



## SWAT model for analysis of pollution load of manganese in rainwater runoff in a manganese mine

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### ABSTRACT

Heavy metal pollution has become one of the crucial global environmental problems with a growing threat to the environment and human health. Therefore, research on the prevention and treatment of heavy metal pollution has attracted extensive concern. Among them, heavy metal pollution in urban rainwater runoff has become a research hotspot. Rainwater runoff is a major pathway for transporting nonpoint-source pollutants or sediment from the watersheds to other environment. In this study, the Soil & Water Assessment Tool (SWAT model) was used to assess the pollution load of manganese in the rainwater runoff discharged from a manganese mine. Results showed that with the modified SWAT model, it exhibited a higher prediction accuracy in pollution load of manganese with coefficients of  $R^2$  and  $Ens$  greater than 0.6 and 0.5, respectively. According to water quality standard for surface water in China, the key contaminated areas corresponding to the pollution load of manganese were obtained, which also reflected an actual situation that the most seriously contaminated sites were located in the mine aperture and mine tailing. This study demonstrated that the modified SWAT model was a promising tool for analysis of the pollution load of manganese in rainwater runoff from a manganese mine.

**Key words:** SWAT model; manganese mine; rainwater runoff; pollution load

### INTRODUCTION

With rapid development in the metal and mining industry, large quantities of heavy metals such as Mn, Ni, Cu, Zn, Cd and Pb, will inevitably be released during manufacturing, application or disposal, and subsequently polluting rainwater runoff. Therefore, rainwater runoff has become a major pathway for transporting heavy metals to other aquatic systems, resulting in contamination of local areas[1-2]. Transportation of heavy metals through rainwater runoff poses a threat to the environment as well as human health. As such, it has attracted extensive attention. Manganese (Mn) that is widely distributed in the ecosystem does not exist in a pure state[3]. For most important manganese-containing minerals, they occur as oxides, carbonates and silicates state while the pyrolusite ( $MnO_2$ ) is the most common manganese compound[3]. However, the crystals manganese is introduced into the atmosphere due to natural and anthropogenic processes such as wind erosion, suspension of soils, construction, quarrying activities, etc.[3]. Among them, the larger particles tend to be deposited near the source of contamination, whereas fine particulate manganese would be distributed very widely. Long-term exposure to these particles would have an adverse effects on human health since these particles contain large quantities of manganese compounds[3, 4]. It has been found that for workers exposed to manganese at average levels below  $5mg/m^3$ [3], there was a neurobehavioral, reproductive, and respiratory effects[3]. Therefore, reducing the diffusion of manganese in the environment is necessary. There is no doubt that the rainwater runoff increases the risk of heavy metals transport and therefore, it must be effectively controlled. The greatest risk source comes from metal mines since the production and discharge of heavy metals produced is high. Therefore, research on pollution load of manganese in rainwater runoff, especially in the manganese mine, would be an interesting contribution to the management of manganese pollution.

SWAT model has been developed by the Agricultural Research Service of the United States Department of

Agriculture (USDA-ARS) since 1994, and has been recognized as a river basin scale model with a strong physical basis. This model in general is used for quantifying the impact of land management practices and complex watersheds in large scale as well as the nutrient loading analysis (nitrogen, phosphorus, etc.) [5-12]. As a hydrology model, it consists of many modules such as surface runoff, pond and reservoir storage, groundwater flow, nutrient and pesticide loading, and water transfer, etc [13]. This model has been successfully applied in many fields. Boini Narsimlu, et al. [14], applied SWAT model to assess the future climate change impacts on water resources of the Upper Sind River Basin; Akansha Kushwaha, et al. [15], used the SWAT model to evaluate runoff and understand sensitiveness of model input parameters in a predominantly forested watershed. These studies all demonstrated that the SWAT model as a potential alternative to analyze the hydrological phenomena. Since analysis for the pollution load of manganese in rainwater runoff with the SWAT model is not well known, the distribution and contamination status of those metals in the manganese mine was herein discussed in detail.

