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METAL CONTAMINATION OF SURFACE WATER RELATED TO PAST MINING ACTIVITY IN IRELAND

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INTRODUCTION

Old mine sites including those in Ireland may cause deterioration of surface water quality and alluvium contamination, mainly due to acid mine drainage (AMD) - metal-rich by-products of ore weathering, which may affect aquatic ecosystem and general water use.

At present three base-metal mines operate in Ireland, producing more then 3 m tones of Zn-Pb ore per year. However there are more then 100 old mine sites where coal and base-metal ore deposits (mainly sulphides) were mined in the past. As part of an ongoing project in association with the Irish EPA on abandoned and inactive mines in Ireland, a classification of the environmental conditions in respect to the risk of surface water quality deterioration caused by old mine sites was developed. This classification aims to allow an initial prioritisation of old mine sites based on their potential effect on surface water quality, and the need for site rehabilitation. Two abandoned mine sites (AMSs) Silvermines and Avoca were chosen as an illustration for the classification.

Classification aims

The main goal of the classification is to assess the possibility of surface water contamination associated with abandoned mine sites. For this reason surface water contamination is considered as an excessive concentration of mine-related compounds in surface water (mainly metal compounds) becoming greater than MAC (Maximum Acceptable Concentration).

Mine drainage chemical composition varies between sites, depending on mine ore types and host rock formations. However in general metal concentrations in mine drainage and their variety become lower when pH declines (Smith et al., 1994).

At regional scale the extent of river contamination depends on environmental conditions and mine characteristics, which together determine both the impact on surface water quality within a mined area and its further distribution along a river/stream course. Potential environmental risk for water, aquatic habitats or sources of water supply with regard to such concentrations should be studied in relation to site-specific conditions. Generally the impact on aquatic life depends on water pH and alkalinity (MAC is lower for acidic soft water) and specific combinations of metals in solution, which may increase the toxicity of each other, for example Zn and Cu in the R. Avoca (Gray, 1998).

The AMD source may be related to surface and underground mine features, contamination from which may be delivered to surface water by means of surface runoff and ground water discharge. Their contribution to river/stream flow varies throughout the year. For instance in Ireland, rivers are dominantly recharged by surface runoff during prolonged wet seasons (October-April). Ground water may prevail during dry periods in mild summers (April - October). River discharge may vary between dry and wet seasons from 3-10 l/s/km^2 to more then 150 l/s/km^2.

Due to the different nature and hydraulic regimes of surface runoff and ground water flow, the risk of surface water contamination associated with them should be considered separately with regard to seasonal flow variation and precipitation (rainfall) regime.

AMS impact on surface water quality is the greatest within a river sector, that is directly affected by mine drainage. Downstream after it has completely mixed with river water the metal load from AMS may change only insignificantly, if surface water pH/hardness remains constant. However river contamination may be reduced due to a dilution factor, which increases downstream.

Discharged into a river/stream, and therefore entering a solution with different redox conditions, metal compounds from mine drainage are precipitated or adsorbed, which results in sediment contamination. The extent of this process and the subsequent impact on the ecosystem may vary depending on environmental conditions. For areas with generally acidic conditions, it may significantly affect aquatic habitats due to ochre development (Hester and Harrison, 1995), which is mainly related to areas of Fe-rich groundwater discharge as diffusion flow or through mine adits (Gray and Sanzolone, 1996), when changes in redox conditions between surface water and its contaminated recharge are greater. It is less likely that surface runoff may cause significant ochre development.

An analysis of seasonal variation of metal concentration in surface water provides valuable information on the mechanisms of metal compound delivery into the surface water network, and may direct rehabilitation measures toward surface or underground mine features as appropriate.

Two AMSs (Silvermines and Avoca) were chosen to demonstrate the classification in practice. The sites were mined for more then two centuries by surface and underground methods. Their characteristics and parameters of water balance and hydrology of the main draining rivers (Kilmastulla and Avoca) are given in Tables 1, 2. Seasonal variations of Zn, Cu and Fe concentrations for both sites, were considered. Water samples were taken upstream from the mined area, at the location of complete mixture between river water and mine drainage and further downstream (locations 1, 2, 3 respectively). Sampling and testing were undertaken by the Irish EPA, University of Limerick (Silvermines) and Trinity College Dublin, Geological Survey of Ireland (Avoca). Metal concentrations in filtrated water were detected using AAS.

