Application of Geochemical Mineral Exploration Techniques to the Cataloguing of Problematic Discharges from Abandoned Mines in North-East England

By P.L. Younger[1] and K.F. Bradley[2]

[1] Department of Civil Engineering, University of Newcastle Upon Tyne NE1 7RU, UK
[2] Department of Geology, University of Leicester. *Current Address:* Knight Piésold and Partners Ltd, Ashford, Kent TN23 1PP, UK.

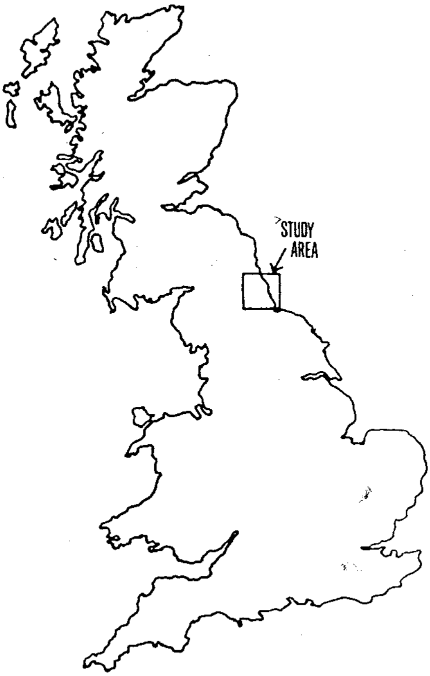
ABSTRACT

Techniques which have traditionally aided in mineral prospecting may assist in the identification of point-source discharges of acidic/ferruginous minewaters after cessation of mining. In North-East England, final closure of a coalfield after nearly three hundred years of continuous extraction and progressive dewatering is anticipated to result in multiple discharges of poor quality minewater. An audit of existing minewater pollution sources prior to abandonment of regional dewatering was undertaken to assess the quality of existing discharges as a guide to future problems, and to define baseline conditions against which future changes may be gauged. In a preliminary reconnaissance, 244 points on the stream system of the coalfield were tested for pH, conductivity, and temperature during periods of baseflow (when most flow comes from groundwater discharge). Screening of these results identified which streams depart significantly from regional background values. From a consideration of known minewater discharge quality elsewhere, the combination of low pH with high TDS was considered as potentially suggestive of ferruginous minewater discharges. 11 such streams were subjected to detailed follow-up surveys; of these, 7 proved to have water quality problems attributable to industrial (non-mining) discharges and runoff from acidifying coniferous plantations. The remaining 4 showed characteristic ochre-staining of the stream beds and clear geographical association with past mining activities. One further discharge eluded detection by geochemical means, as it has flooded pastureland, creating a semi-natural wetland which ameliorates water quality and masks the geochemical anomaly. Natural processes of self-purification include precipitation of sulphate-rich jarositic ochre at the net acidic sites, and incipient microbial sulphate reduction in the near subsurface at the net alkaline sites.

INTRODUCTION

The "Great Northern Coalfield" of England (Figure 1), formerly celebrated as one of the world's most prolific sources of coal, is dying from exhaustion and wanton abandonment. But it is unlikely to rest in peace. Cessation of regional dewatering in the coalfield is anticipated to cause serious and widespread pollution in the River Wear drainage basin and may also lead to geotechnical problems such as subsidence from collapse in ancient "bord and pillar" workings impinged upon by rising groundwater [1,2,3]. The region has been largely spared such problems hitherto, as the nine pumping stations which form the County Durham dewatering scheme (Figure 2) have effectively depressed groundwater levels by as much as 150m over an area of at least 500km^2 for many decades. Indeed such little attention had been paid to the few existing polluting discharges from long-abandoned mines in the far west of the coalfield (beyond the influence of the dewatering scheme) that neither public nor private bodies had chemical analysis results available for these discharges when the

Figure 1 - Location of Study Area.



issue of the potential environmental impact of wholesale cessation of coalfield dewatering arose in late 1992.

Thus in the report to Easington District Council which sparked the first blaze of publicity over this issue [1], the possible quality of future uncontrolled minewater discharges in the coalfield was inferred by analogy with abundant published examples from Scotland and elsewhere. It was an obvious development for the proponents of coalfield abandonment to simply claim (albeit unreasonably) that Scotland is not a suitable analogue for Northern England. In further attempts to allay concerns over potential pollution, those promoting mine closures pointed out that the waters pumped from the long-established dewatering stations are not particularly polluting [4]. While scientists involved with the issue were satisfied that the quality of these pumped discharges is no guide to the quality of water which will emerge at the surface after groundwater rebound [3], the only real proof of the matter to the lay observer would be to analyse the chemistry of existing uncontrolled discharges in the far west of the coalfield. However, consultation of National Rivers Authority records revealed that even the locations of these discharges were not known with any accuracy. Hence analysis of the discharges would only be possible after they had first been located. A survey of existing sites would also serve to provide baseline conditions against which future changes may be gauged.

