Use of multi- parameter sensitivity analysis to determine relative importance of factors influencing natural attenuation of mining contaminants

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ABSTRACT

Combining multi-Parametric Sensitivity Analysis (MPSA) with stream transport modeling is proposed to determine the relative importance of physical and biogeochemical processes controlling natural attenuation of contaminants. The MPSA is based on a large number of Monte-Carlo simulations to identify the sensitive parameters over a broad range of each parameter. This combined approach is applied to the transport of a mining contaminant, dissolved manganese in Pinal Creek basin, Arizona. The MPSA results show that transport of dissolved Mn(II) in Pinal Creek is controlled mainly by ground-water inflow, resulting spatial variation of pH in stream water, and the effect of pH on microbially mediated Mn(II) oxidation in the hyporheic zone.

INTRODUCTION

The fate and transport of contaminants in streams and rivers are controlled by a variety of physical and biogeochemical processes. The physical processes play an important role in determining the fate of solutes in surface-water environments. These physical processes include advection, dispersion, hyporheic exchange, and ground-water interaction. In many situations, however, the transport of contaminants are also greatly affected by biogeochemical processes, such as sorption/desorption, oxidation/reduction, volatilization, hydrolysis, biodegradation, and other biochemical reactions. Therefore, transport of contaminants in natural streams and rivers is best described by considering all of the relevant physical and biogeochemical processes simultaneously (fig. 1).

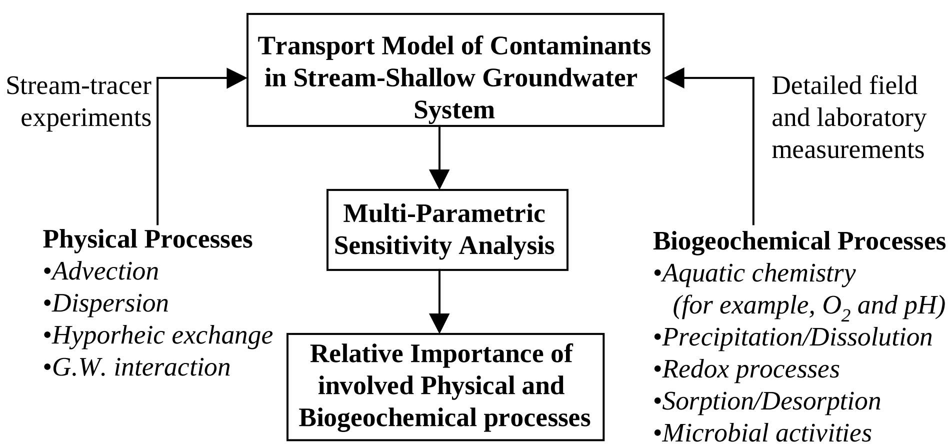

Figure 1. Coulping MPSA with transport model to identify the relative importance of physical and biogeochemical processes.

To answer the question about relative importance of factors, the sensitivity of a numerical transport model needs to be tested for the physical and biogeochemical parameters (processes) that are involved in the forward transport model. However, traditional parameter-sensitivity analysis pertains to a particular point (localized) in the parameter space, which is defined by all possible combinations of parameter values. Also, in the localized sensitivity analysis, the importance or sensitivity of a selected parameter can be affected greatly by the values of other parameters, because the significance of one selected process is usually dependent on other processes. Typically, the importance of biogeochemical processes are highly dependent on the physical processes, whereas the physical processes are not affected by the biogeochemical processes. For example, the biogeochemical reactions of solutes in the hyporheic sediments are enhanced by the prolonged retention time of solutes in these sediments. Therefore, to account for parameter interactions, the relative importance of the physical and biogeochemical processes of the transport model can be evaluated more accurately by a generalized (multi)-parameter sensitivity analysis, which encompasses the entire parameter space (fig. 1).

