Groundwater rebound in the South Yorkshire Coalfield: predicting impacts on water quality

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ABSTRACT
Preliminary characterisation for the Water Framework Directive indicates that 3,500 km of rivers and 18,000 km^2 of groundwater may be at risk from historic mining activities in England and Wales. The Environment Agency is responsible for implementing the Directive by preventing deterioration of water bodies and protecting aquatic ecosystems. The rebound of groundwater after the closure of deep coal mines threatens overlying aquifers and rivers. The GRAM model has been used to estimate future minewater discharge rates. These predictions have been combined with water quality data to assess the impact on receiving rivers using the PHREEQC geochemical speciation model. The simple approach presented here is intended to help catchment managers assess whether new discharges must be treated or if the impact on rivers is acceptable.

INTRODUCTION
The introduction of the EU Water Framework Directive (WaterFD) has prompted a change in the approach taken to protecting the water environment. The new integrated system requires holistic management of rivers and groundwater at the catchment scale. The overall aim of the WaterFD is to achieve "good ecological and good chemical status" in all water bodies by 2015 unless there are grounds for derogation. Deterioration in the existing status of water bodies must be prevented. Significant and sustained upward trends in the concentration of any pollutant in groundwater must be reversed, in order to progressively reduce pollution of groundwater.
The first step towards achieving the WaterFD objectives has been to characterise the risks posed by point and diffuse sources of pollution to groundwater and rivers. In England and Wales, this initial “River Basin Characterisation” (RBC) indicated that pollution from coal and metal mining is a significant potential barrier – over 3,500 km of rivers and 18,000 km^2 of groundwater are at risk or probably at risk from historic mining activities. These water bodies are located in Wales, and the north and west of England. The RBC report will inform the Environment Agency’s management of catchments to ensure that all water bodies are in good status by 2015, and that new pollution is prevented.
The closures of deep mines that had been de-watered for many decades has led to the rebound of contaminated groundwater. This rebound has the potential to lead to a deterioration in the existing status of water bodies and therefore breach the WaterFD. The majority of metal mines closed decades ago and the full recovery of groundwater levels has caused many polluting discharges into rivers. In some former coal mining areas, final recovery levels have not yet been reached. Continuing recovery is expected to lead to increased numbers of discharges into overlying aquifers and rivers. These current and potential discharges must be managed carefully to comply with the WaterFD, and also to protect valuable drinking water abstractions from the overlying Magnesian Limestone and Triassic Sandstone aquifers.
A major challenge for the Environment Agency is to assess the risk from minewater recovery to overlying aquifers and surface waters. Past experience has shown that where recovering minewater have discharged to surface waters then significant pollution has occurred. This has serious cost and time implications for restoring good quality. Options for preventing such discharges include (Younger & Wolkersdorfer, 2004):

- intercepting gravity outflows and diverting the minewater for treatment,
- pumping from shafts or boreholes to maintain water levels below the minimum head level in overlying aquifers or to prevent outflow to surface water.

Whilst discharges will often take place through artificial structures such as drainage adits or shafts, diffuse discharges may also contribute significant pollutant loadings (Younger, 2000b). However the exact location of new gravity outflows is not always predictable since shallow mineworkings are inherently unstable and existing flow paths may become blocked through collapse or precipitation of ochre. There is a temptation to allow minewater to recover until surface discharges occur since the location, flow rate and quality of the outflow can then be measured and a treatment system designed. However this approach will mean the receiving water is polluted for a period of time whilst the discharge stabilises and the treatment system is constructed. It is unlikely that this approach is within the spirit (or letter) of the WaterFD since the ecological status of the surface water body will deteriorate, and the impacts may be unacceptable to local residents.

When the minewater discharge is to an overlying aquifer, this “wait and see” approach is unacceptable since the timescale for ameliorating groundwater pollution is much greater than for surface waters. In addition, the WaterFD requires significant and sustained upward trends in the concentration of any pollutant to be reversed. Pumping to prevent the discharge will therefore be needed in perpetuity which can be very expensive.

