Modelling pH and alkalinity in rivers impacted by acid mine drainage

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Abstract

A model that simulates pH and alkalinity when a river stream is impacted by acid mine drainage or other acidic discharge was developed using the theories of alkalinity and pH in natural waters. The main assumption of the model is that the mixing of the water from the river and acidic discharge is instantaneous. The main principles used in the modelling are that, the total inorganic carbon and total alkalinity are conservative with respect to mixing. Two approaches are used to do simulation using the model: considering the change of volumetric flow of acidic discharge assuming constant pH and considering the change of pH of acidic discharge assuming constant volumetric flow. The modelled results capture clearly the buffer effect of carbonic acid in water.

Furthermore, the model was applied to simulate possible acidification of the main stream of Zambezi River due to acid mine drainage from coal mining. From simulated results it was concluded that the pH of the main stream of Zambezi River will drop to values below 6 if the pH of the water of tributaries coming from the mining area goes below 3.The model is developed to be used to simulate the resulting pH and alkalinity in rivers impacted by acidic discharge but it can be extended to simulate acidification of lagoons or other similar processes. In practice, the model can be used as a decision support tool by authorities for granting new mining licenses, and by different industries that produce acidic wastewaters to manage their discharges to the environment.

Key words: Modelling, alkalinity, river, water quality, acid mine drainage

Introduction

Nowadays, mining activity is common in most developing countries and it brings revenues to the governments (Nhantumbo, et al. 2015). However, mining is also linked to severe impacts to the environment and the water resources can be seriously affected by acid mine drainage (AMD) (Ochieng, et al., 2010; DPLF, 2014; Mishra, et al. 2012). Developing countries lack water quality monitoring programs to assess the impact of mining on the water resources (Nhantumbo, et al. 2015). Financial and other resources limit the possibility of improving the water quality monitoring programs, if such programs exist.

Therefore, the use of indirect methods such as modelling is an alternative avenue to predict water quality changes without extensive sampling and analysis required in the water quality monitoring programs. However, the existing water quality models are not appropriate to simulate rivers impacted by AMD with limited data, and they were not developed to simulate acidification of rivers, which has additional complication (Mosley, et al., 2015; Mosley, et al. 2010).

In this paper we develop a model to simulate the pH and alkalinity in rivers impacted by acid mine drainage or other acidic discharge at the mixing zone. The model can be used to simulate the minimum flow or the high pH of the acidic discharge that would cause a potentially detrimental drop of the pH of the recipient river. The model can also be applied to simulate the discharge of acidic wastewater into lakes, lagoons or similar. The model can be used by water quality monitoring agencies to define limits and standards for acidic wastewater discharges, as well as by mining companies to manage their discharges in terms of flows and acidity.

Methods

Theories of alkalinity and pH in natural waters were combined to develop a model which is easy to apply since it minimizes the input data. The model uses as input pH, alkalinity, flow and average temperature of both, the river water and the acidic discharge, see (fig. 1). When simulating the discharge of a certain volume of water into a body of water such as a lake or lagoon the volumetric flows Q_1, Q_2, and Q_R in m^3/s are replaced by volumes V_1, V_2, and V_R in m^3.

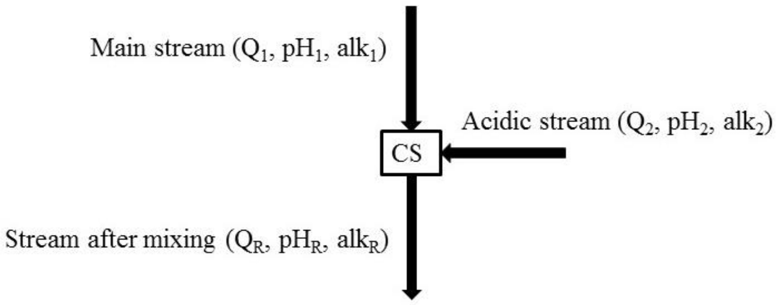

Figure 1 *Schematic representation of the simulated conditions. Q_1, pH_1, alk_1 are the volumetric flow, pH and alkalinity of the main stream. Q_2, pH_2, alk_2 are the volumetric flow, pH and alkalinity of the acidic stream. Q_R, pH_R, alk_R are the volumetric flow, pH and alkalinity of the stream resulting from mixing of the main stream and acidic stream. CS = completely stirred.*

In the development of the model it is assumed that when the streams merge, complete mixed conditions are instantaneously obtained. This is reasonable assumption when dealing with small streams at high velocity. When the streams are large the assumption is less accurate since it might take quite a long distance to have the two streams completely mixed.

