Environmental risk assessment of acid rock drainage under uncertainty: The probability bounds and PHREEQC approach

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HIGHLIGHTS

- A risk assessment methodology for ARD under uncertainty was developed.
- The methodology propagates uncertainties throughout the risk assessment phases.
- The methodology quantifies uncertainties associated with data and parameters.
- The result shows fate-and-transport of heavy metals is well simulated.
- The result shows the methodology estimates ARD risks using two decision measures.

ABSTRACT

Acid rock drainage (ARD) is a major environmental problem that poses significant environmental risks during and after mining activities. A new methodology for environmental risk assessment based on probability bounds and a geochemical speciation model (PHREEQC) is presented. The methodology provides conservative and non-conservative ways of estimating risk of heavy metals posed to selected endpoints probabilistically, while propagating data and parameter uncertainties throughout the risk assessment steps. The methodology is demonstrated at a minesite located in British Columbia, Canada. The result of the methodology for the case study minesite shows the fate-and-transport of heavy metals is well simulated in the mine environment. In addition, the results of risk characterization for the case study show that there is risk due to transport of heavy metals into the environment.

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1. Introduction

Acid rock drainage (ARD) is a major environmental problem caused by mining activities locally and globally [1]. ARD is generated when sulfide-bearing material reacts with oxygen and water during and after mining activities [2,3]. This reaction changes relatively insoluble chemical species in sulfide minerals into more easily dissolved free ionic species (e.g., Cu, As and Zn) or secondary minerals (e.g., sulfate, carbonates and hydroxides). The oxidation of some sulfide minerals produces acidity that may lower the drainage pH, which can increase the rate of sulphide oxidation, the solubility of many products of sulphide oxidation and the rate of weathering for other minerals.

The transport of ARD products into the environment may result in exposure by aquatic life which poses serious ecological risks [1,4–11]. Gray summarized the overall ecological effects of ARD that can include habitat modification, niche loss, bioaccumulation within the food chain, loss of food sources, elimination of sensitive species, reduction in primary productivity, and food chain modification [1]. Ecological risk assessment evaluates the likelihood that adverse ecological effects may occur, or are occurring, as a result of exposure to one or more contaminants [12]. It is imperative to conduct appropriate risk assessment during various phases of mining to minimize ecological risks.

The literature review [3,13–15] shows that there are a few guidelines in the mining industry for risk assessment of ARD. The guidelines that are in place (e.g., Ref. [3]) specify that contaminants...
leached from ARD are predicted (e.g., using fate and transport models). The predicted concentrations are compared with regulatory criteria to assess environmental risks. The models are expected to provide accurate predictions although they have inherent uncertainties such as model, parameter, and data uncertainties [16,17]. In the mining industry, the uncertainties associated with fate and transport modeling are rarely stated or recognized [15]. Regulatory documents quantifying the response of receptors to contaminants are derived from test samples and extrapolating such information to species introduces data uncertainty [19]. Both exposure and effects measures are therefore typically treated deterministically.

Betrie et al. [20] proposed an improved risk assessment methodology using a fugacity-based model which addressed the issue of uncertainties in exposure and effect characterization. The fugacity-based model is a fate and transport model that uses transport parameters (advection and diffusion) to transport metals and a partitioning coefficient ($K_d$) to estimate the distribution of metals into different media such as water and sediment. The model does not have the capability to represent the full range of complex geochemical processes that are going in mine sites and it overestimates the predicted concentrations as a result. The fugacity-based model is very useful for preliminary risk assessment at mine sites where data are limited and results are quickly needed. Geochemical-based models should be used instead of the fugacity-based model for mine sites where adequate data are available.

Geochemical-based models for mine sites are well documented in the literature [21–24]. Examples include MINTEQ [25], PHREEQC [26], MIN3P [27], and others. These models simulate processes such as geochemical speciation, acid-base equilibrium, redox equilibrium, precipitation/dissolution, adsorption/desorption, and transport [28]. This paper presents a new methodology for environmental risk assessment based on the PHREEQC model and demonstrates this methodology using a case study in a mine environment.