A simple tool to quantify the impacts of rising minewaters on receiving waters would assist regulators and catchment managers in deciding whether discharges can be allowed for short time periods. If the impact is small then allowing a new outflow may be acceptable whilst treatment systems are commissioned. This may also assist when the land required for treatment systems does not coincide with the minewater outflow since the results of inaction can be quantified.

Methods for predicting the location, timing, quantity and quality of minewater discharges have been developed (e.g. Robins et al, 2002; Sherwood & Younger, 1997; Younger & Adams, 1999; Younger, 2000a). Tools for estimating the impact of these discharges on receiving surface waters and overlying aquifers have been more elusive. This paper presents a simple approach to this problem by combining the GRAM (Groundwater Rebound in Abandoned Mineworkings) model with the geochemical speciation model PHREEQC (Parkhurst & Appelo, 1999)

GRAM MODELLING OF REBOUND AND FLOW RATES

An assessment of the current and future situation in South Yorkshire has been made by applying the computer model GRAM to predict possible recovery rates in the area (see Burke & Younger, 2000; Burke et al, 2005 for a fuller description). GRAM is based on the mining hydrogeologist's concept of "ponds" in which interconnected mineworkings can be considered together and water balances calculated. The model can be used to estimate the timing and flow from each pond as recovery takes place. This flow may be to surface waters, other mineworkings (ponds) or to overlying aquifers. The location of potential surface discharge points from each pond can be identified by examining where seam outcrops with shallow workings cross valley axes; these are likely to control the final rebound level.

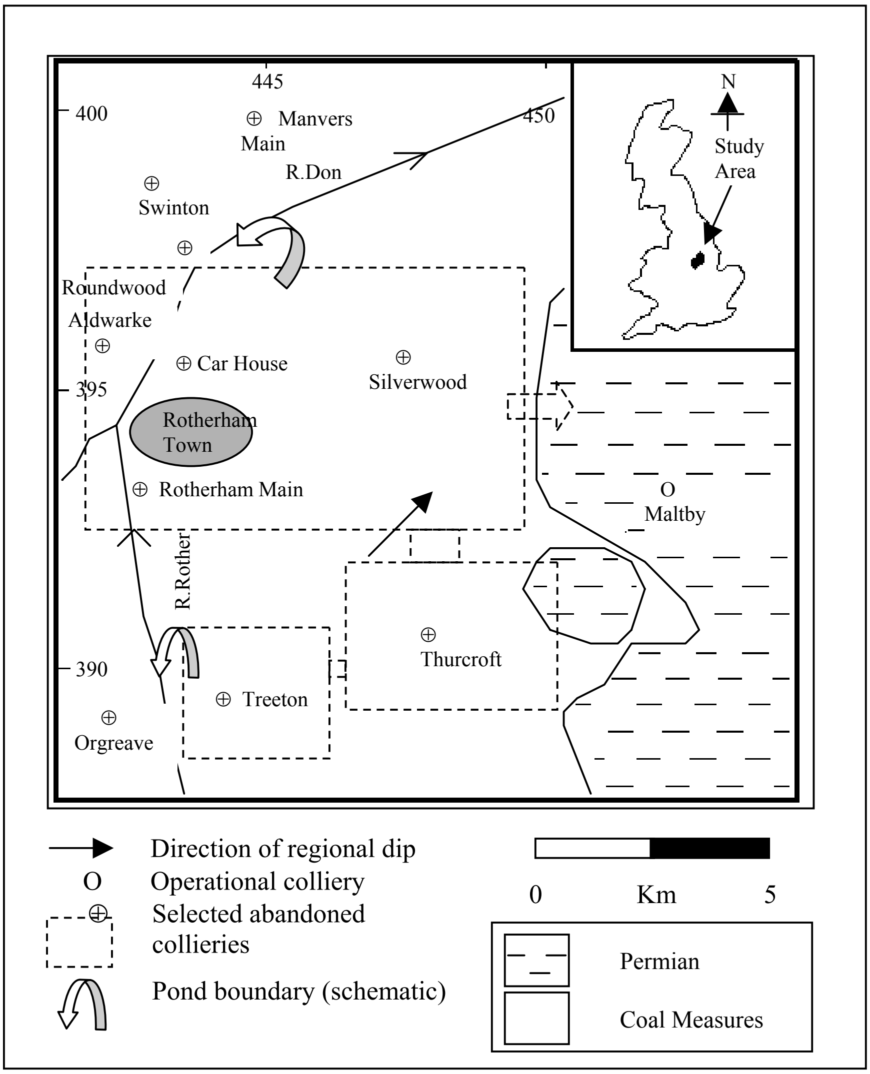


Figure 1. Map of the Rotherham area, showing principal settlements and rivers, the locations of selected collieries, pond boundaries and discharge points, and major geological boundaries (adapted from Burke & Younger, 2000).