There are also two main principles used in the modelling. These principles state that, the total inorganic carbon and total alkalinity are conservative with respect to mixing (Wolf-Gladrow, et al. 2007; Munhoven 2013). The total inorganic carbon (*TIC*) used in the model development is defined by (eq. 1). Carbon acid alkalinity (*TA*) is the only alkalinity considered in the modelling and it is defined by (eq. 2).

$$TIC = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \tag{1}$$

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{2}$$

The concentration of ions in the main steam and in the acidic discharge are calculated using the protolithic water theory and carbonic acid equilibrium theory by (eq. 3, 4, 5, 6 and 7). alk is the alkalinity of the main stream or acidic discharge according to (fig. 1). The equilibrium constants k_w, k_{a1} and k_{a2} are temperature dependent and calculated using empirical equations (Appelo C A J 1999).

$$[H^+] = 10^{-pH} \tag{3}$$

$$[OH^-] = \frac{[H^+]}{k_w} \tag{4}$$

$$[CO_3^{2-}] = \frac{alk - [OH^-] + [H^+]}{2 + [H^+]/k_{a2}} \tag{5}$$

$$[HCO_3^-] = \frac{[H^+] \cdot [CO_3^{2-}]}{k_{a2}} \tag{6}$$

$$[H_2CO_3] = \frac{[H^+]\cdot[HCO_3^-]}{k_{a1}} \tag{7}$$

Total inorganic carbon and total alkalinity in the resulting stream from the mixing of the main stream and acidic water are calculated based on the two main principles of the model as expressed in (eq. 8, and 9) respectively.

$$TIC_R = \frac{TIC_1 \cdot Q_1 + TIC1_2 \cdot Q_2}{Q_1 + Q_2} \tag{8}$$

$$TA_R = \frac{alk_1 \cdot Q_1 + alk_2 \cdot Q_2}{Q_1 + Q_2} \tag{9}$$

Concentrations of carbonate ions in the resulting stream can be written as a function of $[H^+]$ only, (eq. 10, 11 and 12).

$$[H_2CO_3] = \frac{[H^+]^2}{[H^+]^2 + k_{a1}\cdot[H^+] + k_{a1}\cdot k_{a2}} \cdot TIC_R \tag{10}$$

$$[HCO_3^-] = \frac{k_{a1}\cdot[H^+]}{[H^+]^2 + k_{a1}\cdot[H^+] + k_{a1}\cdot k_{a2}} \cdot TIC_R \tag{11}$$

$$[CO_3^{2-}] = \frac{k_{a1}\cdot k_{a2}}{[H^+]^2 + k_{a1}\cdot[H^+] + k_{a1}\cdot k_{a2}} \cdot TIC_R \tag{12}$$

(Eq. 13) is obtained replacing the concentrations of $[OH^-]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ using (eq. 4, 11 and 12) in (eq. 2). The only unknown in (eq. 13) is $[H^-]$.

$$TA_{R'} = \frac{k_{a1}\cdot[H^+] + 2k_{a1}\cdot k_{a2}}{[H^+]^2 + k_{a1}\cdot[H^+] + k_{a1}\cdot k_{a2}} \cdot TIC_R + \frac{k_w}{[H^+]} - [H^+] \tag{13}$$

(Eq. 13) can be written in the form *f(x) = 0*, where x is the hydrogen ions concentration $[H^-]$, and solved numerically using the Newton-Raphson method. The solution of the model was further converted into a computer code using Matlab.

The model developed can be used to simulate contamination of rivers using two different approaches: considering the change of volumetric flow of acidic discharge assuming constant pH or considering the change of pH of acidic discharge assuming constant volumetric flow (fig. 2 and 3), respectively. The (fig. 2 and 3) show results from hypothetic simulation in order to demonstrate the kind of results that can be generated by the model. The values of pH of the main stream and acidic discharge for hypothetic simulation were selected to allow visualization of the quality of the results for a broad range of pH. The alkalinity was selected relatively high to allow the visualization of buffer effect of carbonic acid in water.

Using the two different simulation approaches it is possible to generate graphs showing the resulting pH as function of Q_2/Q_1 for the volume change simulation and as function of pH_2, for the pH change simulation, (fig. 2a and 3a). These kind of results makes it possible to identify the volumetric flow and the pH of the acidic discharge that lowers the pH in the main stream to a predefined threshold. Further analysis can be done by generating the (fig. 2b and 3b). The last two figures show the concentration of carbonate ions, total inorganic carbon and total alkalinity in the resulting stream.

