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Development of Watershed Models for Emerald Lake Watershed in Sequoia National Park and for Other Lakes of the Sierra Nevada

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DEVELOPMENT OF WATERSHED MODELS FOR EMERALD LAKE WATERSHED IN SEQUOIA NATIONAL PARK AND FOR OTHER LAKES OF THE SIERRA NEVADA

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ABSTRACT

Lakes in alpine watersheds in the Sierra Nevada are susceptible to damage by acid deposition due to their generally low buffering capacity and long response time for neutralization to take place. Changes from both repeated, long-term acidic fluxes and intense, short-term depositions/runoff events are expected to cause shifts in the chemical composition and, therefore, in the biotic communities in alpine lakes and streams.

In order to better understand the implications of acid deposition in watershed systems in the Sierra Nevada, the California Air Resources Board (CARB) initiated an intensive integrated watershed study at Emerald Lake in Sequoia National Park. The comprehensive nature of the data obtained from these studies provided an opportunity to develop a quantitative description of how watershed characteristics and inputs to the watershed influence within-watershed fluxes, chemical composition of streams and lakes, and, therefore, biotic processes.

In August 1987, the University of Arizona's research team started work on the development of physical/chemical models of the Emerald Lake watershed as a part of the Sierra Watershed Modeling Project (SWMP).

Two different but closely-related modeling approaches were followed. In the first, the emphasis was placed on the development of "systems-theoretic" models. In the second approach, development of a "compartmental" model was undertaken. The systems-theoretic effort results in simple time-series models that allow the consideration of the stochastic properties of model errors.

One-step-ahead time-series models relating lake outflow as a function of snowmelt estimates were identified and showed good prediction ability. The model for the period of increasing melt contained ten snowmelt terms, indicating longer retention (up to ten days) of water in the watershed. On the other hand, the model for the period of decreasing melt had only three snowmelt terms, indicating short retention (less than three days) and, therefore, faster movement of water through the watershed. The resulting models, however, need to be verified further with independent sets of data from other water years. The results of stepwise regression analysis for the snowmelt period point to flow as being the most influential factor (among temperature and cumulative flow) in deciding the value of acid-neutralizing capacity (ANC). Although the sample of size 17 is too small for strong conclusions, substituting flow as a proxy for cations and anions would amount to a significant reduction in data collection efforts.

On the other hand, the compartmental model [the University of Arizona Alpine Hydrochemical Model (AHM)] is a comprehensive and detailed description of the various interacting physical and chemical processes occurring on the watershed. It is capable of modeling stream hydrology and chemistry at daily time steps. Limited testing of AHM was performed using the 1986 Water Year data.

The results indicate that AHM is capable of providing reasonable estimates of hydrologic and chemical outflows from the Emerald Lake basin. Similarities between this and other basins in the Sierra Nevada suggest that it can be used for evaluations in other basins.

The initial testing has also identified a few potential limitations that should be addressed before the model's full capabilities can be used. For example, more flow-routing information from the watershed is needed, and data for mineral weathering, litter decay, soil mineralization, dry deposition, and other processes and fluxes need further analysis and selective augmentation. A physically-based model of chemical release from the snowpack is also needed. Future efforts should also address coupling the AHM to lake and vegetation models for assessment of deposition and climate changes in alpine watersheds.

CHAPTER ONE
SUMMARY AND CONCLUSIONS

Two different but related modeling approaches were used to interpret and model the hydrology and chemistry of Emerald Lake watershed. The first is a systems-theoretic approach, in which the response (e.g., flow, concentration of a given chemical species) of a natural system is described by a model such as Auto-regressive Moving Average with eXogenous variables (ARMAX). In the case of flow modeling, the system outputs are the time series of flow rates at the watershed (or lake) outlet; possible inputs (exogenous variables) are snowmelt, rain, and other fluxes into the watershed. The second approach involves development of a compartmental model that is based on explicit physical/chemical descriptions of hydrologic and chemical processes in that alpine watershed.

1.1 Systems-Theoretic Modeling

The three main objectives in the analysis of the Emerald Lake watershed data using systems-theoretic models were:

(1) Analyze hydrologic and chemical flux data in order to evaluate the potential information content of data and to see what could be learned about the watershed behavior from the data;

(2) Obtain some idea of watershed response to various system attributes; in particular, identify those attributes having the strongest influence on watershed response and determine which attributes to include in the compartmental model; and

(3) Develop simple predictive models of watershed outputs (both quantity and quality).

Two sets of data, both for Water Year (WY) 86 (October 1, 1985 through September 30, 1986), were available. The first set consisted of hydrologic and meteorologic fluxes at hourly intervals, but it contained several missing periods. The second data set consisted of estimated hydrologic fluxes lumped over the watershed at 24-hr intervals. Therefore, the analysis and modeling effort proceeded in two phases. Phase 1 dealt with the analysis of hourly data, while the focus of Phase 2 was on the analysis of daily data and the development of ARMAX models. Advantages of the ARMAX modeling approach are: (1) analytical model-identification and parameter-estimation techniques are available and well-documented in the literature, (2) previous forecast errors can be included to improve forecasts and to estimate confidence limits for the forecasts, and (3) diagnostic checks are available to determine if the model is performing properly. The primary conclusions of the systems-theoretic modeling are:

(1) The data show that during the snowmelt season, the watershed undergoes a strong diurnal response, whereas this was not the case for the non-snowmelt season;

(2) The result of the Impulse Response Function (IRF) for the snowmelt season suggest that a daily time scale can be used to model the watershed behavior without the need to consider detailed routing of flows in the channel network;

(3) The dominant variable influencing lake output is snowmelt;

(4) The covariance function analysis shows quite different physical mechanisms influencing watershed behavior during the periods of increasing and decreasing melt (days 181-250 and 251-300, respectively). The period corresponding to the early part of the melt season (increasing melt) is consistent with alternating periods of melt and refreezing with poorly-developed runoff pathways. On the other hand, the covariance function results for the period corresponding to the latter part of the melt season (decreasing melt) is consistent with well-established runoff pathways and continuous melting of the snowpack;

(5) One-step-ahead time-series models relating lake outflow as a function of snowmelt estimates were identified and showed good prediction ability. As expected, the model for the period of increasing melt contained ten snowmelt terms indicating longer retention (up to ten days) of water in the watershed. On the other hand, the model for the period of decreasing melt had only three snowmelt terms indicating short retention (less than three days) and, therefore, faster movement of water through the watershed;

(6) A least-squares regression analysis of acid-neutralizing capacity (ANC) in lake inflows, with anion and cation concentrations acting as the input variables, showed very strong correlations, indicating good consistency within the data. The good correlations were found for each inflow for the entire period for which data were available, summer 1984 through fall 1986;

(7) The snowmelt period chemical data were used for systems-theoretic water quality analysis. This decision was based on the fact that the chemical activities, which constitute our key interest, are greatest during this period. The sample size for this period contained only 17 data points; and

(8) The results of stepwise regression analysis for the snowmelt period point to flow as being the most influential factor (among temperature and cumulative

flow) in deciding the value of acid-neutralizing capacity (ANC). Although the sample of size 17 is too small for strong conclusions, substituting flow as a proxy for cations and anions would amount to a significant reduction in data collection efforts.

While it has been demonstrated that the systems-theoretic methodology can result in good predictive/simulation models, the model parameter estimates are based on a limited data sample (WY 86). The resulting models need to be verified further with independent sets of data from other water years. Refinement may be necessary through recalibration.

1.2 Compartmental Modeling

The University of Arizona Alpine Hydrochemical Model (AHM) is the name of the compartmental model developed for modeling alpine watersheds in the Sierra Nevada. AHM is an integrated hydrological/chemical model capable of predicting watershed runoff and chemistry. In its present configuration, AHM is intended to fulfill two primary purposes:

(1) To be used as a research tool to identify which hydrologic and chemical processes are important and when changes due to these processes are occurring. It should also assist in interpreting field monitoring and process-level research and to help plan future research; and

(2) To be used as a predictive model for scenario analysis, displaying changes in watershed outputs resulting from changing input conditions. As such, it enables estimating effects of natural or anthropogenic changes in climate or atmospheric pollutant loading.

Although AHM is relatively complex, the user controls the degree of complexity in modeling a given situation. It can model the movement and chemical changes in numerous compartments of multiple watershed subunits and stream segments.

AHM tracks water and chemical movement, storage, and loss in and between different storage compartments on the watershed, including:

(1) Tree canopies (snowfall and rainfall interception, separately);
(2) Soil or rock surfaces (rainfall interception and storage beneath the snowpack);
(3) Single or multiple soil layers;
(4) Streams or lakes (currently without storage considerations);
(5) Snowpack;

(6) Snowpack free water;

(7) Surface runoff and subsurface horizontal drainage from soil-covered watershed subunits; and

(8) Vegetation (as a source or sink).

To the extent deemed practical, these processes can be modeled in a manner simulating the actual process occurring on the watershed itself, while attempting to avoid extraordinarily detailed modeling of those processes for which supporting data seldom exist. Unique features include the ability to partition outputs from one compartment to several receiving compartments, automatic sequencing of subunit computations, treatment of stream segments as separate compartments, and extraction of streamflow by riparian areas to maintain a minimum soil-water content. AHM can be characterized as a physically-based model and, as such, represents all subprocesses in general terms. Application to a specific watershed will require the necessary data to fit the model parameters. In developing AHM, every attempt has been made to minimize the number of parameters that must be estimated through the calibration process. Most of the parameters are of the type that should be prespecified based on field, laboratory, and other sources of information available on the watershed under investigation.

As a system, AHM is composed of six distinct sections, including (1) data input, (2) water balance, (3) chemical balance, kinetics, and equilibration, and (4) report generation. The program accompanies a user's guide and detailed descriptions of its water and chemical balance. The code implementing the model is modular to enable easily-altering functions describing features such as snowmelt quantity and quality. For example, potential evapotranspiration, potential sublimation, snow-covered area, and snowmelt are computed externally, allowing the user to select the models most appropriate for a given area. Complexity is also controlled by the user's selection of the number of subunits, streams, and soil horizons. Either distributed (spatially and temporally) or lumped parameters can be used.

The WY 86 data were used for initial model testing. The model is designed to use chemical data from most of the watershed-process field and laboratory studies done at Emerald Lake watershed. However, it is currently being run with lumped parameters. Seven watershed subunits were defined by soil and vegetation type. The main conclusions of using the model with these data are:

(1) Modeled basin outflows were very similar in magnitude and distribution to those observed, without adjusting hydrologic parameters. Most apparent differences between modeled and observed runoff can be explained by the input data used (e.g., snowmelt estimates).

(2) There is some indication that predicted basin outflows are relatively insensitive to the choice of hydrologic parameters. Soil volumes on the Emerald Lake

basin may be too small to markedly affect watershed runoff, however, soil does affect the chemistry.

(3) Initial estimates of watershed parameters should be refined when more field data and spatially-distributed snowmelt estimates become available. The model can then be tested using more distributed watershed parameters.

(4) Modeled lake-inflow ANC has average values and seasonal trends that match field observations, with mineral weathering as the only water-soil interaction used. Weathering rates used for the soils and rock outcrops were approximately one percent of those indicated in laboratory weathering studies.

(5) Addition of parameters for nitrogen reactions, ion exchange, and other watershed processes will improve the fit and should be added as more field results become available

(6) AHM is capable of providing reasonable estimates of hydrologic and chemical outflows from the Emerald Lake basin. Similarities between this and other basins in the Sierra Nevada suggest that it can be used for evaluations in other basins.

AHM is capable of very detailed modeling of the hydrology and chemistry of a given watershed and may be applied to a wide range of conditions because so much of the "science" of hydrologic and chemical processes is fed to AHM in the form of input data files. To a large degree, AHM is a large and detailed accounting program, adding up the sum of inputs which the user provides and moving water and chemicals between compartments in response to the directions provided by the input parameters and data. Therefore, AHM may be potentially as accurate as a given set of input data allows it to be.

The initial testing has also identified a few potential limitations that should be addressed before the model's full capabilities can be used. As more of the 1984-87 data become available, and as more critical analyses of the data are reported, parameters such as throughfall, mineral weathering, litter decay, and soil mineralization can be distributed by soil and vegetation type. More flow-routing information from the watershed is needed, and data for mineral weathering, litter decay, soil mineralization, dry deposition, and other processes and fluxes need further analysis and selective augmentation. A physically-based model of chemical release from the snowpack is also needed. Future efforts should also address coupling the AHM to lake and vegetation models for assessment of deposition and climate changes in alpine watersheds.

CHAPTER TWO

RECOMMENDATIONS

Both the systems-theoretic modeling approach and the Alpine Hydrochemical Model (AHM) have been developed under the California Air Resources Board's (CARB's) Acid Deposition Research Program. Both modeling efforts have applications in evaluating the results of field research, in guiding future research, and in assessing the impacts of deposition scenarios on alpine watersheds.

In the future, modeling should proceed in parallel with field measurements of deposition, process-level studies, and related research. Although our efforts to date have yielded modeling tools that can be applied to existing data, some additional model development and testing are needed. This includes:

(1). Further analyze data from process-level studies to develop parameters for the AHM and continue testing with the Water Year 1986 (WY 86) data.

(2). Make improvements to AHM in response to needs that were identified during model testing and do sensitivity analyses of the AHM parameters.

(3). Calibrate AHM since no systematic calibration has yet been performed.

(4). Analyze data for Water Year 1987 (WY 87) (and/or 1985) using systems-theoretic approach as a preliminary step to using the data with the AHM.

(5). Verify AHM with data for WY 87 (and/or 1985).

Table 2.1 indicates the status of chemical data and parameter inputs for the AHM. In some cases, our preliminary analyses of raw data from other investigators have yielded inputs to the model, but further analyses are still needed. In other cases, raw data were not yet available; augmentation to the data sets are also needed for some watershed processes. It is recommended that much of this data analysis be done in the context of the modeling, i.e., specifically with the modeling in mind.

Flow routing or quantification of water movement through soils is a critical need, as is in-situ measurement of weathering rates of rock surfaces and in soils.

Following testing and calibration of the AHM on the Emerald Lake watershed, in use can be extended to other Sierra Nevada watersheds. The critical information needed includes waterflow routing and/or mineral weathering rates (i.e., snowmelt). Hydrologic data and parameters also need to be estimated. For this, further development of snowpack estimation and snowmelt models may be needed. It should first be applied to the four to six watersheds where frequent streamflow and chemistry data are available. It is thought that many model parameters from the Emerald Lake basin can be applied regionally, however better parameter estimates from Emerald Lake are needed first. Other watershed characteristics will need to be estimated from field data.

Table 2.1. CHEMICAL INPUTS AND DATA IN MODEL *(future data needs in italics)*

- ***Dry deposition***
  - average seasonal values for 8 chemical species
  - *temporal resolution for atmospheric concentration, deposition velocity and flux*
  - *distribute data by receptor (vegetation type, snow, rock)*
  - *further analyze the existing data sets for consistency and seasonal values*
- ***Wet deposition*** – data
- ***Throughfall*** – no net uptake
  - lumped data for summer
  - *canopy exchange coefficient*
  - *1985 data (averages only); 1986 data (NO_3^- only)*
  - *extend data seasonally*
- ***Meltwater elution from snow***
  - concentration based on fraction melted; all species same
  - assumed aggregation of point estimates
  - *actual distributed melt and/or energy*
  - *combined snowmelt, snowpack, stream data analysis (1987-88)*
  - *extend conditions/parameters; field validation of point estimates*
  - *multilayer elution model to extend boundary and initial conditions of point estimates*
- ***Mineral weathering***
  - laboratory rates, adjusted for field data
  - stoichiometry from field
  - *different values for upper vs. lower elevation soils*
  - *parameter adjustment for soils, rock, talus*
  - *extend data set – pH dependence*
- ***Litter decay*** – lumped, low
  - constant seasonal release rates for litter (field)
  - lumped by vegetation type
  - *litter amounts by vegetation type and decay products*
- ***Soil mineralization*** - lumped, high
  - apply lab Potentially Mineralizable Nitrogen (PMN) to field rates (NO_3^-) and entire soil volume
  - *resolve large numbers in data sets*
- ***Cation exchange*** – existing lab data
  - *extend data set*
- ***SO_4^{2-} adsorption*** – existing lab data
- ***Plant uptake*** – no data available
- ***Soil lysimeter*** – data
- ***Stream chemistry*** – data
  - *more closely-spaced data during snowmelt*

CHAPTER THREE

INTRODUCTION

Lakes in alpine watersheds in the Sierra Nevada are susceptible to damage by acid deposition due to their generally low buffering capacity and long response time for neutralization to take place. Changes from both repeated, long-term acidic fluxes and intense, short-term depositions/runoff events are expected to cause shifts in the chemical composition and, therefore, in the biotic communities in alpine lakes and streams.

In order to better understand the implications of acid deposition in watershed systems in the Sierra Nevada, the California Air Resources Board (CARB) initiated an intensive integrated watershed study at Emerald Lake in Sequoia National Park. The comprehensive nature of the data obtained from these studies provided an opportunity to develop a quantitative description of how watershed characteristics and inputs to the watershed influence within-watershed fluxes, chemical composition of streams and lakes, and, therefore, biotic processes.

In August 1987, the University of Arizona's research team started work on the development of physical/chemical models of the Emerald Lake watershed as a part of the Sierra Watershed Modeling Project (SWMP).

The primary objectives of the modeling effort were:

(1)To develop a process to identify the most important parameters, inputs, and chemical processes that influence lake/stream chemical composition;

(2)To provide a better understanding of the physical interactions between the various subprocesses of the watershed;

and, finally, based on the results of (1) and (2) above:

(3)To propose a model structure of the Emerald Lake watershed that will facilitate future interpretation and prediction of the response to changes in atmospheric inputs to the watershed.

Two different but closely-related modeling approaches were followed. In the first, the emphasis was placed on the development of "systems-theoretic" models. In the second approach, development of a "compartmental" model was undertaken. The systems-theoretic effort results in simple time-series models that allow consideration of the stochastic properties of model errors, while the compartmental modeling results in a comprehensive and detailed description of the various interacting physical and chemical processes.

The three main objectives in the analysis of the Emerald Lake watershed data using systems-theoretic models, were to:

(1)Analyze hydrologic and chemical flux data in order to evaluate the potential information contents of data and to see what could be learned about the watershed behavior from the data;

(2)Obtain some idea of watershed response to various system attributes; in particular, identify those attributes having the strongest influence on watershed response and determine which attributes to include in the compartmental model; and

(3)Develop simple predictive models of watershed outputs (both quantity and quality).

The primary reason for developing the compartmental model is to provide CARB with a detailed, physically-based tool to assist in evaluating effects caused by acid deposition. The two primary uses of the model are:

(1)As a research tool to identify which hydrologic and chemical processes are important and when changes due to these processes are occurring; it should also assist in interpreting field monitoring and process-level research and to help plan future research; and

(2)As a predictive model for scenario analysis, displaying changes in watershed outputs resulting from changing input conditions. As such, it enables estimating effects of natural or anthropogenic changes in climate or atmospheric pollutant loading.

The model is designed for use in moderate to high elevation mountainous areas where the hydrology is driven largely by snowmelt, and chemical changes in the water passing through the watershed are small but important for stream chemistry. Model flexibility for use in other areas, with different levels of data, and by different users is also an important feature. Therefore, it is designed to overcome the major problems that prohibit use of existing models.

CHAPTER FOUR

SYSTEMS-THEORETIC MODELING

4.1 Introduction

This chapter documents the analysis of the Emerald Lake watershed data using systems-theoretic methods. In specific, there were three main objectives to this study, as follows:

(1) To analyze hydrologic and chemical flux data in order to evaluate the potential information content of the data and to see what could be learned about the watershed behavior from the data;

(2) To obtain some notion of watershed response to various system attributes. In particular, the study was intended to (a) identify those attributes having the strongest influence on watershed response, and (b) determine which attributes to include in the compartmental model; and

(3) To develop simple predictive models of watershed outputs (both quantity and quality).

The first portion of this chapter presents the results of the water quantity (flow) modeling. In the second part, the results of water quality (chemical modeling) analysis are presented.

4.2 Water Quantity Modeling

The first task involved obtaining the Emerald Lake watershed data from the Center for Remote Sensing and Environmental Optics at the University of California at Santa Barbara. Two sets of data, both for Water Year (WY) 86 (October 1, 1985 through September 30, 1986), were available. The first data set (provided in October 1987) consisted of hydrologic and meteorologic fluxes at hourly intervals. This first data set was incomplete, as it contained several missing periods. In addition, some key parameters were not available, notably snowmelt/precipitation and chemistry information. The second data set (provided in February 1988) consisted of estimated hydrologic fluxes lumped over the watershed at 24-hour intervals.

Therefore, the analysis and modeling effort proceeded in two phases. Phase 1 dealt with the analysis of hourly data, while the focus of Phase 2 was on the analysis of daily data and the development of ARMAX (Auto-regressive Moving Average model with eXogenous variable) models. The advantage of the ARMAX modeling approach is that analytical model identification and parameter estimation techniques are available and well-documented in the literature. In addition, previous forecast errors can be included to improve forecasts and to estimate confidence limits for the forecasts. Furthermore, diagnostic checks are available to determine if the model is performing properly. Additional details related to ARMAX modeling and the various stages involved in its development are included in the Appendix accompanying this section of the report.

4.3 Phase 1: Analysis of Hourly Data

The primary objective of Phase 1 of the analysis was to develop and test the algorithms that would be used to develop the systems-theoretic model in Phase 2. Accordingly, some portions of the data were analyzed in detail using the program MATLAB (Moler et al., 1987).

4.3.1 Qualitative Data Analysis

Cumulative daily inflows and outflows for Emerald Lake are plotted in Figure 4.1. The plot shows that there are two distinct runoff seasons. The period from October through March (days 1-180) constitutes a 'dry' season corresponding to winter when snowmelt is minimal. The period from April through September (days 181-365) constitutes a 'wet' season corresponding to summer when the snowpack is melting. Around day 140 (February), we see a large spike in the outflow hydrograph, possibly caused by an avalanche event.

Next, the flow data from inlets 1 and 2 were examined to see how representative they are of the total inflow into the lake. Four distinct inlets contribute water to the lake, along with an unknown amount of other flows. The water budget for the year reveals that 80% of the outflow can be accounted for by inlets 1 and 2. Figures 4.2 and 4.3 show the cumulative flows separately for the 'dry' and 'wet' seasons. It is interesting to note that during the 'dry' season (quarters 1 and 2), a substantial amount of the lake outflow cannot be accounted for by inlets 1 and 2. Much of the outflow not accounted for by the inflows during this period is presumed to be due to avalanche displacement. These data must somehow be estimated, perhaps through the use of the compartmentalized hydrogeochemical model. During the 'wet' season (quarters 3 and 4), the inlet flows comprise a substantially larger percentage of the total lake inflow.

The next step was to look at the data for individual months to determine other behavioral characteristics. Figure 4.4a shows that the data for May clearly depict the transition to daily periodic snowmelt cycles. Figure 4.4b displays some more detail. As can be seen, the time lag between inflow and outflow is smaller than one hour (the time resolution of the data). In addition, the inlet flow troughs occur at about 1:00-3:00 p.m., and the peaks occur at about 8:00-10:00 p.m. Figure 4.4c shows the same detail for July. This is later in the season, and the timing of the inlet flow troughs has advanced to 10:00-12:00 a.m., and that of the peaks has advanced to 5:00-7:00 p.m. For both of these months, the volume of inflow through inlets 1 and 2 is seen to be consistent with the volume of outflow. This is not true for September, when the outlet flow fluctuates dramatically in a manner not accounted

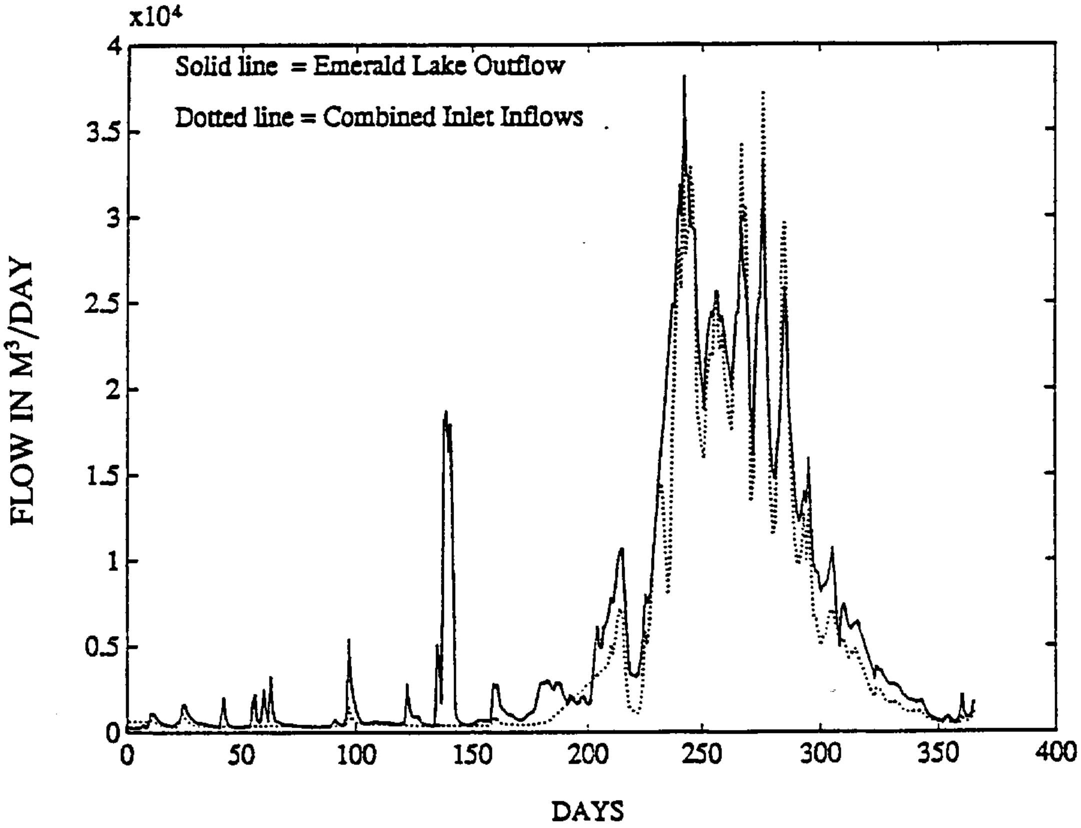


Figure 4.1 Daily flows for water year 86.

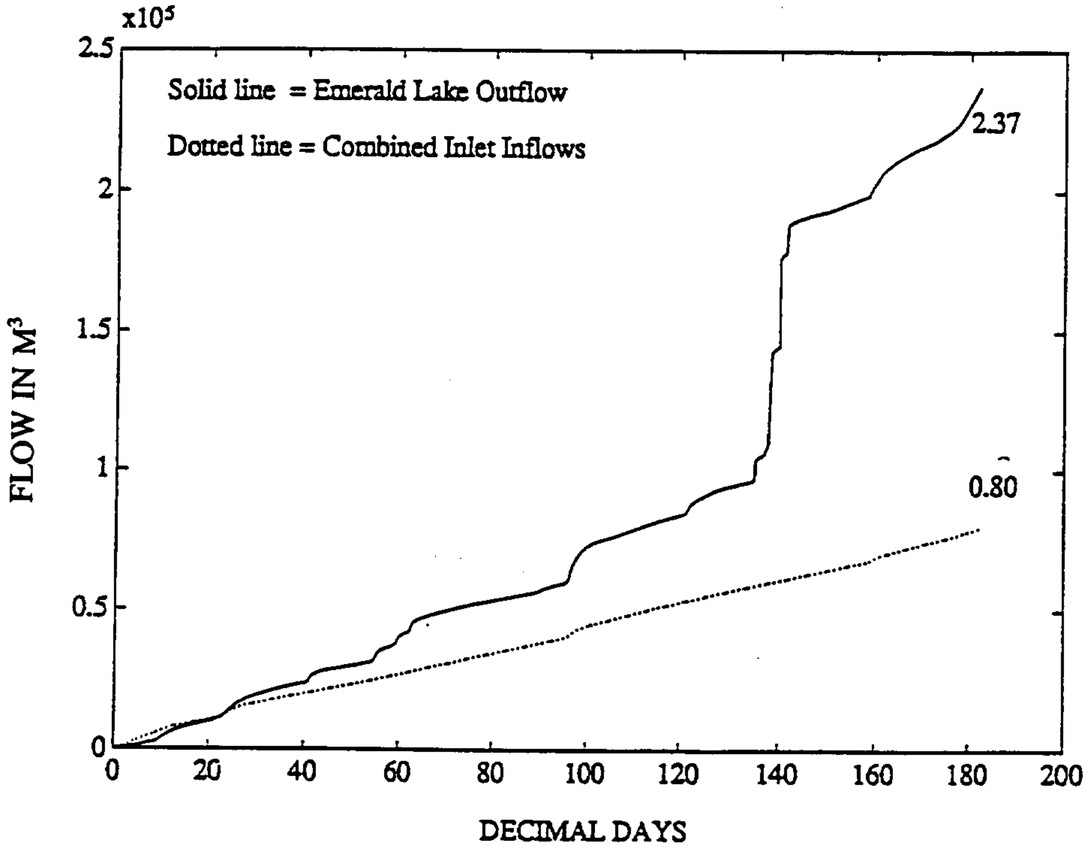


Figure 4.2 Cumulative flows for quarters 1 and 2 only.

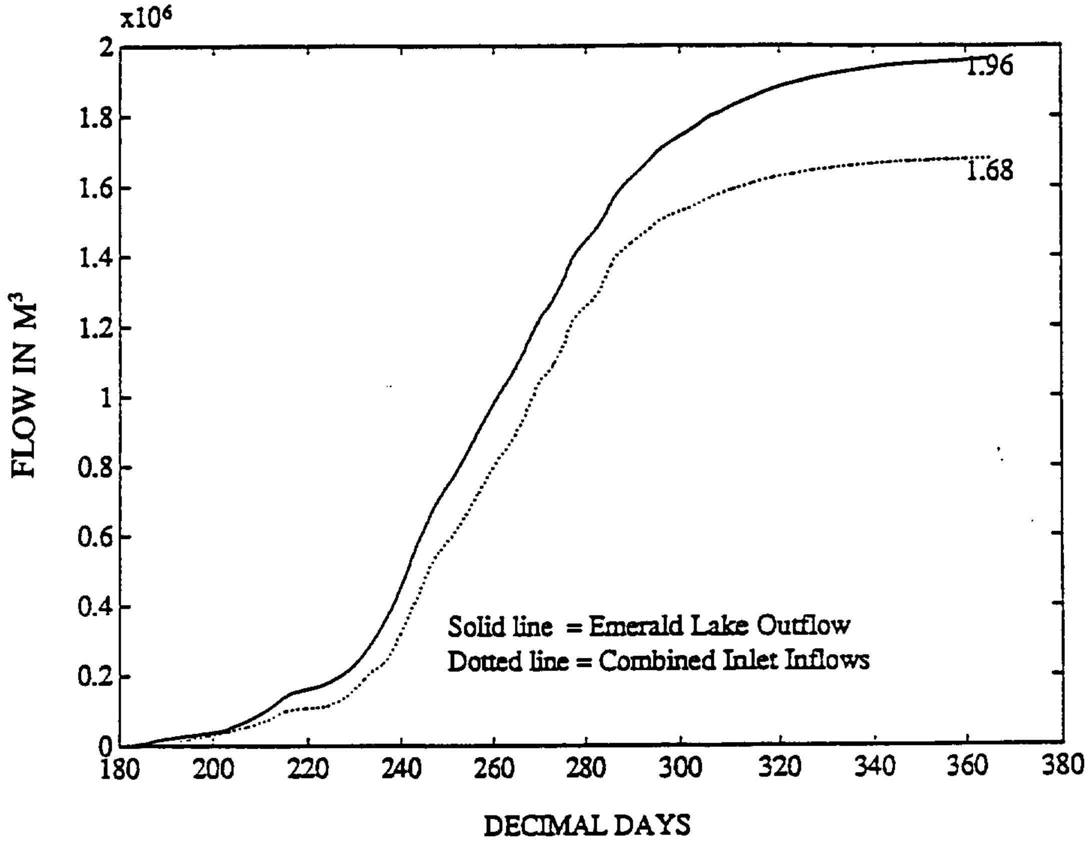


Figure 4.3 Cumulative flows for quarters 3 and 4 only.

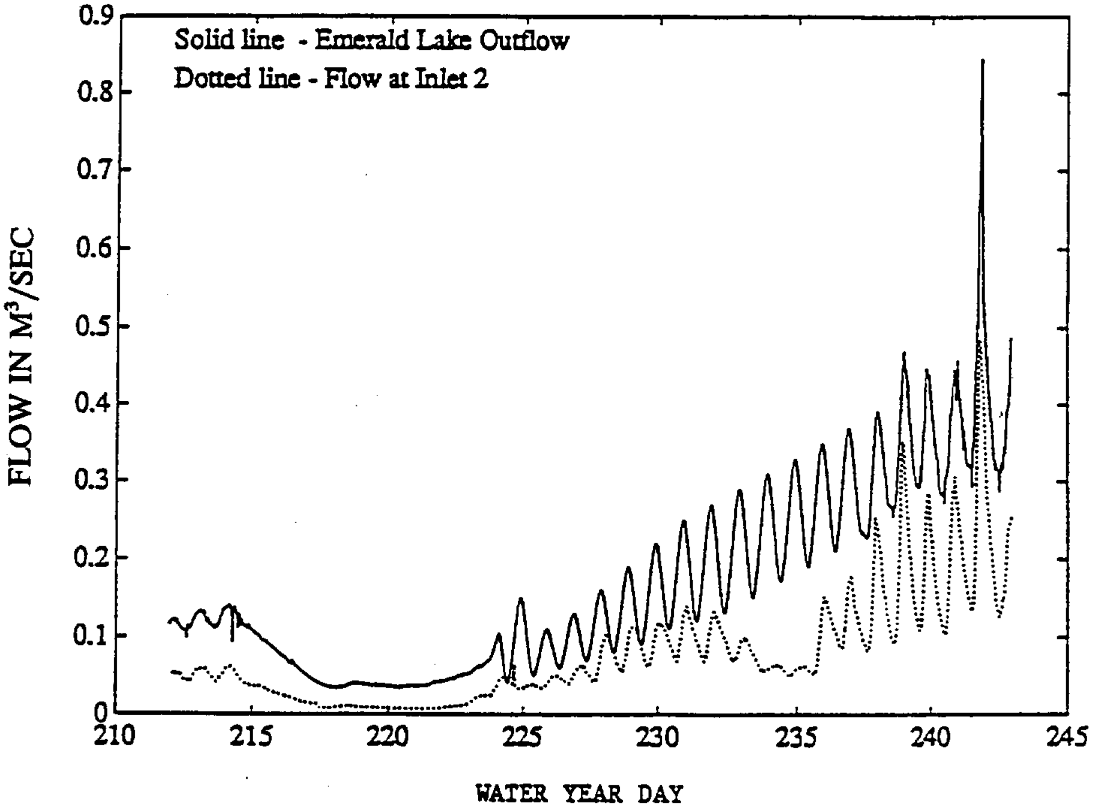


Figure 4.4a May - hourly flows at outlet and inlet 2.

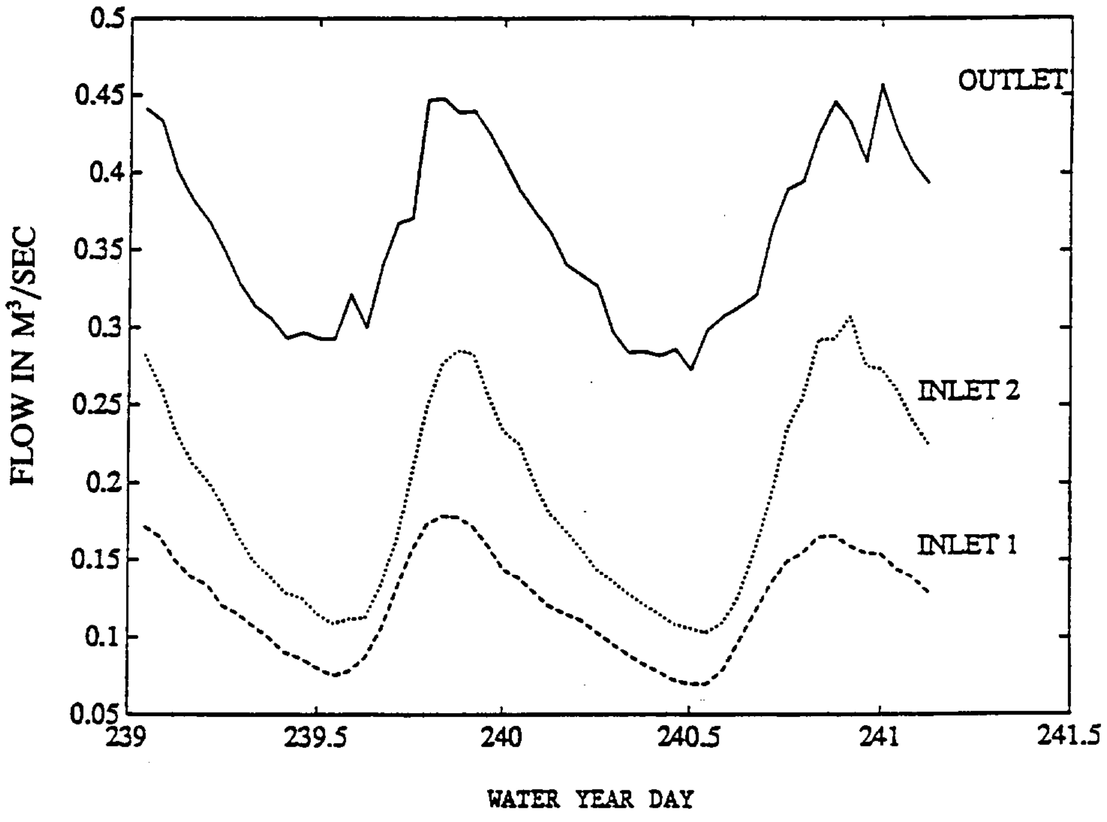


Figure 4.4b May - detail of hourly flows.

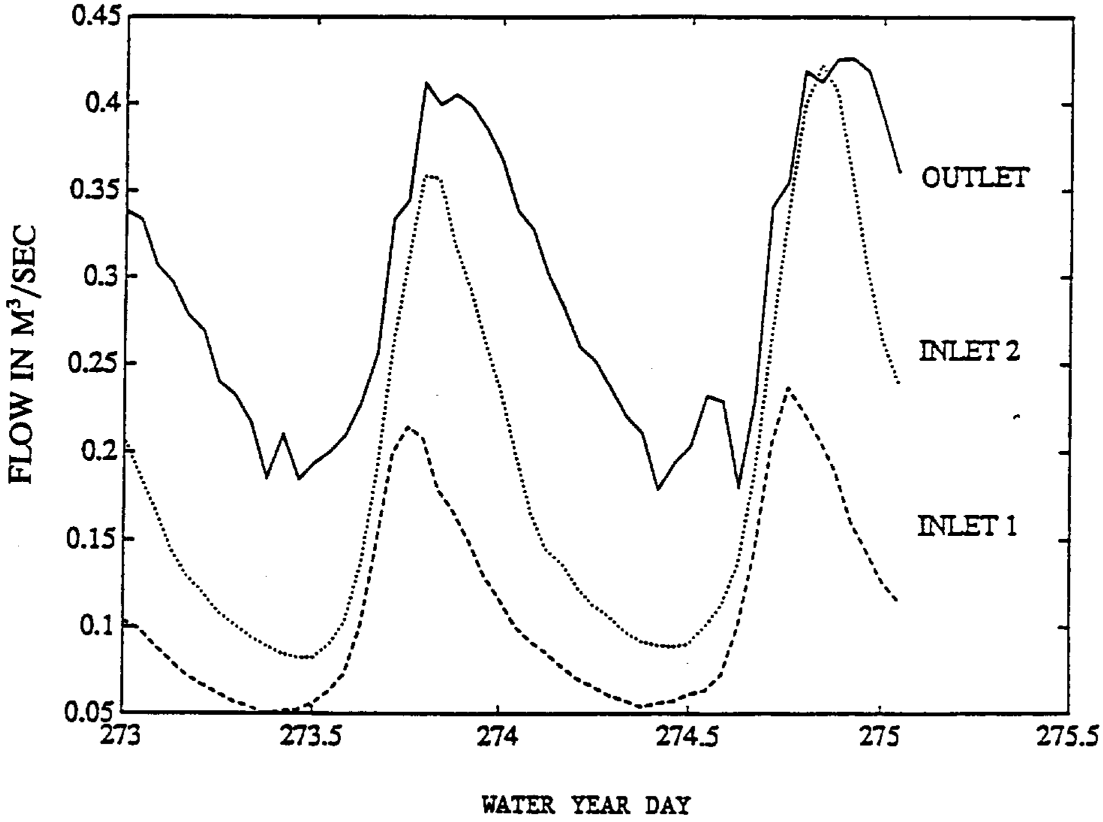


Figure 4.4c July - detail of hourly flows.

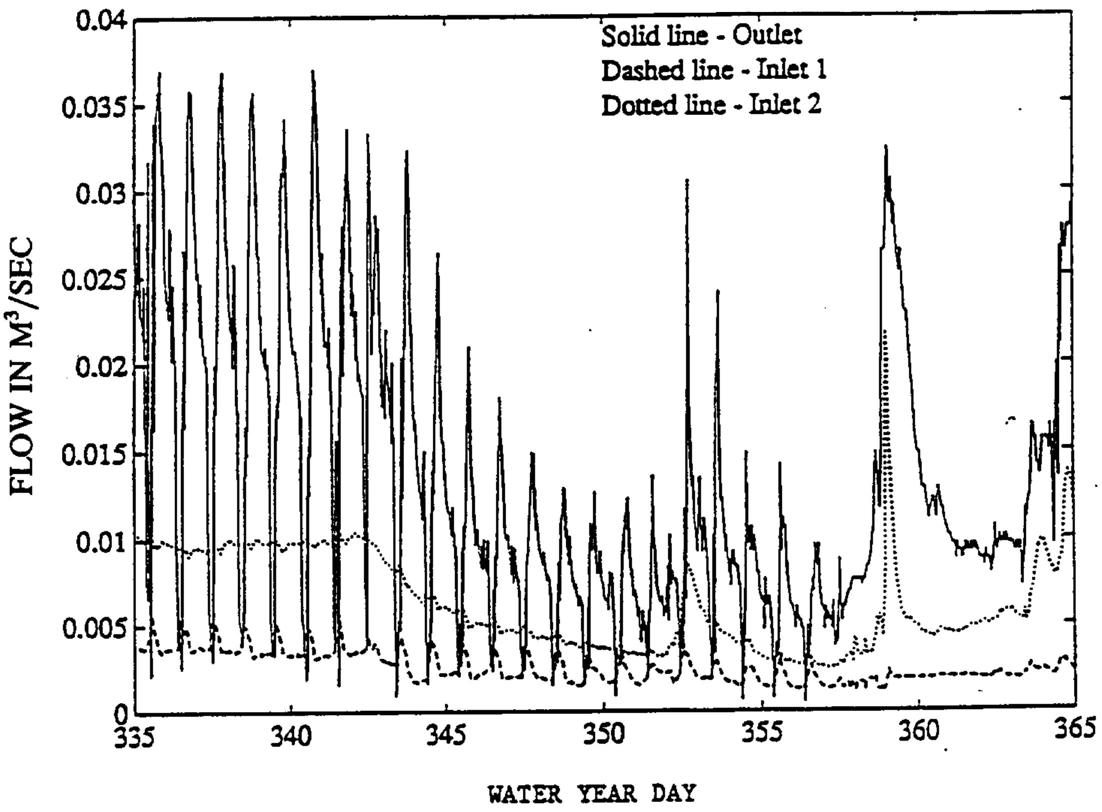


Figure 4.5 September - hourly flows at outlet and inlets.

for by fluctuations in the inlet flows (Figure 4.5). This matter was discussed at the October 1987 meeting of the Integrated Watershed Study researchers and modelers at UCLA, and it was suggested that the outlet fluctuations may be in response to ungaged late season snowmelt and/or due to temperature effects on the transducer at low water level. This matter was not pursued any further.

4.3.2 Quantitative Data Analysis

The objective of the systems-theoretic approach is to establish simple relationships between different observed watershed variables to develop a better understanding of how those variables interact and which variables should be included in the model. Correlation analyses can be used to determine which of several variables are informative and which provide only marginal information. The approach can also be used to establish simple predictive models based on linear relationships.

In order to understand the hydrology of the watershed, the most important relationships of interest are those between the quantity and quality of snowmelt and lake inflow. However, during Phase 1, no snowmelt information was yet available to establish and test the algorithms necessary for the data analysis. Therefore, it was decided to select a surrogate variable for snowmelt from among the available data. The only suitable surrogate variable available was air temperature. Air temperature at the ridge site was used to develop a model predicting lake inlet flows. Figure 4.6 shows a plot of ridge site air temperature for the water year.

The inlet flow estimation algorithms were tested on these data for the month of June (Figure 4.7). An ARMAX predictive model was computed that uses several preceding air temperature values to predict hourly future inflows to the lake. Figure 4.8 shows that a relatively good prediction can be obtained (for June), thereby verifying that the algorithms work satisfactorily. The model parameters are plotted in Figure 4.9 where they indicate the shape of the watershed impulse response function.

The impulse response function (IRF) is the system's response to an isolated unit pulse of input. It completely characterizes the behavior of a system if the system is linear. A relatively flat IRF with many parameters indicates a system with long-term memory, whereas a sharp IRF with fewer parameters indicates that the inputs are rapidly flushed through the system. The time lag of a system (in the case of the present study, roughly the time of concentration of the watershed) is indicated approximately by the time corresponding to the peak of the IRF. The estimated IRF peak, according to Figure 4.9, is at eleven hours, which suggests that if a daily time step is used to model the watershed, overland and streamflow routing will not affect lake inflows. This would eliminate the need for streamflow routing in the watershed model.

4.3.3 Conclusions: Phase 1 Study

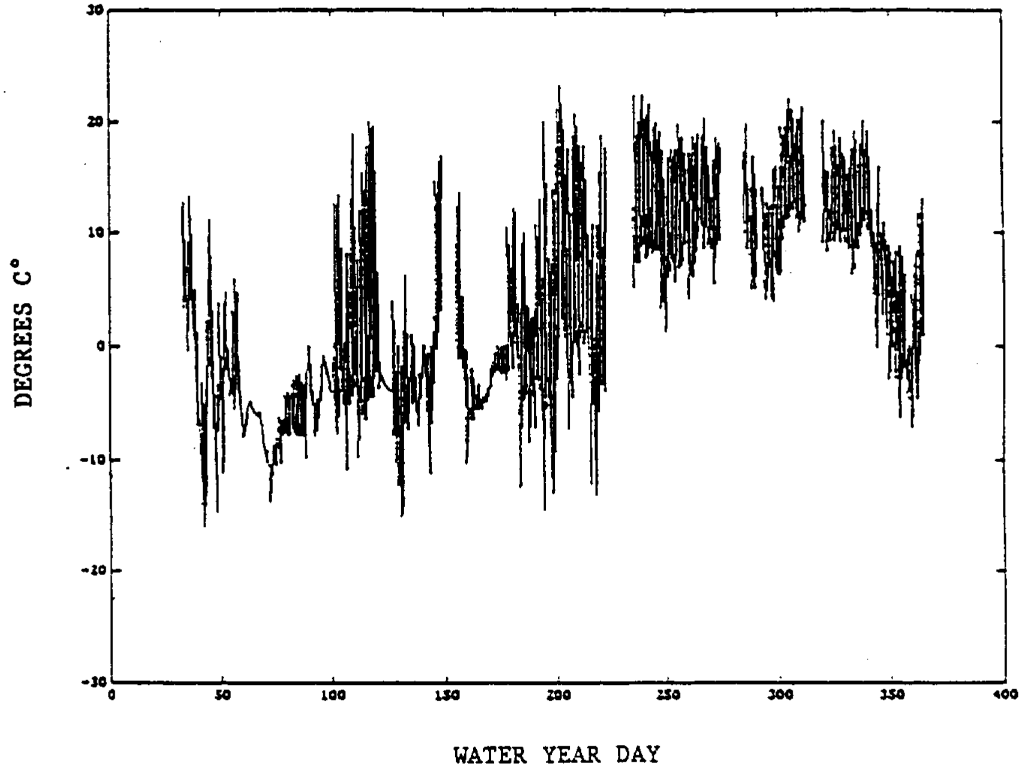


Figure 4.6 Ridge-air temperature at 4.0 m above ground.

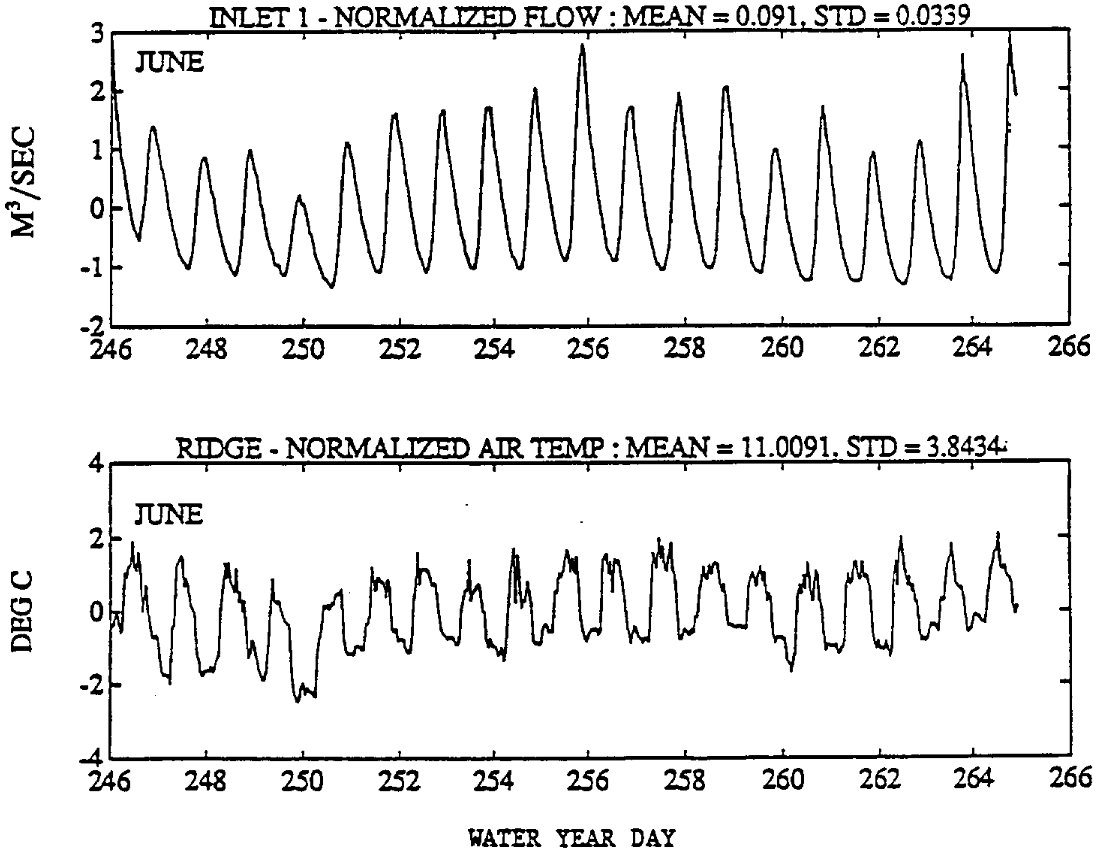


Figure 4.7 Normalized flow at inlet 1, and normalized air temperature at ridge.

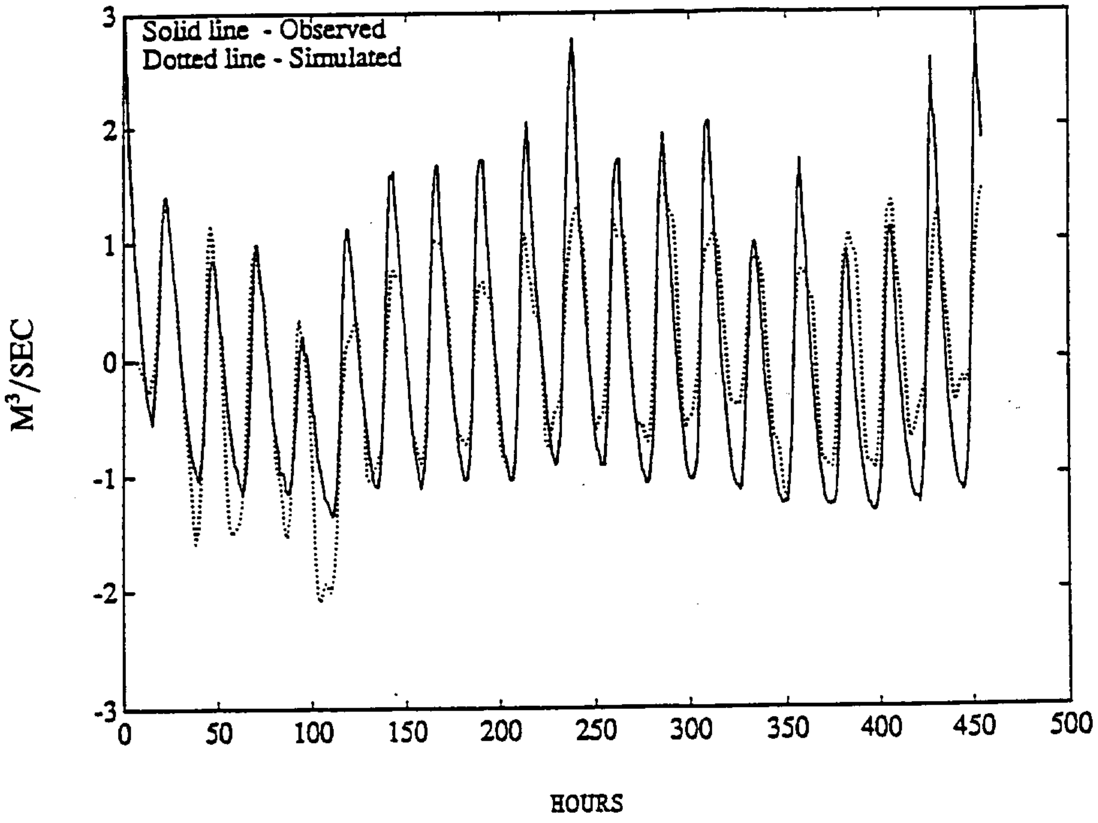


Figure 4.8 Model of inlet 1 flows based on ridge temperature.

