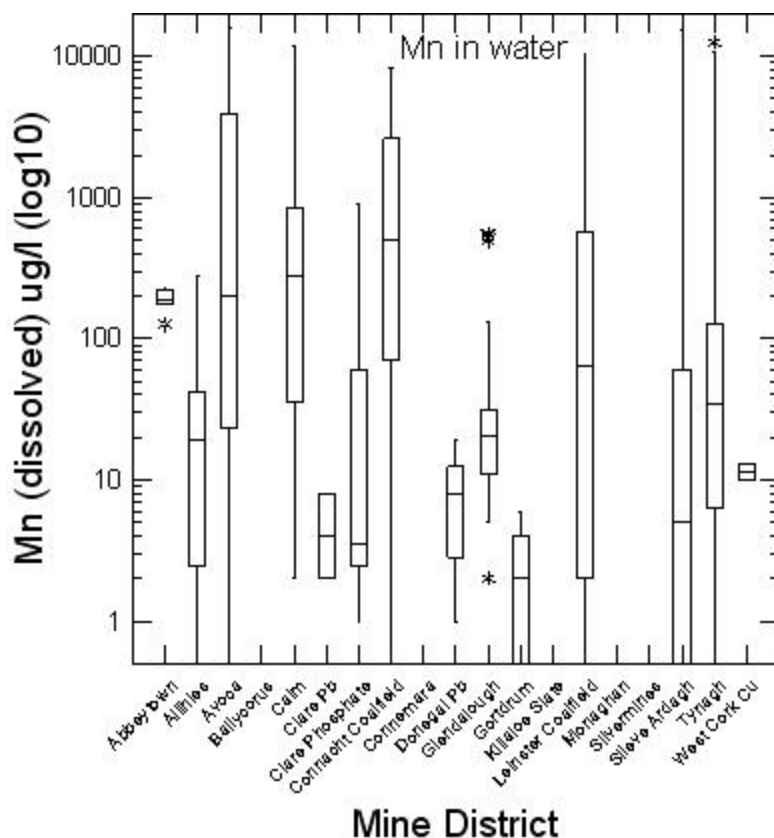


Fig. 34 Mn (dissolved) in all waters analysed, by mine district (log scale)

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).

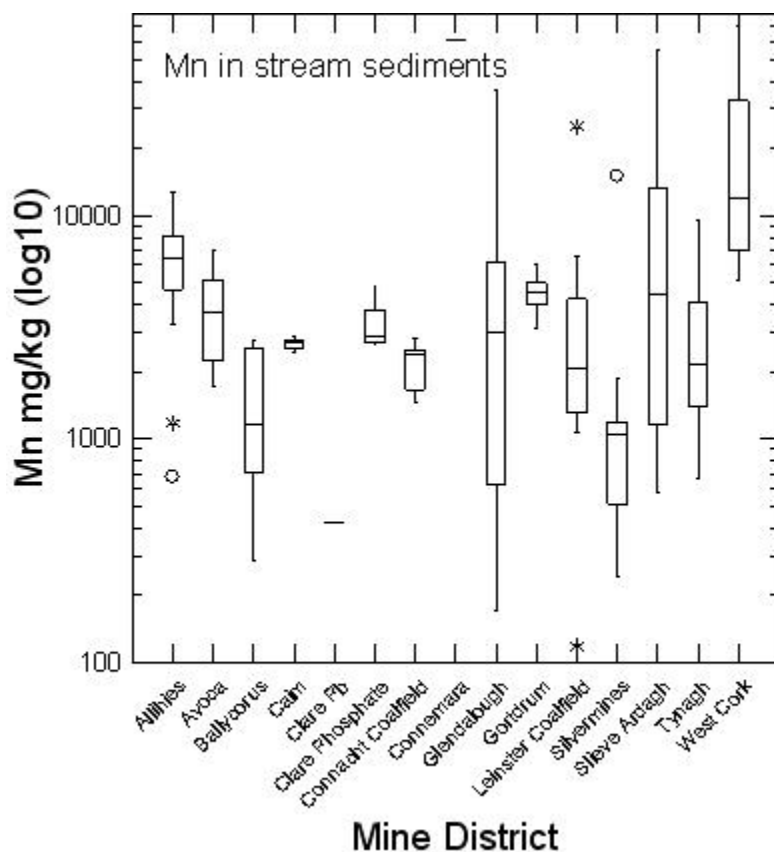


Fig. 35 Mn in stream sediments in mine districts

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. Methylmercury 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.