In this study, the manganese pollution, which was discharged from the Red Flag manganese mine in Xiangtan, China, was investigated. Field experiments and survey were conducted. The SWAT model was not perfect for simulating metal pollution in this mining area, but the model after modification using the metal migration and transformation model exhibited higher simulation accuracy. Firstly, we modified the one-dimensional transport model of mercury developed by Lin [16] on the platform of SWAT software with some assumptions thus obtaining the one-dimensional dynamic model of manganese's migration and transformation. Secondly, the model was coded using Fortran (a computer language) and embedded in the SWAT model. Using the modified SWAT model, we examined the effect of the rainwater runoff on pollution load of manganese in the manganese mine and identified the key polluted areas. This study would give a theoretical and scientific basis for evaluation, control, management and restoration of the heavy metal pollution from the manganese mines and other non-ferrous metal mines.

#### MONITORING SITE AND SAMPLING

Helin town's Red Flag mine in China, is about 12 kilometers north of Xiangtan with longitude between 111°58' and 113°05'E, and latitude between 27°21' and 28°05' N. The area of the mine is approximately 2.6 km<sup>2</sup>. In this study, there were 120 sampling points distributed evenly in the investigated area with sample interval of 0.02-0.04 km<sup>2</sup> (Figure 1). Under natural rainwater conditions, surface runoff would be generated if the rainwater intensity was greater than the infiltration intensity, and therefore at each sample point, 0.5-3L of surface runoff water samples were collected and transferred to a polypropylene container. Subsequently, the container was packed in a black plastic bag and taken to the laboratory for further processing. In the laboratory, the sample was shaken prior to settlement, followed by a natural settlement of 30 min. After settlement, the supernatant was siphoned and filtered through 0.45 μm membrane. Finally, the pH of the sample was lowered to <2 by adding nitric acid (HNO<sub>3</sub>) to the filtered sample and the sample after acidification was stored in the dark at 4 °C for later analysis.

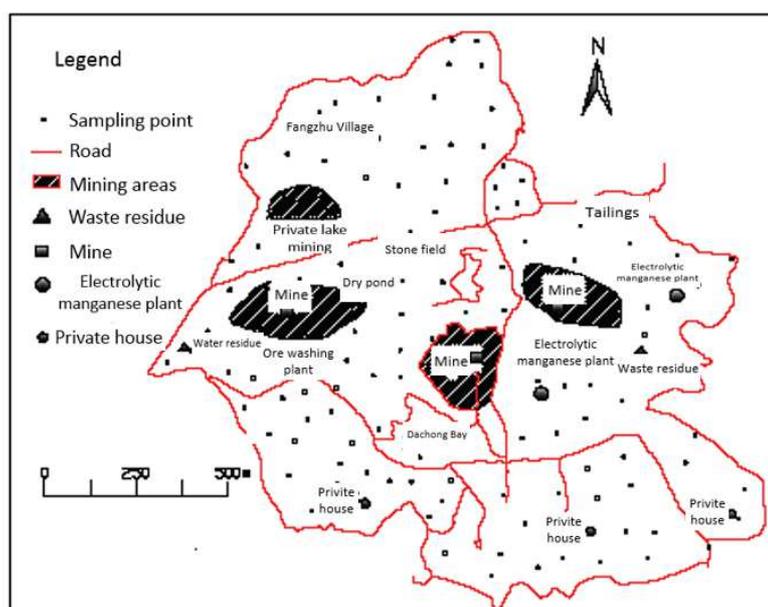


Figure 1. Distribution of sampling points

**SWAT MODEL CONSTRUCTION****3.1 Database**

The SWAT model is a Geographical Information System (GIS)-linked basin scale model which is capable of simulating hydrology and water quality. It was performed based on a relatively complete basic database. The database consisted of property data and the spatial data. In this study, property data was created by some two-dimensional tables which contained the outdoor measuring data and laboratory analysis results. The spatial data is one of the important components for GIS. In this study, it included the Digital Elevation Model data (DEM), land use type, soil type, local meteorological data and hydrological data, as shown in Table 1. Each map was drawn with the albers equal-area conic map projection.

