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The hydrochemistry of coal mine drainage and other ochre waters in North Derbyshire and South Yorkshire, UK

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The hydrochemistry of coal mine drainage and other ochre waters in North Derbyshire and South Yorkshire, UK

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Summary

Fifteen coal mine drainage waters from the Millstone Grit and Coal Measures of Derbyshire and Yorkshire have been hydrochemically compared 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 mgl^{-1} iron, with a range from 0.1 to 101 mgl^{-1}, and sulphate from 60 to over 1000 mgl^{-1}. 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. Coal mine water pH values are typically c. 6, although one water has a pH of 3.6, contains some 17 mgl^{-1} 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 m) 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: Grunnvann	Kull	Gruvevann
England	Jern	Kismineraler
Svovelkis	Vannkjemi	

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THE HYDROCHEMISTRY OF COAL MINE DRAINAGE AND OTHER OCHRE WATERS IN NORTH DERBYSHIRE AND SOUTH YORKSHIRE, UK

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1 OBJECTIVE

Many studies of the problems related to acid or ferruginous mine drainage tend to focus on the parameters having a direct impact on the environment (pH, iron, trace metals, salinity). This report attempts to characterise the hydrochemical composition of drainage waters from abandoned coal mines in one of the most important former mining areas 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 (or ochre) 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. It is also hoped that the results will shed light on the origin of the ferruginous waters and on some of the factors controlling their composition.

This report forms a basic documentation of mining history, site characteristics, analytical and sampling details and analytical results for more concise publications of this material in international journals.

2 INTRODUCTION

As Younger (1995a) and Dumpleton (1995) have pointed out, 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 of at least three dominant types:

(i) ferruginous waters, with sub-neutral pH and high sulphate concentrations. These lead to precipitation of iron (III) oxyhydroxides (or ochre) on stream beds. Their chemistry is dominated by pyrite oxidation processes in workings. Such waters may be net acidic or net alkaline (Hedin et al. 1994). There is 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), whereas more net alkaline waters are derived from more saturated or overflowing workings (Type 2 - see Fig. 1). Younger (1995a) has also speculated whether siderite dissolution may be an important process in the generation of ferruginous coal mine waters.

(ii) saline formation brines (Table 1). These are typically pumped coal mine waters from deep strata and have been recorded in the East Midlands (Downing & Howitt 1969), Tyneside (Anderson 1945, Banks et al. *in press*) and Kent (Buchan 1962). They may contain unacceptable levels of ammoniacal nitrogen (NCB 1982, NRA 1995).

(iii) 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 1995b) coalfields has, at least in part, been responsible for solutions being found to water management problems in these areas. Further south in England 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 its fair share of ferruginous mine waters, but it is important to remember that not all ochre waters are derived from abandoned mines. Spoil tips represent a significant source of contamination and, indeed, natural ochre waters can be found, typically draining broken ground that contains pyrite. Drainage from abandoned boreholes in such strata may also represent another source of iron-rich water. Younger (1995a,b) has criticised the fact that most studies of mine waters have tended to focus on the parameters directly affecting the environment, namely Fe, salinity, some trace metals and pH. He has correctly 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 examines the major and trace element composition of four categories of water from North Derbyshire and South Yorkshire:

(i) mine drainage waters from abandoned mines
(ii) leachates from a number of spoil tips
(iii) natural ferruginous springs
(iv) ochreous lead mine drainage soughs in the Peak District of North Derbyshire.

The locations of the sampled waters are shown in Figs. 2a, b and c.

3 A BRIEF HISTORY OF THE NORTH DERBYSHIRE / SOUTH YORKSHIRE COALFIELD

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 White Limestone, with its rich veins or "rakes" of lead, barite and fluorspar (fluorite) mineralisation, 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 are:

(i) the Ganister or Alton Coal of the Lower Coal Measures, outcropping through the towns of Ogston, Alton, western Sheffield, Loxley and Penistone. The strata have also been mined for refractory ganister for the Bessemer process in the steel industry, causing rejuvenated mining in the western area in around 1856 (Gray 1976).

(ii) the Silkstone (Black Shale) Seam, outcropping through Clay Cross, Chesterfield, Staveley, Sheffield, Pilley and Silkstone itself. The coal is a good quality house, gas and coking coal of c. 1.5 m (5 ft) thickness.

(iii) a little above the Silkstone, still in the Lower Coal Measures, is the Parkgate / Piper Coal.

(iv) probably the main target seam in most modern coal mines has been the Barnsley / Top Hard seam of the Middle Coal Measures, a c. 3 m (9 ft) thick steam coal of low ash content. It is also an ideal coal for hard coke for blast furnaces. The seam crops out through Tibshelf, Renishaw, Elsecar, Worsborough, Barnsley and Gawber.

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 stretching back some 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. There are records of two miners being killed in shallow mines at Rotherham in 1293. In 1370 there are records of leases of pits near Wentworth, while in 1491 the famous Cluniac monks of Pontefract acquired mining rights at Barnsley (Gray 1976). Mining commenced at Barlborough in 1518, while other coal mines active in the 16th century included those at Staveley, Wollaton, Bolsover, Handsworth and Gleadless (Sheffield), Dronfield and the Walton and Beeley Moor areas of Chesterfield. Water drainage soughs are also widely recorded at this time. After the 17th century, coal mining blossomed as a larger scale industry. Pits are recorded at many locations including the Sheffield districts of Crookes, Intake and Ecclesall, Kimberworth, Barnsley, Alfreton, Brimington, Dore, Unstone, Coal Aston, Spital, Wingerworth and Tibshelf (Hopkinson 1976, Griffin 1971).

The depth of workings was still limited by the sough as the most effective drainage technique. Mines below the lowest drainage level could by 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 gradually 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 flows in the mined strata up-dip of the working mines (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. Mine water level recovery has thus taken place, leading to breakouts of polluting ochreous 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. In at least one area (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 mgl^{-1} 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 discharges in the eastern part of the exposed coalfield, ochreous pollution is known to occur from some of the spoil tips associated with these mines.

4 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.

5 THE SAMPLING PROGRAMME

5.1 Organisation of the Studies

The water samples examined in this paper are culled from three separate studies undertaken at the University of Sheffield in 1994/95. The bulk of the samples were taken under study 1, a regional reconnaissance of ochre water hydrochemistry in the study area. Study 2 focused on the sampling and environmental impact assessment of leachates from four spoil tips associated with mines in the eastern part of the exposed coalfield east of Rotherham and Sheffield (Burke 1995). Study 3 was a more detailed environmental impact assessment of the impact of historic ferruginous mine discharges in the catchment of the Limb Brook in southwestern Sheffield

(Gray 1995). The Limb Brook is a minor tributary of the River Sheaf. The sites (Figures 2 a,b,c) are briefly described as follows:

5.2 Sampling Sites: Coal Mine Waters

5.2.1 Bullhouse

The discharge (see Table 2) is derived from the northern workings of the Bullhouse colliery. The colliery was worked for coal from the Halifax Hard seam, together with ganister and fireclay, from the early 1800s (or earlier) until abandonment of the original mine entry in 1915, due to water inflow problems. After 1916, until final abandonment in 1963, the mine's southern area was developed from a new entry through a prominent NE-SW fault (NRA 1994). The workings are interconnected with those of Sheephouse Wood (see below), but the Bullhouse discharge occurs from a drainage level on the northern side of the interfluve into the River Don. The Bullhouse discharge has been flowing since the first world war (abandonment of the original entry) with no apparent decrease in iron content or flow (Dudeney et al. 1994). The Bullhouse discharge drains both saturated and unsaturated workings.

5.2.2 Sheephouse Wood

The Sheephouse Wood adit consists of a brick arched opening draining water from the southern part of the the Bullhouse complex of workings, together with workings associated with the Hand Bank and Hollin Wood collieries, all in the Halifax Hard seam (see above). A 3 km mine water drainage channel (the *ochre track* or *mine water leet*) was constructed from the adit portal to the River Little Don below the dam of the Underbank reservoir to avoid contamination of the reservoir. The Sheephouse Wood adit is widely studied (see Table 2) and documented in reports by Dudeney et al. (1994) and the NRA (1994). Proposals for treatment of the Sheephouse discharge have included its use as a flocculating agent at Langsett Water Treatment Works and settlement following neutralisation by caustic soda and an anionic flocculating agent (Dudeney et al. 1994).

5.2.3 Unstone 2 and 3

Unstone 2 is one of several ochre discharges along the valley of the Drone, mostly derived from the Silkstone (Black Shale) and Parkgate seams (Eden et al. 1957) within the Dronfield syncline. Some of these discharges can be directly related to the Unstone Main Colliery, Summerley Colliery or to Spring Bank Coliery. Unstone 2 and 3 cannot be clearly related to either of these but may conceivably be related to unrecorded workings, in the Parkgate seam or maybe in the higher Deep Hard seam. It is conceivable that Unstone 2 could also be related to old spoil tips. Both discharges emerge on the eastern side of the River Drone and drain into that river. Unstone 2 rises at a high topographic level from a boggy patch in a pasture into a small stream. Sample Unstone 2b (see Table 3) is taken as the combined minewater and streamwater emerges from a culvert near the village hall. Unstone 3 emerges from a pipe at the foot of an embankment at almost river level. Unstone 3 flows perennially, but Unstone 2 dried up during autumn 1995 (a particularly dry year in Yorkshire).

5.2.4 Mill House, Unstone

This discharge emerges in the vegetable garden of Mill House, Unstone, on the west of the Drone. The discharge corresponds to the point at which the outcrop of the Silkstone seam crosses the Drone. Shallow shafts to the Silkstone seam are recorded to the west of the discharge and Battye (1981) documents soughs draining old (18th - 19th) century workings in this area. The persistence of the ochre discharge after over a century should give pause for thought to those designing treatment systems on the basis of a 25 year design life.

5.2.5 Ecclesall Wood

The Ecclesall Wood mine water wells up a short distance from the southwestern bank of the Limb Brook in southwestern Sheffield. The hillside to the west of this location contains a number of old workings in the sulphur-rich Ganister Seam, from which the discharge is believed to be derived. The workings here are also potentially very old, the first recorded mines in the Dore area dating back to the 17th century.

5.2.6 Dore Conduit

The ochre water emerges from pipe in an apparently infilled valley, forming a tributary to the Limb Brook. If the valley has been infilled with spoil, part of the ferruginous nature may be due to leaching of this fill, although it appears likely that mine waters derived from workings in the Ganister Seam may also play a role (see above). Ant minewater is likely to be mixed with surface water drainage.

5.2.7 Ringinglow Mine

The Ringinglow mine worked the pyritiferous Ringinglow Coal (3 - 4 % S) near the top of the Millstone Grit, up until 1911 (Eden et al. 1957). Some 700 m downstream along the Limb Brook from the old colliery site, an ochre spring emerges from the valley side. It is suspected that this is a drainage level from the Ringinglow Colliery or other old workings although it has not been possible to confirm this hypothesis.

5.2.8 Gawber Prospect borehole

Ochre water flows under artesian head from this exploration borehole for a potential opencast site at Gawber, near Barnsley. The borehole is believed to have encountered old workings in the productive Barnsley Seam, at shallow depth, from which the water is derived. At this location the Barnsley seam is near outcrop.

