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**FIELD ASSESSMENT OF ACID MINE DRAINAGE
CONTAMINATION IN SURFACE AND GROUND WATERS**

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EXECUTIVE SUMMARY

Both sulphate and conductivity are excellent indicators of AMD contamination. This is due to sulphate being an end product of pyrite oxidation. Unlike pH, they are both extremely sensitive to AMD even where large dilutions have occurred. The advantage of using sulphate to trace AMD is that unlike other ions it is not removed to any great extent by sorption or precipitation processes, being unaffected by fluctuations in pH. These two parameters are also closely associated as would be expected, as conductivity is especially sensitive to sulphate ions. As sulphate is a difficult anion to measure directly in the field then conductivity, for which accurate and robust electrodes and meters are available, is ideal for routine field screening of water samples for AMD contamination. Sulphate analysis is normally carried out by IC which requires sample dilutions. The use of conductivity ensures accurate sulphate analysis by selecting ideal dilutions. There is also potential to use conductivity to predict approximate concentrations of key metals when the pH of the water is within their respective solubility ranges.

Conductivity can be used to predict sulphate concentration in both AMD and contaminated surface waters using regression analysis. Most accurate predictions are achieved by using equations given for specific conductivity ranges or AMD sources. However, for general use with AMD (including raw AMD, surface runoff from spoil and workings, and leachate streams or adits) then sulphate (y) can be predicted from the conductivity ($\mu\text{S}/\text{cm}$) (x) using the equation:

$$y = -1974 + 1.67x$$

For impacted surface waters the general equation below should be used:

$$y = -69.5 + 0.77x$$

INTRODUCTION

Acid mine drainage (AMD) is a major pollutional problem throughout the world, adversely affecting both surface and ground waters. It is caused by the oxidation and hydrolysis of metal sulphides (in particular pyrite) in water permeable strata or in spoil dumped on the surface. This results in the formation of several soluble hydrous iron sulphates, the production of acidity and the subsequent leaching of metals (Nordstrom, 1982). AMD is principally associated with the mining of sulphide ores. The most commonly associated minerals being sulphur, copper, zinc, silver, gold, lead and uranium. In surface waters it is characterised by elevated concentrations of iron and sulphate, a low pH, and elevated concentrations of a wide variety of metals depending on the host rock geology. The mining and storage of coal can also give rise to AMD.

Avoca mines in County Wicklow, Ireland, are currently being studied in order to characterise AMD generation and the impact of AMD on the environment (Fig 1). At Avoca the important mineral sulphides are pyrite (FeS_2), chalcopyrite (CuFeS_2), and sphalerite (ZnS). The area has been extensively mined underground and in more recent times by open cast techniques. This has resulted in large quantities of spoil being deposited on the surface. AMD is produced by chemical and biological action on the surface spoil, as well as within the underground workings which are partially flooded.

Acid mine drainage (AMD) can cause widespread and often intermittent pollution (Kelly, 1988). Therefore it is necessary to be able to identify contaminated waters in the field in order to rationalise sampling and to design monitoring programmes.

Also, both cation and anion analysis of AMD, and AMD contaminated waters, frequently requires high dilutions of original samples (>10,000 dilution for raw AMD). So in order to identify dilution ranges a rapid screening method for the samples is required.

While pH is a useful indicator of AMD contamination, elevated pH can be due to other causes such as forestry, acid precipitation, natural fulvic and humic acids. pH and H^+ concentration become progressively insensitive to AMD contamination as dilution occurs (i.e. where pH is >4.0), also they