**Table 1. Property database and Special database**

Property data		Special Database		
Type	Source	Type	Source	Precision
Meteorological data	Hunan Provincial Meteorological Bureau	DEM	ASTER_GDEM	30m*30m
Hydrological data	Xiangtan Municipal Water Conservancy Bureau	Land use type	TM data	30m*30m
Soil type	Hunan Provincial Soil Species	Soil type	Paper maps vectorization	1:100000
Land use type	Model			

**3.2 Model Construction and Validation****3.2.1 Improvement of dynamic model and Embedding****3.2.1.1 Kinetics model of migration and transformation of manganese**

There are many important metal migration models and among them, Lin established the one-dimensional model for migration and transformation of mercury. Through comparative analysis, we introduced a correction factor reflecting the difference between elements, and a partition or distribution-coefficient into Lin's model[16], thus obtaining the kinetics model of migration and transformation of manganese as follows:

$$k\delta\left[\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x}\right] = \frac{1}{A}\frac{\partial}{\partial x}\left[D_x A\frac{\partial C}{\partial x}\right] + \frac{1}{H_i}N \quad (1)$$

Where  $\delta$  is the correction factor;  $k$  is the distribution-coefficient ( $\text{m}^3/\text{kg}$ );  $C$  is concentration of manganese ( $\mu\text{g}/\text{ml}$ );  $D_x$  is vertical turbulent diffusion coefficient;  $A$  is the cross-sectional area of the contaminated flowing stream ( $\text{m}^2$ );  $u$  is the velocity of the contaminated flowing stream ( $\text{m}/\text{s}$ );  $x$  is the migration distance ( $\text{m}$ );  $H$  is the water depth ( $\text{m}$ );  $N$  is the pollutant exchange rate between the sediment and the covering water ( $\text{m}/\text{s}$ ).

**3.2.1.2 Determination of  $k$** 

The  $k$  value was determined by the experimental data of the soil-water interface flow, which was assumed that the suspended particulate matters and the layer of soil that was in contact with interface flow contained the same proportion of the active heavy metal manganese.  $k$  was herein expressed as follows:

$$k = C_s / C_w \quad (2)$$

Where  $C_s$  ( $\text{mg}/\text{l}$ ) is the concentration of the manganese of the suspended particulate matters in the soil-water interface flow;  $C_w$  ( $\text{mg}/\text{l}$ ) is the concentration of dissolved manganese in the water from the soil-water interface flow.

**3.2.1.3 Determination of  $\delta$** 

Water samples were measured with an atomic absorption spectroscopy analyzer (AA700, Beijing Dongxi Co., China) and the analytical results of the soil samples were supplied by the local environmental protection bureau, which indicated that the ratio of the mercury to the manganese was in the range of 0.2 to 0.8. In order to achieve better correspondence between the measured and simulated manganese concentrations, Nash-Sutcliffe efficiency coefficient ( $E_{\text{ns}}$ ) and the regression coefficient ( $R^2$ ) were used to assess the simulation accuracy[17, 18]. If the  $E_{\text{ns}}$  and  $R^2$  values were greater than 0.6, it indicated that the simulation results were better. In contrast, the values of the main influence parameters need to be adjusted until the  $E_{\text{ns}}$  and  $R^2$  values were 0.6 or greater. During the adjustment process, we attempted to reduce the  $\delta$  interval values through dichotomy method so as to enable the simulation accuracy to meet the evaluation criteria. It was found that after five attempts and the  $\delta$  interval values was then in the range of 0.36875-0.3875, it could achieve the accuracy requirement and finally the  $\delta$  value of 0.375 was adopted in this study.

