

# TMDL MODEL DEVELOPMENT FOR ACIDIC MINE DRAINAGE

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The quality of Paint Creek and its tributaries in West Virginia are being negatively impacted by the acidic drainage from those mines that were abandoned prior to 1970. The environmental impact of this mine drainage is being manifested in depressed stream pH and elevated concentrations of iron, manganese and aluminum. In order to develop a plan to return the quality of Paint Creek and its tributaries to an acceptable level, the West Virginia Department of Environmental Protection (WVDEP) contracted with the West Virginia Water Resources Institute at West Virginia University to produce the engineering and scientific components of the watershed's TMDL for pH, aluminum, iron and manganese.

Successful development of a TMDL for acidic mine drainage requires that one be able to simulate the evolution of the water quality constituents affected by mining activity, namely pH, total iron, manganese and aluminum concentrations. The one-dimensional advection, dispersion, reaction and loading of these constituents are governed by a hyperbolic, partial differential equation. In order to solve this equation, the Total Acidic Mine Drainage Loading (*TAMD*L) computer program was developed. To reduce the number of constituents that must be simulated, *TAMD*L solves the governing equation for water temperature, net acidity and the concentrations of ferric iron, total aluminum, manganese and dissolved oxygen. The computer program also has the capability to simulate the concentration of ferrous iron, but in most situations, all of the ferrous iron has oxidized into ferric iron before the mine drainage reaches a perennial stream.

This paper describes the theoretical basis of the *TAMD*L computer program and its application in simulating the effects of acidic mine drainage on the water quality of the Paint Creek watershed in West Virginia.

## THEORY

The following partial differential equation is the governing equation for the one-dimensional transport of a water quality constituent in a stream and is solved by *TAMD*L for each of the simulated constituents, except for proton activity.

$$\frac{\partial C_i}{\partial t} = m \frac{\partial^2 C_i}{\partial x^2} - V \frac{\partial C_i}{\partial x} + L_i + S_i \quad (1)$$

Where  $C_i$  are the simulated concentrations of the constituents,  $L_i$  are the model node loading terms for each of the constituents and  $S_i$  are the net chemical and physical reaction source (sink) terms for each constituent. The hydrodynamic dispersion,  $m$  and the mean stream velocity,  $V$ , are simulation parameters. Because these quantities must remain uniform throughout the computational domain, the watershed must be divided into small sub-watersheds before using the computer program. The spatial coordinate,  $x$ , proceeds from the head of the sub-watershed and follows the stream channel to the mouth.

The governing equation is solved using net acidity rather than pH. Net acidity is defined as the total acidity minus the total alkalinity. Total acidity consists of the acidity caused by metal ion hydrolysis and the acidity caused by proton activity. In typical mine drainage, metal ions, rather than protons, constitute the major component of acidity. Therefore, *TAMD*L estimates pH through its relationship with net acidity by subtracting the effect of the metal ions.

If the stream chemistry was simulated with proton activity instead of net acidity, then it would be necessary to also simulate dissolved carbon dioxide, bicarbonate ion, carbonic acid and total sulfate in addition to the other constituents. While this would be more pleasing theoretically, each of the additional parameters would require the estimation of boundary and initial conditions, which would degrade overall simulation precision. When the transport of acidity by the stream is simulated with net acidity instead of proton activity, then a constitutive relationship is required to calculate the pH from the net acidity.

### Net Acidity – pH Constitutive Relationship

The parameter pH must be calculated by the model because water quality standards invariably use pH instead of net acidity and because the kinetic rates of

ferrous iron, aluminum and manganese oxidation and/or precipitation depend heavily upon pH. The following net acidity – pH constitutive relationship was developed through the empirical examination of pH and net acidity data from samples collected in several small watersheds in West Virginia, Maryland, and Pennsylvania (Stiles, Fripp, & Ziemkiewicz, 2000).

$$\text{pH} = -\log_{10}[\text{H}^+] = a \max(1, A^2)^{b \text{sign}(A)} \quad (2)$$

Where  $A$  is the net acidity of the stream in mg/L  $\text{CaCO}_3$  equivalents and  $a$  and  $b$  are empirical constants and normally calibrated from locally obtained water quality data. If local data are unavailable,  $a$  and  $b$  are usually close to 6.5 S.U.- $\text{L}^{2b}/\text{mg}^{2b}\text{-CaCO}_3$  and  $-0.02$ , respectively.

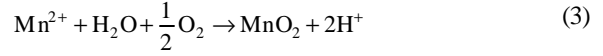
#### Ferric Iron Sedimentation

*TAMDL* assumes that all ferric iron has combined with dissolved oxygen to form ferric hydroxide. The computer program also assumes all of the ferric hydroxide in the stream clings to sediment particles, which leave the computational domain by flowing through the downstream boundary or by sedimentation. The rate at which ferric iron leaves the model domain via sedimentation is assumed to follow Stokes Law. This assumption is valid when the particle Reynolds number is less than unity (Roberson & Crowe, 1980). Given the size of sediment particles most likely to carry ferric hydroxide, this assumption is realistic.

