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Hydrogeochemistry of coal mine drainage and other ferruginous waters in north Derbyshire and south Yorkshire, UK

David Banks[1], Sean P. Burke[2] & Colin G. Gray[3]

[1]Geological Survey of Norway, Postboks 3006 Lade, N7002 Trondheim, Norway
[2]Dept. of Civil Engineering, Cassie Building, University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK
[3]33 Cherrytree Gardens, Low Fell, Gateshead, NE9 6TY, UK

Abstract

Fifteen coal mine drainage waters from the Millstone Grit and Coal Measures of Derbyshire and Yorkshire have been compared hydrochemically with other iron-rich waters from spoil tips, natural springs and lead mine soughs in the area. The coal mine waters typically contained several tens of mg/l iron, with a range from 0.1 to 101 mg/l, and sulphate from 60 to over 1000 mg/l. The waters are undersaturated with respect to siderite. There is a strong linear correlation between iron and sulphate indicating that pyrite weathering is the dominant source of these parameters, although iron appears to be preferentially removed by precipitation or adsorption within the mines. The pH values of coal mine water are typically *c.* 6, although one water has a pH of 3.6, contains some 17 mg/l aluminium and lacks the saturation relative to gibbsite and kaolinite present in the other waters. The coal mine waters may be net acidic or net alkaline: there is some evidence to suggest that the former are typically derived from unsaturated, underdrained (i.e. drained from underneath the workings) shallow workings and the latter from saturated, overflowing workings.

The spoil tip waters are neutral to alkaline and saline. A possible explanation for this is the leaching of residual pore-water brines from the deep (several hundred metres) mined strata. The spoil tip leachates are poor in iron, which may be retained as iron hydroxides, sulphates or even siderite within the spoil.

Keywords: abandoned mines, acid mine drainage, aquifers, coal mines, hydrochemistry

Objective

Younger (1995*a*, *b*) criticized the fact that most studies of mine waters focus on the parameters directly affecting the environment, namely Fe, salinity, some trace metals and pH. He identified the fact that major ion chemistry can shed much light on the origin of, and geochemical processes controlling the composition of, such waters. This paper attempts to characterize the hydrochemical composition of drainage waters from abandoned coal mines in a former mining area of Britain, namely the north Derbyshire and south Yorkshire coalfield, with regard to a full suite of major ions and a selection of trace parameters. The composition of these waters is compared with that of other ferruginous waters in the area (spoil tip leachates, natural ferruginous waters and lead mine drainage). It is hoped that this comparison might allow characteristic features of these water types to be established, which may then be used in identifying sources of ferruginous contamination in surface waters.

As the last mining area in Britain where large-scale underground coal mining is still practised, a hydrochemical characterization of the mine waters of the study area is necessary for developing a management strategy for the operation and eventual closure of the remaining mines. It is hoped that the study will shed light on the origin of the ferruginous waters and on some of the factors controlling their composition.

Detailed descriptions of the studied sites, sampling and analytical procedures and discussions of the data can be found in the report by Banks *et al.* (1996*a*).

Introduction

Younger (1995*a*) and Dumpleton (1995) pointed out that mine water discharges from abandoned coal mines represent one of the most problematic hydrogeological legacies of a decade during which the final closure of all but a handful of the UK's coal mines has taken place. Contaminating coal mine waters may be one of (or a mixture of) at least three dominant types:

- ferruginous waters, with sub-neutral pH and high sulphate concentrations. These lead to precipitation of iron (III) oxyhydroxides (or ochre) on stream beds and their hydrochemistry is dominated by pyrite oxidation processes in workings. Younger (1995*a*) has also speculated whether siderite dissolution may be an important process in the generation of some ferruginous coal mine waters. Such waters may be net acidic or net alkaline (according to the terminology of Hedin *et al.* 1994).
- saline formation brines (Table 1). These are typically pumped coal mine waters from deep strata. Salinities may reach the 61 240 mg/l Cl^- recorded by Downing *et al.* (1970) in water from the Top Hard Coal at Pleasley Colliery, near Manfield. Brines have been

Table 1. *Selected analyses (in mg/l) of deep waters from Coal Measures strata, illustrating possible compositions of saline brines. Compare the acidic iron rich nature of the first drainage (i.e. non-equilibrium) water from Bentinck Colliery with the composition of the pumped (equilibrium) saline water from the nearby Moorgreen and Pye Hill Mines*

	Eakring 8*	Glentworth 5*	Plungar 4*	Tilmanstone Colliery, Kent†	Wardley Colliery Spring‡	St Lawrence Colliery Spring‡	Moorgreen Piper Colliery¶	Pye Hill No. 2 Colliery¶	Bentinck Colliery¶
Source	Crawshaw Sandstone	Lower Coal Measures Sandstones	Crawshaw Sandstone	1948 mine water	Colliery Brine Spring	Colliery Brine Spring	Pumped water	Pumped water	Initial Drainage Water
Na^+	8079	7005	7900	714	20 999	16 511			
K^+	96	9	31						
Ca^{2+}	792	1552	822	45	7443	4586			
Mg^{2+}	218	192	556	27	711	704			
Cl^-	14 555	11 786	14 910	795	47 393	35 329	3600–10 800	1100–3900	31 400
SO_4^{2-}	Nil	2718	342	404	1118	513			
HCO_3^-	73	549	220		207				
TDS	23 776	23 532	24 669	2107	78 180	57 690			
pH	7.1	7.4	7.8	7.7			6.9–7.9	7.3–8.0	5.7
Fe (diss)				0.02					
Fe (total)				25	399		<0.1–7	1–9	150

*From Downing & Howitt (1969)—from boreholes in the deeply concealed East Midlands Coalfield (Nil=not detected).
†From Buchan (1962)—from the concealed Kent Coalfield.
‡From Andersen (1945)—brine springs in collieries in the Tyne Coalfield, N.E. England.
¶From Lemon (1991)—from pumped shafts in the East Midlands Coalfield.

recorded in the East Midlands and Yorkshire coalfields (Downing & Howitt 1969), Tyneside (Anderson 1945; Banks *et al.* 1996*b*) and Kent (Plumptre 1959; Buchan 1962). They may contain unacceptable levels of ammoniacal nitrogen (NCB 1982; NRA 1995). The South Wales coalfield is distinguished by the rather modest salinity of its deep groundwaters (Ineson 1967).

- alkaline, hydrogen sulphide waters. These are derived from sulphate reduction within deeper workings where access of oxygen is limited. The genesis of such waters is not well studied, but methane diffusion from mined strata may be a factor in their formation. Such waters are known, for example, from Hapton Colliery in Lancashire, and are poor in heavy metals, including iron.

Younger's work on the impact of the closure of the Durham (Younger 1993; Younger & Sherwood 1993) and East Fife (Younger 1995*b*) coalfields has, at least in part, been responsible for solutions being found to water management problems in these areas. Further south in Britain lies the nation's largest coalfield; that underlying south Yorkshire and the East Midlands. It is also this coalfield that contains Britain's remaining few deep coal mines, stretching from Asfordby in Nottinghamshire in the south to Selby in north Yorkshire in the north.

The region contains a large number of ferruginous waters, but not all such waters are derived from abandoned mines. Spoil tips (Bell 1996) represent a significant source of contamination and natural ferruginous waters can be found, typically draining broken ground that contains pyrite. Drainage from abandoned boreholes in such strata may represent another source of iron-rich water.

This paper examines the major and trace element composition of four categories of water from north Derbyshire and south Yorkshire:

- mine drainage waters from abandoned coal mines
- leachates from a number of spoil tips
- natural ferruginous groundwaters
- ferruginous lead mine drainage soughs (i.e. discharges from mine drainage systems) in the Peak District of north Derbyshire.

The locations of the sampled waters are shown in Figs 1a, b and c.

Geological and historical setting

The south Yorkshire–north Derbyshire coalfield has been one of the UK's most productive (Allen 1995). It lies on the eastern flank of the dome-shaped Peak District antiform. Lower Carboniferous Limestone, with its rich veins or 'rakes' of lead, barite and fluorspar (fluorite) mineralization, forms the core of the antiform and the hills of the so-called 'White Peak'. The alternating dark shales and resilient sand-and gritstones of the Namurian Millstone Grit overlie the limestone and form the dramatic scarps of the 'Dark Peak'. This, in turn, is overlain by the Westphalian Coal Measures strata, on which the main towns of Sheffield, Barnsley and Chesterfield are built. The main productive seams have been (from oldest to youngest; i.e. from west to east):

- the Ganister or Alton Coal of the Lower Coal Measures. The strata adjacent to this seam have also been mined for refractory ganister for the Bessemer process in the steel industry (Gray 1976).
- the Silkstone (Black Shale) Seam. The coal is a good quality house, gas and coking coal of *c.* 1.5 m (5 ft) thickness.
- a little above the Silkstone, still in the Lower Coal Measures, is the Parkgate/Piper Coal.
- probably the main target seam in most modern coal mines has been the Barnsley/Top Hard seam of the Middle Coal Measures, a 3 m (9 ft) thick steam coal of low ash content. It is also an ideal coal for hard coke for blast furnaces.

East of the Coal Measures outcrop is a low scarp formed by the Permian Magnesian limestone, unconformably overlying the Coal Measures.

The coalfield has a history of production over several hundred years, many of the earliest mines being developed in Upper Namurian and Lower Westphalian seams in the west. The outcrop of the Ringinglow/Baslow coal near the top of the Namurian Millstone Grit often coincides with the location of early lead smelters and lime kilns, being stratigraphically and physically closest to the lead mines of the Lower Carboniferous White Limestone of the White Peak. Prior to the 16th/17th century, most mining was carried out on a 'domestic' basis. After the 17th century, coal mining blossomed as a larger-scale industry (Hopkinson 1976; Griffin 1971). The depth of workings at this time was still limited by the sough as the most effective drainage technique. Mines below the lowest drainage level could be drained by pumping using water, wind, horse or manual power, but this was not especially efficient. The Newcomen engine was invented in around 1710, allowing considerably deeper mines. The first Newcomen engines in the area under consideration were installed at Trowell Field in 1733 and Chapeltown in 1753 (Griffin 1971; Gray 1976). The concealed coalfield, below Permian cover, was first exploited by Shireoaks Colliery in 1854.

Mining activity progressed eastward to greater depths until, today, mining occurs at a number of mines at depths of up to and over 1000 m in the concealed coalfield beneath later Permo-Triassic strata. Strategically placed pumping stations control water

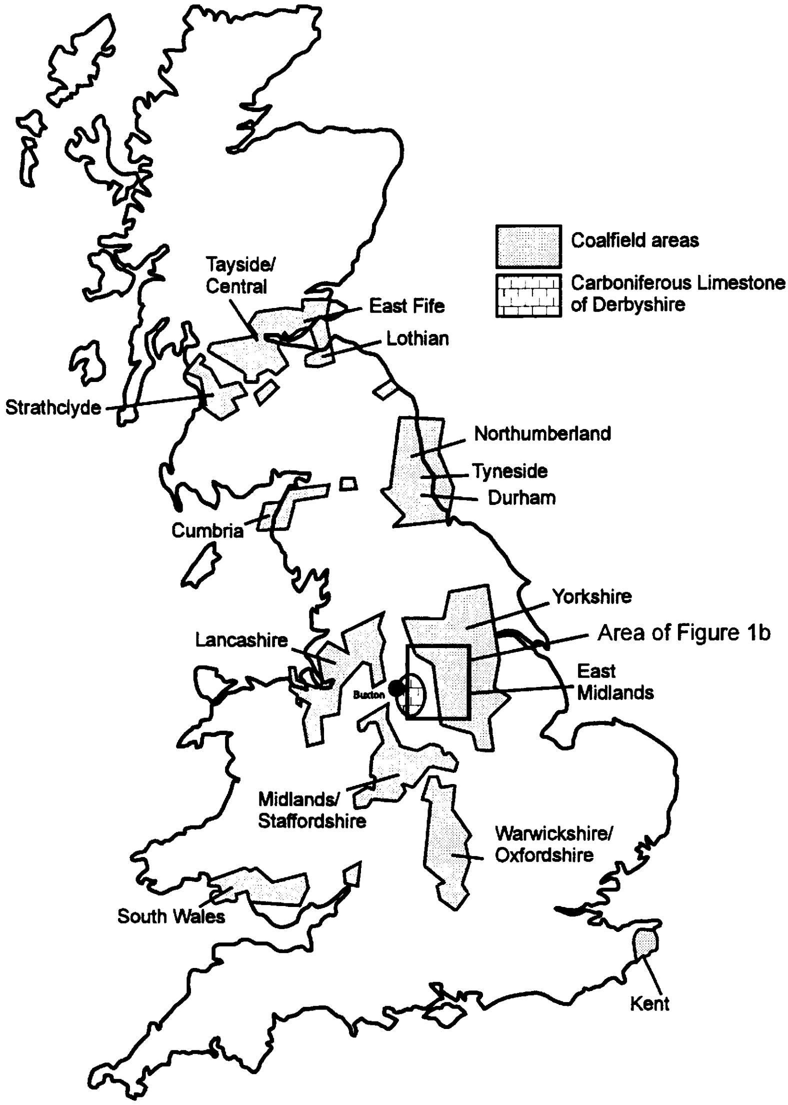

Fig. 1. (a) The coalfields of Britain. The rectangle shows the location of Fig. 1(b).

flows in the mined strata up-dip of the working mines (Gray *et al.* 1969; Downing *et al.* 1970; Awbery 1988; Lemon 1991).