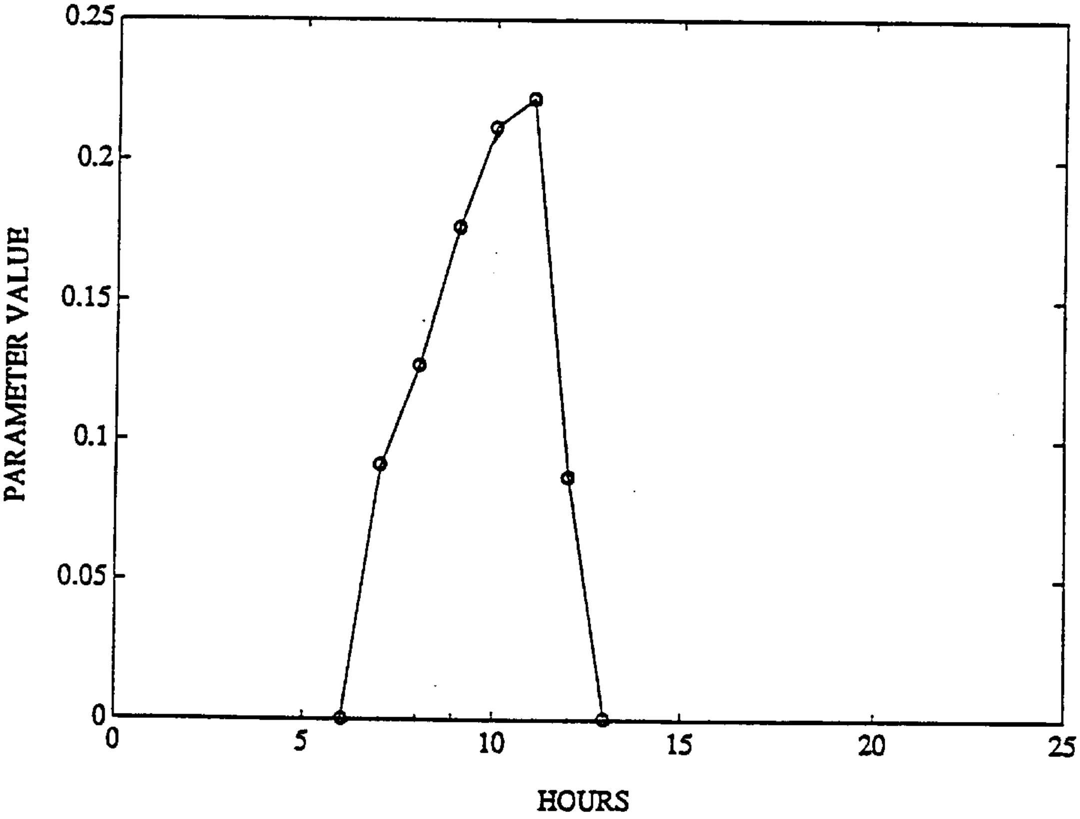


Figure 4.9 Shape of impulse response of inlet 1 flow to ridge temperature.

The following is a summary of the conclusions of the Phase 1 study obtained using WY 86 data. General applicability of these conclusions requires verification with other sets of data.

(1) A significant amount of the lake outflow cannot be accounted for by combined inflows from inlets 1 and 2 during the 'dry' season (first and second quarters of WY 86) (see Figure 4.2). The reason is that much of the outflow not accounted for by the inflows was presumably due to avalanche displacement. The situation during the 'wet' season (third and fourth quarters of WY 86) is somewhat different in that the combined inflows do account for most of the lake outflow (see Figure 4.3).

(2) The data show that during the 'wet' season, the watershed undergoes a strong diurnal response, whereas this is not the case during the 'dry' season (see Figures 4.4a-c and 4.5). Therefore, different models would be needed to best capture the system's behavior during each of the two seasons.

(3) The wet season IRF was found to exhibit a sharp peak at lag time of eleven hours. Therefore, a daily time scale can be used to model the watershed behavior without the need to consider detailed routing of flows in the channel network.

4.4 Phase 2: Analysis of Daily Data

The Phase 1 analysis indicated that a daily time scale would be suitable for modeling of the Emerald Lake watershed response to snowmelt. At this time scale, the diurnal variations would not show up, thereby reducing the complexity of the modeling effort, while preserving the hydrological and geochemical dynamics of interest to the study. This decision was approved by the researchers and modelers at the October 1987 UCLA meeting of the Integrated Watershed Study group. As a result, the Center for Remote Sensing and Environmental Optics at UCSB provided us with hydrologic flux estimates for the watershed on a daily time scale.

The hydrologic data provided for this analysis included ten (10) vectors, consisting of daily values (measured or estimated) of the following hydrologic quantities (m^3/day = cubic meters per day):

Variable Name	Description	Units
psnow	Precipitation as snow	(m^3/day)
prain	Precipitation as rain	(m^3/day)
esnow	Evaporation from snow	(m^3/day)
eet	Evapotranspiration	(m^3/day)
elake	Evaporation from lake	(m^3/day)

rmelt	Runoff from snowmelt *(estimated by UCSB model)*	(m^3/day)
rrain	Runoff from rain	(m^3/day)
Q	Flow at lake outlet	(m^3/day)
schange	Change in watershed storage	(m^3/day)
resid	Mass balance residual	(m^3/day)

These vectors are presented graphically in Figures 4.10a-j. Positive values indicate fluxes into the watershed, and negative values correspond to losses from the watershed.

4.4.1 Covariance Analysis of the Data

The major inputs to the watershed are snow and rain. However, rainfall events are few and far between. In addition, the lake outflow shows little or no response to the individual rainfall events (see Figure 4.11a). The dominant variable influencing lake outflow is clearly snowmelt (see Figure 4.11b). The general pattern of correlation between melt and lake outflow seems quite good. Note that there are some incidences of short-duration spikes in the lake outflow record. These few anomalies, which may be attributable to avalanche events where snow is deposited directly into the lake, should not show up in the snowmelt record.

An important point to be mentioned here is that the available snowmelt estimates assume that the entire watershed behaves as one homogenous unit and do not account for zoning variations. We might expect some errors in timing and volume to be present in the snowmelt estimates.

The various hydrologic variables are presented as cumulative plots for the entire WY in Figure 4.12a. The graph clearly shows that evapotranspiration (eet) is extremely minor in comparison to evaporation from snow (esnow). However, the combined total of the two is only about one-sixth of the total watershed inputs. In addition, while the daily variations are quite significant (see Figures 4.10c, 4.10e), the cumulative pattern indicates that the general trend is fairly constant through the year.

Figure 4.12a also shows the cumulative pattern for the combined inputs (Curve No. 2) and the combined outputs (Curve No. 7), showing the pattern of accumulation and release. The mass balance of the data appears to be quite good. Note again that precipitation as rain (prain) does not contribute significantly.

The data analysis indicates that the only variables worth including in the systems-theoretic evaluation are snowmelt (rmelt) and lake outflow (Q). The cumulative totals of these are presented in Figure 4.12b. The lake outflow is presented in two ways, first including the anomalous events and then excluding volumes from the anomalous events exceeding the current average flow. Note that snowmelt preceeds lake outflow, and that the total cumulative volume of snowmelt ($2.35 \times 10^6 m^3$) exceeds the

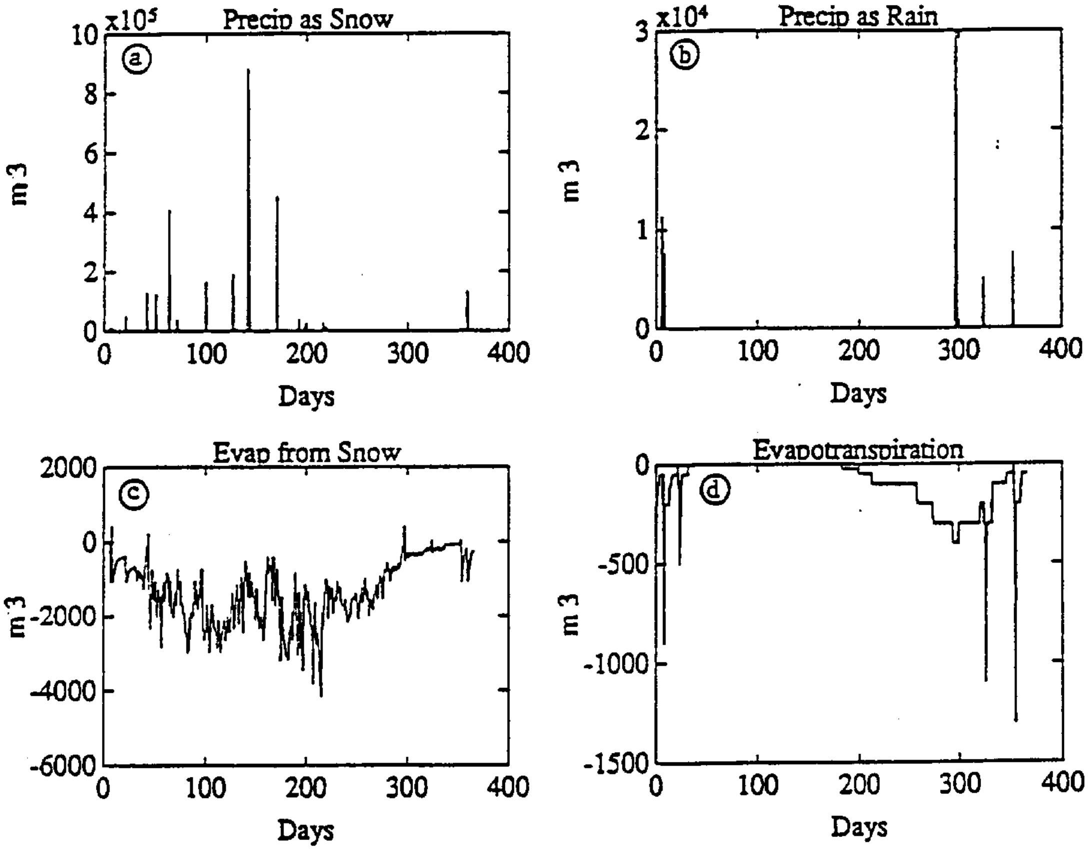


Figure 4.10 Plots of the hydrologic vectors for WY 1986.

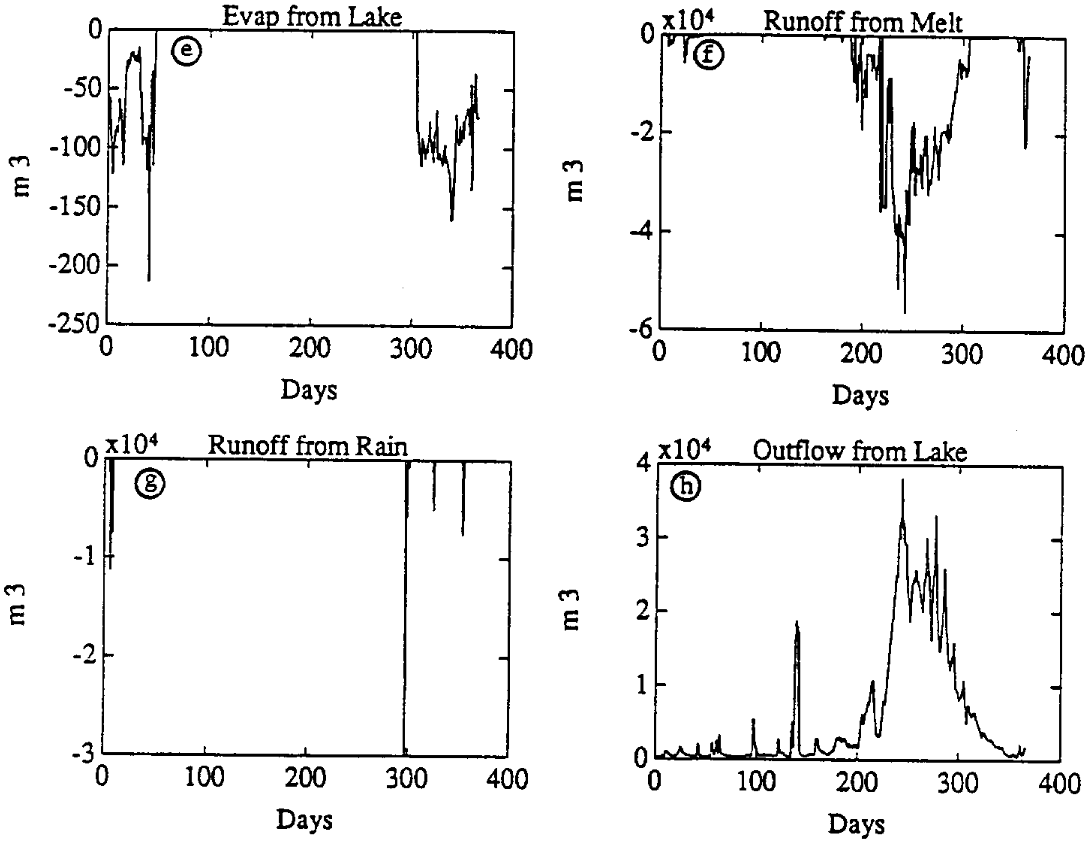


Figure 4.10 cont. Plots of the hydrologic vectors for WY 1986

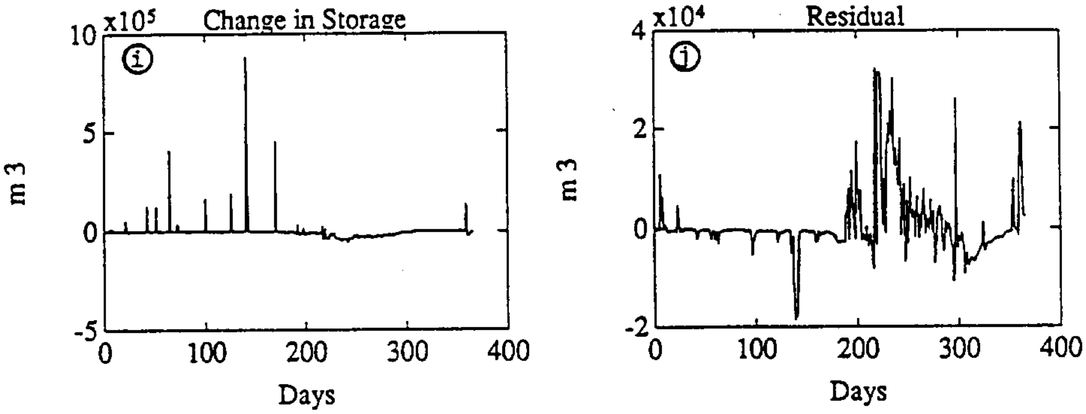


Figure 4.10 cont. Plots of the hydrologic vectors for WY 1986

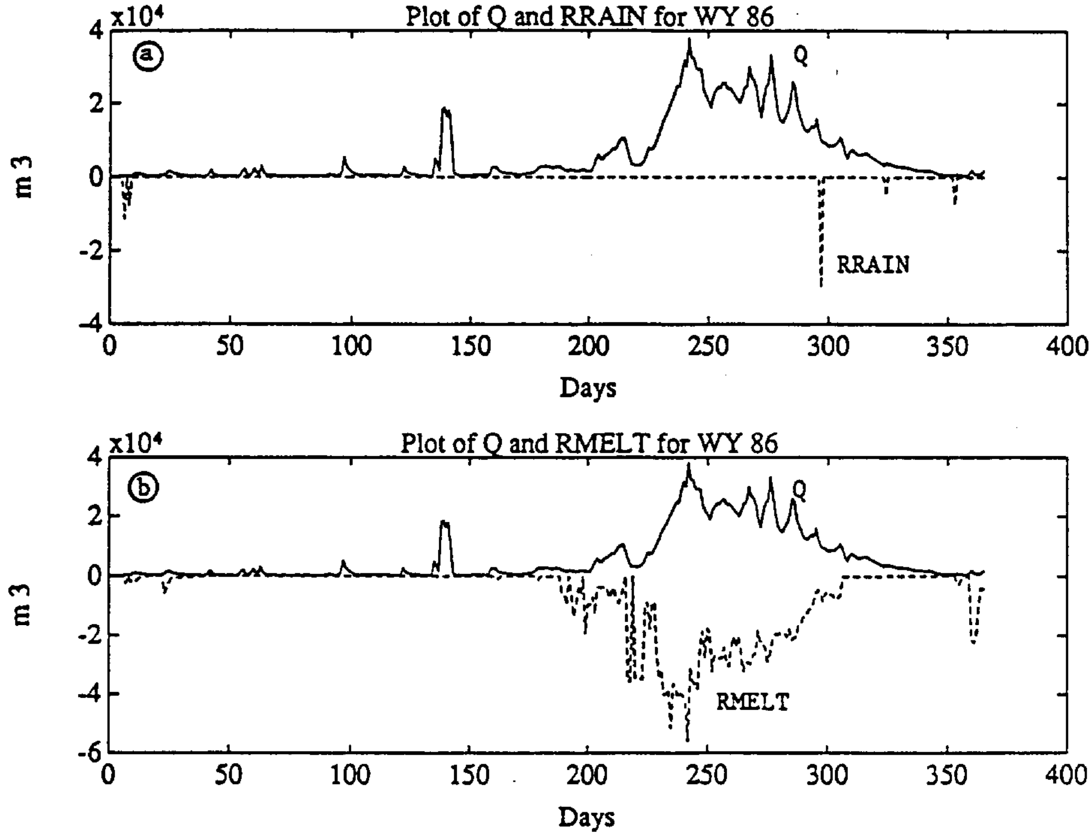


Figure 4.11 Plots of Q with RRAIN and RMELT for Water Year 1986

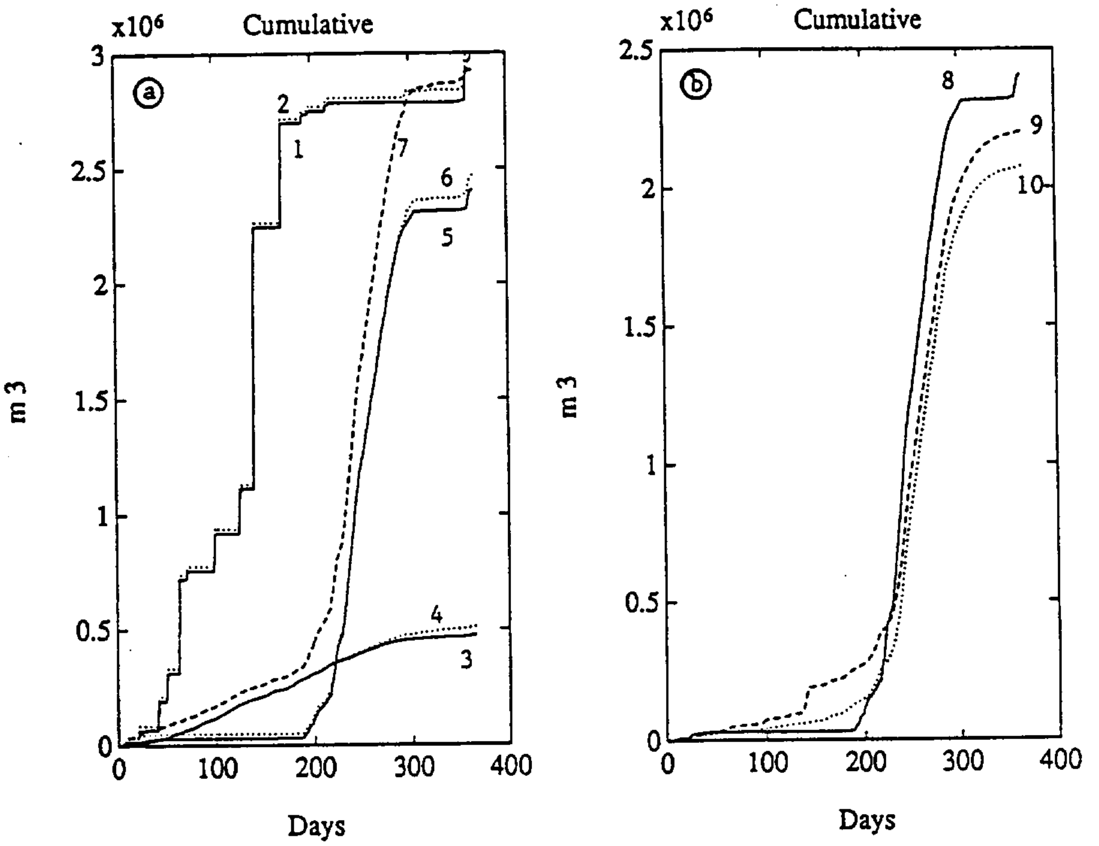


Figure 4.12 Plots of Cumulative values of the vectors

1 - PSNOW
2 - PSNOW + PRAIN
3 - ESNOW
4 - ESNOW + EET
5 - RMELT
6 - RMELT + RRAIN
7 - RMELT + RRAIN + ESNOW + EET
8 - RMELT
9 - Q (including avalanches)
10 - Q (without avalanches)

cumulative volume of lake output ($2.25 \times 10^6 m^3$). However, the difference does not appear significant enough to prevent systems-theoretic models from being developed. (NOTE: Appendix A contains some details related to systems-theoretic modeling. Review of that appendix might be necessary before reading the next sections).

4.4.2 Systems-Theoretic Model-Correlation Analysis

The first step in model development is to establish how well the dependent (Q) and independent (rmelt) variables are related. A plot of rmelt versus Q showed no clear patterns. This result seems inconsistent with Figure 4.11b which shows a good relationship between the two variables. However, a closer look at Figure 4.11b reveals that the relationship is strong only for certain portions of the year, while it appears quite weak at other times. Hence, the data were divided into four portions corresponding to days 1-180 (initial frozen period), days 181-250 (period of increasing melt), days 251-300 (period of decreasing melt), and days 301-365 (tail period). These data are presented in Figures 4.13a-d. Individual correlation plots for these four periods are presented in Figures 4.14a-d. Note that the best relationship emerges for the third period, while the second period is moderately good. The first and last periods show very poor correlation.

The relationship between the variables Q and rmelt was also analyzed by computing the cross-covariance functions for each of the four periods (see Figures 4.15a-d). Note that there are very different patterns for the four periods, indicating that very different mechanisms are operating in the relationship between the variables in each period. The two periods of interest are periods two and three. Note that in period two, the cross-covariance function has a peak at about three days and is quite flat, indicating that several melt periods are contributing to a lake outflow value. In contrast, period three has a cross-covariance, with its maximum at zero lags, falling off rather quickly. This indicates that very few melt periods contribute to a lake outflow value. The behavior of period two is consistent with alternating periods of melting and refreezing and with poorly-developed runoff pathways, as might be expected early in the snowmelt season. The behavior of period three is consistent with continuous melting with well-established runoff pathways, as might be expected later in the snowmelt season. Clearly, different models are required to reproduce the behavior in these two periods.

4.4.3 Systems-Theoretic Model: Model Identification

4.4.3.1 Method of Analysis. The model identification is divided into two parts: the first involves analysis of period two data, and the second involves analysis of period three data. All computations were conducted using the facilities of the MATLAB program for data analysis (Moler et al., 1987). The method used was as follows. First, the variables q (lake outflow) and rmelt (runoff from snowmelt)

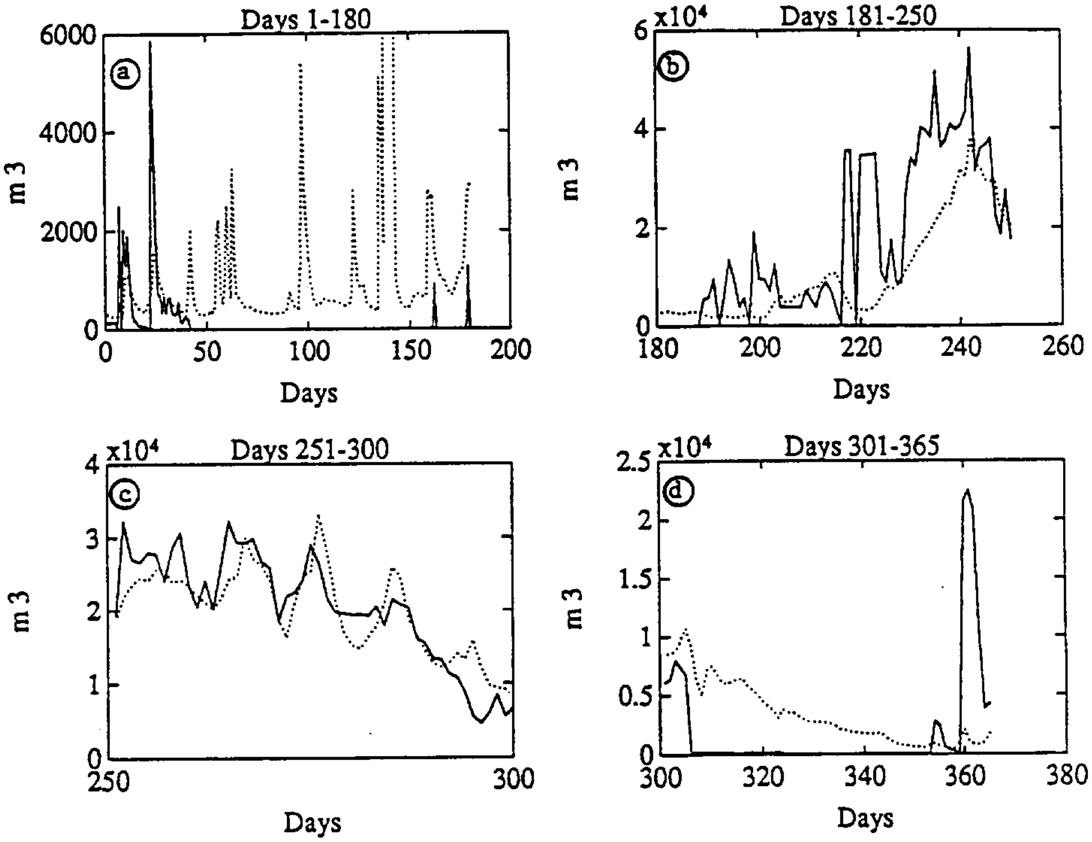


Figure 4.13 Plots showing the division of the data into 4 periods

Solid line = RMELT
Dotted Line = Q

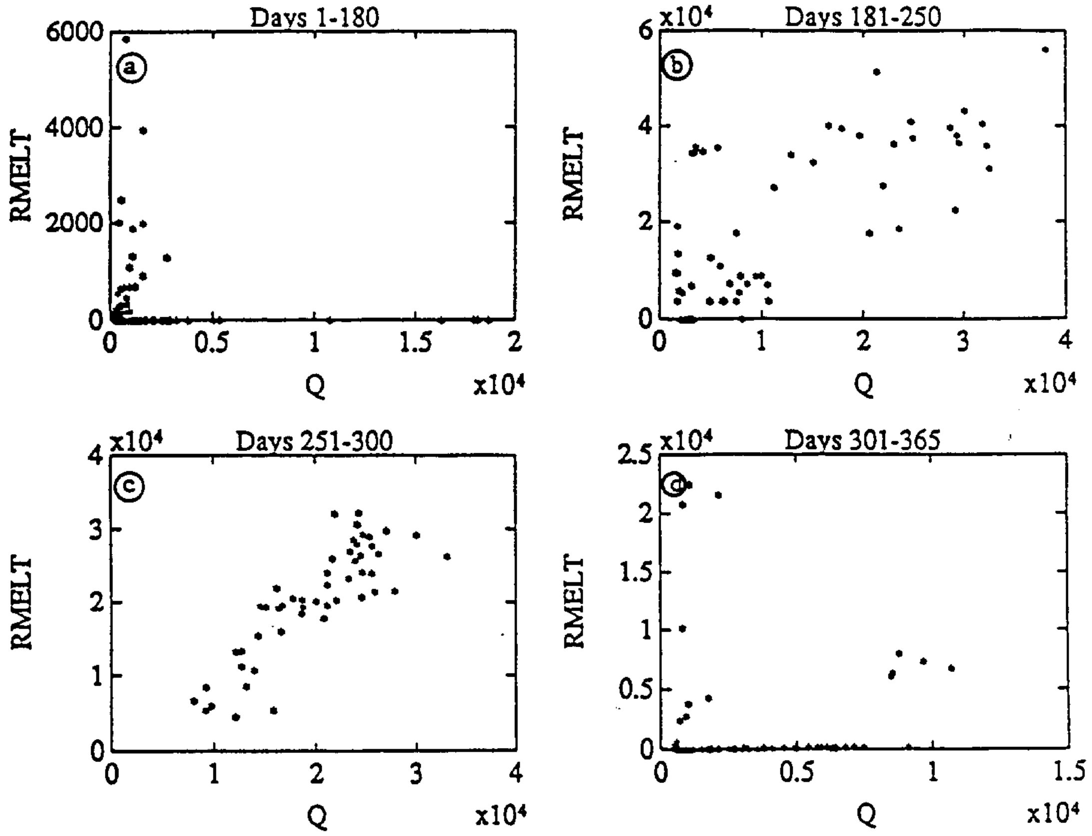


Figure 4.14 Plots showing the correlation between Q (m ^{3}/day) and RMELT (m ^{3}/day) for each of the four periods

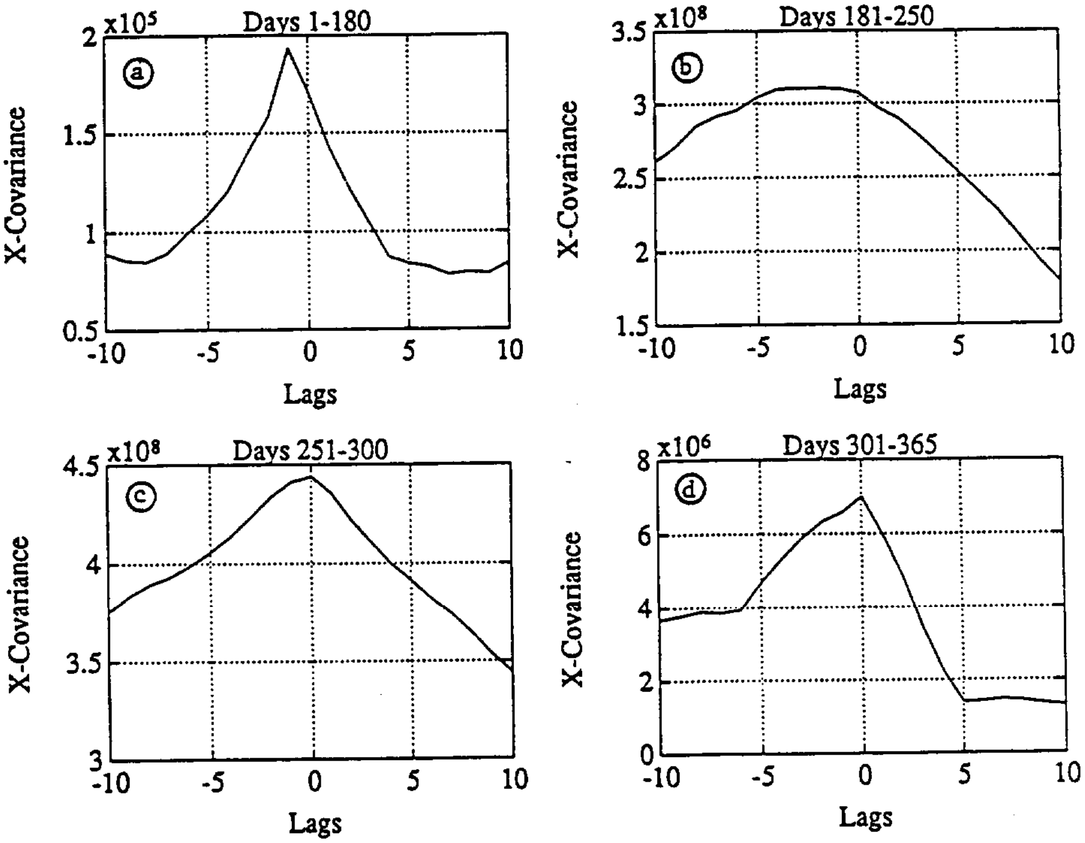


Figure 4.15 Plots of the Cross-correlation functions for each of the four periods

were normalized by subtracting the mean and dividing by the standard deviation (normalization of the variables is necessary to ensure accuracy in the subsequent computations). The normalized variables for period 2 are denoted as nq2 and nr2, respectively, and nq3 and nr3 for period 3. The MATLAB ARMAX modeling facility was then employed to construct several models predicting lake outflow at each time period based on known melt values from previous time periods.

As described in Appendix A, the structure of this model in our case is given by the equation:

$$A(s)Q(t) = B(s)I(t-l) + G(s)e(t)$$

where A(s), B(s) and G(s) are polynomials in the delay operator s (see Appendix A for details):

$$A(s) = \sum_{i=0}^{n} a_i\, s^{-i} \qquad where\ a_0 = 1$$

$$B(s) = \sum_{i=0}^{m} b_i\, s^{-i}$$

$$G(s) = \sum_{i=0}^{v} g_i\, s^{-i}$$

where Q(t), I(t-l), and e(t) are the output (dependent variable), input (independent variable), and error, respectively, and l indicates the number of lags between inputs and outputs (the number of time units before an input value has any effect on the output value).

In this analysis, no autoregressive terms (using past outflows to predict the present outflow) were used. Therefore, A(s) = 1.0. This results in a model similar to the well- known unit hydrograph, such that the parameters of the B(s) polynomial correspond to the impulse response function of the system. The shape of this polynomial, therefore, gives one an idea of the behavioral nature of the system being modeled.

The models were developed in two steps. In the first step, the B(s) polynomial was fitted while assuming G(s) = 1.0. This corresponds to the deterministic case (no consideration of the error term). Once the best B(s) polynomial was found, an error model [G(s) polynomial] was added to improve the predictive ability of the model. Fitting the best polynomial involves fitting several models by varying the maximum power of the polynomial (number of terms). The entire procedure was conducted for the cases of no-lag (l = 0) and one-lag (l = 1) between input and output.

4.4.3.2 Analysis of Period Two. First, several models were fit for the no-lag (l = 0) case. The estimated parameter values for each model are presented in Table 4.1. For each model, the loss

Table 4.1 Parameter values for different ARMAX models fitted to period 2 data assuming no lag term.

	Number of Parameters in the Model											
	1	2	3	4	5	6	7	8	9	10	11	12
1	7.5470	3.6970	2.2430	1.1630	1.0970	1.4630	1.5920	1.7600	1.4680	1.2320	1.2670	1.2130
2	0.0000	4.9410	2.2140	2.1020	1.3140	1.0070	1.1160	1.2850	1.4470	1.3200	1.0190	1.0160
3	0.0000	0.0000	4.7190	2.3030	2.0960	1.6430	1.4810	1.4610	1.6780	1.9580	1.7490	1.5140
4	0.0000	0.0000	0.0000	3.8570	1.4140	9.7800	0.6220	0.4430	0.5430	0.0614	0.0961	-0.0088
5	0.0000	0.0000	0.0000	0.0000	3.7790	1.4730	1.0250	0.5420	0.0523	0.0421	0.0525	0.0797
6	0.0000	0.0000	0.0000	0.0000	0.0000	3.5340	2.2610	1.6090	1.0510	1.1460	0.0094	1.0640
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.3120	1.0490	0.0491	-0.0146	0.0066	-0.0039
8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.7550	1.8500	1.6480	1.0440	1.1250
9	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.1590	1.2880	1.2180	0.0771
10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.9930	1.3790	1.3840
11	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.4850	0.0932
12	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.1480

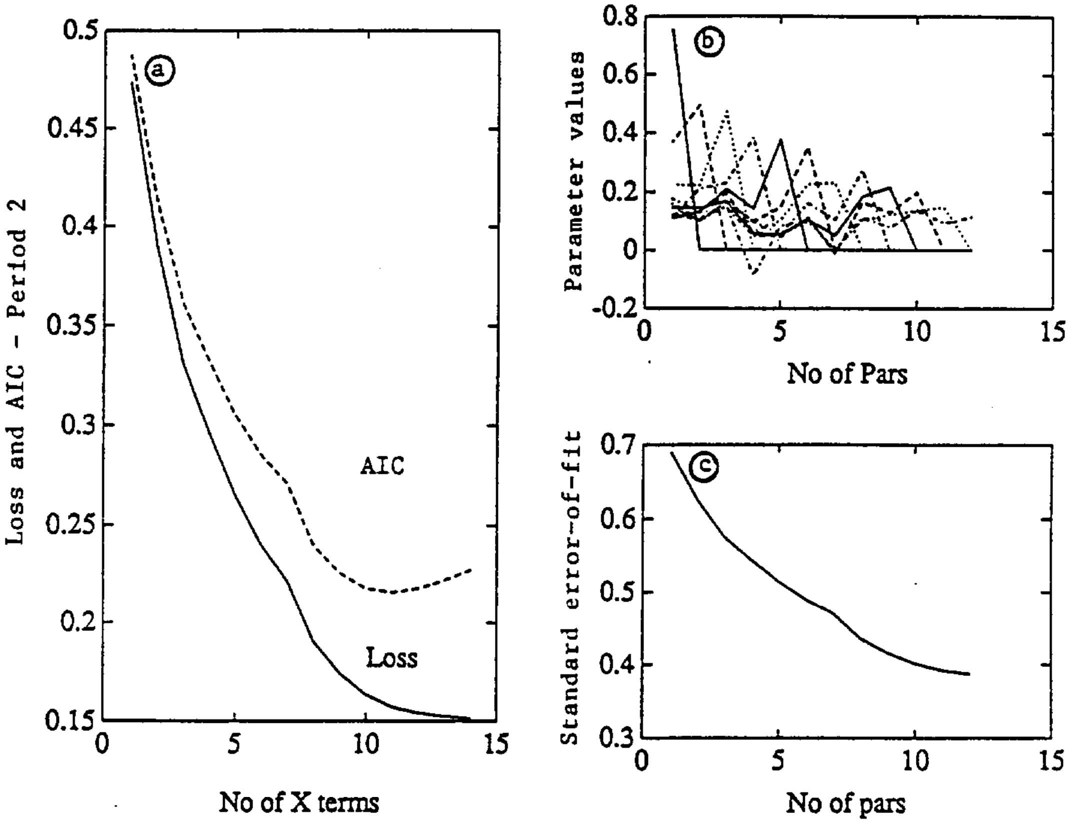


Figure 4.16 Results of model fitting to period 2

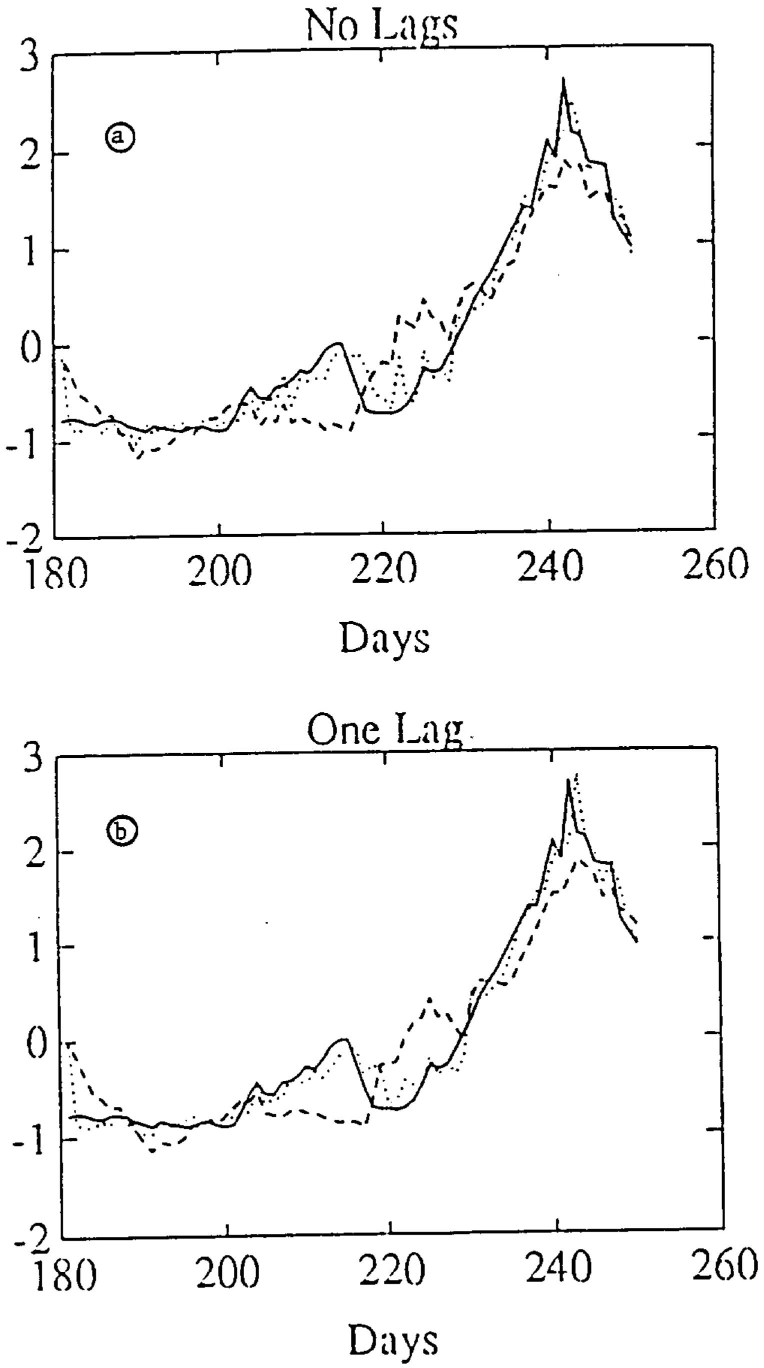


Figure 4.17 Plots comparing the observed and predicted lake outflows for period two (a) no-lag case, (b) one-lag case. Solid line = Q; dashed line = predicted Q without error model; dotted line = predicted Q with error model.

function, (loss), (a quadratic prediction-error criterion; see Ljung, 1987, p. 173) and value of the Akaike Information Criterion (AIC) were computed and are presented graphically in Figure 4.16a. [Note: AIC was proposed by Akaike as a criterion for model selection. It is described in Appendix A]. While the loss continues to decrease, the AIC begins to increase after 10 terms. The parameter values for all the models are presented graphically in Figure 4.16b along with the standard error-of-fit in Figure 4.16c. We note that the impulse response function becomes rather flat as the number of parameters increases; in fact, some of the parameter estimates become insignificant (not significantly different than zero). On the basis of the AIC, the 10-parameter model was selected. The comparison of observed lake outflow (nq2) and values predicted by this model are presented in Figure 4.17a.

Next, a model was fit to the prediction error. A single lag model with the structure:

$$e(t) = 0.8726e(t-1) + a(t)$$

where a(t) is a random error term was found to be satisfactory. The new prediction was also superimposed in Figure 4.17a. Note that except for one area around day 220, the prediction ability of the latter model (i.e., the one with error model added) is superior. The standard error-of-fit for this model is 0.1942.

In a similar manner, a model was fit assuming one lag between input and output. Once again, 10 input parameters were required for the optimal model. The parameters of the B(s) polynomial were found to be:

.1533 .1846 .1573 .0543 .0836 -.0132 .0937 .1317 .1596 .1436

and the error model was:

$$e(t) = 0.8933e(t-1) + a(t)$$

The model predictions (with and without error model) are compared with the observed lake outflows displayed in Figure 4.17b. The behavior of the one-lag model, according to visual inspection (Figures 4.17a-b), is very similar to the no-lag model. However, the standard error-of-fit of 0.2034 (for the case with error model added) shows slight deterioration of fit (as compared to 0.1942 for no-lag case).

4.4.3.3 Analysis of Period Three. The same procedure used for period two was repeated for the period three data. Only three parameters were found to be necessary for the B(s) polynomial of the no-lag model. These parameter values were:

.4547 .3298 .1615

Note the smooth behavior of this impulse response function with its maximum value at zero lags. The optimal error model was found to be:

$$e(t) = 0.7771e(t-1) - 0.3583e(t-2) + a(t)$$

The model predictions are compared, with and without the error model, to the observed lake outflow in Figure 4.18a. The model predictions are extremely good during this period. The standard error-of-fit without the error model was .4600, and improved to 0.3546 with the error model.

Only two parameters of the B(s) polynomial were needed for the one-lag model. The parameter values were:

0.7248 and 0.1985

The optimal error model was found to be:

$$e(t) = 0.6498e(t-1) - 0.2625e(t-2) + a(t)$$

The model predictions are compared with and without the error model in Figure 4.18b. The standard error-of-fit without the error model was 0.4858, and improved slightly to 0.4083 with the error model.

4.4.4 Conclusions: Phase 2 Study

The following is a summary of the results and conclusions of the Phase 2 study using WY 86 daily flux data. General applicability of these conclusions requires verification using data from other water years.

(1) The dominant variable influencing lake output is snowmelt. The output shows little or no response to rainfall events (see Figures 4.11a-b).

(2) The data indicate differing correlation characteristics between melt and lake outflow at different times of the year. The correlation is strongest in period two (days 181-250), which is a period of increasing melt, and period three (days 251-300, which is a period of decreasing melt.

(3) The covariance function for period two is quite different from that of period three, indicating that very different physical mechanisms influence the watershed behavior

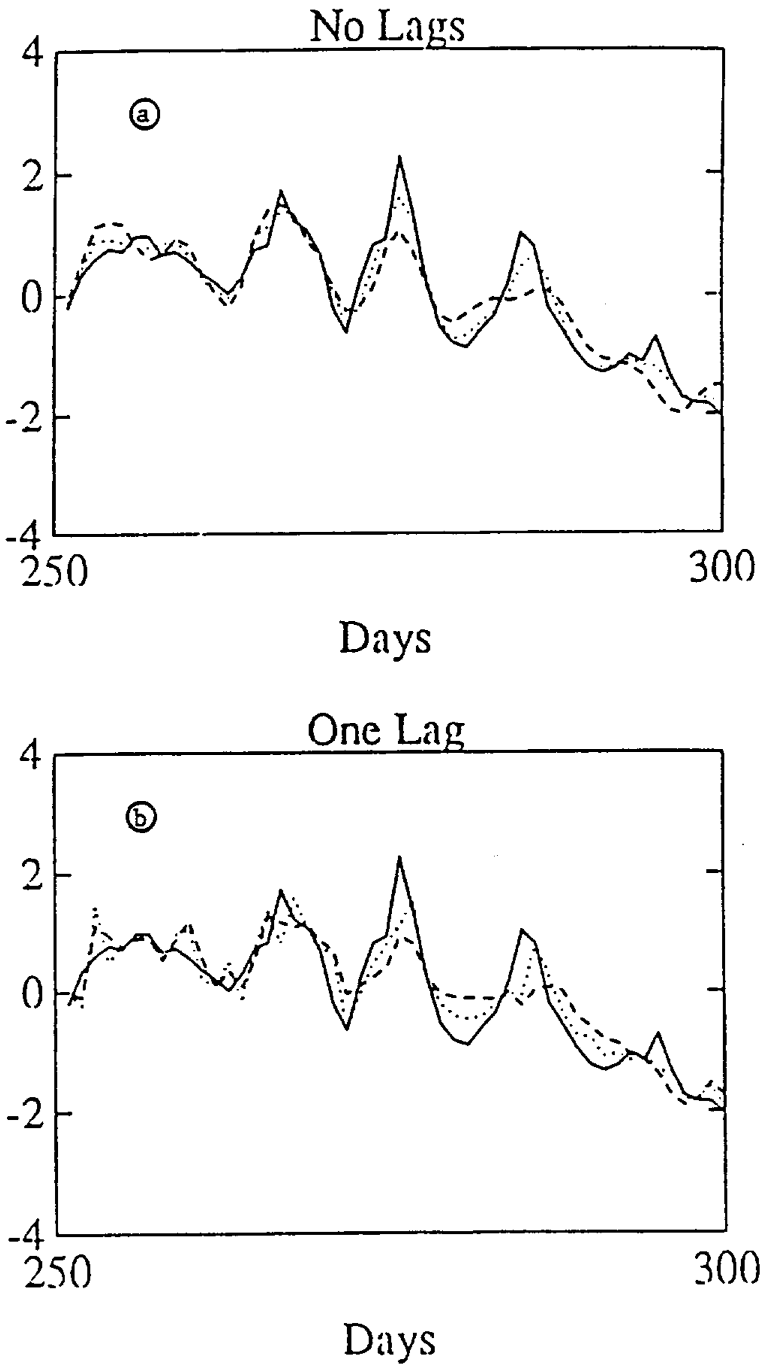


Figure 4.18 Plots comparing the observed and predicted lake outflows for period three (a) no-lag case, (b) one-lag case. Solid line = Q; dashed line = predicted Q without error model; dotted line = predicted Q with error model.

during these periods. Period two covariance is consistent with alternating periods of melt and refreezing with poorly-developed runoff pathways. Period three covariance is consistent with well-established runoff pathways and continuous melting of the snowpack.

(4) ARMAX models were fit to the data from periods two and three for prediction of lake outflow based on snowmelt estimates. The prediction ability of these models is very good. A one-step ahead (one-lag) model was found to give a satisfactory one-day ahead prediction with little decrease in the prediction error over that of a no-lag model. As expected, the models for periods two and three are significantly different; the period two impulse response function contains ten parameters indicating longer retention (up to ten days) of water in the watershed, while the period three impulse response function has only three parameters indicating short retention (less than three days) and, hence, faster movement of water through the watershed.

While it has been demonstrated that the ARMAX methodology can develop with very good predictive/simulation ability, the model parameter estimates reported here are based on a limited data sample. These models need to be verified further with independent sets of data from other WYs. Refinement may be necessary through recalibration.

4.5 Approach to Water Quality (Chemical Modeling)

A total of 99 observations on acid-neutralizing-capacity (ANC), cations (CA), and anions (AN) were available for WY 86. The data for the three main inflows (1, 2, and 4) were collected on 31 different days during the year (Note: multiple observations were available for some of the days).

A least-squares regression analysis of these three variables, with ANC acting as the "output" and CA and AN acting as the "input" variables, shows a very strong correlation, as theoretically expected. The reason for performing this analysis was not to prove the obvious, but rather to check for any inconsistencies and inaccuracies in the measured data. Similar good correlations were found for individual inflows and for the entire period for which data were available (summer 1984 through fall 1986). A simple model using only Ca^{2+} and NO_3^- as input variables also gave a good correlation with ANC. Examples of these and other correlation and time-series analyses that were done to check data for consistency and examine trends are contained in Appendix B.

Once the chemical correlations were shown to be satisfactory, an attempt was made to model lake inflow chemistry (i.e., ANC) as a function of watershed mass and/or energy inputs (e.g., flow (Q), temperature (T), etc.). For the snowmelt period (April 20-August 20), a total of only 52 observations collected over 17 days within this period were available. The ANC values were averaged for the days for which multiple observations were available; hence, the relatively small sample size of only 17 data points. The variables ANC, Q, and T were normalized to have zero mean and unit variance.

Next, the stepwise-regression technique (e.g., Draper and Smith, 1981, Section 6.4) was implemented. This is a commonly-used technique in multiple regression analysis which employs the partial correlation coefficient as the means for entering variables not yet included in the model. Variables already included in the model may be dropped from consideration if enough information can be extracted from a newly-entered variable and the rest of the variables already in the model. Using this technique, the flow, Q, was chosen as the most influential variable during the snowmelt period. Cumulative flow was also examined, but it was a less-influential variable. Figure 4.19 represents the results of the regression fit of ANC versus Q and T. However, because of the small size of the data sample, the conclusion that flow and temperature can adequately represent ANC needs further verification.

4.6 Conclusions and Future Interests

(1) It was decided that the snowmelt period would be used as the analysis period. This decision was based on the fact that the chemical activities, which constitute our key interest, are greatest during this period.

(2) The relationship between ANC and the anions and the cations is theoretically expected, and it has also been verified by our analysis. During the snowmelt period, however, stepwise regression analysis points to flow, Q, as the most influential of all factors in deciding the value of ANC. Although our small sample size of 17 is too small for strong conclusions, substituting flow as a proxy for cations and anions would amount to a significant reduction in data collection efforts.

(3) Further interests in our analysis include investigating the feasibility of some of the following recommendations:

(a) Since all the observations of the input as well as the output variables are noisy, the regression coefficients are known to be biased and inconsistent. The practicality of implementing noise (error)-in-variable modeling techniques should be investigated.