5.2.9 Dunston Colliery, Sheepbridge

This mine water is believed to be derived from the shaft of the old Dunston Colliery in the northern suburbs of Chesterfield and discharges from the northern bank of the Barlow Brook. The mine water is discussed by Eden et al. (1957) who regard the shaft as being the focus of discharge for mine water from workings in the Silkstone Seam from several collieries within the Sheepbridge syncline.

5.2.10 River Hipper discharge

This discharge occurs from the south bank of the Hipper, just before its confluence with the Rother. Its origin is not clearly known, although it may be related to the workings of the Boythorpe Colliery. The chemistry of the water clearly indicates it to be mining related, although oily odours suggest it may be contaminated by effluent from the surrounding industrial area. Unlike the other mine water discharges discussed in the paper, the Hipper discharge precipitates a white material in addition to orange ochre. This is believed to be aluminium hydroxide, typical of highly acidic discharges of this nature.

5.2.11 Hunters Bar Discharge

This discharge emerges from the north side of the Porter Clough from a culvert under the roundabout of Hunters Bar, western Sheffield. It visibly impacts the river for some distance eastward. There are no known mine workings in the vicinity of Hunters Bar and it is thus hypothesised that the culvert may be a storm drain, the mine water entering it at an indeterminate point along its course.

5.2.12 Greystones Discharge

This ochreous discharge emerges in a wood to enter a southern tributary of the Porter Clough in west Sheffield. It is believed to be related to historic workings in the Ganister Coal or Soft Bed (Coking) Coal in the area, described by Eden et al. (1957).

5.2.13 Duke's Level and Goyt Moss Adit, Buxton

Buxton lies in the extreme west of Derbyshire, and differs from the other mine water sites in being situated on the western limb of the Peak District anticline. To the west of Buxton lies a small coalfield which was actively worked between c. 1600 and 1919, extracting the Ringinglow and Goyt coal seams from the top of the Millstone Grit and base of the Coal Measures (Roberts & Leach 1985). The coalfield lies in a small subsidiary synclinal structure and the workings do not exceed a few tens of metres in depth. The underground mines appear to be drained by only two discharges: a "sough" (or adit) out into the Goyt Moss valley (Grid Ref. SK 018 721), draining predominantly workings in the Goyt Seam, and a (now partially infilled) canal named the Duke's Level. The canal (SK 037 723), over 2 miles long, was used both to transport barges underground to the working faces and to drain mine water, mainly from the Ringinglow Seam, into a headwater of the nearby River Wye.

The drainage water from the Duke's Level was typical "ochre water" during the lifetime of the mine, and still is today. The water draining from the Goyt Moss adit, on the other hand, is only very mildly ochrous. There is little visible ochre precipitation on the stream bed, although iron hydroxides can be seen to have accumulated within the foliage of stream bed and stream-side vegetation.

5.3 Sampling Sites: Ochreous Lead Mine Waters

5.3.1 Odin Sough

The Odin Mine is an old lead mine in the Lower Carboniferous Limestone at the foot of Mam Tor. A long sough was driven through the stratigraphically overlying Millstone Grit to a tributary of the Peakshole Water in Castleton to allow deep mining of the rake. Lead mine soughs normally discharge good quality water (Edmunds 1971) but Odin Sough is an exception in discharging a mildly ochreous water with a significant metal content. The metals are 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.

5.3.2 Allen Hill Spaw

This is an adit emerging from Millstone Grit strata at the base of "The Dimple" at Matlock Bank. An inscription states that it was restored as a spa in 1824. The origin of the sough is uncertain but Naylor (1983) and Banks et al. (*in press*) believe it is likely to drain workings in lead ore veins which may extend up from the Carboniferous limestone into the Millstone Grit.

5.4 Sampling Sites: Spoil Tip Waters

The spoil tip waters were collected from 4 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 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.

5.5 Sampling Sites: Natural Ochre Waters

The occurrence of natural ochre 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. *in press*), Ashover, Treeton and Fulwood area, Sheffield (Wilson 1991).

5.5.1 Kilnhurst Boardwalk

At this location, an ochre water discharges into a small stream. No mine workings or spoil tips are recorded in the area. The discharge coincides with the outcrop of the Shafton Coal Seam and Marine Band shale. Such marine bands are associated with high sulphur contents. It is assumed that the ochre water is a natural spring associated with weathering of the outcrop, although there is a possibility that it is derived from very old, unmapped workings in the Shafton Coal.

5.5.2 Mam Tor

Mam Tor, the "Shivering Mountain", is 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 ochreous springs are derived from the disturbed (and hence oxidised) landslip strata. The spring area sampled during this study emerged at the top of the main landfill area, near the base of the slipped wall. The springs of Mam Tor was 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.

5.5.3 Smeekley Borehole

Smeekley was a water supply borehole drilled for N.E.Derbyshire Joint Water Committee in 1952 and now owned by Severn Trent water. Its use was discontinued in c. 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 ferruginous and has a significant visual effect on the bed of the brook. The borehole is 287 m deep, reaching the Chatsworth Grit horizon, and draws the its water from both the Lower Coal Measures (Loxley Edge Rock, Crawshaw Sandstone) and the Upper Millstone Grit (Rough Rock, Longshaw Grit and Chatsworth Grit) (Eden et al. 1957).

5.6 Water Sampling and Analysis

The majority of sampling took place in winter/spring 1995 for study 1 and summer 1995 for studies 2 and 3. Samples were taken as near as was practically possible to the emergence of the ochre discharge. All polythene sampling flasks were rinsed thoroughly three times with groundwater, and (for filtered samples) twice with filtered (0.45 mm Millipore filter) water before sampling.

The following samples were then taken in polythene bottles with screw caps.

(a) 1 x 100 ml unfiltered, unacidified
(b) 2 x 100 ml filtered (0.45 mm Millipore filter and polythene syringe) and acidified (0.5% x 65% Ultrapur nitric acid) in the field.
(c) 1 x 500 ml unfiltered, unacidified

Sample (a) was analyzed for anions (F^-, Br^-, Cl^-, $SO_4^=$, NO_3^-) by ion chromatography by the University of Sheffield Department of Animal and Plant Sciences.

For studies 1 & 2, one quantum of sample (b) was analyzed by inductively coupled plasma emission spectroscopy (ICP-AES) for a suite of elements by the Sheffield Assay office (samples up to 1/6/95) and by the University of Sheffield Department of Earth Sciences following that date. The second quantum of sample (b), where collected, was analyzed by ICP Mass Spectrometry for a suite of elements including Pb, U and Sn by the University of Sheffield joint ICP-MS facility. The purpose of study 3 was to examine total metal content of waters and analysis of Fe, Zn, Cu, Ni, Cd and Pb was performed on unfiltered water samples by furnace atomic adsorption (Cu, Ni, Cd, Pb) and flame atomic adsorption (Fe, Zn). These samples have been identified in Table 3 (Gray 1995).

Where a significant visible precipitation of iron was noted on the 0.45 mm filter during sampling, a parallel unfiltered sample of water was collected and acidified in the same manner as the filtered sample, prior to ICP-AES analysis.

The 500 ml sample (c) was used for laboratory determinations of pH, electrical conductivity and alkalinity. For many mine waters, pH and temperature were also measured in the field using a Palintest Microcomputer 9000 meter. Where water was flowing from an opening full bore (e.g. upwelling mine waters) or from slow, 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 a syringe with disposable tips was used to collect a quantum of 10 ml water directly from the water emergence. This was immediately injected slowly into a 20 ml vial containing 10 ml of prefilled scintillation liquid. Flasks were delivered to the British Geological Survey and analyzed by scintillation counter. Results were back adjusted for radioactive decay to give a radon activity in Bql^{-1} at time of sampling.

Two samples were analyzed 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 in the Figures in this report, analytical values below the detection limit were set to half the detection limit.

6 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.

6.1 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, despite the fact that some deposition of orange ochre could often be seen on the filter disc (Fig. 3). 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 iron values 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 low. The greatest percentage losses upon filtration were observed in three samples with high pH and low iron content (Fig. 3). It can thus be concluded that for most ochre waters with an iron content of > 5 mgl^{-1} 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.

6.2 Analytical Technique

The correlation between analytical results for ICP-AES and ICP-MS varied from good to very poor, depending on the parameter measured. For Mn, for example, a very good correlation was achieved, while acceptable correlations were found for Zn and Fe. For Ni, V and Ba the correlations were less satisfactory (although still in general agreement for most samples) while for Al the correlation was disappointing. For all of these parameters, the ICP-AES results have been taken as the basis for data analysis. Correlations for Cd, Pb and Cu, in particular, showed significant discrepancies. There is evidence to suggest that Cd results by ICP-MS are the more reliable for these parameters and these are presented briefly below. The discrepancies relating to Pb, Cu and Cd in coal mine waters have been noted in sudies performed by other workers and further analytical work on possible interferences is required.

6.3 Laboratory contra Field Determination 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 the fact 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.

6.4 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 ochreous waters was satisfactory (including Sheephouse, Bullhouse, Ecclesall Wood, 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 are a number of waters where alkalinity, as measured in the laboratory, appears to be significantly inaccurate, leading to deviant ionic balances. In conclusion, although laboratory determinations of pH and alkalinity can reproduce field conditions for some ochre waters, they may significantly and unpredictably deviate from field values. The findings thus support the conclusions of several other workers in emphasising the need for organisations engaged in hydrochemical work on mine waters to acquire the necessary equipment for field determinations of pH and alkalinity.

7 OCHRE 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 mobilisation 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 mobilise 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 often assumed to be broadly 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 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 an electron acceptor for pyrite oxidation). As the complete utilisation of oxygen-saturated water (containing approximately 11 mg O_2/l at 10°C) will only release sulphate concentrations of approximately 17 mgl^{-1}, 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 mgl^{-1} 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 oxidised 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.

7.1 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.

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

$$H_2S + 2O_2 \leftrightarrow 2H^+ + SO_4^{=} \qquad (2)$$

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

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).

7.2 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).

$$CaCO_3 + 2H^+ \_ Ca^{2+} + 2HCO_3^- \tag{4}$$

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

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

7.3 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.

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

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

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

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

- sulphate reduction by a carbon substrate or by methane

$2CH_2O + SO_4^{=} \leftrightarrow 2HCO_3^- + H_2S$ (10)

$H^+ + CH_4 + SO_4^{=} \leftrightarrow HCO_3^- + H_2S + H_2O$ (11)

7.4 Mineral Acidity

Hedin et al. (1994) and Younger (1995a) 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:

$$\text{Acidity (meql}^{-1}\text{)} = 1000.10^{-pH} + (Fe^{2+})eq + (Fe^{3+})eq + (Al^{3+})eq + (Mn^{2+})eq + (Zn^{2+})eq \qquad \text{(equation 12)}$$

where (M)eq is the concentration of the metal ion M in $meql^{-1}$. 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 being discussed later and shown in Figure 11.

Acidity is thus generated not only by reactions releasing protons to solution but also reactions releasing the relevant metals.

8 RESULTS

8.1 Organic Contaminants

It has been suspected that refractory organic contaminants may be leached from coal horizons. Evidence for this 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 analyzed by GC-MS in this study, from Ecclesall Woods and Gawber Prospect ochre discharges, both showed no detectable (< 1 ppb) PAH compounds. Further work using excitation-emission matrix spectroscopy is ongoing and will be reported shortly.