This paper describes the geochemical exploration methods applied in finding the existing minewater discharges, and gives a preliminary appraisal of the results of chemical analyses and their implications for possible future pollution elsewhere in the coalfield.

RATIONALE OF STUDY

Geochemical Exploration Methods

Classic methods of geochemical exploration involve surveying soils, rocks, stream sediments, water, vegetation and air in an attempt to identify geochemical "anomalies" which might betray the presence of ore bodies in target areas [5,6]. Surveys of drainage basins for sediment and/or water chemistry are now the most widely used geochemical reconnaissance technique [6]. Where exploring for ore bodies, stream sediment surveys have generally been much more popular than water surveys [5], since stream sediment anomalies are often far more distinguishable from background than water quality anomalies. Furthermore the formerly prohibitive size of water samples required for analysis (a restriction which no longer applies since the advent of ICP spectroscopy) and uncertainties in interpreting temporal changes in water quality have also hindered application of water quality surveys. For these reasons, water surveys are usually restricted to the detailed follow-up stage of geochemical exploration, after anomalies identified in stream sediments are traced to source [6]. Further details of the theory and practice of geochemical exploration may be pursued in the works cited [5,6].

Adapting the classic geochemical exploration techniques to serve present needs gave rise to the following considerations:

- While uncontrolled minewater discharges do produce characteristic sediments (ie ochre deposits), small quantities of finely grained ochre mixed with clastic sediments in areas of a large drainage basin distant from sources will be hard to detect, not least because iron is so ubiquitous an element that subtle anomalies are hard to distinguish.

- Published literature shows that uncontrolled minewater discharges can be reasonably expected to exhibit relatively low pH values, high sulphate concentrations and high salinities relative to "normal" shallow groundwater. Not surprisingly, these characteristics correspond closely to the classic river water quality anomalies associated with sulphide ore bodies [5], which have been successfully investigated in mineral exploration.

- While many abandoned mines discharge their poorest quality water during or shortly after rainfall, as the rising water table flushes fresh pyrite oxidation products into solution, dilution by receiving waters in spate would tend to subdue the geochemical anomalies which will be sought during geochemical exploration. It is therefore preferable to survey the drainage system during periods of little or no rainfall, when most of the water in the stream channels will have originated from groundwater sources (including minewaters).

Selection of Target Area

Where mineral exploration surveys might define a suitable target area on the basis of major geological boundaries etc [6], the target area for this study must also take into account certain mining-related features which act as effective boundaries beyond which uncontrolled surface discharge of minewaters is unlikely. The target area in the present study was selected as follows (see Figures 1 and 2 for orientation):

- Only streams draining the exposed coalfield were sampled in detail. While some minewaters are known to have flowed into the Permian Magnesian Limestone aquifers (Figure 2) to the south of the Butterknowle Fault, such waters have mixed with the native groundwaters producing a water of hybrid quality. No known surface discharges of such waters are known, though there is some evidence from pumped borehole samples for the existence of such waters at depth in the Limestone. Therefore only a few streams draining the Permian outcrop were surveyed, to help in establishing background conditions.