Factors influencing the impact of mine drainage on surface water quality

Since contaminants are delivered to surface water by two major pathways (surface runoff and ground water filtration), factors that determine the origin, quantity and properties (physical or chemical) of these water courses also influence the impact of AMS on surface water quality. They include the following (1) climatic conditions, particular the water balance; (2) geology of the mined area and the river/stream catchment, especially occurrence of carbonate rock; (3) geomorphology of the river/stream catchment; (4) river/stream hydrological regime; (5) hydrodynamic conditions in the catchment; (6) the relative size of the AMS within the catchment; and (7) mining method and mineral processing method adopted (Hester, R.E. and R.M. Harrison, 1995). On a basis of their input into the process of surface water contamination by AMD, these factors may be arranged into three major classes.

F_1 - Factors determining the buffering capacity of the environment in relation to AMD generation and distribution.

F_2 - Factors influencing AMD dilution.

F_3 - Factors influencing contaminant-rich discharge into surface water.

The relative importance of these factors determines the cumulative risk for surface water contamination from AMS. Each factor class (F_1, F_2, F_3) may provide conditions for low, moderate and high risk, with an assigned rank 1, 2 and 3 respectively. The cumulative risk (R) for surface water contamination is estimated by summing individual class ranks, and is classified as low (R=3-4), moderated (R=5-6) and high (R=7-9).

F_1 - factors determining the buffering capacity of the environment in relation to AMD generation and distribution. As is widely accepted, the buffering capacity of the geoenvironment depends on geological formation types, and may be altered by anthropogenic activity. In Ireland, rock formations may be grouped into three categories in relation to their ability to affect the process of AMD generation and distribution (Table 3, 4, Figure 1).

F_2 - dilution factors. The relevant size of the mined area in a river/stream catchment area determines the level of AMD dilution at any point along a river/stream current and influences the extent of surface water contamination by AMD. Together with high water buffering capacity a high dilution rate reduces the risk of surface water contamination. In general the dilution factor (D) increases downstream from the mine area and may be approximately estimated as $D = a_m / A$, where a_m is the portion of the catchment area affected by AMS, and A is the total area of the catchment.

In order to estimate the mitigating effects of AMD dilution, the D factor should be considered simultaneously with a AMD parameter (F_{amd}), describing the excess of metal concentrations in AMD within AMS (C_{amd}) over surface water standards (C_{st}) ($F_{amd} = C_{amd} / C_{st}$). For approximate assessment, typical metal concentrations in AMD and the relevant standards values may be used to estimate potential risk of surface water contamination from a mine site as follows.

	Acidic conditions			Alkaline conditions		
Metal	Typical mine drainage (*2*)	Standard for soft water (salmonid)	Required dilution	Typical mine drainage (*2*)	Standard for hard water (salmonid)	Required dilution
Zn	> 60 mg/l	0.03 mg/l	> 2000	> 6	0.3 mg/l	> 20
Cu	> 5 mg/l	0.005 mg/l	> 1000	> 1	0.1 mg/l	> 10

The risk ranks for the dilution factors are given in Table 5.