The western mines are long since abandoned and are either located in isolated synclinal structures or are generally beyond the reach of dewatering pumping in the eastern and concealed coalfield. Recovery of mine water levels has thus taken place, leading to breakouts of polluting ferruginous discharges in the catchments of the Rivers Don, Little Don, Loxley, Sheaf, Dearne, Drone, Porter Clough, Rother, Hipper and Barlow Brook. Several of these are still substantially contaminating after a period of many decades. At Woolley Colliery, near Barnsley, an abandoned shaft is being pumped by the Coal Authority solely to prevent uncontrolled breakout of contaminating mine waters in the Dearne catchment. The pumped water is saline and contains *c.* 100 mg/l Fe. It is treated using a combination of settlement and constructed wetlands (Coal Authority/ IMC 1996).

The most recent mine closures (e.g. Thurcroft, Dinnington, Treeton, Kiveton Park, Pleasley, Orgreave, Silverwood) have tended to affect those mines near the eastern edge of the exposed coalfield. Mine water levels here are believed to be largely controlled by the current dewatering schemes protecting the concealed coalfield, although some water management uncertainties do still exist. Despite the lack of uncontrolled mine water

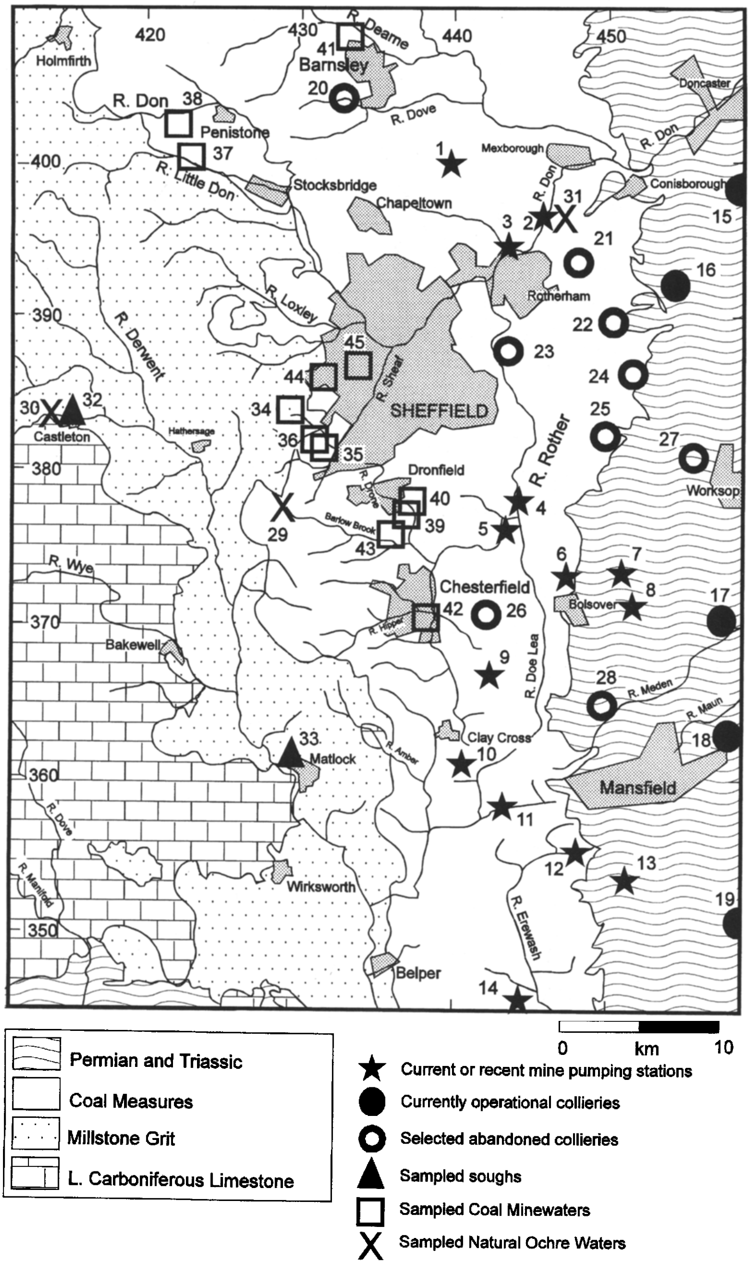

Fig. 1. (b) Map of northern Derbyshire and southern Yorkshire, showing locations of sample localities and selected other features: 1, Elsecar Pumping Station; 2, Kilnhurst P.S.; 3, Carr House P.S.; 4, Blacks P.S.; 5, Hartington P.S.; 6, Oxcroft P.S.; 7, Creswell P.S.; 8, Langwith P.S.; 9, Williamthorpe P.S.; 10, Morton P.S.; 11, Blackwell 'A'-winning P.S.; 12, Bentinck P.S.; 13, Annesley P.S.; 14, Woodside P.S.; 15, Rossington; 16, Maltby; 17, Welbeck; 18, Clipstone; 19, Calverton; 20, Strafford; 21, Silverwood; 22, Thurcroft; 23, Treeton; 24, Dinnington; 25, Kiveton Park; 26, Arkwright; 27, Shireoaks, 28, Pleasley; Sampling Localities: 29, Smeekley Borehole; 30, Mam Tor; 31, Kilnhurst Boardwalk; 32, Odin Sough; 33, Allen Hill Spaw; 34, Ringinglow Colliery; 35, Ecclesall Wood; 36, Dore Conduit; 37, Sheephouse Wood; 38, Bullhouse; 39, Mill House Unstone; 40, Unstone 2 & 3; 41, Gawber Prospect Borehole; 42, River Hipper; 43, Dunston Colliery; 44, Greystones; 45, Hunters Bar.

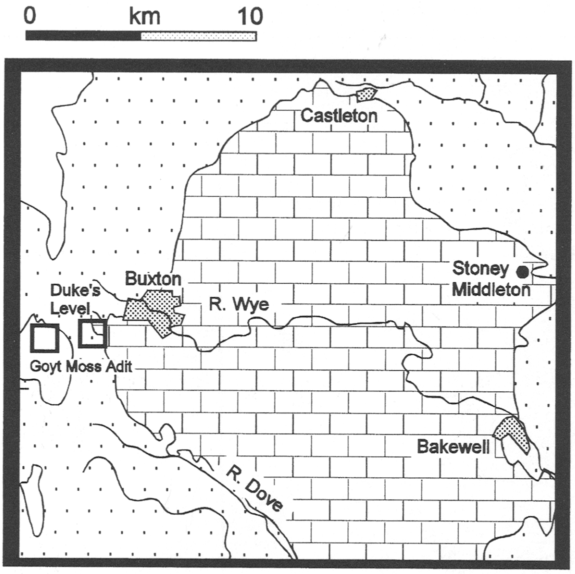

Fig. 1. (c) Map of western Derbyshire, showing locations of the Duke's Level and Goyt Moss Adit, Buxton. Legend as for Fig. 1(b).

discharges in the eastern part of the exposed coalfield, ferruginous pollution is known to occur from some of the spoil tips associated with these mines.

Mineralogy

Coal seams vary considerably in their sulphur content, ranging from 0.8% in the Barnsley, through 2.1% in the Parkgate to some 3–4% in the Ringinglow (Eden *et al.* 1957). This sulphur may exist as organic sulphur, as pyrite framboids or, occasionally, as more massive pyrite.

The Coal Measures sandstones consist of some 55–75% quartz, 24–41% feldspar and mica (both fresh and partially decomposed) and 1–4% limonite, according to samples detailed by Eden *et al.* (1957). Geochemically, this corresponds to 74–88% SiO_2, 6–13% Al_2O_3 and 0.8–4% Fe_2O_3. Siderite is probably the most common carbonate mineral, most prominently cementing mudstones and siltstones to form exploitable ironstone deposits. Ferruginous dolomites and calcite are also known within the Coal Measures sequence. Bell (1996) documents the composition of selected colliery spoils from Yorkshire.

The sampling programme

The water samples examined in this paper are derived from three separate studies undertaken at the University of Sheffield in 1994/95. Samples E20–E81 were taken in winter 1994–spring 1995 and are referred to as Series 1. Series 2 (Burke 1995) and Series 3 (Gray 1995) were taken in Summer 1995. The sampling sites are shown in Fig. 1b,c, listed in Table 2 and are described in detail in Banks *et al.* (1996*a*).

Coal mine waters

Sites for sampling coal mine waters are summarized in Table 2. Two pairs of mine waters (Bullhouse and Sheephouse Wood; Duke's Level and Goyt Moss) drain the opposite ends of the same, interconnected set of mine workings, into different river catchments.

Several of the sampled discharges (e.g. Bullhouse, Sheephouse) are derived from mine drainage adits; others (Dunston) are known to be derived from overflowing shafts. Some of the waters occur as strong seepages with no clear adit or opening visible (Unstone 2). One mine water (Gawber) is derived from an unsealed exploration borehole into the Barnsley Seam and one water (Hunters Bar) emerges from a culvert far from any known mine. It is suspected that the culvert is a storm drain, into which mine water enters at some point along its course.

All the mine waters deposit orange precipitates of iron oxyhydroxide (ochre) on the beds of the recipient watercourses, with the exception of Goyt Moss discharge where the deposit is almost negligible. The Hipper discharge precipitates, in addition, a whitish yellow deposit in the immediate vicinity of the outfall. This is suspected to be aluminium hydroxide.

Spoil tip waters

The spoil tip waters were collected from four spoil tips at collieries in the Rotherham area, referred to as R1–R4 from west to east.

Colliery R1 is situated on Middle Coal Measures outcrop and was operational from 1851 to 1983. The main mined seams were the Barnsley (at 121 m depth), Swallow Wood (at 185 m) and Parkgate (at 353 m).

Colliery R2 is situated on Upper Coal Measures outcrop, and was operational between 1904 and 1995. The main seams worked were the Barnsley (at 681 m depth), Parkgate and Swallow Wood.

Colliery R3 is situated on Upper Coal Measures outcrop adjacent to the Permian unconformity. The main seams worked at the colliery were the Barnsley (at 750 m depth) and Parkgate seams, although deeper seams such as the Swallow Wood and Haigh Moor were also mined. The colliery was operational between 1911 and 1992.

Colliery R4 is situated on Permian Magnesian Limestone. The Coal Measures commence at 68 m

Table 2. *Characteristics of the sampled sites of coal mine drainage waters. Further details are found in Banks* et al. *(1996a)*

Site	Grid. reference	Seam worked Comments	References
Ringinglow	SK 3004 8344	Ringinglow Coal ?	Eden *et al.* 1957
Ecclesall Woods	SK 3184 8175	Ganister Seam ?	
Dore Conduit	SK 3111 8190	Ganister Seam ? possibly spoil material Probably mixed with surface water	
Sheephouse Wood (Handbank/Hollin Wood mines)	SE 2309 0004	Halifax Hard	Dudeney *et al.* 1994 NRA 1994
Bullhouse	SE 2152 0293	Halifax Hard	Dudeney *et al.* 1994 NRA 1994
Mill House Unstone	SK 3759 7691	Silkstone	Battye 1981
Unstone 2	SK 3753 7757	Parkgate?/Deep Hard? Unstone 2b is a mixture with recipient surface water	Eden *et al.* 1957
Unstone 3	SK 3754 7731	Parkgate ?/Deep Hard?	Eden *et al.* 1957
Gawber Prospect	SE 329 086	Barnsley Overflowing exploration borehole	
River Hipper, Chesterfield	SK 3842 7067	Unknown (Boythorpe Colliery ?) Whitish yellow precipitate	
Dunston	SK 3657 7516	Silkstone	Eden *et al.* 1957
Greystones	SK 3143 8506	Ganister Seam or Soft Bed	Eden *et al.* 1957
Hunters Bar	SK 3324 8574	Unknown Mine water entering storm drain conduit ?	
Duke's Level, Buxton	SK 0370 7231	Mainly Ringinglow Coal	Roberts & Leach 1985
Goyt Moss Adit	SK 018 721	Mainly Goyt Seam Little ferruginous deposit	Roberts & Leach 1985

depth. The main seams worked were the Clown (at 318 m) and Barnsley (Top Hard) (at 472 m). The colliery was operational between 1856 and 1986.

Natural ferruginous waters

The occurrence of natural ferruginous waters from Millstone Grit and Coal Measures strata is historically well-known. Chalybeate spa waters from these strata are known from Matlock Bank, Buxton (Albu *et al.* 1997), Ashover, Treeton and Fulwood area, Sheffield (Wilson 1991).