2. Methodology

The proposed methodology for ecological risk assessment consists of problem formulation, uncertainty analysis, exposure characterization, effect characterization, and risk characterization (Fig. 1). Problem formulation defines the assessment endpoints, the conceptual model and analysis plan. In uncertainty analysis, uncertainty in input parameters is represented in a set of special type of probability distribution functions and discrete values are sampled from them to prepare inputs for the PHREEQC model. In exposure characterization, the PHREEQC model simulates the fate and transport of contaminants using the input values. Once all the sampled parameters are used for simulations, the predicted outputs of PHREEQC are used to construct distribution functions and are validated against their observed counterparts. In effect characterization, responses of receptors to stressors (i.e., toxicity data) are collected and the associated uncertainty represented in distribution functions. In risk characterization, the results of exposure and effect characterization are used to quantify the risk. The detail descriptions of each component are presented in the following subsections.

2.1. Problem formulation

Assessment endpoints, the conceptual model and the analysis plan are first defined (Fig. 1). The assessment endpoints express the environmental values that are to be protected. The selection of endpoints characteristics are based on the ecological relevance, susceptibility or relevance to management goals. The conceptual model is the description and visual representation of possible relationships between the endpoints and stressors. The analysis plan evaluates risk hypotheses to determine how they will be assessed using available data.

The case study mine site is located in British Columbia. The mine site consists of waste rock and the aquifer, which has geological units of clay and bedrock (Fig. 2). The waste rock is in the unsaturated zone, and the clay till and bedrock are in the saturated zone. ARD is typically generated in a waste rock or tailings facility, transported vertically to the water table, and then transported laterally within the saturated zone in groundwater. The most common concern is the ecological impact when the groundwater containing leached materials returns to surface water. Sampling was conducted prior to the commencement of mining, and a monitoring plan was carried out in which monthly samples were obtained from groundwater located beneath the waste rock.

In this study, the assessment endpoints are defined based on the example mine’s management goals, which are protecting at least 90% of fish species 90% of the time from stressor exposure in a nearby lake. The conceptual model consists of the source of stressors, media, exposure routes, and receptors. The stressors are elevated copper and zinc released from waste rock. The media that could be contaminated are groundwater and surface water. The two potential exposure routes that are considered at this site are ingestion and contact. The hypothesis evaluated in this study was: copper and zinc may cause permanent reduction of fish species in this lake. The fish species that inhabit the lake are Oncorhynchus mykiss, Oncorhynchus kisutch, Gasterosteus aculeatus, and Oncorhynchus clarki.

2.2. Uncertainty analysis

Uncertainty analysis is conducted in this study using a probability bounds method. The Probability bounds ($p$-box) method is used to represent imprecise probability. Imprecise probability is a generalization of probability when one is not able to define a precise probability function $P$ for an event $x$ [29]. An imprecise probability function $P(x)$ is characterized by its lower probability $p(x)$ and upper probability $P(x)$. Lower probability and upper probability functions map an event $x \in X$ in interval values between zero and one [30]. The lower and upper bounds of a $p$-box associated with a random variable $X$ give the possible range of probabilities that $X$ exceeds any particular value. These bounds are close together when the imprecision is small but may be far apart when it is large.

The uncertainty analysis is done following two steps. First, $p$-boxes are constructed for input and validation parameters of the PHREEQC model. The input parameters of the proposed model include the concentration of cations and anions in input waters, parameters related to chemical reactions and processes (e.g., cation exchange capacity) within the aquifer, and transport parameters related to advection, diffusion, and dispersion. The parameters for model validation are measured concentrations of cations and anions at the assessment point that are used to validate the simulation. Second, a probability level is defined and this is used to cut the $p$-boxes into $j$ intervals (Fig. 3). This figure shows a $p$-box for copper, a defined level of probability and the cuts. In this example, a probability level of 0.2 is defined to cut the $p$-box into 6 cuts ($j = 1\ldots 6$). Each cut has minimum and maximum values from the lower and upper cumulative distribution functions, respectively. For instance, the cut $j = 6$ consists of lower and upper bound values of 0.05 mg/L and 0.263 mg/L, respectively. In this study, Risk Cal 4.0 software [31] was used to conduct the uncertainty analysis.