(b) Instead of choosing a fixed period of time as the snowmelt period, we could incorporate the use of an "indicator-variable" which takes on a value of 1 when the temperature is above a certain threshold, and zero otherwise. This will

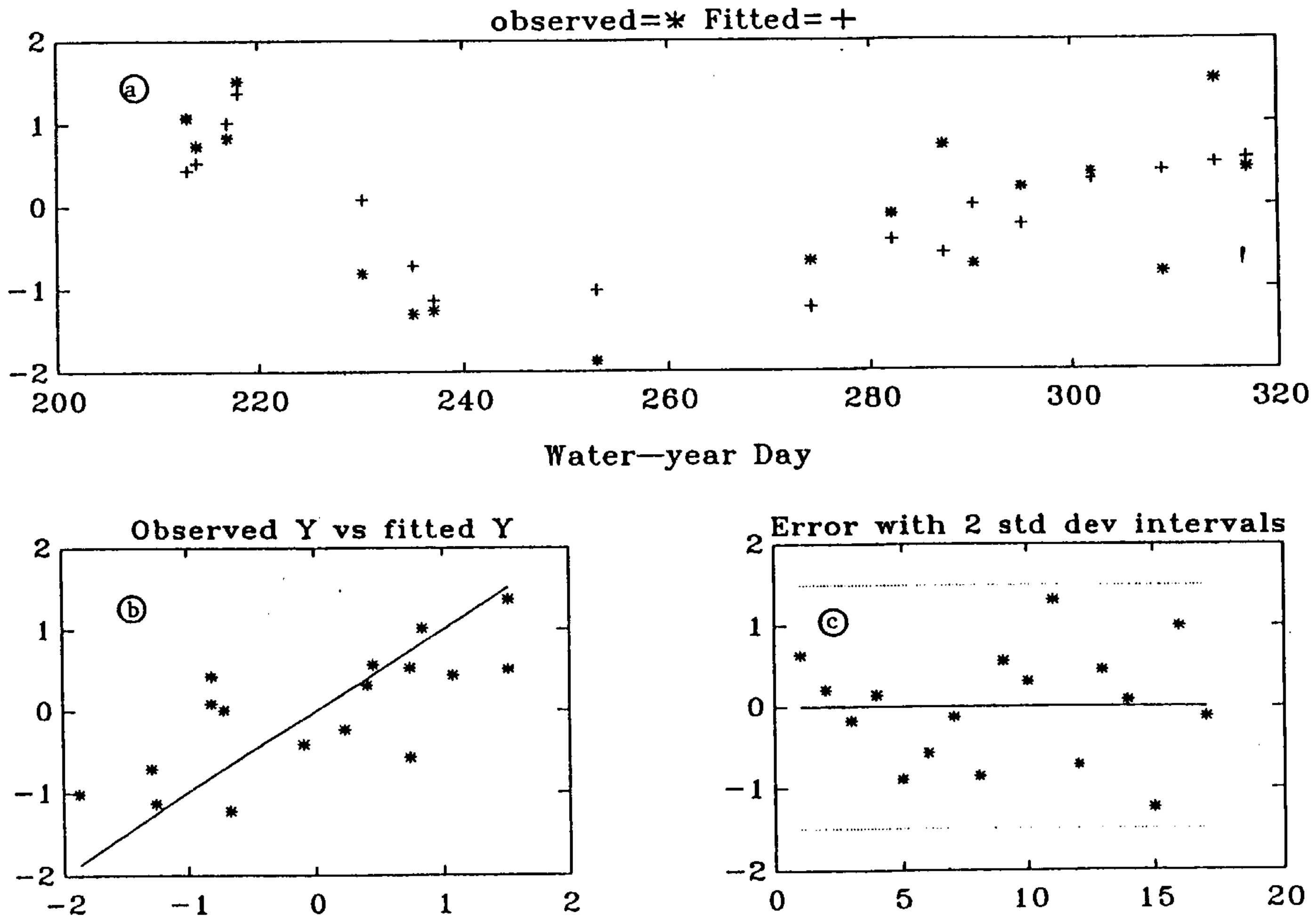


Figure 4.19 (a) Plot of observed values of ANC vs. fitted values of ANC vs. T and Q against water-year day.
(b) Plot of observed values of ANC against fitted values of ANC.
(c) Plot of model residuals with two standard deviation intervals.

enable us to use all of the data, as well as helping us better assess the significance of this particular period in the analysis.

(c) Take individual measurements of temperature and flow every time AN, CA, and ANC are measured. This way, no averaging will be necessary.

(d) With more data, the Fourier series could be implemented to reveal some hidden periodicities in the process.

CHAPTER FIVE

UNIVERSITY OF ARIZONA ALPINE HYDROCHEMICAL MODEL

5.1 Introduction

The University of Arizona Alpine Hydrochemical Model (AHM) is an integrated hydrological/chemical model for predicting watershed runoff and chemistry. AHM is being developed for modeling alpine watersheds in the Sierra Nevada as part of the Sierra Watershed Modeling Project (SWMP) of the California Air Resources Board. Its primary application for SWMP is the evaluation of effects caused by several acid deposition scenarios.

AHM is a compartmental model with six distinct sections, including (1) data input, (2) water balance, (3) chemical balance, kinetics, and equilibration, and (4) report generation.

This chapter provides an introduction to the overall hydrochemical model, and detailed descriptions of its water and chemical balance. Appendix D is a user's guide.

AHM is a set of computer instructions that simulate many of the physical and chemical processes occurring on a watershed. When properly fit to a given watershed, AHM can be used for scenario analysis, displaying changes in watershed outputs resulting from changing input conditions. This enables estimating effects of natural or anthropogenic changes in climate or atmospheric pollutant loading. AHM is also designed as a research tool, to identify what hydrologic and chemical processes are important, and when changes due to these processes are occurring. It should be used both to assist in interpreting field monitoring and process-level research and to help plan future research.

Hydrochemical models may be simple or complex. The most simple might be a "cells in series" mixing model without chemical reactions. The other extreme is a physically-based description of all hydrologic and chemical changes occurring on the watershed. While very simple models may be fit to a watershed's data, they have no physical basis. Knowledge gained by fitting a simple model to one watershed may be of no value in fitting a similar model to a second watershed. For example, if the second watershed has deeper soils, the simple model may have no parameters that directly address this difference. This makes it impractical to transfer such models between watersheds. Physically-based models are transferrable, but if they are too complex, they frequently suffer from a lack of data necessary to fit the model's parameters. Cost of model development, data collection, and computer use increase rapidly with increasing model detail.

AHM is as or more detailed than any other watershed hydrochemical model we are aware of, yet it falls approximately midway between the extremes noted above. Although the model itself is relatively complex, the user controls the degree of complexity in modeling a given situation. AHM can model movement and chemical changes in numerous compartments of multiple watershed subunits and stream segments. When such detailed modeling is not necessary, AHM functions more simply by ignoring certain water storage components (such as tree canopy interception) or modeling an entire watershed as a single subunit. It also contains unique design features which can be used to reduce its operational cost.

AHM tracks water and chemical movement, storage, and loss in and between different storage compartments on the watershed (Figure 5.1), including:

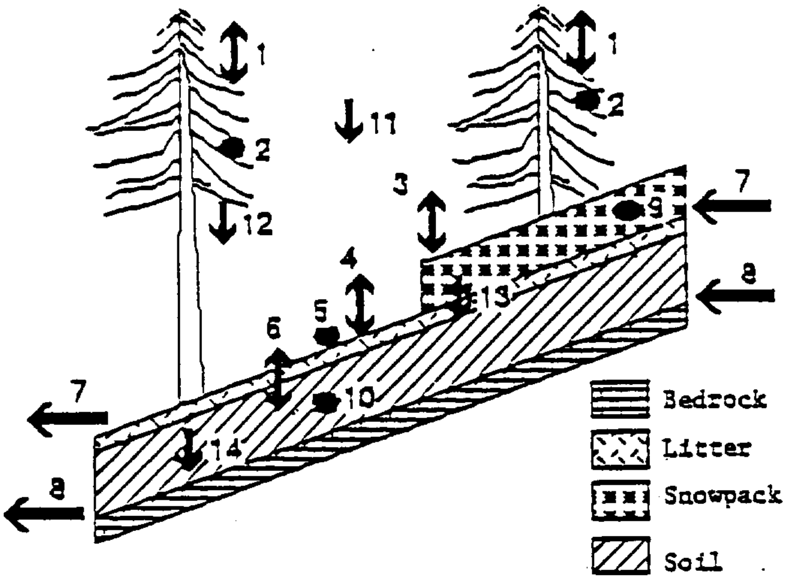
(1) Tree canopies (snowfall and rainfall interception, separately);
(2) Soil or rock surfaces (rainfall interception and storage beneath the snowpack);
(3) Single or multiple soil layers;
(4) Streams or lakes (currently without storage considerations);
(5) Snowpack;
(6) Snowpack free water;
(7) Surface runoff and subsurface horizontal drainage from soil-covered watershed subunits;
(8) Vegetation (as a source or sink).

These various compartments are present (when applicable) on single or multiple watersheds or subunits. Subunits are used to divide the watershed into areas with similar soil, vegetation, slope, snow accumulation, and snowmelt characteristics (Figure 5.2).

Many different types of watershed subunits can be modeled by using appropriate hydrologic parameters, including: (1) soil covered subunits (with or without canopy cover), (2) rock outcrops, or (3) lakes and streams (without storage and assuming complete mixing). Outputs may be obtained in a form suitable for input to a separate, detailed lake model, or with minor modifications, a lake model can be added to AHM.

Model outputs can be obtained for each subunit or storage component within each subunit. Watershed subdivisions can be designed to provide water and chemical outputs at desired locations, enabling the user to monitor specific outputs where verification data are available or where scenario evaluation is desired.

For each watershed subunit, a separate set of parameters is specified to define the physical characteristics of the subunit and its various water and chemical storage compartments. These parameters control physical and chemical processes such as maximum storage, rate of movement into or out of a compartment (which may also be a function of existing storage), routing of water leaving a subunit, etc.



1. Interception and Loss to ET and Sublimation
2. Interception Storage, Rain and Snow
3. Snowfall Accumulation and Sublimation
4. Litter Interception and Loss to ET
5. Litter Interception Storage
6. Soil Infiltration and Loss to ET
7. Surface Runoff
8. Subsurface Drainage
9. Snowpack Water Equivalent and Free Water Storage
10. Soil Water Storage
11. Rainfall and Snowfall
12. Drip from Canopy
13. Drainage from the Snowpack
14. Vertical Drainage in the Soil

Figure 5-1 Illustration of water movement and storage between various compartments within a single watershed subunit.

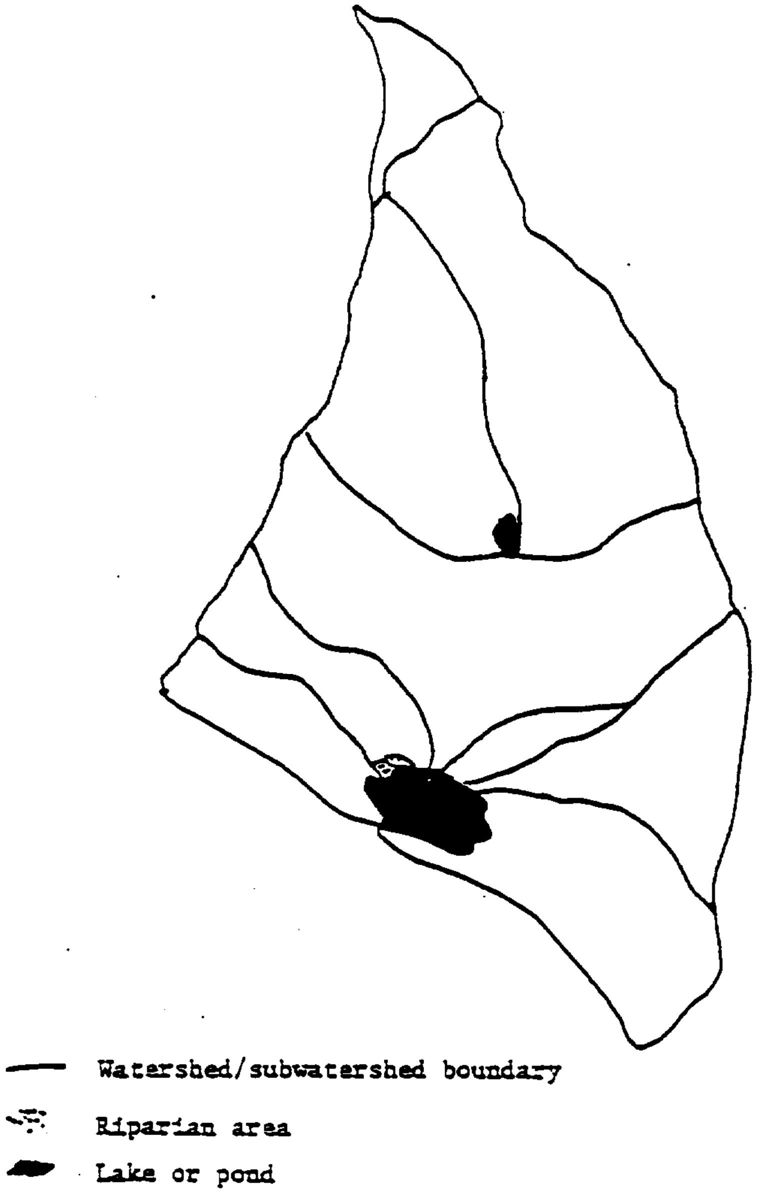


Figure 5-2 Emerald Lake basin showing a potential set of watershed subdivisions. Each subdivision shown could be further subdivided by soil classification, and stream subunits added if desired.

To the extent deemed practical, these processes are modeled in a manner simulating the actual process occurring on the watershed itself, while attempting to avoid extraordinarily detailed modeling of those processes for which supporting data seldom exist. For example, AHM does not attempt to model saturated, free-surface groundwater movement in detail. This is because in most alpine watersheds: (1) subsurface flow pathways are ill-defined, (2) verification measurements of depths of saturated flow are generally lacking, (3) soil subunits typically are irregularly shaped, variable in slope, and not contiguous, and (4) the volume of runoff contributed to a given patch of soil from surrounding rock outcrops is not well-defined. Although very basic, these data are difficult to obtain. Without such data, use of a formal mathematical representation of actual subsurface flow processes provides a false suggestion of extraordinary accuracy. In addition, a detailed evaluation of subsurface flow depths, as provided by a free-surface groundwater model, was not deemed necessary for the modeling task at hand. When inputs of chemical species are evenly distributed over a watershed, a "lumped" modeling approach is generally adequate (Gelhar and Wilson, 1974).

Available data dictated that some hydrologic processes be simulated by simplified modeling procedures, with parameters that must be fit by comparing modeled to observed outputs. For example, AHM uses a simple linear reservoir approach for subsurface flow modeling. The procedures used are described with the descriptions of appropriate program subroutines (Appendix C). Any procedures used by the model can be modified. Physical and chemical processes that are modeled include:

(1) Interception of precipitation;

(2) Spatial distribution of snowmelt and snowpack sublimation (actual snowmelt, sublimation, and evapotranspiration (ET) are determined given user-supplied potential values and snow-covered area. In practice, the user will obtain potential values through the use of independent models);

(3) Flow between various components (tree canopy, soil surface or layers, surface runoff, horizontal drainage, etc.) of subunits;

(4) Infiltration;

(5) Soil water drainage;

(6) Surface runoff;

(7) Distribution of ET between canopy interception, litter (soil or rock surface) interception, water surfaces, or soil layers;

(8) Recharge of riparian areas by streamflow;

(9) Chemical release from snowpacks in meltwater;

(10) Mineral weathering;

(11) Chemical uptake and release by soil and vegetation;

(12) Chemical complexation, precipitation, adsorption, ion-exchange, and oxidation-reduction reactions;

(13) Gas exchange between water and air.

The hydrologic processes included on non-riparian, soil covered subunits are displayed in Figure 5.1. Riparian subunits have the additional capability of withdrawing water and chemicals from streamflow to maintain a specified minimum soil water content.

Water and chemical species may be routed between watershed subunits as well as between different storage compartments of each subunit (Figure 5.3). Flow from individual subunits or groups of subunits may converge or diverge into any number of separate stream channels. Flow routing between subunits can be complex, subject to the limitation that flow from one subunit cannot be routed in a manner resulting in flow contributions to itself (Figure 5.4). Recharge of riparian areas can violate this "uphill" routing prohibition.

AHM was written in FORTRAN 77 and is designed to be compatible with virtually all computers, including IBM-compatible personal computers (PCs), scientific work stations, mainframes, or super-computers. The water balance portion of the program has been successfully tested on PCs and SUN workstations, without alteration of the FORTRAN code. Several hundred watershed subunits can be included in a single run of the water balance model, even when run on a PC; to do so requires only changing the values of two parameters in a single file and re-compiling the program. With the addition of chemical computations, the number of watershed subunits which the program can handle on a given computer will decline.

The FORTRAN code was written in a "long" rather than "short" form; in many cases, separately-coded programming statements could have been condensed into fewer, more concise statements. The form used makes the physical processes being modeled more obvious for those who might wish to evaluate or modify certain procedures. With today's optimizing compilers, the executable program should be practically as efficient as one written with more condensed, "refined" programming.

5.2 Comparison to the ILWAS Model

AHM is similar in terms of purpose and complexity to only one other model, ILWAS (Chen et al., 1983). When an existing model is available, the necessity for development of a new model may be questioned. To answer this, differences between the water balance procedures of the two models are presented here. Those differences particularly important to modeling the Emerald Lake basin are related to the handling of snow and are described separately from minor model differences.

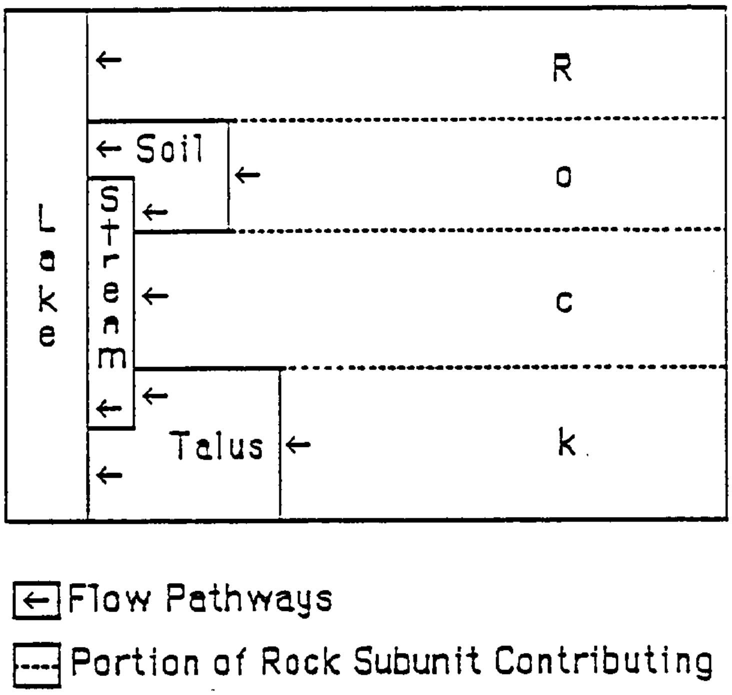


Figure 5-3 Example of flow pathways between watershed subunits. Except for the stream subunit, this diagram is very similar to the pathways used in the model's initial test runs.

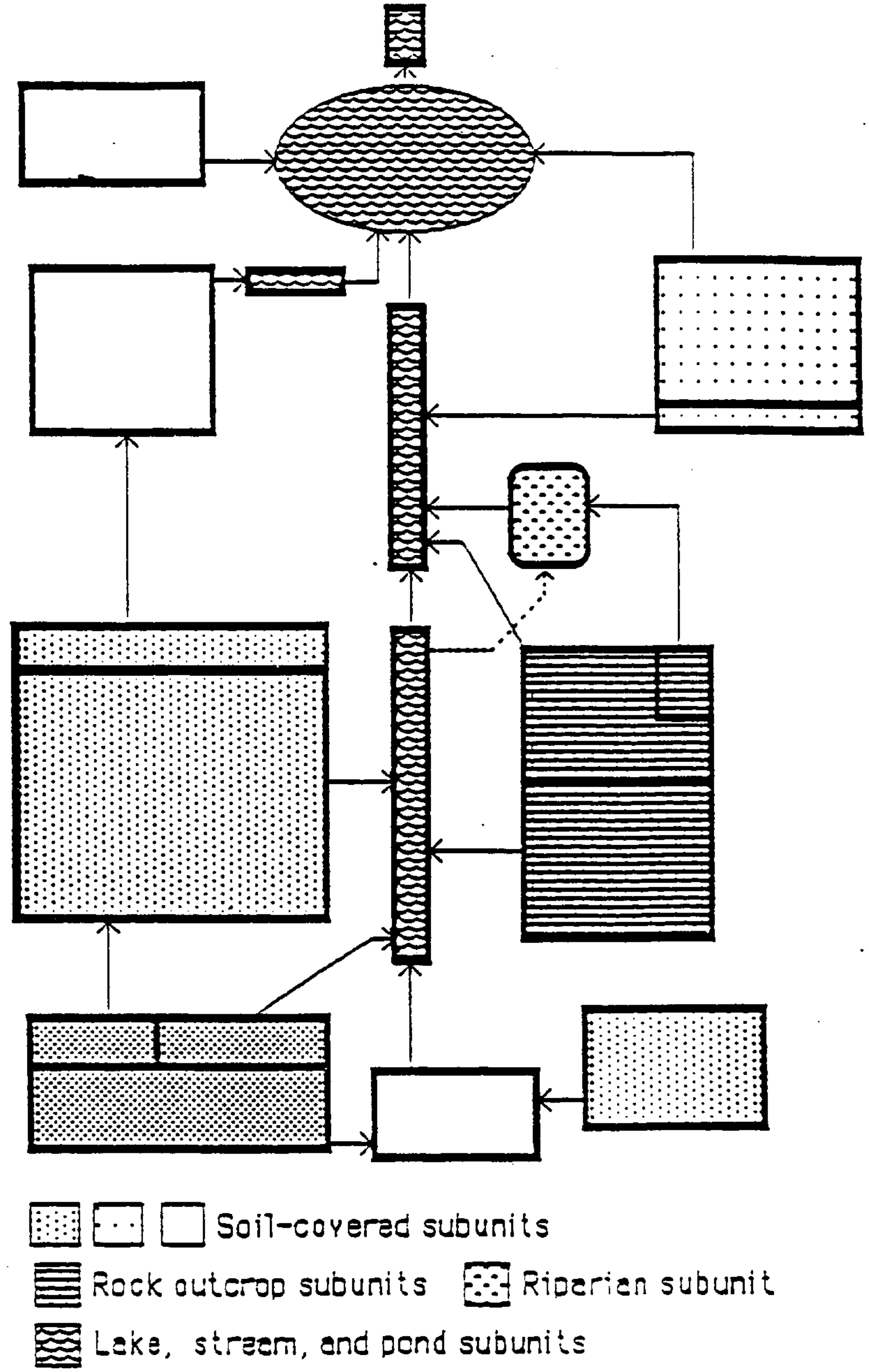


Figure 5-4 Example of relatively complex flow routing possible with AHM. Each "box" represents a watershed subunit. Subdivided boxes represent portioning of outflow from one subunit to several others.

This comparison is hampered by the lack of a comprehensive user's manual for the ILWAS model; that project apparently terminated before user documentation was published. Information about ILWAS presented here was obtained from Chen et al. (1983).

5.2.1 Differences Important to the Sierra Modeling Study

The primary difference between the water balance portions of ILWAS and AHM is in their treatment of snow.

Although it tracks snowfall and snowmelt, ILWAS is not generally oriented toward snow-dominated, mountainous regions. For example:

(1) Snowmelt is modeled by an air-temperature index. Although this is a common modeling practice, it is regarded as inadequate by many snow researchers.

(2) A given subunit is assumed to be either 100 percent snow covered or entirely snow free, while snow-covered area (SCA) on the Emerald Lake basin is continuously variable, typically changing less than a few percent between successive days during the snowmelt season. Under a particular set of conditions, SCA is directly proportional to snowmelt and sublimation and inversely proportional to evapotranspiration (ET) from a watershed.

(3) Sublimation from the snowpack surface appears to be either modeled using the Hargreaves (1974) method, which was not designed for this task, or ignored entirely. Research and the data provided to us suggest that sublimation losses are significant on the Emerald Lake basin (Dozier et al., 1988).

(4) Snowfall interception is not considered.

In contrast, from its conception, AHM was designed for use in moderate to high elevation mountainous areas or other areas with similar snow packs. The hydrology of these areas is dominated by snow; throughout much of the year, the majority of runoff and water storage is directly related to snowfall, snowmelt, and snowpack storage. Preferred methods for determining snowmelt, snow-covered area, sublimation, and potential evapotranspiration (PET) vary regionally; available data limit the methodology selection process. AHM provides the flexibility needed for ranges of data availibility and climatological conditions. Specifically:

(1) Potential snowmelt is obtained from an external model. The snowmelt model most appropriate for a given region may be used to the extent that supporting data are available.

(2) SCA is a driving force in AHM. It is used to determine actual snowmelt, actual sublimation, and actual ET given potential values. It is also used to determine rainfall litter interception losses and storage, and areas left wet behind a receding snowpack. SCA was given particular emphasis because it is frequently variable throughout a given drainage basin in mountainous terrain. SCA values used are independently obtained using best-available data for a given situation.

(3) Potential sublimation from the SCA is independently determined using procedures most appropriate for a given region.

(4) Snowfall interception in tree canopies is a separate variable in AHM. Snowfall interception may drop frozen to the snowpack or melt, becoming rainfall interception storage and/or drip onto the snowpack.

5.2.2 Less Significant Differences Between ILWAS and AHM

There are numerous other differences in computations between the two models. These include the following:

(1) ILWAS uses a single function to define rainfall interception storage capacity only. AHM uses a separate interception storage capacity for rainfall on the canopy, snowfall on the canopy, and rainfall on the litter (or rock surface). The litter interception capacity in AHM is a function of SCA.

(2) ILWAS uses the Hargreaves (1974) method for PET. AHM allows the user to select any technique believed best suited to a given region (AHM does no PET determination).

(3) ILWAS and AHM use different weighting schemes to distribute ET between soil layers.

(4) ILWAS uses one to three layer soil profiles with horizontal movement of water permitted in each; AHM allows for more soil layers, with water moving horizontally only as surface runoff or drainage from the lowest soil layer. AHM's soil drainage model was briefly described in the introduction section of this report, and is fully described in the appendix.

(5) ILWAS uses a streamflow routing procedure that includes a term for storage, while streamflow routing in AHM does not account for storage. In modeling the Emerald Lake basin with a daily time step, storage in stream channels was assumed to be insignificant due to the small size of the watershed and the stream channels themselves.

(6) ILWAS reads one precipitation value and determines whether that precipitation was rain, snow, or a mixture of both through the use of an air temperature function. AHM reads snowfall and rainfall separately, with mixtures of rain and snow permitted.

(7) AHM permits withdrawal of water from streamflow to maintain soil water content on riparian areas.

(8) AHM can distribute outputs from one subunit to a number of other subunits (Figure 5.4). This feature allows use of single, large subunits to represent several smaller watershed areas that are similar in all respects except for the distribution of their outputs. Surface and subsurface outputs from the large subunit are proportionally distributed to other soil-covered or stream subunits based on the fractional area draining in a given direction (this is made possible by the assumption of underlying, impermeable bedrock). This feature can be used to reduce computational time while obtaining more accurate estimates of fluxes within given channels.

The ability to use any number of methods to determine potential snowmelt, sublimation, and ET adds to the flexibility of modeling water movement on a given watershed. While potentially increasing accuracy, this feature makes this model somewhat less convenient for casual use. Currently, the user must obtain independent estimates of these values, which typically will involve running some additional models. Although "user-friendliness" could be built into AHM, defensible model output will always require valid input data. Obtaining valid input data requires knowledge of hydrology, hydrochemistry, and geology.

Addition of a built-in capability to model potential ET, snowmelt, and sublimation is a relatively simple procedure and is a long-range goal.

While oriented toward mountainous terrain, the water-balance portion of AHM is suitable for other areas, particularly those with rock outcrops and relatively impermeable bedrock beneath surface soils.

5.3 Operational Overview

AHM consists of a main program and 66 subroutines and functions. The main program calls other subroutines but performs no computations. Most variables (with the exception of a few temporary or dummy variables used in computations within individual subroutines) are defined near the top of the main program. Chemical variable definitions are currently not present in the main program.

In operation, the program reads files containing watershed parameters and climatological data, combining many separate input files into a few, larger files. Observations for a single time step (currently one day) are then read from a combination of "combined" input files and individual files, and computations are done on all watershed subunits for that time step. With the exception of evaporation and sublimation from stream surfaces, computations for each watershed subunit are done in the same subroutines regardless of subunit type.

5.3.1 Daily Input Data

For each (daily) time step, the following input data are required:

(1) Snowfall and snowfall chemistry;
(2) Rainfall and rainfall chemistry;
(3) Potential snowmelt on snow-covered area (SCA);
(4) Potential sublimation (on SCA);
(5) SCA;
(6) Potential ET (on snow-free area); and
(7) Chemical sources or sinks.

5.3.2 Hydrologic and Chemical Parameters

There are three groups of required parameters, as follows: (1) those that apply to the entire basin being modeled, (2) those applicable to an entire subunit of that basin, and (3) those applicable to a given layer of soil or other compartment of a subunit. Detailed descriptions of these parameters and their use are separately described (Appendix C). Watershed-wide parameters needed include:

(1) Snowpack free water holding capacity, a constant;
(2) Month and day when stream surfaces freeze; and
(3) Month and day when stream surfaces thaw.

Parameters for each subunit include:

(1) Number of soil layers;
(2) Subunit type (soil, rock, or stream);
(3) Area;
(4) Elevation;
(5) Maximum surface infiltration rate;
(6) Stream subunit that serves as this subunit's riparian recharge source, if any;
(7) Method chosen for adjusting the subunit's rainfall and snowfall relative to that observed at a base station;

(8) Initial conditions for snowpack water equivalent, snowpack free water content, and snow-covered area;
(9) Constants describing maximum interception storage capacity for rainfall on the canopy, snowfall on the canopy, and rainfall on the litter, grass, or rock surface;
(10) Initial water storage conditions for the three components in (9); and
(11) Initial chemical species and amounts present in each compartment of the subunit.

Parameters for each soil layer of a subunit include:

(1) A factor used to reduce ET from lower soil layers below that rate occurring under similar conditions from the surface soil layer;
(2) Soil depth;
(3) A parameter used to control the vertical drainage through the soil column;
(4) Saturated hydraulic conductivity;
(5) Soil water content below which hydraulic conductivity is zero;
(6) Soil water content at saturation;
(7) Soil water content not susceptible to loss through ET;
(8) Initial condition for soil water content;
(9) Bulk density;
(10) Specific surface; and
(11) Initial chemical storage by species.

Subunit computations are done in a particular order determined by the program, ensuring that outputs from "donating" subunits are available before computations begin on the subunit receiving those contributions. This is accomplished by rearrangement of a matrix supplied by the user, which provides information on the disposition of flow from each subunit. The program uses this matrix to determine the sources of flow to each subunit and the computational sequence required.

In operation, AHM:

(1) Reads data;
(2) Inputs or extracts chemicals based on source/sink data;
(3) Adjusts certain parameters based on the value of SCA;
(4) Computes interception based on existing available storage;
(5) Adjusts the snowpack and snow water equivalent for snowfall, rainfall, and melt;
(6) Computes influx of water to each subunit, including rainfall, snowfall, snowpack drainage, and surface or subsurface inflows from other subunits;

(7) Drains water through and from the soil, or as surface runoff;

(8) Computes chemical equilibration and kinetics on rock and soil litter surfaces;

(9) Computes actual ET and sublimation;

(10) Computes soil water deficit in riparian areas;

(11) Determines the degree of riparian recharge based on available streamflow;

(12) Computes chemical equilibration and kinetics in the soil and streams; and

(13) Generates outputs.

After output for the time step is generated, computations begin again with a new set of "initial" water and chemical storage conditions.

5.4 General Description of Chemical Model

The chemical model consists of two parts: 1) a general equilibrium model for fast reactions such as complexation, ion exchange and gas dissolution, and 2) difference equations for slow processes such as mineral weathering, oxidation and litter decay. Both equilibrium and kinetic calculations are done at each time step. In addition, at each time step chemical species are transported between compartments and input to the watershed in precipitation and by dry deposition.

The equilibrium model is based on the computer program MINEQL [*Morel and Morgan, 1972; McDuff and Morel, 1973; Westall et al., 1976*] and solves a general set of material-balance and mass-law equations by a series of approximations. This structured approach can be described conceptually by a single tableau containing all of the thermodynamic and stoichiometric information necessary to solve the problem [*Morel, 1983*]. The tableau used for initial testing of the AHM, Table 1, lists all of the chemical species considered along the left. Components, which are a subset of the species and represent the basic components from which other species can be defined, are listed across the top. Note that this definition of components is consistent with that of Gibbs [*Morel, 1983*]. The number of components equals the total number of species minus the number of (mathematically independent) chemical reactions needed to describe the chemical system. The rows of the tableau (for species that are not components) give the stoichiometry for mass-law expressions, with one for each chemical reaction. The *j*th chemical reaction, written in terms of components S_1, S_2 ... and S_j (not a component) is:

$$0 = v_{j1} S_1 + v_{j2} S_2 + \dots v_j S_j \qquad (5.1)$$

were the V_{jk}'s are the stoichiometric coefficients, positive for products and negative for reactants. The corresponding mass-law expression is:

$$[S_j] = K_j \prod_{k=1} [S_k]^{v_{jk}} \qquad (5.2)$$

where V_j is taken to be one and the brackets indicate concentration in mol L^{-1}. K_j is the equilibrium constant, corrected for ionic strength by the Davies equation [*Stumm and Morgan, 1981*]. Temperature corrections are not included in this version of the model. These mass-law expressions are also referred

Table 5.1. Tableau of equations used for initial testing of AHM

	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	CO_3^{2-}	PO_4^{3-}	NH_3	SiO_3^{2-}
H^+	1											
Ca^{2+}		1										
Mg^{2+}			1									
Na^+				1								
K^+					1							
Cl^-						1						
NO_3^-							1					
SO_4^{2-}								1				
CO_3^{2-}									1			
PO_4^{3-}										1		
NH_3											1	
SiO_3^{2-}												1
OH^-	-1											
HCO_3^-	1								1			
$H_2CO_3^*$	2								2			
NH_4^+	1										1	
HPO_4^{2-}	1									1		
$H_2PO_4^-$	2									1		
H_3PO_4	3									1		
$HSiO_3^-$	1											1
H_2SiO_3	2											1
Totals	$(H)_T$	$(Ca)_T$	$(Mg)_T$	$(Na)_T$	$(K)_T$	$(Cl)_T$	$(NO_3)_T$	$(SO_4)_T$	$(CO_3)_T$	$(PO_4)_T$	$(NH_3)_T$	$(SiO_3)_T$

to as equilibrium expressions. The mass-law expressions -- K_j's and v_{jk}'s for the S_{jk}'s -- are contained in a thermodynamic data base that is common to all watershed subunits.

The columns of the tableau are material-balance equations, with one equation expressing the conservation of mass (moles) for each component. The mole-balance equation for component k is:

$$TOT\ C_k = \sum_{i=1}^{m} V_{ik}\,[S_i] = C_{kT} \tag{5.3}$$

where C_{kT} refers to the values along the bottom row of the tableau. The integers in the tableau are the V_{ik} values in equations 1 and 3.

Model inputs for each compartment in the model are the totals listed across the bottom of the tableau -- these are the quantities to be conserved in the calculation. Also needed are initial guesses of the equilibrium concentrations of the species that are components, listed across the top row of the tableau. Figure 1 illustrates the general algorithm used to arrive at a solution. The mass-law expressions -- coefficients are given in each row in the second portion of the tableau -- are used to calculate concentrations of the other species. Concentrations of all species are then summed in each mole-balance equation -- coefficients are given by each column in the tableau. If the difference between the sum of species concentrations and the fixed totals exceeds a set tolerance value, guesses of the component concentrations are updated by a modified Newton method and the computations repeated. If solids subject to precipitation are included, the tableau is modified to include as components any solids whose solubility product is exceeded, and totals adjusted accordingly.

At each time step, totals are adjusted for flux in and out, the equilibrium computed, and additions or losses due to slow reactions computed. The kinetic expressions include terms of any order -- typically zero, first and fractional -- and are of the form:

$$\frac{d[S_k]_T}{dt} = k_{k1} + k_{k2}\,[S_p] + k_{k3}\,[S_1]^{\alpha_q} \tag{5.4}$$

where $\alpha_q < 1$. The $[S_p]$ and $[S_q]$ concentration terms can be any species. Provision is also made to include higher-order terms in the model. The equilibrium component concentrations from one time step serve as the initial guesses for the next time step.

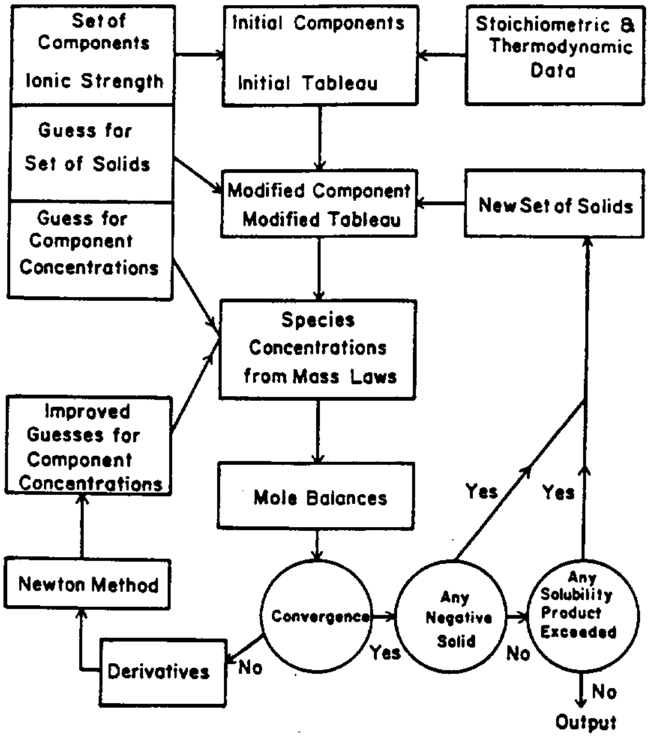


Figure 5.5: Flow chart of a general computer algorithm for solving chemical equilibrium problems.

Arrays are currently dimensioned for up to 25 components. Additional components and species that we plan to add following initial testing are:

Component	*Identity*	*Additional species*
>X	sulfate adsorption site	$>X\text{-}SO_4$
>Y	cation exchange site	>Y-cation
A^-	organic anion	HA
Al^{3+}	dissolved Al(III)	hydroxide complexes
Fe^{3+}	dissolved Fe(III)	hydroxide complexes
Mn^{2+}	dissolved Mn(II)	hydroxide complexes
O_2	dissolved oxygen	electron
ON	dissolved organic N	--

Solid species that are or will be included in the equilibrium model, given the set of components in Table 5.1 and above include primarily carbonates and hydroxides, with some phosphates and silicates (Appendix C). Others can be added to the thermodynamic data base as needed.

5.5 Initial Test Run on Emerald Lake Data

The University of Arizona Alpine Hydrochemical Model has been tested using data collected on or estimated for the Emerald Lake basin. We received the climatological data, lake discharge, and estimated runoff from snowmelt values in tabular, machine-readable form from Dr. D. Marks, (formerly of the University of California, Santa Barbara), on approximately February 3, 1988. Dr. Marks provided estimated snow-covered area (SCA) values in hard copy in September 1988.

Soil parameters were estimated using data received at the July 1988 meeting in Riverside, California.

5.5.1 Hydrologic Data Conversion

The input data provided were not in the exact form required by the model, so adjustments were made to make it compatible. Specific requirements for AHM include the following:

(1) ET, sublimation, and snowmelt must be **potential** values (area cm) that would occur if water or snow is not limiting. (The data received were estimated **actual** values in cubic meters/ day for the entire watershed).

(2) SCA must be the "beginning of time step" value on those days that snowfall occurs.

(3) all input climatological and snow values required by AHM must be positive in sign.

To convert the data for AHM, the data received were adjusted as follows:

(1) On days with snowfall, SCA was set to the preceding day's value. This allows the program to increase SCA internally, permitting appropriate calculations related to rainfall litter interception storage.

(2) Snowmelt values (given as whole-watershed runoff from snowmelt in meters) were divided by (120 hectares x (10,000 square meters/hectare) x .01 meters/cm) to give the watershed average snowmelt in centimeters (cm). This value was divided by the SCA fraction (0 to 1) to obtain potential snowmelt, the snowmelt rate that would occur over the entire area were it completely snow covered. For lack of better information at this time, all subunits used the same potential snowmelt values.

(3) Sublimation values were adjusted like snowmelt values, except that negative values (for those few occasions when condensation on the snowpack resulted in net input to the watershed) were set to zero. All subunits used the same potential sublimation values.

(4) For initial testing, we did not consider it necessary to determine exactly how the ET values we used as a basis for generating PET were generated; initial test runs

serve primarily as a basis for additional discussion among associated researchers. Modifications to ET estimates received were necessary, requiring some additional assumptions. These assumptions included:

- (a) Most of the estimated ET came from soil-covered subunits except on those days when it rained; interception losses from rock areas could be ignored as a first approximation;
- (b) ET from intercepted rainfall could be ignored in generating PET values, because rainfall events were few in number;
- (c) Losses to ET were insignificant relative to total runoff.

(5) Data received with negative values used to imply "water leaving the watershed through some mechanism" were converted to the positive form required by AHM.

(6) Negative values of sublimation, implying condensation of fog on the snowpack surface, were set to zero. No effort has been made to model this with AHM, and total annual inputs from condensation were less than 1 cm in approximately 5 events.

ET values (except for Emerald Lake itself) were converted to potential ET (PET) by dividing first by (24.35 hectares soil-covered area x (10,000 square meters/hectare) x .01 meters/cm) to give the average ET value for the soil-covered area in centimeters (cm). This value was divided by (1 - SCA) to obtain potential ET, the ET value that would occur over the soil-covered area were it completely snow free. In the test run, the PET value generated above was used to estimate ET from rainfall litter (and rock surface) interception, as well as being used as the PET estimate for ET losses from soil and talus-covered areas. PET for Emerald Lake was obtained by converting given lake evaporation values from cubic meters per day (cm^3/day) to centimeters per day (cm/day).

5.5.2 Test Run Model Form and Parameters

The initial run included seven separate watershed subunits (Table 5.2). These were determined by soil type or other subunit type (bedrock or "lake").

A single soil layer was used to model soil-covered subunits. When AHM is restricted to a single soil layer, some soil parameters required by the model for multiple soil layers are not used. Soil parameters that were used included:

(1) Soil depth;

(2) Saturated water content (ThetaS);

Table 5.2: Subunit area and soil parameters used in initial test run of the water balance portion of the model. A "yes" under riparian recharge indicates a soil unit whose soil water content was maintained under dry conditions by recharge from the unit labeled "from".

Subunit	Soil Type Ha	Area cm	Depth cm/cm	Theta R cm/cm	Theta S cm/cm	Theta Wlt Rech.	Ripar.	ETmax
1	Aquept	0.30	100.	0.2	0.5	0.15	yes	1.0
1	Orthod	2.10	80.	0.1	0.5	0.02	NO	1.0
3	Umbrept	18.29	35.	0.2	0.5	0.03	NO	1.0
4	Orthent, Fluvent	3.66	25.	0.075	0.4	0.02	NO	1.0
5	Rock outcrops	69.80	0.0	0.0	0.0	0.00	NO	1.0
6	Talus	23.00	200.	0.075	0.3	0.01	NO	0.6
7	Emerald Lake	2.85	0.	0.0	0.0	0.00	from	1.0

(3) Water content below which drainage is zero and below which ET declines linearly to zero (ThetaR);

(4) Water content at which ET is zero (ThetaWlt);

(5) A horizontal drainage constant (K); and

(6) A parameter that is used to reduce actual ET when the soil is saturated to a level below that which would occur on a saturated surface soil (ETmax, used only on a talus subunit).

The values used were initial "best guesses" based on a review of soil- moisture-release data obtained at the July 1988 meeting in Riverside. The values used are not final, and further input from soil researchers is needed. Those soil parameters used that vary between subunits are shown in Table 5.2.

Other assumptions used in the initial run included:

(1) Maximum daily infiltration on all soil-covered subunits and talus was set at 20 cm/day;

(2) Horizontal drainage from the soil profile for all soil and talus subunits used a value of K = 0.10. Horizontal soil drainage follows the relationship:

$$Q = K \times (\text{Theta} - \text{ThetaR})$$

where: Q is drainage in centimeters (cm);
Theta is volumetric soil water content, dimensionless;
ThetaR is defined above; and
K is a user-supplied constant;

(3) Emerald Lake was assumed to freeze on November 12, 1985 and was thawed August 3, 1986;

(4) Snowpack free-water holding capacity was 0.05 cm/cm;

(5) Rainfall interception constants for "litter" (soil or rock surface) were 0.4 cm on aquept soils, 0.2 cm on umbrept soils, .1 cm on orthent, fluvent, and rock outcrops, 0.2 cm on talus, 0.5 cm on the forested orthod soils, and 0.0 cm on the lake. The forested subunit used canopy interception constants of 0.25 cm for rainfall and 0.25 for snowfall.

(6) 70 percent of the water falling on the rock subunit was routed directly to the lake. The remaining 30 percent was routed to the four soil or talus-covered subunits, in proportion to those subunit's surface areas.

5.5.3 Chemical Inputs

For the initial test run, dry deposition was assumed to occur only between June 1 and September 30, 1986 based on a preliminary scenario suggested by Tonnessen (1988). The input values were proportionately distributed over the entire 120-ha watershed and lake surface based on individual subunit areas. Values were estimated based on results of Wu and Davidson (1989), and Bytnerowicz and Olszyk (1988). We have subsequently analyzed additional data; future runs can use more spatially disaggregated data (see e.g., Noppe, 1989).

Species	mol/day
NO_3^-	14
NH_4^+	10
SO_4^{2-}	10
Cl^-	3
Ca^{2+}	5
Mg^{2+}	3
Na^+	8
H^+	3

Initial (October 1) chemical conditions for the soils in each subunit were calculated using estimated water contents and soil-solution chemistry data; this involved making several assumptions. Estimated October 1 water volumes in each subunit's soil are:

Subunit	Water, L
1	600,000
2	566,000
3	7,243,000
4	1,354,000
5	"0"
6	18,400,000
7	N/A

These were multiplied by averaged soil-solution chemical composition to obtain the total moles of each species in each subunit's soil (Table 5.3). This method of estimating initial chemistry misses any chemicals that may be present as precipitates subject to dissolution or adsorbed species.

Table 5.3. Values Used for Chemical Initial Conditions.

	Component, Moles/Subunit											
Subunit	Ca	Mg	Na	K	H	NH_4	Cl	NO_3	SO_4	PO_4	CO_3	SiO_3
1	14.7	2.88	12.06	3.36	12.63	8.64	33.12	47.34	6.0	0.006	1.02	0.006
2	10.9	2.94	28.62	4.87	6.84	6.62	23.022	0.537	7.69	0.006	0.006	0.006
3	139.8	37.7	366.5	62.3	87.6	84.7	295.0	6.881	98.5	0.072	0.072	0.072
4	26.1	7.04	68.5	11.6	16.4	15.8	55.1	1.29	18.4	0.014	0.014	0.014
5	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
6	355.0	95.7	931.0	158.0	223.0	215.0	749.0	17.48	250.0	0.184	0.184	0.184
7	0	0	0	0	0	0	0	0	0	0	0	0

The kinetic reactions are computed in the form:

$$\frac{\partial S_K}{\partial t} = A \times F \times 1000 \times (K_{k1} + K_{k2} \times [S_p^{\alpha 1}] + K_{k3} \times [S_q^{\alpha 2}])/Q$$

where:

$\frac{\partial S_K}{\partial t}$ = change in molar concentration of the chemical species being adjusted each time step;

A = soil particle or rock outcrop surface area on the subunit, m^2;
F = fraction of subunit wet in this compartment;
S_p,S_q = molar concentration of species which affects that species being adjusted;
Q = volume of water (liters) in the compartment; and
K_1, K_2, K_3, α_1, α_2 = user-supplied parameters to give outputs in millimoles per m^2.

Kinetic parameters (K, K_2, K_3, α_1, α_2) were the same for all soils, talus, and interception storage on the rock and talus. Differences in weathering between these different compartments therefore became functions of the length of time they were wet, their specific surface area (surface area for the rocks), and their relative volumes (area, in the case of rock surfaces) of soil. For an analysis of the weathering stoichiometry used, see Appendix B. Weathering rates were based on data in Brown et al. (1988). The values used are shown in Appendix D, File 6.

5.5.4 Description of Test Run Output

Several observations may be made through examination of initial model output obtained using the hydrologic data and parameters described above (Figure 5.6). These include: (1) modeled flows exceed observed during the highest snowmelt runoff period, (2) mid-December through mid-February (WY days 75-165) peaks are missed entirely by the model, (3) computed flows are less than observed prior to the peak runoff period, and (4) modeled runoff drops to zero before observed in August.

It is obvious that during the early portion of peak snowmelt runoff season, some retardation of runoff is provided by the snowpack itself. This retardation is not included in the model. When snowmelt begins to cause runoff in the model, the modeled runoff responds more rapidly to snowmelt

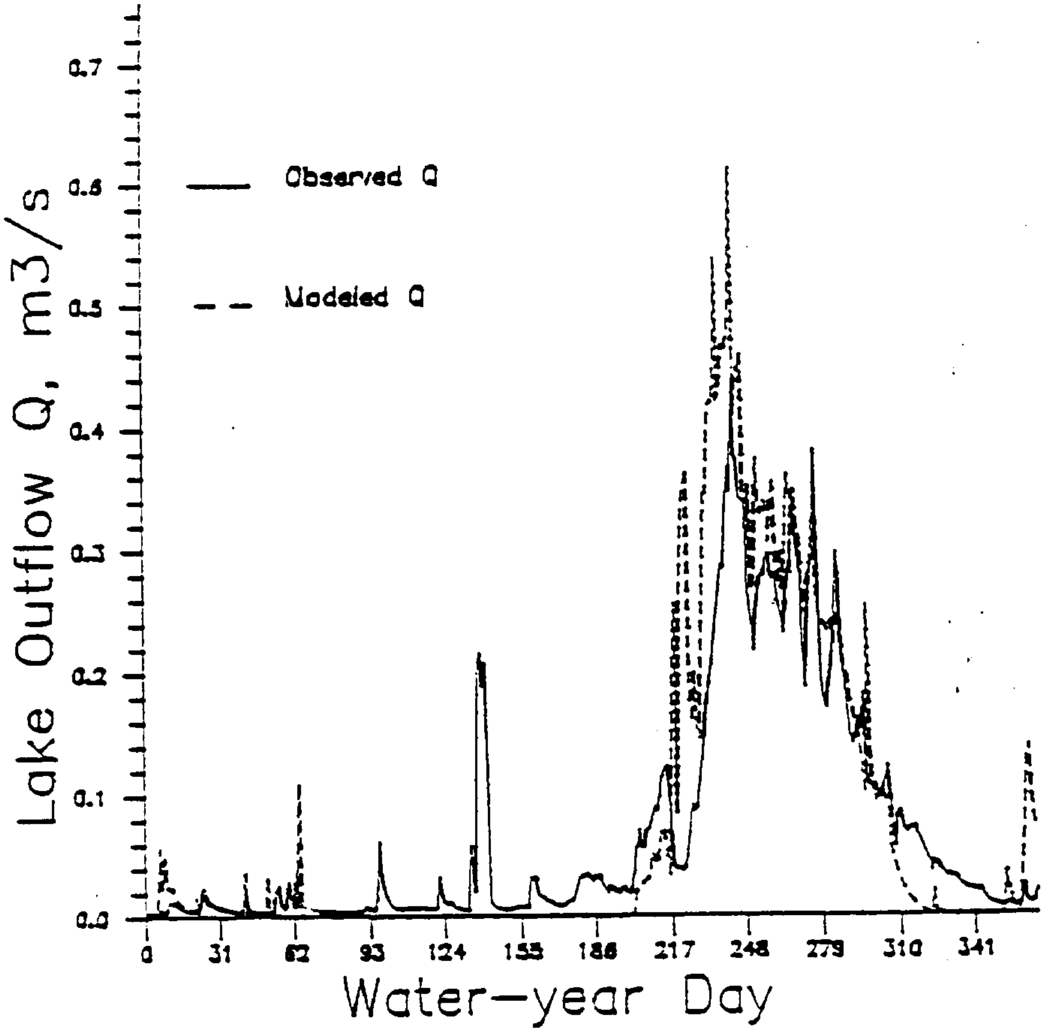


Figure 5-6 Observed and modeled discharge from Emerald Lake, water year 1986. The lake is modeled as frozen between December 15, 1985 and June 30, 1986.

than does observed runoff. This can be seen near WY day 220 (Figure 5.6). Incorporation of a seasonally-variable snowpack streamflow retardation factor or a detailed, free-surface, groundwater-type model for predicting snowpack retardation would solve this problem. Conversely, if higher concentrations of chemical species leave the snowpack with the initial flush of meltwater, our current model formulation will generally result in a "worst case" scenario.

The small flow peaks occurring in midwinter are particularly interesting. The data that we received show no rain or snowmelt (except 0.07 cm on WY day 162) during this period. Further evaluation showed that most of these peaks coincide with fresh snowfall, and it was hypothesized that the weight of the fresh snowpack on the ice-covered lake surface was displacing an amount of water roughly equal to the weight of the snow. To test this hypothesis, the model was re-run with identical data, except that the lake was allowed to retain an open, ice-free surface throughout the year (Figure 5.7). The model results appear to confirm the hypothesis and suggest that the lake model (currently not in the water balance) should incorporate this finding. Using this same hypothesis, it appears that the large snowfall attributed to a single storm of December 3, 1985 may have been the result of three smaller storms, though uneven settling of the lake's ice cover could also be proposed as the cause of the three observed outflow peaks. The largest peak between WY days 124 and 155 has been previously attributed to an avalanche (Dozier et al., 1988). Comparing the modeled to observed outputs around this peak, it can be seen that substantially more volume was observed than computed with the "snowfall-in-the-lake" hypothesis, though the largest daily average lake discharges are similar. "Observed" lake outflow during this period is known to be suspect (Dozier et al., 1988). In conjunction with on-site observations, our modeling effort suggests a combination of avalanches and ordinary snowfall on a combination of sound lake ice (pre-avalanche) and broken or absent ice (post- avalanche) caused the large outflow event, and that the observed snowfall on sound lake ice could cause lake discharge nearly equal to the highest daily average discharge reported. (The latter conclusion is partly a result of the lack of storage in the model's lake subunit).

With the current model formulation, leaving a free-water surface on the lake improves the fit to lake outflows, but would result in erroneous mixing of snowfall with lake water and lake evaporation computations.