Burke & Younger (2000) applied GRAM to the Rotherham area of South Yorkshire (Figure 1). Outflows to surface water and to the active coal mine of Maltby were predicted along with the potential range in 'first flush' and long-term minewater quality. At the present time, groundwater pumping within the modelled area continues to allow extraction of coal from the Maltby mine. Burke & Younger (2000) considered three scenarios which impacted the rate of recovery in the study area:

- no minewater flow to Maltby,
- some flow to Maltby,
- significant flow to Maltby.

The results of the GRAM modelling predicted surface discharges from the Treeton and Silverwood ponds (Figure 1). These discharges would be to the River Rother and River Don respectively, and are likely to occur via old shafts. The approximate flow rates of the discharges and the river flows (mean and 5 percentile; Mark Hutchinson, pers. comm.) are shown in Table 1.

Table 1. Flow rates for discharges and receiving rivers

Flow (Ml/d)	Treeton discharge	Silverwood discharge	River Rother	**River Don**
Mean flow	**2**	**1.5**	**400**	**1,400**
Low flow (5%ile)	**2**	**1.5**	**90**	**500**

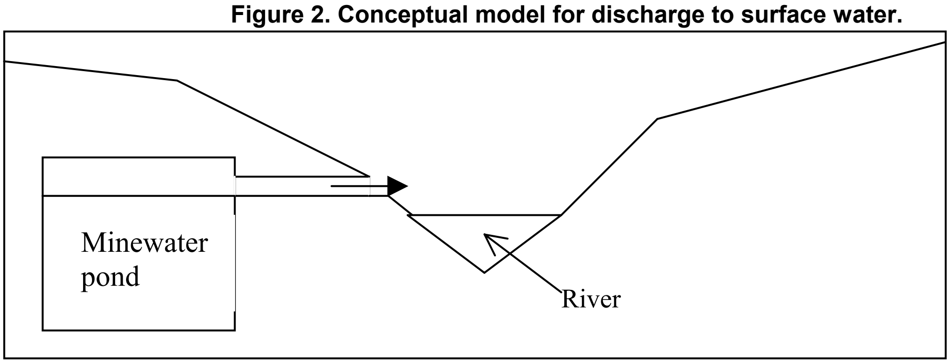
It is recognised that the minewater discharge flow rates will vary in response to rainfall. However, experience from existing discharges is that once the system has fully recovered discharge flow rates are relatively stable in comparison with receiving rivers. The assumption of a constant minewater flow rate is therefore considered reasonable for the purposes of this study.

PHREEQC MODELLING – IMPACT ON RECEIVING WATERS

The flow-rates calculated with the GRAM model have been combined with the geochemical speciation model PHREEQC to predict the impact of the minewater on the water quality in the receiving rivers. It should be emphasised that the approach taken in this paper is deliberately simplistic since the intention is to trial the conceptual approach rather than deliver a management tool at this stage.

The PHREEQC model has been widely used for investigating geochemical processes occurring in aquatic systems (Parkhurst & Appelo, 1999). It can simulate the equilibrium geochemical speciation as a result of mixing of waters and the precipitation and dissolution of solid phases. PHREEQC is based on an ion-association aqueous model. It takes user-defined water chemistry and determines saturation indices for the species present. The potential for precipitation of amorphous and crystalline mineral phases is determined by the model for the defined solution chemistry and environmental conditions (pH, redox). Interaction between dissolved ions and reactive surfaces can also be simulated. PHREEQC can therefore be used to predict the water quality expected as a result of mixing of two waters such as the discharge of minewater into a river. In this study, PHREEQC (version 2.8) has been used to predict the impact on river water quality as a result of the discharge of minewater. The conceptual model for mixing is shown in Figure 2.