This paper presents the concepts and procedures of multi-parameter sensitivity analysis (MPSA) that is used to determine the relative importance of transport processes. In addition, a case study shows how the MPSA can be applied to the transport of metal contaminants in a drainage basin affected by acidic mine drainage.

MULTI-PARAMETRIC SENSITIVITY ANALYSIS

A numerical transport model may include detailed field measurements as well as ill-defined parameters that cannot be measured with a high degree of accuracy in the field or in the laboratory. These ill-defined parameters will severely limit the accuracy of any single simulation and increase the difficulty of assessing the relative importance. In an attempt to overcome this difficulty and to recognize the relative significance of parameters involved in the model, the sensitivities of simulations results to input parameters need to be evaluated by assigning either a range of variation or a degree of uncertainty to each parameter and implementing a generalized sensitivity analysis (Hornberger and Spear, 1980; Chang and Delleur, 1992; Choi et al., 1998; Choi, 1998). This multi-parametric sensitivity analysis (MPSA) followed the procedure proposed by Chang and Delleur (1992) and Choi et al. (1998). The procedure includes the following steps:

1. Select the parameters to be tested.
2. Set the range of each parameter to include the variations experienced in the field and laboratory measurement.
3. For each selected parameter, generate a series of, for example, 500 independent random numbers with a uniform distribution within the design range.
4. Run the model using selected 500 parameter sets and calculate the objective function values.
5. Determine whether the 500 parameter sets are ‘acceptable’ or ‘unacceptable’ by comparing the objective function values to a given criterion (R).
6. Statistically evaluate parametric sensitivity. For each parameter, compare the distributions of the parameter values associated with the acceptable and unacceptable results. If the two distributions are not statistically different, the parameter is classified as insensitive; otherwise, the parameter is classified as sensitive. Relative importance can be evaluated statistically if desired.

The objective function values of the sensitivity analysis usually are calculated from the sum of squared errors between observed and modeled values:

$$f = \sum_{i=1}^{n} [x_0(i) - x_c(i)]^2 \qquad (1)$$

where f is the objective function value and $x_C(i)$ and $x_0(i)$ are calculated and observed values, respectively. Observed values often are obtained from simulations that used the mid-points of the characteristic range for each parameters. The ranges for each parameter are determined from minimum to maximum values that are obtained from parameter estimations and field measurements through the study reaches. If the objectve function value obtained from the simulation is less than a subjective criterion then the result is classified as acceptable, otherwise the result is classified as unacceptable. Three different objective function values often are tested for a subjective criterion. Those values typically define the 33, 50 and 66% divisions of 500 sorted objective functions.

The basic concept of MPSA is illustrated by using a hypothetical model with only two parameters (fig. 2). In addition, the modleing procedure of MPSA described above is summarized using a flowchart (fig. 3).