	Silvermines AMS	**Classification factors**	**Avoca AMS**	**Classification factors**
Topographical location	Northern slope Silvermines mountains (490mOD)	High surface runoff (tab. 2) **(F_3=3-RO)**	Wicklow mountains, upland areas (West and East Avoca)	High surface runoff (tab. 2) **(F_3=3-RO)**
Main ore mined	Mainly Pb, Zn, barites, but also Cu, Ag, S	*Metals considered in the paper Zn, Cu, Fe*	Cu, S	*Metals considered in the paper Zn, Cu, Fe*
Geological setting *(1)*	West wing of Kilmastulla syncline with a core formed by Lower Carboniferous formations	Provides high buffering capacity of surface water (pH>7.5; alkalinity>160mg/l) **(F_1=1)** (tab.3)	Avoca formations (sequence of Ordovician volcanic and sedimentary rocks)	Surface water is acidic and soft (pH<7; hardness<20mg/l **(F_1=3)** (tab.3)
Surface mine features	Open cast (now filled with water) Tailing ponds (66ha, 5ha) Spoil heaps	Composed of 3.5km^2, direct discharge into river from 0.7 km^2, discharge from others are received by Kilmastulla river tributaries. **(F_2=2)** (tab.5)	Open cast (dry) Spoil heaps Tailing pond	Composed 0.65km^2 *(12)* plus tailing pond 10km downstream from the mine site. **(F_2=3)** (tab.5)
Underground mine features	Underground workings (partly refilled and mainly flooded)	Partly coincide with surface features over 2.5km^2 Stretch across groundwater flow lines for about 3 km. Mainly (80%) located below a local erosion basin in the ground water recharge zone **(F_3=1-GW)** (tab.6)	Underground workings, partly flooded	Mainly coincide with surface features over 0.65km^2. Stretch across groundwater flow lines about 1km. Located above a local erosion basin in ground water recharge and discharge zone **(F_3=3-GW)** (tab.6)

Table 1. General characteristics of Silvermines and Avoca AMS and risk rank (F) for surface water contamination.

	Silvermines AMS	**Avoca AMS**
The water balance		
rainfall	1157 mm/pa	1539 mm/pa
evapotranspiration	467 mm/pa	520 mm/pa
surface runoff	564 mm/pa	834 mm/pa
ground water recharge	126 mm/pa	185 mm/pa
Catchment area		
complete mixture of river water and mine drainage	55 km^2	378 km^2
total	99 km^2	652 km^2
River flow		
base flow (dry seasons)	4.8 l/s/km^2	5.1 l/s/km^2
high flow (wet seasons)	28.3 l/s/km^2	42.5 l/s/km^2

Table 2. The water balance and rivers hydrology (parameters are given as a long average).

Risk ranking	**Rock type**	**Formations**	**Effect on surface water** *(13)*
1	Limestones	Lower Carboniferous	"Infinite" buffering capacity
2	Shale and sandstones Sandstones Slate and Shale Basalt	Upper and Lower Carboniferous Devonian Lower Palaeozoic	Medium buffering capacity, acidification restricted to 1st and 2nd-order streams and small lakes and overland runoff
3	Gneiss, schist, quartzite Granite	Late Proterozoic/Cambrian	Low or no buffering capacity, overlying waters very sensitive to acidification

Table 3. Rock formation and their effect on surface water acidification.

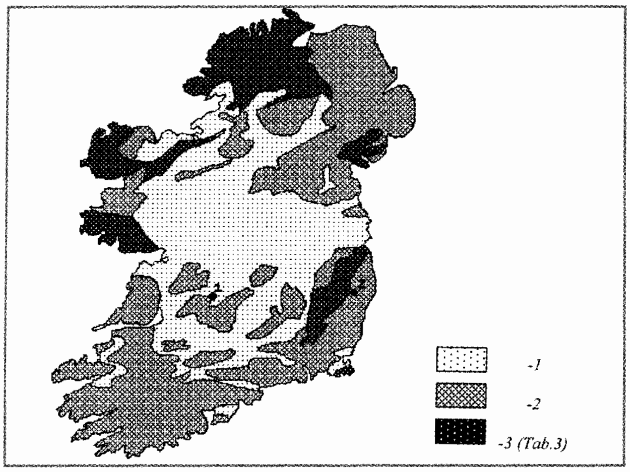

Figure 1. Location of Silvermines (1) and Avoca (2) AMSs and rock formations with relevant risk ranks.

	No buffering capacity			Medium buffering capacity			High buffering capacity		
Rock formation	Volcanic /sedimentary			Sandstones			Limestones		
River catchment	Avonmore			Blackwater			Little Brosna		
pH (downstream from the source)	mean	min	max	mean	min	max	mean	min	max
	6.7	6.0	7.0	7.1	6.5	7.7	8.2	7.9	8.3
	6.8	6.1	7.4	7.2	6.5	8.2	8.1	8.0	8.4
	6.9	5.9	7.4	7.4	6.6	8.5	8.1	7.9	8.6
	6.9	6.1	7.7	7.6	6.7	8.5	8.2	8.0	8.4
Hardness mg/l $CaCO_3$	12 - 66			17 - 277			255 - 387		

Table 4. Surface water parameters in the area of different formations occurrence.

