

An object-oriented particle tracking approach to modelling pyrite oxidation and pollutant transport in mine spoil heaps

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ABSTRACT

At present there is no suitable method to predict either the longevity of contaminant sources within spoil heaps, or the evolution of their strength over the contaminating lifetime of the sites. Existing techniques provide little information relevant to the prediction of field contaminant concentrations and time scales, which is essential for an optimum choice of remediation options. A physically-based contaminant transport model, POTOMAC (Pyrite Oxidation products Transport: Object-oriented Model for Abandoned Colliery sites), has been developed to simulate the pyrite oxidation process in mine spoil heaps and the subsequent transport of the reaction products. This is believed to represent the first particle tracking model created using object-oriented technology. The model conceptualises a spoil heap as a series of 'columns', each representing a portion of the unsaturated zone, where active weathering and precipitation of secondary minerals takes place. The columns are then connected to a saturated zone, beneath the water table, where the contaminants are transported to the heap discharge. POTOMAC has been applied to a case study, the Morrison Busty spoil heap in County Durham, UK.

INTRODUCTION

Polluted discharges from abandoned coal and metal mines are well documented (e.g. Younger *et al.*, 2002) but surface spoil heaps can also be potential long-term sources of contamination for local watercourses and groundwater systems. As they are generally in greater contact with the atmosphere than *in situ* rock, spoil heaps have the potential to be far more vigorous generators of acidic water than flooded underground workings. Oxidative weathering and dissolution of sulphide minerals, particularly pyrite, which are abundant in mine spoil heaps, leads to the release of metals (e.g. iron, copper, zinc), sulphate and, in the case of pyrite, acidity into percolating waters. The discharge of these acidic, metal-rich waters into the wider environment results in the precipitation of iron hydroxides and oxyhydroxides, coating stream beds with ochre and damaging the local ecology.

During the decision making process over whether, and how best, to remediate such polluting discharges from surface spoil heaps, it is important to have a knowledge of the long term evolution of their water quality. Existing methodologies for mine water pollution assessment, such as acid-base accounting techniques, are concerned primarily with the presence or absence of acidity-producing minerals (such as pyrite) and alkalinity-producing minerals (such as calcite) in order to estimate a balance between the two. Such methods do not take into account temporal changes which arise from differential reaction rates and transient hydrological fluxes. In reality, they are more concerned with the possibility of a problem occurring rather than how severe the problem may prove over the long term (Younger, 2000). A more reliable approach is to consider the time scales for removal of oxidation products and for depletion of source minerals by sustained weathering. Estimates of the lifetime of contamination from spoil heaps are therefore essential for an optimum choice of remediation options. In cases where contaminant loadings are high early in the life of a discharge, the predicted time scale for the depletion of source minerals will dictate whether long term remediation must involve expensive techniques, such as chemical dosing, or whether less costly passive treatment methods, e.g. constructed wetlands, will eventually suffice (Wood *et al.*, 1999).

A physically-based contaminant transport model, POTOMAC (Pyrite Oxidation products Transport: Object-oriented Model for Abandoned Colliery sites), has been developed to predict the long term contamination potential of mine spoil heaps (Gandy, 2003). The latest object-oriented techniques have been employed in the development of POTOMAC to produce a computationally fast model capable of simulating the large time scales (on the order of centuries) required for this application. The model has been applied to a case study, the Morrison Busty spoil heap, which lies near the village of Quaking Houses, County Durham, UK, in order to produce estimates of the lifetime of the contaminants discharging from the heap and reveal a pattern of source mineral depletion.

MODEL DESIGN

Conceptual model

A mine spoil heap can be conceptualised as a series of columns (Gandy, 2003), which represent an unsaturated zone where oxidative weathering of pyrite takes place, draining into a saturated zone beneath the water table, which may be within the spoil, effectively producing a perched aquifer, or within the underlying bedrock (Figure 1). This conceptual model represents a pseudo two-dimensional approach to modelling contaminant transport in spoil

heaps, with flow in a vertical direction within the columns and in a lateral direction within the saturated zone. It is assumed there is no lateral flow or transport of contaminants between columns.

