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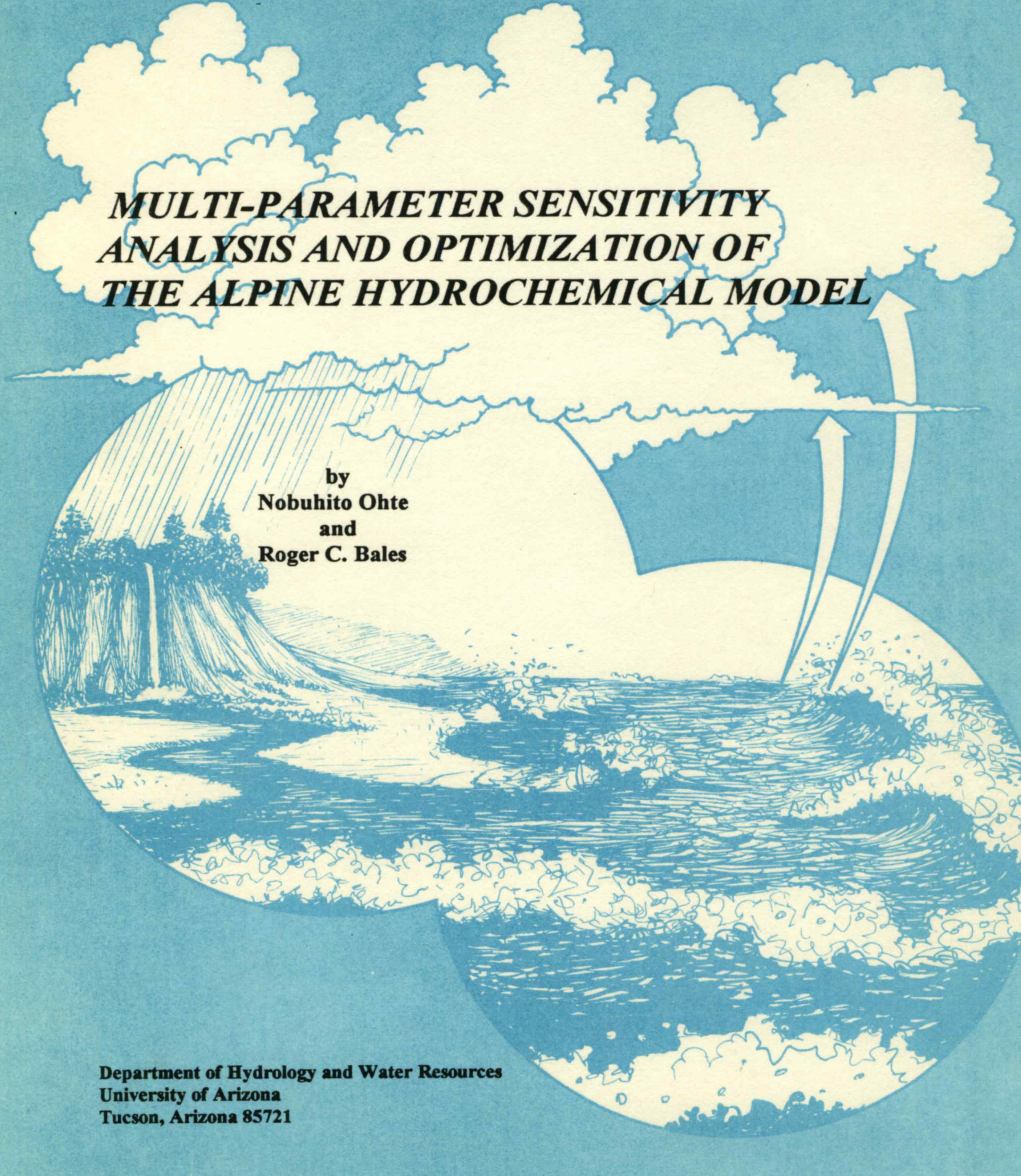

MULTI-PARAMETER SENSITIVITY ANALYSIS AND OPTIMIZATION OF THE ALPINE HYDROCHEMICAL MODEL

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Table of Contents

List of Tables

List of Figures

Abstract

The University of Arizona's Alpine Hydrochemical Model (AHM) is an integrated set of algorithms for water and chemical balances that describes hydrologic and chemical processes in a headwater catchment. We developed AHM for use both as a research tool and as a predictive model for estimating effects of natural and anthropogenic changes in climate or in atmospheric-pollutant loading on alpine watersheds. We initially applied AHM to Emerald Lake watershed in the southern Sierra Nevada, and estimated model parameters by trial and error using a single water year of data and process-level studies. Using the same parameters, AHM successfully reproduced stream chemistry and discharge for a second water year. We have extended that empirical analysis by doing a systematic analysis of parameter sensitivity and an automatic optimization of model parameters. In the sensitivity analysis, a large number of Monte-Carlo simulations done on the multi-dimensional function field were used to identify the sensitive parameters and to set an appropriate range for each parameter. These results were then used to reduce the computational load in the automatic optimization, which is based on the downhill simplex method in multiple dimensions; we estimate the global optimum parameter set according to the fluctuation of the sum of squared errors between observed and modeled stream discharge and chemistry. Sensitive physical and chemical parameters were identified, including those describing evapotranspiration, hydraulic conductivity and soil depth or porosity; and those describing mineral weathering, ion release from the snowpack, ion exchange, soil CO_2 and nitrogen reactions. The automatic optimization method succeeded in estimating a global optimum parameter set from a single water year of data that improved the fitting compared to the set from trial and error manipulation.

1 Introduction

The Alpine Hydrochemical Model (AHM) is an integrated set of algorithms for water and chemical balances that describes hydrologic and chemical processes in a headwater catchment [Wolford, 1992]. AHM was developed for use both as a research tool and as a predictive model for estimating effects of natural and anthropogenic changes in climate or in atmospheric-pollutant loading on alpine watersheds. AHM is capable of predicting watershed hydrologic and hydrochemical responses to inputs and changes in inputs of water and chemicals. The model computes integrated water and chemical balances for a watershed with multiple terrestrial, stream, and lake subunits, each of which can have a variable snow-covered area. Chemical speciation is handled by adapting portions of the model MINEQL [Westall et al., 1976]. The conceptual diagram of the model is showed in Figure 1.

AHM has been applied to Emerald Lake watershed in the southern Sierra Nevada with a daily step. Parameters in the model were lumped, with five subunits defined to describe characteristics of whole watershed: SOIL, TALUS, ROCK, STREAM and LAKE. And also, SOIL and TALUS subunits were given two layers each, with independent soil physical parameters. Model parameters were estimated by trial and error using a single water-year of data and process-level studies [Wolford et al., 1994]. Using the same parameters, AHM successfully reproduced stream discharge and chemical composition for a second water year. AHM runs used some 23 hydrologic and 11 thermodynamic parameters to describe exchange reactions in the soil. In addition, AHM has parameters describing mineral weathering, nitrogen reactions and ion release rate from snowpack.

Wolford [1992] showed that to manually analyze the model sensitivity to all parameters would require on the order of 10^{13} mathematical operations, which would require more than about 400 hours on a computer capable of 20 million floating-point operations per second. Namely, the current model has too many parameters and outputs and consumes too much computer time to attempt to manually find the optimum set of parameters for each application. Moreover, the interdependence between several parameters and the non-linear characteristics of parameters might make the parameter calibration so difficult even in the case of a simpler model [Sorooshian and Gupta, 1983]. Therefore, the decision to fix most parameters, based on independent physical measurements, and to adjust only a few is the preferred way for calibrating this kind of model. However, if relatively small number of parameters can be selected for adjustment, automatic parameter estimation techniques may be used to good effect, as was demonstrated with the ILWAS model [Chang and Delleur, 1992]. This attempt with the ILWAS considered the hydrologic and chemical portions independently for performing their sensitivity analysis, although the chemical calculation may be influenced by not only chemical portion, but the hydrologic portion of the model as well.

The purpose of the work reported in this paper is to develop a systematic procedure for parameter sensitivity analysis for AHM and to automatically identify a global optimum parameter set for both hydrologic and chemical calculation by considering the effects of hydrologic calculation on chemical outputs. We have thus extended the empirical analysis of Wolford et al. [1994] by doing a systematic analysis of parameter sensitivity and an automatic optimization of model parameters.

2 Methods

The parameter estimation of AHM was basically carried out through two steps; i) multi-parametric sensitivity analysis (MPSA), and ii) automatic parameter optimization (APO).

AHM has the two linked functions, simulation of both hydrologic phenomena and biogeochemical phenomena [Wolford 1992]. Although the chemical calculations do not affect the hydrologic calculations, several hydrologic factors influence the simulation of chemical phenomena.. Therefore, to aim for a global optima during the parameter estimation for the both chemical and hydrologic simulation, the both chemical and hydrologic parameters must be examined and optimized together. Thus, to get the global optima, we treat the chemical and hydrologic parameters together instead of estimating them

2.1 Multi-parametric sensitivity analysis

A three-step procedure was used to evaluate parameter sensitivity. First, we identified the sensitive hydrologic parameters using MPSA, with a fit to the basin discharge hydrograph being the objective. Second, we identified the sensitive chemical parameters using MPSA, with a fit to discharge pH, ANC, Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, Cl^-, silica and NO_3^-, i.e. ten objectives. Third, we investigated the sensitivities of chosen chemical and hydrologic parameters together using MPSA with the ten chemical objectives and the discharge hydrograph.

The multi-parametric sensitivity analysis procedure followed the method used by Chang and Delleur [1992]. The steps were as follows.

1. Select the parameters to be tested.
2. Set the range of each selected parameter. The range was determined from independent physical-chemical data or from the literature.
3. Select parameter values randomly within the determined range for each parameter. Here, the distribution of each parameter value must be uniform with in the range.
4. Implement the model and calculate the value of the objective function.
5. Determine whether the parameter set is acceptable or unacceptable by comparing the objective function value to a given criteria (R).
6. Statistically evaluate parameter sensitivity. The two groups (acceptable and unacceptable) of frequency distributions of individual parameters were compared to each other. If the two frequency distributions were not statistically different, the

parameter was classified as insensitive, otherwise the parameter was called sensitive. A Kolmogorov-Smirnov (K-S) test was used to evaluate the difference between two distributions [Stephens, 1970].

Step 3–5 were repeated enough times to assure randomness and uniformity of the distribution of the generated parameter values. These steps were based on the concept of Monte-Carlo simulation on multi-dimensional function field. The flowchart is represented in Figure 2.

2.2 Automatic parameter optimization

In the automatic parameter optimization there were two steps. First was to do hydrologic parameter optimization using only the discharge hydrograph as an objective. Second was to do multi-objective optimization for all eleven objectives (discharge and concentrations) using the Minimum Deviation Method to formulate the global objective function. The individual objective functions (e.g. discharge rate, pH, ANC, etc.) was calculated from the sum of squared errors between observed and modeled values:

$$f = \sum_{i=1}^{n} (x_o(i) - x_c(i))^2 \tag{1}$$

where, $x_c(i)$ and $x_o(i)$ are the calculated and observed values respectively.

To get the global objective function, eleven individual objectives were normalized and combined based on the Minimum Deviation Method:

$$F = \sum_{j=1}^{m} \frac{f_{min}(j) - f(j)}{f_{max}(j) - f_{min}(j)} \tag{2}$$

In equation (2), f_{min} and f_{max} are the least desirable and optimal objective function values, respectively. This formulation is effective when partial information on the objectives is available; that is, the optimal values of the objectives are known but their relative importance is not known [Tabucanon 1988]. Approximate f_{max} and f_{min} of values of each objective were obtained from the multi-parametric sensitivity analysis.

The optimization procedure was based on the Downhill Simplex Method in multiple dimensions [Nelder and Mead 1965]. The procedure was as follows.

1. Select the parameters to be optimized

2. Define a reasonable range of values for each parameter considered.

3. Give several parameter sets to define an initial simplex. If the number of parameters

to be optimized is M, the Downhill Simplex Method requires $M+1$ initial parameter sets and their objective function values.

4. Execute the DownHill Simplex Method to find the parameter set giving the smaller function value.

5. Return to step 4 and repeat the optimization cycle until the function value does not decrease.

The flowchart of APO is showed in Figure 3.

The whole processes of the parameter estimation that was done in this study is illustrated in Figure 4. First, six hydrologic and six chemical parameters were chosen for sensitivity evaluation and optimization. The selection was based on the previous empirical parameter estimation [Wolford, 1992]. Second, MPSA was done to choose four sensitive hydrologic and four sensitive chemical parameters. A fit to discharge hydrograph was used as an objective function for hydrologic parameters. For chemical parameters we used a fit to discharge pH, ANC, Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, Cl^-, silica and NO_3^-, i.e., eleven objectives. Third, MPSA was done to investigate the model sensitivity to four sensitive hydrologic and four sensitive chemical parameters. Ten chemical objectives, the discharge hydrograph and the global objective function were used. Fourth, the hydrologic parameter optimization was done using only the discharge hydrograph as an objective. The initially chosen six parameters were optimized, then the optimization of three most sensitive parameters obtained by MPSA was done to compare its computational load with that of the six-parameter case. Fifth, the multi-objective parameter optimization for all eleven objectives was done using the Minimum Deviation Method. The four hydrologic and four chemical parameters that were selected by MPSA (step II) were optimized, then the optimization of five most sensitive parameters was done to compare its computational load with that of the eight-parameter case. Five parameters were also chosen by MPSA using the global objective function (step III).

2.3 Watershed data

The parameter estimation procedure for AHM was applied to the Emerald Lake watershed using data collected in the 1986 and 1987 water years [Elder et al., 1991; Kattelmann and Elder, 1991; Williams and Melack, 1991a,b]. The water year runs from October 1 of the previous year through September 30. We used the 1986 data for parameter optimization, and used the 1987 data to evaluate model performance.

The Emerald Lake watershed is a 120-ha headwater catchment located in the Sierra Nevada (36'35'N, 118'40'W), with elevations ranging from 2800 m at the lake to 3417 m at the top [Tonnessen, 1991]. It is 20 percent soil covered, with another 23 percent talus and the remainder rock. The detailed description of soil geochemistry and vegetation was reported by Brown et al.[1990].

The input data used in the model implementation include snow covered area, evapotranspiration, sublimation, wet and dry deposition chemistry and soil physical and chemical characteristics. The observed lake outflow data set consists of the daily discharge rate and its pH, acid neutralizing capacity (ANC), and concentrations of Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, Cl^-, NO_3^-, and silica.

AHM simulations were done for lake inflow, and observed lake inflow chemical data were used for computing the values of objective functions. Lake outflow data were used for discharge quantity, because the complete lake inflow was not measured and changes in lake storage were minimal [Wolford, 1992].

3 Results

3.1 Selecting sensitive hydrologic parameters with MPSA

Of the several physical parameters of SOIL and TALUS subunits that influence streamflow [Wolford et al., 1994], six kinds of parameters were chosen for examination: maximum fraction of evapotranspiration that can occur relative to potential evapotranspiration (ET), soil layer thickness (ST), saturated soil water content (TS), saturated hydraulic conductivity (KS), a parameter (N) that determines the relation between soil water content and unsaturated hydraulic conductivity, and soil bulk density (BD) (Table 1). The range to be examined of all parameters were set as 0.5–1.5 (except N which was set as 0.8–1.8) times the values used by Wolford et al. [1994]. In this parameter estimation, we were concerned with the characteristics of each parameter itself rather than individual parameter value of each compartment. Therefore, the same percentage of increase or decrease for each parameter was used for all SOIL and TALUS subunits and their individual layers.

We executed 400 simulations using randomly chosen parameter sets were executed. Three criteria were used to distinguish between acceptable and unacceptable results. First, the frequency of the acceptable and unacceptable cases were made approximately 50% each. For the other two cases, slightly larger and smaller divisions were made. Table 2 shows the results for each case. The *p* values for each parameter represents the probability calculated by K-S test. The probability indicates the smallest level of significance that would lead to the rejection of the null hypothesis that the frequency distributions of the parameter value corresponding to the acceptable and unacceptable cases are not significantly different, i.e. the parameter is insensitive. Therefore, if the calculated probability is less than the critical significance level (we used 1%), this parameter can be evaluated as sensitive. From this table, *p* values of ET and TS were smaller than 0.01 in all three cases, and ST's *p* value was also smaller than 0.01 in two cases. Thus these parameters are evaluated as sensitive. N and KS can be classified relatively insensitive. BD was obviously insensitive for hydrograph generation. The accumulated frequency distributions of acceptable and unacceptable cases in case 2 are shown in Figure 5. The acceptable and unacceptable distributions of ET, ST and TS are relatively different compared to the other three parameters.

3.2 Selecting sensitive chemical parameters with MPSA

Applying AHM to the Emerald Lake watershed, the major factors that we expected to influence stream water chemistry were: ion elution with snow melt, ion exchange, mineral weathering and biological reactions related to nitrogen in soil. Therefore, six parameters were chosen to examine initially; the parameter determining elution rate (EL), the parameter determining the weathering rate (KI), the thermodynamic constants of the major ion exchange reaction (EX), the partial pressure of CO_2 in soil (PC), and two parameters related to nitrogen reaction, the fraction of NH_4^+ to convert to organic nitrogen (NH) and the fraction of NO_3^- in excess of base line concentration (NO) to convert to organic nitrogen (Table 3). Note that EX represents equal percent changes in all major exchange and adsorption reactions. They include ion exchange for Na^+, Ca^{2+}, K^+ and Mg^{2+}, SO_4^{2-} adsorption, and silica adsorption. The reactions were not considered individually. The range to be examine of all parameters were also set as 0.5–1.5 times their values determined by Wolford et al. [1994].

We did 400 simulations for the chemical parameter sets. Hydrologic parameters were left at Wolford et al.'s [1994] values. In this analysis, we evaluated the sensitivities of six parameters for each objective, which are given from simulations of pH, ANC, Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, Cl^-, silica and NO_3^-. Tables 4.1 through 4.10 show probability values from K-S tests of each parameter for each objective. Three different subjective criteria were also used to classify the calculated cases if they are acceptable on each objective. For all objectives, the tendencies of sensitivity are quite consistent through three cases using different criteria. The results for each objective are summarized in Table 5. According to the most sensitive parameter of each objective, EL, EX, PC an NH can be chosen as the main sensitive chemical parameters. The accumulated frequency distributions of the case 2 with 50% acceptable are shown in Figures 6.1 through 6.10.

3.3 Sensitivity analysis of chosen eight parameters

To help identify the global optimal parameter set, the sensitivities of the independently chosen hydrologic and chemical parameters were examined together. The following seven parameters that were chosen the previous step: ET, ST, TS, EL, EX, PC, NH, and the saturated hydraulic conductivity KS were tested. Although KS was not classified as a sensitive parameter for the hydrograph, it was thought to be one of the important factors influencing the chemical reactions in soil. The ranges of these eight parameters were also set as 0.5–1.5 times the optimum values from Wolford et al. [1994].

The probability values in Tables 6.1 through 6.12 were calculated by setting the criteria as in the previous case. The objectives were the above-mentioned ten chemical data sets and the hydrograph. Moreover, the global objective function value from the eleven objectives were examined using equation (2). In this case, 400 simulations were also carried out. Which hydrologic or chemical parameters were sensitive for each objective are summarized in Table 7. The accumulated frequency distributions of the equal- acceptable-unacceptable case are shown in Figures 7.1 through 7.12.

3.4 Parameter optimization for the hydrograph

Table 8 shows the results of parameter optimization for only the hydrograph as a single objective. Runs 1–11 used the six parameters chosen initially; run 12 used the three sensitive parameters chosen by MPSA. In the runs 1–10, the initial simplex points were randomly selected within the range of each parameter. In runs 11 and 12, the seven and four parameter sets from Monte-Carlo simulation in MPSA that gave the smallest objective function values were used to as initial simplex points.

In all six-parameters optimization cases (runs 1–11), the optimized parameter set resulted in a significantly lower objective function value compared to the original set. The three-parameter optimization run also resulted in a lower function value, although it was slightly larger than that of the six-parameter cases. Moreover, in the three-parameter run the number of iterations, which indicates how many times the simplex was regenerated during the APO run, was reduced by almost 50% as compared to the six-parameter cases.

The optimum parameter values obtained by Run 12 were quite similar to those of the six-parameter runs. The simulated hydrograph using the optimized parameter sets (six- and three-parameter cases) are shown in Figure 8.

3.5 Parameter optimization for the global objective

Two cases of parameter optimization for a global objective function were done. Runs 1–3 (Table 9) represent the optimization run using the eight hydrologic and chemical parameters chosen in the sensitivity analysis (ET, ST, KS, TS, EL, EX, PC and NH). Run 4 uses five sensitive parameters; ET, ST, KS and EX, which were evaluated as sensitive at the previous step, and NH. Although NH was not classified as sensitive parameter, it is the only parameter controlling the nitrogen reactions in soil. In runs 1 and 2, the initial simplex points were randomly chosen parameter sets. In runs 3 and 4, the most desirable nine and six parameter sets from MPSA were used as the initial simplex.

The three runs with eight optimized parameters reduced the global objective function value compared to the original parameter sets; run 3 especially gave a small function value.

The five-parameter optimization run also gave a smaller function value; and the number of iterations was reduced to fewer than half as compared to the eight-parameter runs. The simulated hydrograph and chemical changes using optimum parameter sets (eight- and five-parameter cases) are shown in Figures 9, 10.1 and 10.2.

4 Discussion

4.1 Parameter sensitivity for hydrograph

For the Emerald Lake watershed hydrograph, the parameters describing evapotranspiration (ET) and soil thickness (ST) or water storage capacity (TS) are classified as more sensitive rather than the hydraulic conductivity related parameters, which particularly influence an event hydrograph. TE, ST and TS are supposed to exert greater influence on a long-term water budget rather than on an event hydrograph. In the Emerald Lake watershed, snow dominated the water balance during the 1986 and 1987 water year, accounting for 95% of the precipitation, and direct short-term runoff from snowmelt resulted in more than 80% of stream flow. Moreover, 80% of the total release of water was as sublimation from snow surface [Kattelmann and Elder, 1991]. Therefore, during the period of high flow generated by snowmelt (April–August), runoff was supposed to consist mainly of surface runoff rather than subsurface water, and the evaporation rate was quite high. Thus evaporation strongly influenced hydrograph generation in this period. On the other hand, during a low flow period (September–March), the water budget was dominated by release of subsurface water. The amount of event discharge was supposed to be smaller than that of snowmelt season. Thus, the water balance was influenced more by soil water storage factors rather than hydraulic conductivity factors. Moreover, evaporation factors played only small role, because the potential evaporation itself was small in this period.

4.2 Parameter sensitivity for the chemical changes

The sensitivity of parameters depend on which objectives were examined. For instance, for Cl^- concentration change, the parameter EL, which describes ion release rate from snowpack is the only sensitive chemical parameter identified in the MPSA (Table 5). In essence, this shows that the model responds to what we already knew, that Cl^- concentration is influenced by the hydrologic processes like snow melt rather than the chemical reaction such as ion exchange or mineral weathering in soil. For NO_3^- concentration, NH was naturally more sensitive than any other parameter. For the rest of these objectives, PC or EX was classified as the most sensitive parameter. Especially, for Ca^{2+}, Mg^{2+}, K^+ and Na^+, the mineral weathering related parameters such as PC or KI were sensitive. None of these results are counterintuitive or contradictory to the chemical formulations within AHM.