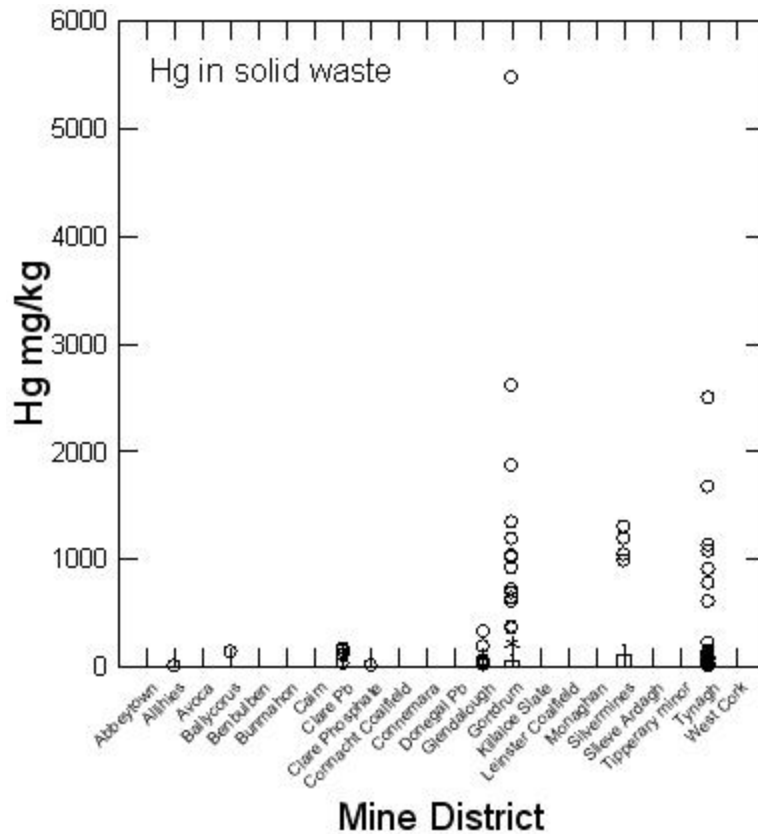


Fig. 36 Measured Hg in solid waste v mine district

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 coordination (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)₉S₈), 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

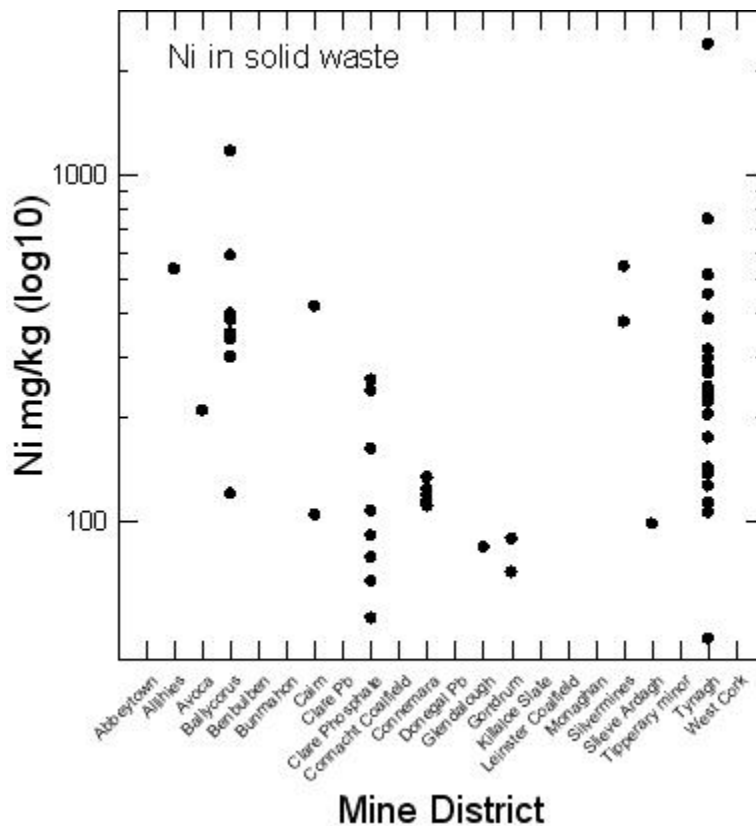


Fig. 37 Scatterplot of Ni v. mine district for HMS-IRC solid waste analyses

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

$\mu\text{g/l Ni}$	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 $\mu\text{g/l}$ (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 $\mu\text{g/l}$) 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.

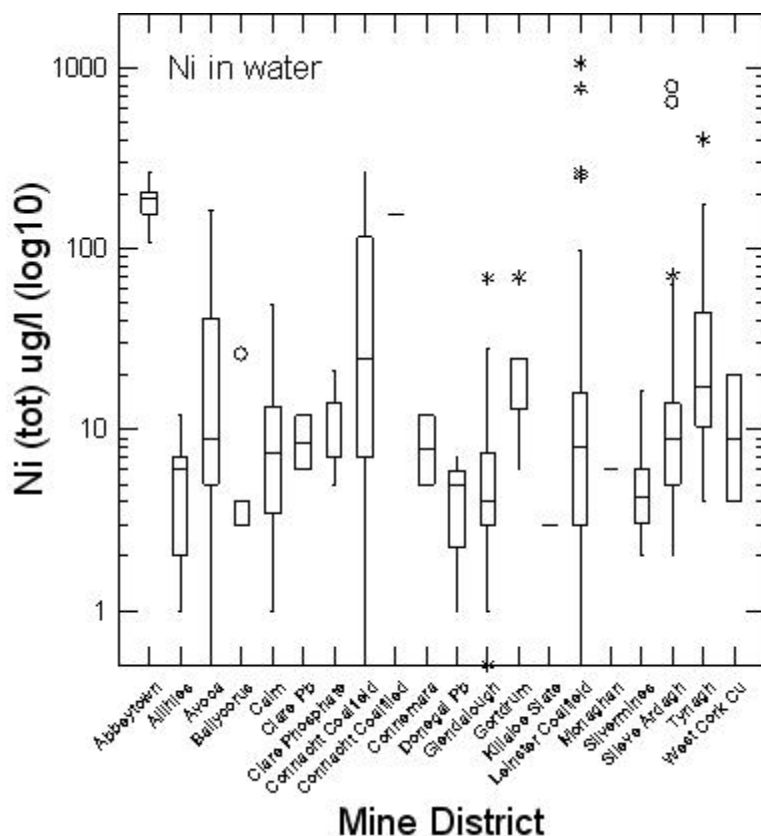


Fig. 38 Total Ni in all waters analysed, by mine district (log scale)

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

$\mu\text{g/l Ni}$	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.