Environmental conditions	Risk ranking			
Dilution factor	*10's*	*100's*	*1000's*	
Alkaline	3	2[1]	1	1
Neutral	3	3	2	1
Acidic	3	3	3[2]	2

Table 5. Risk ranking for various environmental conditions and dilution factors.

***F_3* - factors influencing contaminant-rich discharge into surface water.** **Surface runoff.** Under Irish climatic conditions, with high rainfall (800-2000 mm/pa) and moderate evapotranspiration (450-500 mm/pa), surface runoff (>300 mm/pa and average 46% of the water balance) may be a dominating factor influencing transport of contaminants from surface features of AMSs. Although all Irish territory is located within the same climatic zone, the intensity of surface runoff varies between different regions of the country. Since a distinguishing feature of the Irish landscape is complete vegetation cover throughout the year, such variations are determined (a) by rainfall (Figure 2a), which steadily decreases inland (Collins and Cummins, 1996), and (b) by relief, correlating with its geomorphologic setting (Figure 2b) (Aslibekian, 1999). Here Lower Carboniferous formations underlie the lowland landscape, upland areas are mainly formed either by Devonian or older formations (clastics or magmatic/volcanic rocks) or Upper Carboniferous rock formations (Davis and Stphens, 1978).

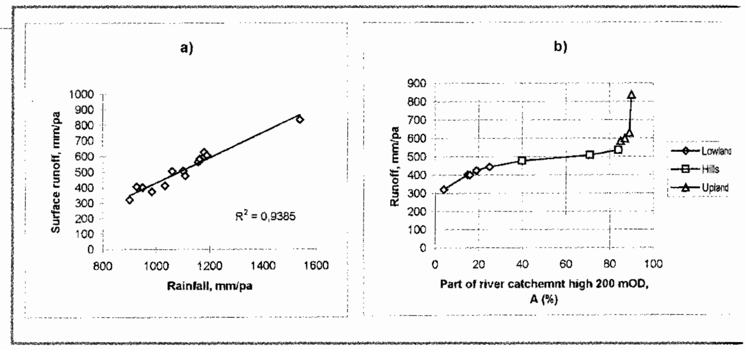

Figure. 2. Relationship between surface runoff and (a) rainfall; (b) surface elevation parameter (A %).

Therefore under Irish environmental conditions, surface runoff is a specific characteristics, as it is a complex parameter reflecting the total rainfall, relief features and geomorphologic structure. It is most intensive in the areas where surface water is most sensitive to acidification (Table 3), which increases the risk of surface water contamination in these regions. Three major runoff conditions were considered: >550 mm/pa (high risk - rank 3-RO); >450 mm/pa and <550 mm/pa (moderate risk - rank 2-RO); <450 mm/pa (low risk - rank 1-RO), corresponding with mountain/plateaux area, high hills/mountain lower slopes, and lowland respectively.

Ground water recharge in Ireland varies within the range 60-250 mm/pa, providing discharge of about 3-6 l/s/km^2 in average. The input of ground water to river/stream flow is generally very low in wet seasons when river discharge may reach more then 100 l/s/km^2. The effect of ground water effect on surface water quality is significant during summer, when river flow is less then 10-12 l/s/km^2.

The impact of ground water discharge affected by AMS depends on the location of the AMD source in relation to an aquifer (Table 6). The risk of receiving river contamination is higher when the sources of ground water contamination (mine workings) are located within the active water exchange zone of an aquifer. In hydrogeological conditions in Ireland this zone is located above the basin of erosion or within a depth of 20-30 m in lowlands (Daly,1995). If the sources of groundwater contamination are below the basin of erosion, the risk of surface water contamination is lower.