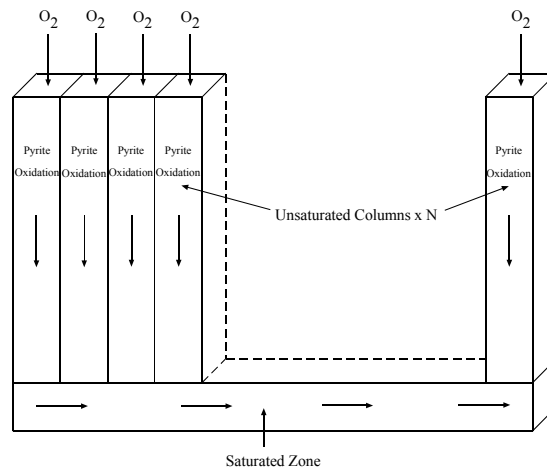


Figure 1: Conceptual model of a mine spoil heap (after Gandy, 2003)

Within the conceptual model, oxygen enters each column at the spoil surface, both in its gaseous form and dissolved in infiltrating rain water, and is transported vertically through the unsaturated spoil. It is assumed that the pore space within the spoil is partly water-filled and partly air-filled. On encountering pyrite (the only source of contamination), oxidation takes place, with the resultant products, ferrous iron and sulphate, joining the transport process. The subsequent oxidation of ferrous iron by any remaining oxygen and precipitation of ferric oxyhydroxide provides an iron 'sink', where iron is effectively removed from the transport process. It is assumed there is no sink for sulphate and, as such, the concentration of sulphate present at each point within the model domain is a representation of the amount of pyrite oxidation taking place. On reaching the saturated zone, each chemical constituent is transported laterally to the spoil heap discharge.

Solute and gaseous transport

The transport of components within POTOMAC is based on a particle tracking technique, the random walk method, in which the fundamental idea is to simulate the concentration distribution of chemical constituents by a finite number of discrete particles, each of which is moved by groundwater flow and is assigned a mass which represents a fraction of the total mass of chemical constituent involved (Prickett *et al.*, 1981).

The governing equation for one-dimensional solute transport in porous media, the advection-dispersion equation, can be written as:

$$\frac{\partial}{\partial x} \left(\frac{D_L}{R_d} \cdot \frac{\partial C}{\partial x} \right) - \frac{V}{R_d} \cdot \frac{\partial C}{\partial x} \pm C_s Q = \frac{\partial C}{\partial t} \quad (1)$$

where V = average linear groundwater velocity, D_L = coefficient of longitudinal hydrodynamic dispersion, x = space dimension, t = time, R_d = retardation factor, C = concentration of solute, $C_s Q$ = source or sink function having a concentration C_s and a flux rate Q . Advection is defined as the movement of solutes by the bulk motion of the flowing groundwater, at the same rate as the average linear velocity of the groundwater (Anderson & Woessner, 1992), where average linear velocity (V) can be defined as:

$$V = \frac{K}{n} \left(\frac{\partial h}{\partial x} \right) \quad (2)$$

where K = hydraulic conductivity, n = mean effective porosity, $\frac{\partial h}{\partial x}$ = head gradient.