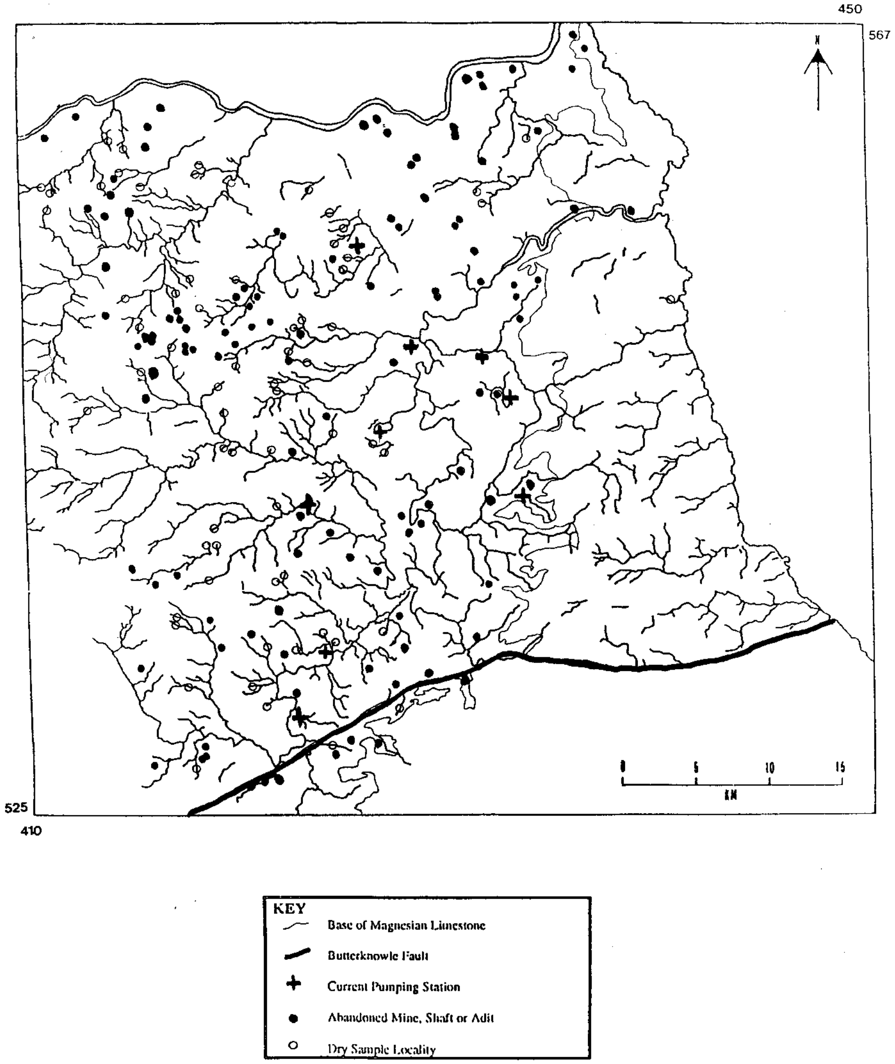
- Western boundary: The outcrop of the Brockwell Seam, which is generally regarded as the lowest widely-worked seam in the Durham Coalfield [7]. Known abandoned mines plotted on Figure 2 all lie to the east of the Brockwell outcrop; therefore intensive stream sampling was generally not pursued west of this line.

- Eastern boundary: The outer limit of the regionally dewatered zone. As insufficient observation boreholes are available to allow precise definition of the combined radius of influence of the nine pumping stations, a conservative boundary definition was obtained by simply drawing straight lines between the outermost pumping stations (whose positions are given on Figure 2). Within the polygon described by this line and the base of the Magnesian Limestone to the east, little sampling was programmed.

- The Butterknowle Fault (Figure 1) is a well known barrier to groundwater flow in the coalfield, for not only does the fault interrupt continuity of permeable units, but the fault plane is generally lined with low permeability fault-gouge, and steep dips in the Coal Measures strata immediately south of the fault (due to fault drag) effectively precluded any mines from working strata on both sides of the fault from single gates. From the vicinity of Bishop Auckland (approximate eastings 420 on Figure 2) eastwards, the Butterknowle Fault acts as the southern limit of the regionally dewatered zone, so no stream sampling was conducted to

Figure 2

Locations of Pumping Stations (Regional Dewatering Scheme), Abandoned Mines and Dry Sample Localities in the Exposed Coalfield of County Durham. Pumping station locations from Younger (1993), abandoned mines from published BGS maps and British Coal mine records.



the north of the fault in this eastern zone. South of the fault, throughout its length, dewatering ceased in the mid-1970's and uncontrolled surface discharges of minewater commenced before the end of the decade. Thus the area of exposed coalfield south of the Butterknowle Fault was surveyed. To the west of Bishop Auckland, the zone of "recovered" groundwater levels south of the fault was assumed to abut an area of at least partially recovered levels to the west of the regionally dewatered zone, so the presence of the Fault had less impact on survey design in the western part of the target area.

PHASES OF EXPLORATION

Reconnaissance Phase

The reasonably dense road network in the area (itself a legacy of mining history) expedited rapid diagonal traversing of the area, so that in 12 days during a mainly dry period in June 1993 it was possible to measure pH, temperature and specific electrical conductance ("conductivity") at 244 sample localities on the drainage system of the target area. Measurements were made using hand-held battery-powered meters (Palintest brand) which were recalibrated before each days' sampling commenced and checked at intervals. Of the programmed sampling sites, more than 90 proved to be dry (these are shown on Figure 2). The locations of all sites where water was flowing (and therefore measurements made) are shown on Figure 3.