In the eight-parameter MPSA with four hydrologic parameters, all chemical objectives except SO_4^{2-} were sensitive to not only chemical, but also parameters related to soil physical properties (Table 7). For example, for Cl^- concentration, two hydrologic parameters

ET and ST were even more sensitive than was EL.

Moreover, for the objectives influenced by soil chemical parameters such as PC or EX, the soil physical parameters KS, ST, or TS were also classified as sensitive. These are the soil physical parameters that strongly influence the residence time of water in soil.

4.3 Parameter sensitivity for global objective function

Which part of the parameter range that was examined is more desirable can be inferred from the shapes of the distribution curves of acceptable and unacceptable cases (Figures 7.1 through 7.12). For instance, in the case of PC distributions with ANC as the objective (Figure 7.3), most of the acceptable cases lie in the parameter value range of approximately 0.8 to 1.2. Namely, this range can be expected to give more parameter values that are desirable. On the other hand, for the ST, KS and TS distributions, the acceptable frequency increases for values greater than 1.0. Which range should be the most desirable values of sensitive parameters are summarized for each objective in Table 10. The desirable ranges of ET, ST, KS and EX are consistent between different objectives. On the other hand, the desirable ranges of TS and PC differ depending on the objective. For example, PC's desirable range is less than 1.0 for pH and SO_4^{2-}, but more than 1.0 for Ca^{2+} and Mg^{2+}, around 1.0 for ANC.

These desirable ranges for individual objectives directly affect the parameter sensitivity for the global objective. ET, ST, KS and EX, which have no inconsistency in desirable parameter ranges for different objectives were naturally classified as sensitive and their desirable ranges corresponded to those of individual objectives. However TS and PC were not classified as sensitive for the global objective, apparently due to the inconsistencies in desirable ranges for different objectives.

4.4 Optimization of the outflow hydrograph

The optimized parameter sets of run 1 to run 10 (Table 8), which used randomly generated parameter values for initial simplex points, converged to quite a small range of parameter values. Thus, the resulting parameter sets were judged to be quite reliable. Run 11, which used the best seven parameter sets obtained from MPSA, gave a function value as small as the best of those optimized using a randomly chosen initial simplex.

The three-parameter run (run 12) gave a small function value and optimum parameter values that corresponded well to those of the six-parameter runs. In addition, the number of iterations was significantly reduced.

Both of these results show that the sensitivity information obtained from MPSA was certainly effective in reducing the computational load during the optimization process.

4.5 Optimization for the global objective function

As noted above, some parameters had inconsistent desirable parameter ranges for different objectives. For example, although TS's desirable range with the hydrograph as the objective was less than 1.0, for pH or ANC it was greater than 1.0. Thus optimization for only the hydrograph did not necessarily give the optimum hydrologic parameters for the entire hydrochemical calculation. Therefore, the multi-objective optimization was required when the global optimum parameter set was sought.

Table 9 shows that although all three runs changing eight parameters could reduce the global objective function value, those of run 1 and run 2 were not as small as that of run 3. Figure 11 is a comparison of the individual function values of runs 1–4. The values on the horizontal axis were ratio to the function values of the original calculation using empirically determined by Wolford et al. [1994]. From this figure, one sees that the individual function values were not always reduced to less than those of the original empirical fit. For example, the function values of K^+ and NO_3^- in run 1 and ANC, Ca^{2+} and SO_4^{2-} in run 2 were larger than those of the original calculation. This suggests that run 1 and run 2 did not reach the best parameter sets.

According to Table 10, the desirable range of the sensitive parameters for the global objective are less than 1.0 for ET and greater than 1.0 for ST, KS and EX. For NH, which was next the most sensitive parameter (see Table 6-12), the desirable range was less than 1.0. In the case of run 1, the NH value obtained was 1.36. But in this run the function value for NO_3^- was not lower than the empirical fit. Also, in run 2, the obtained ET value was not less than 1.0 but was 1.26; and the function values were not as low for some objectives as in other runs. These two cases (runs 1 and 2) suggest that there were local optima on the objective function field.

In the case of run 3, the searching process apparently avoided being trapped by some local optima, such as in the cases of run 1 and run 2. The run 3 parameter set was the best that we found, though we cannot state that it was the global optimum. However, it appears that an effective way to avoid local optima and to get the best parameter estimates is to use the best parameter sets from the Monte-Carlo MPSA simulations as the initial simplex points.

The parameter set obtained by the five-parameter optimization agreed with the expected ranges from the MPSA for the global objective (Table 10). Although the F values, which indicate the global objective function, was larger than that of run 3, the number of iterations was reduced to fewer than half of that of run 3. This further supports our finding that the information from the parameter sensitivity can efficiently reduce the computational load in the optimization.

4.6 Evaluation of the optimum parameter set using the 1987 data

The validation run of the global optimum parameter set was done using the half year data for the 1987 water year. The parameters tested were ET, ST, KS, TS, EL, EX, PC and NH from on run 3 (Table 9). Table 11 shows the individual objective function values compared to those of empirical fit. The global optimum parameter set calibrated on the 1986 data did reduce the objective function values of outflow hydrograph, Na^+, SO_4^{2-}, silica and NO_3^- concentrations. However, the objective function values in pH, ANC, Ca^{2+}, Mg^{2+} and Cl^- were not reduced. One reason that the values for pH, ANC, Ca^{2+} and Mg^{2+} were not reduced was related to the sensitive parameter PC, representing partial pressure of CO_2 in the soil (see Table 7). The time series of PC values are from observed data. Because the two water years had such different snow accumulation and melt, the 1986's optimum value may not be suitable for 1987 data. The simulated outflow hydrograph and chemical changes are shown in Figures 12.1 and 12.2.

5 Conclusions

From the MPSA result with eight parameters, which included four chemical parameters, it was shown that the hydrograph was not sensitive to any chemical parameters, as expected. However, chemical objectives were sensitive to hydrologic parameter choices, highlighting the need to consider both physical and chemical objectives together when doing parameter estimation. The parameters ET, ST, KS and EX, representing the evapotranspiration function, hydraulic conductivity, water capacity of the soil and ion exchange reactions, respectively, were evaluated as sensitive for the global objective and are thus most important for the calculation of the hydrochemical mass balance. This result is quite consistent with the AHM formulation and empirical optimization done by Wolford et al. [1994].

Comparison of optimization runs for both the outflow hydrograph and the global objective function show that the information gained from the sensitivity analysis was effective in both reducing the computational load of the optimization and finding a more-optimum parameter set.

When applied to the 1987 data, the global optimum parameter set estimated for 1986 provided a small improvement in model fit to the data than did the set estimated empirically by Wolford et al. [1994]. However, the fact that improvements in both the calibration and evaluation years were generally small suggests that the empirical procedure used by Wolford et al. [1994] was both a good approach to parameter estimation for a model with so many adjustable parameters, and a necessary first step to finding the optimum parameter set using an automatic procedure.

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Table 1. Initially selected hydrologic parameters and original values.

	Original value				
	Soil subunit		Talus subunit		
Parameter	Horizon 1	Horizon 2	Horizon 1	Horizon 2	Description
ET	0.90	0.40	1.00	0.60	Maximum fraction of evapotranspiration that can occur relative to potential evapotranspiration
ST (cm)	17.67	17.67	12.46	12.46	Soil thickness
KS (cm day^{-1})	400.00	1.25	400.00	3.50	Saturated hydraulic conductivity
N	1.45	10.00	1.45	10.00	Parameter in the equation expressing unsaturated hydraulic conductivity as a function of soil water content
TS (cm^3 cm^{-3})	0.522	0.522	0.543	0.543	Saturated soil water content
BD (g cm^{-3})	1.267	1.267	1.350	1.350	Bulk density of soil

Table 2. Result of MPSA for the AHM hydrologic calculation.

Objective function criteria	0.994×10^9	1.007×10^9	1.020×10^9
Acceptable cases	168	200	236
Unacceptable cases	232	200	164
Percent acceptable:unacceptable	42:58	50:50	59:41

Parameter	*p* values from K-S test			Sensitive
ET	0.0000	0.0000	0.0027	+
ST	0.0428	0.0026	0.0056	+
N	0.0224	0.0197	0.5552	-
KS	0.0374	0.1324	0.4023	-
TS	0.0000	0.0000	0.0000	+
BD	0.5101	0.8537	0.9768	-

Table 3. Initially selected chemical parameters.

Parameters	Original value		Description
EL			Parameter for the function describing ion release from snowpack
KI[a]	Ca^{2+}	0.50×10^{-6}	Parameter for the function describing mineral weathering
	Mg^{2+}	0.85×10^{-7}	
	K^+	1.15×10^{-7}	
	Na^+	4.15×10^{-7}	
	$SiO_2(OH)_2^{2-}$	1.90×10^{-6}	
	L-2	0.60×10^{-6}	
	H^+	1.50×10^{-6}	
EX for soil subunit[b]	$Al^{3+} + 3(XH) \rightleftharpoons AlX_3 + 3H^+$	-5.32	Exchange coefficients of major cations and anions in soil
	$Ca^{2+} + 2(XH) \rightleftharpoons CaX_2 + 2H^+$	-5.23	
	$Mg^{2+} + 2(XH) \rightleftharpoons MgX_2 + 2H^+$	-5.73	
	$K^+ + XH \rightleftharpoons KX + H^+$	-0.85	
	$Na^+ + XH \rightleftharpoons NaX + H^+$	-3.01	
	$SO_4^{2-} + Y + 2H \rightleftharpoons YH_2SO_4$	17.45	
EX for talus subunit[b]	$Al^{3+} + 3(XH) \rightleftharpoons AlX_3 + 3H^+$	-6.82	
	$Ca^{2+} + 2(XH) \rightleftharpoons CaX_2 + 2H^+$	-6.15	
	$Mg^{2+} + 2(XH) \rightleftharpoons MgX_2 + 2H^+$	-6.00	
	$K^+ + XH \rightleftharpoons KX + H^+$	-1.00	
	$Na^+ + XH \rightleftharpoons NaX + H^+$	-2.95	
	$SO_4^{2-} + Y + 2H \rightleftharpoons YH_2SO_4$	27.63	
PC	Soil subunit	20.4	Partial pressure of CO_2 in soil
	Talus subunit	20.5	
NH	0.989		Parameter for the function describing nitrogen reaction in soil (the fraction of NH_4^+ to convert to organic nitrogen)
NO	10/1/85 - 12/14/85	0.7	Parameter for the function describing nitrogen reaction in soil (the fraction of NO_3^- in excess of base line concentration to convert to organic nitrogen)
	1		
	12/15/85 - 6/30/86	-0.7	
	7/15/86 - 9/30/86	0.9	

[a] KI is the parameter for the kinetic reaction. These ions belong to AHM type-1 species.
[b] EX is the thermodynamic $\log_{10}K$ value of association for the main species in each reaction. K values were varied in the parameter estimation, rather than the $\log_{10}$ values themselves.
[c] PC controls changes to partial pressure of CO_2. The K value for CO_2 is the sum of the Henry's law constant and dissociation of CO_2 to CO_3^{2-}. K value itself was varied in the parameter examination.

Table 4.1. Results of MPSA for pH.

Objective function criteria	1.34	1.47	1.72
Acceptable cases	136	200	267
Unacceptable cases	264	200	133
Percent acceptable:unacceptable	34:68	50:50	67:33

Parameter	*p* values from K-S test			Sensitive
EL	0.1019	0.5272	0.2487	-
KI	0.2751	0.6107	0.9297	-
EX	0.4153	0.3767	0.3382	-
PC	0.0000	0.0000	0.0000	+
NH	0.9116	0.6959	0.1514	-
NO	0.2214	0.9154	0.1574	-

Table 4.2. Results of MPSA for ANC.

Objective function criteria	1700	2125	2500
Acceptable cases	148	200	246
Unacceptable cases	252	200	154
Percent acceptable:unacceptable	37:63	50:50	62:38

Parameter	*p* values from K-S test			Sensitive
EL	0.2564	0.2078	0.2776	-
KI	0.7541	0.5272	0.1871	-
EX	0.5719	0.6959	0.5978	-
PC	0.0000	0.0000	0.0000	+
NH	0.8036	0.1668	0.0453	-
NO	0.1868	0.0623	0.0445	-

Table 4.3. Results of MPSA for Ca^{2+}

Objective function criteria	510	600	750
Acceptable cases	148	200	248
Unacceptable cases	252	200	152
Percent acceptable:unacceptable	37:63	50:50	62:38

Parameter	p values from K-S test			Sensitive
EL	0.3977	0.1324	0.3147	-
KI	0.4957	0.6959	0.2377	-
EX	0.1170	0.4486	0.0010	-
PC	0.0000	0.0000	0.0000	+
NH	0.6934	0.6107	0.8940	-
NO	0.0520	0.0358	0.0866	-

Table 4.4. Results of MPSA for Mg^{2+}.

Objective function criteria	38.0	42.6	55.0
Acceptable cases	153	199	258
Unacceptable cases	247	201	142
Percent acceptable:unacceptable	38:62	50:50	65:35

Parameter	*p* values from K-S test			Sensitive
EL	0.9959	0.3302	0.7955	-
KI	0.5805	0.8272	0.1094	-
EX	0.2832	0.0011	0.0000	+
PC	0.0000	0.0000	0.0000	+
NH	0.9735	0.7968	0.9672	-
NO	0.6883	0.7569	0.7881	-

Table 4.5. Results of MPSA for K^+.

Objective function criteria	67	82	126
Acceptable cases	147	199	262
Unacceptable cases	253	201	138
Percent acceptable:unacceptable	37:63	50:50	66:34

Parameter	*p* values from K-S test			Sensitive
EL	0.8815	0.5664	0.5264	-
KI	0.2285	0.0030	0.0031	+
EX	0.0000	0.0000	0.0000	+
PC	0.0000	0.0000	0.0017	+
NH	0.3670	0.2332	0.9948	-
NO	0.4967	0.5399	0.1530	-

Table 4.6. Results of MPSA for Na^+.

Objective function criteria	500	525	570
Acceptable cases	153	200	248
Unacceptable cases	247	200	152
Percent acceptable:unacceptable	38:62	50:50	62:38

Parameter	*p* values from K-S test			Sensitive
EL	0.3637	0.4486	0.3646	-
KI	0.0000	0.0000	0.0001	+
EX	0.0000	0.0000	0.0000	+
PC	0.1189	0.3124	0.0120	-
NH	0.7380	0.9154	0.8813	-
NO	0.8871	0.8537	0.0981	-

Table 4.7. Results of MPSA for SO_4^{2-}.

Objective function criteria	87	117	165
Acceptable cases	151	200	245
Unacceptable cases	249	200	155
Percent acceptable:unacceptable	38:62	50:50	61:39

Parameter	*p* values from K-S test			Sensitive
EL	0.5876	0.5272	0.5682	-
KI	0.0176	0.7787	0.0940	-
EX	0.0000	0.0000	0.0000	+
PC	0.0050	0.1668	0.0114	-
NH	0.8368	0.8537	0.6816	-
NO	0.6733	0.9596	0.3318	-

Table 4.8. Results of MPSA for Cl^-.

Objective function criteria	554	555	556
Acceptable cases	158	198	252
Unacceptable cases	242	202	148
Percent acceptable:unacceptable	40:60	50:50	63:37

Parameter	*p* values from K-S test			Sensitive
EL	0.0000	0.0000	0.0000	+
KI	0.4933	0.9116	0.5443	-
EX	0.5899	0.8896	0.9516	-
PC	0.3790	0.6652	0.2787	-
NH	0.9166	0.8403	0.7284	-
NO	0.2399	0.1939	0.3747	-

Table 4.9. Results of MPSA for silica.

Objective function criteria	3100	3430	4500
Acceptable cases	147	200	243
Unacceptable cases	253	200	157
Percent acceptable:unacceptable	37:63	50:50	61:39

Parameter	*p* values from K-S test			Sensitive
EL	0.7568	0.6959	0.5730	-
KI	0.0309	0.2562	0.4191	-
EX	0.0000	0.0000	0.0000	+
PC	0.2153	0.3767	0.4911	-
NH	0.5796	0.9855	0.9945	-
NO	0.3509	0.1040	0.0753	-

Table 4.10. Results of MPSA for NO_3^-.

Objective function criteria	198	210	222
Acceptable cases	150	200	249
Unacceptable cases	250	200	151
Percent acceptable:unacceptable	38:62	50:50	62:38

Parameter	p values from K-S test			Sensitive
EL	0.9357	0.5272	0.1398	-
KI	0.1684	0.4486	0.5331	-
EX	0.6783	0.9855	0.5946	-
PC	0.9095	0.9966	0.4989	-
NH	0.0000	0.0000	0.0000	+
NO	0.5686	0.7787	0.7790	-

Table 5. Sensitive parameters for each chemical objective.

Objective	Sensitive parameters
pH	PC
ANC	PC
Ca^{2+}	PC
Mg^{2+}	PC, EX
K^+	EX, PC, KI
Na^+	EX, KI
SO_4^{2-}	EX
Cl^-	EL
Silica	EX
NO_3^-	NH

Table 6.1. Results of MPSA for outflow hydrograph.

Objective function criteria	0.985×10^9	1.007×10^9	1.030×10^9
Acceptable cases	148	199	250
Unacceptable cases	252	201	150
Percent acceptable:unacceptable	37:63	50:50	63:37

Parameter	p values from K-S test			Sensitive
ET	0.0000	0.0000	0.0001	+
ST	0.1343	0.0115	0.0003	-
KS	0.0150	0.0550	0.8056	-
TS	0.0000	0.0000	0.0000	+
EL	0.3832	0.3041	0.5051	-
EX	0.9863	0.6123	0.9847	-
PC	0.7057	0.9960	0.6121	-
NH	0.2045	0.9456	0.9657	-

Table 6.2. Results of MPSA for pH.

Objective function criteria	1.570	1.812	2.100
Acceptable cases	146	199	253
Unacceptable cases	254	201	147
Percent acceptable:unacceptable	37:63	50:50	63:37

Parameter	p values from K-S test			Sensitive
ET	0.0003	0.0267	0.1544	-
ST	0.0000	0.0000	0.0000	+
KS	0.0000	0.0000	0.0000	+
TS	0.0000	0.0000	0.0000	+
EL	0.6643	0.9882	0.2903	-
EX	0.1784	0.9006	0.0901	-
PC	0.0000	0.0000	0.0000	+
NH	0.0853	0.0824	0.6444	-

Table 6.3. Results of MPSA for ANC.

Objective function criteria	2400	3150	3900
Acceptable cases	145	200	259
Unacceptable cases	255	200	141
Percent acceptable:unacceptable	36:64	50:50	65:35

Parameter	p values from K-S test			Sensitive
ET	0.0966	0.0809	0.0802	-
ST	0.0000	0.0000	0.0000	+
KS	0.0000	0.0000	0.0016	+
TS	0.0000	0.0000	0.0000	+
EL	0.5723	0.2078	0.8554	-
EX	0.5506	0.2078	0.7319	-
PC	0.0000	0.0000	0.0000	+
NH	0.0736	0.0358	0.1706	-

Table 6.4. Results of MPSA for Ca^{2+}.

Objective function criteria	750	945	1250
Acceptable cases	147	199	255
Unacceptable cases	253	201	145
Percent acceptable:unacceptable	37:63	50:50	64:36

Parameter	*p* values from K-S test			Sensitive
ET	0.1270	0.3635	0.1391	-
ST	0.0349	0.0136	0.2797	-
KS	0.0000	0.0000	0.0018	+
TS	0.2963	0.0866	0.2297	-
EL	0.7765	0.9618	0.5314	-
EX	0.4877	0.4067	0.5103	-
PC	0.0000	0.0000	0.0000	+
NH	0.3577	0.6887	0.5636	-

Table 6.5. Results of MPSA for Mg^{2+}.

Objective function criteria	48.0	56.2	65.0
Acceptable cases	150	199	238
Unacceptable cases	250	201	162
Percent acceptable:unacceptable	38:62	50:50	60:40

Parameter	*p* values from K-S test			Sensitive
ET	0.4257	0.4859	0.5185	-
ST	0.5259	0.9369	0.8606	-
KS	0.0000	0.0001	0.0819	+
TS	0.0087	0.0012	0.0000	+
EL	0.9095	0.7014	0.5569	-
EX	0.0970	0.0541	0.0114	-
PC	0.0000	0.0000	0.0000	+
NH	0.1684	0.2279	0.3318	-

Table 6.6. Results of MPSA for K^+.

Objective function criteria	110	155	225
Acceptable cases	152	199	258
Unacceptable cases	248	201	142
Percent acceptable:unacceptable	38:62	50:50	65:35

Parameter	*p* values from K-S test			Sensitive
ET	0.9857	0.9154	0.1857	-
ST	0.0000	0.0000	0.0000	+
KS	0.0226	0.2173	0.0044	-
TS	0.0000	0.0000	0.0000	+
EL	0.8305	0.9536	0.2869	-
EX	0.0000	0.0000	0.0000	+
PC	0.0016	0.0624	0.0483	-
NH	0.4913	0.4013	0.9132	-

Table 6.7. Results of MPSA for Na^+.

Objective function criteria	530	610	720
Acceptable cases	147	200	251
Unacceptable cases	253	200	149
Percent acceptable:unacceptable	37:63	50:50	63:37

Parameter	*p* values from K-S test			Sensitive
ET	0.0001	0.0002	0.0020	+
ST	0.0000	0.0000	0.0000	+
KS	0.4824	0.0475	0.0914	-
TS	0.8864	0.9154	0.7143	-
EL	0.6315	0.6959	0.2768	-
EX	0.0000	0.0000	0.0000	+
PC	0.3281	0.1324	0.0347	-
NH	0.7154	0.7787	0.9266	-

Table 6.8. Results of MPSA for SO_4^{2-}.

Objective function criteria	180.0	200.5	350.0
Acceptable cases	178	200	245
Unacceptable cases	222	200	155
Percent acceptable:unacceptable	45:55	50:50	61:39

Parameter	*p* values from K-S test			Sensitive
ET	0.7073	0.3767	0.3222	-
ST	0.0414	0.1040	0.2660	-
KS	0.0033	0.0267	0.3021	-
TS	0.1943	0.3767	0.7632	-
EL	0.0068	0.0053	0.0094	+
EX	0.0000	0.0000	0.0000	+
PC	0.0116	0.0001	0.0000	+
NH	0.1495	0.6107	0.7527	-

Table 6.9. Results of MPSA for Cl^-.

Objective function criteria	480	527	620
Acceptable cases	142	200	251
Unacceptable cases	258	200	149
Percent acceptable:unacceptable	36:64	50:50	63:37

Parameter	*p* values from K-S test			Sensitive
ET	0.0086	0.0012	0.0000	+
ST	0.0000	0.0000	0.0000	+
KS	0.8621	0.2562	0.0543	-
TS	0.8052	0.0809	0.0032	-
EL	0.5900	0.7787	0.3046	-
EX	0.8284	0.2078	0.7561	-
PC	0.9188	0.5272	0.6404	-
NH	0.9988	0.2078	0.9294	-

Table 6.10. Results of MPSA for silica.