Because this process is not dependent upon the precise concentration of suspended solids, the simulation of the erosion, transport and deposition of sediment was not required. Since *TAMDL* is often employed to simulate watersheds, like Paint Creek, where very little information on stream hydraulics is available, sediment transport is not simulated and the re-suspension of ferric iron-containing sediment particles must be neglected. Because the computer program can be easily modified to use the results of a sophisticated hydraulics model, the incorporation of a suspended sediment constituent and ferric iron re-suspension into the model would not be difficult.

#### Manganese Oxidation and Precipitation

The formulation used by *TAMDL* to calculate the kinetic rate of manganese oxidation and precipitation was obtained from Stumm and Morgan (1981). When the stream's dissolved oxygen concentration is less than 0.01 mg/L, manganese oxidation and reduction are neglected.



The kinetic rate for the progress of manganese oxidation and precipitation,  $S'_{\text{Mn}}$  is calculated by the program using the following formula.

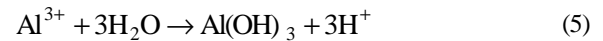
$$S'_{\text{Mn}} = \frac{-a_{\text{Mn}} C_{\text{Mn}} C_{\text{DO}} C_{\text{Fe}^{3+}}}{[\text{H}^+]^2} \exp\left(\frac{-E_{\text{Mn}}}{RT}\right) \quad (4)$$

Where  $E_{\text{Mn}}$  is an empirical rate constant assumed by the program to be 107.987 kJ/mole,  $a_{\text{Mn}}$  is an empirical rate multiplier specified by the user with units of  $\text{L}^4/(\text{mg}^4\text{-day})$  and  $R$  is the universal gas constant,  $8.314 \times 10^{-3}$  kJ/mole/K. The stream water temperature,  $T$ , must be in K,  $C_{\text{Mn}}$  is the manganese concentration,  $C_{\text{DO}}$  is the stream's dissolved oxygen concentration and  $C_{\text{Fe}^{3+}}$  is the ferric iron concentration. All of the concentrations in equation (4) are in mg/L.

The array containing the net rate of production (consumption) for each of the constituents,  $S_i$  is calculated by taking the algebraic sum of the kinetic rates for each chemical and physical reaction being modeled. Because manganese oxidation consumes oxygen, equation (3) is used to calculate the corresponding decline in dissolved oxygen concentration. The effect of this reaction's proton production on the pH and net acidity is calculated with equation (3) and the net acidity – pH constitutive relationship, equation (2).

#### Aluminum Precipitation

The chemical reaction for aluminum precipitation is similar to the equation for manganese oxidation and precipitation except for the absence of oxidation because aluminum has only a single oxidation state.



$$S'_{\text{Al}} = \frac{-a_{\text{Al}} C_{\text{Al}} A_{\text{Al}}}{[\text{H}^+]^3} \exp\left(\frac{-E_{\text{Al}}}{RT}\right) \quad (6)$$

Where  $S'_{\text{Al}}$  is the kinetic rate for aluminum precipitation, equation (5),  $a_{\text{Al}}$  is the dimensionless empirical rate constant specified by the user,  $C_{\text{Al}}$  is the aluminum concentration in mg/L and  $A_{\text{Al}}$  is the empirical rate multiplier assumed by *TAMDL* to be 3160  $\text{mole}^3/\text{L}^3/\text{day}$ . The other empirical rate constant,  $E_{\text{Al}}$ , is assumed by the program to be 58.2 kJ/mole. Like for manganese precipitation and oxidation, the effect of this reaction's production of protons on the pH and the net

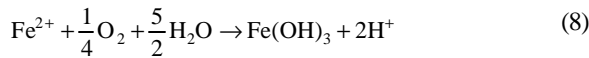
acidity is calculated with equation (5) and the net acidity – pH constitutive relationship, equation (2).

If the user specifies a negative value for the dimensionless empirical rate constant,  $a_{Al}$ , the program does not evaluate equation (6), but does not allow the aluminum concentration to be greater than the solubility limit under equilibrium conditions,  $C_{Al-equ}$ , which is calculated with equation (7).

$$C_{Al-equ} = \exp(35.071 - 6.9078pH) \quad (7)$$

### Ferrous Iron Oxidation

While not necessary for the application that will be discussed in this paper, ferrous iron oxidation can be simulated by *TAMDL* with the following chemical reaction. When the stream's dissolved oxygen concentration is less than 0.01 mg/L, ferrous iron oxidation is neglected.