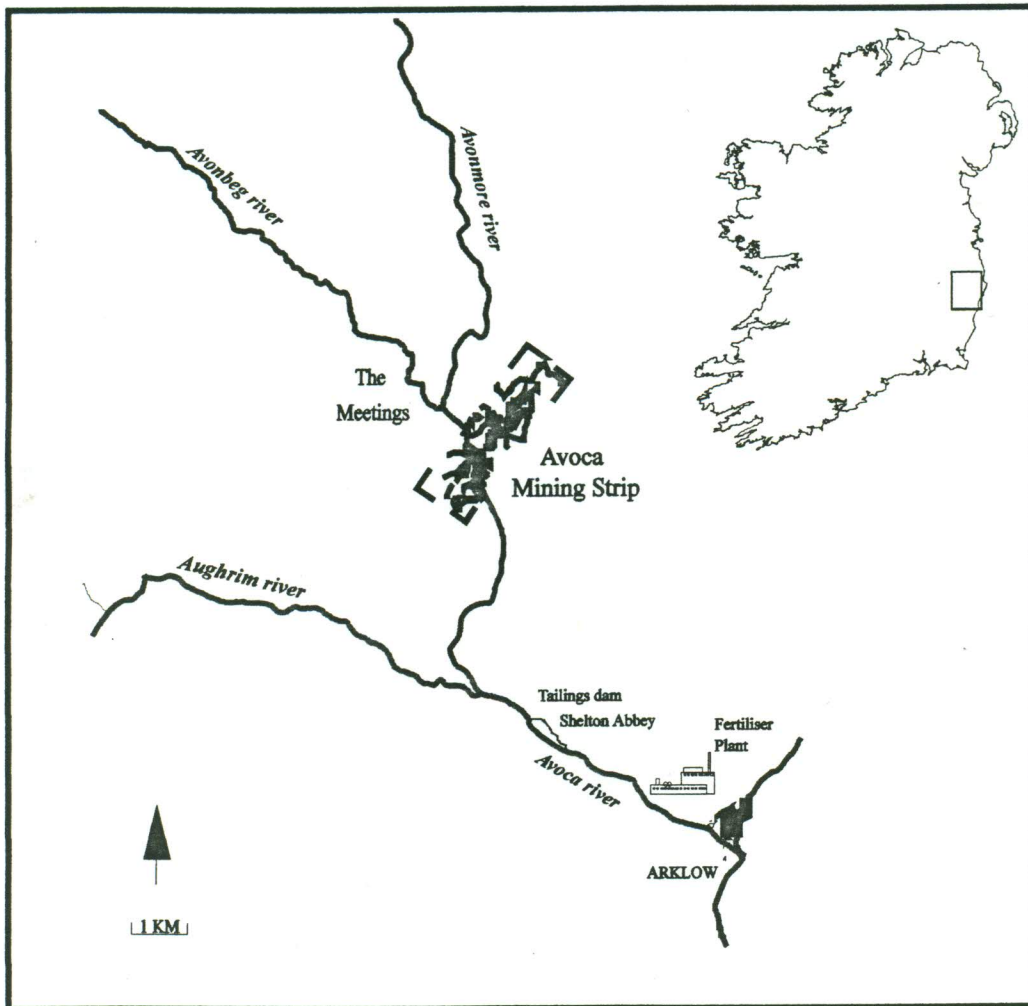


Fig. 1. The location of the Avoca mines in the Avonmore-Avoca catchment of County Wicklow in Ireland. The location of the main tailings dam and the fertilizer factory, which once used the pyrite for sulphuric acid production, is also shown.

can not be used to quantify the strength of AMD or its relative impact.

A number of alternative parameters are explored with the aim of identifying a rapid field and laboratory assessment of AMD.

METHODS

Water samples were filtered in the field through a 0.45 μ m pore diameter Millipore cellulose nitrate membrane, and stored in high density plastic bottles. Although conductivity and sulphate concentrations were found to be very stable over time, they were analysed within 24 hours of collection. Conductivity and pH were also measured within 1 hour of collection in the field. Water samples for cation analysis were acidified with nitric acid and stored at 4°C. All analysis was carried out using standard methods (APHA, 1989). Conductivity was measured using a WTW meter (LF196) and electrode, ion chromatography (IC) using a Dionex (2010-1) system was used for sulphate and chloride analysis, an Orion pH meter and electrode were used (SA250), while Fe, Cu, Zn and Cd were determined using flame atomic absorption spectroscopy (Perkin Elmer 3100).