The best-documented of the sampled natural waters occurs on Mam Tor, a mountain composed of alternating thin sandstone and shale horizons near the base of the Millstone Grit sequence near Castleton. The mountain has suffered severely from landslip and a number of ferruginous springs are derived from the disturbed (and hence oxidized) landslip strata. The springs of Mam Tor were the subject of one of the earliest quantitative studies of pyrite oxidation in the UK (Vear & Curtis 1981), to whose location 7/8 our sampling point corresponds.

At 'Kilnhurst Boardwalk' a ferruginous water seeps into a small stream. No mine workings or spoil tips are recorded in the area. It is assumed that the ferruginous water is a natural spring associated with weathering of the outcrop of the Shafton Coal and Marine Band Shale, although there is a possibility that it is derived from very old, unmapped mine workings.

Smeekley public supply borehole was drilled in 1952 and discontinued around 1987, although it was not securely capped and now discharges an estimated 30 l/s artesian flow into the headwaters of the Barlow Brook. The water is rich in hydrogen sulphide, ferruginous and has a significant visual effect on the bed of the brook. The borehole is 287 m deep and draws its water from both the Lower Coal Measures and the Upper Millstone Grit (Eden *et al.* 1957).

Ferruginous lead mine waters

Lead mine water discharges in the Carboniferous Limestone of the Peak District are normally of such high quality that they can be used as drinking water (Edmunds 1971; Banks *et al.* 1996*b*). Occasionally, however, ferruginous discharges occur, typically where the mine also drains water from the pyrite-bearing Millstone Grit shales overlying the limestone.

One such site is the Odin Mine in the Lower Carboniferous Limestone at the foot of Mam Tor. This was drained by driving a long sough to a tributary of the Peakshole Water in Castleton through the stratigraphically overlying Millstone Grit shales. The sough discharges a mildly ferruginous water. The iron is believed to be derived, not from the mine itself, but from leakage into the sough from overlying pyritiferous Millstone Grit strata and landslipped material from Mam Tor.

The second ferruginous lead mine discharges from an adit in Millstone Grit strata at Matlock Bank. An inscription states that it was restored as 'Allen Hill Spaw' (or spa) in 1824. The origin of the sough is uncertain but Naylor (1983) and Banks *et al.* (1996*b*) believe it is likely to drain workings in lead ore veins which may extend up from the Carboniferous Limestone into the Millstone Grit.

Water sampling

Sampling and analytical details are documented by Banks *et al.* (1996*a*). In summary, samples were analysed in the laboratory for pH, alkalinity, electrical conductivity, a range of elements by ICP-AES (field filtered and acidified samples at 0.45 µm) and/or atomic absorption techniques (sample series 3) and anions by ion chromatography. A selection of field-filtered and acidified samples were analysed for a range of trace elements by ICP-MS techniques.

Where a significant visible precipitation of iron was noted on the 0.45 µm filter during sampling, a parallel unfiltered sample of water was collected and acidified in the same manner as the filtered sample, for comparative ICP-AES analysis. For many mine waters, pH and temperature were also measured in the field using a Palintest Micro 900 meter. Where water was upwelling from an opening or flowing slowly from non-turbulent adits, such that atmospheric contact and admixture were minimal, Eh readings were taken using a standard Eh electrode and the Palintest meter.

For sampling of radon at non-turbulent or upwelling discharges, samples of 10 ml water were taken in a 20 ml vial containing 10 ml of prefilled scintillation liquid. Flasks were delivered to the British Geological Survey and analysed by scintillation counter. Results were back adjusted for radioactive decay to give a radon activity in Bq/l at time of sampling. Two samples were analysed for PAH constituents by GC-MS techniques at the Department of Animal and Plant Sciences, University of Sheffield. Only two of the waters contained hydrogen sulphide gas detectable by odour, namely Smeekley borehole and Bullhouse mine water. For the purposes of statistical analysis and plotting, samples returning values below the analytical detection limit were set to half the analytical detection limit.

Analytical control

In addition to normal laboratory controls, the duplicate analysis of filtered and unfiltered samples and of filtered samples by ICP-MS and ICP-AES gave the opportunity to compare sampling and analytical techniques.

Effect of filtration

The effect of field filtration was found to be low to moderate for most important parameters, including the metals Fe, Al, Mn and Zn (Fig. 2), despite the fact that some deposition of iron could often be seen on the filter disc. Of these four metals, the greatest discrepancy was seen for Al and the least for Mn. This reflects Hedin *et al.*'s (1994) observation that dissolved manganese has a far lower rate of oxidation, hydrolysis and precipitation in treatment systems than does iron. For iron, the deviation in concentrations between filtered and unfiltered samples was less than 10% for all samples, except three. This presumably reflects the fact that the majority of iron is in solution in the ferrous state, and that the rate of oxidation and hydrolysis is slow. The greatest percentage losses upon filtration were observed in three samples with high pH and low iron content (Fig. 2). It can thus be concluded that for most ferruginous waters with an iron content of >5 mg/l and pH<6.5, changes in iron concentration due to field filtration are minor. In the remainder of the paper and the diagrams, the metal concentrations referred to are those in filtered samples.

Laboratory and field determinations of pH

Although a laboratory determination of pH was performed within a short time of arrival of samples at the laboratory, field determinations of pH were regrettably not possible on all sampling occasions (Table 3). This provides an excellent opportunity to assess the correlation of the two measurements. The degree of correlation, although good for many samples, is not good for all samples, confirming that reliable pH determinations on mine waters must be performed in the field. Where significant differences between laboratory and field pH occur, the laboratory pH is usually lower than that in the field, presumably reflecting oxidation and hydrolysis of dissolved iron in the flask.

Laboratory determination of alkalinity

Alkalinity was also determined in the laboratory. As the analyses of major cations and anions are believed (through independent controls) to be accurate, the accuracy of the alkalinity determination can be assessed from the ion balance. In many cases, the ionic balance for the highly ferruginous waters was satisfactory (including Sheephouse, Bullhouse, Ecclesall Wood,

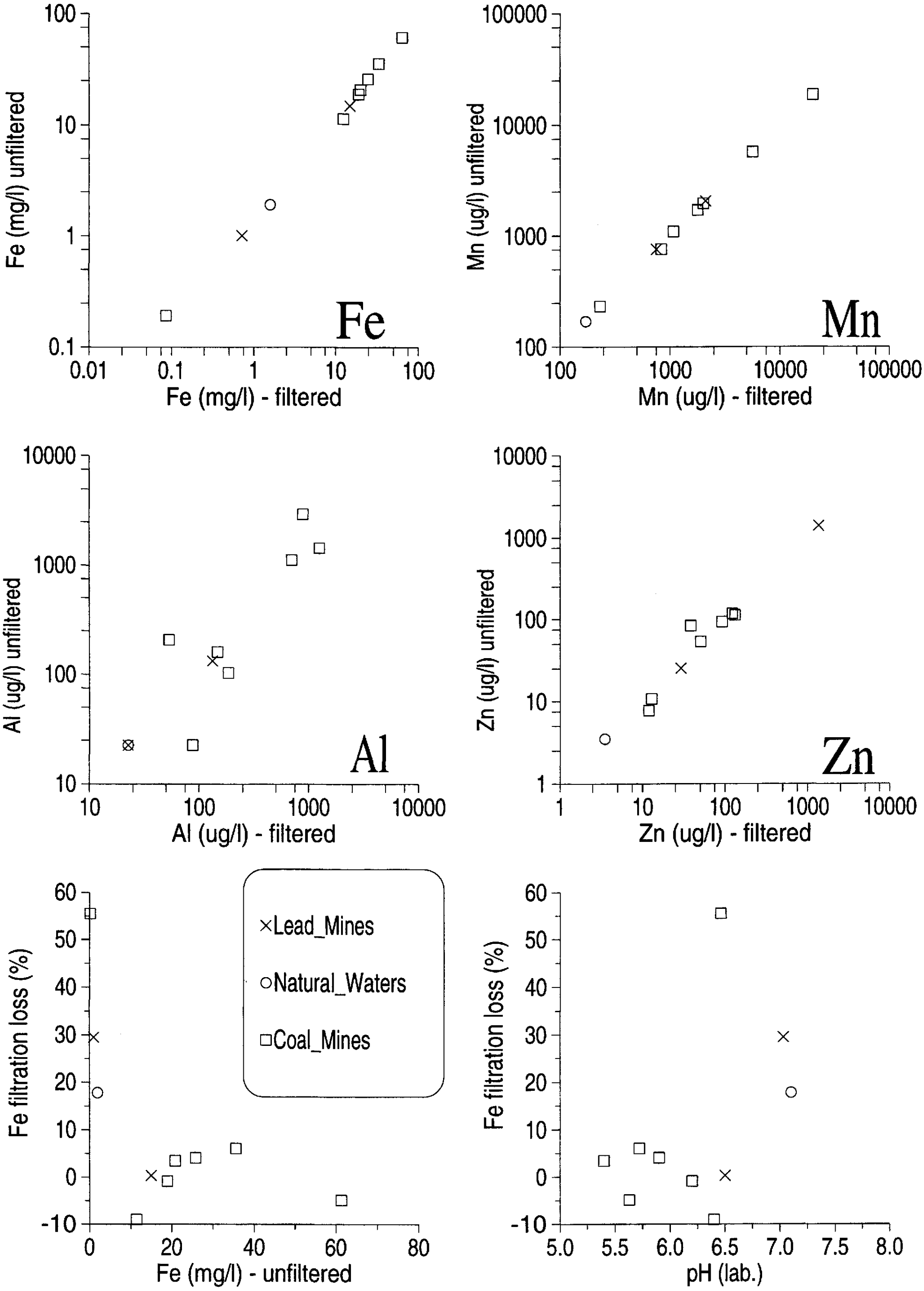

Fig. 2. Plots illustrating correlation between analyses of filtered (0.45 μm) and unfiltered (both acidified with conc. HNO_3) waters, for Fe, Mn, Al and Zn (ICP-AES analyses). N.B. for the purposes of plotting in this and subsequent diagrams, values below detection limit have been set to half the detection limit.

Duke's Level, Goyt Moss, R. Hipper, Unstone 2, Dunston and Hunters Bar), implying that the alkalinity analysis is not significantly in error. However, as with pH, there were a number of waters where alkalinity, as measured in the laboratory, appeared to be significantly inaccurate, leading to deviant ionic balances. In conclusion, although laboratory determinations of pH and alkalinity can reproduce field conditions for some ferruginous waters, they may significantly and unpredictably deviate from field values.

Mine water hydrochemistry

Pyrite (FeS_2) is a common accessory mineral which is found in sulphide mineral deposits, in coal and in many coal-bearing mudstones. It is the bacterially catalysed oxidation of this pyrite that is primarily responsible for the environmental problems created by acid mine drainage (AMD). These problems arise both directly from the mobilization of high concentrations of iron, principally as Fe^{2+}, and also indirectly through the production of large quantities of acid. This acidity is then able to mobilize aluminium and the wide range of trace metals often associated with sulphide-rich deposits. The fundamental geochemical processes occurring in coal and metalliferous mines, tailings dumps and spoil heaps are assumed to be similar. The final pH and chemistry of the discharge water will be controlled by an interaction between (i) access for and diffusion of oxygen to reduced phases (ii) the rates of sulphide oxidation and acid production and (iii) the availability and rates of buffering reactions offered by basic (carbonate, silicate and oxide/hydroxide) mineral phases or sulphate-reducing niches in the mine system as well as by (iv) admixture with other groundwaters.

The pyrite oxidation reaction is normally ultimately limited by the supply of oxygen (although ferric iron or, conceivably, MnO_2 or NO_3^- can also act as electron acceptors for pyrite oxidation). As the complete utilization of oxygen-saturated water (containing approximately 11 mg O_2/l at 10°C) will only release sulphate concentrations of approximately 17 mg/l, the access of free (gas-phase) oxygen to the pyrite-bearing strata is necessary to obtain the typically observed concentrations of several hundreds or thousands of mg/l sulphate. This may be achieved by seasonal variations in water level within mine workings or, of course, in unsaturated workings underdrained by a sough.

Within the mine, cycling of iron between ferrous and ferric phases may occur. Ferrous iron may be oxidized to ferric iron, which may subsequently hydrolyse and precipitate out as ferric oxyhydroxide or as a sulphate phase such as jarosite. Alternatively ferric iron may, as mentioned above, function as an electron acceptor for pyrite oxidation. Thus, ferric iron can conceivably act as a sink for iron within the mine system or promote further pyrite oxidation.

Generation of protons

In mine drainage situations, there are two main generating processes for protons, the oxidation of pyrite (or hydrogen sulphide), and the hydrolysis of metals such as Fe, Al, Zn and Mn.

$$2FeS_2+2H_2O+7O_2 \rightleftharpoons 2Fe^{2+}+4SO_4^{2-}+4H^+ \qquad (1)$$

$$H_2S+2O_2 \rightleftharpoons 2H^+ +SO_4^{2-} \qquad (2)$$

$$Fe^{3+}+3H_2O \rightleftharpoons 3H^+ +Fe(OH)_3. \qquad (3)$$

Although reaction (3) may be important within the mine, Fe(II) will be the dominant oxidation state for dissolved iron in most emerging coal mine waters (Hedin *et al.* 1994) due to the insolubility of Fe(III) in all but the most acidic waters. Once the mine water contacts the atmosphere, reaction (3) will progress resulting in the generation of iron oxyhydroxide flocs and precipitates (and also protons).