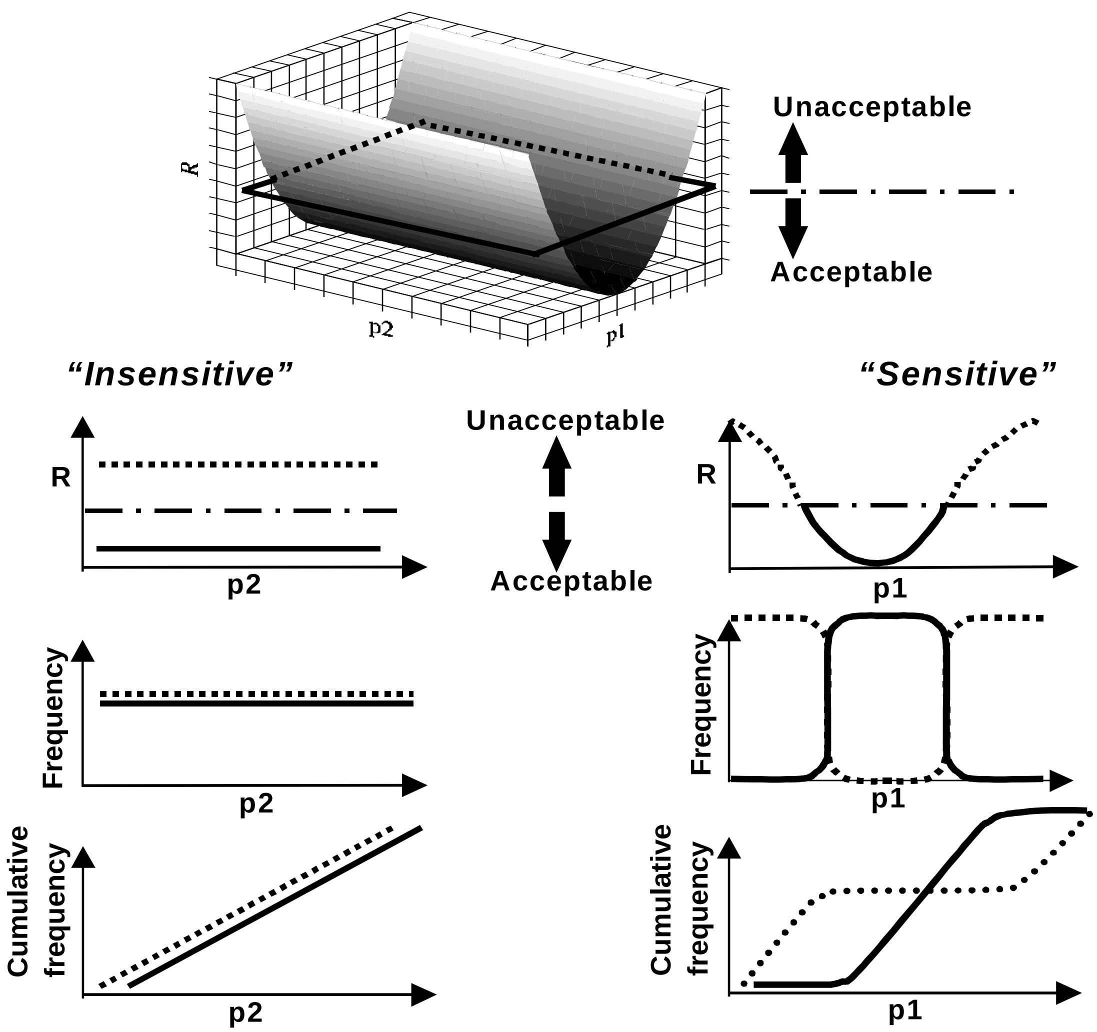

Figure 2. Basic concept of multi-parametric sensitivity analysis (MPSA) using a hypothetical model with only two parameters.

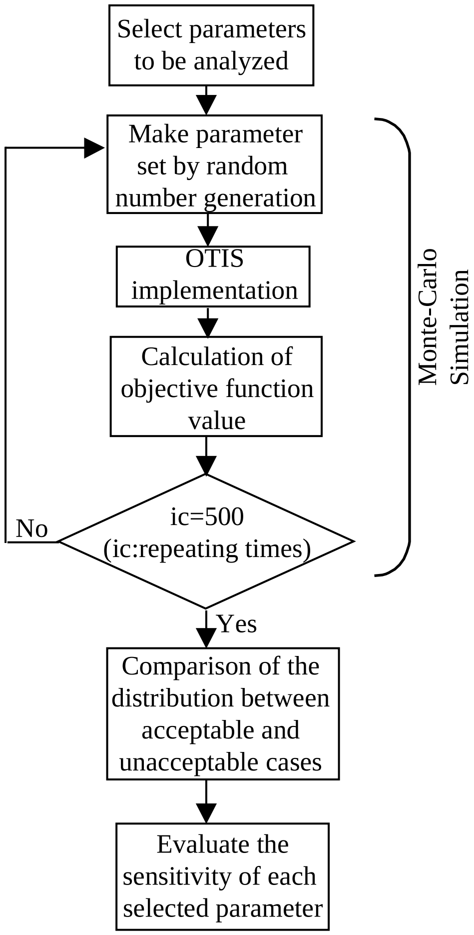

Figure 3. Flow chart illustrating the procedure of multi-parameteric sensitivity analysis (MPSA)