### 3.2.1.4 Modified dynamic model embedding

The modified kinetics model for migration and transformation of manganese was obtained. In order to improve the SWAT model for better simulation of the pollution load of the manganese in rainwater runoff in the manganese mine, it was written in Fortran and embed into the SWAT model containing input/output parameters, custom parameters, and subprogram or performance functions.

### 3.2.2 Spatial discretization

Based on the established database, spatial discretization in the SWAT model mainly includes division of sub-basin and Hydrological Response Unit (HRU) in an analysis area. According to the relationship between every basin outlet location and stream junctions, watershed could be divided into different sub-basins, and generates stream response for every location within the catchment[13]. HRU is the smallest unit operation with a single land use type and soil type. We overlaid layers of the different land use type and soil type in the manganese mine. The overlay analysis showed that there were eighteen sub-basins (see Figure 2) and two hundred thirty-two HRUs.

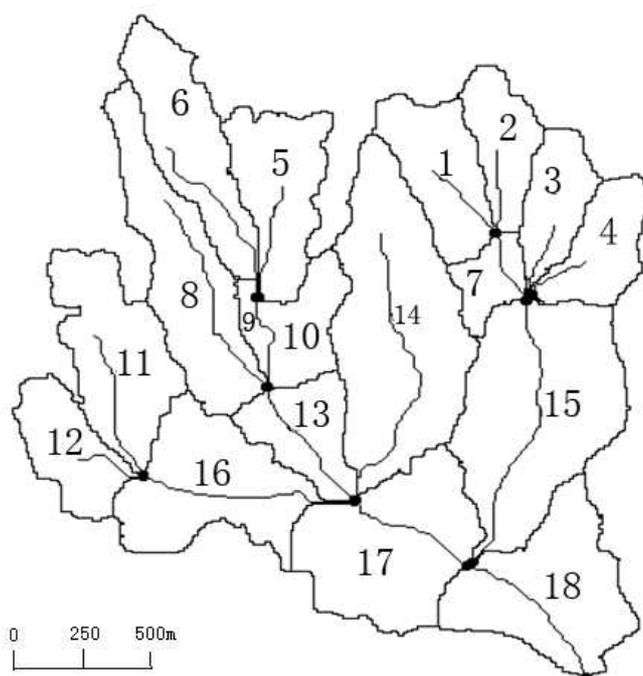


Figure 2. The watershed division of manganese ore areas

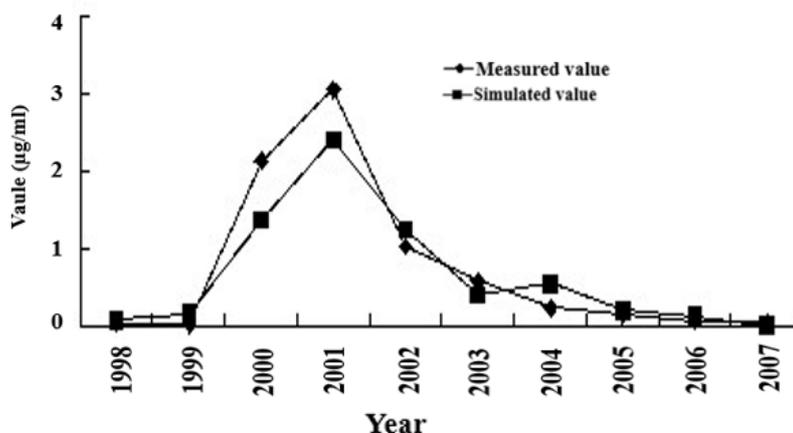


Figure 3. The observed and simulated values of pollution load of manganese with data collected from Jan.,1998 to 2007 for the 4th sub basin in the manganese ore