Consumption of protons

Once protons are generated, they may be consumed by sulphate reduction (essentially the reverse of equations (1) and (2)) or by acid-base weathering of carbonates (equation 4) or silicates (equation 5). Under conditions of very low pH, aluminosilicates such as kaolinite may be dissolved to release Al^{3+} to solution (equation 6):

$$CaCO_3+H^+ \rightleftharpoons Ca^{2+}+HCO_3^- \qquad (4)$$

$$2NaAlSi_3O_8+2H^++H_2O \rightleftharpoons 2Na^+ + Al_2Si_2O_5(OH)_4+4SiO_{2(aq)} \qquad (5)$$

$$Al_2Si_2O_5(OH)_4+6H^+ \rightleftharpoons 2Al^{3+}+2SiO_2+5H_2O \qquad (6)$$

Generation of alkalinity

Bicarbonate alkalinity may be generated by a number of processes, including:

- carbonate or silicate weathering by dissolved carbon dioxide in recharge water.

$$CaCO_3+CO_2+H_2O \rightleftharpoons Ca^{2+}+2HCO_3^- \qquad (7)$$

$$2NaAlSi_3O_8+2CO_2+3H_2O \rightleftharpoons 2Na^+ + 2HCO_3^- +Al_2Si_2O_5(OH)_4+4SiO_2 \qquad (8)$$

Table 3. *Analytical results for selected parameters for the ferruginous waters forming the subject of this paper. Sample numbers prefixed 'E' form part of series 1, those prefixed 'SB' form part of series 2 and those marked 'CG' form part of series 3. All metals analyses from series 3 samples are performed on unfiltered, unacidified samples, analysed by atomic adsorption methods*

Sample	Location	Date	Temp °C	Estimated flow (l/s)	pH (field)	pH (lab)	Eh (mV)	EC (µS/cm)	Ca (mg/l)	Na (mg/l)	Mg (mg/l)	K (mg/l)	Alkalinity (meq/l)	F^- (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Si (µg/l)	Fe (filtered) (mg/l)	Fe (unfiltered) (mg/l)	Al (µg/l)	Mn (µg/l)	Zn (µg/l)	Rn (Bq/l)	U (µg/l)
E29	Smeekley Borehole	23 Jan. 95	9.2	30		7.10		468	38.8	20.6	23.0	3.86	10.01	0.09	21	<1.5	25	9150	1.58	1.92	<45	172	<7		<1
E16	Mam Tor Springs	3 Jan. 95	3.4	0.8		3.08		2200	197	6.8	115	3.70	0.00	i	7.9	<1.5	1480	14 600	27.3		51 300	23 900	1040		13
SB3	Kilnhurst Boardwalk	9 Jul. 95	9.5†	0.083	7.45†	7.28		776	69.1	17.8	49.6	2.38	4.12		40	1.2	141	6030	3.17		<22	619	24		
E13	Odin Sough, Castleton	3 Jan. 95	8.7	4		7.03		549	75.9	24.0	6.3	1.84	2.61	1.53	36	2.4	79	3350	0.71	1.01	<45	749	1360		9
E24	Allen Hill Spaw, Matlock	20 Jan. 95	10.2	0.15		6.50		753	85.3	17.9	20.9	3.50	7.07	i	83	3.9	124	10 200	14.9	15.0	132	2100	29		<1
SB9	Spoil Tip R1	9 Jul. 95		0.033		7.40		6340	136	947	146	32.4	4.72		625	2.5	2370	342	0.27		<22	328	59		
SB5	Spoil Tip R2	9 Jul. 95	10.1†	0.033	7.85†	7.60		8510	131	1490	198	24.4	12.99		996	1.9	3200	4020	<0.002		<22	129	60		
E50	Spoil Tip R3 (Point 1)	Apr. 95	11.0		6.90	6.91		9550	214	1430	132	19.2	10.91	i	1710	1.6	386	5830	17.5		<45	3150	7		
E51	Spoil Tip R3 (Point 3)	Apr. 95	11.9		6.77	6.76		6670	342	762	257	20.9	14.29	i	511	1.72	1330	5330	18.6		<45	2000	<7		
SB1	Spoil Tip R3 (Point 3)	9 Jul. 95		0.083		6.76		6250	136	903	231	22.7	13.89		748	<0.5	2600	4320	15.2		<22	2120	66		
E52	Spoil Tip R3 (Point 4)	Apr. 95							85.3	991	43.7	11.3		i	692	4.68	883	3970	0.17		<45	22	<7		
SB7	Spoil Tip R4	9 Jul. 95		<0.017		8.32		12 770	88.0	2220	227	64.2	4.78		1870	4.6	3580	214	<0.002		79	273	46		
CG	Ringinglow	29 Jun. 95			5.45	5.48		371							43	0.58	86			2.02*			112*		
CG	Ringinglow	10 Jul. 95			5.47	5.45		356							40	0.47	75			2.04*			57*		
CG	Ringinglow	17 Jul. 95				5.40		358							35	0.64	87			2.06*			46*		
CG	Ecclesall Woods	29 Jun. 95			5.84	6.00		848							36	<0.5	333			48.0*			55*		
CG	Ecclesall Woods	10 Jul. 95				5.89		844							33	0.35	334			47.3*			34*		
CG	Ecclesall Woods	17 Jul. 95				5.71		821							31		329			39.5*			31*		
E32	Ecclesall Woods	1 Feb. 95	9.0	2		5.40		617	49.6	14.2	27.7	5.34	0.88	0.48	26	16.2	224	9190	20.1	20.8	703	1070	50		2
E65	Ecclesall Woods	1 May 95		0.5	5.78	4.58		790	70.0	14.9	39.0	6.29	0.01	i	29	0.9	296	11 000	40.8		270	1590	34	24	<2
CG	Dore Conduit	29 Jun. 95			6.58	6.65		590							53	1.18	154			15.1*			42*		
E20	Sheephouse Wood Adit	16 Jan. 95	9.2	10		5.72		838	60.9	62.8	22.4	3.58	1.62	i	18.2	0.6	368	11 400	33.4	35.6	886	1780	92		
E21	Bullhouse	16 Jan. 95				5.63		1583	154	38.1	76.5	7.50	2.20	i	43	<0.5	886	12 600	64.3	61.3	1270	19 900	132		2
E30	Mill House, Unstone	1 Feb. 95	9.2	0.45	6.14	6.20		900	59.5	44.6	42.0	8.33	1.60	i	18.2	0.5	229	6210	19.1	19.0	88	2010	12		
E64	Unstone 2	1 May 95		0.75	6.01	4.86		738	43.6	18.3	43.5	2.25	0.04	i	40	0.7	303	13 500	30.5		<45	6370	54	18	<2
E45	Unstone 2b	22 Mar. 95	8.9		6.94	6.18		706	45.4	20.7	41.9	2.42	0.02	i	35	2.21	211	12 200	16.5		<45	5820	33		
E31	Unstone 3	1 Feb. 95		2	5.98	5.90		730	41.8	20.5	39.7	2.64	9.97	0.47	36	3.7	221	11 000	24.8	25.9	148	5640	38		
E35	Gawber Prospect Borehole	5 Feb. 95	10.2	4.5		6.40		1484	100	60.3	87.2	11.5	16.37	i	91	<0.5	366	7500	12.5	11.4	185	831	13		<1
E46	River Hipper AMD	22 Mar. 95	10.3	0.5	3.81	3.16		1488	98.5	24.5	63.9	5.71	0.00	i	26	0.67	538	18 700	67.3		9410	2650	152		
E60	River Hipper AMD	1 May 95	10.7	0.75	3.61	2.90		2010	127	22.8	94.3	5.78	0.00	i	29	0.6	1040	19 600	101		17 300	4020	221	1	<2
E70	Dunston Colliery	31 May 95	9.4	*c.* 20	6.33	6.31		957	64.5	51.4	48.5	8.93	3.74	i	26	0.49	210	7020	10.6		<45	1260	<7		
E73	Greystones	31 May 95	9.3	0.5	6.02	3.76	+108	789	48.2	17.8	24.4	4.15	0.00	0.44	33	0.41	181	9510	9.61		<45	1640	9		
E74	Hunters Bar	31 May 95	9.8	3.3	6.50	5.96		340	55.4	29.3	27.1	5.79	0.62	i	56	5.92	245	10 300	21.4		223	1880	54		
E43	Duke's Level, Buxton	22 Mar. 95	7.4	15	6.35	6.24		321	25.2	10.6	13.2	2.21	0.73	0.08	18.5	3.8	72	6650	6.08		50	315	49		
E62	Duke's Level, Buxton	1 May 95	7.5	20	6.30	6.71		318	26.1	9.8	13.9	2.30	0.64	<0.15	16.1	3.2	79	6940	5.99		<45	352	44		<2
E71	Duke's Level, Buxton	31 May 95	7.2	*c.* 20	6.25	6.28		213	27.5	10.5	14.5	2.41	0.22	0.13	16.6	2.81	83	7090	5.71		<45	372	49		
E75	Duke's Level, Buxton	29 Jun. 95	7.3	*c.* 20	6.25	6.36	+90	325	25.6	10.1	13.4	2.53	0.66	<0.15	18.0	2.57	83	6550	4.90		78	364	48		
E80	Duke's Level, Buxton	2 Aug. 95	7.3	*c.* 20–30	6.26	6.10	+90	359	26.8	10.6	14.1	2.39	0.84	<0.15	16.9	2.8	84	6130	0.13		29	356	41		
E44	Goyt Moss Adit	22 Mar. 95	6.4	2.5	6.47	6.46		174	11.0	4.5	8.2	1.22	0.10	0.06	6.0	2.04	48	4410	0.09	0.19	53	233	123		<2
E63	Goyt Moss Adit	1 May 95	6.7	1	6.57	5.98		200	12.5	4.7	9.6	1.49	0.18	<0.15	6.5	1.8	53	5390	0.16		<45	186	105		<2
E72	Goyt Moss Adit	31 May 95	6.4	2.5	6.17	5.48	+168	574	12.9	4.9	10.0	1.48	0.26	0.18	5.5	1.86	55	5210	0.09		84	240	122		
E76	Goyt Moss Adit	29 Jun. 95	6.5	*c.* 2.5	6.19	6.41	+193	215	13.6	5.1	10.0	1.58	0.26	<0.15	7.4	1.68	63	5290	0.13		120	170	114		
E81	Goyt Moss Adit	2 Aug. 95	6.5	2.2	6.13	6.20	+158	225	14.6	5.6	10.8	1.53	0.41	<0.15	6.9	2.0	62	5480	0.05		95	130	120		
E77‡	Sheffield Univ. borehole 1	25 Jul. 95	9.4	0.43	7.15	7.06	−35	446	37.8	11.7	21.6	2.35	3.26	<0.15	31	<0.5	36	8860	1.42		<22	201	38		<2
E78‡	Sheffield Univ. borehole 2	25 Jul. 95	9.6	0.38	6.40	6.6	+20	444	34.5	12.6	20.5	3.94	2.58	<0.15	39	<0.5	36	8810	3.05		26	304	26		<2

*For the purposes of data presentation in Figs 3–11, metals analyses from sample series 3 have been regarded as filtered samples compatible with results from series 1 and 2.

†Data from 27/9/95.

‡"Normal" non-mining-related Coal Measures groundwaters, for comparison.

i interference with fluoride determination during ion chromatography.

- dissolution of carbonates (such as siderite, which is the dominant carbonate mineral in many Coal Measures sequences) by protons generated by pyrite oxidation:

$$FeCO_3 + H^+ \rightleftharpoons Fe^{2+} + HCO_3^- \qquad (9)$$

- sulphate reduction with a carbon substrate

$$2CH_2O + SO_4^{2-} \rightleftharpoons 2HCO^-{}_3 + H_2S \qquad (10)$$

Mineral acidity

Hedin *et al.* (1994) and Younger (1995*a*) have both discussed the concept of some dissolved metals representing a form of non-proton acidity, due to their capacity to hydrolyse and generate protons by reactions such as (3) above. Thus, in a sense, Fe^{3+} and Al^{3+} are equivalent to 3 meq · mmol^{-1} acidity, while Fe^{2+}, Zn^{2+} and Mn^{2+} are equivalent to 2 meq · mmol^{-1}. The total acidity of a solution can thus be estimated by:

$$\begin{aligned}\text{Acidity (meql}^{-1}) = 1000 \cdot 10^{-\text{pH}} &+ \\ (Fe^{2+})eq + (Fe^{3+})eq + (Al^{3+})eq &+ \\ (Mn^{2+})eq + (Zn^{2+})eq & \qquad (11)\end{aligned}$$

where (M)eq is the concentration of the metal ion M in meq/l. Acidity has been estimated using this method of Hedin *et al.* (1994) for the mine waters studied (using the admittedly simplified assumption that all iron, manganese and zinc are in the form of divalent ions and all aluminium as trivalent ions). The results are discussed later. Acidity is thus generated not only by reactions releasing protons to solution but also reactions releasing the relevant metals.