8.2 Iron, Sulphate and Acid

8.2.1 Coal Mine Waters

The coal mine waters show a considerable degree of variability (Fig. 4). Iron contents range from 50 mgl^{-1} (at Goyt Moss) to 101 mgl^{-1} (R. Hipper, Chesterfield). The field pH varies from c. 6.6 (Goyt Moss - discounting the samples Unstone 2b and Dore Conduit, which are mixtures of mine- and surface water) to 3.6 (R.Hipper AMD). Sulphate values range from 1044 (R. Hipper AMD) to 48 mgl^{-1} (Goyt Moss). Median values of Fe and sulphate are 12 and 210 mgl^{-1} respectively. The range in pH between the extremes mentioned above conceals the fact that the large majority of measured pH values lie around 6.

As might be expected, a plot of total iron (filtered samples) vs. sulphate (Fig. 4) reveals a strong ($r^2 = 0.872$) linear correlation between the two parameters for coal mine waters. The regression line passes approximately through the origin with a gradient of $Fe/SO_4^=$ (mgl^{-1} ratio) = 0.0986 or $Fe/SO_4^=$ (molar ratio) = 0.17. The pyrite oxidation equation (1) predicts that 2 moles $SO_4^=$ are generated for every mole of Fe^{2+}. The strong linear correlation suggests that the generation of sulphate and iron are ultimately derived from the same process of pyrite oxidation (rather than, for example, siderite dissolution for iron), but simple pyrite oxidation is not the whole story. It appears that iron is being retained within the subsurface system, probably by some form of precipitation or adsorption reaction. Possible solid phases include ferric oxyhydroxides (following oxidation and hydrolosis of Fe^{++}), or sulphates such as jarosite ($KFe^{III}_3(OH)_6(SO_4)_2$). In the case of jarosite, the iron is preferentially removed in a molar ratio of 3/2 relative to sulphate, depressing the $Fe/SO_4^=$ ratio in solution.

The dissolved iron content in coal mine waters decreases with increasing pH (Fig. 5), possibly reflecting both the decreasing solubility of iron with increasing pH and covariation due their common source in pyrite. The correlation between pH and Fe is not as strong as that between iron and sulphate.

8.2.2 Spoil Tips

In spoil tip waters, iron concentrations vary from moderate to non-detectable. There is no positive correlation between iron and sulphate, indeed, there is a slight negative one (Fig. 4). The spoil tip waters have pH values ranging from 6.8 to 8.3. The iron contents decrease with increasing pH. The high pH values may control the solubility of the iron, explaining the low iron concentrations. The chemistry of these waters suggests either that pyrite oxidation is not the major control over the water geochemistry or that acidity derived from pyrite oxidation is being effectively neutralised and iron removed by some mineral phase within the tip.

8.2.3 Natural Ochre Waters

The Smeekley and Kilnhurst waters revealed circum-neutral pH (up to 7.3) and relatively low iron concentrations (1.6 and 3.2 mgl^{-1} respectively). The sulphate concentration at Kilnhurst was 141 mgl^{-1}, indicating pyrite oxidation, whereas the Smeekley water contains only 25 mgl^{-1}, at the lower end of the range found in most non-ochreous Coal Measures and Millstone Grit groundwaters. This is likely to be partially due to the evident sulphate reduction occurring in this water.

The Mam Tor water is exceptional, indicating that very strong pyrite oxidation is taking place in the broken and landslipped strata. The pH, iron and sulphate values are 3.1, 27 mgl^{-1}, 1480 mgl^{-1} respectively. The low temperature is due to the altitude of the spring.

8.2.4 Lead Mine Soughs

The Odin Sough, derived from mines in Carboniferous Limestone, yields water with an understandably high pH value of 7.03 and a relatively low iron content of 0.7 mgl^{-1}. 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.

Allen Hill Spaw has somewhat lower pH, higher iron content (15 mgl^{-1}) and sulphate (124 mgl^{-1}), indicative of pyrite oxidation

8.3 Alkalinity

Substantial alkalinity only begins to be observed at pH values > c. 5.5 (below pH 4.5, alkalinity is, by definition, zero), indicating that there appears to be a pH buffering system at around 5.5 to 6, the pH commonly observed in most coal mine waters. 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 $meql^{-1}$.

8.4 Silicon and Aluminium

Dissolved silicon shows a negative correlation with pH (Fig. 5). In coal mine waters, the maximum silicon concentration is that in the extremely acid mine water of the river Hipper (19.6 mgl^{-1}) and the lowest (4.4 mgl^{-1}) in Goyt Moss adit. The negative correlation (Fig. 6) is likely to be due to the increased weathering of silicates and aluminosilicates at high pH by protons derived from pyrite oxidation.

The abundant aluminium in the Hipper mine water (up to 17 mgl^{-1}) and the Mam Tor spring water (51 mgl^{-1}) are evidence of intense aluminosilicate weathering under conditions of low pH. Aluminium levels not significantly exceeding 1 mgl^{-1} in the other samples (Fig. 5) 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.

8.5 Manganese and Zinc

These are typically the next two most prominent heavy metals in ochre waters after iron. Manganese shows a slight negative correlation with pH in coal mine waters (Fig. 5), with concentrations typically near or greater than 1 mgl^{-1} in waters with $pH < 6$. The highest concentrations are seen in the waters from Bullhouse, with almost 20 mgl^{-1}. Concentrations over 5 mgl^{-1} are also observed at Unstone 2 and Unstone 3. The lowest concentrations of 0.13 mgl^{-1} are observed at Goyt Moss.

The concentrations of manganese in spoil tip waters are typically below 3 mgl^{-1}. The highest measured concentration of manganese in any of the samples was at Mam Tor, almost 24 mgl^{-1}.

Zinc in coal mine waters also shows a negative correlation with pH (Fig. 5) although this is almost entirely controlled by the high values measured in the R. Hipper discharge of up to 0.22 mgl^{-1}. Concentrations of over 1 mgl^{-1} are observed in the springs from Mam Tor and also in 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 mineralisation within the Odin Mine may also contribute to the latter water.

8.6 Fluoride

Surprisingly, fluoride exhibits a fairly strong negative correlation with pH in coal mine waters and a positive correlation with calcium. This is indicates that it is unlikely that anion exchange with, for example, hydroxide or weathering of fluorite (calcium far exceeds fluoride in solution) are sources for fluoride. The source of the fluoride is thus likely to be the same as the source of the bulk of the calcium, i.e. weathering of silicates or carbonates.

8.7 Major Cations

8.7.1 Mine Waters and Natural Ochre Waters

All major cations except sodium show a negative correlation with pH (Fig. 6), the strongest being observed for calcium and magnesium. No correlation with pH is observed for sodium.

The calcium and magnesium may be derived either from weathering of silicates or carbonates or from exchange reactions on clay minerals. It is known that silicate weathering is occurring in the system (negative correlation of Si with pH), and weathering of Ca and Mg-silicates seems a likely source of these cations. The Coal Measures are generally poor in calcium and magnesium carbonates, although small quantities of ankerite and calcite can be found. It should additionally be noted (Fig. 9) that magnesium (in $meql^{-1}$) often equals or exceeds calcium in mine waters. It is conceivable that the source of magnesium is exchange, in ferromagnesian minerals, 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 characterised by pyrite oxidation (e.g. Epsom salts from the Epsom spa in pyritic London Clay - Albu et al. *in press*).

Chloride concentrations in coal mine waters show no correlation with pH and are typically between 10 and c. 40 mgl^{-1}, indicative of derivation from sea salts in evapotranspiratively concentrated precipitation. There is little clear evidence of any admixture with deep-seated Coal

Measures brines. The highest chloride concentration of 91 mgl^{-1} is from the Gawber Prospect Borehole and is indicative of a non-atmospheric source, either contamination from agriculture, industry or road salts or from a geological source. The lowest concentrations are found in the Goyt's Moss Adit, which is also the most elevated and the most westerly of the coal mine waters; interestingly, the concentration is comparable to that of Mam Tor springs, another elevated and westerly water. It is also noteworthy that the chloride concentrations in the Duke's Level water are over twice as great as from the Goyt's Moss adit, despite draining the same complex of workings. The two adits do not, however drain the same seams; it is therefore conceivable that the adits drain areas of workings fed by differing recharge regimes. The higher temperature of the Duke's Level water suggests a lower elevation of the recharge area. Corresponding differences in temperature and chloride are noted between the high level Mam Tor springs and the lower Odin Sough adit.

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. Sodium shows a very strong correlation with chloride (Fig. 7), indicating a similar origin (i.e. marine salt or, possibly, mixing with deep brines). A small excess of sodium over chloride in many samples indicates that some plagioclase weathering is occurring (or, conceivably, ion exchange), although the Na/Cl ratio exceeds unity in only three non-spoil-water samples, namely Sheephouse Wood, Mill House (Unstone) and Dunston.

8.7.2 Spoil Tips

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 mgl^{-1}, potassium at several tens of mgl^{-1} and calcium and magnesium concentrations of over 100 mgl^{-1}. It is suggested that these very saline waters represent the flushing out of residual pore waters brines from the shaley spoil, which represents material from depths of several hundred metres.

The spoil tip waters are also identifiable by their significant non-marine excess of sodium (Na* - i.e. sodium in excess of that expected from the ratio Na/Cl in seawater - Fig. 7). 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.

8.8 Nitrate

Nitrate concentrations in coal mine waters are low in comparison with many UK groundwaters. Only two waters exceed 5 mgl^{-1}, sample E32 from the Ecclesall Woods discharge in February (16 mgl^{-1}) and the Hunters Bar discharge (5.9 mgl^{-1}). The former of these discharges from below agricultural land, the latter from an urban drain which may receive some sewage contamination. The Ecclesall Wood discharge did not, however, contain significant nitrate when sampled in May, possibly indicating rapid travel times and short residence times (this interpretation is supported by observed seasonal variations in flow). The generally low nitrate levels support the opinion (e.g. NRA 1995, Banks et al. *in press*) that coal mine water discharges are important providers of low nitrate baseflow to watercourses

8.9 Non-Heavy Metal Trace Elements

Lithium exhibits a weak negative correlation with pH in the coal mine waters, although the spoil tip waters exhibit elevated Li concentrations of over 150 mgl^{-1} despite their high pH (Fig. 8).

Beryllium exhibits a weak negative correlation with pH (Fig. 8). All concentrations are < 10 mgl^{-1} with the exception of the Mam Tor water (17 mgl^{-1}).

Boron is an important trace constituent in coals, but shows no very convincing correlation either with pH or with salinity. The highest value of almost 600 mgl^{-1} is from the most alkaline spoil tip water, possibly reflecting the mobilisation of boron as anionic borates at high pH (Fig. 8).

Strontium shows a strong correlation with calcium (Fig. 9) in non-spoil waters, indicating a common sources of these two elements (carbonate or silicate weathering). However, the Sr/Ca ($mgl^{-1}:mgl^{-1}$) ratio typically exceeds 0.01 in spoil tip waters. It has been shown that this occurs in groundwaters of high pH in waters from both the Carboniferous Limestone and the Coal Measures of the area (Edmunds 1971 and Banks *in press*), 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. Mg/Ca ratios are also elevated in spoil tip waters (Fig. 9), possibly due to gypsum saturation (limiting calcium solubility) but lack of epsomite saturation controls (see below). The low Mg/Ca ratios observed in the lead mine soughs are compatible with ratios observed in many Carboniferous Limestone groundwaters (Edmunds 1971).