EXAMPLE OF APPLICATION

Problem Statement

Surface-water chemistry of Pinal Creek is dominated by discharge of the neutralized, contaminated ground water in the upper 4-Km of perennial flow. The neutralized contaminated groundwater is characterized by high dissolved solids (sulfate 2200 mg/L; Ca 500 mg/L) with pH of 5.5 to 6 and elevated pCO_2 resulting from neutralization of the acid plume by carbonate minerals, and elevated concentrations of dissolved Mn, Co, Ni and Zn. Beginning at the head of perennial stream flow in Pinal Creek, pH in the stream increases from approximately 6.0 to 7.8, and dissolved manganese, Mn(II) decreases from approximately 70 to 50 mg/L.

Although manganese is a toxic substance, it is not usually one of the more toxic metals present in acidic mine drainage. Manganese is of particular interest at acidic mine drainage sites, however, because precipitation of manganese oxide has a high potential to reduce downstream transport of other dissolved metals (including nickel, cobalt, and zinc at the Pinal Creek basin site). Harvey and Fuller (1998) showed that oxidation of Mn(II) to form manganese precipitates is enhanced by microbial activities in the hyporheic zone of Pinal Creek. Furthermore, the microbial activities in the hyporheic zone are highly dependent on the pH of stream water (Marble, 1998).

Modeling Analysis

The one-dimensional solute transport model (OTIS; Runkel and Broshears, 1991, Runkel, 1998), developed to describe the transport processes in streams and rivers, was used in our study. This transport model was extended to include a pH-dependence of the microbially-mediated uptake processes of manganese (Choi, 1998). The governing equations of the extended pH-dependent transport model are,

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \frac{q_L^{in}}{A}\left(C_L - C\right) + \alpha\left(C_S - C\right) - \lambda(pH)C \qquad (2)$$

$$\frac{\partial C_S}{\partial t} = \alpha\frac{A}{A_S}\left(C - C_S\right) - \lambda_S(pH)C_S \qquad (3)$$

where

- A main channel cross-sectional area $[L^2]$,
- A_S storage zone cross-sectional area $[L^2]$,
- C main channel solute concentration $[ML^{-3}]$,
- C_L lateral inflow solute concentration $[ML^{-3}]$,

C_S	storage zone solute concentration [ML^{-3}],
D	dispersion coefficient [L^2T^{-1}],
Q	volumetric flow rate [L^3T^{-1}],
q^{in}_L	lateral inflow rate [$L^3T^{-1}L^{-1}$],
t	time [T],
x	distance [L],
α	storage zone exchange coefficient [T^{-1}],
λ	main channel first-order decay coefficient [T^{-1}], and
λ_S	storage zone first-order decay coefficient [T^{-1}].

The parameters involved in the model were obtained from field measurements and inverse estimation using tracer dilution data (Harvey and Fuller, 1998). The rate constants for microbial uptake of dissolved Mn(II) were specified on the basis of experimentally-determined net rates of removal of Mn(II) from laboratory experiments (Marble, 1998). On the basis of two different data sets (June, 1994 and June, 1995) from Pinal Creek, the extended pH-dependent model was executed to simulate the transport of dissolved manganese in the stream system. The simulation results are presented on figure 4. As we can see from figure 4, the spatial distributions of dissolved manganese along the Pinal Creek were well simulated by the extended pH-dependent transport model.