2.3. Exposure characterization

Exposure characterization describes the potential or actual contact of stressors with the endpoints. It analyses sources of
contaminants, distribution of contaminants, and co-occurrence of stressors and endpoints. Its objective is to identify endpoints, exposure pathways from source to the endpoint and describes the spatial and temporal distribution and intensity of contaminants [32].

To determine fate and transport of contaminants, the PHREEQC model, its description presented in the subsection below, is run using the input values sampled in the uncertainty analysis step. The total number of runs is $2 \times j$. Next, p-boxes are constructed for each simulated parameter based on the PHREEQC output and validated against p-boxes of the observed parameters. The validation is done by visually comparing the simulated and observed parameters. If an acceptable match is not obtained between simulated and observed p-boxes, the process is reinitiated from constructing input p-boxes (Fig. 1).

2.3.1. Description of PHREEQC

PHREEQC (pH REDox Equilibrium in C) is a computer model that simulates aqueous equilibrium speciation, batch chemical reactions and one-dimensional reactive transport in aqueous
environments [26]. This program has capabilities of simulating: speciation, sorption and desorption; and one dimensional transport through sequential batch reactions. The speciation component calculates concentrations and activities of ionic species and complexes using the law of mass action, mineral saturation indexes as a logarithmic ratio of ionic activity product and solubility product, density and specific conductance of solution compositions. Solute activities are calculated as product of the activity coefficient and concentration of ion. The activity coefficient is determined using Debye-Hückel [33] (Eq. 1), or Pitzer [34] (Eq. 2) depending on the ionic strength of the solution.

$$\log \gamma_i = \frac{-A \beta^0_{i} l^{1/2}}{1 + B q_{i} l^{1/2}}$$

(1)

where $\gamma_i$ is the activity coefficient, $z$ is charge number of ion $i$; $l$ is ionic strength; $A$ and $B$ are temperature dependent constants; and $q_i$ is ion size parameter.

$$\ln \gamma_i = -\frac{A}{3} l^{1/2} f(l) + \frac{2 \nu_i \nu_m}{\nu} B(l) m + \frac{2 (\nu_i \nu_m)^{3/2}}{\nu} C m^2$$

(2)

where

$$f(l) = \frac{l^{1/2}}{1 + 1.2 l^{1/2}} + 1.67 \ln(1 + 1.2 l^{1/2})$$

and

$$B(l) = 2 \beta^0 + \frac{2 \beta}{\alpha l} \left[ 1 - \left( 1 + \alpha l^{1/2} - \frac{1}{2} \nu^2 l \right) e^{-\alpha l^{1/2}} \right]$$

and where $\beta^0$ and $\beta$ are specific-ion parameters, $\alpha$ is a constant for a similarly charged class of electrolytes, $\nu$ is the sum of the stoichiometric coefficients for the cation ($\nu_+$) and the anion ($\nu_-$).

Sorption and desorption are simulated as surface complexation reactions or ion exchange reactions. Surface complexation reactions are simulated either by the Dzombok and Morel database for complexation of heavy metals ions on hydrous ferric oxide or CD-MUSIC (Charge Distribution MultiSite Complexation) for complexation of heavy metals on goethite [26]. There are three conventions to simulate ion-exchange reactions and the Gaines–Thomas convention (Eq. (3)) was used in this study to simulate ion exchange reactions. The Gaines–Thomas convention calculates the activity of exchange species using the equivalent fraction of the exchangeable cation [35].

$$\beta_i = \sum_{l,j,k,...} \frac{\text{meq}_{l-} \cdot x_i}{\text{meq}_{l-} \cdot x_i}$$

(3)

where $\beta_i$ is the activity of an exchangeable ion $l$, meq $x_i$ is concentration of species $i$ on the solid phase expressed in milliequivalents (meq/kg), and $l, j, k, \ldots$ are the exchangeable ions.