Coal mine waters

Characterization

The parameters most characteristic of mine waters are iron, sulphate and H^+, generated by the pyrite oxidation reaction (equation 1), and with regard to these, the coal mine waters show a considerable degree of variability (Fig. 3). Iron contents range from 50 µg/l (at Goyt Moss) to 101 mg/l (R. Hipper, Chesterfield). The field pH varies from 6.6 (Goyt Moss—discounting Dore Conduit and Unstone 2b, both mixtures of mine- and surface water) to 3.6 (R. Hipper). Sulphate values range from 48 mg/l (Goyt Moss) to 1044 mg/l (R. Hipper). Median values of Fe and sulphate are 12 and 210 mg/l respectively. The range in pH between the extremes mentioned above conceals the fact that the large majority of measured pH values lie around 6.

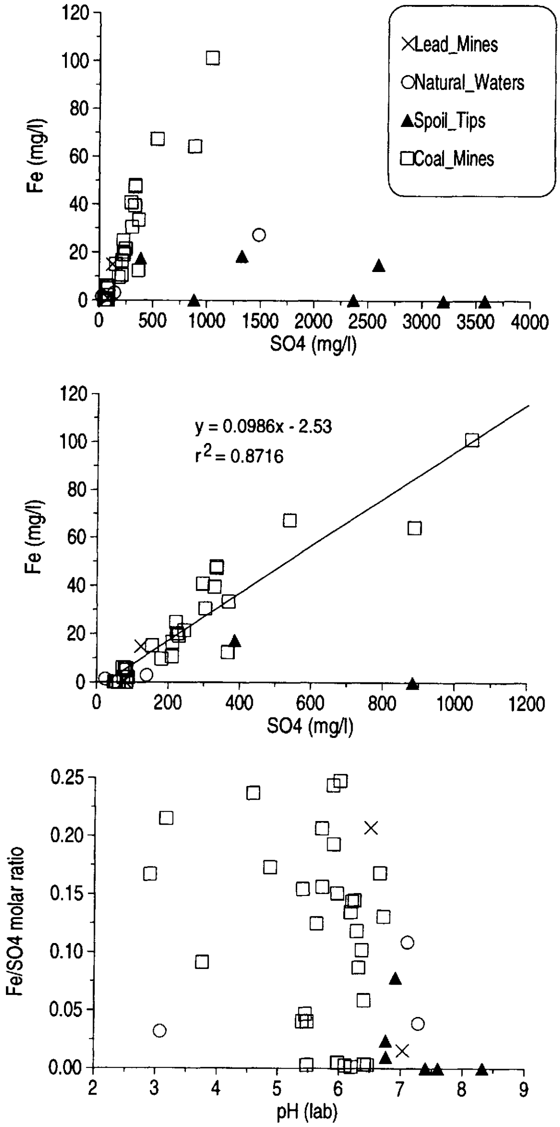

Fig. 3. Plots illustrating the relationship between iron (filtered) and sulphate concentrations in the studied waters. The lower diagram shows the relationship of the molar Fe/SO_4^{2-} ratio to pH. The linear regression for coal mine waters only is shown.

A plot of total iron (filtered samples) vs. sulphate (Fig. 3) reveals a strong ($r^2=0.872$) linear correlation between the two parameters. The regression line passes approximately through the origin with a gradient of Fe/SO_4^{2-} = (mg/l ratio) = 0.0986 or Fe/SO_4^{2-} (molar ratio) = 0.17. The dissolved iron content in coal mine waters decreases with increasing pH (Fig. 4), possibly reflecting both the decreasing solubility of iron with increasing pH and covariation due to their common source in pyrite.

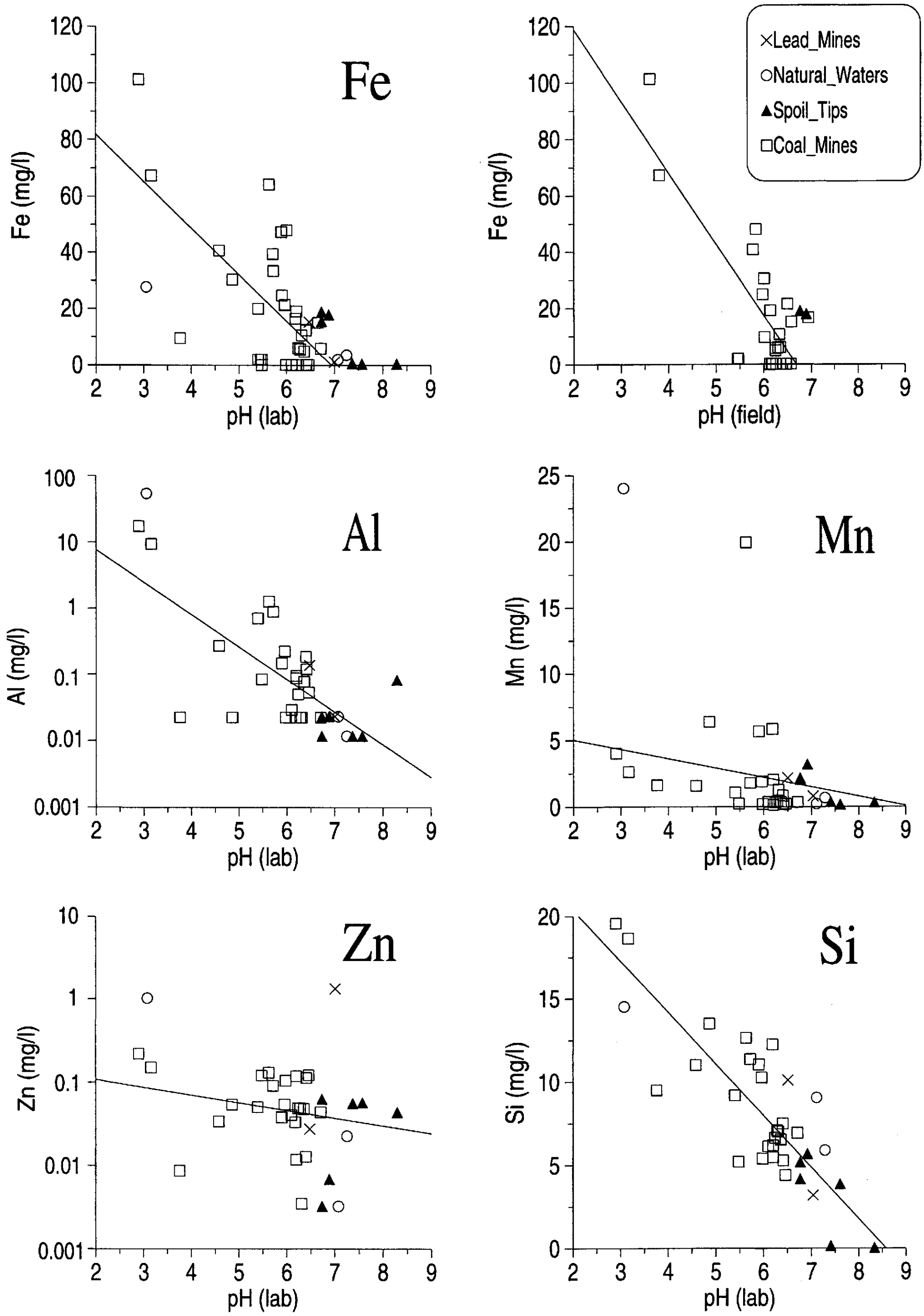

Fig. 4. Relationship of Fe, Al, Mn, Zn and Si (filtered) to pH in the studied waters. The linear regression for coal mine waters only is shown.

Substantial alkalinity only begins to be observed in mine waters as the pH exceeds 5.5. The two highest values of alkalinity in mine waters are thought to be overestimated (on the basis of poor ion balances). Assessment of the corrected alkalinity values from the ion balances still indicates that the Gawber Prospect borehole has the highest alkalinity of over 5 meq/l.

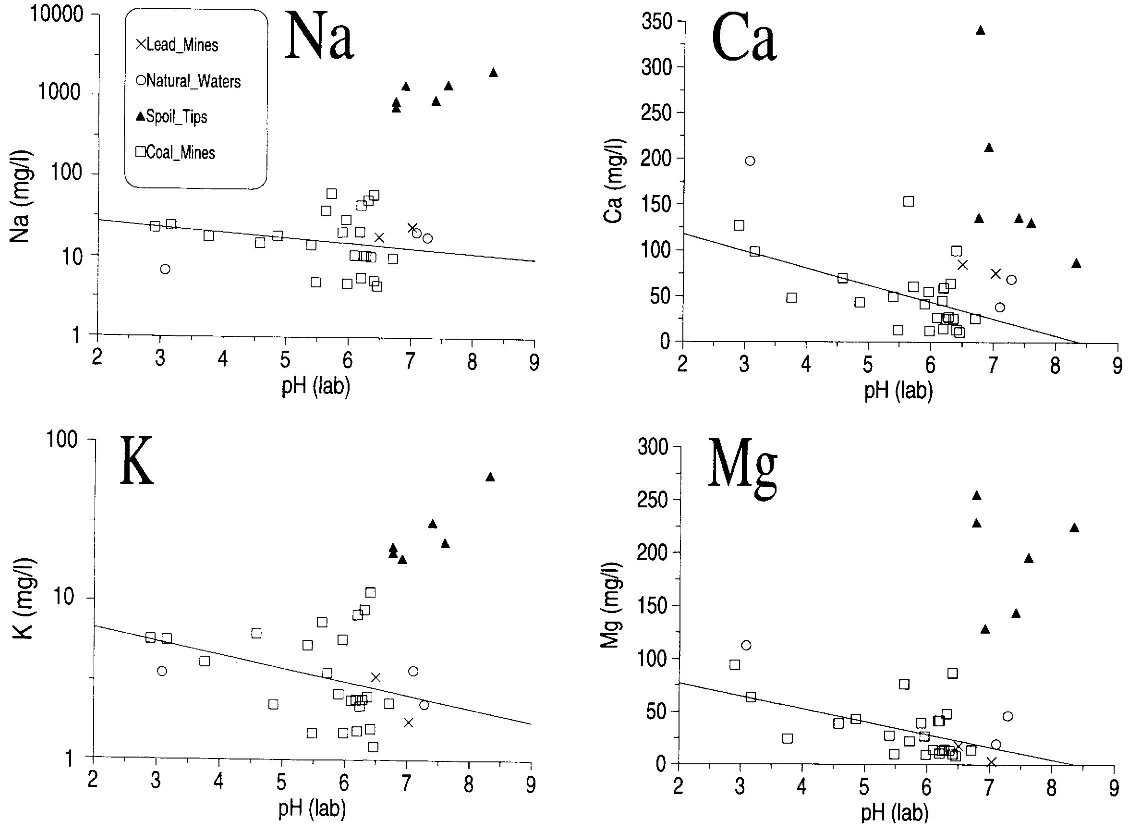

Fig. 5. Relationship of Na, Ca, K and Mg (filtered) to pH in the studied waters. The linear regression for coal mine waters only is shown.

Dissolved silicon shows a negative correlation with pH (Fig. 4). In coal mine waters, the maximum silicon concentration is that in the extremely acid mine water of the river Hipper (19.6 mg/l) and the lowest (4.4 mg/l) in Goyt Moss adit. The abundant aluminium in the Hipper mine water (up to 17 mg/l) is evidence of intense aluminosilicate weathering under conditions of low pH. Aluminium levels not significantly exceeding 1 mg/l in the other samples (Fig. 4) confirm Hedin *et al.*'s (1994) observation that Al is seldom a problematic component of mine drainage waters at pH>4.5, largely due to gibbsite saturation control.

Manganese and zinc are typically the next most abundant metals in the coal mine waters, and also exhibit (albeit very weak) negative correlations with pH (Fig. 4). Manganese concentrations are typically near or greater than 1 mg/l in waters with pH<6. All major cations except sodium show a weak negative correlation with pH (Fig. 5), the strongest being observed for calcium and magnesium. Sodium shows a very strong correlation with chloride (Fig. 6), indicating a similar origin (i.e. marine salt or, possibly, mixing with deep brines). A small but significant non-marine excess of sodium over chloride (Na*—i.e. sodium in excess of that expected from the ratio Na/Cl in seawater) is found in many samples.

Chloride concentrations in coal mine waters show no correlation with pH and are typically between 10 and 40 mg/l, which indicates derivation from salts from precipitation concentrated by evapotranspiration. The most topographically elevated and westerly mine water (Goyt Moss) exhibits the lowest concentrations of chloride. Some samples exhibit chloride at somewhat higher concentrations, notably Gawber Prospect borehole at 91 mg/l. Fluoride exhibits a strong negative correlation with pH in coal mine waters and a positive correlation with calcium. Nitrate concentrations in coal mine waters are low in comparison with many UK groundwaters. Only two waters exceed 5 mg/l, sample E32 from the Ecclesall Woods discharge in February (16 mg/l) and the Hunters Bar discharge (5.9 mg/l). The former of these discharges is from below agricultural land; the latter from an urban drain which may be contaminated by sewage. The generally low nitrate levels support the opinion (e.g. NRA 1995; Banks *et al.* 1996*b*) that coal mine water discharges are important providers of low nitrate baseflow to watercourses.

