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## Field assessment of acid mine drainage contamination in surface and ground water

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**Abstract** Both sulfate and conductivity are useful indicators of acid mine drainage (AMD) contamination. Unlike pH, they are both extremely sensitive to AMD even where large dilutions have occurred. The advantage of using sulfate 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 sulfate ions. Therefore, as sulfate analysis is difficult in the field, conductivity can be used to predict sulfate 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. 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.

**Key words** Acid mine drainage · Conductivity · Sulfate

### Introduction

Acid mine drainage (AMD) is a major pollution problem throughout the world, adversely affecting both surface and groundwaters. It is caused by the oxidation and hydrolysis of metal sulfides (in particular pyrite) in water-permeable strata or in spoil dumped on the surface. This results in the formation of several soluble hydrous iron sulfates, the production of acidity, and the subsequent leaching of metals (Nordstrom 1982). AMD is principally associated with the mining of sulfide ores. The most commonly associated minerals being sulfur, copper, zinc, silver, gold, lead, and uranium. In surface waters it is characterized by elevated

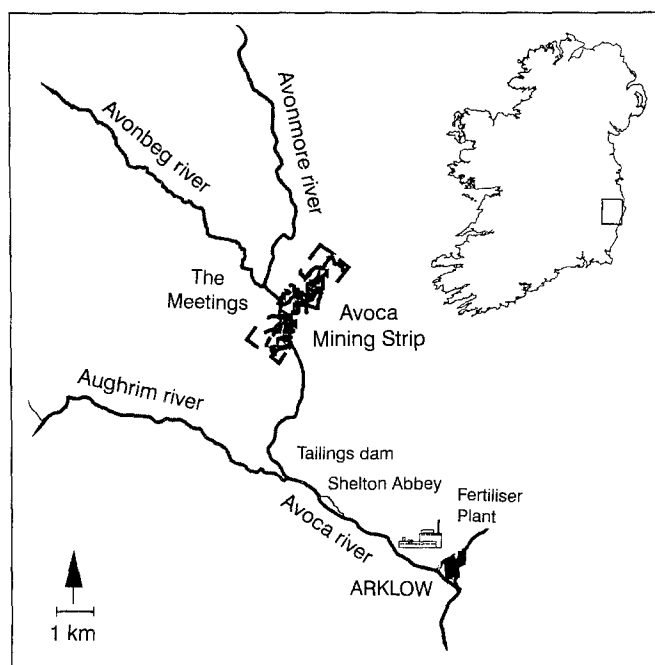
concentrations of iron and sulfate, a low pH, and elevated concentrations of a wide variety of metals, depending on the host rock geology.

Avoca mines in County Wicklow, Ireland, are currently being studied in order to characterize AMD generation and the impact of AMD on the environment (Fig. 1). At Avoca the important mineral sulfides are pyrite ( $\text{FeS}_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ), and sphalerite ( $\text{ZnS}$ ). 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.

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 rationalize sampling and to design monitoring programs. Furthermore, both cation and anion analysis of AMD and AMD-contaminated waters frequently require high dilutions of original samples ( $> 10,000$  dilution for raw AMD). Thus, 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 activity, acid precipitation, and natural fulvic and humic acids. The pH concentration becomes progressively insensitive to AMD contamination as dilution occurs (i.e., where pH is  $> 4.0$ ); it also 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  $0.45\text{-}\mu\text{m}$ -diameter Millipore cellulose nitrate membrane and stored in high-density plastic bottles. Although conductivity and sulfate concentrations were found to be very stable over



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

time, they were analyzed within 24 h of collection. Conductivity and pH were also measured within 1 h 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 sulfate and chloride analysis; an Orion pH meter and electrode were used (SA250); 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). 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 sulfate, 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 sulfate 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).