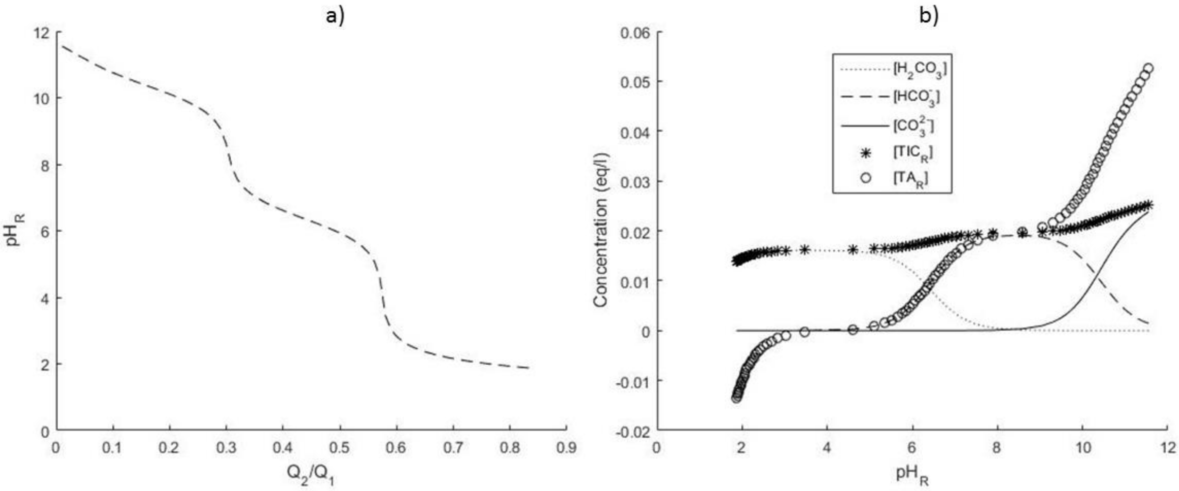

Figure 2 *Hypothetic simulation varying the volumetric flow of the acidic discharge (Q_2). All other parameters are kept constant.(pH_1 =11.6,alk_1 =0.05 eq/l, pH_2 =1.1 and alk_2 =-0.09). a) pH in the resulting stream after complete mixing of main stream (1) and acidic discharge (2). b) concentration of carbonate species, hydrogen and hydroxide ions after complete mixing of main stream (1) and acidic discharge (2) in eq/l.*

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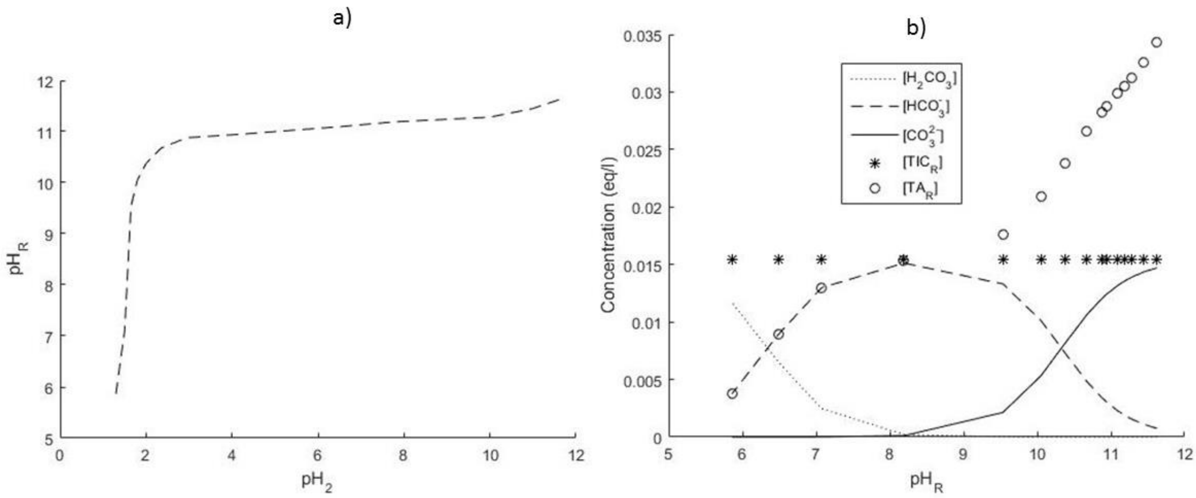

Figure 3 *Hypothetic simulation varying the pH of the acidic discharge (pH_2). The alkalinity of the acidic discharged is computed by the model based on pH_2 and its initial alkalinity. All other parameters are kept constant. (pH_1 =11.6 and alk_1 =0.06 eq/l). a) pH in the resulting stream after complete mixing of main stream (1) and acidic discharge (2). b) Concentration of carbonate species, hydrogen and hydroxide ions after complete mixing of main stream (1) and acidic discharge (2) in eq/l.*

Furthermore data from Zambezi River in Mozambique was used to illustrate a practical application of the model. Zambezi River Basin is the major river basin in Southern Africa with an area of 1.370.000 km^2 and the average discharge at the outlet of 4100 m^3/s. The river is essential for the economy of its riparian countries, which include Angola, Botswana, Malawi, Mozambique, Namibia, Tanzania, Zambia, and Zimbabwe and its outlet is located in Mozambique (Nhantumbo 2013), (fig. 4).