The transport of solutions through a 1D flow path is modeled using the advection–reaction–dispersion equation (Eq. (4)). This equation consists of the transport (i.e., the first two terms) and the chemical reactions (the last term) parts. A finite difference scheme is used in PHREEQC to solve the transport part of the equation. The scheme is forward in time, central in space for dispersion, and upwind for advective transport [26]. First the advective transport is calculated, second the chemical reactions, third the dispersive transport and finally the chemical reactions again.

$$\frac{\partial C}{\partial t} = -\nu \frac{\partial C}{\partial x} + D_l \frac{\partial^2 C}{\partial x^2} - \frac{\partial q}{\partial t}$$

(4)

where $C$ is concentration in water, $t$ is time, $\nu$ is pore water flow velocity, $D_l$ is the hydrodynamic dispersion coefficient, and $q$ is concentration in the solid phase. $D_l$ can be computed from:

$$D_l = \alpha_l v_x + D_s$$

$\alpha_l$ = longitudinal dispersivity

$v_x$ = velocity in x direction

$D_s$ = effective diffusion coefficient
2.3.2. PHREEQC modeling

The modeling assumptions are described as follows. The aquifer is initially filled with native-water and this water represents the pre-mining water chemistry. The aquifer contains clay with cation exchange capacity and calcite. Initially, the cation exchanger is in equilibrium with the native water. Rain water infiltrates through the waste rock surface. The infiltrating water gains cations (e.g., copper, zinc, and iron), anions (sulfate, alkalinity, chloride) and carbon dioxide in the unsaturated zone from oxidation processes. The drainage water enters the saturated zone and reacts with calcite in the presence of the cation exchanger.

The chemistry of the native-water and infiltration-water are presented in Table 1. The chemistry of native-water represents the pre-mine water chemistry obtained from monitoring wells installed during the pre-mining phase in different locations around the minesite. The values presented are the mean of concentration and it was assumed that the uncertainty associated with the values is negligible. The concentrations of sulfate, iron, copper and zinc are below detection-limit, indicating ARD was not there initially as natural phenomena.

The chemistry of infiltration-water represents the water that carries the pyrite oxidation products from the base of the waste rock into the unsaturated zone. This water carries oxidation products (i.e., cations and anions). The datasets were obtained from monitoring stations at the base of the unsaturated zone. These drain water from the waste rock/soil interface, and are used therefore to represent the chemistry of water that continues downwards through the till layer to the underlying aquifer. The uncertainty in these datasets is represented by their statistics, which are minimum, maximum, mean and standard deviation. These statistics are used to construct p-boxes using the RAMAS Risk Calc software [31]. It was assumed for the purposes of this initial model demonstration that the variables are independent. It is worth noting that the concentrations of the chemistry variables for infiltration-water have significantly increased including for sulfate, iron, copper and zinc.

Table 2 shows the model parameter, their values, and whether each parameter is uncertain or constant. The infiltration velocity was obtained from climate data at the minesite and its value is treated in this example as constant (certain). The total number of cells used in the model is 30. Each cell in the model has the same length and has equal residence time. A simulation period of 168 months is used, which is the period between 1978 and 1992. The model was run at a monthly time step and new infiltrating water is picked at each time step. A specified flux was used as the groundwater flow boundary condition at the start and end cells. There are no measured values for diffusion coefficients, dispersivity and CEC at the minesite. Thus, these variables are represented with their minimum and maximum values that are obtained from the literature. Values for diffusion coefficient and longitudinal dispersivity are obtained from Batu [36], and values for CEC are obtained Appelo and Postma [37]. Note CEC is commonly expressed in meq/kg solids. Values are converted to meq/L for use in PHREEQC using representative density and porosity values.