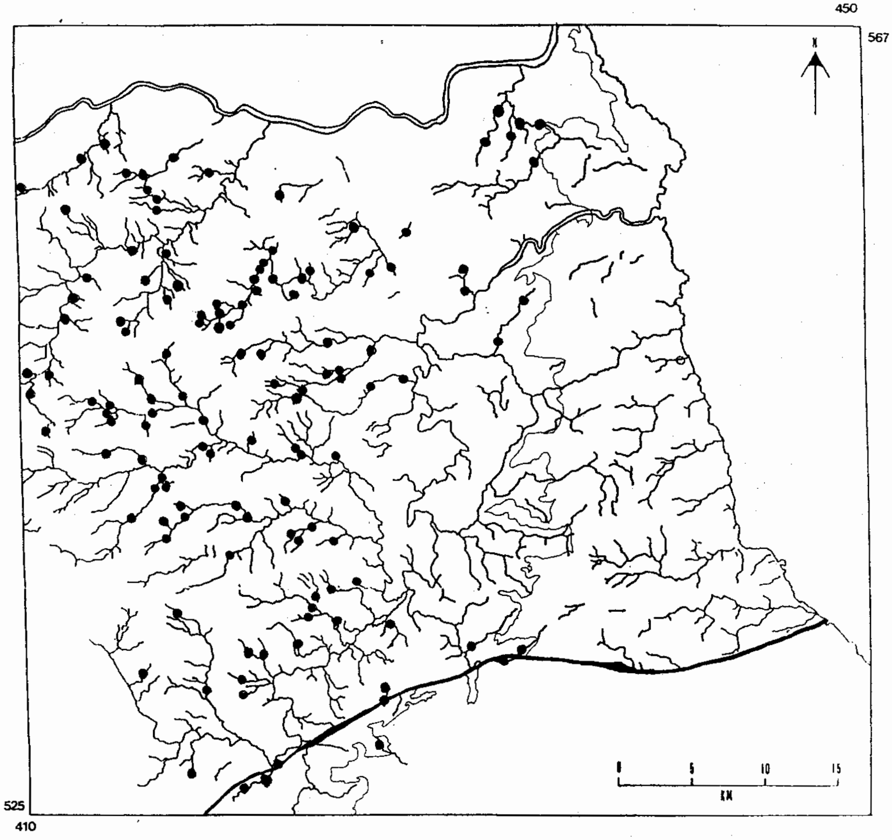
Follow-up Phase

The data set obtained during the reconnaissance phase allowed the identification of regional "background" values for pH and conductivity. The majority of sample localities clustered in a population with pH in the range 7.7 - 8.9 and conductivity in the range 540 - 770mS/cm. Outliers in the data set, representing anomalies in water quality, could then be identified and plotted on the sampling plan (Figure 3).

Anomalously alkaline waters ($pH > 8.6$) were generally associated with streams draining arable land, though one stream draining an old ironworks exhibited a pH of 11.11. By contrast, waters with relatively low pH (in this context meaning < 7.6) and elevated mineralisation ($>$ 770mS/cm) were noted as possible indicators of minewater pollution. A few of these localities exhibited ochre staining of the streambed. 11 localities in all were selected for detailed follow-up, in which anomalies were traced upstream with periodic measurement of pH, Eh and conductivity.

Eh was measured using an ORP probe fitted to the Palintest 900 pH-Eh meter. While field measurements of Eh are notoriously inaccurate and difficult to interpret in strictly quantitative terms [8], positive values ($mV > 0$) associated with oxidising conditions are generally expected in acid minewater discharges as Fe^{2+} oxidises rapidly to Fe^{3+} as the minewater contacts the atmosphere. In the event, semi-quantitative interpretation of Eh values helped in discriminating potential minewater pollution from low-pH/high-conductivity waters arising from other sources. Waters from several of the follow-up localities exhibit markedly negative Eh values; in most cases, industrial effluents with high chemical oxygen demands were found to be responsible for the combination of relatively low pH and negative Eh. In one case, the water quality appeared to be attributable to the effects of organic rich acid soils in a conifer plantation.

Figure 3 - Sites of field water quality measurements during regional reconnaissance.



Four out of the original eleven follow-up localities gave unequivocal minewater signatures; these were traced upstream to source, and then subjected to detailed sampling and analysis. Figure 4 shows the locations of the four minewater discharges identified during the follow-up surveys and Table 1 summarises the site details, with brief notes on the past mining activities with which they are associated, gleaned from examination of abandonment plans held by British Coal. Field measurements were extended to include alkalinity (where pH exceeded 4.5), which was determined by titration against concentrated sulphuric acid in the presence of a bromocresol green - methyl red indicator, using a rugged hand-held digital burette. Flow measurements were made at a time of high groundwater levels in springtime by the velocity-area method, using a Valeport impeller flowmeter. The coincidence of observed water level at that time with the uppermost level of ochre staining on the stream channel indicates that the measured flow rates correspond to the annual maxima (except at Crook, where staining extended above the water line). In the laboratory, filtered and dissolved fractions of field-acidified samples were analysed for 25 metals using ICP-ES, while raw samples were analysed gravimetrically and titrimetrically for sulphate and chloride using standard methods. Charge balance errors were generally less than 10%, though higher values were encountered in some samples, probably where charged colloidal particles were inadequately characterised.