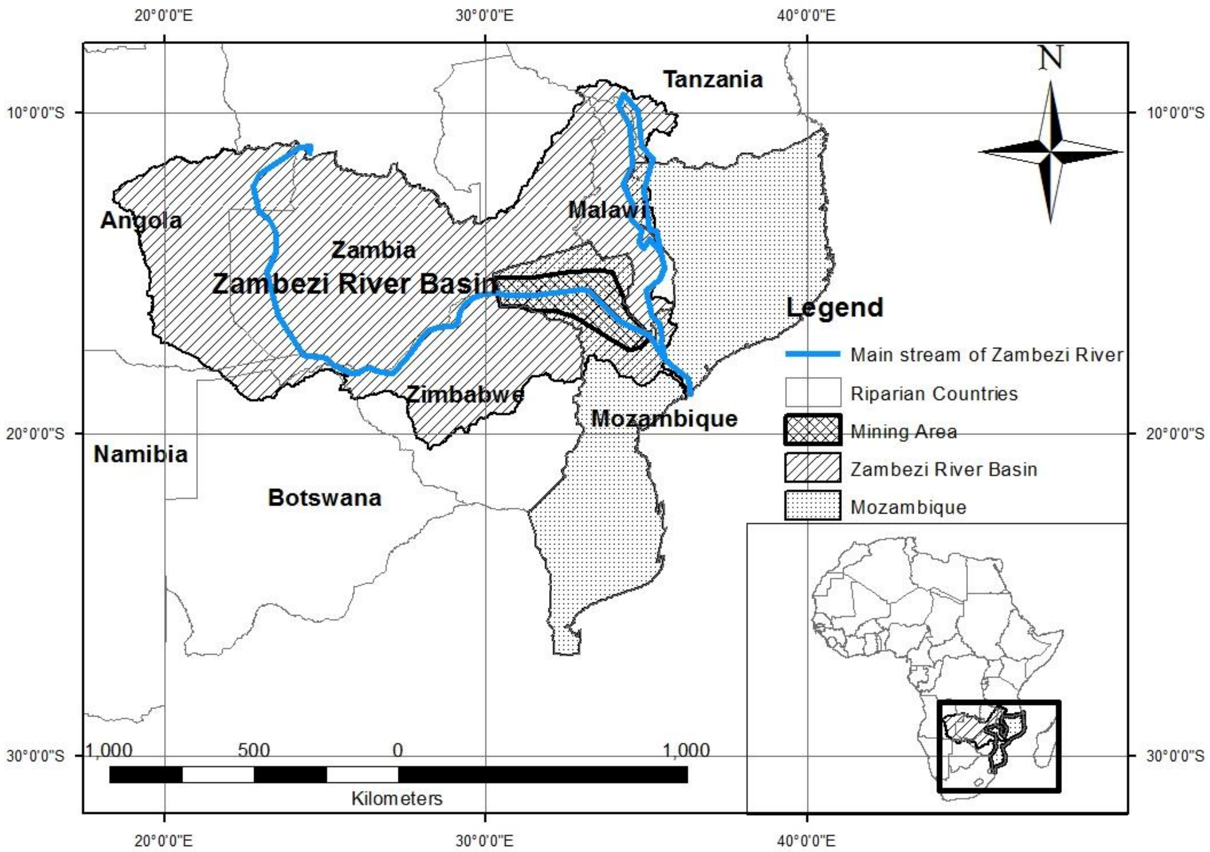

Figure 4 *Zambezi River Basin*

Three major coal reserves of Mozambique are located in the Zambezi River Basin area. Since the last decade, a number of coal mining companies started to exploit coal in the coal reserves and the water quality is at risk of being impacted by acid mine drainage (Nhantumbo 2013). The water quality monitoring agency is not well established to assess the water quality changes and to take actions to protect the water resources. Further on, the lack of resources limits improvement.