The rate of ferrous iron oxidation,  $S'_{Fe^{2+}}$  is calculated by the program with the formulation presented by Kirby, Thomas, Southam and Donald (1998). This formulation has a biotic term as well as an abiotic term to account for the oxidation of ferrous iron by *T. ferrooxidans* bacteria.

$$S'_{Fe^{2+}} = -\frac{U_{DO}A_aC_{Fe^{2+}}C_{DO}}{[H^+]^2} \exp\left(\frac{-E_a}{RT}\right) - U_{DO}A_bC_{Fe^{2+}}C_{DO}C_{TF}[H^+] \exp\left(\frac{-E_b}{RT}\right) \quad (9)$$

Where  $U_{DO}$  converts equation (9) from the units used by Kirby, Thomas, Southam and Donald (1998) to the units employed by *TAMDL* and is  $3.125117192 \times 10^{-5}$  g-moles  $O_2$  / mg  $O_2$ . The empirical abiotic oxidation rate multiplier,  $A_a$ , is  $3.456 \times 10^{10}$  mole/L/day, and the empirical abiotic rate constant,  $E_a$ , is 96 kJ/mole. The ferrous iron concentration in mg/L is  $C_{Fe^{2+}}$ , and the dry biomass concentration of *T. ferrooxidans* bacteria is  $C_{TF}$ . The empirical biotic rate constants,  $A_b$  and  $E_b$ , are  $8.8128 \times 10^{13}$  mole/L/day and 58.77 kJ/mole, respectively. All of the empirical rate constants in equation (9) were determined from the analysis of field data (Kirby, Thomas, Southam & Donald, 1998). Because the results of Kirby, Thomas, Southam and Donald (1998) suggest that the dry biomass concentration of *T. ferrooxidans* bacteria is difficult to measure accurately, it can be used as a model calibration parameter.

### Other Reactions

Because the kinetic rates of manganese oxidation and precipitation, aluminum precipitation and ferrous iron oxidation depend upon the stream temperature and the dissolved oxygen concentration, it is necessary that *TAMDL* simulate these water quality constituents as well. With dissolved oxygen, the user has the option of directing the program to assume that saturated conditions are always present or calculate the dissolved oxygen concentration from stream reaeration and organic material decay. A zeroth order sediment oxygen demand formulation from the lake model *CE-QUAL-W2* (Cole & Buchak, 1995) was adapted for use in *TAMDL*. Stream reaeration is calculated with the O'Conner and Dobbins (1958) formulation. Because stream temperature is not absolutely crucial to the modeling of streams affected by acid mine drainage, the simplified formulation used by the program assumes that the amount of heat transferred between the stream and the atmosphere is directly proportional to the difference in temperature and wind speed and inversely proportional to the depth of the stream.

### Boundary and Initial Conditions

Upstream of the computational domain for each simulation, the user specifies the boundary temperature and concentrations. The specified upstream boundary temperature and concentrations may vary with simulation time. Normally, the upstream boundary condition is calculated from the results of the model for the upstream sub-watershed. If there is no upstream sub-watershed, the upstream boundary condition must be implied from the results of water quality sampling.

At the downstream end of each computational domain, *TAMDL* assumes that the spatial gradient of the temperature and concentration is zero. Downstream boundary conditions are required because of the dispersion (second derivative) term in governing equations. If there is no flow through the computational domain, *TAMDL* automatically applies the downstream boundary condition to the upstream boundary, and the concentrations specified for the upstream boundary are ignored.

The program also requires that the initial temperature and concentration be specified for each node. Initial conditions are not very important when one desires a steady state solution. When one is simulating a transient problem, the precise selection of initial conditions may have an important effect on the results calculated in the early portion of the simulation. Realistic initial conditions can be generated by

simulating water quality conditions for a period prior to the desired simulation period.

### Numerical Algorithm

In order to make efficient use of computational resources, the selection of an appropriate numerical algorithm is very important. In the planning stages of *TAMDL*, it was decided that the selected algorithm should be both explicit and at least second order accurate in both time and space. One well-tested algorithm that satisfies this requirement is the explicit MacCormack predictor – corrector method described by Anderson, Tannehill and Pletcher (1984). Because this finite difference algorithm is normally applied to the solution of the advection – dispersion equation, the loading and chemical reaction terms in the governing equation must be solved analytically or with a numerical technique for first order ordinary differential equations.

Since the equations describing the kinetic rates of the aforementioned reactions are both complex and non-linear, it was decided that both the loading and reaction terms should be solved numerically. First order ordinary differential equations are commonly solved with one of the Runge-Kutta methods (Boyce & DiPrima, 1977). In order to simplify the program's source code, it was decided that intermediate time steps to solve the chemical reaction terms would not be employed. Therefore, to achieve the desirable accuracy, it was decided to use the fourth order Runge-Kutta method to solve the contributions of these terms.

### Source Loads

The source loads applied to finite difference model nodes are represented in *TAMDL*'s governing partial differential equation, equation (1), by the array  $L_i$ . The program allows one to specify thermal, alkaline, acid, ferrous iron, ferric iron, manganese, aluminum and dissolved oxygen loads with this array. The operation of passive acid mine drainage treatment systems can also be simulated for specified model nodes. Because the production of alkalinity by passive acid mine drainage treatment systems depends upon the stream's acidity, the source load terms can be non-linear and the fourth order Runge-Kutta method is also used to calculate the contribution of these terms. When simulating most watersheds for TMDL purposes, only alkaline, acid, ferric iron, manganese and aluminum loads are normally employed.

Most water quality models simulate the transport of constituents whose loading rates are directly proportional to local runoff rates. Because of this proportionality, these models calculate non-point source

loads from either precipitation or runoff rates. However, mine drainage normally has both precipitation driven and non-precipitation driven components and it is normally impossible to generate correlations between precipitation and mine drainage quality or quantity. Because the generation of useful correlations between precipitation rate and loading rates of acidity, aluminum, iron and manganese is impossible, *TAMDL* requires that the user specify these loading rates explicitly in the model input.