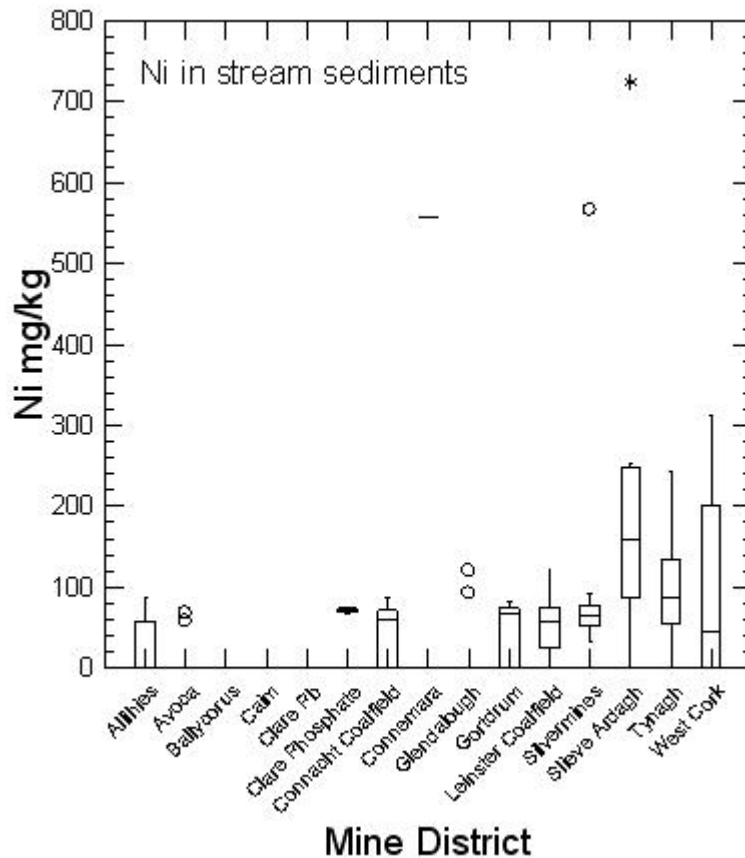


Fig. 39 Boxplot of Ni in stream sediments across all districts

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 $\mu\text{g/l}$ Se. The Canadian water quality guideline for protection of aquatic life is 1 $\mu\text{g/l}$ (Solomon 2007); the Irish Drinking Water standard is 10 $\mu\text{g/l}$.

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 $\mu\text{g/l}$; 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.

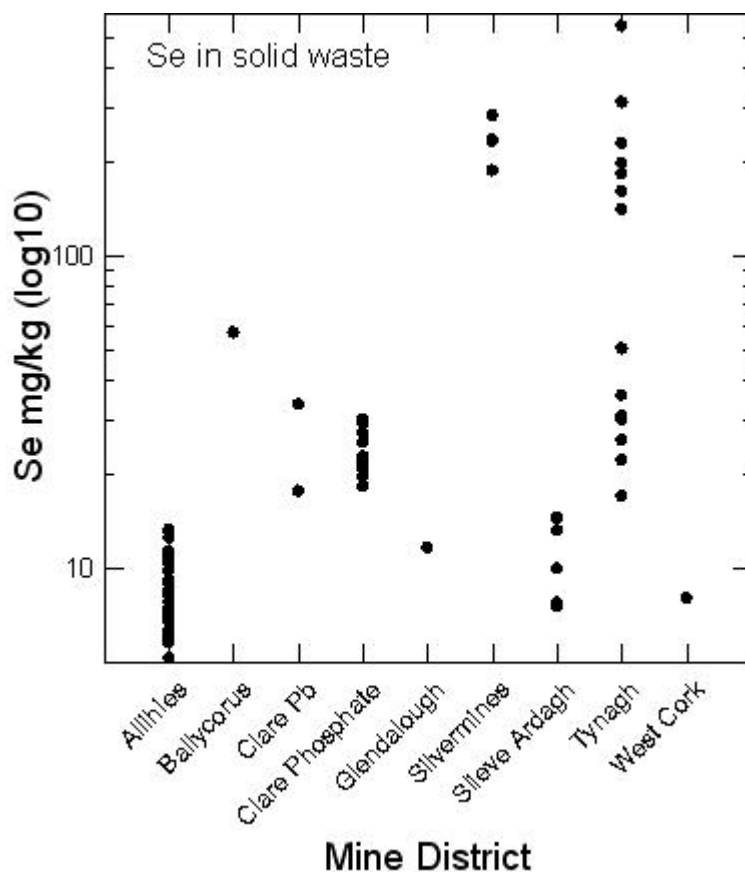


Fig. 40 Scatterplot of Se in solid waste, by district (log scale)

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

$\mu\text{g/l}$ 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 $\mu\text{g/l}$, 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 $\mu\text{g/l}$. This is an unusually very high concentration for which no obvious explanation exists. Dissolved Se in this sample was 3 $\mu\text{g/l}$. The other sample with total Se > 10 $\mu\text{g/l}$ 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** (Ag₂S), **argentopyrite** (AgFe₂S₃), and various antimonides, arsenides and tellurides. Sulphosalts include **proustite** (Ag₃AsS₃) and **tetrahedrite-tennantite** ((Cu,Fe,Ag)₁₂(Sb,As)₄S₁₃) (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 argyria. 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).