Hydrodynamic dispersion refers to the spreading of the contaminant due to the fact that not all of it actually moves at the same speed as the average linear velocity of the groundwater, i.e. the spreading of the contaminant in excess of the displacement attributable to advection alone (Fetter, 1999). Within POTOMAC, the spreading of solute is in the direction of bulk flow only, known as longitudinal dispersion. The longitudinal dispersion coefficient (D_L) in Equation (1) includes both mechanical mixing and molecular diffusion but for the transport of solutes within POTOMAC molecular diffusion is considered to be negligible so the longitudinal dispersion coefficient is given by:

$$D_L = \alpha_L V \quad (3)$$

where α_L = longitudinal dispersivity, which is taken to be a 'characteristic length' of the porous medium. However, for gaseous oxygen transport, diffusion plays an important role. The driving force for diffusive transport of oxygen through a spoil heap is assumed to be the oxygen concentration gradient which develops when oxygen is

consumed by pyrite oxidation reactions (Gerke *et al.*, 1998). The effective diffusion coefficient for gaseous oxygen (D_a) is calculated using the approaches of Elberling *et al.* (1993) and Gerke *et al.* (1998):

$$D_a = 0.273D_a^0 (1 - S_w)^{3.28} + \frac{S_w D_w^0}{H} \quad (4)$$

where D_a^0 = diffusion coefficient for oxygen in air, D_w^0 = diffusion coefficient for oxygen in water, S_w = relative water saturation, H = Henry's constant. It is then incorporated into POTOMAC by way of Equation (3), in place of the mechanical mixing term which is taken to be zero. Therefore:

$$D_L = D_a \quad (5)$$

The random walk method solves Equation (1) by transporting particles at the average linear groundwater velocity to represent advection, then adding a random displacement, tending to the normal distribution, to represent dispersion. The direct result is therefore a particle (mass) distribution which can be converted to a concentration distribution, where required. The fundamental idea is that the concentration distribution of a simple one-dimensional transport problem can be equated to the probability density function of a normally distributed (Gaussian) random variable to establish the following relationships:

$$\begin{aligned} \mu &= Vt \\ \sigma &= \sqrt{2\alpha_l Vt} \end{aligned} \quad (6)$$

where μ = the mean and σ = the standard deviation of a normally distributed random variable. In terms of solute transport, advection represents the mean of a normally distributed random variable and dispersive movement the deviation from the mean. Each particle is therefore moved over a distance x during a single time step of length t according to:

$$x = Vt + Z\sqrt{2\alpha_l Vt} \quad (7)$$

where Z is a normally distributed random variable with zero mean and unit variance. The resulting path lengths are normally distributed with mean Vt and standard deviation $\sqrt{2\alpha_l Vt}$.

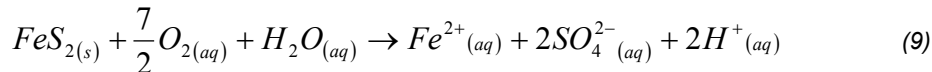
For particles containing gaseous oxygen, the advection component is taken to be zero so that the distance a particle moves in a single time step is given by:

$$x = Z\sqrt{2D_a t} \quad (8)$$

where all terms are as defined above.

Oxidative weathering of pyrite

The controlling chemical reaction taking place within a spoil heap is the oxidative weathering of pyrite by dissolved oxygen. Gaseous oxygen is assumed to dissolve into solution at the pore walls and, along with the dissolved oxygen present within the water-filled pores, reacts with pyrite minerals according to:



The rate of pyrite oxidation is generally believed to be controlled by the availability of oxygen at the pyrite surface (Ritchie & Miskelly, 2000). The rate equation used in POTOMAC is based on that determined by McKibben & Barnes (1986), where the rate of pyrite oxidation is dependent on the square root of oxygen concentration and effectively independent of pH. The rate of dissolved oxygen depletion, in units of moles oxygen $m^{-2} s^{-1}$, according to this approach, is given by:

$$-\frac{d[O_{2(aq)}]}{dt} = k[O_{2(aq)}]^{0.5} \quad (10)$$

where the square brackets indicate species activity and k , the rate constant, has a value of $3 \pm 10^{-8} s^{-1}$. Pyrite content is assumed to vary both laterally and vertically within the columns, and is entered into the model by the user as a percentage by mass. The mass of pyrite within each model cell can then be calculated.