At each of the four sites, changes in dissolved and suspended solids were assessed by sequential sampling downstream from source. Some of the implications of these results are discussed below. Finally, ochre samples from three of the sites were analysed for crystallinity using X-Ray diffractometry (XRD).

A fifth site (site T, Brusselton Farm), which was identified after the end of the survey, is also shown on Figure 4 and detailed in Tables 1 and 2. It is instructive to briefly consider how that site came to be overlooked in the geochemical survey. Although water courses near Brusselton Farm were sampled during the survey, no significant anomaly was detected. This is because flooding of pasture land caused by the discharge at site T has led to the development of a substantial wetland, in which ochre is precipitated, pH raised and conductivity lowered before the flow reaches the Gaunless. The site is therefore an interesting natural analogue for constructed wetlands used in minewater treatment, although the flooding is causing serious nuisance and loss of revenue to the farmer whose land is affected.

WATER QUALITY AND OCHRE DEPOSITS

Table 2 summarises the water quality of the five sites shown on Figure 4 at their points of first emergence. Three of the five discharges are net alkaline, two strongly acidic; all five are depositing ochre.

XRD results show most of the ochre deposits to be amorphous, though the ochre at Broken Banks gives a goethite diffractogram. The ochre at all sites is usually red-orange (consistent with goethite), and varies little through time at the net alkaline sites. However, the colour of the ochre sometimes alters to yellow or even off-white at the net acidic sites. The reasons for these changes are still under investigation, though a change in the chemistry of the dominant precipitate in response to rainfall fluctuations is suspected. Preliminary mineral equilibria modelling for the Crook site, for instance, suggests that the yellow potassic iron sulphate mineral jarosite may precipitate during dry spells, dissolving again to reveal underlying orange amorphous ferric oxyhydroxide after rain. Downstream trends in water quality at Crook and Quaking Houses (Figure 5) support this notion,

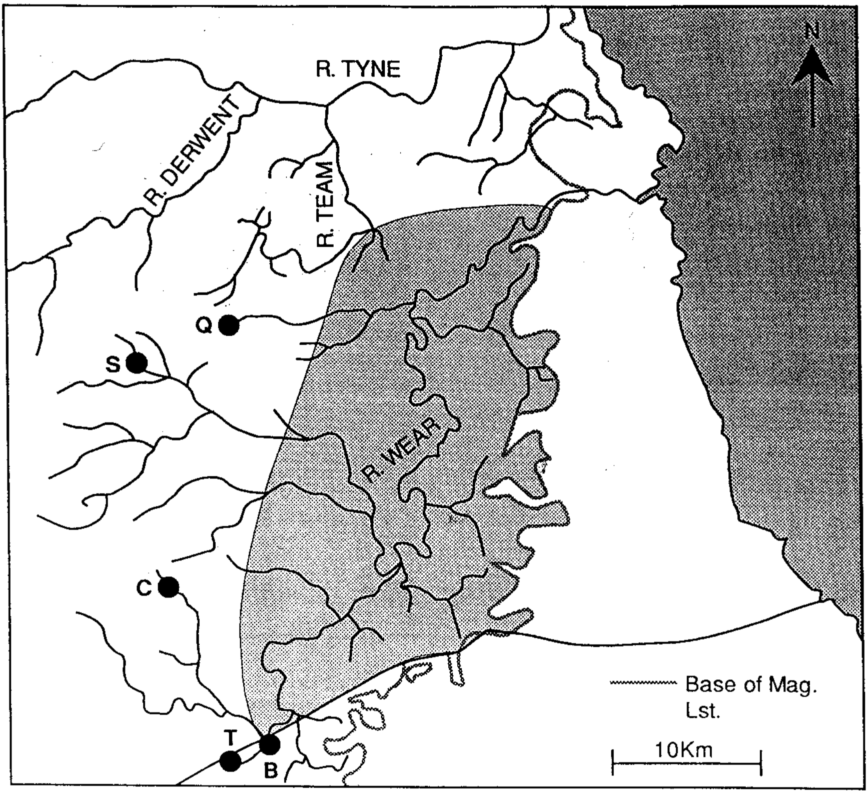
Table 1 - Details of Uncontrolled Minewater Discharges in County Durham, 1994