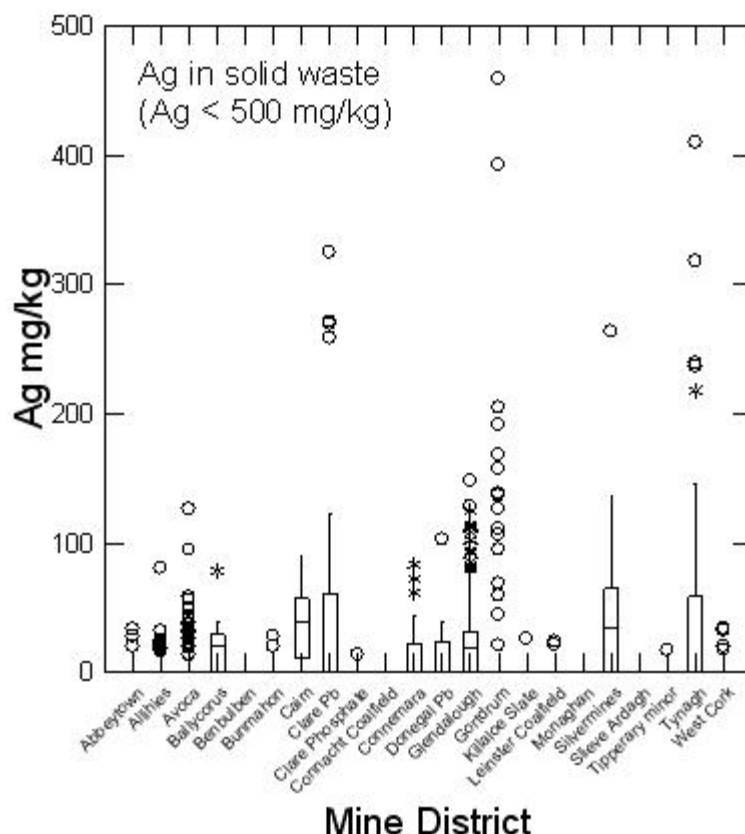


Fig. 41 Boxplots of Ag in solid waste, by district (log scale)

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, Benbulbin 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 Th⁴⁺ ion with an ionic radius comparable to U⁴⁺ and Ce⁴⁺. A considerable number of isostructural compounds of Th, Ce, U and Zr exist (Wedepohl 1978). Pure Th minerals such as **thorianite** (ThO₂) or **thorite** (ThSiO₄) 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)(PO₄,SiO₄)). ThO₂ and UO₂ form a solid solution series and Th is usually present in CeO₂. Unlike UO₂, ThO₂ 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.

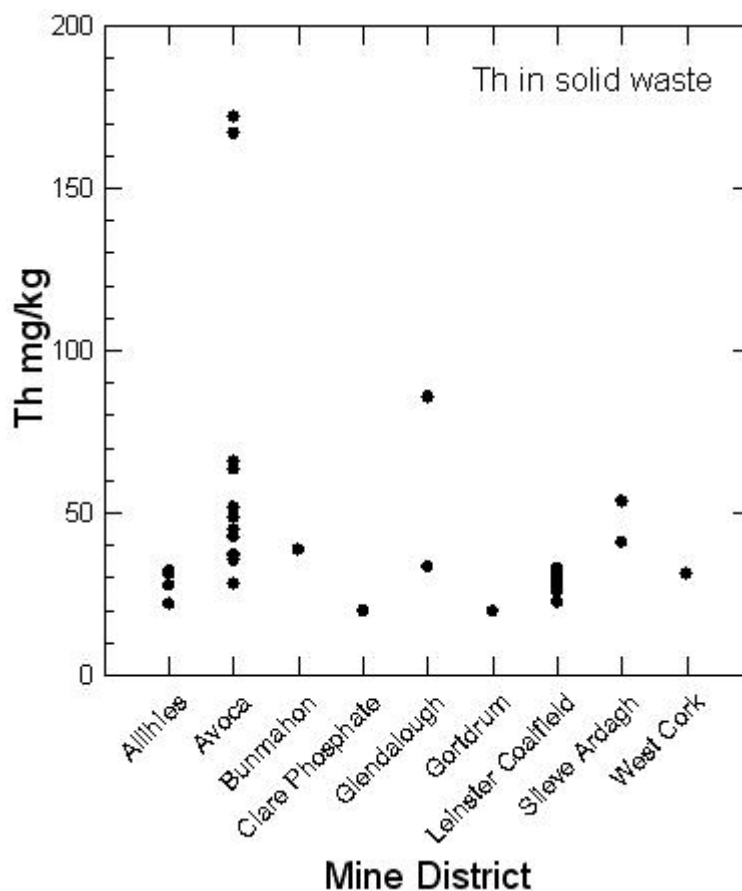


Fig. 42 Scatter plot of Th in solid waste, by district (log scale)

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 U⁴⁺, U⁵⁺ and U⁶⁺ 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 ($\text{UO}_2 - \text{U}_3\text{O}_8$ - 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** ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8-12\text{H}_2\text{O}$) and **torbernite** ($\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$) (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.