RESULTS

Due to the significant difference in water quality between most of the AMD sources examined, specific sources have been considered separately. Table 1 gives the mean concentrations for the main parameters studied showing the wide variation between sources. Raw AMD arises as springs or seepage from spoil heaps, while surface runoff from the spoil occurs during heavy rainfall and is quite variable in quality. While the two sources are similar in pH, Fe and sulphate, the latter source contains significantly less metals. Leachate is raw AMD diluted by groundwater and is significantly less acidic and more diluted in terms of metal and sulphate concentrations. Drainage from the mines enters the Avoca River and its impact is assessed by comparing an upstream unpolluted site with a downstream site below the mixing zone of the leachate streams with the river water. A number of minor streams entering the river are also contaminated by AMD and these are considered as a separate source category. As with the AMD sources, the river samples are also

significantly different from one another in terms of water quality and so are considered separately (Table 1).

Table 1. Mean concentrations of main parameters in a range of acid mine drainage and associated source waters.

	n	pH	Zn (mg/l)	Fe (mg/l)	Cu (mg/l)	Cd (μ g/l)	SO ₄ (mg/l)	Conductivity (μ S/cm)
<i>Acid mine drainage</i>								
Raw AMD	21	2.7	362	1031	243	1198	10579	8010
Surface runoff	16	2.6	93	1050	48	156	5290	4019
Leachate	51	3.6	66	177	9	242	2015	2490
<i>Rivers and streams</i>								
Upstream mines	31	6.8	0.05	0.11	0.01	0	6	78
Downstream mines	11	6.1	0.58	0.61	0.03	0.91	28	113
Contaminated stream	11	4.9	5.5	13.9	2.1	5.8	507	735

Table 2 Correlation between sulphate (mg/l) and pH, zinc (mg/l), iron (mg/l), copper (mg/l), cadmium (μ g/l) and conductivity (Con) (μ S/cm). Levels of significance are $p < 0.05^*$, $p < 0.01^{**}$, and $p < 0.001^{***}$.

n	Correlation between Sulphate and						
	pH	Zn	Fe	Cu	Cd	Con	
<i>Acid mine drainage</i>							
Raw AMD	21	-0.474*	0.249	0.752***	0.986***	0.957***	0.983***
Surface runoff	16	-0.618**	0.430	0.999***	0.918***	0.924***	0.985***
Leachate	51	-0.796***	0.701***	0.881***	0.883***	0.823***	0.862***
<i>Rivers and streams</i>							
Upstream mines	31	0.202	-0.171	-0.029	0.056	-	0.430*
Downstream mines	11	-0.384	0.843***	0.617*	0.661*	0.932	0.743**
Contaminated stream	11	-0.532	0.808**	0.708*	0.693*	0.697*	0.998***

Sulphate is produced during the oxidation of sulphide minerals and so is directly related to AMD production. Unlike metal ions it is unaffected by sorption processes or precipitation. Therefore it is an ideal indicator for

AMD. The correlation between sulphate and conductivity with the other key parameters are shown below (Tables 2 and 3). Both display identical correlations, with the exception that there is only a significant association between Zn and conductivity in surface runoff and raw AMD. Sulphate and conductivity were extremely strongly correlated with each other for all types of AMD and also significantly associated in all surface waters, the strength of the correlation increasing with increasing AMD contamination.