### Hydrology

Because the advection term in the governing partial differential equation, equation (1), contains the mean flow velocity of the stream,  $V$ , the mean velocity must be known for all portions of the computational domain throughout the simulation period. The current formulation of the explicit MacCormack predictor – corrector method requires that the stream velocity and the hydrodynamic dispersion be uniform throughout the computational domain. Therefore, to account for changes in the stream hydraulics, the watershed must be divided into many small sub-watersheds. Because few watersheds possess the quantity of hydrologic data required to warrant a sophisticated simulation of the stream hydrology and hydraulics, the current version of *TAMDL* assumes that the flow within each sub-watershed is governed by the Mannings equation for uniform flow. The program can easily be modified to read the output from a dedicated hydrological simulation package.

## **MODEL APPLICATION**

The Paint Creek watershed has a drainage area of 318 km<sup>2</sup> and covers parts of Kanawha, Fayette and Raleigh counties in south central West Virginia. For the past 90 years, surface and deep coal mines have operated in the watershed. Before 1970, little consideration was given to the environmental degradation that resulted from these activities. The environmental impact of this mine drainage is being manifested in depressed stream pH and elevated concentrations of iron, manganese and aluminum.

In order to develop a plan to return the quality of Paint Creek and its tributaries to an acceptable level, the West Virginia Department of Environmental Protection (WVDEP) contracted with the West Virginia Water Resources Institute at West Virginia University to produce the engineering and scientific components of the watershed's TMDL for pH, aluminum, iron and manganese. The production of these TMDL components will be assisted with a *TAMDL* water quality model of Paint Creek and its tributaries. This

paper describes the results of the calibration water quality model that were used to demonstrate to the WVDEP and other regulatory agencies that the model can adequately simulate the evolution of stream water quality in the watershed.

The Paint Creek watershed calibration model was then modified to form the baseline conditions model with the assumption that all mine outlets with NPDES permits in the watershed were discharging at the reported monthly mean rate. The acidity and metal concentrations in the drainage from these permitted outlets were taken from the discharge permits. Because of the non-linear nature of the kinetic equations simulated by *TAMDL*, an allocation model was needed to determine the required reductions in waste loads from point sources (permitted mine outlets) and loads from non-point sources (abandoned mine sites). The TMDL loads were obtained by reducing the point and non-point source loads in the allocation model from their level in the baseline conditions model until the TMDL endpoints were satisfied. Because of the uncertainties inherent in the allocation process, the selected TMDL endpoints were slightly more restrictive than the actual water quality standards. For the Paint Creek TMDL, the minimum allowable pH was raised by 0.5 SU and the maximum allowable aluminum, iron and manganese concentrations were reduced by five percent.

Figure 1 is a map of the watershed with the 62 sub-watersheds. These stream segments were divided by finite difference nodes. No stream segment had fewer than five finite difference nodes, and the evenly spaced nodes were no more than 200 m apart. The geographical information required to create the model was obtained from the Watershed Characterization and Modeling System (*WCMS*) developed by the National Resource Analysis Center at West Virginia University (Fletcher & Strager, 2000). Both stream and mine drainage source data were obtained from the WVDEP Division of Water Resources and Division of Mining and Reclamation. Because no USGS gauging stations for Paint Creek exist, hydrologic data from a selected gauging station outside the watershed were employed to calculate stream hydraulics. The USGS gauging station on the Coal River at Tornado, WV was selected because of its proximity to the Paint Creek watershed and because the Coal River and Paint Creek watersheds have a similar topography. One disadvantage of using the data from this gauging station is that the drainage area of the Coal River above Tornado, WV is approximately twice that of Paint Creek. Stream discharge hydrographs for the various sub-watersheds were estimated with the unit area method.

### Model Calibration

Water quality data employed in the Paint Creek *TAMDL* calibration model were collected at two types of locations: streams and mine outlets. Water quality data collected from simulated stream segments were used in model calibration. Water quality data collected from stream segments too small to simulate or from mine outlets and seeps were used to estimate the magnitude of acid and metal loads entering the model. Permitted mines report average monthly pH, discharge rates and concentrations electronically to WVDEP via Discharge Monitoring Reports. Stream water quality data and seep data from abandoned mine sites were collected by the WVDEP Stream Restoration Group.

Because the WVDEP Stream Restoration Group collects water quality data primarily in support of WVDEP's abandoned mine land projects, a large quantity of calibration data for Paint Creek *TAMDL* model were not available. Most of the water quality data were collected in the Ten Mile Fork and Long Branch sub-watersheds (Figure 2), which encompass a large amount of abandoned mine land. Some of the sub-watersheds in the upper portions of the Paint Creek watershed have only had two or three samples collected during the seven year duration (October 1, 1992 – September 30, 1999) of the calibration simulations.