### 3.2.3 Model calibration and validation

Sensitivity analysis was an uncertainty method which was used to determine how the different values of independent parameters will influence a particular index[19]. The commonly used method for sensitivity analysis is LH-OAT

method[20-23]. Through sensitivity analysis, the most sensitive parameters were CN2, ALPHA\_BF, SPCON, etc. Based on this method and the measured data, the model calibration and validation could be evaluated[24-27]. In this study, we adjusted the independent parameters to perform the sensitivity analysis following the SCE-UA(Shuffled Complex Evolution) algorithm developed by Duan, et al.[17, 18] in which the Nash-Sutcliffe efficiency coefficient ( $E_{ns}$ ) and regression coefficient ( $R^2$ ) were used for evaluation. This evaluation criteria aimed to make  $E_{ns}$  and  $R^2$  greater than 0.5 and 0.6, respectively, through adjustments of primary sensitivity parameters and finally finding the optimum parameters values. The calibration and validation data were collected from 1998-2002 and 2003-2007, respectively. Taking the sub-basin 4 for example, we showed the measured value and the simulated value in Figure 3. It indicated higher simulation accuracy which achieved the evaluation criteria. The calibration and validation of other basins modeling and parameters adjustments were conducted following the same method.

### RESULTS AND DISCUSSION

Through model calibration and validation, the key parameters values were adjusted enabling  $E_{ns}$  and  $R^2$  values to achieve the evaluation criteria. As a result, key parameter values were obtained. Using parameters values, the simulation for the SWAT model was performed. The results are as shown in Figure 4 and Figure 5.

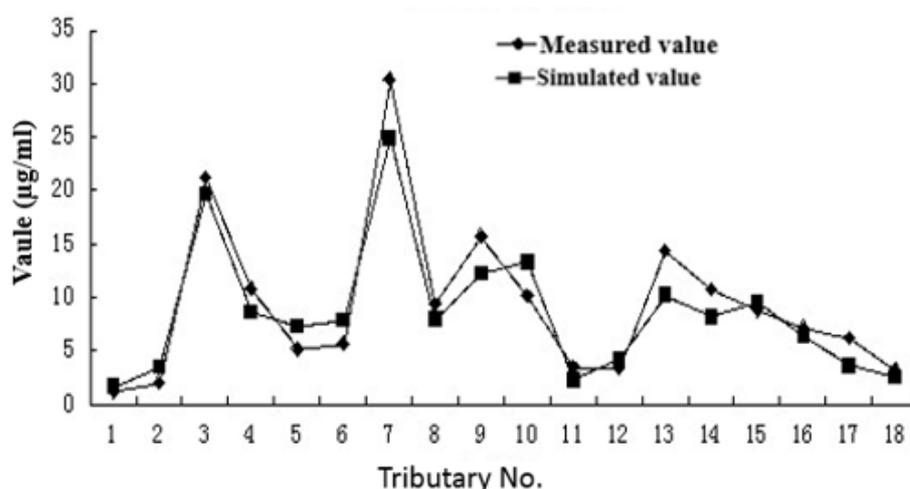


Figure 4. The simulated values and measured values of load pollution of manganese for every tributary in 2012