Table 3. Correlation between conductivity ($\mu\text{S/cm}$), and pH, zinc (mg/l), iron (mg/l), copper (mg/l), cadmium ($\mu\text{g/l}$) and sulphate (mg/l) Levels of significance are $p < 0.05^*$, $p < 0.01^{**}$, and $p < 0.001^{***}$.

	n	Correlation between conductivity and					
		pH	Zn	Fe	Cu	Cd	SO ₄
<i>Acid mine drainage</i>							
Raw AMD	21	-0.628**	0.581**	0.784***	0.976***	0.976***	0.983***
Surface runoff	16	-0.703**	0.518*	0.985***	0.956***	0.926***	0.985***
Leachate	51	-0.768***	0.732***	0.900***	0.891***	0.799***	0.862***
<i>Rivers and streams</i>							
Upstream mines	31	0.218	-0.343	-0.210	0.018	-	0.430*
Downstream mines	11	-0.085	0.850***	0.699*	0.790*	0.337	0.743**
Contaminated stream	11	-0.567	0.813**	0.701*	0.702*	0.694*	0.998***

For AMD sources then both the sulphate and conductivity can be used to predict other parameters with strong correlations between pH, Fe, Cu, and Cd ($p < 0.001$). Zinc is strongly correlated with both sulphate and conductivity in the leachates ($p < 0.001$), but only conductivity is correlated with raw AMD ($p < 0.01$) and surface runoff ($p < 0.05$). In the unpolluted river metal concentrations are low and pH is near neutral, being independent of both sulphate and conductivity. Even though there are strong influences from other ions on conductivity in the unpolluted water, sulphate remained significantly correlated with conductivity ($p < 0.05$). Downstream, in the impacted area, the effect of AMD results in the elimination of the biota and heavy deposition of ferric hydroxide. While the strength of association between sulphate and conductivity improved

($p < 0.01$), only Zn is strongly correlated with either sulphate or conductivity ($p < 0.001$), with Cu and Fe less strongly associated ($p < 0.05$). In the contaminated streams a very strong association is identified between sulphate and conductivity ($p < 0.001$) with correlations between them and Zn ($p < 0.01$), Fe, Cu and Cd ($p < 0.05$) (Tables 2 and 3).

DISCUSSION

Sulphate and conductivity are closely correlated for all types of waters studied, with the strength of the association improving with increasing contamination by AMD.

Conductivity can be measured rapidly using an electrode and meter in the field, while accurate sulphate analysis requires IC analysis and so is both time consuming and restricted to the laboratory. However, conductivity can be reliably used to predict the concentration of sulphate using regression analysis. Due to the wide variation in AMD contamination of surface and ground waters, it is more accurate if predictions are made using equations for different conductivity strengths and AMD sources (Table 4). For example pH or conductivity itself can be used to distinguish the best equation to use for sulphate estimation. So for AMD (i.e. if the pH is < 4.0 and the conductivity is $> 2000 \mu\text{S/cm}$) equation (iii) should be used, while for heavily contaminated surface waters (i.e. the pH > 4.0 and the conductivity is $< 2000 \mu\text{S/cm}$) equation (ii) should be used (Table 4). Prediction of sulphate can be improved in impacted waters if the background conductivity is subtracted from the actual conductivity readings.

Fytas and Hadjigeorgiou (1995) feel that intermittent manual sampling does not adequately describe the variability of AMD, and recommend the use of continuous monitoring. Conductivity is an extremely reliable, accurate, simple and cheap parameter to monitor continuously. In contrast, sulphate is a difficult ion to monitor in the field, and especially continuously, as there is no ion-specific electrode available. Automated calorimetry can be used, however due to the presence of iron oxides in AMD and natural humic acids in rivers such as the Avoca, as well as other influences, automated sulphate analysis in the field is currently unreliable, lacks precision and is very expensive. Therefore conductivity

appears to be the ideal parameter for sampling and monitoring acid mine waters.