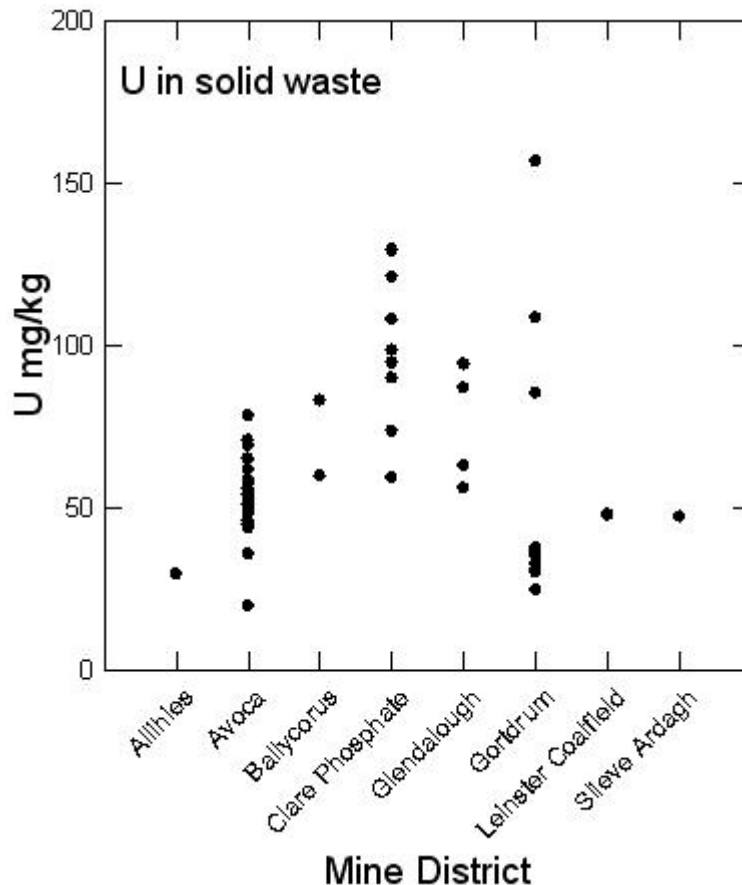


Fig. 43 Scatter plot of U in solid waste, by district (log scale)

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.