The surface area of pyrite crystals is calculated for each model cell using the approach of Bronswijk *et al.* (1993):

$$A_{FeS_2} = \frac{6HA(1-n)X_{FeS_2}}{\rho d} \quad (11)$$

where A_{FeS_2} = surface area of pyrite crystals, X_{FeS_2} = pyrite content, ρ = density of pyrite, d = average diameter of pyrite crystals, and all other parameters are as defined above.

The rate of oxygen depletion (Equation 10) is calculated for each time step and converted to rate of pyrite depletion according to the stoichiometry of Equation 9, i.e. multiplying by 2/7. Since, for particle tracking purposes, the amount of pyrite depletion is required in terms of mass rather than area, a specific surface area

(S_A) is calculated for each model cell, giving the relationship between the surface area of pyrite and mass of pyrite:

$$S_A = \frac{A_{FeS_2}}{M_{FeS_2}} \quad (12)$$

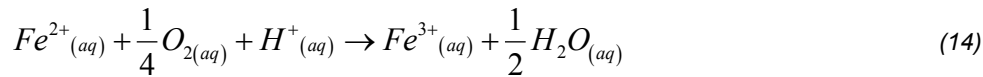
By multiplying the specific surface area by the rate of pyrite depletion, then converting the number of moles to a mass (multiplying by the relative molecular mass of pyrite) and multiplying by the mass of pyrite in each cell, a value can be calculated for the mass of pyrite oxidised in each cell in a single time step. The entire process can be summarised as:

$$-\frac{d(FeS_{2(s)})}{dt} = \frac{2}{7} * 119.967 * S_A M_{FeS_2} k [O_{2(aq)}]^{0.5} \quad (13)$$

where the rate of pyrite depletion is in units of grams per second, the value 119.967 represents the relative molecular mass of pyrite and all other parameters are as defined above. The use of parentheses, as opposed to square brackets, denotes the mass of a solid rather than a concentration.

Incorporation of ferrous iron oxidation

The ferrous iron produced by pyrite oxidation is assumed to oxidise in the presence of dissolved oxygen to produce ferric iron:



The rate of oxidation is dependent upon pH and oxygen concentration and has been studied by a number of authors, e.g. Sung & Morgan (1980). It is agreed that:

$$\frac{-d[Fe^{2+}_{(aq)}]}{dt} = k [Fe^{2+}_{(aq)}] [O_{2(aq)}] \quad pH < 2 \quad (15)$$

$$\frac{-d[Fe^{2+}_{(aq)}]}{dt} = \frac{k [Fe^{2+}_{(aq)}] [O_{2(aq)}]}{[H^+_{(aq)}]} \quad 2 < pH < 5 \quad (16)$$

$$\frac{-d[Fe^{2+}_{(aq)}]}{dt} = \frac{k [Fe^{2+}_{(aq)}] [O_{2(aq)}]}{[H^+_{(aq)}]^2} \quad 5 < pH < 8 \quad (17)$$

where k is the rate constant and has a different value in each case, calculated from reported data. The rates are in units of moles $l^{-1}s^{-1}$ so are converted to grams per time step by multiplying by the relative molecular mass of iron and by the volume of water in the cell and the time step.

The oxidation of ferrous iron is likely to be bacterially mediated, which can increase reaction rates by a factor of up to 10^6 (Singer & Stumm, 1970). Bacterial catalysis is incorporated into POTOMAC by multiplying the rate at a pH less than 2 by a factor of 10^3 and at a pH between 2 and 5 by a factor of 10^2 . At a pH greater than 5, no factor is added since the abiotic rate of ferrous iron oxidation is faster than the bacterially catalysed rate at these higher pH values (Boon *et al.*, 1999). It is assumed that all ferric iron produced in the ferrous iron oxidation process spontaneously precipitates as ferric oxyhydroxide and is therefore removed from the calculations.