At the same time the risk may be lower if contamination sources are located in the groundwater recharge zone, for contamination may fade downgradient due to processes of a chemical nature (precipitation, sorption, exchange reactions) or hydraulic dispersion. The former is more relevant to carbonate rock occurrence, while the role of the hydraulic dispersion may become important in acid rock aquifers.

Environmental conditions	**Below the level of a local erosion basin**		**Above the level of a local erosion basin**	
Zones within GW flow	***Recharge***	***Discharge***	***Recharge***	***Discharge***
Alkaline	1[1]	1	1	2
Neutral	1	2	2	3
Acidic	1	3	3	3[2]

[1]Silvermines AMS positions; [2]Avoca AMS positions.

Table 6. Risk ranking for various environmental conditions and location of contamination sources within an aquifer.

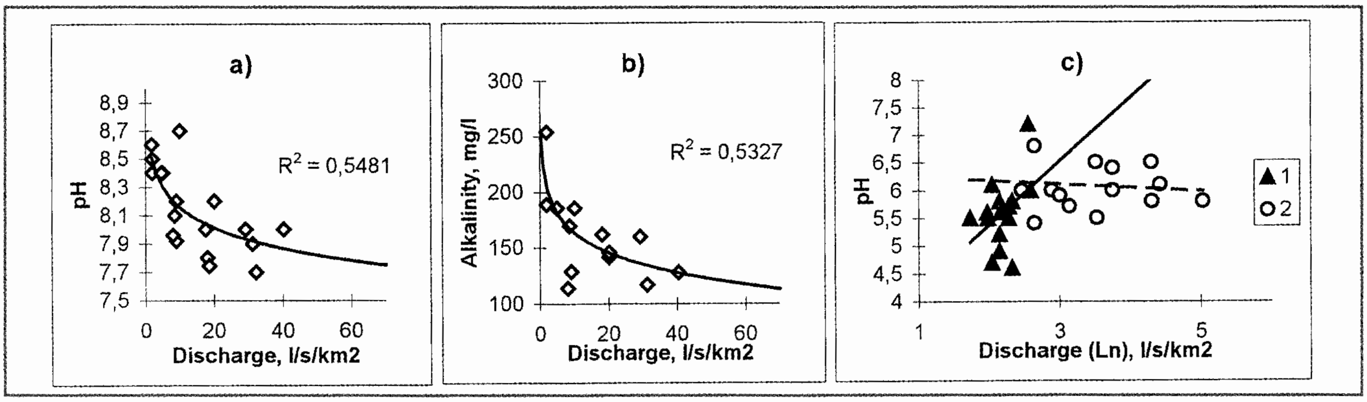

Figure 3. Relationship between pH/alkalinity and river discharge: (a-b) R. Silvermines; (c) R. Avoca.