Figure 2. Conceptual model for discharge to surface water.



The flows calculated by GRAM for the Treeton and Silverwood ponds (Table 1) are mixed with the flow in the River Rother and River Don. PHREEQC was applied as a batch-reaction model by taking the volume of flow in a fixed time period (e.g. 1 second) and mixing the two waters together. It was assumed that the minewater and river water completely mix, and that equilibrium was instantaneous. It is recognised that both these assumptions are simplifications but are deemed appropriate for this study.

Water chemistry

The concentrations of certain parameters in the rivers was taken from Environment Agency records (Mark Hutchinson, pers. comm.). Analysis of the minewater in the Treeton and Silverwood ponds was not available. Burke & Younger (2000) estimated the iron concentrations based on areas with similar geology and the sulphur content of the seams. The sulphur content has been correlated with expected iron concentrations in the short ("first-flush") and long-term (Younger, 2000a). The maximum iron concentration was predicted to be 200-600 mg/l, and the long-term concentration around 20 mg/l. Concentrations of other cations and anions was adapted from minewater analysis reported for a low iron concentration minewater (unpublished data from INWATCO project) and a high iron water (Horden Shaft; Croxford *et al.*, 2004).

Table 2. Input parameters - chemistry (mg/l except pH, pe).

Parameter	Minewater (long-term)	Minewater (first-flush)	River Rother	River Don
pH	6.68	5.9	7.97	7.54
pe	4	4	10	10
Fe	30	400	0.1	0.13
Mg	65	1,000	28	18
Na	615	2,000	65	-
Ca	-	2,000	68	55
Alkalinity (as $CaCO_3$)	390	0	278	212
Cl	145	35,000	104	83
SO_4^{2-}	1290	3,500	-	-
P (o-PO_4^-)		-	1	1.2
NO_3^-		-	6	7
K	65	1,000	-	-

The temperature was fixed at 25ºC. Redox data were not available and pe values of 4 (minewater) and 10 (river) were chosen by comparison with literature values (Appelo & Postma, 1996). Whilst deep minewaters isolated from the atmosphere would have lower pe, it is expected that mixing of minewater within the shaft prior to discharge into the river would increase the redox potential. Na was allowed to vary to satisfy the charge balance.

The influence of varying CO_2 partial pressures in the minewater (Croxford *et al.,* 2004) was ignored for the purposes of this simple modelling exercise. It is recognised that this assumption will need to be reviewed prior to a more detailed application of this approach.

RESULTS

Twelve scenarios were investigated using PHREEQC. The scenarios involved mixing of each minewater with the mean and low flows in each river. In addition, the saturation indices for the four initial solutions were calculated. The minewater has no significant effect on river pH in any scenario.

Minewater

The model indicates hematite is the dominant Fe(III) solid phase in equilibrium with the solution chemistry for both the "first-flush" and "long-term minewaters. Goethite, amorphous $Fe(OH)_3$, and jarosite ($KFe_3(SO_4)_2(OH)_6$) are also expected to be present at equilibrium; in reality, the amorphous phase is likely to form first with subsequent transformation to hematite and goethite. For all modelled scenarios, jarosite is under-saturated after mixing with the river but hematite, goethite and amorphous $Fe(OH)_3$ are calculated to precipitate.

River Rother – Treeton pond discharge

At mean river flows, the "first-flush" discharge is predicted to increase the concentration of iron to 2.1 mg/l. This exceeds the environmental quality standard (EQS) for iron of 1 mg/l (Dangerous Substances Directive, 76/464/EEC). However under low flow conditions (5%ile) the first-flush discharge increases the iron concentration to more than 8 mg/l. The minewater input also increases the chloride concentration to 860 mg/l. Whilst there is no formal EQS for chloride in surface waters, the drinking water standard is 250 mg/l which this discharge clearly breaches.