Just prior to the modeled flow's highest runoff peaks, computed runoff lags behind that observed. This can be seen on the graph in the period near WY day 180, where observed flows rise before modeled flows. This is due to at least two causes. The first is that the melt data which were provided included essentially no melt near that period until WY day 189. Second, when the melt data began to be positive, most of them were used to satisfy the snowpack's free-water holding capacity; therefore, no

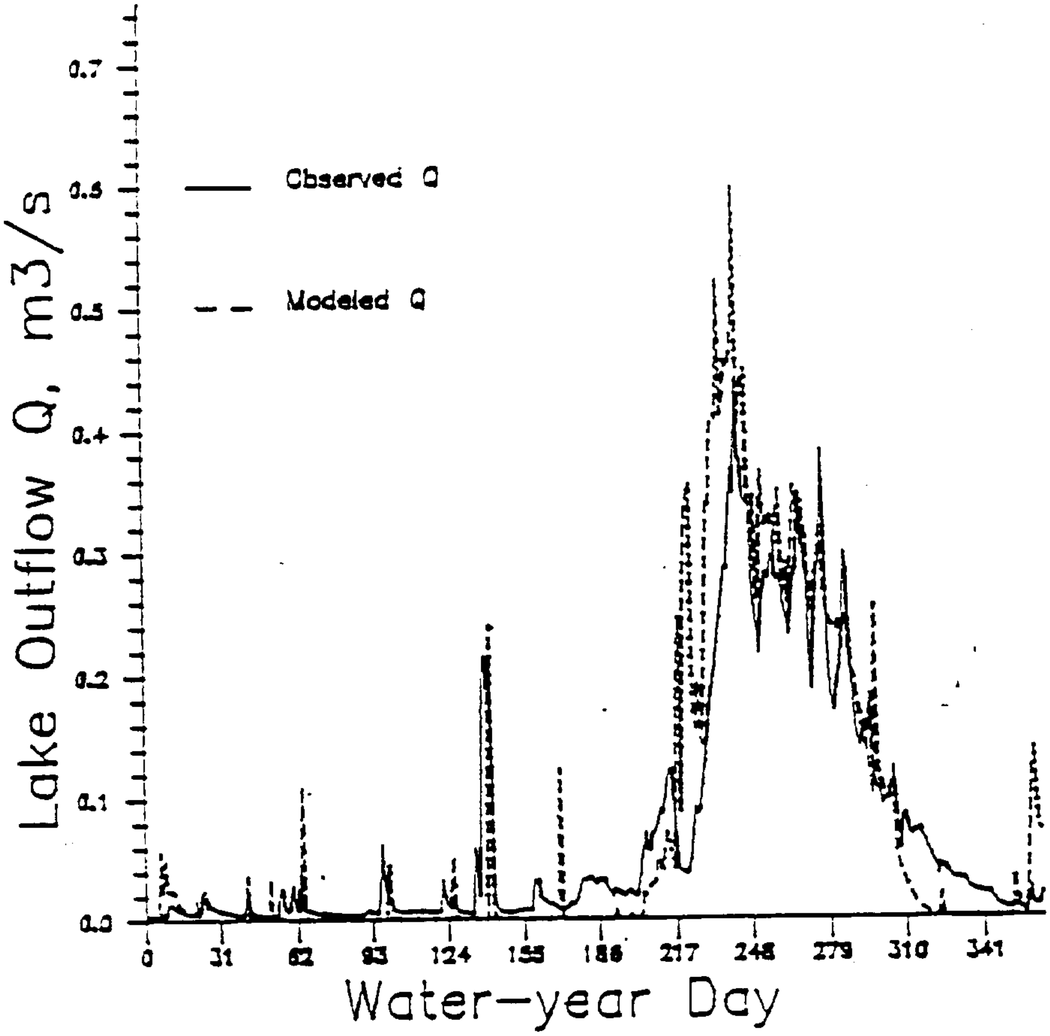


Figure.5-7 Observed and modeled discharge from Emerald Lake, water year 1986. The Lake is modeled as ice-free all year. Note improvement in fit between WY days 93-155.

runoff occurred until WY day 203. Most of the first 10 cm of snowmelt was stored as increases in the snowpack's free-water holding capacity.

The modeled flow drops to zero in early August, while observed flows continue at a higher rate. This apparently is the result of an early disappearance of the snowpack in the model, a result of our making snowpack accumulation and melt uniform on the snow covered area of all subunits. In reality, the late-season snowpack is probably concentrated in a few, relatively small locations, "Danny's Hole" being one example. Besides different melt rates, these "deep-snowpack" locations may also have greater than normal snow accumulation due to redistribution by avalanches, which are outside the realm of automatic computation by AHM. Avalanche redistribution can be manually incorporated into the current model, by restarting the model with new initial snowpack conditions after an avalanche, with locations that receive redistributed snow modeled as separate subunits.

For initial test runs, the only processes involving chemical change that we included were wet and dry inputs to the watershed and mineral weathering. While raw data for the other processes listed in Section 5.1 were available at the time of model testing, most were not yet reduced to a form usable to the model. Further, our approach was to begin with the most important processes and sequentially add others after the importance of the previous step was evaluated.

Calculated pH and ANC for one soil to compartment talus and the lake inflow for WY 1986 are in Figure 5.8a. Examination of these initial test runs for the pH and ANC concentration in both compartments show:

(1) A gradual rise in both during the fall and winter snow accumulation season;
(2) A steep drop at the initiation of snowmelt;
(3) A late spring and early summer plateau;
(4) Followed by a summer rise; and
(5) Late-summer fluctuations caused by rainstorms.

Obvious problems with the lake calculations are: (1) the spikes that occur up to the time of snowmelt, (2) the high peaks in ANC just prior to snowmelt and in mid summer, and (3) the general tendency of the model to overestimate the changes in ANC or pH.

This overestimate of changes, which can be seen more clearly for the snowmelt period on Figure 5.8b, can be addressed by adding more processes, using spatially (and temporally) distributed parameters and model calibration. Recall that in this initial test run, parameters for ion exchange, vegetation uptake, soil mineralization, vegetative throughfall, etc. were set to zero. Also, most parameters were lumped spatially; dry deposition was put in as a two period step function.

The model is sensitive to doubling the annual acid deposition flux, as illustrated on Figure 5.9a for one soil and the inflow subunits. As expected, the pH calculated by the model is most sensitive during snowmelt (Figure 5.9b).

5.5.5 Evaluation of Initial Test Runs

Modeled lake outflows were very similar in magnitude and distribution to those observed. Most apparent differences can be explained by those factors mentioned above. Other, presumably smaller and therefore less apparent differences probably exist, due to process simplification in the model or inaccuracy in the data. Some of this latter group of errors is no doubt due to a misapplication of the snowmelt and ET data used.

The model was written to use potential snowmelt, sublimation, and ET values rather than "actual" values as observed by the difference between inputs, outflows, and on-site storage, because potential values are more easily obtained. In fact, obtaining "actual" values requires the use of some form of complete water-balance model, the use of which would, to a large extent, negate the purpose for developing AHM. In using the best available estimates for actual snowmelt, sublimation, and ET, we were forced to make assumptions about the spatial distribution of these "actual" values, and our initial assumptions probably do not match exactly those used by the generators of that data. We hope to improve model fit by input data adjustments obtained through interaction between researchers, now that our initial assumptions have been recorded.

Typically, matching outflows obtained by a model (using reasonable, physical parameters) to those observed on-site is considered a fair test of a model's performance, particularly so if data not used in model calibration can also be shown to provide an adequate fit. Using this assumption, the "goodness-of-fit" obtained on our initial test with no attempt made to optimize parameters could be considered cause for jubilation. Unfortunately, this is not true.

Several of the researchers working on the AHM modeling effort have had a long-term concern that the nature of the Emerald Lake watershed might preclude hydrologic parameter optimization by calibration against observed streamflow. Our belief has been that, due to the minimal amount of soil present on the watershed, almost any set of hydrologic parameters used to represent soils, rock outcrop areas contributing flows to soils, and parameters influencing ET will result in similar outflows from Emerald Lake. This appears to be the case.

Although we have not done detailed testing of this theory at this time, one simple test was done to demonstrate the problem. Soil depths on all subunits shown in Table 5.2 were doubled and halved, the model was run again, and outputs from this run plotted with those from the preceding (normal soil depth) run (Figure 5.10). Doubling soil depth will generally double the water available for ET, the

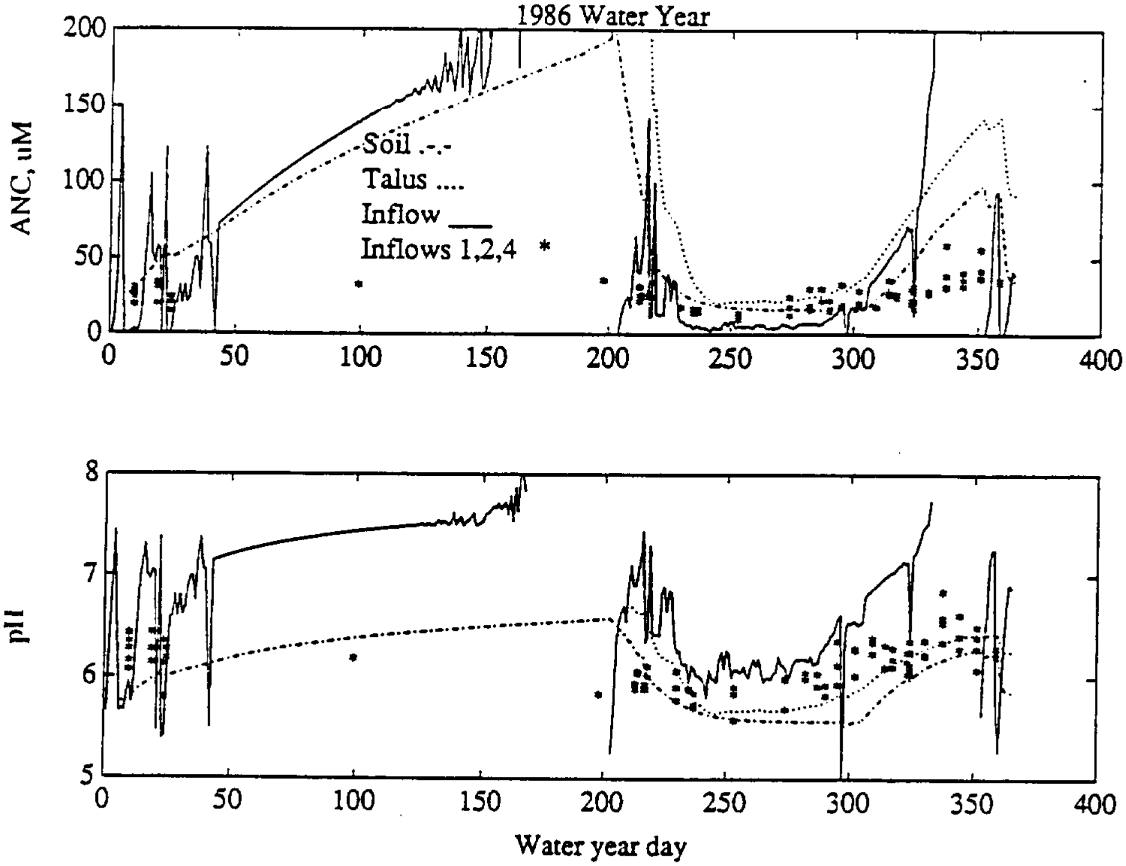


Figure 5.8a: Modeled soil water and streamflow pH and acid-neutralizing capacity compared to lake inflow observations for the 1986 WY.

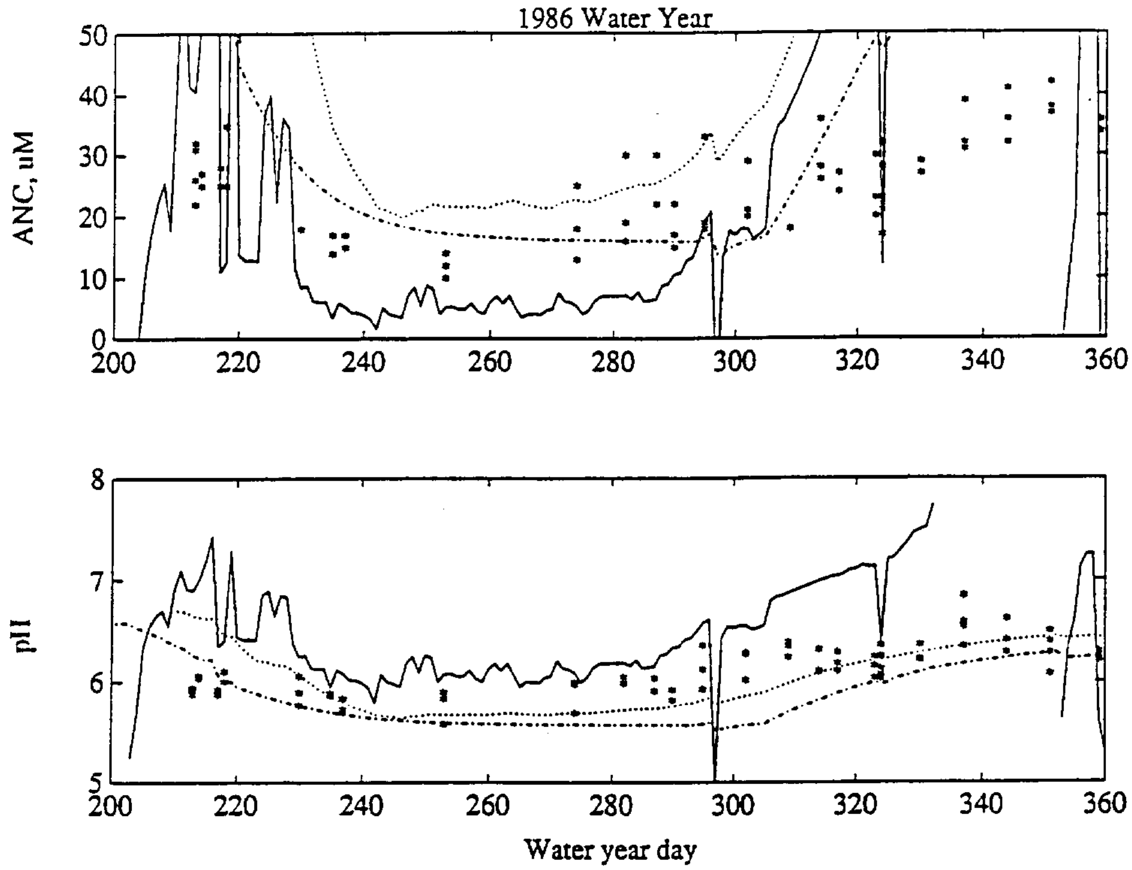


Figure 5.8b: Modeled soil water and streamflow pH and acid-neutralizing capacity compared to lake inflow observations, snowmelt season throughfall, 1986.

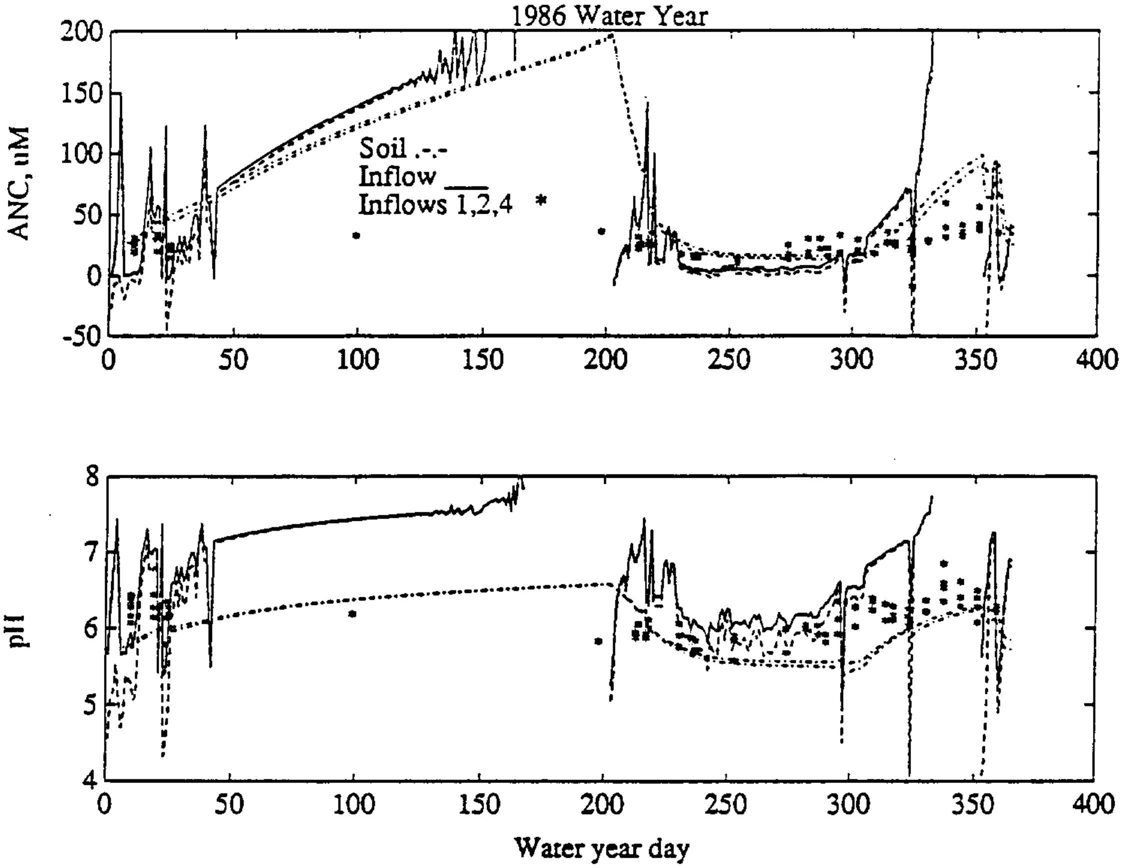


Figure 5.9a: Modeled soil water and streamflow pH and acid-neutralizing capacity compared to lake inflow observations, WY 1986. Acid inputs have been set to twice the estimated actual inputs. Data with normal acid inputs is also shown.

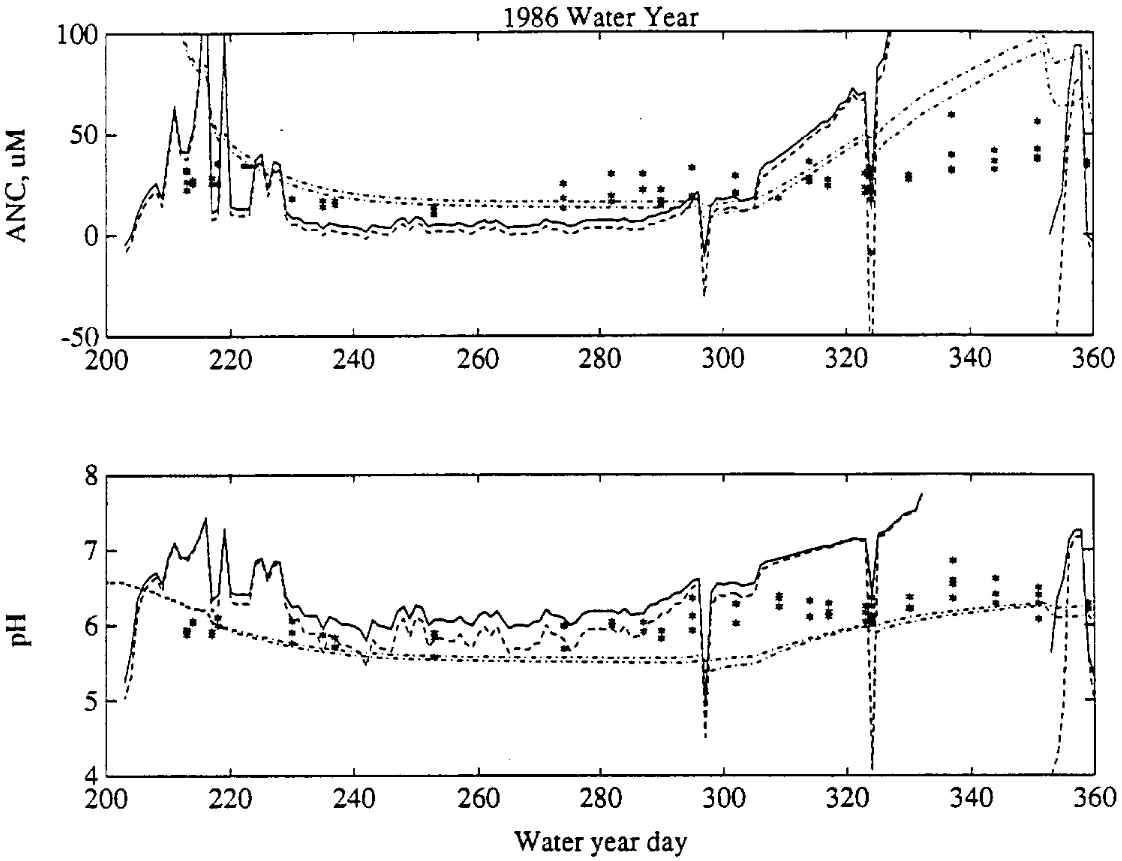


Figure 5.9b: Modeled soil water and streamflow pH and acid neutralizing capacity compared to lake inflow observations, snowmelt through fall seasons, 1986. Acidic inputs have been set to twice the estimated actual inputs. Data with normal acid input is also shown.

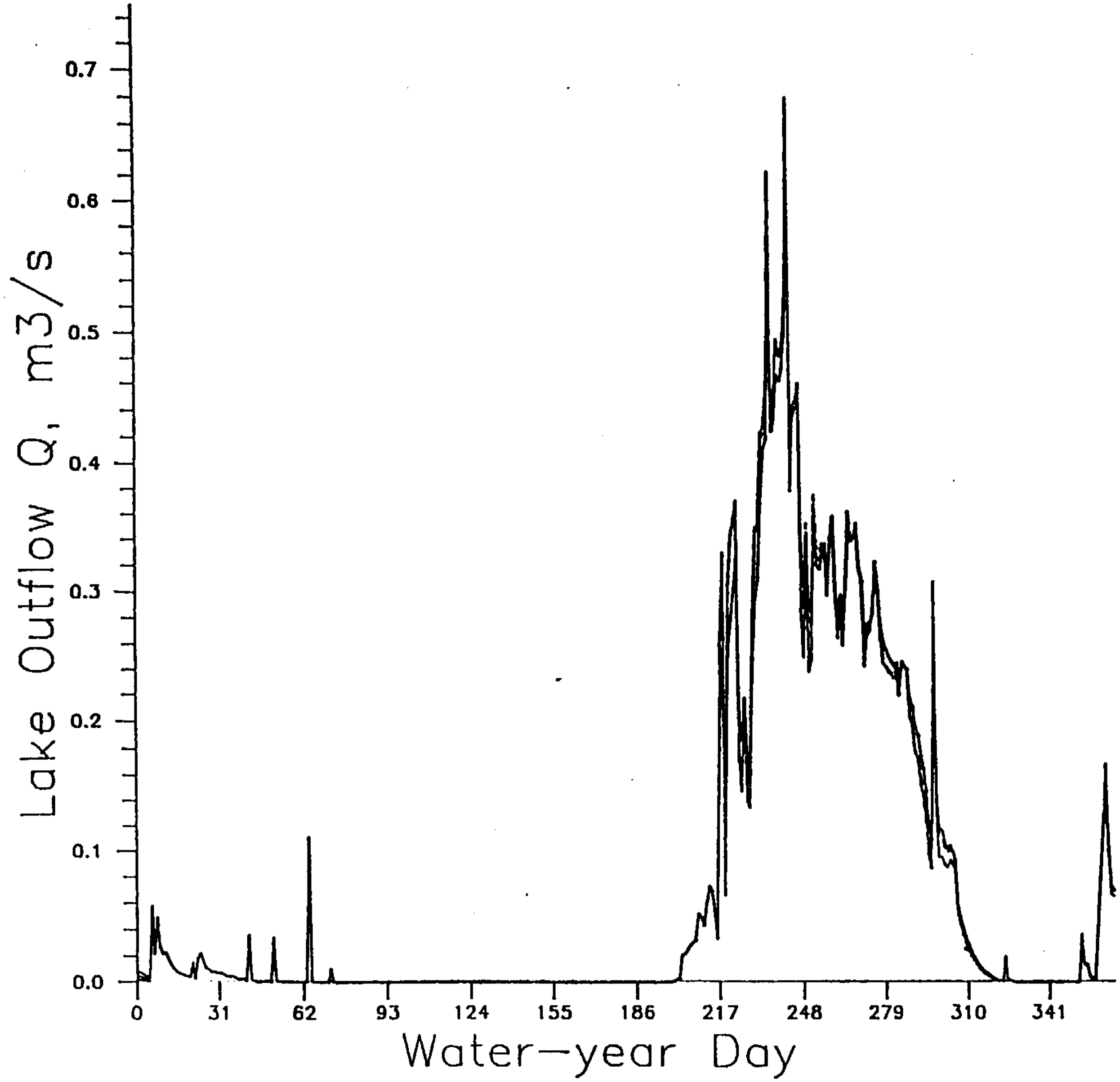


Figure 5.10: Modeled lake outflows with soil depths set to 0.5, 1.0, and 2.0 times those estimated in the field.

"buffering" of peak flows following prolonged dry periods, and the delay in streamflow caused by water residence time in the soil. Although some differences are apparent between the two model runs, those differences are slight in comparison to the relative change made in modeled soil depths.

5.5.6 Influence of Findings on Future Modeling Effort

Our task is to model not only runoff, but also the chemical composition of that runoff. If the kinetics of soil reactions play a significant role in streamflow chemistry, then the residence time of water in the soils is significant to the overall modeling effort. AHM is ideally suited to this modeling task. Unfortunately, if any reasonable range of soil parameters results in essentially equivalent modeled outflow rates, lake or stream outflows give essentially no indication of soil-water residence times. Therefore, lake outflow rate cannot be used to adequately calibrate AHM or any other water balance model for the Emerald Lake basin, for those cases where soil water dynamics are of critical importance. In contrast, the ideal situation for calibration of a hydrochemical model would be one in which flow volumes and rates through chemically reactive soils could be independently confirmed, after which streamflow chemistry and soil water chemistry observations could be used to calibrate the chemical portion of the model.

Given existing data, fitting both chemical and soil parameters simultaneously is probably impossible, as any number of possible combinations of parameters may result in the same fit to observed data. For example, a too-rapid flow rate through the soil can probably be masked by excessively fast chemical-reaction rates.

Therefore, the user is faced with two possible courses of action for water balance model calibration. These are:

(1) More detailed information pertaining to flow pathways of surface and subsurface runoff on the watershed, infiltration, ET, and other related variables must be obtained, and the watershed subdivided accordingly; or

(2) Existing knowledge of streamflow chemistry and soil chemistry must be used to determine the flux of water through the soil.

At this time, option (2) appears to be a viable alternative and should be developed further.

APPENDIX A

SYSTEMS-THEORETIC MODELING

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APPENDIX A

SYSTEMS THEORETIC MODELING

A.1 Description

A possible approach to model the response (e.g., flow, concentration of given chemical species) of a natural system is through systems-theoretic (linear stochastic) models such as Autoregressive Moving Average (ARMA) and ARMA with inclusion of eXogenous Variable (ARMAX). The success of such a modeling approach (especially in the case of water quality variables) is highly dependent on the availability of sufficient data.

In the case of flow modeling, the flows (system output) at the outlet of a watershed (or lake) can be considered as a time series measured directly in time. Possible systems inputs could be some measure of precipitation as snow, precipitation as rain, as well as any other significant inflow source. In system jargon, the inputs are commonly referred to as <u>exogenous</u> variables.

The deterministic component of such a model for Emerald Lake represents the inter-relationship between various measured time-series (e.g., precipitation as snow and/or as rain, temperature, etc.) and lake outflow. For instance:

$$A(s)Q(t) = B(s)p(t-r) + C(s)I(t-f) \tag{A-1}$$

with A(s), B(s), and C(s) being polynomials in s of the form:

$$A(s) = \sum_{1=0}^{n} a_i \, s^{-i} \qquad \text{where } a_0 = 1$$

$$B(s) = \sum_{i=0}^{m} b_i \, s^{-i}$$

$$C(s) = \sum_{i=0}^{k} c_i \, s^{-i}$$

where s^{-i} is the ith backshift operator [i.e., $s^{-i}Q(t) = Q(t-i)$].

The above model represents the relationship between flow, Q(t), and flows measured in previous time intervals, m values of measured precipitation as snow I(·), and k values of measured precipitation as rainfall p(·).

In the above equation, a_i, b_i and c_i, are parameters applied to k previous flow values, to k previous measured rainfall values, and to m previous measured snow values, respectively. The parameters f and r are the respective delay parameters for each of the variables. They can be viewed as representing travel time from the point of measurements P(·) and I(·) to the point where flow is measured.

In order to ensure the selection of best model, a three-stage process is followed. The first step is to identify the form of model which best fits the given data. Extensive correlation analysis of data is critical in this step. In the second stage, the model parameters must be calculated by employing a suitable estimation method. The third and last stage involves checking the model for possible inadequacies. If serious anomalies are detected as a result of tests performed in the third stage, then appropriate model modifications may be necessary by repeating the identification and estimation stages. A detailed discussion of the three stages is provided later in this Appendix.

A.1.1 The Stochastic Component: The Moving Average (MA)

The model described above (Equation A-1) is purely deterministic in the sense that it does not allow the consideration of uncertainty associated with either the measured time-series or the nature of the relationship. In order to introduce some measure of uncertainty into the problem formulation, it is most straightforward and analytically convenient if we assume that all stochastic effects can be lumped into a single stochastic variable, ϵ (t). Without going into much detail, it is also reasonable to assume that the stochastic variable, ϵ (t), may be best represented through an autoregressive structure. Here, we are assuming that the additive error term is an autocorrelated sequence with a memory of residual from previous time steps. In this situation, then, ϵ (t) is modeled according to:

$$\epsilon(t) = G(s)e(t) = g_0 e(t) + g_1 e(t-1) + \dots + g_v e(t-v)$$

$$\text{with } G(s) = \sum_{i=0}^{v} g_i \, s^{-1} \tag{A-2}$$

where g_i's are parameters and e(t) , ... , e(t-v) are a sequence of normally independently-distributed white noise residuals with mean zero and variance α^2. Residuals are defined as the difference between observed and computed values.

Now, if this stochastic component (i.e., Equation A-2) is added to Equation (A-1), then we obtain a mixed model which not only captures the dynamic of the process deterministically, but also incorporates any additional information about the process which may exist in the model residuals.

A.2 Application Procedure

As pointed out, there are three stages involved in the application of systems-theoretic models. The first stage is to identify the form of model which may best fit the given data. In the second stage, the model parameters must be calculated, employing a suitable estimation method. The third and last stage involves checking the model for possible inadequacies. If serious anomalies are detected as a result of tests performed in Stage 3, then appropriate model modifications can be made by repeating the identification and estimation stages.

A.2.1 Stage 1: Identification Stage

The purpose of the identification stage is to determine the differences required to produce the order of both periodical and nonperiodical AR and MA operators for the given time series. The topic of model identification for time-series models is extensively covered in the literature (e.g., Box and Jenkins, 1976; Salas et al., 1980).

A.2.1.1 Plot of the Original Series. The first step in model identification is usually to inspect a time plot of the original series. Strong periodicity, nonstationary trend, outliers, and extreme values should be evident from such plots.

A.2.1.2 Autocorrelation Function (ACF). The ACF measures the amount of linear dependence between observations in a time series that are separated by lag k. The ACF is obtained by taking the ratio of:

$$\rho_k = \frac{cov\ (z_t\ z_{t-k})}{var\ (z_t)} \qquad \text{(A-3)}$$

where ρ_k is autocorrelation at lag k of the series (z). The ACF, ρ_u, of AR models also satisfies the difference equation:

$$\rho_k = \sum_{j=1}^{p} \phi_j\ \rho_{k-j} \quad k > 0 \qquad \text{(A-4)}$$

where ϕj, ... , ϕp are autoregressive coefficients of the AR(p) model of series (z). To use ACF in model identification, calculate and then plot ρ_k against lag k. From the plot, one can observe at which lag the ACF dies out abruptly. ACF is helpful in identifying the order of MA process. For example, if ACF dies out and is not significantly different from zero after lag q, then the model is a pure MA of order

q. However, if ρ_k tails off and does not truncate, this suggests that AR terms are needed to model the time series.

A.2.1.3 Partial Autocorrelation Function (PACF). The PACF, ϕ_k, in an AR process of order k is a measure of linear association between ρ_j and ρ_{j-k} for $j \leq k$. The difference equation for an AR(k) model is:

$$\rho_j = \sum_{i=1}^{k} \phi_i\ (k)\rho_{j-1} \qquad j = 1, \ldots k \tag{A-5}$$

where $\phi_i(k)$ is the i^{th} autoregressive coefficient of the AR(k) model. The PACF is given by the last coefficient, $\phi_k(k)$, $k = 1,2,\ldots$ Note that PACF $\phi_k(k)$ for an AR process of order k satisfies the Yule-Walker equation (see Salas et al., 1980, Appendix A4.2, pp. 179-181). It is obtained by fitting to the given time series (z) AR process of order $k = 1,2,\ldots$

$$z_t = \phi_1\ (k)\ z_{t-1} + \phi_2\ (k)\ z_{t-2} + \ldots\ \phi_j\ (k)\ z_{t-j} + \ldots + \phi_k\ (k)\ z_{t-k} \tag{A-6}$$

The plot of $\phi_k(k)$ versus k is the sample PACF. In a nonperiodic case, for a pure AR process, ϕ_k truncates and is not significantly different from zero after lag p. If ϕ_k tails off, this implies that MA terms are required.

If both ACF and PACF fail to abruptly cut off, it will be an indication of a mixed (ARMA) model. Table A-1 summarizes the expected behavior of AR, MA, and ARMA models.

A.2.1.4 Cross-Correlation Function (CCF). The purpose of a cross-correlation study in the identification phase is to determine the approximate time delay between, say, the streamflow and any of the inputs used as exogenous variables in the model. The CCF between the two time-series (say, streamflow and snow water equivalent sequence) when plotted against time (lag) will peak at some point on the time axis. This time, which corresponds to the largest cross-correlation value on the vertical axis, is a reasonable estimate of the time lag which that specific exogenous variable should be delayed in the ARMAX equation.

A.2.1.5 Akaike Information Criterion (AIC). The Akaike Information Criterion (AIC) is a mathematical formulation which considers the principle of parsimony in model building. AIC was proposed by Akaike (1974) and is used primarily for comparing among competing ARMAX models. AIC is represented as follows:

TABLE A-1. Summary of Autocorrelation and Partial Autocorrelation Relationships for AR(p), MA(q), and ARMA(p,q) Processes.

Process	Autocorrelation (ρ_k)	Partial Autocorrelation (ϕ_k)
AR(p)	$\rho_k = \sum_{j=1}^{p} \phi_j \ \rho_{k-j}$	Peaks at lag 1 through p, then cuts off; zero for lags greater than p.
MA(q)	Zero for lags greater than q	Gradually decays
ARMA(p,q)	Irregular at lags 1 through q, then obeys $\rho_k = \sum_{j=1}^{p} \phi_j \ \rho_{k-j}$ for $k \geq q + 1$	Decays

$$AIC\ (n,\ m,\ v)\ =\ N\ell n\ (\hat{\sigma}_\epsilon^2)\ +\ 2(n\ +\ m\ +\ k\ +\ v)$$

where N is the sample size (number of data points in our time series), and $\hat{\alpha}_\epsilon{}^2$ is the maximum likelihood estimate of the residual variance. The parameters n, m, k, and v represent the number parameters of the polynomials A(s), B(s), C(s), and G(s), respectively. Under this criterion, the model structure which gives the minimum AIC is the "correct" structure among competing ARMAX models and should therefore be selected.

A.3 Stage 2: Parameter Estimation

In the parameter estimation phase, we are concerned with answering the following question. Given information on the model structure, how do we then estimate the values of the coefficients a_1, ... a_k, b_o, ... b_m, c_o, ... , c_s that characterize this structure?

There have been numerous methods proposed to estimate the model parameters. Many of the proposed methods require strong assumptions about the nature of the residuals. For instance, in Box and Jenkins' modeling, the residuals are required to be independent, homoscedastic (i.e., variance is a constant), and usually normally-distributed. The independence assumption is the most important of all, and its violation can cause drastic consequences.

The normality assumption of the residuals is usually not critical for obtaining good parameter estimates. As long as the residuals are independent and possess finite variance, reasonable estimates of the parameters can be obtained. In practice, however, it is advantageous to satisfy the normality assumption reasonably well. Without the normality assumption, for example, calculation of confidence intervals for the forecasted flows would be impossible for practical use. Fortunately, in cases where both heteroscedasticity and non-normality of the residuals are present, these flaws can often be rectified simultaneously by a suitable transformation such as the Box-Cox transformation (Box and Cox, 1964).

For parameter estimation of the models proposed in this project, the maximum likelihood estimation method which accounts for all information contained in the data is used. The parameter estimation routines of the software package MATLAB referenced in the report are used for this purpose.

A.4 Stage 3: Diagnostic Checks

In this step, the identified model for which parameters have also been calculated is checked for possible inadequacies. Most diagnostic tests deal with the residuals. The residual estimates are automatically calculated at the estimation stage and are available. Many tests have been proposed, and most are available in standard statistical packages The following is a list of possible tests which can be conducted to determine model inadequacies:

(1) Overfitting: To check if a more elaborate model than the one estimated will greatly improve the fit;

(2) Test for whiteness of the residuals: To determine whether the final residuals are white noise (i.e., uncorrelated);

(3) Homoscedasticity checks of the residuals: To determine whether the variance of the residuals is constant or not and, hence, a suitable transformation of data might be in order;

(4) Tests for normality of the residuals: To check if the residuals show significant skewness and kurtosis coefficients significantly different than 3. If indications are that the residuals are not normal, then the transformation of data may be in order to reinforce the normality assumptions of the residuals.

A.5 Goodness-of-Fit Tests

Various goodness-of-fit tests are available to check how well the model fits the measured data. In this study, the standard error-of-fit was used as the measure to evaluate the model performances.

APPENDIX B

ANALYSIS OF SNOWPACK AND STREAM CHEMISTRY DATA FOR CONSTRUCTION AND TESTING OF COMPARTMENTAL MODEL

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APPENDIX B

ANALYSIS OF SNOWPACK AND STREAM CHEMISTRY DATA FOR CONSTRUCTION AND TESTING OF COMPARTMENTAL MODEL

B1. Introduction

B1.1. Objectives

To complement the systems-theoretic analysis of the streamflow data, we have undertaken similar analyses on the stream and snowpack chemistry data for Emerald Lake watershed (ELW). This analysis is intended to: (1) identify spatial and temporal correlations, (2) determine the level of consistency or inconsistency in the data sets, and (3) guide development of equations and parameters for the compartmental model.

B1.2. Data Sets

Stream chemistry data used were those provided on a floppy disk by J. Melack and associates (U.C. Santa Barbara) in February 1988. The data were previously presented graphically in the draft final limnology report (Melack et al., 1987). The time period covered was July 1984 to September 1986. Upon receipt, we split the data into separate records by station and by water year. Analyses were reported for 12 constituents (H^+, NH_4^+, PO_4^{3-}, ANC, Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Silica), plus electrical conductivity and temperature. Table B.1 indicates the number of observations reported. Data for 1984-85 and 1985-86 cover the complete water years. The 1984-85 data are most complete for inflow 1, whereas the 1985-86 data are reasonably complete for inflows 1, 2, and 4.

Table B.1. Extent of stream and lake chemistry data set

	Observations per Water Year			
Location	1983-84	1984-85	1985-86	Total
Inflow 1	6	22	34	72
Inflow 2	0	14	35	49
Inflow 3	0	0	7	7
Inflow 4	7	18	27	50
Parsons pond	0	6	15	21
East joint	0	0	7	7
Southeast gulley	0	1	8	8
Other	0	3	2	7
Subtotal, watershed	12	60	133	205
Subsurface				
Site 4[a]	6	14	19	39
Other sites[b]	0	0	15	15
Outflow	6	27	39	72

[a] 35 have data for 4 depths, 2 each have 2 and 3 depths.

[b] 2 have data for 4 depths, 13 have data for 4 depths.

B2. Analysis Methods

Visual comparisons and statistical correlations were as follows.

(1). Time-series plots of chemical species for the different sampling points give a visual indication of trends.

(2). For each sampling point, the degree of correlation between pairs of species was determined. The correlation was expressed as the covariance.

(3). Dependency relations between multiple parameters for a sampling point were determined using a multiple linear regression.

(4). Comparing parameter correlations for different sampling points indicated spatial differences and provided an indication of consistency for the data set.

(5). Comparing parameter correlations for different years or seasons indicated temporal changes.

(6). Snowpack and lake-inlet samples for the period of record were compared to determine what mineral weathering, and biological reactions were responsible for the observed composition changes.

The program MATLAB was used for most of the computations because of power and ease of use in manipulating data in matrix form, ease in program development, and graphics capability.

B2.1. Covariance Analysis

We applied a covariance analysis method used in hydrologic models to determine the correlation between two parameters. Given two zero-mean vectors $X(i)\; i=1, \cdots n$ and $Y(i)\; i=1, \cdots n$, the cross-covariance function is:

$$XCF(l) = \frac{1}{h-l} \sum_{i=1}^{n-l} X(i)\,Y(i+l) \tag{1}$$

where l is the lag between the vectors at which the XCF is computed. By computing $XCF(l)$ for the various l's, one finds the l at which the XCF is largest. This enables determining which variable leads which other variable (possible causality), and at what lag in time the variables are best related.

The primary use for the chemical data was simply to get the cross covariance (zero lag) of two normalized (divided by the mean) vectors of parameters.

B2.2. Linear Regression

The linear regression problem finds the coefficient values $TH1, \cdots THN$, such that the following equations represent the "best" (smallest standard error) linear model for approximating the measured values of the dependent variable (Y by YP), obtained as a linear combination of the independent variables ($X1$ through XN).

$$Yi = YPi + ERi \qquad \text{for i} = 1,2, \cdots M \tag{2}$$

$$YPi = TH1 \times X1i + TH2 \times X2i + \cdots + THN \times XNi + C \qquad \text{for i} = 1,2, \cdots M \tag{3}$$

Y is the observed value of the dependent variable , YP is the estimated value, ER is the error of the estimate, and C is the regression constant. The linear equations can be rewritten in matrix and vector notation.

$$Y = XX \times TH + ER \qquad \text{where } Yi = [Y1, ... YM]^{\mathrm{T}} \tag{4}$$

$$XX = \begin{bmatrix} 1 & 1 & \cdots & 1 \\ X11 & X12 & \cdots & X1M \\ \cdots & \cdots & \cdots & \cdots \\ XN1 & XN2 & \cdots & XNM \end{bmatrix} \tag{5}$$

The snowpack data were taken from the draft final snow-hydrology report (Dozier et al., 1987). Two different sets of measurements are available: (1) the snow-event data and (2) the snow-pit data. The time period covered by the analyses is November 1984 to June 1986, the same two water years as for the stream data. Analyses were reported for 10 constituents (H^+, NH_4^+, PO_4^{3-}, Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, MG^{2+}, Na^+, K^+), plus electrical conductivity and snow-water equivalents.

For 1984-85, event samples were taken near the inlet; snow-pit samples were taken near the inlet and outlet. For 1985-86, event and pit samples were taken at inlet, pond and ridge sites; some were taken near the lake outlet. Fourteen meltwater samples were also taken from snow pits in 1985-86. Table B.2 indicates the distribution of sampling.

Table B.2. Extent of snow chemistry data set

	Observations per Water Year[a]			
	1984-85		1985-86	
Location	Event	Pit	Event	Pit[b]
Inlet		5		9/5
Tower		1		1/2
Bench		2		
Pond		1		3/2
Ridge				7/4
Ramp		1		
Hole		1		2/1
Cirque		1		
Total	10	19	85	23

[a] Individual numbers do not add to total; some samples were apparently combined.
[b] Two numbers for 1985-86 pit are samples/days.

Dozier et al. (1988) noted that spatial variability for event samples and for pit samples during the accumulation season was small. The distribution of event samples was not given in the report; if spatial variability can be neglected, individual data are not needed.

Mineral compositions of rocks for estimating weathering reactions were taken from Clow (1987).

Streamflow data were taken from the final report on hydrologic mass balance (Dracup et al., 1988).

$$TH = [C, TH1, \ldots, XNM]^T \tag{6}$$

$$ER = [ER1, \ldots, ERM]^T \tag{7}$$

where the T indicates transpose. The least squares solution is found by minimizing $ER^T \times ER$ and is given by:

$$TH = \mathrm{inv}(XX^T \times XX) \times XX^T \times Y \tag{8}$$

Parameters are estimated using a standard derivative based optimization algorithm built into MATLAB. On termination of the search, the algorithm returns the "best" parameter estimates as well as the approximate values of the standard error on each parameter estimate. The standard error is compiled by MATLAB using an estimate of the parameter covariance matrix, computed from the final search Hessian (matrix of the second derivatives of the function with respect to the parameters). Using the parameter value ± 2 standard errors, one gets an idea of the 95 percent confidence interval on each parameter estimate. If this interval includes zero, we may assume that the estimated parameter is not significant and can be dropped from the analysis.

The standard error is calculated by:

$$e = \frac{1}{n-1}[ER - \overline{ER}]^T[ER - \overline{ER}] \text{where} \overline{ER} = \frac{1}{m}\sum_{i=1}^{m} ERi \tag{9}$$

A correlation matrix between parameters is also calculated, given by the normalized $[X^T X]^{-1}$ matrix. If $|\ cor(i,j)\ |$ is close to 1.0, then the two parameters have almost a linear dependence; one should thus be removed from the analysis.

Missing data are input as -0.9. By calling a separate MATLAB routine, a search is done through each data vector of dependent and independent variables; those rows in the data matrix with a missing value in one or more columns are deleted. The linear regression is then applied to the remaining data. The coefficient vector and standard error are then reported.

B2.3. Watershed Reactions

Composition of snow and stream water were compared to determine what reactions were responsible for alkalinity generation in the watershed. The principle has been applied many times by others; the method is similiar to that described by Garrels and MacKenzie (1967).

Five weathering reactions were considered for transforming snowpack concentrations into inflow stream concentrations.

(1). 3 biotite + 8 H_2O = 2 vermiculite + 6 K^+ + 3 Mg^{2+} + 3 Fe^{2+} + 8 SiO_2 - 12 H^+

(2). 2 vermiculite - 29 H_2O = 3 kaolinite + 6 Mg^{2+} + 6 Fe^{2+} + 4 SiO_2 - 30 H^+

(3). 8 plagioclase + 5 H_2O = 5 kaolinite + 6.1 Na^+ + 1.9 Ca^{2+} + 12.3 SiO_2 - 10 H^+

(4). anorthite + H_2O = kaolinite + Ca^{2+} - 2 H^+

(5). kaolinite + H_2O = 2 gibbsite + 2 SiO_2

Ammonia assimilation and nitrification were also included in the analysis. The net reaction for ammonia assimilation is:

(6). $NH_4^+ + 5\,CO_2 + 2\,H_2) = C_5H_7NO_2 + 5\,O_2 + H^+$

For nitrification, the sum of the NH_4^+ -> NO_3^- reaction and decomposition (the reverse of reaction 6) was used, giving the net reaction:

(7). $C_5H_7NO_2 + O_2 = NO_3^- + CO_2 + 3\,H_2) + H^+$

Thus, each nitrogen reaction produces one H^+ per NH_4^+ consumed. These reactions were applied to individual samples for the lake inflows.

A FORTRAN program was written to handle the computations to determine the change in ANC for the reactions as applied to the difference between snowpack and streamflow data. As snowpack samples were taken less frequently than streamflow samples, linear interpolation (by day) was used to estimate snowpack composition on the day corresponding to a given stream sample. The two snowpack samples immediately before and after the stream sample were used for the interpolation. Snowpack chemical compositions were adjusted (upward) by a factor accounting for sublimation and evapotranspiration. The factor was computed for each day by dividing the snow volume by snow volume minus the accumulated evaporation loss from the snowpack. For the latter, see Table 23 of Dracup et al. (1988). The actual factors used were essentially 1.00, indicating that the equation in the program may have computed them incorrectly.

Differences between snow and stream compositions were then adjusted for two salts: (1) amounts of Na^+ and Cl^- equal to the Cl^- concentration were subtracted and (2) amounts of Ca^{2+} and SO_4^{2-} equal to the SO_4^{2-} concentration were subtracted. Therefore, it was assumed that within watershed contributions of Cl^- and SO_4^{2-} were from sea salt and $CaSO_4(s)$, respectively.

Reactions (1) - (5) and the nitrogen reactions were then applied stepwise to the remaining concentrations.

(1). Either all Mg^{2+} or all K^+ was assumed to come from biotite to vermiculite weathering, depending on which was limiting.

(2). All Mg^{2+} was assumed to come from vermiculite to kaolinite weathering.

(3). Either all Na^+ (most cases) or all Ca^{2+} was assumed to come from plagioclase to kaolinite weathering.

(4). Any remaining Ca^{2+} was assumed to come from anorthite to kaolinite weathering.

(5). The remaining SiO_2 was assumed to come from kaolinite to gibbsite weathering.

(6). The decrease in NH_4^+ from snowpack to stream was attributed to NH_4^+ assimilation.

(7). Nitrate increases were attributed to decomposition and nitrification.

Note that the sum of steps 6 and 7 is simply nitrification.

The computations were limited to only those in-stream observations obtained within two weeks of the period in which snow chemistry data were available. Combined with the frequency of in-stream measurements, this limited the analysis to water year days 200-274, or mid April through July 1, 1986.

Mass Balances

Comparison of material balances for the different species shows similar trends for some and differences for others. Our analysis basically followed that of Dracup et al. (1988) and will not be repeated here. Our most detailed analysis was for all available nitrogen data, which showed uncertainties in fluxes on the order of atmospheric deposition and lake outflow quantities (Noppe, 1989). Uncertainties in biological uptake, decay, and transformations are the apparent causes of the differences.

B3.2. Time-Series Data

Time-series data for the lake inflows show some qualitatively similar trends for different species. For example, Ca^{2+}, NO_3^-, ANC and SO_4^{2-} in inflow 1 all show summer minima, then rise to higher values for summer, fall, and winter (Figure B.1). For easy reference, Table B.3 lists calendar dates for WY days plotted.

Table B.3. Conversion of calendar date to water year day

Calendar Day	Water Year Day		
October 1	1	366	731
November 1	32	397	762
December 1	62	427	792
January 1	93	458	823
February 1	124	489	854
March 1	152	520	885
April 1	183	551	916
May 1	213	581	946
June 1	244	612	977
July 1	274	642	1007
August 1	305	673	1038
September 1	336	704	1069

The NO_3^- and SO_4^{2-} minima occur about mid-May in 1985 and mid-June in 1986, rising again to higher values through September. The ANC minima occur in early May in both years; however, the date could be as early as mid-April, given the lack of data for the intervening period. Similarly, no spring peaks in NO_3^- and SO_4^{2-} are apparent, but they could have occurred during the same period. Ca^{2+} reaches a minimum somewhat later, mid-June in 1985 and early July in 1986. The later peaks, mid-August through September, are apparently associated with release of soil water due to summer rains.

These trends are consistent with a model reflecting a spring ionic pulse of species from the snowpack, particularly acidic species. The earliest snowmelt sampled appears to contain significant concentrations of base cations from the soil, represented here by Ca^{2+}. That suggests a significant buffering role for the soil during spring melt, due either to release of readily exchangeable material built up during the low-flow fall and winter (e.g. ion exchange) or significant flow through rather than over soil, with asssociated mineral weathering. However, the low ANC earlier in the season does suggest that some, possibly a significant amount, snowmelt reaches the inlet stream with only a small amount of buffering (e.g., via overland flow).

Taking a closer look at the spring snowmelt period for the two water years illustrates further the similarity in trends, especially for Ca^{2+} (Figure B.2). The NO_3^- data for 1986 illustrate the trends noted above better than the 1985 data, which show some temporal inconsistencies (i.e., the wide range of

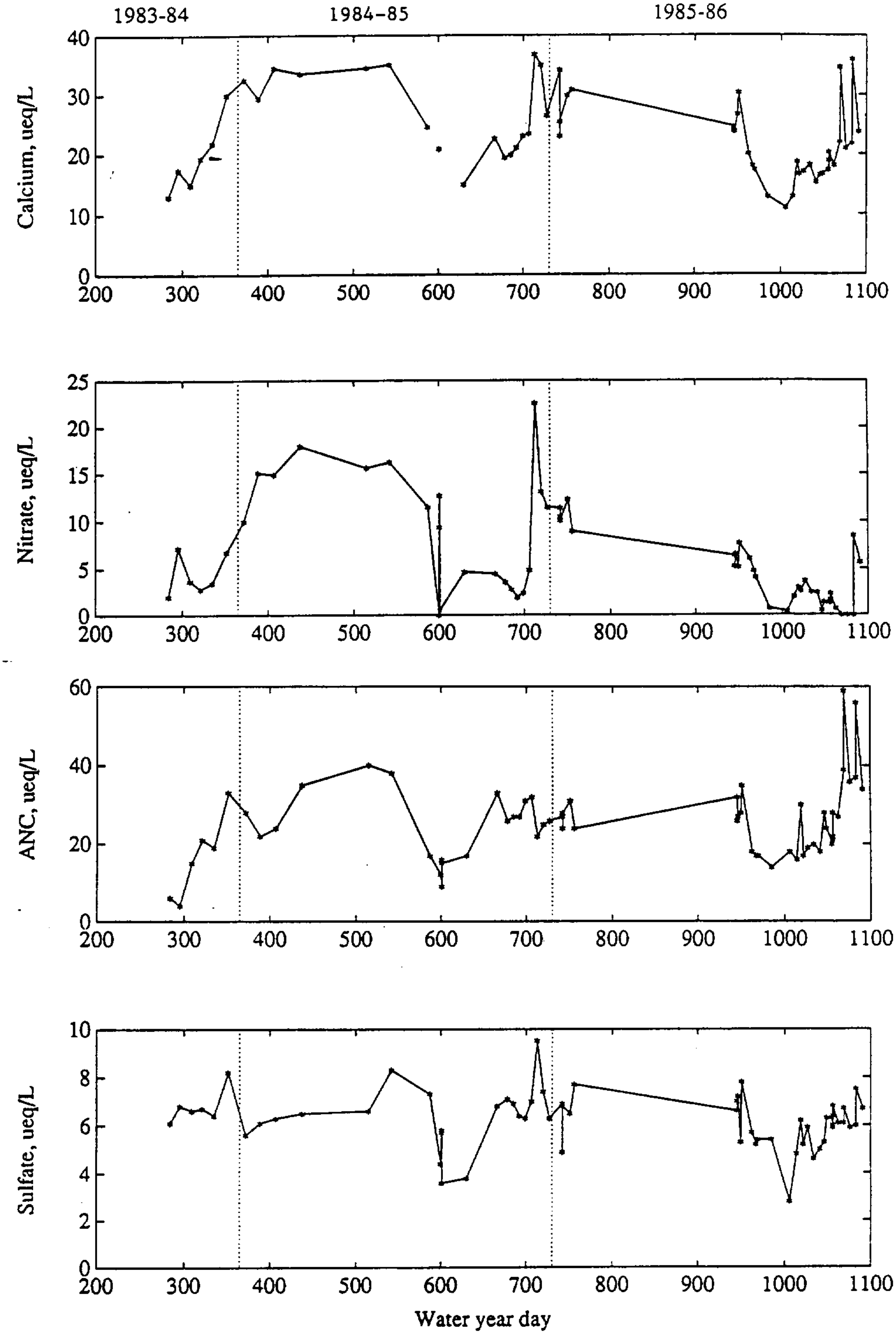

Figure B1. 1984-86 chemistry data set for inflow 1 illustrating high fall and winter concentrations and a drop during snowmelt. The long periods between fall and spring samples and late resumption of spring sampling relative to the beginning of snowmelt are potentially serious data gaps for modeling.