OBJECT-ORIENTED NUMERICAL APPROACH

Object-oriented programming is often referred to as a new paradigm (Budd, 1991). It is a technology that has become increasingly popular over the past ten years and involves concepts that are fundamentally different to those employed in conventional procedural programming techniques. Its major advantage is easily re-useable code, which is also easily extended, allowing future adaptations to be efficiently made. In object-oriented programming technology, an "object" is an individual instance of a "class", where a class is essentially a "template" which defines the properties (variables) and methods (procedures and functions) of a group of objects. POTOMAC has been written in a fully object-oriented style, incorporating the main features of object-oriented programming, and is believed to be the first particle tracking model to be developed using such technology (Gandy, 2003). Each physical element within the conceptual model (Column, Saturated Zone, Node, Particle) is assigned to an object, which contains the properties associated with that element and any methods required to perform the various mathematical calculations with which the element is concerned.

Each one-dimensional column is assigned to an object which is an instance of the class *TPorousMedium*. This object holds the input variables (i.e. column dimensions and physical properties, e.g. porosity, pH, density of

pyrite) for the unsaturated zone and the methods associated with the main calculations carried out there, such as the addition of oxygen particles to each column, oxidation of pyrite and ferrous iron, and transport of particles. Similarly, the saturated zone is assigned to an object, this time an instance of the class *TSaturatedMedium*, which contains the input variables and methods associated with the saturated zone. Nodes are located at the centres of each cell in the finite difference grid and each is assigned to an object which is an instance of the class *TNode*. This object stores variables describing the node's position in the grid, the velocity of any particles passing through that particular cell and the mass of chemical constituents contained within the cell, as well as the physical properties of the cell. Since each node is assigned to a separate object, variations in physical properties between cells can be easily implemented as each can store different values. Particles are unique entities which hold a proportion of the total mass of a particular chemical constituent and are transported throughout the model domain. There are three types of object used to describe particles: those which are instances of the class *TParticle*, to which each particle containing ferrous iron and sulphate is assigned; those which are instances of the class *TOxygenParticle*, which describe particles containing dissolved oxygen; and those which are instances of the class *TOxygenDiffusionParticle*, which describe particles containing gaseous oxygen. Particles are moved vertically through each column before being transferred to the corresponding cell in the saturated zone, where they are transported laterally to the discharge point. As well as containing the mass of the relevant chemical constituent, each object stores the position of the particle in the grid and its velocity. In addition, at the beginning of each simulation one object is created from the *TPorousControl* class, which represents the outer core of the model and stores most inputs before passing them to the other objects, as required. The model structure, incorporating all the objects described above, is shown in Figure 2.

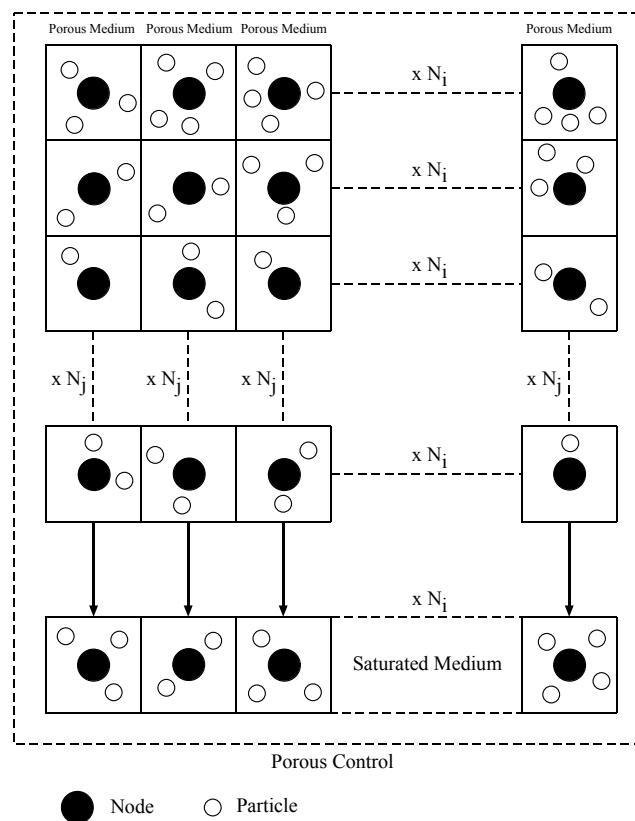


Figure 2: Overall structure of physical system showing objects involved in N_i columns each containing N_j cells (after Gandy, 2003)