The "long-term" discharge has a less significant impact. The iron concentration in the river after mixing is predicted to be 0.25 mg/l (mean flow) and 0.75 mg/l for low flows. The EQS for iron is not exceeded. The Environment Agency policy on new discharges is that individual inputs should not increase the contaminant concentration in clean rivers by more than 10% of the EQS (i.e. 0.1 mg/l). This avoids a single discharge taking up all the dilution capacity within the river. The minewater discharge would therefore be allowed to increase the iron concentration in the river to 0.2 mg/l. The PHREEQC calculations indicate this limit will be breached, particularly at low river flow.

River Don – Silverwood pond discharge

The first-flush discharge increases the dissolved iron in the river to 0.56 mg/l from 0.13 mg/l under mean flow conditions. At low river flow, the iron concentration increases to 1.33 mg/l. The first-flush minewater will therefore exceed the EQS value under low river flow, and be of concern at mean flow.

The PHREEQC modelling indicates that the long-term discharge is unlikely to cause pollution. At mean river flow there is no change in dissolved iron and at low flow, it is calculated to be 0.22 mg/l.

Iron ochre precipitation and smothering.

The PHREEQC modelling indicates that for some scenarios, the “strong” minewater may cause the environmental quality standard for iron to be breached in the receiving river. However, the main reason this regulatory standard is not exceeded for all the scenarios is that iron precipitates out of the dissolved phase to form various Fe(III) minerals. At equilibrium the model predicts the formation of hematite, goethite and amorphous iron oxide for all scenarios. In reality, the majority of iron oxide is likely to be precipitated initially in the amorphous form which will be transformed into crystalline hematite and goethite over time (Schroth & Parnell, 2005).
The formation of ochre typifies iron-rich minewater discharges particularly in coal mining areas. Although the precipitation of ochre removes iron from the dissolved phase, it causes smothering of the river bed and therefore damage to the aquatic ecosystem (Jarvis & Younger, 1997; Younger, 2000b).
The PHREEQC results were used to estimate the mass of iron deposited on the river bed from each of the minewater discharges. The model calculates the iron concentration remaining in solution after mixing of the minewater with the river water. Subtracting this value from the initial iron concentration in the discharge gives the concentration lost from solution, i.e. precipitated. This is multiplied by the minewater flow to give kg of iron precipitated per day. The results are shown in Table 3 below.

Table 3. Amount of iron (oxide) precipitated

Scenario	Mass of iron precipitated (kg Fe/day)
Rother+‘first-flush’ MW (mean flow)	796
Rother+‘first-flush’ MW (low flow)	782
Rother+‘long-term’ MW (mean flow)	60
Rother+‘long-term’ MW (low flow)	59
Don+‘first-flush’ MW (mean flow)	599
Don+‘first-flush’ MW (low flow)	598
Don+‘long-term’ MW (mean flow)	45
Don+‘long-term’ MW (low flow)	45

These calculations illustrate the significant amount of iron that will be deposited from the minewater onto the bed of the river. The “long-term” discharges have a lesser impact of 45-60 kg Fe/day whereas the “first-flush” discharges are predicted to be 600-800 kg Fe/day. The assumptions on which these calculations are based are necessarily simplistic, however the results indicate the seriousness of the potential impact.

DISCUSSION

The calculations presented in this study illustrate the impact of minewater discharges on receiving rivers. These impacts decrease as the concentration of iron and other contaminants decrease from their levels in the first-flush. An important factor when considering management options for dealing with such impacts is the length of time until the discharge concentration has stabilised. Treatment schemes designed for the long-term contaminant loading will invariably be smaller scale and cheaper than for the first-flush. Younger & Adams (1999) suggest the half-life for decline in iron concentration is generally equal to the total time period for rebound. Burke & Younger (2000) estimated recovery would take between 10 and 25 years for the study area. It will therefore take at least 40 years for the initial concentration of 400 mg/l to fall to the long-term level of 30 mg/l.
The PHREEQC modelling demonstrates that allowing the minewater to discharge in an uncontrolled manner from the Treeton pond to the River Rother will cause unacceptable pollution in both the short (first-flush) and long term. Dissolved iron concentrations will exceed environmental quality standards, while the deposition of substantial amounts of ochre will lead to smothering of the river-bed. The installation of a treatment scheme is necessary if the objectives of the Water Framework Directive are to be achieved. It is expected that the treatment scheme would be needed in perpetuity.
The discharge from the Silverwood pond to the River Don is predicted to have a significant impact at first. The modelling indicated the EQS for iron would be breached under low river flow conditions, and substantial ochre deposition would take place. In the longer term however, dilution within the River Don may allow the discharge to continue without treatment although staining of the river-bed may be unacceptable.