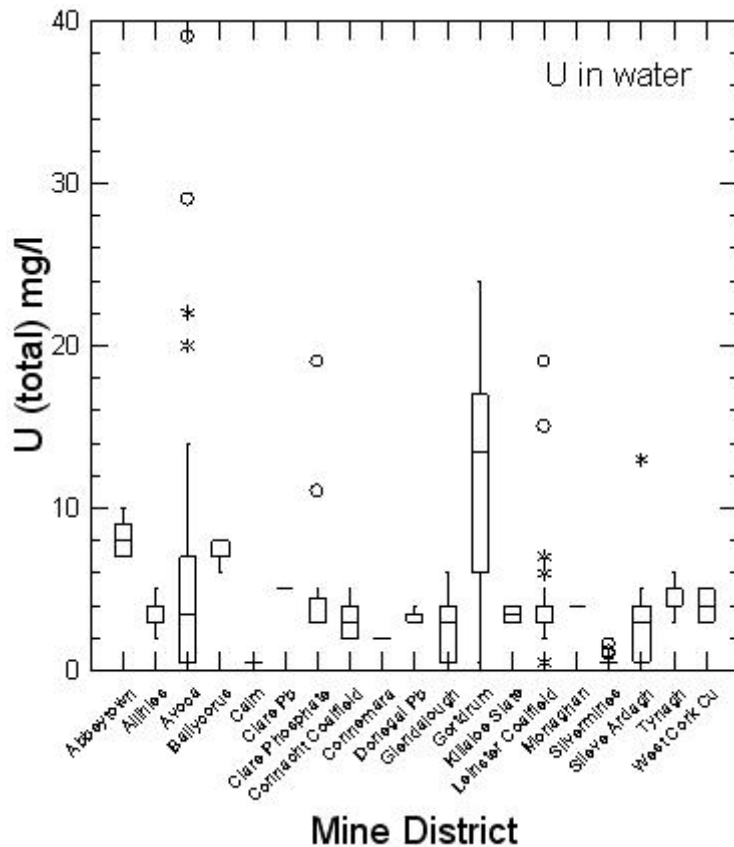


Fig. 44 Boxplots of U (total) in all water samples analysed, by district

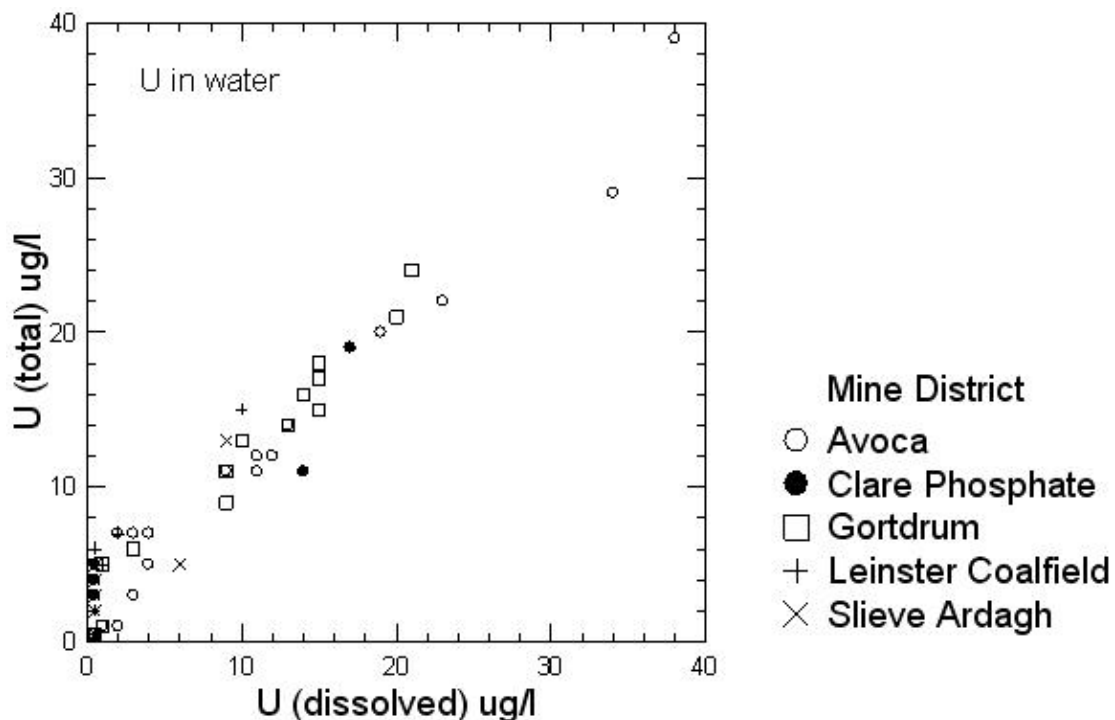


Fig. 45 Scatterplot of U (total) v U (dissolved) for selected mine districts

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 $\mu\text{g/l}$. 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.

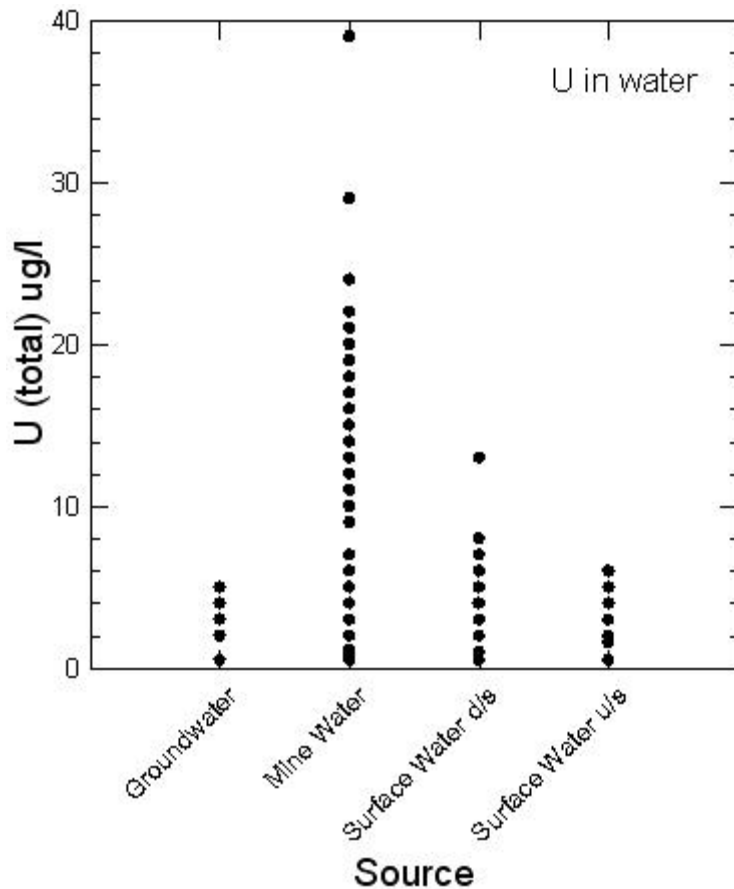


Fig. 46 Scatterplot of U (total) v water source

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.