Objective function criteria	4500	5320	6600
Acceptable cases	156	199	243
Unacceptable cases	244	201	157
Percent acceptable:unacceptable	39:61	50:50	61:39

Parameter	*p* values from K-S test			Sensitive
ET	0.0093	0.0075	0.4726	+
ST	0.0000	0.0102	0.0236	-
KS	0.0007	0.0359	0.4698	-
TS	0.0512	0.4730	0.8209	-
EL	0.2629	0.0188	0.0170	-
EX	0.0000	0.0000	0.0000	+
PC	0.5904	0.2758	0.5210	-
NH	0.5092	0.8050	0.9183	-

Table 6.11. Results of MPSA for NO_3^-.

Objective function criteria	250	295	350
Acceptable cases	141	200	257
Unacceptable cases	259	200	143
Percent acceptable:unacceptable	35:65	50:50	64:36

Parameter	*p* values from K-S test			Sensitive
ET	0.9325	0.6107	0.1835	-
ST	0.0000	0.0000	0.0000	+
KS	0.0000	0.0000	0.0000	+
TS	0.0000	0.0000	0.0000	+
EL	0.9429	0.2562	0.9610	-
EX	0.6127	0.6107	0.3407	-
PC	0.3026	0.3767	0.9355	-
NH	0.0000	0.0000	0.0000	+

Table 6.12. Results of MPSA for global objective function.

Objective function criteria	1.55	1.84	2.2
Acceptable cases	148	199	254
Unacceptable cases	252	201	146
Percent acceptable:unacceptable	37:63	50:50	64:36

Parameter	p values from K-S test			Sensitive
ET	0.0012	0.0000	0.0010	+
ST	0.0000	0.0000	0.0000	+
KS	0.0004	0.0000	0.0024	+
TS	0.3691	0.6605	0.2475	-
EL	0.3947	0.4816	0.7225	-
EX	0.0000	0.0000	0.0000	+
PC	0.0450	0.1815	0.5979	-
NH	0.0203	0.0531	0.2773	-

Table 7. Sensitive parameters for the AHM calculation.

	Sensitive parameters	
Objective	Hydrologic	Chemical
Hydrograph	ET, TS	—
pH	TS, ST, KS	PC
ANC	ST, TS, KS	PC
Ca^{2+}	KS	PC
Mg^{2+}	KS, TS	PC
K^+	ST, TS	EX
Na^+	ST, ET	EX
SO_4^{2-}	—	EX, PC, EL
Cl^-	ST, ET	—
Silica	ET	EX
NO_3^-	KS, ST, TS	NH
Global	ST, KS, ET	EX

Table 8. The optimization results for the outflow hydrograph.[a]

	Optimum parameter value.[b]							
Run	ET	ST	N	KS	TS	BD	$f(10^8)$	
Original	1.0	1.0	1.0	1.0	1.0	1.0	9.951	Iterations
Parameter range	0.5–1.5	0.5–1.5	0.8–1.8	0.5–1.5	0.5–1.5	0.5–1.5	–	
Run 1	0.501	0.566	1.001	1.457	1.160	0.891	9.094	72
Run 2	0.500	0.638	0.990	1.475	1.073	0.817	9.096	116
Run 3	0.501	0.685	1.007	1.295	0.999	0.875	9.109	88
Run 4	0.500	0.664	1.001	1.466	1.031	0.534	9.098	85
Run 5	0.500	0.591	1.006	1.433	1.114	1.144	9.095	80
Run 6	0.512	0.927	1.027	1.385	0.795	1.482	9.128	89
Run 7	0.500	0.795	0.972	1.397	0.899	0.593	9.108	82
Run 8	0.502	0.517	1.004	1.483	1.263	1.375	9.093	117
Run 9	0.551	0.501	1.295	1.491	1.372	0.511	9.178	114
Run 10	0.501	0.569	1.006	1.463	1.159	0.571	9.094	121
Run 11	0.500	0.587	0.994	1.451	1.127	1.498	9.095	127
Run 12	0.503	0.500	1.0[c]	1.0[c]	1.243	1.0[c]	9.197	51

[a] In runs 1–10, the initial simplex points were randomly determined. The most desirable 7 and 4 parameter sets that were obtained from the MPSA were used to give the initial simplex points in runs 11 and 12, respectively.

[b] 1.0 is value from Wolford et al. [1994].

[c] In run 12, N, KS and BD were fixed at 1.0.

Table 9. The optimization results for the global objective.[a]

	Optimum parameter value.[b]									
Run	ET	ST	KS	TS	EL	EX	PC	NH	F	Iterations
Original	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.8153	-
Parameter range		0.5-1.5	0.5-1.5	0.5-1.5	0.5-1.5	0.5-1.5	0.5-1.5	0.5-1.5	0.5-1.5	-
Run 1	0.51	1.25	1.50	0.75	0.84	1.20	1.01	1.36	0.4501	183
Run 2	1.26	1.49	1.20	0.62	0.75	1.27	0.85	0.74	0.6014	168
Run 3	0.50	1.42	1.29	0.68	1.39	1.33	0.86	0.50	0.2533	167
Parameter range	0.5-1.5	0.5-1.5	0.5-1.5	-	-	0.5-1.5	-	0.5-1.5	-	-
Run 4	0.53	1.22	1.50	1.0[c]	1.0[c]	1.30	1.0[c]	0.62	0.4469	82

[a] In Run 1 and 2, the initial simplex points were randomly determined. The most desirable 9 and 6 parameter sets which were obtained from the MPSA were used to give the initial simplex points in Run 3 and 4, respectively.

[b] 1.0 is value from Wolford et al. [1994].

[c] In run 12, N, KS and BD were fixed at 1.0.

Table 10. The desirable range of each sensitive parameter.

Objective	ET	ST	KS	TS	EL	EX	PC	NH
Hydrograph	<1.0	–	–	<1.0	–	–	–	–
pH	–	>1.0	>1.0	>1.0	–	–	<1.0	–
ANC	–	>1.0	>1.0	>1.0	–	–	$\simeq$1.0	–
Ca^{2+}	–	–	>1.0	–	–	–	>1.0	–
Mg^{2+}	–	–	>1.0	<1.0	–	–	>1.0	–
K^+	–	>1.0	–	>1.0	–	>1.0	–	–
Na^+	<1.0	>1.0	–	–	–	>1.0	–	–
SO_4^{2-}	–	–	–	–	<1.0	>1.0	<1.0	–
Cl^-	<1.0	>1.0	–	–	–	–	–	–
Silica	<1.0	–	–	–	–	>1.0	–	–
NO_3^-	–	>1.0	>1.0	>1.0	–	–	–	<1.0
Global	<1.0	>1.0	>1.0	–	–	>1.0	–	–

Table 11. The objective function values of the validation run of the optimum parameter set.

Objective	Original parameters	Optimum parameters	1986
Hydrograph	6.598×10^7	6.033×10^7	reduced
pH	0.9718	1.0110	
ANC	2314	2795	
Ca^{2+}	1189	1266	
Mg^{2+}	66.34	69.05	
K^+	380.2	390.5	
Na^+	359.3	320.3	reduced
SO_4^{2-}	506.5	459.5	reduced
Cl^-	361.9	515.1	
Silica	3705	1458	reduced
NO_3^-	538.3	466.5	reduced

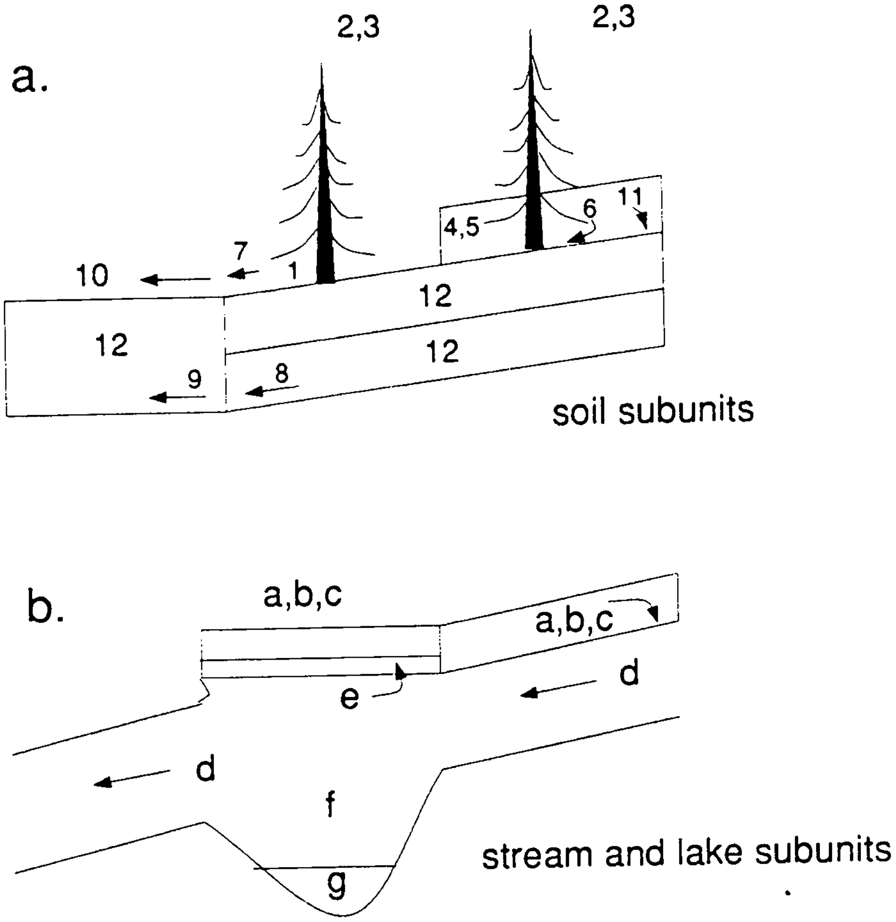


Figure 1: Conceptual diagram of the Alpine Hydrochemical Model.

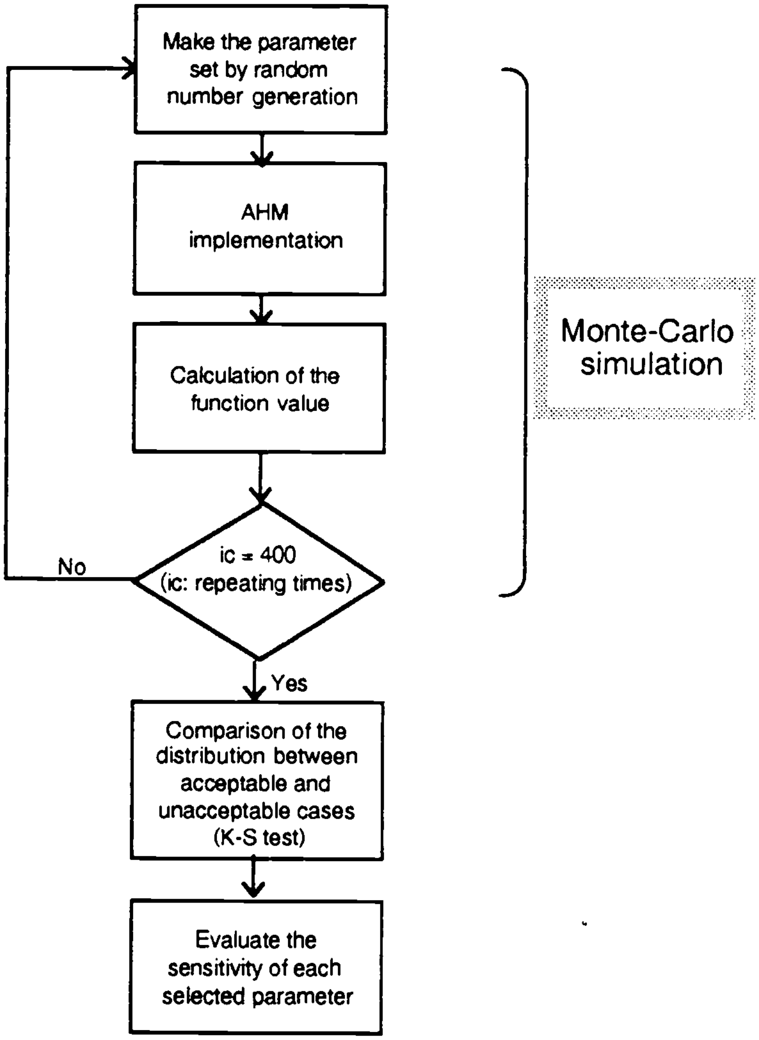


Figure 2: Flow chart of the multi-parametric sensitivity analysis.

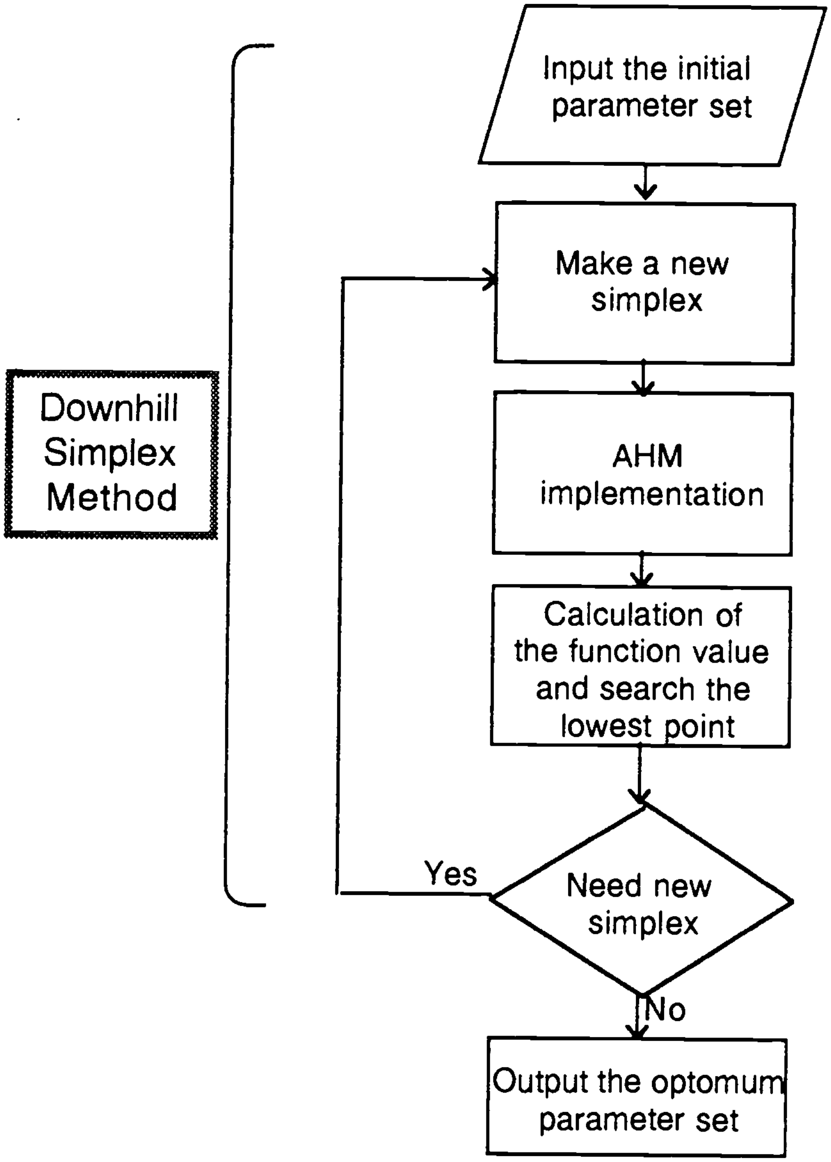


Figure 3: Flow chart of the automatic parameter optimization.

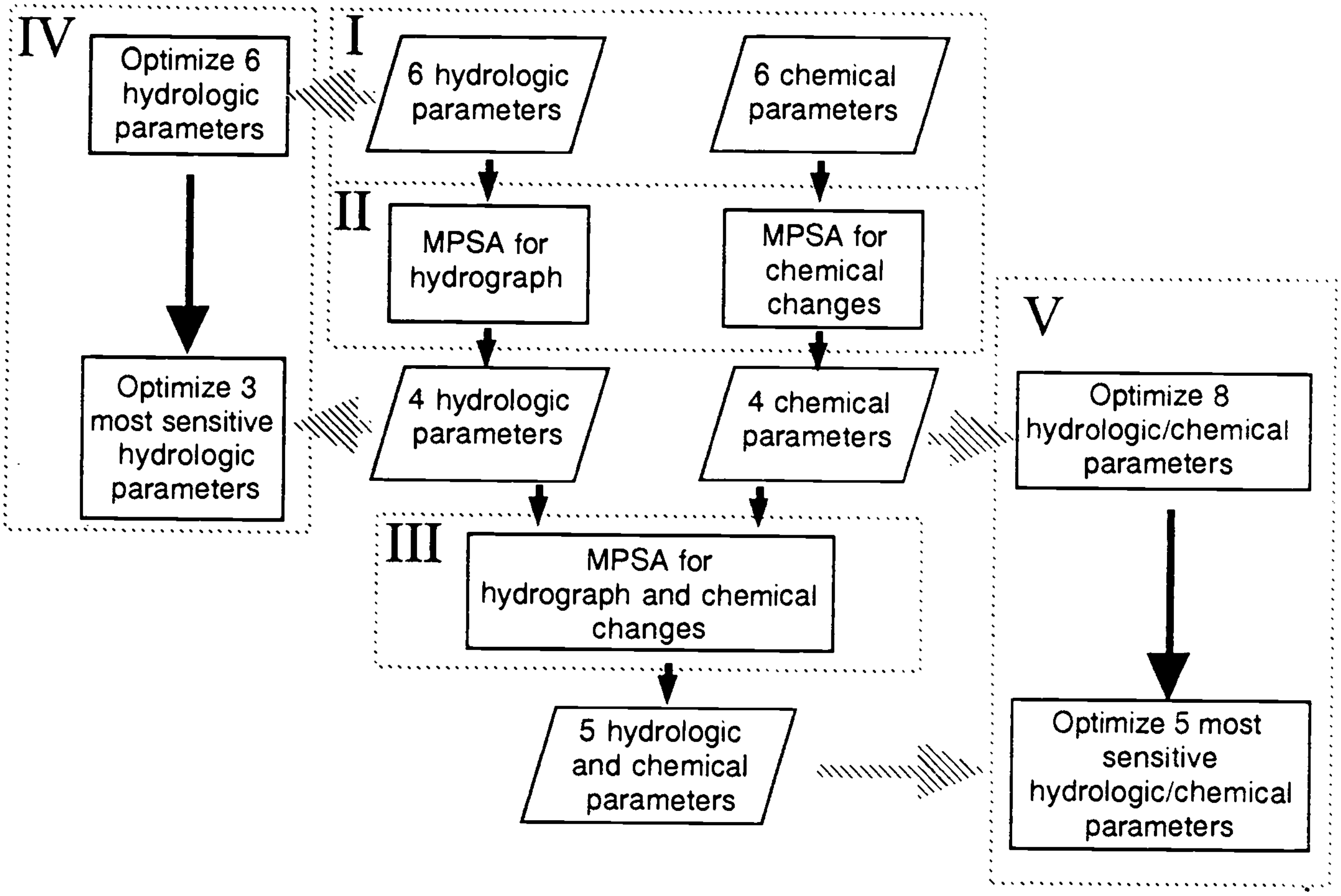


Figure 4: Schematic diagram of parameter estimation process.

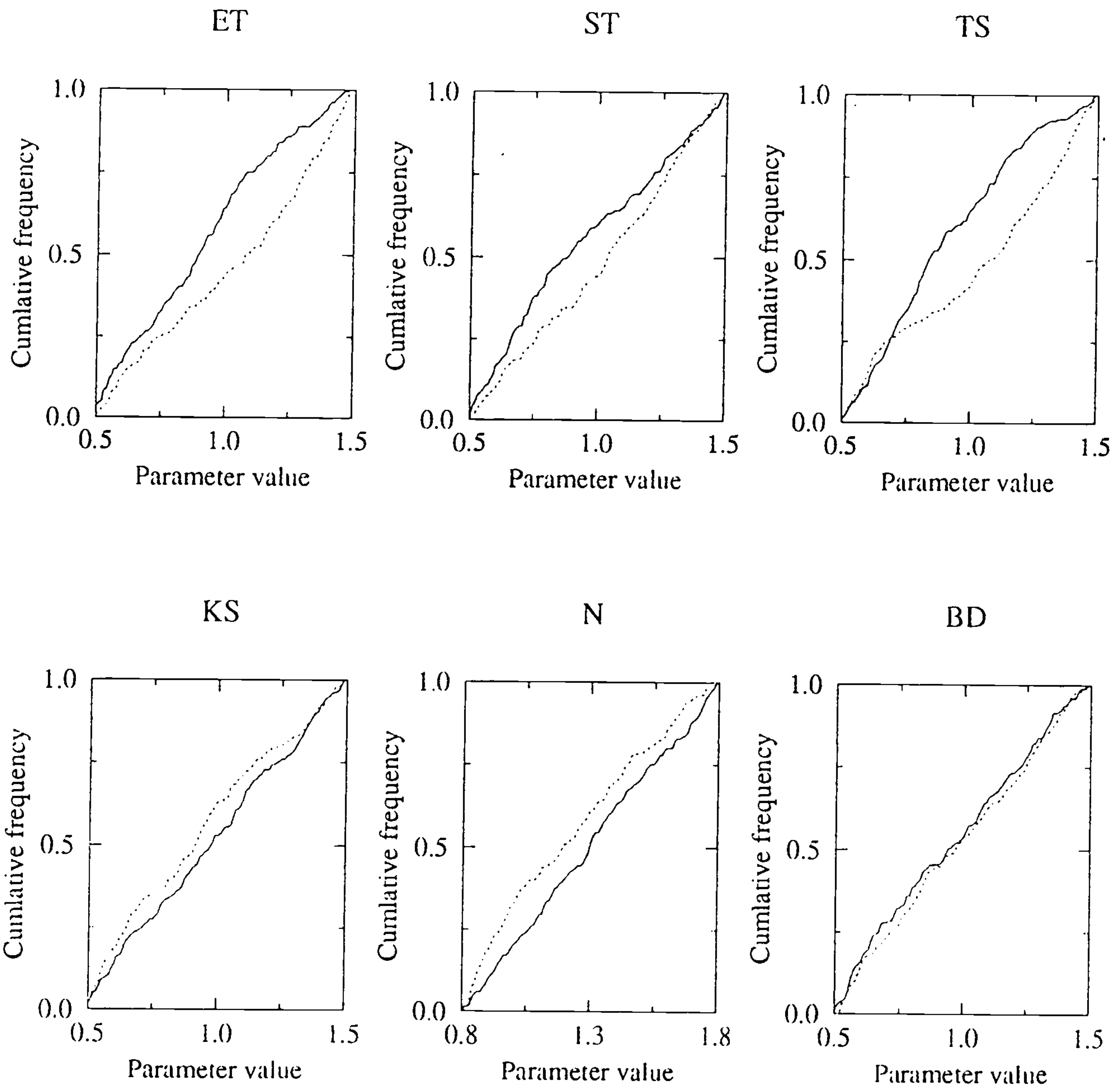


Figure 5: The two cumulative distributions for six soil hydrologic parameters; acceptable (——) and unacceptable (......).