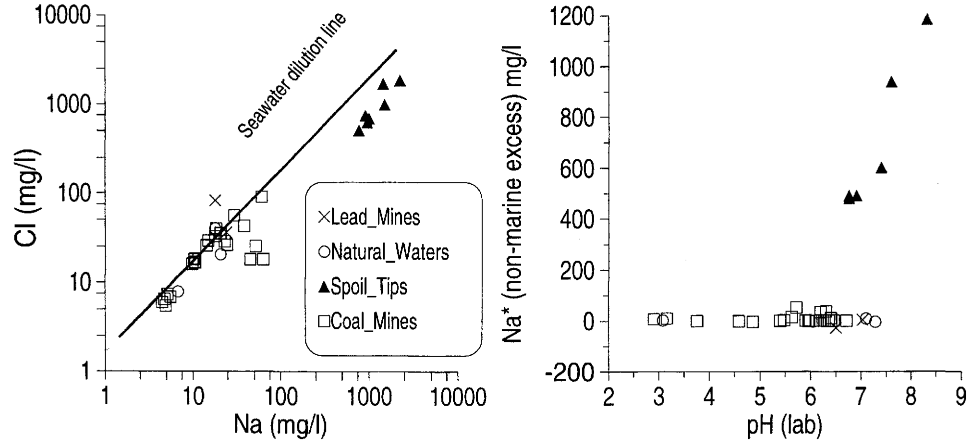

Fig. 6. Relationship of Cl^- to Na (filtered) and of non-marine (excess) Na to pH in the studied waters. In the left hand diagram, the line represents the seawater dilution line.

A range of trace elements have also been determined (Fig. 7). Beryllium and lithium exhibit weak negative correlations with pH with levels typically under 10 μg/l and 100 μg/l respectively. Boron shows no convincing correlation either with pH or with salinity, with concentrations of up to 300 μg/l. Barium exhibits a positive correlation with pH and a negative one with sulphate (Fig. 8). This is indicative of barite ($BaSO_4$) saturation imposing a solubility constraint on barium concentrations. Nickel concentrations are typically in the range 10–100 μg/l and do show some indication of a negative correlation with pH (Fig. 7) and with Fe^{2+} from pyrite oxidation. Cadmium concentrations, as measured by ICP-MS, are very low for all waters of pH>5, but reach values of *c.* 30 μg/l in the Hipper mine water (Fig. 7). Lead, cobalt and copper were also analysed by ICP-MS on nine coal mine waters, and returned median values of <1, 15 and 3 μg/l respectively. Tin, by ICP-MS, on seven waters (six coal mine waters and the Mam Tor water) all returned values <3 μg/l, with the exception of the River Hipper water at 4 μg/l. Uranium concentrations do not exceed 2 μg/l in any of the analysed coal mine waters. Radon concentrations were only determined at three sites, the maximum being 24 Bq/l at Ecclesall Woods, where the water wells up from the ground without opportunity for degassing. A low value (1 Bq/l) was recorded at the River Hipper discharge, where water flows from an open conduit. None of the radon measurements reaches levels which could pose a health hazard.

Some evidence for the leaching of refractory organics from fossil fuels is provided by a study of lignite-bearing strata in the Balkans, where refractory fluorescent organics in groundwater show some correlation with endemic kidney disease (Goldberg *et al.* 1994). The two samples of coal mine water analysed by GC-MS in this study, from Ecclesall Woods and Gawber Prospect ferruginous discharges, both showed no detectable (<1 μg/l) PAH compounds. Further work using excitation-emission matrix spectroscopy is ongoing and will be reported shortly.

Interpretation

The strong linear correlation between iron and sulphate suggests that pyrite oxidation is the dominant reaction characterizing the coal mine discharge waters. There is, however, a large variety in the iron and sulphate concentrations in the waters, suggesting that the reaction is progressing at varying rates within the differing mine systems.

Simple pyrite oxidation is not the whole story, however: equation (1) predicts that 2 moles SO_4^{2-} are generated for every mole of Fe^{2+}, whereas the observed linear regression indicates a ratio of nearer 6:1. It appears that iron is being retained within the subsurface system, probably by some form of precipitation, ion exchange (possibly iron for magnesium, see below) or adsorption reaction. Possible solid phases include ferric oxyhydroxides (following oxidation and hydrolosis of Fe^{2+}), or sulphates such as jarosite ($KFe^{III}_3(OH)_6(SO_4)_2$). In the case of jarosite, the iron is preferentially removed relative to sulphate, depressing the Fe/SO_4^{2-} ratio in solution.

A substantial variation in mine water chemistry can be observed in the data set, even between mine waters derived from different parts of the same mine system (Duke's Level and Goyt Moss). Part of the variety might be explained by differences in pyrite content of the coal, although differences of a few per cent seem insufficient to account for the several orders of magnitude difference in concentrations in the mine waters. It is thus postulated that the main controlling factor is

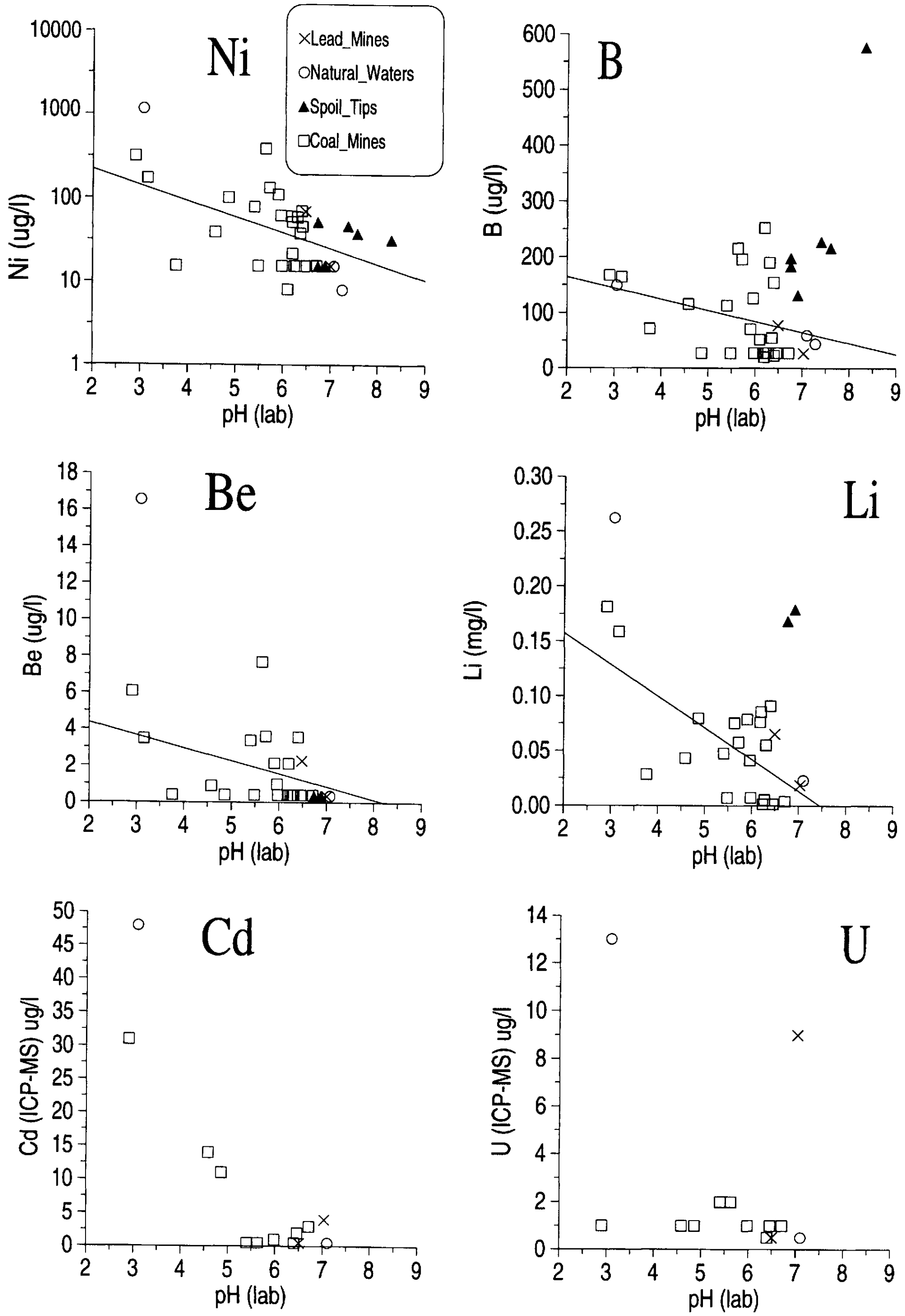

Fig. 7. Relationship of selected trace parameters in filtered samples (Ni, B, Be and Li by ICP-AES; Cd and U by ICP-MS) to pH in the studied waters. The linear regression for coal mine waters only is shown.

related to the hydrodynamics of the mine system and, to some extent, the bulk rock mineralogy, rather than the sulphide content. This theme can be explored further by calculating the net acidity or alkalinity of the mine waters. Where complete analyses were available, acidity was calculated from pH and concentrations of Fe, Mn,

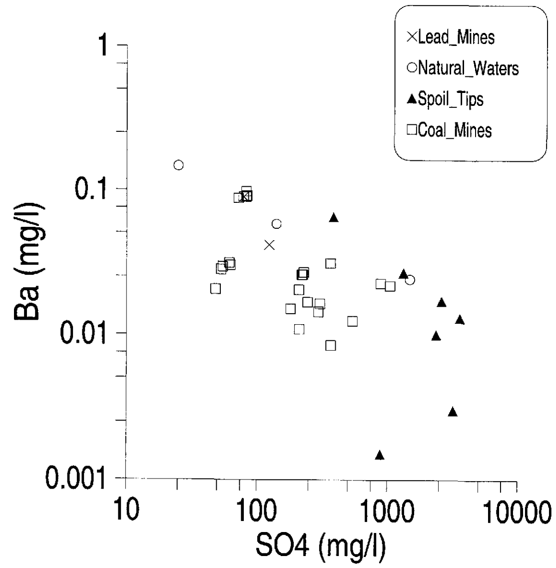

Fig. 8. The relationship of Ba (filtered) to SO_4^{2-} in the studied waters.

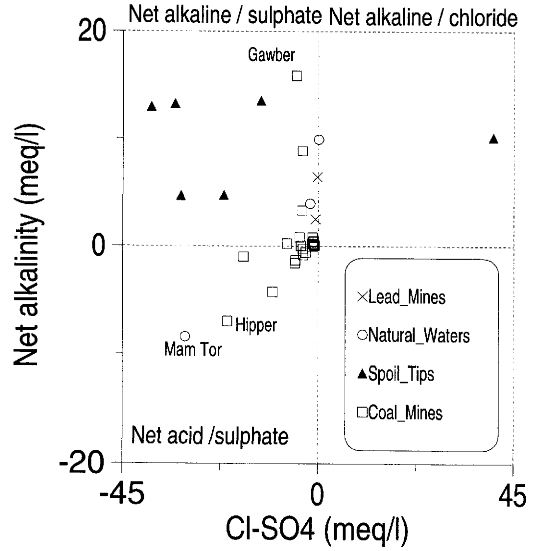

Fig. 9. Plot of net alkalinity (meq/l) versus ($Cl^- - SO_4^{2-}$) (meq/l), for the sampled waters (alkalinities are uncorrected for ionic balance), as recommended by Younger (1995*a*) to distinguish pyrite oxidation waters from saline brines.

Al and Zn (see equation 11), with the assumption that iron and manganese are in the +2 state. Net alkalinity was then calculated by subtracting acidity from determined alkalinity. Most coal mine waters fell in the range − 2 to +2 meq/l net alkalinity (Fig. 9). Two of the most strongly net alkaline waters were Gawber Prospect and Dunston, in both cases consisting of mine waters welling up through a borehole or shaft from deeper, largely saturated workings. The most net acidic workings were the River Hipper discharge, Unstone 2 and Bullhouse. These are all from relatively shallow workings. At least two of the net acidic sites (Bullhouse and Ringinglow) are thought to be drained from below by soughs and largely unsaturated. There is thus some evidence to suggest that the most net acidic waters tend to be derived from free draining, largely unsaturated workings with free access to oxygen (Type 1, see Fig. 10), whereas more net alkaline waters are derived from more saturated or overflowing workings (Type 2), where residence times are longer and sulphate-reducing niches may become established. This is undoubtedly an overidealized picture, however, and it remains a puzzle why Bullhouse, an apparently net acidic and largely unsaturated mine, should be the only system yielding nasally detectable H_2S.

The negative correlation of many elements (Si, Al, Mn, Ca, Mg, heavy metals) with pH probably reflects two factors; (i) pH-related solubility controls and (ii) the enhanced weathering of aluminosilicate and carbonate mineral phases (feldspars, rhodochrosite) by protons released by pyrite oxidation. The relatively rapid kinetics of these reactions allows significant concentrations of, e.g. Si, to occur in solution without being limited by kinetically slow saturation controls due to silica or secondary aluminosilicate phases.