It is assumed that the average flow of the main stream and the water coming from the tributaries do not change a lot and that acid mine drainage can lower the pH of the water coming from the mining area with time. If the major interest is to protect the main stream because it sustains life of the people living in the riparian area of the river basin, it is important to guarantee that the water coming from the mining area does not lower its pH to values that may seriously harm the environment. Fish populations, for example, start to reduce when the pH is below 6 (Jennings, et al. 2008). Thus, it is important to guarantee that the pH in the main stream does not go below that limit.

Table 1*. Input data from Zambezi River used for simulation (Nhantumbo 2013)*

	Main Stream of Zambezi River (1)	Tributaries coming from the mining area (2)
Flow Q ,m^3/s	2330	1120
pH	7.6	7.85 (considering varying to 2)
Alkalinity mg/l. $CaCO_3$, (eq/l)	62 (0.00124)	129 (0.00384)

The input data used for simulation, both of the main stream of Zambezi River and tributaries coming from the mining area is given in (tab. 1). The flows and the pH used for simulation are the average values and the simulated results are affected by these averages. However, the simulated results can be used as a clue on what is going to happen in the main stream of the river if the pH of the water of the tributaries coming from the mining area drops. For simulation, the pH of water coming from the tributaries in the mining area was considered to reduce from its original value 7.85 to 2.

By simulation with the presented model in can be shown (see fig. 5a) that the pH of the main stream will drop to values below 6 if the pH of the water coming from the tributaries is below 3. Supplementary information about the carbonate species (H_2CO_3, HCO_3^-, CO_3^{2-}), total inorganic carbon (TIC), total alkalinity in the main stream (TA_R) is given in (fig. 5b).

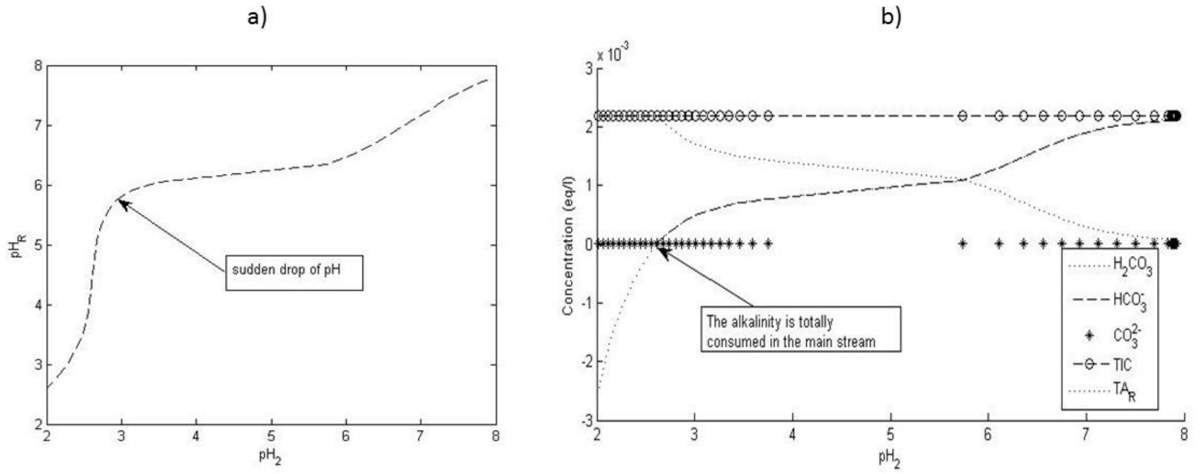

Figure 5 *Simulation results for acidification of the main stream of Zambezi River. a) pH in the resulting stream after complete mixing of main stream (1) and potential acidic water coming from the mining area (2). b) Concentration of carbonate species, hydrogen and hydroxide ions after complete mixing of main stream (1) and potential acidic water coming from the mining area (2) in eq/l. Input data is given in (tab. 1).*

Conclusions

A model that simulates pH and alkalinity when acid mine drainage or other acidic water is discharged into a river was developed based on the theories of alkalinity and pH in natural waters. The model is based on input of flow, pH, alkalinity and average temperature of both, the main stream and acidic discharge. The model was developed assuming complete mixing immediately after the river and the acidic water merge. The model can do simulations considering two different approaches: the change of volumetric flow of acidic discharge assuming constant pH and the change of pH of acidic discharge assuming constant volumetric flow. The modelled results capture clearly the buffer effect of carbonic acid in water.

Furthermore, the model was applied to simulate possible acidification of the main stream of Zambezi River in Mozambique due to acid mine drainage from coal mining. Using the simulated results it was concluded that the pH of the main stream of Zambezi River will drop to values below 6 only if the pH of the water coming from the tributaries in the mining area is below 3.

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