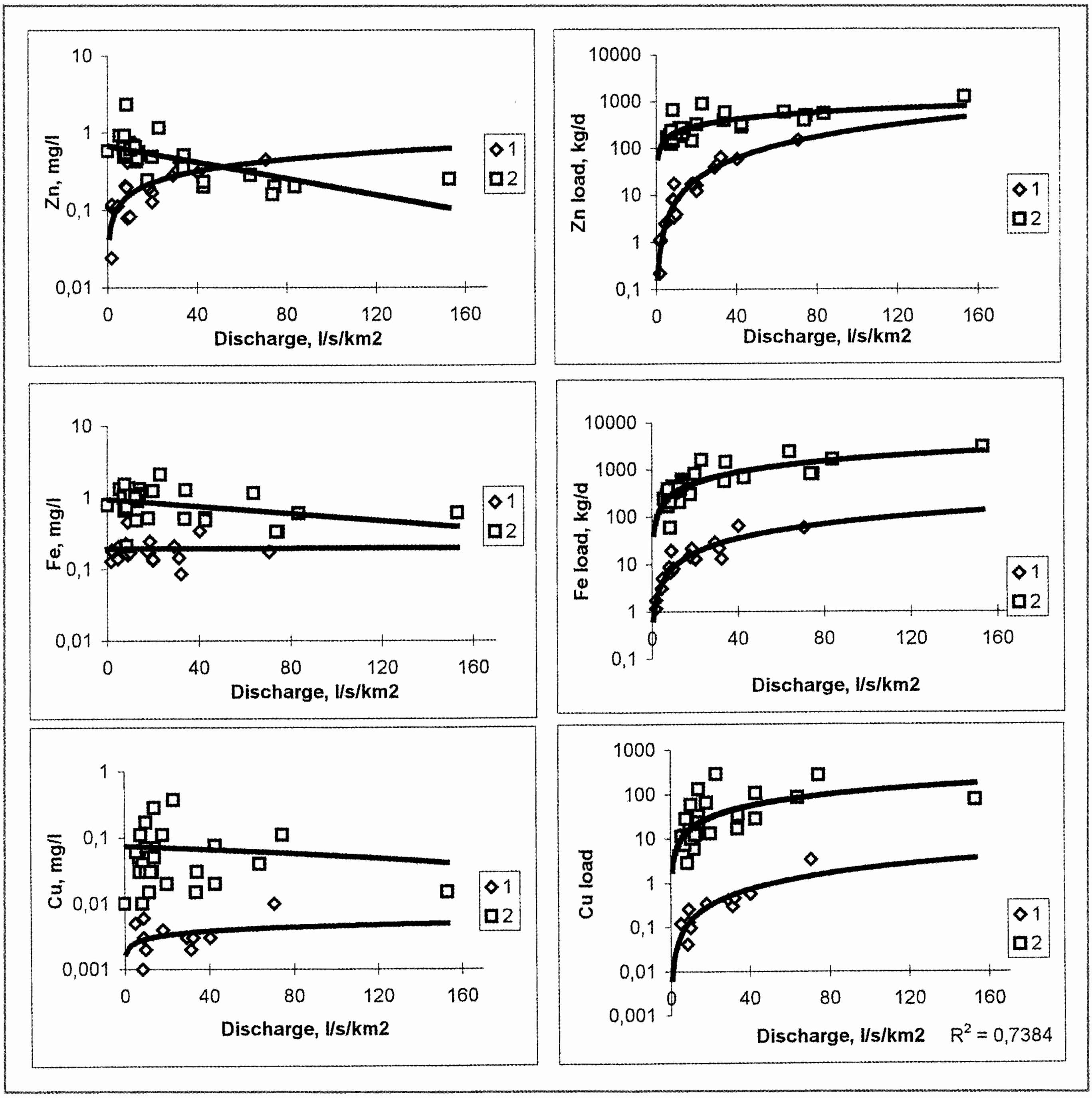

Figure 4. Relationship between metal concentration / metal load and river discharge (1-Silvermines AMS; 2-Avoca AMS).

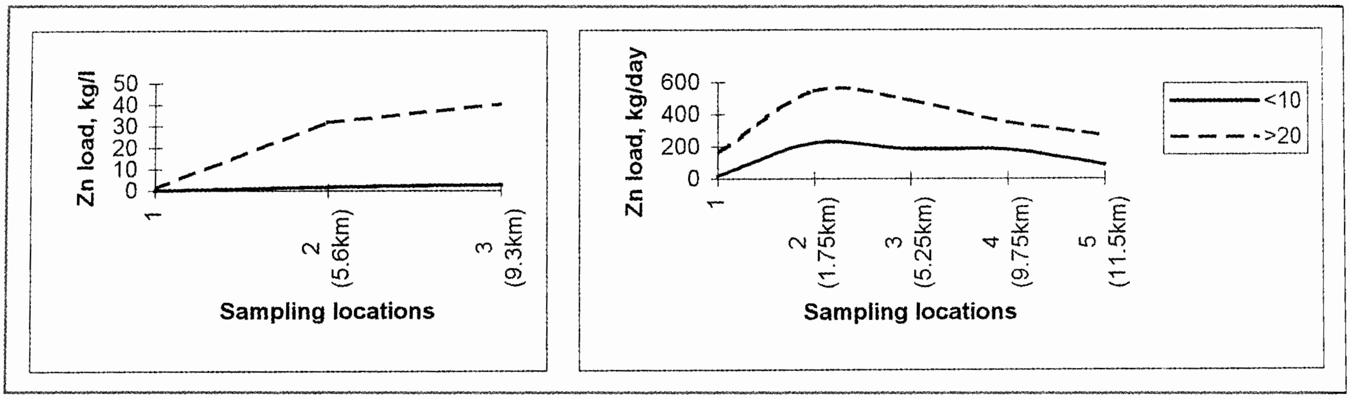

Figure 5. Variation of Zn load along the river current (a) R. Kilmastulla; (b) R. Avoca (for river discharge <10 and > 20 l/s/km^2).