The limited quantities of ankerite and calcite found in the Coal Measures, or Ca- or Mg-rich silicate phases are regarded as the most plausible sources of calcium and magnesium. It should additionally be noted (Fig. 11) that magnesium (in meq/l) often equals or exceeds calcium in mine waters. It is conceivable that the source of some of the magnesium is exchange for iron released by pyrite oxidation. The exact reverse of this mechanism is noted by Drever (1988) in the context of sulphate reduction. It also explains the prevalence of magnesium in some spa waters characterized by pyrite oxidation (e.g. Epsom salts from the Epsom spa in pyritic London Clay: Albu *et al.* 1997).

The fact that potassium and sodium exhibit poor correlations with pH is likely to be indicative of the greater resistance of Na- and K-feldspars to weathering, relative to Ca-feldspars and ferromagnesian silicates. The small non-marine sodium excess in many samples does, however, indicate that limited plagioclase weathering (or, conceivably, ion exchange) is occurring.

The interaction of oxidation-derived protons with other mineral phases can be further explored by the use of speciation modelling, which was carried out on six coal mine waters with field measurements of pH and good ionic balances (hence reliable pH and alkalinity determinations), using the code MINTEQA2 (Allison *et al.* 1991), as shown in Table 4. The modelling attempt must be regarded as preliminary as no information on redox speciation was available (all iron and manganese were assumed to be in +2 state).

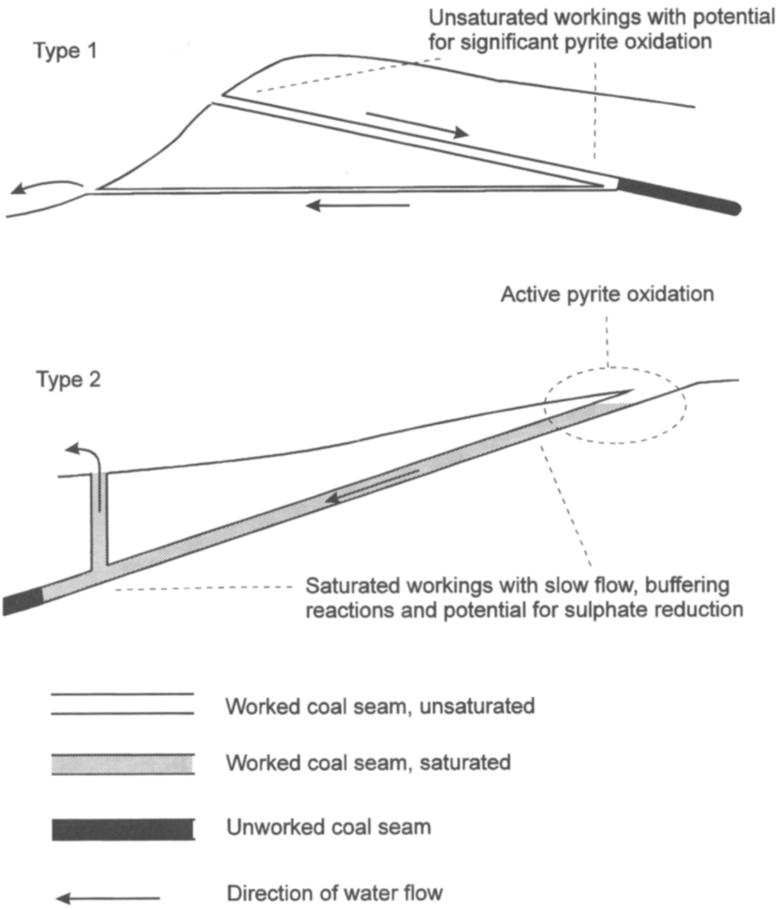

Fig. 10. Two types of mine water discharge: Type 1, non-saturated workings underdrained by a sough; Type 2, deeper saturated workings, overflowing via a borehole or shaft.

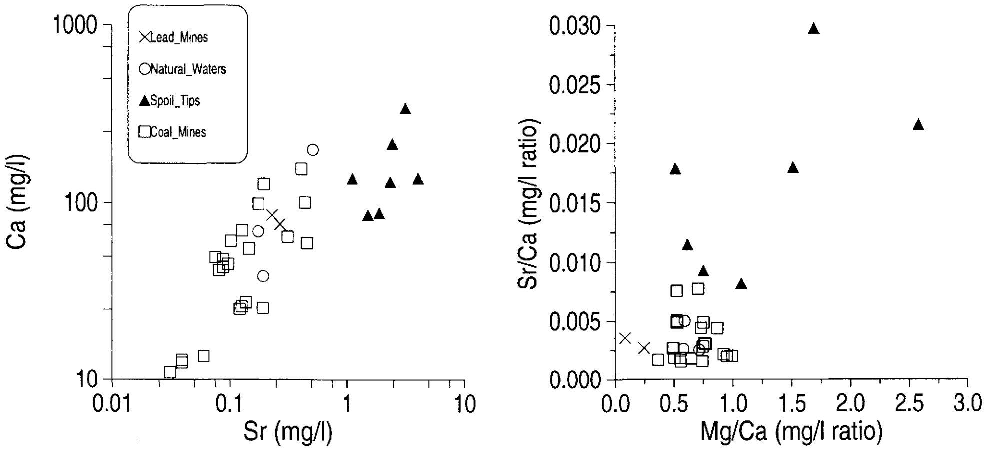

Fig. 11. The relationship of Ca to Sr and the concentration (mg/l) ratios Sr/Ca to Mg/Ca in filtered samples of the studied mine waters.

Table 4. *Saturation indices for selected mineral phases, calculated using the MINTEQA2 code, with the Davies algorithm for activity estimation. Italics show saturation indices of aluminium phases where the aluminium input concentration was below detection limit and has been set to half the detection limit*

	Natural Water	Lead Mine Sough	Coal Mine Spoil Tip	Coal Mine Drainage Waters					
	Kilnhurst SB3	Odin Sough E13	Spoil Tip R3, E51	Dunston Colliery Mine water E70	Hunters Bar Mine water E74	Duke's Level Mine water E62	Goyt Moss Adit Mine water E63	Unstone Fields Mine water E64	R. Hipper Mine water E60
$Al(OH)_3$ (a)	*−1.93*	*−1.74*	*−1.44*	*−1.71*	−0.64	−1.48	−1.59	−2.23	−4.74
$Al(OH)SO_4$	*−4.87*	*−4.36*	*−2.88*	*−2.62*	−1.82	−2.50	−3.20	−2.29	+0.26
$Al_4(OH)_{10}SO_4$	*−2.06*	*−0.94*	*+0.74*	*+0.75*	+4.68	+1.98	+1.14	−0.38	−5.76
Alunite ($KAl_3(OH)_6(SO_4)_2$)	*−2.10*	*−1.22*	*+2.50*	*+2.21*	+4.84	+2.25	+0.89	+1.47	+1.89
Gibbsite ($Al(OH)_3$)	*−0.14*	*+0.05*	*+0.31*	*+0.07*	+1.14	+0.32	+0.23	−0.44	−2.98
Boehmite (AlOOH)	*−0.17*	*+0.01*	*+0.33*	*+0.05*	+1.12	+0.27	+0.17	−0.47	−2.98
Anhydrite ($CaSO_4$)	−1.64	−1.75	−0.50	−1.52	−1.48	−2.14	−2.55	−1.53	−0.81
Gypsum ($CaSO_4 \cdot 2H_2O$)	−1.26	−1.37	−0.15	−1.15	−1.11	−1.74	−2.15	−1.15	−0.45
Epsomite ($MgSO_4 \cdot 7H_2O$)	−3.79	−4.83	−2.68	−3.65	−3.80	−4.39	−4.63	−3.52	−2.96
Barite ($BaSO_4$)	+0.55	+0.59	+0.66	+0.24	+0.28	+0.69	+0.11	+0.34	+0.74
Quartz	+0.60	+0.35	+0.50	+0.66	+0.82	+0.68	+0.59	+0.95	+0.82
Chalcedony	+0.05	−0.21	−0.03	+0.11	+0.27	+0.13	+0.03	+0.40	+0.27
SiO_2 (a)	−0.47	−0.72	−0.54	−0.40	−0.24	−0.39	−0.49	−0.11	−0.24
Kaolinite	*+4.63*	*+4.50*	*+5.37*	*+5.18*	+7.63	+5.72	+5.33	+4.73	−0.07
Halloysite	*+1.18*	*+1.04*	*+1.95*	*+1.73*	+4.18	+2.25	+1.85	+1.28	−3.50
Muscovite	*+5.29*	*+4.74*	*+6.82*	*+5.74*	+9.41	+5.92	+5.42	+4.14	−5.04
Albite	*−0.62*	*−1.31*	*+0.72*	*−0.71*	+0.78	−1.18	−1.67	−1.13	−5.53
Anorthite	*−4.98*	*−5.56*	*−4.58*	*−6.35*	−3.58	−6.35	−6.55	−7.66	−16.78
Microcline	*+0.46*	*−0.46*	*+1.08*	*+0.49*	+2.02	+0.17	−0.14	−0.08	−4.20
Calcite	−0.26	−0.61	+0.16	−1.30	−1.96	−2.39	−2.96	−3.76	—
Dolomite	−0.60	−2.25	+0.31	−2.65	−4.14	−5.02	−6.01	−7.45	—
Siderite	+0.20	−0.85	+0.74	−0.28	−0.56	−1.26	−3.10	−2.12	—
Fluorite	—	−0.03	—	—	—	—	—	—	—

All the modelled coal mine waters were undersaturated with respect to the carbonate phases calcite, dolomite and siderite, saturation being approached most nearly in the most net alkaline water modelled (Dunston colliery). It is thus possible that siderite dissolution from coal-bearing strata, unconstrained by saturation, may be a significant source of iron to coal mine waters. All coal mine waters are saturated with respect to barite, confirming the interpretation of the inverse correlation between barium and sulphate.

All the coal mine waters fell within the range between quartz saturation and amorphous silica saturation. As regards aluminosilicate phases, all coal mine waters were undersaturated with respect to the feldspar phases albite and anorthite (with the exception of Hunters Bar for albite), indicating the potential for active weathering of plagioclase feldspars. Regarding microcline, only the R. Hipper mine water was undersaturated, indicating the highly aggressive nature of this water.

All modelled coal mine waters, excepting the R. Hipper water, were significantly oversaturated with respect to kaolinite and its hydrated form, halloysite. This is thus one of the thermodynamically stable products of feldspar weathering, although its formation appears to be limited by kinetic constraints. All the mine waters, except the Hipper water, are approximately saturated with respect to gibbsite, indicating that this may also be a likely product of aluminosilicate weathering in mine systems and potentially also the main phase limiting aluminium concentrations in most coal mine waters.

The River Hipper mine water is undersaturated with respect to all feldspar phases, halloysite, gibbsite and is also just undersaturated with respect to kaolinite. The water thus lacks the carbonate, silicate and hydroxide buffers potentially present in the other coal mine waters, explaining its low pH and exceptional aluminium concentrations. Eriksson (1981) commented that basic aluminium sulphates, in particular the phase $Al(OH)SO_4$, are the most important buffering phases for aluminium in aluminium-rich sulphate waters, and this is supported by the fact that the Hipper coal mine water is just saturated with respect to this phase (the other coal mine waters are undersaturated).

There is little clear evidence of any admixture of the ferruginous waters with deep-seated Coal Measures brines. However, the elevated concentration of chloride in Gawber Prospect Borehole is possibly indicative of a non-atmospheric source, either contamination from agriculture, industry or road salts or from a geological source. The lowest concentrations of chloride in the mine waters are found in the Goyt Moss Adit, which is also the most elevated and the most westerly of the coal mine waters, indicating a climatic control on chloride concentration. The rainfall in the Buxton area (some 1300 mm, Downing *et al.* 1970) is over twice that in the lower lying areas in the east. A topographic control appears to be confirmed by comparing temperature and chloride in high-altitude waters (Goyt Moss, Mam Tor springs) with lower waters in the same area (Duke's Level and Odin Sough, respectively).

The positive correlation of fluoride with both pH and Ca suggests it is unlikely that anion exchange with hydroxide (as has been suggested by Banks (1997) for non-mine drainage waters in the same area) or weathering of fluorite (calcium far exceeds fluoride in solution) are sources for fluoride. The source of the fluoride is likely to be a dissolution reaction, enhanced under low pH conditions.

Spoil tip leachates

Leachates from coal mine spoil tips are often highly aggressive, with low pH and elevated sulphate, aluminium, iron and heavy metal concentrations. Examples are cited by, for example, Banks (1996), Banks *et al.* (1997), Wiggering (1993) and Madawee (1994). The spoil tip leachates analysed in this study were significantly different in character: iron concentrations vary from moderate to non-detectable. The concentrations of Mn, Al and trace metals are all generally low. There is no positive correlation between iron and sulphate; indeed, there is a slight negative one (Fig. 3). The spoil tip waters have pH values ranging from 6.8 to 8.3. The iron contents decrease with increasing pH, possibly indicating a pH solubility control on iron.