8.10 Trace Heavy Metals

Trace metal hydrochemistry is not dealt with in detail in this paper; however the following brief comments may be made:

Barium exhibits a positive correlation with pH and a negative one with sulphate (Fig. 10). This is indicative of barite ($BaSO_4$) saturation imposing a solubility constraint on barium concentrations.

Nickel concentrations are typically in the range 10 - 100 mgl^{-1} and do show some indication of a negative correlation with pH (Fig. 8).

Cadmium concentrations, as measured by ICP-MS are very low for all waters of $pH > 5$, but reach values of c. 30 and c. 50 mgl^{-1} in the R. Hipper mine water and the Mam Tor springs, respectively. A negative correlation with pH is thus observed (Fig. 8).

Lead, by ICP-MS, on selected samples returned values in a range from < 1 to a maximum of 8 mgl^{-1} in Odin Sough. The other lead mine water (Allen Hill Spaw) returned a value of 5 mgl^{-1}. The median value for the nine analyzed coal mine waters was < 1 mgl^{-1}.

Copper, by ICP-MS, on selected samples returned values in a range from < 1 to a maximum of 230 mgl^{-1} at Mam Tor Springs. The median value for the nine analyzed coal mine waters was 3 mgl^{-1}.

Tin, by ICP-MS, on seven waters (6 coal mine water and Mam Tor), all returned values < 3 mgl^{-1}, with the exception of the River Hipper minewater at 4 mgl^{-1}.

Cobalt, by ICP-MS, on selected samples returned values in a range from < 1 to a maximum of 440 mgl^{-1} at Mam Tor Springs. The median value for the nine analyzed coal mine waters was 15 mgl^{-1}.

8.11 Radioelements

Uranium concentrations show no clear correlation with pH (Fig. 8). Concentrations do not exceed 2 mgl^{-1} in any waters where U was determined, with the exception of Odin Sough (9 mgl^{-1}) and Mam Tor (13 mgl^{-1}). Both of these localities are associated with broken ground in the lower Millstone Grit carbonaceous shales, 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).

Radon determinations were only deemed possible at three sites, the maximum recorded being 24 Bql^{-1} at Ecclesall Woods, where the water wells up from the ground without opportunity for degassing. A low value 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.

Thorium determinations were attempted by ICP-MS on seven of the waters. Problems with internal thorium adsorption hindered quantitative determinations, but in only one sample was thorium detected, at an estimated 7 mgl^{-1}, in the Mam Tor spring water.

8.12 Alkalinity and Acidity

Where complete analyses were available, acidity was calculated from pH and concentrations of Fe, Mn, Al and Zn (see equation 12). It was found to be dominated by iron, which, for the purposes of calculation was assumed to be in a ferrous state. Net alkalinity was then calculated by subtracting acidity from determined alkalinity. Most coal mine waters fell in the range -2 to + 2 $meql^{-1}$ net alkalinity (Fig. 11). 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 underneath by soughs and largely unsaturated.

One can thus hypothesise two types of workings as illustrated in Fig. 1; type 1 yielding typically net acid and type 2 net alkaline waters. This is undoubtedly an overidealised 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.

In almost all coal mine waters, sulphate exceeds chloride in terms of $meql^{-1}$. All the spoil tip waters are net alkaline. It is hypothesised that the spoil tip waters are dominantly derived from leaching of residual pore water brines from the deeply derived spoil. This process may be coupled with varying degrees of pyrite oxidation to generate sulphate.

9 SPECIATION MODELLING

Speciation modelling 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, as shown in Table 4. Speciation modelling was also carried out on one water from each of the other three ochre water groupings, again with good ion balances, namely Kilnhurst Boardwalk, Spoil Tip R3 and Odin Sough. 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 +II state). Anions measured by ion chromatography were assumed to represent total concentrations of those anionic elements in solution, an assumption which could be checked by speciation results from MINTEQA2.

9.1 Coal Mine Waters

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 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. The other coal mine waters were approximately saturated with respect to microcline (with the exception again of Hunters Bar which was oversaturated).

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 the kaolinite. The water thus lacks the carbonate, silicate and hydroxide buffers 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).

All coal mine waters are saturated with respect to barite, confirming the interpretation of the inverse correlation between barium and sulphate.

9.2 Other Ochre Waters

The Kilnhurst natural ochre 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 and indicates that, in this case, siderite saturation is 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, saturated with respect to silica, barite, microcline and gibbsite and oversaturated with respect to kaolinite and halloysite).

The Odin Sough water is remarkable in being slightly undersaturated 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 spoil tip water is interesting from a number of aspects. It is the only water which is saturated with respect to gypsum. It 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.

10 CONCLUSIONS

Fifteen examples of coal mine drainage waters from the North Derbyshire and South Yorkshire area have been sampled and analyzed. 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 ochre springs.

10.1 Coal Mine Waters

The majority of the coal mine waters contain several tens of mgl^{-1} iron, the maximum of 101 mgl^{-1} being from the highly acidic River Hipper discharge in Chesterfield, the lowest, typically some 0.1 mgl^{-1} 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 mgl^{-1} to over 1000 mgl^{-1}. 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 coal mine water pH 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 mgl^{-1} aluminium and precipitates a yellowish white deposit (aluminium hydroxide) in the recipient watercourse, in addition to the typical orange "ochre" deposit left by the other waters. Most of the coal mine waters are of low salinity (c. 10 - 40 mgl^{-1} Cl^{-}) and there is no clear evidence of admixture with deeper Coal Measures brines. Concentrations of Rn do not appear to reach levels exceeding a few tens of Bql^{-1} in the waters studied, and U does not exceed 2 mgl^{-1}.

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, underdrained workings.

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 minewater 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).

10.2 Spoil Tip Waters

The spoil tip waters studied are typically net alkaline and saline. Iron concentrations are relatively low and range from some 19 mgl^{-1} down to < 2 mgl^{-1}. pH values are 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, summarised 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 recognised 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. The relatively benign nature of these leachates is thought to be due to their derivation from deep, recently mined strata containing highly saline, high pH pore water. 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.

10.3 Natural Ochre Waters

The natural ochre 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 in 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 mobilised under reducing conditions in the ferrous state from oxides and carbonates in the aquifer matrix.

10.4 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 Carboniferous 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 (9 mgl^{-1}) reflect the uraniferous nature of the lower Millstone Grit shales and the reef edge Carboniferous Limestone environment of the Castleton area.

10.5 Summary

Drainage waters from abandoned coal mines are characterised by pyrite oxidation as the dominant reaction, although the importance of, for example, siderite dissolution as a source of iron, cannot be discounted. There is some suggestion that net alkaline waters tend to be derived from overflowing, saturated workings with long residence times, whilst the more aggressive, net acidic waters tend to be derived from underdrained aerated working.

Natural ferruginous waters, e.g. Mam Tor, may emerge from broken pyritiferous strata which have essentially an undistinguisable chemistry from acidic coal mine drainage. The strata at Mam Tor are, however, exceptionally disturbed and one might expect most natural ferruginous springs to exhibit a more buffered chemistry (as seen at Kilnhurst) due to less oxygenation and longer residence times. Ferruginous waters may also occur under highly reducing conditions where iron is mobilised from oxide and carbonate phases in the aquifer matrix, as seems to be the case at Smeekley.

Lead mine soughs may emit ferruginous waters where they pass through and drain pyritiferous strata. The hydrochemistry is similar to coal mine drainage but parameters related to the mine source (e.g. Pb, Zn or even bicarbonate, if the mine itself is in limestone) may be elevated.

The spoil tip waters studied have a completely different character to the other ferruginous waters. They are generally low in iron, high in chloride and exhibit an elevated pH. These leachates are not typical of spoil tip leachates in general, but appear to characterise relatively fresh spoil, where buffering phases are still present and where leaching of residual deep pore waters brines is taking place.

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	Eakring 8[1]	Glentworth 5[1]	Plungar 4[1]	Tilmanstone Colliery, Kent[2]	Wardley Colliery Spring[3]	St.Lawrence Colliery Spring[3]	Moorgreen Piper Colliery[4]	Pye Hill No. 2 Colliery[4]	Bentinck Colliery[4]
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	20999	16511			
K^+	96	9	31						
Ca^{2+}	792	1552	822	45	7443	4586			
Mg^{2+}	218	192	556	27	711	704			
Cl^-	14555	11786	14910	795	47393	35329	3600-10800	1100-3900	31400
$SO_4^{=}$	ND	2718	342	404	1118	513			
HCO_3^-	73	549	220		207				
TDS	23776	23532	24669	2107	78180	57690			
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

Table 1. Selected analyses for 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.

[1] - from Downing and Howitt (1969) - from boreholes in the deeply concealed East Midlands Coalfield (ND = not detectable).

[2] - from Buchan (1962) - from the concealed Kent Coalfield

[3] - from Andersen (1945) - brine springs in collieries in the Tyne Coalfields, N.E. England.

[4] - from Lemon (1991) - from pumped shafts in the East Midlands Coalfield.

Table 2. Results of accumulated data for Sheephouse Wood and Bullhouse discharges for the period 1979-91 (after Dudeney et al. 1994), showing mean values (± range).

	Bullhouse	Sheephouse Wood
pH	5.8 (0.4)	6.6 (0.7)
EC mS/cm	1285 (432)	855 (128)
Fe (total) mgl^{-1}	51 (24)	54 (109)
Cl^- mgl^{-1}	56 (38)	20 (5)
$SO_4^=$ mgl^{-1}	660 (88)	389 (82)
Flow m3/d	1500-3000	1000-2000

Sample	Location	NGR	Date	Temp	Estimated Flow	pH (field)	pH (lab)	Eh	EC	Ca	Na	Mg	K	Alkalinity	F$^-$	Cl$^-$	NO$_3^-$	SO$_4^=$	Si	Fe (filtered)	Fe (unfiltered)	Al	Mn	Zn	Rn	U
				°C	l/s			mV	mS/cm	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	meql^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	Bql^{-1}	mgl^{-1}
E29	Smeekley Borehole	SK 2960 7656	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	SK 1308 8350	03-Jan-95	3.4	0.8		3.08		2200	197	6.8	115	3.70	0.00	i	7.9	< 1.5	1480	14600	27.3		51300	23900	1040		13
SB3	Kilnhurst Boardwalk	SK 4715 9710	09-Jul-95	9.5^b	0.083	7.45^b	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	SK 1499 8323	03-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	SK 2962 6044	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	10200	14.9	15.0	132	2100	29		< 1
SB9	Spoil Tip R1		09-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		09-Jul-95	10.1^b	0.033	7.85^b	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)		09-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		09-Jul-95		<0.017		8.32		12770	88.0	2220	227	64.2	4.78		1870	4.6	3580	214	< 0.002		79	273	46		
CG	Ringinglow	SK 3004 8344	29-Jun-95			5.45	5.48		371							43	0.58	86			2.02^a			112^a		
CG	Ringinglow		10-Jul-95			5.47	5.45		356							40	0.47	75			2.04^a			57^a		
CG	Ringinglow		17-Jul-95				5.40		358							35	0.64	87			2.06^a			46^a		
CG	Ecclesall Woods	SK 3184 8175	29-Jun-95			5.84	6.00		848							36	< 0.5	333			48.0^a			55^a		
CG	Ecclesall Woods		10-Jul-95				5.89		844							33	0.35	334			47.3^a			34^a		
CG	Ecclesall Woods		17-Jul-95				5.71		821							31		329			39.5^a			31^a		
E32	Ecclesall Woods		01-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		01-May-95		0.5	5.78	4.58		790	70.0	14.9	39.0	6.29	0.01	i	29	0.9	296	11000	40.8		270	1590	34	24	< 2
CG	Dore Conduit	SK 3111 8190	29-Jun-95			6.58	6.65		590							53	1.18	154			15.1^a			42^a		
E20	Sheephouse Wood Adit	SE 2309 0004	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	11400	33.4	35.6	886	1780	92		
E21	Bullhouse	SE 2152 0293	16-Jan-95				5.63		1583	154	38.1	76.5	7.50	2.20	i	43	< 0.5	886	12600	64.3	61.3	1270	19900	132		2
E30	Mill House, Unstone	SK 3759 7691	01-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	SK 3753 7757	01-May-95		0.75	6.01	4.86		738	43.6	18.3	43.5	2.25	0.04	i	40	0.7	303	13500	30.5		< 45	6370	54	18	< 2
E45	Unstone 2b	SK 3749 7734	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	12200	16.5		< 45	5820	33		
E31	Unstone 3	SK 3754 7731	01-Feb-95		2	5.98	5.90		730	41.8	20.5	39.7	2.64	9.97	0.47	36	3.7	221	11000	24.8	25.9	148	5640	38		
E35	Gawber Prospect Borehole	SE 329 086	05-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	SK 3842 7067	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	18700	67.3		9410	2650	152		
E60	River Hipper AMD		01-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	19600	101		17300	4020	221	1	< 2
E70	Dunston Colliery	SK 3657 7516	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	SK 3143 8506	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	SK 3324 8574	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	10300	21.4		223	1880	54		
E43	Duke's Level, Buxton	SK 0370 7231	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		01-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		02-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	SK 018 721	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		01-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		02-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	SK 3343 8727	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	SK 3348 8731	25-Jul-95	9.6	0.38	6.40	6.60	+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