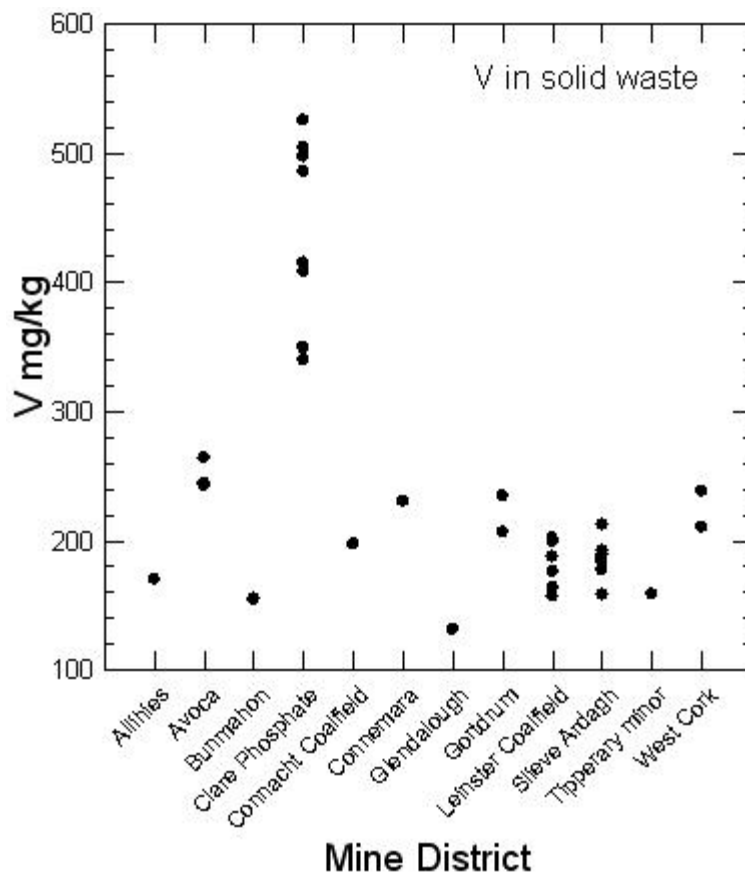


Fig. 47 Scatterplot of V in solid waste samples (> detection limit)

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 $\mu\text{g/l}$; the rest had a concentration of 3 $\mu\text{g/l}$ 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.

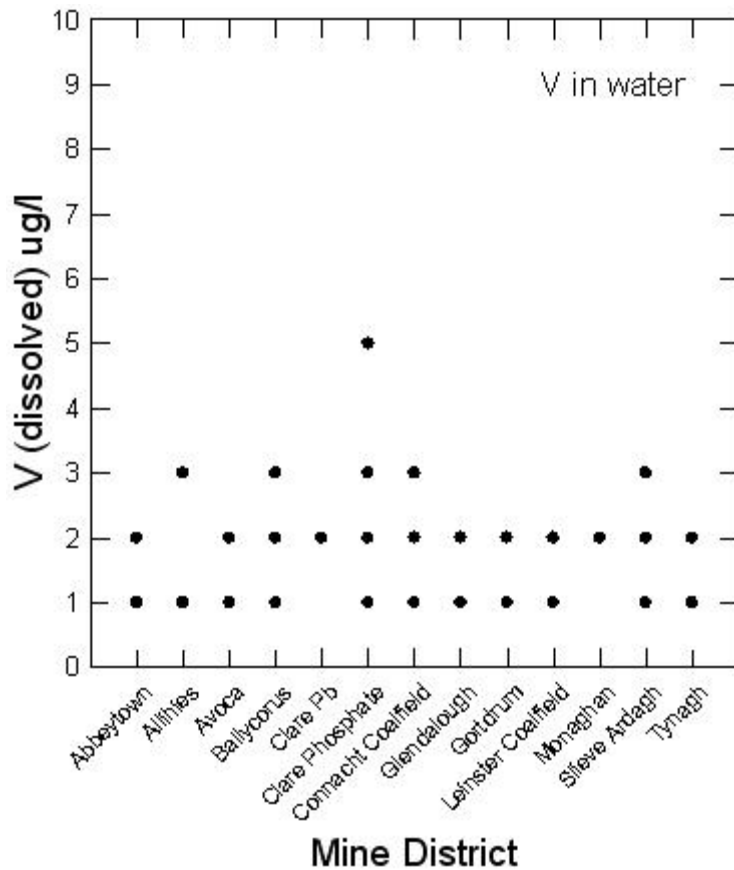


Fig. 48 Scatterplot of V (dissolved) in water, by district

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 $\mu\text{g/l}$ 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)₄S₁₃), oxides including **zincite** (ZnO); carbonates, e.g. **smithsonite** (ZnCO₃) 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).

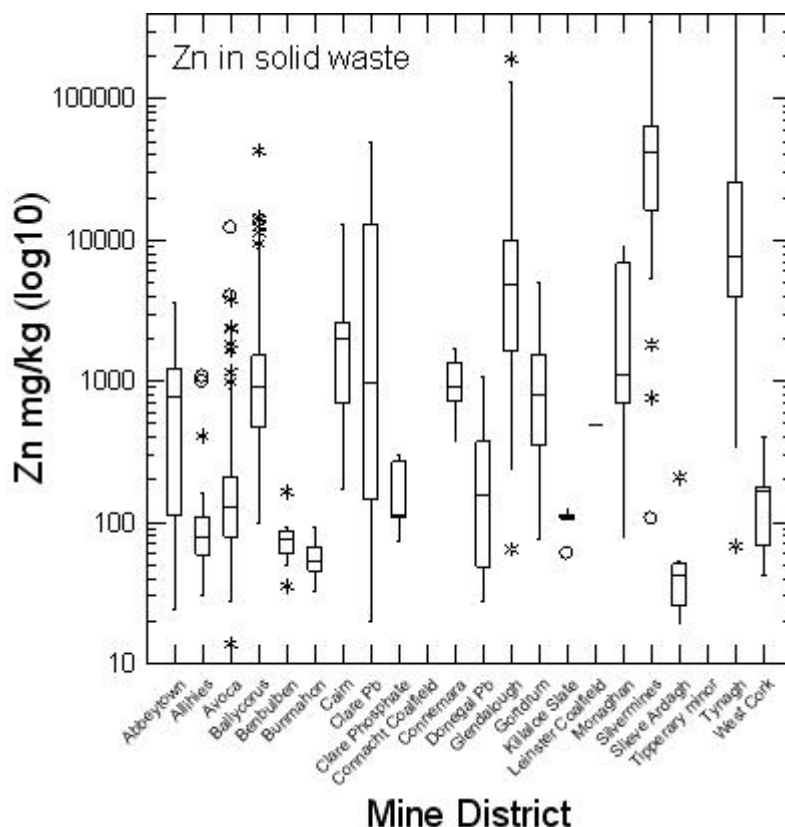


Fig. 49 Boxplots of Zn (log scale) in solid mine waste v mine district

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 CaCO₃) to 100 µg/l (hardness > 100 mg/l CaCO₃). 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 CaCO₃, 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 CaCO₃), 15 µg/l (hardness = 100 mg/l CaCO₃), 90 µg/l (hardness = 200 mg/l CaCO₃), 165 µg/l (hardness = 300 mg/l CaCO₃) and 240 µg/l (hardness = 400 mg/l CaCO₃). On this basis, over 80% of surface water samples analysed for HMS-IRC, with hardness < 300 mg/l CaCO₃, 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.