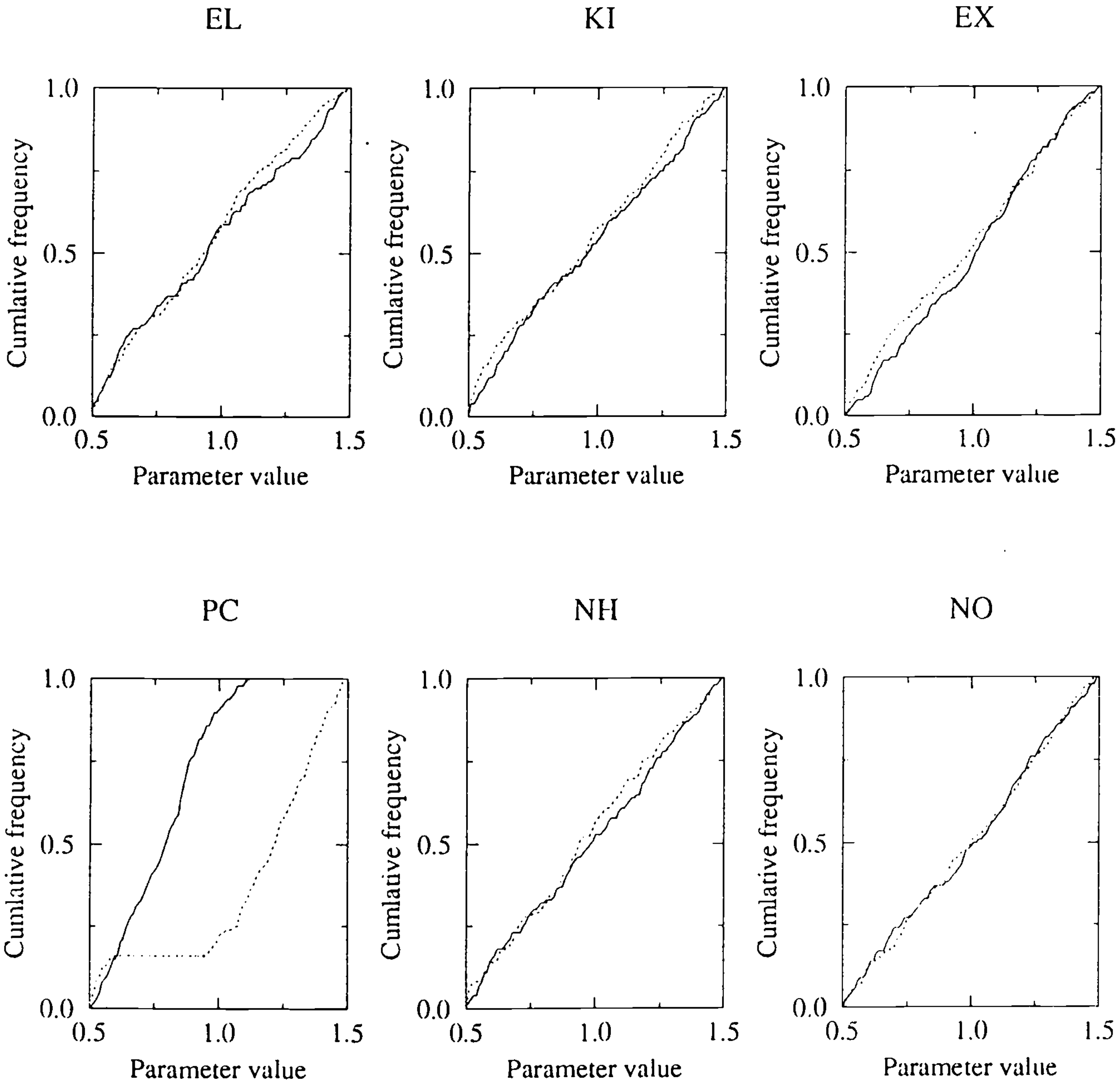


Figure 6.1: The two cumulative distributions for six soil hydrologic parameters. with pH as objective function; acceptable (——) and unacceptable (......).

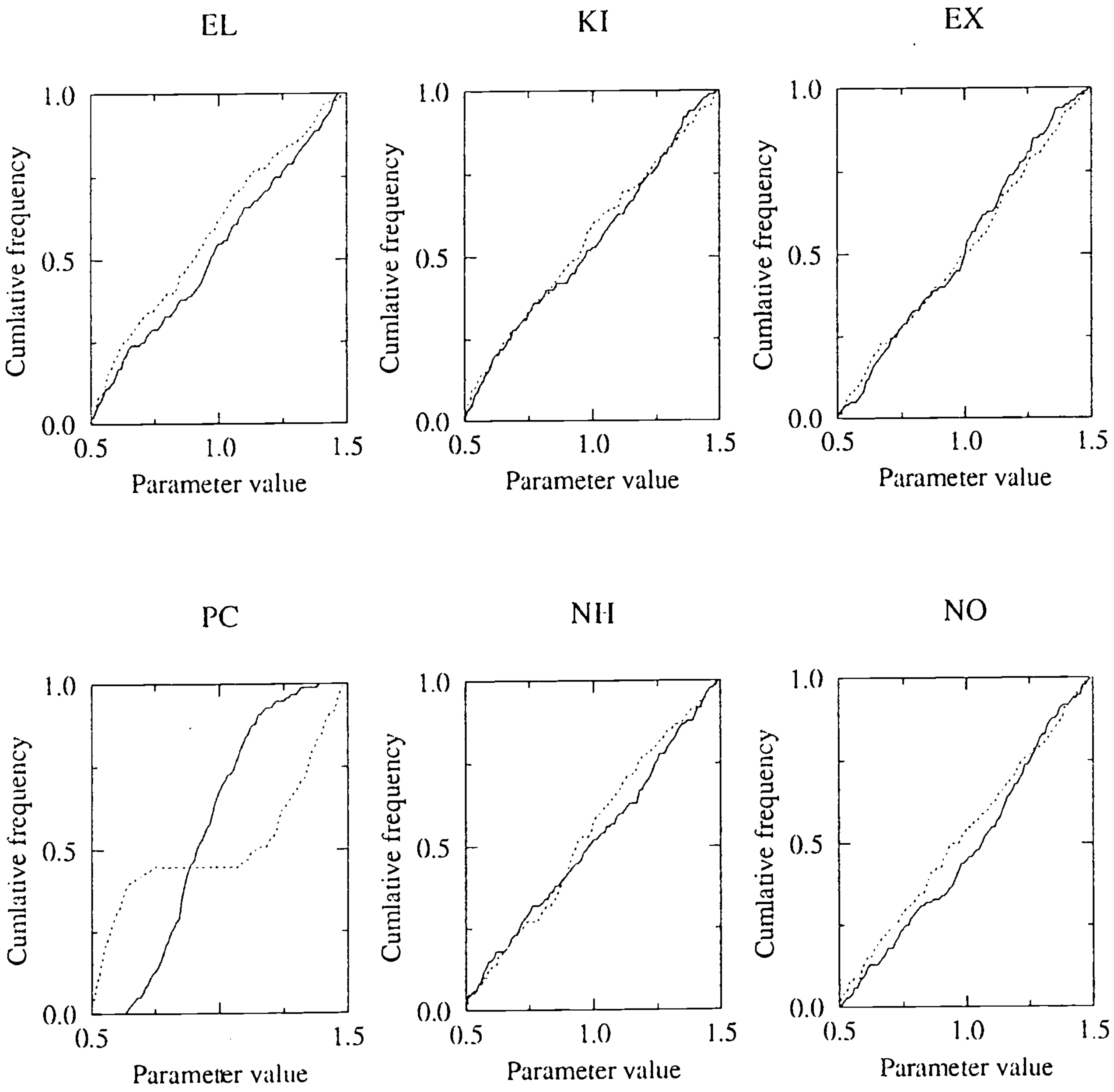


Figure 6.2: The two cumulative distributions for six soil hydrologic parameters, with ANC as objective function; acceptable (——) and unacceptable (......).

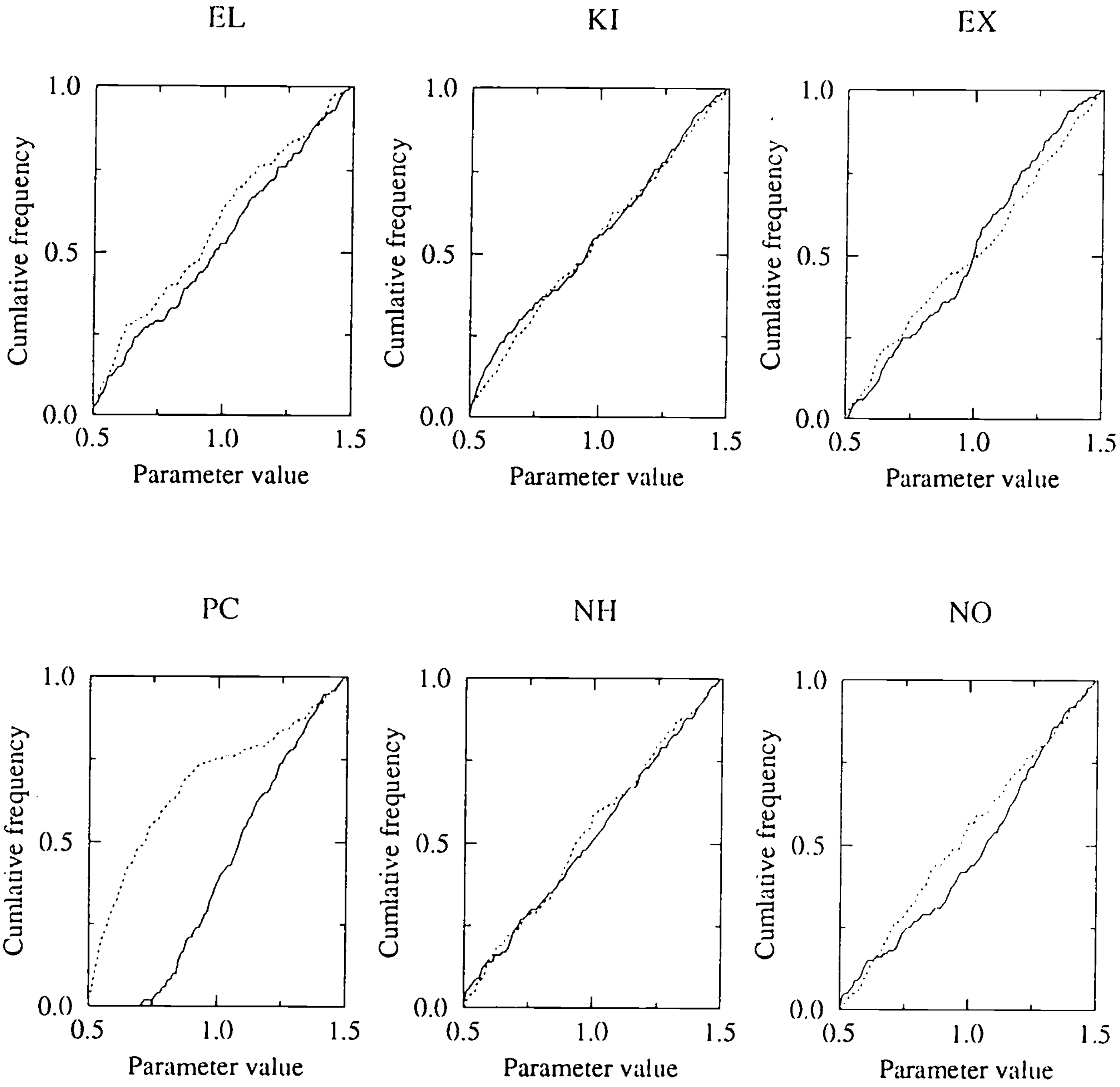


Figure 6.3: The two cumulative distributions for six soil hydrologic parameters, with Ca^{2+} as objective function; acceptable (——) and unacceptable (......).

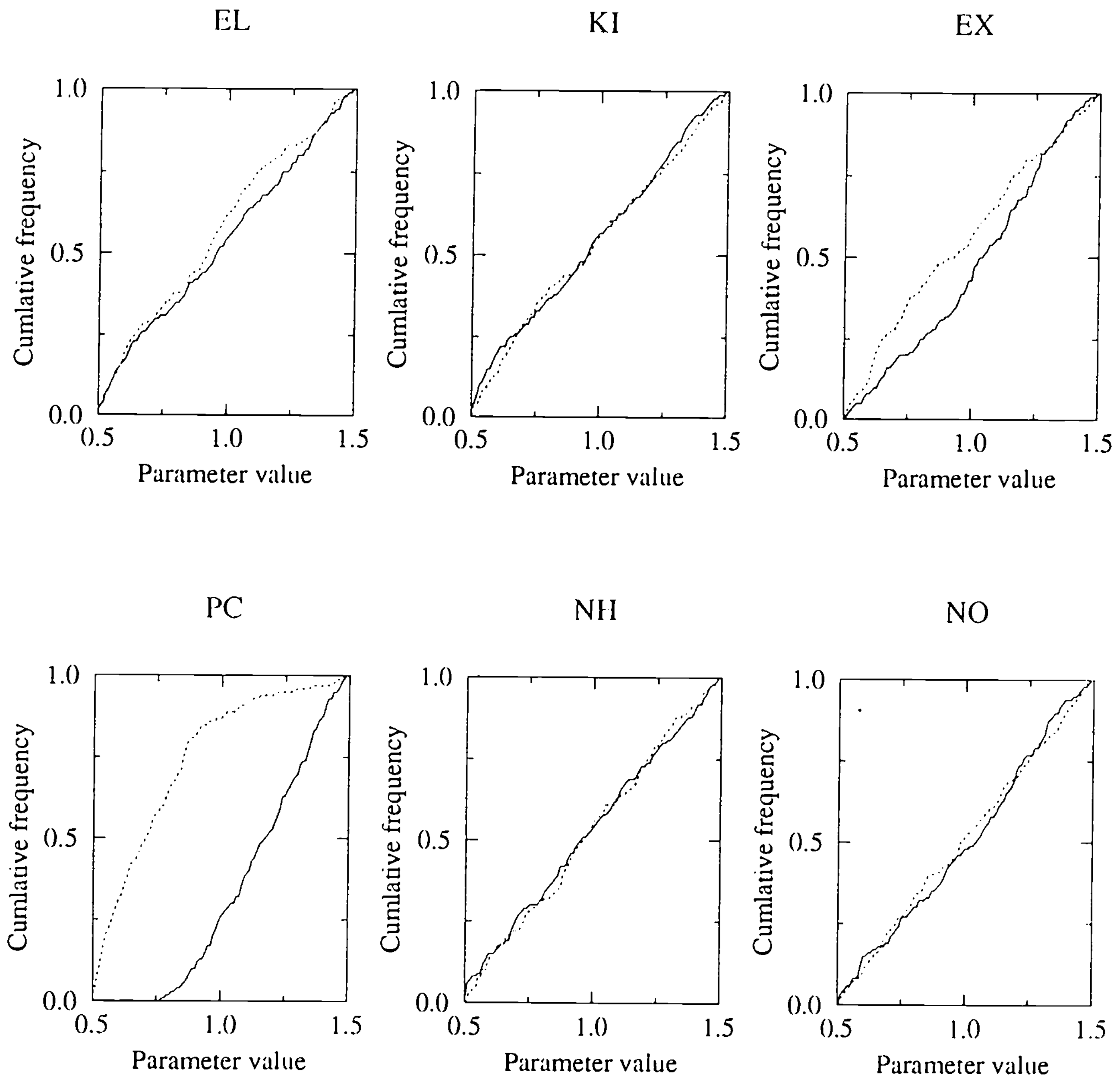


Figure 6.4: The two cumulative distributions for six soil hydrologic parameters, with Mg^{2+} as objective function; acceptable (——) and unacceptable (......).

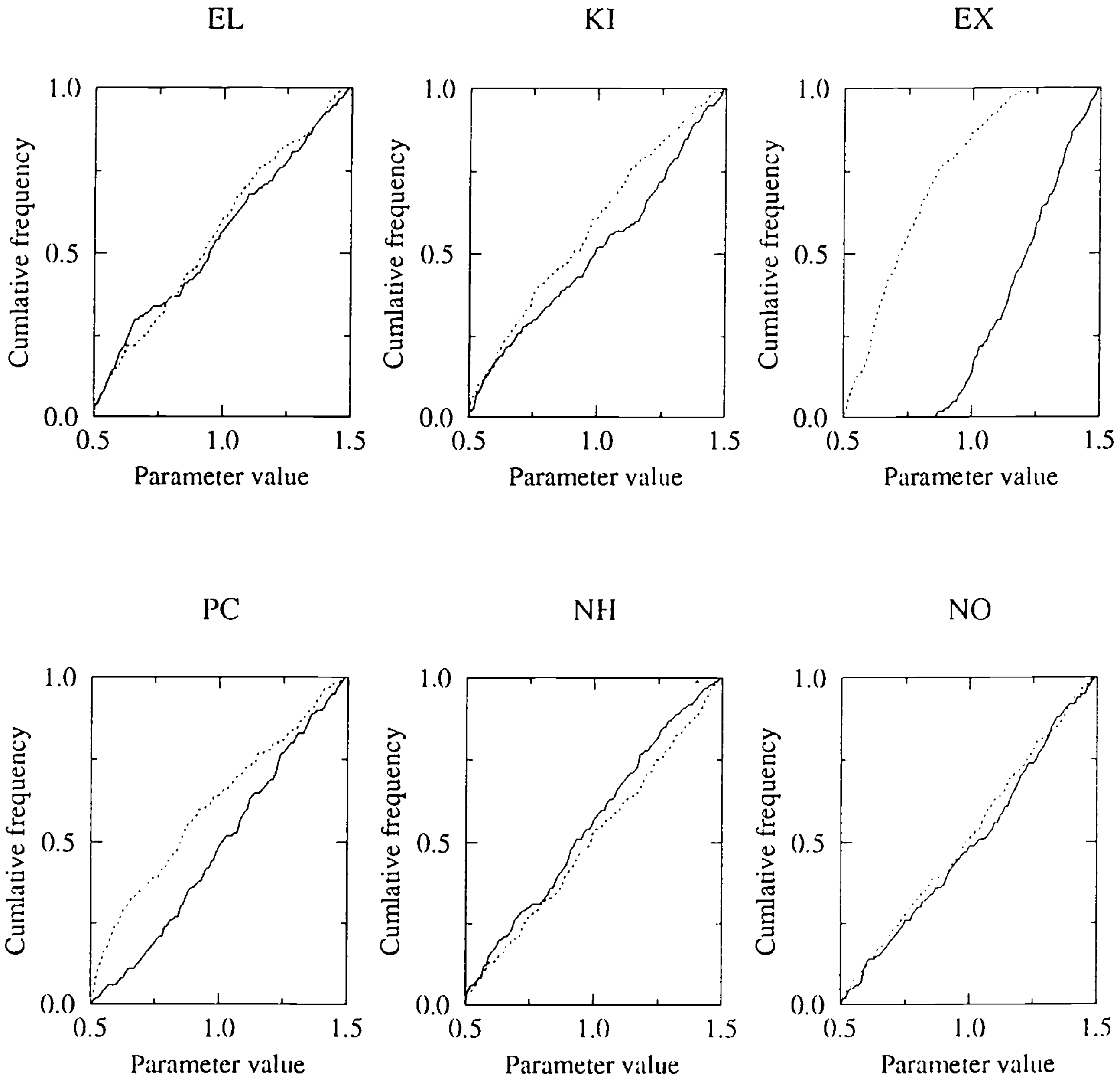


Figure 6.5: The two cumulative distributions for six soil hydrologic parameters, with K^+ as objective function; acceptable (——) and unacceptable (......).

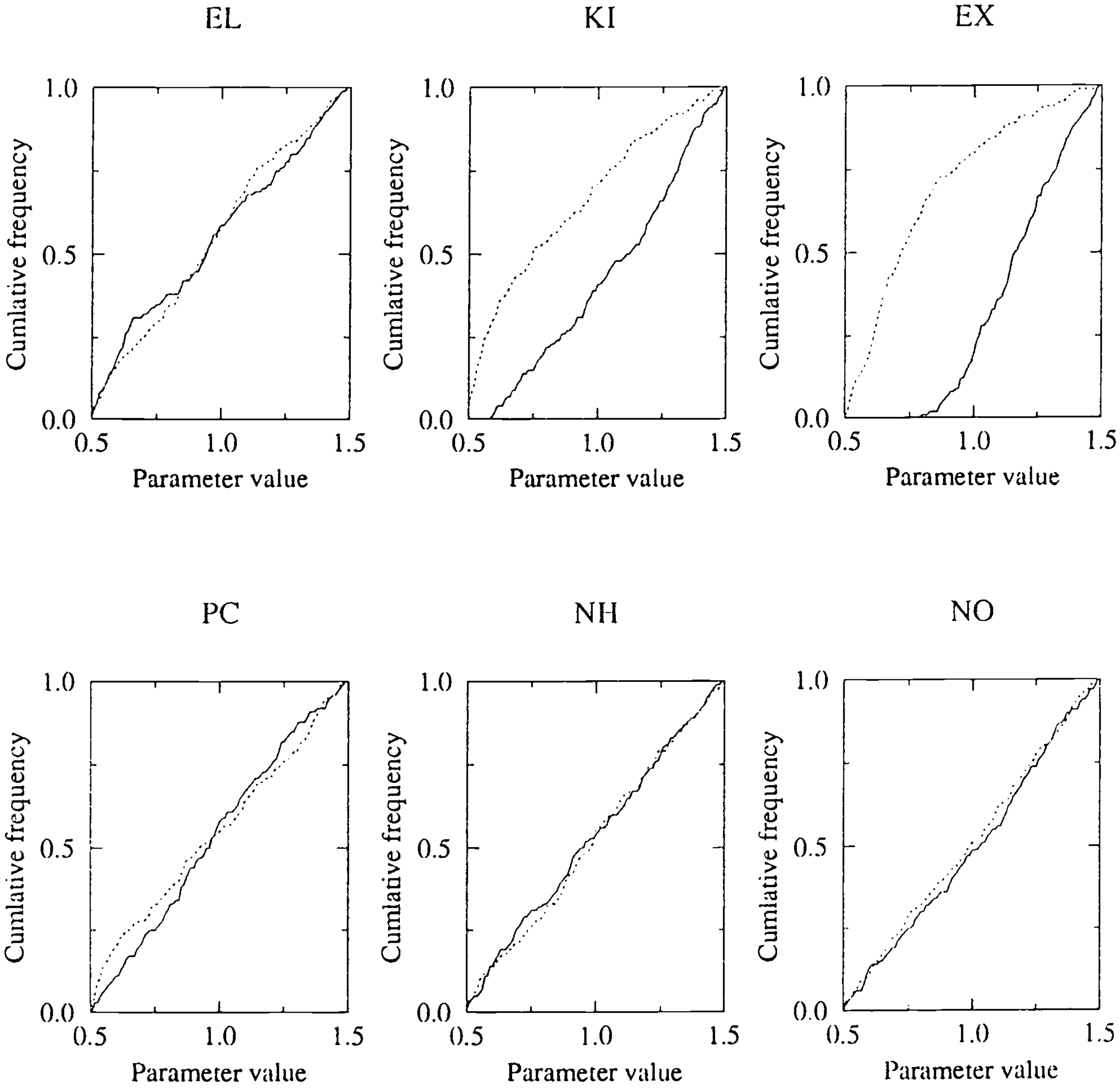


Figure 6.6: The two cumulative distributions for six soil hydrologic parameters, with Na^+ as objective function; acceptable (——) and unacceptable (......).