Table 3: Analytical results for selected parameters for the minewaters forming the subject of this paper. Sample numbers prefixed "E" form part of study 1, those prefixed "SB" form part of study 2 and those marked "C" form part of study 3. All metals analyses for study 3 samples are performed on unfiltered, unacidified samples, analyzed by atomic adsorption methods.

[a] For the purposes of data presentation on plotting metals analyses from study 3 have been treated as filtered samples compatible with results from studies 1 & 2. [b] Data from 27/9/95

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 Minewater E70	Hunters Bar Minewater E74	Duke's Level Minewater E62	Goyt Moss Adit Minewater E63	Unstone Fields Minewater E64	R. Hipper Minewater 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 ($CaSO_4.2H_2O$)	-1.26	-1.37	-0.15	-1.15	-1.11	-1.74	-2.15	-1.15	-0.45
Epsomite ($MgSO_4.7H_2O$)	-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	-	-	-	-	-	-	-

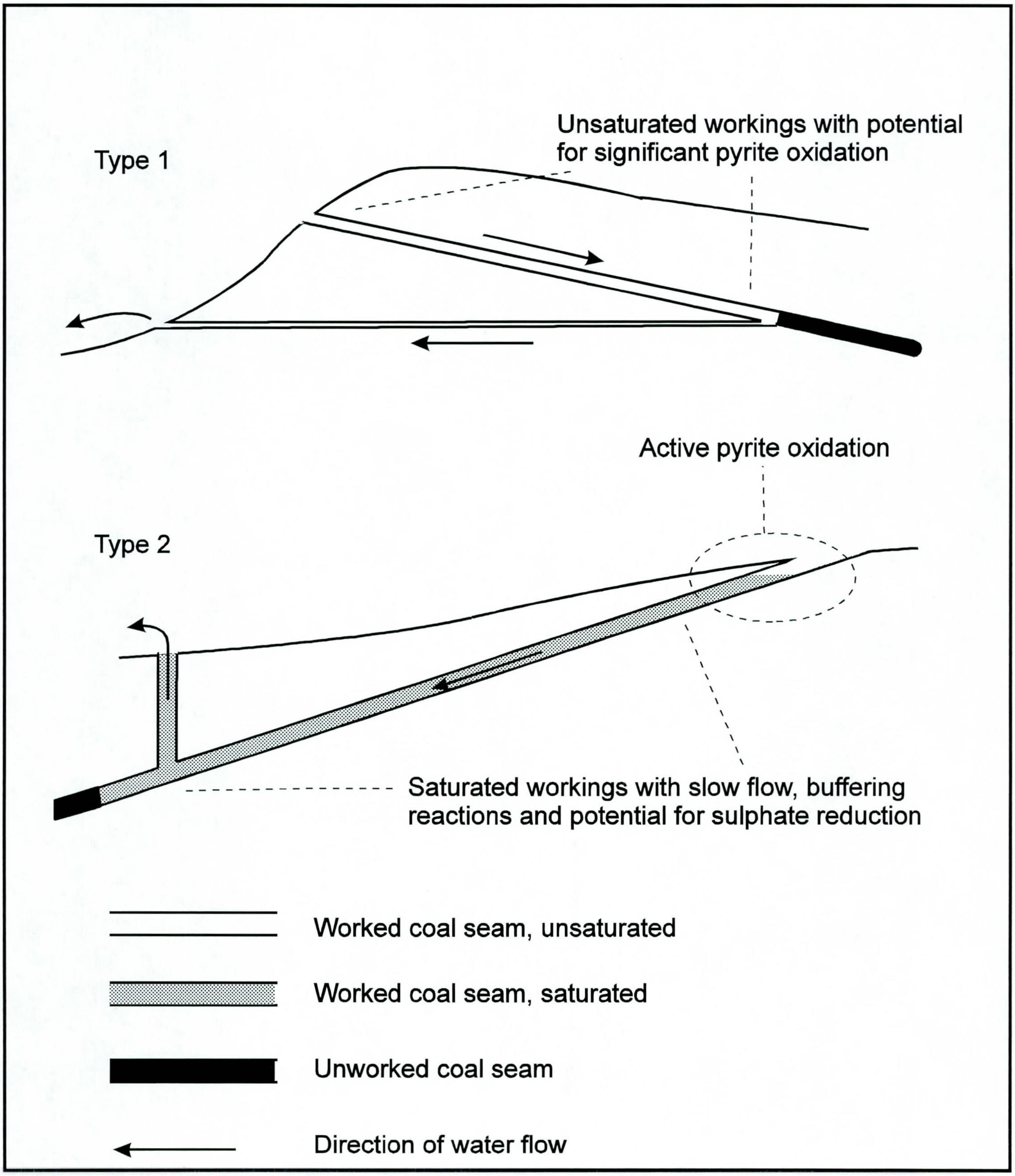


Figure 1. Two types of mine water discharge: Type 1 - non-saturated workings underdrained by a sough; Type 2 - deeper saturated workings, overflowing via a borehole or shaft.

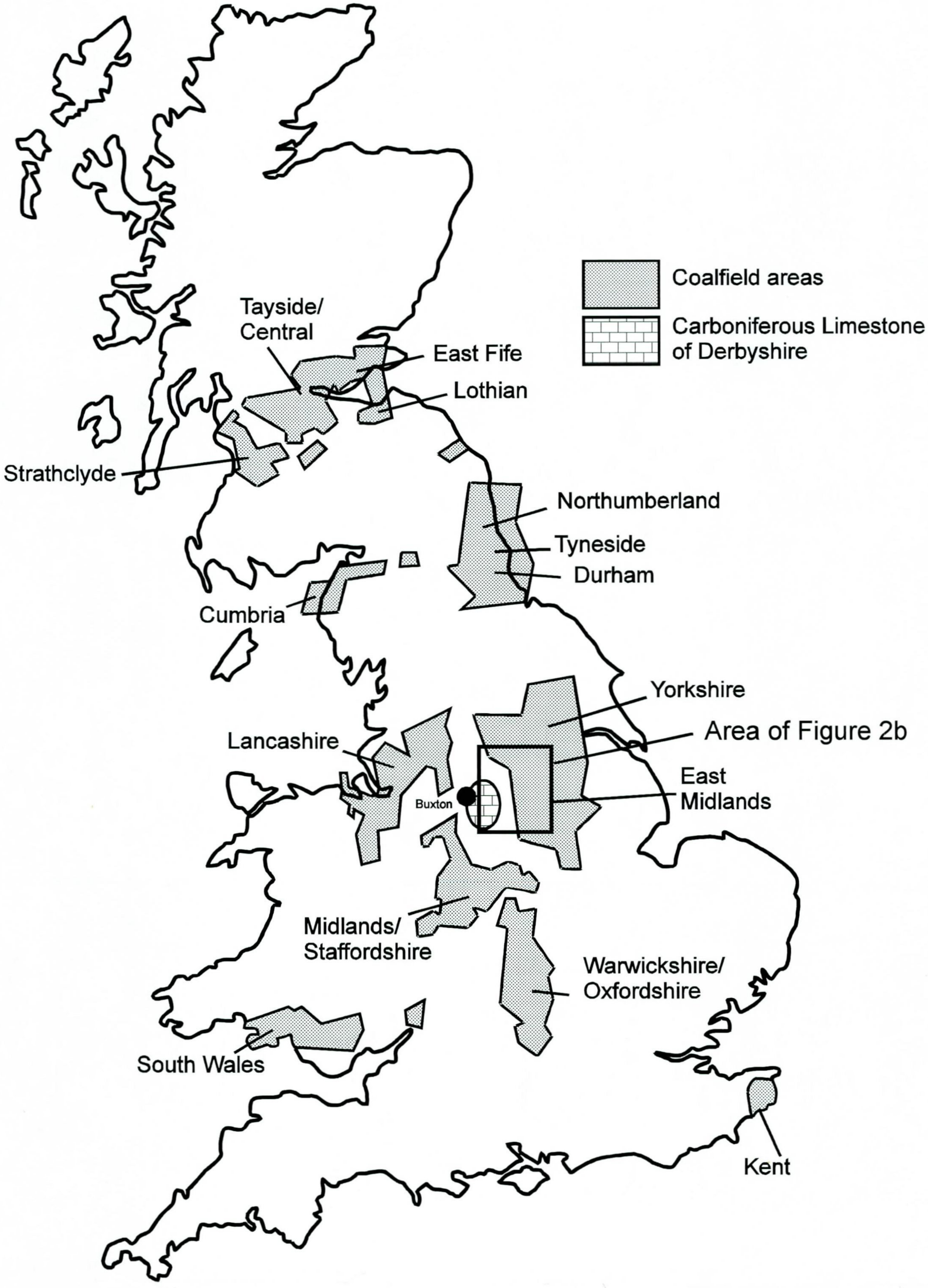


Figure 2a. The coalfields of Britain. The rectangle shows the location of Figure 2b.