Table 4. Regression equations for the prediction of sulphate (mg/l) using conductivity ($\mu\text{S}/\text{cm}$). Equations are derived using various categories of data. Some equations are non-linear.

	n	Numeric	Logarimic
<i>Acid mine drainage</i>			
(A) Raw AMD	21	$y = -3029 + 1.73x$ R^2 0.966	$y = -1.33 + 1.36x$ R^2 0.988
(B) Surface runoff	16	$y = -1849 + 1.78x$ R^2 0.971	$y = -1.49 + 1.41x$ R^2 0.974
(C) Leachate	51	$y = -435 + 0.99x$ R^2 0.746	$y = -0.25 + 1.04x$ R^2 0.767
(A+B)	37	$y = -2175 + 1.69x$ R^2 0.965	$y = -1.46 + 1.40x$ R^2 0.984
(A+B+C)	88	$y = -1974 + 1.67x$ R^2 0.972	$y = -1.31 + 1.36x$ R^2 0.965
<i>Rivers and streams</i>			
(D) Upstream mines	31	$y = 3.19 + 4.24e^{-2x}$ R^2 0.186	$y = -0.57 + 0.72$ R^2 0.327
(E) Downstream mines	11	$y = 6.89x10^{(5.1e^{-3x})}$ R^2 0.566	$y = 0.24x10^{(0.38x)}$ R^2 0.616
(F) Contaminated streams	11	$y = -123.7 + 0.80x$ R^2 0.995	$y = -1.73 + 1.49x$ R^2 0.941
(E+F)	22	$y = -69.5 + 0.77x$ R^2 0.993	$y = -1.44 + 1.40x$ R^2 0.953
(D+E+F)	53	$y = -61.2 + 0.76x$ R^2 0.991	$y = -2.13 + 1.65x$ R^2 0.870
(A+B+C+D+E+F)	141	$y = -871 + 1.50x$ R^2 0.949	$y = -1.85 + 1.51x$ R^2 0.981
<i>Conductivity only</i>			
(i) Contaminated and uncontaminated waters: Conductivity <200 $\mu\text{S}/\text{cm}$	61	$y = 1.79x10^{(8.9e^{-3x})}$ R^2 0.619	$y = -3.04 + 2.12x$ R^2 0.678
(ii) Heavily impacted surface waters Conductivity <2000 $\mu\text{S}/\text{cm}$	59	$y = -51.9 + 0.67x$ R^2 0.862	$y = -2.14 + 1.65x$ R^2 0.889
(iii) AMD and leachate streams: Conductivity >2000 $\mu\text{S}/\text{cm}$	83	$y = 2252 + 1.68x$ R^2 0.965	$y = 1.27 + 1.35x$ R^2 0.963

CONCLUSIONS

Both sulphate and conductivity are excellent indicators of AMD contamination. This is due to sulphate being an end product of pyrite

oxidation. Unlike pH, they are both extremely sensitive to AMD even where large dilutions have occurred. The advantage of using sulphate to trace AMD is that unlike other ions it is not removed to any great extent by sorption or precipitation processes, being unaffected by fluctuations in pH. These two parameters are also closely associated as would be expected, as conductivity is especially sensitive to sulphate ions. Chloride was found to be a good tracer for mine waters at the Twelveheads and Wheal Jane mine complex in Cornwall by Johnson and Thornton (1987). The source of the chloride ion being either seawater infiltration or naissant waters from the granite rock beneath the mine. In the immediate Avoca mine catchment chloride is only present in very low concentrations and is independent of all the other parameters measured. As sulphate is a difficult anion to measure directly in the field then conductivity, for which accurate and robust electrodes and meters are available, is ideal for routine field screening of water samples for AMD contamination. Sulphate analysis is normally carried out by IC which requires sample dilutions. The use of conductivity ensures accurate sulphate analysis by selecting ideal dilutions. There is also potential to use conductivity to predict approximate concentrations of key metals when the pH of the water is within their respective solubility ranges.

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$$y = -1974 + 1.67x$$

For impacted surface waters the general equation below should be used:

$$y = -69.5 + 0.77x$$

Conductivity is the convenient parameter with which to monitor AMD on a continuous basis being an extremely reliable, accurate, simple and cheap.

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