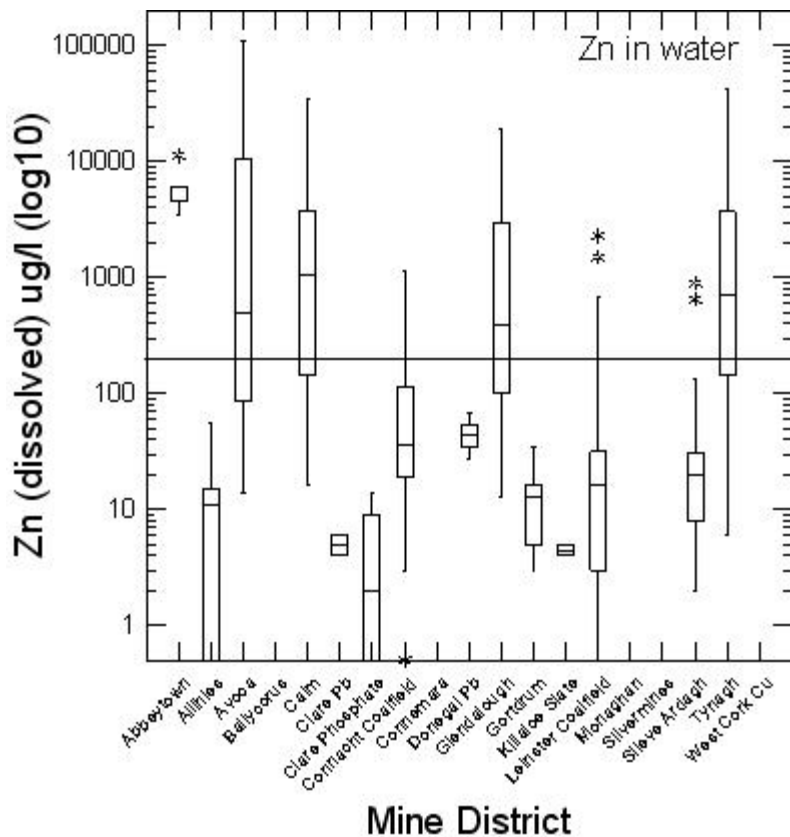


Fig. 50 Dissolved Zn in all waters analysed, by mine district (log scale)

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.

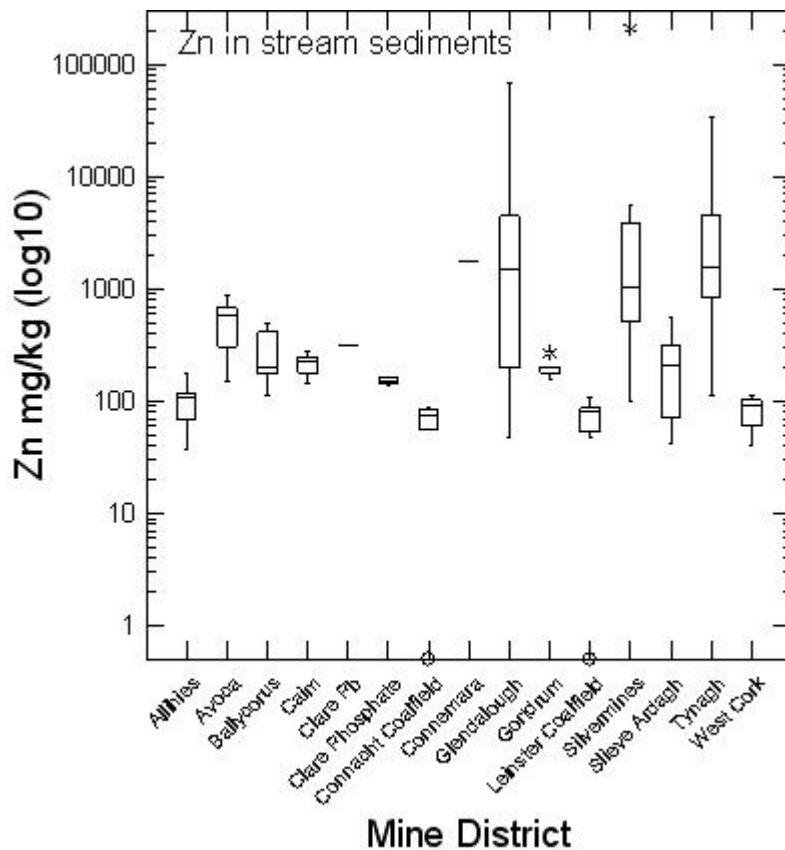


Fig. 51 Zn in stream sediments in mine districts

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.

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