2.4. Effect characterization

Effect characterization evaluates the relationship between stressor levels and ecological effects, the plausibility that the effect may occur and the linkage between stressors and effects [32]. The stressor-response relationships used in a particular assessment depend on the scope and nature of the ecological risk assessment, as defined in the problem formulation. The shape of the stressor-response curve is useful to determine the presence of effects for evaluating risk. The characterization begins by collecting effects data and fitting distribution functions (Fig. 1). Such data can be obtained either from laboratory tests or micro/mesocosm studies [38]. For example, laboratory tests on target fish species to determine the effects of dissolved metals (Cu, Zn, As) include median lethal concentration (LC50) and no observed effect concentration (NOEC). LC50 is the concentration that is required to kill 50% of the test population, whereas, the NOEC is the concentration at which no long-term or chronic effects occur on the test population.

In this study, LC50 data are used to evaluate the relationship between stressors and effects. The LC50 response of the fish species to copper and zinc were obtained from the AQUIRE database [39] (Table 3). The values of LC50 were divided by 10 to calculate the predicted-no-effect-concentration (PNEC) [40]. The PNEC values were assumed to represent any possible exposure pathways such as ingestion of contaminated water and consumption of the lower trophic level organisms. For each stressor, the calculated PNEC values of all species are combined to construct a p-box. This p-box assumes to represent the response of the entire fish species.

2.5. Risk characterization

The risk characterization step (Fig. 1) involves estimation of the probability of adverse effects on selected endpoints. The risks of stressors are estimated and described, and uncertainties and assumptions are summarized. Risks are estimated by comparing exposure and effects data using either the risk-quotient method or distributions [19,32,38,41]. The risk-quotient method compares the maximum exposure concentration and effect concentration of the most sensitive species. This method may not be suitable to evaluate the impact of mitigation measures in reducing the estimated risk [42]. In this study, the degree of overlap between the probability bounds of exposure and effect were compared.

Ecological risks are estimated on selected endpoints using three steps. First, the effect concentration that is defined to protect the assessment endpoints is estimated from the lower and upper distributions of effect. Second, the probabilities of exceedance for these concentrations are determined from their corresponding exposure distributions. The results of the second step inform the percentage of time the assessment endpoints is exposed to a stressor and whether the defined protection level is satisfied. There will be a risk if the defined protection level is violated. Third, the risk is estimated, which is equal to one minus the probability of exceedance.

3. Results and discussion

The p-boxes of the observed and simulated concentrations of cations and anions in water were compared to validate the PHREEQC outputs (Figs. 4 and 5). For sodium, the lower bound of the observed concentration is well simulated by PHREEQC, whereas, the upper bound of the observed concentration is underestimated (Fig. 4). A detailed analysis of the lower bounds of sodium reveals that the predictions underestimate the observed values at the 10th and 99th and overestimate at the 50th percentiles (Table 4), respectively. For the upper bound of sodium, the predictions are overestimated at 10th percentile and underestimated at the, 50th and 99th percentiles.

The PHREEQC simulations for calcium overestimate both the lower and upper bounds of the observed p-box. The predicted values of calcium at the lower bound overestimate at the 10th and 50th percentiles, and underestimate the observed values at the 99th percentiles. For the upper bound of calcium, the prediction values overestimate the observed calcium at the 10th, 50th, and 99th percentiles.

For magnesium, the simulations of PHREEQC slightly overestimate the lower and upper bounds of the observed p-box. Table 4 shows that the predicted values of magnesium at the 10th, 50th,
Table 1
Chemistry of native-water and infiltration-water in mmol/L.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Native-water</th>
<th>Infiltration-water</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8</td>
<td>5</td>
<td>0.3</td>
<td>11.4</td>
<td>6.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Alk. (meq/L)</td>
<td>2.68</td>
<td>0.5</td>
<td>70</td>
<td>3118</td>
<td>290</td>
<td>590</td>
</tr>
<tr>
<td>SO₄ (mg/L)</td>
<td>–</td>
<td>70</td>
<td>0.005</td>
<td>21000</td>
<td>1567</td>
<td>900</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>–</td>
<td></td>
<td>0.007</td>
<td>239</td>
<td>23</td>
<td>12</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>5.48</td>
<td></td>
<td>0.01</td>
<td>798</td>
<td>23</td>
<td>6</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>0.65</td>
<td></td>
<td>0.001</td>
<td>1430</td>
<td>35</td>
<td>1</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>0.37</td>
<td></td>
<td>0.001</td>
<td>2520</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>–</td>
<td></td>
<td>0.001</td>
<td>650</td>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>–</td>
<td></td>
<td>0.001</td>
<td>40</td>
<td>10</td>
<td>0.421</td>
</tr>
</tbody>
</table>