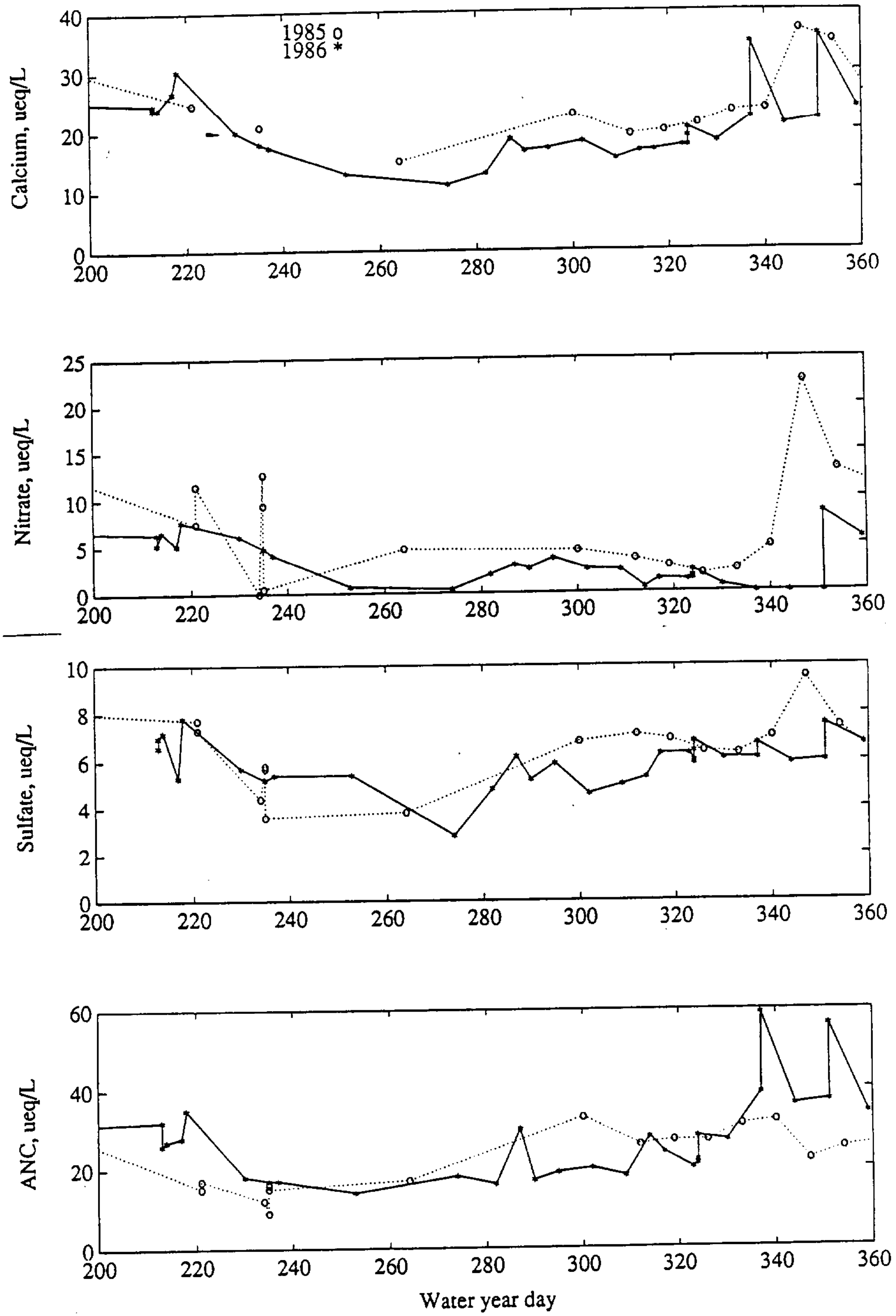

Figure B2. Ca^{+2}, SO_4^{2-} and ANC concentrations in inflow 1 are similar for 1985 and 1986, but NO_3^- data show some inconsistencies in late May 1985 (days 234-5) and higher values thereafter. The 1985 data are less closely-spaced; during the early part of snowmelt, even the weekly spacing of 1986 data may miss peak concentrations..

values on May 21-22, day 234-235).

Inflows 2 and 4 suggest further that a spring pulse occurred just prior to mid-April 1986, from the 10-fold drops in NO_3^- concentrations from late April to late June (Figure B.3). After the minimum in late June, there is a second peak in mid to late July, then generally lower concentrations the rest of the year. Possibly plant uptake of nitrogen and thus low soil unbound nitrogen concentrations during the summer are responsible for this. Inflows 1-4 show quite similar concentrations of NO_3^-. Parson's pond is a little higher, although data are limited to summer, and the southeast joint samples have lower concentrations than the inflows.

Although the Ca^{2+} concentrations exhibit the same minimum in late June and same second peak in mid to late July, there are two differences. The April peak is not as high (relatively), and the Ca^{2+} concentration goes back up from late August onward. That suggests that mineral weathering occurs in wet soils and rock all summer, versus the limited NO_3^- release. Presumably, the two peaks in inflow 1 are associated with summer rains. The fact that they do not occur in other inflows suggests that contamination of samples is a possibility that should be further checked, however.

The relative differences in spring values for NO_3^-, possibly representing snowpack species, and Ca^{2+}, possibly representing species from the soil, are further illustrated in Figure B.4, where inflow 2 concentrations are divided by the annual average for inflows 1 and 2. Recall that the two inflow concentrations are essentially the same, except that inflow 2 has a higher spring peak (Figure B.3). The trend does not show up on inflow 1, possibly reflecting an earlier spring peak.

In order to model these data and trends, one must separate snowpack from soil influences. That is, the Ca^{2+} (and base cations, which are essentially the same) comes largely from the soil. The annual mass balance supports this. However, the NO_3^- could be coming from either the snow or from the soil. Part of the NO_3^- peak could represent washout of winter accumulation from the soil, assuming that mineralization rather than uptake occurs in the winter, beneath the snowpack. In addition, the peak could represent preferential release of NO_3^- from the snowpack. The lack of coincidence of the acid-anion and base-cation high values in early May argues against soil contributions of NO_3^-.

The ANC and H^+ data (Figure B.3 and B.5) suggest that there are contributions from both soil water and snow melt during the period sampled; Southeast Gully (SEG) and East Joint (EJ) ANC (and Ca^{2+}) values are as high or higher than for the numbered inflows, reflecting soil and mineral weathering. As these two inflows apparently drain areas that melt more completely earlier in the season, the peaks in species concentrations may occur slightly earlier, before sampling of the two streams. On the other hand, NO_3^- for the SEG and EJ are quite low, having reached very low values early in the season. If there was a peak, it occurred before any sampling. H^+ concentrations fail to exhibit a distinct peak as the same time NO_3^- does, but do show a decline with time.

Of the other base cations (Figure B.6), Na^+ and K^+ follow the same general trend during spring and summer as does Ca^{2+}; but Mg^{2+} drops off to less than 1 μM in summer and remains low the rest of the year. Cl^- (Figure B.6) also drops during the year.

Silica data also indicate mineral weathering, as it is absent in the snowpack. Note the lack of a high spring peak relative to the ions (Figure B.5).

The lake outflow data qualitatively follow the same trends for NO_3^- and Ca^{2+} as do the inflow data (Figure B.7). The additional outflow (versus inflow) data support the existence of a spring peak associated with snowmelt. Also note the less-distinct later-season peaks in outflow (versus inflow) Ca^{2+}. The within-lake data could also be used to extend the time-series coverage.

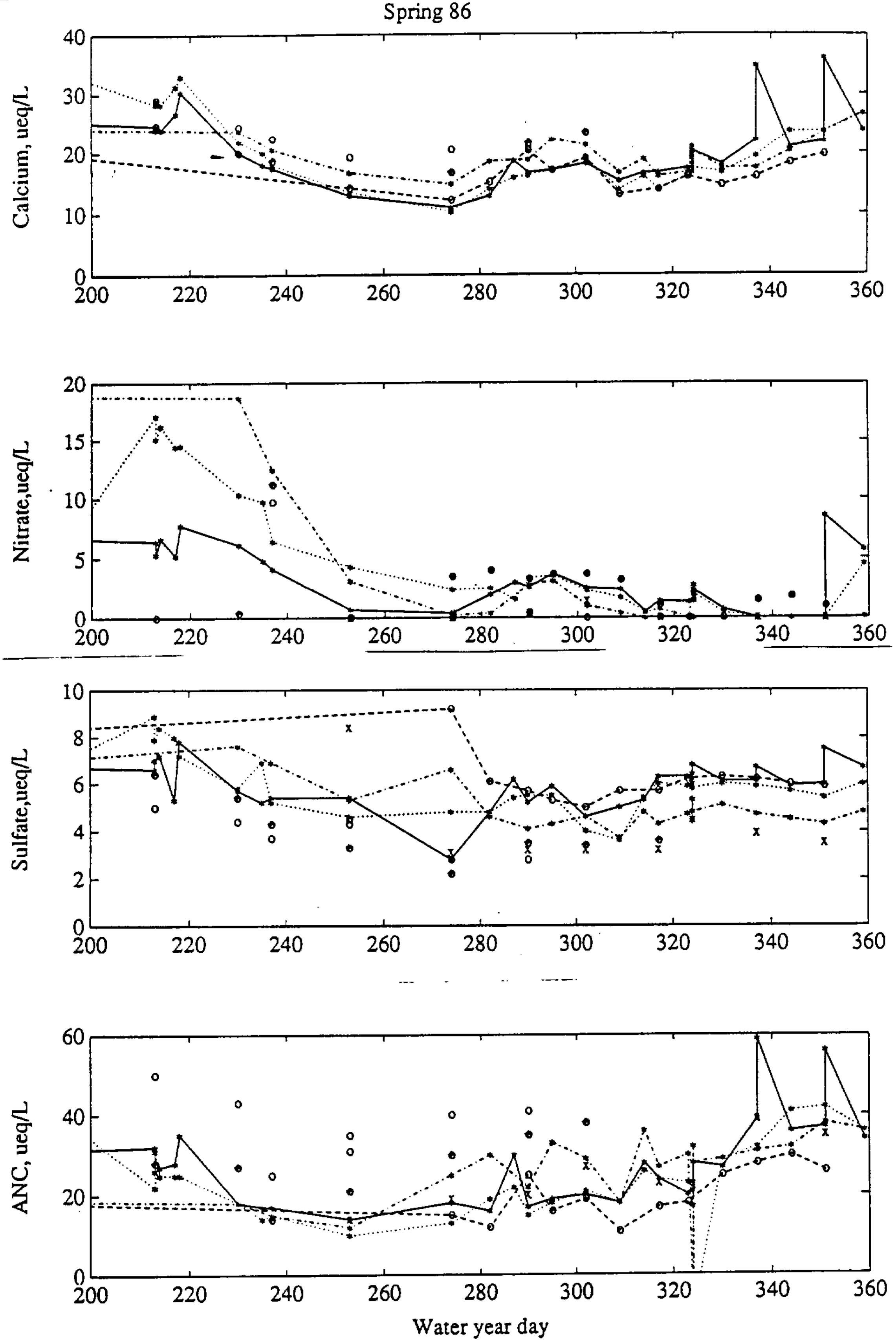

Figure B3. Comparison of Ca^{+2}, NO_3^-, SO_4^{2-} and ANC for inflows, 1986 snowmelt period.

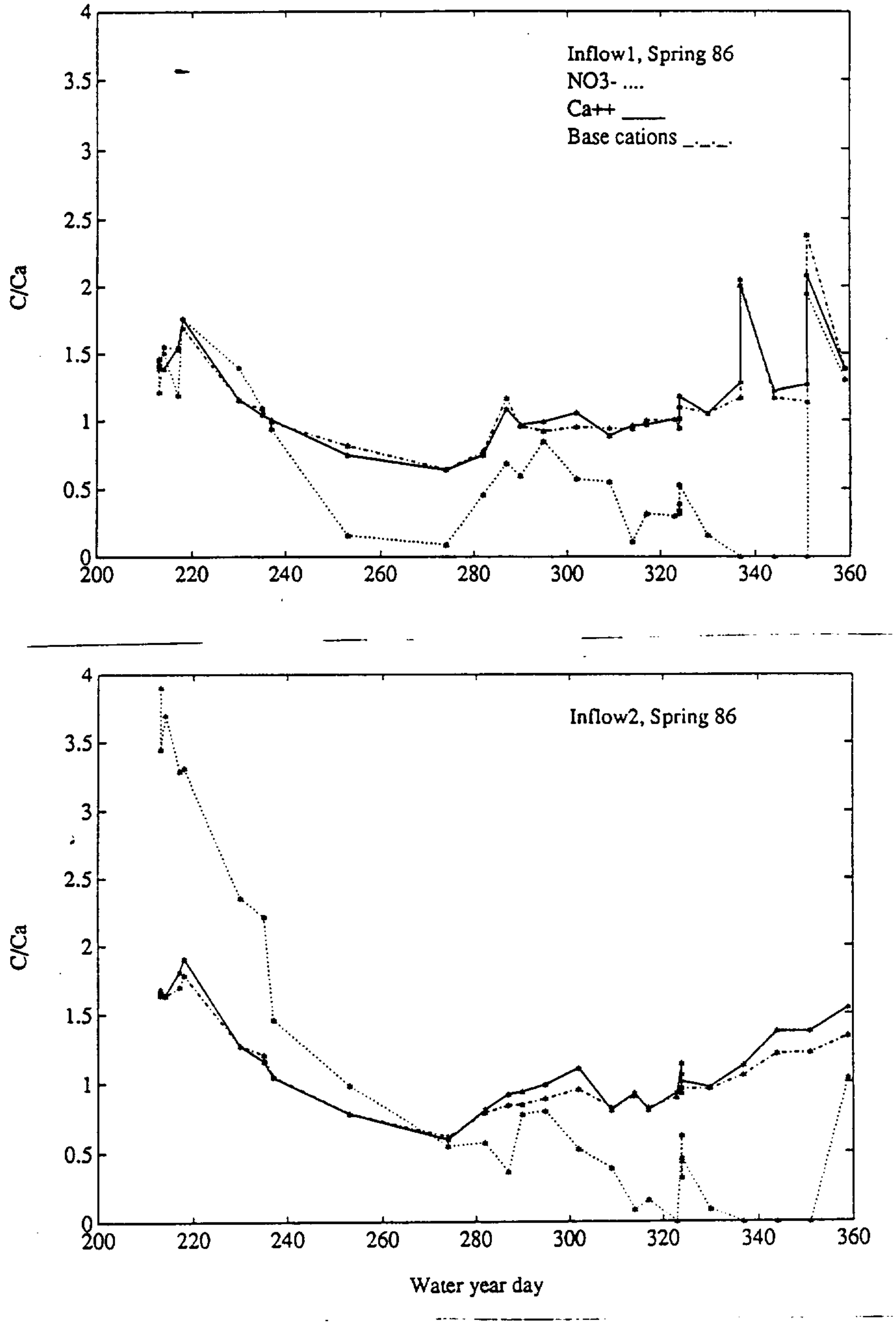

Figure B4. Normalized NO_3^-, Ca^{+2} and sum-of-base-cation concentrations for inflows 1 and 2. Inflow 2 shows a NO_3^- peak, but inflow 1 does not, possibly to different timing of melts and run-off.

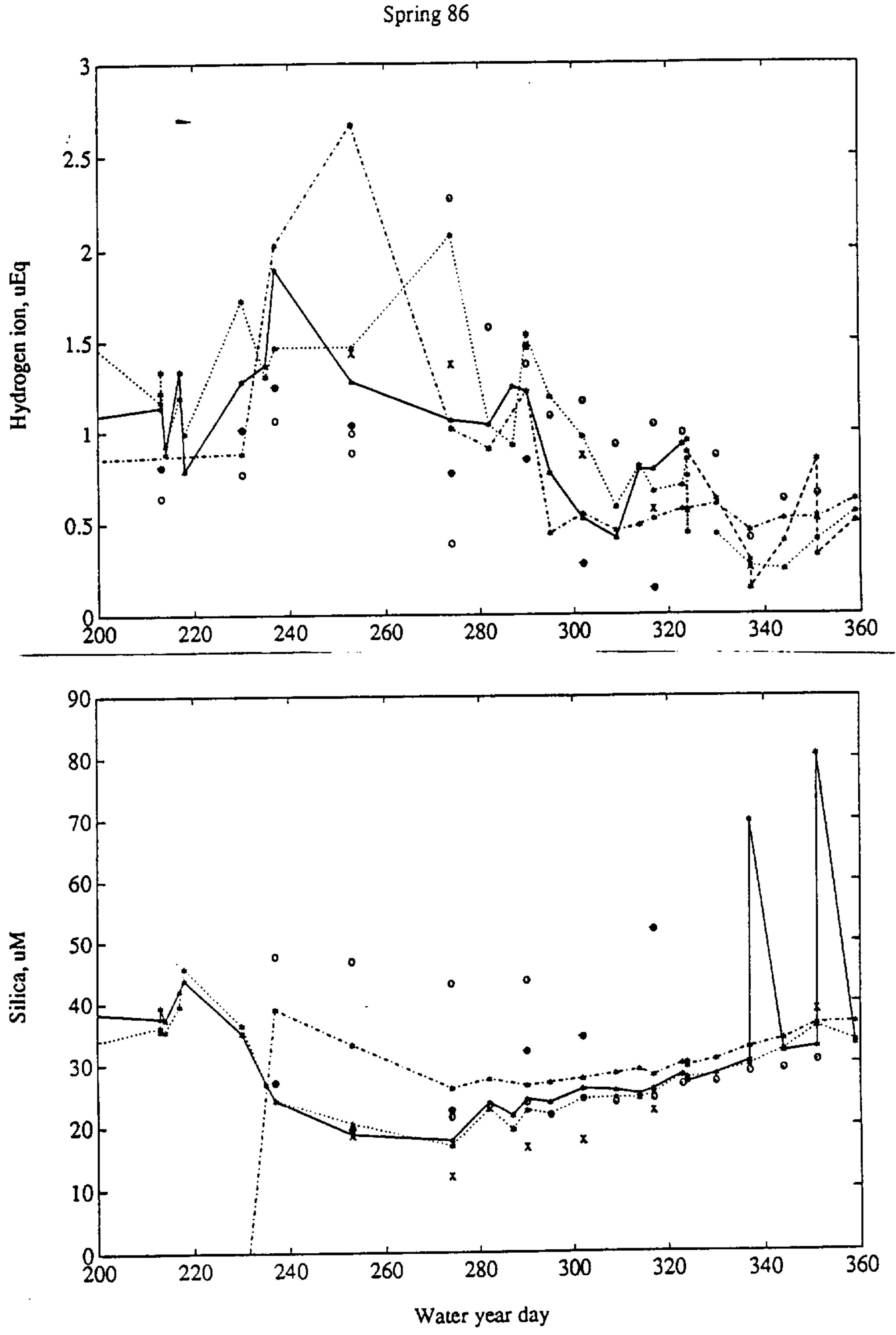
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Figure B5. H⁺ and silica in lake inflows.

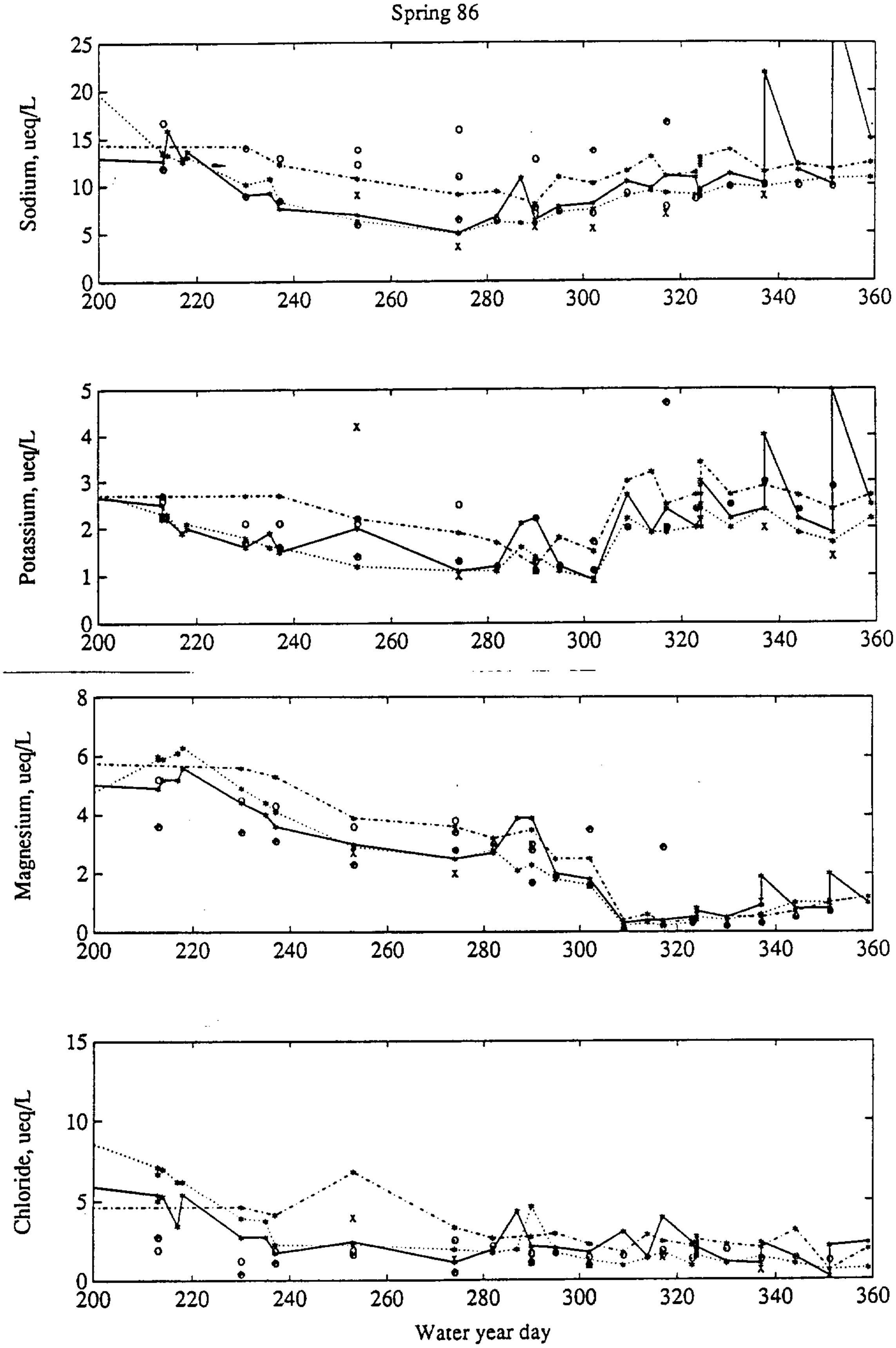


Figure B6. Na⁺ K⁺ and Mg⁺² in lake inflows.

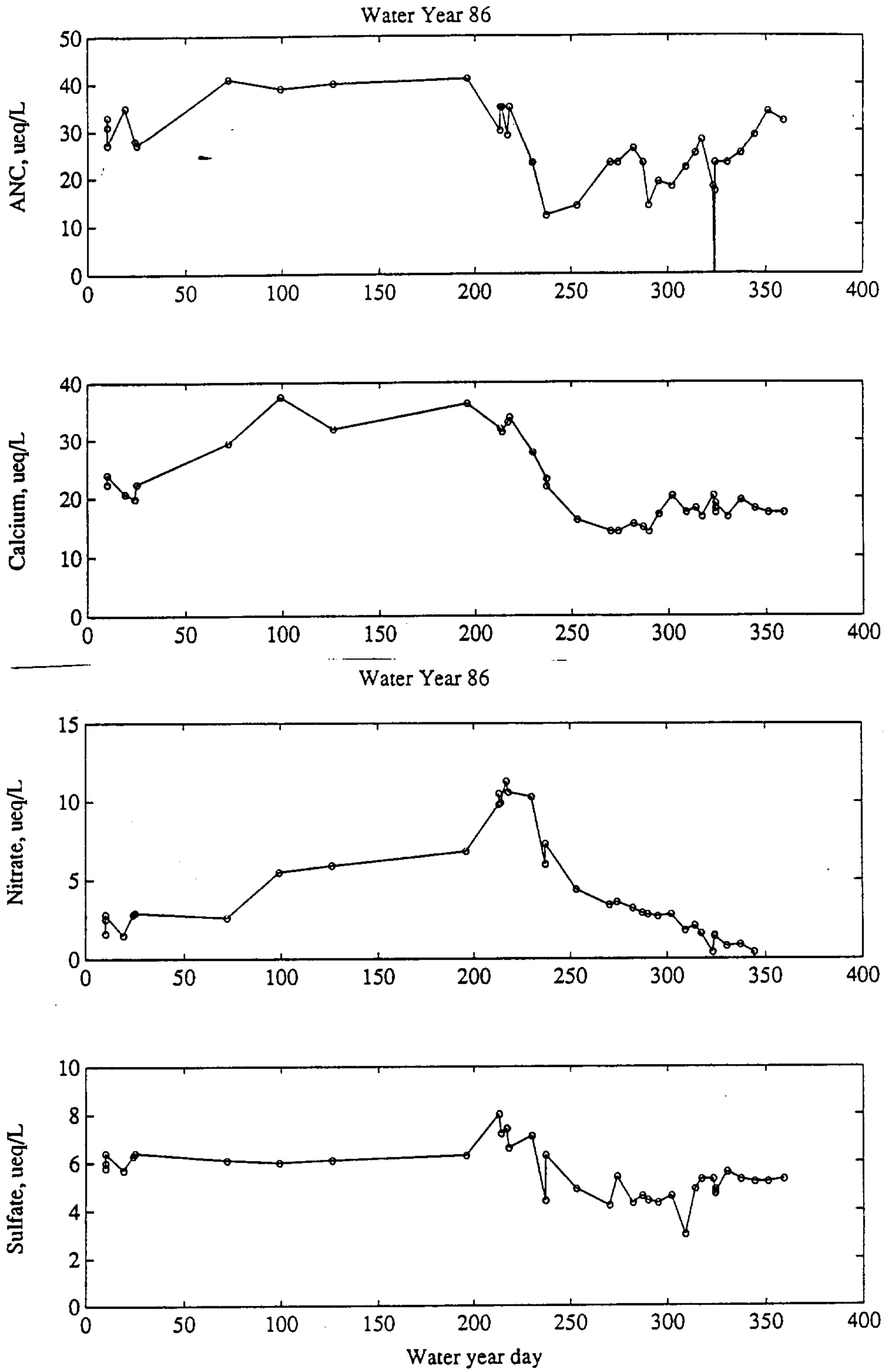


Figure B7. Ca^{+2}, NO_3^-, SO_4^{2-} and ANC data in the outflow show a qualitatively similar trend as the inflows.

B3.3. Covariance Analyses

Covariance analyses comparing the sum of base cations, silica, and ANC suggest that all three major inflows have similar mineral-weathering stoichiometry (Figure B.8). There is a good correlation between silica and sum of base cations. The two water years do not have the same slopes (Figure B.8), and the plot of all data together shows considerable scatter at the higher concentrations (Figure B.9). The silica-ANC correlation was not as good (Figure B.10), and the correlation between ANC and base cations was poor (Figure B.10), suggesting that there are processes other than mineral weathering that contribute to the alkalinity during the periods sampled. Plots for these ANC correlations for each inflow are not shown, but none had as good a covariance as did those of Figure B.8.

From Figure B.11, one can see that NO_3^- greatly exceeded SO_4^{2-}, with essentially no correlation between the two. SO_4^{2-} varies little between samples, whereas the NO_3^- changes may reflect an active nitrogen cycle in the watershed. This may also play a major role in the lack of balance for the ANC correlations in Figure B.10. Adding in Cl^- illustrates that NO_3^- is a good indicator of $Cl^- + NO_3^- + SO_4^{2-}$ (Figure B.11). The non-zero intercept is due to the sulfate. Figure B.12 illustrates that Ca^{2+} is a good indicator of the sum of base cations. It is not, however that will correlate with Mg^{2+}. The data that appear to fall along a lower line in the Ca vs. Mg plot were from the end of WY 1980, and should be checked; they may be 10-fold low.

B3.4. Linear Regressions

Regressions were done on the entire data set, on the two individual water years (1984-85 and 1985-86), and on seasonal data. The best fit estimate for alkalinity for all WY data lumped together gave the coefficients:

	const	Ca^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	se
All inflows, 1984-86								
param	0.7	1.4	0.6	0.6	-1.1	-1.0	-0.8	4.4
error	1.7	0.1	0.1	0.4	0.2	0.1	0.3	
Inflow 1, 1984-86								
parm	-4.6	1.8	0.3	0.2	-1.3	-0.9	-0.5	4.6
error	4.0	0.2	0.2	0.7	0.2	0.3	0.8	
Inflow 2, 1984-86								
parm	-4.0	1.0	0.7	1.5	-1.1	-1.1	0.9	3.7
error	3.8	0.2	0.3	0.6	0.3	0.2	0.8	
Inflow 4, 1984-86								
parm	-2.1	1.3	0.8	0.5	-2.0	-0.9	0.1	4.1
error	7.0	0.2	0.5	1.2	0.6	0.1	1.0	

Data for all inflows together and for inflow 1 (Figure B.12) illustrate that the regressions give a good fit to the data. Including Mg^{2+} provides no better fit as $[Ca^{2+}]$ and $[Mg^{2+}]$ are highly correlated, as are Ca^{2+} and the sum of base cations (see above):

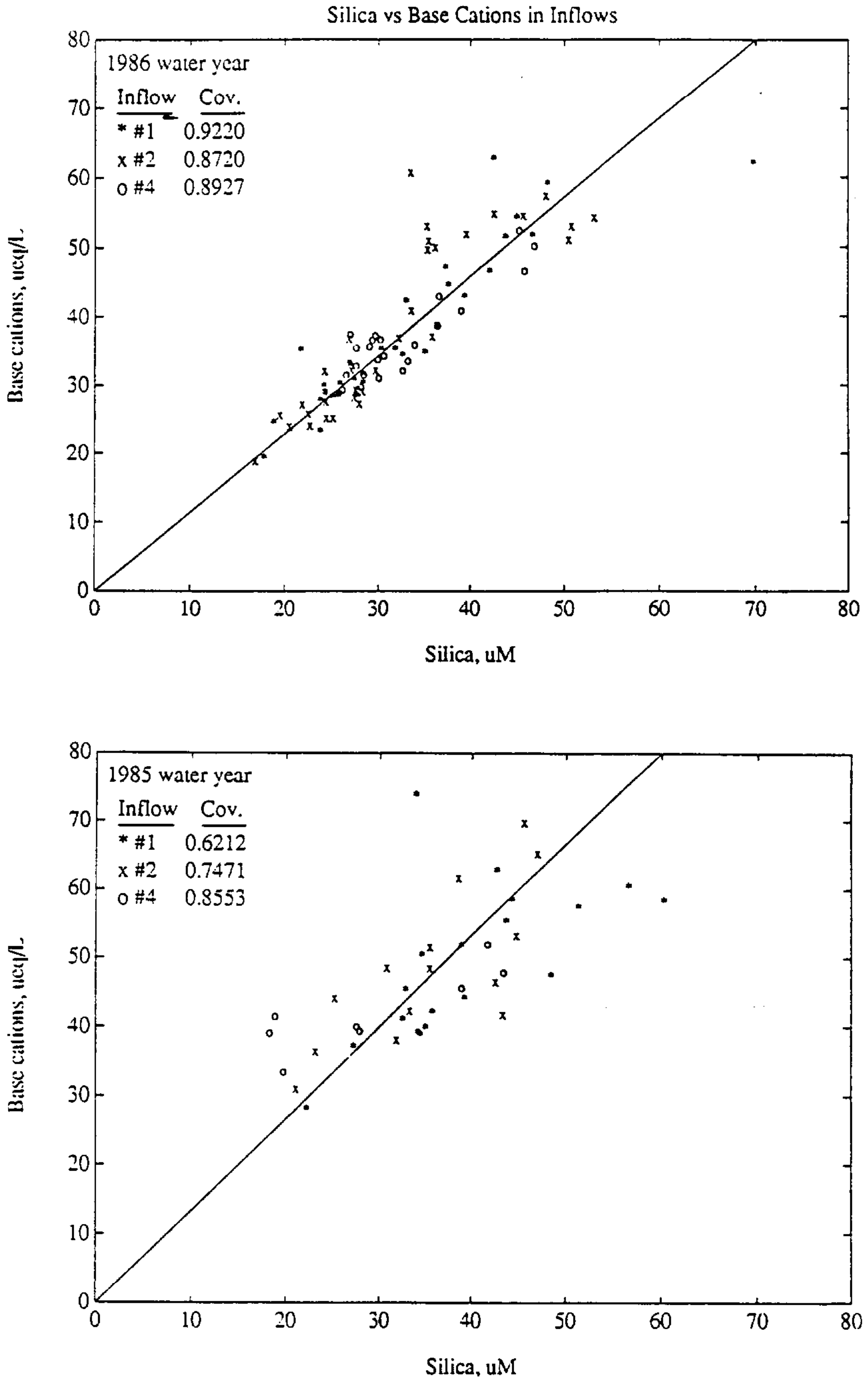


Figure B8. There is a good correlation between silica and base cations on the three main inflows.

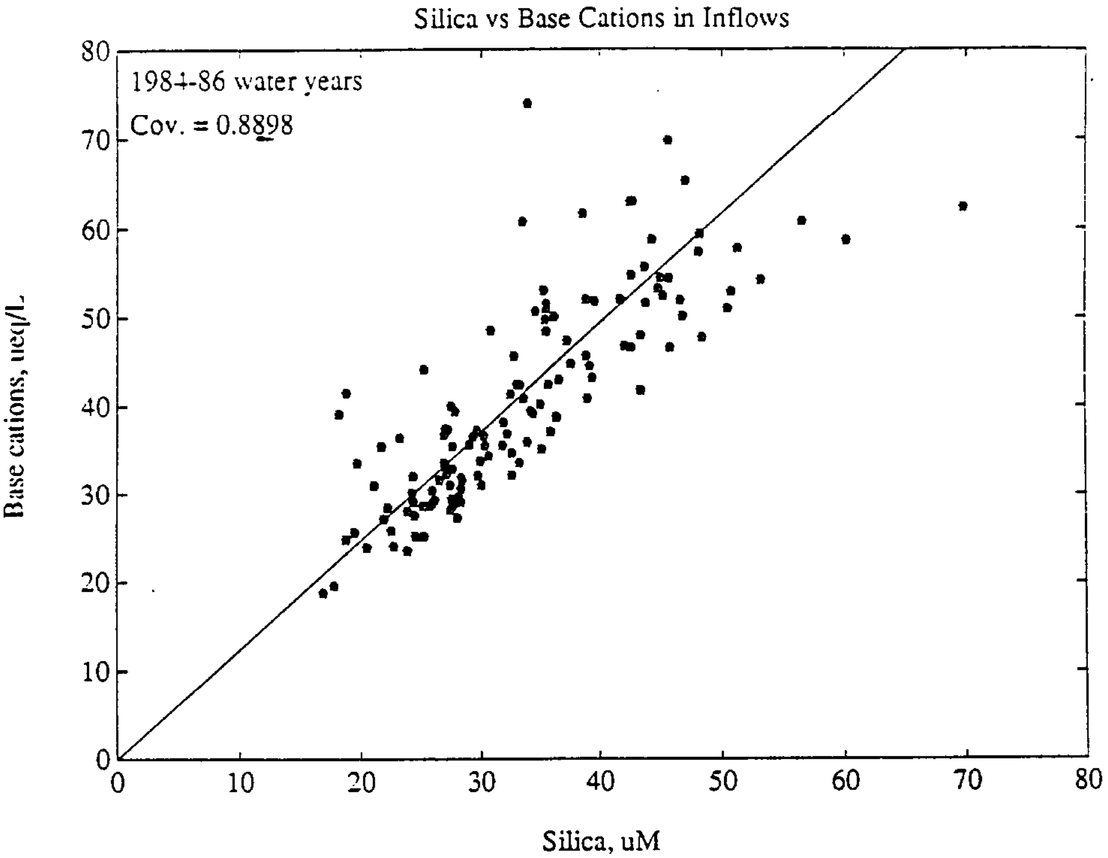
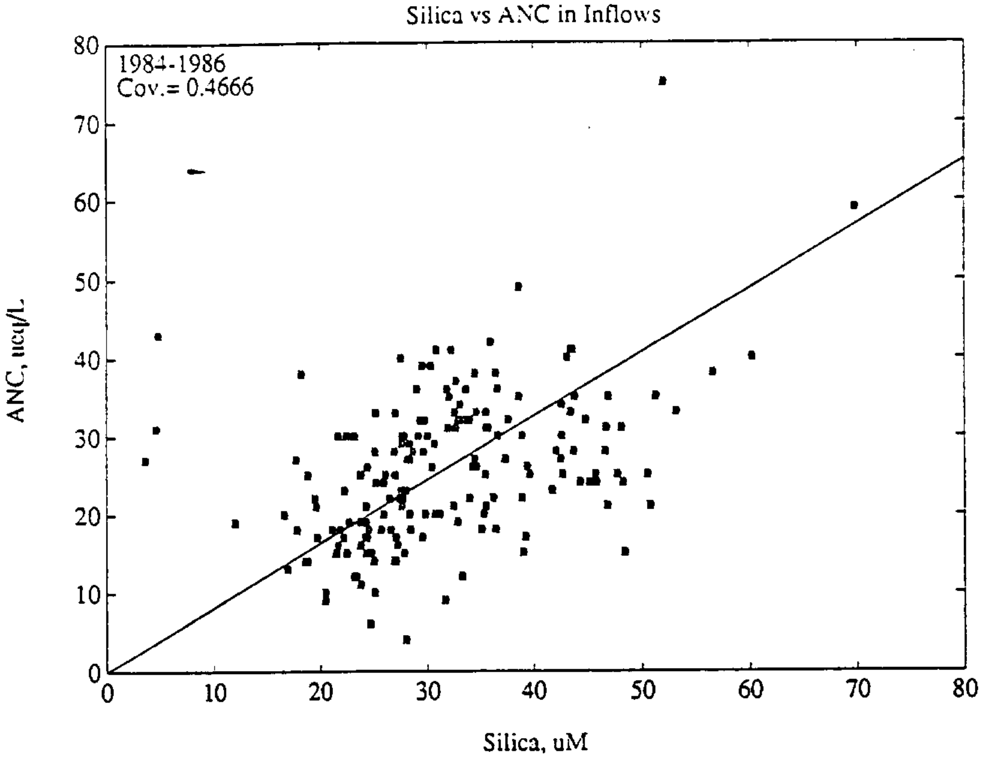


Figure B9. Plotting two water years together for inflows 1, 2, and 4 shows more scatter at higher concentrations.


Silica vs ANC in Inflows

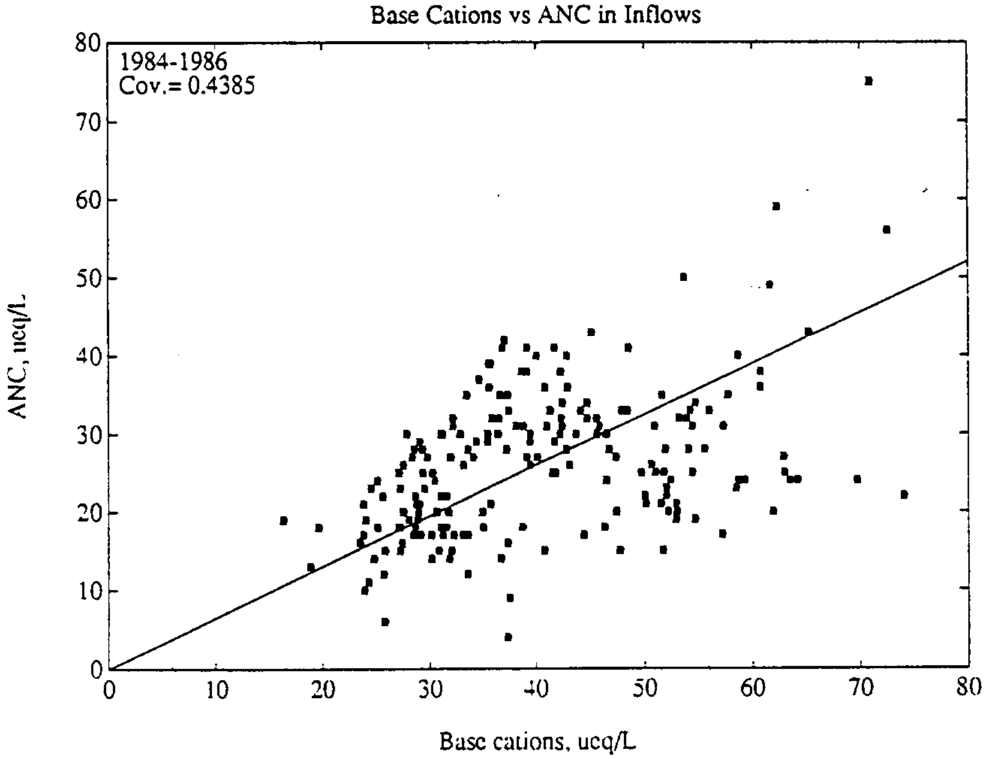
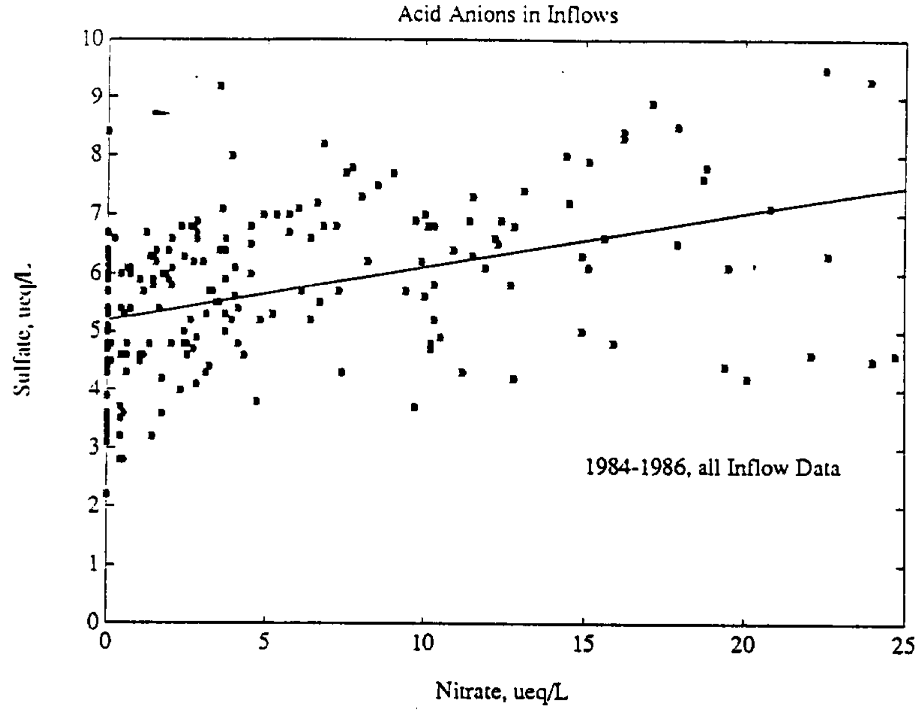

Base Cations vs ANC in Inflows

Figure B10. Correlations between silica and ANC were poor, as were those between base cations and ANC.



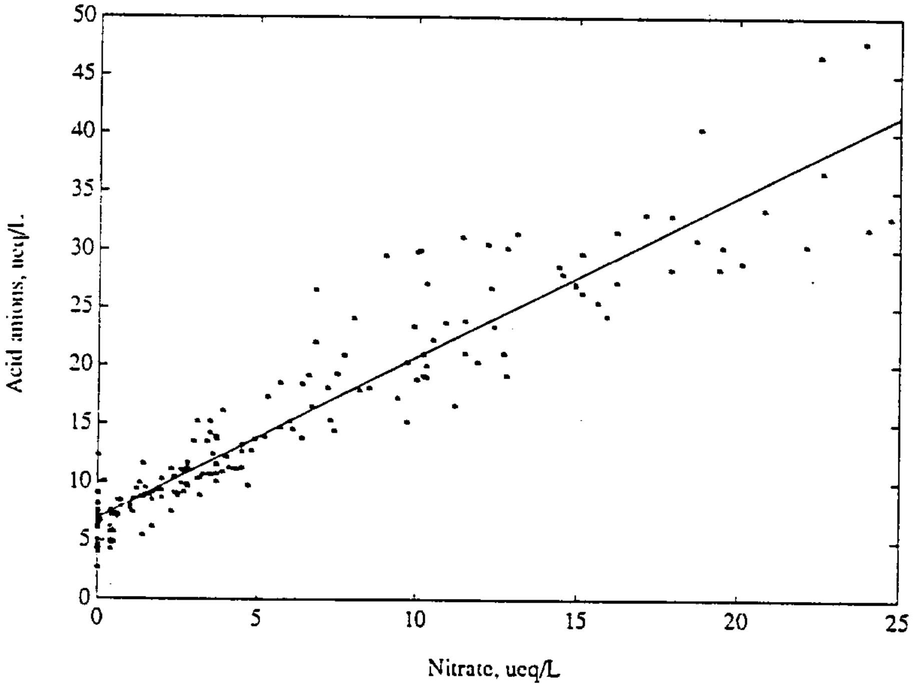
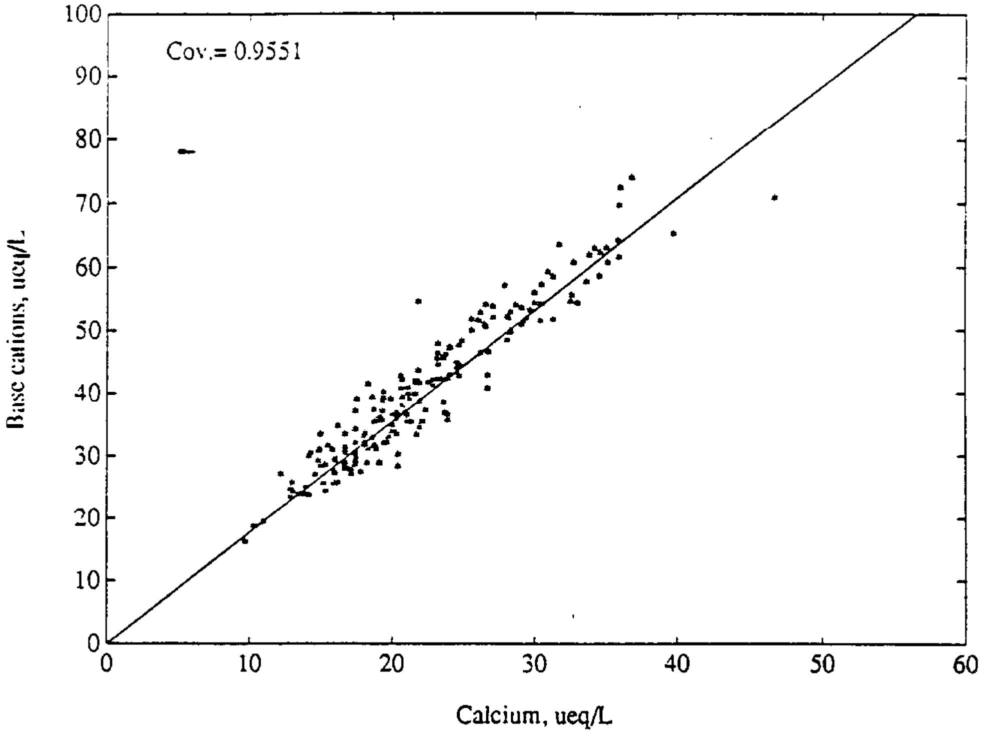


Figure B11. SO_4^{2-} was relatively constant between samples, whereas NO_3^- varied widely. Cl^- and NO_3^- are well correlated at low concentrations.



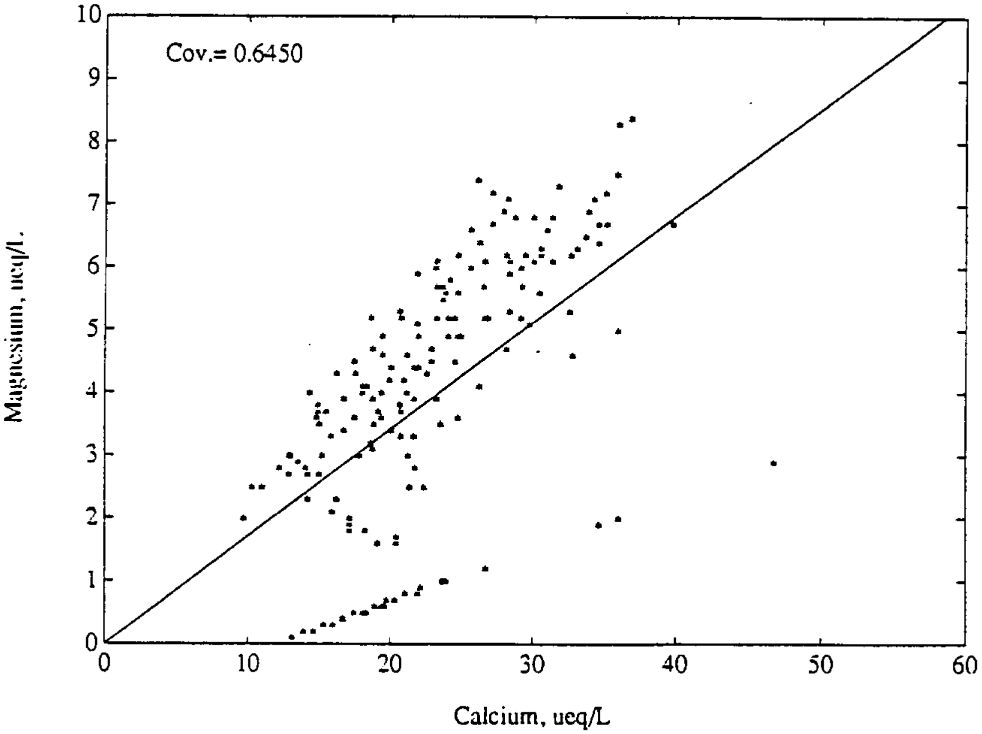


Figure B12. Ca^{-2} dominates base cations, and is a good indicator of the sum. Ca^{-2} and Mg^{-2} are not well correlated, however.

	const	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	se
All inflows, 1984-86									
param	1.2	1.4	-0.5	0.7	0.4	-0.9	-0.9	-0.9	4.4
error	1.7	0.1	0.2	0.1	0.4	0.2	0.1	0.3	
Inflow 1, 1984-84									
parm	-3.9	1.8	-1.3	0.3	-0.6	-1.0	-0.5	-0.2	4.4
error	3.8	0.2	0.5	0.2	0.7	0.2	0.3	0.8	
Inflow 2, 1984-86									
parm	-4.6	1.1	-0.5	0.7	1.3	-1.0	-1.1	0.9	3.6
error	3.8	0.2	0.5	0.3	0.7	0.2	0.3	0.8	
Inflow 4, 1984-86									
parm	2.2	0.9	0.8	1.2	-2.1	-1.0	-0.2	4.6	
error	7.6	0.2	0.5	1.4	0.7	0.2	1.0		

Summing Ca^{2+} and Mg^{2+} gives a similar fit:

	const	Ca^{2+} & Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	se
All inflows, 1984-86								
parm	1.2	1.1	0.7	1.1	-1.3	-1.2	-0.7	4.9
error	2.0	0.1	0.2	0.4	0.2	0.1	0.3	
Inflow 1, 1984-86								
parm	-3.7	1.4	0.5	1.0	-1.3	-1.5	-0.5	5.5
error	4.8	0.2	0.3	0.8	0.3	0.3	1.0	
Inflow 2, 1984-86								
parm	-2.8	0.9	0.7	1.8	-1.2	-1.2	0.9	4.0
error	4.0	0.2	0.3	0.7	0.3	0.2	0.8	
Inflow 4, 1984-86								
parm	2.2	0.9	0.8	1.2	-2.1	-1.0	-0.2	4.6
error	7.6	0.2	0.5	1.4	0.7	0.2	1.0	

Two different two-parameter models provides a reasonable estimate:

	const	Ca^{2+}	NO_3^-	se
All inflows, 1984-84				
parm	0.2	1.5	-1.3	5.2
error	1.5	0.1	0.1	
Inflow 1, 1984-86				
parm	-6.1	1.8	-1.7	5.1
error	2.7	0.1	0.2	
Inflow 2, 1984-86				
parm	2.5	1.4	-1.3	4.4
error	2.4	0.1	0.1	
Inflow 4, 1984-86				
parm	1.6	1.5	-1.0	4.8
error	4.5	0.2	0.1	

	const	base cations	acid anions	se
All inflows, 1984-86				
parm	3.3	1.0	-1.1	5.0
error	1.4	0.0	0.1	
Inflow 1, 1984-86				
parm	1.3	1.0	-1.2	5.7
error	2.7	0.1	0.2	
Inflow 2, 1984-86				
parm	5.7	0.9	-1.0	4.2
error	2.2	0.1	0.1	
Inflow 4, 1984-86				
parm	5.1	0.9	-1.1	4.7
error	4.6	0.1	0.1	

As Figures B.14 and B.15 illustrate, there is little difference between the two-parameter and multi-parameter models.

These equations can be viewed essentially as definitions of alkalinity for the watershed. The good fits indicate consistency of the data sets. Errors were randomly distributed, as illustrated in the figures.