One of the WVDEP sample collection stations with a relatively large quantity of calibration water quality data is station 54 near the mouth of the Long Branch of Ten Mile Fork sub-watershed. The location of this station is shown in Figure 3. Figure 4 is a plot of the simulated and observed stream pH at this station. Observed data are represented on all the time series plots in this paper as dark circles, and the results of the simulation, instantaneous pH and concentration values, are represented by solid lines. While the pH calculated by the model for this station is reasonably well calibrated, some of the higher pH readings are overestimated by the model. The net acidity – pH constitutive relationship used  $6.41421 \text{ SU} \cdot (\text{mg/L})^{-2b}$  and  $-0.04643$  for  $a$  and  $b$ , respectively, within this sub-watershed. Because the oxidation and/or hydrolysis precipitation of aluminum and manganese increase the concentration of free protons in the solution, this discrepancy suggests that the kinetic constants for aluminum,  $10^{-18}$ , and manganese,  $10^0 \text{ (mg/L)}^{-4}/\text{day}$ , may have been underestimated. With an increased sample collection frequency (i.e., monthly), it may have been possible to directly calculate the aluminum and manganese kinetic rate constants for this sub-watershed.

Figure 5 is a plot of the simulated and observed ferric iron concentration for WVDEP station 54. As was

mentioned earlier, the Paint Creek *TAMDL* model assumes that the iron has been completely oxidized and is in the form of ferric hydroxide which settles to the bottom of the channel after clinging to stream sediment particles. Therefore the total iron concentration simulated by the model is a function of the iron load, the hydraulics of the sub-watershed and the calibrated mean sediment diameter, 2.0  $\mu\text{m}$  for this sub-watershed. While the maximums and minimums of the simulated and observed iron concentrations are similar, there appears to be a phase shift between the simulated and observed concentrations. Because ferric iron sedimentation has a great deal of dependence on the stream hydraulics, this discrepancy may indicate that improved definition of stream hydraulics is in order for this sub-watershed.

Figures 6 and 7 are plots of the simulated and observed manganese and aluminum concentrations for WVDEP station 54. While the model appears to replicate most of the observed concentrations well, the maximum simulated concentrations are significantly greater than the maximum observed concentrations. The existence of this type of discrepancy can lead the modeler's customers to question the degree to which the model has been calibrated. For the model's results at this station, it appears that this discrepancy is a result of either the failure of the data collection effort to collect enough samples to adequately define water quality at the station or the possible underestimation of the manganese and aluminum kinetic factors discussed earlier. Given that ten samples were collected at the station during the seven year simulation period, both factors probably contribute to the discrepancy.

To further illustrate the deficiencies in the calibration of a water quality model, a direct comparison of the simulated and observed pH and metals concentrations for station number 54 is given in Tables 1 through 4. The expected model error magnitude,  $S$ , with  $n$  observed samples was calculated using the following equation.

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (C_{i, \text{model}} - C_{i, \text{observed}})^2} \quad (10)$$

Where,  $C_{i, \text{model}}$  and  $C_{i, \text{observed}}$  are the simulated and observed constituent values.

## CONCLUSIONS

The computer program *TAMDL* was designed to simulate the stream transport, reaction and loading of temperature, net acidity, pH, dissolved oxygen, ferrous iron, ferric iron, manganese and aluminum. The advection and dispersion terms of the governing

equation for these constituents are solved using the explicit MacCormack predictor - corrector finite difference method, and the loading and reaction terms are solved with the fourth order Runge-Kutta method. Because *TAMDL* uses net acidity to model solution buffering, an empirical relationship is used to calculate stream pH during the simulation. The computer program has demonstrated the ability to simulate the stream water quality of watersheds affected by acid mine drainage (AMD).

Currently *TAMDL* is being used to construct a pH, iron, aluminum and manganese TMDL model of the Paint Creek watershed. Both the calibration of this model and interaction with the model's future users have impressed upon the author the need for adequate calibration data. Given enough effort it is possible to make any model appear to be calibrated against any set of data, but the degree to which the model will be useful will depend upon both the technical validity of the computer program and the degree to which the calibration data represents the long-term behavior of the system.

Future applications of *TAMDL* will include the simulation of in-stream AMD treatment for selected portions of the Paint Creek watershed. Future development of the program should be devoted toward increasing the number of water quality constituents that can be simulated and improving the program's simulation of sub-watershed hydrology. Building links between the program and one or more Geographical Information System or Computer Aided Design packages would allow the user to quickly design and execute watershed models of AMD and its treatment. Currently, programmers are working to build links between the program and the Watershed Characterization and Modeling System developed by the National Resource Analysis Center at West Virginia University.

## ACKNOWLEDGMENTS

The computer program *TAMDL* was developed with the financial and technical assistance of the West Virginia Water Resources Institute at West Virginia University. The application of the computer program to constructing a pH, aluminum, iron and manganese TMDL model of the Paint Creek watershed was conducted under the research project WRI24 - Enhanced Decision Support for TMDL's, which was funded by the West Virginia Department of Environmental Protection, Division of Water Resources.