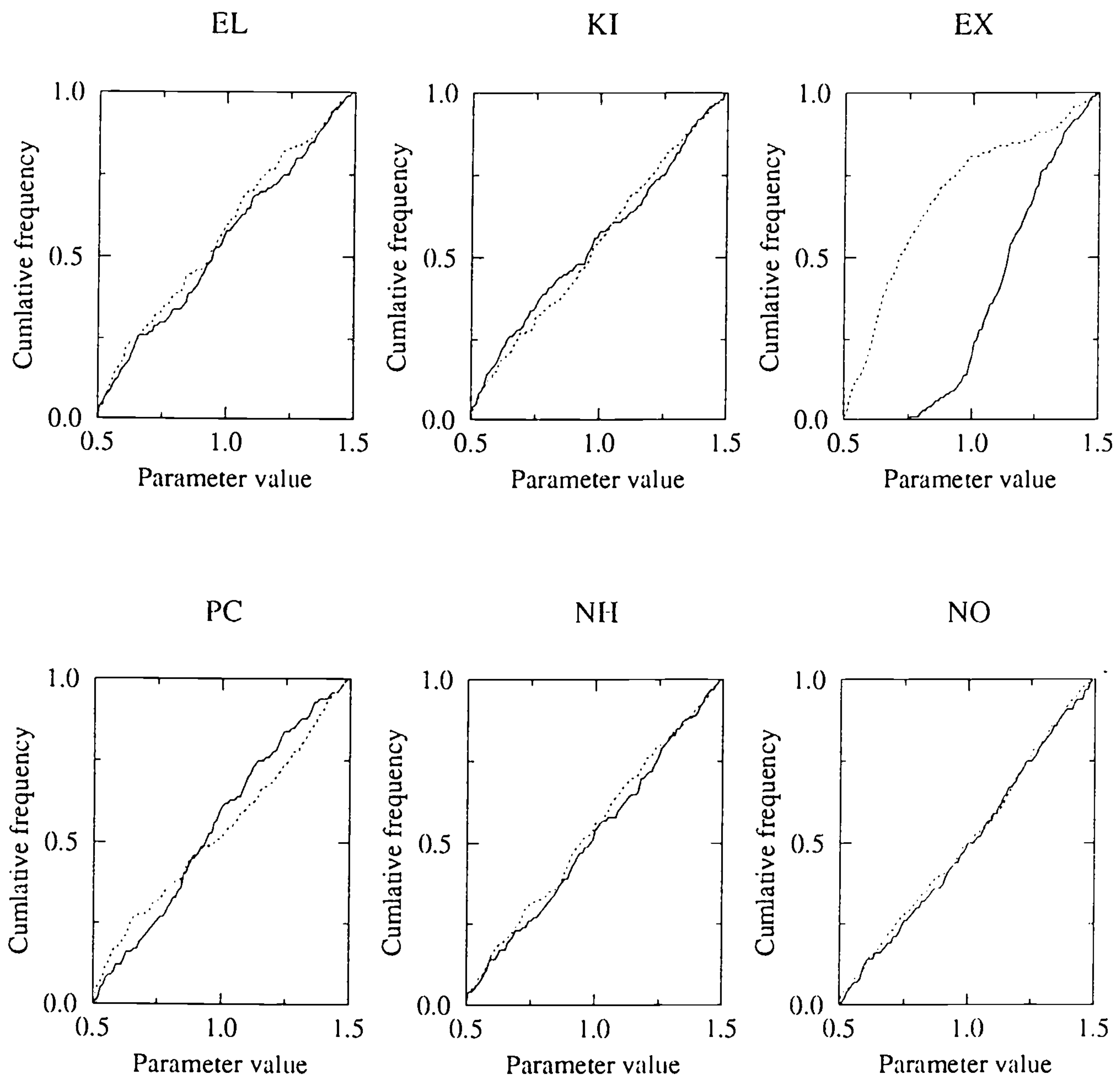


Figure 6.7: The two cumulative distributions for six soil hydrologic parameters, with SO_4^{2-} as objective function; acceptable (——) and unacceptable (......).

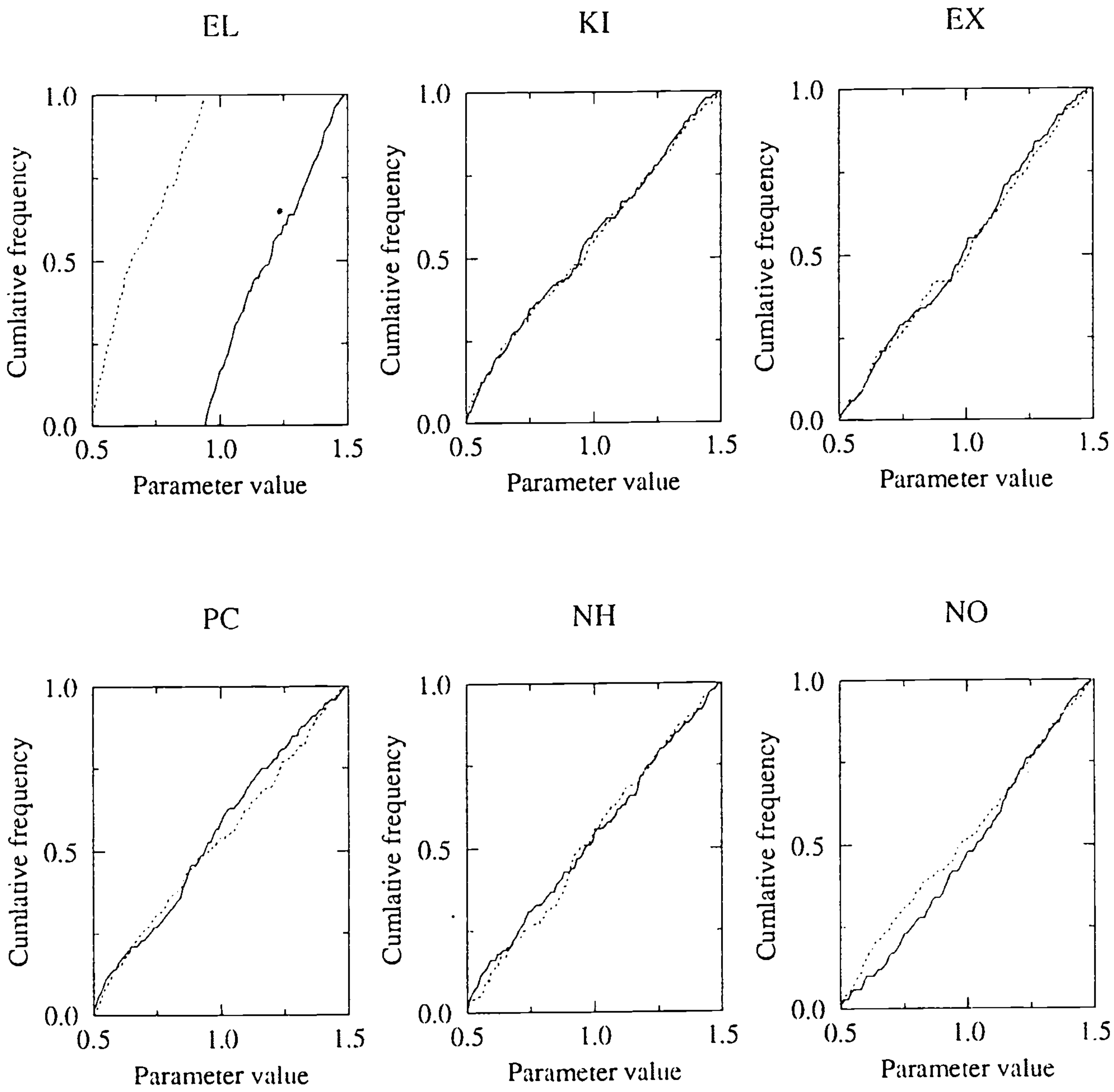


Figure 6.8: The two cumulative distributions for six soil hydrologic parameters, with Cl^- as objective function; acceptable (——) and unacceptable (......).

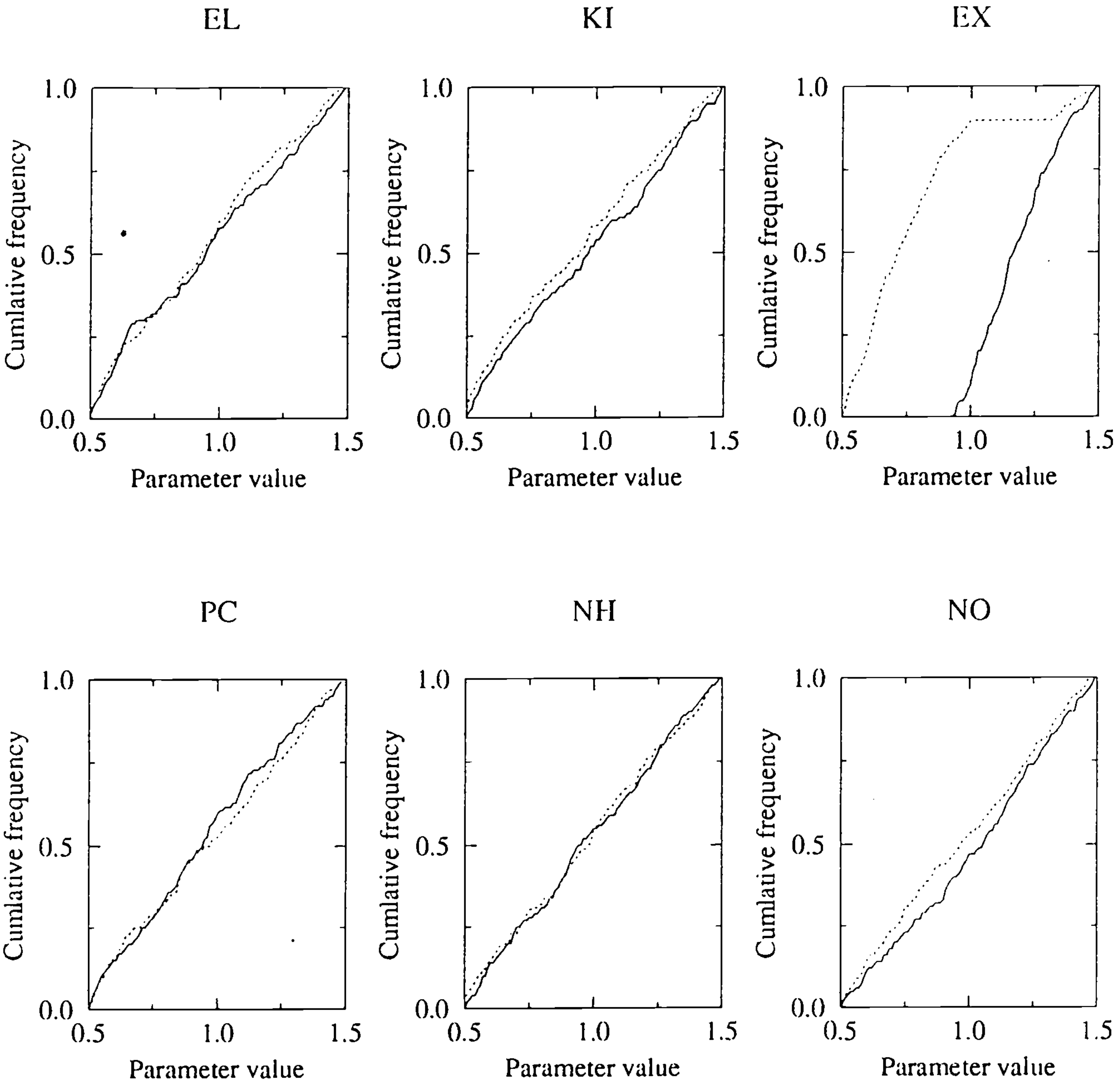


Figure 6.9: The two cumulative distributions for six soil hydrologic parameters, with silica as objective function; acceptable (——) and unacceptable (......).

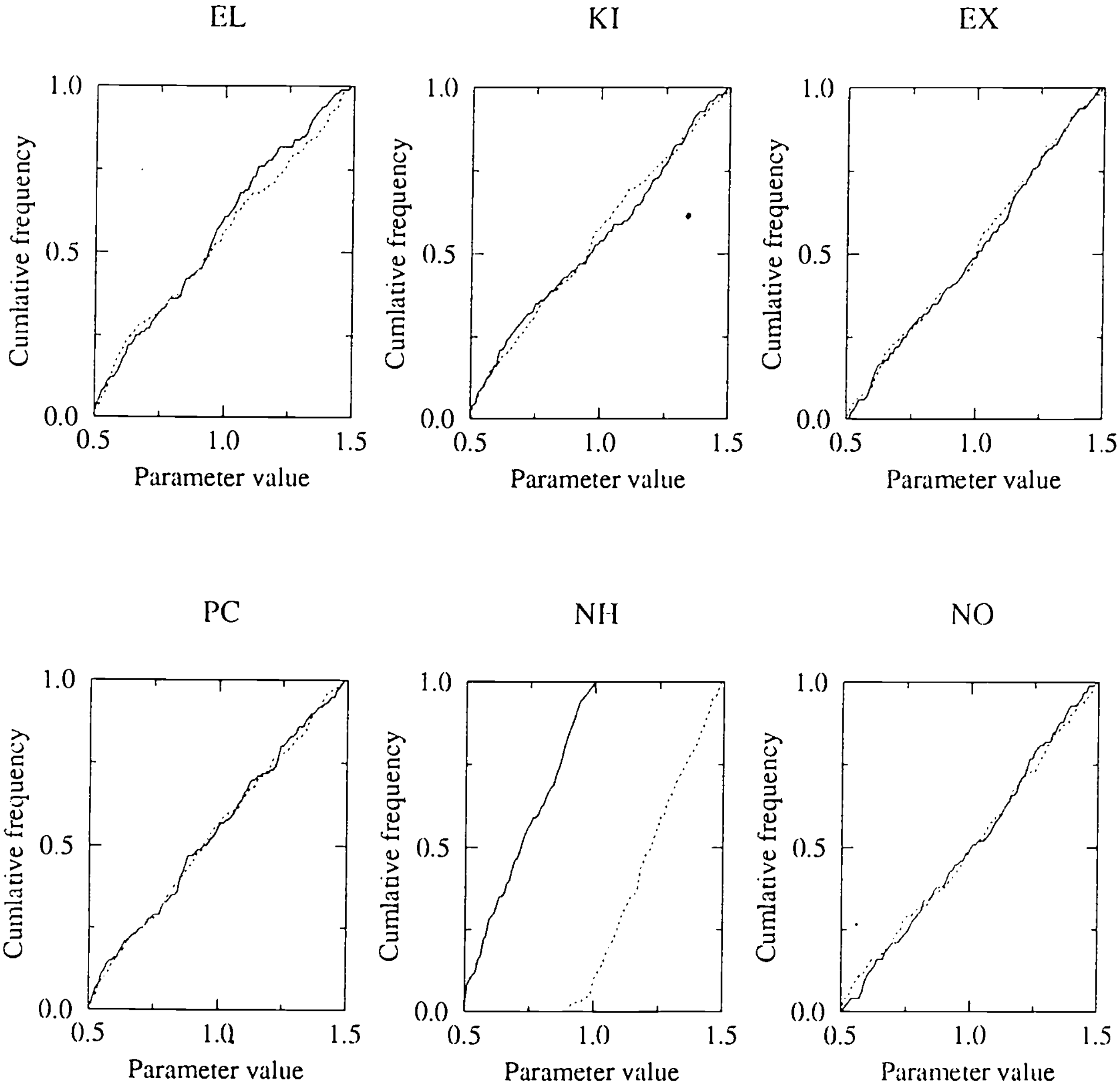


Figure 6.10: The two cumulative distributions for six soil hydrologic parameters, with NO_3^- as objective function; acceptable (——) and unacceptable (......).

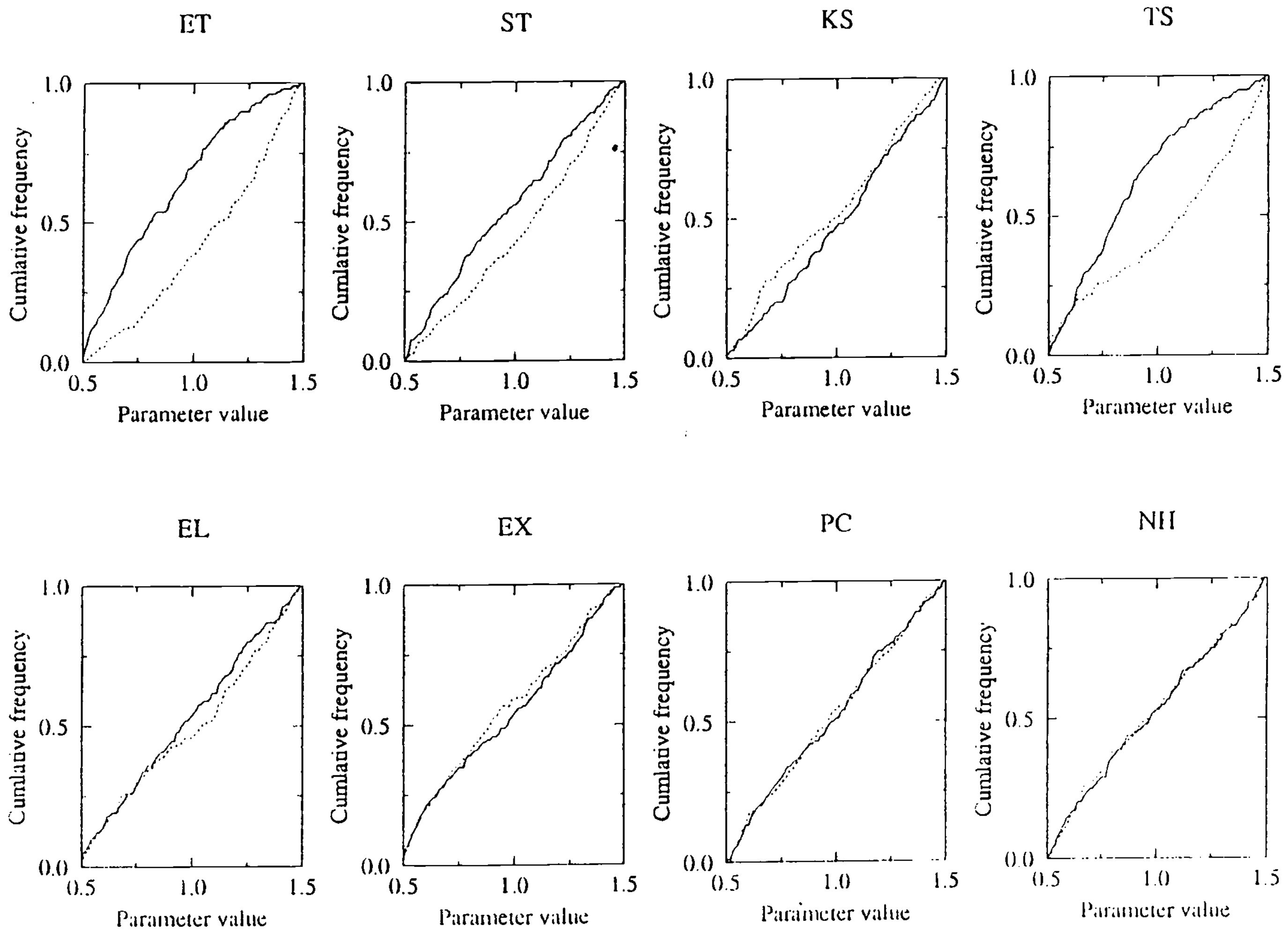


Figure 7.1: The two cumulative distributions for six soil hydrologic parameters: acceptable (——) and unacceptable (......). Global objective is outflow discharge.

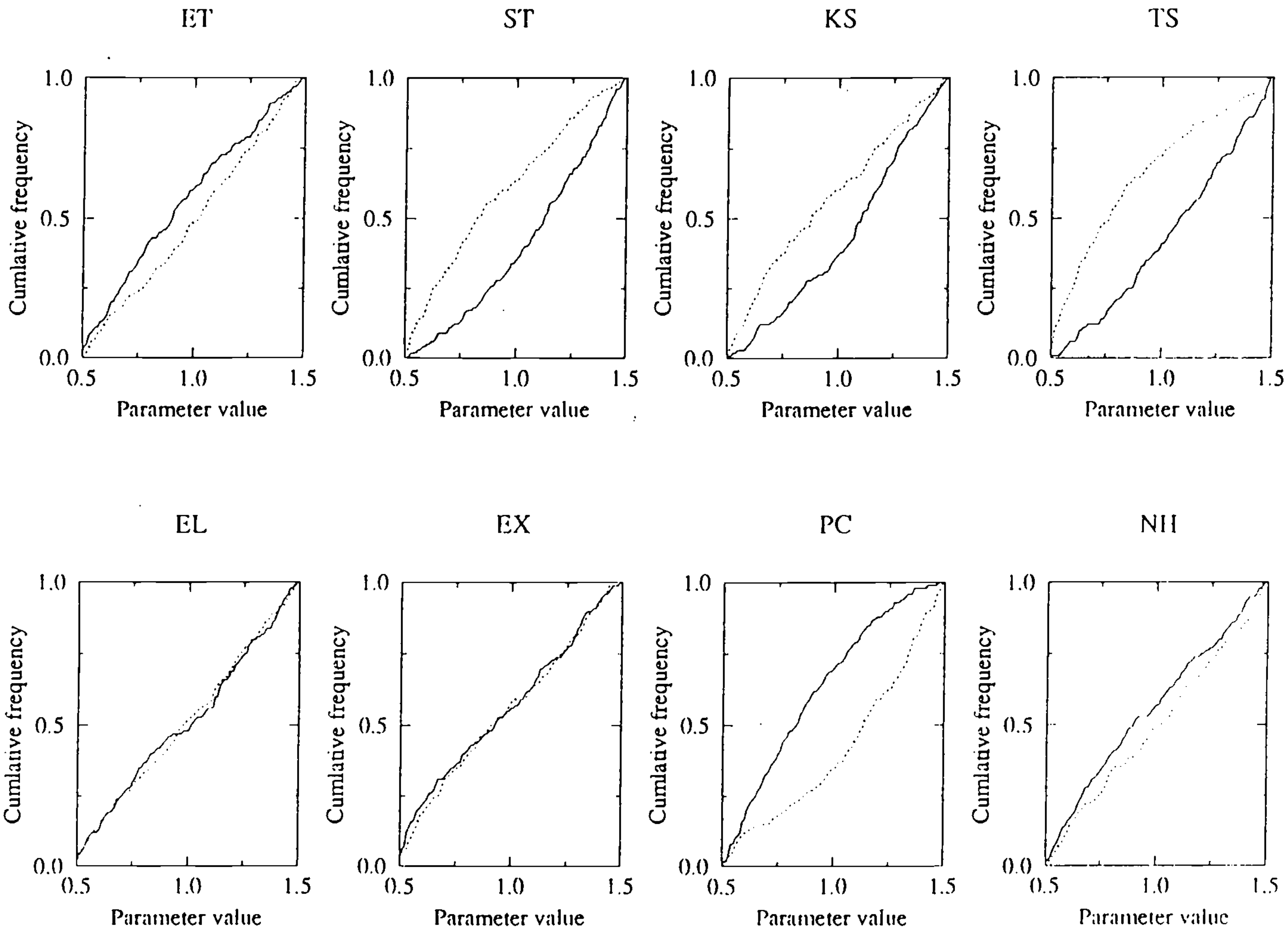


Figure 7.2: The two cumulative distributions for six soil hydrologic parameters; acceptable (——) and unacceptable (......). Global objective is pH.