APPLICATION OF POTOMAC TO A CASE STUDY

POTOMAC has been applied to the Morrison Busty spoil heap, which lies near the village of Quaking Houses in County Durham, UK, in order to predict the contamination potential of the waste material and assess the long-term water quality evolution. The spoil heap covers an area of approximately 35 hectares and varies in thickness from 4 to 10 m. It comprises colliery waste in the form of grey and black weathered shale, ash, coal and coal dust, and overlies glacial clay and sandy drift deposits which in turn overlie Carboniferous Coal Measures beds. A perched water table appears to exist within the heap, above the impermeable clay layer at the base of the spoil, at a depth of approximately 6 to 9 m, while the most significant discharge enters a local watercourse, the Stanley Burn. Further details on the Morrison Busty spoil heap are given in Gandy & Younger (2003). Since only a small part of the spoil heap is pollutant-generating, a 500 m by 125 m section of the heap was taken for modelling and

the perched water level was kept constant at a depth of 8 m below the spoil surface, producing a saturated zone of constant thickness 2 m. For the POTOMAC simulation, the area was divided into 20 columns each containing 8 cells. Pyrite content was allowed to vary in each cell, according to analysis of spoil samples collected during borehole construction, which revealed that pyrite content is limited above a depth of 4 m (Evans *et al.*, 2003). It is assumed that oxidative weathering, since the emplacement of the spoil heap some 80 years ago, is exhausting the supply of pyrite in these upper layers.

Following successful calibration against observed iron and sulphate concentrations in the perched groundwater and discharge from Morrison Busty spoil heap, a long-term simulation was carried out to predict the contamination over a 500 year period. Results for the perched groundwater are shown in Figures 3 and 4, with an exponential decline in concentration with time shown for iron and sulphate and both predicted to persist for several centuries. Similar results were achieved for the heap effluent into the Stanley Burn, although concentrations are predicted to be significantly lower than the perched groundwater, probably due to dilution by water of a much higher quality, generated in less contaminated parts of the spoil heap.

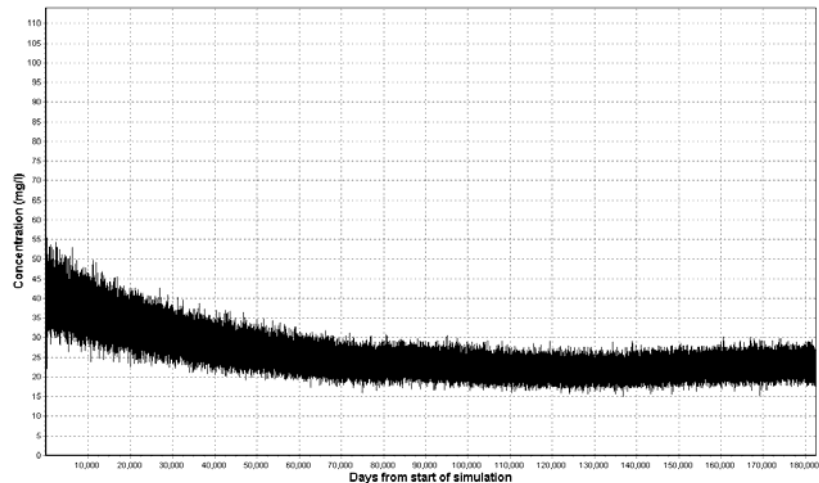


Figure 3: Predicted iron concentration in perched groundwater of Morrison Busty spoil heap over a 500 year period