Discharge Name and Grid Reference	Letter Code[1]	Mines with which discharge is associated	Closure year[2]	Notes
Broken Banks (NZ 197295)	B	Etherley Dene Colliery, Dene Pit, Pity Me Pit	1955	Discharge arises from a stone-lined conduit thought to have been part of drainage system of old Pity Me shaft. Water derived from workings to south of Butterknowle Fault, forced to surface by unworked/impermeable fault plane. Underground brickwork dams were constructed in 1952 (within a few metres of present discharge coordinates) where saturated boulder clay was encountered. These dams appear to have been breached by minewater flowing to the surface. Water make during mining: 330m^3/d
Crook (Helmington Row) (NZ 185356)	C	Stonechester, Bowden Colliery, Sunny Brow	1970	Mapped positions of drives correspond with reduction in pH in stream. Marked increase in metal concentrations adjacent to bricked shaft at 450m from source.
Quaking Houses (NZ 178509)	Q	Hedley Pit, South Moor Morrison Busty Pit, Stanley Burn Drift	1973	Earlier workings in west were allowed to waterlog after extraction and mining continued further east. Pressure grouting of some strata was undertaken prior to abandonment. Water make during mining: 3900m^3/d.
Stoney Heap (NZ 147515)	S	Stoney Heap Colliery, Eden Colliery, Dipton Colliery, South Medomsley Colliery	1980	The discharge arises from an "amphitheatre" formed by collapse of one of several medieval bell-pits which worked outcropping Main Coal adjacent to a fault. During modern deep mining, feeders of up to 720m^3/d arose from the fault plane almost directly below the current discharge location; these were controlled by inclined boreholes feeding a pumping sump. Total water make during mining: 3500m^3/d.
Tindale Colliery (Brusselton Farm) (NZ 197269)	T	Ladysmith Colliery, Tindale Pit, West Auckland Colliery	1967	After closure of the mine, dewatering continued (with pumping from the nearby Ladysmith shaft) until 1976 to protect the workings at Mainsforth further east; uncontrolled surface discharge began 1979 after a spectacular outburst through the floor of a workshop which had been constructed over a back-filled shaft. Site drainage works resulted in the discharge being diverted to its current outfall from a concrete culvert.

Notes: 1. As given on Figure 4. 2. Final closure of mines in area with cessation of local dewatering.

Figure 4

Map of major uncontrolled discharges from abandoned mineworkings identified during the study. Shading denotes the approximate area of the exposed coalfield affected by the long-term regional dewatering scheme. Site identities - Q: Quaking Houses; S: Stoney Heap; C: Helmington Row, near Crook; T: Brusselton Farm, at old Tindale Colliery site; B: Broken Banks, at old Etherley Dene Colliery site.



with a pronounced decrease in sulphate suggestive of incorporation in the solid phase. The grey-white deposits seen at Crook and Quaking Houses are possibly aluminium hydroxides.

The existence of net alkaline minewater discharges has baffled many researchers, for the high sulphate and high iron loadings which characterise such discharges clearly result from the acid-generating pyrite oxidation process. Most commentators ascribe circum-neutral pH and associated bicarbonate alkalinity to carbonate dissolution after acid generation [9]. This is a reasonable postulate where the coal-bearing strata include limestones, or at least carbonate nodules, or where groundwater flows into the Coal Measures from a limestone aquifer. Indeed the latter possibility can be invoked to explain observed water chemistry at the old Tindale Colliery site, which lies south of the Butterknowle Fault in an area where substantial inflows of water from the Magnesian Limestone were observed during mining [10]. In general, however, the Durham coal measures are utterly devoid of carbonate minerals, and in the west of the coalfield, there is no possibility of ingress of limestone groundwaters. It is therefore pertinent to enquire about the source of the alkalinity in the Stoney Heap and Broken Banks waters which occur in that area.

Even if it is argued that carbonates are present in the sequence but have simply been overlooked (unlikely in view of the mass of geological data for the region), there are three lines of hydrochemical evidence which strongly support the notion that the Stoney Heap and Broken Banks waters do not derive their alkalinity from carbonate dissolution:

1. At both sites, Ca and Mg are present at even lower concentrations than at the net-acidic sites (Crook and Quaking Houses); this is hardly consistent with carbonate dissolution at the net alkaline sites.

2. Mineral equilibria modelling using the USGS WATEQ4F software [11] reveals that both waters are undersaturated with respect to calcite (the saturation index Log{IAP/KT} falls in the range -0.6 to -1.2). Saturation indices closer to (or greater than) 0 might reasonably be expected if carbonate dissolution had generated the alkalinity.

3. There is an excess of HCO_3^- over Ca^{2+} on a molar basis (3.5 to one at Broken Banks; nearly 6 to one at Stoney Heap), whereas approximate equality would be expected if both species were derived from carbonate dissolution.

An alternative explanation for the observed water chemistry could be that incipient microbial sulphate reduction is occurring in the near sub-surface, since this process generates alkalinity. There are three hydrochemical observations which support this possibility.

1. Sulphate concentrations are up to 10 times lower at these two sites than at the net acidic sites, suggesting the existence of a significant sulphate sink.

2. There is a strong odour of H_2S where water first emerges at both Stoney Heap and Broken Banks, but not at the net-acidic sites.