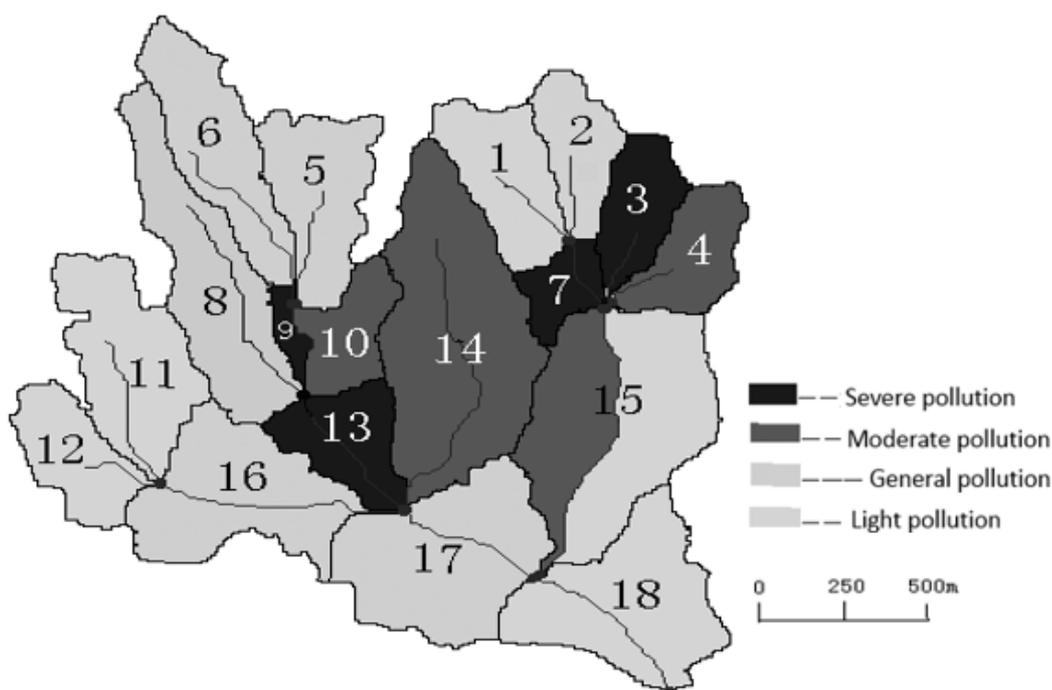


Figure 5. Area distribution of manganese pollution in manganese ore

Figure 4 shows the simulated and measured pollution load of manganese in tributaries. The results indicates that  $E_{ns}$  and  $R^2$  were 0.91 and 0.88, respectively. At the soil-water interface flow in the manganese mine, the simulated values after adjustment of parameter was closer to the measured values than that without adjustment. This indicates the modified SWAT model was better for the pollution load simulation resulting in successful adjustment of parameter.

According to the Chinese water quality standards (GB/T 3838-2002) for surface water, and its classification on the pollution load of manganese in rainwater runoff from the manganese mine, there was no direct relationship between the manganese concentration and water quality classification. However, through analysis of six metal concentrations in the mine, it was found that there was only metallic lead concentration similar to the pollution loading concentration of manganese. Therefore, the manganese pollution classification was classified according to the lead pollution classification corresponding to severe pollution, moderate pollution, general pollution and light pollution as shown in Table 2. At the manganese mine, the key areas with pollution load of manganese in the rainwater runoff were therefore identified.

**Table 2. China water quality standard and manganese pollution standard**

Category	Pollution levels	Pb (mg/L) ( $\leq$ )	Mn(mg/L)( $\leq$ )
□	Light pollution	0.01	1
□	General pollution	0.01	5
□	Moderate pollution	0.05	10
□	severe pollution	0.05	20
□		0.1	

As seen from the Figures 4 and 5, the most polluted areas were sub-basins 3 and 7, which corresponded to the mine tailings disposal areas and the mine-mouth, respectively. The simulation results were very consistent with the actual pollution. Since the rainwater runoff (#9,#10,#13 and #15) crossed the main transport routes of the mine and other treated slag areas, there was serious pollution, which also reflected the actual pollution situation. Overall, the simulation results achieved the desired effects, and therefore the SWAT model played an important role in improving the forecast of the pollution loads of contaminants from non-ferrous metal mine.

## CONCLUSION

In this study, based on the modification of the migration and transformation model of mercury, the kinetics model of migration and transformation of manganese was obtained. Subsequently, the model was written in Fortran and embedded in the SWAT model. To improve the SWAT model, it was calibrated and validated using the measured data and during the calibration and the validation, the sensitivity analysis was examined in which the key parameters were adjusted until the  $E_{ns}$  and  $R^2$  achieved the desired values. According to water quality standard for the lead in the surface water of China, the key polluted areas corresponding to the pollution load of manganese were identified. It was found that the most seriously contaminated sites were located in the mine mouth and mine tailing, which reflected the actual situation. Results showed that the modification of the SWAT model and the identification of key polluted areas were contributed to the analysis of the pollution load of the heavy metal in the rainwater runoff in the metal mine, which gave a significance to engineering treatment and a profoundly scientific guidance.

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