RISK RANKS AND CASE-STUDIES

Often AMSs may be composed of surface and underground mine features, affecting both surface runoff and ground water quality. In such a case an assessment of the potential risk for surface water depends on the hydrological regime of a river/stream and may be estimated separately for the periods when river/stream recharge dominantly by (i) surface runoff (RO) or (ii) ground water (GW). For instance, the cumulative risk of R. Kilmastulla contamination from the Silvermines AMS is moderate (6-RO) and low (4-GW), while the cumulative risk of R. Avoca contamination from the Silvermines AMS is high for both cases (9-RO and 9-GW)

Silvermines site. The risk of surface water contamination at this site is estimated as moderate in wet seasons and low in dry seasons. When the river is dominantly recharged by ground water high pH (>8.3) and alkalinity (>200 mg/l) provide conditions in which metal concentration in water is low.

At the site, surface runoff is the main source of metal compounds in R. Kilmastulla water. During the period when river is mainly recharged by surface runoff, rainwater input reduces river water alkalinity and pH (Figure 3a-b). Hence metal concentrations increase with river discharge at location (2) (Figure 4). However downstream from the site, metal concentrations become lower mainly due to the dilution factor and metal load in the river remains unchanging (Figure 5).

Sediment contamination is significant within the mine discharge zone due to high rates of metal removal from water (C_{zn} = 2850 mg/kg (samples sieved <2 mm)). Metal precipitation is more intensive during wet seasons when surface runoff is high and river pH and alkalinity remain high (7.9-8.0 and 160-200 mg/l) (Aslibekian Childs and Moles). High river flow during these periods (> 20 l/s/km^2) transports suspended metal compounds downstream, resulting in high metal concentration in river at considerable distances from the AMS (C_{zn} = 765 mg/kg at 13 km downstream from AMS). However due to low Fe concentration at the given redox conditions, there is no ochre development on the river bed. According to bio-assay Kilmastulla river is moderately polluted, and invertebrates analysis indicates the river as unpolluted (Application for license to discharge treated mine water at the Garryard west and Gortshaneroe townland, 1998).

Avoca AMS. According to the classification, the risk of R. Avoca contamination is high for both types of contamination delivery (9-RO and 9-GW), which suggests excessive metal concentration in the river throughout a year.

Metal concentrations in R Avoca decrease when river flow increases, which provides dilution for ground water discharge into the river (Figure 4). At the same time metal load increases also, reflecting runoff input of metal compounds into the river. However due to greater rainfall rates in the catchment area upstream from the site (1539 mm/pa for catchment against 1171 mm/pa at the site (O´Sulliaghain, 1996) the dilution factor in wet seasons may be greater then in dry.

Metals remains in water downstream from the mine site: metal loads in river water decrease only slightly (Figure 5). Zn and Fe load reduces considerably when river pH rises (up to 9) at the inflow from a fertiliser factory some 12 km downstream from the site.

Seasonal pH variation in the river water within the mined area (2) is also affected by this seasonal variation in dilution. pH in the R. Avoca does not vary significantly upstream from the AMS, providing constant conditions in the inflow into the mined area (pHmean=6.7, STD=0.4), and there is little variation in pH of adit discharges also (pHmean=3.6, STD=0.2). However water pH at location (2) tends to increase within the range 4.5-6.5 when flow is lower than 10-11 l/s/km^2, reflecting the dilution of contaminated ground water discharge from the mine site. pH varies little when river discharge is higher (pHav = 6) (Figure 3c).