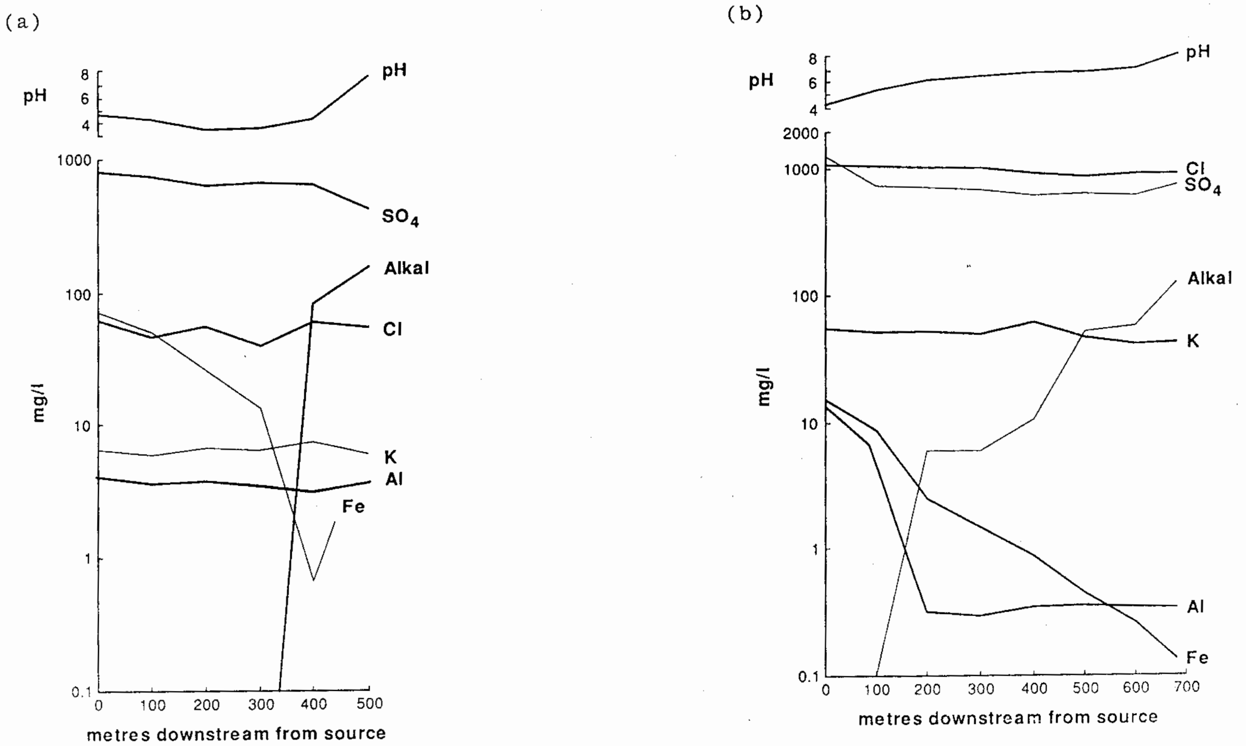
3. Both of these sites display Eh values an order of magnitude lower than Crook and Quaking Houses, suggesting the waters are rather more reduced.

If sulphate reduction is occurring, then bio-precipitation of metallic sulphides may be occurring in microniches in the subsurface, in a manner analogous to the alkalinity-generating metallic

Table 2 - Hydrochemistry of Durham AMD Discharges at First Emergence

Site: (Grid Reference)	Broken Banks NZ 197295	Crook NZ185356	Quaking Houses NZ178509	Stoney Heap NZ147515	Tindale Colliery (Brusselton) NZ197269
Flow rate (m^3/s) on 15-4-94	0.1328	0.00194	0.0067	0.0256	0.010
Calcium (mg/l)	100.70	185.29	255.20	83.58	262
Magnesium (mg/l)	61.23	93.15	102.79	49.69	107
Sodium (mg/l)	26.86	21.52	463.62	27.87	80
Potassium (mg/l)	10.69	6.78	57.04	6.70	13
Iron (total) (mg/l)	1.76	79.84	17.96	26.32	1.84
Manganese (mg/l)	0.998	6.97	4.78	1.20	1.68
Aluminium (mg/l)	0.261	4.18	12.94	0.156	0.0413
Zinc (mg/l)	0.023	0.045	0.040	0.022	0.0184
Copper (mg/l)	0.110	0.230	0.228	0.097	0.0110
Alkalinity (mg/l as $CaCO_3$)	364.0	0.000	0.0	188.0	357
Sulphate (mg/l)	137.0	810.00	1358.0	325.0	890
Chloride (mg/l)	60.0	65.00	1012.0	102.0	75
pH	6.5	4.8	4.1	6.3	6.4
Temperature (°C)	10.9	11.8	11.2	10.3	12.0
Eh (mV)	39	264	327	36	- 50
Conductivity (mS/cm)	1177	1563	3560	1134	2360

