



Modelling tool for predicting and simulating nitrogen concentrations in cold-climate mining ponds

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ABSTRACT

A nitrogen model was developed with the aim to trace nitrogen cycling in a cold climate-mining pond at the Aitik copper mine in northern Sweden. The model contains 10 state variables and 19 nitrogen cycling reactions. The model also includes sediment and physical properties of the pond, such as evaporation, freezing and thawing. The model was written in Mathworks MATLAB and was calibrated and validated using environmental monitoring data for the clarification pond at the Aitik mine. The data used comprised monthly values of nitrogen speciation, phosphorous and water flow. The model accurately predicts ammonium ($r^2 = 0.84$) and nitrate ($r^2 = 0.82$) concentrations in a time series from February 2012–August 2014. The model did not accurately predict nitrate concentrations ($r^2 = 0.11$), presumably due to high oxygen concentration in the pond water that prevented denitrification in the water column. The transport of organic material to the sediment was also limiting denitrification in the sediment. When allowing denitrification in the water column as well as increasing the rate of transport of organic material to the sediment the nitrate prediction capacity increased to a satisfactory level ($r^2 = 0.54$). A sensitivity analysis for the system showed that the most sensitive reactions for the water column were oxic mineralisation as well as the nitrification rate.

1. Introduction

Nitrogen discharge from mining sites causing local eutrophication in natural receiving waters has been a known problem for over a decade (Mattila et al., 2007, Chlot et al., 2013). The source of nitrogen is predominantly from ammonium-nitrate based explosives used in blasting operations (Mattila et al., 2007). Furthermore, recirculation of mining pond water back to the ore refining process enhances the nitrogen concentration in the process waters, which in the long term could affect the quality of the effluent waters. This paper presents a model that can be used to predict nitrogen concentrations and effects of biogeochemical reactions in cold-climate mining ponds. McLemore et al. (2014) published guidelines for the design of sampling and monitoring programmes at mine sites and pointed out the importance of collecting data that are acceptable for environmental modelling and prediction studies. Here we present a case study where ammonium, nitrite, and nitrate concentrations in a mining pond in northern Sweden are modelled based on regular environmental monitoring data collected by the mining company.

There is an increasing demand from the mining industry on the ability to investigate the complex biogeochemical cycle of nitrogen and predict the behaviour of nitrogen and nitrogen related compounds

released from mine sites. Most geochemical models focus on speciation modelling, groundwater flow or coupled groundwater flow with kinetic reactions added (PhreeqC, Visual minteq, Geochemist's Workbench), which are considered inadequate for modelling a water column, sediments and their interaction in a dynamic system. During the last years a few models have been presented that focus on modelling inorganic nitrogen and its interaction with organic material, some of which have focused on large-scale applications such as nitrogen, phosphorus and oxygen fluxes in the Baltic Sea. Eilola et al. (2011) summarised three of these models (BALTSEM, ERGOM and RCO-SCOBI). For detailed model description of the three large-scale nitrogen models see Marmefelt et al. (1999) or Eilola et al. (2009). We implemented the SCOBI model (Swedish Coastal and Ocean Biogeochemical model) in Mathworks Matlab and tested to predict nitrogen concentrations in a small scale mining pond affected by high nitrogen mining discharge, but it showed poor prediction capacity. The reason was not investigated in great depth but it could be due to the large horizontal discretisation or phytoplankton kinetics adapted to marine systems as the SCOBI model was originally developed for large-scale marine systems.

Chlot et al. (2011) presented a model aiming to predict inorganic nitrogen concentrations and growth of phytoplankton and macrophytes in cold-climate lakes receiving nitrogen-rich mining effluents. The

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model presented in this study focuses on cold-climate mining pond systems and the interaction between nitrogen, phosphorous, oxygen and organic material in the water column and in the sediment. Compared to the model of Chlot et al. (2011), the present model contains more state variables and a refined discretisation of the sediment. The sediment–water interface is particularly important in this context since this is the sub-oxic environment where most denitrification occurs in natural systems (Seitzinger 1988; Meyer et al., 2008). The aim of this study is twofold: 1) to present a model that is useful in development and testing of different treatment methods for nitrogen removal within mining ponds, where proper modelling of the sediment and the interaction between water column and sediment are of vital importance, and 2) to demonstrate that regular environmental monitoring data can be used as model input data although it was not primarily collected for modelling purposes.

For the present model, an extension of a previously used redox-model was developed in Mathworks Matlab with extensions programmed in JAVA (predominantly UI elements). The model is based on Yakushev (2013) redox layer model (ROLM) and, with some modifications, biogeochemical reactions are parameterised according to Yakushev (2013). The model was adapted to a mass balance concept for the water column. The surface sediment is modelled using discrete depth layers according to the implicit Euler Backwards finite difference method (Butcher, 2003). Water concentration/dilution due to evaporation and precipitation as well as input and output water flow was also added. Evaporation was modelled using the semi-empirical Penman formula (Penman, 1948). The model was coupled with a snow model to accurately model dilution during spring flood (Kokkonen et al., 2006). The model was also coupled with a water temperature model that estimates water temperature from air temperature (Piccolroaz et al., 2013). The presented model is simple, fast and can be applied to different systems to estimate nitrogen concentrations in mining ponds with high accuracy.