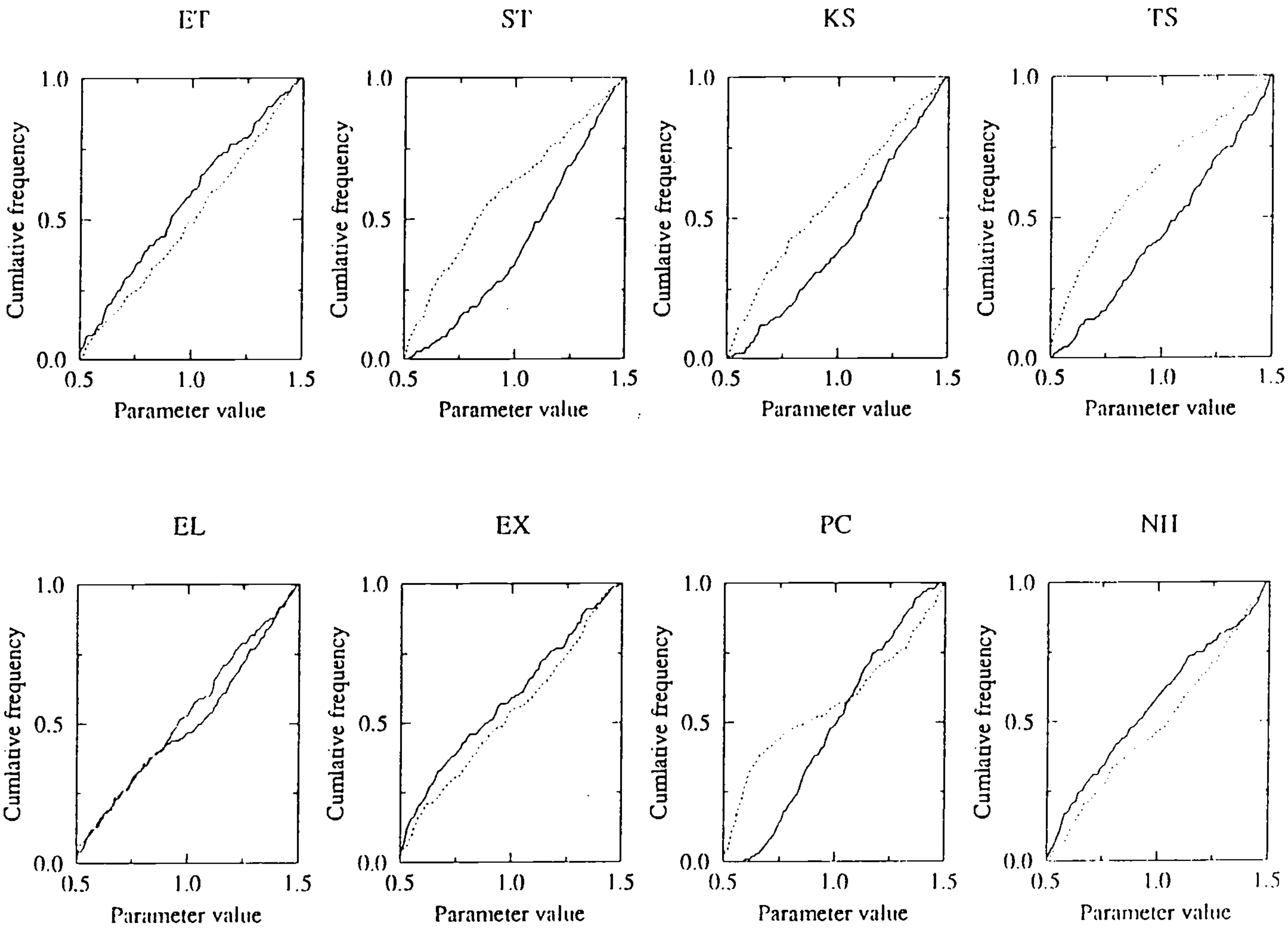


Figure 7.3: The two cumulative distributions for six soil hydrologic parameters: acceptable (——) and unacceptable (......). Global objective is ANC.

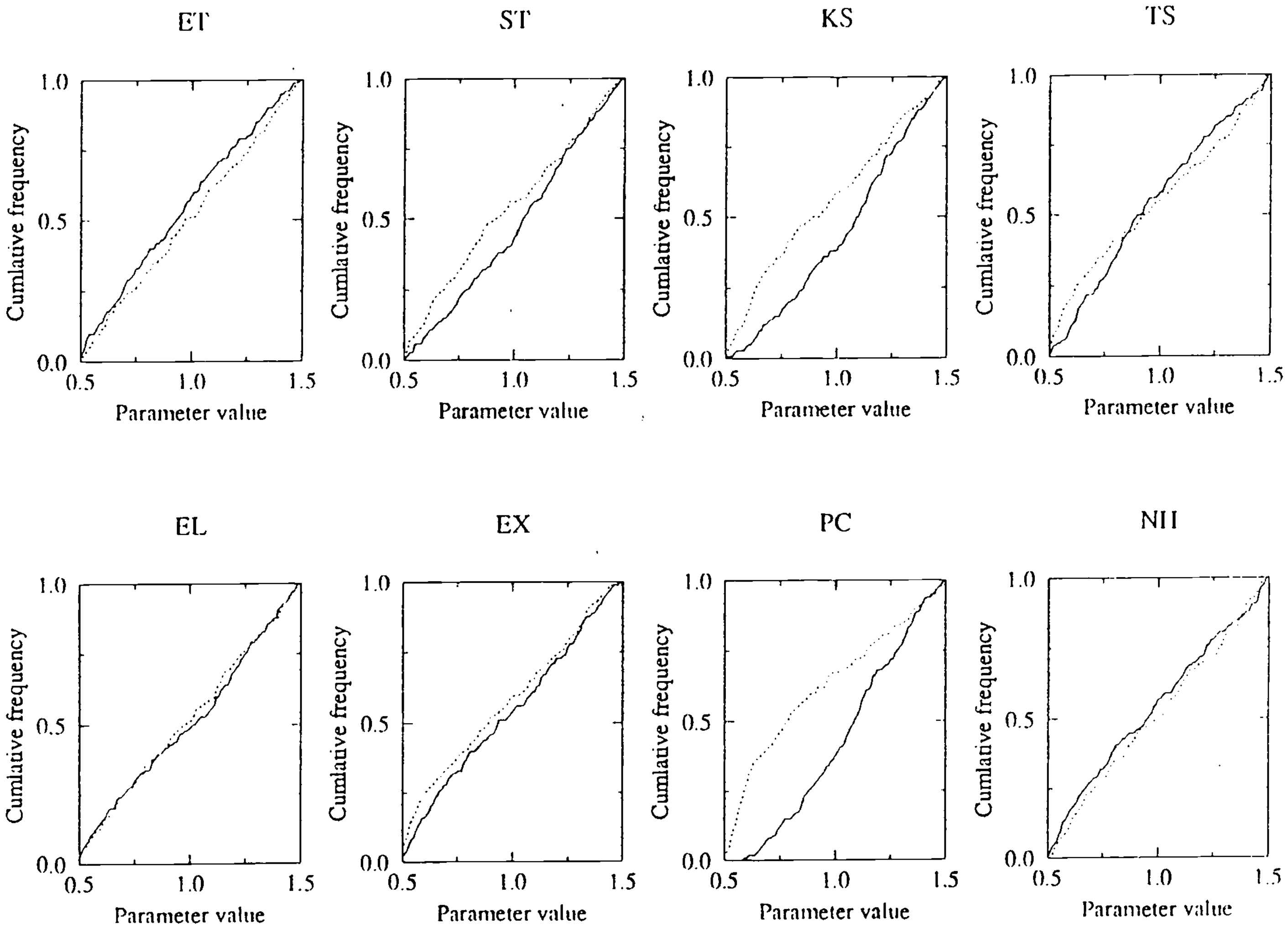


Figure 7.4: The two cumulative distributions for six soil hydrologic parameters; acceptable (——) and unacceptable (……). Global objective is Ca^{2+}.

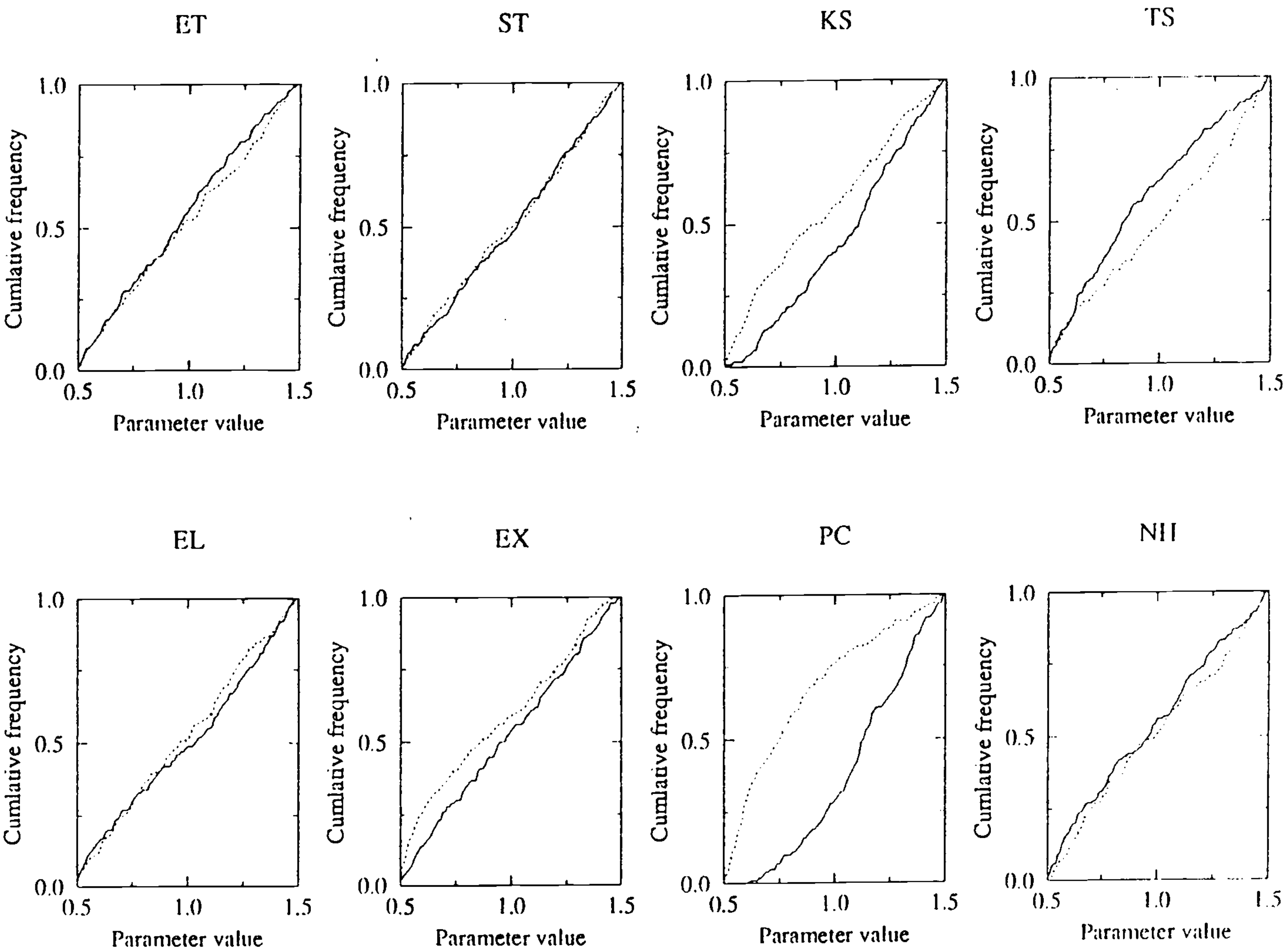


Figure 7.5: The two cumulative distributions for six soil hydrologic parameters; acceptable (——) and unacceptable (......). Global objective is Mg^{2+}.

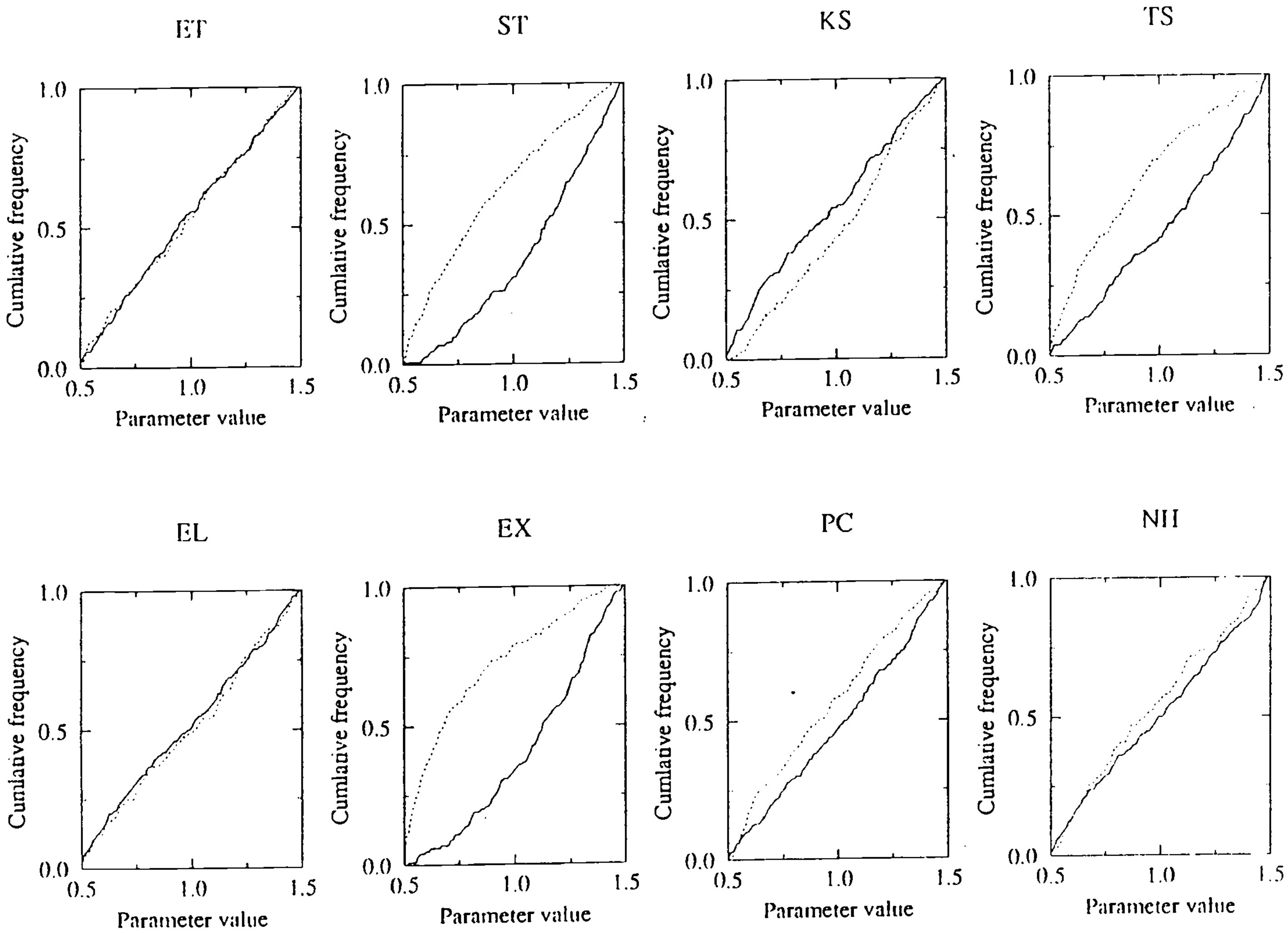


Figure 7.6: The two cumulative distributions for six soil hydrologic parameters; acceptable (——) and unacceptable (......). Global objective is K^+.

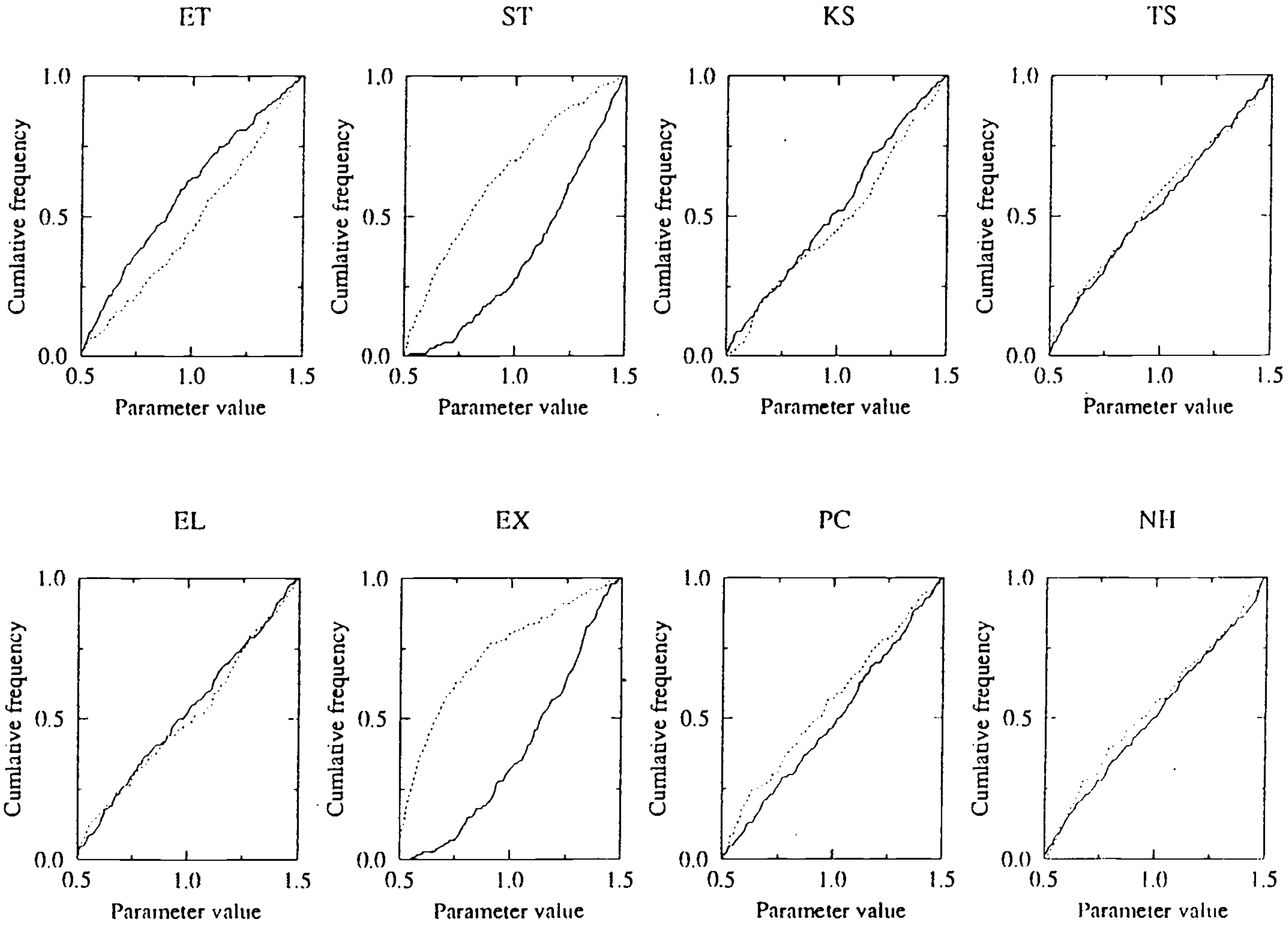


Figure 7.7: The two cumulative distributions for six soil hydrologic parameters; acceptable (——) and unacceptable (......). Global objective is Na^+.

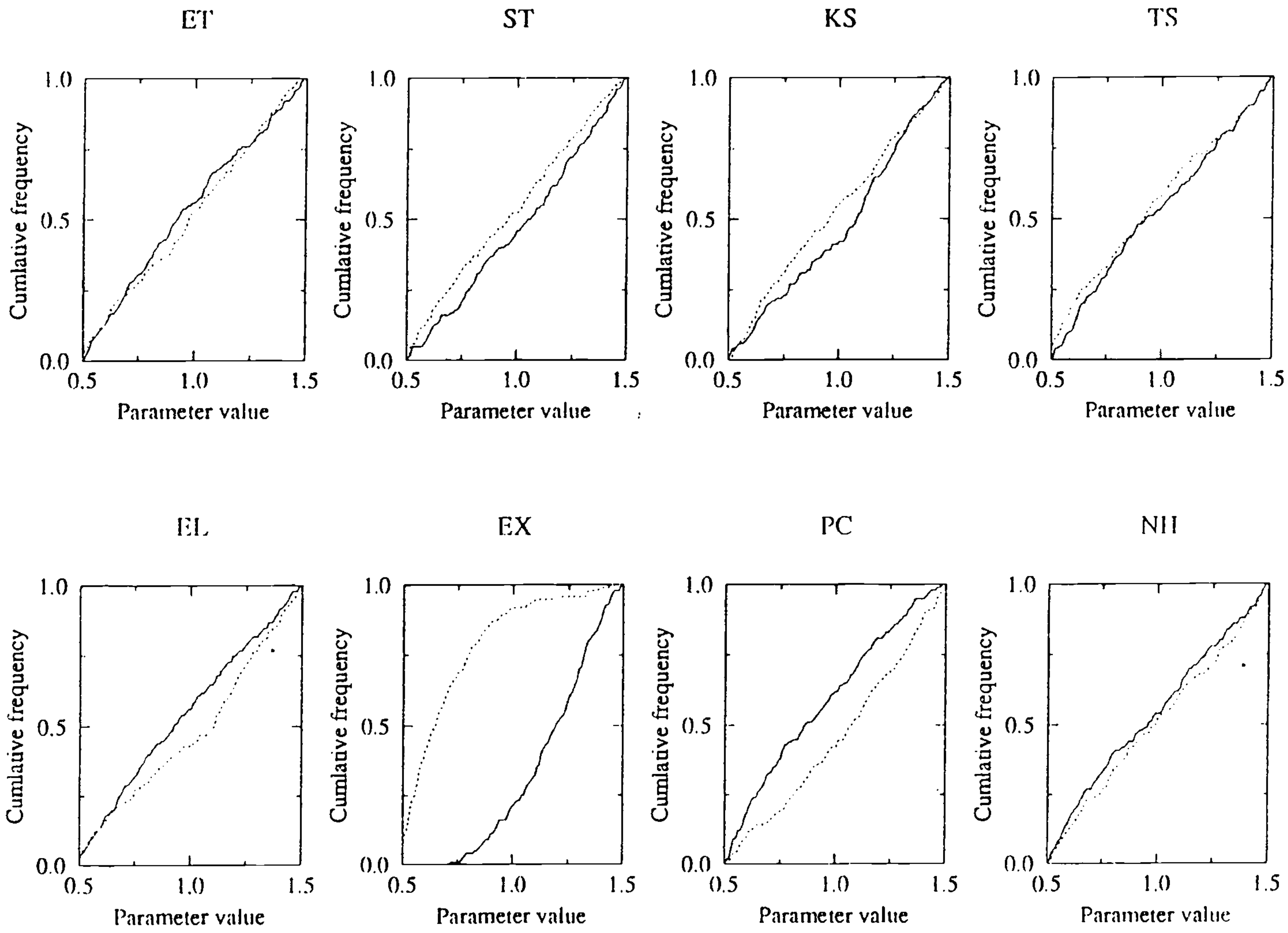


Figure 7.8: The two cumulative distributions for six soil hydrologic parameters; acceptable (——) and unacceptable (……). Global objective is SO_4^{2-}.