## AUTHOR

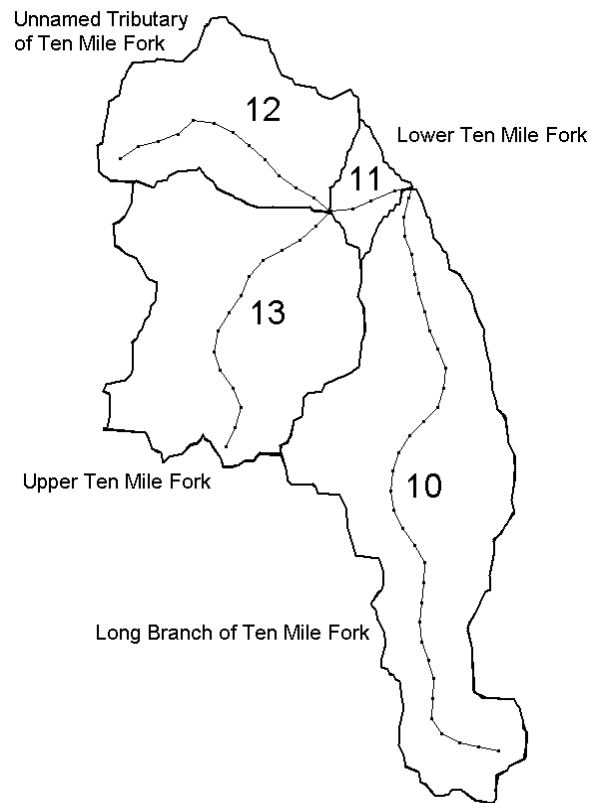
**James M. Stiles** is a registered professional environmental engineer whose wide ranging professional interests include non-linear optimization and fluid mechanics as well as environmental systems analysis and modeling. He recently finished his doctorate in Civil Engineering at West Virginia University and is employed as a research environmental engineer at the West Virginia Water Resources Institute at West Virginia University.

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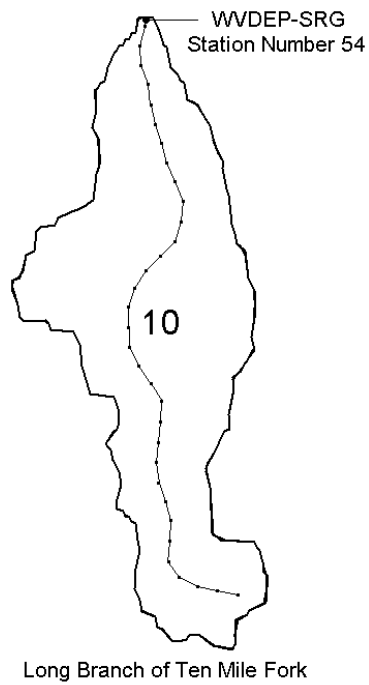
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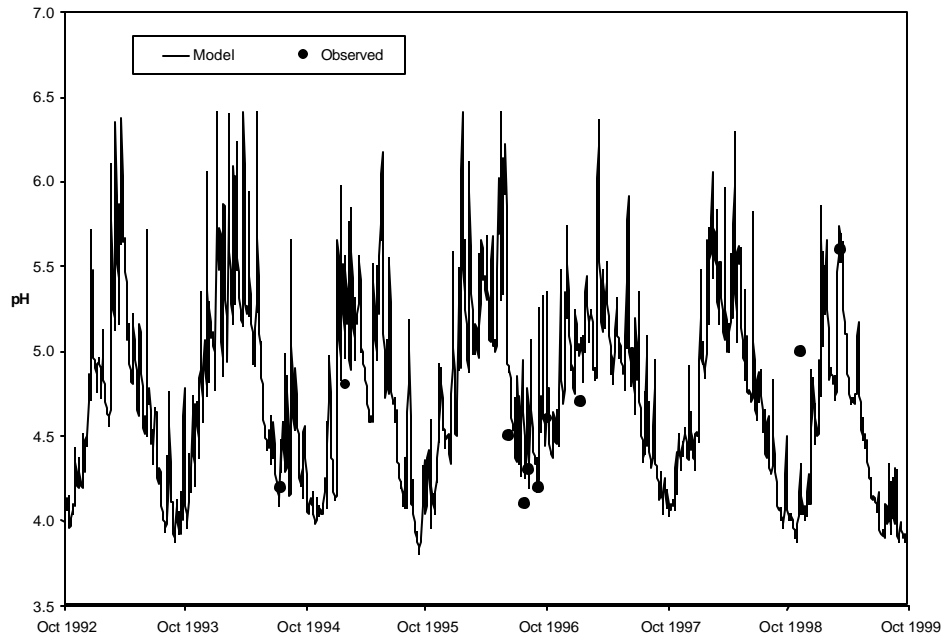
Figure 1. Map of Paint Creek Watershed with the *TAMDL* Sub-watersheds.