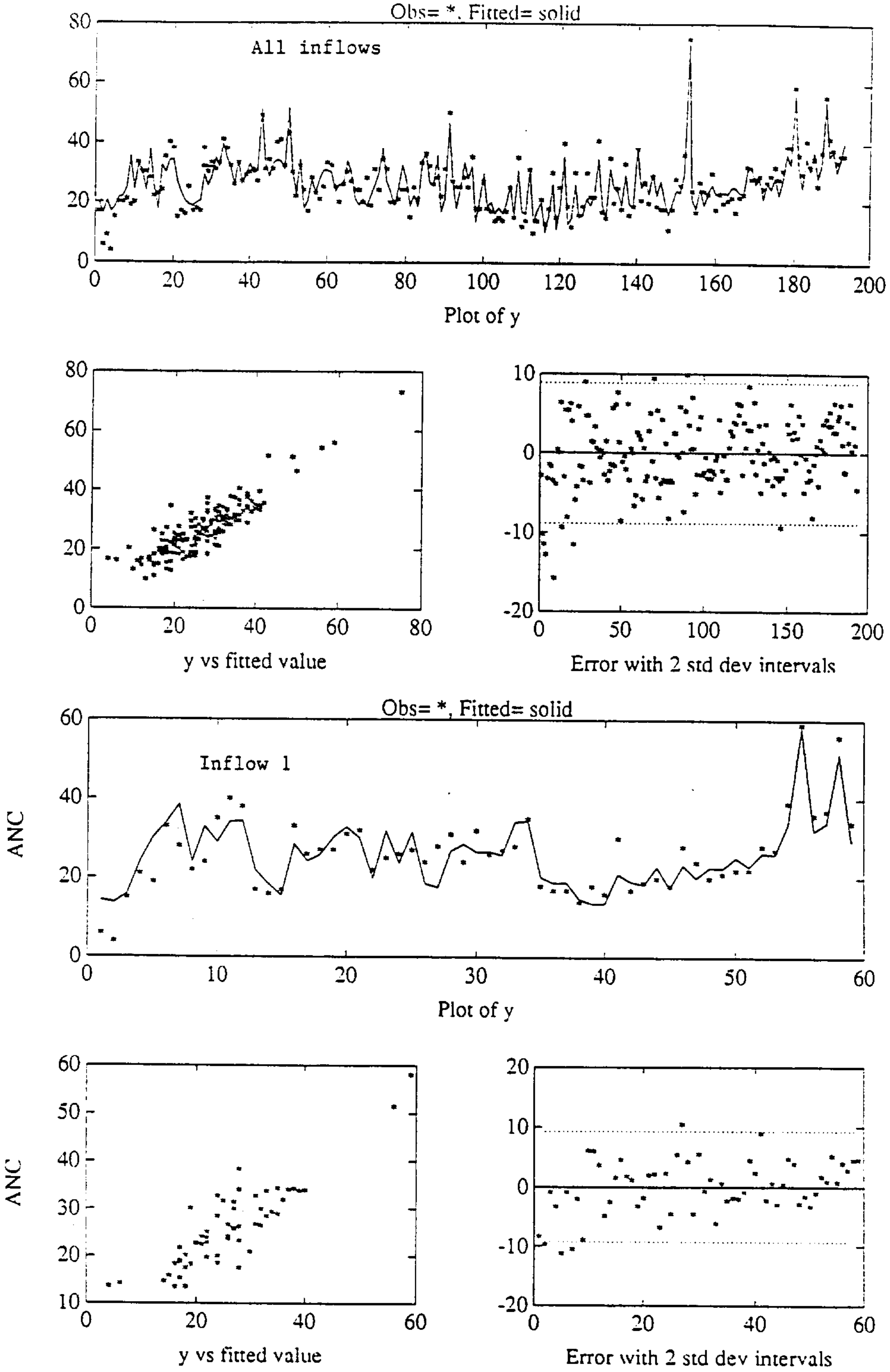


Figure B13. Linear regression fit for all inflow data together, and inflow 1 alone, water years 1984-86.

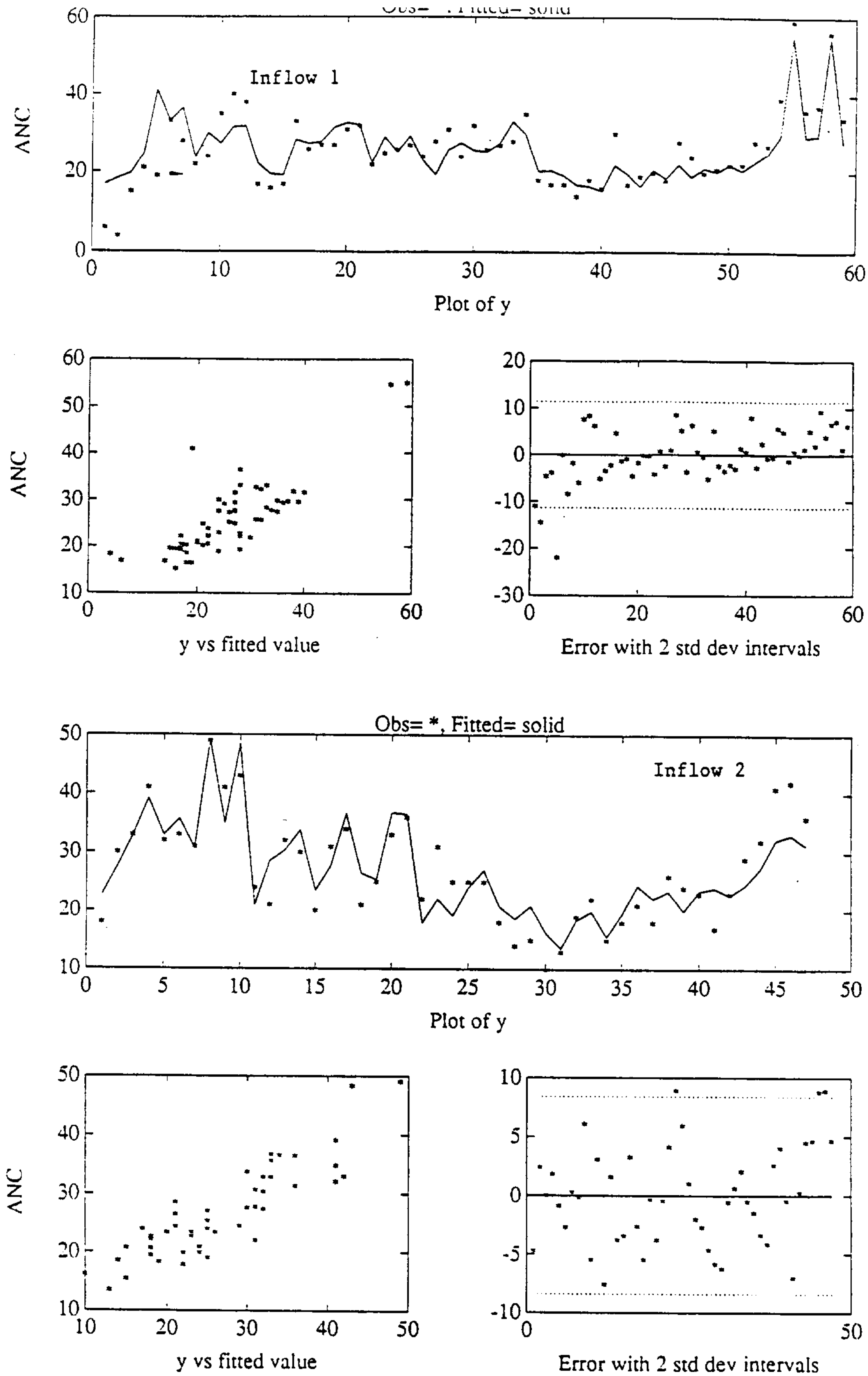


Figure B14. Linear regression fit for inflows 1 and 2, and water years 1984-86. Independent variables are Ca^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, and SO_4^{2-}; all concentrations in μeqL^{-1}.

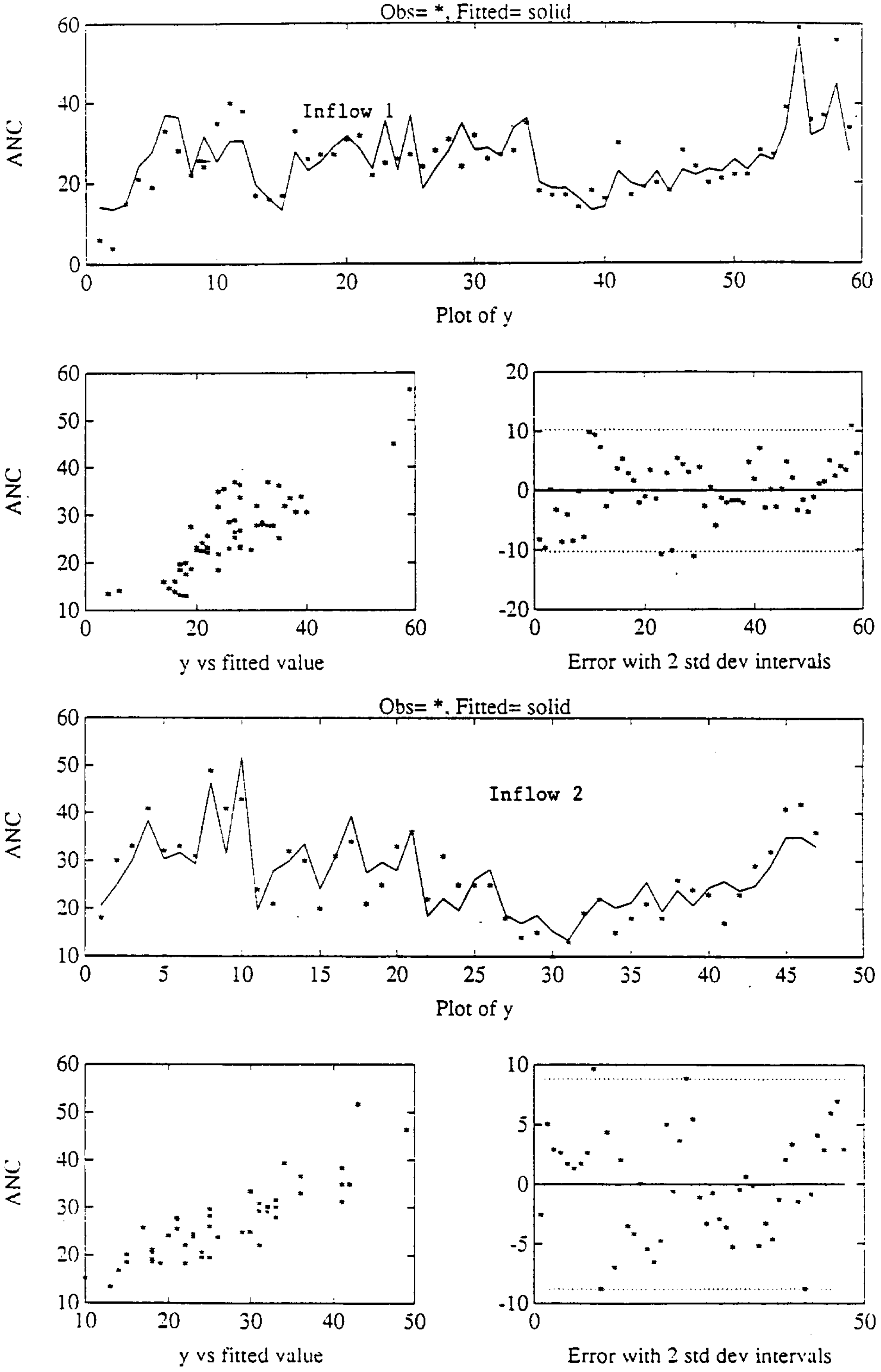


Figure B15. Linear regression fit for inflows 1 and 2, water years 1984-86. Independent variables are $Ca^{-2} + Mg^{-2} + Na^{-}, +K^{+}$ and $Cl^{-} + NO_3^{-} + SO_4^{2-}$, i.e., base cations and acid anions.

The within-lake and outflow data do not fit these models as well, having higher standard errors; in addition, coefficients differ quite a bit from the inflow values. For example:

	const	Ca^{2+}	NO_3^-	se
Lake site 4, 1984-84				
parm	-2.3	1.6	-1.1	7.9
error				
Outflow , 1984-86				
parm	4.2	1.3	-1.4	5.5
error				

B3.5. Watershed Reactions

Combining weathering reactions (1) - (7) in the proportions needed to give lake inflow concentrations results in assigning stoichiometric coefficients to each, from which "net" weathering and ANC-generation reactions can be written. For example, Figure B.16 gives the fraction of ANC produced by each of the four weathering reactions for each of the 38 data points. Note than ammonia uptake and oxidation consumes 20 percent of the ANC produced by mineral weathering. There appears to be a seasonal difference in the importance of the nitrogen reactions, particularly in inflow 1; there is also an apparent difference between the importance between inflows 1 and 2. With regard to modeling, this suggests using disaggregated modeling of the nitrogen reactions (i.e., to each soil and vegetation type, and spatially). Similarly, Figure B.17 gives the fraction of silica produced by each reaction. Note that half of the silica is assigned to the kaolinite --> gibbsite reaction, rather than weathering of primary minerals.

These analyses give stoichiometric coefficients for each weathering reaction of:

1.	biotite --> vermiculite	0.25
2.	vermiculite --> kaolinite	0.18
3.	plagioclase --> kaolinite	1.10
4.	anorthite --> kaolinite	4.90
5.	kaolinite --> gibbsite	15.35

The weighted sum gives an overall whole-watershed weathering reaction:

Composite rock -->
$1.5\ K^+ + 1.8\ Mg^{2+} + 1.8\ Fe^{3+} + 6.7\ Na^+ + 7.0\ Ca^{2+} + 46.6\ SiO_2 - 29.4\ H^+$

The small differences seasonally and between inflows suggest that this composite function can be used for all three inflows; it will thus be applied watershed wide for modeling. The proportion of each base cation from the composite weathering is also relatively constant across all samples (Figure B.18).

Contributions from individual reactions for inflow 1 (21 samples) are noted in Table B.4. The average error as a percent of calculated ANC ranged from -4.4 percent on inflow 2 to -16.6 on inflow 1. These data suggest that for inflow 1, weathering of plagioclase contributes about 50 percent more than biotite, with anorthite being slightly more than biotite. For inflow 2, the three reactions are of about equal importance. For inflows 1, 2 and 4, 21, 13 and 3, stream observations were included in the analysis, respectively.

Table B.4. Contribution of individual reactions to alkalinity generation

	Inflow 1			Inflow 2			Overall
Reaction	Range	Ave	Error	Range	Ave	Error	Ave
1. Biotite → vermiculite	0.08 - 0.31	0.14	0.05	0.10 - 0.23	0.13	0.03	0.14
2. Vermiculite → kaolinite	0.00 - 0.30	0.19	0.08	0.21 - 0.42	0.31	0.08	0.24
3. Plagioclase → kaolinite	0.27 - 0.71	0.47	0.11	0.36 - 0.60	0.47	0.07	0.47
4. Anorthite → kaolinite	0.21 - 0.63	0.38	0.11	0.26 - 0.68	0.51	0.13	0.42
5. Kaolinite → gibbsite							
6. NH_4^+ → organic N	-0.09 - -0.02	0.04	0.02	-0.07 - -0.01	-0.05	0.02	-0.04
7. Organic N → NO_3^-	-0.68 - 0.03	-0.13	0.17	-0.68 - -0.16	-0.38	0.17	-0.23
Error	-1.53 - 0.17	-0.23	0.37	-1.26 - 0.16	-0.22	0.37	-0.22

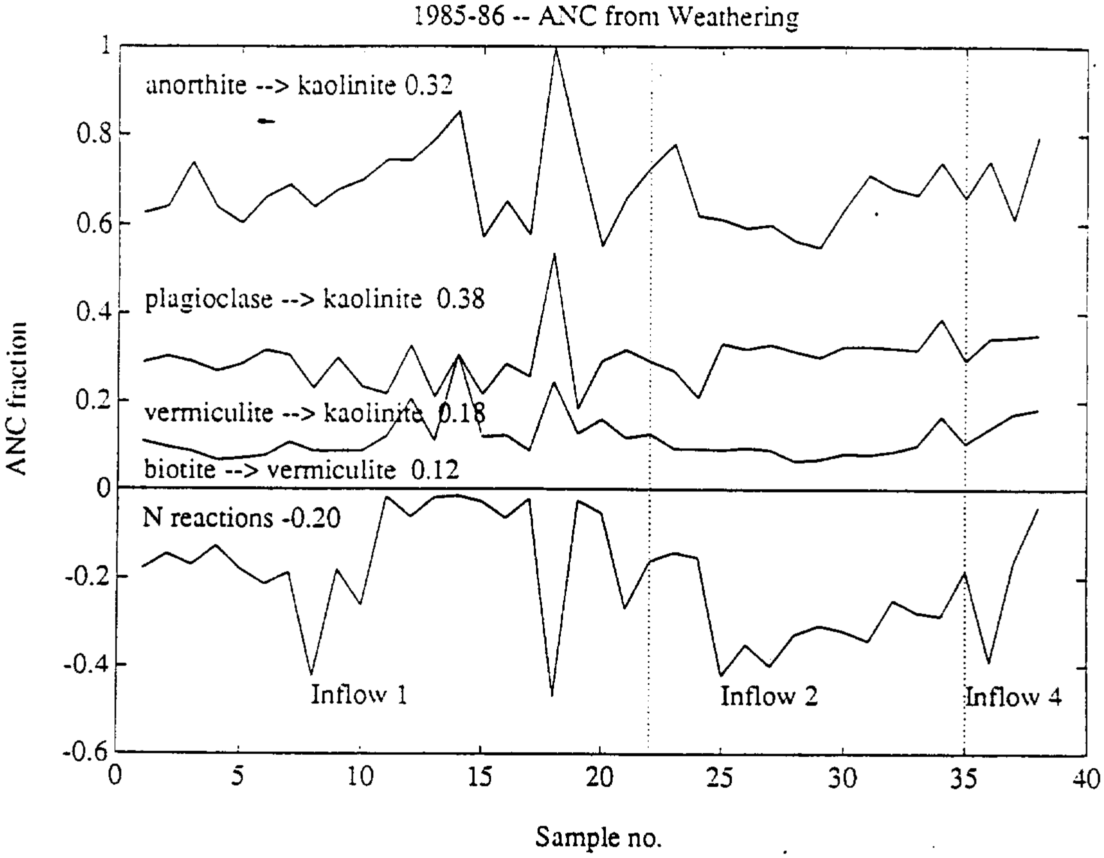


Figure B16. Fraction of ANC produced by each mineral-weathering reaction and consumed by NH_4^+ uptake and oxidation. Independent variables are Ca^{+2} and NO_3^-.

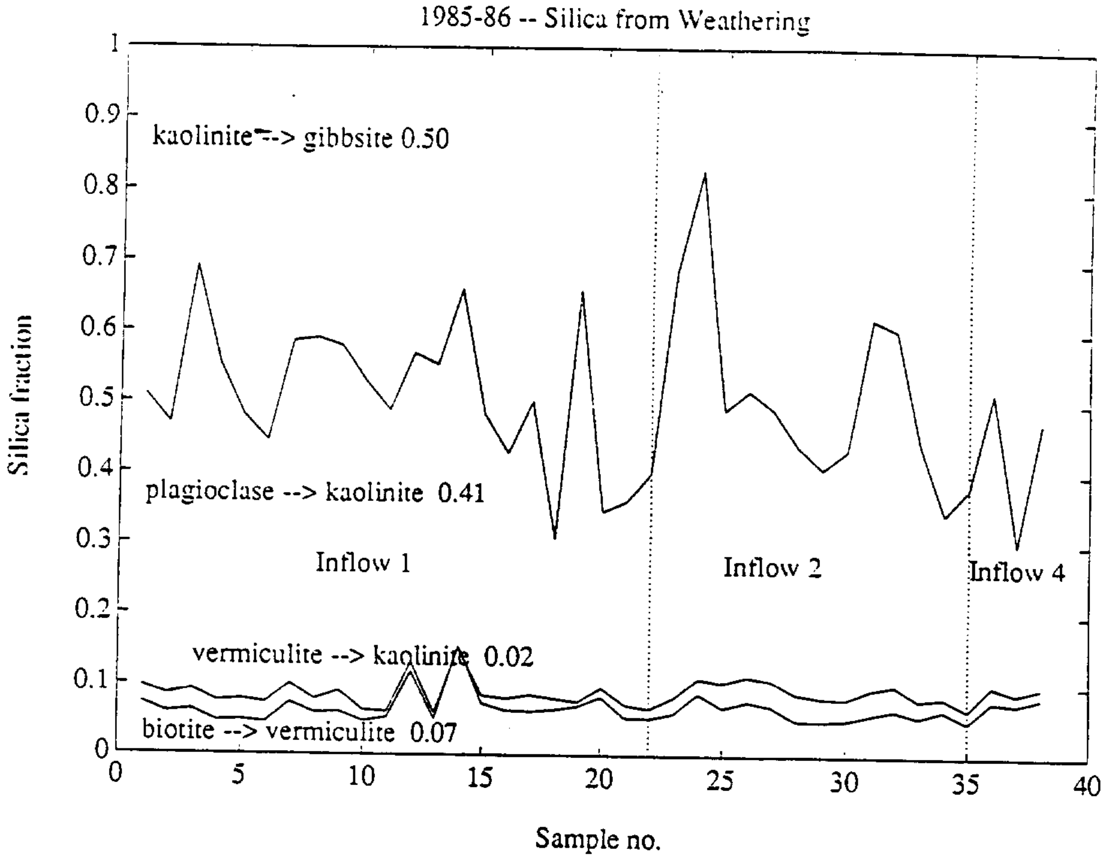


Figure B17. Fraction of silica contributed by each mineral-weathering reaction.

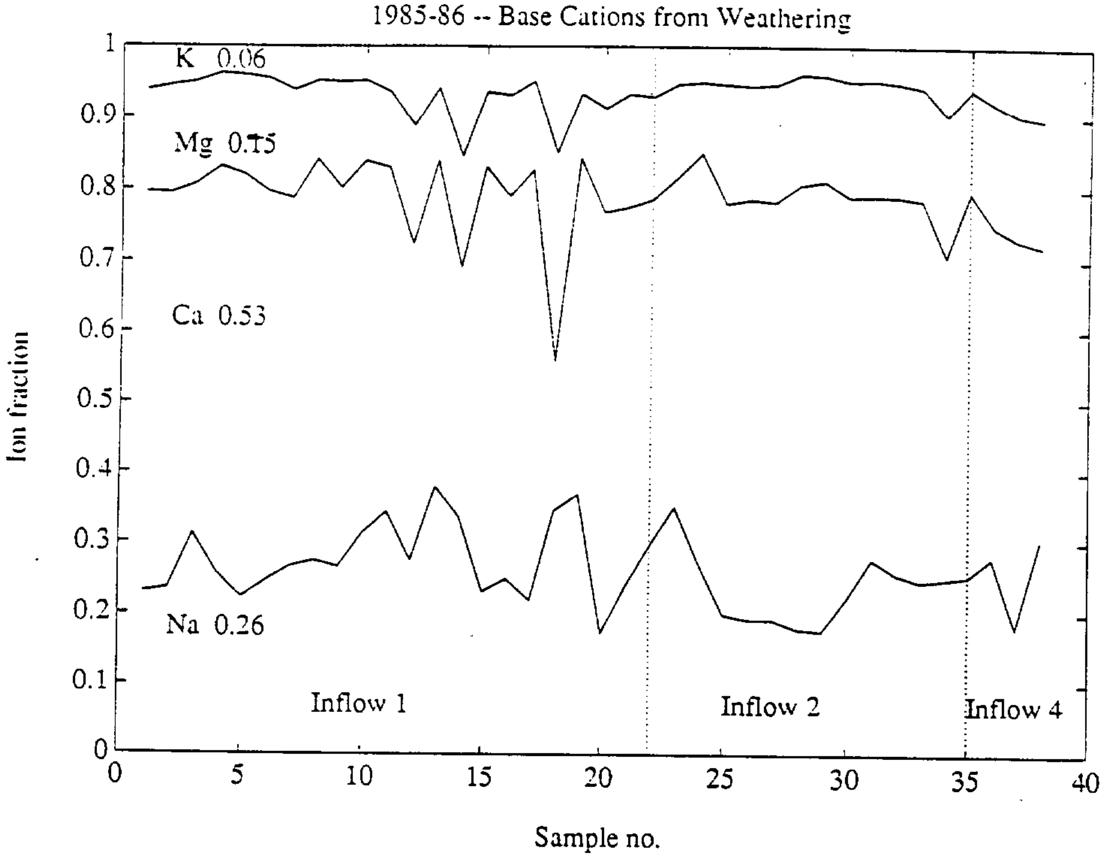


Figure B18. Fraction that each base cation contributes to the sum of base cations from mineral weathering.

The resulting ratio of silica to base cations from weathering, shown in Figure B.19, is about 0.83. The positive intercept on the silica axis suggests that some silica is produced even without base-cation production, i.e., without weathering of primary minerals. While this was attributed to the kaolinite --> gibbsite reaction in the above analysis, it could also be due to dissolution of SiO_2. Given the limited evidence for gibbsite accumulation in the watershed, this is probably the case.

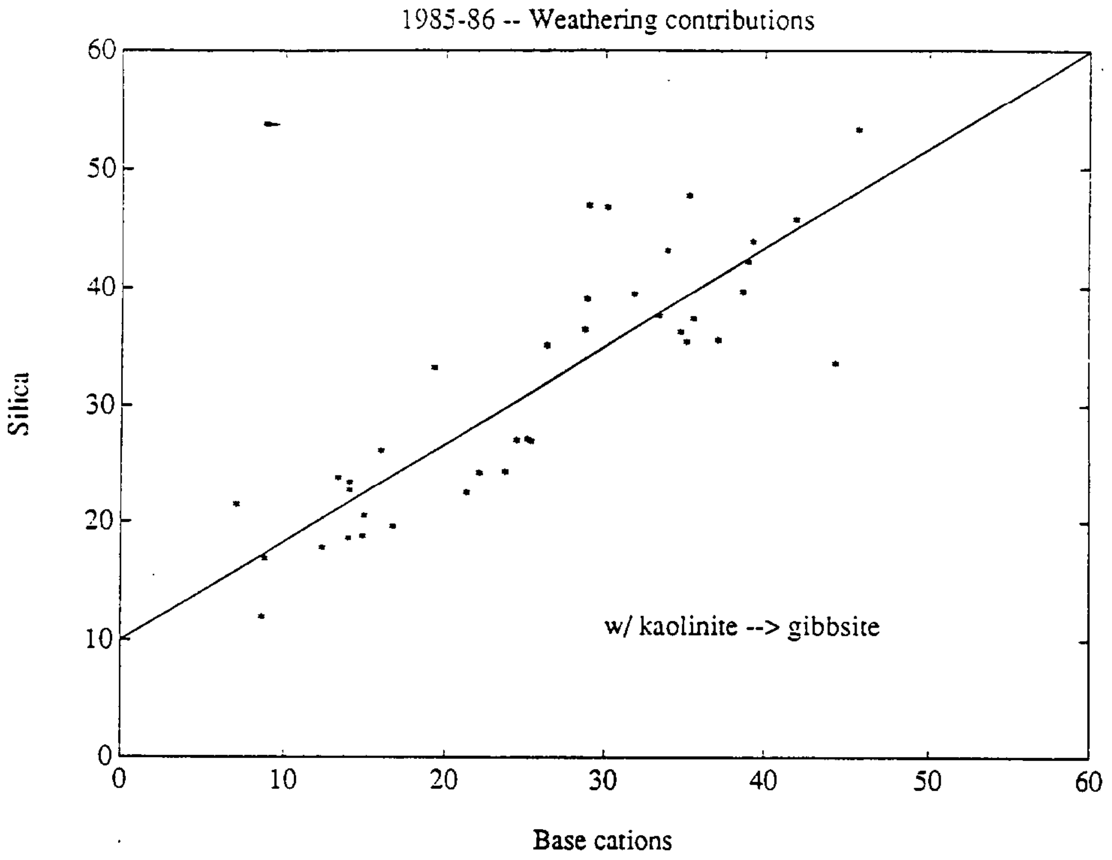


Figure B19. Relation between silica and base cations for weathering reactions.

APPENDIX C

DESCRIPTIONS OF INDIVIDUAL SUBROUTINES

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APPENDIX C

DESCRIPTIONS OF INDIVIDUAL SUBROUTINES

This section consists of descriptions of the various subroutines within the program. Each subsection opens with a description of the general computations done by the subroutine, followed by a detailed, virtually step-by-step description of subroutine operation. The latter is probably of interest only to technically-inclined readers, while the opening paragraphs may be considered a detailed summary.

C.1 Hydrologic Data Input (Subroutine READDAT)

READDAT reads most of the data necessary for a given run of the program. To do so, it calls several other subroutines that also read input data, including:

(1) READORD (called by SUBUSEQ, which is called by READDAT), which reads subunit computational sequencing information
(2) READCHEM, which reads chemical initial condition, kinetics, stochiometry, and thermodynamic data
(3) READKIN, which reads chemical kinetic inputs (called from READCHEM)
(4) RAINCHEM, which reads concentration of chemical components in rainfall and snowfall

Chemical input routines are described separately.

Hydrological data read by READDAT includes:

(1) physical constants and initial conditions of the various forms of water storage on each subunit
(2) rainfall and snowfall
(3) parameters to adjust rainfall and snowfall as required for each subunit
(4) snowmelt, SCA, and potential sublimation on each subunit
(5) potential evapotranspiration on each subunit
(6) a matrix showing the subunit(s) that receive flow from each subunit

READDAT prompts the user for responses relating to the period of time to be covered by a given program run, the type of output required (including choice of output units), and the name of a file of "file names" that directs the program to necessary input data files. These input files include hydrologic and climatic parameters and daily input data. Hydrologic parameters required include:

(1) elevation of the site where climatic data are recorded
(2) snowpack free-water holding capacity (a constant)
(3) month and day when streams freeze
(4) month and day when streams thaw

(5) subunit number (consecutive)

(6) number of soil layers

(7) subunit type (n = normal soil covered, s = stream, r = rock)

(8) subunit name (optional)

(9) subunit area (ha)

(10) subunit elevation

(11) subunit maximum infiltration rate (cm/day)

(12) stream subunit number of that stream subunit (if any) that is used as this subunit's riparian recharge source

(13) parameters used to adjust rainfall and snowfall for the subunit to a different value than that observed at the climatic station (can be set for no change)

(14) initial conditions for snowpack water equivalent, free water content, and snow-covered area

(15) interception capacity for rainfall in the canopy, snowfall in the canopy and rainfall on the litter or rock surface

(16) initial conditions for the above interception storages

(17) for each soil layer:
 (a) a parameter used to reduce ET below that which would occur under identical conditions from the surface soil layer
 (b) soil depth (cm)
 (c) a parameter used to calculate unsaturated hydraulic conductivity
 (d) soil water content below which unsaturated hydraulic conductivity is zero (cm/cm)
 (e) saturated soil water content (cm/cm)
 (f) soil water content below which ET is zero (cm/cm)
 (g) initial soil water content (cm/cm)
 (h) specific surface (obtained in chemical initial condition file)

(18) a matrix showing the subunits to which surface runoff and horizontal drainage from each subunit is delivered

The parameters listed above are labeled and stored in a file ("XCHECK") for reference (Figure C-1). XCHECK also lists chemical initial conditions and data prior to each equilibration, which is not shown in Figure C-1.

Daily hydrologic input values are input in separate files and include:

(1) rainfall at the climatic station

(2) snowfall at the climatic station

(3) potential ET for each subunit

Figure C-1: AHM output file "XCHECK", a listing of input parameters and error messages generated when reading those parameters. This file also lists chemical initial condition inputs, and chemical inputs prior to each chemical equilibration (not shown).

```
          Cross check of input parameters:

                 AREA WIDE PARAMETERS

 base elevation =    3000.00000000000000000
 Dry temp. lapse rate (per 1000 units) =      10.00000000000000000
 Wet temp. lapse rate (per 1000 units) =       5.45000000000000018
 Snow free water holding Cap., Fract.  =   5.00000000000000028E-02
 Streams freeze on          10          1
 Streams thaw on            10          1
 Total watershed area                  =     119.99999999999998600


Subunit  1  Type=N   Number soil layers= 1
    Aquept Soils on Emerald Lake WS
 Area =      0.300 Elev.=  3700.000
 Max. Infilt. rate =     20.000 Ripar. Rech. from  7
Rainfall   Rainfall   Snowfall   Snowfall  Snowpack  SnowFrW  T-step -1
Adj. Typ  Adj. Fact.  Adj. Typ  Adj. Fact.   I.C.      I.C.    Snow C.A.
       1     0.000           1      0.000   13.760    0.680      0.028

  Rain Lit.  Rain Lit.  Snow Can.  Snow Can.  Rain Can.  Rain Can.
 Int. Const    I.C.    Int. Const    I.C.    Int. Const    I.C.
      0.100     0.000      0.000      0.000      0.000      0.000

   Max ET      Soil       Soil   Sat. Hyd.    Resid.   Saturated   Wilting  Soil M.
 fraction     Depth        N     Conduct.    Soil M.    Soil M.      Pt.     I.C.
    1.000   100.000      0.150    150.000     0.200      0.500     0.150    0.200

( parameters from other subunits normally are listed here)
```

Figure C-1 (continued): AHM output file "XCHECK", a listing of input parameters and error messages generated when reading those parameters.

```
              USER INPUT - WHERE FLOW GOES:

SUB-   | Fractional %  of subunits flow going to subunit N
UNIT   | N     %    N     %    N     %    N     %    N     %    N     %    N     %    N     %
------|----------------------------------------------------
   1   | 7 1.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   2   | 7 1.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   3   | 7 1.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   4   | 7 1.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   5   | 7 0.350   1 0.004   2 0.027   3 0.232   4 0.046   6 0.291   0 0.000   0 0.000
   6   | 7 1.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   7   | 0 1.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000

            PROGRAM DETERMINATION - SUBUNIT INFLOWS

SUB-   | Fractional %  of subunit N's outflow received
UNIT   | N     %    N     %    N     %    N     %    N     %    N     %    N     %    N     %
------|----------------------------------------------------
   1   | 5 0.004   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   2   | 5 0.027   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   3   | 5 0.232   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   4   | 5 0.046   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   5   | 0 0.000   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   6   | 5 0.291   0 0.000   0 0.000   0 0.000   0 0.000   0 0.000
   7   | 1 1.000   2 1.000   3 1.000   4 1.000   5 0.350   6 1.000


 COMPUTATIONAL ORDER (PROGRAM DETERMINED):

 SUBUNIT # | SUBUNIT TYPE
----------|------------------------------
    5      |  Rock outcrop
    1      |  Normal soil covered subunit *
    2      |  Normal soil covered subunit *
    3      |  Normal soil covered subunit *
    4      |  Normal soil covered subunit *
    6      |  Normal soil covered subunit *
    7      |  Steam channel segment
```

(4) potential snowmelt, potential sublimation, and snow-covered area for each subunit

The program combines required input files into fewer, larger files to facilitate examination of input data and to reduce the number of files the computer must keep open at any given time (Figures A-2 through A-4). The "combined" input files permit even personal computers to run the program with large numbers of watershed subunits and provide a convenient means of reviewing the input data driving a given program run.

Chemical Inputs (subroutines READCHEM, READKIN, SSINK, GASK)

Chemical initial conditions, stoichiometry, alkalinity definition, and thermodynamic data are read by subroutine READCHEM. Form and function of these inputs is described more fully in the users guide portion of this appendix.

Chemical initial condition files define for each compartment of each subunit the total number of moles of chemical component species present, and an initial guess at the fraction of the total of each component present in the "free species" form (e.g. fraction of total Na as Na^+).

The stoichiometry file is fixed and not altered by the user.

The alkalinity definition file is a listing of those chemical species output by the chemical equilibration routine that generate acid neutralizing capacity (ANC), and their contribution to ANC relative to their concentration in solution (e.g. 1 mole of NaOH contributes 1 mole of ANC).

READCHEM calls subroutine READKIN, which reads chemical kinetic data (weathering, etc.).

Subroutine GASK is called from the main program. It reads a file permitting day-by-day adjustment of the partial pressure of gases, such as CO_3^{2-}, present during chemical equilibration.

Subroutine SSINK is also called from the main program, and reads a file detailing daily addition or subtraction of individual chemical species to or from specific compartments. It may be used for input dry deposition data, or nutrient uptake and release by plants.

Initial Conditions (subroutine INCOND)

This subroutine sets initial conditions on each subunit. This enables a given modeling effort to begin at any time of the year under any condition of snowpack, recent rainfall, or soil water content. Variables initialized include:

(1) snowpack water equivalent depth (SWE) (water equivalent in area cm on SCA)
(2) snowpack volume (cubic meters of water equivalent)
(3) snowpack free water content (SFW) (water equivalent in area cm of unfrozen water within the snowpack)
(4) "litter" (or rock outcrop surface) rainfall interception storage, (water storage in area cm on snow-free area)

Figure C-2: File "ARIZCLIM", a consolidated input file generated by AHM. Values are adjusted rainfall, snowfall, and air temperature for each subunit. Air temperature currently plays no internal role in the AHM model, because potential snowmelt, sublimation, and ET are data values supplied to the program by the user.

```
Adjusted climatic data, day   1, FROZEN = F
SUB|      RAIN|       SNOW| Air TEMP
  1     0.0000    0.0000   -7.0000
  2     0.0000    0.0000   -7.0000
  3     0.0000    0.0000   -7.0000
  4     0.0000    0.0000   -7.0000
  5     0.0000    0.0000   -7.0000
  6     0.0000    0.0000   -7.0000
  7     0.0000    0.0000   -7.0000
Adjusted climatic data, day   2, FROZEN = F
SUB|      RAIN|       SNOW| Air TEMP
  1     0.0000    0.0000   -7.0000
  2     0.0000    0.0000   -7.0000
  3     0.0000    0.0000   -7.0000
  4     0.0000    0.0000   -7.0000
  5     0.0000    0.0000   -7.0000
  6     0.0000    0.0000   -7.0000
  7     0.0000    0.0000   -7.0000
.
.
```

Figure C-3: File "AZSNOMn", a consolidated input file generated by AHM. Values are potential snowmelt, snow-covered area, and potential sublimation for each subunit. One to multiple files of this type may be generated, depending on the number of subunits used in a particular model run. Each file holds values for up to 15 subunits, with the file name incremented by the numerical "n" term in its name as more files are created.

```
Snowmelt/Snow C. A./Sublim. Data, Day   1, Subunits  1 through  7
    0.3786    0.0280    0.0964
    0.3786    0.0280    0.0964
    0.3786    0.0280    0.0964
    0.3786    0.0280    0.0964
    0.3786    0.0280    0.0964
    0.3786    0.0280    0.0964
    0.3786    0.0280    0.0964
Snowmelt/Snow C. A./Sublim. Data, Day   2, Subunits  1 through  7
    0.4192    0.0260    0.0962
    0.4192    0.0260    0.0962
```

Figure A-4: File "ARIZETn", a consolidated input file generated by AHM. Values are potential evapotranspiration for each subunit. One to multiple files of this type may be generated, depending on the number of subunits used in a particular model run. Each file holds values for up to 15 subunits, with the file name incremented by the numerical "n" term in its name as more files are created.

```
Potential ET Data, Day   1, Subunits  1 through  7
    0.0845
    0.0845
    0.0845
    0.0845
    0.0845
    0.0845
    0.2421
Potential ET Data, Day   2, Subunits  1 through  7
    0.0422
    0.0422
    0.0422
    0.0422
    0.0422
    0.0422
    0.2035
Potential ET Data, Day   3, Subunits  1 through  7
.
.
.
```

(5) "litter" rainfall interception storage volume (cubic meters of water stored in litter interception)

(6) canopy rainfall interception storage (water storage in area cm)

(7) canopy snowfall interception storage (stored water equivalent in area cm)

Data Input Each Time Step (Subroutine REREAD)

This subroutine reads the consolidated input files created by READDAT (see Figures C-2 through C-4), allowing the program to track only initial (or previous time step) conditions and the effect of the current time step's data on water storage conditions. Currently, the program uses daily time steps, but could be modified for any desired time increment.

Data Conversion (Subroutine CONVERT)

This subroutine currently performs no function, but can be modified to allow data stored in English units to be converted to the metric (cm) values required by this program. Its presence serves to identify the location in the program most appropriate for such conversion if it is desired.

Adjustment for Variable Snow-Covered Area (Subroutine SNOINI)

SWE and SFW are treated as constant across the SCA of the subunit. Rainfall litter interception is treated as a constant depth of water on the snow-free area (SFA). When SCA changes, the depths of the SWE, SFW, and rainfall "litter" interception must be adjusted to maintain constant volumes, or the water balance will have an apparent error. This routine makes adjustments to those values as required to establish new beginning-of-time-step initial conditions as SCA changes. Computationally:

(1) If no snow is present either on the ground surface or in canopy interception storage, SWE, snowpack volume, and SFW are set to zero. Water and chemicals stored in the "interception" component beneath the snowpack are added to existing rainfall "litter" interception water and chemicals, and the water and chemicals are distributed over the entire subunit.

(2) If the snowpack volume is greater than zero, but the read-in value of SCA was zero, SCA is set to the previous time step's SCA if that was non-zero, or to a built-in constant (currently .1) if the "old" SCA was also zero.

(3) Rainfall litter interception, SWE, and SFW and new initial conditions for those values are adjusted for SCA, whether obtained from (1) or (2).

Interception (Subroutine SNTERCPT)

Interception is the loss from rainfall or snowfall due to rain or snow being trapped by the forest canopy, surface litter, or rock surfaces. Such interception is typically (though not always) returned to the atmosphere. This subroutine separately accounts for rainfall and snowfall interception in the tree canopy and rainfall interception on litter (rock surface). Of these three interception types, only rainfall interception on litter (rock) is physically influenced by SCA. Within this routine, litter interception depth is computed as though SCA is zero. SCA enters computations in this routine only in the determination of litter interception volume.

Computationally:

(1) Chemicals present in rainfall are split into 2 fractions, one on the snow-covered area, the other on the snow-free area.

(2) If the subunit is a stream segment, no interception is computed, and all interception values are set to zero. Control returns to the main program.

(3) New initial conditions for rain and snow canopy interception are set equal to the current storage value.

If no rain or snow occurred, then

(a) the current time step's (new) interception is set to zero

(b) rainfall and snowfall depths adjusted for interception are set to zero

(c) the volume of rainfall litter interception is set to correspond to the current depth on the snow-free area, and

(d) control is returned to the main program

(4) If precipitation occurred, available interception storage capacities for this time step are computed as the differences between interception storage capacities and existing interception storage in rainfall litter, rainfall canopy, and snowfall canopy compartments. SCA is not considered at this point. The actual interception for the time step is equal to available capacities except when:

(a) the subunit's rainfall times a factor (RIntFrac) is less than available canopy interception storage, rain canopy storage is set equal to subunit rainfall times that factor, and rainfall adjusted for the interception loss. The factor RIntFrac allows some throughfall to occur even with light rains; it is currently fixed at 0.30.

(b) the subunit's rainfall is less than the sum of available rainfall canopy and litter storage, this time step's rainfall canopy storage equals available storage capacity and its litter interception storage equals rainfall left after satisfying canopy storage.

(c) snowfall on the subunit is less than available snowfall canopy interception storage capacity, this time step's canopy interception is set equal to snowfall.

(d) chemicals in rainfall or snowfall are distributed to appropriate interception storage proportionately to the fraction of rainfall or snowfall entering that storage compartment.

(5) Values of time-step interception storage are subtracted from subunit rainfall and snowfall, and added to initial interception storage. Litter interception volume is computed from adjusted litter interception storage depth adjusted for SCA.

Snowmelt and Snowfall effects (subroutine SnowComp)

This subroutine computes changes to the snowpack, snowpack free water, intercepted snow, rainfall litter interception, drainage from the snowpack caused by snowmelt, rainfall, or snowfall, and associated chemical mixing between compartments. It also adjusts SCA (which is otherwise read from an external file) when it snows, when the snowpack is zero upon entering the routine, or in a few other cases described below.

Chemical transfer between compartments taking place in this subroutine is proportional to the water moved and left behind; this may be overridden later by subroutines SNOWRAIN and SNOWMIX when the user selects the "decay" option to concentrate chemicals in early-season drainage from the pack.

Snowmelt, SCA, and sublimation data values are supplied to AHM in data files. These values are interpreted as potential (subject to availability of snow) snowmelt and sublimation that occur on the SCA, not a subunit average.

This routine initially stores current values of the three interception types (rain on canopy and litter and snow on canopy) for internal use; these are initial conditions for this subroutine. Computationally:

(1) If it snowed during a time step:
  (a) rainfall litter interception water and chemicals are added to existing snowpack free water content; this procedure was used due to the preponderance of rock outcrops at Emerald Lake Basin.
  (b) SCA is internally increased to 1.0. (The user's input SCA value should reflect SCA prior to this days new snowfall, or adjustments to litter interception may be inappropriate.)
  (c) Snowpack chemical content, SWE, and snowpack volume are adjusted for new snow additions.

(2) If no snow is present, including new snowfall and snowfall interception storage:
  (a) SWE, SFW, SCA, snowmelt, snowfall canopy interception, and snowpack volume are set to zero;
  (b) rainfall litter interception storage depth is determined by the volume of that interception divided by subunit area;
  (c) SCA as it exists leaving this subroutine is recorded in a new variable; this value will replace the subsequent time step's SCA if during that step snowpack volume is non-zero but the read-in value of SCA is zero.

(d) Control returns to the main program.

(3) If snow is present on the ground or in the canopy, but no melt occurred, then:

(a) if this time step's snowfall is less than snowfall canopy interception storage, a fixed amount (currently 20 percent) of that storage is dropped from the canopy to the snowpack. If some snow dropped from canopy interception:

(a1) Snowfall canopy interception (ice and chemicals) are reduced by that amount; chemicals are added to snowpack.

(a2) If the current SCA is zero, SCA is increased to the previous time step's SCA if that is positive, or to a fixed value (currently .1). In this case, SWE and SFW also were zero; SFW now equals the depth of rainfall litter interception, and volume of rainfall litter interception is reduced a like amount. Rainfall litter interception depth remains unchanged, because this value is applicable only on the snow-free area.

(a3) SWE is set equal to [(initial SWE plus snowfall) -(the time step's canopy interception) + (dropped snow)/SCA]

(b) snowpack volume is re-computed based on SWE and SCA.

(c) rainfall (depth) less canopy interception is added to SFW (rainfall on snow-free area is separate). Chemicals remaining in rain on SCA (after canopy interception are added to chemicals in snowpack's free water.

(d) if rainfall caused SFW to exceed the snowpack's storage capacity (no melt occurred here), the excess becomes snowpack drainage, and SFW is set to capacity. Chemicals in snowpack drainage are proportional to the fraction of free-water lost to drainage.

(e) SCA as it exists leaving this subroutine is recorded in a new variable; this value will replace the subsequent time step's SCA if during that step snowpack volume is non-zero but the read-in value of SCA is zero.

(f) Control returns to the main program.

(4) If potential snowmelt exceeds the sum of snowfall canopy interception plus SWE, all snow will melt. Operationally:

(a) snowmelt is set to a subunit average value.

(b) snow canopy interception storage water-equivalent and chemicals are added to rain canopy interception storage. If this raises rain canopy storage above its capacity, the excess is "dripped" to snowpack drainage from the current SCA, and rainfall canopy storage is set to capacity. Chemicals from rainfall canopy interception storage are distributed proportionately between remaining interception storage and the fraction "dripped" to snowpack drainage.

(c) snowpack drainage is computed as the sum of SFW, SWE, rainfall less interception, and "drip" from the canopy. Chemicals in SFW, SWE, and rain-on-SCA are added to snowpack drainage. In addition, if it snowed this time step, chemicals in rainfall on the snow-free area are also added to snowpack drainage, because the program internally resets SCA to 1.0 when it snows.

- (d) subroutine WETMELT is called to determine the volumes of water left behind the receding snowpack, with a wetted area equal to the (still current) SCA. Although there is no remaining snowpack, SCA cannot be reset to zero yet, because the drainage from the snowpack is effective only on the SCA.
- (e) SWE, SFW, snowfall canopy interception, and snowpack volume are set equal to zero. This precludes losses from sublimation, while ET only effects the snow-free area. Because snow-free area remains unchanged until this time step is completed, ET will not effect the area left wet behind the receding snowpack the day SCA declines.
- (f) SCA as it exists leaving this subroutine is recorded in a new variable; this value will replace the subsequent time step's SCA if during that step snowpack volume is non-zero but the read-in value of SCA is zero.
- (g) Control returns to the main program.

(5) If potential snowmelt is positive, but less than the sum of snowfall canopy interception plus SWE on the SCA, some snow will remain. Operationally:

- (a) Intercepted snow is reduced by up fixed percentage of potential melt (currently 30 percent). If remaining potential snowmelt results in a negative snowpack, then more snow must exist in the canopy, and it is melted.
- (b) Melted snowfall interception is added to rainfall interception storage. Chemicals from the fraction of snowfall canopy interception melted are added to rainfall canopy interception.
- (c) If rain interception storage exceeds maximum capacity, the amount that will "drip" is computed and intercepted water is reduced. "Dripped" chemicals are added to the snowpack's free water.
- (d) SWE and snowpack volume are reduced by remaining potential snowmelt.
- (e) Chemicals from the portion of the snowpack melted are added to snowpack free water. Chemicals from rain on the snow covered area, or all chemicals in rain if fresh snowfall occurred, are added to the snowpack's free water content.
- (f) SFW is computed by adding rainfall plus snowmelt minus melt of intercepted snow plus water dripped from rain interception storage plus the time step's litter interception value, which previously was subtracted from rainfall.
- (g) Snowmelt is converted from melt on the SCA to subunit average melt.
- (h) If the snowpack's free-water holding capacity has been exceeded, snowpack drainage is computed, along with chemicals lost from the free-water to drainage.

(i) Subroutine WETMELT is called to determine the volumes of water left behind the receding snowpack, with a wetted area equal to the difference between the previous and current time step's SCA. Although melt may have changed the SCA, SCA cannot be reset yet, because the drainage from the snowpack takes place only on the SCA.

(j) SCA as it exists leaving this subroutine is recorded in a new variable; this value will replace the subsequent time step's SCA if during that step snowpack volume is non-zero but the read-in value of SCA is zero.

(k) Control returns to the main program.

Wetted Area Behind Receding Snowpack (subroutine WETMELT)

This subroutine determines the amount of water left in "litter" interception storage behind a receding snowpack.

(1) If it snowed this time step and all the snowpack melted, all snowpack drainage is added to rainfall interception storage, and snowpack drainage set to zero. Snow-covered area is set to zero, and excess rainfall interception storage (on "litter") is added back to rainfall adjusted for canopy interception, from where it can become surface runoff or infiltration later. (This unusual step is taken because with SCA = 0.0, no snowpack drainage will occur.) Chemicals from snowpack drainage are added to rainfall litter interception, with the excess going back to rainfall on the snow-free area. Control returns to the main program.

(2) If the volume of snowpack drainage is greater than maximum possible rainfall litter interception on the wet area left behind a receding snowpack, that volume of interception is added to existing litter interception on the snow-free area and subtracted from snowpack drainage. Chemicals move proportionately to water transfered from snowpack drainage. Chemicals and water added to the newly wetted area are distributed over the entire snow-free area.

(3) If the volume of snowpack drainage is less than maximum possible rainfall litter interception on the newly wetted area, all snowpack drainage goes to litter interception on the newly-wetted area, and snowpack drainage is set to zero. All snowpack drainage chemicals go into rainfall litter interception on the snow-free area. Chemicals and water added to the newly wetted area are distributed over the entire snow-free area.

(4) The depth of interception storage on the snow-free area is determined, and control returns to subroutine SNOWCOMP.

Snowpack Initial Chemical Conditions for "Decay" type Chemical Elution (subroutine SNOWRAIN)

The user interactively selects an option for chemical elution from the snowpack. If that choice is to use a "decay"-type method that concentrates chemicals in early snowpack drainage, subroutine SNOWRAIN will be called. Then:

(1) If no rainfall or snowfall occurred this time-step, control reurns to the main program.

(2) If it snowed or rained, SNOWRAIN updates a whole-snowpack chemical initial condition array, which is the total of each chemical species in the sum of the snowpack's ice, free water, and drainage, and the total volume of water in the sum of those compartments. These become the initial conditions for subsequent computations of chemical elution from the snowpack.

Accelerated Chemical Elution from the Snowpack (subroutine SNOWMIX)

If the user selects the "decay" or accelerated method of snowpack chemistry elution from the snowpack, subroutine SNOWMIX is called. SNOWMIX negates the proportional mixing of chemicals in the snowpack that has occured so far, and recomputes the concentration of chemicals in snowpack drainage using an accelerated scheme. Computationally:

(1) Chemicals in the snowpack's drainage and free water are added to the snowpack's water equivalent (ice) compartment, and chemicals in free water and drainage set to zero.

(2) If the snowpack is entirely gone, all remaining chemicals in the snowpack's water equivalent (ice) are added to snowpack drainage, unless that too is zero, in which case the chemicals are added to litter interception on terrestrial subunits or surface runoff on stream subunits. Control returns to the main program.

(3) Total current volume of water stored in the snowpack's ice, free water, and drainage is compared to the initial value stored after the last precipitation event by subroutine SNOWRAIN. The fraction of initial water storage missing is computed, and the concentration in the snowpack's drainage and free water as a fraction of initial concentration (as defined by subroutine SNOWRAIN's initial conditions) is computed as:

$$Y = A \times B \times EXP(- B \times X) + (1 - A) \times D \times EXP(- D \times X)$$

where:

Y = fraction of "initial condition" concentration currently in snowpack drainage and free water;
A, B, D = parameters entered interactively by the user when this snowpack chemistry option is selected;
X = fraction of "initial" (as defined by SNOWRAIN) total snowpack water missing.

(4) Chemical concentration of each species in snowpack drainage and free water (same concentration) is determined by multiplying "initial" concentration by the fraction Y. Remaining chemicals in the pack are adjusted for the loss to drainage, and control returns to the main program.