Sulfate is produced during the oxidation of sulfide minerals and so is directly related to AMD production. Unlike metal ions it is unaffected by sorption processes or precipitation. Reduction of sulfate also is unlikely to occur in surface waters that are predominantly aerobic or to be significant in most groundwaters in mining areas such as Avoca due to a lack of suitable carbon sources or low enough redox potential in groundwaters. Therefore, it is an ideal indicator for AMD. For AMD sources, then, either sulfate or conductivity can be used to predict other parameter concentrations, with strong correlations between pH, Fe, Cu, and Cd ( $P < 0.001$ ). Zinc is strongly correlated with both sulfate and conductivity in the leachates ( $P < 0.001$ ), but only conductivity is correlated with raw AMD ( $P < 0.01$ ) and surface runoff ( $P < 0.05$ ) (Tables 2 and 3). Sulfate 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.

In the unpolluted river, metal concentrations are low and pH is near neutral, being independent of both sulfate and conductivity. Even though there are strong influences from other ions on conductivity in the unpolluted water, sulfate remained 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

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

	Samples (n)	pH	Zn (mg l <sup>-1</sup> )	Fe (mg l <sup>-1</sup> )	Cu (mg l <sup>-1</sup> )	Cd (μg l <sup>-1</sup> )	SO <sub>4</sub> (mg l <sup>-1</sup> )	Conductivity (μS cm <sup>-1</sup> )
Acid mine drainage								
Raw AMD	21	2.7	362	1031	243	1198	10,579	8,010
Surface runoff	16	2.6	93	1050	48	156	5,290	4,019
Leachate	51	3.6	66	177	9	242	2,015	2,490
Rivers and streams								
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 sulfate and pH, zinc, iron, copper, cadmium, and conductivity

	Samples ( <i>n</i> )	Correlation between sulfate (mg l <sup>-1</sup> ) and					Conductivity (μS cm <sup>-1</sup> )
		pH	Zn (mg l <sup>-1</sup> )	Fe (mg l <sup>-1</sup> )	Cu (mg l <sup>-1</sup> )	Cd (μg l <sup>-1</sup> )	
Acid mine drainage							
Raw AMD	21	-0.474 <sup>a</sup>	0.249	0.752 <sup>***</sup>	0.986 <sup>***</sup>	0.957 <sup>***</sup>	0.983 <sup>***</sup>
Surface runoff	16	-0.618 <sup>**</sup>	0.430	0.999 <sup>***</sup>	0.918 <sup>***</sup>	0.924 <sup>***</sup>	0.985 <sup>***</sup>
Leachate	51	-0.796 <sup>***</sup>	0.701 <sup>***</sup>	0.881 <sup>***</sup>	0.883 <sup>***</sup>	0.823 <sup>***</sup>	0.862 <sup>***</sup>
Rivers and streams							
Upstream mines	31	0.202	-0.171	-0.029	0.056		0.430 <sup>*</sup>
Downstream mines	11	-0.384	0.843 <sup>***</sup>	0.617 <sup>*</sup>	0.661 <sup>*</sup>	0.932	0.743 <sup>**</sup>
Contaminated stream	11	-0.532	0.808 <sup>**</sup>	0.708 <sup>*</sup>	0.693 <sup>*</sup>	0.697 <sup>*</sup>	0.998 <sup>***</sup>

<sup>a</sup> Levels of significance are \**P* < 0.05, \*\**P* < 0.01, and \*\*\**P* < 0.001