CONCLUSIONS

This paper has presented a simple approach for assessing the impacts of rising minewater on receiving surface waters. Outputs from the GRAM model for rebound have been used in the geochemical speciation model PHREEQC to calculate contaminant concentrations in rivers and the deposition of ochre. This approach is based on a number of simplifying assumptions that must be further explored and tested before it can be used as a management tool for regulators. Comparison of the predictions with field data is planned. The approach will then be extended to investigate the impact of minewater discharges on overlying aquifers.

DISCLAIMER

The views expressed in this document are not necessarily those of the Environment Agency.

REFERENCES

Appelo, C.A.J., & Postma, D. 1996. *Geochemistry, Groundwater and Pollution.* A.A. Balkema Publishers, Rotterdam. 649pp.

Burke, S.P., & Younger, P.L. 2000. Groundwater rebound in the South Yorkshire coalfield: a first approximation using the GRAM model. *Quarterly Journal of Engineering Geology and Hydrogeology,* 33, 149-160.

Burke, S.P., Potter, H.A.B., & Jarvis, A.P. 2005. Groundwater rebound in the South Yorkshire coalfield: a review of initial modelling. *Proceedings of IMWA '05: Mine Closure.* 5-7 September 2005, Oviedo, Spain.

Croxford, S.J., England, A., Jarvis, A.P. 2004. Application of the PHREEQC geochemical computer model during the design and operation of UK mine water treatment schemes. *In:* Jarvis, A.P., Dudgeon, B.A., & Younger, P.L. (Eds.) *Mine Water 2004: Process, Policy and Progress.* Proceedings of IMWA conference, Newcastle upon Tyne, September 2004. University of Newcastle upon Tyne. Volume 2, 125-134.

Jarvis, A.P., & Younger, P.L. 1997. Dominating chemical factors in mine water induced impoverishment of the invertebrate fauna of two streams in the Durham Coalfield, UK. *Chemical Ecology,* 13, 249–270.

Parkhurst,D.L., & Appelo, C.A.J. 1999. *User's guide to PHREEQC (Version 2) – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.* U.S. Geological Survey Water Resources Investigations Report 99-4259. 310pp.

Robins, N.S., Dumpleton, S., & Walker, J. 2002. Coalfield closure and environmental consequence – the case in south Nottinghamshire. *In:* Younger, P.L., & Robins, N.S. (eds). *Mine Water Hydrogeology and Geochemistry.* Geological Society, London, Special Publications, 198, 89-97.

Schroth, A.W., & Parnell, R.A. 2005. Trace metal retention through the schwertmannite to goethite transformation as observed in a field setting, Alta Mine, MT. *Applied Geochemistry,* 20, 907-917.

Sherwood, J.M. & Younger, P.L. 1997. Modelling groundwater rebound after coalfield closure. *In:* Chilton, P.J. *et al.* (eds). *Groundwater in the Urban Environment, Volume 1: Problems, processes and management.* A.A. Balkema Publishers, Rotterdam, 165-170.

Younger, P.L. & Adams, R. 1999. *Predicting Mine Water Rebound.* Environment Agency R&D Technical Report W179. Bristol, UK. 108 pp.

Younger, P.L. 2000a. Predicting temporal changes in total iron concentrations in groundwaters flowing from abandoned deep mines: a first approximation. *Journal of Contaminant Hydrology,* 44, 47-69.

Younger, P.L. 2000b. Iron. *In:* D'Arcy, B.J., Ellis, J.B., Ferrier, R.C., Jenkins, A., & Dils, R. (eds). Diffuse Pollution Impacts. Chartered Institution of Water and Environmental Management.

Younger, P.L., & Wolkersdorfer, C.H. (eds). 2004. Mining impacts on the fresh water environment: technical and managerial guidelines for catchment scale management. *Mine Water and the Environment,* 23, S2-S80.