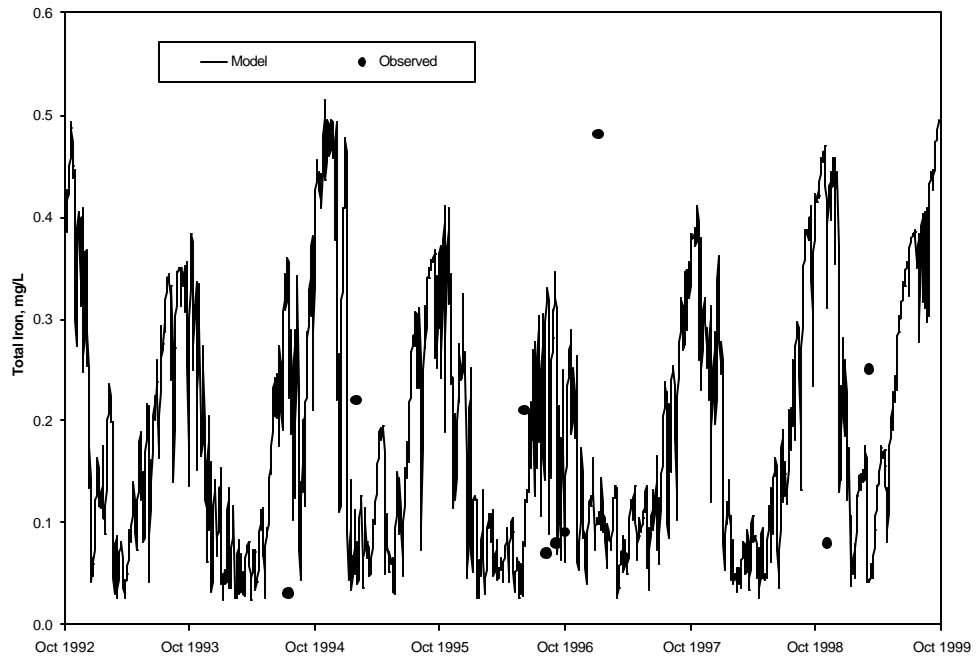
**Figure 2. Ten Mile Fork and Long Branch of Ten Mile Fork Sub-watersheds**



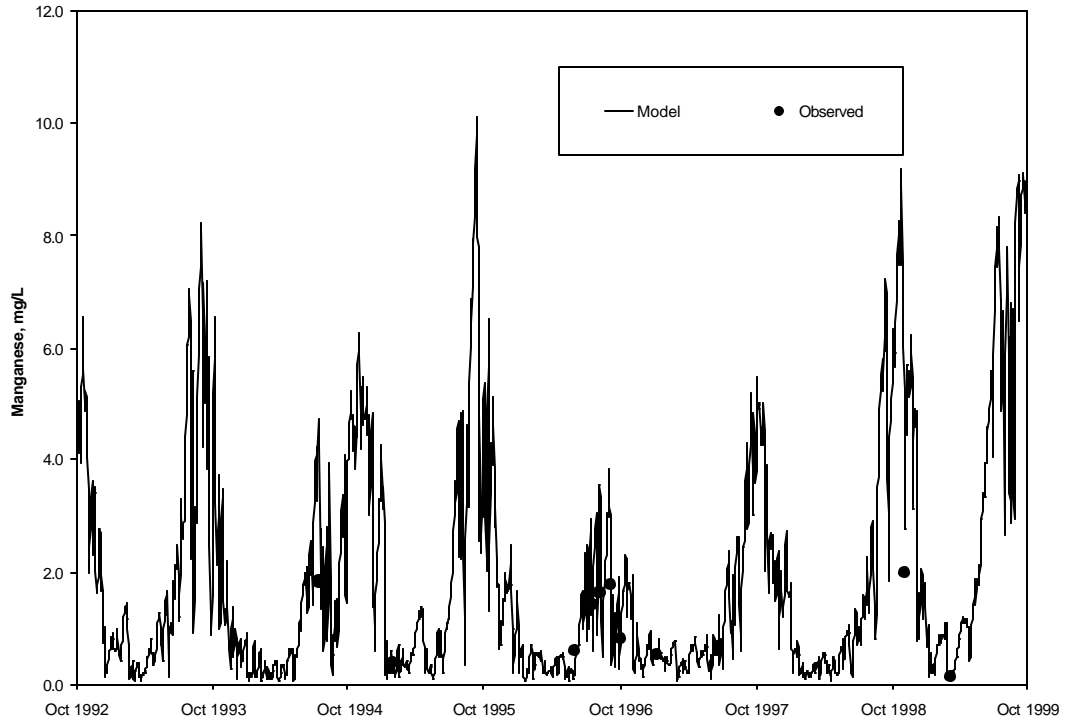
**Figure 3. Long Branch of Ten Mile Fork and WVDEP Station 54.**



