Coupled Hydrological and Chemical Model of Coal Mine Dumps at As Pontes, A Coruña (Spain)

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Abstract
Mine wastes from the operation of As Pontes coal mine in A Coruña (Spain) contain pyrite and have the potential to generate acid waters when rainwater interacts with them. Their runoff waters are collected into two main channels (North and South) and taken to the liquid-effluent treatment plant. After mine closure in December 2007, dump runoff waters are diverted into the open-pit mine to contribute to the filling of the future open pit lake. The chemistry of dump runoff waters changes seasonally in response to hydrological events. Here we present a coupled hydrological and geochemical model to predict daily stream flows and chemical quality. The coupled model accounts for three end-member waters and reproduces most of the chemical data measured at the South channel during 2006. Once calibrated, the model has been tested and verified with data collected during 2007 and not used for calibration.

Key words: coal mine dump, hydrological model, geochemical model, As Pontes

Introduction

As Pontes coal mine dump is situated in Galicia (N.W. Spain) and it has a surface area of 13 km$^2$ (see Figure 1). Mine wastes from the operation of As Pontes coal mine in A Coruña (Spain) contain pyrite and have the potential to generate acid waters when rainwater interacts with them. Their runoff waters are collected into two main channels (North and South) and taken to the liquid-effluent treatment plant. After mine closure in December 2007, dump runoff waters are diverted into the open-pit mine to contribute to the filling of the future open pit lake. The climate of the study area is temperate and wet. This favors weathering and leaching processes. As Pontes dumps contain a wide variety of mine soils of various weathering stages and physical and chemical properties. Pyrite present in some of these materials caused soil and water acidification during the construction of the dumps (Monterroso, 1995). Acidity promoted also the dissolution of great amounts of aluminum and iron. Recent chemical analyses of dump runoff waters show seasonal trends in response to hydrological events. Water quality is good during the rainy season and gets worse during the summer when runoff decreases drastically.

Figure 1 Location of As Pontes coal mine and outside dumps in Coruña, Spain.
Mixing of dump runoff waters

It is assumed that runoff waters from the dump come from mixing of 3 end-member waters which have different chemical characteristics. Fractions of each member in the measured sample are called mixing fractions which add to 1. Mixing fractions of samples were estimated with a statistical mixing fraction model. VISUAL-BALAN (Samper et al., 1999) was used for hydrological modeling and estimating hydrological components from precipitation (evapotranspiration, surface runoff, interflow and groundwater flow). CORE2DV4 (Samper et al., 2003) was used to model dump water mixing and chemical reactions. This model uses stream flows $Q$ computed with VISUAL-BALAN and concentrations of chemical species $c$ of each type of water stream flow derived from a statistical mixing model.

Hydrological model

VISUAL-BALAN is a hydrological code which solves the daily water balance in the soil layer, the unsaturated zone and the aquifer. VISUAL-BALAN was run for the basin of the sampling point 16B. Dumps occupy a total area of 12 km$^2$. Catchment area of sampling point 16B is 12.6 km$^2$ out of which 8.4 km$^2$ is occupied by dumps and the rest of 4.2 km$^2$ corresponds to natural basins which have natural waters. Stream flows from natural basins, and surface runoff, interflow and groundwater flows from dumps are computed from VISUAL-BALAN.

Results of hydrological model were tested and compared to stream flows measured at the liquid-effluent treatment plant (Planta TEL in Spanish). Monthly flows computed with VISUAL-BALAN (VB) agree well with those measured at Planta TEL (Figure 2).

Figure 2 Comparison of monthly flows computed with VISUAL-BALAN and measured values.

Geochemical model

The geochemical model assumes that there are the following 3 end-member waters: 1) Natural Water (NW), Acid Water (AW) and Neutral Mineralized Water (NMW). A statistical method was used to estimate the concentrations of the three uncertain end-members (Samper et al., 2008) and compute chemical mixing fractions by assuming pure mixing without chemical reactions. Chemical mixing fractions were coupled later with hydrological and geochemical models. Chemical fractions derived from the statistical model and hydrological fractions derived from the hydrological model are related through a matrix $H$ of chemical-to-hydrological fractions. Best estimates of the entries of matrix $H$ are listed in Table 1.

The geochemical model considers aqueous complexation, dissolution/exsolution of O$_2$(g) and CO$_2$(g), precipitation of ferrihydrite and surface complexation of proton on iron oxides and is solved in terms of H$^+$, Fe, Mn, Al, SO$_4^{2-}$, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$ and HCO$_3^-$.
Table 1 Best estimates of chemical-hydrological mixing fraction matrix $H$.

<table>
<thead>
<tr>
<th>Flows</th>
<th>Neutralized mine water</th>
<th>Acid mine water</th>
<th>Natural water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural basins</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Dumps: Surface runoff</td>
<td>0.00</td>
<td>0.10</td>
<td>0.90</td>
</tr>
<tr>
<td>Dumps: Interflow</td>
<td>0.35</td>
<td>0.00</td>
<td>0.65</td>
</tr>
<tr>
<td>Dumps: Groundwater</td>
<td>0.00</td>
<td>1.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Coupled hydrological and geochemical model**

The coupled model was calibrated using data from point 16B from 01/12/2006 to 05/05/2007. Data from 06/05/2007 to 30/11/2007 were used to test the predictive capabilities of the model. The chemistry of dump runoff waters changes seasonally in response to hydrological events. Precipitation causes dilution of dump runoff. Water quality improves during rain events and gets worse during the summer when runoff decreases drastically.

Results of the calibration and testing stages for the main chemical species are shown in Figure 3. One can see that the model reproduces the trends of most measured data during the calibration period. Most chemical species and especially sulfate show sharp dilution patterns caused by rainfall events. Such dilution events are followed by recovery periods. In the testing period the model predicts properly the trends of Mn, sulfate, Ca and Na. For pH the model predicts a decrease during the summer while measured values keep increasing modestly. Possible reasons for such deviation should be analyzed in future studies.

Sensitivity runs have been performed to evaluate uncertainties in model parameters such as pH of end member waters. Results are most sensitive to pH of neutralized water (NM) which controls the mean pH while the slope of pH curve is controlled by pH of acid water. It is found that HCO$_3^-$ concentration of NM water affects significantly computed pH. Mn concentration of acid water controls the recovery stages. Sulfate concentration of NM water controls mainly the mean computed concentration while the SO$_4^{2-}$ concentration of AM water controls the shape of the recovery curves.

**Conclusions**

A coupled hydrological and geochemical model has been presented for the stream flows and chemical quality of As Pontes dumps. The coupled model accounts for three end-member waters and reproduces most of the chemical data measured at point 16B during 2006. Once calibrated, the model has been tested and verified with data collected during 2007 and not used for calibration.

**Figure 3** Comparison of measured and calculated results for pH, Mn, sulfate, Na and Ca during calibration (01/12/2006 to 05/05/2007) and testing (06/05/2007 to 30/11/2007) periods.
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References