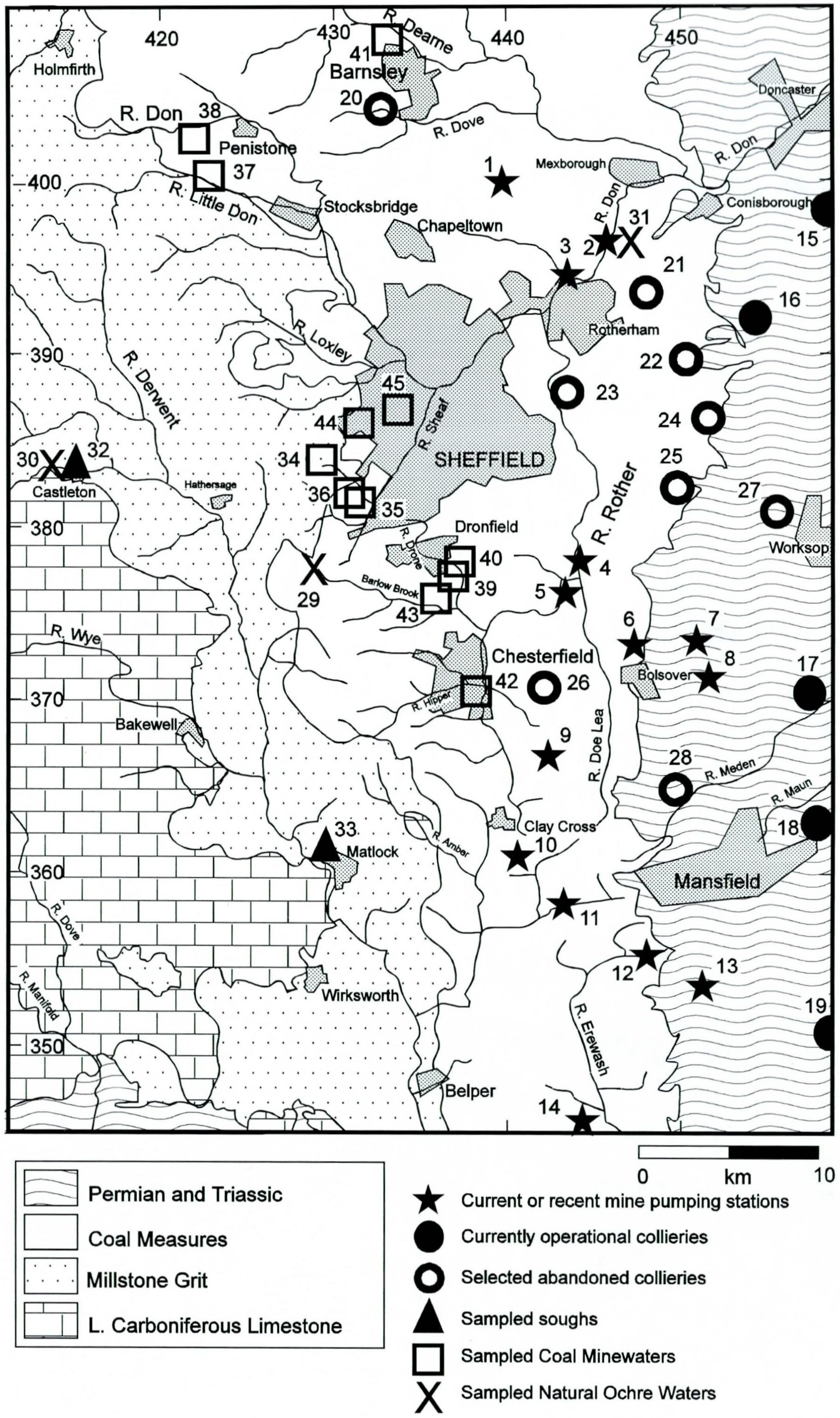


Figure 2b. Map of northern Derbyshire and southern Yorkshire, showing locations of sample localities and selected other features; 1 - Elsecar Pumping Station; 2 - Kilnhurst P.S.; 3 - Carr House P.S.; 4 - Blacks P.S.; 5 - Hartington P.S.; 6 - Oxcroft P.S.; 7 - Creswell P.S.; 8 - Langwith P.S.; 9 - Williamthorpe 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 Hose Unstone; 40 - Unstone 2 & 3; 41 - Gawber Prospect Borehole; 42 - River Hipper; 43 - Dunston Colliery; 44 - Greystones; 45 - Hunters Bar.

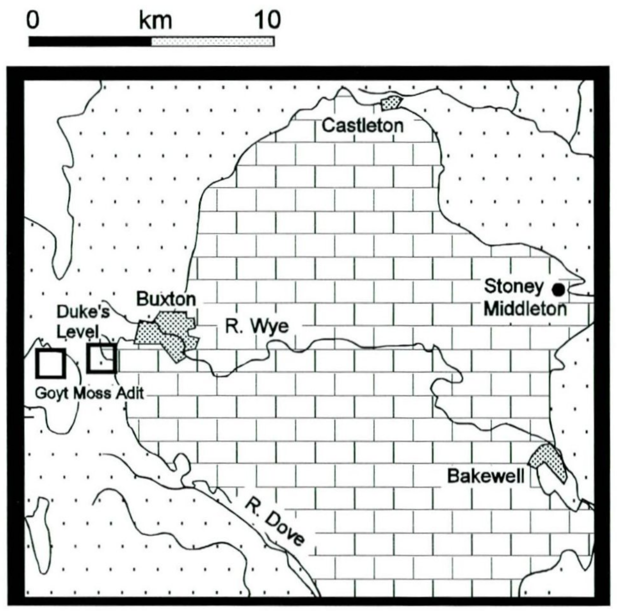
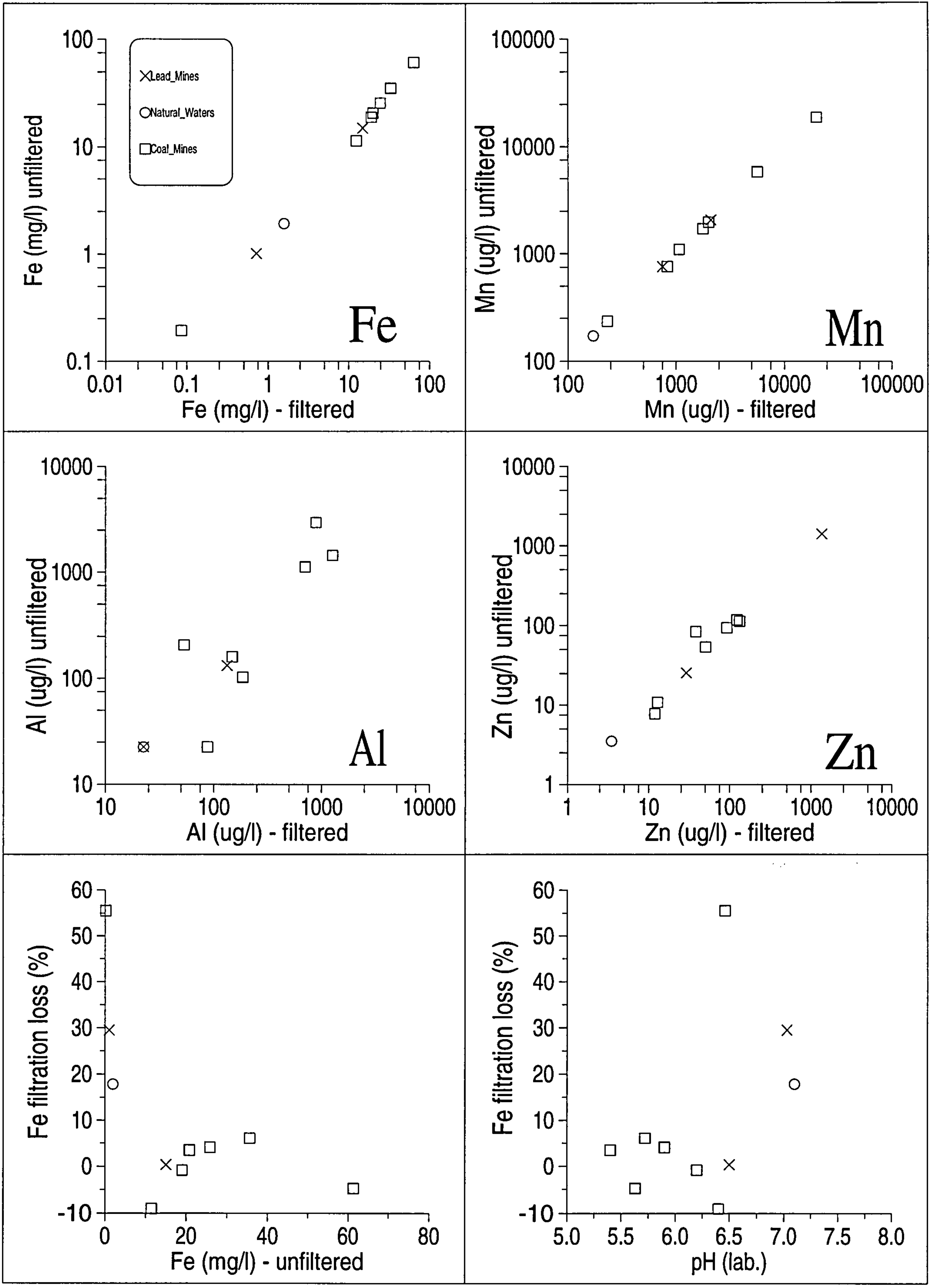


Figure 2c. Map of western Derbyshire, showing locations of the Duke's Level and Goyt Moss Adit, Buxton.

Figure 3. 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).

NB: In this and subsequent diagrams, analytical parameters returning values below instrumental detection limit have been set to half the value of the detection limit for the purposes of plotting and statistical presentation.