The model was calibrated and validated using monitoring data from the clarification pond at the Aitik copper mine in northern Sweden, where it accurately predicts ammonium and nitrite concentrations. The input data for the Aitik pond was obtained from the Boliden Mineral AB mining company. The data was collected from 2012-02-01 to 2014-07-31, and consists of dissolved ammonium, nitrite, nitrate, filtered-(outflow) and unfiltered (inflow) phosphorous, as well as total nitrogen concentrations. Chemical data was sampled monthly during late spring to early autumn. Water inflow and outflow to/from the pond was measured daily.

2. Methods

2.1. Study site

The developed model was calibrated using data from the clarification pond at the Aitik copper mine (Wanhainen et al., 2006), where high concentrations of dissolved inorganic nitrogen have been observed. The Aitik mine is located ~15 km SE of the town of Gällivare in northern Sweden (Fig. 1), which is located roughly 60 km north of the Arctic Circle. The annual average air temperature at the Aitik mine is $-2\text{ }^{\circ}\text{C}$, the average precipitation is 700 mm year^{-1} , and snow coverage is 200 days year^{-1} (SMHI, 2016).

The Aitik mine is an open pit copper mine with an annual production of 36 Mtons of ore. The source of nitrogen in the process water and clarification pond is the explosives used in blasting operations (Mattila et al., 2007). The explosive used is an emulsion type explosive with 10–30% ammonium-nitrate addition as oxidiser (Forcit, 2016). Blasting is generally performed weekly, where 200–300 holes drilled into the ore body are filled with approximately 1 ton of explosives each. During 2014 a total amount of 32 Ktons were used (Forcit, 2016). A major part of ammonium and nitrate in the mine water originates from undetonated explosives that dissolve when groundwater infiltrates into

boreholes charged with explosives. The water from the open pit mine is pumped up and used in ore-refining processes and subsequently discharged into the tailings and clarification pond system. The clarification pond at the Aitik mine has an area of $1.54 \times 10^6\text{ m}^2$ and the volume is on average $1.09 \times 10^7\text{ m}^3$.

For the clarification pond, water discharge data is collected daily and chemical data at the inlet and outlet are collected on a monthly basis by Boliden Mineral AB. For this model development, physical parameters such as air temperature, wind speed and incoming solar radiation were obtained from the Swedish Meteorological and Hydrological Institute (SMHI, 2016).

The predominant inorganic nitrogen species in the clarification pond, both in the inlet and outlet water is nitrate, which accounts for approximately 78% and 84% of total inorganic N in the inlet and outlet water, respectively (Table 1). The higher percentage in the outlet water (84%) indicates nitrification during water transport through the pond. The second most common species is nitrite (5–31% of total inorganic nitrogen), while ammonium accounts for only around 5% of the total inorganic nitrogen concentration (Table 1). The monitoring data only contains total (unfiltered) phosphorous in the inlet water (average 0.186 mg/l), and dissolved (filtered) phosphorous in the outlet water (average 0.0009 mg/l) (Table 1). The inlet phosphorous concentration shows a large span ranging from 0.030 to 1.1 mg/l . pH is generally close to neutral both in inflowing and outflowing water.

2.1.1. Water flow

Water inflow and outflow to/from the clarification pond was measured daily during the period between 2012-02-01 and 2014-08-01 (Fig. 2).

There are two outlets where water is pumped from the clarification pond, one is water pumped back into the ore refining process and the other is overflow water that is discharged to Lina älv. After passing through the ore concentrating plant, this water is discharged to the tailings pond and is then gathered in a small stream which discharges into the clarification pond. There is also a significant flow of $\sim 950\text{ m}^3/\text{h}$ from the tailings pond originating from precipitation.

The average water retention time in the clarification pond is 88 days but varies significantly during the year. The average for the summer months (June–August) is 59 days, with the lowest measured water retention time for the summer 2013, when the average residence time was 50 days.

2.2. Analytical methods

The obtained chemical data for inlet and effluent water as well as chemical composition of the clarification pond were obtained from Boliden Mineral AB mining company. The analyses were performed by an external accredited laboratory. All inorganic nitrogen species ($\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{NO}_2\text{-N}$) were determined by flow analysis (CFA and FIA) and spectrometric detection. The analytical precision for $\text{NH}_4\text{-N}$ was $\pm 15\%$, and for $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ the precision was $\pm 20\%$. Chlorophyll- α samples were collected from the clarification pond during summer 2015 and filtered onto Whatman GF/C glass fibre filters (pore size $1.2\text{ }\mu\text{m}$) and determined spectrophotometrically on a Shimadzu instrument (detection limit $0.5\text{ }\mu\text{g/L}$).

2.3. Model description and differential equation set up

The model utilises the following four different sub-models to calculate the concentration of the different state variables:

- Biogeochemical reactions in water column
- Biogeochemical reactions and diffusion in discrete sediment layers
- Dilution and enrichment due to water inflow and outflow, precipitation and evaporation
- Sedimentation and diffusive flux to and from sediment

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