Figure 5 - Variation in major water quality parameters downstream from point of first emergence of minewater at (a) Crook (Helmington Row) and (b) Quaking Houses.



sulphide precipitation processes which occur in constructed anaerobic wetlands. The circumstances which give rise to the reducing conditions may be a simple function of high flow rate and the geometry of old workings: Stoney Heap and Broken Banks have flow rates one to two orders of magnitude greater than the net-acidic sites, ensuring that the flow always emerges "full bore" from the openings which conduct the water to the land surface (fractures associated with collapsed bell-pits at Stoney Heap, and an old stone conduit at Broken Banks). Thus confined and quite probably anoxic conditions prevail in the shallow sub-surface at these two sites, whereas the net acidic waters flow through large conduits which are fully aerated. While all discharges obviously originate in oxidising sub-surface environments, the sulphate in the Broken Banks and Stoney Heap discharges may be consumed by sulphate reducing bacteria where they enter fully saturated subsurface passageways near their points of emergence. Exsolution of hydrogen sulphide gas therefore occurs when the waters flow out at the surface.

CONCLUSIONS

Exploration techniques generally used to locate mineable ore reserves at the very outset of the resource exploitation cycle can also be applied in environmental auditing after extraction ceases, to detect point sources of pollution emanating from abandoned mineworkings. Application of such techniques in North East England has led to the identification of four polluting discharges in the west of the exposed coalfield, beyond the limits of the regional dewatering scheme. A fifth site eluded detection by these methods because it has flooded a large area of pasture-land, forming a semi-natural wetland which serves to ameliorate water chemistry, masking the geochemical anomaly which might have been expected in receiving water courses. Approximately 15 Ml/d of polluting waters are currently flowing from abandoned workings outside the regionally dewatered zone of the Durham coalfield. According to latest model predictions [3], similarly poor-quality waters might emerge at eight times this rate throughout the exposed coalfield if dewatering is discontinued. This would clearly result in serious environmental degradation. Studies of water chemistry and ochre deposits suggest that self-purification processes which may help to improve water quality in the natural environment include precipitation of jarositic sulphate-bearing ochre at net acidic sites, and microbial sulphate reduction in the near subsurface, which is argued to be the source of most of the alkalinity measured in waters at the net-alkaline sites.

ACKNOWLEDGEMENTS

We would like to thank the following for practical assistance in field and lab: Pat Johnston, Bryn Jones, Julia Sherwood and Trevor Elliot (Newcastle University); Brian Dickie, Charlie Moon and Mike Whateley (Leicester University); Stewart Turner (Imperial College); Peter Raine (Brusselton Farm). Staff of the British Coal Records Office at Bretby are also thanked for their assistance.

REFERENCES

1. Younger P.L. Probable Environmental Impact of the Closure of Vane Tempest and Easington Collieries, County Durham. Report to Easington District Council for Submission to the Coal Review. 9pp. (1992).
2. Younger P.L. Possible Environmental Impact of the Closure of Two Collieries in County Durham. Journal of the Institution of Water and Environmental Management. Vol. 7, pp.521-531. (1993)

3. Younger P.L. and Sherwood J.M. The Cost of Decommissioning a Coalfield: Potential Environmental Problems in County Durham. Mineral Planning. Vol. 57, pp.26-29. (1993).
4. Clarke J.N. Letter from the Chairman of British Coal to the Chief Executive of Easington District Council, Dated 11th February 1993. 4pp. (1993).
5. Levinson A.A. Introduction to Exploration Geochemistry. Applied Publishing Ltd, Calgary. 612pp. (1974).
6. Rose A.W., Hawkes H.E. and Webb J.S. Geochemistry in Mineral Exploration (Second Edition). Academic Press, London. 657 pp. (1979).
7. Smith D.B. and Francis E.A. Geology of the Country between Durham and West Hartlepool. Memoir of the Geological Survey of Great Britain. Explanation of One-inch Geological Sheet 27, New Series. HMSO, London. 354pp. (1967).
8. Appelo C.A.J. and Postma D. Geochemistry, Groundwater and Pollution. A.A. Balkema Publishers, Rotterdam. 536pp. (1993).
9. National Rivers Authority. Abandoned Mines and the Water Environment. Report of the National Rivers Authority (UK), Water Quality Series No. 14. London, HMSO. 46pp. (1994).
10. Cairney T., and Frost R.C. A case study of mine water quality deterioration, Mainsforth Colliery, County Durham. Journal of Hydrology Vol. 25, pp.275 - 293. (1975).
11. Ball J.W. and Nordstrom D.K. User's Manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. Geological Survey Open-File Report 91-183. 189pp. (1991).