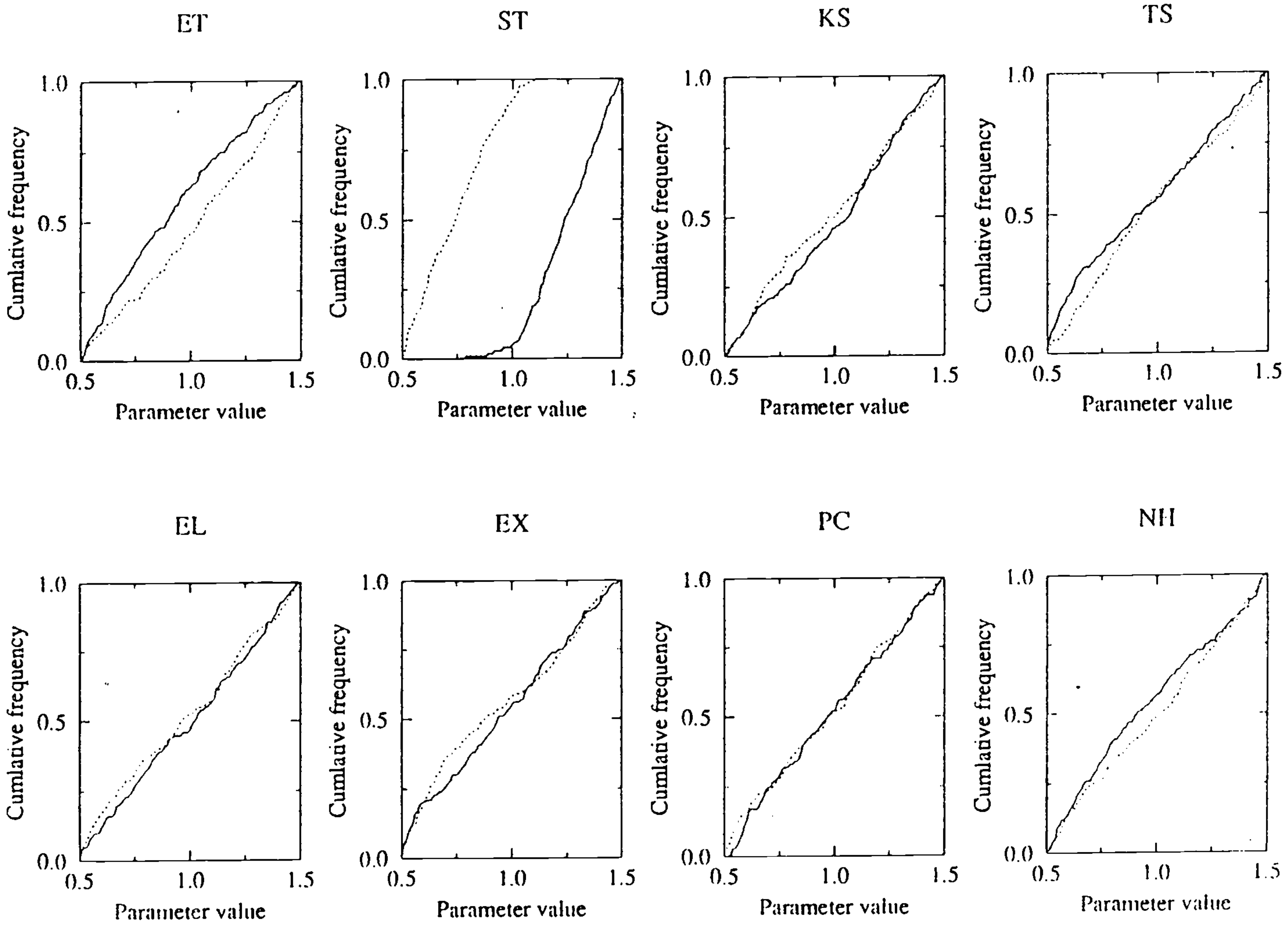


Figure 7.9: The two cumulative distributions for six soil hydrologic parameters; acceptable (——) and unacceptable (......). Global objective is Cl$^-$.

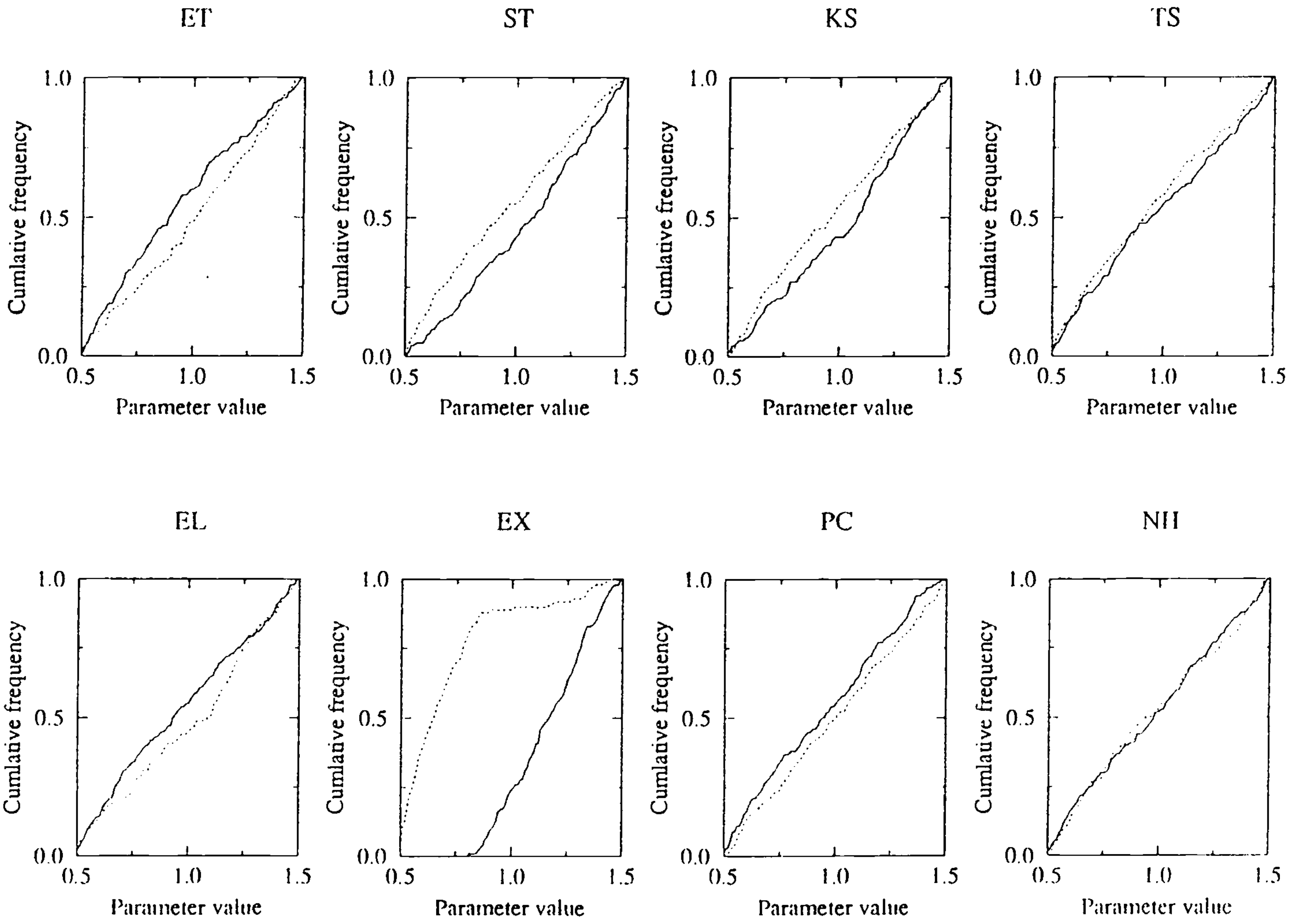
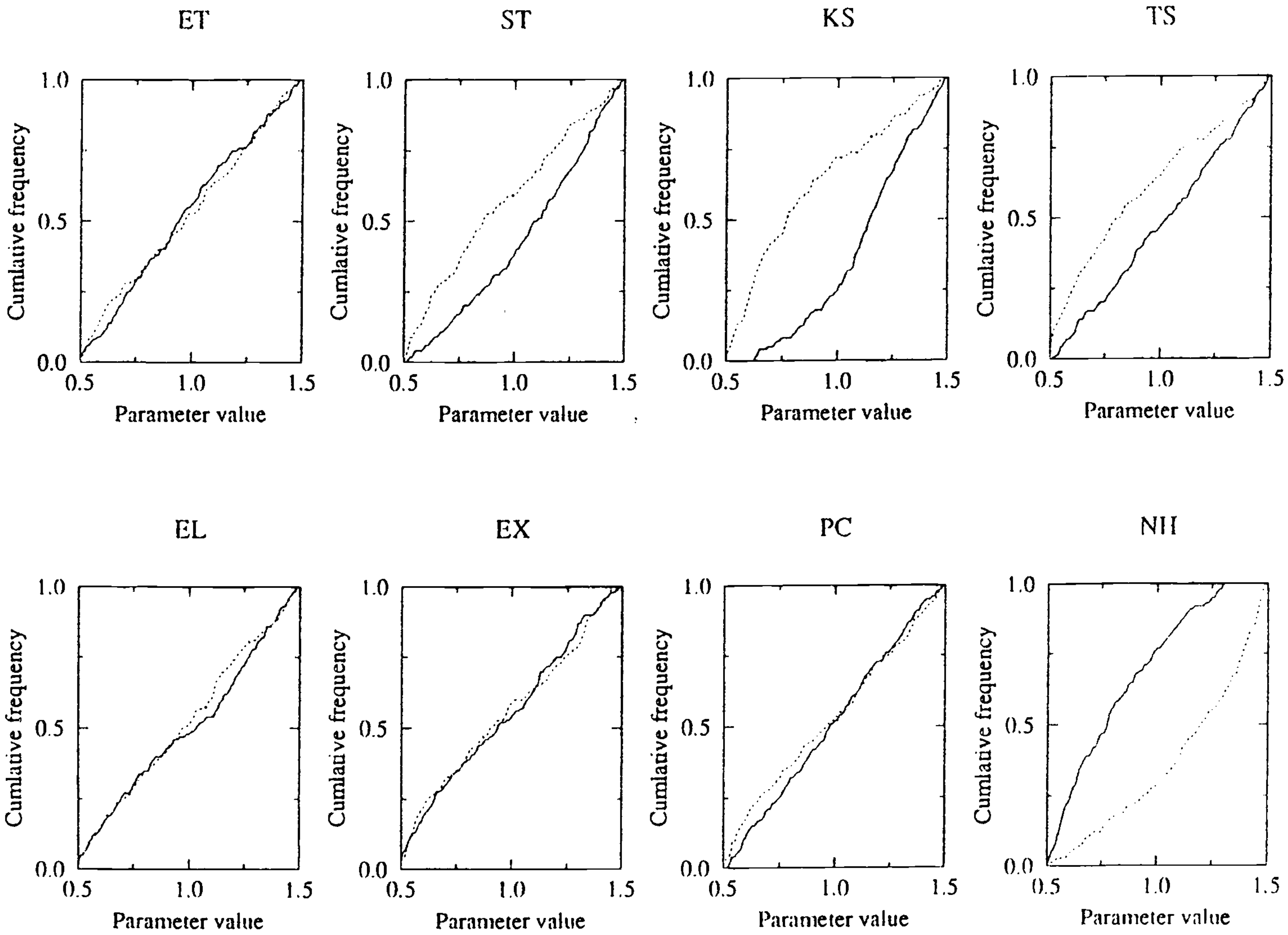


Figure 7.10: The two cumulative distributions for six soil hydrologic parameters: acceptable (——) and unacceptable (......). Global objective is silica.


ET ST KS TS

EL EX PC NH

Figure 7.11: The two cumulative distributions for six soil hydrologic parameters; acceptable (——) and unacceptable (......). Global objective is NO_3^-.

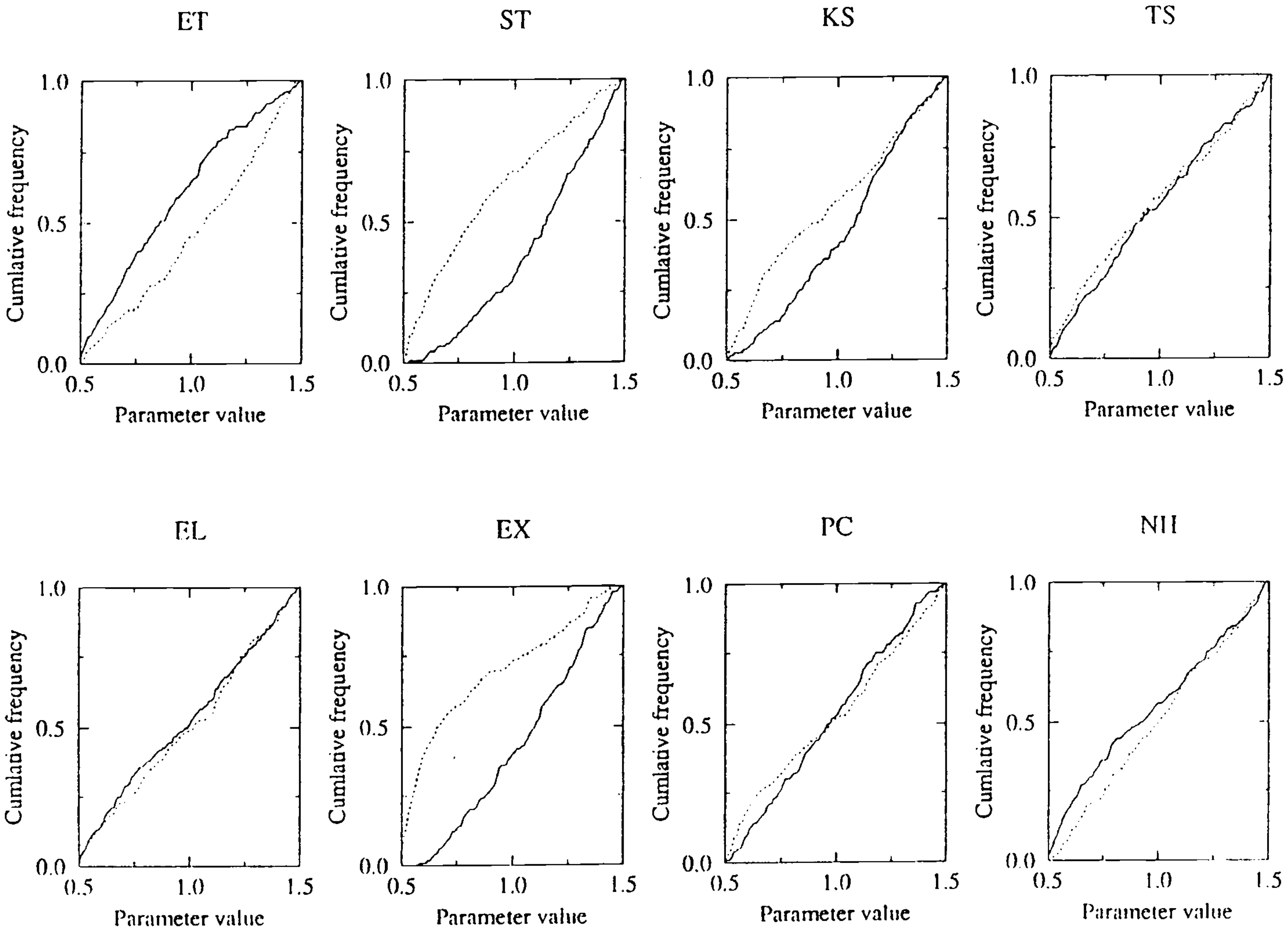
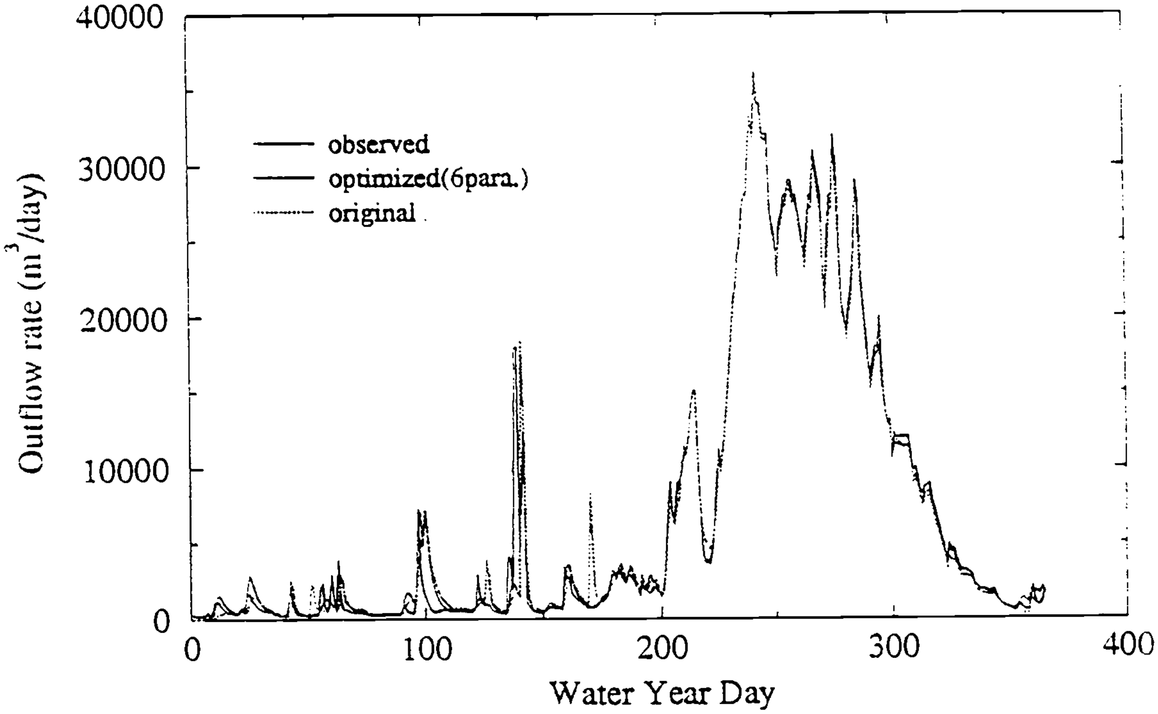


Figure 7.12: The two cumulative distributions for six soil hydrologic parameters; acceptable (——) and unacceptable (......). Global objective is combination of all.



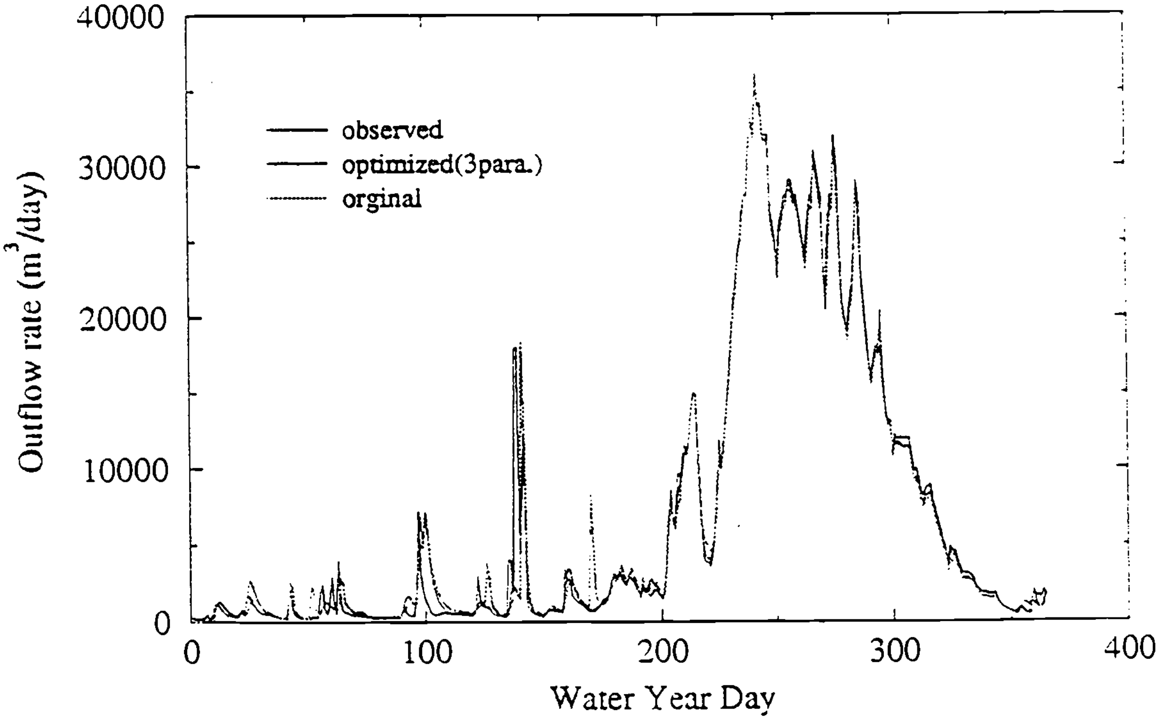


Figure 8: The simulated outflow hydrograph using optimized parameter sets (six and three hydrologic parameters cases).