Water in "Interception Storage" beneath Snowpack (subroutine USNOW)

Subroutine USNOW computes the volume of water and quantity of chemicals stored in the "litter" interception compartment beneath the snowpack after snowpack drainage occurs. Computationally:

(1) If no snowpack drainage occurred this time step, or if this is a stream subunit, control returns to the main program.
(2) Water and chemicals in snowpack drainage are added to litter interception beneath the pack. The amount in excess of litter interception capacity is determined, and water and chemicals partitioned between drainage and that left in interception beneath the pack.
(3) The volume of litter interception beneath the snowpack is stored in a separate variable, and control returns to the main program.

Total Effective Water Inputs to a Subunit (subroutine INFLOW)

This routine sums total inputs with the potential for reaching a subunit's soil reservoir or surface runoff. These inputs normally include surface runoff, horizontal drainage, rainfall, and drainage from the snowpack. When the subunit is a thawed stream segment, the snowpack and snowpack free water content remaining or created due to snowfall and rainfall this time step are added to other inputs. Rainfall and snowpack drainage are adjusted for SCA. Computationally:

(1) Rain and snowpack drainage are adjusted for SCA, summed, and converted to volume in cubic meters.
(2) If this is a thawed stream subunit, SWE and SFW are added to the value in (1), and SCA, SWE, SFW, and snowpack volume are set to zero. Chemicals in the snowpack's water equivalent (ice), free water, and drainage are temporarily moved to "rainfall litter interception" compartment, from where they will be added to surface runoff of the stream later (in subroutine SOILDRAN). This is done because subroutine SOILDRAN zeros chemistry

and surface runoff of stream subunits before computing surface runoff for this time-step. Subroutine SOILDRAN will also add snowpack drainage water to the stream's surface runoff.

(3) Surface runoff and horizontal drainage inputs from up to eight contributing subunits summed, and chemicals from those contributions recorded.

(4) Items (1), (2), and (3) are converted back to area cm, and control is returned to the main program.

Drainage and Recharge to the Soil Profile, and Surface Runoff (subroutine SOILDRAN)

The soil simulation model is a mixture of physically-based and systems techniques. This came about due to the nature of the Emerald Lake watershed itself.

Soils within the Emerald lake basin tend to be located in isolated patches with ill-defined drainage patterns. Unless each soil patch was modeled separately (which would require a very detailed survey), it is impossible to accurately define runoff-contributing rock outcrop areas, gradients, and widths of the subsurface flow profiles for soils. Contributing outcrop areas can increase effective precipitation many times above that which would otherwise fall on a soil patch. Gradients and the widths of flow profiles have direct, positive correlations with rates of saturated flow through soils. Without accurate estimates of these parameters for a given soil patch, detailed modeling of subsurface flow patterns serves no purpose.

Conversely, systems-type soil models requiring the fitting of numerous parameters to observed flows would be hampered by the limited influence of soils on runoff in the Emerald Lake watershed; from a hydrological perspective, very little soil is present.

The model we developed is capable of handling multiple soil layers, with different numbers of layers on each subunit. The topmost layer has a parameter controlling maximum infiltration rate; excess surface inputs become surface runoff. Storage in each layer is limited by depth and porosity. Any layer can limit downward infiltration. Vertical drainage is controlled by unsaturated hydraulic conductivity in upper layers, while the bottom layer drains "horizontally" as a simple linear reservoir. Subunits modeled with single-layer soils use only the linear reservoir methodology. Use of unsaturated hydraulic conductivity in upper layers reduces the number of parameters that must be calibrated using streamflow; these parameters can be obtained from soil moisture release data. Horizontal drainage inputs from contributing soil units are added first to the bottom layer of the receiving subunit, then successive higher layers until available storage is filled, with excess inputs becoming surface runoff from the receiving subunit. While this procedure may be somewhat questionable, excess inputs end up as surface runoff, where they belong. Computationally:

(1) Soil water content of each layer is recorded as an "initial condition" (in terms of this subroutine).

(2) Chemical content of surface runoff and horizontal drainage from this subunit is set to zero.

(3) If this is a stream subunit, subroutine SSINK may have allowed (dry deposition) chemicals to be added to "litter interception" as a temporary location before adding them to surface runoff in the stream. Additionally, subroutine INFLOW adds chemicals from the snowpack when a frozen stream thaws. Both of these moves were necessary because this subroutine zeroed the chemical content of surface runoff. Now the chemicals in "litter interception storage" are added to surface runoff.

(4) On rock outcrop or stream subunits, surface runoff is equal to the sum of horizontal drainage and surface runoff inputs plus rain (less time-step interception) plus snowpack drainage. Soil water content is set to zero, and control is returned to the main program.

(5) On soil-covered subunits, the lowest soil layer (or the only layer if a single soil layer is used) is (horizontally) drained using a linear reservoir model of the form:

$$Q = K\,(\text{Theta} - \text{ThetaR})$$

where: Q is drainage from the soil profile in area cm
K is a fitted parameter
Theta is soil water content, cm/cm
ThetaR is residual soil water content at which unsaturated hydraulic conductivity becomes 0.

(6) Soil water content of the bottom layer is adjusted for horizontal drainage.

(7) Chemicals from soil water in the bottom layer are added to horizontal drainage.

(8) Soil layers above the bottom layer are drained, with the lesser of unsaturated hydraulic conductivity (function HYDK) or storage available in the next lower layer being limiting. (Drainage is not allowed to reduce soil water content below the level at which unsaturated hydraulic conductivity is zero). Soil water and chemical contents are adjusted in both affected layers.

(9) Horizontal drainage from contributing subunits is added starting from the bottom layer and progressing toward the top layer as storage permits. Any excess after filling one soil layer is available as input to the next higher layer, without restriction by physical impediments to flow. Excess available after filling the uppermost soil

layer is added to surface runoff. Chemicals are transferred proportionately with water transfers.

(10) When the uppermost soil layer is reached, any excess incoming horizontal drainage from other subunits becomes surface runoff, and remaining chemicals in incoming horizontal drainage are added to surface runoff from this subunit. Chemicals in rain on the snow-free area, snowpack drainage, and incoming surface runoff are added to the surface runoff from this subunit. Unless this is a rock subunit (on which all contributed horizontal drainage always becomes surface runoff and control is passed to item 12), chemicals in litter interception storage are added to surface runoff. Litter interception is set to capacity (on non-rock subunits), and a proportionate amount of the water and chemicals in surface runoff are moved back to litter interception storage.

(11) Surface runoff is computed as surface runoff computed to this point less the change in litter interception storage on the snow-free area. Litter interception storage (depth) on the snow-free area is set to capacity, and the volume of that storage is computed.

(12) If this is a rock or stream subunit, surface runoff is set equal to incoming horizontal drainage, and chemicals in incoming horizontal drainage are transferred to surface runoff.

(13) If no excess incoming horizontal drainage exists, additional water inputs from rain, externally-added surface runoff, and snowpack drainage are compared to maximum infiltration capacity. Surface runoff and the fraction of that water which can infiltrate is computed. The appropriate fraction of chemicals from each of these input sources is added to the surface runoff.

(14) For rock and stream subunits, control returns to the main program.

(15) Available storage capacity in the uppermost soil layer is computed. Water left over after computing the excess of rainfall, snowmelt, and surface runoff beyond maximum infiltration capacity is added to the uppermost soil layer to the extent storage space is available; excess is added to surface runoff. Chemicals in remaining rainfall, snowpack drainage, and incoming surface runoff are partitioned between the uppermost soil layer and surface runoff. Control returns to the main program.

A modification to this soil drainage procedure is under consideration. The modified procedure would drain the lowest level of each soil first, computing drainage from each subunit in the opposite computational order used in the remainder of the program. This would permit storage space for "upstream" drainage to be created before that drainage is computed. Drainage from a subunit would enter the lowest soil layer of the appropriate downstream subunit to the extent space was available; any excess would remain in place.

Determination of Unsaturated Hydraulic Conductivity (Function HYDK)

The function HYDK computes unsaturated hydraulic conductivity (UHC) as a function of volumetric soil water content. The computational procedure is that described by Warrick et al. (1985).

If soil water content is below the residual value at which UHC goes to zero, UHC is set to zero, and control is returned to the main program.

At higher water contents, the computation used is:

UHC = HC* x HCs

where: UHC is unsaturated hydraulic conductivity at this water content
HCs is saturated hydraulic conductivity
HC* is computed as:

HC* = SQW x (1 - (1 - W**(N/(N-1)))**(1-1/N)) **2

where: SQW = square root of W
W = (TH - THr) / (THs - THr)]
N = a parameter fitted to a given soil
TH = volumetric soil water content
THr = soil water content where UHC = 0
THs = soil water content at saturation
** = exponentiation

Water Volume Stored for Equilibration (Subroutine DOCHEM)

Subroutine DOCHEM is called whenever it is desired to compute the equilibrium concentrations of chemical species in solution in a given compartment of a subunit, or when kinetically-based (dependent on concentrations of one or two chemical species) chemical reactions are to be computed, such as soil weathering. Its calling arguments include the compartment number, and the number of centimeters of water are stored in that compartment. (Adding equilibration and kinetics to other than the currently included "litter" (rock surface) compartment (under the snow and snow-free) and soil layers will require minor modifications to the program).

When called, DOCHEM computes the total number of liters of water in the compartment using centimeters of water in the compartment and snow-covered area when necessary. It then calls the routines MINEQL, ANC, COMPKIN, and MATBAL2, then returns control to the main program.

Chemical Equilibration (Subroutine MINEQL)

MINEQL consists of a number of separate subroutines and functions, which have largely been stored in the single file "mineql.for" for convenience. These subfiles include (1) MINEQL, (2) EXCOL, (3) EXROW, (4) IADY, (5) IADX, (6) IONCOR, (7) SIMQ, (8) SOLID, (9) SOLIDX, (10) SOLVE, (11) INCASE (temporary), (12) SURFIN, (13) SURFPR, (14) SURFT, (15) SURFZ, (16) INPUT, (17) OUTPUT, (18) MBUST, and (19) MBUST2.

Collectively, these routines compute chemical equilibration on the mix of chemical components and water in the given compartment at one time-step. The version of MINEQL we used was a functioning program before work on the AHM model began; any changes made to it have been cosmetic.

MINEQL creates an enormous output file named bigchem.out (Figure C-5), listing input and output species concentrations for each equilibration that occurred during the run.

When equilibration is complete for this compartment, control returns to subroutine DOCHEM.

Computation of Acid-Neutralizing Capacity (Subroutine ANC)

Subroutine ANC computes acid-neutralizing capacity of the equilibrium solution computed by MINEQL. It accomplishes this through the use of a user-supplied file listing the chemical species and their stochiometric contributions to acid-neutralizing capacity. The species concentrations from MINEQL are multiplied by the matching species' stochiometric coefficients from the user's input file and summed to compute acid-neutralizing capacity.

Subroutine ANC writes an output file named phalk.out that includes water year day, subunit, compartment, pH, acid-neutralizing capacity, and the volume of water in that compartment (m^3) (Figure C-6). A supplemental program is available for creating files for plotting from file phalk.out (an appendix to AHM user's guide).

When completed, control returns to subroutine DOCHEM.

Chemical Kinetics (Subroutine COMPKIN)

Chemical kinetics are computed using a separate set of parameters for each subunit and compartment. Currently, this includes only the litter or rock surface and soil layers. The kinetic reactions are computed in the form:

$$C1 = C1 + A \times F \times 1000 \times (K1 + K2 \times C2^{\alpha 1} + K3 \times C3^{\alpha 2})/Q$$

Figure C5: AHM output file "bigchem.out". This file is created by AHM's MINEQL routine, and includes output similar to that shown here for every equilibrated compartment each time step. The size of this file is a function or run length, the number of subunits and compartments present, and the number of species present in chemical initial condition files and in the thermodynamic input file "thrm.dat".

```
  INPUT: Subunit  2 Compart. 12 WYDAY   1 Total Liters  5.559E+05

    ID  Conc. M/l   LOG C  Total M/l    TYPE 1 - COMPONENTS
     1   1.96E-05   -4.71   1.96E-05    CA
     2   5.29E-06   -5.28   5.29E-06    MG
     4   8.76E-06   -5.06   8.76E-06    K
     5   5.07E-05   -4.29   5.07E-05    NA
    50   2.45E-06   -5.61   1.23E-05    H
   157   9.66E-07   -6.01   9.66E-07    NO3
   102   1.38E-05   -4.86   1.38E-05    SO4
   103   4.14E-05   -4.38   4.14E-05    CL
   107   4.87E-09   -8.31   1.19E-05    NH3
   109   2.60E-17  -16.59   1.10E-08    PO4
   112   3.97E-20  -19.40   1.10E-08    SIO3
   101   5.74E-11  -10.24   1.10E-08    CO3-

    ID     LOGK      SPECIES:  TYPE II - COMPLEXES  (these come from file
 12530    10.18      H       1   CO3-    1            "thrm.dat" )
 12540    16.46      H       2   CO3-    1
 12570     9.00      H       1   NH3     1
 12600    12.46      H       1   PO4     1
 12610    19.84      H       2   PO4     1
 12620    21.83      H       3   PO4     1
 12710    13.08      H       1   SIO3    1
 12720    22.66      H       2   SIO3    1
 13595   -13.99      H      -1

    ID     LOGK      SPECIES:  TYPE III - FIXED SOLIDS
 25000    21.46      H       2   CO3-    1

    ID     LOGK      SPECIES:  TYPE V - DISSOLVED SOLIDS
 20010     4.65      CA      1   SO4     1
 20030    44.83      CA      5   H      -1    PO4     3
 20050    19.22      CA      1   H       1    PO4     1
 20070     8.65      CA      1   SIO3    1
 20130   -21.91      CA      1   H      -2
 20140     5.35      MG      1   CO3-    1
 20160    28.22      MG      3   PO4     2
 20200   -16.41      MG      1   H      -2
 21440    25.36      H       2   SIO3    1
 20000     8.25      CA      1   CO3-    1
```

Figure C5: AHM output file "bigchem.out" (continued).

```
 OUTPUT: Subunit  2 Compart. 12 WYDAY   1 ITERATIONS =  13
  IONIC STRENGTH =  1.37E-04      LOG F(Z=1) = -0.01
   ID  Conc. M/l   LOG C  Total M/l   Residual     COMPONENT SPECIES
    1   1.96E-05   -4.71   1.96E-05   7.28E-12     CA
    2   5.29E-06   -5.28   5.29E-06   1.36E-12     MG
    4   8.76E-06   -5.06   8.76E-06   2.73E-12     K
    5   5.07E-05   -4.29   5.07E-05  -1.82E-11     NA
   50   2.45E-06   -5.61   1.23E-05   2.22E-11     H
  157   9.66E-07   -6.01   9.66E-07   3.41E-13     NO3
  102   1.38E-05   -4.86   1.38E-05  -4.55E-12     SO4
  103   4.14E-05   -4.38   4.14E-05  -1.09E-11     CL
  107   4.87E-09   -8.31   1.19E-05   1.91E-11     NH3
  109   2.60E-17  -16.59   1.10E-08   1.86E-14     PO4
  112   3.97E-20  -19.40   1.10E-08  -3.46E-14     SIO3
  101   5.74E-11  -10.24   1.10E-08   0.00E-01     CO3-
   ID  Conc. M/l   LOG C   LOG K      SPECIES:  TYPE II - COMPLEXES

12530   2.11E-06   -5.68   10.18     H       1    CO3-    1
12540   1.00E-05   -5.00   16.46     H       2    CO3-    1
12570   1.19E-05   -4.92    9.00     H       1    NH3     1
12600   1.85E-10   -9.73   12.46     H       1    PO4     1
12610   1.08E-08   -7.97   19.84     H       2    PO4     1
12620   2.57E-12  -11.59   21.83     H       3    PO4     1
12710   1.16E-12  -11.94   13.08     H       1    SIO3    1
12720   1.10E-08   -7.96   22.66     H       2    SIO3    1
13595   4.20E-09   -8.38  -13.99     H      -1
   ID  Conc. M/l   LOG C   LOG K      SPECIES:  TYPE III - FIXED SOLIDS

25000  -1.21E-05   -4.92   21.46     H       2    CO3-    1
   ID  Conc. M/l   LOG C   LOG K      SPECIES:  TYPE V - DISSOLVED SOLIDS

20010   1.22E-05   -4.91    4.65     CA      1    SO4     1
20030   1.41E-23  -22.85   44.83     CA      5    H      -1     PO4     3
20050   2.06E-08   -7.69   19.22     CA      1    H       1     PO4     1
20070   3.50E-16  -15.46    8.65     CA      1    SIO3    1
20130   4.02E-16  -15.40  -21.91     CA      1    H      -2
20140   6.84E-11  -10.16    5.35     MG      1    CO3-    1
20160   1.67E-21  -20.78   28.22     MG      3    PO4     2
20200   3.43E-11  -10.46  -16.41     MG      1    H      -2
21440   5.50E-06   -5.26   25.36     H       2    SIO3    1
20000   2.01E-07   -6.70    8.25     CA      1    CO3-    1
```

Figure C6: AHM output file "phalk.out". This file is created by subroutine ANC and includes the values of WY day, subunit, compartment, pH, acid-neutralizing capacity (eq/l), and total water in the compartment (m^3).

```
 1    5 11       5.651 0.2601E-007      0.6549E-03
 1    1 11       6.177 0.8194E-005      0.0000E+00
 1    2 11       5.720 0.8644E-006      0.0000E+00
 1    3 11       5.660 0.1344E-006      0.0000E+00
 1    4 11       5.690 0.4960E-006      0.0000E+00
 1    6 11       5.655 0.7893E-007      0.0000E+00
 1    1 12       5.357-0.3199E-005      0.0000E+00
 1    2 12       5.612-0.3189E-006      0.0000E+00
 1    3 12       5.611-0.3260E-006      0.0000E+00
 1    4 12       5.610-0.3350E-006      0.0000E+00
 1    6 12       5.608-0.3630E-006      0.0000E+00
 1    7  7       5.656 0.3216E-006      0.4085E-03
 2    5  1       5.657 0.1003E-006      0.9240E-03
 2    5 11       5.654 0.5248E-007      0.9240E-03
 2    1  1       6.067 0.5933E-005      0.0000E+00
 2    1 11       5.710 0.7497E-006      0.0000E+00
 2    2  1       5.704 0.6677E-006      0.0000E+00
 2    2 11       5.650 0.1808E-007      0.0000E+00
 2    3  1       5.665 0.1930E-006      0.0000E+00
 2    3 11       5.650 0.1532E-007      0.0000E+00
 2    4  1       5.803 0.1913E-005      0.0000E+00
 2    4 11       5.650 0.8765E-008      0.0000E+00
 2    6  1       5.661 0.1523E-006      0.0000E+00
 2    6 11       5.653 0.4506E-007      0.0000E+00
 2    1 12       9.572 0.4420E-001      0.0000E+00
 2    2 12       9.619 0.7741E-001      0.0000E+00
 2    3 12       9.523 0.4735E-001      0.0000E+00
 2    4 12       9.493 0.4115E-001      0.0000E+00
 2    6 12       9.691 0.1179E+000      0.0000E+00
 2    7  7       9.499 0.4244E-001      0.6373E-03
 3    5  1       5.659 0.1202E-006      0.9580E-03
```

where:

$C1$ = concentration of the chemical species being adjusted

A = soil particle or rock outcrop surface area on the subunit, m^2

F = fraction of subunit wet in this compartment

$C2$, $C3$ = concentration of species that effect that species being adjusted

Q = volume of water (liters) in the compartment

$K1$, $K2$, $K3$, $a1$, $a2$ = user-supplied parameters to give outputs in millimoles per m^2

Computationally:

(1) the number of species output by MINEQL is determined.

(2) a set of parameters and species for a kinetic reaction affecting one species is selected, and the corresponding concentrations are found among MINEQL's output concentrations.

(3) the kinetic reactions are computed.

(4) items 2 and 3 are repeated for all kinetic reactions for the compartment of the subunit, and control returns to subroutine DOCHEM.

Total Chemical Species in a Compartment (Subroutine MATBAL2)

Kinetic reactions computed by subroutine COMPKIN change the concentration of specific MINEQL chemical species; these are not the values tracked between compartments by the remainder of the AHM program. MINEQL species may include some created by combinations of AHM's input components (type 1 components). Subroutine MATBAL2 recomputes the values of the total chemical component species that are tracked by AHM by extraction from those species present as determined by MINEQL. Computationally:

(1) The total number of MINEQL species types 1-4 is computed.

(2) Initially, the total concentration of each MINEQL type 1 species is set equal to the concentration of the "free" species (e.g., total H = H^+).

(3) The total concentration of each species set in item 1 above is increased to reflect the presence and stoichiometry of that type 1 component in MINEQL species types 2 and 4. MINEQL type 3 species are not included in the total concentrations. Type 3 species are "precipitated solids" that are not allowed to dissolve, even if their concentration becomes negative. Because type 3 species are not allowed to dissolve, they can be used to represent gases at fixed partial pressures. The gas carbon dioxide is entered as a type 3 species and has gone negative during initial testing (see MINEQL documentation).

(4) A new "guess" at the fraction of the total type 1 component species that is present in the "free" state is obtained by dividing the current value of the "free" species by the total obtained in item 3, above. If the species in question is H^+, the guess at the fraction "free" is set to a fixed value .0001, because total H may be negative, and the "guess" must be positive. This operation probably should be moved elsewhere, as the concentrations of the "free" species in MINEQL have been adjusted by COMPKIN.

(5) In the case where only a small portion of the "litter" interception area was left wet behind a receding snowpack, the concentrations of species computed by MINEQL reflect only a small portion of the total chemistry. In this case, the existing total moles in the AHM chemical species on the dry fraction of litter interception storage plus the moles computed by (total concentration times total liters) from the MINEQL variables on the wetted area are added to obtain new total moles of type 1 component species.

In all other cases, the total moles of type 1 chemical components in the compartment are computed by total concentration times total liters, and control returns to subroutine DOCHEM, and then directly to the main program.

Evapotranspiration Losses (subroutine ET)

This subroutine adjusts potential ET and sublimation on non-stream units for available water or snow. No changes in chemicals stored in affected compartments occur.

ET proceeds at potential rates from litter and canopy rainfall interception storage. Canopy-intercepted rainfall evaporates over the entire subunit, while litter-intercepted rainfall evaporates only on the snow free area. ET from soil layers is a function of remaining PET after reductions for interception losses, soil water content, and the relative location of the soil layer. The latter is controlled by a parameter that limits ET to some fraction of that which would otherwise occur; this parameter should generally be smaller as depth of the layer increases. ET from soil water storage occurs only on the snow free area.

Sublimation proceeds at potential rates given the presence of either intercepted snow or a snowpack. Intercepted snow sublimates on the entire subunit area, while the snowpack sublimates only from the SCA.

Input values of PET and potential sublimation are in area cm of loss that would occur if snowpack or water were not limiting; the program adjusts for SCA by applying ET only to snow free areas or the canopy, and potential sublimation only to canopy-intercepted snow or the SCA.

ET Computations

Actual ET, sublimation, the time step's interception losses, and values of ET from each soil layer are set to zero. Then three different, mutually-exclusive cases involving canopy-intercepted rainfall are considered, including (1) canopy interception alone is greater than PET, (2) the sum of canopy plus litter interception is greater than PET, and (3) the sum of canopy plus litter interception is less than PET.

(1) If rainfall-canopy interception exceeds potential ET:
  (a) Rainfall canopy interception is reduced by the amount of PET.
  (b) Interception loss is set equal to PET.
  (c) Litter interception volume is recorded, and control moves to that portion of the subroutine that computes sublimation; no PET remains for soil water adjustment.

(2) If the sum of rainfall canopy and litter interception exceeds potential ET:
  (a) Interception loss from rainfall canopy interception is set equal to existing interception.
  (b) Existing interception is set to zero.
  (c) Interception loss from the litter is computed as the remaining PET, adjusted for SCA.
  (d) Litter interception depth (on snow-free area) is reduced by remaining PET.
  (e) Litter interception volume is recorded, and control moves to that portion of the subroutine that computes sublimation; no PET remains for soil water adjustment.

(3) If the sum of rainfall canopy and litter interception is less than potential ET, some potential ET remains to affect soil water:
  (a) Rainfall litter interception loss is set equal to that total storage (adjusted for SCA). Litter interception depth and volume are set to zero.
  (b) Rainfall-canopy interception loss is equal to that total storage. Rainfall-canopy interception depth is set equal to zero.
  (c) If there is 100 percent snow cover, control moves to the portion of the subroutine that computes sublimation; no soil water adjustments are made (no provision for transpiration by trees through a snowpack currently exists).
  (d) With less than 100 percent snow cover, a determination of the fraction of remaining PET that can be realized from soil water is made. This fraction is a piece-wise (2-part) linear function of soil water content, similar to functions used by other researchers studying wildland ET (Black, 1979):

$$F = 1 - .1 \times (1 - (TH - THr) / (THs - THr)) \qquad TH > THr$$

$$F = .9 \times (TH - THw)/(THr - THw) \qquad THr > TH > THw$$

where: F = the fraction of PET that can be realized from a soil layer

TH = volumetric soil water content

THr = soil water content at which hydraulic conductivity becomes zero

THs = soil water content at saturation

THw = residual soil water content which cannot be lost to ET

(e) Total water available for ET from the soil is determined as:

$$W = (TH - THw) \times (\text{ soil depth })$$

where: TH = volumetric soil water content

THw = residual soil water content which cannot be lost to ET

(f) ET loss from the top (next iteration layer 2, etc.) soil layer is determined, and this value is added to total soil ET for this subunit. Each layer has a second parameter used to limit ET rates from lower layers to some fraction of that possible at the surface layer under similar soil water contents, which is a reflection of increasing resistance to evaporation increasing with soil depth. A layer-sensitive approach has been strongly recommended by other researchers (Sherratt and Wheater, 1984).

(g) Procedures (4) through (6) are repeated for each successively lower soil layer, then the program begins sublimation computations.

Sublimation Computations and Final ET Calculations

(1) If SWE and canopy-intercepted snow are zero, sublimation and time-step interception loss from the canopy are equal to zero, and:

(a) Values of ET from each soil layer are adjusted for SCA.

(b) Soil water content of each layer is adjusted for ET.

(c) Total subunit ET from the soil is adjusted for SCA.

(d) ET losses from intercepted water are added to subunit wide ET.

(e) Total sublimation loss is computed as the sum of sublimation from the snowpack surface and from snow interception (in this case, both are zero).

(f) Snowpack volume is computed after sublimation loss adjustment (here resulting in no change).

(g) Control is returned to the main program.

(2) If snowfall-canopy interception exceeds potential sublimation:

(a) Intercepted snow is reduced by the value of potential sublimation.

(b) Actual sublimation is set equal to potential sublimation.

(c) Values of ET from each soil layer are adjusted for SCA.

(d) Soil water content of each layer is adjusted for ET.
(e) Total subunit ET from the soil is adjusted for SCA.
(f) ET losses from intercepted water are added to subunit wide ET.
(g) Total sublimation loss is equal to that from snow interception.
(h) Snowpack volume is computed but unchanged by sublimation.
(i) Control is returned to the main program.

(3) If snowfall-canopy interception is less than potential sublimation:
(a) Snowfall-canopy interception loss is equal to that storage, and snowfall-canopy interception storage is set equal to zero.
(b) If SWE is positive, the ratio of SFW to SWE is computed, and potential sublimation (less that used on canopy interception) extracts snow and water from SWE and SFW in that ratio to the extent that SWE and SFW are available. SWE and SFW values are adjusted for this loss.
(c) Actual sublimation realized from the snowpack surface is adjusted for SCA.
(d) Values of ET from each soil layer are adjusted for SCA.
(e) Soil water content of each layer is adjusted for ET.
(f) Total subunit ET from the soil is adjusted for SCA.
(g) ET losses from intercepted water are added to subunit wide ET.
(h) Total sublimation loss is equal to that from snow interception plus that lost from SWE.
(i) Snowpack volume is computed with changes caused by sublimation, and control is returned to the main program.

Soil Water Deficit on Riparian Areas (Subroutine RIPARIAN)

This subroutine computes the soil water deficit of riparian areas. Riparian areas are those lands adjacent to a stream or other body of water, or that have a saturated or seasonally-saturated subsurface layer within the rooting zone. For purposes of this program, riparian areas are those areas which can replace evapotranspired water by withdrawing water from a stream subunit. This enables them to maintain a minimum soil water content as long as sufficient water flows within the stream segment (or lake or pond) defined by that subunit as its recharge source. The minimum soil water content maintained has been fixed at the water content at which unsaturated conductivity reaches zero, which allows ET to occur at 90 percent (currently) of the potential rate.

The stream subunit that serves as a recharge source for a riparian subunit is defined by the user in the hydrologic constants input file.

No chemical changes occur in this subroutine. Operationally:

(1) If the subunit has no designated recharge stream, initial and adjusted values of the soil water deficit are set to zero, and control is returned to the main program.

(2) The initial and adjusted deficit values on subunits with designated recharge streams are set to zero.

(3) Each layer is checked for a deficit, and existing deficits recorded.

(4) Control is returned to the main program.

Recharge of Depleted Riparian Areas from Streamflow (Subroutine RIPCHARG)

This subroutine determines if streamflow is available for riparian recharge and, if so, adds streamflow to the soil of those riparian areas from their designated recharge stream.

RIPCHARG is called from outside the main programs time step and subunit loop, so that before it is reached, most other computations have been accomplished on all other subunits for the current time step. Exceptions to this are limited to stream subunits, for which subroutines INFLOW, SOILDRAN, and STREAMET are called from within this routine. This shift is necessary because computations for a given subunit cannot be completed before those for all subunits that may contribute water and chemical constituents to it. In contrast, riparian recharge may flow "upstream"; a subunit that contributes flows to a stream subunit during wet seasons may be recharged by it during dry seasons.

When called, RIPCHARG goes through the stream subunits in their program-determined computational order. Inflows, surface runoff, and evaporation are first determined for the stream subunit. Any surface runoff left after evaporation may then be used to recharge riparian areas dependent on this stream. Computationally:

(1) The routine looks at stream subunits from upstream to downstream order.

(2) Inflow, surface runoff, and evaporation are computed.

(3) All subunits are checked to see if this stream subunit is their designated recharge source. If it is the designated recharge source and a deficit exists, then:

(4) streamflow is reduced, soil water content of the recharged subunit is increased, chemicals are moved from the streamflow to the soil, and the adjusted (or eliminated) deficit is recorded.

(5) The amount of streamflow lost (if any) due to recharging this riparian subunit is added to existing loss caused by recharge of other riparian subunits, and control returns to the main program.

Evaporation and Sublimation on Streams (Subroutine STREAMET)

Given potential ET and potential sublimation (from files), this routine computes adjusted sublimation and ET values for stream subunits. Lakes or ponds can also be entered as stream subunits, with the recognized limitation that storage is not tracked on stream subunits. Computationally:

(1) Interception losses and soil water content are set to zero.
(2) If both potential sublimation and potential evapotranspiration are zero, control returns to the main program
(3) If the stream is thawed, PET is used to the extent possible to reduce surface runoff, which is equivalent to streamflow on stream subunits. Sublimation is set to zero.
(4) If the stream is frozen, computations are selected from a set of mutually exclusive alternatives:
    (a) If the sum of SWE and SFW exceeds potential sublimation, SWE is reduced by potential sublimation. In those few cases where this results in a negative snowpack (SFW was needed to make the sum SFW + SWE exceed sublimation), sublimation is reduced enough to make the snowpack zero, and SFW is set to zero as it is presumed insignificant.
    (b) If the snowpack on ice is gone but the stream received surface runoff from other subunits, this "over ice" flow is reduced using the greater of ET or sublimation.
    (c) If SWE + SFW on the ice is less than potential sublimation, sublimation is equal to that sum, and SFW, SWE, and ET are set to zero. Ice other than that tracked as SWE does not sublimate in this model.
(5) Snowpack volume is adjusted to account for sublimation loss.
(6) Control is returned to the main program.

Water Balance Outputs (subroutine WATERBAL)

This subroutine does the computations necessary to create the inputs and outputs, storage, and changes in storage files described under the heading "Output". It is self-explanatory.

Miscellaneous Subroutines and Files

CHEMBAL

This subroutine was primarily used during debugging of chemical mass balance computations, but may be worth saving for modification as a standard output. It creates a file called "chembal.out" which shows chemical storage and outputs from each subunits various compartments. Currently, only the number of moles of the first type 1 input component are output, but it could be easily modified to include all type 1 component species. This modification has not been made to date because of the size of the resulting output file.

Figure C-7: AHM output file "INOUT.OUT". This file contains a list of the inputs and outputs (water) for each subunit.

```
SUBUNIT INPUTS AND OUTPUTS
         *                  INPUTS (cm )                                 *              OUTPUTS (cm )
SUB TY  WY*   Rain        Snow        Ripar. Pr   Horiz. Pr  Surface Pr* Surface     Evapo-     Sublim-     Horiz.      Ripar
 #  PE DAY*                           Rechar. U#  drain. U#   Runoff U#*  Runoff     Trans.      ation     Drainage     Rechar

 1  N    1 0.0000E+00 0.0000E+00 0.5338E-01  7                          0.0000E+00 0.7393E-01 0.2699E-02 0.0000E+00 0.0000E+0
                                              0.0000  5    0.0096  5
 2  N    1 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.0000E+00 0.7393E-01 0.2699E-02 0.0000E+00 0.0000E+0
                                              0.0000  5    0.0096  5
 3  N    1 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.0000E+00 0.7394E-01 0.2699E-02 0.0000E+00 0.0000E+0
                                              0.0000  5    0.0096  5
 4  N    1 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.0000E+00 0.7405E-01 0.2699E-02 0.1875E-01 0.0000E+0
                                              0.0000  5    0.0097  5
 5  R    1 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.1091E-01 0.0000E+00 0.2699E-02 0.0000E+00 0.0000E+0
 6  n    1 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.0000E+00 0.4445E-01 0.2699E-02 0.1500E+00 0.0000E+0
                                              0.0000  5    0.0096  5
 7  S    1 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.1080E+01 0.2421E+00 0.0000E+00 0.0000E+00 0.5619E-0
                                              0.0000  1    0.0000  1
                                              0.0000  2    0.0000  2
                                              0.0000  3    0.0000  3
                                              0.0241  4    0.0000  4
                                              0.0000  5    0.0935  5
                                              1.2105  6    0.0000  6

 1  N    2 0.0000E+00 0.0000E+00 0.1545E-01  7                          0.0000E+00 0.3700E-01 0.2501E-02 0.0000E+00 0.0000E+0
                                              0.0000  5    0.0101  5
 2  N    2 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.0000E+00 0.3670E-01 0.2501E-02 0.0000E+00 0.0000E+0
                                              0.0000  5    0.0101  5
 3  N    2 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.0000E+00 0.3632E-01 0.2501E-02 0.0000E+00 0.0000E+0
                                              0.0000  5    0.0101  5
 4  N    2 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.0000E+00 0.3703E-01 0.2501E-02 0.7914E-02 0.0000E+0
                                              0.0000  5    0.0101  5
 5  R    2 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.1144E-01 0.0000E+00 0.2501E-02 0.0000E+00 0.0000E+0
 6  n    2 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.0000E+00 0.2224E-01 0.2501E-02 0.1239E+00 0.0000E+0
                                              0.0000  5    0.0101  5
 7  S    2 0.0000E+00 0.0000E+00 0.0000E+00  0                          0.9031E+00 0.2035E+00 0.0000E+00 0.0000E+00 0.1626E-0
                                              0.0000  1    0.0000  1
                                              0.0000  2    0.0000  2
                                              0.0000  3    0.0000  3
                                              0.0102  4    0.0000  4
                                              0.0000  5    0.0980  5
                                              1.0000  6    0.0000  6
```

Figure C-8: AHM output file "STOR.OUT". This file is a listing of the water storage in various compartments of each subunit at the end of each time-step.

```
                                       Subunit Average Storage (cm )

SUB  TY  WY    Rain    Rain     Snow   Snowpack Snowpack TOT Soil  Soil by     TOTAL     Snow    I-O-STOR
 #   PE  DAY  Litter  Canopy   Canopy  Free H20  H20 Eq.  Storage   LAYER     STORAGE  Cov. Area  BALANCE

 1   N    1   0.0000  0.0000   0.0000   0.0186   0.3721  20.0000  20.0000     20.3907   0.0280    0.0000
 2   N    1   0.0000  0.0000   0.0000   0.0186   0.3721   7.9466   7.9466      8.3373   0.0280    0.0000
 3   N    1   0.0000  0.0000   0.0000   0.0186   0.3721   6.9466   6.9466      7.3373   0.0280    0.0000
 4   N    1   0.0000  0.0000   0.0000   0.0186   0.3721   1.9278   1.9278      2.3185   0.0280    0.0000
 5   R    1   0.0000  0.0000   0.0000   0.0186   0.3721   0.0000   0.0000      0.3907   0.0280    0.0000
 6   n    1   0.0000  0.0000   0.0000   0.0186   0.3721  15.8261  15.8261     16.2168   0.0280    0.0000
 7   S    1   0.0000  0.0000   0.0000   0.0000   0.0000   0.0000   0.0000      0.0000   0.0000    0.0000

 1   N    2   0.0000  0.0000   0.0000   0.0179   0.3588  20.0000  20.0000     20.3768   0.0260    0.0000
 2   N    2   0.0000  0.0000   0.0000   0.0179   0.3588   7.9315   7.9315      8.3083   0.0260    0.0000
 3   N    2   0.0000  0.0000   0.0000   0.0179   0.3588   6.9319   6.9319      7.3086   0.0260    0.0000
 4   N    2   0.0000  0.0000   0.0000   0.0179   0.3588   1.9044   1.9044      2.2812   0.0260    0.0000
 5   R    2   0.0000  0.0000   0.0000   0.0179   0.3588   0.0000   0.0000      0.3768   0.0260    0.0000
 6   n    2   0.0000  0.0000   0.0000   0.0179   0.3588  15.7015  15.7015     16.0783   0.0260    0.0000
 7   S    2   0.0000  0.0000   0.0000   0.0000   0.0000   0.0000   0.0000      0.0000   0.0000    0.0000
```

Figure C-9: AHM output file "DSTOR.OUT". This file is a listing of the changes in water storage in various compartments of each subunit between the end of the previous and current time step.

```
                                        Subunit Average Changes in Storage (cm )

SUB  TY   WY    Rain      Rain      Snow   Snowpack  Snowpack  Soil H20     TOTAL     TOTAL     TOTAL  I-O-STOR
 #   PE  DAY   Litter    Canopy    Canopy  Free H20   H20 Eq.   Storage    INPUTS   OUTPUTS Chng STOR   BALANCE

  1   N    1   0.0000    0.0000    0.0000   -0.0004   -0.0132    0.0000    0.0630    0.0766   -0.0136     0.0000
  2   N    1   0.0000    0.0000    0.0000   -0.0004   -0.0132   -0.0534    0.0096    0.0766   -0.0670     0.0000
  3   N    1   0.0000    0.0000    0.0000   -0.0004   -0.0132   -0.0534    0.0096    0.0766   -0.0670     0.0000
  4   N    1   0.0000    0.0000    0.0000   -0.0004   -0.0132   -0.0722    0.0097    0.0955   -0.0858     0.0000
  5   R    1   0.0000    0.0000    0.0000   -0.0004   -0.0132    0.0000    0.0000    0.0136   -0.0136     0.0000
  6   n    1   0.0000    0.0000    0.0000   -0.0004   -0.0132   -0.1739    0.0096    0.1971   -0.1875     0.0000
  7   S    1   0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    1.3281    1.3281    0.0000     0.0000

  1   N    2   0.0000    0.0000    0.0000   -0.0007   -0.0133    0.0000    0.0256    0.0395   -0.0139     0.0000
  2   N    2   0.0000    0.0000    0.0000   -0.0007   -0.0133   -0.0151    0.0101    0.0392   -0.0291     0.0000
  3   N    2   0.0000    0.0000    0.0000   -0.0007   -0.0133   -0.0148    0.0101    0.0388   -0.0287     0.0000
  4   N    2   0.0000    0.0000    0.0000   -0.0007   -0.0133   -0.0234    0.0101    0.0474   -0.0373     0.0000
  5   R    2   0.0000    0.0000    0.0000   -0.0007   -0.0133    0.0000    0.0000    0.0139   -0.0139     0.0000
  6   n    2   0.0000    0.0000    0.0000   -0.0007   -0.0133   -0.1246    0.0101    0.1487   -0.1385     0.0000
  7   S    2   0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    1.1082    1.1082    0.0000     0.0000
.
.
.
```

COMMON.FOR

The file "common.for" contains what is known as a "blank common" list of variables and their (matrix) dimensions that are obtained from reading the data supplied by the user. It also contains a "named common" block of those variables which are initial conditions. There are also two parameter sets in this file which can be adjusted as needed, after which the source code for the entire program must be re-compiled. These parameters are NNU, the maximum number of subunits that can be user defined (currently set to 25), and NL, the maximum number of soil layers that may be present in single subunit (currently set to 3). The variables in this file are defined in the main program listing.

Common.for is read in by the FORTRAN compiler during program compilation and becomes a part of essentially all subroutines in the program. Placing common variables in a separate file greatly simplifies modifications to the program that involve addition or deletion of these variables.

COMMON2.FOR

The file "common2.for" contains a "labeled common" block called "compute", which are those common variables obtained through computations done by the program. The variables in this file are defined in the main program listing. As with "common.for", placing common variables in a separate file greatly simplifies modifications to the program that involve addition or deletion of these variables.

COMMONC.FOR

This file contains chemical values in common storage that are used throughout AHM and are transferred to the MINEQL routine before equilibration. It does not include common variables used only within the MINEQL routine.

DEPTH

DEPTH is a subroutine that converts selected variables from volumes in cubic meters to areal depths in centimeters. It is used only after subroutine VOLUME has converted the same variables to cubic meters from depths in centimeters. The conversion to meters occurs because areal depths are not additive when flow from one subunit enters another.

Generally, subroutines DEPTH and VOLUME convert more values than necessary for a given computation; this allows the same subroutines to be used whenever conversion is necessary.

FLAG.FOR

FLAG.FOR is an include file that must be present during compilation. It contains a few common variables specific to the MINEQL routine.

GHSTBST, GHSTBST1, MBUST, and MBUST1

These subroutines are present to check for cases where array dimensions may be exceeded in the course of a program run. If a compiler is used that can detect runtime array limit violations, these routines may be removed if desired.

IONC.DAT

IONC.DAT is an input data file that must be present when running the program; it should not be modified by the user. It contains stoichiometry data used in chemical equilibration. It may subsequently be moved into the program with a data statement, eliminating the need for the external file.

IONIC.FOR

IONIC.FOR is an include file that must be present during compilation. It contains a few common variables specific to the MINEQL routine.

IWYDATE

This function converts month and day to water year day, where October 1 equals 1, and September 30 equals 365. Currently, no adjustment for leap years is made. It is called from READDAT for determining the starting date of the data, the date streams freeze and thaw, and dates of rainfall or snowfall.

PARAMETR.FOR

PARAMETR.FOR is an include file that must be present during compilation. It sets limits for array sizes and a few other parameters. These include:

ITMAX = maximum number of iterations MINEQL routine will make before ending attempts to reach a solution.

MCHNG = a number 1 greater than max number of MINEQL type 7 species which user can enter in his chemical initial condition file.

MCOMP = max number of MINEQL type 1 components

MCOMPART = number of water storing compartments in most complex watershed subunit (must equal 10 plus the number of soil layers on the subunit with the most soil layers)

MTYP36 = max number of combined species types 2-6 which user can enter, including the blank line after each type's list of species ID's; this limitation applies only to input in the chemical initial condition files (more species may be present in the THRM.DAT file)

MSPEC = max number of species in equilibration computation

MTHERM = max number of species for which thermodynamic data may be included in file thrm.dat

NPRECOMP = (Max) number of chemical components in precipitation

NNalk = max number of species that can be used to make up total acid-neutalizing capacity. All compartments that are run through MINEQL must contain at least those species which the user enters in the alkalinity computation input file

NNU = maximum number of subunits program can handle; value larger than necessary is OK.

NL = maximum number of soil layers program can handle; a value larger than necessary for a given run is OK.

RIntFrac = fraction of rainfall that passes into canopy interception and that mixes with canopy interception; for snowfall fraction that passes into interception

PARM.FOR

PARM.FOR is an include file that must be present during program compilation. It contains some parameters specific to chemical equilibration, kinetics, and mass balance routines.

RAINADJ

This subroutine can be used to provide adjusted rainfall values on a subunit when the station measuring precipitation is some distance away. Two methods are available. These are:

$$PRECIP = PRECIP + F \times ((Elev - BaseElev)/1000.) \times PRECIP$$

and

$$PRECIP = PRECIP \times F$$

where: PRECIP = rainfall or snowfall, centimeters

F = a parameter supplied by the user

Elev= elevation of the subunit, meters

BaseElev = elevation where precipitation is measured

For modeling work done on the Emerald Lake basin, we averaged precipitation values from two measurement sites for the value PRECIP as used above. Precipitation was adjusted using the first method above with F = 0.0, giving each subunit the same, watershed-wide average precipitation.

SNOWADJ

This subroutine is functionally identical to subroutine RAINADJ, except that it adjusts snowfall values. Its function was once performed by subroutine RAINADJ, and this routine was added only for purposes of avoiding some duplication of memory storage locations that were required when only one routine was used. All comments about subroutine RAINADJ are applicable, but refer to snowfall adjustment.

SUBUSEQ, READORD, UORDER, ORIOIN, ORINIU

This group of subroutines is lumped together because together they perform a single task, which is determination of the order in which watershed subunits are selected for computation. With this subroutine, the user need only provide the program with the subunit(s) that receive flow from each subunit individually. Given this, these subroutines determine the source of inflows to each subunit, and the order in which outflows from each subunit must be made available so that inflows to the next watershed subunit are available when required for its set of hydrological computations. This frees the user from the task of determining computational order and from requirements to input hydrological parameters for subunits in any specific sequence.

Subroutine SUBUSEQ writes a summary table to the output file XCHECK, and READORD reads the user supplied matrix showing the subsequent disposition of flow from each subunit.

SURFCOM.FOR

SURFCOM.FOR is an include file that must be present during program compilation. It includes common variables specific to chemical reactions on surfaces in the MINEQL routine.

TEMPADJ

This subroutine adjusts air temperature for each subunit based on moist or dry adiabatic air temperature lapse rates, subunit unit and base station elevation, and presence or absence of precipitation on a given day.

The presence of this subroutine is a holdover from an earlier version of the model that calculated PET. Currently, it remains in the program only because it may become useful later on in program development.

Without PET computation, air temperature plays no role in the water balance as currently formulated; therefore, further discussion of this subroutine is unnecessary.

VAR.FOR

VAR.FOR is an include file that must be present during program compilation. It includes common variables specific to chemical equilibration, kinetics, and mass balance routines.

VOLUME

VOLUME is a subroutine that converts selected variables from areal depths in centimeters to volumes in cubic meters. The conversion to meters occurs because areal depths are not additive when flow from one subunit enters another. After this subroutine is called and volumes are no longer necessary for the computation at hand, subroutine DEPTH is called for reconversion to areal depth.

Generally, subroutines DEPTH and VOLUME convert more values than necessary for a given computation; this allows the same subroutines to be used whenever conversion is necessary.

ZERO

When called, this subroutine sets values of selected variables to zero.

Program Outputs

With a large computer program such as AHM, it is difficult to determine in advance what the form of output values should be. Outputs desired will vary with the particular use being made of the program, and can readily be tailored to specific user needs.

Currently, several standardized output files are generated whenever the program is run. These include:

(1) a file that is used by the user to cross check the validity of input values (Figure C-1)
(2) consolidated input files (Figures C-2 through C-4)
(3) a detailed chemical equilibration output summary by subunit and compartment; this file can become massive, (over 20 megabytes in our test runs) so it can optionally be avoided (Figure C-5)
(4) a file with subunit, compartment, pH, ANC, water discharge, and water year day; this file is used (in conjunction with supplemental program graphanc) to create output files for graphing (Figure C-6)
(5) a summary file showing inputs and outputs by subunit (Figure C-7)
(6) a summary file showing subunit-average storage in various components of each subunit (Figure C-8)
(7) a summary file showing subunit-average changes in storage in various components of each subunit (Figure C-9)

There is also a subroutine present for generating custom outputs for any given run. This subroutine must be modified as required by someone with some knowledge of FORTRAN programing and AHM. Currently it creates a file with the water year day, surface runoff from stream subunit 7 (Emerald Lake, in our initial test run) in cubic meters/day, and calculated ET in centimeters from each of the seven subunits used in our initial test runs. The latter file was used to generate the plots of modeled lake outflows from initial tests with Emerald Lake data (text, Figures 5-6, 5-7).

Table C1. Components and Identification Numbers

1	Ca^{2+}	101	CO_3^{2-}
2	Mg^{2+}	102	SO_4^{2-}
3	Sr^{2+}	104	F^-
4	K^+	105	Br^-
5	Na^+	106	I^-
6	Fe^{3+}	107	NH_3
7	Fe^{2+}	108	S^{2-}
8	Mn^{2+}	109	PO_4^{3-}
9	Cu^{2+}	112	SiO_3^{2-}
10	Ba^{2+}	149	SO_3^{2-}
20	Al^{3+}	157	NO_3^-
22	Li^+	159	SOH
34	M^+	160	ECM0
35	M^{2+}	163	L^-
36	M^{3+}	164	L^{2-}
37	M^{4+}	165	L^{3-}
38	X38	166	L^{4-}
39	X39	167	X167
40	X40	168	X168
50	H^+	169	X169
99	e^-		

APPENDIX D

AHM USER'S GUIDE

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APPENDIX D

AHM USER'S GUIDE

AHM is a large, detailed, and flexible model. A substantial portion of its flexibility is obtained through the use of external input files in place of built-in functions.

One drawback to this structure is that a large number of input files, some of which are very large themselves, may be required for a given run.

This appendix provides the following:

(1) An overview necessary to understanding the remainder of the user's guide;

(2) Descriptions of the input files required for a run;

(3) An example of interactively starting the program once the input files are prepared; and

(4) A listing of the FORTRAN modules that are compiled and linked to create the program.

There are three types of exhibits used here: Figures, Tables, and Files. "Files" are essentially figures showing examples of the files used for various input data. In most cases, the files shown correspond to the actual files, or truncated versions of those files, used in initial test runs on the Emerald Lake basin. These files are provided in machine-readable form along with this documentation. Required input values and formats are described in the Files.

This appendix cannot stand alone. Ambiguities in the text, the figures, or files of this appendix will most often be clarified by Appendix C, which contains descriptions of the subroutines.

D1 Watershed Subdivisions

Prior to running the program, the user subdivides the watershed(s) to be analyzed into a number of subunits. Individual subunits should have similar elevation, slope, aspect, soils, vegetation, snowmelt, and ET rates. The subunits need not be contiguous, and portions of a given subunit may be tributary to different stream segments or a mixture of stream and non-stream subunits if so desired. Surface and subsurface drainage from a given subunit may be routed to up to eight different receiving subunits, based on the portion of the subunit's area contributing flows to the individual receiving subunits. The primary purpose of this feature is to reduce the total number of computations required by a given run. Computational time required and the size of output files are approximately proportional to the total number of subunits selected.

File 1: AHM input file named *seq.rw1* used in initial test runs. This file describes routing of flows between watershed subunits and enables AHM to determine computational sequence necessary for a given run. Data is number of the subunit(s) which receive(s) flows from a subunit (in order by line), and portion of the subunit's flows received by receiving subunit. Portions of flow from a subunit may be received by up to eight other subunits. In this example, subunit number 5 is all rock outcrops on the Emerald Lake basin. The rock outcrop is contributing flows to the lake (70%), subunit 1 (0.19%), subunit 2 (1.33%), subunit 3 (11.59%), etc. Flows from subunit 7 (Emerald Lake) go to subunit "zero", effectively leaving the model. Format 8(I5, F5.0).

```
 7   1.
 7   1.
 7   1.
 7   1.
 7   .7    1.0019    2.0133    3.1159    4.0232    6.1457
 7   1.
 0   1.
```

The subunit's flow and chemical outputs are apportioned to the receiving subunits based on the user's inputs (File 1). File 1 contains one line for each subunit used in a run, the first line corresponding to flows from subunit one, the second flows from subunit two, etc. Each line lists the number(s) of the receiving subunit(s) and the proportion(s) of the total flux from the "donating" subunit received.

In addition to watershed subdivisions, AHM internally subdivides individual subunits into a number of compartments based on subunit type and other user inputs. For example, if a positive canopy rainfall interception storage is entered, the subunit acquires a compartment internally tracked as compartment 3 (Table D1). While internally defined, it is important that the user remember those compartments present on a given subunit, as chemical initial conditions, kinetics, and some inputs must be added on a subunit and compartment basis.

Table D1: Compartment numbers used by AHM

Compartment Number	Description
1	Rainfall litter interception on snow-free area (SFA)
2	Canopy snowfall interception
3	Canopy rainfall interception
4	Snowpack water equivalent (frozen portion)
5	Snowpack free water
6	Snowpack drainage
7	Surface runoff from the subunit
8	Soil horizontal drainage from the subunit
9	Soil horizontal drainage received by the subunit
10	Surface runoff received by the subunit
11	"Interception" storage on litter (or rock) beneath the snowpack (from snowpack drainage)
12+	Soil water in each layer

D2.Running the Program

AHM uses a combination of interactive and file based inputs. This enables the user to have a degree of interactive control over the program on an individual run, while allowing the majority of the data inputs to be separately stored in files which can be re-used for a number of separate runs.

When WY date is required as an input in a file, October 1 is treated as day one. No provision has been made for leap years.

D3 Interactive Input

Interactive selections include:

(1) Choice of debugging options (debug generates a great deal of output to the screen that should be useful in tracking errors, particularly if program modifications are attempted)

(2) Period of run (with appropriate data files)

(3) Output units

(4) Water balance only or water balance with chemistry

(5) Amount of chemical data output

(6) "First flush" type snowpack chemistry elution or chemical movement from snowpack proportional to fraction of total snowpack melted (only the latter method is recommended at this time due to a problem related to discrete time-steps with a continuous function)

Figure D.1 contains an example of interactive input and output.

D4. Calculation of Chemical Equilibrium

Chemical equilibration is accomplished by a set of subroutines collectively referred to as MINEQL in this document. These routines were developed independently of AHM and have been adapted with only cosmetic and I/O modifications. Each chemical species is assigned a unique ID number.

D5. Input Data Files

AHM requires 15 types of input data files; the actual number of unique input files needed varies with the number of watershed subunits, the options chosen in a run, and the number of files which may be re-used by other subunits and compartments.