The exponential decline in concentration shown by Figures 3 and 4 reflects the progressive decrease in rate of pyrite oxidation as the surface area of pyrite crystals is reduced. In terms of pyrite depletion, after 500 years pyrite oxidation is predicted to have taken place down to a depth of 4 m but below this depth the spoil remains undisturbed. This corresponds to almost all the pyrite in the upper 2 metres being exhausted with progressively less beneath this depth down to a depth of 4 m. The lack of pyrite oxidation at depths below 4 m suggests that oxygen is not being transported to such depths since it is exhausted by the oxidation of pyrite in the upper layers. This is confirmed in Figure 5, which shows the modelled distribution of gaseous oxygen in the most pollutant-generating part of the spoil heap at the end of the simulation. It is predicted that there will be no oxygen present beneath a depth of 4 m. From these results, it can be seen that the longevity of pollution from mine spoil heaps is heavily dependent upon the transport of oxygen to pyrite mineral surfaces. If it is also assumed (as is likely in coal-rich wastes) that oxygen takes part in other oxidation reactions, it is possible that the pyrite at greater depths will always remain undisturbed.

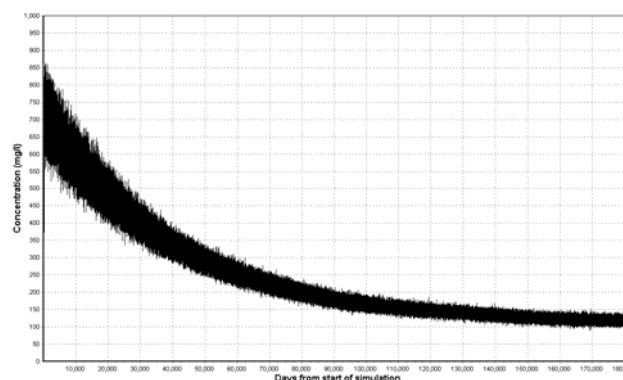


Figure 4: Predicted sulphate concentration in perched groundwater of Morrison Busty spoil heap over a 500 year period

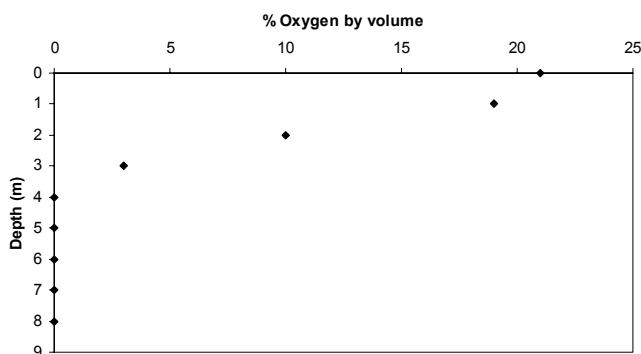


Figure 5: Modelled gaseous oxygen distribution in perched groundwater of Morrison Busty spoil heap at the end of a 500 year simulation

CONCLUSIONS

A physically-based pollutant transport model, POTOMAC, has been developed to predict the long-term quality of discharges from surface spoil heaps undergoing pyrite oxidation. The latest object-oriented techniques have been used to produce a computationally fast model capable of simulating the large timescales (on the order of centuries) required. A particle tracking approach, the 'random walk method', is used to simulate the transport of contaminants, as well as oxygen in both its dissolved and gaseous forms, while reaction kinetics are included to govern the rate of pyrite and ferrous iron oxidation.

Application of POTOMAC to the Morrison Busty spoil heap in County Durham, UK, has enabled a prediction to be made of the contaminating lifetime of the spoil heap and the pattern of pyrite depletion. Results show that the spoil heap could remain polluting for several centuries, while the governing factor in the magnitude of pollution is the transport of oxygen to pyrite mineral surfaces.

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