The difference between coal mine water discharges and spoil tip leachates is possibly most pronounced regarding their major ion chemistry. The spoil tip waters have elevated chloride and sodium concentrations, often exceeding 1000 mg/l, potassium at several tens of mg/l and calcium and magnesium concentrations of over 100 mg/l. All the spoil tip waters are net alkaline and sulphate usually, though not always, exceeds chloride (in meq/l). The hydrochemistry of these waters suggests either that pyrite oxidation is not the major control over the water geochemistry or that acidity derived by pyrite oxidation is being effectively neutralized and iron removed by reactions within the tip. It is suggested that these saline waters represent the flushing out of residual pore water brines from the shaley spoil, ultimately derived from depths of several hundred metres (see Table 1). Wiggering (1993) has similarly explained high pH, saline spoil leachates in the Ruhr area of Germany, although he regards them as a transitory phase, reverting to acidic, metal-rich leachates after buffering carbonate phases have been used up and saline pore waters washed out.

Two minor elements, boron and strontium, also exhibit patterns which are characteristic for the spoil leachates. The highest value of almost 600 μg/l for boron is from the most alkaline spoil tip water, possibly reflecting the mobilization of boron as anionic borates at high pH (Fig. 7). Strontium shows a strong correlation with calcium (Fig. 11) in non-spoil waters, indicating a common sources of these two elements (carbonate or silicate weathering). However, the Sr/Ca (mg/l:mg/l) ratio typically exceeds 0.01 in spoil tip waters. It has been shown that this occurs in groundwaters of high pH in both the Carboniferous Limestone and the Coal Measures of the area (Edmunds 1971; Banks 1997), possibly due to calcite saturation being reached earlier in the groundwater evolution than strontianite (or even strontium sulphate) saturation, imposing a limit on calcium but not strontium in solution. The spoil tip waters are also identifiable by their significant non-marine excess of sodium. It has been noted (Eden *et al.* 1957; Banks in press) that sodium carbonate waters are often encountered in deep Coal Measures strata, due to ion exchange with calcium and/or magnesium.

Speciation modelling (see above) reveals that the spoil-tip water is the only one of the modelled waters which approaches saturation with respect to gypsum. Gypsum saturation, with a lack of epsomite saturation may explain the elevated Mg/Ca ratios observed (Fig. 11) in the spoil leachates. The modelled water is also saturated with respect to the carbonates calcite, siderite and dolomite. The siderite saturation could be one explanation for the apparent pH-related constraint on iron concentrations generated in the spoil tip leachates (there may also be constraints related to iron (III) phases, but such redox aspects could not be investigated in the current study). The spoil tip water is also saturated with respect to quartz, gibbsite, barite, albite and microcline, but not anorthite.

Natural ferruginous waters

The Smeekley and Kilnhurst waters had approximately neutral pHs (up to 7.3) and relatively low iron concentrations (1.6 and 3.2 mg/l respectively). The sulphate concentration at Kilnhurst was 141 mg/l, consistent with pyrite oxidation, whereas the Smeekley water contains only 25 mg/l, at the lower end of the range typical of most non-ferruginous Coal Measures and Millstone Grit groundwaters (Banks 1997). The reducing conditions at Smeekley, evidenced by the H_2S odour in the water, suggest that pyrite oxidation is unlikely to be a major source of dissolved iron. A more probable source is dissolution and mobilization as ferrous iron of iron derived from siderite or iron oxyhydroxides in the aquifer matrix.

Speciation modelling indicates that the Kilnhurst water differs from the coal mine waters in being saturated with respect to siderite and approximately saturated with respect to calcite. This may be indicative of longer residence times or more intimate contact with carbonates. Furthermore, in this case, siderite saturation may be a constraint on iron concentrations which may be produced by pyrite oxidation. In other aspects, the saturation indices are similar to those for coal mine waters such as Dunston (i.e. unsaturated with respect to albite and anorthite, approximately saturated with respect to silica, barite, microcline and gibbsite and oversaturated with respect to kaolinite and halloysite).

The Mam Tor water is exceptional due to the very intense pyrite oxidation taking place in the broken and landslipped strata. The pH, iron and sulphate concentrations are 3.1, 27 mg/l and 1480 mg/l respectively. The abundant aluminium (51 mg/l) is evidence of intense aluminosilicate weathering under conditions of low pH. The Mam Tor water also exhibits the highest concentrations of many of the minor elements including Be (17 μg/l), Cd (almost 50 μg/l), Cu (230 μg/l), Co (440 μg/l), Mn (almost 24 mg/l) and U (13 μg/l). Zinc occurs at over 1 mg/l. Thorium determinations were attempted by ICP-MS on seven of the waters sampled in this study. Problems with the analysis hindered quantitative determinations, but in only one sample was thorium detected, at an estimated 7 μg/l, namely the Mam Tor spring water.

The low temperature and chloride concentrations at Mam Tor are related to the altitude and high rainfall at the spring.

Lead mine drainage waters

The water from Allen Hill Spaw has a pH of 6.5 and contents of iron (15 mg/l) and sulphate (124 mg/l) consistent with pyrite oxidation. The Odin Sough, derived from mines in Carboniferous Limestone, yields water with a higher pH value of 7.03 and a relatively low iron content of 0.7 mg/l. This is consistent with the bulk of the water being derived from the limestone, with a component of leakage from pyrite weathering in Millstone Grit. As at the Mam Tor spring, over 1 mg/l zinc is observed in water from the Odin Sough. The source may the same in both instances, namely the weathering of sulphide-rich marine shales near the base of the Millstone Grit, although zinc mineralization within the Odin Mine may also contribute to the latter water.

Odin Sough and Mam Tor are also noteworthy in being the only two waters analysed that returned uranium concentrations greater than 2 μg/l (9 μg/l and 13 μg/l respectively). The source is likely to be cabonaceous shales of the lower Millstone Grit, which are known to contain elevated uranium and pose a radon hazard to houses constructed on them. In addition, the reef-edge Carboniferous Limestone environment occupied by Odin Mine is known to be rich in uranium (Ball *et al.* 1992). Speciation modelling of the Odin Sough water reveals slight undersaturation with respect to calcite, despite being derived from a limestone lead mine. This may reflect the impact of leakage of acidic pyrite oxidation waters into the sough. The water is saturated with respect to fluorite and barite. The low Mg/Ca ratios observed in the lead mine soughs are compatible with ratios observed in many Carboniferous Limestone groundwaters (Edmunds 1971). In contrast to the generally low concentrations of lead (by ICP-MS) in the coal mine waters, values of 8 µg/l and 5 µg/l were found in waters from Odin Sough and Allen Hill Spaw respectively.

Conclusions

Fifteen examples of coal mine drainage water from the north Derbyshire and south Yorkshire area have been sampled and analysed. The hydrochemistry has been compared with other ochre-precipitating waters from the area, including those from spoil tips, from lead mine soughs and from natural ferruginous springs.

Coal mine waters

The majority of the coal mine waters contain several tens of mg/l iron, the maximum of 101 mg/l being from the highly acidic River Hipper discharge in Chesterfield, the lowest, typically some 0.1 mg/l, from the Goyt Moss Adit in the Buxton Coalfield. These two discharges provide the 'end-point' examples for several other parameters, including sulphate, ranging from some 60 mg/l to over 1000 mg/l. There is a strong correlation between iron and sulphate, indicating pyrite oxidation to be the main source of these parameters, although iron seems to generally be preferentially retained within the mine systems, possibly as a ferric hydroxide or sulphate phase. The pH of coal mine waters is typically around 6, with the exception of the River Hipper discharge with a pH of as low as 3.6. The Hipper water contains concentrations of up to 17 mg/l aluminium and precipitates a yellowish white deposit (aluminium hydroxide) in the recipient watercourse, as opposed to the typical orange ochre deposit left by the other waters. Most of the coal mine waters are of low salinity (*c.* 10–40 mg/l Cl^-) and there is little clear evidence of admixture with deeper Coal Measures brines.

The coal mine waters may be net alkaline or net acidic. There is evidence to suggest that net alkaline waters are preferentially derived from saturated, overflowing workings, whereas net acidic waters tend to be derived from shallower, unsaturated workings, drained from beneath by soughs.

The coal mine waters are typically undersaturated with respect to anorthite, albite, calcite, dolomite and siderite, indicating the potential for weathering of these phases. Siderite may thus be an important contributor of iron to Coal Measures mine waters. The waters are typically saturated with respect to gibbsite and microcline and oversaturated with respect to kaolinite. The high-aluminium, low-pH River Hipper mine water is undersaturated with respect to gibbsite, kaolinite and microcline, although it appears that $Al(OH)SO_4$ may be an important buffering phase (Eriksson 1981).

Many of the waters presented in this study do not fit the image popularly presented in the media of 'acid mine drainage'. The waters are not especially acid and, aside from iron and manganese, do not contain especially high concentrations of heavy metals. These waters are not believed to be in any way unrepresentative of the typical chemistry of coalfield mine drainage; indeed, the relatively unaggressive nature of many coal mine waters is recognized in the USA (Hedin *et al.* 1994). Robbins *et al.* (1995) have advocated the use of remote sensing to distinguish the most environmentally aggressive mine waters (yellowish precipitates, e.g. Hipper discharge) from waters of more neutral pH (orange precipitates).

Spoil tip waters

The spoil tip waters studied are typically net alkaline and saline. Iron concentrations are relatively low and range from some 19 mg/l down to <2 µg/l. pH values are around neutral or alkaline, exceeding pH 8 in one case. It is suggested that the leachates from the spoil tips contain a significant proportion of residual, high pH, saline pore water from the deep strata (several hundred metres) mined at the sites, although the Mg/Ca ratios and the sulphate concentrations observed do appear inconsistently high compared with typical Coal Measures brines, summarized in Table 1. Any such residual pore water is likely to combined with a component of aluminosilicate weathering and pyrite oxidation to produce the final leachate composition. The low iron concentrations may be due to precipitation of ferric hydroxide, ferric or ferrous sulphate phases or even siderite (as indicated by siderite saturation) within the spoil.

Although chloride-rich leachates derived from coal mine spoil tips are recognized both from the UK (Bell 1996) and internationally (e.g. from the Ruhr area, Wiggering 1993), it must be stressed that the spoil tip leachates forming part of this study are not typical of all coal spoil leachates. Spoil tips often generate highly aggressive acidic, heavy-metal-rich leachates. Wiggering (1993) believes the well-buffered chloride-rich leachates merely represent an initial phase, with a transition to acidic, ferruginous leachates as the spoil tip ages, residual pore waters are leached out and buffering phases consumed.

Natural ferruginous waters

The natural ferruginous waters show considerable variability, from the low pH Mam Tor springs, containing high concentrations of aluminium and most heavy metals (reflecting intense aluminosilicate weathering and pyrite oxidation in the landslipped, faulted and broken strata), to the relatively highly evolved waters of Kilnhurst and Smeekley, which have a slightly alkaline pH, relatively low iron concentrations and, in the case of Kilnhurst, are approximately saturated with respect to siderite and calcite. The iron in the Smeekley water is unlikely to be derived from pyrite oxidation, due to the reducing conditions indicated by the H_2S content of the water. The iron is more likely mobilized under reducing conditions in the ferrous state from oxides and carbonates in the aquifer matrix.

Ferruginous lead mine waters

Of the two lead mine soughs, Allen Hill Spaw, in Millstone Grit, generates a water of similar composition to many of the coal mine waters. Odin Sough combines features of a limestone-hosted lead mine water (high pH, elevated Pb and Zn, fluorite saturation) with leakage from pyritiferous, broken Millstone Grit strata at the foot of Mam Tor (sufficient iron to cause ochre precipitation). The uranium content of the Odin Sough water (9 μg/l) reflects the uraniferous nature of the lower Millstone Grit shales and the reef edge Carboniferous Limestone environment of the Castleton area.

Summary

'Acid mine drainage' in north Derbyshire and southern Yorkshire is, in most cases, not especially acid. Concentrations of toxic heavy metals and nutrient compounds (e.g. nitrate) are low, rendering mine drainage a potentially useful source of baseflow to the region's watercourses. The main environmental concern is related to moderate to high concentrations of iron which precipitate out on river beds as ochre deposits, smothering benthic flora and fauna. A limited number of mine waters are more acidic and may have a significant content of other metals, notably aluminium, resulting typically in lighter, more yellowish precipitates than the nearer neutral waters. The wide variety in iron and sulphate contents and other hydrochemical parameters is difficult to explain purely on the basis of lithological or coal composition. Hydrodynamic factors (residence time, access of oxygen to workings), microbiological factors (sulphate reducing niches) and kinetics are believed to be of greater importance, casting significant doubt on the widespread practice of acid-base accounting to assess the contamination potential of mine systems. Several of the studied mine waters continue to emit significant iron loadings to the environment almost a century after abandonment (e.g. Duke's Level).

This study has also indicated that ferruginous waters that have a negative visual impact on watercourses (assuming orange streams are deemed unattractive) are not only generated by abandoned mines. They may also be released by natural springs or overflowing abandoned boreholes. In one case, natural springs at Mam Tor generated waters with higher metals loadings and lower pH values than any of the mine waters studied.

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