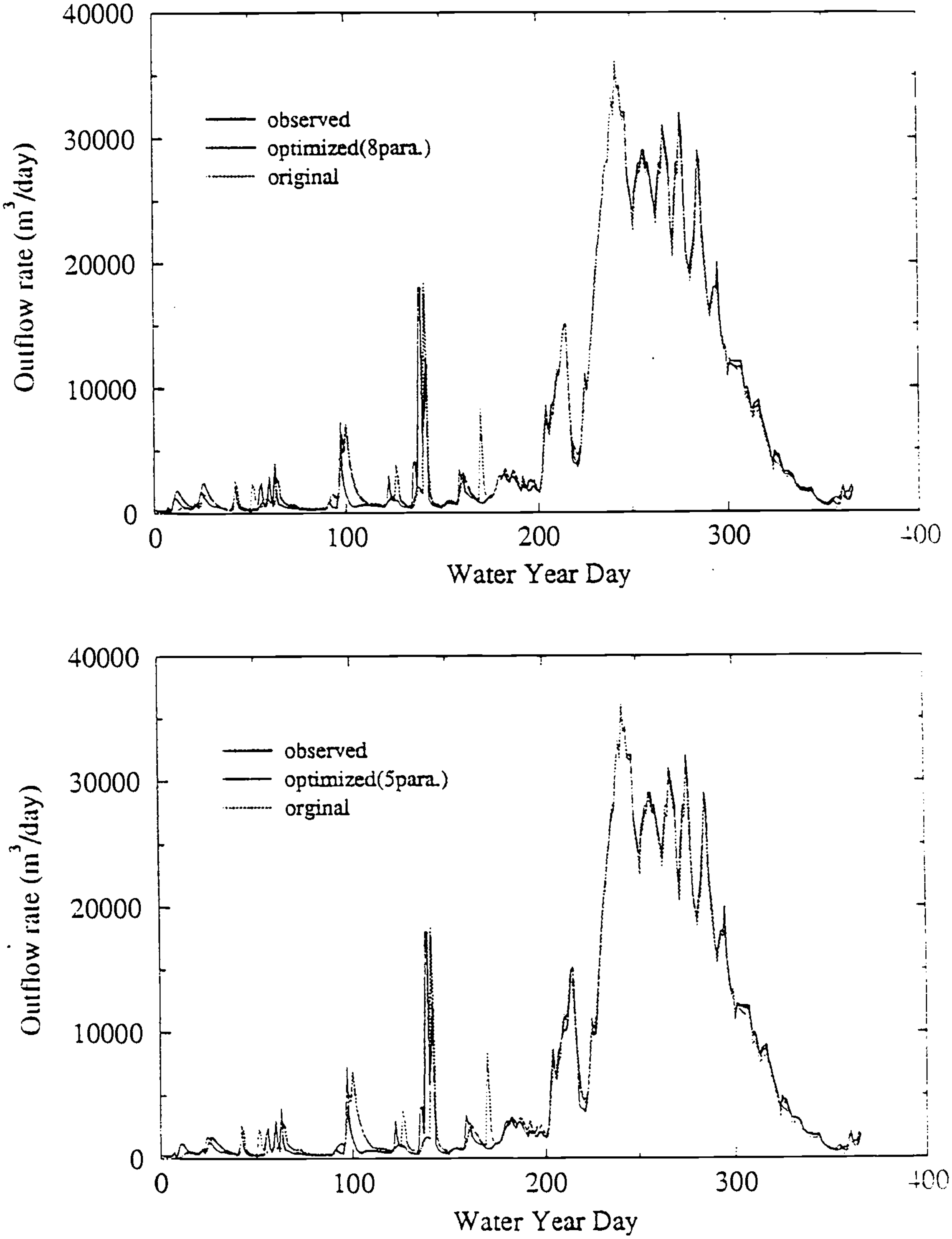


Figure 9: The simulated outflow hydrograph using optimized parameter sets: a) eight and b) five hydrologic and chemical parameter cases.

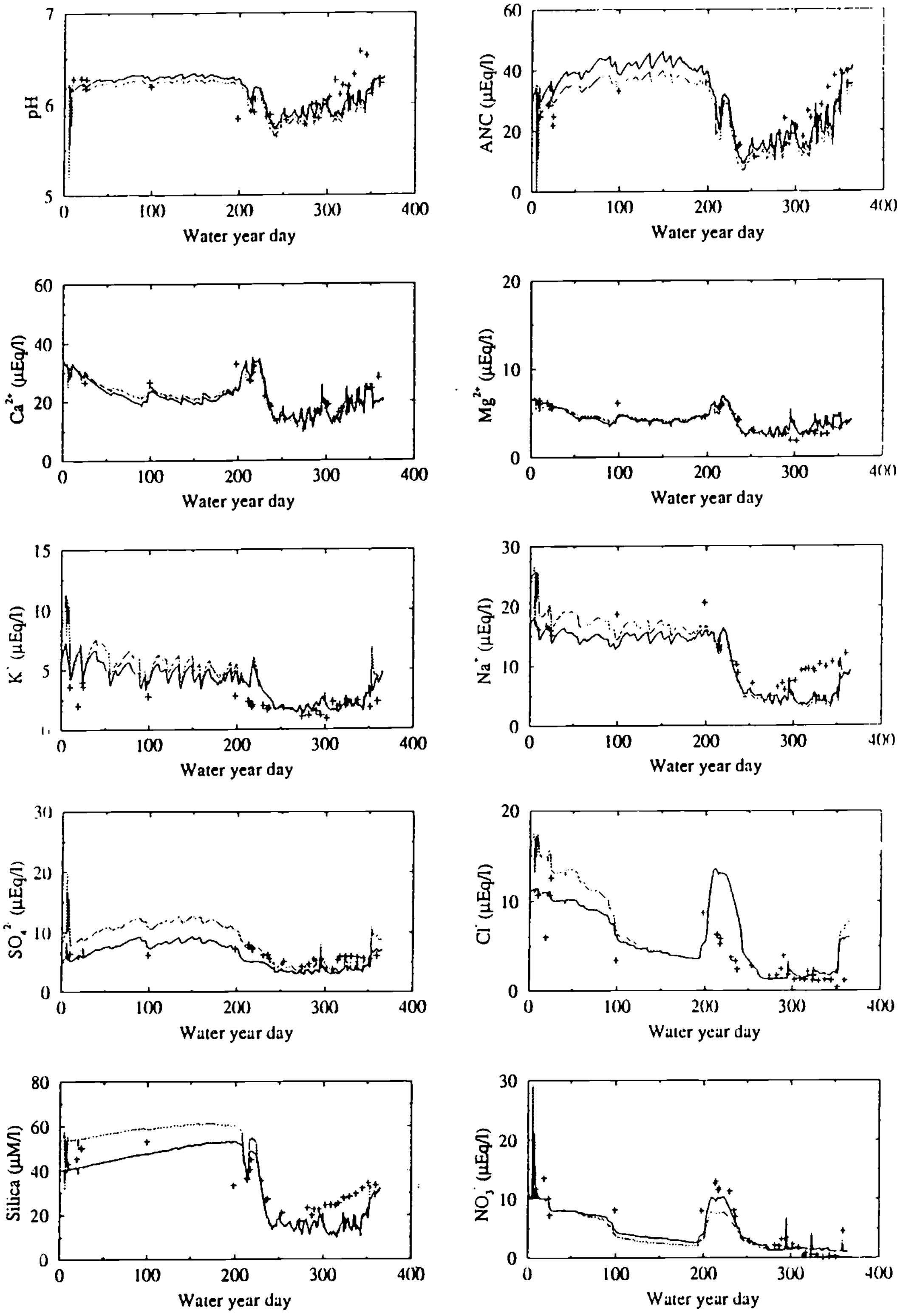


Figure 10.1: The simulated outflow chemical composition using optimized parameter sets: 8-parameter case. Original (......), optimized('86) (——) and observed (+).

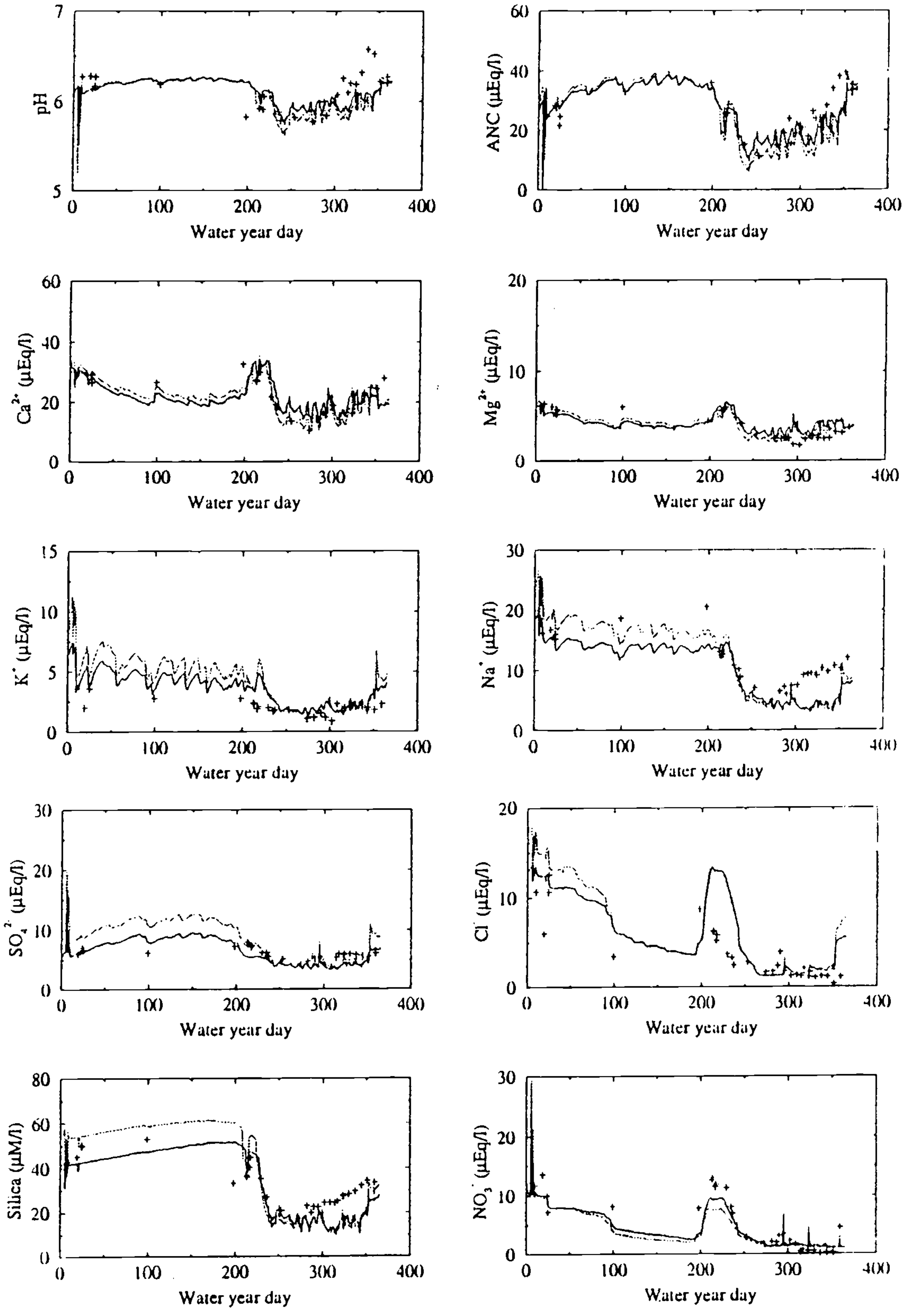


Figure 10.2: The simulated outflow chemical composition using optimized parameter sets: 5-parameter case. Original (......), optimized('86) (——) and observed (+).

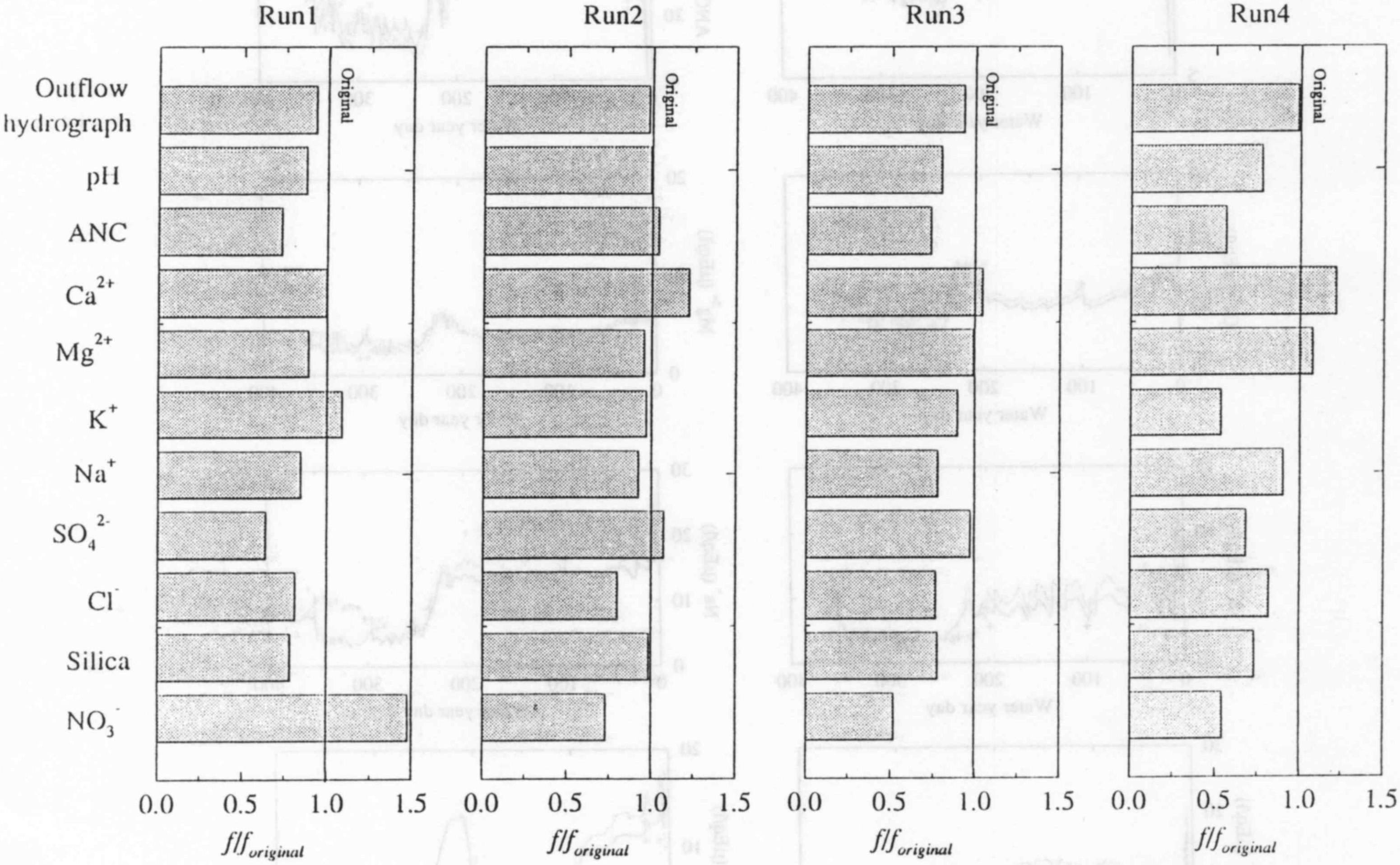


Figure 11: The individual objective function values of the four optimization run. Each function value represents the ratio to its value obtained by original calculation. Runs 1–4 correspond to those of Table 9.

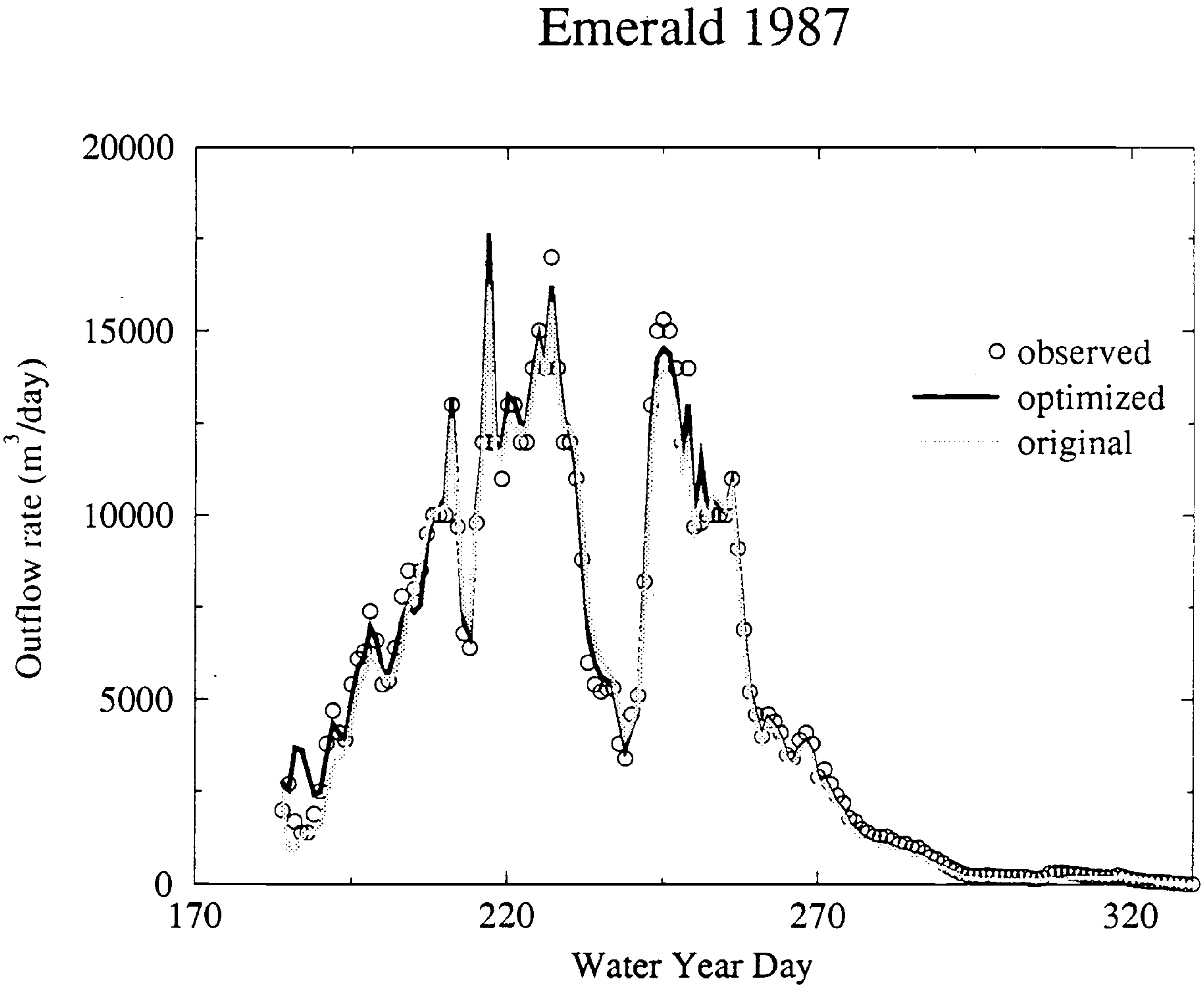


Figure 12.1: Results of validation of the optimum parameter set on the 1987 data for the outflow hydrograph.

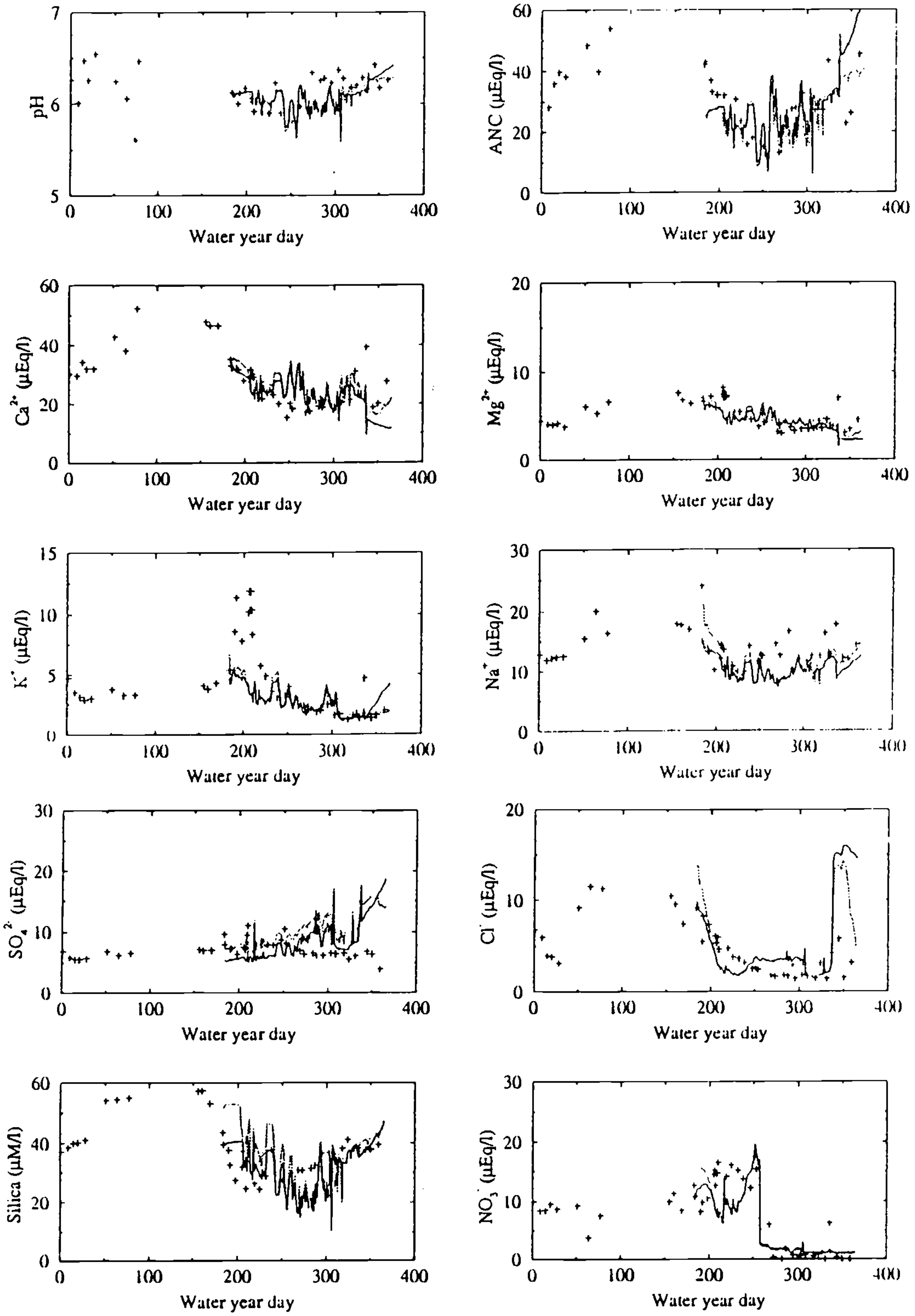


Figure 12.2: Results of validation of the optimum parameter set on the 1987 data for the outflow chemical composition; original (……), optimized('86) (——) and observed (+).