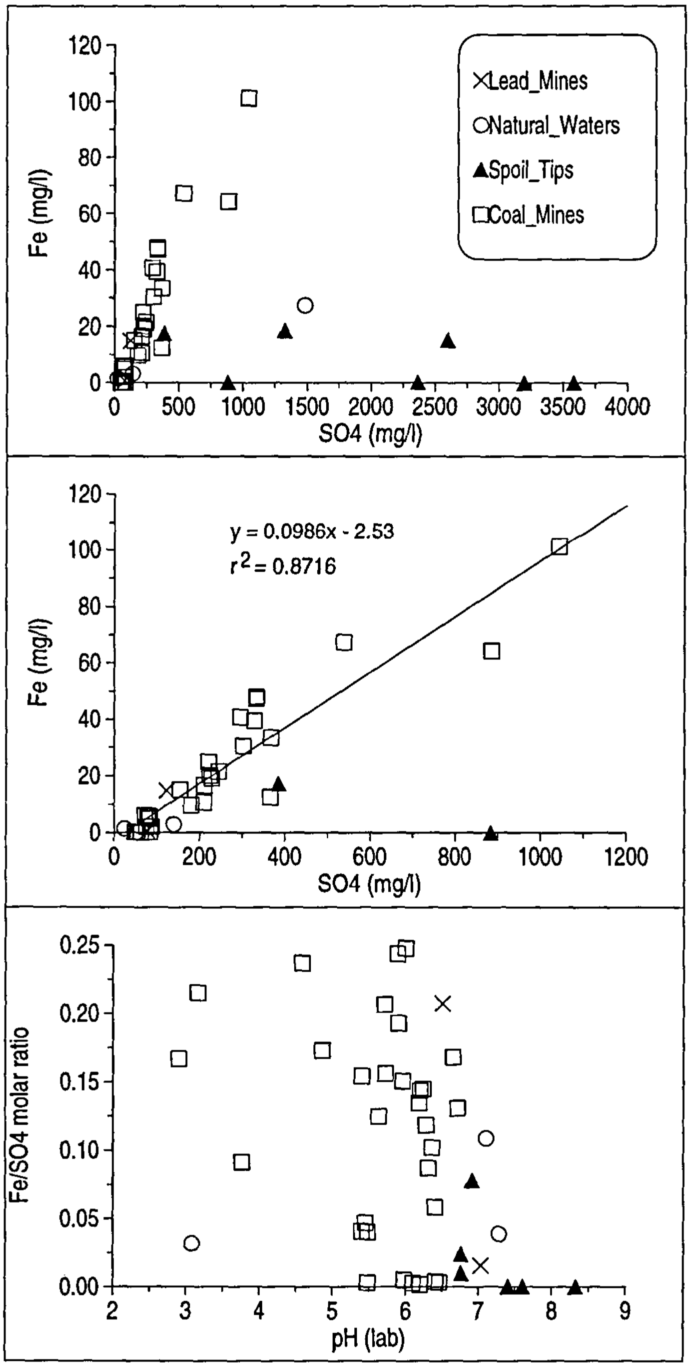
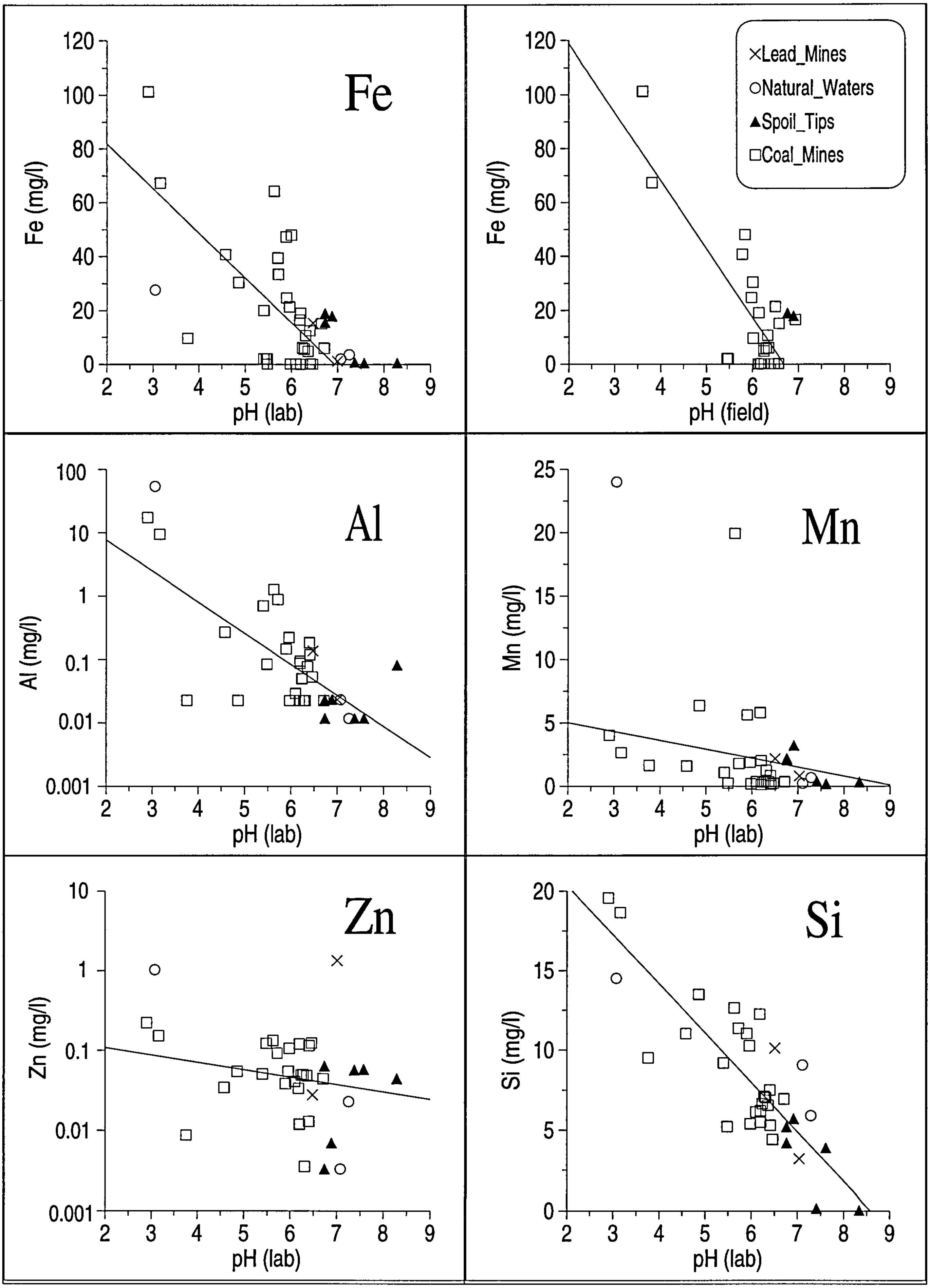


Figure 4. Plots illustrating the relationship between iron (filtered) and sulphate concentrations in the studied waters. The lower diagram shows the relationship of the molar $Fe/SO_4^{=}$ ratio to pH. The linear regression for coal mine waters only is shown.

Figure 5. 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.



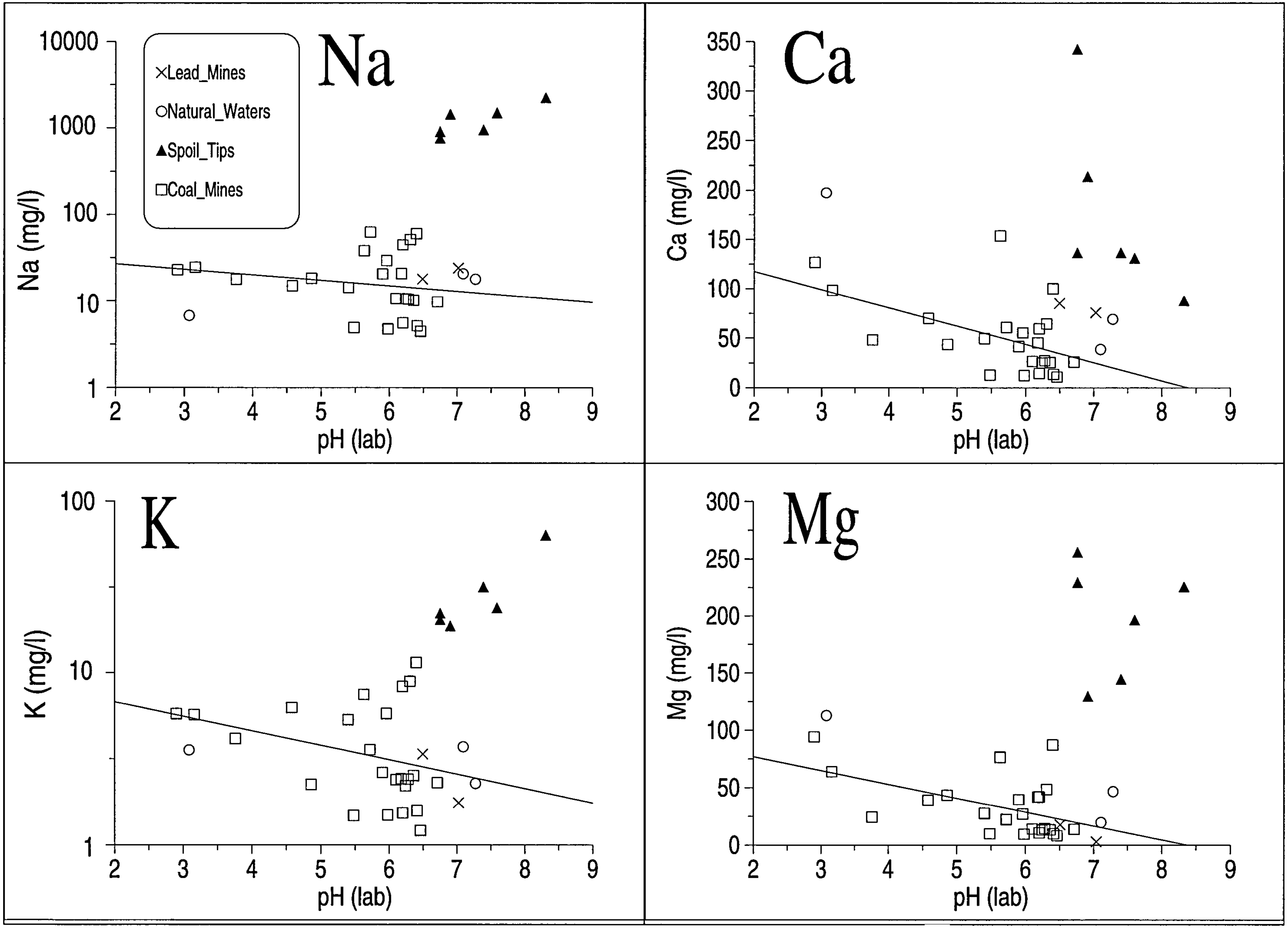


Figure 6. Relationship of Na, Ca, K and Mg (filtered) to pH in the studied waters. The linear regression for coal mine waters only is shown.