**Table 3** Correlation between conductivity and pH, zinc, iron, copper, cadmium, and sulfate

	Samples ( <i>n</i> )	Correlation between conductivity (μS cm <sup>-1</sup> ) and					SO <sub>4</sub> (mg l <sup>-1</sup> )
		pH	Zn (mg l <sup>-1</sup> )	Fe (mg l <sup>-1</sup> )	Cu (mg l <sup>-1</sup> )	Cd (μg l <sup>-1</sup> )	
Acid mine drainage							
Raw AMD	21	-0.628 <sup>***</sup>	0.581 <sup>**</sup>	0.784 <sup>***</sup>	0.976 <sup>***</sup>	0.976 <sup>***</sup>	0.983 <sup>***</sup>
Surface runoff	16	-0.703 <sup>**</sup>	0.518 <sup>*</sup>	0.985 <sup>***</sup>	0.956 <sup>***</sup>	0.926 <sup>***</sup>	0.985 <sup>***</sup>
Leachate	51	-0.768 <sup>***</sup>	0.732 <sup>***</sup>	0.900 <sup>***</sup>	0.891 <sup>***</sup>	0.799 <sup>***</sup>	0.862 <sup>***</sup>
Rivers and streams							
Upstream mines	31	0.218	-0.343	-0.210	0.018		0.430 <sup>*</sup>
Downstream mines	11	-0.085	0.850 <sup>***</sup>	0.699 <sup>*</sup>	0.790 <sup>*</sup>	0.337	0.743 <sup>**</sup>
Contaminated stream	11	-0.567	0.813 <sup>**</sup>	0.701 <sup>*</sup>	0.702 <sup>*</sup>	0.694 <sup>*</sup>	0.998 <sup>***</sup>

<sup>a</sup> Levels of significance are \**P* < 0.05, \*\**P* < 0.01, and \*\*\**P* < 0.001

between sulfate and conductivity improved (*P* < 0.01), only Zn is strongly correlated with either sulfate 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 sulfate 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

Both sulfate and conductivity are useful indicators of AMD contamination. This is due to sulfate 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 sulfate 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 sulfate 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 was either seawater infiltration or naissant waters from the granite rock beneath the mine. In the immediate Avoca mine catchment, chloride is present only in very low concentrations and is independent of all the other parameters measured.

As sulfate is a difficult anion to measure directly in the field, conductivity, for which accurate and robust electrodes and meters are available, is ideal for routine field screening of water samples for AMD contamination. Sulfate analysis is normally carried out by IC, which requires sample dilutions, is time consuming, and is restricted to the laboratory (Department of the Environment 1988). Sulfate and conductivity are closely correlated for all types of waters studied, with the strength of the association improving with increasing contamination by AMD. The use of conductivity ensures accurate sulfate 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 sulfate concentration in both AMD and contaminated surface waters using regression analysis (Table 4). Most accurate predictions are achieved by using equations given for specific conduc-

**Table 4** Regression equations for the prediction of sulphate ( $\text{mg l}^{-1}$ ) using conductivity ( $\mu\text{S cm}^{-1}$ )<sup>a</sup>

	Samples (n)	Numeric			Logarimic		
Acid mine drainage							
(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
Rivers and streams							
(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	$y = 6.89 \times 10^{(5.1e-3x)}$	$R^2$	0.566	$y = 0.24 \times 10^{(0.38x)}$	$R^2$	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
Conductivity only							
Conductivity < 200 $\mu\text{S cm}^{-1}$	61	$y = 1.79 \times 10^{(8.9e-3x)}$	$R^2$	0.619	$y = -3.04 + 2.12x$	$R^2$	0.678
Conductivity < 2000 $\mu\text{S cm}^{-1}$	59	$y = -51.9 + 0.67x$	$R^2$	0.862	$y = -2.14 + 1.65x$	$R^2$	0.889
Conductivity > 2000 $\mu\text{S cm}^{-1}$	83	$y = 2252 + 1.68x$	$R^2$	0.965	$y = 1.27 + 1.35x$	$R^2$	0.963

<sup>a</sup> Equations are derived using various categories of data. Some equations are nonlinear

tivity ranges or AMD sources. Prediction of sulfate can be improved in impacted waters if the background conductivity is subtracted from the actual conductivity readings. However, for general use with AMD (including raw AMD, surface runoff from spoil and workings, and leachate streams or adits) then sulfate (milligrams per liter) ( $y$ ) can be predicted from the conductivity (microsiemens per centimeter) ( $x$ ) using the equation:

$$y = -1974 + 1.67x$$

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

$$y = -69.5 + 0.77x$$

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, sulfate is a difficult ion to monitor in the field, 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 sulfate 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.

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