Significant differences between redox condition in adit discharge and R. Avoca (e.g. pH is 3.6 and 6.7) and high Fe concentration in AMD (>100 mg/l) cause the high rate of ochre development, significantly damaging river habitats (Herr and Gray, 1997). Zn concentration in alluvium is 1187, 330 and 966 mg/kg at the AMS, at the sampling location (2) and after the fertiliser factory outflow respectively (samples sieved <63 µm).

Seasonal variations of metal concentrations in adit discharges may provide more details on the process of R. Avoca contamination. Metal concentration curves (Figure 6) demonstrate a cyclical nature of their seasonal variation: at the aquifer refilling stage Cu concentration becomes lower, while Zn and particularly Fe concentrations are greater. This suggests higher Cu concentration in the R. Avoca in the early summer, than in the early autumn, which was confirmed during site investigations.

	May-June (pH=5.5)	August-September (pH=5.5)
Cu	0.054 mg/l	0.035 mg/l
Zn	0.63 mg/l	0.68 mg/l
Fe	0.95 mg/l	1.00 mg/l

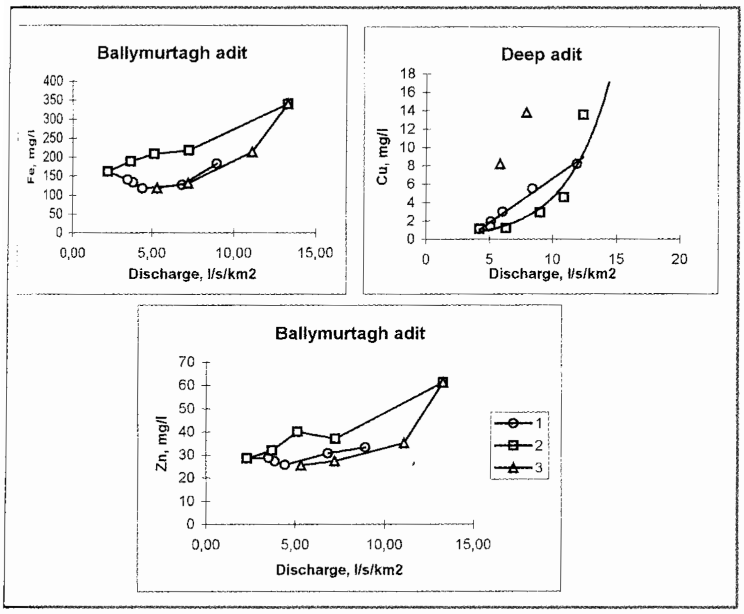

Figure 6. Relationship between Avoca adits discharge and metal concentrations (aquifer discharge: spring/summers '94 (1) and '95 (3), and recharge: autumn/winter '94/95 (2)).

CONCLUSIONS

1. The risk of surface water contamination from old mine sites is determined by environment characteristics and mine site parameters. Factors that strongly influence the process of surface water contamination fall into three classes. They include buffering capacity of the environment, the AMD dilution factor, and the mechanisms of mine drainage delivery to the surface water (by surface runoff or ground water).
2. The cumulative risk of surface water contamination was qualitatively classified as low, moderate or high. This allows ranking of abandoned and inactive mines in Ireland in relation to their environmental impact on surface water. Applicability of the classification was demonstrated in two case studies which differed mainly in relation to their environmental setting.
3. This approach to risk assessment allows evaluation of the contamination input, related to surface runoff or ground water discharge, into surface water. It identifies also appropriate approachs to AMS rehabilitation and monitoring measures. For instance the site rehabilitation programme in the Silvermines AMS case should be focused on surface runoff diversion and decontamination. Adits discharge management at the Avoca AMS (Table 1) and their neutralisation, flow re-route or metal recovery measures may considerably improve river water quality though the adits provide 50-90% of river metal load throughout a year (Gray, N.F., 1998).
4. The classification may be useful for currently active Irish mines, which exploit ore deposits hosted by carbonate rocks (F1=1). The mines adopted underground mine methods, where the main workings are located far the below erosion basin (F3=1). If surface mine features (e.g. mine waste) and leakage from them are controlled, the risk of surface water contamination from these mines after cessation is expected to be low (R<5-GW).

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