Table 2
Model parameters and their values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Constant</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infiltration velocity (mm/year)</td>
<td>100</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cell length (m)</td>
<td>1.25</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Number of cells</td>
<td>30</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Simulation period month</td>
<td>168 months (1978-1992)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Time step (s)</td>
<td>2.63 × 10⁻⁶</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Diffusion coefficient (D*, m² s⁻¹)</td>
<td>–</td>
<td>0.1 × 10⁻⁹</td>
<td>2 × 10⁻⁹</td>
</tr>
<tr>
<td>Longitudinal dispersivity (αL, m)</td>
<td>–</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>CEC (meq/L)</td>
<td>–</td>
<td>0.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 3
LC₅₀ data for fish species found in the study area; data compiled from multiple studies [39].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Oncorhynchus mykiss</th>
<th>Oncorhynchus clarkii</th>
<th>Oncorhynchus kisutch</th>
<th>Gasterosteus aculeatus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (mg/L)</td>
<td>0.004</td>
<td>0.021</td>
<td>0.014</td>
<td>0.185</td>
</tr>
<tr>
<td>Zinc (mg/L)</td>
<td>–</td>
<td>0.061</td>
<td>0.15</td>
<td>4.82</td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
<td>0.00034</td>
<td>0.001</td>
<td>–</td>
<td>0.01</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>15.61</td>
<td>7</td>
<td>6.04</td>
<td>9.33</td>
</tr>
<tr>
<td>Magnesium (mg/L)</td>
<td>3.175</td>
<td>0.289</td>
<td>1.662</td>
<td>2.05</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>1.05</td>
<td>0.01</td>
<td>0.001</td>
<td>–</td>
</tr>
<tr>
<td>Alkalinity (meq/L)</td>
<td>1.63</td>
<td>0.003</td>
<td>0.001</td>
<td>0.16</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>2.68</td>
<td>0.009</td>
<td>0.003</td>
<td>0.062</td>
</tr>
<tr>
<td>Alkalinity (meq/L)</td>
<td>3.19</td>
<td>0.01</td>
<td>0.01</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 4
Predicted and observed values at different percentiles.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>10th percentile</th>
<th>50th percentile</th>
<th>99th percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (Simulated) (mg/L)</td>
<td>0.01</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>Na (Observed) (mg/L)</td>
<td>0.07</td>
<td>1</td>
<td>19</td>
</tr>
<tr>
<td>Ca (Simulated) (mg/L)</td>
<td>9.1</td>
<td>576</td>
<td>789</td>
</tr>
<tr>
<td>Ca (Observed) (mg/L)</td>
<td>3.4</td>
<td>218</td>
<td>789</td>
</tr>
<tr>
<td>Mg (Simulated) (mg/L)</td>
<td>33</td>
<td>196</td>
<td>120</td>
</tr>
<tr>
<td>Mg (Observed) (mg/L)</td>
<td>7</td>
<td>106</td>
<td>7</td>
</tr>
<tr>
<td>Fe (Simulated) (mg/L)</td>
<td>0.001</td>
<td>1.5</td>
<td>16.59</td>
</tr>
<tr>
<td>Fe (Observed) (mg/L)</td>
<td>0.001</td>
<td>9</td>
<td>16.59</td>
</tr>
<tr>
<td>Cu (Simulated) (mg/L)</td>
<td>0.001</td>
<td>0.004</td>
<td>0.019</td>
</tr>
<tr>
<td>Cu (Observed) (mg/L)</td>
<td>0.001</td>
<td>0.008</td>
<td>0.014</td>
</tr>
<tr>
<td>Zn (Simulated) (mg/L)</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>Zn (Observed) (mg/L)</td>
<td>0.003</td>
<td>0.009</td>
<td>0.016</td>
</tr>
</tbody>
</table>

and 99th percentiles slightly overestimate their observed counterparts for both the lower and upper bounds of the p-box.