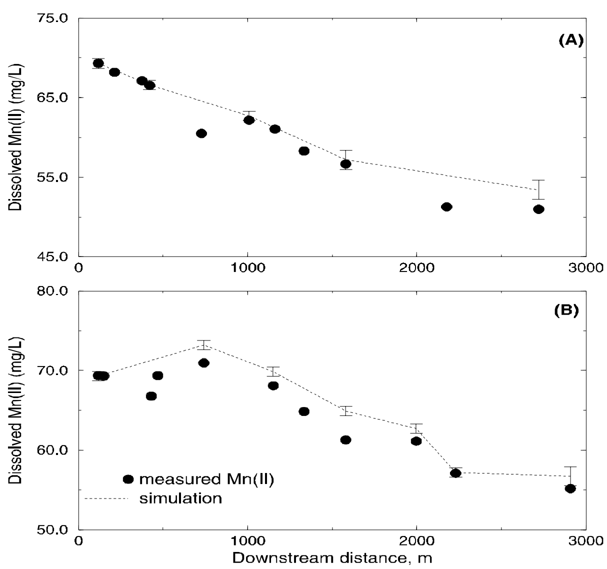

Figure 4. Simulation results from forword modeling approach. (June, 1994 (A) and June 1995 (B)).

Even though there were good agreements bewteen observations and simulation results from predictive forward modeling approach (fig. 4), it is not possible to identify the relative importance of each physical and biogeochemical processes from the graph alone.

Application of MPSA

As one example of the application of the proposed sensitivity analysis, MPSA was applied to the transport of dissolved manganese in Pinal Creek. Using MPSA, the physical and biogeochemical processes involved in the extended pH-dependent transport model were evaluated for their relative importance.

MPSA was performed for selected physical parameters of ground-water inflow/outflow, cross-sectional area of main channel and storage zone, exchange rate with storage zone and dispersion coefficient, and chemical parameters of Mn(II) concentration of ground-water inflow and pH of stream water. The ranges for each parameter determined from parameter estimation and field/laboratory measurements are shown in table 1. The objective functions are calculated by the departure of the modeling results (Mn(II) concentration of streamwater at downstream) from a standard result, which is obtained by using the midpoint values from selected parameter ranges.

Table 1. Ranges of parameters used in multi-parametric sensitivity analysis

parameters	test range
cross-sectional area of main channel (A)	0.1 - 0.5 [m^2]
Dispersion coefficient (D)	0.5 - 8.0 [m^2s^{-1}]
cross-sectional area of storage zone (A_s)	0.02 - 0.15 [m^2]
exchange rate (α)	4.0×10^{-4} - 2.0×10^{-3} [s^{-1}]
pH	5.5 - 8.0
Groundwater (GW) inflow rate (q_L^{in})	0.0 - 1.5×10^{-4} [$m^3s^{-1}m^{-1}$]
GW outflow rate (q_L^{out})	0.0 - 4.0×10^{-5} [$m^3s^{-1}m^{-1}$]
Mn(II) concentration of GW inflow (C_L)	0.3 - 55.0 [mgL^{-1}]

The resulting cumulative frequency distributions of acceptable and unacceptable cases, which are divided by comparing subjective criteria and objective function values are shown in figure 5. If the two distributions are not statistically different, the parameter is classified as insensitive; otherwise, the parameter is classified as sensitive. The objective function values were compared with 3 different subjective criteria, which define the 33-, 50-, and 66-percent divisions of 500 sorted objective function values. In this example, however, the MPSA results were not affected by the choice of the subjective criterion. Therefore, the 50 percent criterion was used to obtain the resulting cumulative frequency distributions of acceptable and unacceptable cases in Figure 5.

The multi-parametric sensitivity analysis identified the ground-water inflow rate (q_L^{in}), Mn(II) concentration in ground-water inflow (C_L), and resulting pH variation in the system as the most important parameters (fig. 5). This indicates that the transport of dissolved manganese in this small stream system is mainly controlled by ground-water inputs with low-Mn(II) and high alkalinity, and the resulting spatial variation of pH through influencing the rate of Mn(II) oxidation. The moderate sensitivity of Mn(II) transport to cross-sectional area (A_S) and exchange rate (α) of storage zone (fig. 5) can be explained by the fact that A_s and α control the retention time and influence the amount of uptake of dissolved manganese in the hyporheic zone. On the basis of these results, it can be inferred that the difference between observation and simulation (fig. 4) may have resulted from the uncertainties in estimating the parameters, such as ground-water inflow rate (q_L^{in}), hyporheic parameters (A_s and α), or pH measurement.