As some of these input files may become quite large and cumbersome, some additional support programs have been written that can greatly simplify input file creation. These programs are described in the Appendix E.

Figure D1: Example of the AHM program's interactive user interface.

```
Enter 1 to run in debug mode, any other number to not debug > 2
Enter 3 to limit normal output to selected period. > 2
How many subunits (including stream segments)
are in the watershed? > 7
 Enter month, day data files (and run) is to begin > 10 1
 How many days do you want the program to run? > 365
 Select output units; 1=m3, 2=cm, 3=ft3, 4=in. > 2
 Enter name of file with NAMES of files containing
 hydrologic and chemical constants and observed
 climatic data > infiles3.289                          (see File 2)
 Enter 1 for water balance only (no chemistry) > 2
 Enter 1 if massive chemical output is desired > 1
 Snow chemistry option: for decay option, enter 1 > 2

File emlhcons.289[1]          - phys. hydrol. const.     (see File 3)
File chemname.f               - chemical I.C. Fnames     (see File 4)
File rain.rwl                 - observed rainfall        (see File 5)
File snow.rwl                 - observed snowfall        (see File 6)
File seq.rwl                  - flow routing matrix      (see File 7)

 Reading chemical initial condition/kinetics files[2]

 Completed reading thrm.dat; reading ionc.dat
                                Reading rainfall, snowfall, WY Day    1
                                Reading rainfall, snowfall, WY Day    2
```

---

[1] The following 5 lines are output for the user to cross-check whether or not the input file names (from Figure 2) were input in correct sequence; the comment following the name indicates the file type being sought by the program.

[2] This output indicates (1) the number of chemical components present in each subunit/compartment's initial condition file, and the number of compartments in a subunit; soil covered units have 11 + number of soil layers, rock units have 11, and "streams" have 10.

Figure D1 (continued): Example of the AHM program's interactive user interface.

```
File smcasub.1                - snow melt/C. A. SUB.
File smcasub.2                - snow melt/C. A. SUB.
File smcasub.3                - snow melt/C. A. SUB.
File smcasub.4                - snow melt/C. A. SUB.
File smcasub.5                - snow melt/C. A. SUB.
File smcasub.6                - snow melt/C. A. SUB.
File smcasub.7                - snow melt/C. A. SUB.

Creating consolidated input file, subunits  1 through  7
for snow melt/C. A. SUB.

File petrwl.1                 - Potential ET
File petrwl.2                 - Potential ET
File petrwl.3                 - Potential ET
File petrwl.4                 - Potential ET
File petrwl.5                 - Potential ET
File petrwl.6                 - Potential ET
File elake.cm                 - Potential ET
Creating consolidated input file, subunits  1 through  7 for PET

                             Water balance complete, water year day #  1

Adjusting K values, type 3 Chem. species, WY Day   2

                             Water balance complete, water year day #  2
...
 AHM run ended normally.
```

Seven species types are used in the MINEQL routine. As they are referred to by terms that have a particular significance outside of their normal use they will be defined.

Type I Species are the dissolved species that correspond to the components and have ID numbers below 200 (Table D2). In a mathematical sense components are the independent basis set from which every species can be defined and upon which the mass balance equations are based. In a chemical sense, the components are a set of chemical entities such that every species can be represented as the product of a reaction involving only these components, and no component can be represented as the product of a reaction involving only these components, and no component can be represented as the product of a reaction involving only the other components. The particular set of components for a given problem is certainly not unique, but once a set of components has been chosen, every species has a unique representation in terms of this set. Numbers from Table D2 much be used for components; there are user-defined components in the table.

There are two different groups of "Type II" species. Those entered by the user as Type II in initial condition files (File 5, no Type II species shown) are simply those Type I component species that do not mix between compartments; an example is soil surface reaction sites. These are known as AHM Type II species, or non-mixing MINEQL Type I species. The other Type II species (MINEQL Type II) are the first species listed in the thermodynamic data file thrm.dat (File 11). This latter group is also listed in the output file BIGCHEM.OUT, and discussed next. The latter group of Type II species cannot be entered in initial condition files.

Type II Species are the complexes -- all dissolved species that are not components. They have ID numbers from 1000 to 20000, and are in the file THERM.DAT. Mathematically, a species represents a log-linear combination of the components; chemically, a species is the product of a chemical reaction involving the components as reactants. The concentration (activity) of every dissolved species is variable, being a function of the concentration of the components of which the species is composed. There are two types of Type II species in AHM, those that are transported between compartments and those that are fixed (i.e. adsorption sites on soil).

Type III Species are precipitated solids that are not allowed to dissolve, even if the amount of these solids becomes negative. Examples are gases at a fixed partial pressure, or simply a solid phase that is specified to be present. Mathematically, Type III species are represented in the same manner as Type II species. Only $CO_2(g)$, species 25000, is defined in THERM.DAT.

Type IV Species are precipitated solids that are subject to dissolution if the amount present becomes less than zero. Mathematically, solid species are represented in the same manner as aqueous species. Solids are species of a fixed activity -- for normal solid phases such as $CaCO_3$, $Ca(OH)_2$, etc. this fixed activity is set equal to one. This implies a certain fixed relationship among the components, with the result that the chemical equilibrium-problem loses one degree of freedom. This is equivalent to transforming the set of components to include the solid phase, which is then set at fixed activity. If, after a chemical equilibrium computation has been made with a given solid phase, the amount of that solid phase is calculated to be negative, the solid may be dissolved, (i.e., removed from the computation) and the fixed relationship among the constituents removed. These have ID's from 20000 to 25000 and are found in THERM.DAT.

Type V Species are dissolved solids that are subject to precipitation if the solubility product is exceeded. The mass-law expression is the same as when the species is listed as a precipitated solid. Type V dissolved solids play no direct role in a chemical equilibrium computation. The fact that a dissolved solid exists indicates simply that the solubility data for the solid are present, and after an equilibrium computation has been made, the solubility of this solid phase may be checked. If the solubility product is exceeded, the solid may be precipitated and become directly involved in the computation. ID's are the same as for Type IV.

Table D2. Components and Identification Numbers

1	Ca^{2+}	101	CO_3^{2-}
2	Mg^{2+}	102	SO_4^{2-}
3	Sr^{2+}	104	F^-
4	K^+	105	Br^-
5	Na^+	106	I^-
6	Fe^{3+}	107	NH_3
7	Fe^{2+}	108	S^{2-}
8	Mn^{2+}	109	PO_4^{3-}
9	Cu^{2+}	112	SiO_3^{2-}
10	Ba^{2+}	149	SO_3^{2-}
20	Al^{3+}	157	NO_3^-
22	Li^+	159	SOH
34	M^+	160	ECM0
35	M^{2+}	163	L^-
36	M^{3+}	164	L^{2-}
37	M^{4+}	165	L^{3-}
38	X38	166	L^{4-}
39	X39	167	X167
40	X40	168	X168
50	H^+	169	X169
99	e^-		

File 5: AHM input data file with user-selected name *chemicl.289* used in initial test runs. This file contains chemical initial conditions and parameters for a given compartment of a single subunit. Data include:
line

1: Capacitance (F/m^2) and specific surface area (m^2/g), format 2F10.0 (capacitance is only used if adsorption includes electrostatic corrections). Specific surface (or area of rock interception surface relative to planimetric area) is used in determining weathering rates as well a surface adsorption reactions. Leave both values blank on dummy files for compartments not present on a given subunit. Enter a non-zero dummy number for specific surface on stream (subunits surface runoff compartment).

2+: AHM type 1 species (component) ID numbers, total number of moles initially present in the compartment, and estimated fraction of that total expected to exist as the component (e.g., fraction of total ammonia present as NH_3). Format I5, 5X, E10.2, F10.2.

Blank line

Next: the number 2-7, corresponding to AHM species type, Format I5. AHM type 2 species are MINEQL type 1 species, but only those which do not move between compartments, such as soil surface reaction sites. AHM type 2 species are entered with the same format as AHM type 1 species, above. (MINEQL type 2 species cannot be entered in this file). Others (MINEQL types 3-7) are equivalent to those defined in MINEQL documentation, except stoichiometry data may not be entered in this file, only log Ks. This is useful if different log Ks or partial pressures apply to different compartments.

Following AHM species type number are individual species ID numbers, and the $\log_{10}$ of their K values (if different from those in file thrm.dat). Format is I5, 5X, F10.2.

A blank line is inserted before each group of a given species type (2-7).

At least two blank lines are used to end the input file.

```
         1.      1.20
    1         1.470E+1         1.
    2         2.880E+0         1.
    4         3.360E+0         1.
    5         1.206E+1         1.
   50         1.263E+1         .1
  101         1.020E+0         .5
  102         6.000E+0         .1
  103         3.312E+1         1.
  107         8.640E+0         .1
  109         6.000E-3         .5
  112         6.000E-3         .5
```

```
  157       4.734E+1        1.

    3
25000          20.50
```

File 11: Example of AHM input file *thrm.dat* (this example was not used in the initial test runs). This file contains thermodynamic data and stochiometry for MINEQL type 2-6 species. It is identical in format to the file used by the original MINEQL program, except the number of species of each type need not be defined at the beginning of each group of a single type. Species types 2, 3, 4, 5, 6, and 7 are separated by a single blank line, or two blank lines if two successive types are not present in the file. The user can add to this file if more species are to be considered.

Parameter MTHERM in FORTRAN ("include") file parametr.for limits the maximum number of species which may be entered in the thrm.dat file. Data in each line include primary chemical species (such as HCO_3^-) ID number (can be user-assigned, so long as it is greater than 200), log10 K value, ID number (1-200) of component(s) of the complex (such as HCO_3^-) and stoichiometric coefficient of the component(s) molecule of the species ($NaHCO_3$). Up to 4 component/coefficient pairs can be used to define a species. Format is I5, 2X, F7.2, 4(I4,I3).

```
 2670    -1.70   6  1  50 -1               (MINEQL type II species
 2680    -4.70   6  1  50 -2
 2690   -20.10   6  1  50 -3               (this line represents FeOH3)
 2700   -21.50   6  1  50 -4
10340    -4.50  20  1  50 -1
10341   -12.00  20  1  50 -2                                         swag
10350   -23.10  20  1  50 -4
12530    10.20  50  1 101  1
12540    16.50  50  2 101  1
12570     9.00  50  1 107  1
12600    12.50  50  1 109  1
12610    19.90  50  2 109  1
12620    21.90  50  3 109  1                 (this line represents H3PO4)
12710    13.10  50  1 112  1
12720    22.70  50  2 112  1
13591     7.40  50  1 167  1 160  1
13592   -10.00  50 -1 167  1 160 -1
13593    22.00  50  1 167  1 102  1 160 -1
13595   -14.00  50 -1

15000    13.20   6  1   7 -1  99  1        ( MINEQL Type 3 species )

                                           ( MINEQL Type 4 species (none))
20000     8.30   1  1 101  1               ( MINEQL Type 5 species )
20010     4.70   1  1 102  1
20030    45.10   1  5  50 -1 109  3
20050    19.30   1  1  50  1 109  1
20070     8.70   1  1 112  1
20130   -21.90   1  1  50 -2
20140     5.40   2  1 101  1
20160    28.40   2  3 109  2
20200   -16.40   2  1  50 -2
```

```
20280    25.80   6  1 109  1
20310    -3.00   6  1  50 -3
20370    10.40   8  1 101  1
20400    10.70   8  1 112  1
20430   -14.50   8  1  50 -2
21150    22.50  20  1 109  1
21160    39.70  20  2  50 -2 112  2
21180    -7.40  20  1  50 -3
21440    25.40  50  2 112  1

25000    18.00  50  2 101  1            ( MINEQL Type 6 species )
```

Type VI Species are species that are not to be considered, e.g., dissolved solids not subject to precipitation, the electron, which does not exist in solution, or electrostatic components of surface complexes. Any previously defined species may be listed as Type VI. Using Type VI Species can set aside the need to edit THERM.DAT if one wants to run the program but omit temporarily one or more species from equilibrium calculations.

Type VII Species are species (which must be defined either in the thermodynamic data or as another species type) whose formation constants are not to be corrected for ionic strength effects. Surface adsorption sites should be designated as Type VII. No more then ten species may be designated as Type VII.

To include redox reactions in a computation it is necessary to include the electron, component identification number 99. Normally the pε ($-\log_{10}$ electron activity) will be fixed at a given value for a computation; thus species 99 should be included as a Type III (fixed component) species. If the pε is to be calculated, species 99 must be included as a Type VI (species not included) species since the free electron does not exist in solution. The default type specification for redox complexes is Type II; for redox solids it is Type V (dissolved solids subject to precipitation), and for redox reactions which relate two components, e.g., Fe^{3+}/Fe^{2+}, Type III.

To include a gas phase at fixed partial pressure, it is necessary to include the gas as a Type III species (fixed solid) and to specify its partial pressure. The formation expression for $CO_2(g)$ is, under ideal conditions:

$$[H^+]^2\,[CO_3^{2-}]\,K = [CO_2(g)] = P_{CO_2} \qquad \log K = 10^{18.0}$$

Since computationally every solid phase has an activity of one, the expression is rearranged to

$$[H^+]^2\,[CO_3^{2-}]\,\frac{K}{P_{CO_2}} = 1$$

and the effective constant for the phase at a fixed partial pressure, P_{CO_2} becomes:

$$\log K' = \log K - \log P_{CO_2}$$

Then to have the aqueous phase in equilibrium with the atmosphere ($P_{CO_2} = 10^{-3.5}$)

$$\log K' = 18.0 - (-3.5) = 21.5$$

Use the following input group in the chemical initial condition input file for the compartment of the subunit to make that specification:

00003		Type III species
25000	21.5	ID# of $CO_2(g)$; log K'
blank line		termination of group

The default species type for gases is Type VI, species not considered. Thus if the gas is not explicitly specified, it will not be considered.

Three surface-complexation models are included in SURFEQL: the constant-capacitance (CCM), triple-layer (TLM) and diffuse-layer (DLM) models. Electrostatic corrections to dissolved species involved in surface reactions are given by:

$$[S_j]_s = [S_j] exp(-\frac{e\Psi}{kT})$$

The subscript s refers to surface concentrations. The undissociated (uncharged) surface group (>S-OH) is species 159. For the CCM, the electrostatic "component" is species 160. Surface protonation and deprotonation are then characterized by:

$$K_{a1}^{s} = \frac{[>S{-}OH][H^+]}{[>S{-}OH_2^+]} \exp(-\frac{e\psi_0}{kT})$$

$$K_{a2}^{s} = \frac{[>S{-}O^-][H^+]}{[>S{-}OH]} \exp(-\frac{e\psi_0}{kT})$$

The protonated and deprotonated species must be entered into the input file by the user as type II complexes. The charge-potential relation is:

$$C = \sigma_0 / \psi_0$$

Surface charge (σ_0) is calculated from the difference between the concentrations of positively and negatively charged sites. Two parameters must be in the chemical input file for the subunit, the capacitance (C, in Farad m^{-2}), the solid surface area (S_A, in $m^2\,g^{-1}$). Note that surface species must be expressed in mol L^{-1}, not moles per unit area, thus including the solid-to-water ratio.

Other Type II complexes may also be entered. For example, Me^{2+} adsorption could be given by one or more constants of the form:

$$K_1^{s} = \frac{[>S{-}OH][Me^{2+}]}{[>S{-}OMe^+]} \exp(-\frac{e\psi_0}{kT})$$

$$K_2^{s} = \frac{[>S{-}OH][Me^{2+}]}{[>S{-}OMeOH][H^+]^2}$$

K_2^s is a composite constant including complexation of Me^{2+} with OH^- in solution and adsorption of the $MEOH^+$ complex.

Since under the CCM, all species are taken to be adsorbed at the same plane, there is only one potential, ψ_0 and the electrostatic correction is the same as above for H^+. Any unused species number can be used for the corresponding species definitions. The electrostatic component should be entered as Type I, with a concentration of 0.00. It should also be listed as Type VI.

Documentation for use of the TLM is not included, as there are insufficient data to support it in any field situation. The diffuse-layer model can be used; the charge-potential relation is in the program, so it does not require that a capacitance value be input. To date, we have not run AHM with any surface reactions present.

File 2: AHM input file with user-selected name *infiles.289* for initial test run; this file contains a list of certain other file names needed for input to the run.

```
emlhcons.289             (see File 3)
chemname.f3              (see File 4) *
rain.rwl                 (see File 12)
snow.rwl                 (see File 12)
seq.rwl                  (see File 1)
smcasub.1                (Snowmelt, snow-covered area, sublimation files;
smcasub.2                 one per subunit.  See File 14)
smcasub.3
smcasub.4
smcasub.5
smcasub.6
smcasub.7
petrwl.1                 (PET files, one per subunit; see File 13)
petrwl.2
petrwl.3
petrwl.4
petrwl.5
petrwl.6
elake.cm
```

* The name of the chemical namelist file (File 4) must be present even for water-balance only runs.

File 4: AHM input file with user-selected name *chemname.f3* used in initial test runs. This file contains an ordered list of the names of chemical initial condition and kinetic files used for the various compartments of each subunit and the acid-neutralizing capacity definition file.

IC and kinetic file names may be repeated for subsequent subunits/ compartments, and "dummy" file names (files that exist but contain no data) are permissible where given compartments are not present in a subunit (e.g., canopy interception (compartments 2 and 3) on a rock subunit). Compartments include (1) rainfall litter interception, (2) canopy snowfall interception, (3) canopy rainfall interception, (4) snowpack water equivalent (frozen), (5) snowpack free water, (6) drainage from snowpack, (7) surface runoff from a subunit, (8) subsurface (horizontal) drainage from a subunit, (9) horizontal drainage received by a subunit, (10) surface runoff received by a subunit, (11) water in "litter (rock surface) interception" storage beneath the snowpack, and (12+) water stored in one to several soil layers. Kinetic file name immediately follows initial condition file name for a compartment. The last file name present in this file is that file used to define how acid-neutralizing capacity is to be computed.

```
minichem.289                                     (#1) LITTER, RAIN [1]
dummy
dummy                                               Canopy, Snow
dummy
dummy                                               Canopy, RAIN
dummy
chemlist                                            Snowpack W.E.
dummy
minichem.289                                        Snowpack F.W.
dummy
chemlist                                            Snowpack Drainage
dummy
chemlist                                            SRO
dummy
chemlist                                            HDRAIN
dummy
chemlist                                            H2Oin3 Hdrain
dummy
chemlist                                            H2Oin2 SRO
dummy
minichem.289                                        U-Snow Int.
litkin.kin
chemicl.289          (see File 5)                   soil layer 1
skin100.389           (see File 6)
```

---

[1] Chemical initial condition (IC) and kinetic file names for subunit number 1. This subunit has 12 compartments, including one soil layer. Compartment type is listed to the right of each IC file name. Lines between IC file names are kinetics files for preceding compartment.

File 4 (continued): AHM input file *chemname.f*; chemical initial condition and kinetic files names used in initial test runs.

```
minichem.289                              (#2) LITTER, RAIN[2]
dummy
chemlist                                     Canopy, Snow
dummy
chemlist                                     Canopy, RAIN
dummy
minichem.289                                 Snowpack W.E.
dummy
chemlist                                     Snowpack F.W.
dummy
chemlist                                     Snowpack Drainage
dummy
chemlist                                     SRO
dummy
chemlist                                     HDRAIN
dummy
chemlist                                     H2Oin3 Hdrain
dummy
chemlist                                     H2Oin2 SRO
dummy
minichem.289                                  U-Snow Int.
dummy
chemic2.289                                  soil layer 1
skin100.389
minichem.289                              (#3) LITTER, RAIN[3]
dummy
dummy                                        Canopy, Snow
dummy
dummy                                        Canopy, RAIN
dummy
chemlist                                     Snowpack W.E.
dummy
minichem.289                                 Snowpack F.W.
dummy
chemlist                                     Snowpack Drainage
dummy
chemlist                                     SRO
dummy
chemlist                                     HDRAIN
dummy
chemlist                                     H2Oin3 Hdrain
dummy
chemlist                                     H2Oin2 SRO
```

---

[2] Begining of chemical IC/kinetics file name list for subunit 2.

[3] Beginning of chemical IC/kinetics file names for subunit 3.

File 4 (continued): Input file *chemname.f*; chemical initial condition and kinetic files names used in initial test runs.

```
dummy
minichem.289                             U-Snow Int.
dummy
chemic3.289                              soil layer 1
skin100.389
minichem.289                          (#4) LITTER, RAIN[4]
dummy
dummy                                    Canopy, Snow
dummy
dummy                                    Canopy, RAIN
dummy
minichem.289                             Snowpack W.E.
dummy
chemlist                                 Snowpack F.W.
dummy
chemlist                                 Snowpack Drainage
dummy
chemlist                                 SRO
dummy
hemlist                                 HDRAIN
dummy
chemlist                                 H2Oin3 Hdrain
dummy
chemlist                                 H2Oin2 SRO
dummy
minichem.289                             U-Snow Int.
dummy
chemic4.289                              soil layer 1
skin100.389
chemic5.289                           (#5) LITTER, RAIN[5]
skin100.389
dummy                                    Canopy, Snow
dummy
dummy                                    Canopy, RAIN
dummy
minichem.289                             Snowpack W.E.
dummy
chemlist                                 Snowpack F.W.
```

---

[4] Beginning of chemical IC/kinetics file names for subunit 4.

[5] Beginning of chemical IC/kinetics file names for subunit 5; this is a rock-outcrop subunit and thus has no "soil" files.

File 4 (continued): Input file *chemname.f*; chemical initial condition and kinetic files names used in initial test runs.

```
dummy
chemlist                                             Snowpack Drainage
dummy
chemlist                                             SRO
dummy
chemlist                                             HDRAIN
dummy
chemlist                                             H2Oin3 Hdrain
dummy
chemlist                                             H2Oin2 SRO
dummy
minichem.289                                         U-Snow Int.
skin100.389
minichem.289                                    (#6) LITTER, RAIN[6]
skin100.389
dummy                                                Canopy, Snow
dummy
dummy                                                Canopy, RAIN
dummy
minichem.289                                         Snowpack W.E.
dummy
chemlist                                             Snowpack F.W.
dummy
chemlist                                             Snowpack Drainage
dummy
chemlist                                             SRO
dummy
chemlist                                             HDRAIN
dummy
chemlist                                             H2Oin3 Hdrain
dummy
chemlist                                             H2Oin2 SRO
dummy
minichem.289                                         U-Snow Int.
skin100.389
chemic6.289                                          soil layer 1
skin100.389
dummy                                           (#7) LITTER, RAIN[7]
```

---

[6] Beginning of chemical IC/kinetics file names for subunit 6; this is a talus subunit, but was treated as a soil subunit permiting water storage/chemistry beyond that occurring in interception storage.

[7] Beginning of chemical IC/kinetics file names for subunit 7; this is a stream/lake subunit and has no soil or "interception beneath the snowpack" files.

File 4 (continued): Input file *chemname.f*; chemical initial condition and kinetic files names used in initial test runs.

```
dummy
dummy                                                Canopy, Snow
dummy
dummy                                                Canopy, RAIN
dummy
chemlist                                             Snowpack W.E.
dummy
chemlist                                             Snowpack F.W.
dummy
chemlist                                             Snowpack Drainage
dummy
chemic7.289                                          SRO
dummy
dummy                                                HDRAIN
dummy
chemlist                                             H2Oin3 Hdrain
dummy
chemlist                                             H2Oin2 SRO
dummy
alk2489[8]          (see File 7)
```

---

[8] This file name is that of the file used to define the chemical species and stochiometry used to compute acid-neutralizing capacity.

File 12: AHM input file with user-supplied name *rain.rw1* for initial test run. This file contains the dates (yymm) and amounts (cm) of rainfall and the names of the files with chemical concentrations for each rainfall event. Snowfall files have identical format. Format 2I2,1X,F10.3, A50.

```
1006     .9375 rch00685    (see File 8 for rain chem. file rch00685)
1008     .6250 rch00885
0724    2.5    rch72486
0820     .4167 rch82086
0918     .625  rch91886
```

The number of input files can become so large that input of even the file names can become tedious. Consequently, several input data files consist either of lists of file names or a combination of data and file names (Files 2, 4, 12).

One data file that is used for flow routing was described previously under the section on Watershed Subdivisions. Others will be described below.

D5.1 File of File Names

File 2 is the file of file names. The example in File 2 is largely self-explanatory or cross-referenced to appropriate Files. This file itself is selected by the user employing interactive input (Figure D1).

The name of the file containing chemical initial condition kinetics files (File 4) must be present in File 2 even if the user selects the "water balance only" option (Figure D1). In that case, it can be a dummy (empty) file.

D5.2 Hydrologic Parameters File

Most hydrologic parameters are entered in a single input file (File 3). The inputs include parameters applicable to the entire area being modeled, to individual subunits and to individual soil layers within each subunit. While most inputs in this file are explained by the footnotes with the file, some require additional descriptions.

Subunit hydrologic parameters must be entered by order of increasing subunit number; subunits must be numbered consecutively.

All subunits (including stream segments) must have a positive surface area.

"Subunit type" currently may be one of three categories, (1) "N", for a "normal" soil-covered subunit, "R" for rock outcrop subunits, and "S" for stream (or lake) subunits. "Normal" subunits include those with at least one soil layer; we also used this category for talus subunits where some water storage in addition to rock-surface interception was presumed to exist at depth in the subunit. Rock outcrop subunits have no soil layer, but may be defined as having interception storage and surface weathering.

File 3: AHM input file with user-selected name *emlhcons.289* in test initial run. This file contains area-wide, subunit-wide, and soil layer hydrologic parameters. First line is a heading which is skipped by AHM.

```
    base elev Dry Lapse   W Lapse  SnowFrWK    FREEZE      THAW
        3000.      10.0      5.45       .05      1112      0803 [1]
       1     1 N   Aquept Soils on Emerald Lake WS [2]
          0.3      3700.      20.         7         [3]
1        .001       .00     13.76       .68      .028 [4]
           .4       .00       .00       .00       .00       .00 [5]
          1.0    100.00       .10    150.00       .20       .50       .15       .20
         1.15 [6]
```

---

[1] Area-wide parameters. Elevation of climatic measurements, dry adiabatic air temp. lapse rate (no effect), moist adiabatic air temp. lapse rate (no effect), snowpack free-water holding capacity, (cm water / cm SWE), date streams freeze (mmdd), date streams thaw (mmdd). Format 4F10.0, 2(6X,2I2).

[2] Subunit number, number of soil layers, subunit type, and subunit name. Format 2I5, 1X, A1, 3X, A64.

[3] Subunit area (ha), elevation (no effect), max. infilt. rate, I.D. number of stream subunit (if any) from which this subunit can extract water to maintain minimum soil water content (for riparian areas). Format 3F10.0, I10.

[4] Rainfall adj. type, rainfall adj. factor, snowfall adj. type, snowfall adj. factor, snowpack initial condition (I.C.) (cm WE on SCA), snowpack free water IC (cm on SCA), initial snow-covered area (SCA), and initial water in "litter" interception storage beneath the snowpack on SCA. Format 2(I1,F9.0), 4F10.0.

[5] Litter interception cap. for rainfall (and snowmelt beneath snowpack), litter interception I.C., canopy-interception capacity, canopy snowfall interception I.C., canopy rainfall interception capacity, and canopy rainfall interception I.C. All values in cm. Format 6F10.0.

[6] Data for first soil layer (other layers follow immediately if present), maximum evaporation rate as compared to free water surface when soil saturated, soil depth (cm), soil parameter N (see text), saturated hydraulic conductivity (cm/day), residual soil water content below which drainage is zero (cm water/cm soil), saturated water content (cm/cm), zero ET water content (cm/cm), initial water content (cm/cm), bulk density (g/cm^3). Format 8F10.0/F10.0.

File 3 (continued): File *emlhcons.289*, subunits 2-7 as used in initial test runs. Data follow same format as for first subunit (previous page).

```
    2    1 N   Orthod Soils, forested area of Emerald Lake Basin
       2.1     3700.      20.         0
1     .001      .00     13.76        .68       .028
      .50       .00       .25        .00        .25       .00
      1.0     36.40       .10     920.00        .10       .50      .02     .074
     1.15
    3    1 N     Umbrept Soils on Emerald Lake WS
     18.29     3700.      20.         0
1     .001      .00     13.76        .68       .028
      .20       .00       .00        .00        .00       .00
      1.0     33.00       .10     385.00        .20       .50      .03      .12
     1.15
    4    1 N     Orthent and Fluvent Soils on Emerald Lake WS
      3.66     3700.      20.         0
1     .001      .00     13.76        .68       .028
      .10       .00       .00        .00        .00       .00
      1.0     25.00       .10     365.00       .075       .40      .02     .148
     1.15
    5    1 R     Rock (jointed and unjointed, and inclusions in soil map units)
     69.80     3700.       0.         0
1     .001      .00     13.76        .68       .028
      .10       .00       .00        .00        .00       .00
      1.0       .00        .0        .00        .00       .00      .00      .00
    6    1 n     Talus and units G, K, and F-K
     23.00     3700.      20.         0
1     .001      .00     13.76        .68       .028
      .20       .00       .00        .00        .00       .00
      .60    200.00       .10     500.00       .075       .30      .01      .04
     1.15
    7    1 S     Emerald Lake, the lake
      2.85     3700.       0.         0
1     .001      .00        0.         .0        .00
      .00       .00       .00        .00        .00       .00
      1.0       .00        .0        .00        .00       .00      .00      .00
```

Stream subunits are treated distinctly in that they must have no litter or canopy interception, and they are also subject to freezing and thawing. When streams are defined as frozen, evaporation is limited to sublimation from the snowpack on the stream surface or evaporation from surface runoff reaching the stream from another subunit; subsurface water inputs from other subunits to a given stream segment are not subject to evaporation from the stream when it is frozen. On thawed streams, any precipitation (including snow) becomes surface runoff subject to evaporation by ET.

Riparian areas are defined by AHM to be those areas that can extract water from a stream subunit to maintain a minimum soil water content. A riparian area is created by specifying the stream segment from which such water can be extracted.

Rainfall and snowfall for a subunit may be adjusted by either of two built-in methods to account for the elevation difference between the subunit and the point where rainfall or snowfall was measured. The details of the methods employed are described in the section of Appendix C describing subroutine RAINADJ.

The soil parameter "N" is related to unsaturated hydraulic conductivity in upper soil layers. This relationship is that described by Warrick et al. (1985) and is also described in the description of function HYDK in Appendix C. In the bottom soil layer (or <u>the</u> soil layer, if only one used), this same parameter is used in the simple linear reservoir model:

$$Q = N \times S$$

where: Q is drainage from the bottom soil layer to the receiving subunit in cm

N is the parameter being described

S is the storage in the subunit in cm of water in excess of the water content at which unsaturated hydraulic conductivity goes to zero

The value of the soil parameter should typically exceed two in upper layers, and must be less than one on the bottom soil layer.

The residual soil water content below which unsaturated hydraulic conductivity is zero is also used in a piece-wise linear relationship to determine actual ET; this is described in the ET Computations section of Appendix C.

D5.3 Chemical IC and Kinetics Files

File 4 shows the list of chemical initial condition (IC) and kinetics file names used in the initial test runs. These files are input for each compartment of each subunit. These file names are input one per line, with the chemical IC file name on the line immediately preceding the kinetic reaction file name for the same compartment of the subunit. File names are input in numerical order of subunits and compartments; file names for all compartments in subunit 1 are followed by all compartments in subunit 2, etc. A list of AHM compartments is given in Table B1.

A given subunit may not have all possible compartments. Specifically, type S (stream or lake) subunits never have compartments 1, 2, 3, 8, 11, or 12+, and type R (rock outcrop) subunits typically may not have compartments 2 or 3 and never have 8 or 12+. However, file names must be listed for all compartments (1-12+) except that no file name is listed for compartments 11 or 12+ on type S subunits, and no file name is entered for compartments 12+ for type R subunits. In summary, soil-covered subunits will have 2 x 11 + 2 x (number of soil layers), rock subunits will have 2 x 11, and stream subunits will have 2 x 10 file names listed in File 4.

While their presence is required, chemical IC and kinetics files are ignored on those compartments which do not in fact exist on a given subunit. Additionally, data in kinetics files are only used on those compartments where the chemical equilibration routine is run (currently only on compartments 1, 7, 11, and 12). Therefore, the names of one or more dummy files (files that exist but contain no data) may be used for IC input files or for kinetics files where chemical equilibration is not occurring (File 4).

On those compartments that exist, the chemical IC file is used to define (File 5):

(1) Chemical component (MINEQL type 1) species to be considered in the compartment. All chemical species to be encountered by the compartment during the run must be identified in this file, even if not initially present. A compartment must include all chemical species present or added to compartments tributary to it or an error condition will result. Because CO_3^{2-} species are present in rainfall, all compartments must include CO_3^{2-} as a component.

(2) Total number of moles of each component species initially present.

(3) A guess at the fraction of the total concentration of a component species present in the form of the component (e.g., the fraction of total CO_3^{2-} present as CO_3^{2-}, rather than as HCO_3^-, H_2CO_3, etc.

(4) Type II species, which are equivalent to MINEQL Type I species, but that do not mix between compartments.

(5) MINEQL Type III species and their $\log_{10}$ K values.

(6) MINEQL Type IV-VI species whose $\log_{10}$ K values differ from those in THRM.DAT.

While there is no requirement that chemical components be entered in the same order in each compartment, doing so (by copying and modifying chemical IC files from one compartment to create another) is a logical way to avoid having a compartment receive a species that has not been defined as existing there.

AHM will accept soil surface reaction sites (total moles/subunit) as input and is capable of computing soil surface reactions such as cation exchange, etc. These surface reaction sites are input as AHM Type II species. However, in our limited testing to date, we have experienced some problems obtaining convergence in the chemical equilibration routines when such surface reactions are present. We anticipate continuing work on this problem.

Kinetics files can operate only on compartments where and when equilibration takes place. Chemical equilibration does not occur on any compartment that is dry. If a dummy file is input for a compartment where equilibration occurs, no kinetic reactions will occur on that compartment.

Kinetic input files compute reactions of the form (File 6):

$$C_1 = C_1 + A \times F \times 1000 \times (k_1 + k_2 \times C_2^{\alpha_1} + k_3 \times C_3^{\alpha_2})/Q$$

where:

C_1 = Concentration of the chemical species being adjusted;

A = Soil particle or rock outcrop surface area on the subunit, m^2;

F = Fraction of subunit wet in this compartment;

C_2, C_3 = Concentration of species that affect species being adjusted;

Q = Volume of water (liters) in the compartment;

k_1, k_2, k_3, α_1, α_2 = User-supplied parameters to give outputs to millimoles per m^2.

File 6: AHM input data file with user-selected name *skin100.389* used in initial test runs. Each compartment present on a given subunit requires a kinetics input file, but the same file can be used for a number of different subunits/compartments if desired. Dummy files (existing but empty) may also be used. Kinetics present in these files affect only those compartments on which chemical equilibration also occurs. Although easily extended to other compartments, this currently includes only soil layers and litter or rock surfaces.

For those compartments where kinetics are active, only those species which are to be adjusted for kinetic reactions need to be included in the input file.

The kinetic reactions are computed in the form:

$$\frac{\partial S_K}{\partial t} = +A \times F \times 1000 \times (K_{k1} + K_{k2} \times [S_p^{\alpha_1}] + K_{k3} \times [S_q^{\alpha_2}]\ )/Q$$

where:

$\frac{\partial S_K}{\partial t}$ = Change in molar concentration of the chemical species being adjusted each time step;

A = Soil particle or rock outcrop surface area on the subunit, m^2;
F = Fraction of subunit wet in this compartment;
S_p, S_q = Molar concentration of species which affects that species being adjusted;
Q = Volume of water (liters) in the compartment; and
K_1, K_2, K_3, α_1, α_2 = User-supplied parameters to give outputs in millimoles per m^2.

Input data include ID number of species being adjusted, K_1, K_2, ID number of first species that affects species being adjusted, α_1, K_3, ID number of second species that affects species being adjusted, and α_2. Example file ends following α_1.

Format I10, F10.0, 2(F10.0, I10, F10.0)

```
         4        0.    .00011        50       .77
         2        0.    .00017        50       .77
         5        0.    .00162        50       .77
         1        0.    .00065        50       .77
       112        0.    .00428        50       .77
        50        0.   -.00270        50       .77
```

The parameters k_1-k_3 and α_1-α_2 should be selected to give inputs in the form of moles per subunit per day; the program adjusts for snow-covered area and area left wet behind receding snowpacks.

When creating input data for kinetics files, keep in mind that order of input is important. If the concentration of a given "Species 2" or "Species 3" is modified by kinetics prior to being used in adjusting the concentration of another Species 1, that and other subsequent adjustments involving Species 2 or 3 may be in error.

D5.4 ANC Definition File

The last file name encountered in the list of chemical IC/kinetics file names (File 4) is the name of the file defining acid-neutralizing capacity (File 7). This file defines the effect of all MINEQL type 1 and 2 chemical species present (after equilibration) on acid-neutralizing capacity and is applicable to the entire run. Values present in the file include the ID number of the species that affect alkalinity and a stoichiometric number defining the extent of that effect (e.g., for CO_3^{2-}, the factor is two times mol L^{-1} of CO_3^{2-}).

D5.5 Precipitation Event Chemistry Files

Each rainfall or snowfall event requires a separate chemical file to define the concentration of the chemical species present in rainfall (File 8). Input data in these files are in mol L^{-1} of each species present. Total molar chemical inputs to a subunit from precipitation account for area of the subunit and changes in precipitation with elevation as defined in the hydrologic parameters file (File 3). Total chemical inputs to a given subunit will be proportional to the total precipitation received.

D5.6 Variable Gas Pressure Files

Partial pressures of gases may be varied as often as every day if desired. This is accomplished through the use of a file which has the (currently-fixed) name gasdate.dat (File 9). This file adjusts for varying partial pressures of gases by changing the log10 of the K value used for the gaseous MINEQL type 3 species (only) which represents a fixed (for a given equilibration) partial pressure of the gas.

File 7: AHM input file named *alk2489* as used in initial test runs. This file defines how acid-neutralizing capacity is to be determined based on concentrations of various species as determined by the chemical equilibration subroutine.

```
   50       -1
  101        2
  107        1
  109        3
  112        2
12530        1
12600        2
12620        1
12710        1
13595        1
```

File 8: AHM input file with user-selected name *rch00685* used in initial test runs. This file contains precipitation chemistry data for a single rainfall (or snowfall) event. Entries include chemical species ID number and concentrations (mol L^{-1}) of each species. Format I5, 5X, E10.2. Tentatively, it appears species 101 and 112 may need to be present at some level to avoid problems with chemical equilibration routine.

50	9.878E-5
5	5.655E-6
4	3.836E-6
1	7.485E-6
2	1.645E-6
107	8.648E-5
103	7.334E-6
157	5.242E-5
102	1.603E-5
101	.001E-06
112	.001E-06

File 9: AHM input file with the (currently) fixed name *gasdate.dat*. An input file with this name must be present, but it may be an empty, dummy file. The file is used to specify the dates (if any) of the year in which the chemical equilibrium "K" values are to change for specified type 3 chemical species. This permits seasonal adjustment of values such as partial pressure of carbon dioxide in the soil. Input data include a date line (mmdd) followed by separate lines for each set of subunit number, compartment number, chemical species identification number, and the new "K" value. K values remain as input in initial condition files (File 5) until the first date set in this file. Then those that were changed remain at their newly-specified K value until the next date specified in this file, when they may be modified again. A blank line follows each group for a given date, followed by a new date line. Format 2I2 / 3I10, F10.0.

```
1002
         1         12       25000        20.5          unit, comp, spec, K

1005
         1         12       25000        20.49
         2         12       25000        22.49
...
```

The first line in this file must begin with a month and day greater than the beginning month and day specified interactively by the user.

D5.7 Chemical Sources and Sinks

Chemical sources and sinks can be used to simulate dry deposition from the atmosphere, nutrient uptake or release by plants and plant materials, or other effects. Daily source and sink data are input from a file with the (currently-fixed) name ssink.dat (File 10). This file permits source and sink input to be specified by subunit, compartment, and chemical component species (MINEQL Type I). This flexibility requires a potentially very large input file. For example, if an entire WY run were made with 10 subunits, each having 5 compartments with daily sources or sinks including 15 chemical species, the input file would be approximately 10 x 5 x 15 x 365 = 274,000 lines in length.

A supplemental program was written to help create this file (Appendix E).

The file must begin with the WY date corresponding to the month and day the run is to begin as specified interactively by the user.

D5.8 Thermodynamic Data

Chemical thermodynamics are obtained from a single input file named thrm.dat (File 11). Blank lines separate groups of different MINEQL species types. In addition, Type 7 species are not allowed in the thrm.dat file for AHM.

D5.9 Rainfall and Snowfall

Rainfall and snowfall are input in separate files, although the files have the same structure (File 12). Unlike many AHM input files, these files have data input by month and day rather than WY day. Rainfall and snowfall data can be present in these files for periods preceding the run's beginning water year date (as specified in Figure D1). The data cannot precede WY day 1, however. Rainfall and snowfall represented by these two input files applies to the entire watershed under consideration, except as adjusted by subroutines RAINADJ or SNOWADJ which are described in Appendix C.

File 10: AHM input file *ssink.dat*. A file with this name must be present and available to AHM at run-time. The file contains data used to determine the number of moles of various chemical species added or subtracted from a given compartment each day. Examples of practical uses include dry deposition or nutrient uptake by plants. Unlike kinetic input files (File 6), inputs present in this file may be added to a compartment whether or not water is present or chemical equilibration has been computed.

The minimum file contains water year day, blank line, water year day, blank line, etc. for the run period specified by the user (Figure D1). When sources and sinks are present, the file also contains one to several lines each including subunit, compartment, chemical species ID, and number of moles to add to that compartment. Format I3 for water year day, 3I10, F10.0 for subunit/compartment/species/number of moles added to entire compartment of subunit. Subunit and compartment in a given day's data can be left blank and will default to the last-read subunit and compartment in that day's data. A supplemental program is available to help generate this file, which can be quite large (Appendix E).

```
  1

  2

  3
         1         1         1 0.0035000
         1         4         1 0.0090000
         1         1         2 0.0021000
         1         4         2 0.0054000
         1         1         5 0.0056000
         1         4         5 0.0144000
         1         1        50 0.0021000
         1         4        50 0.0054000
         1         1       102 0.0070000
         1         4       102 0.0180000
         1         1       103 0.0021000
         1         4       103 0.0054000
         1         1       107 0.0070000
         1         4       107 0.0180000
         1         1       157 0.0098000
         1         4       157 0.0252000
         2         1         1 0.0245000
         2         4         1 0.0630000
         2         1         2 0.0147000
         2         1         5 0.0392000

  4

  5

  6
...
```

D5.10 Potential Evapotranspiration

Each subunit requires a separate potential evapotranspiration (PET) file. These files each consist of a single vector of PET values for the subunit (File 13). PET files must begin with the WY day corresponding to the starting month and day interactively entered by the user (Figure D1).

Actual PET is dependent on water storage, as defined in Appendix C.

D5.11 Snowmelt, Snow-Covered Area, and Sublimation

Each subunit requires a separate file containing values of potential snowmelt, snow-covered area, and potential sublimation. The "potential" as used here implies that snowmelt or sublimation rate that would occur if the entire subunit was snow-covered (actual melt and sublimation are reduced proportionately with decreasing SCA). These values are entered in 3 vectors, each line corresponding to the respective values for a single water-year day (File 14). The files must begin with the WY day corresponding to the starting month and day interactively entered by the user.

On days when snowfall occurs, snow-covered area entered in this file should equal that at the end of the preceding day; SCA is internally set to 1.0 on those days with fresh snowfall.

D5.12 Other Files

The chemical equilibration routine requires an input file named ionc.dat to define the stoichiometry of the component species. This file should not be modified by the user.

D6 Precautions and Problems

Variable snow-covered area is handled by applying snowmelt and sublimation to snow-covered area, ET to snow-free area, etc. as explained in Appendix C. When fresh snowfall occurs, snow-covered area becomes 1.0, and snow water equivalent depth is assumed to be uniformly distributed (Figure D2). If potential snowmelt during the period when SCA is 1.0 exceeds the assumed uniform snowpack depth, all snow will melt, while the user may have intended to leave a persistent, smaller patch of snow on the subunit. To avoid this, the user must adjust potential snowmelt following a snowfall that was preceded by a period with a large snow-free area to maintain the desired residual snowpack. Doing so will require accounting for adjustments to snowfall made by subroutine RAINADJ (Appendix C).

File 13: AHM input file named *petrw1.1* in initial test runs. This file contains daily potential evapotranspiration data for watershed subunit number one. Each subunit (including those representing streams or lakes) must have a separate file containing these data. First line must correspond to beginning month and day of the run, and file(s) must contain enough lines for total number of days that user specified interactively (Figure D1). Format F10.0.

```
0.0845
0.0422
0.0421
0.0210
0.0209
...
```

File 14: AHM input file with user-supplied name *smcasub.1* in initial test runs. This file contains daily potential snowmelt, snow-covered area, and potential sublimation data (respectively) for watershed subunit number one. Each subunit (including those representing streams or lakes) must have a separate file containing these data. First line must correspond to beginning month and day of the run, and file(s) must contain enough lines for total number of days that user specified interactively (Figure D1). format 3F10.0.

```
0.3786  0.0280  0.0964
0.4192  0.0260  0.0962
0.4708  0.0240  0.0958
0.5364  0.0220  0.1000
0.6200  0.0200  0.0950
0.0000  0.0200  0.0000
```

Weathering of minerals under wet or moist conditions would typically be input in the kinetics files (File 6). Kinetic reactions are computed based on concentrations of species computed by the MINEQL routines. Outputs from the kinetic reactions add to the total number of moles of each component species, but do not affect the variable reflecting concentrations of individual species from the MINEQL equilibration. Acid-neutralizing capacity is computed using those concentrations. Therefore, pH, ANC, and other dissolved species concentrations that are output are not affected by weathering that occurs in the current time step. This can lead to erratic results in stream (or lake) subunits which currently store no water between time steps. This is particularly true when surface runoff from those subunits is generated solely from inputs to the stream (or lake) surface itself.

While the chemical equilibration routine computes precipitation of solids, AHM currently moves these precipitated solids from the compartment in direct proportion to the fraction of water storage leaving a compartment. This will be modified to leave precipitated solids in place.

The MINEQL routine's treatment of Type III chemical species as "solids that don't dissolve, even if their concentration becomes negative" can cause an error message to appear related to taking the log of a negative number. This occurs just prior to chemical output each time step and should have no ill effect on the outcome of the run. This will be fixed in subsequent versions.

The method used to accelerate elution of chemicals from the snowpack is not yet functional. The user must select the option for proportional loss of chemicals with snowpack drainage.

D7 Limits

The majority of variable dimensions which impose limits on AHM are defined in the FORTRAN file parametr.for (Appendix C). Parametr.for is an "include" file and is incorporated into the AHM program when it is recompiled. If any values in this file are changed, the entire program should be recompiled.

AHM consolidates a number of snowmelt/snow-covered area/sublimation (SmCaSub) and ET files into fewer, larger files to minimize the number of input data files that must be kept open at one time. Twelve input files (for 12 subunits) become 1 input file. With more than 12 subunits, additional consolidated files are created. Without modification to the FORTRAN code, this permits about 108 subunits to be used, providing: (1) Parameter NNU is changed to 108 in file parametr.for and the program is recompiled; and (2) The computer on which it is run has enough memory to run with the number of subunits, soil layers, chemical species, and thermodynamic inputs chosen. Minor modifications to the code could increase the maximum number of subunits to whatever hardware limitations apply.

As supplied, the default values included in the parametr.for file permit:

12 watershed subunits with up to 3 soil layers each;
19 chemical component (MINEQL type 1) species;
120 total chemical species;
20 chemical species that can be included in computing acid-neutralizing capacity.

The executable version for personal computers requires about 440,000 bytes of memory to run with these default values. On smaller systems, available disk space is also a consideration. The user can interactively select whether or not "massive" chemical output is desired. With the problem formulation we used for the Emerald Lake basin, this output file alone occupies some 22 megabytes, while other output files collectively total about 5 megabytes.

D8 Program Compilation

If modifications are made or if AHM is to be compiled for use on a different computer, a number of program modules must be compiled and linked (Table D3).

Table D3: AHM program modules. Some of these modules contain a number of FORTRAN subroutines.

AMAIN.FOR ANC.FOR CHKCHM.FOR CHEMBAL.FOR COMPKIN.FOR
CONVERT.FOR DEPTH.FOR DOCHEM.FOR ET.FOR GASK.FOR
GHSTBST.FOR GHSTBST1.FOR HYDK.FOR INCOND.FORINFLOW.FOR
INPUT.FOR IWYDATE.FOR MATBAL2.FOR MINEQL.FORMIX.FOR
PRECMIX.FOR PRINTCHM.FOR RAINADJ.FOR RAINCHEM.FOR READCHEM.FOR
READDAT.FOR READKIN.FOR REREAD.FOR RIPARIAN.FOR RIPCHARG.FOR

SNOINI.FOR SNOWADJ.FOR SNOWCOMP.FOR SNOWMIX.FOR SNOWRAIN.FOR
SNTERCPT.FOR SOILDRAN.FOR SPECIAL.FOR SSINK.FOR STREAMET.FOR
SUBUSEQ.FOR USNOW.FOR WATERBAL.FOR WETMELT.FOR VOLUME.FOR
ZERO.FOR

"Include" files that must be present during program compilation:

COMMON.FOR COMMON2.FOR COMMONC.FOR FLAG.FOR IONIC.FOR
PARAMETR.FOR PARM.FOR SURFCOM.FOR VAR.FOR

APPENDIX E

SUPPLEMENTAL PROGRAMS FOR AHM

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APPENDIX E
SUPPLEMENTAL PROGRAMS FOR AHM

READBIG

The output file from the chemical equilibrium routine can be very large. In our test runs with 7 subunits, it averaged approximately 23 megabytes. The supplemental program READBIG reads file BIGCHEM.OUT and selectes from it output data for a specific subunit and compartment. The selected data re copied to a smaller file.

The program is interactive. An example runstream is shown in Figure E1.

Figure E1: Example run of the AHM supplemental program READBIG. User inputs are in boldface.

```
= = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
select subunit and compartment from BIGCHEM FILE
input filename (default bigchem.out) > bigchem.out
output filename > bigout
SUBUNIT = ?7
COMPARTMENT = ?7
Water year day to start copying? > 340
= = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
```

READX

Although smaller than the chemical equilibration file, file XCHECK can also become quite large; in our test runs, it approached 5 megabytes. This file contains a listing of hydrological parameters, initial chemical conditions, and the chemical mass/water volume passed to the equilibration routine from each subunit/compartment every time step.

While the hydrological parameters are easily checked by looking at the file from the top, finding specific chemical entries of interest at a given time step can be difficult. Supplemental program READX reads file XCHECK and extracts chemical mass/water volume entries for a given subunit/compartment.

The program is interactive. An example runstream is contained in Figure E2. The "WY day" entry is the date you wish to begin copying to the new file.

Figure E2: Example runstream with AHM supplemental program READX. User inputs are in boldface.

```
= = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
read xcheck, determine where to start copying
input filename (default xcheck) >
output filename > xout
SUBUNIT = ?1
COMPARTMENT = ?12
WY day ? > 1
= = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = = =
```

DRYDEP

The required source-sink input file SSINK.DAT may be very large. The supplemental program DRYDEP may aid in creating this file.

DRYDEP uses the snowmelt/snow-covered area/sublimation input files used for AHM runs. It is interactively given the names of those files and inputs of the number of moles of each chemical component species per day over the entire watershed and a specific time period. For that time period, it outputs the amount of source or sink chemicals added or subtracted from each compartment of each subunit, proportioned according to subunit area, and presence or absence of snow. In its current form, the chemical inputs/losses are only added to the subunits litter interception or snowpack water equivalent.

If only one period of source/sink activity is present, and daily input is constant during that period, the user can specify that other dates be entered with zero input, in which case the SSINK.DAT AHM input file will be ready to run for the entire year upon completion of this program. If source/sink rates vary seasonally, several runs of this program may be made and the separate output files from each run pieced together to create the AHM input file SSINK.DAT.

DRYDEP was written specifically for the Emerald Lake basin, divided into 7 subunits, and it will require minor modifications before being used with different subunit divisions or for use elsewhere.

The interactive input required is displayed in Figure E3.

Figure E3: Example run with AHM supplemental program DRYDEP. User inputs are in boldface.

```
DRYDEP: expect trouble with leap years
enter SM/CA/SUB file, subunit 1 > smcasub.1
enter SM/CA/SUB file, subunit 2 > smcasub.2
enter SM/CA/SUB file, subunit 3 > smcasub.3
enter SM/CA/SUB file, subunit 4 > smcasub.4
enter SM/CA/SUB file, subunit 5 > smcasub.5
enter SM/CA/SUB file, subunit 6 > smcasub.6
enter SM/CA/SUB file, subunit 7 > smcasub.7
enter output file (rename ssink.dat for use) > ssink.dat
enter starting month, day > 6,1
enter ending month, day > 9,30
ENTER 1 to enter other dates as zero input > 1
ENTER moles (not Equiv.) / Watershed (=120 ha)
157 enter NO3  >14
107 enter NH4  >10
102 enter SO4  >10
103 enter Cl   >3
1 enter Ca  >5
2 enter Mg  >3
5 enter Na  >8
50 enter H+  >3
```

GRAPHANC

The AHM output file phalk.out contains the values of pH, acid-neutralizing capacity, and cubic meters of water in several compartments of each subunit. Phalk.out is not a convenient file for creating plots. Program GRAPHANC separates data for a specific subunit and compartment and stores it in a new file for subsequent plotting. The programs interactive runstream is shown in Figure E4, and an example output file is shown in Figure E5.

Figure E4: Example runstream of AHM supplemental program GRAPHANC. User inputs are in boldface.

```
Program to read phalk.out file from AHM
Enter input filename > phalk.out
output file name ? > graphsoil.2
enter subunit#, compartment# > 2,12
```

Figure E5: Example output file from AHM supplemental program GRAPHANC. Values include water-year day, subunit, pH, acid-neutralizing capacity, and cubic meters of water in the compartment.

```
 1  2   5.612  -0.3189E-006   0.5559E+003
 2  2   6.828   0.3480E-004   0.5537E+003
 3  2   6.877   0.3896E-004   0.5523E+003
...
```

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