The PHREEQC simulations for iron well capture the lower and upper bounds of the observed p-box. For the lower bound of iron, the prediction values are equal to the observed values at the 10th, 50th, and 99th percentiles (Table 4). For the upper bound of iron, the prediction values are equal to the observed values at the 50th and 99th percentiles, and underestimate the observed values at the 10th percentile.

For copper, the PHREEQC simulations reproduce the lower and upper bounds of the observed p-box. The predicted values of copper are equal to the observed values at the 10th, 50th, and 99th percentiles of lower bound. For the upper bound, the prediction values are slightly lower at the 10th percentiles and higher than the observed values, at the 50th and 90th percentiles. The comparison of the simulated and observed copper at the given percentile level reveals that copper is simulated very well by PHREEQC.

The PHREEQC simulation for zinc at the lower bound slightly underestimates its observed counterpart. The simulation at the
upper bound slightly overestimates the observed upper bound for probability level greater than 0.6 and underestimates the observed upper bound for the probability level less than 0.6. For instance, comparisons between the predicted and observed values of the lower bounds at the 10th, 50th, and 99th percentiles reveal that the predicted values underestimate the observed values. For the upper bound, the predicted values slightly underestimate the observed value at the 10th and 50th percentiles and overestimate the observed value at the 99th percentile, respectively.

For sulfate, the PHREEQC predictions overestimate the observed p-box except in the lower portion of the lower bound. For instance, the predicted values of the lower bound slightly underestimate at the 10th percentile and overestimate at the 50th and 99th percentiles the observed values, respectively. For the upper bound, the prediction values overestimate or are equal to the observed values at the 10th and 50th percentiles, and the 99th percentile, respectively. The comparisons at the given percentiles reveal that sulfate is poorly simulated.

The prediction of alkalinity overestimates and underestimates the lower bound of the observed p-box at probability level less or greater than 0.5, respectively. The prediction of alkalinity underestimates and overestimates the upper bound of the observed p-box at probability level less or greater than 0.7. For instance, the predicted values of the lower bound overestimate, equal to, and underestimate the observed values at the 10th, 50th and 99th percentiles, respectively. For the upper bound, the predicted values underestimate the observed values at the 10th and 50th percentiles, and overestimate the observed values at the 99th percentile. The comparison between the simulated and observed concentrations reveals that the simulated alkalinity is acceptable.

The disparity between the simulated and observed values could be attributed to lack of mineralogical composition data for the aquifer and database uncertainties. As noted in the modeling section, there are no measurements for model parameters related to aquifer and mineralogy of the aquifer. A report from the mine-site only indicates presence of calcite in the aquifer, which was considered in the simulation; no other mineralogical assessment of the aquifer was reported. Thus, the overestimation of the simulated and observed values could be due to precipitation and coprecipitation of some minerals that were not included in the simulations. When the acidic water (Eq. (5)) that infiltrates from the waste rock reacts with calcite (Eq. (6)) in the aquifer, it dissociates into calcium ion and carbonic acid. The excess calcium ion reacts with sulfate ion and gypsum precipitates as the result of this reaction (Eq. (7)). The formation gypsum consumes calcium and sulfate ions. The excess carbonic acid reacts with ferrous iron and siderite precipitates (Eq. (8)). The formation of siderite consumes carbonate ions. Moreover, the coprecipitation of metals with minerals (e.g., aluminum hydroxide) is very common [43]. The literature review shows that previous studies conducted at well characterized mine sites obtained significant discrepancy between simulated and observed values [44–46]. These studies reported that the lack of mineralogical characterization hinders their ability to predict fate and transport of toxic metals.