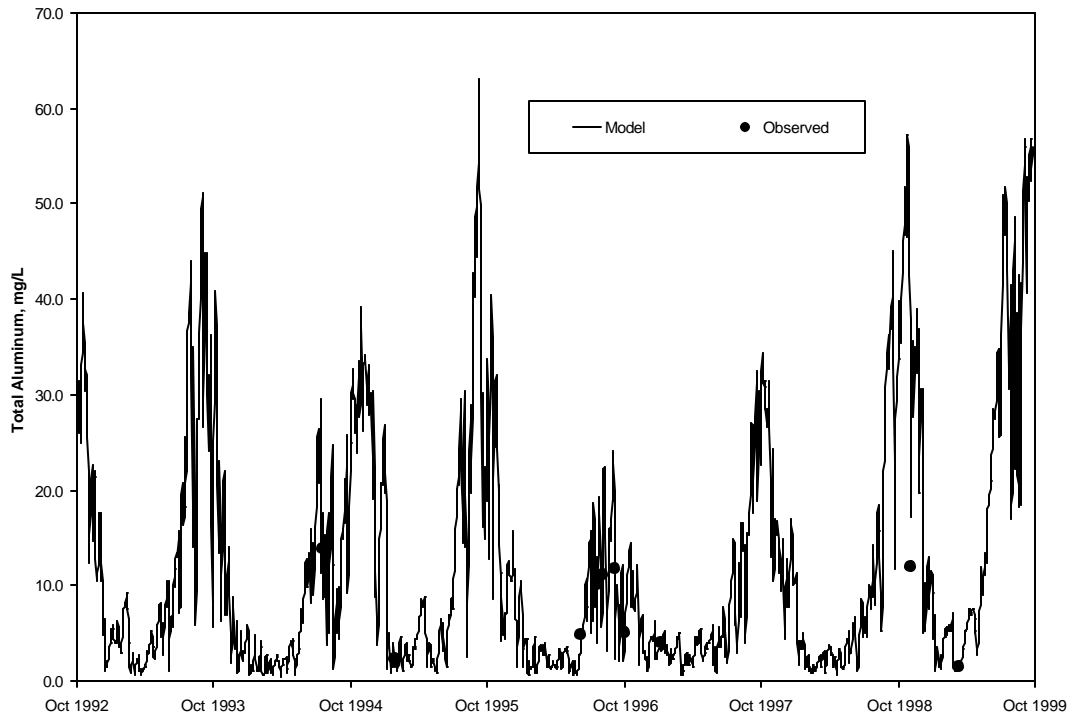
**Figure 4. Simulated and Observed pH at WVDEP Station 54.**



**Figure 5. Simulated and Observed Iron at WVDEP Station 54.**



**Figure 6. Simulated and Observed Manganese at WVDEP Station 54.**



**Figure 7. Simulated and Observed Aluminum at WVDEP Station 54.**

**Table 1. Direct Comparison of Simulated and Observed stream pH for WVDEP Station 54.**

Date	Model pH (SU)	Observed pH (SU)	Error Squared (SU <sup>2</sup> )
07/18/1994	4.4	4.2	0.0518
01/30/1995	5.5	4.8	0.4560
06/05/1996	5.1	4.5	0.3722
07/23/1996	4.5	4.1	0.1648
08/08/1996	4.2	4.3	0.0115
09/05/1996	4.3	4.2	0.0027
10/01/1996	4.9	4.6	0.0774
01/06/1997	5.0	4.7	0.1168
11/05/1998	4.3	5.0	0.4509
03/10/1999	5.6	5.6	0.0000
n =			10
S =			0.4

**Table 2. Direct Comparison of Simulated and Observed Iron Concentration for Station 54.**

Date	Model Iron (mg/L)	Observed Iron (mg/L)	Error Squared (mg <sup>2</sup> /L <sup>2</sup> )
07/18/1994	0.24	0.03	0.0434
01/30/1995	0.05	0.22	0.0277
06/05/1996	0.09	0.21	0.0154
07/23/1996	0.22	0.19	0.0007
08/08/1996	0.33	0.07	0.0672
09/05/1996	0.31	0.08	0.0537
10/01/1996	0.12	0.09	0.0012
01/06/1997	0.10	0.48	0.1451
11/05/1998	0.31	0.08	0.0544
03/10/1999	0.05	0.25	0.0410
n =			10
S =			0.22

**Table 3. Direct Comparison of Simulated and Observed Manganese Concentration for Station 54.**

Date	Model Manganese (mg/L)	Observed Manganese (mg/L)	Error Squared ( $\text{mg}^2/\text{L}^2$ )
07/18/1994	1.99	1.84	0.0213
01/30/1995	0.23	0.39	0.0262
06/05/1996	0.45	0.62	0.0299
07/23/1996	1.65	1.41	0.0592
08/08/1996	3.54	1.64	3.6096
09/05/1996	3.03	1.79	1.5480
10/01/1996	0.72	0.83	0.0123
01/06/1997	0.51	0.54	0.0008
11/05/1998	2.78	2.00	0.6026
03/10/1999	0.20	0.16	0.0013
n =			10
S =			0.81

**Table 4. Direct Comparison of Simulated and Observed Aluminum Concentration for Station 54.**

Date	Model Aluminum (mg/L)	Observed Aluminum (mg/L)	Error Squared ( $\text{mg}^2/\text{L}^2$ )
07/18/1994	12.53	13.80	1.6157
01/30/1995	1.61	2.41	0.6357
06/05/1996	2.97	4.80	3.3387
07/23/1996	10.44	10.10	0.1127
08/08/1996	22.22	11.00	125.8323
09/05/1996	19.16	11.80	54.1049
10/01/1996	4.66	4.90	0.0596
01/06/1997	3.38	3.92	0.2950
11/05/1998	17.28	12.00	27.8932
03/10/1999	1.42	1.51	0.0087
n =			10
S =			4.88