In conclusion, the combined efforts of forward modeling approach and generalized sensitivity analysis can provide an integrated view of contaminant transport processes in natural stream systems. The multi- parametric sensitivity analysis especially helps identify the relative importance of physical and

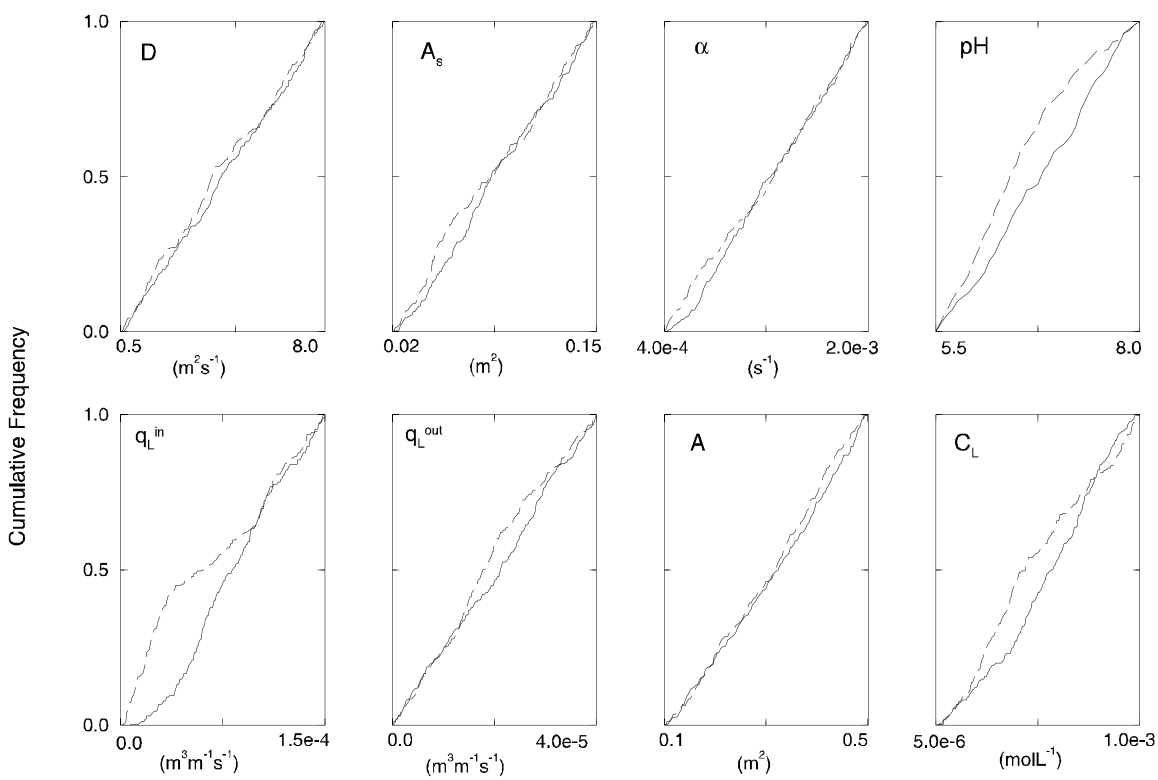

Figure 5. Results of MPSA for transport of dissolved Mn(II) in Pinal Creek, AZ. Solid and dashed lines indicate acceptable and unacceptable cases, respectively. Extent of separation between two cases represents degree of sensitivity of each parameter.

biogeochemical processes controlling the transport of contaminants. Furthermore, this methodology can provide a guide for future data-collection efforts and to order research priorities.

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