\[
2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2 = 2\text{Fe}^{2+} + 4\text{H}^+ + 4\text{SO}_4^{2-} \tag{5}
\]

\[
\text{CaCO}_3 + 2\text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{CO}_3 \tag{6}
\]
validated the solubility of Fe2 and Ca2+ 1.56 at values of 10th, 50th, and 99th percentile, respectively. These p-boxes are validated by comparing them with Canadian water quality guideline (Guideline-PNEC) for aquatic life. For the copper effect, the results show that the guideline value and the lower bound of the derived p-box are almost equal, whereas the upper bound of the derived p-box is greater than the guideline value. For zinc, the result of the validation shows the guideline value is slightly greater than the lower bound of the derived p-box for a probability level less than or equal to 67%, whereas, the guideline value is slightly less than the lower bound of the derived p-box for the probability level greater than 67%. The upper bound of the derived zinc is greater than the guideline value at all probability levels. These comparisons reveal that Derived-PNECs are acceptable. It is worth noting that the guideline values are constant at various probability levels since they are deterministic estimates.

The results of risk characterization show the exposure and effect p-boxes for copper are overlapped both on their lower and upper
bounds (Fig. 7). This overlap suggests that there would be risk from the exposure concentration at both bounds. The method presented in Section 2.5 is used to quantify the risks. The computed risk of copper based on the lower bound shows that the effect concentration (0.001 mg/L) is not exceeded 92% of the time and the associated risk is equal to 8%. The computed risk of copper based on the upper bound shows that the effect concentration (0.021 mg/L) is not exceeded 52% of the time and the associated risk is 48%. These results reveal that the computed risk of copper based on the lower bound is acceptable, whereas, the risk of copper based on the upper bound is not acceptable since it violates the defined assessment endpoint (10%).

In case of zinc, the exposure and PNEC concentrations are overlapped only at their lower bounds (Fig. 7). This overlap suggests that there would be risk from exposure concentration at the lower bound. The computed risk based on the lower bound of zinc shows the effect concentration (0.001 mg/L) is not exceeded 50% of the time and the resulting risk is 50%. In addition, the computed risk based on the upper bound shows that the effect concentration (0.2 mg/L) is exceeded 80% of the time and the associated risk is 20%. These results reveal that the risk of zinc is not acceptable based the lower and upper bound measures since it violates the acceptable risk, which is equal to 10%.

The methodology presented for risk characterization provides two ways to estimate a risk based on the lower and upper bounds. Risk characterization based on the upper and lower bounds provides conservative and non-conservative risk estimates, respectively. It is the task of decision-makers to choose lower or upper bounds to estimate a risk but it is often recommended to use the conservative one [50]. In this study, the risk of copper to fish species is not acceptable based on the conservative measure. On the other hand, the risk of zinc is not acceptable based on the both non-conservative and conservative measures.

4. Summary and conclusion

This paper presents a new methodology for environmental risk assessment of acid rock drainage under uncertainty at minesites and demonstrates it using a case study. The methodology consists of problem formulation, exposure characterization using PHREEQC, effect characterization, and risk characterization and uncertainty analysis using the probability bounds method.

The simulations of PHREEQC estimated the concentrations of cations and anions that are produced as result of the transport of acidic water from waste rock and reaction with the aquifer matrix. The results of simulations are acceptable except for calcium, sulfate, and alkalinity. The overestimation of the simulated variables could be attributed to input uncertainties that arise due to lack of information on aquifer characteristics (e.g., mineralogy and transport parameters), thermodynamic database, and model conceptualization. The methodology also quantifies the simulation, observation, and predicted–no-effect–concentration uncertainties and shows them by the distance between the upper and lower bounds of the p-box. In addition, the methodology propagates these uncertainties and estimates a risk based on non-conservative and conservative measures. For the case study mine, the risk characterization result shows that there is adverse environmental risk due to metals transported into groundwater based on the conservative measure. Simulations result of the case study mine show the need to characterize and collect mineralogical compositions of an underlying aquifer to accurately simulate the fate–and–transport of metals in the environment although it is not required environmental regulatory agencies. The presented methodology could be applied to conduct risk assessments at various phases of the mining life cycle.

References