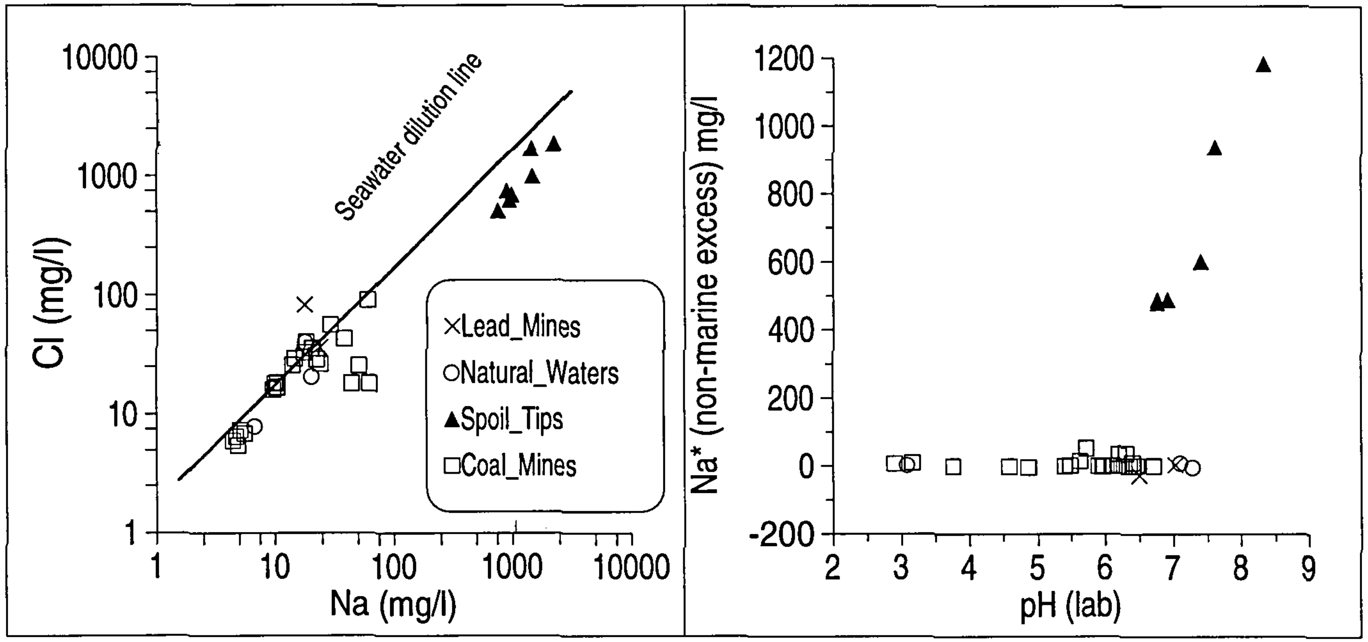
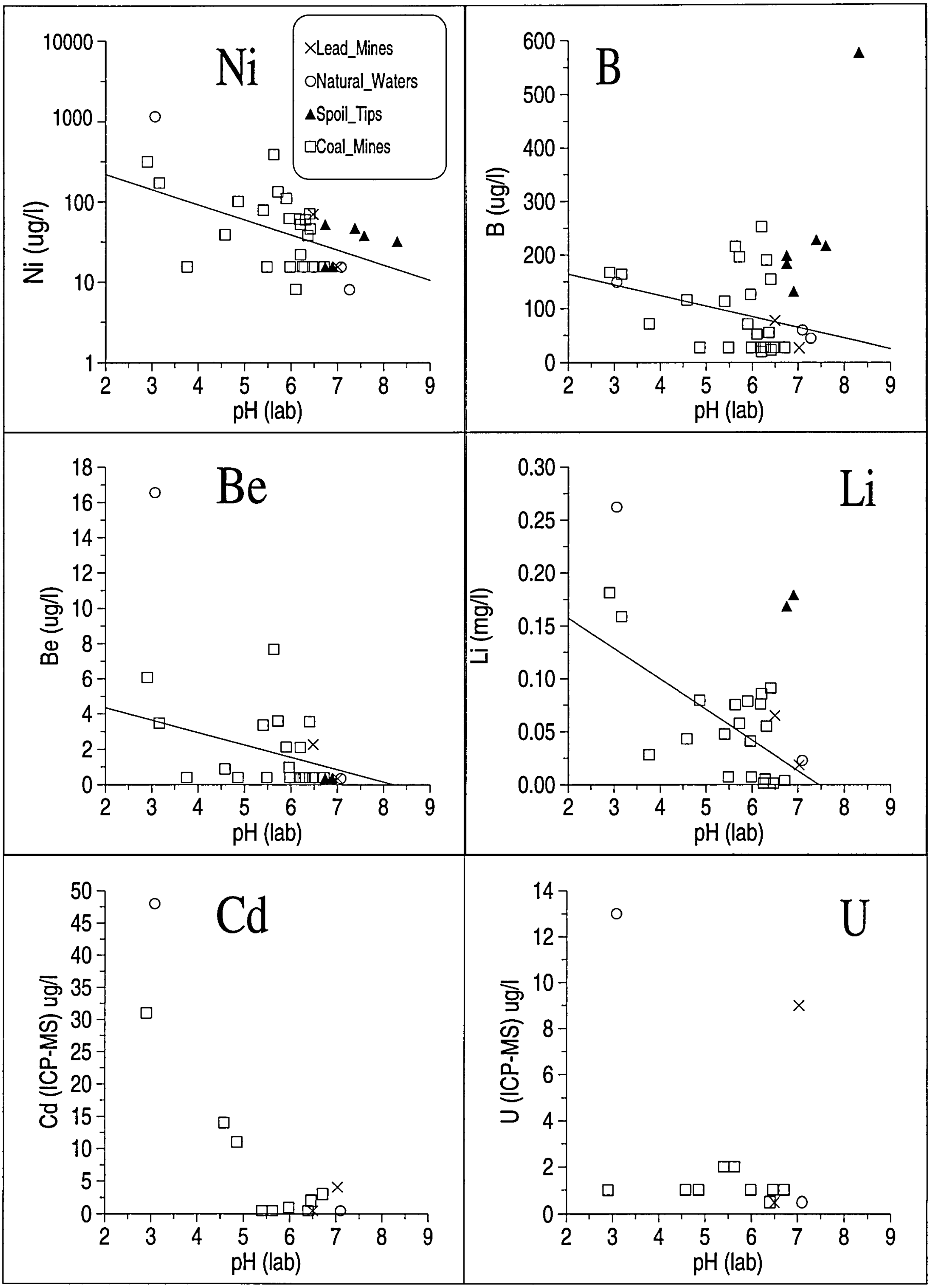


Figure 7. Relationship of Cl^- to Na (filtered) and of non-marine (excess) Na to pH in the studied waters. In the left hand diagram, the line represents the seawater dilution line.

Figure 8. 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.



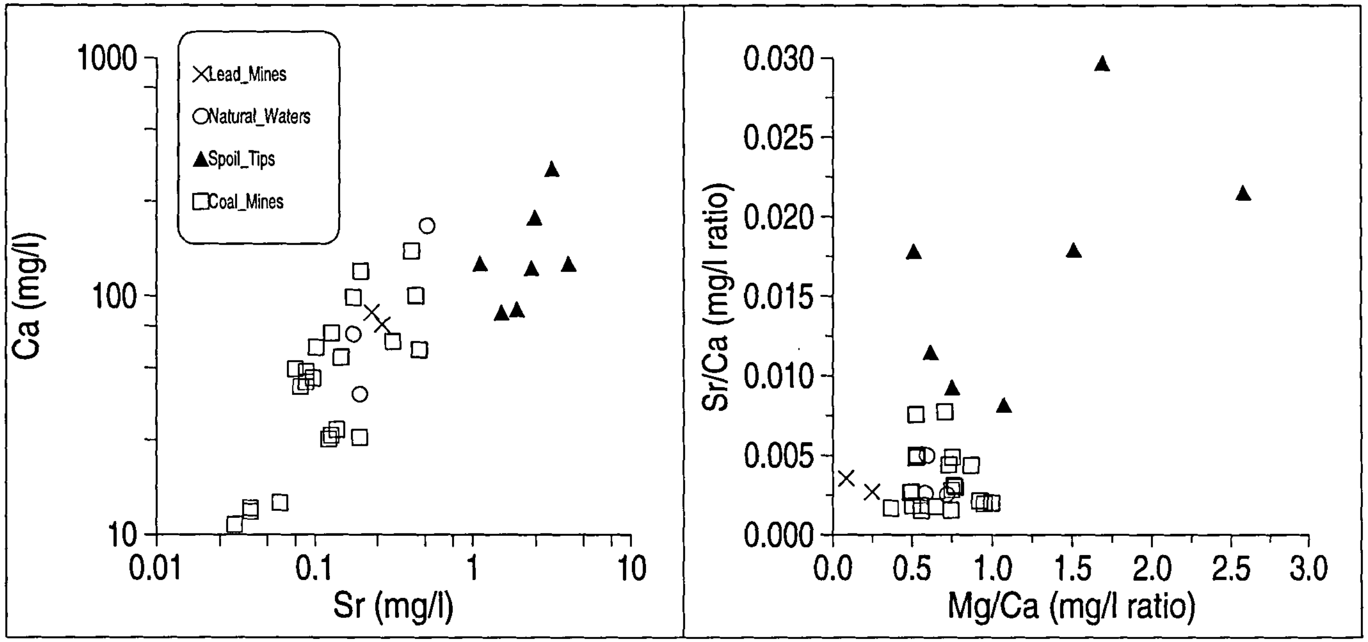


Figure 9. The relationship of Ca to Sr and the concentration (mgl^{-1}) ratios Sr/Ca to Mg/Ca in filtered samples of the studied waters.

Figure 10. The relationship of Ba (filtered) to $SO_4^=$ in the studied waters.

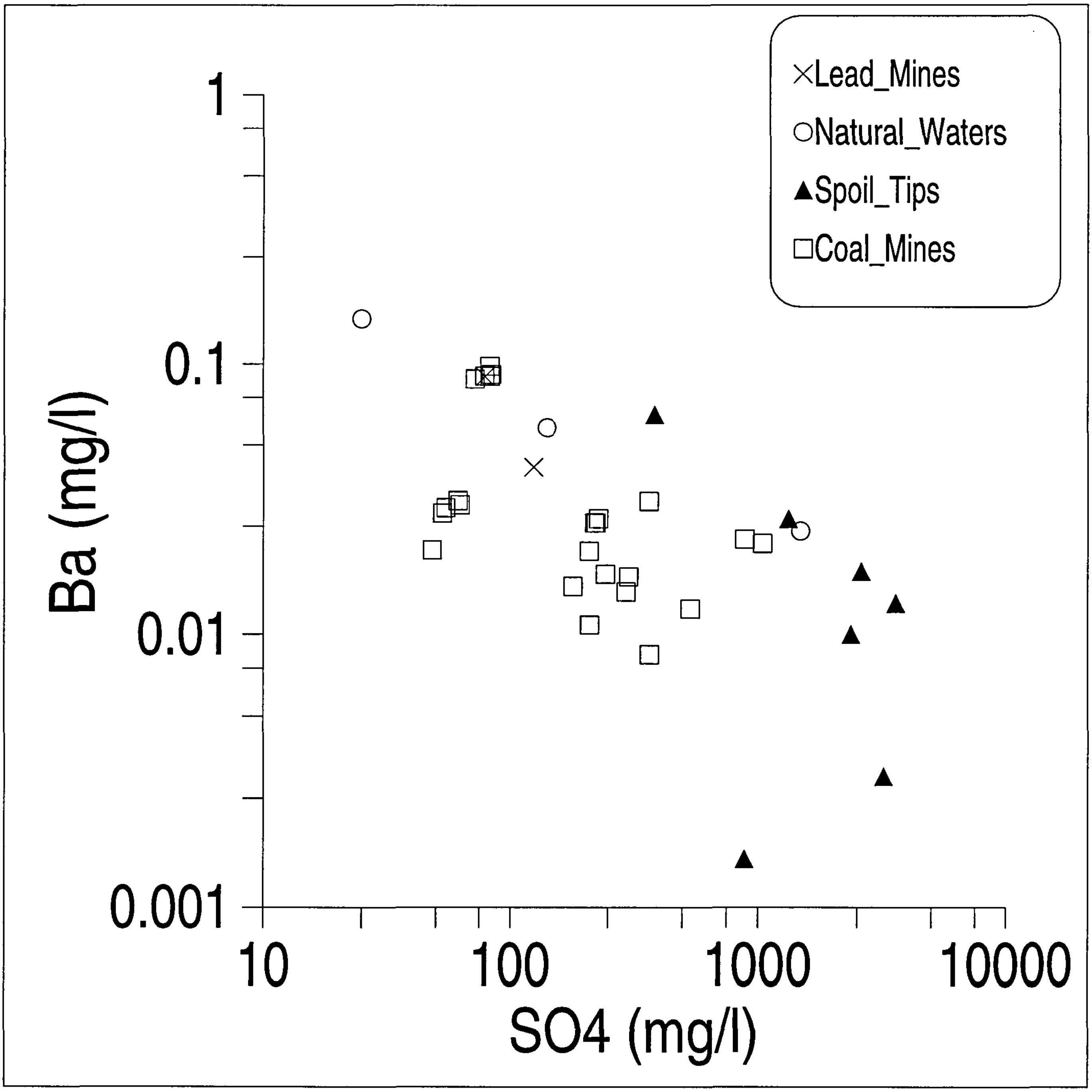


Figure 11. Plot of net alkalinity (meql^{-1}) versus (Cl$^-$ - SO$_4^=$) (meql^{-1}), for the sampled waters (alkalinities are uncorrected for ionic balance), as recommended by Younger (1995a) to distinguish pyrite oxidation waters from saline brines.